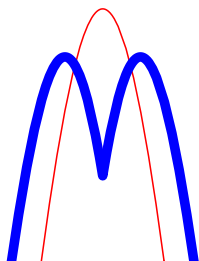# MOLPRO

Users Manual
Version 2015.1

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Introduction to MOLPRO

MOLPRO is a complete system of *ab initio* programs for molecular electronic structure calculations, designed and maintained by H.-J. Werner and P. J. Knowles, and containing contributions from a number of other authors. As distinct from other commonly used quantum chemistry packages, the emphasis is on highly accurate computations, with extensive treatment of the electron correlation problem through the multiconfiguration-reference CI, coupled cluster and associated methods. The recently developed explicitly correlated coupled-cluster methods yield CCSD(T) results with near basis set limit accuracy already with double$-\zeta$ or triple$-\zeta$ basis sets, thus reducing the computational effort for calculations of this quality by two orders of magnitude. Using local electron correlation methods, which significantly reduce the increase of the computational cost with molecular size, accurate *ab initio* calculations can be performed for much larger molecules than with most other programs. These methods have recently been augmented by explicitly correlated terms, which strongly reduce both the basis set truncation errors and the errors of the local approximations.

The heart of the program consists of the multiconfiguration SCF, multireference CI, and coupled-cluster routines, and these are accompanied by a full set of supporting features. The package comprises

- Integral generation for generally contracted symmetry adapted gaussian basis functions ($spdfghi$). There are two programs with identical functionality: the preferred code is SEWARD (R. Lindh) which is the best on most machines; ARGOS (R. M. Pitzer) is available as an alternative, and in some cases is optimum for small memory scalar machines. Also two different gradient integral codes, namely CADPAC (R. Amos) and ALASKA (R. Lindh) are available. Only the latter allows the use of generally contracted symmetry adapted gaussian basis functions.

- Effective Core Potentials (contributions from H. Stoll).

- Many one-electron properties.

- Some two-electron properties, e.g. L_x^2, L_y^2, L_z^2, $L_x L_y$ etc..

- Closed-shell and open-shell (spin restricted and unrestricted) self consistent field.

- Density-functional theory in the Kohn-Sham framework with various gradient corrected exchange and correlation potentials.

- Multiconfiguration self consistent field. This is the quadratically convergent MCSCF procedure described in J. Chem. Phys. 82 (1985) 5053. The program can optimize a weighted energy average of several states, and is capable of treating both completely general configuration expansions and also long CASSCF expansions as described in Chem. Phys. Letters 115 (1985) 259.

- Multireference perturbation theory (MRPT2, CASPT2, CASPT3), including (extended) multi-state methods MS-CASPT2 and XMS-CASPT2 as described in Mol. Phys. **89**, 645 (1996), J. Chem. Phys. **112**, 5546 (2000), J. Chem. Phys. **135**, 081106 (2011).

- Multireference CI. As well as the usual single reference function approaches (MP2, SDCI, CEPA), this module implements the internally contracted multireference CI method as described in J. Chem. Phys. 89 (1988) 5803 and Chem. Phys. Lett. 145 (1988) 514. Non variational variants (e.g. MR-ACPF), as described in Theor. Chim. Acta 78 (1990) 175, are also available. Electronically excited states can be computed as described in Theor. Chim. Acta, **84** 95 (1992). A new more efficient MRCI implementation is described in J. Chem. Phys. **135**, 054101 (2011).

- Møller-Plesset perturbation theory (MPPT), Coupled-Cluster (CCSD), Quadratic configuration interaction (QCISD), and Brueckner Coupled-Cluster (BCCD) for closed shell systems, as described in Chem. Phys. Lett. 190 (1992) 1. Perturbative corrections for triple excitations can also be calculated (Chem. Phys. Letters **227** (1994) 321).

- Open-shell coupled cluster theories as described in J. Chem. Phys. 99 (1993) 5219, Chem. Phys. Letters **227** (1994) 321.

- An interface to the MRCC program of M. Kallay, allowing coupled-cluster calculations with arbitrary excitation level.

- Full Configuration Interaction. This is the determinant based benchmarking program described in Comp. Phys. Commun. 54 (1989) 75.

- Analytical energy gradients for SCF, DFT, state-averaged MCSCF/CASSCF, MRPT2/CASPT2, MP2 and QCISD(T) methods.

- Analytical non-adiabatic coupling matrix elements for MCSCF.

- Valence-Bond analysis of CASSCF wavefunction, and energy-optimized valence bond wavefunctions as described in Int. J. Quant. Chem. **65**, 439 (1997).

- One-electron transition properties for MCSCF, MRCI, and EOM-CCSD wavefunctions, CASSCF and MRCI transition properties also between wavefunctions with different orbitals, as described in Mol. Phys. **105**, 1239, (2007).

- Spin-orbit coupling, as described in Mol. Phys., **98**, 1823 (2000). More recently, a new spin-orbit integral program for generally contracted basis sets has been implemented.

- Douglas-Kroll-Hess Hamiltonian up to arbitrary order and the eXact-2-Component (X2C) Hamiltonian.

- Density-functional theory symmetry-adapted intermolecular perturbation theory (with density fitting), DFT-SAPT , as described in J. Chem. Phys. **122**, 014103 (2005).

- Some two-electron transition properties for MCSCF wavefunctions (e.g., L_x^2 etc.).

- Mulliken population analysis and Natural Population Analysis (NPA)

- Orbital localization.

- Natural bond orbitals (NBOs).

- Distributed Multipole Analysis (A. J. Stone).

- Automatic geometry optimization as described in J. Comp. Chem. **18**, (1997), 1473. Constrained optimization is also possible.

- Automatic calculation of vibrational frequencies, intensities, and thermodynamic properties.

- Reaction path following, as described in Theor. Chem. Acc. **100**, (1998), 21.

- Efficient facilities to treat large lattices of point charges for QM/MM calculations, including lattice gradients.

- Various utilities allowing other more general optimizations, looping and branching (e.g., for automatic generation of complete potential energy surfaces), general housekeeping operations.

- Geometry output in XYZ, MOLDEN and Gaussian formats; molecular orbital and frequency output in MOLDEN format.

- Integral-direct implementation of all Hartree-Fock, DFT and pair-correlated methods (MP, CCSD, MRCI etc.), as described in Mol. Phys., **96**, (1999), 719. At present, perturbative triple excitation methods are not implemented.

- Local second-order Møller-Plesset perturbation theory (LMP2) and local coupled cluster methods, as described in in J. Chem. Phys. **104**, 6286 (1996), Chem. Phys. Lett. **290**, 143 (1998), J. Chem. Phys. **111**, 5691 (1999), J. Chem. Phys. **113**, 9443 (2000), J. Chem. Phys. **113**, 9986 (2000), Chem. Phys. Letters **318**, 370 (2000), J. Chem. Phys. **114**, 661 (2001), Phys. Chem. Chem. Phys. **4**, 3941 (2002), J. Chem. Phys. **116**, 8772 (2002).

- Local density fitting methods, as described in J. Chem. Phys. **118**, 8149 (2003), Phys. Chem. Chem. Phys. **5**, 3349 (2003), Mol. Phys. **102**, 2311 (2004).

- Analytical energy gradients for LMP2, DF-LMP2, and LQCISD as described in J. Chem. Phys. **108**, 5185, (1998), Phys. Chem. Chem. Phys. **3**, 4853 (2001), J. Chem. Phys. **121**, 737 (2004).

- Analytical energy gradients for CASSCF, CASPT2, MS-CASPT2, and XMS-CASPT2 as described in J. Chem. Phys. **119**, 5044 (2003). J. Chem. Phys. **135**, 081106 (2011), J. Chem. Phys., **138**, 104104 (2013).

- Explicitly correlated MP2-F12 and CCSD(T)-F12 methods, as described in J. Chem. Phys. **119**, 4607 (2003), J. Chem. Phys. **121**, 4479 (2004), J. Chem. Phys. **124**, 054114 (2006), J. Chem. Phys. **124**, 094103 (2006), J. Chem. Phys. **127**, 221106 (2007), J. Chem. Phys. **130**, 054104 (2009).

- Explicitly correlated local LMP2-F12 and LCCSD(T)-F12 methods, as described in J. Chem. Phys. **129**, 101103 (2009), J. Chem. Phys. **130**, 054106 (2009), J. Chem. Phys. **130**, 241101 (2009), J. Chem. Phys. **135**, 144117 (2011), Phys. Chem. Chem. Phys. **14**, 7591 (2012).

- Explicitly correlated multireference methods (CASPT2-F12, MRCI-F12), as described in J. Chem. Phys. **133**, 141103 (2010), J. Chem. Phys. **134**, 034113 (2011), J. Chem. Phys. **134**, 184104 (2011), Mol. Phys. **111**, 607 (2013).

- Parallel execution on distributed memory machines, as described in J. Comp. Chem. **19**, (1998), 1215. At present, SCF, DFT, MRCI, MP2, LMP2, CCSD(T), LCCSD(T) energies and SCF, DFT gradients are parallelized. Most density fitted codes such as DF-HF, DF-KS, DF-LMP2, DF-LMP2 gradients, DF-LCCSD(T), DF-MP2-F12, DF-DFT-SAPT, and GIAO-DF-HF NMR shieldings are also parallelized.

- Automatic *embarrassingly parallel* computation of numerical gradients and Hessians (`mppx Version`).

The program is written mostly in standard Fortran–90. Those parts which are machine dependent are maintained through the use of a supplied preprocessor, which allows easy interconversion between versions for different machines. Each release of the program is ported and tested on a number of systems. A large library of commonly used orbital basis sets is available, which can be extended as required. There is a comprehensive users' manual, which includes installation instructions. The manual is available in PDF and also in HTML for mounting on a Worldwide Web server.

More recent methods and enhancements include:

1. Explicitly correlated MP2-F12 (closed-shell) and RMP2-F12 (open-shell) methods with many many different ansätze, as described in *H.-J. Werner, T. B. Adler, and F. R. Manby*, J. Chem. Phys. **126**, 164102 (2007) and *G. Knizia and H.-J. Werner*, J. Chem. Phys. **128**, 154103 (2008).

2. Explicitly correlated CCSD(T)-F12 methods as described in *T. B. Adler, G. Knizia, and H.-J. Werner*, J. Chem. Phys. **127**, 221106 (2007) (closed-shell) and *G. Knizia, T. B. Adler, and H.-J. Werner*, J. Chem. Phys. **130**, 054104 (2009) (open-shell).

3. Explicitly correlated LMP2-F12 and LCCSD-F12 methods as described in *H.-J. Werner*, J. Chem. Phys. **129**, 101103 (2009), *T. B. Adler, H.-J. Werner*, and F. R. Manby, J. Chem. Phys. **130**, 054106 (2009), and *T. B. Adler and H.-J. Werner*, J. Chem. Phys. **130**, 241101 (2009).

4. Natural localized orbitals, NPA and NBO analysis and improved methods for domain selection in local correlation calculations as described in *R. A. Mata and H.-J. Werner*, Mol. Phys. **105**, 2753 (2007); see also *R. A. Mata and H.-J. Werner*, J. Chem. Phys. **125**, 184110 (2006).

5. Correlation regions in local correlation calculations as described in *R. A. Mata, H.-J. Werner and M. Schütz*, J. Chem. Phys. **128**, 144106 (2008).

6. Beyond LMP2 treatment of intermolecular pairs in local coupled cluster methods as described in *O. Masur, D. Usvyat and M. Schütz*, J. Chem. Phys., **139**, 164116 (2013), *M. Schütz, O. Masur and D. Usvyat*, J. Chem. Phys., **140**, 244107 (2014).

7. Automated calculation of anharmonic vibrational frequencies and zero-point energies using VCI methods as described in *T. Hrenar, H.-J. Werner, and G. Rauhut*, J. Chem. Phys. 126, 134108 (2007) and references therein.

8. Dynamical state weighting as described in *M. P. Deskevich and D. J. Nesbitt, and H.-J. Werner*, J. Chem. Phys. **120**, 7281 (2004).

9. Coupling of DFT and coupled cluster methods as described in *E. Goll, T. Leininger, F. R. Manby, A. Mitrushchenkov, H.-J. Werner, and H. Stoll*, Phys. Chem. Chem. Phys. 10, 3353 (2008) and references therein.

10. NMR chemical shifts, magnetizability, and rotational g-tensor using London atomic orbitals for density-fitted Hartree-Fock, and local MP2, as described in *S. Loibl, F.R. Manby, M. Schütz*, Mol. Phys. *108*, 1362 (2010), *S. Loibl, M. Schütz*, J. Chem. Phys. *137*, 084107 (2012), and *S. Loibl and M. Schütz*, J. Chem. Phys., **141**, 024108 (2014).

11. Local response methods (LCC2) for computing excitation energies and transition properties in large molecule as described in *D. Kats, T. Korona, M. Schütz*, J. Chem. Phys. *125*, 104106 (2006), *D. Kats, T. Korona, M. Schütz*, J. Chem. Phys. *127*, 064107 (2007), *D. Kats, M. Schütz*, J. Chem. Phys. *131*, 124117 (2009), and *K. Freundorfer, D. Kats, T. Korona, M. Schütz*, J. Chem. Phys. *133*, 244110 (2010).

12. LCC2 response and LADC(2) orbital relaxed properties and analytical nuclear gradients as described in *K. Ledermüller, D.Kats and M. Schütz*, J. Chem. Phys. *139*, 084111 (2013), *K. Ledermüller and M. Schütz*, J. Chem. Phys. *140*, 164113 (2014), *M. Schütz*, J. Chem. Phys. *142*, 214103 (2015).

13. Automatic basis set extrapolation.

14. Enhanced connections to other programs, including graphical display of output and 3-dimensional structures.

15. Support for Mac OS X

16. Ring-polymer instanton methods for rate and tunnelling-splitting calculations, as described in *J. O. Richardson and S. C. Althorpe*, J. Chem. Phys. **131**, 214106 (2009), and *ibid.* **134**, 054109 (2011).

17. Full Configuration Interation Quantum Monte Carlo (FCIQMC) as described in *G. H. Booth, A. J. W. Thom, and A. Alavi*, J. Chem. Phys. **131**, 054106 (2009), *D. M. Cleland, G. H. Booth, and A. Alavi*, J. Chem. Phys. **134**, 024112 (2011), and *G. H. Booth, D. M. Cleland, A. J. W. Thom, and A. Alavi*, J. Chem. Phys. **135**, 084104 (2011).

18. DMRG calculations through the BLOCK code of the Chan group.

Future enhancements presently under development include

- Analytical energy gradients for CCSD(T) and CCSD(T)-F12.

- Analytic second derivatives for DFT.

- New, more efficient MRCI methods for larger molecules.

These features will be included in the base version at later stages. The above list is for information only, and no representation is made that any of the above will be available within any particular time.

MOLPRO on the WWW

The latest information on MOLPRO, including program updates, can be found on the worldwide web at location `http://www.molpro.net/`.

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All publications resulting from use of this program must acknowledge the following two references.

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Some journals insist on a shorter list of authors; in such a case, the following should be used instead.

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1 HOW TO READ THIS MANUAL

This manual is organized as follows: The next chapter gives an overview of the general structure of MOLPRO. It is essential for the new user to read this chapter, in order to understand the conventions used to define the symmetry, records and files, orbital spaces and so on. The later chapters, which describe the input of the individual program modules in detail, assume that you are familiar with these concepts. The appendices describe details of running the program, and the installation procedure.

Throughout this manual, words in `Typewriter Font` denote keywords recognized by MOLPRO. In the input, these have to be typed as shown, but may be in upper or lower case. Numbers or options which must be supplied by the user are in *italic*. In some cases, various different forms of an input record are possible. This is indicated as [*options*], and the possible options are described individually in subsequent subsections.

2 RUNNING MOLPRO

On Unix systems, MOLPRO is accessed using the *molpro* unix command. The syntax is

`molpro`   [*options*] [*datafile*]

MOLPRO's execution is controlled by user-prepared data; if *datafile* is not given on the command line, the data is read from standard input, and program results go to standard output. Otherwise, data is taken from *datafile,* and the output is written to a file whose name is generated from *datafile* by removing any trailing suffix, and appending `.out`. If the output file already exists, then the old file is appended to the same name with suffix `.out_1`, and then deleted. This provides a mechanism for saving old output files from overwriting. Note that the above behaviour can be modified with the `-o` or `-s` options.

2.1 Options

Most options are not required, since sensible system defaults are usually set. Options as detailed below may be given, in order of decreasing priority, on the command line, in the environment variable MOLPRO_OPTIONS, or in the files `./molpro.rc`, `$HOME/.molprorc`, and `tuning.rc` in the library files directory.

`-d` *dir1:dir2:...*   where *dir1:dir2:...* is a list of directories which may be used for creating scratch files. Each of the directories should be writable by those who will use the program, and the directory specification may contain embedded environment variables in shell form, for example `$TMPDIR` or `/tmp/$USER`; these will be expanded at run time. If multiple scratch file systems are available, it is advantageous to present a list of directories of which there is one in each file system. Some parts of MOLPRO present extreme I/O demands, and it is therefore important to be careful in optimizing the provision and specification of scratch directories.

Note that in the building of `bin/molpro`, the environment variables `$TMPDIR`, `$TMPDIR2`, `$TMPDIR3,...` are used to construct the list of scratch directories for the `-d` option. Thus, these environment variables should at make time be filled with the names

of directories on each available scratch file system (cf. section A.2.3).

-o | --output *outfile* specifies a different output file.

-x | --executable *executable* specifies an alternative MOLPRO executable file.

-d | --directory *directory1*:*directory2...* specifies a list of directories in which the program will place scratch files. For detailed discussion of optimal specification, see the installation guide.

--backup *nfile* enables the saving of previous output files, up to a maximum of *nfile*. If *nfile* is omitted, it defaults to infinity. The names of the backup files are constructed by appending _ and a sequence number to the output file name, and both regular and xml-format files are processed, together with any log file.

-a | --append-backup Previous output files are concatenated by appending, instead of being kept separate.

--directory-backup Backup files are stored in a single separate subdirectory, named *datafile*.d, with subdirectories 01, 02, ... --directory-backup and --append-backup are mutually exclusive, and switching one of them on will force the other to be switched off.

--backup-directory *dir* In the case of --directory-backup, use *dir* as the location of backup files instead of the default.

-s | --nobackup disables the mechanism whereby an existing output file is saved.

-v | --verbose causes the procedure to echo debugging information; --noverbose selects quiet operation (default).

-k *key* where *key* is the licence key. This is normally not necessary since the key should be installed globally when installing MOLPRO.

-m | --memory *memory* specifies the working memory to be assigned to the program, in 8-byte words. For details, see section 4.6.

-I | --main-file-repository *directory* specifies the directory where the permanent copy of any integral file (file 1) resides. This may be a pathname which is absolute or relative to the current directory (e.g., '.' would specify the current directory). Normally, the -I directory should be equal to the -d working directory to avoid copying of large integral files, since after completion of the job the file will be copied to the directory given after -I. On some main frames, the scratch directory is erased automatically after a job has terminated, and in such cases a different -I directory, e.g., $HOME/int, can be specified (environment variables will be expanded at run time). In view of the large integral file sizes, this should be used with care, however. Note that in parallel runs with more than 1 processor the integral file will never be copied, and cannot be restarted.

-W | --wavefunction-file-repository *directory* is similar to --main-file-repository except that it refers to the directory for the wavefunction files (2,3 and 4). This determines the destination of permanent wavefunction (dump) files used for storing information like orbitals or CI-vectors etc. These files are essential for restarting a job. As explained for the integral files above, permanent wavefunction files will be copied to *directory* after completion of the job. The default for *directory* is $HOME/wfu.

-X | --xml-output   specifies that the output file will be a well-formed XML file suitable for automatic post-processing. Important data such as input, geometries, and results are tagged, and the bulk of the normal descriptive output is wrapped as XML comments. --no-xml-output switches off this behaviour and forces a plain-text output file to be produced.

-L | --library *directory* specifies the directory where the basis set library files (LIBMOL*) are found.

-1 | --file-1-directory *directory:directory:...* specifies the directory where the runtime file 1 will be placed, overriding --directory for this file only. -2, -3, -4, -5, -6, -7, -8 and -9 may be used similarly. Normally these options should not be given, since the program tries to use what is given in -d to optimally distribute the I/O.

-t | --omp-num-threads *n* Specify the number of OpenMP threads, as if the environment variable OMP_NUM_THREADS were set to *n*.

--xml2txt   Convert Molpro XML output file to plain text. In this mode the input file should refer to a Molpro XML output file.

--no-flush6   Don't flush the output, this might increase performance on some systems as the expense of being able to poll the output.

-g | --use-logfile   Use a separate logfile for more in-depth output.

--nouse-logfile   All output will be in the regular output file.

-E | --exclusive-file-implementation Specify file implementation. This is mainly for debugging, eg. reproducing non-shared file problems on a system with shared files, normally the default should be used.

--init   Run the initialization job, this is called as part of the build process and should not be used directly.

-k | --licence-token Specify licence token on the command line.

--version   Print Molpro version and exit

--sysid   For debugging when the getinfo.sh script does not give the correct sysid.

There are a number of other options, specific to parallel execution, which are summarized below and described in detail in the next section. All of the followng options are ignored when using serial MOLPRO.

-n | --tasks *tasks/tasks_per_node:smp_threads tasks* specifies the number of parallel processes to be set up.

-N | --task-specification *user1:node1:tasks1,user2:node2:tasks2... node1, node2* etc. specify the host names of the nodes on which to run.

-S | --shared-file-implementation *method* specifies the method by which the shared data are held in parallel.

--multiple-helper-server *nprocs_per_server* enables the multiple helper servers.

--node-helper-server specifies one helper server on every node.

--single-helper-server specifies only one single helper server for all processes.

--no-helper-server   disables the helper server.

`--all-outputs`	produces an output file for each process when running in parallel.
`--ga-debug`	activates GA debugging statements.
`--check-collective`	check collective operations when debugging
`--mpp`	run conventional parallel (default)
`--mppx`	run identical independent tasks parallel (eg. for frequencies).
`--gpu` | `--gpus` *n*	number of GPUs
`--tuning-mincuda` *n*	minimum dimension for using GPUs (CUDA), currently unused
`--nclearsp` *n*	for clearspeed, obsolete
`--tuning-mpplat` *n*	mpp latency in microseconds
`--tuning-mppspeed` *n*	mpp bandwidth in MB/sec
`-G` | `--global-memory` *n*	total amount of GA space initially allocated
`-M` | `--ga-stack` *n*	stack option to MA_init() call
`--ga-heap` *n*	heap option to MA_init() call

There are a number of other options for tuning and system parameters, but these do not usually concern the general user.

Tuning parameters for blas routines (mxma,, mxmb, mxva, mxvb):

`--tuning-flopdgm` *n*	speed of dgemm in MFLOPS
`--tuning-flopdgv` *n*	speed of dgemv in MFLOPS
`--tuning-flopmxm` *n*	speed of fortran mxma in MFLOPS
`--tuning-flopmxv` *n*	speed of fortran mxva in MFLOPS
`--tuning-mindgv` *n*	use dgemv from mxva/mxvb if matrix dimensions are ge. mindgv
`--tuning-mindgm` *n*	use dgemm from mxma/mxmb if all matrix dimensions are ge. mindgm
`--tuning-mindgc` *n*	use dgemm from mxma/mxmb if column dimension is ge. mindgc and other dimensions larger than mindgm2
`--tuning-mindgr` *n*	use dgemm from mxma/mxmb if row dimension is ge. mindgr and other dimensions larger than mindgm2
`--tuning-mindgl` *n*	use dgemm from mxma/mxmb if link dimension is ge. mindgl and other dimensions larger than mindgm2
`--tuning-mindgf` *n*	for old Fujitsu machines, probably obsolete

Tuning parameters for fortran versions of mxma/mxmb:

`--tuning-unroll` *n*	level of unrolling in (2,3, or 4)
`-b` | `--matrix-block-link` | `--tuning-mxmbln` *n*	block dimension for link dimension
`-B` | `--matrix-block` | `--tuning-mxmblk` *n*	block dimension for rows and columns of result matrix
`-K` | `--cache` | `--tuning-cache` *n*	cache size in words. If the total size of the 3 matrices is smaller than this, no blocking.

It is not usually necessary to specify any of these options as there are sensible defaults. Sometimes installation dependent options can be found in the system configuration file `molpro.rc` in the same directory as the MOLPROlibrary files.

2.2   Running MOLPRO on parallel computers

MOLPRO will run on distributed-memory multiprocessor systems, including workstation clusters, under the control of the Global Arrays parallel toolkit or the MPI-2 library. There are also some parts of the code that can take advantage of shared memory parallelism through the OpenMP protocol, although these are somewhat limited, and this facility is not at present recommended. It should be noted that there remain some parts of the code that are not, or only partly, parallelized, and therefore run with replicated work. Additionally, some of those parts which have been parallelized rely on fast inter-node communications, and can be very inefficient across ordinary networks. Therefore some caution and experimentation is needed to avoid waste of resources in a multiuser environment.

MOLPRO effects interprocess cooperation through the *ppidd* library, which, depending on how it was configured and built, draws on either the Global Arrays parallel toolkit or pure MPI. *ppidd* is described in Comp. Phys. Commun. 180, 2673-2679 (2009). Global Arrays handles distributed data objects using whatever one-sided remote memory access facilities are provided and supported. In the case of the MPI implementation, there is a choice of using either MPI-2 one-sided memory access, or devoting some of the processes to act as data 'helpers'. It is generally found that performance is significantly better, and competitive with Global Arrays, if at least one dedicated helper is used, and in some cases it is advisable to specify more. The scalable limit is to devote one core on each node in a typical multi-core cluster machine, but in most cases it is possible to manage with fewer, thereby making more cores available for computation. This aspect of configuration can be tuned through the `*-helper-server` options described below.

Molpro can be compiled in three different ways:

1. Serial execution only. In this case, no parallelism is possible at run time.

2. 'MPP': a number of copies of the program execute simultaneously a single task. For example, a single CCSD(T) calculation can run in parallel, with the work divided between the processors in order to achieve a reduced elapsed time.

3. 'MPPX': a number of copies of the program run in serial executing identical independent tasks. An example of this is the calculation of gradients and frequencies by finite difference: for the initial wavefunction calculation, the calculation is replicated on all processes, but thereafter each process works in serial on a different displaced geometry. At present, this is implemented only for numerical gradients and Hessians.

Which of these three modes is available is fixed at compilation time, and is reported in the job output. The options, described below, for selecting the number and location of processors are identical for MPP and MPPX.

2.2.1   Specifying parallel execution

The following additional options for the `molpro` command may be used to specify and control parallel execution.

`-n`│`--tasks` *tasks/tasks_per_node:smp_threads tasks* specifies the number of parallel processes to be set up, and defaults to 1. *tasks_per_node* sets the number of GA(or MPI-2) processes to run on each node, where appropriate. The default is installation dependent. In some environments (e.g., IBM running under Loadleveler; PBS batch job),

the value given by $-n$ is capped to the maximum allowed by the environment; in such circumstances it can be useful to give a very large number as the value for $-n$ so that the control of the number of processes is by the batch job specification. *smp_threads* relates to the use of OpenMP shared-memory parallelism, and specifies the maximum number of OpenMP threads that will be opened, and defaults to 1. Any of these three components may be omitted, and appropriate combinations will allow GA(or MPI-2)-only, OpenMP-only, or mixed parallelism.

-N | --task-specification *user1:node1:tasks1,user2:node2:tasks2... node1, node2* etc. specify the host names of the nodes on which to run. On most parallel systems, node1 defaults to the local host name, and there is no default for node2 and higher. On Cray T3E and IBM SP systems, and on systems running under the PBS batch system, if -N is not specified, nodes are obtained from the system in the standard way. *tasks1, tasks2* etc. may be used to control the number of tasks on each node as a more flexible alternative to $-n$ / *tasks_per_node*. If omitted, they are each set equal to $-n$ / *tasks_per_node*. *user1, user2* etc. give the username under which processes are to be created. Most of these parameters may be omitted in favour of the usually sensible default values.

-S | --shared-file-implementation *method* specifies the method by which the shared data are held in parallel. *method* can be *sf* or *ga*, and it is set automatically according to the properties of scratch directories by default. If *method* is manually set to *sf*, please ensure all the scratch directories are shared by all processes. Note that for GA version of MOLPRO, if *method* is set to *sf* manually or by default, the scratch directories can't be located in NFS when running molpro job on multiple nodes. The reason is that the SF facility in Global Arrays doesn't work well on multiple nodes with NFS. There is no such restriction for MPI-2 version of MOLPRO.

--multiple-helper-server *nprocs_per_server* enables the multiple helper servers, and *nprocs_per_server* sets how many processes own one helper server. For example, when total number of processes is specified as 32 and *nprocs_per_server* = 8, then every 8 processes(including helper server) will own one helper server, and there are 4 helper servers in total. For any unreasonable value of *nprocs_per_server* (i.e., any integer less than 2), it will be reset to a very large number automatically, and this will be equivalent to option --single-helper-server.

--node-helper-server specifies one helper server on every node if all the nodes are symmetric and have reasonable processes (i.e., every node has the same number of processes, and the number should be greater than 1), and this is the default behaviour. Otherwise, only one single helper server for all processes/nodes will be used, and this will be equivalent to option --single-helper-server

--single-helper-server specifies only one single helper server for all processes.

--no-helper-server disables the helper server.

-t | --omp-num-threads *n* Specify the number of OpenMP threads, as if the environment variable OMP_NUM_THREADS were set to *n*.

Note that options `--multiple-helper-server`, `--node-helper-server`, `--single-helper-server`, and `--no-helper-server` are only effective for MOL-PRO built with MPI-2 library. In the cases of one or more helper servers enabled, one or more processes act as data helper servers, and the rest processes are used for computation. Even so, it is quite competitive in performance when it is run with a large number of processes. In the case of helper server disabled, all processes are used for computation; however, the performance may not be good because of the poor performance of some existing implementations of the MPI-2 standard for one-sided operations.

In addition, for MOLPRO built with GA library (MPI over InfiniBand), GA data structures can't be too large (e.g., 2GB per node) when running `molpro` job on multiple nodes. In this case, setting environment variable ARMCI_DEFAULT_SHMMAX might be helpful. The number should be less than 2GB (e.g., to set 1600MB for ARMCI_DEFAULT_SHMMAX in bash: export ARMCI_DEFAULT_SHMMAX=1600). One can also use more computer nodes to run such jobs, thus allocated memory for GA data structures on each node becomes smaller. There is no such restriction for MPI-2 version of MOLPRO.

3 DEFINITION OF MOLPRO INPUT LANGUAGE

3.1 Input format

MOLPRO's execution is controlled by an input file. In general, each input record begins with a keyword, which may be followed by data or other keywords. Molpro input contains commands, directives, options and data. The commands and directives are sequentially executed in the order they are encountered. Furthermore, procedures can be defined anywhere in the input, which can include any number of commands and directives. They are only executed when called (which may be before or after the definition in the input file).

The input file can be written in free format. The following conversions take place:

, (comma)	move to next tab stop, i.e. this delimits input fields
; (semicolon)	end of record, i.e. a new record is started
! (exclamation mark)	ignore rest of input line (useful for comments)
――― (three dashes)	end of file (rest of input is ignored)

Input may be given upper or lower case. The input processor converts all characters to upper case. All integers are appended with "." (only floating point numbers are read by the program).

Several logical input records can actually be typed on one line and separated by semicolons, i.e., a given input line may contain many actual commands (separated by semicolons), or just one, as you prefer. These basic command units (records) delimited by semicolons are also frequently referred to as *cards* throughout this manual.

Exception to these general rules are:

***	first data line always
INCLUDE	include other input file
FILE	definition of named files
TEXT	prints text
TITLE	defines a title for the run or a table
CON	specifies orbital configurations
―――	last line of input

These commands always occupy a whole line. Using `INCLUDE` it is possible to open secondary input files. If an `INCLUDE` command is encountered, the new input file is opened and read until its end. Input is then continued after the include card in the first file. `INCLUDE`'s may be nested.

A MOLPRO input record (card) contains a number of input *fields*. Input fields may be up to 256 characters wide and contain either expressions or strings. The fields can be separated by commas or blanks. We recommend the general use of commas in order to avoid unexpected results.

Each line may start with a label. A label is separated from the body of the line by a colon (:). The colon is part of the label. The length of the label must not exceed 6 characters (including the colon) and the labels must be unique. Labels may be useful with `GOTO` commands. Example:

```
GOTO,START:
...
START: CCSD(T)
```

Here `START:` is a label, and `CCSD(T)` is a command.

Strings containing blanks can be entered using quotes. For instance, `'This is a string'` is interpreted as one string, but `This is a string` is a sequence of four strings in four subsequent fields. Strings in quotes are not converted to upper case.

Input lines may be concatenated using `\` at the end of the line(s) to be continued. Any number of lines may be concatenated up to a total length of 1024 characters (only 500 characters are possible on older IBM systems).

Filenames may be up to 31 characters long, provided that long filenames are supported by the Unix system used. An exception are older CRAY systems, which allow only 8 characters for the names of binary MOLPRO files.

3.2   Commands

A command invokes a particular program. It may be followed by local input for this program, enclosed in curley brackets[1]

The general format is either

`COMMAND,` *options*

or

`{ COMMAND,`*options*
directives
data
`}`

Examples for commands are `HF, MP2, CCSD(T), MCSCF, MRCI`. Examples for directives are `OCC, CLOSED, WF, PRINT`. Directives can be in any order, unless otherwise noted. Data can follow certain directives. For the format of options, directives and data see subsections 3.3, 3.5, and 3.6, respectively.

In the following, such a sequence of input will be denoted a *command block*. Special command blocks are the geometry and basis blocks.

The options given on the command line may include any options relevant to the current program. For instance, in DF-LMP2-R12 this could be options for density fitting, local, explicit, and/or thresholds. Alternatively, options can be specified on individual directives like

`DFIT,`*options*
`LOCAL,`*options*
`EXPLICIT,`*options*
`THRESH,`*options*

In these cases, only the options belong to the corresponding directive are valid; thus, if an option for `EXPLICIT` would be specified, e.g., on the `DFIT` directive, an error would result. This error would be detected already in the input prechecking stage.

---

[1]Depending on the parameter `STRICTCHECK` in file `lib/variable.registry` the program may tolerate directives given after commands without curley brackets. The program checks for ambiguities in the input. A directive is considered ambiguous if a command or procedure with the same name is known, and the directive is not in a command block (i.e., no curley brackets are used). `STRICTCHECK=0`: The input checker tolerates ambiguous directives if they are followed by a non ambiguous directive which is valid for the current command. `STRICTCHECK=1`: The input checker does not tolerate any ambiguous directives. `STRICTCHECK=2`: The input checker does not tolerate any directives outside curley brackets. The default is `STRICTCHECK=0`, which gives the maximum possible compatibility to previous Molpro versions.

As already mentioned, the use of curly brackets is normally compulsary if more than one input line is needed. In the case of one-line commands, curley brackets are needed as well if the next command or procedure has the same name as a directive valid for the current command.

Note: `DIRECT` and associated options cannot be specified on command lines any more.

3.3 Directives

Directives serve to specify input data and special options for programs. They start with a keyword, followed by data and/or options. The general format is

`DIRECTIVE,`*data*`,`*options*

The format of data and options is specified in the subsequent sections. Data must always be given before any options.

Examples for directives are

`OCC,CORE, CLOSED, WF, LOCAL, DFIT, ...`

3.4 Global directives

Certain directives can be given anywhere in the input, i.e. either inside or outside command blocks. If they are given inside of command blocks, the specified options are valid only locally for the current program. However, if they are given outside a command block, they act globally, and are used for all programs executed after the input has been encountered. Local options have preference over global options.

The following directives can be either local or global:

Wavefunction definition: `OCC,CORE, CLOSED, FROZEN, WF`
Thresholds and options: `LOCAL, DFIT, DIRECT, EXPLICIT, THRESH, PRINT, GRID`

If such options are given outside a command block, a context can be specifified

`DIRECTIVE,`*data*`,CONTEXT=`*context*`,`

e.g.,

`OCC,3,1,1,CONTEXT=HF`
`OCC,4,1,2,CONTEXT=MCSCF`

`CONTEXT` can be any valid command name (or any valid alias for this), but internally these are converted to one of the following: `HF` (Hartree-Fock and DFT), `MC` (MCSCF and CASSCF), `CC` (single reference correlation methods, as implemented in the CCSD program), `CI` (multireference correlation methods, as implemented in the MRCI program). The directive will then be applied to one of the four cases. Several contexts can be specified separated by colon, e.g.,

`CONTEXT=HF:CCSD`

If only a single context is given (no colon), shortcuts for the specifying the `CONTEXT` option are obtained by postfixing *context* to the command name, e.g.,

`OCC_HF,3,1,1`
`OCC_MCSCF,4,1,2`

If no context is given, the default is `HF`. The default occupations for single reference methods (e.g., MP2, CCSD) are the ones used in `HF`, the defaults for multireference methods (e.g. RS2, MRCI) correspond to those used in `MCSCF`.

3.5 Options

Options have the general form NAME[=*value*]

where value can be a number, and expression, or a string. Several options are separated by comma or blank. NAME must begin with a character [A-Z]. If options are given on a COMMAND line or on directives within a command block, they are valid only for the corresponding program (see Sec. 3.3). If options are given in a procedure, they are valid only in the procedure and procedures called from the current procedure; whenever a procedure is terminated, the options of the previous level are restored.

Options can also be single keywords, like SYM or NOSYM. In this case, the option is switched on or off, depending whether or not the key begins with NO. Alternatively, such logical options can also be set or unset using NAME=ON or NAME=OFF. For instance, SYM=OFF is equivalent to NOSYM. Furthermore, YES and NO are aliases for ON and OFF, respectively.

3.6 Data

Data are defined as a sequence of numbers, expressions, or strings, separated by commas or blanks. Generally, the order of data is essential. Empty fields are interpreted as zeros. Strings and variables must begin with a character [A-Z]. If + or − follows blank and directly precedes a number or variable it is interpreted as sign and not a binary operator. If there are no blanks before and after such operators, or blanks follow them, they are interpreted as binary operators. Examples:

```
3 − 4 4     yields [-1,4]
3−4 4       yields [-1,4]
3 −4 4      yields [3,-4,4]
3,−4 4      yields [3,-4,4]
3, −4, 4    yields [3,-4,4]
```

Expressions (including numbers) may contain variables.

Examples for the use of data: geometry and basis input, LATTICE, OCC, CLOSED, CORE, WF directives.

In some cases several lines of data are needed for a certain command or directive; in such cases the data must follow directly the corresponding command|directive, and must be enclosed in square brackets:

COMMAND,options
[*data*]

Normally, the input format of data is MOLPRO style, i.e., numbers are separated by commas, and variables as well as expressions can be used.

If data are included using external files, the input format of *data* is free format: no commas are needed, but no variables and expressions can be used.

3.7 Expressions

In any input field, data can be entered in the form of expressions. Numbers and variables are special cases of expressions. An expression is typed in Fortran style and may contain any number of nested parenthesis. The standard intrinsic functions are also available (see next section).

MOLPRO understands both arithmetic and logical expressions. The result of an arithmetic expression is a *real* (double precision) number. Internally, all integers are also converted to *real* numbers. The result of a logical expression is either `.TRUE.` or `.FALSE.`. Internally, `.TRUE.` is stored as a one (1.0), and `.FALSE.` as zero (0.0). Expressions may contain any number of variables.

The following standard operations can be performed :

expr + *expr*	Addition
expr − *expr*	Subtraction
expr * *expr*	Multiplication
expr / *expr*	Division
expr `.OR.` *expr*	Logical `OR`
expr `.AND.` *expr*	Logical `AND`
expr `.XOR.` *expr*	Exclusive `OR`
`.NOT.`*expr*	Logical `NOT`
expr `.GT.` *expr*	Greater Than
expr `.EQ.` *expr*	Equal
expr `.LT.` *expr*	Less Than
expr `.GE.` *expr*	Greater Equal
expr `.LE.` *expr*	Less Equal
expr `.NE.` *expr*	Not Equal
expr **expr*	Exponentiation
expr ˆ *expr*	Exponentiation
(*expr*)	Parenthesis (no effect)
−*expr*	Change sign
+*expr*	Keep sign (no effect)

3.8   Intrinsic functions

Expressions may contain the following intrinsic functions:

`ABS`(*expr*)	Absolute value
`MAX`(*expr*,*expr*, `...`)	Largest value of arbitrary number of numbers or expressions
`MIN`(*expr*,*expr*, `...`)	Smallest value of arbitrary number of numbers of expressions
`EXP`(*expr*)	Exponential
`LOG`(*expr*)	Natural Logarithm
`LOG10`(*expr*)	Common Logarithm
`SQRT`(*expr*)	Square Root
`NINT`(*expr*)	Next nearest integer
`INT`(*expr*)	Truncate to integer
`SIN`(*expr*)	Sine

`COS(`*expr*`)`	Cosine
`TAN(`*expr*`)`	Tangent
`ASIN(`*expr*`)`	Arcsine
`ACOS(`*expr*`)`	Arccosine
`ATAN(`*expr*`)`	Arctangent
`COSH(`*expr*`)`	Hyperbolic cosine
`SINH(`*expr*`)`	Hyperbolic sine
`TANH(`*expr*`)`	Hyperbolic tangent
`MOD(`*expr1*`,`*expr2*`)`	Remainder: `expr1-INT(expr1/expr2)*expr2`

Note: all trigonometric functions use or produce angles in degrees.

3.9   Variables

3.9.1   Setting variables

Data and results can be stored in MOLPRO variables. Variables can be of type string, floating, or logical and may be used anywhere in the input.

The syntax for setting variables is

`VARNAME1=`*expression* [unit]`,VARNAME2=`*expression* [unit]

where unit is optional. If a variable is undefined, zero is assumed.

Variables are useful for running the same input with different actual parameters (e.g. geometries or basis function exponents), and to store and manipulate the results. *Arrays* are variables with an index in parenthesis, e.g., `var(1)`. The number of elements in an array `var` is `#var`. The array length can be reset to zero by the `CLEAR` directive or simply by modifying `#var`. Variables and variable arrays may be displayed at any place in the output by the `SHOW` command, and whole tables of variables can be generated using the `TABLE` command. For more details about variables see section 8.

3.9.2   String variables

Special care is necessary when using strings. In order to avoid unexpected results, either a $ has to be prefixed whenever a string variable is set, or the string has to be given in quotes. Possible forms are

`$name=`string
`name=`'string'
`name=`*string variable*
`$name=`*string variable*

Examples:

```
 string1='This is a string'  !define a string variable. Text in quotes is not
                             ! converted to upper case.
 string2=string1             !assign string variable string1 to a new variable.
 $string3=string1            !equivalent to previous case.
 $string4=mystring           !define a string variable. Since ''mystring'' is not
                             !given in quotes, !it will be converted to upper case.
 string5=mystring            !string5 will not be a string variable since $ is missing.
```

yields

```
SETTING STRING1        =     This is a string
SETTING STRING2        =     This is a string
SETTING STRING3        =     This is a string
SETTING STRING4        =     MYSTRING
VARIABLE MYSTRING UNDEFINED, ASSUMING 0
SETTING STRING5        =            0.00000000
```

For more information concerning strings and string variables, see section 8.3

3.10 Procedures

3.10.1 Procedure definition

Procedures are sequences of commands and/or options. They can be defined anywhere in the input as

[PROC]*procname*={
command blocks
directives
}

or

PROC *procname*
command blocks
directives
ENDPROC

In order to avoid unexpected results, *procname* must differ from all known command names. Procedures must not contain geometry blocks.

Note that procedures are not executed when encountered in the input, but only when called. Procedure definitions must not be nested. Procedures can contain procedure calls up to a nesting level of 10.

3.10.2 Procedure calls

Procedures can be called anywhere in the input. The syntax is the same as for commands (cf. section 3.2), except that the procedure name replaces the command name.

PROCEDURE

No options are allowed on procedure calls. However, specific options may be set using directives within the procedure, and these are then valid for all programs within the procedure which follow the directive. When execution of the procedure is finished, the previous global options are restored. The hierarchy in which options are processed is as follows:

Global options
Options in procedures
Command line options
Options given on directives within a command block

The last option set is then actually used. Thus, options specified on command lines or within command blocks have preference over procedure options, and procedure options have preference over global options.

4 GENERAL PROGRAM STRUCTURE

This chapter gives an overview of the most important features of MOLPRO. For the new user, it is essential to understand the strategies and conventions described in this section, in particular the meaning of *files* and *records*, and the use of *symmetry*. This chapter will focus on general aspects; detailed information about each command will be given in later chapters. Information about commands and parameters can also be obtained using the MOLPRO help facility (see section 4.13).

4.1 Input structure

A typical MOLPRO input has the following structure:

```
***,title                    !title (optional)
memory,4,m                   !memory specification (optional)
file,1,name.int              !permanent named integral file (optional)
file,2,name.wfu              !permanent named wavefunction file (optional)

gprint,options               !global print options (optional)
gthresh,options              !global thresholds (optional)
gdirect[,options]            !global direct (optional)
gexpec,opnames               !global definition of one-electron operators (optional)

basis=basisname              !basis specification. If not present, cc-pVDZ is used
geometry={...}               !geometry specification

var1=value,var2=value,...    !setting variables for geometry and/or wavefunction definitions

{command,options             !program or procedure name
 directive,data,option       !directives for command (optional)
...
}                            !end of command block
---                          !end of input (optional)
```

If the memory card is given, it should be the first card (after the optional title card). If any file cards are given, they should follow immediately. The order of `basis`, `geometry`, `gprint`, `gdirect`, `gthresh`, `gexpec`, and variable definitions is arbitrary. It is possible to call several programs one after each other. It is also possible to redefine basis set and/or geometry between the call to programs; the program will recognize automatically if the integrals have to be recomputed.

4.2 Files

MOLPRO uses three sequential text files, namely the *input file*, the *output file*, and the *punch file*. The punch file is a short form of the output which contains the most important data and results, such as geometries, energies, dipole moments, etc. The punch file can be processed by the separate program *READPUN*, which selects specific results by keywords and is able to produce ordered tables in user supplied format. Furthermore, there are up to 9 binary MOLPRO

files available, each one known to the program simply by its number (1 to 9). By default, they are temporary files, usually allocated dynamically by the program, but they can be connected to permanent files with the `FILE` command. Each file is direct access, and word addressable (word=64 bit usually), but is organised in *records* of any length. The name, address and length of each record is held in a directory at the start of the file.

File 1 is the *main file*, holding basis set, geometry, and the one and two electron integrals. By default, file 2 is the *dump file* and used to store the wavefunction information, i.e. orbitals, CI coefficients, and density matrices. File 3 is an auxiliary file which can be used in addition to file 2 for restart purposes. Often files 1 and 2 (and 3) are declared as permanent files (see `FILE`) to enable restarts. Storing the wavefunction information on file 2 is useful, since the integral file is overwritten at each new geometry, while the orbitals and CI coefficients of one calculation can be used as a starting guess for the next calculation at a neighbouring geometry. Files 4 to 8 are used as scratch space, e.g., for sorting the integrals, storage of transformed integrals and of the CI vectors. These files should normally not be made permanent.

Note that the file name appearing in molpro input is always converted to lower case on unix machines.

4.3   Records

Record names are positive integers, and are usually referred to in the format *record.file*, e.g., 2100.2 means the record called 2100 on file 2. Note that these names are quite arbitrary, and their numerical values have nothing to do with the order of the records in the file. Record names ≤ 2000 are reserved for standard quantities (e.g. integrals, properties etc.) and you should never use these in an input, unless you know exactly what you are doing. Some important default records to remember are

2100	RHF dump record (closed and open-shell)
2200	UHF dump record
2140	MCSCF dump record
4100	CPHF restart information
5000	MCSCF gradient information
5100	CP-MCSCF gradient information
5200	MP2 gradient information
5300	Hessian restart information
5400	Frequencies restart information
6300	Domain restart information

If an input contains several wavefunction calculations of the same type, e.g., several MCSCF calculations with different active spaces, the record number will be increased by 1 for each calculation of the same type. Thus, the results of the first SCF calculation in an input are stored in dump record 2100.2, the second SCF in record 2101.2, the first MCSCF in 2140.2, the second MCSCF in 2141.2 and so on. Note that these numbers refer to the occurrence in the input and not on the order in which the calculations are performed in the actual run. If an input or part of it is repeated using `DO` loops, this ensures that each calculation will start with the orbitals from the corresponding orbitals from the previous cycle, as long as the order of the commands in the input remains unchanged. If for instance the first SCF would be skipped in the second cycle using some `IF` / `ENDIF` structure, the second SCF would still use record 2101.2. Thus, under

most circumstances the program defaults are appropriate, and the user does not have to specify the records.

After a restart this logic will still work correctly if the number and sequence of `SCF` and `MCSCF` commands is kept unchanged. Thus, if you want to skip certain parts of the input after a restart, it is recommended to use `IF` / `ENDIF` structures or the `GOTO` command rather than to delete or comment certain commands. If for some reason this is not possible, the `START` and `ORBITAL` directives can be used to specify explicitely the records to be used.

In general we recommend the use of program defaults whenever possible, since this minimizes the probability of input errors and frustration!

After completion of each program step, MOLPRO prints a summary of the records on each file.

4.4   Restart

Information from the permanent files is automatically recovered in subsequent calculations. This can be controlled using the `RESTART` directive.

4.5   Data set manipulation

It is possible to truncate files and rename or copy records using the `DATA` command. Several standard matrix operations can be performed with `MATROP`, e.g., printing records, linearly combining or multiplying matrices, or forming the trace of a product of two matrices.

4.6   Memory allocation

MOLPRO can allocate memory dynamically as required by the user. Thus it is not necessary to maintain different versions of the program with different memory sizes. There are two ways to specify the memory: (1) `MEMORY` card in MOLPRO input file; (2) option `-m` or `--memory` in MOLPRO command line. If memory is specified using both methods at the same time, `MEMORY` card will take precedence. If both ways are omitted, the program will use a default memory size (currently it is 8000000 words, i.e. 64000000 bytes). Please note that: (1) memory specification is in words. 1 word is 8 bytes (i.e., the memory size to store one double precision data). (2) memory specification is for each process.

4.6.1   Memory card in input file

`MEMORY,`*n,scale*`;`

If *scale* is given as `K`, *n* is multiplied by 1000; if *scale* is `M`, *n* is multiplied by 1 000 000; if *scale* is `G`, *n* is multiplied by 10^9. The *scale* is case insensitive. So there is no difference between `M` and `m` (`K` and `k`, or `G` and `g`).

Note: The `MEMORY` card must precede all `FILE` cards!

Examples:

`MEMORY,90000`	requests 90 000 words of memory
`MEMORY,500,K`	requests 500 000 words of memory
`MEMORY,2,M`	requests 2 000 000 words of memory

`MEMORY,100,M`	requests 100 000 000 words of memory
`memory,100,m`	requests 100 000 000 words of memory
`MEMORY,1,G`	requests 10^9 words of memory

4.6.2   Memory option in command line

`-m` | `--memory` *n*`scale`

The `scale` (`k`, `m`, `g` and `K`, `M`, `G`) is case sensitive, lower case for decimal and upper case for binary. `k`, `m`, `g` stand for 1000, 1000 000 and 10^9; `K`, `M`, `G` stand for 2^{10}, 2^{20} and 2^{30}.

Examples:

`-m 1k`	requests 1000 words of memory
`-m 1K`	requests 1024 words of memory
`-m 1m`	requests 1000000 words of memory
`-m 1M`	requests 1048576 words of memory
`-m 1g`	requests 10^9 words of memory
`-m 1G`	requests 2^{30} words of memory

4.6.3   Memory in parallel

The memory specification is for each process. So the total requested memory in parallel calculation will be the specified memory amount multiplied by the number of compute processes. For example, specifying $100*10^6$ words for a job with 4 compute processes:

| `memory,100,m` | in input file |
| `-m 100m` | in command line |

the total requested memory will be $100*10^6*8*4 = 3.2*10^9$ bytes.

4.7   Multiple passes through the input

It is possible to perform loops over parts of the input using `DO` loops, very much as in `FORTRAN` programs. `DO` loops may be nested to any reasonable depth. This can be conveniently used, for instance, to compute automatically whole potential energy surfaces.

4.8   Symmetry

MOLPRO can use Abelian point group symmetry only. For molecules with degenerate symmetry, an Abelian subgroup must be used — e.g., C_{2v} or D_{2h} for linear molecules. The symmetry group which is used is defined in the integral input by combinations of the symmetry elements *x*, *y*, and *z*, which specify which coordinate axes change sign under the corresponding generating symmetry operation. It is usually wise to choose *z* to be the unique axis where appropriate (essential for C_2 and C_{2h}). The possibilities in this case are shown in Table 1.

Table 1: The symmetry generators for the point groups

Generators	Point group
(null card)	C_1 (i.e. no point group symmetry)
X (or Y or Z)	C_s
XY	C_2
XYZ	C_i
X,Y	C_{2v}
XY,Z	C_{2h}
XZ,YZ	D_2
X,Y,Z	D_{2h}

Table 2: Numbering of the irreducible representations in D_{2h}

No.	Name	Function
1	A_g	s
2	B_{3u}	x
3	B_{2u}	y
4	B_{1g}	xy
5	B_{1u}	z
6	B_{2g}	xz
7	B_{3g}	yz
8	A_u	xyz

Normally, MOLPRO determines the symmetry automatically, and rotates and translates the molecule accordingly. However, explicit symmetry specification is sometimes useful to fix the orientation of the molecule or to use lower symmetries.

The irreducible representations of each group are numbered 1 to 8. Their ordering is important and given in Tables $2-4$. Also shown in the tables are the transformation properties of products of x, y, and z. s stands for an isotropic function, e.g., s orbital, and for these groups, this gives also the transformation properties of x^2, y^2, and z^2. Orbitals or basis functions are generally referred to in the format *number.irrep*, i.e. 3.2 means the third orbital in the second irreducible representation of the point group used.

4.9   Defining the wavefunction

In all program modules where such information is required, the total symmetry of the *N*-electron wavefunction is defined on WF (wavefunction) cards in the following way:

Table 3: Numbering of the irreducible representations in the four-dimensional groups

	C_{2v}		C_{2h}		D_2	
No.	Name	Function	Name	Function	Name	Function
1	A_1	s,z	A_g	s,xy	A	s
2	B_1	x,xz	A_u	z	B_3	x,yz
3	B_2	y,yz	B_u	x,y	B_2	y,xz
4	A_2	xy	B_g	xz,yz	B_1	xy

Table 4: Numbering of the irreducible representations in the two-dimensional groups

	C_s		C_2		C_i	
No.	Name	Function	Name	Function	Name	Function
1	A'	s,x,y,xy	A	s,z,xy	A_g	s,xy,xz,yz
2	A''	z,xz,yz	B	x,y,xz,yz	A_u	x,y,z

`WF,`*nelec,irrep,spin*

or, alternatively

`WF,[NELEC=`*nelec*`],[SYM[METRY]=`*irrep*`],[spin=`*spin*`],[CHARGE=`*charge*`]`

where *nelec* is the total number of electrons, *irrep* is the number of the irreducible representation, and *spin* equals $2 \times S$, where S is the total spin quantum number. Instead of *nelec* also *charge* can be given, which specifies the total charge of the molecule. For instance, for a calculation in C_{2v} symmetry with 10 electrons, `WF,10,3,0` denotes a $^1B_2$ state, and `WF,10,1,2` a $^3A_1$ state. The charge can also be defined by setting the variable `CHARGE`:

`SET,CHARGE=`*charge*

This charge will be used in all energy calculations following this input. Note that `SET` is required, since `CHARGE` is a system variable (cf. section 8.4).

Although in principle each program unit requires a `WF` command, in practice it is seldom necessary to give it. The program remembers the information on the `WF` card, and so one might typically specify the information in an SCF calculation, but then not in subsequent MCSCF or CI calculations; this also applies across restarts. Furthermore, *nelec* defaults to the sum of the nuclear charges, *irrep* to 1 and *spin* to 0 or 1; thus in many cases, it is not necessary to specify a `WF` card at all.

If the `WF` directive is given outside an command input block, it is treated as global, i.e., the given values are used for all subsequent calculations. Setting the variables `NELEC`, `SPIN`, or `SYMMETRY`, has the same effect giving these on a global `WF` directive. If the global `WF` directive is given after the variable definition, the values of the variables are replaced by the values given on the `WF` directive. Vice versa, if a variable definition follows a global `WF` directive, the new value of the variable is used in the following. Note that `WF` input cards in command blocks have preference over global `WF` directives or input variables.

4.10 Defining orbital subspaces

In the SCF, MCSCF, and CI programs it may be necessary to specify how many orbitals in each symmetry are *occupied* (or *internal* in CI), and which of these are *core* or *closed shell* (doubly occupied in all CSFs). This information is provided on the OCC, CORE, and CLOSED cards in the following way:

OCC,$m_1, m_2, \ldots, m_8$; CORE,$co_1, co_2, \ldots, co_8$; CLOSED,$cl_1, cl_2, \ldots, cl_8$; FROZEN,$fr_1, fr_2, \ldots, fr_8$;

where m_i is the number of occupied orbitals (including core/frozen and closed), co_i the number of core orbitals, and cl_i is the number of closed-shell orbitals (including the core orbitals) in the irreducible representation i. In general, $m_i \geq cl_i$, and $cl_i \geq co_i$. It is assumed that these numbers refer to the first orbitals in each irrep. FROZEN only exists in the MCSCF program and denotes frozen core orbitals that are not optimized (note that in older MOLPRO versions frozen core orbitals were denoted CORE).

Note that the OCC and CLOSED cards have slightly different meanings in the SCF, MCSCF and CI or CCSD programs. In SCF and MCSCF, *occupied* orbitals are those which occur in any of the CSFs. In electron correlation methods (CI, MPn, CCSD etc), however, OCC denotes the orbitals which are occupied in any of the *reference* CSFs. In the MCSCF, FROZEN orbitals are doubly occupied in all CSFs and *frozen* (not optimized), while *closed* denotes all doubly occupied orbitals (frozen plus optimized). In the CI and CCSD programs, *core* orbitals are those which are not correlated and *closed* orbitals are those which are doubly occupied in all reference CSFs.

OCC, CORE and CLOSED directives are generally required in each program module where they are relevant; however, the program remembers the most recently used values, and so the directives may be omitted if the orbital spaces are not to be changed from their previous values. Note that this information is also preserved across restarts. Note also, as with the WF information, sensible defaults are assumed for these orbital spaces. For full details, see the appropriate program description.

The orbital spaces may also be defined outside command blocks, and then the directive is treated as global, i.e., it is used in all subsequent programs. Spaces specific to certain wavefunction types can be defined by specifying the program name with a CONTEXT option, e.g.,

OCC,4,2,1,CONTEXT=MULTI

Alternatively, the context can be appended to the directive name with an underscore. For example

OCC_MULTI,4,2,1

is equivalent to the previous form.

Local input given within command blocks has preference over global input.

4.11 Selecting orbitals and density matrices (ORBITAL, DENSITY)

As outlined in section 4.3, the information for each SCF or MCSCF calculation is stored in a *dump record*. Dump records contain orbitals, density matrices, orbital energies, occupation numbers, fock matrices and other information as wavefunction symmetries etc. Subsequent calculation can access the orbitals and density matrices from a particular record using the ORBITAL and DENSITY directives, respectively. These input cards have the same structure in all programs. The general format of the ORBITAL and DENSITY directives is as follows:

ORBITAL[, [RECORD=]*record*] [, [TYPE=]*orbtype*] [, STATE=*state*] [, SYM[METRY]=*symmetry*]
[, SPIN=*spin*] [, MS2=*ms2*] [, [N]ELEC=*nelec*] [, SET=*iset*] [, OVL] [, NOCHECK] [, IGNORE[_ERROR]]

DENSITY[, [RECORD=]*record*] [, [TYPE=]*dentype*] [, STATE[B]=*stateb*] [, SYM[B]=*symb*]
[, SPIN[B]=*spinb*] [, MS2[B]=*ms2b*] [, STATEK=*statek*] [, SYMK=*symk*] [, SPINK=*spink*]
[, MS2K=*ms2k*] [, [N]ELEC=*nelec*] [, SET=*iset*]

where the (optional) specifications can be used to select specific orbitals or densities, if several different orbital sets are stored in the same record. If a specification is not given, it is not checked and the last written set that fullfills all other criteria is used. The meaning of the individual specifications are as follows:

orbtype	Orbital type. This can be one of CANONICAL: canonical or pseudo-canonical orbitals; NATURAL: natural orbitals; LOCAL: localized orbitals; LOCAL(PM): localized Pipek-Mezey orbitals; LOCAL(BOYS): localized Boys orbitals; PROJECTED: projected virtual orbitals used in local calculations. Without further specification, the most recently computed orbitals of the specified type are used. If the orbital type is not specified, the program will try to find the most suitable orbitals automatically. For instance, in MRCI calculations NATURAL orbitals will be used preferentially if available; MRPT (CASPT2) calculations will first search for CANONICAL orbitals, and local calculations will first look for LOCAL orbitals. Therefore, in most cases the orbital type needs not to be specified.
state	Specifies a particular state in the form *istate.isym*. For instance, 2.1 refers to the second state in symmetry 1. This can be used if density matrices or natural orbitals have been computed for different states in a state-averaged CASSCF calculation. If not given, the last written orbitals are used. A state-averaged density can be selected using STATE=AV[ERAGED]. The specification of *isym* is optional; it can also be defined using the SYMMETRY key.
dentype	Density type. This can be one of CHARGE: charge density; SPIN: UHF spin density; TRANSITION: transition density matrix; The default is CHARGE.
symmetry	Specifies a particular state symmetry. Alternatively, the state symmetry can be specified using STATE (see above).
spin	Spin quantum number, i.e. 0 for singlet, 1/2 for doublet, 1 for triplet, etc. Alternatively MS2 can be used.
ms2	$2M_S$, i.e. 0 for singlet, 1 for doublet, 2 for triplet etc. Alternatively, SPIN can be used.
nelec	Number of electrons.
iset	Set number of orbitals. The orbital sets are numbered in the order they are stored.

In some cases (e.g. in MATROP) transition density matrices can be specified. In this case STATEB, SYMB, MS2B, SPINB refer to the bra state and STATEK, SYMK, MS2K, SPINK refer to the ket state. If bra and ket differ, TYPE=TRANSITION is implied, and SYMMETRY is automatically set to the product symmetry of bra and ket. If STATEK, SYMK, MS2K, SPINK are not given, they are assumed to be equal to the corresponding bra quantities. See section 65 for examples.

If OVL is specified, the starting orbitals are obtained by maximizing the overlap with previous orbitals. By default, this is used if the basis dimension of the previous orbitals is different then the current one. If OVL is specified this procedure is used even if the basis dimensions are the same, which is occasionally useful if the contraction scheme changed.

If NOCHECK is specified, some consistency checks for finding correct orbitals are skipped, and error messages like "ORBITALS CORRESPOND TO DIFFERENT GEOMETRY" are ignored.

If IGNORE_ERROR is specified, MPn or triples calculations can be forced with other than canonical orbitals. Note that this can lead to meaningless results! Note that in MULTI IGNORE_ERROR must be given on the START directive, since in this program ORBITAL is used to define the new orbitals.

If any of the above options are given, they must be obeyed strictly, i.e., the program aborts if the request cannot be fulfilled.

Examples:

```
ORBITAL,2100.2                       !Use SCF orbitals
ORBITAL,2140.2                       !Use (state-averaged) MCSCF orbitals
ORBITAL,2140.2,CANONICAL             !use canonical MCSCF orbitals
ORBITAL,2140.2,NATURAL,STATE=2.1     !use natural MCSCF orbitals for second state in sym. 1
```

4.12 Summary of keywords known to the controlling program

This is a summary of all keywords presently implemented in the controlling program. Each module knows further keywords, which are described in the chapters about the individual programs. For detailed information about the use of the commands listed below, consult the following chapters.

Program control:

`***`	indicates start of a new calculation
`MEMORY`	allocates dynamic memory
`PUNCH`	opens a punch file
`FILE`	connects units to permanent files
`RESTART`	recovers file information
`INCLUDE`	includes other input files
`BASIS`	can be used to define default basis sets
`GEOMETRY`	can be used to specify the geometry
`ZMAT`	can be used to define the Z-matrix
`PARALLEL`	can be used to control parallelization
`STATUS`	checks status of program steps
`PRINT,GPRINT`	controls global print levels
`THRESH,GTHRESH`	controls global thresholds
`DIRECT,GDIRECT`	flags direct computation of integrals and for setting direct options
`EXPEC,GEXPEC`	controls computation of expectation values
`TEXT`	prints text
`EXIT`	stops execution
`DO`	controls do loops
`ENDDO`	end of do loops
`IF`	controls conditional actions
`ELSEIF`	controls conditional actions
`ENDIF`	end of `IF block`
`GOTO`	used to skip part of input and for loops over input
`LABEL`	no action
`DATA`	data set management
`DELETE, ERASE`	data set deletion
`MATROP`	performs matrix operations
`GRID`	Define grid
`CUBE`	Dump data to grid
`CARTESIAN`	Use cartesian basis functions
`SPHERICAL`	Use spherical harmonic basis functions
`USER`	calls user-supplied subroutine
`---`	last line of input

Variables:

`SET`	sets variables (obsolete)
`SETI`	sets variables or numbers to their inverse (obsolete)
`SETA`	sets variable arrays (obsolete)
`CLEAR`	clears variables

`CLEARALL`	clears all variables
`GETVAR`	recovers variables from file
`SHOW`	displays the values of variables
`TABLE`	prints tables

Wave function optimization:

`INT`	calls the machine default integral program. This is optional and needs not to be given.
`LSINT`	calls the spin-orbit integral program
`SORT`	calls two-electron sorting program. This is called automatically and needs not to be given
`CPP`	compute core polarization potential integrals
`HF`, `RHF`, `HF-SCF`, or `RHF-SCF`	calls spin-restricted Hartree-Fock program (open or closed shell)
`UHF` or `UHF-SCF`	calls spin-unrestricted Hartree-Fock program
`DFT`	calls the density functional program
`KS`, `RKS`	call the Kohn-Sham spin restricted density functional program
`UKS`	call the Kohn-Sham spin-unrestricted density functional program
`MULTI`, `MCSCF`, or `CASSCF`	calls MCSCF/CASSCF program
`CASVB`	calls the CASVB valence bond program
`CI`, `MRCI`, or `CI-PRO`	calls internally contracted MRCI program
`MRCI-F12`	calls the explicitly correlated internally contracted MRCI program
`CIPT2`	calls internally contracted CIPT2 program
`ACPF`, `AQCC`	calls internally contracted MR-ACPF program
`CEPA`	calls single-reference CEPA program (closed- or open-shell)
`RS2`, `RS3`	calls internally contracted multireference perturbation theory program
`RS2-F12`	calls the explicitly correlated multireference perturbation theory program
`RS2C`	faster program for internally contracted multireference perturbation theory
`MP2`	calls closed-shell MP2 program
`MP3`	calls closed-shell MP3 program
`MP4`	calls closed-shell MP4 program
`CISD`	calls closed-shell CISD program
`CCSD`	calls closed-shell coupled cluster program
`BCCD`	calls closed-shell Brueckner CCD program
`QCI`,`QCSID`	calls closed-shell quadratic configuration interaction program
`UCCSD`	calls spin-unrestricted open-shell coupled cluster program
`RCCSD`	calls spin-restricted open-shell coupled cluster program
`FCI` or `FULLCI`	calls determinant based full CI program

Local correlation methods:

`LMP2`	calls closed-shell local MP2 program

`LMP3`	calls closed-shell local MP3 program
`LMP4`	calls closed-shell local MP4 program
`LCISD`	calls closed-shell local CISD program
`LCCSD`	calls closed-shell local coupled cluster program

Explicitly correlated methods:

`DF-MP2-R12`	MP2-R12 program with density fitting
`DF-MP2-F12`	MP2-F12 program with density fitting
`DF-LMP2-R12`	Local MP2-R12 program with density fitting
`DF-LMP2-F12`	Local MP2-F12 program with density fitting

Orbital manipulation:

`LOCALI`	calls orbital localization program
`MERGE`	calls orbital manipulation program

Properties and wavefunction analysis:

`POP`	calls population analysis program
`DMA`	calls distributed multipole analysis program
`PROPERTY`	calls properties program
`DIP`	adds dipole field to h
`QUAD`	adds quadrupole field to h
`LATTICE`	read or disable lattice of point charges

Gradients and geometry optimization:

`FORCES`	calls gradient program
`OPTG`	performs automatic geometry optimization
`MIN`	performs energy minimization with respect to some parameters
`PUT`	print or write geometry to a file
`HESSIAN`	calculate Hessian
`FREQUENCY`	calculate vibrational frequencies
`MASS`	define atomic masses
`DDR`	evaluates approximate non-adiabatic coupling matrix elements

The command names for single reference coupled cluster methods `QCISD, CCSD, LQCISD,` `LCCSD` can be appended by `(T)` and then a perturbative correction for triple excitations will be computed (e.g., `CCSD(T)`).

`HF, KS, MP2` and all local correlation methods can be prepended by `DF-` to invoke density fitting.

4.13 MOLPRO **help**

The help command can be used to obtain a short description of commands, input parameters, and variables. The syntax is:

`HELP`,*set*,*name*,[*keys*]

where *set* is either COMMAND, VARIABLE, or the name of the input set (e.g., THRESH, PRINT, LOCAL, EOM, CFIT), and *name* is the name of the parameter. If *name* is blank, all parameters of the set are shown. Optionally, *keys* can be specified to request specific information (e.g., short_description, long_description, default_value, type, program). If *keys* are not given, short_description is assumed.

Currently, help is only available for a limited number of parameters and commands. However, the database will be extended in the near future.

5 INTRODUCTORY EXAMPLES

This section explains some very simple calculations in order to help the new user to understand how easy things can be.

5.1 Using the molpro command

1. Perform a simple SCF calculation for molecular hydrogen. The input is typed in directly and the output is sent to the terminal:

   ```
   molpro <<!
   basis=vdz;
   geometry={angstrom;h1;h2,h1,.74}
   hf
   !
   ```

2. The same calculation, with the data taken from the file h2.com. The output is sent to h2.out. On completion, the file h2.pun is returned to the current directory and the file h2.wf to the directory $HOME/wfu (this is the default):

   ```
   molpro h2.com
   ```

   h2.com contains:

   ```
   ***,H2
   file,2,h2.wf,new;
   punch,h2.pun;
   basis=vdz;
   geometry={angstrom;h1;h2,h1,.74}
   hf
   ```

   ```
   http://www.molpro.net/info/current/examples/h2.com
   ```

3. As before, but the file h2.wf is sent to the directory /tmp/wfu:

   ```
   molpro -W /tmp/wfu h2.com
   ```

5.2 Simple SCF calculations

The first example does an SCF calculation for H_2O, using all possible defaults.

```
***,h2o                  !A title
r=1.85,theta=104         !set geometry parameters
geometry={O;             !z-matrix geometry input
         H1,O,r;
         H2,O,r,H1,theta}
hf                       !closed-shell scf
```

http://www.molpro.net/info/current/examples/h2o_scf.com

In the above example, the default basis set (VDZ) is used. We can modify the default basis using a BASIS directive.

```
***,h2o cc-pVTZ basis    !A title
r=1.85,theta=104         !set geometry parameters
geometry={O;             !z-matrix geometry input
         H1,O,r;
         H2,O,r,H1,theta}
basis=VTZ                !use VTZ basis
hf                       !closed-shell scf
```

http://www.molpro.net/info/current/examples/h2o_scf_vtz.com

5.3 Geometry optimizations

Now we can also do a geometry optimization, simply by adding the card OPTG.

```
***,h2o                  !A title
r=1.85,theta=104         !set geometry parameters
geometry={O;             !z-matrix geometry input
         H1,O,r;
         H2,O,r,H1,theta}
basis=6-31g**            !use Pople basis set
hf                       !closed-shell scf
optg                     !do scf geometry optimization
```

http://www.molpro.net/info/current/examples/h2o_scfopt_631g.com

5.4 CCSD(T)

The following job does a CCSD(T) calculation using a larger (VTZ) basis (this includes an f function on oxygen and a d function on the hydrogens).

```
***,h2o                  !A title
r=1.85,theta=104         !set geometry parameters
geometry={O;             !z-matrix geometry input
         H1,O,r;
         H2,O,r,H1,theta}
basis=VTZ                !use VTZ basis
hf                       !closed-shell scf
ccsd(t)                  !do ccsd(t) calculation
```

http://www.molpro.net/info/current/examples/h2o_ccsdt_vtz.com

5.5 CASSCF and MRCI

Perhaps you want to do a CASSCF and subsequent MRCI for comparison. The following uses the full valence active space in the CASSCF and MRCI reference function.

```
***,h2o                  !A title
r=1.85,theta=104         !set geometry parameters
geometry={o;             !z-matrix geometry input
        h1,O,r;
        h2,O,r,H1,theta}
basis=vtz                !use VTZ basis
hf                       !closed-shell scf
ccsd(t)                  !do ccsd(t) calculation
casscf                   !do casscf calculation
mrci                     !do mrci calculation
```

    http://www.molpro.net/info/current/examples/h2o_mrci_vtz.com

5.6 Tables

You may now want to print a summary of all results in a table. To do so, you must store the computed energies in variables:

```
***,h2o                  !A title
r=1.85,theta=104         !set geometry parameters
geometry={o;             !z-matrix geometry input
        h1,O,r;
        h2,O,r,H1,theta}
basis=vtz                !use VTZ basis
hf                       !closed-shell scf
e(1)=energy              !save scf energy in variable e(1)
method(1)=program        !save the string 'HF' in variable method(1)

ccsd(t)                  !do ccsd(t) calculation
e(2)=energy              !save ccsd(t) energy in variable e(2)
method(2)=program        !save the string 'CCSD(T)' in variable method(2)

casscf                   !do casscf calculation
e(3)=energy              !save scf energy in variable e(3)
method(3)=program        !save the string 'CASSCF' in variable method(3)
mrci                     !do mrci calculation
e(4)=energy              !save scf energy in variable e(4)
method(4)=program        !save the string 'MRCI' in variable method(4)

table,method,e           !print a table with results
title,Results for H2O, basis=$basis  !title for the table
```

    http://www.molpro.net/info/current/examples/h2o_table.com

This job produces the following table:

```
 Results for H2O, basis=VTZ

 METHOD        E
 HF        -76.05480122
 CCSD(T)   -76.33149220
 CASSCF    -76.11006259
 MRCI      -76.31960943
```

5.7   Procedures

You could simplify this job by defining a procedure SAVE_E as follows:

```
***,h2o                  !A title

proc save_e              !define procedure save_e
if(#i.eq.0) i=0          !initialize variable i if it does not exist
i=i+1                    !increment i
e(i)=energy              !save scf energy in variable e(i)
method(i)=program        !save the present method in variable method(i)
endproc                  !end of procedure


r=1.85,theta=104         !set geometry parameters
geometry={o;             !z-matrix geometry input
        h1,O,r;
        h2,O,r,H1,theta}
basis=vtz                !use VTZ basis
hf                       !closed-shell scf
save_e                   !call procedure, save results

ccsd(t)                  !do ccsd(t) calculation
save_e                   !call procedure, save results

casscf                   !do casscf calculation
save_e                   !call procedure, save results

mrci                     !do mrci calculation
save_e                   !call procedure, save results

table,method,e           !print a table with results
title,Results for H2O, basis=$basis  !title for the table
```

   http://www.molpro.net/info/current/examples/h2o_proce.com

The job produces the same table as before.

5.8   Do loops

Now you have the idea that one geometry is not enough. Why not compute the whole surface? DO loops make it easy. Here is an example, which computes a whole potential energy surface for H_2O.

```
***,H2O potential
symmetry,x                           !use cs symmetry
geometry={
        o;                           !z-matrix
        h1,o,r1(i);
        h2,o,r2(i),h1,theta(i) }
basis=vdz                            !define basis set
angles=[100,104,110]                 !list of angles
distances=[1.6,1.7,1.8,1.9,2.0]      !list of distances
i=0                                  !initialize a counter
do ith=1,#angles                     !loop over all angles H1-O-H2
do ir1=1,#distances                  !loop over distances for O-H1
do ir2=1,ir1                         !loop over O-H2 distances(r1.ge.r2)
i=i+1                                !increment counter
r1(i)=distances(ir1)                 !save r1 for this geometry
r2(i)=distances(ir2)                 !save r2 for this geometry
theta(i)=angles(ith)                 !save theta for this geometry
hf;                                  !do SCF calculation
escf(i)=energy                       !save scf energy for this geometry
ccsd(t);                             !do CCSD(T) calculation
eccsd(i)=energc                      !save CCSD energy
eccsdt(i)=energy                     !save CCSD(T) energy
enddo                                !end of do loop ith
enddo                                !end of do loop ir1
enddo                                !end of do loop ir2
{table,r1,r2,theta,escf,eccsd,eccsdt  !produce a table with results
head, r1,r2,theta,scf,ccsd,ccsd(t)   !modify column headers for table
save,h2o.tab                         !save the table in file h2o.tab
title,Results for H2O, basis $basis  !title for table
sort,3,1,2}                          !sort table
```

```
 http://www.molpro.net/info/current/examples/h2o_pes_ccsdt.com
```

This produces the following table.

```
 Results for H2O, basis VDZ

    R1    R2    THETA       SCF            CCSD          CCSD(T)
   1.6   1.6   100.0   -75.99757338   -76.20140563   -76.20403920
   1.7   1.6   100.0   -76.00908379   -76.21474489   -76.21747582
   1.7   1.7   100.0   -76.02060127   -76.22812261   -76.23095473
   ...
   2.0   1.9   110.0   -76.01128923   -76.22745359   -76.23081968
   2.0   2.0   110.0   -76.00369171   -76.22185092   -76.22537212
```

You can use also use `DO` loops to repeat your input for different methods.

```
***,h2o benchmark
$method=[hf,fci,ci,cepa(0),cepa(1),cepa(2),cepa(3),mp2,mp3,mp4,\
      qci,ccsd,bccd,qci(t),ccsd(t),bccd(t),casscf,mrci,acpf]
basis=dz                                  !Double zeta basis set
geometry={o;h1,o,r;h2,o,r,h1,theta}       !Z-matrix for geometry
r=1 ang, theta=104                        !Geometry parameters
do i=1,#method                            !Loop over all requested methods
$method(i);                               !call program
e(i)=energy                               !save energy for this method
enddo
escf=e(1)                                 !scf energy
efci=e(2)                                 !fci energy
table,method,e,e-escf,e-efci              !print a table with results
!Title for table:
title,Results for H2O, basis $basis, R=$r Ang, Theta=$theta degree


http://www.molpro.net/info/current/examples/h2o_manymethods.com
```

This calculation produces the following table.

```
Results for H2O, basis DZ, R=1 Ang, Theta=104 degree

METHOD       E             E-ESCF       E-EFCI
HF        -75.99897339    .00000000    .13712077
FCI       -76.13609416   -.13712077    .00000000
CI        -76.12844693   -.12947355    .00764722
CEPA(0)   -76.13490643   -.13593304    .00118773
CEPA(1)   -76.13304720   -.13407381    .00304696
CEPA(2)   -76.13431548   -.13534209    .00177868
CEPA(3)   -76.13179688   -.13282349    .00429728
MP2       -76.12767140   -.12869801    .00842276
MP3       -76.12839400   -.12942062    .00770015
MP4       -76.13487266   -.13589927    .00122149
QCI       -76.13461684   -.13564345    .00147732
CCSD      -76.13431854   -.13534515    .00177561
BCCD      -76.13410586   -.13513247    .00198830
QCI(T)    -76.13555640   -.13658301    .00053776
CCSD(T)   -76.13546225   -.13648886    .00063191
BCCD(T)   -76.13546100   -.13648762    .00063315
CASSCF    -76.05876129   -.05978790    .07733286
MRCI      -76.13311835   -.13414496    .00297580
ACPF      -76.13463018   -.13565679    .00146398
```

One can do even more fancy things, like, for instance, using macros, stored as string variables. See example oh_macros.com for a demonstration.

6 PROGRAM CONTROL

6.1 Starting a job (***)

The first card of each input should be:

***,*text*

where *text* is arbitrary. If file 1 is restarted, *text* must always be the same. The effect of this card is to reset all program counters, etc. If the *** card is omitted, *text* assumes its default value, which is all blank.

6.2   Ending a job (`---`)

The end of the input is signaled by either an end of file, or a

`---`

card. All input following the `---` card is ignored.

Alternatively, a job can be stopped at at some place by inserting an `EXIT` card. This could also be in the middle of a `DO` loop or an `IF` block. If in such a case the `---` card would be used, an error would result, since the `ENDDO` or `ENDIF` cards would not be found.

6.3   Restarting a job (`RESTART`)

In contrast to MOLPRO92 and older versions, the current version of MOLPRO attempts to recover all information from all permanent files by default. If a restart is unwanted, the `NEW` option can be used on the `FILE` directive. The `RESTART` directive as described below can still be used as in MOLPRO92, but is usually not needed.

`RESTART,`$r_1,r_2,r_3,r_4,\ldots$`;`

The r_i specify which files are restarted. These files must have been allocated before using `FILE` cards. There are two possible formats for the r_i:

a) $0 < r_i < 10$:   Restart file r_i and restore all information.

b) $r_i = $ *name.nr*:   Restart file *nr* but truncate before record *name*.

If all $r_i = 0$, then all permanent files are restarted. However, if at least one r_i is not equal to zero, only the specified files are restarted.

Examples:

`RESTART;`   will restart all permanent files allocated with `FILE` cards (default)

`RESTART,1;`   will restart file 1 only

`RESTART,2;`   will restart file 2 only

`RESTART,1,2,3;`   will restart files 1-3

`RESTART,2000.1;`   will restart file 1 and truncate before record 2000.

6.4   Including secondary input files (`INCLUDE`)

`INCLUDE,`*file*`[,ECHO];`

Insert the contents of the specified *file* in the input stream. In most implementations the file name given is used directly in a Fortran open statement. If *file* begins with the character `'/'`, then it will be interpreted as an absolute file name. Otherwise, it will be assumed to be a path relative to the directory from which the Molpro has been launched. If, however, the file is not found, an attempt will be made instead to read it relative to the system `lib/include` directory, where any standard procedures may be found.

If the `ECHO` option is specified, the included file is echoed to the output in the normal way, but by default its contents are not printed. The included file may itself contain `INCLUDE` commands up to a maximum nesting depth of 10.

6.5   Allocating dynamic memory (`MEMORY`)

`MEMORY`,*n*,*scale*;

Sets the limit on dynamic memory to *n* floating point words. For details, see section 4.6.

6.6   `DO` loops (`DO`/`ENDDO`)

`DO` loops can be constructed using the `DO` and `ENDDO` commands. The general format of the `DO` command is similar to Fortran:

`DO` *variable=start, end* [[,]*increment*] [[,]*unit*]

where *start, end, increment* may be expressions or variables. The default for *increment* is 1. In contrast to Fortran, these variables can be modified within the loop (to be used with care!). For instance:


```
DR=0.2
DO R=1.0,6.0,DR,ANG
IF (R.EQ.2) DR=0.5
IF (R.EQ.3) DR=1.0
....
ENDDO
```


performs the loop for the following values of R: `1.0, 1.2, 1.4, 1.6, 1.8, 2.0, 2.5, 3.0, 4.0, 5.0, 6.0` Ångstrøm. The same could be achieved as follows:


```
RVEC=[1.0,1.2,1.4,1.6,1.8,2.0,2.5,3.0,4.0,5.0,6.0] ANG
DO I=1,#RVEC
R=RVEC(I)
....
ENDDO
```


Up to 20 `DO` loops may be nested. Each `DO` must end with its own `ENDDO`.

Jumps into `DO` loops are possible if the `DO` variables are known. This can be useful in restarts, since it allows to continue an interrupted calculation without changing the input (all variables are recovered in a restart).

6.6.1   Examples for do loops

The first example shows how to compute a potential energy surface for water.

```
***,H2O potential
symmetry,x                          !use cs symmetry
geometry={
        o;                          !z-matrix
        h1,o,r1(i);
        h2,o,r2(i),h1,theta(i) }
basis=vdz                           !define basis set
angles=[100,104,110]                !list of angles
distances=[1.6,1.7,1.8,1.9,2.0]     !list of distances
i=0                                 !initialize a counter
do ith=1,#angles                    !loop over all angles H1-O-H2
do ir1=1,#distances                 !loop over distances for O-H1
do ir2=1,ir1                        !loop over O-H2 distances(r1.ge.r2)
i=i+1                               !increment counter
r1(i)=distances(ir1)               !save r1 for this geometry
r2(i)=distances(ir2)               !save r2 for this geometry
theta(i)=angles(ith)               !save theta for this geometry
hf;                                 !do SCF calculation
escf(i)=energy                      !save scf energy for this geometry
ccsd(t);                            !do CCSD(T) calculation
eccsd(i)=energc                     !save CCSD energy
eccsdt(i)=energy                    !save CCSD(T) energy
enddo                               !end of do loop ith
enddo                               !end of do loop ir1
enddo                               !end of do loop ir2
{table,r1,r2,theta,escf,eccsd,eccsdt  !produce a table with results
head, r1,r2,theta,scf,ccsd,ccsd(t)   !modify column headers for table
save,h2o.tab                        !save the table in file h2o.tab
title,Results for H2O, basis $basis  !title for table
sort,3,1,2}                         !sort table
```

  http://www.molpro.net/info/current/examples/h2o_pes_ccsdt.com

The next example shows how to loop over many methods.

```
***,h2o benchmark
$method=[hf,fci,ci,cepa(0),cepa(1),cepa(2),cepa(3),mp2,mp3,mp4,\
     qci,ccsd,bccd,qci(t),ccsd(t),bccd(t),casscf,mrci,acpf]
basis=dz                            !Double zeta basis set
geometry={o;h1,o,r;h2,o,r,h1,theta} !Z-matrix for geometry
r=1 ang, theta=104                  !Geometry parameters
do i=1,#method                      !Loop over all requested methods
$method(i);                         !call program
e(i)=energy                         !save energy for this method
enddo
escf=e(1)                           !scf energy
efci=e(2)                           !fci energy
table,method,e,e-escf,e-efci        !print a table with results
!Title for table:
title,Results for H2O, basis $basis, R=$r Ang, Theta=$theta degree
```

http://www.molpro.net/info/current/examples/h2o_manymethods.com

6.7   Branching (IF/ELSEIF/ENDIF)

IF blocks and IF/ELSEIF blocks can be constructed as in FORTRAN.

6.7.1   IF statements

IF blocks have the same form as in Fortran:

```
IF (logical expression) THEN
statements
ENDIF
```

If only one statement is needed, the one-line form

```
IF (logical expression) statement
```

can be used, except if *statement* is a procedure name.

`ELSE` and `ELSE IF` can be used exactly as in Fortran. `IF` statements may be arbitrarily nested. Jumps into `IF` or `ELSE IF` blocks are allowed. In this case no testing is performed; when an `ELSE` is reached, control continues after `ENDIF`.

The logical expression may involve logical comparisons of algebraic expressions or of strings. Examples:

```
IF(STATUS.LT.0) THEN
TEXT,An error occurred, calculation stopped
STOP
ENDIF
```

```
IF($method.eq.'HF') then
...
ENDIF
```

In the previous example the dollar and the quotes are optional:

```
IF(METHOD.EQ.HF) then
...
ENDIF
```

6.7.2 `GOTO` **commands**

`GOTO` commands can be used to skip over parts of the input. The general form is

`GOTO,`*command,* `[`*n*`],[`*nrep*`]`

Program control skips to the $|n|$'th occurrence of *command* (Default: $n = 1$). *command* must be a keyword in the first field of an input line. If *n* is positive, the search is forward starting from the current position. If *n* is negative, search starts from the top of the input. The `GOTO` command is executed at most *nrep* times. The default for *nrep* is 1 if $n < 0$ and infinity otherwise. We recommend that `GOTO` commands are never used to construct loops.

Alternatively, one can jump to labels using

`GOTO,`*label*

Since labels must be unique, the search starts always from the top of the input. It is required that the *label* ends with a colon.

6.7.3 **Labels (**`LABEL`**)**

```
LABEL
```

This is a dummy command, sometimes useful in conjunction with `GOTO`.

6.8 **Procedures** (`PROC`/`ENDPROC`)

Procedures can be defined at the top of the input or in `INCLUDE` files as follows:

`PROC` *name*
statements
`ENDPROC`

Alternatively, one can use the form

`PROC` *name*`[=]`{*statements*}

In the latter case, it is required that the left curly bracket ({) appears on the same line as `PROC`, but *statements* can consist of several lines. If in the subsequent input *name* is found as a command *in the first field* of a line, it is substituted by the *statements*. Example:

```
PROC SCF
IF (#SPIN.EQ.0.OR.MOD(SPIN,2).NE.MOD(NELEC,2)) SET,SPIN=MOD(NELEC,2)
IF (SPIN.EQ.0) THEN
  HF
ELSE
  RHF
ENDIF
ENDPROC
```

Alternatively, this could be written as

```
PROC SCF={
IF (#SPIN.EQ.0.OR.MOD(SPIN,2).NE.MOD(NELEC,2)) SET,SPIN=MOD(NELEC,2)
IF (SPIN.EQ.0) THEN; HF; ELSE; RHF; ENDIF}
```

Procedures may be nested up to a depth of 10. In the following example `SCF` is a procedure:

```
PROC CC
SCF
IF (SPIN.EQ.0) THEN
  CCSD
ELSE
  RCCSD
ENDPROC
```

Note: Procedure names are substituted only if found in the first field of an input line. Therefore, they must not be used on one-line `IF` statements; please use `IF` / `ENDIF` structures instead.

If as first statement of a procedure `ECHO` is specified, the substituted commands of the present and lower level procedures will be printed. If `ECHO` is specified in the main input file, all subsequent procedures are printed.

Certain important input data can be passed to the program using variables. For instance, occupancy patterns, symmetries, number of electrons, and multiplicity can be defined in this way (see section 8.8 for more details). This allows the quite general use of procedures. For example, assume the following procedure has been defined at the top of the input:

```
PROC MRCI
IF (INTDONE.EQ.0) INT
IF (SCFDONE.EQ.0) THEN
SCF
ENDIF
MULTI
CI
ENDPROC
```

This procedure can be used for a calculation of a vertical ionization potential of H_2O as follows:

```
R=1 ANG            !Set bond distance
THETA=104 DEGREE   !Set bond angle

BASIS=VTZ          !Define basis set

GEOMETRY           !Geometry input block
O                  !Z-matrix
H1,O,R
H2,O,R,H1,THETA
ENDG               !End of geometry input
HF
MRCI               !Compute mrci energy of water using defaults
EH2O=ENERGY        !save mrci energy in variable EH2O

SET,NELEC=9        !Set number of electrons to 9
SET,SYMMETRY=2     !Set wavefunction symmetry to 2
HF
MRCI               !Compute mrci energy of H2O+ (2B2 state)

IPCI=(ENERGY-EH2O)*TOEV  !Compute MRCI ionization potential in eV
```

Note: At present, all variables are *global*, i.e., variables are commonly known to all procedures and all variables defined in procedures will be subsequently known outside the procedures as well. The reason is that procedures are included into the internal input deck at the beginning of the job and not at execution time; for the same reason, variable substitution of procedure names is not possible, e.g. one cannot use constructs like

```
method=scf
$method         !this does not work!
```

6.9   Text cards (`TEXT`)

`TEXT,`*xxxxxx*

will just print *xxxxxx* in the output. If the text contains variables which are preceded by a dollar ($), these are replaced by their actual values, e.g.

```
r=2.1
text,Results for R=$r
```

will print

```
Results for R=2.1
```

6.10   Checking the program status (`STATUS`)

`STATUS,[ALL|LAST|`*commands*`],[IGNORE|STOP|CRASH],[CLEAR]`

This command checks and prints the status of the specified program steps. *commands* may be a list of commands for wavefunction calculations previously executed in the current job. If no *command* or `LAST` is specified, the status of the last step is checked. If `ALL` is given, all program steps are checked.

If `CRASH` or `STOP` is given, the program will crash or stop, respectively, if the status was not o.k. (`STOP` is default). If `IGNORE` is given, any bad status is ignored. If `CLEAR` is specified, all status information for the checked program steps is erased, so there will be no crash at subsequent status checks.

Examples:

`STATUS,HF,CRASH;`	will check the status of the last `HF-SCF` step and crash if it was not o.k. (i.e. no convergence). `CRASH` is useful to avoid that the next program in a chain is executed.
`STATUS,MULTI,CI,STOP;`	will check the status of the most previous `MULTI` and `CI` steps and stop if something did not converge.
`STATUS,RHF,CLEAR;`	will clear the status flag for last `RHF`. No action even if `RHF` did not converge.

Note that the status variables are not recovered in a restart.

By default, the program automatically does the following checks:

1.) If an orbital optimization did not converge, and the resulting orbitals are used in a subsequent correlation calculation, an error will result. This error exit can be avoided using the `IGNORE_ERROR` option on the `ORBITAL` directive.

2.) If a `CCSD|QCI|BCC|LMPn` calculation did not converge, further program steps which depend on the solution (e.g, Triples, CPHF, EOM) will not be done and an error will result. This can be avoided using the `NOCHECK` option on the command line.

3.) In geometry optimizations or frequency calculations no convergence will lead to immediate error exits.

6.11   Global Thresholds (`GTHRESH`)

A number of global thresholds can be set using the `GTHRESH` command outside the individual programs (the first letter `G` is optional, but should be used to avoid confusion with program specific `THRESH` cards). The syntax is

`GTHRESH,`*key1=value1,key2=value2,...*

key can be one of the following.

`ZERO`	Numerical zero (default 1.d-12)
`ONEINT`	Threshold for one-electron integrals (default 1.d-12, but not used at present)
`TWOINT`	Threshold for the neglect of two-electron integrals (default 1.d-12)
`PREFAC`	Threshold for test of prefactor in `TWOINT` (default 1.d-14)
`LOCALI`	Threshold for orbital localization (default 1.d-8)
`EORDER`	Threshold for reordering of orbital after localization (default 1.d-4)
`ENERGY`	Convergence threshold for energy (default 1.d-6)
`GRADIENT`	Convergence threshold for orbital gradient in `MCSCF` (default 1.d-2)
`STEP`	Convergence threshold for step length in MCSCF orbital optimization (default 1.d-3)

ORBITAL	Convergence threshold for orbital optimization in the SCF program (default 1.d-5).
CIVEC	Convergence threshold for CI coefficients in `MCSCF` and reference vector in `CI` (default 1.-d.5)
COEFF	Convergence threshold for coefficients in `CI` and `CCSD` (default 1.d-4)
PRINTCI	Threshold for printing CI coefficients (default 0.05)
PUNCHCI	Threshold for punching CI coefficients (default 99 - no punch)
SYMTOL	Threshold for finding symmetry equivalent atoms (default 1.d-6)
GRADTOL	Threshold for symmetry in gradient (default 1.d-6).
THROVL	Threshold for smallest allowed eigenvalue of the overlap matrix (default 1.d-8)
THRORTH	Threshold for orthonormality check (default 1.d-8)

6.12   Global Print Options (`GPRINT/NOGPRINT`)

Global print options can be set using the `GPRINT` command outside the individual programs (the first letter `G` is optional, but should be used to avoid confusion with program specific `PRINT` cards). The syntax is

GPRINT,*key1*[=*value1*],*key2*[=*value2*],...
NOGPRINT,*key1*,*key2*,...

Normally, *value* can be omitted, but values > 0 may be used for debugging purposes, giving more information in some cases. The default is no print for all options, except for `DISTANCE`, `ANGLES` (default=0), and `VARIABLE`. NOGPRINT,*key* is equivalent to PRINT,*key*=−1. *key* can be one of the following:

BASIS	Print basis information
DISTANCE	Print bond distances (default)
ANGLES	Print bond angle information (default). If > 0, dihedral angles are also printed.
ORBITAL	Print orbitals in `SCF` and `MCSCF`
ORBEN	Print orbital energies in `SCF`
CIVECTOR	Print `CI` vector in `MCSCF`
PAIRS	Print pair list in `CI, CCSD`
CS	Print information for singles in `CI, CCSD`
CP	Print information for pairs in `CI, CCSD`
REF	Print reference CSFs and their coefficients in `CI`
PSPACE	Print p-space configurations
MICRO	Print micro-iterations in `MCSCF` and `CI`
CPU	Print detailed CPU information
IO	Print detailed I/O information
VARIABLE	Print variables each time they are set or changed (default).

6.13 One-electron operators and expectation values (`GEXPEC`)

The operators for which expectation values are requested, are specified by keywords on the global `GEXPEC` directive. By default, only dipole moments are computed. The first letter `G` is optional, but should be used to avoid confusion with program specific `EXPEC` cards, which have the same form as `GEXPEC`. For all operators specified on the `GEXPEC` card, expectation values are computed in all subsequent programs that generate the first-order density matix. This is always the case for variational wavefunctions, i.e., HF, DFT, MCSCF, MRCI. For non-variational wavefunctions such as MP2, MP3, QCISD, QCISD(T), CCSD, or CCSD(T) the density matix is not computed by default, since this requires considerable additional effort (solving z-vector equations). The GEXPEC directive does not affect such programs. In some cases [currently for MP2, MP3, QCISD, QCISD(T), and CCSD] the `EXPEC` directive that is specific to those programs can be used to request the property calculation.

For a number of operators it is possible to use *generic* operator names, e.g., `DM` for dipole moments, which means that all three components `DMX`, `DMY`, and `DMZ` are computed. Alternatively, individual components may be requested.

The general format is as follows:

`[G]EXPEC`,*opname*[,][*icen*,[*x,y,z*]],...

where

opname	operator name (string), either generic or component.
icen	z-matrix row number or z-matrix symbol used to determine the origin (x,y,z must not be specified). If *icen*= 0 or blank, the origin must be specified in *x,y,z*

Several `GEXPEC` cards may follow each other, or several operators may be specified on one card.

Examples:

`GEXPEC,QM` computes quadrupole moments with origin at (0,0,0),

`GEXPEC,QM1` computes quadrupole moments with origin at centre 1.

`GEXPEC,QM,O1` computes quadrupole moments with origin at atom `O1`.

`GEXPEC,QM,,1,2,3` computes quadrupole moments with origin at (1,2,3).

The following table summarizes all available operators:

Expectation values are only nonzero for symmetric operators (parity=1). Other operators can be used to compute transition quantities (spin-orbit operators need a special treatment).

6.13.1 Example for computing expectation values

The following job computes dipole and quadrupole moments for H_2O.

```
***,h2o properties
geometry={o;h1,o,r;h2,o,r,h1,theta}   !Z-matrix geometry input
r=1 ang                               !bond length
theta=104                             !bond angle
gexpec,dm,sm,qm                       !compute dipole and quarupole moments
$methods=[hf,multi,ci]                !do hf, casscf, mrci
do i=1,#methods                       !loop over methods
$methods(i)                           !run energy calculation
e(i)=energy
dip(i)=dmz                            !save dipole moment in variable dip
quadxx(i)=qmxx                        !save quadrupole momemts
quadyy(i)=qmyy
quadzz(i)=qmzz
smxx(i)=xx                            !save second momemts
smyy(i)=yy
smzz(i)=zz
enddo
table,methods,dip,smxx,smyy,smzz       !print table of first and second moments
table,methods,e,quadxx,quadyy,quadzz   !print table of quadrupole moments
```

     http://www.molpro.net/info/current/examples/h2o_gexpec2.com

This Job produces the following tables

METHODS	DIP	SMXX	SMYY	SMZZ
HF	0.82747571	−5.30079792	−3.01408114	−4.20611391
MULTI	0.76285513	−5.29145148	−3.11711397	−4.25941000
CI	0.76868508	−5.32191822	−3.15540500	−4.28542917

METHODS	E	QUADXX	QUADYY	QUADZZ
HF	−76.02145798	−1.69070039	1.73937477	−0.04867438
MULTI	−76.07843443	−1.60318949	1.65831677	−0.05512728
CI	−76.23369821	−1.60150114	1.64826869	−0.04676756

6.13.2 Example for computing relativistic corrections

```
***,ar2
geometry={ar1;ar2,ar1,r}  !geometry definition
r=2.5 ang                 !bond distance
{hf;                      !non-relativisitic scf calculation
expec,rel,darwin,massv}   !compute relativistic correction using Cowan-Griffin operator
e_nrel=energy             !save non-relativistic energy in variable enrel
show,massv,darwin,erel    !show individual contribution and their sum

dkroll=1                  !use douglas-kroll one-electron integrals
hf;                       !relativistic scf calculation
e_dk=energy               !save relativistic scf energy in variable e_dk.
show,massv,darwin,erel    !show mass-velocity and darwin contributions and their sum
show,e_dk-e_nrel          !show relativistic correction using Douglas-Kroll
```

      http://www.molpro.net/info/current/examples/ar2_rel.com

This jobs shows at the end the following variables:


```
 MASSV / AU          =       −14.84964285
 DARWIN / AU         =        11.25455679
 EREL / AU           =        −3.59508606
```

Table 5: One-electron operators and their components

Generic name	Parity	Components	Description
OV	1		Overlap
EKIN	1		Kinetic energy
POT	1		potential energy
DELTA	1		delta function
DEL4	1		Δ^4
DARW	1		one-electron Darwin term, i.e., DELTA with appropriate factors summed over atoms.
MASSV	1		mass-velocity term, i.e., DEL4 with appropriate factor.
REL	1		total Cowan-Griffin Relativistic correction, i.e., DARW+MASSV.
DM	1	DMX, DMY, DMZ	dipole moments
SM	1	XX, YY, ZZ, XY, XZ, YZ	second moments
TM	1	XXX, XXY, XXZ, XYY, XYZ, XZZ, YYY, YYZ, YZZ, ZZZ	third moments
MLTPn	1	all unique Cartesian products of order n	multipole moments
QM	1	QMXX, QMYY, QMZZ, QMXY, QMXZ, QMYZ, QMRR=XX + YY + ZZ, QMXX=(3 XX - RR)/2, QMXY=3 *XY* / 2 etc.	quadrupole moments and R^2
EF	1	EFX, EFY, EFZ	electric field
FG	1	FGXX, FGYY, FGZZ, FGXY, FGXZ, FGYZ	electric field gradients
DMS	1	DMSXX, DMSYX, DMSZX, DMSXY, DMSYY, DMSZY, DMSXZ, DMSYZ, DMSZZ	diamagnetic shielding tensor
LOP	-1	LX, LY, LZ	Angular momentum operators $\hat{L}_x, \hat{L}_y, \hat{L}_z$
LOP2	1	LXLX, LYLY, LZLZ, LXLY, LXLZ, LYLZ The symmetric combinations	one electron parts of products of angular momentum operators. $\frac{1}{2}(\hat{L}_x\hat{L}_y + \hat{L}_y\hat{L}_x)$ etc. are computed
VELO	-1	D/DX, D/DY, D/DZ	velocity
LS	-1	LSX, LSY, LSZ	spin-orbit operators
ECPLS	-1	ECPLSX, ECPLSY, ECPLSZ	ECP spin-orbit operators

7 FILE HANDLING

7.1 FILE

The FILE directive is used to open permanent files, which can be used for later restarts. The syntax in MOLPRO94 and later versions is

FILE,*file*,*name*,[*status*]

file is the logical MOLPRO file number (1-9). *name* is the file name (will be converted to lower case). *status* can be one of the following:

UNKNOWN	A permanent file is opened. If it exists, it is automatically restarted. This is the default.
OLD	Same effect as UNKNOWN. No error occurs if the file does not exist.
NEW	A permanent file is opened. If it already exists, it is erased and not restarted.
ERASE	Same effect as NEW.
SCRATCH	A temporary file is opened. If it already exists, it is erased and not restarted. After the job has finished, the file is no longer existent.
DELETE	Same effect as SCRATCH.

Note that RESTART is now the default for all permanent files. All temporary files are usually allocated automatically where needed. I/O buffers are allocated at the top of the dynamic memory, and the available memory decreases by the size of the buffers. The MEMORY card must therefore be presented before the first FILE card!

Examples:

FILE,1,H2O.INT	allocates permanent file 1 with name H2O.INT. Previous information on the file is recovered.
FILE,2,H2O.WFU,NEW	allocates permanent file 2 with name H2O.WFU. All previous information on the file is erased.

Note that filenames are converted to lower case on unix machines.

7.2 DELETE

DELETE,*file1, file2, . . .*

Deletes the specified files. *file* refers to the logical MOLPRO file numbers as specified on the FILE card.

7.3 ERASE

ERASE,*file1, file2, . . .*

Erases the specified files. *file* refers to the logical MOLPRO file numbers as specified on the FILE card.

7.4 `DATA`

The `DATA` command can be used to modify the MOLPRO binary files.

UNIT	Alias for `NPL` (should never be used)
RENAME,*rec1*,*rec2*	used to rename *rec1* to *rec2*. *rec1* and *rec2* must be given in the form *name.ifil*, where *ifil* is the number of a MOLPRO binary file (alias for `NAME`).
TRUNCATE,*nen*	used to truncate files after *nen-1* records (alias for `NEN`).
TRUNCATE,*rec*	used to truncate before record *rec*. *rec* must be given in the form *name.ifil*, where *ifil* is the number of a MOLPRO binary file.
COUNT	Alias for `NRE` (presently not used)
COPY,*rec1*,*rec2*	Copies record *rec1* to *rec2*. *rec1* and *rec2* must be given in the form *nam1.ifil1*, *nam2.ifil2*. If *nam2=0*, *nam2=nam1*. If *nam1=0*, all records are copied from file *ifil1* to file *ifil2*.

7.5 Assigning punch files (`PUNCH`)

`PUNCH`,*filename*,`[REWIND]`

Opens punch file named *filename*. If this file already exists, it is appended, unless the `REWIND` or `NEW` option is specified; in that case, any previous information on the punch file is overwritten. See `FILE` for machine dependent interpretation of filename. The punch file contains all important results (geometries, energies, dipole, transition moments etc). It can be read by a separate program *READPUN*, which can produce tables in user supplied format.

Example:

`PUNCH,H2O.PUN` allocates punch file `H2O.PUN`

Note that the file name is converted to lower case on unix machines.

7.6 MOLPRO system parameters (`GPARAM`)

The `GPARAM` card allows to change MOLPRO system parameters. This should only be used by experts!

`GPARAM`,*option=value*,...

The following options can be given in any order.

NOBUFF	if present, disable system buffering
LSEG	disk sector length
INTREL	number of integer words per real word (should never be modified!)
IBANK	number of memory banks. Default is 2, which should always be o.k.
IVECT	0=scalar, 1=vector machine
MINVEC	minimum vector length for call to mxmb
LTRACK	page size in buffer routines (must be multiple of *lseg*)

LENBUF	length of integral buffer (file 1)
NTR	length of integral records (must be multiple of 3·*ltrack*)
LTR	disk sector length assumed in CI (default 1 is reasonable)
NCACHE	machine cache size in bytes
IASYN	if nonzero, use asynchronous I/O on CONVEX
MXMBLK	column/row block size for mxma
MXMBLN	link block size for mxma
NCPUS	maximum number of cpus to be used in multitasking
MINBR1	min number of floating point ops per processor
MXDMP	highest file number to be treated as dump file with full functionality ($1 \leq$. MXDMP$\leq$ .3).

The MXDMP option is for experts only! This prevents basis and geometry information from being written to dump files with higher file number than the given *value*, and can sometimes be useful for counterpoise corrected geometry optimizations. Note that some functionality is lost by giving this option, and errors will result unless all input is correct!

8 VARIABLES

Data may be stored in *variables*. A variable can be of type *string*, *real* or *logical*, depending on the type of the expression in its definition. Any sequence of characters which is not recognized as expression or variable is treated as string. In this section, we will discuss only *real* and *logical* variables. *String* variables will be discussed in more detail in section 8.3. Variables can be used anywhere in the input, but they can be set only outside the input blocks for specific programs. For example, if a variable is used within the input block for HF, it must have been set before the HF{...} input block.

MOLPRO automatically stores various results and data in system variables (see section 8.8.1), which can be used for further processing. A new feature of MOLPRO2002 is that most system variables are write protected and cannot be overwritten by the user. The input is automatically checked before the job starts, and should a system variable be set in the input the job will stop immediately with an error message. Only in some exceptions (see section 8.4), system variables can be modified using the SET command (but not with the simple NAME=*value* syntax). Note that due to the changed usage and syntax of the SET command, compatibility with MOLPRO92 input syntax is no longer maintained.

8.1 Setting variables

A variable can be defined using

variable1=value1, *variable2=value2*, . . .

A variable definition is recognized by the equals sign in the *first* field of the input card. For example,

THRESH,ENERGY=1.d-8,GRADIENT=1.d-5

does *not* define variables; here ENERGY and GRADIENT are options for the THRESH directive.

Variables can have different types:

Numbers: The value is a number or an expression. The general form of *value* is
                    expression [,] [*unit*]
                    unit is an optional string which can be used to associate a unit to the value.
                    `ANG[STROM]`, `DEGREE`, `HARTREE` are examples. Undefined variables in
                    expressions are assumed to be zero (and defined to be zero at the same time).

Logicals: The value can be `.TRUE.` or `.FALSE.` (`.T.` and .F. also work), or a logical
                    expression. Internally, `.TRUE.` is stored as 1 and `.FALSE.` as zero.

Strings: The value can either be a string enclosed in quotes or a string variable. See
                    section 8.3 for more details.

8.2   Indexed variables

Variables can be indexed, but only one-dimensional indexing is available. Indexed variables can
be defined either individually, e.g.

```
R(1)=1.0 ANG
R(2)=1.2 ANG
R(3)=1.3 ANG
```

or as a vector of values enclosed by square brackets:

```
R=[1.0,1.1,1.2] ANG
```

Subranges can also be defined, e.g.

```
R(1)=1.0 ANG
R(2:3)=[1.1,1.2] ANG
```

leads to the same result as the above two forms.

The type of each element depends on the type of the assigned value, and it is possible to mix
types in one variable. Example:

```
geometry={he}
hf
result=[program,energy,status.gt.0]
```

yields:

```
RESULT(1)      =    HF-SCF
RESULT(2)      =       -2.85516048  AU
RESULT(3)      =    TRUE
```

In this example the variables `PROGRAM`, `ENERGY`, and `STATUS` are system variables, which
are set by the program (see section 8.4).

8.3   String variables

As explained already in section 8.1, string variables can be set as other variables in the form

variable = 'string'
variable = string_variable

Strings must be enclosed by quotes. Otherwise the string is assumed to be a variable, and if this is undefined it is assumed to be zero.

Alternatively, if the name of the variable is preceded by a dollar ($), all values are assumed to be a string. This can be a string variable, a quoted string, or an unquoted string. Note that unquoted strings are converted to upper case. Also note that quotes are compulsory if the string contains blanks.

Example:

```
$str=[a,b+4,'This is an example for strings']
```

yields

```
STR(1)          =    A
STR(2)          =    B+4
STR(3)          =    This is an example for strings
```

As a general rule, string variables are replaced by their value only if they are preceded by a dollar ($) (exceptions: in variable definitions, on `SHOW` cards, and in logical expressions on `IF` cards, the dollar is optional). This is a precaution to avoid commands which have the same name as a variable being interpreted as variables. Variables may also appear on `TEXT` or `TITLE` cards or in strings, but must be preceded by $ in these cases. Example:

```
$METHOD=MCSCF
R=1.5
TEXT,$method results for R=$R Bohr
```

prints

```
MCSCF results for R=1.5 Bohr
```

String variables can be concatenated with strings or other string variables in the following way. Assume that variable `PROGRAM` has the value `MRCI`. Setting

```
METHOD='$PROGRAM+Q'
```

sets `METHOD` to `MRCI+Q`. Alternatively, if we would also have a variable `VERSION` with value `Q`, we could write

```
METHOD='$PROGRAM+$VERSION'
```

Again, the value of `METHOD` would be `MRCI+Q`. Note that the quotes are necessary in these cases.

Substring operations are not implemented.

8.4   System variables

As mentioned above, most system variables cannot be written by the user. In some exceptions, it is possible to redefine them using the `SET` command:

`SET,`*variable = expression* [,] [*unit*]

This holds for the following variables:

`CHARGE`	Total charge of the molecule
`NELEC`	Number of electrons
`SPIN`	Spin quantum number, given as $2 \cdot M\_S$ (integer)
`SCFSPIN`	Same as `SPIN`, but only for HF
`MCSPIN`	Same as `SPIN`, but only for MCSCF
`CISPIN`	Same as `SPIN`, but only for MRCI
`STATE`	State to be optimized
`MCSTATE`	Same as `STATE` but only for MCSCF
`CISTATE`	Same as `STATE` but only for MRCI
`SYMMETRY`	State symmetry
`SCFSYM[METRY]`	Same as `SYMMETRY` but only for HF
`MCSYM[METRY]`	Same as `SYMMETRY` but only for MCSCF
`CISYM[METRY]`	Same as `SYMMETRY` but only for MRCI
`ZSYMEL`	Symmetry elements
`LQUANT`	Lambda quantum number for linear molecules
`OPTCONV`	Geometry optimization convergence criterion
`PROGRAM`	Last program name
`CPUSTEP`	CPU-time of last program step
`SYSSTEP`	System-time of last program step
`WALLSTEP`	Elapsed-time of last program step
`FOCKDONE`	Indicates if closed-shell fock operator is available.
`MAXBASIS`	Max number of basis sets stored on dump files. If the maximum is reached, the last one is overwritten when a new one is made, and all information (including dump records etc) of the previous basis is lost. The default is the maximum possible number of basis sets (30), which cannot be exceeded.

8.5   Macro definitions using string variables

String variables for which the stored string has the form of an algebraic expression are evaluated to a number if they are preceded by two dollars ($$). Example:

```
string='a+b'
a=3
b=4
text,This is string $string which evaluates to $$string
```

prints

```
** This is string a+b which evaluates to 7
```

This can be used to define simple macros, which can be used at various places in the subsequent input. For instance,

```
ECORR='ENERGY-ESCF'  !define a macro
HF                   !do SCF calculation
ESCF=ENERGY          !store SCF energy in variable ESCF
MULTI                !do CASSCF
DEMC=$$ECORR         !store CASSCF correlation energy in variable DEMC
MRCI                 !do MRCI
DECI=$$ECORR         !store MRCI correlation energy in variable DECI
```

Here is an example of advanced use of macros and string variables:

```
***,test for parser
text,This fancy input demonstrates how string variables and macros can be used
text
basis=vdz              !define basis set
geometry={O;H,O,r}     !define geometry (z-matrix)

text,methods
$method=[rhf,2[casscf,2[mrci]]]
text,active spaces
$spaces=['[3,1,1]',3['[4,2,2]'],3['[5,2,2]']]
text,symmetries
$symset=['1',2['[1,2,3]','1','2']]
text,weight factors for state averaged casscf
$weights=['1','[1,1,1]',2[' '],'[1,0.5,0.5]',2[' ']]
text,scf occupation
set,scfocc=[3,2[1]]
text,bond distance
r=1.85

hf
do i=1,#method          !loop over methods
mcocc=$$spaces(i)       !set active space for this run
set,symmetry=$$symset(i)   !set symmetries for this run
set,weight=$$weights(i)    !set weights for this run
$method(i)              !now run method
e(i)='$energy'          !save energies in strings
dipol(i)='$dmz'         !save dipole moments in strings
enddo
table,method,spaces,symset,weights,e,dipol
title,Results for OH, r=$r, basis=$basis
head,method,spaces,symmetries,weights,energies,'dipole moments'
exit
```

        http://www.molpro.net/info/current/examples/oh_macros.com

8.6 Indexed Variables (Vectors)

Variables may be indexed, but only one-dimensional arrays (vectors) are supported. The index may itself be a variable. For instance

```
METHOD(I)=PROGRAM
E(I)=ENERGY
```

are valid variable definitions, provided I, PROGRAM, and ENERGY are also defined variables. Indices may be nested to any depth.

Different elements of an array can be of different type (either *real* or *logical*). However, only one *unit* can be assigned to an array. String variables have no associated value and cannot be mixed with the other variable types. Therefore, a given variable name can only be used either for a *string* variable or a *real* (*logical*) variable.

Vectors (arrays) can be conveniently defined using square brackets:

R=[1.0,1.2,1.3] ANG

This defines an array with three elements, which can be accessed using indices; for instance, R(2) has the value 1.2 ANG. A repeat specifier can be given in front of the left bracket: 5[0] is equivalent to [0,0,0,0,0]. Brackets can even be nested: for instance, 2[1,2,2[2.1,3.1]] is equivalent to [1,2,2.1,3.1,2.1,3.1,1,2,2.1,3.1,2.1,3.1].

Arrays can be appended from a given position just by entering additional elements; for instance,

R(4)=[1.4,1.5] ANG

or

R(4:)=[1.4,1.5] ANG

extends the above array to length 5. Previously defined values can be overwritten. For instance

R(2)=[1.25,1.35,1.45]

modifies the above vector to (1.0, 1.25, 1.35, 1.45, 1.5).

If no index is given on the left hand side of the equal sign, an existing variable of the same name is replaced by the new values, and all old values are lost. For instance

```
THETA=[100,110,120,130]  set four values
...
THETA(1)=104          replace THETA(1) by a new value; THETA(2:4) are unchanged
...
THETA=[140,150]     old variable THETA is replaced; THETA(3:4) are deleted
```

Square brackets can also be used to define an array of strings, e.g.,

METHOD=[INT,HF,CASSCF,MRCI]

These could be used as follows:

```
DO I=1,4
$METHOD(I)
ENDDO
```

The above input would be equivalent to

```
INT
HF
CASSCF
MRCI
```

The current length of an array can be accessed by preceding # to the variable name. For instance, in the above examples `#R` and `#METHOD` have the values 5 and 4, respectively. If a variable is not defined, zero is returned but no error occurs. This can be used to test for the existence of a variable, for example:

```
IF(#SPIN.EQ.0.AND.#NELEC.EQ.1) SET,SPIN=MOD(NELEC,2)
```

This defines variable `SPIN` if it is unknown and if `NELEC` is a scalar (one dimensional) variable.

8.7 Vector operations

The following simple vector operations are possible:

- Copying or appending a vector to another vector. For instance `S=R` copies a vector `R` to a vector `S`. `S(3)=R` copies `R` to `S(3)`, `S(4)`, `....` `S(#S+1)=R` appends vector `R` to vector `S`. It is also possible to access a range of subsequent elements in a vector: `S=R(2:4)` copies elements 2 to 4 of `R` to `S(1)`, `S(2)`, `S(3)`. Note that `R(2:)` denotes elements `R(2)` to `R(#R)`, but `R(2)` denotes a single element of `R`.

- Vector-scalar operations: `R=R*2` multiplies each element of `R` by 2. Instead of the number 2, also scalar (one dimensional) variables or expressions can be used, e.g., `R=R*ANG` converts all elements of `R` from Ångstrøm to bohr, or `Z=R*COS(THETA)` creates a vector `Z` with elements `Z(i) = R(i)*COS(THETA)`. All other algebraic operators can be used instead of "*". Note that the scalar must come last since the first variable in the expression determines the vector length.

- Vector-vector operations: If `A` and `B` are vectors of the same length, then `A × B` is also a vector of this length. Here `×` stands for any algebraic operator, and the operation is done for each pair of corresponding elements. For instance, `A + B` adds the vectors `A` and `B`, and `A * B` multiplies their elements. Note that the latter case is not a scalar product. If an attempt is made to connect two vectors of different lengths by an algebraic operator, an error occurs.

- Intrinsic functions: Assume `THETA=[100,110,120,-130]` to be a vector of angles (in degrees). In this case `X=2*COS(THETA)` is also a vector containing the cosines of each element of `THETA` multiplied by two, i.e., `X(i) = 2*COS(THETA(i))`. `MAX(THETA)` or `MIN(THETA)` return the maximum and minimum values, respectively, in array `THETA`. Vector operations can also be nested, e.g., `MAX(ABS(THETA))` returns the maximum value in array `ABS(THETA)`.

At present, vector operations are not supported with `string` variables.

8.8 Special variables

8.8.1 Variables set by the program

A number of variables are predefined by the program. The following variables can be used to convert between atomic units and other units:

```
EV=1.d0/27.2113839d0 HARTREE
KELVIN=1.d0/3.157747d5 HARTREE
KJOULE=1.d0/2625.500d0 HARTREE
```

```
KCAL=1.d0/627.5096d0 HARTREE
CM=1.d0/219474.63067d0 HARTREE
CM-1=1.d0/219474.63067d0 HARTREE
HZ=1.d0/6.5796839207d15 HARTREE
HERTZ=1.d0/6.5796839207d15 HARTREE
ANG=1.d0/0.529177209d0 BOHR
ANGSTROM=1.d0/0.529177209d0 BOHR

TOEV=27.2113839d0 EV
TOK=3.157747d5 K
TOKELVIN=3.157747d5 K
TOCM=219474.63067d0 CM-1
TOHERTZ=6.5796839207d15 HZ
TOHZ=6.5796839207d15 HZ
TOKJ=2625.500d0 KJ/MOL
TOKJOULE=2625.500d0 KJ/MOL
TOKCAL=627.5096d0 KCAL/MOL
TOA=0.529177209d0 ANGSTROM
TOANG=0.529177209d0 ANGSTROM
TODEBYE=2.54158d0 DEBYE
```

Further variables which are set during execution of the program:

INTYP	defines integral program to be used. Either INTS (Seward) or INTP (Argos).
INTDONE	has the value .true. if the integrals are done for the current geometry.
CARTESIAN	Set to one if Cartesian basis functions are used.
SCFDONE	has the value .true. if an SCF calculation has been done for the current geometry.
NUMVAR	number of variables presently defined
STATUS	status of last step (1=no error, -1=error or no convergence)
CHARGE	Total charge of the molecule
NELEC	number of electrons in last wavefunction
SPIN	spin multiplicity minus one of last wavefunction
ORBITAL	record of last optimized orbitals (set but never used in the program)
LASTORB	Type of last optimized orbitals (RHF, UHF, UHFNAT, or MCSCF.
LASTSYM	Symmetry of wavefunction for last optimized orbitals.
LASTSPIN	$2 * M_S$ for wavefunctions for last optimized orbitals.
LASTNELEC	Number of electrons in wavefunction for last optimized orbitals.
ENERGR(istate)	Reference energy for state *istate* in MRCI and CCSD.
ENERGY(istate)	last computed total energy for state *istate* for the method specified in the input (e.g., HF, MULTI, CCSD(T), or CCSD[T].
ENERGY_METHOD	String variable holding name of the method used for calculating ENERGY
ENERGY_BASIS	String variable holding name of the orbital basis-set used for calculating ENERGY
GEOMETRY_METHOD	Equal to the value of ENERGY_METHOD for the most recent geometry optimisation

GEOMETRY_BASIS	Equal to the value of ENERGY_BASIS for the most recent geometry optimisation
ENERGD(istate)	Total energy for state *istate* including Davidson correction (set only in CI).
ENERGP(istate)	Total energy for state *istate* including Pople correction (set only in CI).
ENERGT(1)	Total energy including perturbative triples (T) correction (set only in CCSD(T), QCI(T)).
ENERGT(2)	Total energy including perturbative triples [T] correction (set only in CCSD(T), QCI(T)).
ENERGT(3)	Total energy including perturbative triples -t correction (set only in CCSD(T), QCI(T)).
EMP2	holds MP2 energy in MPn, CCSD, BCCD, or QCISD calculations, and RS2 energy in MRPT2 (CASPT2) calculations.
EMP3	holds MP3 energy in MP3 and MP4 calculations, and RS3 energy in MRPR3 (CASPT3) calculations.
EMP4	holds MP4(SDQ) energy in MP4 calculations. The MP4(SDTQ) energy is stored in variable ENERGY.
METHODC	String variable holding name of the methods used for ENERGC, e.g., CCSD, BCCD, QCI.
METHODT(1)	String variable holding name of the methods used for ENERGT(1), e.g., CCSD(T), BCCD(T), QCI(T).
METHODT(2)	String variable holding name of the methods used for ENERGT(2), e.g., CCSD[T], BCCD[T], QCI[T].
METHODT(3)	String variable holding name of the methods used for ENERGT(3), e.g., CCSD-T, BCCD-T, QCI-T.
ENERGC	Total energy excluding perturbative triples correction (set only in QCI or CCSD with triples correction enabled).
DFTFUN	total value of density functional in DFT or KS.
DFTFUNS(ifun)	value of ifun'th component of density functional in DFT or KS.
DFTNAME(ifun)	name of ifun'th component of density functional in DFT or KS.
DFTFAC(ifun)	factor multiplying ifun'th component of density functional in DFT or KS.
DFTEXFAC	factor multiplying exact exchange in KS.
PROP(istate)	computed property for state *istate*. See below for the names PROP of various properties.
PROGRAM	last program called, as specified in the input (e.g., HF, CCSD(T), etc.)
ITERATIONS	Number of iterations used. Set negative if no convergence or max number of iterations reached.
CPUSTEP	User-CPU time in seconds for last program called.
SYSSTEP	System-CPU time in seconds for last program called.
WALLSTEP	Elapsed time in seconds for last program called.

The variable names for properties are the same as used on the EXPEC input cards.

`OV`	Overlap
`EKIN`	Kinetic energy
`POT`	Potential
`DELTA`	Delta function
`DEL4`	∇^4
`DARWIN`	Darwin term of relativistic correction
`MASSV`	Mass-velocity term of relativistic correction
`EREL`	Total relativistic correction
`DMX, DMY, DMZ`	Dipole moments
`XX, YY, ZZ, XY, XZ, XY`	Second moments
`XXX, XXY, XXZ, XYY, XYZ, XZZ, YYY, YYZ, YZZ, ZZZ`	Third moments
`QMXX, QMYY, QMZZ, QMXY, QMXZ, QMXY`	Quadrupole moments
`EFX, EFY, EFZ`	Electric field
`FGXX, FGYY, FGZZ, FGXY, FGXZ, FGXY`	Electric field gradients
`D/DX, D/DY, D/DZ`	Velocity
`LSX, LSY, LSZ`	One-electron spin-orbit
`LL`	Total angular momentum squared L^2
`LX, LY, LZ`	Electronic angular momentum
`LXLX, LYLY, LZLZ, LXLY, LXLZ, LYLZ`	Two-electron angular momentum

By default, only the dipole moments are computed and defined. The values of other properties are only stored in variables if they are requested by `EXPEC` cards. If more than one state is computed (e.g., in state-averaged MCSCF, corresponding arrays `PROP(istate)` are returned. If properties are computed for more than one center, the center number is appended to the name, e.g. `EFX1`, `EFX2` etc.

If transition properties are computed, their values are stored in corresponding variables with prefix `TR`, e.g., `TRDMX`, `TRDMY`, `TRDMZ` for transition dipole moments. If more than two states are computed, the index is $(i-1)*(i-2)/2+j$, where $i > j \geq 1$ are state numbers. In a state-averaged calculation, states are counted sequentially for all state symmetries.

For instance, in the following state-averaged MCSCF

`MULTI;WF,14,1,0;STATE,3;WF,14,2,0;STATE,2;WF,14,3,0`

the states are counted as

i	1	2	3	4	5	6
Symmetry	1	1	1	2	2	3
Root in Sym.	1	2	3	1	2	1

8.8.2 Variables recognized by the program

All variables described below are checked by the program, but not set (except `NELEC` and `SPIN`). If these are not defined by the user, the program uses its internal defaults. The variables are only recognized and used if defined using the `SET` command, e.g.

```
SET,MCOCC=[6,3,2]
SET,STATE=2
```

etc.

Variables recognized by the SCF program:

CHARGE	Total charge of the molecule (can be given instead of nelec)
NELEC	number of electrons
SPIN	spin multiplicity minus one
SCFSYM[METRY]	wavefunction symmetry
SYMMETRY	as SCFSYMM; only used if SCFSYMM is not present.
SCFOC[C]	number of occupied orbitals in each symmetry for SCF
SCFCL[OSED]	number of closed-shell orbitals in each symmetry for SCF
SCFORB	record of saved orbitals in SCF
SCFSTART	record of starting orbitals used in SCF

Variables recognized by the MCSCF program:

CHARGE	Total charge of the molecule (can be given instead of nelec)
NELEC	number of electrons
MCSYM[METRY]	wavefunction symmetry. This can be an array for state-averaged calculations.
SYMMETRY	as MCSYMM; only used if MCSYMM is not present.
MCSPIN	spin multiplicity minus one. This can be an array for state-averaged calculations, but different spin multiplicities can only be used in determinant CASSCF. If only one value is specified, this is used for all states
SPIN	as MCSPIN; only used if MCSPIN is not present.
MCSTATE	number of states for each symmetry in MCSCF
STATE	as MCSTATE; only used if MCSTATE is not present.
WEIGHT	weight factors for all states defined by SYMMETRY and STATE
LQUANT	Eigenvalues of L_z^2 for linear molecules for each state defined by SYMMETRY and STATE.
MCSELECT	records from which configurations can be selected and selection threshold
SELECT	as MCSELECT; only used if MCSELECT is not present.
MCRESTRICT	can be used to define occupancy restrictions
RESTRICT	as MCRESTRCT; only used if MCRESTRICT is not present:
CONFIG	if set to .true. or to one triggers use of CSFs
MCOC[C]	number of occupied orbitals in each symmetry
OCC	as MCOCC; only used if MCOCC is not present.
MCCL[OSED]	number of optimized closed-shell orbitals in each symmetry
CLOSED	as MCCLOSED; only used if MCCLOSED is not present.
MCFROZEN	number of frozen core orbitals in each symmetry
FROZEN	as MCFROZEN; only used if MCFROZEN is not present.

MCSTART	record of starting orbitals
COREORB	record of frozen core orbitals
MCORB	record for saving optimized orbitals
MCSAVE	records for saving CI wavefunction (like SAVE card in MCSCF)

Variables recognized by the CI/CCSD program:

CHARGE	Total charge of the molecule (can be given instead of nelec)
NELEC	number of electrons
SPIN	spin multiplicity minus one
CISYM[METRY]	wavefunction symmetry. If this is an array, only SYMMETRY(1) is used.
SYMMETRY	as CISYMM; only used if CISYMM is not present.
CISTATE	number of states in CI
STATE	as CISTATE, only used if CISTATE is not present.
CISELECT	records from which configurations can be selected
SELECT	as CISELECT; only used if CISELCT is not present.
CIRESTRICT	defines occupancy restrictions
RESTRICT	as RESTRICT; only used if CIRESTRICT is not present.
CIOC[C]	number of occupied orbitals in each symmetry
OCC	as CIOCC; only used if CIOCC is not present.
CICL[OSED]	number of closed-shell orbitals in each symmetry
CLOSED	as CICLOSED; only used if CICLOSED is not present.
CICO[RE]	number of core orbitals in each symmetry
CORE	as CICORE; only used if CICORE is not present.
CIORB	record of orbitals used in CI
CISAVE	records for saving CI wavefunction (like SAVE card in CI)
CISTART	records for restarting with previous CI wavefunction (like START card in CI)

Variables recognized by the DFT/KS program:

DF(ifun) or DFTNAME(ifun)	name of ifun'th component of density functional.
DFTFAC(ifun)	factor multiplying ifun'th component of density functional.
DFTEXFAC	factor multiplying exact exchange in KS.

Example for the use of these variables for a state-averaged MCSCF (note that system variables can only be modified using the SET command, see section 8.4):

SET,NELEC=9	defines number of electrons
SET,SPIN=1	defines wavefunction to be a doublet
SET,SYMMETRY=[1,2,3]	defines wavefunction symmetries for state averaged calculation

```
SET,STATE=[2,1,1]   defines number of states to be averaged in each symmetry
WEIGHT=[2,2,1,1]    defines weights for the above four states
OCC=[5,2,2]         number of occupied orbitals in each symmetry
CLOSED=2            number of closed-shell orbitals in symmetry 1
MCORB=3100.2        record for optimized orbitals
MULTI               do mcscf with above parameters
```

Note: Setting the variables `NELEC`, `SPIN`, or `SYMMETRY`, has the same effect giving these on a gobal `WF` directive. If the global `WF` directive is given after the variable definition, the values of the variables are replaced by the values given on the `WF` directive. Vice versa, if a variable definition follows a gobal `WF` directive, the new value of the variable is used in the following. Note that `WF` input cards in command blocks have preference over global `WF` directives or input variables.

8.9   Displaying variables

Variables or the results of expressions can be displayed in the output using `SHOW` and `TABLE`.

8.9.1   The `SHOW` command

The general form of the `SHOW` command is as follows:

`SHOW[`*ncol,format*`],`*expression*

where *expression* can be an expression or variable, *ncol* is the number of values printed per line (default 6), and *format* is a format (default 6F15.8). This can be used to print vectors in matrix form. The specification of *ncol* and *format* is optional. Assume that `E` is a vector:

```
SHOW,E          prints E using defaults.
SHOW[n],E       prints E with n elements per line; (if n>6, more than one line is needed, but
                in any case a new line is started after n elements).
SHOW[n,10f10.4],E prints E in the format given, with newline forced after n elements.
```

Note that the total length of the format should not exceed 100 characters (a left margin of 30 characters is always needed).

A *wild card* format can be used to show several variables more easily:

`SHOW,qm*,dm*`

shows all variables whose names begin with `QM` and `DM`. Note that no letters must appear after the `*`, i.e., the wild card format is less general than in `UNIX` commands.

See the `TABLE` command for another possibility to tabulate results.

8.10   Clearing variables

Variables can be deleted using

CLEAR,*name1, name2, . . .*

Wild cards can be used as in SHOW, e.g.,

CLEAR,ENERG*

clears all variables whose names begin with ENERG. All variables can be cleared using

CLEARALL

The length of vectors can be truncated simply by redefining the length specifier: #R=2 truncates the array R to length 2. Higher elements are no longer available (but could be redefined). Setting #R=0 is equivalent to the command CLEAR,R.

8.11   Reading variables from an external file

Variables can be read from an external file using

READVAR, *filename*, [*option*]

Such files can be saved, for instance by the geometry optimization program, and reused later to recover a certain optimized geometry. The format of the input in *filename* is the same as for ordinary input.

If *option*=NOINDEX|IGNOREINDEX is given then variable indices are ignored and only the last value saved is read (without index). This can be useful if for example a file saved with SAVEACT in a geometry optimization is read, and it is intended to continue with the variables that were saved last.

9   TABLES AND PLOTTING

9.1   Tables

Variables can be printed in Table form using the command

TABLE,*var1*,*var2*,...

The values of each variable are printed in one column, so all variables used must be defined for the same range, and corresponding elements should belong together. For example, if in a calculation one has stored R(i), THETA(i), ECI(i) for each geometry *i*, one can print these data simply using

TABLE, R, THETA, ECI

By default, the number of rows equals the number of elements of the first variable. This can be changed, however, using the RANGE subcommand.

The first ten columns of a table may contain string variables. For instance,

```
hf;etot(1)=energy;method(1)=program;cpu(1)=cpustep
ccsd;etot(2)=energy;method(2)=program;cpu(2)=cpustep
qci;etot(3)=energy;method(3)=program;cpu(3)=cpustep
table,method,etot,cpu
```

prints a table with the `SCF`, `CCSD`, and `QCI` results in the first, second, and third row, respectively. For other use of string variables and tables see, e.g. the examples `h2o_tab.com` and `oh_macros.com`

The apparence of the table may be modified using the following commands, which may be given (in any order) directly after the the `TABLE` card:

`HEADING,`*head1, head2,...*	Specify a heading for each column. By default, the names of the variables are used as headings.
`FORMAT,`*format*	Specify a format for each row in fortran style. *format* must be enclosed by quotes. Normally, the program determines automatically an appropriate format, which depends on the type and size of the printed data.
`FTYP,`*typ1, typ2, typ3, ...*	Simplified form to modify the format. This gives the type (`A`, `F`, or `D`) for each column (sensible defaults are normally used).
`DIGITS,`*dig1, dig2, dig3, ...*	Give the number of digits after the decimal points to be printed for each column (sensible defaults are normally used).
`TYPE`	Specify a data format for the table. The default is `TEXT` which gives a plain text file. Other possibilities are `CSV` (comma-separated fields suitable for a spreadsheet), `LATEX` (a LaTeX `table` environment), `MATHEMATICA` (Mathematica code that assigns the table to an array), `MATLAB` (Matlab code that assigns the table to an array), `MAPLE` (Maple code that assigns the table to an array), `HTML` (an HTML TABLE construction), and `XML` (an XML document containing a tree representing the table. The actual format is XHTML).
`SAVE,`*file,status*	Specify a file on which the table will be written. If status is `NEW`, the file is rewound, otherwise it is appended. If *file* has a suffix that is one of `txt, csv, tex, m, mpl, html, xml`, and a `TYPE` command is not specified, then the type will be set to that which is conventionally appropriate for the suffix. If *file* is omitted, then a file name is automatically generated, with the form *input*`.table`*n.ext*: *input* is the basename of the input file (or `molpro` if running from standard input); *n* is a sequence number that is incremented by one each time a table is produced; *ext* is a suffix appropriate to the file format, eg `txt`, `html`, etc.
`TITLE,`*title*	Specify one line of a title (several `TITLE` cards may follow each other). Note that titles are only displayed in the `SAVE` file, if the `SAVE` command is given before the `TITLE` card.
`SORT,`*col1,col2,...*	Sort rows according to increasing values of the given columns. The columns are sorted in the order they are specified.
`PRINT,`*key1,key2,...*	Specify print options (`TABLE, HEADING, TITLE, WARNING, FORMAT, SORT`). The default is print for the first three, and noprint for the last three.
`NOPRINT,`*key1,key2,...*	Disable print for given keys.
`NOPUNCH`	Don't write data to the punch file (data are written by default).
`RANGE,`*start,end*	Specify start and end indices of the variables to be printed.

`STATISTICS`	Print also linear regression, upper and lower bounding lines, and quadratic fits of the data columns. The slopes and intercepts of these lines are saved in the Molpro variables `REGRESSION_SLOPE`, `REGRESSION_INTERCEPT`, `LOWERBOUNDMIN_SLOPE`, `LOWERBOUNDMIN_INTERCEPT`, `UPPERBOUNDMIN_SLOPE`, `UPPERBOUNDMIN_INTERCEPT`, `LOWERBOUNDMAX_SLOPE`, `LOWERBOUNDMAX_INTERCEPT`, `UPPERBOUNDMAX_SLOPE`, `UPPERBOUNDMAX_INTERCEPT`.

9.2 Plotting

[`PLOT`[,*col1*,*col2*,...][,*options*]

Construct input for a plotting program using the table as data. `PLOT` is a subcommand of `TABLE` and must follow `TABLE` or any of its valid subcommands given in the previous section. More than one `PLOT` command can be included within a single `TABLE`, and each invocation generates a new plot. However, `PLOT` must appear after all other `TABLE` subcommands.

col1, *col2*,... are the names of the table columns to be plotted. These must be an exact subset of those given on the `TABLE` command. The first column is taken as abscissa, and the values of the remainder will be plotted against it. If no columns are specified, then the entire table is plotted; if a single column is specified, it will be used as abscissa, and all other columns in the table will be plotted as ordinate. *options* can be chosen from the following.

`CMD=`*unix_plot_command*	*unix_plot_command* consists of the system command needed to start the plotting program, followed by any required options. The whole thing should normally be enclosed in quotation marks to preserve lower-case letters. The default is `'xmgrace'`. At present, the *Grace* program (also known as *xmgrace, grace, gracebat*), with only numerical data, is supported. The output is also compatible with the portable drop-in replacement for Grace, *AptPlot*, and if *Grace* is not found on the system, Molpro will attempt to use *AptPlot* as default instead.
`FILE=`*plotfile*	By default the input file for the plotting program is saved in *input*.`table`*n*.`plot`*m*.`agr`, where *m* is an automatically generated sequence number. The name of the plotfile can be modified using the `FILE` option.
`INTERACTIVE`	By default, the plot is not shown on the screen but all plot data are saved in the given file. The plotting program can be started interactively by giving the `INTERACTIVE` option.
`TYPE=`*type*	If `TYPE` is specified, *type* should be set to one of `pdf`, `svg`, `png`, `jpeg` or `eps`. The result is that the `gracebat` program is executed on the plot input file to generate the graph output file in the desired format. This feature depends on the availability of `gracebat`, and on it supporting the requested output format (for example, at present pdf is supported under Mac OS X, but not in some Linux systems).
`BACKGROUND=`*rgb*	*rgb* should be a string of six hexadecimal digits specifying the red-green-blue colour to use for the background of the plot.
`BACKGROUND=TRANSPARENT`	The background of the plot is made transparent (currently implemented only for `TYPE=svg`).

NOSPLINE	Prevents spline interpolation of data points
CURVE=*type*	Specifies type of curve to be drawn with points. Possibilities are SPLINE (default; spline interpolation); NONE (equivalent to NOSPLINE); REGRESSION (linear regression line); UPPERBOUNDMAX (maximum gradient line that bounds points from above); UPPERBOUNDMIN (minimum gradient line that bounds points from above); LOWERBOUNDMAX (maximum gradient line that bounds points from below); LOWERBOUNDMIN (minimum gradient line that bounds points from below).
NSPLINE=*number*	Number of interpolation points (default 20)
LEGEND=' *x, y*'	Position legend at (x, y) on plot.
LEGEND=OFF	Do not draw legend; this behaviour is chosen automatically when there is only a single ordinate dataset.
PCOMMAND=' *command*'	Insert arbitrary *Grace* command into the plot file; for details, consult http://plasma-gate.weizmann.ac.il/Grace/doc/UsersGuide.html#s5.

The following additional directives can be given *before* the PLOT directive:

COLOUR,*icolour1, icolour2,...*	Colour map to be used for columns 1,2,...; zero means to use default values (colours black, blue, red, green cycle)
COLOUR,*rgb1, rgb2,...*	Absolute colours (6-hex-digit rgb values) to be used for columns 1,2,...;
SYMBOL,*isymb1, isymb2,...*	Symbol types to be used for columns 1,2,...; -1 means no symbols; zero means to use default values.
LINEWIDTH,*width1, width2,...*	Line widths to be used for columns 1,2,...; omit to use default values.
LINESTYLE,*style1, style2,...*	Line styles to be used for columns 1,2,...; omit to use default values.

9.3   Diatomic potential curve analysis

For the case that a table contains one or more potential energy functions for a diatomic molecule, with the first column containing bond lengths in Bohr or Ångstrom, it is possible to calculate spectroscopic constants using

DIATOMIC[, DEGREE=*n*][, MASS=*m*][, PRINT=*p*]

The data are fitted to a polynomial of degree *n* (default is number of points minus 1, ie interpolation), and spectroscopic constants calculated using reduced mass *m* expressed in u. Note that it is possible to constrain which bond lengths are used through the use of the RANGE subcommand.

10   MOLECULAR GEOMETRY

10.1   Geometry specifications

The geometry may be given in standard Z-matrix form, or XYZ form. The geometry specifications are given in the form

```
[SYMMETRY, options ]
```

```
[ORIENT, options ]
```

```
[ANGSTROM]
```

```
GEOMETRY={
```
atom specifications
```
}
```

`GEOMETRY` must come after the other commands that modify the way the geometry is constructed. The following are permitted as `SYMMETRY` options:

	Any valid combination of symmetry generators, as described in section 10.2 below.
NOSYM	Disable use of symmetry. Instead of `SYMMETRY,NOSYM` also just `NOSYM` can be used.

The following are permitted as `ORIENT` options:

CHARGE	Orient molecule such that origin is centre of charge, and axes are eigenvectors of quadrupole moment.
MASS	Orient molecule such that origin is centre of mass, and axes are eigenvectors of inertia tensor (default for Z-matrix input). Alternatively, the symmetry centre can be specified as `CENTRE=MASS|CHARGE`.
NOORIENT	Disable re-orientation of molecule (default for XYZ-input).
SIGNX=±1	Force first non-zero x-coordinate to be positive or negative, respectively. Similarly, `SIGNY`, `SIGNZ` can be set for the y- and z-coordinates, respectively. This can be useful to fix the orientation of the molecule across different calculations and geometries. Alternatively, the system variables `ZSIGNX`, `ZSIGNY`, `ZSIGNZ` can be set to positive or negative values to achieve the same effect.
PLANEXZ	For the C_{2v} and D_{2h} point groups, force the primary plane to be *xz* instead of the default *yz*. The geometry builder attempts by swapping coordinate axes to place as many atoms as possible in the primary plane, so for the particular case of a planar molecule, this means that all the atoms will lie in the primary plane. The default implements recommendation 5*a* and the first part of recommendation 5*b* specified in J. Chem. Phys. 55, 1997 (1955). `PLANEYZ` and `PLANEXY` may also be specified, but note that the latter presently generates an error for C_{2v}.

`ANGSTROM` Forces bond lengths that are specified by numbers, or variables without associated units, to use the values as a number of Ångstrom, rather than Bohr.

10.1.1   Z-matrix input

The general form of an atom specification line is

[*group*`[,]`]*atom*, p_1, r, p_2, α, p_3, β, *J*

or, alternatively,

[*group* [**,**]] *atom*, p_1, x, y, z

where

group	atomic group number (optional). Can be used if different basis sets are used for different atoms of the same kind. The basis set is then referred to by this group number and not by the atomic symbol.
atom	chemical symbol of the new atom placed at position p_0. This may optionally be appended (without blank) by an integer, which can act as sequence number, e.g., C1, H2, etc. Dummy centres with no charge and basis functions are denoted either Q or X, optionally appended by a number, e.g, Q1; note that the first atom in the z-matrix must not be called X, since this may be confused with a symmetry specification (use Q instead).
p_1	atom to which the present atom is connected. This may be either a number *n*, where *n* refers to the *n*'th line of the Z-matrix, or an alphanumeric string as specified in the *atom* field of a previous card, e.g., C1, H2 etc. The latter form works only if the atoms are numbered in a unique way.
r	Distance of new atom from p_1. This value is given in bohr, unless ANG has been specified directly before or after the symmetry specification.
p_2	A second atom needed to define the angle $\alpha(p_0, p_1, p_2)$. The same rules hold for the specification as for p_1.
α	Internuclear angle $\alpha(p_0, p_1, p_2)$. This angle is given in degrees and must be in the range $0 < \alpha < 180^0$.
p_3	A third atom needed to define the dihedral angle $\beta(p_0, p_1, p_2, p_3)$. Only applies if $J = 0$, see below.
β	Dihedral angle $\beta(p_0, p_1, p_2, p_3)$ in degree. This angle is defined as the angle between the planes defined by (p_0, p_1, p_2) and (p_1, p_2, p_3) $(-180^0 \leq \beta \leq 180^o)$. Only applies if $J = 0$, see below.
J	If this is specified and nonzero, the new position is specified by two bond angles rather than a bond angle and a dihedral angle. If $J = \pm 1$, β is the angle $\beta(p_0, p_1, p_3)$. If $J = 1$, the triple vector product $(\mathbf{p}_1 - \mathbf{p}_0) \cdot [(\mathbf{p}_1 - \mathbf{p}_2) \times (\mathbf{p}_1 - \mathbf{p}_3)]$ is positive, while this quantity is negative if $J = -1$.
x,y,z	Cartesian coordinates of the new atom. This form is assumed if $p_1 \leq 0$; if $p_1 < 0$, the coordinates are frozen in geometry optimizations.

All atoms, including those related by symmetry transformations, should be specified in the Z-matrix. Note that for the first atom, no coordinates need be given, for the second atom only p_1, r are needed, whilst for the third atom p_3, β, J may be omitted. The 6 missing coordinates are obtained automatically by the program, which translates and re-orients the molecule such that the origin is at the centre of mass, and the axes correspond to the eigenvectors of the inertia tensor (see also CHARGE option above).

Variable names, and in general expressions that are linear in all dependent variables, may be used as well as fixed numerical values for the parameters r, α and β. These expressions are evaluated as late as possible, so that it is possible, for example, to set up loops in which these parameters are changed; the geometry optimizer also understands this construction, and will optimize the energy with respect to the value of the variables. Non-linear expressions should not be used, because the geometry optimization module is unable to differentiate them.

Once the reorientation has been done, the program then looks for symmetry (D_{2h} and sub-groups), unless the NOSYM option has been given. It is possible to request that reduced symmetry be used by using appropriate combinations of the options X, Y, Z, XY, XZ, YZ, XYZ. These specify symmetry operations, the symbol defining which coordinate axes change sign under the operation. The point group is constructed by taking all combinations of specified elements. If symmetry is explicitly specified in this way, the program checks to see that the group requested can be used, swapping the coordinate axes if necessary. This provides a mechanism for ensuring that the same point group is used, for example, at all points in the complete generation of a potential energy surface, allowing the safe re-utilization of neighbouring geometry molecular orbitals as starting guesses, etc..

Note that symmetry is not implemented in density fitting methods, and in these cases the NOSYM option is implied automatically.

Also note that by default the automatic orientation of the molecule only takes place if the geometry is defined by internal (Z-matrix) coordinates. In case of XYZ Input the orientation is unchanged, unless the MASS option is specified in the geometry block.

10.1.2 *XYZ input*

Simple cartesian coordinates in Ångstrom units can be read as an alternative to a Z matrix. This facility is triggered by setting the MOLPRO variable GEOMTYP to the value XYZ before the geometry specification is given, but usually this does not need to be done, as a geometry specification where the first line is a single integer will be recognized as XYZ format, as will the case of the first line consisting of a chemical symbol followed by three cartesian coordinates. The geometry block should then contain the cartesian coordinates in Minnesota Computer Centre, Inc. XYZ format. Variable names, and in general expressions that are linear in all dependent variables, may be used as well as fixed numerical values. Non-linear expressions should not be used, because the geometry optimization module is unable to differentiate them.

The XYZ file format consists of two header lines, the first of which contains the number of atoms, and the second of which is a title. The remaining lines each specify the coordinates of one atom, with the chemical symbol in the first field, and the x, y, z coordinates following. A sequence number may be appended to the chemical symbol; it is then interpreted as the atomic group number, which can be used when different basis sets are wanted for different atoms of the same kind. The basis set is then specified for this group number rather than the atomic symbol. As a further extension, the first two header lines can be omitted.

Note that for XYZ input the default is not to reorient the molecule. Orientation can be forced, however, by the MASS or CHARGE options on the ORIENT directive.

```
geomtyp=xyz
geometry={
3            ! number of atoms
This is an example of geometry input for water with an XYZ file
O ,0.0000000000,0.0000000000,-0.1302052882
H ,1.4891244004,0.0000000000, 1.0332262019
H,-1.4891244004,0.0000000000, 1.0332262019
}
hf
```

> http://www.molpro.net/info/current/examples/h2o_xyzinput.com

The XYZ format had been specified within the documentation distributed with the Minnesota Supercomputer Center's XMol package. Note that MOLPRO has the facility to write XYZ files with the PUT command (see section 10.3).

10.2 Symmetry specification

If standard Z-matrix input is used, MOLPRO determines the symmetry automatically by default. However, sometimes it is necessary to use a lower symmetry or a different orientation than obtained by the default, and this can be achieved by explicit specification of the symmetry elements to be used, as described below.

Generating symmetry elements, which uniquely specify the point group, can be specified on the SYMMETRY directive. This must be given *before* the geometry block. Each symmetry directive only affects the subsequent geometry block; after a geometry block has been processed, the defaults are restored. Note that the specification of symmetry elements inside the geometry block is no longer allowed.

The dimension of the point group is 2**(number of fields given). Each field consists of one or more of X, Y, or Z (with no intervening spaces) which specify which coordinate axes change sign under the corresponding generating symmetry operation. It is usually wise to choose z to be the unique axis where appropriate (essential for C_2 and C_{2h}). In that case, the possibilities are:

(null card)	C_1 (i.e., no point group symmetry)
Z	C_s
XY	C_2
XYZ	C_i
X,Y	C_{2v}
XY,Z	C_{2h}
XZ,YZ	D_2
X,Y,Z	D_{2h}

Note that Abelian point group symmetry only is available, so for molecules with degenerate symmetry, an Abelian subgroup must be used — e.g, C_{2v} or D_{2h} for linear molecules.

See section 4.8 for more details of symmetry groups and ordering of the irreducible representations. Also see section 10.1.1 for more information about automatic generation of symmetry planes.

Note that by default the automatic orientation of the molecule only takes place if the geometry is defined by internal (Z-matrix) coordinates. In case of XYZ Input the orientation is unchanged, unless the MASS option is specified in the geometry block.

10.3 Writing files for postprocessing(`PUT`)

The `PUT` command may be used at any point in the input to print, or write to a file, the current geometry. The syntax is

`PUT`,*style,file,status,info*

If *style* is `GAUSSIAN`, a complete Gaussian input file will be written; in that case, `info` will be used for the first (route) data line, and defaults to '`# SP`'.

If *style* is `XYZ`, an XYZ file will be written (see also section 10.1.2). If *style* is `XYZGRAD`, an XYZ file including energy gradients will be written (columns are: x,y,z,charge,gx,gy,gz; gradient is given in -1*eV/A) If *style* is `CRD`, the coordinates will be written in CHARMm CRD format.

If *style* is `MOLDEN`, an interface file for the MOLDEN visualization program is created; further details and examples are given below.

If *style* is `IRSPEC`, a gnuplot input file will be written, which can be used to plot an IR spectrum. The gnuplot file contains Lorentz functions with the results of the previous vibrational calculation (`VSCF` 54.1, `VCI` 55.1). Input examples can be found in these chapters.

If *style* is `XML`, a dump of the current state is written, including variables, geometry, basis set, latest orbitals. The file format is well-formed XML, according to the https://www.molpro.net/info/2015.1/lib/schema/molpro-output.html schema. In this case, additional options can be given:

`INDEX`,*n*	Insert an `index=``n''` attribute into the `<molecule>` node that is produced.
`NOFREQUENCIES`	Skip output of normal modes
`NOORBITALS`	Skip output of molecular orbitals
`SKIPVIRT`	Skip output of virtual molecular orbitals
`NOBASIS`	Skip output of basis set specification
`NOVARIABLES`	Skip output of Molpro variables
`KEEPSPH`	Express orbitals in terms of spherical-harmonic functions rather than converting to cartesian

If *style* is of the form `BABEL`/*format*, then, where possible, the external shell command `obabel` will be used to convert the geometry to any format supported by the OpenBabel package. For the possible values of *format*, see OpenBabel's documentation. If `obabel` is not installed on the system, then nothing happens.

If *style* is omitted, the Z-matrix, current geometry, and, where applicable, gradient are written.

file specifies a file name to which the data is written; if blank, the data is written to the output stream. If *status* is omitted or set to `NEW`, any old contents of the file are destroyed; otherwise the file is appended.

10.3.1 Visualization of results using Molden

Geometry, molecular orbital, and normal mode information, when available, is dumped by `PUT,MOLDEN` in the format that is usable by MOLDEN.

The interface to the gOpenMol program offers an alternative visualization possibility, and is described in section 38.8.

The example below generates all the information required to plot the molecular orbitals of water, and to visualize the normal modes of vibration:

```
***,H2O
geometry={angstrom;o;h,o,roh;h,o,roh,h,theta};
roh=1.0
theta=104.0
rhf;
optg;
{frequencies;
print,low,img;}
put,molden,h2o.molden;
```

> http://www.molpro.net/info/current/examples/h2o_put_molden.com

The example below does a difference density by presenting its natural orbitals to MOLDEN. Note that although MOLDEN has internal features for difference density plots, the approach shown here is more general in that it bypasses the restriction to STO-3G, 3-21G, 4-31G and 6-31G basis sets.

```
gprint,orbitals
symmetry,y,planexz
geometry={O;H1,O,r;h2,O,r,h1,alpha}
r=1.8
alpha=104
int;
{hf;wf,10,1;orbital,2100.2}
{multi;wf,10,1;orbital,2140.2}

{matrop
load,dscf,density,2100.2        !load scf density
load,dmcscf,density,2140.2      !load mcscf density
add,ddiff,dmcscf,-1,dscf        !compute dmcscf-dscf
natorb,neworb1,dscf
natorb,neworb2,dmcscf
natorb,neworbs,ddiff
save,neworbs,2110.2
save,ddiff,2110.2}

put,molden,h2o_ddens.molden;orb,2110.2
```

> http:
> //www.molpro.net/info/current/examples/h2o_diffden_molden.com

10.4 Geometry Files

Using the format

GEOMETRY=*file*

the geometry definitions are read from *file*, instead of inline.

10.5 Lattice of point charges

LATTICE,[INFILE=*input_file*,] [OUTFILE=*output_file*,] [VARGRAD,] [NUCONLY,] [REMOVE]

Includes a lattice of point charges, for use in QM/MM calculations for example (see section 59). An external file (*input_file*) should be given as input, with the following format:

Comment line
number of point charges N
*x*1,*y*1,*z*1,*q*1,*flag*1
⋮
xN,*yN*,*zN*,*qN*,*flagN*

The *x*, *y* and *z* fields stand for the point charge coordinates (in Å), *q* for its charge and *flag=1* indicates that gradients should be computed for this lattice point (0 means no gradient).

outfile specifies a file name to which the lattice gradient is written; if blank, it will be written to the output stream.

VARGRAD	(logical) Stores the lattice gradient in variable VARGRAD.
NUCONLY	(logical) Disables gradient evaluation with respect to the lattice, independent of *flag* in the lattice file.
REMOVE	(logical) Removes the lattice.

Symmetry is not supported for lattice gradients.

10.6   Redefining and printing atomic masses

The current masses of all atoms can be printed using

MASS,PRINT

The atomic masses can be redefined using

MASS, [*type*,] [*symbol=mass*, . . .]

The optional keyword *type* can take either the value AVER[AGE] for using average isotope masses, or ISO[TOPE] for using the masses of the most abundant isotopes. This affects only the rotational constants and vibrational frequencies. As in most quantum chemistry packages, the default for *type* is AVERAGE. If INIT is given, all previous mass definitions are deleted and the defaults are reset.

Individual masses can be changed by the following entries, where *symbol* is the chemical symbol of the atom and *mass* is the associated mass. Several entries can be given on one MASS card, and/or several MASS cards can follow each other. The last given mass is used.

Note that specifying different isotope masses for symmetry related atoms lowers the symmetry of the system if the molecular centre of mass is taken as the origin. This effect can be avoided by using the charge centre as origin, i.e., specifying CHARGE as the option to an ORIENT directive before the GEOMETRY input:

ORIENT,CHARGE; GEOMETRY={ ...}

10.7   Dummy centres

DUMMY,*atom1,atom2,...*

Sets nuclear charges on atoms 1,2 etc. to zero, for doing counterpoise calculations, for example. *atom1, atom2,...* can be Z-matrix row numbers or tag names. Note that the current setting of dummies is remembered by the program across restarts via the MOLPRO variable DUMMYATOMS. Dummies can be reset to their original charges using a DUMMY card with no entries. Dummy centres are also reset to their original charges if (i) an INT command is encountered, or (ii) a new geometry input is encountered.

The program does not recognize automatically if the symmetry is reduced by defining dummy atoms. Therefore, for a given dummy atom, either all symmetry equivalent atoms must also be dummies, or the symmetry must be reduced manually as required. An error will result if the symmetry is not consistent with the dummy centre definitions.

10.7.1   Counterpoise calculations

Counterpoise corrections are easily performed using dummy cards. One first computes the energy of the total system, and then for the subsystems using dummy cards. The process can, however, be automated using the command

COUNTERPOISE [, *key1=value, key2=value,......*]

Without any options, this will calculate the ghost-orbital corrections to dimer interaction energies using the last energy calculation to define the dimer and the methods to be used. First of all, the molecule is automatically partitioned into two optimally separated fragments. This is done by finding the partitioning that has the largest minimum distance between any pair of atoms in different fragments. Optionally, one may give the option SEPARATION=*distance*; if the optimum fragment separation is smaller than *distance*, then it will be assumed that the system is not a non-bonded complex, and the counterpoise calculation will not be done at all. This gives support for running the same Molpro input for both dimers and monomers.

The counterpoise procedure performs four calculations. For each of the identified monomers, it calculates the energy at the dimer geometry using first the dimer basis set, and secondly just the basis functions tied to the monomer atoms. The difference between these, the counterpoise correction, is reported, and added to the previously-calculated dimer energy.

Further options that specify the calculation to be run can be specified exactly as for geometry optimisations; see section 46.1.1 for further details.

10.7.2   Example: interaction energy of OH-Ar

```
***,OH(2Sig+)-Ar linear
memory,2,m
geometry={q1;               !dummy center in center of mass
o,q1,ro;h,q1,rh,o,180;      !geometry of OH
ar,q1,rar,o,theta,h,0}      !geometry of Ar
roh=1.8                     !OH bond-length
rar=7.5                     !distance of Ar from center of mass
theta=0                     !angle OH-Ar
ro=roh*16/17                !distance of O from center of mass
rh=roh*1/17                 !distance of H from center of mass
basis=avdz                  !basis set

text,calculation for complex
{rhf;occ,8,3,3;wf,27,1,1}   !RHF for total system
rccsd(t)                    !CCSD(T) for total system
e_ohar=energy               !save energy in variable e_ohar

text,cp calculation for OH
dummy,ar                    !make Ar a dummy center
{rhf;occ,3,1,1;wf,9,1,1}    !RHF for OH
rccsd(t)                    !CCSD(T) for OH
e_oh=energy                 !save energy in variable e_oh

text,cp calculation for Ar
dummy,o,h                   !make OH dummy
hf                          !scf for Ar
ccsd(t)                     !CCSD(T) for Ar
e_ar=energy                 !save energy in variable e_ar

text,separate calculation for OH
geometry={O;H,O,roh}        !geometry for OH alone
{rhf;occ,3,1,1;wf,9,1,1}    !RHF for OH
rccsd(t)                    !CCSD(T) for OH
e_oh_inf=energy             !save energy in variable e_oh_inf

text,separate calculation for Ar
geometry={AR}               !geometry for OH alone
hf                          !scf for Ar
ccsd(t)                     !CCSD(T) for Ar
e_ar_inf=energy             !save energy in variable e_ar_inf

de=(e_ohar-e_oh_inf-e_ar_inf)*tocm   !compute uncorrected interaction energy
de_cp=(e_ohar-e_oh-e_ar)*tocm        !compute counter-poise corrected interaction energy
bsse_oh=(e_oh-e_oh_inf)*tocm         !BSSE for OH
bsse_ar=(e_ar-e_ar_inf)*tocm         !BSSE for Ar
bsse_tot=bsse_oh+bsse_ar             !total BSSE
```

http://www.molpro.net/info/current/examples/ohar_bsse.com

For performing counterpoise corrected geometry optimizations see section 46.4.7.

11   BASIS INPUT

11.1   Overview: sets and the basis library

Basis functions are used in Molpro not just for representing orbitals, but also for providing auxiliary sets for density fitting (see 15) and for simplifying integrals through approximate identity

resolution in explicitly-correlated methods (see 35). In order to accommodate this, the program maintains internally a number of different *sets*. The first of these always has the name ORBITAL and is the primary basis set for representing orbitals, and others can be defined as necessary as described below, or else are constructed automatically by the program when required. In the latter case, the density-fitting and other modules attempt to guess a reasonable libary fitting basis that should be appropriate for the orbital basis set; it is advisable to check the choice when using anything other than a standard orbital basis set.

The basis sets may either be taken from the library, or may be specified explicitly, or any combination. Optionally, the basis function type can be chosen using the CARTESIAN or SPHERICAL commands.

11.2   Cartesian and spherical harmonic basis functions

MOLPRO uses spherical harmonics ($5d$, $7f$, etc) by default, even for Pople basis sets like 6-31G**. This behaviour may be different to that of other programs; However, cartesian functions can be requested using the CARTESIAN command.

CARTESIAN

If this command is encountered, the logical **MOLPRO** variable CARTESIAN is set to true (1.0), and all subsequent calculations use cartesian basis functions. This is remembered across restarts. One can switch back to spherical harmonics using the command

SPHERICAL

11.3   The basis set library

The basis set library consists of a set of plain text files, together with an associated index, that constitute a database of commonly-used basis sets (primitive gaussians and associated contractions) and effective core potentials. These files can be found in the source tree as lib/*.libmol and lib/libmol.index, but it is usually more convenient to query the database using one of the provided tools.

Many of the basis sets are taken directly from the Pacific Northwest National Laboratory basis set database, but there are others, notably the Stuttgart effective core potentials and bases.

A simple command-line interface to the database is provided through the libmol program. It requires the environment variable LIBMOL to point to the lib/ directory, but this will default to the location of the source tree at compile time, so it is often not necessary to specify it. The command-line syntax is

libmol [-p *print*] [-e *element*] [-k *key*] [-t *type*]   [-f *format*]

where the parameters are

print:	Output level; 0 means list matching keys, 1 means print also the entry.
element:	Specify chemical element. If omitted, all elements are searched.
key:	Specify record key. If omitted, all keys are searched.
type:	Specify entry type, i.e. $s, p, \ldots$. If omitted, all types are searched.
format:	One of text (default), molpro (**MOLPRO** input format), table (tabular) or html (html table) to govern the output format.

A more convenient way of browsing the basis library is through the web interface at http://www.molpro.net/info/basis.

11.4 Default basis sets

If a basis is not specified at all for any unique atom group, then the program assumes a global default. Presently, this default is `VDZ`, but may be overridden using

`BASIS,`*basis*

or

`BASIS=`*basis*

basis is looked up in the file `lib/defbas`, which generates an appropriate request for a complete contracted set, together in some cases with an ECP, from the library. This mapping includes the following commonly-used basis sets:

- All of the Dunning correlation consistent basis sets, through the use of either the standard name of the basis set (`cc-pVXZ`, `aug-cc-pVXZ`) or an abbreviation (`VXZ`, `AVXZ`). For Al-Ar the tight-d augmented sets are obtained through the standard name `cc-pV(X+d)Z`, `aug-cc-pV(X+d)Z` or `VXZ+d`, `AVXZ+d`. Sets X=D,T,Q,5 are available for H-Kr with X=6 available for B-Ne and Al-Ar.

- The correlation consistent basis sets for core correlation, `cc-pCVXZ`, `aug-cc-pCVXZ` or `CVXZ`, `ACVXZ` (X=D,T,Q,5), and the newer "weighted sets" `cc-pwCVXZ`, `aug-cc-pwCVXZ` or `WCVXZ`, `AWCVXZ` (X=D,T,Q,5). These are available for Li-Kr (CVXZ do not include Sc-Zn).

- Douglas-Kroll-Hess relativistic versions of the correlation consistent basis sets are available through use of the standard or abbreviated names with extension -DK, e.g., `cc-pVXZ-DK` or `VXZ-DK`. X=D-5 are available for H-Kr, while X=T are available for Y-Cd and Hf-Hg. Sets contracted for 3rd-order DKH are available for Hf-Hg with extension -DK3.

- The F12 basis sets of Peterson et al. for explicitly correlated calculations, `cc-pVXZ-F12`, `cc-pCVXZ-F12` or `VXZ-F12`, `CVXZ-F12` with X=D,T,Q. These are available for H-Ar.

- The Turbomole def2 family of basis sets, `SV(P)`, `SVP`, `TZVP`, `TZVPP`, `QZVP`, and `QZVPP`. These are available for the entire periodic table except for the f-block elements.

- The older segmented Dunning/Hay double-zeta sets for the first row (`DZ` and `DZP`).

- The Roos ANO basis sets for H-Ar (`ROOS`).

- The Stuttgart ECPs and associated basis sets (e.g., `ECP10MDF`), as well as the ECP-based correlation consistent basis sets of Peterson and co-workers, `cc-pVXZ-PP`, `aug-cc-pVXZ-PP`, `cc-pwCVXZ-PP`, `aug-cc-pwCVXZ-PP` or `VXZ-PP`, `AVXZ-PP`, `WCVXZ-PP`, `AWCVXZ-PP`. The latter are available for Cu-Kr, Y-Xe, and Hf-Rn (core correlation sets currently only for transition metals).

- The Hay ECPs and corresponding basis sets (`ECP1` and `ECP2`).

- Other members of the Karslruhe basis sets (`SV`, `TZV`, and, for some elements, `TZVPPP`).

- The Binning/Curtiss sets for Ga–Kr (`BINNING-SV`, `BINNING-SVP`, `BINNING-VTZ` and `BINNING-VTZP`)

- Most of the Pople basis sets, using their standard names (e.g., `6-31G*, 6-311++G(D,P)`, etc.). Note that specially in this case, the mechanism described below using parenthesized modifiers to restrict the basis set is disabled to allow the full range of standard basis sets to be specified.

In addition, many density fitting and resolution of the identity (RI) basis sets are available. For the correlation consistent basis sets of Dunning, the appropriate VXZ/JKFIT, VXZ/MP2FIT, AVXZ/MP2FIT sets of Weigend are chosen automatically in density fitted calculations (augmented versions AVXZ/JKFIT for Fock-matrix fitting are also available, but not used by default). For the def2 family of orbital basis sets, the appropriate auxiliary sets (e.g., TZVPP/JFIT, TZVPP/JKFIT, TZVPP/MP2FIT) are used. In principle these JKFIT sets are universal and also applicable in combination with the AVXZ basis sets. Initial results indicate that they also work well with the cc-pVXZ-PP and aug-cc-pVXZ-PP series of basis sets.

For explicitly correlated F12 calculations that use the cc-pVXZ-F12 orbital basis sets, the corresponding VXZ-F12/OPTRI basis sets are used by default to construct the complementary auxiliary orbital basis (CABS). For other orbital basis sets, appropriate JKFIT sets are utilized by default.

Example:

```
BASIS=VTZ
```

generates valence triple zeta basis set for all atoms. Thus, the input

```
***,h2o cc-pVTZ basis      !A title
r=1.85,theta=104           !set geometry parameters
geometry={O;               !z-matrix geometry input
        H1,O,r;
        H2,O,r,H1,theta}
basis=VTZ                  !use VTZ basis
hf                         !closed-shell scf
```

http://www.molpro.net/info/current/examples/h2o_scf_vtz.com

performs a Hartree-Fock calculation for H_2O using the cc-pVTZ basis set.

Default basis sets can be defined anywhere in the input before the energy calculation to which it should apply using a single `BASIS` card as shown above. The default basis set applies to all types of atoms but can be superceded by different basis sets for specific atoms as explained in the next section. Some restrictions concerning the maximum angular momentum functions to be used, or the number of contracted functions are possible as follows:

The maximum angular momentum in the basis set can be reduced using syntax such as

```
BASIS,VQZ(D)
```

which would omit the *f* and *g* functions that would normally be present in the VQZ basis set.

```
BASIS,VQZ(D/P)
```

would specify additionally a maximum angular momentum of 1 on hydrogen, i.e. would omit *d* orbitals on hydrogen.

For generally contracted basis sets, an extended syntax can be used to explicitly give the number of contracted functions of each angular momentum. For example,

```
BASIS,ROOS(3s2p1d/2s)
```

generates a `6-31G*`-sized basis set from the Roos ANO compilation.

Notes: *basis* must not be variable called BASIS. Furthermore, input like

```
$BASIS=[AVDZ, AVTZ, AVQZ]
```

is not allowed, i.e. the keyword BASIS must not be preceded with $. One can loop over several basis sets using, for example, using

```
$aobases=[AVDZ, AVTZ, AVQZ]
do ibas=1,#aobases
basis=aobases(ibas)
...
enddo
```

11.5   Default basis sets for individual atoms

Different default basis sets for individual atoms can be specified with one-line BASIS commands by adding after the default basis *atom1=name1, atom2=name2,...*, where *atomi* are the chemical symbols, and *namei* are the associated basis set names. The name conventions for the atom specific basis sets work exactly as described above for default basis sets. Examples:

```
basis=vtz,h=vdz
```

uses cc-pVTZ as a general default, but for hydrogen atoms cc-pVDZ is used.

```
basis,vtz,h=vdz
```

or

```
basis,default=vtz,h=vdz
```

are equivalent to the above. Note that the default basis has to be specified before any atom specific sets.

11.6   Basis blocks

More specific basis set definitions for individual atoms can be given in BASIS input blocks, which have the following general form:

```
BASIS
SET,setname1,[options]
DEFAULT=name
atom1=name1
atom2=name2
primitive basis set specifications
SET,setname2,[options]
...
END
```

Instead of the BASIS ... END block one can also use the structure BASIS={...}

Any number of basis sets can be be given in a basis block. The definition of each basis set is started by a SET directive, on which the name of the basis and further options can be specified.

By default, the first set in a basis block is the orbital basis, and in this case the directive SET,ORBITAL can be omitted.

DEFAULT specifies the default basis set, exactly as on one line basis input. It can be followed by specifications for individual atoms, e.g. O=AVTZ. The default and atom specifications can also be merged to one line, separated by commas, e.g.

DEFAULT=VTZ,O=AVTZ,H=VDZ

Here the basis sets AVTZ, VDZ overwrite the default basis set VTZ for the atoms O and H, respectively. This is exactly as described in section 11.5 for one-line basis inputs.

The specifications SET, DEFAULT, atom=name are all optional. If DEFAULT is not given, the previous default, as specified on the last previous BASIS card, is used.

Several BASIS cards and/or blocks can immediately follow each other. Always the last specification for a given atom and setname is used (the default setname is ORBITAL).

If a basis is not specified at all for any unique atom group, then the program assumes VDZ.

11.7   Auxiliary basis sets for density fitting or resolution of the identity

As described in the previous section, several basis sets can be defined in a basis block. The definition of each basis starts with a line

SET,*name*,[CONTEXT=*context*]

where *name* is an arbitary name that can be used later to choose the basis set using options like df_basis=*name*, ri_basis=*name* etc. CONTEXT can optionally be specified to select the basis types JFIT, JKFIT, MP2FIT, CCSDFIT, or OPTRI. This affects the choice of default basis sets. For example

```
basis={
default=avtz     !default orbital basis set
set,df,context=mp2fit
default,avtz     !use avtz/mp2fit
set,jk,context=jkfit
default,avtz     !use avtz/jkfit
}
```

is equivalent to

```
basis={
default=avtz           !default orbital basis set
set,df
default,avtz/mp2fit    !use avtz/mp2fit
set,jk
default,avtz/jkfit     !use vtz/jkfit
}
```

If the setname begins with JFIT, JKFIT, MP2FIT, CCSDFIT, or OPTRI, these strings define the default context.

Specific basis sets for individual atoms or explicit input of exponents and contraction coefficients can be given exactly in the same way as for orbital basis sets.

11.8   Primitive set definition

Default basis sets given using one-line `BASIS` commands or `DEFAULT` directives in a basis block can be overwritten by explicit specifications of basis functions (type, exponents, contraction coefficients).

A group of basis functions is defined by a data card specifying a set of primitive gaussians, optionally followed by one or more cards specifying particular contractions of primitives to be included in the final basis (see section 11.9 for specification of contractions).

If an individual basis function type (*s*, *p*, *d*, etc.) is specified for an atom, it is required that all other types are also defined, i.e., as soon as an explicit definition of a basis function for an atom is given, all defaults are erased for this atom.

There are four different input forms for basis functions, as explained below under a) to d). In case that options (e.g. SCALE, NPRIM) are specified, they can be given in any order, but no value without option key must be given after an option.

In all four cases *type* defines the angular symmetry (S, P, D, F, G, H, or I). *type* can include several types, e.g., SPD or DF (this usually makes sense only with default library contractions or no contractions). The basis is loaded for all atoms with tag name *atom* in the geometry input. If *atom* is an integer, it refers to a z-matrix row.

a) Library basis sets:

type,atom,name,scale2,nprim;

or

type,atom,name,[SCALE=*scale*|SCALE2=*scale2*],[NPRIM=*nprim*|DELETE=*ndel*];

Load basis named *name* from the library

If *scale* or *scale2* is present, all exponents are scaled by *scale* or *scale**2*, respectively. If *nprim* is specified, the first *nprim* exponents only are taken from the library. If *nprim* is negative or *ndel* is given, the last |*nprim*| (*ndel*) basis functions from the library set are deleted. Associated with the library basis may be a set of default contraction coefficients which may be accessed in subsequent contraction cards. *type* can include several types, e.g., SPD or DF. This usually makes sense only with default contractions, i.e., such cards should be followed only by "C" without any other specifications for contractions.

b) Explicit basis input:

type,atom,exp1,exp2,…expn;expn+1,…;

General specification of exponents; continuation onto subsequent cards (separated by semicolon) is permitted as shown (the first card can hold up to 19 exponents, each following card 20 exponents).

The exponents (and other numerical parameters described below such as numbers of functions, and contraction coefficients) can be given as general input expressions, possibly involving variables. It is important to note, however, that these expressions are evaluated typically just once, at the same time as the complete basis set is parsed. This generally happens the first time that the basis set is required, perhaps before the first SCF calculation can be done. If the variables on which the basis depends are altered, this will not be noticed by the program, and the new basis set will not be used for subsequent stages of the computation. If, however, a new basis block is presented in the input, then the program marks as outdated any quantities such as integrals that have been calculated with the old basis set; subsequent job steps will then use the new basis.

c) Even tempered basis sets:

*type,atom,*EVEN*,nprim,ratio,centre,dratio*

or

*type,atom,*EVEN*,*NPRIM=*nprim,*[RATIO=*ratio*],[CENTRE=*centre*],[DRATIO=*dratio*]*

Generates a generalized even tempered set of functions. The number of functions *n* is specified by *nprim*, their geometric mean *c* by *centre*, the mean ratio of successive exponents *r* by *ratio*, and the variation of this ratio, *d*, by *dratio*. If *centre* is not given, the previous basis of the same type is extended by diffuse functions. If in this case *ratio* is not given, *r* is determined from the exponents of the last two function of the previous basis. If this is not possible, the default $r = 2.5$ is adopted. $d = 1$ (the default) specifies a true even-tempered set, but otherwise the ratio between successive exponents changes linearly; the exponents are given explicitly by

$$\log e_i = \log c + ((n+1)/2 - i)\log r + \frac{1}{2}((n+1)/2 - i)^2 \log d \quad i = 1, 2, \ldots, n$$

Example 1   `SP,1,VTZ;C;SP,1,EVEN,1;`
generates the generally contracted *s* and *p* triple-zeta basis sets for atom 1 and extends these by one diffuse function.

Example 2   `SPD,1,VTZ,DELETE=1;C;`
`SP,1,EVEN,NPRIM=2,RATIO=2.5;`
generates the generally contracted *s*, *p* triple-zeta basis sets for atom 1. Two energy optimized *d*-functions of Dunning are included. The last *s* and *p* functions are deleted and replaced by two even tempered functions with ratio 2.5.

d) 3-term tempered basis sets:

*type,atom,*EVEN3*,nprim,*α, β, γ

Generates a 3-parameter set of *nprim* functions with exponents given by

$$e_0 = \alpha; \qquad e_i = e_{i-1}\beta\left(1 + \frac{\gamma i^2}{(nprim+1)^2}\right), \quad i = 1, \ldots nprim - 1$$

e) Regular even tempered basis sets:

*type,atom,*EVENR*,nprim,aa,ap,bb,bp*

Generates an even tempered set of *nprim* functions according to the "regular" prescription described in M W Schmidt and K Ruedenberg, J. Chem. Phys. 71 (1970) 3951. If any of the parameters *aa, ap, bb, bp* is zero or omitted, the values are taken from table III of the above.

f) Even tempered basis set with confined progression:

*type,atom,*EVENP*,nprim,*α, β, γ

Generates an even tempered basis set with *nprim* functions and a maximal exponent given by α. The progression (ratio) between the first and second exponent is adjusted using parameter β and the progression between the last but one and the last exponent is adjusted with parameter γ. In between the progression is linearly interpolated. The explicit values of the progression factors are given by:

$$p(\beta) = \frac{\text{exponent}^i}{\text{exponent}^{i+1}} = \frac{5}{\pi}\left(\arctan(\beta - 2.5) + \frac{\pi}{2}\right) + \sqrt{2}$$

so that for $\beta \ll 0 : p \to \sqrt{2}$ and for $\beta \gg 0 : p \to 5 + \sqrt{2}$ which limits the progression factors in between these two values and enables unconstrained basis set optimisations. For $\beta \approx 0$ the progression has a factor of about 2.

*type,atom,*EVENP2,*nprim,*$\alpha,\beta,\gamma,\delta$

Generalises confined progression tempered basis sets by a third paramter (now γ) which defines the progression as above in the centre. The ratio factors are then determined by interpolating between $p(\beta) \to p(\gamma)$ and $p(\gamma) \to p(\delta)$.

11.9 Contracted set definitions

a) C,*first.last,c1,c2,…cn;cn+1,…*;

General specification of a contracted function. *first.last* defines the range of primitives to be contracted. The order corresponds to the primitives as specified on the previous input card. *c1, c2…* are the *last* − *first* + 1 contraction coefficients. Continuation onto a subsequent card is permitted as shown.

b) C;

Use default contractions from the library. This applies to both the number of contracted primitives and also to the number of different contraction sets.

c) *n*C,*first.last*;

n contracted functions taken from library. *first.last* defines the range of primitives to be contracted. If *n* is omitted and *first.last* is specified, *n* = 1. If *first.last* is omitted, the library default values are used. If both *n* and *first.last* are omitted, default values for both are used.

d) *n*C,*first.last,record.file,orb.sym*;

n contracted functions taken from orbitals *orb*, *orb*+1,..,*orb*+*n*−1 of symmetry *sym* on molpro file *record.file*. The first nonzero coefficient in the specified orbital corresponds to the first associated basis function. *first.last* specifies the range of primitives to be contracted. If *first.last* is omitted, all coefficients from the specified orbitals are used.

Example

2C,1.12,2100.2,1.1
generates two contractions, using the first 12 coefficients from orbitals 1.1 and 2.1. The orbitals are read from record 2100.2.

11.10 Examples

This shows the use of default basis sets for H_2O:

```
***,H2O
basis=VQZ(f/p)
R=0.95 ANG,THETA=104 DEGREE
geometry={O;H1,O,R;H2,O,R,H1,THETA}
hf              !do closed-shell SCF
```

   http://www.molpro.net/info/current/examples/h2o_vqz_fp.com

This is equivalent to the explicit input form

```
***,H2O
R=0.95 ANG,THETA=104 DEGREE
geometry={O;H1,O,R;H2,O,R,H1,THETA}
basis={spdf,o,vqz;c;sp,h,vqz,c;}
hf               !do closed-shell SCF
```

                            http:
 //www.molpro.net/info/current/examples/h2o_vqz_fp_explicit.com

This is an example for using multiple basis sets for density fitting and resolution of the identity

```
***,h2o
geom={o;
      h1,o,r;
      h2,o,r,h1,theta}
r=0.97 ang
theta=104

basis={
default,avtz
set,df
default,avtz/mp2fit    !density fitting basis
set,jk
default,avtz/jkfit     !density fitting basis for Fock and exchange matrices
set,ri
default,avtz/optri     !ri cabs basis
}
hf
ccsd(t)-f12,df_basis=df,df_basis_exch=jk,ri_basis=ri
```

 http://www.molpro.net/info/current/examples/h2o_basissets1.com

The following two examples yield identical results:

```
***,h2o
geom={o;
      h1,o,r;
      h2,o,r,h1,theta}
r=0.97 ang
theta=104

basis={
default,avtz
set,df,context=mp2fit
default,avtz           !density fitting basis
set,jk,context=jkfit
default,avtz           !density fitting basis for Fock and exchange matrices
set,ri,context=optri
default,avtz           !ri cabs basis
}
hf
ccsd(t)-f12,df_basis=df,df_basis_exch=jk,ri_basis=ri
```

 http://www.molpro.net/info/current/examples/h2o_basissets2.com

```
***,h2o
geom={o;
      h1,o,r;
      h2,o,r,h1,theta}
r=0.97 ang
theta=104

basis=avtz
hf
ccsd(t)-f12,df_basis=avtz/mp2fit,df_basis_exch=avtz/jkfit,ri_basis=avtz/optri
```

`http://www.molpro.net/info/current/examples/h2o_basissets3.com`

In the latter example, the speciations mp2fit and jkfit, respectively, can be omitted since these contexts are defaults for df_basis and df_basis_exch, respectively.

12   EFFECTIVE CORE POTENTIALS

Pseudopotentials (effective core potentials, ECPs) may be defined at the beginning of `BASIS` blocks.

The general form of the input cards is

`ECP`,*atom*,[*ECP specification*]

which defines a pseudopotential for an atom specified either by a chemical symbol or a group number. The *ECP specification* may consist either of a single keyword, which references a pseudopotential stored in the library, or else of an explicit definition (extending over several input cards), cf. below.

12.1   Input from ECP library

The basis set library presently contains the pseudopotentials and associated valence basis sets by a) the Los Alamos group (P. J. Hay and W. R. Wadt, J. Chem. Phys. **82**, 270 (1985) and following two papers), and b) the Stuttgart/Köln group (e.g., A. Nicklass, M. Dolg, H. Stoll and H. Preuß, J. Chem. Phys. **102**, 8942 (1995); for more details and proper references, see the web page `http://www.tc.uni-koeln.de/PP/index.en.html`). Pseudopotentials a) are adjusted to orbital energies and densities of a suitable atomic reference state, while pseudopotentials b) are generated using total valence energies of a multitude of atomic states.

Library keywords in case a) are `ECP1` and `ECP2`; `ECP2` is used when more than one pseudopotential is available for a given atom and then denotes the ECP with the smaller core definition. (For Cu, e.g., `ECP1` refers to an Ar-like $18e^-$-core, while `ECP2` simulates a Ne-like $10e^-$ one with the $3s$ and $3p$ electrons promoted to the valence shell). For accurate calculations including electron correlation, promotion of all core orbitals with main quantum number equal to any of the valence orbitals is recommended.

Library keywords in case b) are of the form `ECP`*nXY*; *n* is the number of core electrons which are replaced by the pseudopotential, *X* denotes the reference system used for generating the pseudopotential ($X = S$: states of the single-valence-electron ion; $X = M$: states of the neutral atom and of ions with low charge), and *Y* stands for the theoretical level of the reference data ($Y = HF$: Hartree-Fock, $Y = WB$: quasi-relativistic; $Y = DF$: relativistic). For one- or two-valence electron atoms $X = S$, $Y = DF$ is a good choice, while otherwise $X = M$, $Y = WB$ (or $Y = DF$) is recommended. (For light atoms, or for the discussion of relativistic effects, the

corresponding $Y = HF$ pseudopotentials may be useful.) Additionally, spin-orbit (SO) potentials and core-polarization potentials (CPP) are available, to be used in connection with case b) ECPs, but these are not currently contained in the library, so explicit input is necessary here (cf. below).

In both cases, a) and b), the same keywords refer to the pseudopotential and the corresponding basis set, with a prefix `MBS-`... in case a).

12.2   Explicit input for ECPs

For each of the pseudopotentials the following information has to be provided:

- a card of the form
  `ECP`,*atom*,n_{core},l_{max},l'_{max};
  where n_{core} is the number of core electrons replaced by the pseudopotential V_{ps}, l_{max} is the number of semi-local terms in the scalar-relativistic part of V_{ps}, while l'_{max} is the corresponding number of terms in the SO part:

$$V_{ps} = -\frac{Z - n_{core}}{r} + V_{l_{max}} + \sum_{l=0}^{l_{max}-1} (V_l - V_{l_{max}})\mathscr{P}_l + \sum_{l=1}^{l'max} \Delta V_l \mathscr{P}_l \vec{l} \cdot \vec{s} \mathscr{P}_l;$$

  the semi-local terms (with angular-momentum projectors $\mathscr{P}_l$) are supplemented by a local term for $l = l_{max}$.

- a number of cards specifying $V_{l_{max}}$, the first giving the expansion length $n_{l_{max}}$ in

$$V_{l_{max}} = \sum_{j=1}^{n_{l_{max}}} c_j r^{m_j-2} e^{-\gamma_j r^2}$$

  and the following $n_{l_{max}}$ ones giving the parameters in the form

$$m_1, \gamma_1, c_1; m_2, \gamma_2, c_2; \ldots$$

- a number of cards specifying the scalar-relativistic semi-local terms in the order $l = 0, 1, \ldots, l_{max} - 1$. For each of these terms a card with the expansion length n_l in

$$V_l - V_{l_{max}} = \sum_{j=1}^{n_l} c_j^l r^{m_j^l-2} e^{-\gamma_j^l r^2}$$

  has to be given, and immediately following n_l cards with the corresponding parameters in the form $m_1^l, \gamma_1^l, c_1^l; m_2^l, \gamma_2^l, c_2^l; \ldots$

- analogously, a number of cards specifying the coefficients of the radial potentials ΔV_l of the SO part of V_{ps}.

12.3   Example for explicit ECP input

```
***,CU
! SCF d10s1 -> d9s2 excitation energy of the Cu atom
!  using the relativistic Ne-core pseudopotential
! and basis of the Stuttgart/Koeln group.
gprint,basis,orbitals
geometry={cu}
basis
ECP,1,10,3;    ! ECP input
 1; ! NO LOCAL POTENTIAL
 2,1.,0.;
 2; ! S POTENTIAL
 2,30.22,355.770158;2,13.19,70.865357;
 2; ! P POTENTIAL
 2,33.13,233.891976;2,13.22,53.947299;
 2; ! D POTENTIAL
 2,38.42,-31.272165;2,13.26,-2.741104;
! (8s7p6d)/[6s5p3d] BASIS SET
s,1,27.69632,13.50535,8.815355,2.380805,.952616,.112662,.040486,.01;
c,1.3,.231132,-.656811,-.545875;
p,1,93.504327,16.285464,5.994236,2.536875,.897934,.131729,.030878;
c,1.2,.022829,-1.009513;C,3.4,.24645,.792024;
d,1,41.225006,12.34325,4.20192,1.379825,.383453,.1;
c,1.4,.044694,.212106,.453423,.533465;
end
rhf;
e1=energy
{rhf;occ,4,1,1,1,1,1,1;closed,4,1,1,1,1,1;wf,19,7,1;}
e2=energy
de=(e2-e1)*toev  ! Delta E = -0.075 eV
```

http://www.molpro.net/info/current/examples/cu_ecp_explicit.com

12.4   Example for ECP input from library

```
***,AuH
! CCSD(T) binding energy of the AuH molecule at r(exp)
! using the scalar-relativistic 19-valence-electron
! pseudopotential of the Stuttgart/Koeln group
gprint,basis,orbitals;
geometry={au}
basis={
ecp,au,ECP60MWB;              ! ECP input
spd,au,ECP60MWB;c,1.2;        ! basis set
f,au,1.41,0.47,0.15;
g,au,1.2,0.4;
spd,h,avtz;c;
}
rhf;
{rccsd(t);core,1,1,1,,1;}
e1=energy
geometry={h}
rhf
e2=energy;
rAuH=1.524 ang                ! molecular calculation
geometry={au;h,au,rAuH}
hf;
{ccsd(t);core,2,1,1;}
e3=energy
de=(e3-e2-e1)*toev            ! binding energy = 3.11 eV
```

    http://www.molpro.net/info/current/examples/auh_ecp_lib.com

13   CORE POLARIZATION POTENTIALS

13.1   Input options

The calculation of core-polarization matrix elements is invoked by the CPP card, which can be called at an arbitrary position in the MOLPRO input, provided the usual AO integrals have been calculated before. The CPP card can have the following formats:

- CPP,INIT,*ncentres*;

- CPP,ADD[,*factor*];

- CPP,AE[,*record.file*];

- CPP,SET[,*fcpp*];

CPP,INIT,$< ncentres >$;

abs($< ncentres >$) further cards will be read in the following format:

$< atomtype >,< ntype >,< \alpha_d >,< \alpha_q >,< \beta_d >,< cutoff >,< q_{eff} >$;

$< atomtype >$ specifies an atomic centre with polarizable core,
$< ntype >$ fixes the form of the cutoff-function (choose 1 for Fuentealba/Stoll and 2 for Mueller/Meyer);
$< \alpha_d >$ is the static dipole polarizability,
$< \alpha_q >$ is the static quadrupole polarizability,
$< \beta_d >$ is the first non-adiabatic correction to the dipole polarizability,

$< cutoff >$ is the exponential parameter of the cutoff-function, and
$< q_{eff}$ is the effective charge of the core with which it polarizes its surroundings (only needed if it contributes orbitals to the CPP core (see below)).

When $< ncentres >$ is lower than zero, only CPP integrals are calculated and saved in record 1490.1. Otherwise, the h_0 matrix (records 1200.1 and 1210.1) and the two-electron-integrals (record 1300.1) will be modified.

CPP,ADD,$< factor >$;

With this variant, previously calculated matrix elements of the polarization matrix can be added with the variable factor $< factor >$ (default: $< factor > = 1$) to the h_0-matrix as well as to the two-electron integrals. In particular, CPP,ADD,-1.; can be used to retrieve the integrals without the polarization contribution.

CPP,AE,$< record.file >$;

This is equivalent to the CPP,ADD command (with factor 1), but additionally sets a flag that CPP integrals projected with respect to core orbitals should be used. The projection is necessary whenever explicitly treated polarizable cores are present. The core orbitals are taken from *record.file*, and the CPP,AE command should be followed by a *core* card specifying the numbers of these orbitals in the various irreducible representations. Currently, the code assumes that the polarizable cores are spherically symmetric.

CPP,SET,$< fcpp >$;

normally not necessary but may be used to tell MOLPRO after a restart, with what factor the polarization integrals are effective at the moment. Currently the CPP integrals are restricted to basis functions up to and including angular momentum 4, i.e. g functions.

13.2 Example for ECP/CPP

```
***,Na2
! Potential curve of the Na2 molecule
! using 1-ve ECP + CPP
gprint,basis,orbitals;
rvec=[2.9,3.0,3.1,3.2,3.3] ang
do i=1,#rvec
rNa2=vec(i)
rNa2=rvec(i)
geometry={na;na,na,rNa2}
basis={
ecp,na,ecp10sdf;         ! ecp input
s,na,even,8,3,.5;        ! basis input
p,na,even,6,3,.2;
d,na,.12,.03;
}
cpp,init,1;              ! CPP input
na,1,.9947,,,.62;
hf;
ehf(i)=energy
{cisd;core;}
eci(i)=energy
enddo
table,rvec,ehf,eci
---
```

13.3   Example for use of CPP in all-electron calculations

```
***, P_2: All-electron calculation with polarizable P(+5) cores; calculation of the potential

print,basis,orbital;

basis=vtz

dist = [2000.,1.84,1.86,1.88,1.90,1.92,1.94,1.96] ang
do ii=1,#dist

geometry={P1;P2,P1,dist(ii)}

if (ii.eq.1) then
!calculation of free atoms at large distance
!the resulting cores are kept frozen in subsequent calculations
{rhf;closed,4,1,1,,4,1,1;wf,spin=6;save,2101.2}
e_scf(1)=energy

else


!symmetric orthogonalization of the cores for current distance
{merge,2102.2;orbital,2101.2;move;orth,3,1,1,,3,1,1;}

!calculation without CPP
{multi;occ,5,2,2,,4,1,1;frozen,3,1,1,,3,1,1,2102.2;start,2102.2;wf,30,1,0;canorb,2140.2;}
e_scf(ii)=energy

!calculating CPP integrals
cpp,init,-1;P,1,0.1057,,,1.6132,5;

!projecting CPP integrals onto valence space
{cpp,ae,2102.2;core,3,1,1,,3,1,1;}

!following calculations are done with CPP; core must be frozen
{multi;occ,5,2,2,,4,1,1;frozen,3,1,1,,3,1,1,2102.2;start,2140.2;wf,30,1,0;canorb,2141.2;}
e_scf_cpp(ii)=energy

{ccsd(t);occ,5,2,2,,4,1,1;core,3,1,1,,3,1,1;orbital,2141.2;}
e_ccsdt_cpp(ii)=energy
endif

table,dist,e_scf,e_scf_cpp,e_ccsdt_cpp
enddo
---
```

> http://www.molpro.net/info/current/examples/p2_cpp.com

14   INTEGRATION

Before starting any energy calculations, the geometry and basis set must be defined in GEOMETRY and BASIS blocks, respectively. By default, two electron integrals are evaluated once and stored on disk. This behaviour may be overridden by using the input command gdirect (see section 14.3) to force evaluation of integrals on the fly. MOLPRO checks if the one-and two-electron integrals are available for the current basis set and geometry, automatically computing them if necessary. The program also recognizes automatically if only the nuclear charges have been changed, as is the case in counterpoise calculations. In this case, the two-electron integrals are not recomputed.

14.1 Sorted integrals

If the integrals are stored on disk, immediately after evaluation they are sorted into complete symmetry-packed matrices, so that later program modules that use them can do so as efficiently as possible. As discussed above, it is normally not necessary to call the integral and sorting programs explicitly, but sometimes additional options are desired, and can be specified using the `INT` command, which should appear after geometry and basis specifications, and before any commands to evaluate an energy.

`INT,` [[`NO`]`SORT,`] [`SPRI=`*value*]

`SORT,` [`SPRI=`*value*]

`INT,NOSORT;SORT` can be used to explicitly separate the integral evaluation and sorting steps, for example to collect separate timing data. With *value* set to more than 1 in the `SPRI` option, all the two-electron integrals are printed.

The detailed options for the integral sort can be specified using the `AOINT` parameter set, using the input form

`AOINT,` *key1=value1*, *key2=value2*, ...

`AOINT` can be used with or without an explicit `INT` command.

The following summarizes the possible keys, together with their meaning, and default values.

c_final	Integer specifying the compression algorithm to be used for the final sorted integrals. Possible values are 0 (no compression), 1 (compression using 1, 2, 4 or 8-byte values), 2 (2, 4 or 8 bytes), 4 (4, 8 bytes) and 8. Default: 0
c_sort1	Integer specifying the compression algorithm for the intermediate file during the sort. Default: 0
c_seward	Integer specifying the format of label tagging and compression written by the integral program and read by the sort program. Default: 0
compress	Overall compression; c_final, c_seward and c_sort1 are forced internally to be not less than this parameter. Default: 1
thresh	Real giving the truncation threshold for compression. Default: 0.0, which means use the integral evaluation threshold (`GTHRESH, TWOINT`)
io	String specifying how the sorted integrals are written. Possible values are `molpro` (standard MOLPRO record on file 1) and `eaf` (Exclusive-access file). `eaf` is permissible only if the program has been configured for MPP usage, and at present `molpro` is implemented only for serial execution. `molpro` is required if the integrals are to be used in a restart job. For maximum efficiency on a parallel machine, `eaf` should be used, since in that case the integrals are distributed on separate processor-local files.

For backward-compatibility purposes, two convenience commands are also defined: `COMPRESS` is equivalent to `AOINT,COMPRESS=1`, and `UNCOMPRESS` is equivalent to `AOINT,COMPRESS=0`.

14.2 Imported hamiltonian

It is possible to import the second-quantised hamiltonian completely from outside MOLPRO. In order to do so, it is necessary to set up a job that simulates the desired calculation by having a basis set of exactly the same dimensions as the one to be imported. One can then import the hamiltonian using the command

`HAMILTONIAN`,*filename*

filename is the name of a file that contains the hamiltonian in FCIDUMP format, which can be produced using Molpro's `{FCI;DUMP}` facility, or by another method.

Note that this facility is fragile, and is limited to energy-only calculations. Attempts to calculate gradients or other properties will inevitably fail. At present, the implementation does not support the use of point-group symmetry.

14.3 INTEGRAL-DIRECT CALCULATIONS (`GDIRECT`)

References:

Direct methods, general: M. Schütz, R. Lindh, and H.-J. Werner, Mol. Phys. 96, 719 (1999).
Linear scaling LMP2: M. Schütz, G. Hetzer, and H.-J. Werner J. Chem. Phys. **111**, 5691 (1999).

Most methods implemented in MOLPRO can be performed integral-direct, i.e., the methods are integral driven with the two-electron integrals in the AO basis being recomputed whenever needed, avoiding the bottleneck of storing these quantities on disk. Exceptions are currently full CI (FCI), perturbative triple excitations (T), `UMP2`, `RMP2`, `CPP`, `MRCI-F12`, and `RS2-F12`. For small molecules, this requires significantly more CPU time, but reduces the disk space requirements when using large basis sets. However, due to efficient prescreening techniques, the scaling of the computational cost with molecular size is lower in integral-direct mode than in conventional mode, and therefore integral-direct calculations for extended molecules may even be less expensive than conventional ones. The break-even point depends strongly on the size of the molecule, the hardware, and the basis set. Depending on the available disk space, calculations with more than 150–200 basis functions in one symmetry should normally be done in integral-direct mode.

Integral-direct calculations are requested by the `DIRECT` or `GDIRECT` directives. If one of these cards is given outside the input of specific programs it acts globally, i.e. all subsequent calculations are performed in integral-direct mode. On the other hand, if the `DIRECT` card is part of the input of specific programs (e.g. `HF`, `CCSD`), it affects only this program. The `GDIRECT` directive is not recognized by individual programs and always acts globally. Normally, all calculations in one job will be done integral-direct, and then a `DIRECT or GDIRECT` card is required before the first energy calculation. However, further `DIRECT` or `GDIRECT` directives can be given in order to modify specific options or thresholds for particular programs.

The integral-direct implementation in MOLPRO involves three different procedures: (i) Fock matrix evaluation (`DFOCK`), (ii) integral transformation (`DTRAF`), and (iii) external exchange operators (`DKEXT`). Specific options and thresholds exist for all three programs, but it is also possible to specify the most important thresholds by general parameters, which are used as defaults for all programs.

Normally, appropriate default values are automatically used by the program, and in most cases no parameters need to be specified on the `DIRECT` directive. However, in order to guarantee sufficient accuracy, the default thresholds are quite strict, and in calculations for extended systems larger values might be useful to reduce the CPU time.

The format of the `DIRECT` directive is

`DIRECT,` `key1=`*value1*`,` `key2=`*value2...*

The following table summarizes the possible keys and their meaning. The default values are given in the subsequent table. In various cases there is a hierarchy of default values. For instance, if `THREST_D2EXT` is not given, one of the following is used: [`THR_D2EXT`, `THREST_DTRAF`, `THR_DTRAF`, `THREST`, *default*]. The list in brackets is checked from left to right, and the first one found in the input is used. *default* is a default value which depends on the energy threshold and the basis set (the threshold is reduced if the overlap matrix contains very small eigenvalues).

General Options (apply to all programs):

THREST	Integral prescreening threshold. The calculation of an integral shell block is skipped if the product of the largest estimated integral value (based on the Cauchy-Schwarz inequality) and the largest density matrix element contributing to the shell block is smaller than this value. In `DTRAF` and `DKEXT` effective density matrices are constructed from the MO coefficients and amplitudes, respectively.
THRINT	Integral prescreening threshold. This applies to the product of the exact (i.e. computed) integral value and a density matrix. This threshold is only used in `DTRAF` and `DKEXT`. A shell block of integrals is skipped if the product of the largest integral and the largest element of the effective density matrix contributing to the shell block is smaller than this threshold. If it is set negative, no computed integrals will be neglected.
THRPROD	Prescreening threshold for products of integrals and MO-coefficients (`DTRAF`) or amplitudes (`DKEXT`). Shell blocks of MO coefficients or amplitudes are neglected if the product of the largest integral in the shell block and the largest coefficient is smaller than this value. If this is set negative, no product screening is performed.
THRMAX	Initial value of the prescreening threshold `THREST` for `DFOCK` and `DKEXT` in iterative methods (`SCF`, `CI`, `CCSD`). If nonzero, it will also be used for `DKEXT` in `MP3` and `MP4(SDQ)` calculations. The threshold will be reduced to `THREST` once a certain accuracy has been reached (see `VARRED`), or latest after `MAXRED` iterations. In `CI` and `CCSD` calculations, also the initial thresholds `THRINT_DKEXT` and `THRPROD_DKEXT` are influenced by this value. For a description, see `THRMAX_DKEXT`. If `THRMAX=0`, the final thresholds will be used from the beginning in all methods.
SCREEN	Enables or disables prescreening. `SCREEN≥ 0`: full screening enabled. `SCREEN< 0`: `THRPROD` is unused. No density screening in direct SCF. `SCREEN< −1`: `THRINT` is unused. `SCREEN< −2`: `THREST` is unused.
MAXRED	Maximum number of iterations after which thresholds are reduced to their final values in `CI` and `CCSD` calculations. If `MAXRED=0`, the final thresholds will be used in `CI` and `CCSD`

	from the beginning (same as `THRMAX=0`, but `MAXRED` has no effect on `DSCF`. In the latter case a fixed value of 10 is used.
VARRED	Thresholds are reduced to their final values if the sum of squared amplitude changes is smaller than this value.
SWAP	Enables or disables label swapping in `SEWARD`. Test purpose only.

Specific options for direct SCF (`DFOCK`)**:**

THREST_DSCF	Final prescreening threshold in direct SCF. If given, it replaces the value of `THREST`.
THRMAX_DSCF	Initial prescreening threshold in direct SCF. This is used for the first 7-10 iterations. Once a certain accuracy is reached, the threshold is reduced to `THREST_DSCF`
SWAP_DFOCK	Enables or disables label swapping in fock matrix calculation (test purpose only).

General options for direct integral transformation (`DTRAF`)**:**

PAGE_DTRAF	Selects the transformation method. `PAGE_DTRAF=0`: use minimum memory algorithm, requiring four integral evaluations. `PAGE_DTRAF=1`: use paging algorithm,leading to the minimum CPU time (one integral evaluation for DMP2/LMP2 and two otherwise).
SCREEN_DTRAF	If given, replaces value of **SCREEN** for `DTRAF`.
MAXSHLQ1_DTRAF	Maximum size of merged shells in the first quarter transformation step (0: not used).
MINSHLQ1_DTRAF	Shells are only merged if their size is smaller than this value (0: not used).
MAXSHLQ2_DTRAF	Maximum size of merged shells in the second quarter transformation step (0: not used).
MINSHLQ2_DTRAF	Shells are only merged if their size is smaller than this value (0: not used).
MAXCEN_DTRAF	Maximum number of centres in merged shells (0: no limit).
PRINT_DTRAF	Print parameter for `DTRAF`.

General thresholds for all direct integral transformations:

THR_DTRAF	General threshold for `DTRAF`. If given, this is taken as default value for all thresholds described below.
THREST_DTRAF	AO prescreening threshold for `DTRAF`. Defaults: [`THR_DTRAF`, `THREST`, *default*].
THRINT_DTRAF	Integral threshold for `DTRAF`. Defaults: [`THR_DTRAF`, `THRINT`, *default*].
THRPROD_DTRAF	Product threshold for `DTRAF`. Defaults: [`THR_DTRAF`, `THRPROD`, *default*].

Thresholds specific to direct integral transformations:

THR_D2EXT	General threshold for generation of 2-external integrals. If given, this is used as a default for all D2EXT thresholds described below.
THREST_D2EXT	Prescreening threshold for generation of 2-external integrals. Defaults: [THR_D2EXT, THREST_DTRAF, THR_DTRAF, THREST, *default*].
THRINT_D2EXT	Integral threshold for generation of 2-external integrals. Defaults: [THR_D2EXT, THRINT_DTRAF, THR_DTRAF, THRINT, *default*].
THRPROD_D2EXT	Product threshold for generation of 2-external integrals. Defaults: [THR_D2EXT, THRPROD_DTRAF, THR_DTRAF, THRPROD, *default*].
THR_D3EXT	General threshold for generation of 3-external integrals. If given, this is used as a default for all D3EXT thresholds described below.
THREST_D3EXT	Prescreening threshold for generation of 3-external integrals. Defaults: [THR_D3EXT, THREST_DTRAF, THR_DTRAF, THREST, *default*].
THRINT_D3EXT	Integral threshold for generation of 3-external integrals. Defaults: [THR_D3EXT, THRINT_DTRAF, THR_DTRAF, THRINT, *default*].
THRPROD_D3EXT	Product threshold for generation of 3-external integrals. Defaults: [THR_D3EXT, THRPROD_DTRAF, THR_DTRAF, THRPROD, *default*].
THR_D4EXT	General threshold for generation of 4-external integrals. If given, this is used as a default for all D4EXT thresholds described below.
THREST_D4EXT	Prescreening threshold for generation of 4-external integrals. Defaults: [THR_D4EXT, THREST_DTRAF, THR_DTRAF, THREST, *default*].
THRINT_D4EXT	Integral threshold for generation of 4-external integrals. Defaults: [THR_D4EXT, THRINT_DTRAF, THR_DTRAF, THRINT, *default*].
THRPROD_D4EXT	Product threshold for generation of 4-external integrals. Defaults: [THR_D4EXT, THRPROD_DTRAF, THR_DTRAF, THRPROD, *default*].
THR_DCCSD	General threshold for generalized transformation needed in each CCSD iteration. If given, this is used as a default for THREST_DCCSD, THRINT_DCCSD, and THRPROD_DCCSD described below.
THREST_DCCSD	Prescreening threshold for DCCSD transformation. Defaults: [THR_DCCSD, THREST_DTRAF, THR_DTRAF, THREST, *default*].

THRINT_DCCSD	Integral threshold for DCCSD transformation. Defaults: [THR_DCCSD, THRINT_DTRAF, THR_DTRAF, THRINT, *default*].
THRPROD_DCCSD	Product threshold for DCCSD transformation. Defaults: [THR_DCCSD, THRPROD_DTRAF, THR_DTRAF, THRPROD, *default*].
THRMAX_DCCSD	Initial value for THREST_DCCSD in CCSD calculations. The threshold will be reduced to THREST_DCCSD once a certain accuracy has been reached (see VARRED), or latest after MAXRED iterations. The initial thresholds THRINT_DCCSD and THRPROD_DCCSD are obtained by multiplying their input (or default) values by THRMAX_DCCSD/THREST_DCCSD, with the restriction that the initial values cannot be smaller than the final ones.

Specific options for direct MP2 (DMP2):

DMP2	Selects the transformation method for direct MP2: DMP2=−1: automatic selection, depending on the available memory. DMP2=0: use fully direct method for DMP2 (min. two integral evaluations, possibly multipassing, no disk space). DMP2=1: use semi-direct method for DMP2 (one to four integral evaluations, depending on PAGE_DTRAF). DMP2=2: use DKEXT to compute exchange operators in DMP2 (one integral evaluation). This is only useful in local DMP2 calculations with many distant pairs.
THR_DMP2	General threshold for generation of 2-external integrals in DMP2. If given, this is used as a default for all DMP2 thresholds described below.
THREST_DMP2	Prescreening threshold for generation of 2-external integrals. Defaults: [THR_DMP2, THREST_DTRAF, THR_DTRAF, THREST, *default*].
THRINT_DMP2	Integral threshold for generation of 2-external integrals. Defaults: [THR_DMP2, THRINT_DTRAF, THR_DTRAF, THRINT, *default*].
THRPROD_DMP2	Product threshold for generation of 2-external integrals Defaults: [THR_DMP2, THRPROD_DTRAF, THR_DTRAF, THRPROD, *default*].

Specific options for direct local MP2 (LMP2):

DTRAF	Selects the transformation method for direct LMP2: DTRAF $\geq$ 0: generates the 2-external integrals (exchange operators) first in AO basis and transforms these thereafter in a second step to the projected, local basis. The disk storage requirements hence scale cubically with molecular size. DTRAF = −1: generates the 2-external integrals (exchange operators) directly in projected basis. The disk storage requirements hence scale linearly with molecular size. This (together with PAGE_DTRAF = 0) is the recommended algorithm for very

large molecules (cf. linear scaling LMP2, chapter 32).

$DTRAF = -2$: alternative algorithm to generate the exchange operators directly in projected basis. Usually, this algorithm turns out to be computationally more expensive than the one selected with $DTRAF = -1$. Note, that neither $DTRAF = -1$ nor $DTRAF = -2$ work in the context of LMP2 gradients.

THR_LMP2	General threshold for generation of 2-external integrals in linear scaling LMP2. If given, this is used as a default for all LMP2 thresholds described below.
THREST_LMP2	Prescreening threshold for generation of 2-external integrals. Defaults: [THR_LMP2, THREST_DTRAF, THR_DTRAF, THREST, *default*].
THRQ1_LMP2	Threshold used in the first quarter transformation. Defaults: [THR_LMP2, THRPROD_DTRAF, THR_DTRAF, THRPROD, *default*].
THRQ2_LMP2	Threshold used in the second and subsequent quarter transformations. Defaults: [THR_LMP2, THRINT_DTRAF, THR_DTRAF, THRINT, *default*].
THRAO_ATTEN	Special threshold for prescreening of attenuated integrals $(\mu\mu\vert\nu\nu)$ Default: THREST_LMP2

Options for integral-direct computation of external exchange operators (DKEXT):

DKEXT	Selects driver for DKEXT. DKEXT=-1: use paging algorithm (minimum memory). This is automatically used if in-core algorithm would need more than one integral pass. DKEXT=0: use in-core algorithm, no integral triples. DKEXT=1: use in-core algorithm and integral triples. DKEXT=2: use in-core algorithm and integral triples if at least two integrals of a triple differ. DKEXT=3: use in-core algorithm and integral triples if all integrals of a triple differ.
SCREEN_DKEXT	if given, replaces value of **SCREEN** for DKEXT.
MAXSIZE_DKEXT	Largest size of merged shells in DKEXT (0: not used).
MINSIZE_DKEXT	Shells are only merged if their size is smaller than this value. (0: not used).
MAXCEN_DKEXT	Maximum number of centres in merged shells (0: no limit).
SCREEN_DKEXT	Enables of disables screening in DKEXT.
PRINT_DKEXT	Print parameter for DKEXT.
SWAP_DKEXT	Enables of disables label swapping in DKEXT (test purpose only)
MXMBLK_DKEXT	Largest matrix block size in DKEXT (only used with DKEXT$\geq$ 1).

Thresholds for integral-direct computation of external exchange operators (DKEXT)**:**

THR_DKEXT	General threshold for DKEXT. If given, this is used as a default for all DKEXT thresholds described below.
THREST_DKEXT	Prescreening threshold for DKEXT. Defaults: [THR_DKEXT, THREST, *default*].
THRINT_DKEXT	Integral threshold for DKEXT. Defaults: [THR_DKEXT, THRINT, *default*].
THRPROD_DKEXT	Product threshold for DKEXT. Defaults: [THR_DKEXT, THRPROD, *default*].
THRMAX_DKEXT	Initial value for THREST_DKEXT in CI, and CCSD calculations. If nonzero. it will also be used for DKEXT in MP3 and MP4(SDQ) calculations. The threshold will be reduced to THREST_DKEXT once a certain accuracy has been reached (see VARRED), or latest after MAXRED iterations. The initial thresholds THRINT_DKEXT and THRPROD_DKEXT are obtained by multiplying their input (or default) values by THRMAX_DKEXT/THREST_DKEXT, with the restriction that the initial values cannot be smaller than the final ones.

For historical reasons, many options have alias names. The following tables summarize the default values for all options and thresholds and also gives possible alias names.

Table 6: Default values and alias names for `direct` options.

Parameter	Alias	Default value
SCREEN		1
MAXRED		7
VARRED		1.d-7
SWAP		1
SWAP_DFOCK		SWAP
DMP2	DTRAF	−1
PAGE_DTRAF	PAGE	1
SCREEN_DTRAF		SCREEN
MAXSHLQ1_DTRAF	NSHLQ1	32
MINSHLQ1_DTRAF		0
MAXSHLQ2_DTRAF	NSHLQ2	16
MINSHLQ2_DTRAF		0
MAXCEN_DTRAF		0
PRINT_DTRAF		−1
SWAP_DTRAF		SWAP
DKEXT	DRVKEXT	3
SCREEN_DKEXT		SCREEN
MAXSIZE_DKEXT		0
MINSIZE_DKEXT		5
MAXCEN_DKEXT		1
PRINT_DKEXT		−1
SWAP_DKEXT		SWAP
MXMBLK_DKEXT		depends on hardware (-B parameter on `molpro` command)

Table 7: Default thresholds and alias names for `direct` calculations

Parameter	Alias	Default value
THREST	THRAO	$\min(\Delta E \cdot 1.d-2, 1.d-9)^{a,b}$
THRINT	THRSO	$\min(\Delta E \cdot 1.d-2, 1.d-9)^{a,b}$
THRPROD	THRP	$\min(\Delta E \cdot 1.d-3, 1.d-10)^{a,b}$
THRMAX		1.d-8^b
THREST_DSCF	THRDSCF	$\leq$ 1.d-10 (depending on accuracy and basis set)
THRMAX_DSCF	THRDSCF_MAX	THRMAX
THR_DTRAF	THRDTRAF	
THREST_DTRAF	THRAO_DTRAF	[THR_DTRAF, THREST]
THRINT_DTRAF	THRAO_DTRAF	[THR_DTRAF, THRINT]
THRPROD_DTRAF	THRP_DTRAF	[THR_DTRAF, THRPROD]
THR_D2EXT	THR2EXT	THR_DTRAF
THREST_D2EXT	THRAO_D2EXT	[THR_D2EXT, THREST_DTRAF]
THRINT_D2EXT	THRSO_D2EXT	[THR_D2EXT, THRINT_DTRAF]
THRPROD_D2EXT	THRP_D2EXT	[THR_D2EXT, THRPROD_DTRAF]
THR_D3EXT	THR3EXT	THR_DTRAF
THREST_D3EXT	THRAO_D3EXT	[THR_D3EXT, THREST_DTRAF]
THRINT_D3EXT	THRSO_D3EXT	[THR_D3EXT, THRINT_DTRAF]
THRPROD_D3EXT	THRP_D3EXT	[THR_D3EXT, THRPROD_DTRAF]
THR_D4EXT	THR4EXT	THR_DTRAF
THREST_D4EXT	THRAO_D4EXT	[THR_D4EXT, THREST_DTRAF]
THRINT_D4EXT	THRSO_D4EXT	[THR_D4EXT, THRINT_DTRAF]
THRPROD_D4EXT	THRP_D4EXT	[THR_D4EXT, THRPROD_DTRAF]
THR_DCCSD	THRCCSD	THR_DTRAF
THREST_DCCSD	THRAO_DCCSD	[THR_DCCSD, THREST_DTRAF]
THRINT_DCCSD	THRSO_DCCSD	[THR_DCCSD, THRINT_DTRAF]
THRPROD_DCCSD	THRP_DCCSD	[THR_DCCSD, THRPROD_DTRAF]
THRMAX_DCCSD	THRMAX_DTRAF	THRMAX
THR_DMP2	THRDMP2	THR_DTRAF
THREST_DMP2	THRAO_DMP2	[THR_DMP2, THREST_DTRAF, *default^c*]
THRINT_DMP2	THRSO_DMP2	[THR_DMP2, THRINT_DTRAF, *default^c*]
THRPROD_DMP2	THRP_DMP2	[THR_DMP2, THRPROD_DTRAF, *default^c*]
THR_LMP2	THRLMP2	THR_DTRAF
THREST_LMP2	THRAO_LMP2	[THR_LMP2, THREST_DTRAF, *default^c*]
THRQ1_LMP2	THRQ1	[THR_LMP2, THRPROD_DTRAF, *default^c*]
THRQ2_LMP2	THRQ2	[THR_LMP2, THRINT_DTRAF, *default^c*]
THRAO_ATTEN]	THRATTEN	THREST_LMP2
THR_DKEXT	THRKEXT	
THREST_DKEXT	THRAO_DKEXT	[THR_DKEXT, THREST]
THRINT_DKEXT	THRSO_DKEXT	[THR_DKEXT, THRINT]
THRPROD_DKEXT	THRP_DKEXT	[THR_DKEXT, THRPROD]
THRMAX_DKEXT		THRMAX

a) ΔE is the requested accuracy in the energy (default 1.d-6).

b) The thresholds are reduced if the overlap matrix has small eigenvalues.

c) The default thresholds for DMP2 and LMP2 are $0.1 \cdot \Delta E$.

14.3.1   Example for integral-direct calculations

```
memory,2,m
$method=[hf,mp2,ccsd,qci,bccd,multi,mrci,acpf,rs3]          !some methods
basis=vdz                                                   !basis
geometry={o;h1,o,r;h2,o,r,h1,theta}                         !geometry
gdirect                                                     !direct option
r=1 ang,theta=104                                           !bond length and angle
do i=1,#method                                              !loop over methods
$method(i)                                                  !run method(i)
e(i)=energy                                                 !save results in variables
dip(i)=dmz
enddo
table,method,e,dip                                          !print table of results
```

http://www.molpro.net/info/current/examples/h2o_direct.com

This job produces the following table:

```
METHOD       E           DIP
HF        -76.02145798  0.82747348
MP2       -76.22620591  0.00000000
CCSD      -76.23580191  0.00000000
QCI       -76.23596211  0.00000000
BCCD      -76.23565813  0.00000000
MULTI     -76.07843443  0.76283026
MRCI      -76.23369819  0.76875001
ACPF      -76.23820180  0.76872802
RS3       -76.23549448  0.75869972
```

15   DENSITY FITTING

Density fitting can be used to approximate the integrals in spin restricted Hartree-Fock (HF), density functional theory (KS), second-order Møller-Plesset perturbation theory (MP2 and RMP2), explicitly correlated MP2 (MP2-F12), all levels of closed-shell local correlation methods (LCC2, LMP2-LMP4, LQCISD(T), LCCSD(T)), as well as for CASSCF and CASPT2 methods. Density fitting is invoked by adding the prefix DF- to the command name, e.g. DF-HF, DF-KS, DF-MP2 and so on. Gradients are available for DF-HF, DF-KS, DF-MP2, DF-LMP2, DF-CASSCF, and DF-CASPT2. Symmetry is not implemented for density fitting programs. Therefore, symmetry is turned off automatically if DF- is found in the input.

By default, a fitting basis set will be chosen automatically that corresponds to the current orbital basis set and is appropriate for the method. For instance, if the orbital basis set is VTZ, the default fitting basis is VTZ/JKFIT for DF-HF or DF-KS, and VTZ/MP2FIT for DF-MP2. Other fitting basis sets from the library can be chosen using the DF_BASIS option, e.g.

```
BASIS=VTZ               !use VTZ orbital basis
DF-HF,DF_BASIS=VQZ      !use VQZ/JKFIT fitting basis
DF-MP2,DF_BASIS=VQZ     !use VQZ/MP2FIT fitting basis
```

The program then chooses automatically the set which is appropriate for the method. Optionally, the basis type can appended to the basis name and then this supercedes the default, e.g.

```
DF-HF,DF_BASIS=VQZ/JKFIT     !use VQZ/JKFIT fitting basis
```

Orbital basis sets can be chosen using type `ORBITAL` (but this is not recommended normally!). Contraction/uncontraction can be forced appending (CONTRACT) or (UNCONTRACT) to the basis name, e.g.
`DF_BASIS=AVQZ(UNCONTRACT)/ORBITAL`.
If other options are given in parenthesis, these can be separated by commas, e.g.
`DF_BASIS=AVQZ(f/d,UNCONTRACT)/ORBITAL`.
Alternative forms, which should work as well, are
`DF_BASIS=AVQZ(f/d)(UNCONTRACT)/ORBITAL`
or
`DF_BASIS=AVQZ(f/d)/ORBITAL(UNCONTRACT)`.
Note that the CONTRACT/UNCONTRACT option cannot be used with basis set names previously defined in a basis block (see below).

Alternatively, fitting basis sets can be defined in a preceding basis block (see 11), and then be refered to with their set names, e.g.,

```
DF-HF, DF_BASIS=MYJKBASIS
DF-MP2, DF_BASIS=MYMP2BASIS
```

where `MYJKBASIS` and `MYMP2BASIS` are sets defined in a basis block. In this case it is the responsibility of the user to ensure that the basis set is appropriate for the method.

Further options, as fully described in section 15.1, can be added on the command line. In this case they are valid only for the current command. Alternatively, the options can be specifed on a separate `DFIT` directive. If this is given within a command block, the options are used only for the current program; this is entirely equivalent to the case that the options are specified on the command line. However, if a `DFIT` (or `GDFIT`) directive is given outside of a command block, the specified options are used globally in all subsequent density fitting calculations in the same run.

The options specified on a global `DFIT` directive are also passed down to procedures. However, if a `DFIT` is given within a procedure, the corresponding options are used only in the same procedure and procedures called from it. When the procedure terminates, the options from the previous level are recovered.

15.1 Options for density fitting

The options described in this section have sensible default values and usually do not have to be given. Many options described below have alias names. These can be obtained using

`HELP,CFIT,ALIASES`.

15.1.1 Options to select the fitting basis sets

BASIS	Basis set for fitting (Default: set corresponding to the orbital basis)
BASIS_COUL	Basis set for Coulomb fitting (default `BASIS`)
BASIS_EXCH	Basis set for exchange fitting (default `BASIS`)
BASIS_MP2	Fitting basis set for DF-MP2 (default `BASIS`)
BASIS_CCSD	Fitting basis set for DF-LCCSD (default `BASIS`)

15.1.2 Screening thresholds

`THRAO`	Threshold for neglecting contracted 3-index integrals in the AO basis (default 1.d-8).
`THRMO`	Threshold for neglecting half-transformed 3-index integrals (default 1.d-8).
`THRSW`	Threshold for Schwarz screening (default 1.d-5).
`THROV`	Threshold for neglecting 2-index integrals in the AO (default 1.d-10.
`THRPROD`	Product screening threshold for first half transformation (default 1.d-8).

Analogous thresholds for specfic programs can be set by appending the above keywords by the following specifications

`_SCF`	Coulomb and exchange fitting in DF-HF/DF-KS
`_COUL`	Coulomb fitting in DF-HF/DF-KS
`_EXCH`	Exchange fitting in DF-HF/DF-KS
`_CPHF`	Coulomb and exchange fitting in CPHF
`_SCFGRD`	Coulomb and exchange fitting in DF-HF/DF-KS gradients

The default values are the same as for the general thresholds.

Further thresholds:

`THR2HLF`	Threshold for second-half transformation in exchange fitting (default `THRAO_SCF`)
`THRASM_SCF`	Threshold for local assembly of exchange matrix (default `THRAO_SCF`)
`THRAO_FOCK`	Threshold for Coulomb fitting in DF-KS (default `MIN(THRAO_SCF*1.d-2,1.d-12)`)

15.1.3 Parameters to enable local fitting

Local fitting as described in H.-J. Werner, F. R. Manby, and P. J. Knowles, J. Chem. Phys. **118**, 8149 (2003), Polly, H.-J. Werner, F. R. Manby, and Peter J. Knowles, Mol. Phys. **102**, 2311 (2004), and M. Schütz, H.-J. Werner, R. Lindh and F. R. Manby, J. Chem. Phys. **121**, 737 (2004) can be activated by setting `LOCFIT=1`. By default, local fitting is disabled, because under certain circumstances it can lead to unacceptable errors. For instance, local fitting must not be used in counter-poise calculations, since the lack of fitting functions at the dummy atoms can lead to wrong results.

Local fitting can be restricted to certain programs, using the following options:

`LOCFIT`	If positive, use local fitting in all programs in which it is available (default 0).
`LOCFIT_SCF`	If positive, use local fitting in SCF (default `LOCFIT`)
`LOCFIT_MP2`	If positive, use local fitting in DF-LMP2; 1: use orbital domains; 2: use pair domains (default `LOCFIT`)

LOCFIT_F12	If positive, use local fitting in DF-LMP2-F12 (default LOCFIT)
LOCFIT_CCSD	If positive, use local fitting in DF-LCCSD (default LOCFIT)
LOCFIT_2EXT	If positive, use local fitting in LCCSD 2ext transformation (default LOCFIT_CCSD)
LOCFIT_3EXT	If positive, use local fitting in LCCSD 3ext transformation (default LOCFIT_CCSD)
LOCFIT_4EXT	If positive, use local fitting in LCCSD 4ext transformation (default LOCFIT_CCSD)
LOCFIT_CPHF	If positive, use local fitting in CPHF (default LOCFIT)
LOCFIT_SCFGRD	If positive, use local fitting in gradient calculations (default LOCFIT)
LOCORB	If positive, use localized orbitals in DF-HF (default 1)
LOCTRA	If positive, use local screening in first half transformation (default LOCFIT).
DSCREEN	If positive, enable density screening in LMP2 (default 0)
KSCREEN	If positive, enable fit-basis Schwarz screening in LMP2 (default depends on LOCTRA).

15.1.4   Parameters for fitting domains

The following options can be used to modify the domains used in local fitting. These parameters only have an effect if LOCFIT=1. The local fitting domains are determined in two steps: first *primary* orbital domains are determined. In the LMP2 and LCCSD programs, the primary orbital domains are the same as used for excitation domains and determined by the Boughton-Pulay procedure, as described in Sect. 32. Depending on the value of FITDOM_MP2 or FITDOM_CCSD for LMP2 and LCCSD, respectively, either the orbital domains are used directly or united pair domains are generated. In DF-HF the primary orbital domains include all basis functions at atoms which have Löwdin charges greater or equal to THRCHG_SCF. In the second step the primary fitting domains are extended using either distance criteria (RDOMAUX, in bohr) or bond connectivity criteria (IDOMAUX). IDOMAUX=1 means to include all functions at atoms wich are at most one bond distant from the primary domains. By default, distance criteria are used. However, if IDOMAUX.ge.0, the distance criteria are ignored and connectivity is used.

THRCHG_SCF	Parameter to select the primary orbital domains in local exchange fitting (default 0.1). All atoms are included which have Löwdin charges greater than this value. The primary domains are extended according to RDOMAUX_SCF or IDOMAUX_SCF.
FITDOM_MP2	Parameter to select primary fitting domains in LMP2 transformation (default 3). 1: use orbital domains; 2: use united orbital domains of strong pairs; 3: use united orbital domains of strong and weak pairs (default 3). The primary domains are extended according to RDOMAUX_MP2 or IDOMAUX_MP2
FITDOM_CCSD	Similar to FITDOM_MP2 but used for LCCSD 2-ext transformation.
RDOMAUX_SCF	Distance criterion for fitting domain extension in SCF (default 5.0)

IDOMAUX_SCF	Connectivity criterion for fitting domain extension in SCF (default 0)
RDOMAUX_CORE	Distance criterion for core orbital fitting domain extension in SCF (default RDOMAUX_SCF).
IDOMAUX_CORE	Connectivity criterion for core orbital fitting domain extension in SCF (default IDOMAUX_SCF).
RDOMSCF_START	Distance criterion for fitting domain extension in the initial SCF iterations (default 3.0).
IDOMSCF_START	Connectivity criterion for fitting domain extension in the initial SCF iterations (default 1).
RDOMSCF_FINAL	Distance criterion for fitting domain extension in the final SCF iterations (default RDOMAUX_SCF).
IDOMSCF_FINAL	Connectivity criterion for fitting domain extension in the final SCF iterations (default IDOMAUX_SCF).
RDOMAUX_MP2	Distance criterion for fitting domain extension in LMP2. The default value depends on FITDOM_MP2
IDOMAUX_MP2	Connectivity criterion for fitting domain extension in LMP2. The default value depends on FITDOM_MP2
RDOMAUX_CCSD	Distance criterion for fitting domain extension in LCCSD. The default value depends on FITDOM_CCSD).
IDOMAUX_CCSD	Connectivity criterion for fitting domain extension in LCCSD. The default value depends on FITDOM_CCSD.
RDOMAUX_CPHF	Distance criterion for fitting domain extension in CPHF (default 3.0).
RDOMAUX_SCFGRD	Distance criterion for fitting domain extension in gradients (default 5.0).
SCSGRD	Switches the DF-LMP2 analytic gradient to Grimmes SCS scaled MP2 energy functional (default 0).

15.1.5   Miscellaneous control options

There is a rather large number of parameters. Many of these should normally not be changed, and therefore only a subset is described here. A full list can be obtained using

HELP,CFIT

16   THE SCF PROGRAM

The Hartree-Fock self-consistent field program is invoked by one of the following commands:

`HF` or `RHF`	calls the spin-restricted Hartree-Fock program
`UHF` or `UHF-SCF`,*options*	calls the spin-unrestricted Hartree-Fock program

In contrast to older versions of MOLPRO, the `HF` and `RHF` directives have identical functionality and can both be used for closed-shell or open-shell calculations. Other aliases are `HF-SCF` or `RHF-SCF`.

Often, no further input is necessary. By default, the number of electrons is equal to the nuclear charge, the spin multiplicity is 1 (singlet) for an even number of electrons and 2 (doublet) otherwise, and the wavefunction is assumed to be totally symmetric (symmetry 1) for singlet calculations. The Aufbau principle is used to determine the occupation numbers in each symmetry. Normally, this works well in closed-shell and many open-shell cases, but sometimes wrong occupations are obtained. In such cases, the `OCC` and/or `CLOSED` directives can be used to force convergence to the desired state. The default behaviour can be modified either by options on the command line, or by directives.

In open-shell cases, we recommend to use the `WF`, `OCC`, `CLOSED`, or `OPEN` cards to define the wavefunction uniquely. Other commands frequently used are `START` and `ORBITAL` (or `SAVE`) to modify the default records for starting and optimized orbitals, respectively. The `SHIFT` option or directive allows to modify the level shift in the RHF program, and `EXPEC` to calculate expectation values of one-electron operators (see section 6.13). Section 16.10 discusses strategies for dealing difficult molecules and convergence problems.

Density fitting can be used for closed and open-shell spin-restricted HF and is invoked by a prefix `DF-` (`DF-HF` or `DF-RHF`, see section 15). For UHF, only Coulomb fitting is possible (`CF-UHF`). Density fitting very much speeds up calculations for large molecules. The greatest savings are seen for large basis sets with high angular momentum functions. For details see R. Polly, H.-J. Werner, F. R. Manby, and Peter J. Knowles, *Fast Hartree-Fock theory using local density fitting approximations*, Mol. Phys. **102**, 2311 (2004). **All publications resulting from DF-HF or DF-KS calculations should cite this work.**

16.1   Options

In this section the options for `HF | RHF | UHF` are described. For further options affecting Kohn-Sham calculations see section 17. For compatibility with previous *MOLPRO* versions, options can also be given on subsequent directives, as described in later sections.

16.1.1   Options to control HF convergence

`ACCU[RACY]=`*accu*	Convergence threshold for the density matrix (square sum of the density matrix element changes). If *accu* > 1, a threshold of 10^{-accu}) is used. The default depends on the global `ENERGY` threshold, and the threshold is automatically tightened in geometry optimizations or frequency calculations (unless a tight threshold is given).
`ENERGY=`*thrden*	The convergence threshold for the energy. The default depends on the global `ENERGY` threshold.

START=*record*	Record holding start orbitals.
SAVE|ORBITAL=*record*	Dump record for orbitals.
MAXIT=*maxit*	Maximum number of iterations (default 60)
SHIFTA|SHIFTC=*shifta*	Level shift for closed-shell orbitals in RHF (default -0.3) and α-spin orbitals in UHF (default 0).
SHIFTB|SHIFTO=*shiftb*	Level shift for open-shell orbitals in RHF and β-spin orbitals in UHF (default 0)
NITORD|NITORDER=*nitord*	Starting with iteration *nitocc*, the orbital occupation pattern is kept fixed: The orbitals are reordered after each iteration to obtain maximum overlap with the closed-shell/open-shell/virtual spaces from the previous iteration. This takes only effect after *nitord* iterations. The default depends on the quality of the starting guess.
NITSH|NITSHIFT=*nitsh*	If the iteration count is smaller than *nitsh*, the shifts are set to zero. The default depends on the quality of the starting guess.
NITCL|NITCLOSED=*nitcl*	If the iteration count is smaller than *nitcl*, only the closed-shell part of the Fock matrix is used (default *nitcl*= 0). This option is left for compatibility purposes, it almost never helps.
NITOCC=*nitocc*	Starting with iteration *nitocc* the occupation pattern is kept fixed. The default depends on the quality of the starting guess.
NITORT|NITORTH=*nitort*	The orbitals are reorthonormalized after every *nitort* iterations. The default is *nitort*= 10.

Note that in case of a restart the iteration count starts with 3.

16.1.2 Options for the diagonalization method

In calculations with very large basis sets, the diagonalization time becomes a significant fraction of the total CPU time. This can be reduced using the orbital rotation method as described in R. Polly, H.-J. Werner, F. R. Manby, and Peter J. Knowles, Mol. Phys. **102**, 2311 (2004))

MINROT=*minrot*	If *minrot*≥ 0, the orbital rotation method is employed. Explicit diagonalization of the full Fock matrix is performed in the first *minrot* iterations and in the last iteration. If *minrot*=0, a default is used which depends on the starting guess.
NEXPR=*nexpr*	Number of terms used in the exponential expansion of the unitary orbital transformation matrix (default 4).
DEROT=*nexpr*	Energy gap used in the orbital rotation method. For orbitals within $\pm$*derot* hartree of the HOMO orbital energy the Fock matrix is constructed and diagonalized (default 1.0)
JACOBI=*jacobi*	If nonzero, use Jacobi diagonalization.

16.1.3 Options for convergence acceleration methods (DIIS)

For more details, see IPOL directive.

IPTYP=*iptyp*	Interpolation type (default DIIS, see IPOL directive).

IPNIT|DIIS_START=*ipnit*	First iteration for DIIS interpolation.
IPSTEP|DIIS_STEP=*ipstep*	Iteration increment for DIIS interpolation.
MAXDIS|MAXDIIS=*maxdis*	Max number of Fock matrices used in DIIS interpolation (default 10).

16.1.4 Options for integral direct calculations

DIRECT	(logical). If given, do integral-direct HF.
THRMIN|THRDSCF_MIN=*value*	Final integral screening threshold for DSCF.
THRMAX|THRDSCF_MAX=*value*	Initial integral screening threshold for DSCF.
THRINT|THRDSCF=*value*	Same as THRDSCF_MIN.
PRESCREEN=*value*	If nonzero, use density screening (default).
DISKSIZE]=*value*	Max disk size in Byte for semi-direct calculations (currently disabled).
BUFSIZE=*value*	Max memory buffer size for semi-direct calculations (currently disabled).
THRDISK=*value*	Threshold for writing integrals to disk (currently disabled).
PRINT_DFOCK=*value*	Print option for direct Fock matrix calculation.

16.1.5 Special options for UHF calculations

NATORB=*record*	Save natural charge orbitals in given record.
UNOMIN=*unomin*	Minimum occpation number for UNO-CAS (default 0.02)
UNOMAX=*unomax*	Maximum occupation number for UNO-CAS (default 1.98)

16.1.6 Options for local density-fitting calculations

Please refer section 15 for more options regarding density fitting. The following options affect local density fitting, as described in H.-J. Werner, F. R. Manby, and P. J. Knowles, J. Chem. Phys. **118**, 8149 (2003), and R. Polly, H.-J. Werner, F. R. Manby, and Peter J. Knowles, Mol. Phys. **102**, 2311 (2004)). Note that local fitting affects the accuracy.

LOCFIT=*locfit*	If nonzero, use local fitting for exchange. If > 1, also use local fitting for Coulomb (not recommended).
RDOM=*locfit*	Radius for fitting domain selection in local fitting (default 5 bohr).
RDOMC=*locfit*	Radius for fitting domain selection for core orbitas in local fitting (default RDOM).
DOMSEL=*domesel*	Criterion for selecting orbital domains in local fitting (default 0.1).

16.1.7 Options for polarizabilities

POLARI=*value*	If nonzero, compute analytical dipole polarizabilities. See also the POLARI directive (section 16.8), which allows to specify various one-electron operators (by default, the dipole operator is used).
THRCPHF=*thresh*	Threshold for CPHF if polarizabilities are computed (default 1.d-6).

16.1.8 Printing options

PRINT|ORBPRINT=*value*	Number of virtual orbitals to be printed. If *value*=0, the occupied orbitals are printed.
DEBUG=*value*	Option for debug print.

16.2 Defining the wavefunction

The number of electrons and the total symmetry of the wavefunction are specified on the WF card:

WF,*elec,sym,spin*

where

elec	is the number of electrons
sym	is the number of the irreducible representation
spin	defines the spin symmetry, $spin = 2*S$ (singlet=0, doublet=1, triplet=2 etc.)

Note that these values take sensible defaults if any or all are not specified (see section 4.8). For example, {rhf; wf,sym=N,spin=M} gives the explicit values N for the symmetry and M for the spin of the wave function, but uses the default number of electrons.

16.2.1 Defining the number of occupied orbitals in each symmetry

OCC,$n_1, n_2, \ldots, n_8$

To avoid convergence problems in cases with high symmetry, this card should be included whenever the occupation pattern is known in advance. n_i is the number of occupied orbitals in the irreducible representation *i*. The total number of orbitals must be equal to (*elec*+*spin*)/2 (see WF card).

16.2.2 Specifying closed-shell orbitals

CLOSED,$n_1, n_2, \ldots, n_8$

This optional card can be used in open-shell calculations to specify the number of closed-shell orbitals in each symmetry. This makes possible to force specific states in the absence of an OPEN card.

16.2.3 Specifying open-shell orbitals

OPEN,*orb*$_1$.*sym*$_1$,*orb*$_2$.*sym*$_2$,...,*orb*$_n$.*sym*$_n$

This optional card can be used to specify the singly occupied orbitals. The number of singly occupied orbitals must be equal to *spin*, and their symmetry product must be equal to *sym* (see WF card). If the OPEN card is not present, the open shell orbitals are selected automatically. The algorithm tries to find the ground state, but it might happen that a wrong state is obtained if there are several possibilities for distributing the open shell electrons among the available orbitals. This can also be avoided using the CLOSED card. If *orb*$_i$.*sym* is negative, this orbital will be occupied with negative spin (only allowed in UHF).

16.3 Saving the final orbitals

ORBITAL,*record.file*
SAVE,*record.file*

The optimized orbitals, and the corresponding density matrix, fock matrix, and orbital energies are saved on *record.file*. SAVE is an alias for ORBITAL. If this card is not present, the defaults for *record* are:

RHF	2100	
UHF	2200	(holds both α and β-spin orbitals and related quantities)

These numbers are incremented by one for each subsequent calculation of the same type in the same input. Note that this holds for the sequence number in the input, independently in which order they are executed (see section 4.3).

The default for *file* is 2.

16.4 Starting orbitals

The START directive can be used to specify the initial orbitals used in the SCF iteration. It is either possible to generate an initial orbital guess, or to start with previously optimized orbitals. Alternatively, one can also use a previous density matrix to construct the first fock operator.

If the START card is absent, the program tries to find suitable starting orbitals as follows:

First:	Try to read orbitals from *record* specified on the ORBITAL or SAVE card or the corresponding default (see ORBITAL). All files are searched.
Second:	Try to find orbitals from a previous SCF or MCSCF calculation. All files are searched.
Third:	If no orbitals are found, the starting orbitals are generated using approximate atomic densities or eigenvectors of *h* (see below).

Since these defaults are usually appropriate, the START card is not required in most cases.

16.4.1 Initial orbital guess

An initial orbital guess can be requested as follows:

START,[TYPE=]*option*

The *option* keyword can be:

H0	Use eigenvectors of *h* (core Hamiltonian) as starting guess.
ATDEN	Use natural orbitals of a diagonal density matrix constructed using atomic orbitals and atomic occupation numbers (default).

Note that it is also possible to use orbitals from previous (e.g., smaller basis set) calculations as starting orbitals (see section 16.4.2 below).

Example:

```
r=1.85,theta=104          !set geometry parameters
geometry={O;              !z-matrix geometry input
        H1,O,r;
        H2,O,r,H1,theta}
basis=STO-3G              !first basis set
hf                        !scf using STO-3G basis
basis=6-311G              !second basis set
hf                        !scf using 6-311G basis set
```

http://www.molpro.net/info/current/examples/h2o_sto3gstart1.com

The second calculation uses the optimized orbitals of the STO-3G calculation as starting guess. This is done by default and no START card is necessary. The explicit use of START and SAVE cards is demonstrated in the example in the next section.

The following input is entirely equivalent to the one in the previous section:

```
r=1.85,theta=104          !set geometry parameters
geometry={O;              !z-matrix geometry input
        H1,O,r;
        H2,O,r,H1,theta}
basis=STO-3G              !first basis set
hf                        !scf using STO-3G basis
start,atdens              !use atomic density guess
save,2100.2               !save orbitals to record 2100.2
basis=6-311G              !second basis set
hf                        !scf using 6-311G basis set
start,2100.2              !start with orbitals from the previous STO-3G calculation.
save,2101.2               !save optimized orbitals to record 2101.2
```

http://www.molpro.net/info/current/examples/h2o_sto3gstart2.com

Beware, however, that STO-3G is a very poor basis set and usually gives very bad starting vectors. This technique is best used in combination with reasonable small basis sets (e.g., cc-pVDZ or def2-SVP) or minimal basis sets with a proper repesentation of the occupied atomic orbitals (e.g, 6-31G or MINAO/MINAO-PP):

```
memory,50,m

! CuO2(NH3)4
geometry={
 N    -2.244097     0.000000    -0.017684
 N     1.111652    -1.671116    -0.178974
 N     1.111652     1.671116    -0.178974
 N    -0.306059     0.000000    -2.311080
Cu   -0.179579     0.000000    -0.290548
 O    -0.184327     0.000000     1.594789
 O     1.053213     0.000000     2.103145
 H    -2.331519     0.000000     1.002818
 H     0.614110     0.000000    -2.753879
 H    -0.793743     0.815054    -2.687415
 H    -0.793743    -0.815054    -2.687415
 H    -2.764729     0.814552    -0.345484
 H    -2.764729    -0.814552    -0.345484
 H     0.635193     2.543632     0.052739
 H     0.635193    -2.543632     0.052739
 H     1.616225     1.397092     0.672915
 H     1.616225    -1.397092     0.672915
 H     1.809254     1.910324    -0.883324
 H     1.809254    -1.910324    -0.883324
}
wf,charge=1,spin=2

! select all-electron minimal basis sets for H,N,O and ECP10 based basis
! set for Cu; using MINAO-PP here instead of MINAO allows us to project
! the obtained wave function on the cc-pVTZ-PP basis later on.
basis=MINAO,Cu=MINAO-PP

! Run HF to get an initial guess for the valence electronic
! structure. The level shifts damp and stabilize the convergence.
{rhf; shift,-1.0,-0.5; save,2100.2}

! select the actual basis set and start RHF with projected wave function
! from MINAO basis. nitord=1 asks RHF to reorder orbitals in each
! iteration to maximize overlap with the closed and active space
! from the last iteration.
basis=AVTZ,Cu=VTZ-PP,H=VDZ(p)
{df-rhf,nitord=1; start,2100.2}
```

```
http://www.molpro.net/info/current/examples/minao_startorb.com
```

16.4.2   Starting with previous orbitals

START,[RECORD=]*record.file*,[*specifications*]

reads previously optimized orbitals from record *record* on file *file*. Optionally, a specific orbital set can be specified as described in section 4.11.

The specified dump record may correspond to a different geometry, basis set, and/or symmetry than used in the present calculation. Using starting orbitals from a different basis set can be useful if no previous orbitals are available and the ATDENS option cannot be used (see above).

The following example shows how to change the symmetry between scf calculations. Of course, this example is quite useless, but sometimes it might be easier first to obtain a solution in higher symmetry and then convert this to lower symmetry for further calculations.

```
r1=1.85,r2=1.85,theta=104        !set geometry parameters
geometry={O;                     !z-matrix geometry input
         H1,O,r1;
         H2,O,r2,H1,theta}
basis=vdz
hf                               !scf using c2v symmetry
orbital,2100.2                   !save on record 2100.2

symmetry,x

hf
start,2100.2                     !start with previous orbitals from c2v symmetry
orbital,2101.2                   !save new orbitals

geometry={O;                     ! geometry has to be respecified so that
         H1,O,r1;                  ! H1 and H2 can be retagged as symmetry related
         H2,O,r2,H1,theta}
symmetry,x,y
hf
start,2101.2                     !start with orbitals from cs symmetry
orbital,2102.2                   save new orbitals
```

```
                                 http:
   //www.molpro.net/info/current/examples/h2o_c2v_cs_start.com
```

Note, however, that this only works well if the orientation of the molecule does not change. Sometimes it might be helpful to use the `noorient` option.

Note also that a single dump record cannot hold orbitals for different basis dimensions. Using `save=2100.2` in the second calculation would therefore produce an error.

If orbitals from a corresponding SCF calculation at a neighbouring geometry are available, these should be used as starting guess.

16.4.3   Starting with a previous density matrix

START,DENSITY=*record.file*,[*specifications*]

A density matrix is read from the given dump record and used for constructing the first fock matrix. A specific density matrix can be specified as described in section 4.11. It is normally not recommended to use the DENSITY option.

16.5   Rotating pairs of orbitals

ROTATE,*orb$_1$.sym*,*orb$_2$.sym*,*angle*

Performs a 2×2 rotation of the initial orbitals *orb$_1$* and *orb$_2$* in symmetry *sym* by *angle* degrees. With *angle*= 0 the orbitals are exchanged. See MERGE for other possibilities to manipulate orbitals. In UHF, by default only the β-spin orbitals are rotated. The initial α-spin orbitals can be rotated using

ROTATEA,*orb$_1$.sym*,*orb$_2$.sym*,*angle*

In this case ROTATEB is an alias for ROTATE.

16.6   Using additional point-group symmetry

Since *MOLPRO* can handle only Abelian point-groups, there may be more symmetry than explicitly used. For instance, if linear molecules are treated in C_{2v} instead of $C_{\infty v}$, the $\delta_{(x^2-y^2)}$-orbitals appear in symmetry 1 (A_1). In other cases, a linear geometry may occur as a special case of calculations in C_S symmetry, and then one component of the π-orbitals occurs in symmetry 1 (A'). The program is able to detect such hidden "extra" symmetries by blockings in the one-electron hamiltonian h and the overlap matrix S. Within each irreducible representation, an "extra" symmetry number is then assigned to each basis function. These numbers are printed at the end of the integral output. Usually, the extra symmetries are ordered with increasing l-quantum number of the basis functions. This information can be used to determine and fix the extra symmetries of the molecular orbitals by means of the SYM command.

SYM,*irrep,sym*(1),*sym*(2),,,*sym*(*n*)

sym(i) are the extra symmetries for the first n orbitals in the irreducible representation *irrep*. For instance, if you want that in a linear molecule the orbitals 1.1 to 3.1 are σ and 4.1, 5.1 δ, the SYM card would read (calculation done with X,Y as symmetry generators):

SYM,1,1,1,1,2,2

If necessary, the program will reorder the orbitals in each iteration to force this occupation. The symmetries of occupied and virtual orbitals may be specified. By default, symmetry contaminations are not removed. If *irrep* is set negative, however, symmetry contaminations are removed. Note that this may prevent convergence if degenerate orbitals are present.

16.7   Expectation values

EXPEC,*oper*$_1$,*oper*$_2$,...,*oper*$_n$

Calculates expectation values for one-electron operators *oper*$_1$, *oper*$_2$, ..., *oper*$_n$. See section 6.13 for the available operators. By default, the dipole moments are computed. Normally, it is recommended to use the GEXPEC directive if expectation values for other operators are of interest. See section 6.13 for details.

16.8   Polarizabilities

POLARIZABILITY[,*oper*$_1$,*oper*$_2$,...,*oper*$_n$]

Calculates polarizabilities for the given operators *oper*$_1$, *oper*$_2$, ..., *oper*$_n$.. See section 6.13 for the available operators. If no operators are specified, the dipole polarizabilities are computed.

Presently, this is working only for closed-shell without direct option.

The polarizabilities are stored in the variables POLXX, POLXY, POLXZ, POLYY, POLYZ, POLZZ.

16.9   Miscellaneous directives

All commands described in this section are optional. Appropriate default values are normally used.

16.9.1   Level shifts

`SHIFT`,*shifta,shiftb*

A level shift of *shifta* and *shiftb* hartree for α- and β-spin orbitals, respectively, is applied. This can improve convergence, but has no effect on the solution. *shifta*$= -0.2$ to -0.3 are typical values. The defaults are *shifta*$= 0$ and *shifta*$= -0.3$ in closed and open-shell calculations, respectively, and *shiftb*$= 0$.

Applying large negative level shifts like $\{$`rhf; shift,-1.0,-0.5`$\}$ will often stabilize convergence at the expense of making it somewhat slower. See section 16.10.

16.9.2   Maximum number of iterations

`MAXIT`,*maxit*

sets the maximum number of iterations to *maxit*. The default is *maxit*$= 60$.

16.9.3   Convergence threshold

`ACCU`,*accu*

This threshold applies to the square sum of the density matrix element changes (same as option `ACCU`). If *accu*> 1, a threshold of 10^{-accu}) is used. The default depends on the global `ENERGY` threshold, and the threshold is automatically tightened in geometry optimizations or frequency calculations (unless a tight threshold is given).

16.9.4   Sanity check on the energy

`NOENEST`

This disables the sanity check on the energy even if the energy value is unreasonable. Otherwise, the energy will be automatically checked by default.

16.9.5   Print options

`ORBPRINT`,*print,test*

This determines the number of virtual orbitals printed at the end of the calculation. By default, *print*$= 0$, i.e., only the occupied orbitals are printed. *print*$= -1$ suppresses printing of orbitals entirely. *test*$= 1$ has the additional effect of printing the orbitals after each iteration.

16.9.6   Interpolation

`IPOL`,*iptyp,ipnit,ipstep,maxdis*

This command controls iterative subspace interpolation. *iptyp* can be:

`DIIS`	direct inversion of the iterative subspace. This is the default and usually yields fast and stable convergence.
`KAIN`	Krylov-subspace accelerated inexact newton. A method similar to DIIS.

NONE   No interpolation.

ipnit is the number of the iteration in which the interpolation starts (default: as soon as possible). *ipstep* is the iteration increment between interpolations (default: 1, i.e., every iteration). *maxdis* is the maximum dimension of the DIIS matrix (default 10). *iptyp* and *maxdis* can also be set as options. E.g.,

```
{rhf,maxdis=20,iptyp='DIIS'; shift,-1.0,-0.5}
```

16.9.7   Reorthonormalization of the orbitals

ORTH,*nitort*

The orbitals are reorthonormalized after every *nitort* iterations. The default is *nitort*= 10.

16.9.8   Direct SCF

DIRECT,*options*

If this card is present, the calculation is done in direct mode. See section 14.3 for options. Normally, it is recommended to use the global GDIRECT command to request the direct mode. See section 14.3 for details.

16.10   Handling difficult cases: When SCF does not converge

General suggestions:

- Carry out convergence experiments with a small but reasonable basis set (e.g., cc-pVDZ, def2-SVP, aug-cc-pVDZ, ASVP). STO-3G is *not* a reasonable basis set.

Before you start you should check:

- Whether your geometry is sensible (e.g., look for Angstrom/Bohr conversion issues). Note that Molpro prints bond distances in both Angstroms and atomic units at the top of an output.

- Whether you have selected the correct electronic state (spin and symmetry). Molpro tries to guess spatial symmetries of open-shell compounds automatically if none are provided. However, the guess is not always right. In such a case you need to give the symmetry manually (in the simplest case as wf,sym=N,spin=M. See section 16.2). Molpro does *not* attempt to guess the spin state of the input compound automatically; it defaults to spin=0 for systems with even numbers of electrons and spin=1 for odd-numbered species.

If convergence problems persist, the following techniques can be attempted:

Hartree-Fock options & Small-basis initial guess:

- **Level shifts:** Adding a level shift like {rhf; shift,-1.0,-0.5} stabilizes the current RHF solution against changes and leads to smoother (but slower) convergence. That should be your first try; it is often sufficient.

- **Occupation freezing:** The option $\{\texttt{rhf,nitord=N}\}$ can be used to freeze orbital occupations at iteration N. When the programs emits warnings about reassigned orbital occupations, you could try to freeze the occupations only later (give a higher N) or earlier (give a smaller N).

  By freezing the occupation pattern you tell the RHF program to try to lock on whatever solution it currently is pursuing. This often helps if multiple RHF solutions with similar energies are present and otherwise the program would oscillate between some of them.

  Note that $\{\texttt{rhf,nitord=1}\}$ will tell RHF to lock onto the initial occupation; if combined with orbital rotation or advanced initial guesses this can often be used to converge to specific solutions (e.g., some excited states).

- **Minimal-basis SCF guess:** Try to obtain a Hartree-Fock solution with a minimal-basis AO set first and to use this as initial guess for the actual Hartree-Fock calculation. For this purpose we provided the basis set definition "MINAO" (to complement cc-pVnZ basis sets) and "MINAO-PP" (to complement cc-pVnZ-PP sets with ECPs). See section 16.4.1 for an example. These sets simply consist of the AO part of the cc-pVTZ or cc-pVTZ-PP basis sets, stripped of all their polarization functions. Since a minimal basis has fewer degrees of freedom than a real basis set, convergence is often easier, and it can still provide reasonable guess for the valence electronic structure.

  Note: The MINAO basis sets are very small, so conventional Hartree-Fock (in integral-direct mode if necessary) is typically much faster than density-fitting Hartree-Fock.

- **Increasing the DIIS dimension:** In rare cases

  $\{\texttt{rhf,maxdis=30,iptyp='DIIS',nitord=20; shift,-1.0,-0.5}\}$

  can find solutions which are not found in the standard settings. Usually increasing the DIIS dimension beyond 10 (the default) just slows down convergence. It is also worthwhile to try a variation of DIIS known as KAIN (Krylov-subspace accelerated inexact Newton):

  $\{\texttt{rhf,maxdis=10,iptyp='KAIN',nitord=10; shift,-1.0,-0.5}\}$

  which sometimes shows different convergence behavior than straight DIIS.

Cationic or Anionic initial guess:

- If molecule X does not converge, it might still be possible to converge X^+ (X^{2+}, ..) and use this as initial guess for the actual computation. Particularly if X^+ is a closed-shell compound this will often work. If using this technique, you need to be careful about the final state you arrive in. Because your initial guess is biased, the X calculation might converge to an excited state.

Density-functional initial guess:

- For transition metals and transition states sometimes DFT methods show better convergence behavior than RHF. You might perform a DFT calculation (possibly with a smaller basis set) and use it as initial guess for the SCF. E.g.,

  $\{\texttt{df-rks,b-lyp; coarsegrid; save,2100.2}\}$

  $\{\texttt{df-rhf,nitord=1; orbital,2100.2}\}$

If all else fails: Use the MCSCF program. The MCSCF program uses an advanced orbital optimization algorithm which is much more robust than the SCF method, and which can converge almost everything you give to it (but it is often slower and sometimes locks on an excited state if started from an atomic density guess). MCSCF can also calculate Hartree-Fock solutions if used with suitable input cards.

16.11   Advanced use: Core-excited states

Some kinds of excited or higher ionized states can be calculated using a so-called delta-SCF procedure. Here the excitation/ionization energy is obtained as difference of the SCF solutions for the ground state and the excited/ionized state. If the excited state is reasonably well described by a single determinant, this procedure is normally quite accurate.

The example

```
! This example calculates the N 1s core-hole binding energy of pyridine
! using a delta-SCF procedure. It calculates a SCF solution in the
! ground state, then in the core-excited state, and reports the
! difference. The example shows how to obtain the core-excited state
! of a core of your choice.
memory,20,m;
geometry=pyridine.xyz

! we use default basis sets for all atoms except the one we wish
! to calculate the core hole of, in this case N 1s. For this atom,
! we uncontract the s and p functions of the basis to give the core
! hole more opportunities for relaxation.
!
! Notes:
!   - Uncontracting the complete basis would of course also work,
!     but might be more expensive
!   - For correlated calculations, you would need additional tight
!     correlation functions for the hole (e.g., use a cc-pwCVnZ basis
!     on the affected atom and cc-pVTZ on the rest)
basis={
   default,def2-TZVPP
   sp,N,def2-TZVPP     ! no "c;" following -- uncontracted.
   df,N,def2-TZVPP;c;  ! use d and f functions with contractions.
}

! reference calculation, normal DFT. We also uncontract the fitting
! basis to fit the core region more accurately.
{df-rks,pbe,df_basis=def2-tzvpp(u)}
ENORMAL = ENERGY       ! remember energy of ground state calculation.

! localize orbitals. This isolates the cores of the individual atoms
! also in the case of degeneracy. And, in particular, it shows us which
! orbital is the N 1s we are looking for. It comes out as orbital 1.1.
{ibba; save,2101.2}

! do the core-hole calculation. Additionally to the previous command, we
! specify nitord=1, which asks SCF to fix orbital order & occupations
! starting at iteration 1. This should prevent SCF from dropping down to
! the ground state SCF solution.
!
! With this, SCF will emit warnings about strongly deviating orbital
! occupations in the first iterations. This is to be expected when
! treating instable states and no reason for concern.
{df-rks,pbe,df_basis=def2-tzvpp(u),nitord=1;
   ! in the program, closed-shell orbitals always have lower numbers
   ! than open-shell orbitals. In order to get the core hole state, we
   ! thus need to exchange the localized N1s orbital (1.1) with whatever
   ! came out at the highest orbital number (21.1) before. [Because the
   ! latter one will be considered as singly-occupied. If we would not use
   ! localized orbitals, 21.1 would be the HOMO].
   rotate,1.1,21.1;    ! exchange orbitals 1.1 and 21.1
   orbital,2101.2;     ! use the localized orbitals as input
   wf,spin=1,charge=1  ! one open-shell orbital (implicitly 21.1)
}
EWITH_HOLE = ENERGY
! run population analysis again to see if we arrived at the right
! state. This should be indicated by an active orbital occupation
! of about 1.0 on the N 1s orbital.
{ibba}
! show the result, converted to electron volts.
{table,(EWITH_HOLE-ENORMAL)*toev
 title,N 1s core hole binding energy [Exp. value: (404.94 +/- 0.03) eV. [Can J. Chem 58 694 (1
}
```

shows how to use the delta-SCF procedure to calculate the N 1s core binding energy in pyridine, by employing localized orbtials and moving them to the HOMO position using a ROTATE card (Sec. 16.5). In the core-excited state calculation, SCF is prevented from collapsing to the ground state by using the option NITORD=1 (Sec. 16.1), which asks SCF to lock onto the input solution.

17 THE DENSITY FUNCTIONAL PROGRAM

Density-functional theory calculations may be performed using one of the following commands:

`DFT`	calculate functional of a previously computed density.
`RKS` or `RKS-SCF`	calls the spin-restricted Kohn-Sham program. `KS` and `KS-SCF` are aliases for `RKS`.
`UKS` or `UKS-SCF`	calls the spin-unrestricted Kohn-Sham program

Each of these commands may be qualified with the key-names of the functional(s) which are to be used, and further options:

command, key1, key2, key3, …, options

If no functional keyname is given, the default is `LDA` (see below). Following this command may appear directives specifying options for the density-functional modules (see section 17.2) or the Hartree-Fock program (see section 16.1).

On completion of the functional evaluation, or self-consistent Kohn-Sham calculation, the values of the individual functionals are stored in the MOLPRO vector variable `DFTFUNS`; the total is in `DFTFUN`, and the corresponding individual functional names in `DFTNAME`.

Energy gradients are available for self-consistent Kohn-Sham calculations.

Density fitting can be used for closed and open-shell spin-restricted KF and is involked by a prefix `DF-` (`DF-KS` or `DF-RKS`, see section 15). For UKS, only Coulomb fitting is possible (`CF-UKS`). Density fitting is highly recommended (unless explicit symmetry handling is required), as the induced errors are negligible and it offers *massive* speed increases, particularly for pure functionals. For details see R. Polly, H.-J. Werner, F. R. Manby, and Peter J. Knowles, *Fast Hartree-Fock theory using local density fitting approximations*, Mol. Phys. **102**, 2311 (2004). **All publications resulting from DF-HF or DF-KS calculations should cite this work.**

Normally, sensible defaults are used to define the integration grid. The accuracy can be controlled using options as described in section 17.1 or directives as described in section 17.2). More control is provided by the `GRID` command, as described in section 17.3.

17.1 Options

The following options may be specified on the `KS` or `UKS` command lines:

`GRID=`*target*	Specifies the grid target accuracy (per atom). The default is 1.d-6 unless this has been modeified using a global `THRESH,` `GRID` option.
`COARSE` (logical)	If *true*, perform initial iterations with a coarser grid. Default is *false*.
`GRIDMAX=`*gridmax*	In the initial iterations, the grid accuracy is min(*gridmax, target*coarsefac*) (only if COARSE is set).
`COARSEFAC=`*coarsefac*	Factor for initial grid accuracy (see above). The default is 1000.
`GRIDGRAD=`*0 or 1*	Defines whether grid weight derivatives are included in analytical gradient calculations (default: 1). Disabling these can improve convergence in geometry optimizations.

DFTFAC=[*fac1,fac2,..*]	Factors for each functional. The number of given values must agree with the number of functionals.
EXFAC=*factor*	Fraction of exact exchange added to the functional. The default depends on the functional.
TOLORB=*value*	Threshold for orbital screening (default depends on energy threshold).

In addition, all options valid for HF (see section 16.1) can be given.

17.2 Directives

The following options may be used to control the operation of the DFT modules. In the Kohn-Sham case, these may come in any order before or after directives for the SCF program as described in Section 16.

17.2.1 Density source (DENSITY, ODENSITY)

DENSITY,*orbc.filec,*... ODENSITY,*orbo.fileo,*...

For non-self-consistent DFT calculations, specifies the source of the density matrix. The total density is read from *orbc.filec*, with further options specifying density sets in the standard way as described in Section 4.11. ODENSITY can be used to specify the spin density. The defaults are the densities last written by an SCF or MCSCF program.

17.2.2 Thresholds (DFTTHRESH)

DFTTHRESH,*key1=value1,key2=value2*...

Sets various truncation thresholds. *key* can be one of the following.

TOTAL	Overall target accuracy (per atom) of density functional. Defaults to the value of the global threshold GRID or the value specified by option GRID. For proper use of this threshold, other thresholds should be left at their default value of zero.
ORBITAL	Orbital truncation threshold.
DENSITY	Density truncation threshold.
FOCK	Fock matrix truncation threshold.

17.2.3 Exact exchange computation (EXCHANGE)

EXCHANGE,*factor*

For Kohn-Sham calculations, compute exchange energy according to Hartree-Fock formalism and add the contribution scaled by *factor* to the fock matrix and the energy functional. Otherwise, the default is *factor=0*, i.e., the exchange is assumed to be contained in the functional, and only the Coulomb interaction is calculated explicitly.

DFTFACTOR,*fac1, fac2, ...*

Provide a factor for each functional specified. The functionals will be combined accordingly. By default, all factors are one.

17.2.4 Double-hybrid functionals (`DH`, `DSDH`)

`DH`, *ax*, *ac*

initiates a double-hybrid calculation (Ref. [1]) where a_x is the fraction of HF exchange and a_c is the fraction of MP2 correlation. A self-consistent KS calculation is performed with functional $a_x E_x^{\mathrm{HF}} + (1 - a_x) E_x^{\mathrm{DFT}}[\rho] + (1 - a_c) E_c^{\mathrm{DFT}}[\rho]$. One then needs to call the MP2 program to add the MP2 contribution $a_c E_c^{\mathrm{MP2}}$. If a_c is not given, $a_c = a_x^2$ is assumed, according to Ref. [2].

`DSDH`, *ax*, *ac*

initiates a density-scaled double-hybrid calculation (Ref. [2]) where a_x is the fraction of HF exchange and a_c is the fraction of MP2 correlation. A self-consistent KS calculation is performed with functional $a_x E_x^{\mathrm{HF}} + (1 - a_x) E_x^{\mathrm{DFT}}[\rho] + E_c^{\mathrm{DFT}}[\rho] - a_c E_c^{\mathrm{DFT}}[\rho_{1/\sqrt{a_c}}]$, where $\rho_{1/\sqrt{a_c}}$ is the scaled density. In the case of meta-GGA functionals, the kinetic energy density τ is also scaled, according to Ref. [3]. One then needs to call the MP2 program to add the MP2 contribution $a_c E_c^{\mathrm{MP2}}$. If a_c is not given, $a_c = a_x^2$ is assumed, according to Ref. [2].

Example of input for B2-PLYP calculation (Ref. [1]):
```
{ks,b,lyp;dh,0.53,0.27;}
mp2;
```

Example of input for 1DH-BLYP calculation (Ref. [2]):
```
{ks,b,lyp;dh,0.65;}
mp2;
```

Example of input for DS1DH-TPSS calculation (Ref. [3]):
```
{ks,tpss;dsdh,0.725;}
mp2;
```

Unrestricted calculations (`uks`, `ump2`) can also be done.

References:
[1] S. Grimme, J. Chem. Phys. **124**, 034108 (2006).
[2] K. Sharkas, J. Toulouse, A. Savin, J. Chem. Phys. **134**, 064113 (2011).
[3] S. M. O. Souvi, K. Sharkas, J. Toulouse, J. Chem. Phys. **140**, 084107 (2014).

17.2.5 Rangehybrid methods (`RANGEHYBRID`)

For coupling of short-range (sr-)DFT with long-range (lr-)ab-initio methods, one first has to specify the coupling parameter μ in the sr interelectronic interaction $\sum_{i<j} \mathrm{erf}(\mu r_{ij})/r_{ij}$; this can be done by setting a variable (e.g. `mu=0.5`). As a next step, long-range ERIs have to be calculated by calling the integral program (e.g. `int;erf,mu;`).

Then sr-DFT/lr-HF calculations can be performed by calling the RKS program with the additional subcommand `rangehybrid`. Available short-range functionals are `exerf` and `ecerf` for sr-LDA, and `exerfpbe` and `ecerfpbe` for sr-PBE; as usual, the functionals have to be specified after the `rks` command (e.g. `rks,exerf,ecerf;`). The underlying short-range LDA correlation functional is that of S. Paziani, S. Moroni, P. Gori-Giorgi, G.B. Bachelet, Phys. Rev. B 73, 155111 (2006).

Finally, sr-DFT/lr-post-HF calculations can be done by adding, within a call of the chosen post-HF program, two subcommands: `srxcdft` followed by the desired short-range functionals (e.g. `srxcdft,exerf,ecerf;`), and `dftden` followed by the record number from which the density for the sr functionals is taken. Implementations are available for `ci`, `mp2`, `ccsd`, `ccsd(t)`, and the corresponding local MP2 and CC methods w/wo density-fitting.

17.2.6   Exchange-correlation potential (`POTENTIAL`)

`POTENTIAL`,*rec.fil*

For stand-alone DFT calculations, compute exchange-correlation potential pseudo-matrix elements, defined formally as the differential of the sum of all specified functionals with respect to elements of the atomic orbital density matrix. The matrix is written to record *rec* on file *fil*.

17.2.7   Grid blocking factor (`DFTBLOCK`)

`DFTBLOCK`,*nblock*

Respecify the number of spatial integration points treated together as a block in the DFT integration routines (default 128). Increasing *nblock* may enhance efficiency on, e.g., vector architectures, but leads to increased memory usage.

17.2.8   Dump integrand values(`DFTDUMP`)

`DFTDUMP`,*file,status*

Write out values of the integrand at grid points to the file *file*. The first line of *file* contains the number of functional components; there then follows a line for each functional giving the input key of the functional. Subsequent lines give the functional number, cartesian coordinates, integrand value and integration weight with Fortran format (`I2,3F15.10,F23.15`).

17.2.9   Asymptotic correction for xc-potentials(`ASYMP`)

`ASYMP`,*shift,α,β,b*

Activates the gradient-regulated asymptotic correction (GRAC) approach for exchange-correlation potentials of Grüning *et al.* (J. Chem. Phys. **114**, 652 (2001)). The user has to supply a *shift* parameter (Δ_{xc}) for the bulk potential which should approximate the difference between the HOMO energy (ε_{HOMO}) obtained from the respective standard Kohn-Sham calculation and the (negative) ionisation potential of the monomer (IP):

$$\Delta_{xc} = \varepsilon_{HOMO} - (-IP) \tag{1}$$

This method accounts for the derivative discontinuity of the exact xc-potential and that is missing in approximate ones. The parameters α and β determine the interpolation function (see Eq. (2.3) in the above reference) and are set to $\alpha = 0.5$ and $\beta = 40$ by default, respectively. The parameter b is the parameter of the asymptotic xc-potential from van Leeuwen and Baerends (Phys. Rev. A **49**, 2421 (1994), Eqns. (54,55)) and is set to $b=0.05$ by default.

In case of gradient or laplacian functionals the modified GRAC scheme of Bast *et al.* (Chem. Phys. Chem. **9**, 445 (2008)) is used.

If *shift* is set to zero in the input the program will estimate the ionisation energy from the HOMO energy during the SCF (as soon as the HOMO energy is converged to a given threshold) and then sets the bulk shift automatically. This is done by using a linear fit of DFT HOMO energies to ionisation energies calculated with the ΔSCF method for a range of molecules (see also S. Hirata *et al.*, J. Phys. Chem. A, **107**, 10154 (2003)).

17.3 Numerical integration grid control (GRID)

Density functionals are evaluated through numerical quadrature on a grid in three-dimensional space. Although the sensible defaults will usually suffice, the parameters that define the grid can be specified by using the GRID top-level command, which should be presented *before* the the DFT or KS commands that will use the grid. Alternatively, GRID and its subcommands can be presented as directives within the KS program.

GRID,*orb.file*,*status*

The integration grid is stored on record *orb.file* (default 1800.2). The information on disk consists of two parts: the parameters necessary to define the grid, and a cache of the evaluated grid points and weights. The latter is flagged as 'dirty' whenever any parameters are changed, and whenever the geometry changes; if the cache is dirty, then when an attempt is made to use the grid, it will be recalculated, otherwise the cached values are used.

If *status* is OLD, an attempt to restore the grid from a previous calculation is performed; effectively, the old grid provides a template of parameters which can be adjusted using the parameter commands described below. If *status* is NEW, the grid is always created with default parameters. If *status* is UNKNOWN (the default), a new grid is created either if record *orb.file* does not exist; otherwise the old grid is used.

The GRID command may be followed by a number of parameter-modifying subcommands. The currently implemented default parameters are equivalent to the following input commands.

```
GRIDTHRESH,1e-5,0,0
RADIAL,LOG,3,1.0,20,25,25,30
ANGULAR,LEBEDEV,0.0,0.0
LMIN,0,0,0,0
LMAX,53,53,53,53
VORONOI,10
GRIDSAVE
GRIDSYM
```

17.3.1 Target quadrature accuracy (GRIDTHRESH)

GRIDTHRESH,*acc*,*accr*,*acca*

Specify the target accuracy of integration. Radial and angular grids are generated adaptively, with the aim of integrating the Slater-Dirac functional to the specified accuracy. *acc* is an overall target accuracy, and is the one that should normally be used; radial and angular grid target accuracies are generated algorithmically from it. However, they can be adjusted individually by specifying *accr* and *acca* respectively.

17.3.2 Radial integration grid (RADIAL)

RADIAL,*method*,m_r,*scale*,n_0,n_1,n_2,n_3

Specify the details of the radial quadrature scheme. Four different radial schemes are available, specified by *method* = EM, BECKE, AHLRICHS or LOG, with the latter being the default.

EM is the Euler-Maclaurin scheme defined by C. W. Murray, N. C. Handy and G. J. Laming, Mol. Phys. 78 (1993) 997. m_r, for which the default value is 2, is defined in equation (6) of the above as

$$r = \alpha \frac{x^{m_r}}{(1-x)^{m_r}} \qquad (2)$$

whilst *scale* (default value 1) multiplied by the Bragg-Slater radius of the atom gives the scaling parameter α.

`LOG` is the scheme described by M. E. Mura and P. J. Knowles, J. Chem. Phys. 104 (1996) 9848. It is based on the transformation

$$r = -\alpha \log_e(1 - x^{m_r}) \,, \tag{3}$$

with $0 \leq x \leq 1$ and simple Gauss quadrature in x-space. The recommended value of m_r is 3 for molecular systems, giving rise to the Log3 grid; $m_r{=}4$ is more efficient for atoms. α is taken to be *scale* times the recommended value for α given by Mura and Knowles, and *scale* defaults to 1.

`BECKE` is as defined by A. D. Becke, J. Chem. Phys. 88 (1988) 2547. It is based on the transformation

$$r = \alpha \frac{(1+x)}{(1-x)} \,, \tag{4}$$

using points in $-1 \leq x \leq +1$ and standard Gauss-Chebyshev quadrature of the second kind for the x-space quadrature. Becke chose his scaling parameters to be half the Bragg-Slater radius except for hydrogen, for which the whole Bragg-Slater radius was used, and setting *scale* to a value other than 1 allows a different α to be used. m_r is not necessary for this radial scheme.

`AHLRICHS` is the radial scheme defined by O. Treutler and R. Ahlrichs, J. Chem. Phys. 102 (1995) 346. It is based on the transformation their M4 mapping

$$r = \frac{\alpha}{\log_e 2}(1+x)^{0.6} \log_e\left(\frac{2}{1-x}\right) \,, \tag{5}$$

with using standard Gauss-Chebyshev quadrature of the second kind for the x-space integration. m_r is not necessary for this radial scheme.

n_0, n_1, n_2, n_3 are the degrees of quadrature n_r (see equation (3) of Murray et al.), for hydrogen/helium, first row, second row, and other elements respectively.

`accr` as given by the `THR` command specifies a target accuracy; the number of radial points is chosen according to a model, instead of using an explicit n_i. The stricter of n_i, `accr` is used, unless either is zero, in which case it is ignored.

17.3.3   Angular integration grid (`ANGULAR`)

`ANGULAR`,*method,acca,crowd*
`LMIN`,$l_0^{\min}$,$l_1^{\min}$,$l_2^{\min}$,$l_3^{\min}$
`LMAX`,$l_0^{\max}$,$l_1^{\max}$,$l_2^{\max}$,$l_3^{\max}$

Specify the details of the angular quadrature scheme. The default choice for *method* is `LEBEDEV` (ie. as in A. D. Becke, J. Chem. Phys. 88 (1988) 2547) which provides angular grids of octahedral symmetry. The alternative choice for *method* is `LEGENDRE` which gives Gauss-Legendre quadrature in θ and simple quadrature in ϕ, as defined by C. W. Murray, N. C. Handy and G. J. Laming, Mol. Phys. 78 (1993) 997.

Each type of grid specifies a family of which the various members are characterized by a single quantum number l; spherical harmonics up to degree l are integrated exactly. $l_i^{\min}$ and $l_i^{\max}, i = 0, 1, 2, 3$ specify allowed ranges of l for H–Be, B–Ca, Sc–Ba, and La– respectively. The $l_i^{\min}$ are

further moderated at run time so that for any given atom they are not less than $2i+4$ or twice the maximum angular momentum of the basis set on the atom; this constraint can be overridden by giving a negative value in LMIN, and in this case just its absolute value will be used as the lower bound. For the Lebedev grids, if the value of l is not one of the set implemented in MOLPRO (3, 5, 7, 9, 11, 13, 15, 17, 19, 23, 29, 41, 47, 53), then l is increased to give the next largest angular grid available. In general, different radial points will have different l, and in the absence of any moderation described below, will be taken from $l_i^{\max}$.

crowd is a parameter to control the reduction of the degree of quadrature close to the nucleus, where points would otherwise be unnecessarily close together; larger values of crowd mean less reduction thus larger grids. A very large value of this parameter, or, conventionally, setting it to zero, will switch off this feature.

acca is a target energy accuracy. It is used to reduce l for a given radial point as far as possible below $l_i^{\max}$ but not lower than $l_i^{\max}$. The implementation uses the error in the angular integral of the kernel of the Slater-Dirac exchange functional using a sum of approximate atomic densities. If *acca* is zero, the global threshold is used instead, or else it is ignored.

17.3.4   Atom partitioning of integration grid (VORONOI)

VORONOI,m_μ

Controls Becke-Voronoi partitioning of space. The algorithm of C. W. Murray, N. C. Handy and G. J. Laming, Mol. Phys. 78 (1993) 997 is used, with m_μ defined by equation (24). The default value is 10.

17.3.5   Grid caching (GRIDSAVE, NOGRIDSAVE)

NOGRIDSAVE

disables the disk caching of the grid, i.e, forces the recalculation of the grid each time it is needed.

GRIDSAVE

forces the use of a grid cache where possible.

17.3.6   Grid symmetry (GRIDSYM, NOGRIDSYM)

NOGRIDSYM

switches off the use of symmetry in generating the integration grid, whereas

GRIDSYM

forces the use of any point-group symmetry.

17.3.7   Grid printing (GRIDPRINT)

GRIDPRINT,*key=value*,...

controls printing of the grid, which by default is not done. At present, the only possible value for *key* is GRID, and *value* should be specified as an integer. GRID=0 causes the total number of integration points to be evaluated and reported; GRID=1 additionally shows the number of points on each atom; GRID=2 causes the complete set of grid points and weights to be printed.

17.4 Density Functionals

Widely used functional combinations can be specified via convenient keywords. These can be entered, for example via {df-rks,pbe} (do a single KS calculation with PBE) or {dfunc,pbe} (which will instruct all following KS calculations to use PBE by default). The following table lists the defined alias density functional combinations:

alias	functionals	factors	Ref
B	B88	1	doi:10.1103/PhysRevA.38.3098
B-LYP	B88:LYP	1:1	
BLYP	B88:LYP	1:1	
B-P	B88:P86	1:1	
BP86	B88:P86	1:1	
B-VWN	B88:VWN5	1:1	
B3LYP	EXACT:B88:DIRAC:LYP:VWN5	0.2:0.72:0.08:0.81:0.19	
B3LYP3	EXACT:B88:DIRAC:LYP:VWN3	0.2:0.72:0.08:0.81:0.19	
B3LYP5	EXACT:B88:DIRAC:LYP:VWN5	0.2:0.72:0.08:0.81:0.19	
B88X	B88	1	doi:10.1103/PhysRevA.38.3098
B97	EXACT:B97DF	0.1943:1	
B97R	EXACT:B97RDF	0.21:1	
BECKE	B88	1	doi:10.1103/PhysRevA.38.3098
BH-LYP	EXACT:B88:LYP	0.5:0.5:1	
CS	CS1	1	
D	DIRAC	1	
HFB	B88	1	doi:10.1103/PhysRevA.38.3098
HFS	DIRAC	1	
LDA	DIRAC:VWN5	1:1	
LSDAC	PW92C	1	doi:10.1103/PhysRevB.45.13244
LSDC	PW92C	1	doi:10.1103/PhysRevB.45.13244
LYP88	LYP	1	
MM05	EXACT:M05X:M05C	0.28:0.72:1	doi:10.1063/1.2126975
MM05-2X	EXACT:M052XX:M052XC	0.56:0.44:1	doi:10.1021/ct0502763
MM06	EXACT:M06X:M06C	0.27:0.73:1	doi:10.1007/s00214-007-0310-x
MM06-2X	EXACT:M062XX:M062XC	0.54:0.46:1	doi:10.1007/s00214-007-0310-x
MM06-L	M06LX:M06LC	1:1	doi:10.1063/1.2370993
MM06-HF	EXACT:M06HFX:M06HFC	1:1:1	doi:10.1021/jp066479k
PBE	PBEX:PBEC	1:1	doi:10.1103/PhysRevLett.77.3865
PBE0	EXACT:PBEX:PBEC	0.25:0.75:1	doi:10.1063/1.478522
PBE0MOL	EXACT:PBEX:PW91C	0.25:0.75:1	
PBEREV	PBEXREV:PBEC	1:1	
PW91	PW91X:PW91C	1:1	doi:10.1103/PhysRevB.46.6671
S	DIRAC	1	
S-VWN	DIRAC:VWN5	1:1	
SLATER	DIRAC	1	
VS99	VSXC	1	
VWN	VWN5	1	
VWN80	VWN5	1	
M05	EXACT:XC-M05	0.28:1	doi:10.1063/1.2126975
M05-2X	EXACT:XC-M05-2X	0.56:1	doi:10.1021/ct0502763
M06	EXACT:XC-M06	0.27:1	doi:10.1007/s00214-007-0310-x
M06-2X	EXACT:XC-M06-2X	0.54:1	doi:10.1007/s00214-007-0310-x
M06-L	XC-M06-L	1	doi:10.1063/1.2370993
M06-HF	EXACT:XC-M06-HF	1:1	doi:10.1021/jp066479k
M08-HX	EXACT:XC-M08-HX	0.5223:1	
M08-SO	EXACT:XC-M08-SO	0.5679:1	
M11-L	XC-M11-L	1	
SOGGA	XC-SOGGA	1	
SOGGA11	XC-SOGGA11	1	
SOGGA11-X	EXACT:XC-SOGGA11-X	0.4015:1	
TPSS	TPSSX:TPSSC	1:1	doi:10.1103/PhysRevLett.91.146401
TPSSH	EXACT:TPSSX:TPSSC	0.1:0.9:1	doi:10.1063/1.1626543
M12HFC	EXACT:M12C	1:1	doi:10.1063/1.4768228
HJSWPBE	HJSWPBEX:PBEC	1:1	doi:10.1063/1.2921797
HJSWPBEH	EXACT:HJSWPBEX:PBEC	0.2:0.8:1	doi:10.1063/1.3073302
TCSWPBE	EXERFPBE:ECERFPBE	1:1	doi:10.1063/1.1824896
PBESOL	PBESOLX:PBESOLC	1:1	doi:10.1103/PhysRevLett.100.136406

17.4.1 Technical definitions of density functional inputs

In the following, ρ_α and ρ_β are the α and β spin densities; the total spin density is ρ;

The gradients of the density enter through

$$
\begin{aligned}
\sigma_{\alpha\alpha} &= \nabla\rho_\alpha \cdot \nabla\rho_\alpha \,, \sigma_{\beta\beta} = \nabla\rho_\beta \cdot \nabla\rho_\beta \,, \sigma_{\alpha\beta} = \nabla\rho_\alpha \cdot \nabla\rho_\beta \,, \\
\sigma &= \sigma_{\alpha\alpha} + \sigma_{\beta\beta} + 2\sigma_{\alpha\beta}.
\end{aligned} \tag{6}
$$

$$
\chi_\alpha = \frac{\sqrt{\sigma_{\alpha\alpha}}}{\rho_\alpha^{4/3}} \,, \chi_\beta = \frac{\sqrt{\sigma_{\beta\beta}}}{\rho_\beta^{4/3}} \,. \tag{7}
$$

$$
\upsilon_\alpha = \nabla^2\rho_\alpha \,, \upsilon_\beta = \nabla^2\rho_\beta \,, \upsilon = \upsilon_\alpha + \upsilon_\beta \,. \tag{8}
$$

Additionally, the kinetic energy density for a set of (Kohn-Sham) orbitals generating the density can be introduced through

$$
\tau_\alpha = \sum_i^\alpha |\nabla\phi_i|^2 \,, \tau_\beta = \sum_i^\beta |\nabla\phi_i|^2 \,, \tau = \tau_\alpha + \tau_\beta \,. \tag{9}
$$

All of the available functionals are of the general form

$$
F\left[\rho_s, \rho_{\bar{s}}, \sigma_{ss}, \sigma_{\bar{s}\bar{s}}, \sigma_{s\bar{s}}, \tau_s, \tau_{\bar{s}}, \upsilon_s, \upsilon_{\bar{s}}\right] = \int d^3\mathbf{r}\, K\left(\rho_s, \rho_{\bar{s}}, \sigma_{ss}, \sigma_{\bar{s}\bar{s}}, \sigma_{s\bar{s}}, \tau_s, \tau_{\bar{s}}, \upsilon_s, \upsilon_{\bar{s}}\right) \tag{10}
$$

where $\bar{s}$ is the conjugate spin to s.

17.4.2 Lists of component density functionals

Below is a list of the primary correlation and exchange functionals supported by MOLPRO. These can be combined into total density functionals. For example, the following input will produce a B3LYP calculation:

```
{dfunc,B88,DIRAC,LYP,VWN5,dftfac=[0.72,0.08,0.81,0.19],exfac=0.2}
{df-rks}
```

Note that many commonly used combinations of primary functionals are predefined as alias keywords (e.g., {df-rks,b3lyp} is an equivalent input. See above).

B86	$X\alpha\beta\gamma$. Divergence free semiempirical gradient-corrected exchange energy functional. $\lambda = \gamma$ in ref. doi:10.1063/1.450025
B86MGC	$X\alpha\beta\gamma$ with Modified Gradient Correction. B86 with modified gradient correction for large density gradients. doi:10.1063/1.451353
B86R	$X\alpha\beta\gamma$ Re-optimised. Re-optimised β of B86 used in part 3 of Becke's 1997 paper. doi:10.1063/1.475007
B88	Becke 1988 Exchange Functional doi:10.1103/PhysRevA.38.3098

`B88C`	Becke 1988 Correlation Functional. Correlation functional depending on B86MGC exchange functional with empirical atomic parameters, t and u. The exchange functional that is used in conjunction with B88C should replace B88MGC here. doi:10.1063/1.454274
`B95`	Becke 1995 Correlation Functional. *tau* dependent Dynamical correlation functional. doi:10.1063/1.470829
`B97DF`	Density functional part of B97. This functional needs to be mixed with 0.1943*exact exchange. doi:10.1063/1.475007
`B97RDF`	Density functional part of B97 Re-parameterized by Hamprecht et al. Re-parameterization of the B97 functional in a self-consistent procedure by Hamprecht et al. This functional needs to be mixed with 0.21*exact exchange. doi:10.1063/1.477267
`BR`	Becke-Roussel Exchange Functional. A. D. Becke and M. R. Roussel,Phys. Rev. A 39, 3761 (1989)

$$K = \frac{1}{2}\sum_s \rho_s U_s, \tag{11}$$

where

$$U_s = -(1 - e^{-x} - xe^{-x}/2)/b, \tag{12}$$

$$b = \frac{x^3 e^{-x}}{8\pi\rho_s} \tag{13}$$

and x is defined by the nonlinear equation

$$\frac{xe^{-2x/3}}{x-2} = \frac{2\pi^{2/3}\rho_s^{5/3}}{3Q_s}, \tag{14}$$

where

$$Q_s = (\upsilon_s - 2\gamma D_s)/6, \tag{15}$$

$$D_s = \tau_s - \frac{\sigma_{ss}}{4\rho_s} \tag{16}$$

and

$$\gamma = 1. \tag{17}$$

`BRUEG`	Becke-Roussel Exchange Functional — Uniform Electron Gas Limit. A. D. Becke and M. R. Roussel,Phys. Rev. A 39, 3761 (1989)

As for `BR` but with $\gamma = 0.8$.

BW   Becke-Wigner Exchange-Correlation Functional. Hybrid exchange-correlation functional comprimising Becke's 1998 exchange and Wigner's spin-polarised correlation functionals.
doi:10.1039/FT9959104337

CS1   Colle-Salvetti correlation functional. R. Colle and O. Salvetti, Theor. Chim. Acta 37, 329 (1974); C. Lee, W. Yang and R. G. Parr, Phys. Rev. B 37, 785(1988)

CS1 is formally identical to CS2, except for a reformulation in which the terms involving υ are eliminated by integration by parts. This makes the functional more economical to evaluate. In the limit of exact quadrature, CS1 and CS2 are identical, but small numerical differences appear with finite integration grids.

CS2   Colle-Salvetti correlation functional. R. Colle and O. Salvetti, Theor. Chim. Acta 37, 329 (1974); C. Lee, W. Yang and R. G. Parr, Phys. Rev. B 37, 785(1988)

CS2 is defined through

$$K = -a \left(\frac{\rho + 2b\rho^{-5/3} \left[\rho_\alpha t_\alpha + \rho_\beta t_\beta - \rho t_W \right] e^{-c\rho^{-1/3}}}{1 + d\rho^{-1/3}} \right) \tag{18}$$

where

$$t_\alpha = \frac{\tau_\alpha}{2} - \frac{\upsilon_\alpha}{8} \tag{19}$$

$$t_\beta = \frac{\tau_\beta}{2} - \frac{\upsilon_\beta}{8} \tag{20}$$

$$t_W = \frac{1}{8}\frac{\sigma}{\rho} - \frac{1}{2}\upsilon \tag{21}$$

and the constants are $a = 0.04918, b = 0.132, c = 0.2533, d = 0.349$.

DIRAC   Slater-Dirac Exchange Energy. Automatically generated Slater-Dirac exchange.
doi:10.1103/PhysRev.81.385

ECERF   Short-range LDA correlation functional. Local-density approximation of correlation energy
for short-range interelectronic interaction $\mathrm{erf}(\mu r_{21})/r_{12}$,
S. Paziani, S. Moroni, P. Gori-Giorgi, and G. B. Bachelet, Phys. Rev. B 73, 155111 (2006).

$$\varepsilon_c^{\mathrm{SR}}(r_s,\zeta,\mu) = \varepsilon_c^{\mathrm{PW92}}(r_s,\zeta) - \frac{[\phi_2(\zeta)]^3 Q\left(\frac{\mu\sqrt{r_s}}{\phi_2(\zeta)}\right) + a_1\mu^3 + a_2\mu^4 + a_3\mu^5 + a_4\mu}{(1+b_0^2\mu^2)^4}$$

where

$$Q(x) = \frac{2\ln(2)-2}{\pi^2} \ln\left(\frac{1+ax+bx^2+cx^3}{1+ax+dx^2}\right), \tag{23}$$

with $a = 5.84605$, $c = 3.91744$, $d = 3.44851$, and $b = d - 3\pi\alpha/(4\ln(2) - 4)$. The parameters $a_i(r_s, \zeta)$ are given by

$$
\begin{aligned}
a_1 &= 4b_0^6 C_3 + b_0^8 C_5, \\
a_2 &= 4b_0^6 C_2 + b_0^8 C_4 + 6b_0^4 \varepsilon_c^{\mathrm{PW92}}, \\
a_3 &= b_0^8 C_3, \\
a_4 &= b_0^8 C_2 + 4b_0^6 \varepsilon_c^{\mathrm{PW92}}, \\
a_5 &= b_0^8 \varepsilon_c^{\mathrm{PW92}},
\end{aligned}
$$

with

$$
\begin{aligned}
C_2 &= -\frac{3(1-\zeta^2)\, g_c(0, r_s, \zeta = 0)}{8 r_s^3} \\[2mm]
C_3 &= -(1-\zeta^2)\frac{g(0, r_s, \zeta = 0)}{\sqrt{2\pi}\, r_s^3} \\[2mm]
C_4 &= -\frac{9 c_4(r_s, \zeta)}{64 r_s^3} \\[2mm]
C_5 &= -\frac{9 c_5(r_s, \zeta)}{40\sqrt{2\pi} r_s^3} \\[2mm]
c_4(r_s, \zeta) &= \left(\frac{1+\zeta}{2}\right)^2 g''\left(0, r_s \left(\frac{2}{1+\zeta}\right)^{1/3}, \zeta = 1\right) + \left(\frac{1-\zeta}{2}\right)^2 \times \\
&\qquad g''\left(0, r_s \left(\frac{2}{1-\zeta}\right)^{1/3}, \zeta = 1\right) + (1-\zeta^2)D_2(r_s) - \frac{\phi_8(\zeta)}{5\alpha^2 r_s^2} \\
c_5(r_s, \zeta) &= \left(\frac{1+\zeta}{2}\right)^2 g''\left(0, r_s \left(\frac{2}{1+\zeta}\right)^{1/3}, \zeta = 1\right) + \left(\frac{1-\zeta}{2}\right)^2 \times \\
&\qquad g''\left(0, r_s \left(\frac{2}{1-\zeta}\right)^{1/3}, \zeta = 1\right) + (1-\zeta^2)D_3(r_s), \qquad (24)
\end{aligned}
$$

and

$$
b_0(r_s) = 0.784949\, r_s \qquad (25)
$$

$$
g''(0, r_s, \zeta = 1) = \frac{2^{5/3}}{5\,\alpha^2\, r_s^2}\frac{1 - 0.02267 r_s}{(1 + 0.4319 r_s + 0.04 r_s^2)} \qquad (26)
$$

$$
D_2(r_s) = \frac{e^{-0.547 r_s}}{r_s^2}\left(-0.388 r_s + 0.676 r_s^2\right) \qquad (27)
$$

$$
D_3(r_s) = \frac{e^{-0.31 r_s}}{r_s^3}\left(-4.95 r_s + r_s^2\right). \qquad (28)
$$

Finally, $\varepsilon_c^{\mathrm{PW92}}(r_s, \zeta)$ is the Perdew-Wang parametrization of the correlation energy of the standard uniform electron gas [J.P. Perdew and Y. Wang, Phys. Rev. B **45**, 13244 (1992)], and

$$
g(0, r_s, \zeta = 0) = \frac{1}{2}\left(1 - B r_s + C r_s^2 + D r_s^3 + E r_s^4\right)e^{-d r_s}, \qquad (29)
$$

is the on-top pair-distribution function of the standard jellium model [P. Gori-Giorgi and J.P. Perdew, Phys. Rev. B **64**, 155102

(2001)], where $B = -0.0207$, $C = 0.08193$, $D = -0.01277$, $E = 0.001859$, $d = 0.7524$. The correlation part of the on-top pair-distribution function is $g_c(0, r_s, \zeta = 0) = g(0, r_s, \zeta = 0) - \frac{1}{2}$.

`ECERFPBE`	Range-Separated Correlation Functional. Toulouse-Colonna-Savin range-separated correlation functional based on PBE, see J. Toulouse et al., J. Chem. Phys. 122, 014110 (2005). doi:10.1063/1.1824896
`EXACT`	Exact Exchange Functional. Hartree-Fock exact exchange functional can be used to construct hybrid exchange-correlation functional.
`EXERF`	Short-range LDA correlation functional. Local-density approximation of exchange energy for short-range interelectronic interaction $\text{erf}(\mu r_{12})/r_{12}$, A. Savin, in Recent Developments and Applications of Modern Density Functional Theory, edited by J.M. Seminario (Elsevier, Amsterdam, 1996).

$$\varepsilon_x^{\text{SR}}(r_s, \zeta, \mu) = \frac{3}{4\pi} \frac{\phi_4(\zeta)}{\alpha r_s} - \frac{1}{2}(1+\zeta)^{4/3} f_x\left(r_s, \mu(1+\zeta)^{-1/3}\right) + \frac{1}{2}(1-\zeta)^{4/3} f_x\left(r_s, \right.$$

with

$$\phi_n(\zeta) = \frac{1}{2}\left[(1+\zeta)^{n/3} + (1-\zeta)^{n/3}\right], \qquad (31)$$

$$f_x(r_s, \mu) = -\frac{\mu}{\pi}\left[(2y - 4y^3)e^{-1/4y^2} - 3y + 4y^3 + \sqrt{\pi}\,\text{erf}\left(\frac{1}{2y}\right)\right], \qquad y = \frac{\mu\,\alpha\,r_s}{2}$$

and $\alpha = (4/9\pi)^{1/3}$.

`EXERFPBE`	Range-Separated Exchange Functional. Toulouse-Colonna-Savin range-separated exchange functional based on PBE, see J. Toulouse et al., J. Chem. Phys. 122, 014110 (2005). doi:10.1063/1.1824896
`G96`	Gill's 1996 Gradient Corrected Exchange Functional doi:G96
`HCTH120`	Handy least squares fitted functional doi:10.1063/1.480732
`HCTH147`	Handy least squares fitted functional doi:10.1063/1.480732
`HCTH93`	Handy least squares fitted functional doi:10.1063/1.477267
`HJSWPBEX`	Meta GGA Correlation Functional. Henderson-Janesko-Scuseria range-separated exchange functional based on a model of an exchange hole derived by a constraint-satisfaction technique, see T. M. Henderson et al., J. Chem. Phys. 128, 194105 (2008). doi:10.1063/1.2921797
`LTA`	Local τ Approximation. LSDA exchange functional with density represented as a function of τ. doi:10.1063/1.479374

LYP	Lee, Yang and Parr Correlation Functional. C. Lee, W. Yang and R. G. Parr, Phys. Rev. B 37, 785(1988); B. Miehlich, A. Savin, H. Stoll and H. Preuss, Chem. Phys. Letters 157, 200 (1989). doi:10.1103/PhysRevB.37.785,10.1016/0009-2614(89)87234-3
M052XC	M05-2X Meta-GGA Correlation Functional doi:10.1021/ct0502763
M052XX	M05-2X Meta-GGA Exchange Functional doi:10.1021/ct0502763
M05C	M05 Meta-GGA Correlation Functional doi:10.1063/1.2126975
M05X	M05 Meta-GGA Exchange Functional doi:10.1063/1.2126975
M062XC	M06-2X Meta-GGA Correlation Functional doi:10.1007/s00214-007-0310-x
M062XX	M06-2X Meta-GGA Exchange Functional doi:10.1007/s00214-007-0310-x
M06C	M06 Meta-GGA Correlation Functional doi:10.1007/s00214-007-0310-x
M06HFC	M06-HF Meta-GGA Correlation Functional doi:10.1021/jp066479k
M06HFX	M06-HF Meta-GGA Exchange Functional doi:10.1021/jp066479k
M06LC	M06-L Meta-GGA Correlation Functional doi:10.1063/1.2370993
M06LX	M06-L Meta-GGA Exchange Functional doi:10.1063/1.2370993
M06X	M06 Meta-GGA Exchange Functional doi:10.1007/s00214-007-0310-x
M12C	Meta GGA Correlation Functional. Meta-GGA correlation functional based on first principles, see M. Modrzejewski et al., J. Chem. Phys. 137 204121 (2012). doi:10.1063/1.4768228
MK00	Exchange Functional for Accurate Virtual Orbital Energies doi:10.1063/1.481298
MK00B	Exchange Functional for Accurate Virtual Orbital Energies. MK00 with gradient correction of the form of B88X but with different empirical parameter. doi:10.1063/1.481298
P86	.. Gradient correction to VWN. doi:10.1103/PhysRevB.33.8822
PBEC	PBE Correlation Functional doi:10.1103/PhysRevLett.77.3865
PBESOLC	PBEsol Correlation Functional doi:10.1103/PhysRevLett.100.136406

PBESOLX	PBEsol Exchange Functional doi:10.1103/PhysRevLett.100.136406
PBEX	PBE Exchange Functional doi:10.1103/PhysRevLett.77.3865
PBEXREV	Revised PBE Exchange Functional. Changes the value of the constant R from the original PBEX functional doi:10.1103/PhysRevLett.80.890
PW86	.. GGA Exchange Functional. doi:10.1103/PhysRevB.33.8800
PW91C	Perdew-Wang 1991 GGA Correlation Functional doi:10.1103/PhysRevB.46.6671
PW91X	Perdew-Wang 1991 GGA Exchange Functional doi:10.1103/PhysRevB.46.6671
PW92C	Perdew-Wang 1992 GGA Correlation Functional. Electron-gas correlation energy. doi:10.1103/PhysRevB.45.13244
STEST	Test for number of electrons
TFKE	Thomas-Fermi Kinetic Energy. Automatically generated Thomas-Fermi Kinetic Energy. doi:10.1017/S0305004100011683
TH1	Tozer and Handy 1998. Density and gradient dependent first row exchange-correlation functional. doi:10.1063/1.475638
TH2	.. Density and gradient dependent first row exchange-correlation functional. doi:10.1021/jp980259s
TH3	.. Density and gradient dependent first and second row exchange-correlation functional. doi:TH3/4
TH4	.. Density an gradient dependent first and second row exchange-correlation functional. doi:TH3/4
THGFC	.. Density and gradient dependent first row exchange-correlation functional for closed shell systems. Total energies are improved by adding DN, where N is the number of electrons and $D = 0.1863$. doi:10.1016/S0009-2614(97)00586-1
THGFCFO	.. Density and gradient dependent first row exchange-correlation functional. FCFO = FC + open shell fitting. doi:10.1016/S0009-2614(97)00586-1
THGFCO	.. Density and gradient dependent first row exchange-correlation functional. doi:10.1016/S0009-2614(97)00586-1
THGFL	.. Density dependent first row exchange-correlation functional for closed shell systems. doi:10.1016/S0009-2614(97)00586-1

TPSSC	TPSS Correlation Functional. J. Tao, J. P. Perdew, V. N. Staroverov, and G. E. Scuseria, Phys. Rev. Lett. 91, 146401 (2003). doi:10.1103/PhysRevLett.91.146401
TPSSX	TPSS Exchange Functional. J. Tao, J. P. Perdew, V. N. Staroverov, and G. E. Scuseria, Phys. Rev. Lett. 91, 146401 (2003). doi:10.1103/PhysRevLett.91.146401
VSXC	. doi:10.1063/1.476577
VW	von Weizsäcker kinetic energy. Automatically generated von Weizsäcker kinetic energy. doi:10.1007/BF01337700
VWN3	Vosko-Wilk-Nusair (1980) III local correlation energy. VWN 1980(III) functional doi:VWN80
VWN5	Vosko-Wilk-Nusair (1980) V local correlation energy. VWN 1980(V) functional. The fitting parameters for $\Delta\varepsilon_c(r_s,\zeta)_V$ appear in the caption of table 7 in the reference. doi:VWN80
XC-M05-2X	M05-2X Meta-GGA Exchange-Correlation Functional. Here it means M05-2X exchange-correlation part which excludes HF exact exchange term. Y. Zhao, N. E. Schultz, and D. G. Truhlar, J. Chem. Theory Comput. 2, 364 (2006). doi:10.1021/ct0502763
XC-M05	M05 Meta-GGA Exchange-Correlation Functional. Here it means M05 exchange-correlation part which excludes HF exact exchange term. Y. Zhao, N. E. Schultz, and D. G. Truhlar, J. Chem. Phys. 123, 161103 (2005). doi:10.1063/1.2126975
XC-M06-2X	M06-2X Meta-GGA Exchange-Correlation Functional. Here it means M06-2X exchange-correlation part which excludes HF exact exchange term. Y. Zhao and D. G. Truhlar, Theor. Chem. Acc. 120, 215 (2008). doi:10.1007/s00214-007-0310-x
XC-M06-HF	M06-HF Meta-GGA Exchange-Correlation Functional. Here it means M06-HF exchange-correlation part which excludes HF exact exchange term. Y. Zhao and D. G. Truhlar, J. Phys. Chem. A 110, 13126 (2006). doi:10.1021/jp066479k
XC-M06-L	M06-L Meta-GGA Exchange-Correlation Functional. Y. Zhao and D. G. Truhlar, J. Chem. Phys. 125, 194101 (2006). doi:10.1063/1.2370993
XC-M06	M06 Meta-GGA Exchange-Correlation Functional. Here it means M06 exchange-correlation part which excludes HF exact exchange term. Y. Zhao and D. G. Truhlar, Theor. Chem. Acc. 120, 215 (2008). doi:10.1007/s00214-007-0310-x
XC-M08-HX	M08-HX Meta-GGA Exchange-Correlation Functional. Here it means M08-HX exchange-correlation part which excludes

	HF exact exchange term. Y. Zhao and D. G. Truhlar, J. Chem. Theory Comput. 4, 1849 (2008). doi:10.1021/ct800246v
`XC-M08-SO`	M08-SO Meta-GGA Exchange-Correlation Functional. Here it means M08-SO exchange-correlation part which excludes HF exact exchange term. Y. Zhao and D. G. Truhlar, J. Chem. Theory Comput. 4, 1849 (2008). doi:10.1021/ct800246v
`XC-M11-L`	M11-L Exchange-Correlation Functional. R. Peverati and D. G. Truhlar, Journal of Physical Chemistry Letters 3, 117 (2012). doi:10.1021/jz201525m
`XC-SOGGA`	SOGGA Exchange-Correlation Functional. Y. Zhao and D. G. Truhlar, J. Chem. Phys. 128, 184109 (2008). doi:10.1063/1.2912068
`XC-SOGGA11-X`	SOGGA11-X Exchange-Correlation Functional. Here it means SOGGA11-X exchange-correlation part which excludes HF exact exchange term. R. Peverati and D. G. Truhlar, J. Chem. Phys. 135, 191102 (2011). doi:10.1063/1.3663871
`XC-SOGGA11`	SOGGA11 Exchange-Correlation Functional. R. Peverati, Y. Zhao and D. G. Truhlar, J. Phys. Chem. Lett. 2 (16), 1991 (2011). doi:10.1021/jz200616w

17.4.3 Implementing new functionals

New functionals are implemented based upon the automatic code generation (ACG) program (doi:10.1016/S0010-4655(01)00148-5). In order to work the program requires the maple mathematics program and an XSLT parser, defined by the variable XSLT in CONFIG.

The format of the input file is an XML file containing all of the information about the new functional. All density functional XML files are placed in the directory `lib/df` and are automatically activated on the next instance of the `make` command in the MOLPRO base directory.

The root element of the XML document is `content`. At the next level the element, `functional` is expected, 1 per file.

The `functional` element has an `id` attribute which is used as the keyword for the functional in MOLPRO, and optional `doi` attribute for specifying a reference. The allowed elements are defined in table 8. The final element is `maple` for which multiple cases are allowed. A typical

title	Text to appear as a heading for the functional documentation
tex	Text to document the functional

Table 8: Elements allowed for defining functionals

maple expression such as

```
A:=1.2:
```

is written as

```
<maple lhs="A">1.2</maple>.
```

To input a Maple procedure such as

```
add_together:=proc(a,b) a+b end:
```

one should write

```
<maple lhs="add_together" proc="a,b">a+b</maple>.
```

As an example the Perdew-Wang 1991 GGA exchange functional is given below:

```
<?xml version="1.0" encoding="ISO-8859-1"?>
<content>
 <functional id="PW91X">
  <title>Perdew-Wang 1991 GGA Exchange Functional</title>
  <maple lhs="g">1/2*E(2*rho(s))</maple>
  <maple lhs="G">1/2*E(2*rho(s))</maple>
  <maple lhs="E" proc="n"> -3/(4*Pi)*(3*Pi^2)^(1/3)*n^(4/3)*F(S)</maple>
  <maple lhs="S">chi(s)/(2*(6*Pi^2)^(1/3))</maple>
  <maple lhs="F" proc="S">
   (1+0.19645*S*arcsinh(7.7956*S) + (0.2743-0.1508*exp(-100*S^2))*S^2)/
   (1+0.19645*S*arcsinh(7.7956*S)+0.004*S^4)
  </maple>
 </functional>
</content>
```

17.4.4   Implementing new hybrid-functionals

Hybrid functionals are defined in the file `lib/dalias.registry`. Entries can be added to this file as required, and then run `make` to update the other registry files.

17.5   Empirical damped dispersion correction

Empirical damped dispersion corrections can be calculated in addition to Kohn-Sham calculations. This is particularly important in cases where long-range correlation effects become dominant.

The dispersion correction can be added to the DFT energy by using

```
 ks,<func>; disp
```

The total energy will then be calculated as

$$E_{\text{DFT-D}} = E_{\text{DFT}} + E_{\text{disp}} \tag{33}$$

Currently the default dispersion correction added to the DFT energy is the D3 dispersion correction developed by Grimme *et al.*, see Ref. [1]. The `disp` keyword can have the following additional options:

FUNC	Functional name (default: FUNC='pbe').
VERSION	Can have values 2 and 3 according to parametrisations from Refs. [2] and [3] (default: VERSION=3)
ANAL	Performs a detailed analysis of pair contributions.

GRAD	Cartesian gradients are computed. (note that geometry optimisations with `DFT+dispcorr3` are currently not yet possible).
TZ	Use special parameters for calculations with triple-zeta basis sets. Preliminary results in the SI of Ref. [3] indicate that results are slightly worse than with the default parameters and QZVP type basis sets. This option should be carfully tested for future use in very large computations.

(see also `http://toc.uni-muenster.de/DFTD3/index.html` for further documentation).

Alternatively, the D3 dispersion correction can also be calculated separately from the DFT calculation using the following template:

```
ks,<func>
eks=energy
dispcorr3
eks_plus_disp=eks+edisp
```

The older DFT-D1 [2] or DFT-D2 [3] methods by Grimme can still be used invoking

```
ks,<func>
eks=energy
dispcorr
eks_plus_disp=eks+edisp
```

with the following options to `dispcorr`:

MODE	Adjusts the parametrisation used: `MODE=1` uses parameters from Ref. [1] and `MODE=2` uses parameters from Ref. [2] (default: `MODE=1`)
SCALE	Overall scaling parameter s_6 (see Eq. (34) and Refs. [2,3] for optimised values).
ALPHA	Damping function parameter (see Eq. (37)). Smaller values lead to larger corrections for intermediate distances.

In the DFT-D1 and DFT-D2 method the dispersion energy is calculated as

$$E_{\text{disp}} = -s_6 \sum_{i,j<i}^{N_{\text{atoms}}} f_{\text{damp}}(R_{ij}) \frac{C_6^{ij}}{R_{ij}^6} \ . \tag{34}$$

where N_{atoms} is the total number of atoms, R_{ij} is the interatomic distance of atoms i and j, s_6 is a global scaling parameter depending on the choice of the functional used and the C_6^{ij} values are calculated from atomic dispersion coefficients C_6^i and C_6^j in the following way:

$$C_6^{ij} = 2\frac{C_6^i C_6^j}{C_6^i + C_6^j} \quad \text{(Ref. [1])} \tag{35}$$

$$C_6^{ij} = \sqrt{C_6^i C_6^j} \quad \text{(Ref. [2])} \tag{36}$$

The function f_{damp} damps the dispersion correction for shorter interatomic distances and is given by:

$$f_{\text{damp}}(R_{ij}) = \frac{1}{1 + \exp\left[-\alpha(R_{ij}/(R^i_{\text{vdW}} + R^j_{\text{vdW}}) - 1)\right]} \tag{37}$$

whith R^i_{vdW} being the van-der-Waals radius for atom i and α is a parameter that is usually set to 23 (Ref. [1]) or 20 (Ref. [2]).

References:

[1] S. Grimme, J. Antony, S. Ehrlich and H. Krieg, J. Chem. Phys. **132**, 154104 (2010)
[2] S. Grimme, J. Comp. Chem. **25**, 1463 (2004).
[3] S. Grimme, J. Comp. Chem. **27**, 1787 (2006).

17.6   Time-dependent density functional theory

The time-dependent density functional linear response theory program can be used to calculate excitation energies or response properties for molecules. The program currently has the following restrictions:

- No point-group symmetry can be used in TDDFT.

- The program only works in conjunction with density-fitting of electron repulsion integrals, i.e., the user must supply an auxiliary basis set, see section 15 for details.

- Currently the exchange-correlation kernel is approximated by the adiabatic local density approximation (ALDA).

- In case of the calculation of excitation energies using hybrid-DFT functionals the reduced hessian matrix is approximated by the hermitian matrix $\mathbf{A}^2 - \mathbf{B}^2$, i.e., it is assumed that $\mathbf{A}$ and $\mathbf{B}$ commute. This works well for small systems/basis sets, but the excitation energies may deviate more strongly from the eigenvalues of the full hessian in case of larger systems/basis sets.

A typical input for calculating the ten lowest excitation energies is given by:

```
ks,<func>; save,2100.2
df-tddft,orb=2100.2,nexcit=10
```

yielding, e.g., the following output:

```
   n      eig                oscill.stren.           eig (eV)
   1      0.15429481          0.00000361             4.19857508
  12->  13    0.999706         0.14361479
  11->  14    0.000034         0.35333048
  10->  20    0.000027         0.58330205
  10->  16    0.000016         0.43005338

   n      eig                oscill.stren.           eig (eV)
   2      0.24134275          0.10469512             6.56727008
  ...
```

As shown by the above snippet, the output will contain the excitation energies, oscillator strengths and the four most important orbital contributions to the respective transition. The latter is characterised by the orbital index pairs (`<occ> -> <virt>`), the coefficient of this index pair in the eigenvector, and the orbital energy differences contained in the last column showing the uncoupled excitation energy for comparison.

For the calculation of frequency-dependent dipole-dipole polarisabilities use, e.g.:

```
ks,<func>; save,2100.2
df-tddft,orb=2100.2,pert='DMX',pert='DMY',pert='DMZ',om=[0.0,1.0]
```

which calculates $\alpha(\omega)$ and its cartesian components at the frequencies $\omega = 0$ (static response) and $\omega = 1$. Response property calculations are possible for all properties described in section 6.13.

The following list summarises the possible options to TDDFT:

ORB	Record for input orbitals (required).
AUXBAS	Auxiliary basis set (default: 'MP2FIT')
FEXX	Factor for nonlocal exchange.
FXC	Factor for local exchange-correlation.
FU	Factor for Coulomb kernel contribution (default: 1).
MAXIT	Maximum number of iterations in Davidson and conjugate-gradient solver.
NEXCIT	Number of excitation energies requested (default: 0).
DAV	Switches (1,2) between two different Davidson eigensolvers (default: 2).
OM	Real frequencies for which the linear response is calculated, example: `OM=[0.0,1.0,2.0]` calculates the response at $\omega = 0.0$, 1.0 and 2.0.
OMI	Imaginary frequencies for which the linear response is calculated.
PERT	Perturbations for which the linear response is calculated, example: `PERT='DMX',PERT='DMY',PERT='DMZ'` calculates the dipole-dipole polarisabilities for the three cartesian components (see section 6.13 for available properties).
TOLDAV	Convergence tolerance used in the Davidson eigensolver.
THRCG	Convergence tolerance used in the conjugate-gradient solver.
NSUBMAX	Maximum subspace used in Davidson eigensolver (default: `10*NEXCIT`)
TRIP	Set to '1' for triplet excitation energies (default: 0).
C6	Set to '1' for calculating C_6 dispersion coefficients (default: 0).
NQUAD	Number of quadrature points used in the calculation of dispersion coefficients.
FXCFIT	Set to '1' for approximating the exchange-correlation kernel matrix with density-fitting (default: 0).
DENTHR	Threshold for density in the calculation of the exchange-correlation kernel matrix on the auxiliary basis set (default: 1d-7).

FULL	Set to '1' for a full diagonalisation of the hessian matrix (experimental).
CRITC	Convergence threshold for the coefficients of the last added basis vector in the 2nd Davidson eigensolver (default: 1d-7).
CRITR	Convergence threshold for residual vector norms in the 2nd Davidson eigensolver (default: 1d-7).
ORTHO	The threshold over which loss of orthogonality is assumed in the 2nd Davidson eigensolver (default: 1d-8).
NDUMP	Number of excitation vectors (transformed to AO basis) written to file (default: 0).
DUMP	Record for dump of excitation vectors (default: 5000.2).

17.7 Random-phase approximation

The random-phase approximation program (`rpatddft`) can be used to calculate RPA correlation energies after a SCF calculation. Additionnally, it can be used to calculate dynamic dipole polarizabilities, C_6 dispersion coefficients, and excitation energies. The program currently works without point-group symmetry.

List of the main keywords:

`ECORR, <list of methods>`
> Calculation of RPA correlation energies [1] (see options below)

`PROPERTIES, <list of methods>`
> Calculation of dynamic dipole polarizabilities and C_6 dispersion coefficients [10] (see options below)

`EXCIT, <list of methods>`
> Calculation of excitation energies [11] (see options below)

as well as:

| `ORB,<orbrec>` | Record for input orbitals (required). |
| `STAB` | Check matrices stability conditions in RPA calculations. When used without an `ECORR`, `EXCIT` or `PROPERTIES` keyword, check the Hessian and RPA matrices eigenvalues and do nothing more. |

`INTAC,NLAMBDA=<n>[,LAMBDA=<lambda>,WEIGHT=<weight>]`
> Number of quadrature points for the Gauss-Legendre numerical integration along the adiabatic connection for RPA calculations (default is 7). If `LAMBDA` and `WEIGHT` are given, assumes a one-point quadrature with given abscissa and weight.

`INTFREQ,METHFREQ=<methfrq>,NFREQ=<nfreq>`
> Options for the numerical integration over the frequency variable of RPA calculations. `METHFREQ` governs the type of quadrature used (0(default) is Gauss-Chebyshev, 1 and 2 are Gauss-Legendre, 3 is Clenshaw-Curtis) and `NFREQ` governs the number of quadrature points (default is 16).

`INTEGRAL,<nbr>`	Specify the two-electron integral transformation routine: 0 (still the default for spin-unrestricted and gradient calculations) is the 'old' one, 1 is the 'old' one that has been cleaned up, and 2 (default otherwise) is a much more efficient transformation using Molpro's "transform" routine.
`DFTKERNEL,<funcx>[,<funcc>]`	
	Specify the exchange and correlation kernel for `EXCIT` (if only one argument is given, it is understood to be the exchange-correlation kernel).
`NOMP2`	The MP2 energy is calculated in certain situations where it is available almost for free, provided that some matrices are allocated. This behavior can be switched off by this `NOMP2` keyword.
`DIELSOLID`	Use the solid-state variant when performing DIEL calculations.
`NOSPINBLOCK`	For spin-unrestricted calculations, use a formalism where matrices are of $\alpha\alpha + \alpha\beta + \beta\alpha + \beta\beta$ dimensions (the default is to use a formalism with a nospinflip/splinflip block structure)
`NOSPINFLIP`	Exclude spin-flip dimensions of unrestricted RPA calculations that use the `NOSPINBLOCK` formalism (not suitable for all RPA variants).
`C6`	Computes C6 coefficients from last two saved polarizabilities.
`TDA`	Tamm-Dancoff approximation for `EXCIT` and `PROPERTIES`.
`OCC,<nocc>`	Explicitly specify the number of occupied orbitals (useful for fake pseudopotential calculations).
`CORE,<core>`	Specify core orbitals (default: last specified core orbitals or, if none, atomic inner shells)
`PRINT,<nbr>`	Level of print expected from the output (from 0(default) to 3).

Calculation of RPA correlation energies

`ECORR, <list of methods>`
If no method is given, a `SO2-RCCD` calculation will be done (see below).

There are two main RPA *variants* [1]: dRPA (direct RPA, without the inclusion of an Hartree-Fock exchange kernel in the response function) and RPAx (with the Hartree-Fock exchange kernel included in the response function).

There are four main *formulations* in which the RPA equations can be derived. The adiabatic-connection fluctuation-dissipation theorem (ACFDT) equation involves integrations both over frequency and coupling constant: an analytical integration along the frequency variable followed by a quadrature on the coupling constant yields the adiabatic connection formulation (AC) [1], while an analytic integration on the coupling constant followed by a numerical integration over the frequency yields the dielectric formulation (DIEL) [2]. Two other formulations are obtained when the two integrations are carried out analytically: the plasmon formula (PLASMON) [1] and the ring coupled cluster doubles formulation (RCCD) [3]. These four formulations are not in general equivalent.

Most variants+formulations can readily by used in a spin-unrestricted context [6]. This is implemented in the code and does not need any further input from the user: the RPA program

recognizes the spin-unrestricted character of a SCF calculation that was done beforehand and acts accordingly.

Gradients of most of the RCCD-formulation RPA energies are available, both without range-separation with RHF orbitals and with range-separation with RSH orbitals [9]. The calculations are triggered by the presence of the keyword FORCE or OPTG *after* the energy-related section (see examples at the end of the section).

The user can test the RPA program using make rpatddfttest, which proposes a variety of tests for RPA correlation energy calculations.

The keywords for the methods are constructed on the model:

<variant>-<formulation>-<alternative>

For the AC formulation, the available methods are:

DRPAI-AC	dRPA calculation (see Refs. [1] and [4]).
DRPAII-AC	dRPA calculation, using antisymmetrized two-electron integrals (see Refs. [1] and [4]).
RPAXI-AC	RPAx calculation (see Refs. [1] and [5]).
RPAXII-AC	RPAx calculation, using antisymmetrized two-electron integrals (see Refs. [1] and [5]).
DRPAI-AC-ALT	dRPA calculation using an alternative derivation (see Ref. [7]).
RPAXI-AC-ALT	RPAx calculation using an alternative derivation (see Ref. [7]).
DRPAI-AC-NOINT	dRPA calculation without integration along the adiabatic connection (using the "kinetic" and "potential" contributions, sometimes called the "alternative plasmon formula", see Ref. [1]).
RPAXII-AC-NOINT	RPAx calculation without integration along the adiabatic connection (using the "kinetic" and "potential" contributions, sometimes called the "alternative plasmon formula", see Ref. [1]).

For the DIEL formulation, the available methods are:

DRPAI-DIEL	dRPA calculation (see Ref. [2]).
DRPAIIA-DIEL	dRPA-IIa approximation (see Ref. [2]).
RPAXIA-DIEL	RPAx-Ia approximation (see Ref. [2]).

For the RCCD formulation, the available methods are:

DRPAI-RCCD	dRPA-I calculation (see Ref. [3]).
RPAXII-RCCD	RPAx-II calculation (Szabo-Ostlund variant 1 is calculated too, see Ref. [3]).
SO2-RCCD	Szabo-Ostlund variant 2 (see Ref. [3]).
SOSEX-RCCD	dRPA-I+SOSEX correction (see Ref. [3]).
RPAX2-RCCD	RPAX2 approximation (see Ref. [8]).

For the PLASMON formulation, the available methods are:

DRPAI-PLASMON   dRPA-I calculation (see Ref. [1]).

RPAXII-PLASMON   RPAx-II calculation (see Ref. [1]).

Note that to all these keywords are associated energy variables defined as :

<div align="center">

ECORR_VARIANT_FORMULATION_ALTERNATIVE

</div>

(see the examples below).

Example of a dRPA-I calculation using the PBE functional:

```
{rks,pbe,orbital,2101.2}
{rhf,start=2101.2,maxit=0}
{rpatddft;
 orb,2101.2;
 ecorr,DRPAI-AC
}
e=ECORR_DRPAI_AC
```

Example of a range-separated RPAx-I calculation using the short-range PBE exchange-correlation functional and the range-separated parameter mu=0.5:

```
{int;erf,0.5}
{rks,exerfpbe,ecerfpbe;rangehybrid;orbital,2101.2}
{rpatddft;
 orb,2101.2;
 ecorr,RPAXI-AC
}
```

Example of several RPA calculations in the same run:

```
{rhf,orbital,2101.2}
{rpatddft;
 orb,2101.2;
 ecorr,DRPAI-AC,RPAXII-RCCD,DRPAI-DIEL
}
e1=ECORR_DRPAI_AC
e2=ECORR_RPAXII_RCCD
e3=ECORR_DRPAI_DIEL
```

(the calculations are done with the same transformed integrals, *i.e.* without redoing the integral transformation).

Example of a dRPA-I gradient calculation:

```
{rks,pbe,orbital,2101.2}
{rpatddft;
 orb,2101.2;
 ecorr,DRPAI-RCCD
}
force
```

Example of a geometry optimization at the LDA+dRPA-I level:

```
{int;erf,0.5}
{rks,exerf,ecerf;rangehybrid;orbital,2101.2}
{rpatddft;
 orb,2101.2;
 ecorr,DRPAI-RCCD
}
optg
```

Calculation of properties, excitation energies and oscillator strengths

```
PROPERTIES, METHOD=<method>
EXCIT, METHOD=<method>
```

The `EXCIT` calculations output shows the excitation energies in ua, eV and nm, the oscillator strengths in length and velocity gauge, as well as the major excitations involved in each mode.

The methods available are:

DRPA	Direct random-phase approximation (or time-dependent Hartree).
TDHF	Time-dependent Hartree-Fock.
TDDFT	Time-dependent density-functional theory.
RS-TDDFT	Range-separated time-dependent density-functional theory [11].

The exchange density functionals (FUNCX) available are:

LDAXERF	(short-range LDA exchange density functional for the erf interaction [12]).

The correlation density functionals (FUNCC) available are:

LDAC	(Perdew-Wang-92 LDA correlation density functional)
LDACERF	(short-range LDA correlation density functional for the erf interaction [13]).

Example of a range-separated time-dependent density-functional theory calculation using the short-range LDA exchange-correlation functional and the range-separated parameter mu=0.5:

```
mu=0.5
{int;erf,mu;save}
{rks,exerf,ecerf;rangehybrid;orbital,2101.2}
{int}
{setmu,mu}
{rpatddft;
 orb,2101.2;
 excit,method=rs-tddft;
 dftkernel,funcx=ldaxerf,funcc=ldacerf
}
```

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17.8   Examples

The following shows the use of both non-self-consistent and self-consistent DFT.

```
geometry={c;n,c,r}
r=1.1 angstrom
dfunc,b-lyp
rhf;method(1)=program
dft;edf(1)=dftfun
uhf;method(2)=program
dft;edf(2)=dftfun
uks;method(3)=program,edf(3)=dftfun
dft;method(4)=program,edf(4)=dftfun
table,dftname,dftfuns
table,method,edf
```

          http://www.molpro.net/info/current/examples/cndft.com

18   ORBITAL LOCALIZATION

Localized orbitals are calculated according to the Boys, Pipek-Mezey or NLMO criteria. Localization takes place within each symmetry species separately. If complete localization is desired, no symmetry should be used. All subcommands can be abbreviated by three characters.

The localization program is invoked by the `LOCALI` command

`LOCALI` [,*method*],[`LOCMETHOD`=*locmethod*],[`REFORB`=*record*]

The keyword *method* can be either `BOYS`, `PIPEK` or `NATURAL`. By default, the valence orbitals from the last energy calculation are localized using the Boys criterion. Only orbital subsets which leave the energy invariant are transformed. These defaults can be modified using the optional commands described in the following sections.

The option `LOCMETHOD` only applies to Pipek-Mezey localization. The value *locmethod* can take the following values:

locmethod=1:	Standard iterative localization method
locmethod=2:	Use second-order localization method. Redundant rotations will be eliminated.
locmethod=3:	First do a first iterations using the standard method, then invoke locmethod=2. This option is recommended in cases with redundant rotations, e.g., benzene.

The option `REFORB` has the same effect as the directive `REFORB` described further below.

18.1   Defining the input orbitals (`ORBITAL`)

`ORBITAL`,*record.file*,*specifications*

The orbitals to be localized are read from dump record *record.file*. A state specific orbital set can be selected using *specifications*, as explained in section 4.11. Default are the orbitals calculated last.

18.2   Saving the localized orbitals (`SAVE`)

`SAVE`,*record.file*

This specifies the dump record where the localized orbitals are stored. If the dump record already exists, the localized orbitals are added to it. Default is the input record (cf. `ORBITAL`).

18.3   Choosing the localization method (`METHOD`)

`METHOD`,*method*

The localization method *method* can be either `BOYS`, `PIPEK` or `NATURAL`. This can also be specified as argument on the `LOCALI` card (see above).

18.4   Delocalization of orbitals (`DELOCAL`)

`DELOCAL`

If this card is present, the orbitals are delocalized.

18.5   Localizing AOs(`LOCAO`)

`LOCAO`

If this card is present, the number of AOs contributing to each MO is minimized. This can be useful to rotate degenerate orbitals (e.g., px, py, pz in an atom) so that pure orbitals (in this case px, py, pz) result.

This implies Pipek-Mezey localization.

18.6   Selecting the orbital space

By default, only the valence orbitals are localized, in order to ensure invariance of subsequent electron correlation treatments. This behaviour can be modified using the `OCC` and `CORE` directives.

18.6.1   Defining the occupied space (`OCC`)

`OCC,` $o_1, o_2 \dots$

defines the highest orbital o_i in each symmetry i to be localized.

18.6.2   Defining the core orbitals (`CORE`)

`CORE,` $c_1, c_2 \dots$

The first c_i orbitals in each symmetry are treated as core orbitals and not localized. Thus, orbitals $c_i + 1$ to o_i are localized in symmetry i.

18.6.3   Defining groups of orbitals (`GROUP`, `OFFDIAG`)

`GROUP,`*orb1,orb2,orb3,...*

This card defines groups of orbitals to be localized as follows:

`GROUP,1.1,2.1,3.1`	a group of orbitals 1-3 in symmetry 1
`GROUP,1.1,-3.1`	equivalent to previous example
`GROUP,3.1,5.1,-8.1`	this group includes orbitals 3,5,6,7,8 in symmetry 1

Orbitals in different groups are localized independently. Orbitals not included in any group are unchanged.

18.6.4   Localization between groups (`OFFDIAG`)

`OFFDIAG`

If this card is present, localize between groups instead of within groups.

18.7   Ordering of localized orbitals

`ORDER,`*type*

If *type*=`CHARGE`, the orbitals are ordered according to their charge centroids (default).

If *type*=`FOCK`, the orbitals are ordered according to increasing diagonal elements of the fock operator (PIPEK) or increasing Coulson-additive orbital energies (BOYS). This requires a Fock operator from the preceding energy calculation. For localization of Hartree-Fock orbitals, this operator is stored in the dump record and automatically found. For localization of MCSCF orbitals, an effective fock operator is computed from the MCSCF density matrix (see `DENSITY` option). Alternatively, a dump record of a previous SCF calculation can be specified on the

FOCK card, and then the fock operator is read from this record. For degenerate orbitals, further ordering according to the the coordinates of charge centres is attempted (first according to largest z-coordinates, then according to x, then y).

This card does not apply to NLMO localization.

18.7.1   No reordering (NOORDER)

NOORDER

If this card is present, the localized orbitals are not reordered. This is useful if localized orbitals are used as starting guess, and it is intended that their order remains unchanged.

18.7.2   Ordering using domains (SORT)

SORT,[THRCHCHG=*charge*][THREIG=*eps*],GROUP=*igrp*],[REVERT],*centrelist*

This directive only works for Pipek-Mezey localization. The orbitals are ordered according to domains and the given centrelist. The contributions of the centres to domains are determined by Löwdin charges. Only centres with charges greater than THRCHCHG (default 0.4) are included in these domains. The orbitals are reordered according to the following criteria:

1.) The primary centre in a domain is the one with largest charge, the secondary centre the one with the next largest charge. Orbitals are reordered separately within each localization group. First all orbitals are sorted so that the primary centres are in the order of the given *centrelist*. Orbitals with primary centres which are not in *centrelist* come last.

2.) Within each group of orbitals found for a given primary centre, those containing only one centre (lone pairs) are included first. The remaining ones are ordered so that the secondary atoms are in the order of *centrelist*. Orbitals with secondary centres which are not in *centrelist* come last.

3.) If REVERT is given, the order in each localization group is reverted.

4.) If GROUP is given, only the orbitals in the given group are reordered. *igrp* is 2 for closed shells and inactive orbitals, 1 for open-shells in single reference methods, and 3 for active orbitals in CASSCF calculations.

5.) If THREIG is given, only orbitals with energies larger than the given value are reordered. *eps* must be negative. The remaining orbitals come last (first if REVERT is given).

Note that core orbitals are neither localized nor reordered.

18.7.3   Defining reference orbitals (REFORB)

REFORB,*record.file*,*specifications*

The localized orbitals are reordered such that the overlap with the reference orbitals read from *record.file* is maximized. This is useful for local correlation treatments for keeping the order of the localized constant for different geometries. A state specific orbital set can be selected using *specifications*, as explained in section 4.11.

18.7.4   Selecting the fock matrix (`FOCK`)

`FOCK`,*record.file*

This specifies a record holding a Fock operator to be used for ordering the orbitals. Note that only SCF dump records hold fock operators. Default is the Fock operator from the energy calculation which produced the input orbitals.

18.7.5   Selecting a density matrix (`DENSITY`)

`DENSITY`,*record.file*,*specifications*

This specifies a record holding a density matrix for construction of a fock operator used for ordering the orbitals. This can be used if no fock operator is available, and has only an effect for MCSCF localizations. By default, the (state averaged) MCSCF density is used. A state specific density matrix can be selected using *specifications* as described in section 4.11.

18.8   Localization thresholds (`THRESH`)

`THRESH`,*thresh*,*eorder*

thresh is a threshold for localization (default 1.d-12). If *eorder* is nonzero (default 1.d-4), the orbitals whose energy difference is smaller then *eorder* are considered to be degenerate and reordered according to the position of their charge centres (see section 18.7).

18.9   Options for PM localization (`PIPEK`)

Some special options exist for Pipek-Mezey localization (all optional):

`PIPEK`,`METHOD=`*method*,`DELETE=`*ndel*,`MAXDL=`*maxdl*,`THRESH=`*thresh*,`ORDER=`*iorder*,`STEP=`*step*

`METHOD`:	*method=1*: use 2x2 rotation method (default); *method=2*: use Newton-Raphson method; *method=3*: Initial iterations using 2x2 rotation method , final convergence using NR method.
`DELETE`:	Delete the last *ndel* basis functions of each angular momentum type for each atom in PM localization. This can be useful to achieve proper localization with diffuse (augmented) basis sets.
`MAXDL`:	If *ndel*>0 delete functions only up to angular momentum *maxdl*.
`ORDER`:	If *iorder=1*, order final orbitals according to increasing diagonal fock matrix elements; If *iorder=2*, order final orbitals according charge centres (default).
`THRESH`:	Localization threshold (same as on `THRESH` directive).
`STEP`:	Max step size in NR method (default 0.1d0).

18.10   Printing options (`PRINT`)

`PRINT,[ORBITAL=]`*pri*`[,CHARGE][,CENTRES][,TEST][,TRAN];`

If `ORB[ITAL]` is given, the localized orbitals are printed.
If `CHA[RGE]` or `CEN[TRES]` is given, the charge centres of the localized orbitals are printed.
If `TRAN` is given, the transformation matrix is printed (Boys only).
If `TEST` is given, intermediate information is printed.

19   THE MCSCF PROGRAM MULTI

MULTI is a general MCSCF/CASSCF program written by
P. J. Knowles and H.-J. Werner (1984).

Bibliography:

H.-J. Werner and P. J. Knowles, J. Chem. Phys. **82**, 5053 (1985).
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All publications resulting from use of this program must acknowledge the above. See also:

H.-J. Werner and W. Meyer, J. Chem. Phys. **73**, 2342 (1980).
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This program allows one to perform CASSCF as well as general MCSCF calculations. For CASSCF calculations, one can optionally use Slater determinants or CSFs as a *N*-electron basis. In most cases, the use of Slater determinants is more efficient. General MCSCF calculations must use CSFs as a basis.

A quite sophisticated optimization method is used. The algorithm is second-order in the orbital and CI coefficient changes and is therefore quadratically convergent. Since important higher order terms in the independent orbital parameters are included, almost cubic convergence is often observed. For simple cases, convergence is usually achieved in 2-3 iterations. However, convergence problems can still occur in certain applications, and usually indicate that the active space is not adequately chosen. For instance, if two weakly occupied orbitals are of similar importance to the energy, but only one of them is included in the active set, the program might alternate between them. In such cases either reduction or enlargement of the active orbital space can solve the problem. In other cases difficulties can occur if two electronic states in the same symmetry are almost or exactly degenerate, since then the program can switch from one state to the other. This might happen near avoided crossings or near an asymptote. Problems of this sort can be avoided by optimizing the energy average of the particular states. It is also possible to force convergence to specific states by choosing a subset of configurations as primary space (`PSPACE`). The hamiltonian is constructed and diagonalized explicitly in this space; the coefficients of the remaining configurations are optimized iteratively using the P-space wavefunction as zeroth order approximation. For linear molecules, another possibility is to use the `LQUANT` option, which makes it possible to force convergence to states with definite Λ quantum number, i.e., Σ, Π, Δ, etc. states.

19.1   Structure of the input

All sub-commands known to *MULTI* may be abbreviated by four letters. The input commands fall into several logical groups; within each group commands may appear in any order, but the groups must come in correct order.

   a) The program is invoked by the command `MULTI` or `MCSCF`

   b) cards defining partitioning of orbitals spaces – `OCC,FROZEN,CLOSED`

   c) general options (most commands not otherwise specified here)

   d) a `WF` card defining a state symmetry

e) options pertaining to that state symmetry – `WEIGHT`, `STATE`, `LQUANT` (must be given after `WF`)

f) configuration specification for that state symmetry – `SELECT`, `CON`, `RESTRICT`

g) definition of the primary configurations for that state symmetry - `PSPACE`

h) further general options

Stages d) through to h) may be repeated several times; this is the way in which you specify an average energy of several states of different symmetry.

Some options can be specified on the `MULTI` command line:

`MULTI,`*options*

Selected options:

`MAXIT`	Max. number of iterations (default 10)
`ENERGY`	Convergence threshold for energy
`GRADIENT`	Convergence threshold for gradient
`STEP`	Convergence threshold for steplength
`FAILSAFE`	(logical) Use options for more robust convergence
`FORCEINP`	(logical) If true, process all input in geometry optimizations and frequency calculations (Default is false). By default, most input is ignored in these cases and taken from the initial calculation; also, the orbitals are taken from the previous geometry (`OPTG` or the reference point (`FREQUENCIES`). Disabling this behaviour by setting `FORCEINP` is normally not recommended. See also the `FORCEINP` directive for `OPTG`.

Many further options and thresholds, which can also be given on the command line, are described in section 19.8.5.

19.2   Defining the orbital subspaces

19.2.1   Occupied orbitals

`OCC,`$n_1, n_2, \ldots, n_8$;

n_i specifies numbers of occupied orbitals (including FROZEN and CLOSED) in irreducible representation number i. In the absence of an `OCC` card, the information from the most recent MCSCF calculation is used, or, if there is none, those orbitals corresponding to a minimal valence set, i.e., full valence space, are used.

19.2.2   Frozen-core orbitals

`FROZEN,`$n_1, n_2, \ldots,$*record.file,type*;

n_i is the number of frozen-core orbitals in irrep number i. These orbitals are doubly occupied in all configurations and not optimized. Note that in earlier MOLPRO versions this directive was

called `CORE` and has now been renamed to avoid confusion with `CORE` orbitals in the MRCI and CCSD programs.

record.file is the record name for frozen core orbitals; if not supplied, taken from *orb* on `START` card. *record.file* can be specified in any field after the last nonzero n_i. It should always be given if the orbital guess is from a neighbouring geometry and should then specify the SCF orbitals calculated at the present geometry. If a subsequent gradient calculation is performed with this wavefunction, *record.file* is mandatory and must specify closed-shell SCF orbitals at the present geometry. Note that *record* must be larger than 2000.

type optionally specified the orbital type, e.g., ALPHA, BETA, or NATURAL if UHF/UKS orbitals are used.

If the `FROZEN` card is omitted, then the numbers of core orbitals are taken from the most recent MCSCF calculation, or otherwise no orbitals are frozen. If the `FROZEN` card is given as `FROZEN,record.file`, then the orbitals corresponding to atomic inner shells are taken, i.e., $1s$ for Li–Ne, $1s2s2p$ for Na–Ar, etc. A `FROZEN` card without any specification resets the number of frozen core orbitals to zero.

19.2.3 Closed-shell orbitals

`CLOSED,`$n_1,n_2,\ldots,n_8$

n_i is the number of closed-shell orbitals in irrep number i, inclusive of any `FROZEN` orbitals. These orbitals do not form part of the active space, i.e., they are doubly occupied in all CSFs. In contrast to the core orbitals (see `FROZEN`), these orbitals are fully optimized.

If the `CLOSED` card is omitted, then the data defaults to that of the most recent MCSCF calculation, or else the atomic inner shells as described above for `FROZEN`.

19.2.4 Freezing orbitals

`FREEZE,`*orb.sym*;

The specified orbital will not be optimized and will remain identical to the starting guess. *orb.sym* should be an active or closed-shell orbital. If *orb.sym* is a frozen core orbital, this card has no effect.

19.3 Defining the optimized states

Each state symmetry to be optimized is specified by one WF card, which may optionally be followed by `STATE`, `WEIGHT`, `RESTRICT`, `SELECT`, `CON`, and/or `PSPACE` cards. All cards belonging to a particular state symmetry as defined on the `WF` card must form a block which comes directly after the `WF` card. The cards can be in any order, however.

19.3.1 Defining the state symmetry

The number of electrons and the total symmetry of the wavefunction are specified on the WF card:

`WF,`*elec,sym,spin*

where

elec	is the number of electrons
sym	is the number of the irreducible representation
spin	defines the spin symmetry, *spin*$= 2S$ (singlet=0, doublet=1, triplet=2, etc.)

Note that these values take sensible defaults if any or all are not specified (see section 4.8).

The input directives `STATE`, `WEIGHT`, `LQUANT`, `SELECT`, `PUNCSF` always refer to the state symmetry as defined on the previous `WF` card. If such a directive is found before a `WF` card has been given, an error occurs. If any of these cards and a `WF` card is given, the variables `STATE`, `WEIGHT`, `LQUANT`, `SELECT` are *not* used, and the number of state symmetries defaults to one, regardless of how many symmetries are specified in variable `[MC]SYMMETRY`.

19.3.2   Defining the number of states in the present symmetry

`STATE`,*nstate*;

nstate is the number of states in the present symmetry. By default, all states are optimized with weight 1 (see `WEIGHT` card). The `STATE` directive must follow a `WF` card.

19.3.3   Specifying weights in state-averaged calculations

`WEIGHT`,$w(1), w(2), \ldots, w(nstate)$;

$w(i)$ is the weight for the state i in the present symmetry. By default, all weights are 1.0. See also `STATE` card. If you want to optimize the second state of a particular state symmetry alone, specify

`STATE,2;WEIGHT,0,1;`

Note, however, that this might lead to root-flipping problems. `WEIGHT` should follow a `STATE` directive.

19.3.4   Dynamical weighting

Dynamical weighting, as described in J. Chem. Phys. **120**, 7281 (2004), can be activated using

`DYNW`,*dynfac*

The weights for each state are then computed as

$$w = 1/\cosh(dynfac * \Delta E)^2 \tag{38}$$

where ΔE is the energy difference (in Hartree) between the state under consideration and the ground state. This is dynamically adjusted during the optimization process.

19.4   Defining the configuration space

By default, the program generates a complete configuration set (CAS) in the active space. The full space may be restricted to a certain occupation pattern using the `RESTRICT` option. Alternatively, configurations may be selected from the wavefunction of a previous calculation using `SELECT`, or explicitly specified on `CON` cards. Note that this program only allows to select or

specify orbital configurations. For each orbital configuration, all spin couplings are always included. Possible RESTRICT, SELECT and CON cards must immediately follow the WF card which defines the corresponding state symmetry.

19.4.1 Occupation restrictions

RESTRICT,*nmin,nmax,orb$_1$,orb$_2$,...orb$_n$*;

This card can be used to restrict the occupation patterns. Only configurations containing between *nmin* and *nmax* electrons in the specified orbitals *orb$_1$*, *orb$_2$*,...,*orb$_n$* are included in the wavefunction. If *nmin* and *nmax* are negative, configurations with exactly abs(*nmin*) and abs(*nmax*) electrons in the specified orbitals are deleted. This can be used, for instance, to omit singly excited configurations. The orbitals are specified in the form *number.sym*, where *number* is the number of the orbital in irrep *sym*. Several RESTRICT cards may follow each other. RESTRICT only works if a CONFIG card is specified before the first WF card.

RESTRICT cards given before the first WF cards are global, i.e., are active for all state symmetries. If such a global restrict card is given, variable [MC]RESTRICT is *not* used.

Additional state-specific RESTRICT cards may be given after a WF card. These are used in addition to the global orbital restrictions.

If neither state-specific nor global RESTRICT cards are found, the values from the variable [MC]RESTRICT are used.

19.4.2 Selecting configurations

SELECT,*ref1,ref2,refthr,refstat,mxshrf*;

This card is used to specify a configuration set other than a CAS, which is the default. This option automatically triggers the CONFIG option, which selects CSFs rather than determinants. Configurations can be defined using CON cards, which must follow immediately the SELECT card. Alternatively, if *ref1* is an existing MOLPRO record name, the configurations are read in from that record and may be selected according to a given threshold.

ref1=rec1.file	(*rec1*> 2000) The configurations are read in from the specified record. If *ref1* is not specified, the program assumes that the configurations are read from subsequent CON cards (see CON).
ref2=rec2.file	(*rec2*> 2000) Additional configurations are read from the specified record. If *rec2* is negative, all records between *rec1* and abs(*rec2*) are read. All configurations found in this way are merged.
refthr	Selection threshold for configurations read from disc (records *rec1–rec2*). This applies to the norm of all CSFs for each orbital configuration.
refstat	Specifies from which state vector the configurations are selected. This only applies to the case that the configurations were saved in a state-averaged calculation. If *refstat* is not specified, the configurations are selected from all states.
mxshrf	max. number of open shells in the selected or generated configurations.

19.4.3 Specifying orbital configurations

`CON,`$n_1,n_2,n_3,n_4,\ldots$

Specifies an orbital configuration to be included in the present symmetry. The first `CON` card must be preceded by a `SELECT` card. n_1, n_2 etc. are the occupation numbers of the active orbitals (0,1,or 2). For example, for
`OCC,5,2,2;CLOSED,2,1,1;`
n_1 is the occupation of orbital 3.1 (number.sym), n_2 is the occupation of orbital 4.1, n_3 of 5.1, n_4 of 2.2, and n_5 of 2.3 Any number of `CON` cards may follow each other.

Example for the BH molecule:

```
OCC,4,1,1;              ! four sigma, one pi orbitals are occupied
FROZEN,1;               ! first sigma orbital is doubly occupied and frozen
WF,6,1;                 ! 6 electrons, singlet Sigma+ state
SELECT                  ! triggers configuration input
CON,2,2                 ! 2sigma**2, 3sigma**2
CON,2,1,1               ! 2sigma**2, 3sigma, 4sigma
CON,2,0,2               ! 2sigma**2, 4sigma**2
CON,2,0,0,2             ! 2sigma**2, 1pi_x**2
CON,2,0,0,0,2           ! 2sigma**2, 1pi_y**2
```

19.4.4 Selecting the primary configuration set

`PSPACE,`*thresh*

The hamiltonian is constructed and diagonalized explicitly in the primary configuration space, which can be selected with the `PSPACE` card. The coefficients of the remaining configurations (Q-space) are optimized iteratively using the P-space wavefunction as zeroth order approximation.

If *thresh* is nonzero, it is a threshold for automatically selecting all configurations as P-space configurations which have energies less then *emin* + *thresh*, where *emin* is the lowest energy of all configurations. Further P-space configurations can be specified using `CON` cards, which must follow immediately after the `PSPACE` card. These are merged with the ones selected according to the threshold. Automatic selection can be avoided by specifying a very small threshold. There is a sensible default value for thresh (0.4), so you usually don't need a `pspace` card in your input. Furthermore, if the number of configurations in the MCSCF is less than 20, all configurations go into the P-space unless you give a PSPACE card in the input.

A P-space threshold defined on a `PSPACE` card before the first `WF` (or `STATE`, `WEIGHT`, `SELECT`, `PUNCSF` if `WF` is not given) card is global, i.e., valid for all state symmetries. State-specific thresholds can be defined by placing a `PSPACE` card after the corresponding `WF` card. In the latter case the `PSPACE` card can be followed by `CON` cards, which define state-specific P-space configurations.

19.4.5 Projection to specific Λ states in linear molecules

Since MOLPRO can only use Abelian point groups (e.g. C_{2v} instead of $C_{\infty v}$ for linear molecules), $\Delta_{x^2-y^2}$ states as well as Σ^+ states occur in the irreducible representation number 1, for example. Sometimes it is not possible to predict in advance to which state(s) the program will converge. In such cases the `LQUANT` option can be used to specify which states are desired.

`LQUANT,`*lam(1),lam(2),...,lam(nstate)*;

lam(i) is the Λ quantum number of state *i*, i.e., 0 for Σ states, 1 for Π states, 2 for Δ states, etc. The matrix over Λ^2 will be constructed and diagonalized in the P-space configuration basis. The eigenvectors are used to transform the P-space hamiltonian into a symmetry adapted basis, and the program then selects the eigenvectors of the correct symmetry. The states will be ordered by symmetry as specified on the LQUANT card; within each symmetry, the states will be ordered according to increasing energy.

19.5   Restoring and saving the orbitals and CI vectors

MULTI normally requires a starting orbital guess. In this section we describe how to define these orbitals, and how to save the optimized orbitals. In a CASSCF calculation, one has the choice of transforming the final orbitals to natural orbitals (the first order density matrix is diagonalized), to pseudo-canonical orbitals (an effective Fock-operator is diagonalized), or of localizing the orbitals.

19.5.1   Defining the starting orbitals

START,*record,[options]*;

record: dump record containing starting orbitals. As usual, *record* has the form *irec.ifil*, where *irec* is the record number (e.g., 2140), and *ifil* the file number (usually 2). The *options* can be used to select orbitals of a specific type; for details, see section 4.11.

If this card is missing, the program tries to find suitable starting orbitals as follows:

First:	Try to read orbitals from the record specified on the ORBITAL card (or the corresponding default, see ORBITAL). All files are searched.
Second:	Try to find orbitals from the most recent MCSCF calculation. All files are searched.
Third:	Try to find orbitals from the most recent SCF calculation. All files are searched.

If no orbitals are found, a starting orbital guess is generated.

It is often useful to employ MCSCF orbitals from a neighbouring geometry as starting guess (this will happen automatically if orbitals are found, see the above defaults). Note, however, that frozen-core orbitals should always be taken from an SCF or MCSCF calculation at the present geometry and must be specified separately on the FROZEN card. Otherwise the program is likely to stop with error "non-orthogonal core orbitals". The program remembers where to take the core orbitals from if these have been specified on a FROZEN card in a previous MCSCF calculation.

19.5.2   Defining the starting CI coefficients

MULTI normally obtains configuration mixing coefficients by a robust eigenvector solver that converges on the lowest eigenvalues, and applies a phase convention such that the largest coefficient is forced to be positive. For most purposes, this approach is satisfactory.

Sometimes one wants a guarantee that the CI vector is phase matched to that of a previous geometry. This can be achieved by using SAVE,CI=*record.file* (see section 19.5.5) in the first job, and in the restart,

CIGUESS,*record.file*

The phase convention applied for the rest of the calculation is then that, for each optimised state, the largest coefficient in the original CI vector defines the sign of the corresponding coefficient in the optimised vector.

19.5.3   Rotating pairs of initial orbitals

ROTATE,*orb1.sym,orb2.sym,angle*

Performs a 2×2 rotation of the initial orbitals *orb1* and *orb2* in symmetry *sym* by *angle* degrees. With *angle*=0 the orbitals are exchanged. ROTATE is meaningful only after the START card. See MERGE for other possibilities to manipulate orbitals.

19.5.4   Saving the final orbitals

ORBITAL,*record.file*

The orbitals are dumped to record *record.file*. Default for *record* is 2140 and *file=2*. This default record number is incremented by one for each subsequent MCSCF calculation in the same job (see section 4.11). Therefore, if several different MCSCF calculations at several geometries are performed in one job, each MCSCF will normally start with appropriate orbitals even if no ORBITAL or START card is present.

The ORBITAL card can be omitted if a NATORB, CANORB or LOCORB card is present, since *orb* can also be specified on these cards (the same defaults for *orb* as above apply in these cases).

19.5.5   Saving the CI vectors and information for a gradient calculation

Old form (obsolete):

SAVE,*cidump,refsav,grdsav*;

New form:

SAVE,[CI=*cidump*,] [REF=*refsav*,] [GRD=*grdsav*];

This directive must be placed before any WF or STATE cards. The options can be given in any order.

cidump: record name for saving the CI vectors. By default, the vectors are only written to a scratch file. If NATORB, CANORB or LOCORB cards are present, *cidump* should be specified on these cards. At present, there is hardly any use of saved CI vectors, and therefore this option is rarely needed.

refsav: record name for saving the orbital configurations and their weights for use in subsequent MULTI or CI calculations using the SELECT directive. If wavefunctions for more than one state symmetry are optimized in a state-averaged calculation, the weights for each state symmetry are saved separately on records *refsav*+($istsym$−1)∗100, where *istsym* is the sequence number of the WF card in the input. If several NATORB, CANORB, or LOCORB cards are present, the record number is increased by 1000 for each subsequent orbital set. Note that this option implies the use of CSFs, even of no CONFIG card (see section 19.6.1) is present.

grdsav: record name for saving the information which is needed in a subsequent gradient calculation. This save is done automatically to record 5000.1 if the input contains a FORCE or OPTG card, and therefore the GRD option is normally not required.

19.5.6 Natural orbitals

NATORB,[*record,*] [*options*]

Request to calculate final natural orbitals and write them to record *record*. The default for *record* is 2140.2, or what else has been specified on an ORBITAL card, if present. By default, the orbitals are not printed and the hamiltonian is not diagonalized for the new orbitals The following *options* can be specified (in any order):

CI	Diagonalize the hamiltonian in the basis of the computed natural orbitals and print the configurations and their associated coefficients. This has the same effect as the GPRINT, CIVECTOR directive (see section 6.12. By default, only configurations with coefficients larger than 0.05 are printed. This threshold can be modified using the THRESH (see section 19.8.2) or GTHRESH (see section 6.11) options.
STATE=*state*	Compute natural orbitals for the specified state. *state* has the form *istate.isym*, e.g., 3.2 for the third state in symmetry 2. In contrast to earlier versions, *isym* refers to the number of the irreducible representation, and not the sequence number of the state symmetry. It is therefore independent of the order in which WF cards are given. The specified state must have been optimized. If STATE is not given and two or more states are averaged, the natural orbitals are calculated with the state-averaged density matrix (default).
SPIN=*ms2*	Compute natural orbitals for states with the specified spin. *ms2* equals $2 * S$, i.e., 0 for singlet, 1 for doublet etc. This can be used to together with STATE to select a specific state in case that states of different spin are averaged. If STATE is not specified, the state-averaged density for all states of the given spin is used.
SAVE=*record*	Request to save the civector(s) to the specified record.
ORBITAL=*record*	Request to save the orbitals to the specified record (same effect as specifying *record* as first agrument (see above).
PRINT=*nvirt*	Request to print *nvirt* virtual orbitals in each symmetry. By default, the orbitals are not printed unless the ORBPRINT option (see section 19.8.1 is present or the global GPRINT, ORBITALS (see section 6.12) directive has been given before. The PRINT option on this card applies only to the current orbitals.

Several NATORB, CANORB, and LOCORB cards (for different states) may follow each other. In contrast to earlier versions of MOLPRO the different orbital sets can all be stored in one dump record (but different records still work). See section 4.11 for information about dump records and how specific orbital sets can be requested in a later calculation.

19.5.7 Pseudo-canonical orbitals

CANORB,[*record,*] [*options*]

or

CANONICAL,[*record*,] [*options*]

Request to canonicalize the final orbitals, and writing them to record *record*. All options have the same effect as described for NATORB.

19.5.8   Localized orbitals

LOCORB,[*record*,] [*options*]

or

LOCAL,[*record*,] [*options*]

Request to localize the final orbitals, and writing them to record *record*. All options have the same effect as described for NATORB.

Note: LOCAL is interpreted by MULTI, but LOCALI is a separate command which calls the localization program and not recognized by MULTI. In order to avoid confusion, it is recommended to use LOCORB rather then LOCAL as subcommand within MULTI.

19.5.9   Diabatic orbitals

In order to construct diabatic states, it is necessary to determine the mixing of the diabatic states in the adiabatic wavefunctions. In principle, this mixing can be obtained by integration of the non-adiabatic coupling matrix elements. Often, it is much easier to use an approximate method, in which the mixing is determined by inspection of the CI coefficients of the MCSCF or CI wavefunctions. This method is applicable only if the orbital mixing is negligible. For CASSCF wavefunctions this can be achieved by maximizing the overlap of the active orbitals with those of a reference geometry, at which the wavefunctions are assumed to be diabatic (e.g. for symmetry reasons). The orbital overlap is maximized using using the new DIAB command in the MCSCF program. Only the active orbitals are transformed.

This procedure works as follows: first, the orbitals are determined at the reference geometry. Then, the calculations are performed at displaced geometries, and the "diabatic" active orbitals, which have maximum overlap with the active orbitals at the reference geometry, are obtained by adding a DIAB directive to the input:

Old form (Molpro96, obsolete):

DIAB,*orbref, orbsav, orb1,orb2,pri*

New form:

DIAB,*orbref* [,TYPE=*orbtype*] [,STATE=*state*] [,SPIN=*spin*] [,*MS2=ms2*] [,SAVE=*orbsav*] [,ORB1=*orb1*, ORB2=*orb2*] [,*PRINT=pri*] [,*METHOD=method*]

Here *orbref* is the record holding the orbitals of the reference geometry, and *orbsav* is the record on which the new orbitals are stored. If *orbsav* is not given (recommended!) the new orbitals are stored in the default dump record (2140.2) or the one given on the ORBITAL directive (see section 19.5.4). In contrast to earlier versions of MOLPRO it is possible that *orbref* and *orbsav* are the same. The specifications TYPE, STATE, SPIN can be used to select specific sets of reference orbitals, as described in section 4.11. *orb1, orb2* is a pair of orbitals for which the overlap is to be maximized. These orbitals are specified in the form *number.sym*, e.g. 3.1 means the third orbital in symmetry 1. If *orb1, orb2* are not given, the overlap of all active orbitals is maximized. *pri* is a print parameter. If this is set to 1, the transformation angles for each orbital are printed for each Jacobi iteration. *method* determines the diabatization method.

method=1 (default): use Jacobi rotations; *method=2*: use block diagonalization. Both methods yield very similar results. *method=2* must only be used for CASSCF wavefunctions. *method=-1* and *method=-2*: as the positive values, but AO overlap matrix of the current geometry is used. This minimizes the change of the MO coefficients, rather than maximizing the overlap to the neighbouring orbitals.

Using the defaults described above, the following input is sufficient in most cases:

DIAB,*orbref*

Using `Molpro98` is is not necessary any more to give any GEOM and DISPL cards. The displacements and overlap matrices are computed automatically (the geometries are stored in the dump records, along with the orbitals).

The diabatic orbitals have the property that the sum of orbital and overlap contributions in the non-adiabatic coupling matrix elements become approximately zero, such that the adiabatic mixing occurs only through changes of the CI coefficients. This allows to determine the mixing angle directly from the CI coefficients, either in a simple way as described for instance in J. Chem. Phys. **89**, 3139 (1988), or in a more advanced manner as described by Pacher, Cederbaum, and Köppel in J. Chem. Phys. **89**, 7367 (1988). Recently, an automatic procedure, as described in J. Chem. Phys. **102**, 0000, (1999) has been implemented into MOLPRO. This is available in Version 99.1 and later and is described in section 42.

Below we present an example for the first two excited states of H_2S, which have B_1 and A_2 symmetry in C_{2v}, and A'' symmetry in C_S. We first perform a reference calculation in C_{2v} symmetry, and then determine the diabatic orbitals for displaced geometries in C_S symmetry. Each subsequent calculation uses the previous orbitals as reference. One could also use the orbitals of the C_{2v} calculation as reference for all other calculations. In this case one would have to take out the second-last input card, which sets `reforb=2141.2`.

```
***,H2S diabatic A" states

basis=VDZ                                 !use cc-pVDZ basis set
symmetry,x,planeyz                        !use Cs symmetry & fix orientation of the molecule
orient,noorient                           !dont allow automatic reorientation
geometry={s;h1,s,r1;h2,s,r2,h1,theta}     !Z-matrix geometry input

gprint,orbitals,civector                  !global print options

text,reference calculation for C2V
theta=92.12,r1=2.3,r2=2.3                 !reference geometry

{hf;occ,7,2;wf,18,1}                      !scf calculation for ground state

{multi;occ,9,2;closed,4,1;                !define active and inactive spaces
wf,18,2;state,2;                          !two A" states (1B1 and 1A2 in C2v)
orbital,2140.2}                           !save orbitals to 2140.2
reforb=2140.2

text,calculations at displaced geometries

rd=[2.4,2.5,2.6]                          !define a range of bond distances

do i=1,#rd                               !loop over displaced geometries

r2=rd(i)                                 !set r2 to current distance

{multi;occ,9,2;closed,4,1;               !same wavefunction definition as at reference geom.
wf,18,2;state,2;
orbital,2141.2                           !save new orbitals to record
diab,reforb}                             !compute diabatic orbitals using reference orbitals
                                         !stored on record reforb
reforb=2141.2                            !set variable reforb to the new orbitals.
enddo
```

    http://www.molpro.net/info/current/examples/h2s_diab.com

See section 42 for the automatic generation of diabatic energies.

19.6   Selecting the optimization methods

By default, MULTI uses the non-linear optimization method developed by Werner, Meyer, and
Knowles. Other methods, such as the Newton-Raphson procedure or the Augmented Hessian
procedure, are also implemented and can be selected using the ITERATIONS directive (for
state-averaged calculations, only the non-linear optimization method can be used). For CASSCF
calculations, the CI problem is solved in a basis of Slater determinants, unless a CONFIG card
is given. Some procedures may be disabled using the DONT directive.

19.6.1   Selecting the CI method

CONFIG,*key*;

key may be DET or CSF, and defaults to CSF. If no CONFIG or SELECT card is given, the
default is determinants (CASSCF).

19.6.2 Selecting the orbital optimization method

The ITERATIONS directive can be use to modify the defaults for the optimization method. It consists of a sequence of several cards, which should be enclosed in a pair of curly brackets.

{ ITERATIONS;
DO,*method1,iter1*[,TO,*iter2*];
DONT,*method2,iter3*[,TO,*iter4*];
...
}

method can be one of the following:

DIAGCI	Diagonalize hamiltonian in the beginning of the specified iterations. This is the default for iteration 1.
INTERNAL	Optimize internal orbitals at the beginning of the specified iterations. This is default for second and subsequent iterations.
WERNER	use Werner-Meyer-Knowles non-linear optimization method for the specified iterations. This is the default for all iterations.
AUGMENT	Use step-restricted Augmented Hessian method for the specified iterations.
NEWTON	Use Newton-Raphson method for specified iterations.
UNCOUPLE	Do not optimize orbitals and CI coefficients simultaneously in the specified iterations. This option will set DIAGCI for these iterations.
NULL	No orbital optimization.

19.6.3 Disabling the optimization

In addition to the ITERATIONS directive described above, some procedures can be be disabled more simply using the DONT directive. DONT,*code*

code may be

ORBITAL	Do initial CI but don't optimize orbitals.
WAVEFUNC	Do not optimize the orbitals and CI coefficients (i.e. do only wavefunction analysis, provided the orbitals and CI coefficients are supplied (see START card)).
WVFN	Alias for WAVEFUNC.
ANAL	Do no wavefunction analysis.

19.6.4 Disabling the extra symmetry mechanism

NOEXTRA

This card disables the search for extra symmetries. By default, if extra symmetries are present, each orbital is assigned to such an extra symmetry and rotations between orbitals of different extra symmetry are not performed.

19.7 Calculating expectation values

By default, the program calculates the dipole expectation and transition moments. Further expectation values or transition properties can be computed using the `TRAN, TRAN2` and `EXPEC, EXPEC2` directives.

19.7.1 Matrix elements over one-electron operators

`EXPEC,`*oper*$_1$`,`*oper*$_2$`,...,`*oper*$_n$
`TRAN,`*oper*$_1$`,`*oper*$_2$`,...,`*oper*$_n$

Calculate expectation values and transition matrix elements for the given one-electron operators. With `EXPEC` only expectation values are calculated. *oper*$_i$ is a codeword for the operator. The available operators and their associated keywords are given in section 6.13.

19.7.2 Matrix elements over two-electron operators

`EXPEC2,`*oper*$_1$`,`*oper*$_2$`,...,`*oper*$_n$
`TRAN2,`*oper*$_1$`,`*oper*$_2$`,...,`*oper*$_n$

Calculate transition matrix elements for two-electron operators. This is presently only useful for angular momentum operators. With `EXPEC2` only diagonal matrix elements will be computed. For instance

`TRAN2,LXX`	calculates matrix elements for L_x^2
`TRAN2,LYY`	calculates matrix elements for L_y^2
`TRAN2,LXZ`	calculates matrix elements for $\frac{1}{2}(L_x L_z + L_z L_x)$
`TRAN2,LXX,LYY,LZZ`	calculates matrix elements for L_x^2, L_y^2, and L_z^2. The matrix elements for the sum L^2 are also printed.

19.7.3 Saving the density matrix

`DM,`[*spindens*]

If the `DM` directive is given, the first order density matrix in AO basis is written to the dump record specified on the `ORBITAL` card (default 2140.2). If no `ORBITAL` card is present, but a record is specified on a `NATORB`, `CANORB`, or `LOCORB` card, the densities are saved to the first record occurring in the input. In a state-averaged calculation the SA-density, as well the individual state densities, are saved. See section 4.11 for information about how to recover any of these densities for use in later programs.

If *spindens* is a number greater than zero, the spin density matrices are also saved. Note that a maximum of 50 density matrices can be saved in one dump record.

If no `DM` directive is given), the first order density matrix is saved in single-state calculations, and only the stage-averaged density matrix in state-averaged calculations.

19.8 Miscellaneous options

All commands described in this section are optional. Appropriate default values are normally used. Note that printing of the orbitals and civectors can also be requested using the global `GPRINT` command, or by giving `NATORB` or `CANORB` options.

19.8.1 Print options

`ORBPRINT`[,*nvirt*]

requests the occupied and *nvirt* virtual orbitals in each symmetry to be printed (default *nvirt*=0). By default, the program does not print the orbitals, unless the `ORBPRINT` directive or a global `GPRINT,ORBITALS` (see section 6.12) command is present. Specific orbital sets can be printed using the `PRINT` option on a `NATORB`, `CANORB`, or `LOCORB` card (see section 19.5.6). To print additional information at the end of the calculation, use

`PRINT`,*key1,key2,…*;

Printing is switched on for *key1*, *key2*,… . To print information in each iteration, use

`IPRINT`,*key1,key2,…*;

Possible print keys are:

`MICRO`	print details of "microiterations" — useful for finding out what's going wrong if no convergence
`REF`	print summary of configuration set (CSFs only)
`REF1`	print list of configuration set (CSFs only)
`COR`	print summary of intermediate spaces used in CSF calculation
`COR1`	print list of intermediate configuration sets (CSFs only)
`PSPACE`	print list of configurations making up the "primary" space
`ORBITALS`	print orbitals (see also `ORBPRINT`)
`NATORB`	print natural orbitals (see also `ORBPRINT`)
`VIRTUALS`	print virtual orbitals (see also `ORBPRINT`)
`CIVECTOR`	print CI vector (better use `CANORB` or `NATORB`)
`INTEGRAL`	print transformed integrals (for testing only!)
`DENSITY`	print density matrices
`HESSIAN`	print hessian
`DIAGONAL`	print diagonal elements of hessian
`GRADIENT`	print gradient
`LAGRANGI`	print Lagrangian
`STEP`	print update vector
`ADDRESS`	print addressing information (for testing only!)
`DEBUG`	print debugging information
`CI2`	print debugging information in routine ci2 (Warning: may be long!!)
`IO`	print debugging information in I/O routines

19.8.2 Convergence thresholds

Convergence thresholds can be modified using

`ACCURACY`,[`GRADIENT`=*conv*] [,`STEP`=*sconv*] [,`ENERGY`=*econv*]

where

conv	Threshold for orbital gradient (default 10^{-2}).)
econv	Threshold for change of total energy (default 10^{-6}).
sconv	Threshold for size of step (default 10^{-3}).

The default values can be modified using the global GTHRESH command (see section 6.11). Normally, the above default values are appropriate.

19.8.3 Maximum number of iterations

MAXITER,*maxit*;

maxit is maximum number of iterations (default 20). If the calculation does not converge in the default number of iterations, you should first think about the reason before increasing the limit. In most cases the choice of active orbitals or of the optimized states is not appropriate (see introduction of MULTI). The maximum allowed value of *maxit* is 40. If the calculation has not converged in this number of iterations, it is likely that the active space is not reasonable. Note: slow convergence can occur in RASSCF calculations if single excitations into weakly occupied orbitals are present. These should be eliminated using

RESTRICT,-1,-1,*orbital list*

19.8.4 Test options

TEST,*i1*,*i2*,*i3*,...;

Activate testing options numbered $i1$, $i2$, ... Please do not use unless you know what you are doing!

19.8.5 Special optimization parameters

The following parameters can also be given as options on the MULTI command line.

STEP,*radius,trust1,tfac1,trust2,tfac2*;

Special parameters for augmented hessian method. For experts only!

GOPER,*igop*;

Use G-operator technique in microiterations (Default). If igop.lt.0 do not use G-operators.

COPT,*ciacc,copvar,maxci,cishft,icimax,icimx1,icimx2,icstrt,icstep*;

Special parameters for the direct CI method. For experts only!

ciacc	grad threshold for CI diagonalization
copvar	start threshold for CI-optimization
maxci	max. number of CI-optimizations per microiteration
cishft	denominator shift for q-space
icimax	max. number of CI-optimizations in first macroiteration
icimx1	max. number of CI-optimizations in second and subsequent iterations
icimx2	max. number of CI-optimizations in internal absorption step

icstrt	first microiteration with CI-optimization
icstep	microiteration increment between CI-optimizations

INTOPT,*maxito,maxitc,maxrep,nitrep,iuprod*;

Special parameters for internal optimization scheme. For experts only!

NONLINEAR,*itmaxr,ipri,drmax,drdamp,gfak1,gfak2,gfak3,irdamp,ntexp*

Special parameters for non-linear optimization scheme. For experts only!

Old form (obsolete):

THRESH,*thrpri,thrpun,varmin,varmax,thrdiv,thrdoub*

New form:

THRESH [,THRPRI=*thrpri*] [,THRPUN=*thrpun*] [,VARMIN=*varmin*]
[,VARMAX=*varmax*] [,THRDIV=*thrdiv*] [,THRDOUB=*thrdoub*]

thrpri	threshold for printing CI coefficients (default 0.04)
thrpun	threshold for writing CI coefficients to the punch file. Default is no write to the punch file
varmin,varmax	thresholds for non-linear optimization scheme. For experts only!
thrdoub	threshold for detecting almost doubly occupied orbitals for inclusion into the pseudo canonical set (default 0, i.e. the feature is disabled).

DIIS,*disvar,augvar,maxdis,maxaug,idsci,igwgt,igvec,idstrt,idstep*;

Special parameters for DIIS convergence acceleration. For experts only!

19.8.6   Saving wavefunction information for CASVB

VBDUMP[,*vbdump*];

For users of the valence bond program *CASVB*, all wavefunction information that may subsequently be required is saved to the record *vbdump*. The default is not to write this information. If the keyword is specified without a value for *vbdump*, then record 4299.2 is used. This keyword is not needed prior to variational *CASVB* calculations.

19.8.7   Saving transformed integrals

TRNINT,*trnint*;

trnint specifies the record name for integrals in the basis of active CASSCF MOs. These are used for example by *CASVB* (see section 43.5). The default value for *trnint* is 1900.1.

19.9   Coupled-perturbed MCSCF

The coupled-perturbed MCSCF is required for computing gradients with state-averaged orbitals, non-adiabatic couplings, difference gradients or polarizabilities. We note that the present implementation is somewhat preliminary and not very efficient.

19.9.1 Gradients for SA-MCSCF

For computing state-averaged gradients, use

`CPMCSCF,GRAD,`*state*`,[`SPIN`=`*spin*`],[`MS2`=`*ms2*`],[`ACCU`=`*thresh*`],[`RECORD`=`*record*`]`

where *state* specifies the state (e.g., 2.1 for the second state in symmetry 1) for which the gradients will computed. *spin* specifies the spin of the state: this is half the value used in the corresponding WF card (e.g., 0=Singlet, 0.5=Doublet, 1=Triplet). Alternatively, MS2 can be used, where *ms2* = 2*spin, i.e., the same as specified on WF cards. The specification of SPIN or MS2 is only necessary if states with different spin are state-averaged. *record* specifies a record on which the gradient information is stored (the default is 5101.1). *thresh* is a threshold for the accuracy of the CP-MCSCF solution. The default is 1.d-7.

The gradients are computed by a subsequent call to FORCES or OPTG.

Note: if for some reason the gradients are to be computed numerically from finite energy differences, it is in state-averaged calculations necessary to give, instead of the CPMCSCF input, the following:

`SAVE,GRAD=-1`

Otherwise the program will stop with an error message.

19.9.2 Difference gradients for SA-MCSCF

For computing difference gradients, use

`CPMCSCF,DGRAD,`*state1*`,`*state2*`,[`ACCU`=`*thresh*`],[`RECORD`=`*record*`]`

where *state1* and *state2* specify the two states considered. (e.g., 2.1,3.1 for the second and third states in symmetry 1) The gradient of the energy difference will be computed. Both states must have the same symmetry. *record* specifies a record on which the gradient information is stored (the default is 5101.1). *thresh* is a threshold for the accuracy of the CP-MCSCF solution. The default is 1.d-7.

The gradients are computed by a subsequent call to FORCES or OPTG.

19.9.3 Non-adiabatic coupling matrix elements for SA-MCSCF

For computing non-adiabatic coupling matrix elements analytically, use

`CPMCSCF,NACM,`*state1*`,`*state2*`,[`ACCU`=`*thresh*`],[`RECORD`=`*record*`]`

where *state1* and *state2* specify the two states considered. (e.g., 2.1,3.1 for the second and third states in symmetry 1) Both states must have the same symmetry. *record* specifies a record on which the gradient information is stored (the default is 5101.1). This will be read in the subsequent gradient calculation. *thresh* is a threshold for the accuracy of the CP-MCSCF solution. The default is 1.d-7.

NADC and NADK are an aliases for NADC, and SAVE is an alias for RECORD.

The matrix elements for each atom are computed by a subsequent call to FORCES.

Note: this program is not yet extensively tested and should be used with care!

19.9.4 MCSCF hessians

The MCSCF/CASSCF hessian can be computed analytically (only without symmetry) using

`CPMCSCF,HESS,[ACCU=`*value*`]`

where the `ACCU` option specifies the convergence threshold in the CPMCSCF calculation (default 1.d-4). The hessian is stored on record 5300.2 and can be used in a subsequent frequency calculation.

Example:

```
{multi;cpmcscf,hess,accu=1.d-5}
frequencies
```

Note that the `NOEXTRA` option is used when computing a hessian.

19.10 Optimizing valence bond wavefunctions

`VB={...}`

Using this keyword, the optimization of the CI coefficients is carried out by *CASVB*. The `VB` keyword can be followed by any of the directives described in section 43. Energy-based optimization of the VB parameters is the default, and the output level for the main *CASVB* iterations is reduced to -1.

19.11 Total Position-Spread tensor (TPS)

Bibliography:

M. El Khatib, T. Leininger, G.L. Bendazzoli, and S. Evangelisti, Chem. Phys. Lett. 591, 58 (2014).

O. Brea, M. El Khatib, C. Angeli, G.L. Bendazzoli, S. Evangelisti, and T. Leininger, J. Chem. Theory Comput. 9, 5286 (2013).

All publications resulting from use of this program must acknowledge the above. See also:

W. Kohn, Phys. Rev. 133 (1964) A171.
R. Resta, S. Sorella, Phys. Rev. Lett. 82 (1999) 370.

The total position-spread (TPS) tensor is a quantity originally introduced in the modern theory of electrical conductivity. In the case of molecular systems, this tensor measures the fluctuation of the electrons around their mean positions, which corresponds to the delocalization of the electronic charge within a molecular system. The TPS can discriminate between metals and insulators taking information from the ground state wave function. This quantity can be very useful as an indicator to characterize Intervalence charge transfer processes, the bond nature of molecules (covalent, ionic or weakly bonded), and Metalinsulator transition.

The program is invoked by `TRAN2` inside the `MULTI` input block:

`TRAN2,RXX,RYY,RZZ,RXY,RXZ,RYZ;`

The three different classes of contributions to the CASSCF wave function can be printed by using the keyword:

```
IPRINT,TPS1;
```

This will print the core-core, core-active, and active-active contributions of the TPS tensor are printed.

19.12 Hints and strategies

MCSCF is not a "black box" procedure like SCF! For simple cases, for example a simple CASSCF with no `CLOSED` orbitals, this program will converge in two or three iterations. For more complicated cases, you may have more trouble. In that case, consider the following:

- Always start from neighbouring geometry orbitals when available (this is the default).

- The convergence algorithm is more stable when there are no `CLOSED` orbitals, i.e., orbitals doubly occupied in all configurations, but fully optimized. Thus a reasonable approach is to make an initial calculation with `CLOSED` replaced by `FROZEN` (all doubly occ. frozen).

- If still no success, you can switch off the coupling between CI coefficients and orbital rotations for a few iterations, e.g.:

  { `ITERATIONS;DO,UNCOUPLE,1,TO,2; }`

  and/or disable the simultaneous optimization of internal orbitals & CI, e.g.:

  { `ITERATIONS;DONT,INTERNAL,1,TO,2; }`

You can often get a clue about where the program starts to diverge if you include:

```
IPRINT,MICRO;
```

in the data. Also consider the general remarks at the beginning of this chapter. For the details of the algorithms used, see J. Chem. Phys 82, 5053 (1985); Chem. Phys. Letters 115, 259 (1985); Advan. Chem. Phys. 59, 1 (1987);

19.13 Examples

The simplest input for a CASSCF calculation for H_2O, C_{2v} symmetry, is simply:

```
geometry={o;h1,o,r;h2,o,r,h1,theta}    !Z-matrix geometry input
r=1 ang                                !bond length
theta=104                              !bond angle
hf                                     !do scf calculation
multi                                  !do full valence casscf
```

> http://www.molpro.net/info/current/examples/h2o_casscf.com

This could be extended, for instance, by the following input cards

```
OCC,4,1,2;        !  specify occupied space
CLOSED,2          !  specify closed-shell (inactive) orbitals
FROZEN,1;         !  specify frozen core orbitals
WF,10,1;          !  define wavefunction symmetry
START,2100.2;     !  read guess orbitals from record 2100, file 2
ORBITAL,2140.2;   !  save final orbitals to record 2140, file 2
NATORB,PRINT,CI   !  print natural orbitals and diagonalize the hamiltonian
                  !  for the natural orbitals. The largest CI coefficients
                  !  are printed.
```

Example for a state-averaged calculation for CN, X and B $^2\Sigma^+$ states, and A $^2\Pi_x$, $^2\Pi_y$ states averaged. A full valence CASSCF calculation is performed

```
***,cn
r=2.2                               !define bond length
geometry={c;n,c,r}
{rhf;occ,5,1,1;wf,13,1,1;            !RHF calculation for sigma state
orbital,2100.2}                     !save orbitals to record 2100.2 (default)

{multi;occ,6,2,2;closed,2;           !Define active and inactive orbitals
start,2100.2;                       !Start with RHF orbitals from above
save,ref=4000.2                     !Save configuration weights for CI in record 4000.2
wf,13,1,1;state,2;wf,13,2,1;wf,13,3,1;!Define the four states
natorb,ci,print;                    !Print natural orbitals and associated ci-coefficients
tran,lz                             !Compute matrix elements over LZ
expec2,lzz}                         !compute expectation values for LZZ
```

        http://www.molpro.net/info/current/examples/cn_sa_casscf.com

Example for an RASSCF (restricted active space) calculation for N$_2$, including SCF determinant plus all double excitations into valence orbitals. The single excitations are excluded. D_{2h} symmetry, CSF method used:

```
***,N2
geometry={N1;N2,N1,r}               !geometry input
r=2.2                               !bond length
{hf;occ,3,1,1,,2;wf,14,1;save,2100.2} !scf calculation

{multi;occ,3,1,1,,3,1,1;             !Define occupied orbitals
frozen,1,,,,1,2100.2;                !Define frozen core scf orbitals
config;                             !Use CSF method
wf,14,1;                            !Define state symmetry
restrict,0,2,3.5,1.6,1.7;           !Restriction to singles and doubles
restrict,-1,-1,3.5,1.6,1.7;         !Take out singles
print,ref1                          !Print configurations
natorb,ci,print}                    !Print natural orbitals and CI coeffs
```

        http://www.molpro.net/info/current/examples/n2_rasscf.com

20 THE CI PROGRAM

Multiconfiguration reference internally contracted configuration interaction

Bibliography:

H.-J. Werner and P.J. Knowles, J. Chem. Phys. 89, 5803 (1988).
P.J. Knowles and H.-J. Werner, Chem. Phys. Lett. 145, 514 (1988).

For excited state calculations:

P. J. Knowles and H.-J. Werner, Theor. Chim. Acta **84**, 95 (1992).

For explicitly correlated MRCI (MRCI-F12):

T. Shiozaki, G. Knizia, and H.-J. Werner, J. Chem. Phys. **134**, 034113 (2011);
T. Shiozaki and H.-J. Werner, J. Chem. Phys. **134**, 184104 (2011);
T. Shiozaki and H.-J. Werner, Mol. Phys. **111**, 607 (2013).

All publications resulting from use of the corresponding methods must acknowledge the above.

The first internally correlated MRCI program was described in:

H.-J. Werner and E.A. Reinsch, J. Chem. Phys. 76, 3144 (1982).
H.-J. Werner, Adv. Chem. Phys. 59, 1 (1987).

The command `CI` or `CI-PRO` or `MRCI` calls the MRCI program.
The command `MRCI-F12` calls the explicitly correlated MRCI-F12 program.
The command `CISD` calls fast closed-shell CISD program.
The command `QCI` calls closed-shell quadratic CI program.
The command `CCSD` calls closed-shell coupled-cluster program.

The following options may be specified on the command line:

NOCHECK	Do not stop if no convergence.
DIRECT	Do calculation integral direct.
NOSING	Do not include singly external configurations.
NOPAIR	Do not include doubly external configurations (not valid for single reference methods).
MAXIT=*value*	Maximum number of iterations.
MAXITI=*value*	Maximum number of microiterations (for internals).
SHIFTI=*value*	Denominator shift for update of internal configurations.
SHIFTS=*value*	Denominator shift for update of singles.
SHIFTP=*value*	Denominator shift for update of doubles.
THRDEN=*value*	Convergence threshold for the energy.
THRVAR=*value*	Convergence threshold for the CI-vector. This applies to the square sum of the changes of the CI-coefficients.
SWAP|NOSWAP	If `SWAP` is given, the MRCI wavefunctions are reordered according to maximum overlap with the reference functions (this only applies in multi-state calculations). The default is `NOSWAP`, i.e. the states are ordered according to increasing MRCI energy.
ROTREF=*value*	If *value*=0 the cluster corrections are not printed for the rotated reference energies (cf. Section 20.7). If *value*=1 all corrections are printed. If *value*=-1 the 2009.1 behaviour is recovered.

20.1 Introduction

The internally contracted MRCI program is called by the CI command. This includes as special cases single reference CI, CEPA, ACPF, MR-ACPF and MR-AQCC. For closed-shell reference functions, a special faster code exists, which can be called using the CISD, QCI, or CCSD commands. This also allows to calculate Brueckner orbitals for all three cases (QCI and CCSD are identical in this case).

The explicitly correlated variant is called by the command `MRCI-F12`, see section 20.8.

With no further input cards, the wavefunction definition (core, closed, and active orbital spaces, symmetry) corresponds to the one used in the most recently done SCF or MCSCF calculation. By default, a CASSCF reference space is generated. Other choices can be made using the `OCC`, `CORE`, `CLOSED`, `WF`, `SELECT`, `CON`, and `RESTRICT` cards. The orbitals are taken from the corresponding SCF or MCSCF calculation unless an `ORBITAL` directive is given. The

wavefunction may be saved using the SAVE directive, and restarted using START. The EXPEC directive allows to compute expectation values over one-electron operators, and the TRAN directive can be used to compute transition matrix elements for one-electron properties. Natural orbitals can be printed and saved using the NATORB directive.

For excited state calculations see STATE, REFSTATE, and PROJECT.

20.2 Specifying the wavefunction

Note: All occupations must be given before WF, PAIRSS, DOMAIN, REGION or other directives that need the occupations.

20.2.1 Occupied orbitals

OCC,$n_1,n_2,\ldots,n_8$;

n_i specifies numbers of occupied orbitals (including CORE and CLOSED) in irreducible representation number i. If not given, the information defaults to that from the most recent SCF, MCSCF or CI calculation.

20.2.2 Frozen-core orbitals

CORE,$n_1,n_2,\ldots,n_8$;

n_i is the number of frozen-core orbitals in irrep number i. These orbitals are doubly occupied in all configurations, i.e., not correlated. If no CORE card is given, the program uses the same core orbitals as the last CI calculation; if there was none, then the atomic inner shells are taken as core. To avoid this behaviour and correlate all electrons, specify

CORE

20.2.3 Closed-shell orbitals

CLOSED,$n_1,n_2,\ldots,n_8$

n_i is the number of closed-shell orbitals in irrep number i, inclusive of any core orbitals. These orbitals do not form part of the active space, i.e., they are doubly occupied in all reference CSFs; however, in contrast to the core orbitals (see CORE), these orbitals are correlated through single and double excitations. If not given, the information defaults to that from the most recent SCF, MCSCF or CI calculation. For calculations with closed-shell reference function (closed=occ), see CISD, QCI, and CCSD.

20.2.4 Defining the orbitals

ORBIT,*name.file*,[*specifications*];

name.file specifies the record from which orbitals are read. Optionally, various *specifications* can be given to select specific orbitals if *name.file* contains more than one orbital set. For details see section 4.11. Note that the IGNORE_ERROR option can be used to force MPn or triples calculations with non-canonical orbitals.

The default is the set of orbitals from the last SCF, MCSCF or CI calculation.

20.2.5   Defining the state symmetry

The number of electrons and the total symmetry of the wavefunction are specified on the `WF` card:

`WF`,*elec,sym,spin*

where

elec:	is the number of electrons
sym:	is the number of the irreducible representation
spin:	defines the spin symmetry, *spin*= $2S$ (singlet=0, doublet=1, triplet=2, etc.)

The WF card must be placed after any cards defining the orbital spaces `OCC`, `CORE`, `CLOSED`.

The `REF` card can be used to define further reference symmetries used for generating the configuration space, see `REF`.

20.2.6   Additional reference symmetries

`REF`,*sym*;

This card, which must come after the `WF` directive, defines an additional reference symmetry used for generating the uncontracted internal and singly external configuration spaces. This is sometimes useful in order to obtain the same configuration spaces when different point group symmetries are used. For instance, if a calculation is done in C_s symmetry, it may happen that the two components of a Π state, one of which appears in A' and the other in A'', come out not exactly degenerate. This problem can be avoided as in the following example:

for a doublet A' state:

```
WF,15,1,1;       !define wavefunction symmetry (1)
REF,2;           !define additional reference symmetry (2)
```

and for the doublet A" state:

```
WF,15,2,1;       !define wavefunction symmetry (2)
REF,1;           !define additional reference symmetry (1)
```

For linear geometries the same results can be obtained more cheaply using C_{2v} symmetry,

```
WF,15,2,1;       !define wavefunction symmetry (2)
REF,1;           !define additional reference symmetry (1)
REF,3;           !define additional reference symmetry (3)
```

or

```
WF,15,3,1;       !define wavefunction symmetry (2)
REF,1;           !define additional reference symmetry (1)
REF,2;           !define additional reference symmetry (2)
```

Each `REF` card may be followed by `RESTRICT`, `SELECT`, and `CON` cards, in the given order.

20.2.7 Selecting configurations

SELECT,*ref1,ref2,refthr,refstat,mxshrf*;

This card is used to specify a reference configuration set other than a CAS, which is the default. Configurations can be defined using CON cards, which must appear after the *SELECT* card. Alternatively, if *ref1* is an existing MOLPRO record name, the configurations are read in from that record and may be selected according to a given threshold.

The select card must be placed directly after the *WF* or *REF* card(s), or, if present, the RESTRICT cards. The general order of these cards is

WF (or REF)
RESTRICT (optional)
SELECT   (optional)
CON   (optional)

ref1=rec1.file:	(*rec1>2000*) The configurations are read in from the specified record. See section 19.5.5 about how to save the configurations in the MCSCF calculation. If *ref1* is not specified, the program assumes that the configurations are read from subsequent CON cards (see CON).
ref2=rec2.file:	(*rec2>2000*) additional configurations are read from the specified record. If *rec2* is negative, all records between *rec1* and abs(*rec2*) are read. All configurations found in this way are merged.
refthr:	Selection threshold for configurations read from disc (records *rec1–rec2*). This applies to the norm of all CSFs for each orbital configuration.
refstat:	Specifies from which state vector the configurations are selected. This only applies to the case that the configurations were saved in a state-averaged calculation. If *refstat* is zero or not specified, the configurations are selected from all states. If *refstat* is greater than zero, then the specified reference state is used. If *refstat* is less than zero, then all appropriate reference states are used. Lastly, if *refstat* is of the form *istat1.istat2*, states *istat1* through *istat2* are used.
mxshrf:	maximum number of open shells in the selected or generated configurations.

20.2.8 Occupation restrictions

RESTRICT,*nmin,nmax,orb$_1$,orb$_2$,...orb$_n$*;

This card can be used to restrict the occupation patterns in the reference configurations. Only configurations containing between *nmin* and *nmax* electrons in the specified orbitals *orb$_1$*, *orb$_2$*, ..., *orb$_n$* are included in the reference function. If *nmin* and *nmax* are negative, configurations with exactly abs(*nmin*) and abs(*nmax*) electrons in the specified orbitals are deleted. This can be used, for instance, to omit singly excited configurations. The orbitals are specified in the form *number.sym*, where *number* is the number of the orbital in irrep *sym*. Several RESTRICT cards may follow each other.

The `RESTRICT` cards must follow the `WF` or `REF` cards to which they apply. The general order of these cards is

```
WF (or REF)
RESTRICT (optional)
SELECT  (optional)
CON  (optional)
```

If a `RESTRICT` cards precedes the `WF` card, it applies to all reference symmetries. Note that `RESTRICT` also affects the spaces generated by `SELECT` and/or `CON` cards.

20.2.9 Explicitly specifying reference configurations

`CON`,$n_1,n_2,n_3,n_4,\ldots$

Specifies an orbital configuration to be included in the reference function. n_1, n_2 etc. are the occupation numbers of the active orbitals (0,1,or 2). Any number of `CON` cards may follow each other, but they must all appear directly after a `SELECT` card.

20.2.10 Defining state numbers

`STATE`,*nstate,nroot(1),nroot(2),...,nroot(nstate)*;

nstate is the number of states treated simultaneously; *nroot(i)* are the root numbers to be calculated. These apply to the order of the states in the initial internal CI. If not specified, *nroot(i)=i*. Note that it is possible to leave out states, i.e.,

```
STATE,1,2;    ! calculates second state
STATE,2,1,3;  ! calculates first and third state
```

All states specified must be reasonably described by the internal configuration space. It is possible to have different convergence thresholds for each state (see `ACCU` card). It is also possible not to converge some lower roots which are included in the list *nroot(i)* (see `REFSTATE` card). For examples, see `REFSTATE` card.

20.2.11 Defining reference state numbers

`REFSTATE`,*nstatr,nrootr(1),nrootr(2),...,nrootr(nstatr)*;

nstatr is the number of reference states for generating contracted pairs. This may be larger or smaller than *nstate*. If this card is not present, *nstatr=nstate* and *nrootr(i)=nroot(i)*. Roots for which no reference states are specified but which are specified on the `STATE` card (or included by default if the *nroot(i)* are not specified explicitly on the `STATE` card) will not be converged, since the result will be bad anyway. However, it is often useful to include these states in the list *nroot(i)*, since it helps to avoid root flipping problems. Examples:

```
state,2;
```

will calculate two states with two reference states.

```
state,2;refstate,1,2;
```

will optimize second state with one reference state. One external expansion vector will be generated for the ground state in order to avoid root flipping. The results printed for state 1 are bad and should not be used (unless the pair space is complete, which might happen in very small calculations).

```
state,1,2;refstate,1,2;
```

As the second example, but no external expansion vectors will be generated for the ground state. This should give exactly the same energy for state 2 as before if there is no root flipping (which, however, frequently occurs).

```
state,2;accu,1,1,1;
```

Will calculate second state with two reference states. The ground state will not be converged (only one iteration is done for state 1) This should give exactly the same energy for state 2 as the first example.

20.2.12   Specifying correlation of orbital pairs

`PAIR`,*iorb1.isy1,iorb2.isy2,np*;

is a request to correlate a given orbital pair.

np=1:	singlet pair
np=-1:	triplet pair
np=0:	singlet and triplet pair (if possible)

Default is to correlate all electron pairs in active and closed orbitals. See also `PAIRS` card.

`PAIRS`,*iorb1.isy,iorb2.isy,np*;

Correlate all pairs which can be formed from orbitals *iorb1.isy1* through *iorb2.isy2*. Core orbitals are excluded. Either *iorb2* must be larger than *iorb1* or *isy2* larger than *isy1*. If *iorb1.isy1=iorb2.isy2* the `PAIRS` card has the same effect as a `PAIR` card. `PAIR` and `PAIRS` cards may be combined.

If no `PAIR` and no `PAIRS` card is specified, all valence orbitals are correlated. The created pair list restricts not only the doubly external configurations, but also the all internal and semi internals.

20.2.13   Restriction of classes of excitations

`NOPAIR;`

No doubly external configurations are included.

`NOSINGLE;`

No singly external configurations are included.

`NOEXC;`

Perform CI with the reference configurations only.

20.3   Options

20.3.1   Coupled Electron Pair Approximation

CEPA(*ncepa*);

($0 \leq ncepa \leq 3$). Instead of diagonalizing the hamiltonian, perform CEPA calculation, CEPA type *ncepa*. This is currently available only for single configuration reference functions.

20.3.2   Coupled Pair Functional (ACPF, AQCC)

ACPF,*options*
AQCC,*options*

where options can be

GACPFI=*gacpfi*

GACPFE=*gacpfe*

Instead of diagonalizing the hamiltonian, perform ACPF calculation or AQCC calculation. Using the options GACPFI and GAPCPE The internal and external normalization factors *gacpfi*, *gacpfe* may be reset from their default values of 1, 2/*nelec* and 1, 1-(*nelec*-2)(*nelec*-3)/*nelec*(*nelec*-1), respectively.

The ACPF and related methods are currently not robustly working for excited states. Even though it sometimes works, we do not currently recommend and support these methods for excited state calculations.

20.3.3   Projected excited state calculations

PROJECT,*record,nprojc*;

Initiate or continue a projected excited state calculation, with information stored on *record*. If *nprojc*> 0, the internal CI vectors of *nprojc* previous calculations are used to make a projection operator. If *nprojc*= −1, this calculation is forced to be the first, i.e. ground state, with no projection. If *nprojc*= 0, then if *record* does not exist, the effect is the same as *nprojc*= −1; otherwise *nprojc* is recovered from the dump in *record*. Thus for the start up calculation, it is best to use project,*record*,-1; for the following excited calculations, use project,*record*; At the end of the calculation, the wavefunction is saved, and the information in the dump *record* updated. The project card also sets the tranh option, so by default, transition hamiltonian matrices are calculated.

For example, to do successive calculations for three states, use

```
ci;...;project,3000.3,-1;
ci;...;project,3000.3;
ci;...;project,3000.3;
```

20.3.4   Transition matrix element options

TRANH,*option*;

If *option*> −1, this forces calculation of transition hamiltonian matrix elements in a TRANS or PROJECT calculation. If *option*< 1, this forces calculation of one electron transition properties.

20.3.5   Convergence thresholds

`ACCU`,*istate,energy,coeff*;

Convergence thresholds for state *istate*. The actual thresholds for the energy and the CI coefficients are 10**(-*energy*) and 10**-(*coeff*). If this card is not present, the thresholds for all states are the default values or those specified on the `THRESH` card.

20.3.6   Level shifts

`SHIFT`,*shiftp,shifts,shifti*;

Denominator shifts for pairs, singles, and internals, respectively.

20.3.7   Maximum number of iterations

`MAXITER`,*maxit,maxiti*;

maxit:	maximum number of macroiterations;
maxiti:	maximum number of microiterations (internal CI).

20.3.8   Restricting numbers of expansion vectors

`MAXDAV`,*maxdav,maxvi*;

maxdav:	maximum number of external expansion vectors in macroiterations;
maxvi:	maximum number of internal expansion vectors in internal CI.

20.3.9   Selecting the primary configuration set

`PSPACE`,*select,npspac*;

select:	energy criterion for selecting p-space configurations. If negative, a test for p-space H is performed.
npspac:	minimum number of p-space configurations. Further configurations are added if either required by select or if configurations are found which are degenerate to the last p-space configuration. A minimum number of npspace is automatically determined from the state specifications.

20.3.10   Canonicalizing external orbitals

`FOCK`,$n_1,n_2,\ldots$;

External orbitals are obtained as eigenfunctions of a Fock operator with the specified occupation numbers n_i. Occupation numbers must be provided for all valence orbitals.

20.3.11   Saving the wavefunction

SAVE,*savecp*,*saveco*,*idelcg*;

or

SAVE [,CIVEC=*savecp*] [,CONFIG=*saveco*] [,DENSITY=*dumprec*] [,NATORB=*dumprec*] [,FILES]

savecp:	record name for save of wavefunction. If negative the wavefunction is saved after each iteration, else at the end of the job. In case of coupled cluster methods (CCSD, QCISD, BCCD), the wavefunction is saved in each iteration in any case.
saveco:	record name for save of internal configurations and their maximum weight over all states for subsequent use as reference input (see SELECT card). If the record already exists, the record name is incremented by one until a new record is created.
idelcg:	if nonzero or FILES is specified, don't erase icfil and igfil (holding CI and residual vectors) at the end of the calculation.
dumprec:	Dump record for saving density matrix and natural orbitals. Only one dump record must be given. In any case the density matrix and the natural orbitals are saved. See also DM or NATORB cards.

20.3.12   Starting wavefunction

START,*readc1*,*irest*;

readc1:	record name from which the wavefunction is restored for a restart. In the case of coupled cluster methods (CCSD, QCISD, BCCD), the amplitudes are read from record *readc1* and used for restart.
irest:	If nonzero, the CI coefficients are read and used for the restart; otherwise, only the wavefunction definition is read in.

20.3.13   One electron properties

EXPEC,*oper*$_1$,*oper*$_2$,*oper*$_3$,... ;

After the wavefunction determination, calculate expectation values for one-electron operators *oper*$_i$. See section 6.13 for the available operators and their keywords. In multi-state calculations or in projected calculations, also the transition matrix elements are calculated.

20.3.14   Transition moment calculations

TRANS,*readc1*,*readc2*,[BIORTH],[*oper*$_1$,*oper*$_2$,*oper*$_3$,...];

Instead of performing an energy calculation, only calculate transition matrix elements between wavefunctions saved on records *readc1* and *readc2*. See section 6.13 for a list of available operators and their corresponding keywords. If no operator names are specified, the dipole transition moments are calculated.

If option `BIORTH` is given, the two wavefunctions may use different orbitals. However, the number of active and inactive orbitals must be the same in each case. Note that `BIORTH` is not working for spin-orbit matrix elements. Under certain conditions it may happen that biorthogonalization is not possible, and then an error message will be printed.

20.3.15   Saving the density matrix

`DM`,*record.ifil*,[*idip*];

The first order density matrices for all computed states are stored in record *record* on file *ifil*. If *idip* is not zero, the dipole moments are printed starting at iteration *idip*. See also `NATORB`. In case of transition moment calculation, the transition densities are also stored, provided both states involved have the same symmetry.

20.3.16   Natural orbitals

`NATORB`,[`RECORD=`]*record.ifil*,[`PRINT=`*nprint*],[`CORE`[=*natcor*]];

Calculate natural orbitals. The number of printed external orbitals in any given symmetry is *nprint*) (default 2). *nprint=-1* suppressed the printing. If *record* is nonzero, the natural orbitals and density matrices for all states are saved in a dump record *record* on file *ifil*. If *record.ifil* is specified on a `DM` card (see above), this record is used. If different records are specified on the `DM` and `NATORB` cards, an error will result. The record can also be given on the `SAVE` card. If `CORE` is specified, core orbitals are not printed.

Note: The dump record must not be the same as *savecp* or *saveco* on the `SAVE` card, or the record given on the `PROJECT`.

20.3.17   Miscellaneous options

`OPTION`,*code1=value,code2=value,...*

Can be used to specify program parameters and options. If no codes and values are specified, active values are displayed. The equal signs may be omitted. The following codes are allowed (max 7 per card):

NSTATE:	see `state` card
NSTATI:	number of states calculated in internal CI
NSTATR:	see `refstat` card
NCEPA:	see `CEPA` card
NOKOP:	if nonzero, skip integral transformation
ITRDM:	if .ge. 0 transition moments are calculated
ITRANS:	if nonzero, perform full integral transformation (not yet implemented)
IDIP:	Print dipole moments from iteration number *value*
REFOPT:	if nonzero, optimize reference coefficients; otherwise extract reference coefficients from internal CI
IAVDEN:	average HII and HSS denominators over spin couplings if nonzero

IDELCG:	if.ne.0 then destroy files icfil,igfil at end
IREST:	if nonzero, restart
NATORB:	if nonzero, natural orbitals are calculated and printed. The number of printed external orbitals per symmetry is min(*natorb*,2)
WFNAT:	if nonzero, natural orbitals are saved to this record
IPUNRF:	if nonzero, punch coefficients of reference configurations
NPUPD:	if nonzero, update pairs in nonorthogonal basis, otherwise in orthogonal basis.
MAXIT:	see `maxiter` card
MAXITI:	see `maxiter` card
MAXDAV:	see `maxdav` card
MAXVI:	see `maxdav` card
NOSING:	see `nosing` card
NOPAIR:	see `nopair` card
MXSHRF:	see `select` card
IKCPS=0:	In CIKEXT, only K(CP) is calculated; this option taken when and only when no singles.
IKCPS=1:	only K(CP') is calculated. Implies that modified coupling coefficients are used.
IKCPS=2:	K(CP) and K(CP') are calculated. Default is IKCPS=2 except when single reference configuration, when IKCPS=1.
IOPTGM:	Option for density matrix routines.
IOPTGM=0:	all quantities in density matrix routines are recalculated for each intermediate symmetry (max. CPU, min. core).
IOPTGM=1:	quantities precalculated and stored on disk (max. I/O, min. core).
IOPTGM=2:	quantities precalculated and kept in core (min. CPU, max. core).
IOPTOR:	If nonzero, calculate intermediate orbitals for each pair. Might improve convergence in some cases, in particular if localized orbitals are used.

20.3.18   Miscellaneous parameters

PARAM,*code1=value,code2=value*...

Redefine system parameters. If no codes are specified, the default values are displayed. The following codes are allowed:

LSEG:	disc sector length
INTREL:	number of integers per REAL*8 word
IVECT=0:	scalar machine
IVECT=1:	vector machine

MINVEC:	call MXMB in coupling coefficient routines if vector length larger than this value.
IBANK:	number of memory banks for vector machines. If IBANK>1, vector strides which are multiples of IBANK are avoided where appropriate.
LTRACK:	number of REAL*8 words per track or block (for file allocation)
LTR:	determines how matrices are stored on disc. If LTR=LSEG, all matrices start at sector boundaries (which optimizes I/O), but unused space is between matrices (both on disc and in core). With LTR=1 all matrices are stored dense. This might increase I/O if much paging is necessary, but reduce I/O if everything fits in core.
NCPUS:	Maximum number of CPUs to be used in multitasking.

20.4   Miscellaneous thresholds

THRESH,*code1=value,code2=value*...

If *value*=0, the corresponding threshold is set to zero, otherwise 10**(-*value*). The equal signs may be omitted. If no codes are specified, the default values are printed. The following codes are allowed (max 7 per card):

ZERO:	numerical zero
THRDLP:	delete pairs if eigenvalue of overlap matrix is smaller than this threshold.
PNORM:	delete pair if its norm is smaller than this threshold (all pairs are normalized to one for a closed shell case).
PRINTCI:	print CI coefficients which are larger than this value.
INTEG:	omit two-electron integrals which are smaller than this value.
ENERGY:	convergence threshold for energy; see also: ACCU card.
COEFF:	convergence threshold for coefficients; see also: ACCU card.
SPARSE:	omit coefficient changes which are smaller than this value.
EQUAL:	set values in the internal vector and the diagonal elements equal if they differ by less than this value. Useful for keeping track of symmetry.

20.5   Print options

PRINT,*code1=value,code2=value*,...

Print options. Generally, the value determines how much intermediate information is printed. *value*=-1 means no print (default for all codes). In some of the cases listed below the specification of higher values will generate even more output than described. The equal signs and zeros may be omitted. All codes may be truncated to three characters. The following codes are allowed (max 7 per card):

ORBITALS:	print orbitals

`JOP=0:`	print operator list
`JOP=1:`	print coulomb operators in MO basis
`JOP=2:`	print coulomb operators in AO and MO basis
`KOP:`	as `JOP` for internal exchange operators
`KCP=0:`	print paging information for CIKEXT
`KCP=1:`	print external exchange operators in MO basis
`KCP=2:`	print operators in AO and MO basis
`DM=0:`	print paging information for CIDIMA
`DM=1:`	print density matrix in MO basis
`DM=2:`	print density matrix in AO and MO basis
`FPP=0:`	print energy denominators for pairs
`FPP=1:`	in addition, print diagonal coupling coefficients in orthogonal basis.
`FPP=2:`	print operators FPP
`CP=0:`	print update information for pairs in each iteration
`CP=1:`	print pair matrix updates (MO basis)
`CP=2:`	in addition print pair matrices (MO basis)
`CP=3:`	print CP in AO basis (in CIKEXT)
`CI=0:`	print convergence information for internal CI
`CI=1:`	print internal CI coefficients and external expansion coefficients
`CS:`	as CP for singles
`CPS=0:`	print paging information for CICPS
`CPS=1:`	print matrices CPS in MO basis
`GPP=0:`	print paging information for CIGPQ
`GPP=1:`	print matrices GP at exit of CIGPQ
`GPS=0:`	print paging information for CIGPS
`GPS=1:`	print vectors GS at exit CIGPS
`GSP=1:`	print matrices GP at exit CIGPS
`GPI=0:`	print paging information for CIGPI
`GPI=1:`	print total GP in orthogonal basis
`GPI=2:`	print matrices GP and TP
`GIP=0:`	print paging information for CIGIP
`GIP=1:`	print GI at exit CIGIP
`GSS=0:`	print paging information for CIGSS
`GSS=1:`	print vectors GS at exit CIGSS
`GSI=0:`	print paging information for CIGSI
`GSI=1:`	print GS at exit CIGSI
`GIS=0:`	print paging information for CIGIS
`GIS=1:`	print GI at exit CIGIS
`GII:`	print intermediate information in internal CI

`DPQ:`	print coupling coefficients $\alpha(P,Q)$
`EPQ:`	print coupling coefficients $\beta(P,Q)$
`HPQ:`	print coupling coefficients $\gamma(P,Q)$
`DPI:`	print coupling coefficients for pair-internal interactions
`DSS:`	not yet used
`DSI:`	not yet used
`LOG:`	At end of each iteration, write summary to log file. Delete at end of job if `LOG=0`
`CC=0:`	print address lists for coupling coefficients
`CC=1:`	print coupling coefficients
`DEN=1:`	print internal first order density
`DEN=2:`	print internal second order density
`DEN=3:`	print internal third order density
`DEN=4:`	print first, second and third order densities
`GAM=1:`	print first order transition densities
`GAM=2:`	print second order transition densities
`GAM=3:`	print first and second order transition densities
`PAIRS=0:`	print list of non redundant pairs
`PAIRS=1:`	print list of all pairs
`CORE=0:`	print summary of internal configurations ($N, N-1$ and $N-2$ electron)
`CORE=1:`	print internal configurations ($N, N-1, N-2$)
`REF=0:`	print summary of reference configurations
`REF=1:`	print reference configurations and their coefficients
`PSPACE:`	print p-space configurations
`HII:`	print diagonal elements for internals
`HSS:`	print diagonal elements for singles
`SPQ:`	various levels of intermediate information in pair orthogonalization routine.
`TEST=0:`	print information at each subroutine call
`TEST=1:`	print in addition information about I/O in LESW, SREIBW
`TEST=2:`	print also information about I/O in FREAD, FWRITE
`CPU:`	print analysis of CPU and I/O times
`ALL:`	print everything at given level (be careful!)

20.6   Examples

```
***,Single reference CISD and CEPA-1 for water
r=0.957,angstrom
theta=104.6,degree;
geometry={O;               !z-matrix geometry input
          H1,O,r;
          H2,O,r,H1,theta}
{hf;wf,10,1;}                          !TOTAL SCF ENERGY     -76.02680642
{ci;occ,3,1,1;core,1;wf,10,1;}        !TOTAL CI(SD) ENERGY  -76.22994348
{cepa(1);occ,3,1,1;core,1;wf,10,1;}   !TOTAL CEPA(1) ENERGY -76.23799334
```

```
***,Valence multireference CI for X and A states of H2O
gthresh,energy=1.d-8
r=0.957,angstrom,theta=104.6,degree;
geometry={O;               !z-matrix geometry input
          H1,O,r;
          H2,O,r,H1,theta}
{hf;wf,10,1;}          !TOTAL SCF ENERGY               -76.02680642
{multi;occ,4,1,2;closed,2;frozen,1;wf,9,2,1;wf,9,1,1;tran,ly}
                  !MCSCF ENERGY                   -75.66755631
                  !MCSCF ENERGY                   -75.56605896
{ci;occ,4,1,2;closed,2;core,1;wf,9,2,1;save,7300.1}
                  !TOTAL MRCI ENERGY              -75.79831209
{ci;occ,4,1,2;closed,2;core,1;wf,9,1,1;save,7100.1}
                  !TOTAL MRCI ENERGY              -75.71309879
{ci;trans,7300.1,7100.1,ly}
                  !Transition moment <1.3|X|1.1> = -0.14659810  a.u.
                  !Transition moment <1.3|LY|1.1> = 0.96200488i a.u.
```

```
***,BH singlet Sigma and Delta states
r=2.1
geometry={b;h,b,r}
{hf;occ,3;wf,6,1;}
{multi;
occ,3,1,1;frozen,1;wf,6,1;state,3;lquant,0,2,0;wf,6,4;lquant,2;
tran,lz;
expec2,lzlz;}
! Sigma states:- energies -25.20509620 -24.94085861
{ci;occ,3,1,1;core,1;wf,6,1;state,2,1,3;}
! Delta states:- energies -24.98625171
{ci;occ,3,1,1;core,1;wf,6,1;state,1,2;}
! Delta state:- xy component
{ci;occ,3,1,1;core,1;wf,6,4;}
```

20.7   Cluster corrections for multi-state MRCI

In the following, we assume that

$$\Psi_{\text{ref}}^{(n)} = \sum_R C_{Rn}^{(0)} \Phi_R \tag{39}$$

$$\Psi_{\text{mrci}}^{(n)} = \sum_R C_{Rn} \Phi_R + \Psi_c \tag{40}$$

are the normalized reference and MRCI wave functions for state n, respectively. $C_R^{(0)}$ are the coefficients of the reference configurations in the initial reference functions and C_{Rn} are the relaxed coefficients of these configurations in the final MRCI wave function. Ψ_c is the remainder of the MRCI wave function, which is orthogonal to all reference configurations Φ_R.

The corresponding energies are defined as

$$E_{\text{ref}}^{(n)} = \langle \Psi_{\text{ref}}^{(n)} | \hat{H} | \Psi_{\text{ref}}^{(n)} \rangle, \tag{41}$$

$$E_{\text{mrci}}^{(n)} = \langle \Psi_{\text{mrci}}^{(n)} | \hat{H} | \Psi_{\text{mrci}}^{(n)} \rangle. \tag{42}$$

The standard Davidson corrected correlation energies are defined as

$$E_{\text{D}}^n = E_{\text{corr}}^{(n)} \cdot \frac{1 - c_n^2}{c_n^2} \tag{43}$$

where c_n is the coefficient of the (fixed) reference function in the MRCI wave function:

$$c_n = \langle \Psi_{\text{ref}}^{(n)} | \Psi_{\text{mrci}}^{(n)} \rangle = \sum_R C_{Rn}^{(0)} C_{Rn}, \tag{44}$$

and the correlation energies are

$$E_{\text{corr}}^{(n)} = E_{\text{mrci}}^{(n)} - E_{\text{ref}}^{(n)}. \tag{45}$$

In the vicinity of avoided crossings this correction may give unreasonable results since the reference function may get a small overlap with the MRCI wave function. One way to avoid this problem is to replace the reference wave function $\Psi_{\text{ref}}^{(n)}$ by the the relaxed reference functions

$$\Psi_{\text{rlx}}^{(n)} = \frac{\sum_R C_{Rn} \Phi_R}{\sqrt{\sum_R C_{Rn}^2}}, \tag{46}$$

which simply leads to

$$c_n^2 = \sum_R C_{Rn}^2. \tag{47}$$

Alternatively, one can linearly combine the fixed reference functions to maximize the overlap with the MRCI wave functions. This yields projected functions

$$\Psi_{\text{prj}}^{(n)} = \sum_m |\Psi_{\text{ref}}^{(m)}\rangle \langle \Psi_{\text{ref}}^{(m)} | \Psi_{\text{mrci}}^{(n)} \rangle = \sum_m |\Psi_{\text{ref}}^{(m)}\rangle d_{mn} \tag{48}$$

with

$$d_{mn} = \langle \Psi_{\text{ref}}^{(m)} | \Psi_{\text{mrci}}^{(n)} \rangle = \sum_R C_{Rm}^{(0)} C_{Rn}. \tag{49}$$

These projected functions are not orthonormal. The overlap is

$$\langle \Psi_{\text{prj}}^{(m)} | \Psi_{\text{prj}}^{(n)} \rangle = (\mathbf{d}^\dagger \mathbf{d})_{mn}. \tag{50}$$

Symmetrical orthonormalization, which changes the functions as little as possible, yields

$$\Psi_{\text{rot}}^{(n)} \quad = \quad \sum_m |\Psi_{\text{ref}}^{(m)}\rangle u_{mn}, \tag{51}$$

$$\mathbf{u} \quad = \quad \mathbf{d}(\mathbf{d}^\dagger\mathbf{d})^{-1/2}. \tag{52}$$

The overlap of these functions with the MRCI wave functions is

$$\langle\Psi_{\text{rot}}^{(m)}|\Psi_{\text{mrci}}^{(n)}\rangle \quad = \quad [(\mathbf{d}^\dagger\mathbf{d})(\mathbf{d}^\dagger\mathbf{d})^{-1/2}]_{mn} \quad = \quad [(\mathbf{d}^\dagger\mathbf{d})^{1/2}]_{mn}. \tag{53}$$

Thus, in this case we use for the Davidson correction

$$c_n \quad = \quad [(\mathbf{d}^\dagger\mathbf{d})^{1/2}]_{nn}. \tag{54}$$

The final question is which reference energy to use to compute the correlation energy used in eq. (43). In older MOLPRO version (to 2009.1) the reference wave function which has the largest overlap with the MRCI wave function was used to compute the reference energy for the corresponding state. But this can lead to steps of the Davidson corrected energies if the order of the states swaps along potential energy functions. In this version there are two options: the default is to use for state *n* the reference energy *n*, cf. eq. (45) (assuming the states are ordered according to increasing energy). The second option is to recompute the correlation energies using the rotated reference functions

$$E_{corr}^{(n)} \quad = \quad E_{\text{MRCI}}^{(n)} - \langle\Psi_{\text{rot}}^{(n)}|\hat{H}|\Psi_{\text{rot}}^{(n)}\rangle \tag{55}$$

Both should give smooth potentials (unless at conical intersections or crossings of states with different symmetries), but there is no guarantee that the Davidson corrected energies of different states don't cross. This problem is unavoidable for non-variational energies. The relaxed and rotated Davidson corrections give rather similar results; the rotated one yields somewhat larger cluster corrections and was found to give better results in the case of the F + H_2 potential [see J. Chem. Phys. **128**, 034305 (2008)].

By default, the different cluster corrections listed in Table 9 are computed in multi-state MRCI calculations. and stored in variables. By default, `ENERGD(n)=ENERGD0(n)`. This can be

Table 9: Cluster corrections computed in multi-state MRCI calculations. By default, the energies are in increasing order of the MRCI total energy. In single-state calculations only the fixed and relaxed values are available.

Name	c_n (Eq.)	$E_{corr}^{(n)}$ (Eq.)	Variable
Using standard reference energies:			
Fixed	(44)	(45)	`ENERGD1(n)`
Relaxed	(47)	(45)	`ENERGD0(n)`
Rotated	(54)	(45)	`ENERGD2(n)`
Using rotated reference energies:			
Relaxed	(47)	(55)	`ENERGD3(n)`
Rotated	(54)	(55)	`ENERGD4(n)`

changed by setting `OPTION,CLUSTER=`*x*; then `ENERGD(n)=ENERGD`*x*`(n)` (default *x* = 0). The behaviour of Molpro 2009.1 and older can be retrieved using

`MRCI,SWAP,ROTREF=-1.`

20.8   Explicitly correlated MRCI-F12

The only change needed for including explicitly correlated terms is to append `-F12` to the `MRCI` command. All other options work as described before. It is recommended to use correlation consistent basis sets (aug-cc-pVnZ or VnZ-F12) since for these the appropriate fitting and RI auxiliary basis sets are chosen automatically. Otherwise it max be necessary to specify these basis sets as described for single-reference methods in section 35.

The following options (to be given on the `MRCI-F12` command line) are specific to MRCI-F12:

`SCALF12=`*scalf12*	If `scalf12=1` (default) the explicitly correlated contributions are treated variationally (`SFIX` ansatz, see J. Chem. Phys. **134**, 034113 (2011). If `scalf12=0` intermediate normalization is used (`FIX` ansatz).
`SINGLES=`*isingles*	`isingles=1`: use singles-CI CABS singles correction (default); `isingles=2`: use perturbational CABS singles correction; `isingles=3`: include couplings of CABS singles with MRCI terms.

For a description of the various singles corrections see Mol. Phys. **111**, 607 (2013).

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Bibliography:

Original RS2/RS3:

H.-J. Werner, Mol. Phys. 89, 645-661 (1996)

New internally contracted RS2C:

P. Celani and H.-J. Werner, J. Chem. Phys. 112, 5546 (2000)

All publications resulting from use of this program must acknowledge the above.

The commands

`RS2`,*options*
`RS2C`,*options*
`RS3`,*options*

are used to perform second or third-order perturbation calculations. `RS3` always includes `RS2` as a first step. For closed-shell single-reference cases, this is equivalent to `MP2` or `MP3` (but a different program is used). `RS2C` calls a new more efficient second-order program (see below), which should normally be used if third-order is not required (note that `RS3C` is not available).

for `RS2` an explicitly correlated version as described in T. Shiozaki and H.-J. Werner, J. Chem. Phys. **133**, 141103 (2010) is available. This is called using the command

`RS2-F12`, *options*

Options can be the following:

`Gn`	Use modified zeroth order Hamiltonian, see section 21.4

`SHIFT=`*value*	Level shift, see section 21.5
`IPEA=`*value*	IPEA shift proposed by G. Ghigo, B. O. Roos, and P.A. Malmqvist, Chem. Phys. Lett. **396**, 142 (2004), see section 21.5.
`MIX=`*nstates*	Invokes multi-state (MS-CASPT2) treatment using *nstates* states. See section 21.3 for more details.
`XMS=0:`	MS-CASPT2 method of Finley et al. CPL 288, 299 (1998)
`XMS=1:`	Extended multi-state CASPT2 (XMS-CASPT2) method as described in J. Chem. Phys. **135**, 081106 (2011). fully invariant treatment of level shifts (recommended).
`XMS=2:`	XMS-CASPT2 method; level shift is only applied to the diagonal of H0.
`ROOT=`*ioptroot*	Root number to be optimized in geometry optimization. This refers to the *nstates* included in the MS-CASPT2. See section 21.7 for more details.
`SAVEH=`*record*	Record for saving the effective Hamiltonian in MS-CASPT2 calculations. If this is not given, a default record will be used (recommended).
`INIT`	(logical) Initializes a MS-CASPT2 with single state reference functions, see section 21.3
`IGNORE`	(logical) Flags an approximate gradient calculation without CP-CASPT2; see section 21.7 for details.

In addition, all valid options for `MRCI` can be given (see Sect. 20).

21.1 Introduction

Multireference perturbation calculations are performed by the MRCI program as a special case. For RS2 (CASPT2,RASPT2) only matrix elements over a one-electron operator need to be computed, and therefore the computational effort is much smaller than for a corresponding MRCI. For RS3 (CASPT3) the energy expectation value for the first-order wavefunction must be computed and the computational effort is about the same as for one MRCI iteration. The RS2 and RS3 programs use the same configuration spaces as the MRCI, i.e., only the doubly external configurations are internally contracted.

A new version of the program has been implemented in which also subspaces of the singly external and internal configuration spaces are internally contracted (see reference given above). This program, which is called using the keyword `RS2C`, is more efficient than `RS2`, in particular for large molecules with many closed-shell (inactive) orbitals. It is recommended to use this program for normal applications of second-order multireference perturbation theory (CASPT2, RASPT2). Note that it gives slightly different results than `RS2` due to the different contraction scheme. It should also be noted that neither `RS2` or `RS2C` are identical with the CASPT2 of Roos et al. [J. Chem. Phys. **96**, 1218 (1992)], since certain configuration subspaces are left uncontracted. However, the differences are normally very small. The last point that should be mentioned is that the calculation of CASPT2/RASPT2 density matrices (and therefore molecular properties) is presently possible only with the RS2 command and *not* with RS2C.

The results of multireference perturbation theory may be sensitive to the choice of the zeroth-order Hamiltonian. This dependence is more pronounced in second-order than in third-order. Several options are available, which will be described in the following sections. It may also

happen that $(\hat{H}^{(0)} - E^{(0)})$ in the basis of the configuration state functions becomes (nearly) singular. This is known as "intruder state problem" and can cause convergence problems or lead to a blow-up of the wavefunction. Often, such problems can be eliminated by including more orbitals into the reference wavefunction, but of course this leads to an increase of the CPU time. The use of modified Fock operators (see below) or level shifts, as proposed by Roos and Andersson [Chem. Phys. Lett. **245**, 215 (1995)] may also be helpful. Presently, only "real" level shifts have been implemented.

With no further input cards, the wavefunction definition (core, closed, and active orbital spaces, symmetry) corresponds to the one used in the most recently done SCF or MCSCF calculation. By default, a CASSCF reference space is generated. Other choices can be made using the OCC, CORE, CLOSED, WF, SELECT, CON, and RESTRICT cards, as described for the CI program. The orbitals are taken from the corresponding SCF or MCSCF calculation unless an ORBITAL directive is given.

For a CASPT2 calculation, the zeroth-order Hamiltonian can be brought to a block-diagonal form when (pseudo)canonical orbitals are used. This leads to fastest convergence. It is therefore recommended that in the preceding MULTI calculation the orbitals are saved using the CANONICAL directive (note that the default is NATORB).

Most options for MRCI calculations (like STATE, REFSTATE etc.) apply also for RS2(C) and RS3 and are not described here again. Some additional options which specific for CASPT2/3 and are described below.

21.2   Excited state calculations

There are two possibilities to perform excited state calculations:

1) One can calculate each state separately. This is done using the card

STATE,1,*root*

where *root* is the desired root (i.e., 2 for the first excited state). In this case the Fock operator used in the zeroth-order Hamiltonian is computed using the density for the given state.

2) Alternatively, two or more states can be computed simultaneously, using

STATE, *n* [,*root1, root2, . . . , rootn*]

where *n* is the number of states to be computed. The default is to compute the lowest *n* roots. Optionally, this default can be modified by specifying the desired roots *rooti* as shown. One should note that this *does not* correspond to the multi-state CASPT2 as described in section 21.3.

In the case that several states are computed simultaneously, the fock operator employed in the zeroth-order Hamiltonian is computed from a state-averaged density matrix, and the zeroth-order Hamiltonians for all states are constructed from the same fock operator. By default, equal weights for all states are used. This default can be modified using the WEIGHT directive

WEIGHT,*w1, w2,. . . ,wn.*

If a REFSTATE card is given (see section 20.2.11), the state-averaged fock operator is made for all reference states, and the WEIGHT card refers to the corresponding states.

21.3 Multi-State CASPT2

Multi-state CASPT2 is implemented as described by Finley et al. CPL **288**, 299 (1998). Currently this can only be used with the `RS2` program (i.e., not with `RS2C`). There are two different modes in which MS-CASPT2 calculations can be performed:

(i) Each of the states to be mixed is computed independently, and finally all states are mixed. In the following, such calculations will be denoted SS-SR-CASPT2 (single-state, single reference CASPT2). There is one contracted reference state for each CASPT2 calculation that is specific for the state under consideration. This is the cheapest method, but there are no gradients available in this case. It is the users responsibility to make sure that no state is computed twice.

(ii) All *nstates* states are treated together, with *nstates* contracted reference states. This is more expensive, but should give a more balanced description since the different reference states can mix in the CASPT2. It is required that *nstates* equals the number of states specified on the `STATE` directive. For this case, denoted "MS-MR-CASPT2" (multi-state multi reference CASPT2), analytical energy gradients are available, see section 21.7. It is recommended to use the "extended" (XMS) multi-state CASPT2 option, which guarantees invariance of the theory with respect to unitary rotations of the reference functions. The method yields improved potentials in the vicinity of avoided crossings and conical intersections [see T. Shiozaki and H.-J. Werner, J. Chem. Phys. **133**, 141103 (2010) and T. Shiozaki, C. Woywod and H.-J. Werner, Phys. Chem. Chem. Phys. **15**, 262 (2013)].

21.3.1 Performing SS-SR-CASPT2 calculations

If one wants to mix together *nstates* CASPT2 wavefunctions, a *nstates* single-state, single-reference CASPT2 calculations must be run.

The first calculation must use

{`RS2`,`MIX`=*nstates*, `INIT`, *options*
`STATE`,`1`,`1`;}

and the subsequent ones

{`RS2`,`MIX`=*nstates*, *options*
`STATE`,`1`,*istate*;}

for *istate* = 2, . . . , *nstates*. Further *options* can be given, for instance a level shift.

At the end of each calculation, the CASPT2 wavefunction is stored, and at the end of the last CASPT2 calculation the Bloch Hamiltonian and the corresponding overlap matrix are automatically assembled and printed. The Hamiltonian is diagonalized after symmetrization following Brandow IJQC 15, 207 (1979), as well as with simple half-sum (averaging). The MS-CASPT2 energy and mixing coefficients printed in each case.

The variable MSENERGY(i) (with i=1,...nstates) is set to the multi-state energies obtained with half-sum diagonalization. If a Level Shift is present, MSENERGY(i) contains the multi-state energies obtained with half-sum diagonalization of the Bloch Hamiltonian whose diagonal elements (CASPT2 energies) have been corrected with the level shift.

Example: SS-SR-CASPT2 calculation for LiF

```
r=[3,4,5,6,7,8,9,10] ang

i=1
geometry={Li
          F,1,r(i)}

basis=vtz,F=avtz

hf                        !Hartree-Fock

do i=1,#r                 !loop over range of bond distances
{multi
closed,3,0,0,0
occ,   5,2,2,0
wf;state,2                !SA-CASSCF for 2 states
canonical,ci}

{rs2,MIX=2,INIT
wf;state,1,1}             !single state CASPT2 for reference state 1

e1_caspt2(i)=energy       !unmixed caspt2 energy for ground state

{rs2,MIX=2
wf;state,1,2}             !single state CASPT2 for reference state 2

e2_caspt2(i)=energy       !unmixed caspt2 energy for excited state
e1_mscaspt2(i)=msenergy(1)  !ms-caspt2 energy for ground state
e2_mscaspt2(i)=msenergy(2)  !ms-caspt2 energy for excited state
enddo

{table,r,e1_caspt2,e2_caspt2,e1_mscaspt2,e2_mscaspt2
title,SS-SR-CASPT2 for LiF
plot,file='lif_sr_mscaspt2.plot'
}
```

http://www.molpro.net/info/current/examples/lif_sr_mscaspt2.com

This produces the plot

SS-SR-CASPT2 for LiF
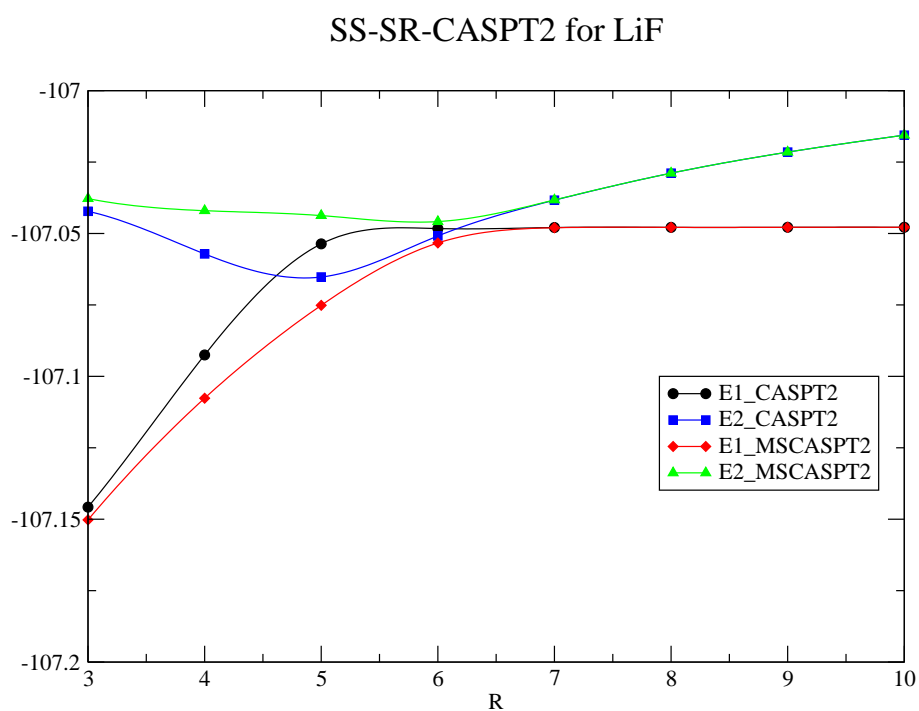
21.3.2 Performing MS-MR-CASPT2 calculations

In the case of multi-state multi-reference CASPT2 calculations, only a single run is needed:

{RS2,MIX=*nstates*,*options*
STATE,*nstates*}

For using the XMS-CASPT2 method option XMS=1 or XMS=2 has to be set. The two variants differ in the treatment of level shifts. XMS=1 is a fully invariant treatment (recommended), while with XMS=2 the level shift is only applied to the diagonal of H0.

Example: MS-MR-CASPT2 calculation for LiF

```
r=[3,4,5,6,7,8,9,10] ang

i=1
geometry={Li
        F,1,r(i)}

basis=vtz,F=avtz

hf                      !Hartree-Fock

do i=1,#r               !loop over range of bond distances
{multi
closed,3,0,0,0
occ,   5,2,2,0
wf;state,2              !SA-CASSCF for 2 states
canonical,ci}

{rs2,MIX=2
wf;state,2}             !2-state MS-CASPT2 with 2 reference states

e1_caspt2(i)=energu(1)     !unmixed caspt2 energy for ground state
e2_caspt2(i)=energu(2)     !unmixed caspt2 energy for ground state

e1_mscaspt2(i)=msenergy(1)  !ms-caspt2 energy for ground state
e2_mscaspt2(i)=msenergy(2)  !ms-caspt2 energy for excited state

{rs2,MIX=2,XMS=1
wf;state,2}             !2-state XMS-CASPT2 with 2 reference states

e1_xmscaspt2(i)=msenergy(1)  !ms-caspt2 energy for ground state
e2_xmscaspt2(i)=msenergy(2)  !ms-caspt2 energy for excited state
enddo

{table,r,e1_caspt2,e2_caspt2,e1_mscaspt2,e2_mscaspt2,e1_xmscaspt2,e2_xmscaspt2
title,MS-MR-CASPT2 for LiF
plot,file='lif_mr_mscaspt2.plot'
}
```

http://www.molpro.net/info/current/examples/lif_mr_mscaspt2.com

This produces the plot

MS-MR-CASPT2 for LiF
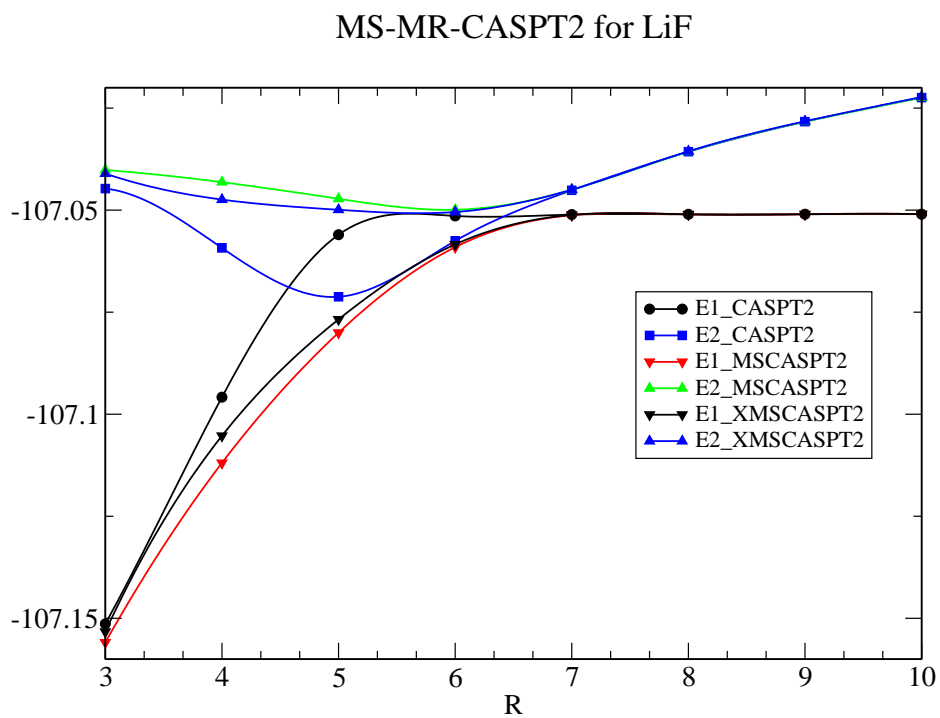
One can clearly see that this gives smoother potentials than the SS-SR-CASPT2 calculation in the previous section. Also, the avoided crossing is shifted to longer distances, which is due to the improvement of the electron affinity of F.

Example for xms-caspt2 for pyrrole B1 states

```
 ***,Pyrrole
memory,128,M;

geometry={
   10
 RS2/VTZ   ENERGY=-209.73179172
 H        0.0000000000      -0.0000000001       2.1166896815
 H        0.0000000000      -2.1059182363       0.7619888215
 H        0.0000000000       2.1059182368       0.7619888221
 H        0.0000000000       1.3572481815      -1.8483571903
 H        0.0000000000      -1.3572481818      -1.8483571900
 N        0.0000000000      -0.0000000001       1.1133413258
 C        0.0000000000       1.1228834673       0.3278824921
 C        0.0000000000      -1.1228834675       0.3278824917
 C        0.0000000000      -0.7098361247      -0.9897171173
 C        0.0000000000       0.7098361249      -0.9897171174
}
gexpec,sm

basis=avtz

{hf;wf,symmetry=1,spin=0}

{multi
occ,11,3,7,2;closed,9,0,6,0;
wf,symmetry=1,spin=0;state,1;   !1A1 state
wf,symmetry=2,spin=0;state,2;   !B1 states
wf,symmetry=4,spin=0;state,2;   !A2 states
}
ecas=energy

shift=0.2

{rs2,shift=shift;               !caspt2 for 1A1 state
wf,symmetry=1,spin=0;state,1,1}
ers2(1)=energy

{rs2,shift=shift,mix=2,xms=1;    !xms-caspt2 for B1 states
wf,symmetry=2,spin=0;state,2}
ers2(2)=msenergy(1)
ers2(3)=msenergy(2)

decas=(ecas-ecas(1))*toev        !vertical excitation energies in eV
ders2=(ers2-ers2(1))*toev

$state=[1A1,1B1,2B1]
table,state,ecas,ers2,decas,ders2
digits,,7,7,7,3,3,3,3
---
```

```
                       http:
 //www.molpro.net/info/current/examples/pyrrole_xms_caspt2.com
```

This produces:

```
 STATE        ECAS           ERS2        DECAS      DERS2
 1A1     -208.9123879   -209.7458973   0.0000000   0.000
 1B1     -208.7459999   -209.5298616   4.5276489   5.879
 2B1     -208.7397557   -209.5261196   4.6975625   5.980
```

21.4 Modified Fock-operators in the zeroth-order Hamiltonian.

The g_1, g_2, and g_3 operators proposed by Andersson [Theor. Chim. Acta **91**, 31 (1995)] as well as a further g_4 operator may be used. g_4 makes CASPT2 calculations size extensive for cases in which a molecule dissociates to high-spin open-shell (RHF) atoms.

The index *n* of the operator to be used is specified on the `RS2`, `RS2C`, or `RS3` card:

`RS2`,*option*
`RS2C`,*option*
`RS3`,*option*

where *option* can be `G1`, `G2`, `G3`, or `G4`. This option can be followed or preceded by other valid options.

21.5 Level shifts

Level shifts are often useful to avoid intruder state problems in excited state calculations. MOL-PRO allows the use of shifts as described by Roos and Andersson, [Chem. Phys. Lett. **245**, 215 (1995)]. The shift can be specified on the `RS2` or `RS2C` card

`RS2` [,`G`*n*] [,`SHIFT=`*shift*],`IPEA=`*value*
`RS2C` [,`G`*n*] [,`SHIFT=`*shift*],`IPEA=`*value*

Typical choices for the shift is are $0.1 - 0.3$. Only two figures after the decimal point are considered. The shift affects the results, the printed energies as well as the `ENERGY` variable include the energy correction for the shift as proposed by Roos and Andersson. At convergence, also the uncorrected energies are printed for comparison.

Alternatively (or in addition), the IPEA shift of G. Ghigo, B. O. Roos, and P.A. Malmqvist, Chem. Phys. Lett. **396**, 142 (2004) can be used. The implementation is not exactly identical to the one in MOLCAS, since in our program the singly external configurations are not (RS2) or only partially (RS2C) contracted. In Molpro, the shift is implemented as follows:

$\frac{1}{2}D_{pp}\varepsilon$ is added to the occupied part of the Fock matrix; in addition, 2ε is added as a general shift (not corrected). ε is the value specified with the `IPEA` option (default 0). A value of 0.20-0.25 is recommended. This removes intruder state problems to a large extent and usually improves the results. Note that the method is not exactly orbital invariant, and pseudo-canonical orbitals should be used (see `CANONICAL` option in MULTI).

It is possible to use `SHIFT` and `IPEA` simultaneously, but it does not make sense to use one of the `G`-options together with `IPEA`.

21.6 Integral direct calculations

`RS2`, `RS2C`, and `RS3` calculations with very large basis sets can be performed in integral-direct mode. The calculation will be direct if a global `DIRECT` or `GDIRECT` card appears earlier in the input. Alternatively, (mainly for testing) `DIRECT` can be specified as an option on the `RS`*n*[`C`] card:

`RS2` [,`G`*n*] [,`SHIFT=`*shift*] [,`DIRECT`]
`RS2C` [,`G`*n*] [,`SHIFT=`*shift*] [,`DIRECT`]

Density fitting is also available, and as usual invoked by the prefix `DF-`, i.e. `DF-RS2`, `DF-RS2C`.

21.7 CASPT2 gradients

P. Celani and H.-J. Werner, J. Chem. Phys. **119**, 5044 (2003))

CASPT2 analytic energy gradients are computed automatically if a `FORCE` or `OPTG` command follows (see sections 45 and 46). Analytical gradients are presently only available for `RS2` calculations (not `RS2C`), and only for the standard $\hat{H}^{(0)}$ (not G1, G2 etc). Gradients can be computed for single-state calculations, as well as multi-state MS-MR-CASPT2 (see section 21.3. However, only states with the same symmetry and spin and the same number of electrons as in the optimized state can be included in the preceding SA-CASSCF (CONFIG,DET must not be given in the CASSCF).

In single state calculations, the gradient is automatically computed for the state computed in CASPT2/RSPT2 (i.e., using `STATE,1,2` the second state in the symmetry under consideration is computed, see section 21.2). The program works with state-averaged MCSCF (CASSCF) orbitals, and no `CPMCSCF` directive is needed. It is necessary that the state under consideration is included in the preceding (state-averaged) MCSCF/CASSCF. The RS2 gradient program can also be used to compute state-averaged MCSCF/CASSCF gradients by using the `NOEXC` directive.

In a multi-state MS-MR-CASPT2 calculation, the state for which the gradient is computed must be specified using the `ROOT` option (default `ROOT=1`), i.e.,

`RS2,MIX=`*nstates*`, ROOT=`*ioptroot*

where $1 \leq ioptroot \leq nstates$.

Level shifts can be used. By default, the exact gradient of the level-shift corrected energy is computed. For a non-zero shift, this requires to solve the CASPT2 Z-vector equations, which roughly doubles the computational effort. In single state calculations it is possible to ignore the effect of the level shift on the gradient and not to solve the Z-vector equation. This variant, which is described in the above paper, may be sufficiently accurate for many purposes. It is invoked using the `IGNORE` option, e.g.

```
RS2,SHIFT=0.2,IGNORE
OPTG
```

Any publications employing the CASPT2 gradients should cite the above paper. A citation for MS-CASPT2 gradient method is P. Celani and H.-J. Werner, *to be published*.

Example:

CASPT2 geometry optimizations for H_2O:

```
***
memory,8,m
gthresh,energy=1.d-10
!
basis=vdz
R=2.0
R0=R
Theta=100
geometry={O
          H1,O,R;
          H2,O,R,H1,THETA}

hf;accu,12

{multi;closed,2}

rs2,shift=0.3,ignoreshift      !ignore shift in computing gradient, i.e., no cp-caspt2
optg,gradient=1.d-5
e_opt(1)=energy
r_opt(1)=r
theta_opt(1)=theta
method(1)='rs2,analytical,ignore'

rs2,shift=0.3                  !exact gradient with shift
optg,gradient=1.d-5
e_opt(2)=energy
r_opt(2)=r
theta_opt(2)=theta
method(2)='rs2,analytical,exact'

rs2,shift=0.3                  !numerical gradient with shift
optg,gradient=1.d-5,numerical,fourpoint !use four-point numerical gradient
e_opt(3)=energy
r_opt(3)=r
theta_opt(3)=theta
method(3)='rs2,numerical'

rs2c,shift=0.3                 !numerical gradient of rs2c with shift
optg,gradient=1.d-5,fourpoint  !use four-point numerical gradient
e_opt(4)=energy
r_opt(4)=r
theta_opt(4)=theta
method(4)='rs2c,numerical'

table,method,r_opt,theta_opt,e_opt
digits,,4,4,8
```

http://www.molpro.net/info/current/examples/h2o_caspt2_opt.com

This produces the Table

```
 METHOD                R_OPT   THETA_OPT       E_OPT
 rs2,analytical,ignore  1.8250   102.1069   -76.22789382
 rs2,analytical,exact   1.8261   102.1168   -76.22789441
 rs2,numerical          1.8261   102.1168   -76.22789441
 rs2c,numerical         1.8260   102.1187   -76.22787681
```

MS-CASPT2 geometry optimization for the second excited $^3B_2$ state if H_2O:

```
***
memory,8,m
gthresh,energy=1.d-12
!
basis=vdz
R=2.0
R0=R
Theta=100
step=0.001
geometry={O
          H1,O,R;
          H2,O,R,H1,THETA}

hf;accu,12

multi        !state averaged casscf for various triplet states
closed,2
wf,10,1,2
state,3
wf,10,2,2
state,2
wf,10,3,2
state,3
canonical,2140.2

rs2,mix=3,root=2,shift=0.2   !optimized second 3B2 state
wf,10,3,2                    !3B2 wavefunction symmetry
state,3                      !include 3 states
optg,gradient=1.d-5          !geometry optimization using analytical gradients

e_opt(1)=msenergy(2)         !optimized ms-caspt2 energy
r_opt(1)=r                   !optimized bond distance
theta_opt(1)=theta           !optimized bond angle
method(1)='rs2,analytical'

rs2,mix=3,shift=0.2
wf,10,3,2                    !3B2 wavefunction symmetry
state,3                      !include 3 states
optg,variable=msenergy(2),gradient=1.d-5,fourpoint
                             !geometry optimization using numerical gradients

e_opt(2)=msenergy(2)         !optimized ms-caspt2 energy
r_opt(2)=r                   !optimized bond distance
theta_opt(2)=theta           !optimized bond angle
method(2)='rs2,numerical'

table,method,r_opt,theta_opt,e_opt
digits,,4,4,8
```

http:
//www.molpro.net/info/current/examples/h2o_mscaspt2_opt.com

This produces the table

METHOD	R_OPT	THETA_OPT	E_OPT
rs2,analytical	2.4259	96.7213	-75.81630628
rs2,numerical	2.4259	96.7213	-75.81630628

21.8 Coupling MRCI and MRPT2: The CIPT2 method

P. Celani, H. Stoll, H.-J. Werner and P. J. Knowles, Mol. Phys. **102**, 2369 (2004).

For particularly difficult cases with strong intruder problems, or in which second-order perturbation theory fails to predict reliable results, a new method that couples MRCI and CASPT2 has been developed. This variant is invoked using the `CIPT2` directive:

`CIPT2`

In this case all excitations solely from active orbitals are treated by MRCI, while the remaining excitations involving inactive (closed-shell) orbitals are treated by second-order perturbation theory. Both methods are coupled by minimizing an appropriate energy functional. Of course, this method is much more expensive that MRPT2. The cost is comparable to the cost for an MRCI without correlating the inactive orbitals.

21.9 Further options for CASPT2 and CASPT3

Other options can be set using the `OPTION` command. These options are mainly used for testing purposes and should be used with care. It should be noted that the only option that can be modified in the RS2C program is `IFDIA`: all others only work with RS2/RS3.

`OPTION,`*code1=value,code2=value,...*

Of relevance for the CASPT2/3 program are the following options:

`IPROCS=0`	(Default). Calculation uses uncontracted singles with `RS2`.
`IPROCS=1`	Non-interacting singles are projected out during update. This is an approximate procedure which should be used with care.
`IPROCS=2`	The singles are fully internally contracted in `RS2`. This is achieved via a projection operator during the coefficient update and may be inefficient. G
`IPROCS=3`	Only singles with one or two holes in the closed-shells are internally contracted in `RS2` using a projection operator.
`IPROCI=0`	(Default). Calculation uses uncontracted internals with `RS2`.
`IPROCI=1`	Internals with two holes in the inactive space are internally contracted in `RS2` using a projection operator.
`IPROCS=3,IPROCI=1`	This combination of options reproduces with `RS2` the `RS2C` result using projection operators. This requires lot of memory and disk space and it is feasible only for small molecules.
`IFDIA=0`	(Default). All off-diagonal elements of the effective Fock matrix are included.
`IFDIA=1`	The internal-external block of the Fock-matrix is neglected. This eliminates the single-pair coupling.
`IFDIA=2`	All off-diagonal elements of the Fock matrix are neglected. This corresponds to CASPT2D of Andersson et al. Note: in this case the result is not invariant to rotations among active orbitals!
`IHINT=0`	(Default). Only one-electron integrals are used in the zeroth-order Hamiltonian for all interactions.
`IHINT=1`	The all-internal two-electron integrals are used in the zeroth-order Hamiltonian for the internal-internal and single-single interactions.

`IHINT=2`	The all-internal two-electron integrals in the zeroth-order Hamiltonian are used for the internal-internal, single-single, and pair-pair interactions. Using `IHINT=2` and `IDFIA=1` corresponds to Dyall's CAS/A method for the case that CASSCF references with no closed-shells (inactive orbitals) are used. Note that this requires more CPU time than a standard CASPT2 calculation. Moreover, convergence of the CAS/A method is often slow (denominator shifts specified on a `SHIFT` card may be helpful in such cases). In general, we do not recommend the use of `IHINT` with nonzero values.
`NOREF=1`	(Default). Interactions between reference configurations and singles are omitted.
`NOREF=0`	Interactions between reference configurations and singles are included. This causes a relaxation of the reference coefficients but may lead to intruder-state problems.
`IMP3=2`	After CASPT2 do variational CI using all internal configurations and the first-order wavefunctions of all states as a basis. In this case the second-order energy will correspond to the variational energy, and the third-order energy approximately to a Davidson-corrected energy. This is useful in excited state calculations with near-degeneracy situations.

22   NEVPT2 calculations

Reference literature:

C. Angeli, R. Cimiraglia, S. Evangelisti, T. Leininger and J. P. Malrieu, *J. Chem. Phys.*, **114**, 10252, (2001)

C. Angeli, R. Cimiraglia and J. P. Malrieu, *J. Chem. Phys.*, **117**, 9138, (2002)

C. Angeli, M. Pastore and R. Cimiraglia, *Theor. Chem. Acc.*, **117**, 743 (2007)

All publications resulting from use of this program must acknowledge the above.

22.1   General considerations

NEVPT2 is a form of second-order multireference perturbation theory which can be applied to CAS–SCF wavefunctions or, more generally, to CAS–CI wavefunctions. The term NEVPT is an acronym for *"n–electron valence state perturbation theory"*. While we refer the reader to the pertinent literature (see above), we limit ourselves to recalling here that the most relevant feature of NEVPT2 consists in that the first order correction to the wave function is expanded over a set of properly chosen *multireference* functions which correctly take into consideration the two–electron interactions occurring among the active electrons. Among the properties ensured by NEVPT2 we quote:

- Strict separability (size consistence): the energy of a collection of non–interacting systems equals the sum of the energies of the isolated systems

- Absence of intruder states: the zero-order energies associated to the functions of the outer space are well separated from the zero-order energy of the state being studied, thus avoiding divergences in the perturbation summation

- The first order correction to the wavefunction is an eigenfunction of the spin operators S^2 and S_z

- Electronically excited states are dealt with at the same level of accuracy as the ground state

- NEVPT2 energies are invariant under a unitary transformation of the active orbitals. Furthermore, the choice of canonical orbitals for the core and virtual orbitals (the default choice) ensure that the results coincide with those of an enlarged version of the theory fully invariant under rotations in the core and virtual orbital spaces, respectively

- NEVPT2 coincides with MP2 in the case of a HF wave function

NEVPT2 has been implemented in two variants both of which are present in MOLPRO, these are the *strongly contracted* (SC) and the *partially contracted* (PC) variants. The two variants differ by the number of perturber functions employed in the perturbation summation. The PC–NEVPT2 uses a richer function space and is in general more accurate than the SC–NEVPT2. The results of SC–NEVPT2 and PC–NEVPT2 are anyway usually very close to one another.

22.2 Input description

NEVPT2 must follow a CAS–SCF or CAS–CI calculation. The command

`NEVPT2,`*options*
has to be specified to carry out a second–order perturbation calculation. NEVPT2 is part of the MRCI program and uses the options of the latter. Of particular relevance are the options `CORE`, `CLOSED`, `OCC`, `WF` and `STATE` of the MRCI program. There is, at the moment, only one option specific to NEVPT2 which can be provided by the user:

`THRNEVPT2`   The threshold to discard small coefficients in the CAS wavefunction (default = 0.0),

The present implementation of NEVPT2 is state–specific, *i.e.* the perturbation theory can only be applied to a single state. The multi–state (or quasi–degenerate) version of NEVPT2 will be implemented in MOLPRO in the near future.

An example is provided where the energies of the ground state and of the first $^1A_2$ ($n \rightarrow \pi^*$) excited state of formaldehyde are calculated.

```
***,
memory,20,m
file,1,h2co.int,new
file,2,h2co.wf,new
gthresh,energy=1.d-9
gthresh,orbital=1.d-8
gthresh,civec=1.d-8

geomtyp=zmat
geometry
 O,,            0.000000000,     0.000000000,    0.0196594609
 C,,            0.000000000,     0.000000000,    2.3248507925
 H1,,           0.000000000,     1.7597110083,   3.3972521023
 H2,,           0.000000000,    -1.7597110083,   3.3972521023
end

basis=6-31G*

{hf
wf,16,1,0}

{multi
closed,4,0,1,0
occ,6,2,4,0
wf,16,1,0
state,1
natorb,2140.2,state=1.1
}

{nevpt2,thrden=1.0d-10,thrvar=1.0d-10
core,2,0,0,0
closed,4,0,1,0
occ,6,2,4,0
orbit,2140.2,state=1.1
wf,16,1,0
state,1,1
}

{multi
closed,4,0,1,0
occ,6,2,4,0
wf,16,4,0
state,1
start,2140.2
natorb,2141.2,state=1.4
}
{nevpt2,thrden=1.0d-10,thrvar=1.0d-10
core,2,0,0,0
closed,4,0,1,0
occ,6,2,4,0
orbit,2141.2,state=1.4
wf,16,4,0
state,1,1
}
```

    http://www.molpro.net/info/current/examples/form_nevpt2.com

23   MØLLER PLESSET PERTURBATION THEORY

Closed-shell Møller-Plesset perturbation theory up to full fourth order [MP4(SDTQ)] is part of
the coupled-cluster program.

The commands `MP2,  MP3,  MP4` perform the MP calculations up to the specified order (lower orders are included).

`MP4;NOTRIPL;` performs MP4(SDQ) calculations.

Normally, no further input is needed if the `MPn` card directly follows the corresponding HF-SCF. Otherwise, occupancies and orbitals can be specified as in the CI program. The resulting energies are stored in variables as explained in section 8.8.

Dual basis set calculations are possible for the closed-shell methods, see section 24.14.

23.1   Expectation values for MP2

`EXPEC[,[TYPE=]`*type*`][,`*opname*`]`

One-electron properties can be computed if an `EXPEC` card follows the `MP2` card (the `GEXPEC` directive has no effect in this case). Properties are obtained as analytical energy derivatives with or without taking into account the orbital relaxation, which can be specified as

`TYPE:`   *type*`=RELAX`: Compute fully relaxed properties with taking into account the orbital relaxation (default). Nonrelaxed properties are also computed and printed. For MP2, this option is highly recommended.

type`=NORELAX`: Compute properties without taking into account the orbital relaxation.

Note that, in MP2, calculation of fully relaxed properties may be much more expensive than computing only the energy or properties without the orbital relaxation effect. The syntax for operators *opname* is explained in section 6.13. See also `DM` in section 23.3, and `NATORB` in section 23.4.

23.2   Expectation values for MP3

`EXPEC[,`*opname*`]` Fully relaxed one-electron properties are available for MP3 (see section 25.6, Paper 2). Currently, this is only working without frozen core orbitals, i.e. `CORE,0` must be specified. MP2 properties are also computed and printed.

23.3   Saving the density matrix

`DM,`*record.ifil*;

The first-order density matrix in AO basis is stored in record *record* on file *ifil*. Two types of density matrices are stored in the same record: the one without orbital relaxation contribution is stored as *set 1*, meanwhile with the orbital relaxation contribution, it is stored as *set 2*. If the `NORELAX` directive is given on the `EXPEC` card prior to the `DM` card, only the orbital unrelaxed density matrix is computed and stored. See also `NATORB` in section 23.4.

23.4   Natural orbitals

`NATORB,[RECORD=]`*record.ifil*`,[PRINT=`*nprint*`],[CORE[=`*natcor*`]];`

Calculate natural orbitals. The number of printed external orbitals in any given symmetry is *nprint*) (default 2). *nprint=-1* suppressed the printing. The natural orbitals and the density matrix are saved in a dump record *record* on file *ifil*. If *record.ifil* is specified on a DM card (see above), this record is used. If different records are specified on the DM and NATORB cards, an error will result. The record can also be given on the SAVE card. Natural orbitals are computed for both the nonrelaxed and relaxed density matrices if available, which are stored in the same record as *set 1* and *set 2*, respectively.

Note that the effective (relaxed) density matrix of non-variational methods like MP2 or CCSD does not strictly behave as a density matrix. For instance, it has non-zero matrix elements between core and valence orbitals, and therefore core orbitals are affected by the natural orbital transformation. Also, occupation numbers can be greater than 2.0 or less than 0.0. If CORE is given (*natcor=1*), the core orbitals are frozen by excluding them from the natural orbital transformation.

23.5 Polarizabilities and second-order properties for MP2

Analytical MP2 static dipole polarizabilities and other second order properties can be computed using the POLARI. By default the dipole operator is used, but other one-electron operators can be specified on the POLARI directive. Currently, this is only working without frozen core orbitals, i.e., $\hat{\text{C}}$ORE,0 must be given. This option is only available without using the density fitting approximation. The dipole polarizabilities are stored in the variables POLXX, POLXY, POLXZ, POLYY, POLYZ, POLZZ.

Example:

```
{ mp2
 core,0
 polari,dm,qm}
```

Computes the full tensors for the dipole and quadrupole operators.

Nonsymmetrized first-order perturbed density matrix resulting from CP equations for MP2 can be stored for further use if RECMP2=*record.ifil* is given.

23.6 CPHF for gradients, expectation values and polarizabilities

The accuracy and other parameters of the CPHF calculations necessary to compute gradients and response properties can be modified using the CPHF directive:

CPHF, [THRMIN=*thrmin*], [THRMAX=*thrmax*], [MAXIT=*maxit*], [SHIFT=*shift*], [*SAVE=record*], [*START=record*], [DIIS=*idiis*], [DISM=idism]

THRMIN	CPHF convergence threshold (default 1.d-6). THRESH and ACCU are aliases for this.
THRMAX	initial CPHF convergence threshold in geometry optimizations. Once the geometry is converged to a certain accuarcy (depending on OPTCONV), the threshold is stepwise reduced to THRMIN. The default is THRMAX=min(1.d-6,THRMIN*100); Values larger than 1.d-6 are ignored.
MAXIT	Maxmimum number of iterations (default 50).

SHIFT	Level shift for CPHF (default 0.1).
DIIS	First macroiteration in which DIIS is used (default 1)
DISM	First microiteration in which DIIS is used (default 1; in microiterations the core contribution is frozen).
SAVE	Record on which the CPHF solution can be saved for later restarts. The solution is saved automatically in geometry optimizations and frequency calculations.
START	Record from which initial guess is read. A starting guess is read automatically in geometry optimizations and frequency calculations.

In density-fitting MP2, only `THRMIN` is active, the rest of the options are handled automatically.

23.7 Density-fitting MP2 (DF-MP2, RI-MP2)

`DF-MP2`,*options*

invokes the density fitted MP2 program. The present implementation works only without symmetry. `RI-MP2` is an alias for the command `DF-MP2`.

The following options can be specified:

BASIS_MP2=*basis*:	Fitting basis set. *basis* can either refer to a basis set defined in a `BASIS` block, or to a default fitting basis set (only available for correlation consistent basis sets). If a correlation consistent orbital basis set is used, the corresponding MP2 fitting basis is generated by default. In all other cases, the fitting basis must be defined.
THRAO=*value*:	Screening threshold for 3-index integrals in the AO basis
THRMO=*value*:	Screening threshold for 3-index integrals in the MO basis
THROV=*value*:	Screening threshold for 2-index integrals of fitting basis.
THRPROD=*value*:	Screening product threshold for first half transformation.
SPARSE=*value*:	If Non-zero, use sparse algorithm in second-half transformation (default).

See section 15 for a more general description of density fitting. Expectation values and gradients can also be computed with `DF-MP2`.

23.8 Spin-component scaled MP2 (SCS-MP2)

The spin-component scaled MP2 energy as proposed by Grimme (J. Chem. Phys. **118**, 9095 (2003)) is printed automatically using the default scaling factors (1.2 for antiparallel spin, 1/3 for parallel spin). These factors can be modified using the options `SCSFACS` and `SCSFACT`, respectively, i.e.

`MP2`, `SCSFACS`=*facs*, `SCSFACT`=*fact*

The SCS-MP2 total energy is stored in the variable `EMP2_SCS`. Gradients and first-order properties can be computed for SCS-MP2 by setting the option `SCSGRD=1`. This only operational for density fitted MP2 and local MP2 methods, i.e. using

`DF-MP2,[DF_BASIS=`*fitbasis*`],SCSGRD=1,[ SCSFACS=`*facs*`], [SCSFACT=`*fact*`]`

followed by `FORCES` or `OPTG`. In these cases, the SCS-MP2 total energy replaces the MP2 total energy in the variable `EMP2`. Expectation values can also be computed with `DF-SCS-MP2`, where the SCS-MP2 density matrix is used instead of the MP2 density matrix (see section 23.1). For DF-LMP2 see section 32.

24 THE CLOSED SHELL CCSD PROGRAM

Bibliography:

C. Hampel, K. Peterson, and H.-J. Werner, Chem. Phys. Lett. 190, 1 (1992)

All publications resulting from use of this program must acknowledge the above.

The CCSD program is called by the CISD, CCSD, BCCD, or QCI directives. CID or CCD can be done as special cases using the `NOSINGL` directive. The code also allows to calculate Brueckner orbitals (QCI and CCSD are identical in this case). Normally, no further input is needed if the `CCSD` card follows the corresponding HF-SCF. Optional `ORBITAL`, `OCC`, `CLOSED`, `CORE`, `SAVE`, `START`, `PRINT` options work as described for the MRCI program in section 20. The only special input directives for this code are `BRUECKNER` and `DIIS`, as described below.

The following options may be specified on the command line:

`NOCHECK`	Ignore convergence checks.
`DIRECT`	Do calculation integral direct.
`NOSING`	Do not include singly external configurations.
`MAXIT=`*value*	Maximum number of iterations.
`SHIFTS=`*value*	Denominator shift for update of singles.
`SHIFTP=`*value*	Denominator shift for update of doubles.
`THRDEN=`*value*	Convergence threshold for the energy.
`THRVAR=`*value*	Convergence threshold for CC amplitudes. This applies to the square sum of the changes of the amplitudes.
`SAVE=`*record*	Save CCSD wavefunction to this record
`START=`*record*	Restart CCSD wavefunction from a previously written record

The convergence thresholds can also be modified using

`THRESH,ENERGY=`*thrden*`,COEFF=`*thrvar*

Convergence is reached if the energy change is smaller than *thrden* (default 1.d-6) *and* the square sum of the amplitude changes is smaller than *thrvar* (default (1.d-10). The `THRESH` card must follow the command for the method (e.g., `CCSD`) and then overwrites the corresponding global options (see `GTHRESH`, sec. 6.11).

The computed energies are stored in variables as explained in section 8.8. As well as the energy, the T_1 diagnostic (T. J. Lee and P. R. Taylor, Int. J. Quant. Chem. S23 (1989) 199) and the D_1 diagnostic (C. L. Janssen and I. M. B. Nielsen, Chem. Phys. Lett. 290 (1998), 423, and T. J. Lee. Chem. Phys. Lett. 372 (2003), 362) are printed and stored for later analysis in the variables T1DIAG and D1DIAG, respectively.

For geometry optimization and computing first-order properties see section 24.11.

24.1 Coupled-cluster, CCSD

The command `CCSD` performs a closed-shell coupled-cluster calculation. Using the `CCSD(T)` command, the perturbative contributions of connected triple excitations are also computed.

If the CCSD is not converged, an error exit will occur if triples are requested. This can be avoided using the `NOCHECK` option:

```
CCSD(T),NOCHECK
```

In this case the (T) correction will be computed even if the CCSD did not converge. Note: `NOCHECK` has no effect in geometry optimizations or frequency calculations.

For further information on triples corrections see under RCCSD.

In cases that the Hartree-Fock reference determinant does not sufficiently dominate the wavefunction, the program will stop with a message `UNREASONABLE NORM. CALCULATION STOPPED`. This can be avoided by setting the option `CC_NORM_MAX=`*value* on the CCSD command line. The calculation is stopped if the square norm of the wavefunction (in intermediate normalization) exceeds `1+nval*CC_NORM_MAX`, where nval is the number of correlated valence orbitals. The default value is `CC_NORM_MAX=0.2`.

24.2 Quadratic configuration interaction, QCI

`QCI` or `QCISD` performs quadratic configuration interaction, QCISD. Using the `QCI(T)` or `QCISD(T)` commands, the contributions of connected triples are also computed by perturbation theory. Normally, no further input is needed if the `QCI` card follows the corresponding HF-SCF. Otherwise, occupancies and orbitals can be specified as in the CI program. For modifying DIIS directives, see section 24.7.

For avoiding error exits in case of no convergence, see `CCSD(T)`.

24.3 Brueckner coupled-cluster calculations, BCCD

`BCCD,[SAVEORB=`*record*`],[PRINT],[TYPE=,`*type*`]`

In addition, the same options as for CCSD can be used.

`BCCD` performs a Brueckner coupled-cluster calculation and computes Brueckner orbitals. With these orbitals, the amplitudes of the singles vanish at convergence. Using the `BCCD(T)` command, the contributions of connected triples are also computed by perturbation theory. Normally, no further input is needed if the `BCCD` card follows the corresponding HF-SCF. Otherwise, occupancies and orbitals can be specified as in the CI program. `BRUECKNER` parameters can be modified using the `BRUECKNER` directive.

The Brueckner orbitals and approximate density matrix can be saved on a `MOLPRO` dump record using the `SAVEORB` option. The orbitals are printed if the `PRINT` option is given. `TYPE` can be used to specify the type of the approximate density to be computed:

`TYPE=REF`	Compute and store density of reference determinant only (default). This corresponds to the BOX (Brueckner orbital expectation value) method of Chem. Phys. Lett. **315**, 248 (1999).
`TYPE=TOT`	Compute and store density with contribution of pair amplitudes (linear terms). Normally, this does not seem to lead to an improvement.
`TYPE=ALL`	Compute and store both densities

Note: The expectation variables are stored in variables as usual. In the case that both densities are made, the variables contain two values, the first corresponding to `REF` and the second to `TOT` (e.g., DMZ(1) and DMZ(2)). If `TYPE=REF` or `TYPE=TOT` is give, only the corresponding values are stored.

For avoiding error exits in case of no convergence, see `CCSD(T)`.

24.3.1 The `BRUECKNER` directive

`BRUECKNER,`*orbbrk,ibrstr,ibrueck,brsfak*`;`

This directive allows the modification of options for Brueckner calculations. Normally, none of the options has to be specified, and the `BCCD` command can be used to perform a Brueckner CCD calculation.

orbbrk:	if nonzero, the Brueckner orbitals are saved on this record.
ibrstr:	First iteration in which orbitals are modified (default=3).
ibrueck:	Iteration increment between orbital updates (default=1).
brsfak:	Scaling factor for singles in orbital updates (default=1).

24.4 Singles-doubles configuration interaction, CISD

Performs closed-shell configuration interaction, CISD. The same results as with the CI program are obtained, but this code is somewhat faster. Normally, no further input is needed. For specifying DIIS directives, see section 24.7

24.5 Quasi-variational coupled cluster, QVCCD

Performs closed-shell quasi-variational coupled cluster, QVCCD (J. B. Robinson and P. J. Knowles, J. Chem. Phys. **136**, 054114 (2012), doi:10.1063/1.3680560). Normally the effect of single excitations needs to be included through orbital optimisation, and this can be done either through the Brueckner condition (`BQVCCD`), or through variational minimisation of the energy functional with respect to orbital rotations (`OQVCCD`). The effects of triple excitations can be included using the standard perturbation theory, `BQVCCD(T)` or `OQVCCD(T)` (J. B. Robinson and P. J. Knowles, Phys. Chem. Chem. Phys. **14**, 6729-6732 (2012), doi:10.1039/C2CP40698E).

24.6 Distinguishable cluster, DCD

`DCSD`, `BDCD`, or `ODCD` perform closed-shell distinguishable cluster calculations with singles, Brueckner orbitals, or optimized orbitals, respectively. All CCSD and BCCD options (24) can be also used for distinguishable cluster calculations. The analytical gradients (45.1), explicit correlation (35), open-shell versions (26), and a linear-scaling implementation (32) are all available for the DCSD method. All reported calculations using this feature should cite:

D. Kats and F. R. Manby, J. Chem. Phys. **139**, 021102 (2013)

D. Kats, J. Chem. Phys. **141**, 061101 (2014)

24.7 The `DIIS` directive

`DIIS,`*itedis,incdis,maxdis,itydis*`;`

This directive allows to modify the DIIS parameters for CCSD, QCISD, or BCCD calculations.

itedis:	First iteration in which DIIS extrapolation may be performed (default=2).

incdis:	Increment between DIIS iterations (default=1).
maxdis:	Maximum number of expansion vectors to be used (default=6).
itydis:	DIIS extrapolation type. itydis=1 (default): residual is minimized. itydis=2: ΔT is minimized.

In addition, there is a threshold *THRDIS* which may be modified with the THRESH directive. DIIS extrapolation is only done if the variance is smaller than *THRDIS*.

24.8   Saving the wavefunction

SAVE,*record*;

record:	record name for save of wavefunction. The wavefunction is saved in each iteration. This has the same effect as the SAVE option.

24.9   Starting wavefunction

START,*record*;

record:	record name from which the wavefunction is restored for a restart. This has the same effect as the START option.
	If the option MAXIT=1 is set on the CCSD command line, no further iterations will be performed. (Note: in this case there is no check whether the previous wavefunction was converged.) It is then for example possible to compute the triples correction using the restarted CCSD wavefunction.

24.10   Examples

24.10.1   Single-reference correlation treatments for H₂O

```
***,h2o test
memory,1,m                              !allocate 1 MW dynamic memory
geometry={o;h1,o,r;h2,o,r,h1,theta}     !Z-matrix geometry input
basis=vtz                               !cc-pVTZ basis set
r=1 ang                                 !bond length
theta=104                               !bond angle
hf                                      !do scf calculation

text,examples for single-reference correlation treatments

ci                                      !CISD using MRCI code
cepa(1)                                 !cepa-1 using MRCI code
mp2                                     !Second-order Moeller-Plesset
mp3                                     !Second and third-order MP
mp4                                     !Second, third, and fourth-order MP4(SDTQ)
mp4;notripl                             !MP4(SDQ)
cisd                                    !CISD using special closed-shell code
ccsd(t)                                 !coupled-cluster CCSD(T)
qci(t)                                  !quadratic configuration interaction QCISD(T)
bccd(t)                                 !Brueckner CCD(T) calculation
---
```

http://www.molpro.net/info/current/examples/h2o_ccsd.com

24.10.2   Single-reference correlation treatments for N₂F₂

```
***,N2F2 CIS GEOMETRY (C2h)
rnn=1.223,ang                           !define N-N distance
rnf=1.398,ang                           !define N-F distance
alpha=114.5;                            !define FNN angle
geometry={N1
         N2,N1,rnn
         F1,N1,rnf,N2,alpha
         F2,N2,rnf,N1,alpha,F1,180}
basis=vtz                               !cc-pVTZ basis set
$method=[hf,cisd,ccsd(t),qcisd(t),bccd(t)]  !all methods to use
do i=1,#method                          !loop over requested methods
$method(i)                              !perform calculation for given methods
e(i)=energy                             !save energy in variable e
enddo                                   !end loop over methods
table,method,e                          !print a table with results
title,Results for n2f2, basis=$basis    !title of table
```

http://www.molpro.net/info/current/examples/n2f2_ccsd.com

This calculation produces the following table:

```
 Results for n2f2, basis=VTZ

 METHOD          E            E-ESCF
 CISD      -308.4634948   -0.78283137
 BCCD(T)   -308.6251173   -0.94445391
 CCSD(T)   -308.6257931   -0.94512967
 QCISD(T)  -308.6274755   -0.94681207
```

24.11 Expectation values

`EXPEC[,[METHOD=]`*method*`][,[TYPE=]`*type*`][,`*opname*`]`

One-electron properties in closed-shell QCISD, QCISD(T), CCD, CCSD, and DCSD can be computed by using `EXPEC`. (the `GEXPEC` directive has no effect in this case). The following options can be specified

`METHOD:`	*method*`=EDERIV`: Default case. Properties are obtained as analytical energy derivatives. *method*`=XCCSD`: eXpectation-value CCSD method (with the exponential ansatz used also for bra) – see section 25.6. *method*`=XCCSD(3)`: A simplified version of XCCSD – see section 25.6. It is also available for the local CCSD method.
`TYPE:`	*type*`=RELAX`: Compute fully relaxed properties with taking into account the orbital relaxation (default). Nonrelaxed properties are also computed and printed. *type*`=NORELAX`: Compute properties without taking into account the orbital relaxation. The `TYPE` option has only effect for the analytical energy derivatives.

Note that, in CCSD, the orbital relaxation effect on properties is less pronounced than, for example, in MP2. By default, only dipole moments are computed. The syntax for operators *opname* is explained in section 6.13. See also `DM` in section 24.12, and `NATORB` in section 24.13.

24.12 Saving the density matrix

`DM,`*record.ifil*`;`

The first-order density matrix in AO basis is stored in record *record* on file *ifil*. For details, see section 23.3. See also `NATORB` in section 24.13.

24.13 Natural orbitals

`NATORB,[RECORD=]`*record.ifil*`,[PRINT=]`*nprint*`],[CORE[=]`*natcor*`]];`

Calculate natural orbitals. The options are the same as for MP2. For details, see section 23.4.

24.14 Dual basis set calculations

Dual basis set calculations are possible with the closed-shell MP2 and CCSD codes (conventional and local, also with density fitting where available). Normally this means that the Hartree-Fock calculation is done with a smaller basis set than the correlation calculation. In MOLPRO, two possibilities exist: the recommended one is to perform the HF and MP2 or CCSD calculations using the same basis set, and only omit higher angular momentum functions in the HF. This means that the resulting HF orbitals can be used directly in the correlation calculation. Alternatively, one can use entirely different basis sets in HF and the correlation calculation; in this case the orbitals in the correlation calculation are determined by a least square fit to the HF orbitals. This is less efficient (in particular in fully direct calculations) and somewhat less

accurate. In any case, a new Fock matrix is computed in the MP2/CCSD program and block diagonalized in the occupied and virtual orbital subspaces. A perturbative singles correction is applied in the MP2 in order to reduce the HF basis set error.

Typically, the input is as follows:

```
basis=vtz(d/p)    !triple zeta basis set without f on heavy atoms and without d on hydrogen
hf                !Hartree-Fock in the small basis
basis=vtz         !full cc-pVTZ basis set to be used in ccsd
ccsd(t),dual=1    !ccsd calculation
```

The option `dual=1` is required, otherwise the program will stop with an error message saying that the basis set of the reference orbitals is inconsistent. This is a precaution in order to avoid unexpected results.

Similarly, this works for other closed-shell single reference methods such as `MP2`, `QCISD`, `MP2-F12`, `CCSD-F12`, and for the local variants `LMP2`, `LQCISD`, `LCCSD` in either conventional or direct mode. Furthermore, dual basis set `DF-LMP2`, `DF-LCCSD`, `DF-LMP2-F12` calculations are possible.

25 EXCITED STATES WITH EQUATION-OF-MOTION CCSD (EOM-CCSD)

Excitation energies for singlet states can be computed using equation-of-motion (EOM) approach. For the excitation energies the EOM-CCSD method gives the same results as linear response CCSD (LR-CCSD) theory. Accurate results can only be expected for excited states dominated by single excitations. The states to be computed are specified on an `EOM` input card, which is a subcommand of `CCSD`. The following input forms are possible

`EOM`, *state1, state2, state3, . . .*

Computes the given states. Each state is specified in the form *number.sym*, e.g., 5.3 means the fifth state in symmetry 3. Note that state 1.1 corresponds to the ground state CCSD wavefunction and is ignored if given.

`EOM`, $-n1.sym1$, $-n2, sym2$, . . .

computes the first $n1$ states in symmetry *sym1*, $n2$ in *sym2* etc.

`EOM`, $n1.sym1$, $-n2, sym1$, . . .

computes states $n1$ through $n2$ in symmetry *sym1*.

The different forms can be combined, e.g.,

`EOM`, $-3.1, 2.2, 2.3, -5.3$

computes states 1-3 in symmetry 1, the second excited state in symmetry 2, and the second through fifth excited states in symmetry 3. Note that state 1.1 is the ground-state CCSD wavefunction.

By default, an error exit will result if the CCSD did not converge and a subsequent EOM calculation is attempted. The error exit can be avoided using the `NOCHECK` option on the CCSD command (see also CCSD(T)).

25.1 Options for `EOM`

Normally, no further input is needed for the calculation of excitation energies.

EOM-CCSD amplitudes can be saved using `SAVE`=*record.ifil*. The vectors will be saved after every refreshing of the iteration space and at the end of the calculation. The calculation can be restarted from the saved vectors, if `START`=*record.ifil* is specified. The set of vectors to be computed can be different in old and restarted calculations. However, if both cards (`SAVE` and `START`) are specified and the records for saving and restarting are identical, the sets of vectors should be also identical, otherwise chaos. The identical `SAVE` and `START` records can be useful for potential energy surfaces calculations, see section 25.4.1.

By default, only excitation energies are calculated, since the calculation of properties is about two times as expensive, as the calculation of energies only. The one-electron properties and transition moments (expectation type, as defined in: J.F. Stanton and R.J. Bartlett, J. Chem. Phys., **98** 7029 (1993)) can be calculated by adding `TRANS=1` to `EOM` card. The CCSD ground state is treated as a special case. If `RELAX` option is specified on the `EXPEC` card, also the relaxed one-electron density matrix is calculated for the ground state. (Currently, the relaxed CCSD density matrix through the EOM program is available for all-electron calculations only.) By default, dipole moments are calculated. Other required properties can be specified using `EXPEC` card. Properties are saved in MOLPRO variables, e.g. the *x*-component of the dipole moment is saved in `DMX`, its pure electron part in `DMXE`, transition moment – in `TRDMX` (left and

right transition moments are stored separately). If DENSAVE=*record.ifil* is specified, excited-state densities are saved to *record.ifil*, otherwise they are saved to the record given in DM card. If TRANS=2, transition density matrices from/to the ground state will be saved provided that DENSAVE=*record.ifil* or DM card are specified and nonzero. If TRANS=3, transition moments among excited states are also calculated, and finally if TRANS=4, all transition densities will be saved (note that the last option should be used with caution because the number of densities to be stored will quickly exceed the allowed maximum). For an example see section 25.4.2.

When properties are needed, the left EOM-CCSD wave functions are calculated first. It is possible to use them as starting guesses for the right EOM-CCSD wave functions. This option is controlled by STARTLE (default 0). If STARTLE=1, left vectors are just used as a start for right vectors; if STARTLE=2, starting vectors, obtained from the left vectors are additionally biorthogonalized to the left vectors; finally, if STARTLE=3, also the final right vectors are biorthogonalized to the left vectors. The last possibility is of particular importance for degenerate states.

It is possible to make the program to converge to a vector, which resembles a specified singles vector. This option is switched on by FOLLOW=*n* card (usually *n*=2 should be set). FOLLOW card should be always accompanied with EXFILE=*record.ifil* card, where *record.ifil* contains singles vectors from a previous calculation, see section 25.4.3.

25.2 Options for EOMPAR card

Normally, no further input is needed. However, some defaults can be changed using the EOMPAR directive:

EOMPAR, key1=*value1*, key2=*value2*,...

where the following keywords key are possible:

MAXDAV=*nv*	Maximum value of expansion vectors per state in Davidson procedure (default 20).
INISINGL=*ns*	Number of singly excited configurations to be included in initial Hamiltonian (default 20; the configurations are ordered according to their energy). Sometimes INISINGL should be put to zero in order to catch states dominated by double excitations.
INIDOUBL=*nd*	Number of doubly excited configurations to be included in initial Hamiltonian (default 10).
INIMAX=*nmax*	Maximum number of excited configurations to be included in initial Hamiltonian. By default, $nmax = ns + nd$.
MAXITER=*itmax*	Maximum number of iterations in EOM-CCSD (default 50).
MAXEXTRA=*maxex*	Maximum number of extra configurations allowed to be included in initial Hamiltonian (default 0). In the case of near degeneracy it is better to include a few extra configurations to avoid a slow convergence.
EOMLOCAL=*eoml*	If set to 0, non-local calculation (default). EOMLOCAL=1 switchs on the local module (experimental!).
INIMAX=*ini*	Number of CSFs included in initial Hamiltonian, used only if INISINGL and INIDOUBL are both zero.

All keywords can be abbreviated by at least four characters.

25.3   Options for `EOMPRINT` card

The following print options are mostly for testing purposes and for looking for the convergence problems.

`EOMPRINT`, `key1`=*value1*, `key2`=*value2*,...

where the following keywords `key` are possible:

`DAVIDSON`=*ipr*	Information about Davidson procedure: *ipr=1* print results of each "small diagonalization" *ipr=2* also print warning information about complex eigenvalues *ipr=3* also print hamiltonian and overlap matrix in trial space.
`DIAGONAL`=*ipr*	Information about configurations: *ipr=1* print the lowest approximate diagonal elements of the transformed hamiltonian *ipr=2* print orbital labels of important configurations *ipr=3* print all approximate diagonal elements *ipr=4* also print the long form of above.
`PSPACE`=*ipr*	Print information about the initial approximate hamiltonian: *ipr=2* print the approximate hamiltonian used to find the first approximation.
`HEFF`=*ipr*	Print information about effective Hamiltonian: *ipr=2* print columns of effective hamiltonian and overlap matrix in each iteration
`RESIDUUM`=*ipr*	Print information about residual vectors: *ipr=-1* no print in iteration *ipr=0* print energy values + residuum norm (squared) for each iteration (default) *ipr=1* also print warning about complex eigenvalue, and a warning when no new vectors is added to the trial space due to the too small norm of the residuum vector. *ipr=2* also print how many vectors are left
`LOCEOM`=*ipr*	*ipr=1* prints overlaps of sample and tested vectors in each iteration, if `FOLLOW` card is present. Increasing *ipr* switches on more and more printing, mostly related to the local EOM-CCSD method.
`POPUL`=*ipr*	if *ipr=1*, do a population analysis of the singles part of the rhs EOM-CCSD wave function. By default the Löwdin method is used. The Mulliken analysis can be forced by adding `MULLPRINT=1` to `EOM` card. Note that a more correct (but more expensive) approach is to calculate and analyse the EOM-CCSD density matrix, see section 25.1.
`INTERMED`=*ipr*	Print intermediates dependent on ground state CCSD amplitudes: *ipr=0* no print (default) *ipr=1* print newly created intermediates *ipr=2* also print more intermediates-related information

25.4 Examples

25.4.1 PES for lowest excited states for hydrogen fluride

This example shows how to calculate potential energy surfaces for several excited states using restart from a previous calculation.

```
***, PES for several lowest states of hydrogen fluoride
memory,2,m
basis=avdz                                     ! define basis set
geometry={h;f,h,r}                             ! z-matrix
r=0.8 Ang                                      ! start from this distance
do n=1,100                                     ! loop over distances
rr(n)=r                                        ! save distance for table
hf                                             ! do SCF calculation
ccsd                                           ! do CCSD calculation, try to restart
start,4000.2,save,4000.2                       ! and save final T amplitudes
eom,-2.1,-1.2,-1.4,start=6000.2,save=6000.2    ! do EOM-CCSD calculation, try to restart
                                               ! and save final excited states' amplitudes


ebase(n)=energy(1)                             ! save ground state energy for this geometry
e2(n)=energy(2)-energy(1)                      ! save excitation energies for this geometry
e3(n)=energy(3)-energy(1)
e4(n)=energy(4)-energy(1)
r=r+0.01                                       ! increment distance
enddo                                          ! end of do loop
table,rr,ebase,e2,e3,e4                         ! make table with results
digits,2,8,5,5,5,5,5,5,5,5                      ! modify number of digits
head,R(Ang),EGRST,E_EXC(2.1),E_EXC(1.2),E_EXC(1.4)! modify headers of table
! title of table
title,EOM-CCSD excitation energies for hydrogen fluoride (in hartree), basis $basis
save,hf_eom_ccsd.tab                           ! save table in file
```

   http://www.molpro.net/info/current/examples/hf_eom_pes.com

This calculation produces the following table:

```
 EOM-CCSD excitation energies for hydrogen fluoride (in hartree), basis AVDZ

   R(ANG)          EGRST      E_EXC(2.1)  E_EXC(1.2)  E_EXC(1.4)
     0.80    -100.23687380     0.56664     0.41204     0.56934
     0.81    -100.24094256     0.56543     0.40952     0.56812
     0.82    -100.24451598     0.56422     0.40695     0.56690
```

etc.

25.4.2 EOM-CCSD transition moments for hydrogen fluoride

This example shows how to calculate and store CCSD and EOM-CCSD density matrices, calculate dipole and quadrupole moments (transition moments from the ground to excited states are calculated), and how to use the EOM-CCSD excited state density for Mulliken population analysis.

```
***, Properties and transition moments for several lowest states of hydrogen fluoride
memory,2,m
basis=avdz                                    ! define basis set
geometry={h;f,h,r}                            ! z-matrix
r=0.92 Ang                                    ! define distance

hf                                            ! do SCF calculation
{ccsd                                         ! do CCSD calculation
dm,5600.2                                     ! density matrices will be stored here
expec,response,qm                             ! require quadrupole moments
eom,-3.1,-2.2,-2.3,-2.4,trans=1}              ! do EOM-CCSD calculation + properties

pop;density,5600.2,state=2.4                  ! make population analysis for state 2.4
```

http://www.molpro.net/info/current/examples/hf_eom_prop.com

This calculation produces the following table:

```
--------------------------------------------------------------------------------
                      Final Results for EOM-CCSD
                          (moments in a.u.)
--------------------------------------------------------------------------------

   State     Exc. Energy (eV)          X              Y              Z
    2.1         14.436

 Right transition moment          0.00000000     0.00000000     0.65349466
 Left  transition moment          0.00000000     0.00000000     0.68871635
 Dipole strength                  0.45007246
 Oscillator strength              0.15917669
 Dipole moment                    0.00000000     0.00000000     0.88758090
```

etc.

25.4.3 Calculate an EOM-CCSD state most similar to a given CIS state

This example shows how to force the convergence of the EOM-CCSD program to a state, which resembles at most a given CIS state.

```
***, EOM-CCSD, vector following procedure
memory,2,m
basis=avdz                                    ! define basis set
geometry={h;f,h,r}                            ! z-matrix
r=0.92 Ang                                    ! define distance
hf;save,2100.2                                ! do SCF calculation, save orbitals
cis,-4.4,exfile=6000.2                         ! do CIS calculation, save amplitudes
ccsd;save,4000.2                              ! do CCSD calculation, save amplitudes
eom,-4.4,checkovlp=1,exfile=6000.2            ! do EOM-CCSD calculation,
                                              ! check overlap of singles with CIS vectors
                                              ! stored in record given in exfile
eompar,inisingl=200,inidoubl=0                ! for first approximation take 200 single CSF
                                              ! of approximate hamiltonian
ccsd;start,4000.2                             ! do CCSD calculation, try to restart
eom,2.4,follow=2,exfile=6000.2,checkovlp=1    ! do EOM-CCSD calculation for state closest
                                              ! to 2.4 CIS state, check overlap of singles
                                              ! with CIS vectors stored in exfile
eompar,inisingl=200,inidoubl=0
eomprint,loce=1                               ! print overlaps of sample and EOM vectors in
                                              ! each iteration
```

http://www.molpro.net/info/current/examples/hf_eom_conv.com

In this example the CIS state 2.4 corresponds to the EOM-CCSD state 1.4!

25.5   Excited states with CIS

Excitation energies can also be calculated using the Configuration-Interaction Singles (CIS) method. By default, singlet excited states are calculated. Triplet excited states can be obtained by setting `triplet`=1 in `EOM` card. This method cannot be expected to give accurate results, but can be used for quite large molecules. The states to be computed are specified as in `EOM`. Setting `trans`=1 switches on the calculation of dipole transition moments (length gauge), while `trans`=2 allows to obtain additionally one-electron properties of excited states. By default, dipole moments are calculated. Other required properties can be specified using `EXPEC` card. `trans`=0 and 1 work in direct mode.

```
hf
cis,-3.1,1.2,trans=2
```

25.6   First- and second-order properties for CCSD from expectation-value CC theory (XCCSD)

First-order and frequency-dependent second-order properties, derived from the expressions based on the expectation value of a one-electron operator, can be obtained with the `CPROP` directive for the closed-shell CCSD method. For first-order properties obtained from the energy-derivative approach see section 24.11. The expectation-value methods utilized in the program are described in the following papers:

[1] B. Jeziorski and R. Moszynski, *Int. J. Quantum Chem.*, **48**, 161 (1993);
[2] T. Korona and B. Jeziorski, *J. Chem. Phys.*, **125**, 184109 (2006);
[3] R. Moszynski, P. S. Żuchowski and B. Jeziorski, *Coll. Czech. Chem. Commun.*, **70**, 1109 (2005);
[4] T. Korona, M. Przybytek and B. Jeziorski, *Mol. Phys.*, **104**, 2303 (2006),
[5] T. Korona, *Theor. Chem. Acc.*, **129**, 15 (2011).

Note that properties obtained from the expectation-value expression with the coupled cluster wave function **are not** equivalent to these derived from gradient or linear-response methods, although the results obtained with both methods are quite similar. In XCC the exponential ansatz for the wave function is utilized for the bra side, too.

For the first-order properties the one-electron operators should be specified in the `EXPEC` card, while for the second-order properties – in the `POLARI` card. A density can be saved by specifying the `DM` card.

For the first-order properties the option `XDEN`=1 should be usually given. Other options specify a type of the one-electron density, which can be either the density directly derived from the expectation-value expression, see Eq. (8) of Paper 2, or the modified formula, rigorously correct through the $\mathcal{O}(W^3)$ Møller-Plesser (MP) order, denoted as $\bar{X}(3)_{\text{resp}}$ in Papers 1 and 2. In the first case the option `PROP_ORDER`=n can be used to specify the approximation level for single and double excitation parts of the so-called S operator (see [2], Eq. (9)); $n = \pm2, \pm3, \pm4$, where for a positive n: all approximations to S up to n are used, and for a negative n only a density with S obtained on the $|n|$ level will be calculated. Another option related to the S operator is `HIGHW`=n, where $n = 0, 1$; if n=0, some parts of S_1 and S_2 operators of a high MP order are neglected. Below an example of a standard use of this method is given:

```
CPROP,XDEN=1,PROP_ORDER=-3,HIGHW=0
```

The combination above is also available by writing `EXPEC,XCCSD` after the `CCSD` card. A cheap method denoted as XCCSD(3), obtained by a simplification of the original XCCSD formula, is available by setting

`CPROP,XDEN=-21`

or by writing `EXPEC,XCCSD(3)` after the `CCSD` card.

In the second case the options `X3RESP=1` and the `CPHF,1` card (or alternatively the `EXPEC` card) should be specified,

`CPROP,XDEN=1,X3RESP=1;CPHF,1`

For the second-order properties always the following options should be given:

`CPROP,PROPAGATOR=1,EOMPROP=1`

The recommended CCSD(3) model from Paper 4 requires that additionally the `PROP_ORDER=3` and `HIGHW=0` options are specified. Frequencies for dynamic properties (in atomic units) should be given in variables `OMEGA_RE` (real parts) and `OMEGA_IM` (imaginary parts). If one of these arrays is not given, it is filled with zeros. Other options for the second-order properties involve

`OMEGAG`	(default 0.3). There are two linear-equation solvers, `OMEGAG` is a minimum frequency, for which the second solver (working for large frequencies) is used.
`DISPCOEF=`*n*	if $n > 0$, calculate dispersion integrals for the van der Waals coefficients with operators given in the `POLARI` card, using *n* as a number of frequencies for the numerical integration. In this case the frequency values given in `OMEGA_RE` and `OMEGA_IM` are ignored. If two molecules are calculated in the same script one after another, also the mixed dispersion integrals are calculated. The isotropic C_6 coefficient is stored in a variable `DISPC6`, the isotropic C_9 nonadditive coefficient – in a variable `DISPC9`. All necessary informations for the calculation of dispersion integrals are written to the ascii file *name.dispinfo*, where *name* is the name of the MOLPRO script.
`THRPROPAG`	if given, use this threshold as a convergence criterion for the linear-equation solver for the first-order perturbed CCSD amplitudes.
`STARTT1=`*n*	various start options for the iterative linear-equation solver for the first-order perturbed CCSD amplitudes, the most useful is $n = 0$ (zero start) and $n = 7$ (start from the negative of the r.h.s. vector rescaled by some energetic factors dependent on the diagonal of the Fock matrix and the specified frequency).

26   OPEN-SHELL COUPLED CLUSTER THEORIES

Spin unrestricted (`RHF-UCCSD`) and partially spin restricted (`RHF-RCCSD`) open-shell coupled cluster theories as described in J. Chem. Phys. **99** (1993) 5219 (see also erratum, J. Chem. Phys., **112** (2000) 3106) are available in MOLPRO. In both cases a high-spin `RHF` reference wavefunction is used. No coupled cluster methods based on UHF orbitals are implemented in MOLPRO (the only correlation method in MOLPRO which uses UHF orbitals is `UMP2`). In the

description that follows, the acronyms RCCSD and UCCSD are used, but the theories should normally be referred to as RHF-RCCSD, RHF-UCCSD, in order to distinguish them from alternative ansätze based on spin-unrestricted orbitals. The program will accept either the full or abbreviated acronyms as input commands.

In the RCCSD theory certain restrictions among the amplitudes are introduced, such that the linear part of the wavefunction becomes a spin eigenfunction (this is not the case in the UCCSD method, even if an RHF reference function is used). At present, the implementation of RCCSD is only preliminary, and no CPU time is saved by as compared to UCCSD. However, improved algorithms, as described in the above publication, are currently being implemented, and will be available in the near future.

The input and the options are exactly the same as for closed-shell CCSD, except that RCCSD or UCCSD are used as keywords. By default, the open-shell orbitals are the same as used in the RHF reference function, but this can be modified using OCC, CLOSED, and WF cards.

Distinguishable cluster calculations can be performed using RDCSD or UDCSD commands.

Perturbative triples corrections are computed as follows:

RCCSD(T), UCCSD(T)	triples corrections are computed as defined by J. D. Watts, J. Gauss and R. J. Bartlett, J. Chem. Phys. **98** 8718 (1993).
RCCSD[T], UCCSD[T]	corrections are computed without contributions of single excitations (sometimes called CCSD+T(CCSD)) .
RCCSD-T, UCCSD-T	triples corrections are computed as defined by M. J. O. Deegan and P. J. Knowles, Chem. Phys. Letters 227 (1994) 321.

In fact, all three contributions are always computed and printed. The following variables are used to store the results (here CCSD stands for either UCCSD or RCCSD):

ENERGY	total energy for method specified in the input.
ENERGC	total CCSD energy without triples.
ENERGT(1)	total CCSD(T) energy.
ENERGT(2)	total CCSD[T] energy.
ENERGT(3)	total CCSD-T energy.

It should be noted that in open-shell cases the triples energy slightly depends on the treatment of core orbitals. In MOLPRO pseudo-canonical alpha and beta spin orbitals (Chem. Phys. Letters **186** (1991) 130) are generated by block-diagonalizing the corresponding Fock matrices in the space of valence orbitals, leaving frozen core orbitals untouched. Some other programs include the frozen core orbitals in the canonicalization and transformation. Because of core-valence mixing this leads to slightly different energies. Neither of the two methods can be regarded as better or more justified — it is just a matter of definition. However, the method in MOLPRO is more efficient since the subsequent integral transformation involves only valence orbitals and no core orbitals.

27 The MRCC program of M. Kallay (MRCC)

An interface exists to use the MRCC program of M. Kallay and J. Gauss within Molpro. The license and source code of the MRCC program must be obtained from Mihaly Kallay

`http://www.mrcc.hu/`. Currently, only single reference methods with `RHF` reference functions are supported. Perturbative methods and CCn methods are only available for closed-shell. Furthermore, only serial execution is supported under MOLPRO, i.e. the mpp version cannot be used.

27.1 **Installing** `MRCC`

Please refer to the MRCC documentation on how to install the MRCC program. The MRCC executables must be found in PATH in order for Molpro to use them.

27.2 **Running** `MRCC`

The `MRCC` program is invoked by the command

`MRCC`,*options*
directives

The available options summarized in Table 10. For a detailed description please refer to the MRCC manual of M. Kallay (file "manual" the mrcc directory)

In MOLPRO the method to be used can be given as a string (option `METHOD`=*string*). The available methods and the corresponding `MRCC` input parameters (see MRCC manual) as specified in Table 11.

Directives are usually not necessary, but the `CORE`, `OCC`, `ORBITAL`, `MAXIT`, directives work as in the MOLPRO CCSD program. In addition, the number of states can be given on a `STATE` directive and this has the same meaning as the `EOM_NSTATES` option.

Table 10: Options for MRCC

Option	Alias	Default value[a]	Meaning
METHOD	CALC	CC(n)	Computational method. See Table 11.
EXCITATION	LEVEL	-1	Excitation level in cluster operator
RESTART_CC	RESTART	0	Restart option. If 1, restart with previous amplitudes.
DIRECTORY	DIR	' '	Subdirectory in which MRCC runs (necessary for restart jobs)
EOM_NSING	NSING	-1	Number of excited singlet states in closed-shell case
EOM_NTRIP	NTRIP	0	Number of excited triplet states in closed-shell case
EOM_NSTATES	NDOUB	-1	Number of states in open shell case.
SYMM	SYMMETRY	-1	Symmetry of excited states
DENSITY	IDENS	0	Parameter for density calculation
HF		1	1 for canonical Hartree-Fock orbitals, 0 otherwise
SPATIAL		1	0 for spin-restricted orbitals, 1 for spin-unrestricted orbitals
NACTO		0	Number of active occupied orbitals
NACTV		0	Number of active virtual orbitals
SACC		0	Spin-adapted coupled cluster
DBOC		0	Diagonal BO correction
MEMORY		-1	Memory
TOL	ENERGY	-1.0	Energy convergence threshold
FREQ		0.0	Frequency for dynamic polarizabilities
FILE		fort	Name for MRCC fortran files
CONVER	ICONV	0	See mrcc manual
CS		1	See mrcc manual
DIAG		0	See mrcc manual
MAXEX		0	See mrcc manual

a) -1 means default value taken from MOLPRO

Table 11: Methods available in the MRCC program

| Key | MRCC parameters | | Notes |
	METHOD	LEVEL	
CI(n) configuration interaction methods			
CISD	0	2	
CISDT	0	3	
CISDTQ	0	4	
CI(N)	0	N	Specify excitation level N using LEVEL
CC(N) coupled cluster methods			
CCSD	1	2	
CCSDT	1	3	
CCSDTQ	1	4	
CC(N)	1	N	Specify excitation level N using LEVEL
CC(N-1)[N] coupled cluster methods			
CCSD[T]	2	3	
CCSDT[Q]	2	4	
CC(N-1)[N]	2	N	Specify excitation level N using LEVEL
CC(N-1)(N) coupled cluster methods. Also computes [n] corrections			
CCSD(T)	3	3	
CCSDT(Q)	3	4	
CC(N-1)(N)	3	N	Specify excitation level N using LEVEL
CC(n-1)(n)_L methods (also computes (n) and [n] corrections)			
CCSD(T)_L	4	3	
CCSDT(Q)_L	4	4	
CC(N-1)(N)_L	4	N	Specify excitation level N using LEVEL
CC(n)-1a methods			
CCSDT-1A	5	3	
CCSDTQ-1A	5	4	
CC(N)-1A	5	N	Specify excitation level N using LEVEL
CC(n)-1b methods			
CCSDT-1B	6	3	
CCSDTQ-1B	6	4	
CC(N)-1B	6	N	Specify excitation level N using LEVEL
CCn methods (only for ground states)			
CC3	7	3	
CC4	7	4	
CCN	7	N	Specify excitation level N using LEVEL
CC(n)-3 methods			
CCSDT-3	8	3	
CCSDTQ-3	8	4	
CC(N)-3	8	N	Specify excitation level N using LEVEL

Examples: Closed-shell ground-state calculations for H2O:

```
***,mrcc calculations for h2o
memory,8,m
gthresh,energy=1.d-8

geometry={
o;h1,o,r;h2,o,r,h1,theta}
theta=104
r=1 ang
basis=vdz

hf
mrcc,method=cc3;                    !CC3 calculation
method(1)=program
e(1)=energy                         !the final energy is returned in variable energy

ccsd(t)                             !CCSD(T) calculation using Molpro
method(2)='CCSD(T) (MOLPRO)'
e(2)=energy

mrcc,method=ccsd(t)                 !CCSD(T) calculation using MRCC
method(3)='CCSD(T) (MRCC)'
e(3)=energy

mrcc,method=ccsdt,dir=mrccdir       !CCSDT calculation, run in directory mrccdir
method(4)=program
e(4)=energy

mrcc,method=ccsdt(q),restart=1,dir=mrccdir !CCSDT(Q) calculation
                                   !restart with previous amplitudes
method(5)=program
e(5)=energy

mrcc,method=CC(n),excitation=4,restart=1,dir=mrccdir !CCSDTQ calculation
method(6)=program
e(6)=energy

table,method,e
```

```
    http://www.molpro.net/info/current/examples/h2o_mrcc.com
```

This yields

```
 METHOD               E
 CC3                 -76.23912734
 CCSD(T) (MOLPRO)    -76.23905150
 CCSD(T) (MRCC)      -76.23905150
 CCSDT               -76.23922746
 CCSDT(Q)            -76.23976632
 CCSDTQ              -76.23973043
```

Excitation energies for H2O:

```
***,h2o excitation energies
memory,8,m
gthresh,energy=1.d-8
geometry={
o;h1,o,r;h2,o,r,h1,theta}
theta=104
r=1 ang
basis=vdz
hf

ii=0
s=2                       !number of states in each symmetry
do sym=1,4                !loop over irreps
ccsd;eom,-(s+0.1*sym);$p=molpro;save_energy
mrcc,method=ccsd, symm=sym,nstates=2;$p=mrcc;save_energy
mrcc,method=ccsdt,symm=sym,nstates=2;$p=mrcc;save_energy
s=1
enddo

{table,method,prog,states,e,exc
 sort,3}

save_energy={        !procedure to save results in variables
!nogprint,variable
e1=energy(1)
do i=1,#energy
ii=ii+1
e(ii)=energy(i)
method(ii)=program
prog(ii)=p
states(ii)=i+0.1*sym
exc(ii)=(e(ii)-e1)*toev
end do
}
```

   http://www.molpro.net/info/current/examples/h2o_mrcc_eom.com

This yields

```
  METHOD    PROG    STATES      E          EXC
  CCSD     MOLPRO    1.1   -76.23580212    0.000
  CCSD     MRCC      1.1   -76.23580212    0.000
  CCSDT    MRCC      1.1   -76.23922746    0.000
  CCSD     MOLPRO    1.2   -76.23580212    0.000
  CCSD     MRCC      1.2   -76.23580212    0.000
  CCSDT    MRCC      1.2   -76.23922746    0.000
  CCSD     MOLPRO    1.3   -76.23580212    0.000
  CCSD     MRCC      1.3   -76.23580212    0.000
  CCSDT    MRCC      1.3   -76.23922746    0.000
  CCSD     MOLPRO    1.4   -76.23580212    0.000
  CCSD     MRCC      1.4   -76.23580212    0.000
  CCSDT    MRCC      1.4   -76.23922746    0.000
  CCSD     MOLPRO    2.1   -75.85033256   10.489
  CCSD     MRCC      2.1   -75.85033257   10.489
  CCSDT    MRCC      2.1   -75.85316687   10.505
  CCSD     MOLPRO    2.2   -75.95093334    7.752
  CCSD     MRCC      2.2   -75.95093335    7.752
  CCSDT    MRCC      2.2   -75.95299013    7.789
  CCSD     MOLPRO    2.3   -75.77630664   12.504
  CCSD     MRCC      2.3   -75.77630665   12.504
  CCSDT    MRCC      2.3   -75.77972816   12.504
  CCSD     MOLPRO    2.4   -75.87776149    9.743
  CCSD     MRCC      2.4   -75.87776150    9.743
```

```
   CCSDT    MRCC        2.4   -75.88051189    9.761
```

Open-shell ground-state calculations for O2:

```
***,O2 tests
memory,8,m
gthresh,energy=1.d-8

geometry={o1;o2,o1,r1}
r1=2.2
set,state=1,symmetry=4,spin=2  ! Triplet sigma- state
basis=vdz

rhf
uccsd(t)
method(1)='UCCSD(T) MOLPRO'
e(1)=energy

rccsd(t)
method(2)='RCCSD(T) MOLPRO'
e(2)=energy

mrcc,method=ccsdt,dir=mrccdir
method(3)='CCSDT MRCC'
e(3)=energy

mrcc,method=ccsdtq,restart=1,dir=mrccdir
method(4)='CCSDT MRCC'
e(4)=energy

table,method,e
```

http://www.molpro.net/info/current/examples/o2_mrcc.com

This yields

```
METHOD                E
UCCSD(T) MOLPRO   -149.9815472
RCCSD(T) MOLPRO   -149.9812566
CCSDT MRCC        -149.9816705
CCSDT MRCC        -149.9832255
```

28 The FCIQMC program (`FCIQMC`)

The FCIQMC program exists through an interface to the `NECI` codebase, which is actively developed in the group of A. Alavi, and has been integrated into the MOLPRO code. The FCIQMC method is a recently introduced stochastic method which can calculate in principle FCI-quality energies for small to medium-sized molecules. The method should also be suitable for large-scale parallel application across distributed memory architecture. However, it should be noted that since the method relies on random number strings, the exact path of the simulation will change with number of MPI tasks used, although converged results should agree. Since the method is new, the code is also somewhat developmental, and updates and improvements are to be expected. Any user hoping to use the FCIQMC package for a study is welcome to get in contact directly with A. Alavi (`asa10@cam.ac.uk`), and the lead developer of the code, G. Booth (`ghb24@cam.ac.uk`), for technical help, advice and access to undocumented options.

It is also highly recommended to invoke the command-line option `--no-helper-server`, which will ensure that when running in parallel, all MPI processes are utilized. Multiple files are created in addition to the standard output, and dynamic adjustment to the calculation can only take place from the working directory. Therefore it may be useful to assign a convenient working directory from the command-line when MOLPRO is run. This can be done with the *-d* flag, with *-d .* setting the current directory as the working directory. Also, since the printing to the output file is buffered, it may be better to view the running simulation from the .xml file.

28.1 The FCIQMC Method

Details of the FCIQMC algorithm are best obtained from various publications on the method, which include:

G. H. Booth, A. J. W. Thom, and A. Alavi, J. Chem. Phys. **131**, 054106 (2009) (Full FCIQMC),
D. M. Cleland, G. H. Booth, and A. Alavi, J. Chem. Phys. **134**, 024112 (2011) (*i*-FCIQMC) and
G. H. Booth, D. M. Cleland, A. J. W. Thom, and A. Alavi, J. Chem. Phys. **135**, 084104 (2011),

and which should be cited in published work resulting from the use of this module.

Briefly, the FCIQMC method involves discretizing the wavefunction amplitudes over the full Slater determinant space into a number of signed 'walkers'. These walkers represent a coarse-grained snapshot of the wavefunction at any given instant. Through a population dynamics of these walkers evolving in imaginary-time, the ground-state energy and wavefunction can be resolved to arbitrary accuracy (in principle FCI quality), in a time-averaged fashion, without the need for any explicit diagonalization steps. The master equations which are stochastically realized and govern this dynamic, are given by

$$ -\frac{dN_i}{d\tau} = (H_{ii} - E_{ref} - S)N_i + \sum_{j \neq i} H_{ij}N_j \,, \tag{56} $$

where τ represents the evolution in imaginary-time, N_i is the walker population on configuration i, and S is the energy 'shift', which can be used as a measure of the correlation energy once the walker population is stable. In the original formulation, this dynamic is integrated exactly over imaginary-time, and converges to the exact basis-set correlation energy of the system within systematically reducible random errors, as long as the number of walkers in the system exceeds a system-dependent number, required to overcome the 'sign-problem' present in the space. This number is indicated by the appearance of a plateau in the growth profile of the walkers for a given value of S.

However, in a modification to the algorithm which allows for a generally smooth convergence to the FCIQMC result with increasing walker number, the sum in Eq. 56 is truncated, such that when considering a configuration *i* whose population is zero, this sum then only runs over those configurations who are deemed 'initiator' configurations. These initiator configurations are ones which have an instantaneous population of above a parameter n_{add}, or are the chosen 'reference' configuration. This modification to the algorithm rigorously converges to the full FCIQMC result in the limit of a large number of walkers, or as $n_{add} \to 0$, and is dubbed '*i*-FCIQMC'. This is the default algorithm used in the FCIQMC module.

Note that the choice of reference configuration, or indeed orbital space, should be independent of the final energy obtained, and the method thus constitutes a multiconfigurational correlation treatment, suitable for strongly-correlated problems. However, the choice of reference configuration and orbital space may affect rate of convergence and random error decay.

28.2 Running FCIQMC

Although many options and details are provided here, often FCIQMC calculations can be performed using default parameters in a relatively 'black-box' fashion, requiring knowledge of only a few key options.

The FCIQMC program is invoked by the command

FCIQMC,*OPTION=value*
directives

The simulation will then run within an orbital space obtained from the previous calculation (generally Restricted Hartree–Fock, although MCSCF/CASSCF/localized/unrestricted orbitals, as well as orbital subspaces can also be used with care). The electron number, spin-polarization and symmetry block of the FCIQMC calculation will also be presumed to be the same as specified for this preceding calculation, unless directives specify otherwise, and therefore should result in the FCIQMC module defining a 'reference' configuration which is the same as the Hartree–Fock determinant in the previous calculation. The symmetry and energy of this determinant should be checked to avoid slow convergence, or one to an incorrect symmetry solution.

Directives are usually not necessary, but the CORE, OCC, ORBITAL and WF directives work as in the MOLPRO CCSD program if core electrons are to be correlated, or if alternative orbital subsets or wavefunctions wish to be defined contrary to the previous mean-field calculation.

The default running procedure is an *i*-FCIQMC calculation, initialized with a single walker at the reference determinant, and the *S* shift parameter fixed at zero. The number of initial walkers, or value for the shift can be adjusted from their default settings with the STARTWALKERS and FIXEDSHIFT options. This initial stage should result in an exponential growth of walkers, whose rate of growth depends on the timestep, value of the fixed shift, and the correlation energy of the problem. This phase of the calculation is called 'fixed shift mode'. Once the total number of walkers has reached a number given by TARGETWALKERS, the shift is updated every INTERVAL iterations, in order to stabilize the walker growth.

The default behavior is to run for only 100 iterations. This is generally far too short, and should be changed using the ITERATIONS command, the TIME command, or dynamically with the CHANGEVARS facility, which will be detailed in section 28.5. In addition, the timestep will be initially chosen as a reasonable upper-bound, and then dynamically updated through the initial part of the calculation in order to eliminate walker 'blooming' events, where multiple walkers (of more than MAXWALKERBLOOM are created in a single spawning attempt. However, this initial upper-bound can be a poor guess if the system is especially small, and so alternatively,

the timestep can be specified and fixed for the entire calculation with the `TIMESTEP` option. Generally this wants to be as large as possible without causing frequent blooming events.

The available options are summarized in Table 12, and those requiring a more detailed explanation are expanded on in section 28.3.

Table 12: Options for FCIQMC

Option	Default	Allowed values	Short description
SYMMETRY	ON	'ON/OFF'	Whether to use point-group symmetry
SPIN	OFF	'EVEN/ODD'	Whether to use spin-reversal symmetry
ITERATIONS	100	INT	Maximum number of iterations
TIME	OFF	REAL	Runtime in minutes
TIMESTEP	N/A	REAL	Timestep for use in calculation
STARTWALKERS	1	INT	Number of initial walkers on reference configuration
TARGETWALKERS	10,000	INT	Target number of total walkers for entry to variable shift mode
SEED	-7	INT	Random number seed
STARTMP1	OFF	INT	Initialize *value* walkers at MP1 wavefunction distribution
MAXATREF	OFF	INT	Target number of walkers on reference configuration for variable shift mode
FIXEDSHIFT	0.0	REAL	Initial value of the fixed shift
SHIFTDAMPING	0.1	REAL	Damping parameter for adjustment of the shift in variable shift mode
INTERVAL	10	INT	Iteration interval for writing out statistics and updating of the shift
PROJE-CHANGEREF	OFF	INT	Percentage increase from the current reference population required to change reference dynamically
FULL_FCIQMC	False	True/False	Flag to determine whether to run full FCIQMC or *i*-FCIQMC algorithms
INITIATOR_THRESH	3	INT	n_{add} parameter for initiator criterion
MAXWALKERBLOOM	INIT_THSH	INT	Maximum allowed spawning probability if automatically adjusting timestep
TRUNCATE	OFF	INT(n)	Truncate space by excitation level n
PARTIALFREEZEOCC	OFF	INT	Number of lowest energy occupied spin-orbitals to partially freeze
PARTIALFREEZEHOLES	OFF	INT	Number of holes allowed in the PARTIALFREEZEOCC orbital space
PARTIALFREEZEVIRT	OFF	INT	Number of highest energy virtual spin-orbitals to partially freeze
PARTIALFREEZEVIRTELECS	OFF	INT	Number of electrons allowed in the PARTIALFREEZEVIRT orbital space

Table 13: Options for FCIQMC cont.

Option	Default	Allowed values	Short description
`MEMORYFACWALKERS`	1.5	REAL	Memory factor for main walker array
`MEMORYFACSPAWNED`	0.3	REAL	Memory factor for spawned walker arrays
`SINGLESBIAS`	OFF	REAL	Singles biasing factor in excitations
`READWALKERS`	False	True/False	Option to read in walker distribution from previous run (requires POPSFILEs)
`CONTINUEWALKERGROWTH`	False	True/False	If restarting, indicates whether to resume calculation in fixed/variable shift mode
`WRITEPOPSFILE`	OFF	INT	Write a restart file (POPSFILE) every *value* iterations
`POPSFILETIMER`	OFF	REAL	Write a restart file (POPSFILE) every *value* hours
`INCREMENTPOPSFILES`	False	True/False	If True preserve previous POPSFILEs
`REBLOCKSHIFT`	OFF	INT	Perform error analysis on data from previous calculation with specified iteration equilibration time for shift estimate
`REBLOCKPROJE`	OFF	INT	Perform error analysis on data from previous calculation with specified iteration equilibration time for projected energy estimate
`NOMCOUTPUT`	False	True/False	Suppress iteration-specific output (Note all data still written to **FCIQMCStats** file)
`CALCMCSIZESPACE`	OFF	INT	Run routine to stochastically calculate size of symmetry-allowed FCI space

28.3   More advanced options

The following section provides more detail on some of the more advanced options described in Table 12.

`SPIN`=*'EVEN'/'ODD'*   Rather than perform the FCIQMC dynamic in a space of Slater determinants, this option combines each determinant with its spin-flipped partner to create a new space, which exactly spans either the space of even or odd spin eigenfunctions of the system. This effectively halves the number of functions on which the walkers can reside, reducing the overall number of walkers required for a given accuracy, as well as potentially allowing for a larger timestep, and the ability to converge to the lowest energy state of odd and even spin quantum number separately. These functions can be considered a compromise between a determinant and configuration state function space which are true spin eigenfunctions, and thus should reduce the instantaneous spin-contamination of the wavefunction, with only small additional computation overhead. This option is only available for $M_s = 0$ states.

`CALCMCSIZESPACE`=*value*   This option will provide an estimate for the dimensionality of the space in which the FCIQMC dynamic will evolve, prior to

the start of the FCIQMC calculation. This is done via a stochastic sampling of the space, and will write out the evolution of this estimate to a file called '`SpaceMCStats`'. The value that this option takes gives the number of iterations (per MPI task) to sample the space for. A final estimate is written to the standard output. All spin and symmetry constraints are considered.

STARTMP1=*value*   This option distributes *value* number of walkers initially at a distribution proportional to that of the MP1 wavefunction. The initial projected energy should therefore agree well with the MP2 energy. This can allow for faster equilibration of the population. If the *value* given here is the same as the TARGETWALKERS, then the simulation will begin in variable shift mode, with the initial shift set to the MP2 energy. Note that this will only work correctly if the orbitals come from a prior RHF calculation.

MAXATREF=*value*   If present, this option provides an additional condition by which the variable shift mode of the calculation can begin. Either if the number of walkers exceeds that specified by TARGETWALKERS, or the number of walkers specifically residing on the reference configuration exceeds the *value* specified in this option, then the shift will be allowed to vary to stabilize walker growth.

PROJE-CHANGEREF=*value*   If present, then this option allows the choice of reference configuration for the calculation of the projected energy to dynamically change during the course of the simulation. As will be seen in section 28.6, the variance of the projected energy estimate is dependent on the choice of reference configuration, but the specifics of the walker dynamic are independent. Therefore, maximizing the population on the reference configuration can be beneficial, especially in strongly-correlated cases where the initial reference (often Hartree–Fock) may have a relatively small weight in the final wavefunction, or where canonical Hartree–Fock orbitals are not used, and so no obvious choice of reference configuration presents itself. The *value* that this option takes is the percentage by which a configuration population is required to exceed the population of the current reference determinant, before the reference is changed to this highest populated configuration, i.e. PROJE-CHANGEREF=15 indicates that if a population on any configuration exceeds 115% of the current reference, it will become the new reference.

MEMORYFACWALKERS=*value*   This is a memory parameter, which determines the available storage for the main walker array. Its value should not affect the calculation if large enough. The *value* given is the fraction of the number of walkers specified by the TARGETWALKERS parameter which can be held in memory (assuming perfect load balancing across MPI tasks). Therefore, the default value of 1.5 should theoretically allow for growth of walkers up to 50% larger than that specified by by TARGETWALKERS. This should be more than sufficient for most applications, however if memory errors or unexpected termination of the program are encountered, these memory parameters may need to be increased.

MEMORYFACSPAWNED=*value*   This memory parameter is of a similar type to MEMORYFACWALKERS, but governs the memory allocated for the spawned walker ar-

rays at each iteration. Once again, it is given as a fraction of the walker number specified by `TARGETWALKERS`, and so the default value of 0.3 should theoretically allow for up to 30% of the `TARGETWALKERS` number of walkers to be created each iteration (again assuming perfect load balancing).

As well as specifying orbital subspaces, it is also possible to perform various truncated determinant space calculations within the FCIQMC dynamic, which although not strictly size-consistent, can nevertheless be used to obtain well equilibrated initial walker populations (which can then be read back in), or often accurate approximations to FCI energies in their own right. A common choice of truncated CI space is based on an excitation level criteria, which can be specified with the `TRUNCATE` keyword.

`TRUNCATE=`*value*	If present, this truncates the CI space based on the excitation rank of the function from the specified reference determinant. This results in FCIQMC energies which converge on the CIS, CISD, CISDT, CISDTQ, ... CI(*value*) hierarchy of approximations.

Another truncated space is one is not in the CI literature to the best of our knowledge, and is based upon either specifying a low-energy occupied orbital space, in which configurations sampled must not contain larger than a given number of holes, and/or a high-energy virtual subspace in which the determinant space must not contain more than a specified number of electrons. Because this reduces to the frozen-core approximation in the case of zero allowed holes in an occupied subspace, or amounts to deleting high-energy virtuals in the limit of no electrons allowed in the virtual subspace, this is denoted 'partial freezing'. This can also be considered as limiting the excitation level for an electron subset.

`PARTIALFREEZEOCC=`*value*	Indicates the number of lowest energy electrons to partially freeze (can be considered a core or semi-core space). Requires the `PARTIALFREEZEHOLES` option to also be specified.
`PARTIALFREEZEHOLES=`*value*	Indicates the number of holes allowed in this partially frozen space. Requires the `PARTIALFREEZEOCC` option to also be specified.
`PARTIALFREEZEVIRT=`*value*	Indicates the number of highest energy virtual spin-orbitals to partially freeze, restricting the number of electrons which can simultaneously occupy them. Requires the `PARTIALFREEZEVIRTELECS` option to also be specified.
`PARTIALFREEZEVIRTELECS=`*value*	Indicates the number of electrons allowed to simultaneously occupy the highest energy virtual space, as specified in the required `PARTIALFREEZEVIRT` option.

28.4 Restarting `FCIQMC` jobs

Another important facility of the `FCIQMC` module is the ability to write out restart files (POPS-FILEs), detailing the specific number and distribution of the walkers throughout the space. These files can then be copied between systems if desired, and the calculation continued from where it left off. Writing out these POPSFILEs is recommended in case further accuracy is required at a later stage. If the previous **FCIQMCStats** file is also present in the working directory

of the restarted calculation, then the new data obtained will be simply appended to the end of the previous **FCIQMCStats** file. Two files are required to restart a calculation: **POPSFILEHEAD** and **POPSFILEBIN**. Options to control their use include:

Writing POPSFILEs:

WRITEPOPSFILE=*value*   If this option is specified, then the required POPSFILEs are written out in the event of a clean exit from the calculation, either via the ITERATIONS or TIME options, or the CHANGEVARS facility. In addition, the POPSFILEs are written out in iteration intervals specified by the *value* given. If a *value* of zero is given, the POPSFILEs will only be written out at the end of the calculation.

POPSFILETIMER=*value*   This option will write out POPSFILEs at time intervals of *value* hours, as well as the end of the calculation.

INCREMENTPOPSFILES=*True*   This option will ensure that if multiple POPSFILEs are written out in one simulation, they will not overwrite previous versions, but rather append incrementing numerical suffixes to the filenames, i.e. POPSFILEHEAD.x. These must be renamed/linked as files called simply POPSFILEHEAD and POPSFILEBIN for reading in for subsequent calculations.

Reading POPSFILES:

READWALKERS=*True*   This option must be present in order to read back in walkers from POPSFILEs.

CONTINUEWALKERGROWTH=*True*   By default, the simulation will resume in variable shift mode. This option will resume the calculation in variable shift mode.

28.5   CHANGEVARS **facility**

The CHANGEVARS facility allows for a real-time dynamic adjustment of many of the parameters of the FCIQMC calculation. A file (which must be named CHANGEVARS) can be created in the working directory of the calculation, which contains one or more lines detailing changes to system parameters, as OPTION *new_value* (note no '='). Each updated option must be specified on a separate line. The options available via the CHANGEVARS interface are summarized in Table 14.

28.6   FCIQMC **output**

The estimate of the energy is extracted from the simulation in various ways. Once in variable shift phase of the calculation, where the walker number is stabilised (column 5 in output and **FCIQMCStats** file), the shift parameter (column 2) should vary about the correlation energy (S in Eq. 56) after equilibration. Alternatively, a projected energy estimate can be obtained through

Table 14: Options available via `CHANGEVARS` interface

Option	Allowed argument	Short description
`EXIT`	NONE	Exit FCIQMC calculation (note: this can also separately exit from `CALCMCSIZESPACE` calculation
`VARYSHIFT`	NONE	Instantaneously leave fixed shift mode and enter variable shift
`ZEROPROJE`	NONE	Zero all averaged energy estimators
`ITERATIONS`	INT	See table 12
`TIMESTEP`	REAL	See table 12
`TRUNCATE`	INT	See table 12 (note: must be increased from current value)
`SHIFT`	REAL	Instantaneously change value of shift (available in fixed and variable shift mode)
`SHIFTDAMPING`	REAL	See table 12
`INTERVAL`	INT	See table 12
`CHANGEREF`	NONE	Instantaneously change reference function to highest currently populated
`INITIATOR_THRESH`	INT	See table 12
`SINGLESBIAS`	REAL	See table 12
`WRITEPOPSFILE`	NONE	Instantaneously write out a restart file (POPSFILE)

the projection of the walker distribution onto a reference configuration (column 9, 11 and 23 – see below for details), as

$$E_{proj} = \frac{\langle D_0|H|\Psi_{FCIQMC}\rangle}{\langle D_0|\Psi_{FCIQMC}\rangle} \tag{57}$$

$$= E_0 + \sum_j \frac{n_j}{n_0}\langle D_0|H|D_j\rangle \tag{58}$$

It is clear that this estimate is sensitive to the number of walkers on the reference configuration (D_0), which is why the use of the `PROJE-CHANGEREF` option is encouraged if it is unclear which the most highly weighted configuration is from the outset of calculation. Initially, this reference will be chosen as the Hartree–Fock determinant, or the configuration resulting from the occupation of the highest weighted orbitals in the case of a prior CASSCF/MCSCF calculation. Unless the system is very strongly correlated and no dominant single reference exists, the projected energy estimate will usually have smaller errorbars, while at convergence the two values should provide relatively independent energy estimates which should agree to within random errors.

The output file contains the following columns of data every `INTERVAL` iterations from the calculation, unless the `NOMCOUTPUT` option is given.

1. Iteration number

2. Current shift value

3. Walker change from previous interval

4. Walker growth rate

5. Total walkers

6. Total annihilated walkers over last interval

7. Total walkers that died over last interval

8. Total spawned walkers over last interval

9. Averaged projected correlation energy estimate from beginning of calculation $\left(\sum_j \frac{\langle n_j H_{0j} \rangle}{\langle n_0 \rangle} \right)$

10. Averaged shift correlation energy estimate from 1000 iterations after entry into variable shift mode

11. Instantaneous projected correlation energy estimate averaged only over last `INTERVAL` iterations

12. Number of walkers currently residing on reference configuration

13. Number of walkers currently residing on single or double excitations of reference configuration (that contribute to the sum in Eq. 58)

14. Fraction of spawning attempts which are successful

15. Total number of currently occupied configurations

16. Time taken for last iteration

   The end of the output also contains a summary of the most highly weighted configurations at the end of the simulation.
   The **FCIQMCStats** file also contains this data, in a way that can easily be plotted, and also contains additional diagnostic information, detailed below

17. Fraction of successful spawning events to single, rather than double excitations

18. Range of occupied configuration number over between MPI processes – a measure of the parallel load-balancing of the simulation

19. Total imaginary-time which has elapsed in the calculation

20. Ignore column

21. Expected shift value obtained in fixed shift mode calculated from rate of growth of reference configuration

22. Expected shift value obtained in fixed shift mode calculated from rate of growth of total walker number

23. Projected total energy estimate averaged only over last `INTERVAL` iterations (col. 11 + reference energy)

24. Denominator of projected energy estimate averaged only over last `INTERVAL` iterations

25. Numerator of projected energy estimate averaged only over last `INTERVAL` iterations

26. Instantaneous normalised weight of reference configuration in FCIQMC wavefunction

27. Instantaneous normalisation factor of FCIQMC wavefunction

In addition to the **FCIQMCStats** file, unless the full scheme is being used, a file called **INITIATORStats** is created. Of interest in this file are column 7: the number of 'initiator' configurations, column 9: the number of walkers residing on 'initiator' configurations and column 11: the number of spawned walkers which were aborted due to the initiator approximation in the last `INTERVAL`

iterations. A **NodeFile** file is also created for each MPI process. Generally, these files will contain nothing that is not mirrored in the output file, however if the calculation terminates unexpectedly, these files will often contain information on the process-specific reason for this, and should be checked in this instance. At the end of a calculation, the output will print the highest weighted configurations in the calculation, as well as attempting an automatic error analysis on the final energies, which is discussed in the next section.

Especially for initial investigations into a new system, it can be instructive to graphically view the progress of the simulation as it proceeds, to determine whether the simulation can enter the variable shift phase, whether the population on the reference configuration is sufficient, or whether any other parameters should be adjusted via the `CHANGEVARS` facility. Examples of typical plots starting from a single walker are shown in Fig. 1 and 2.
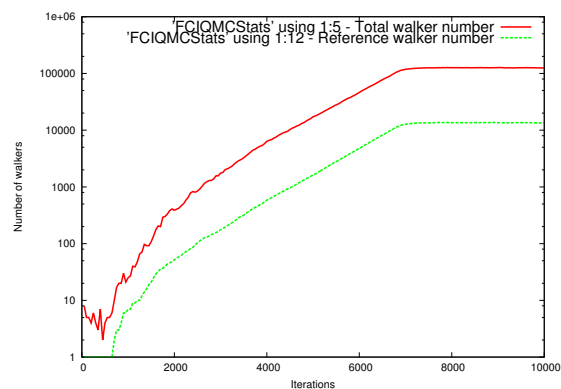
Figure 1: Growth in total walker population (column 5), and population on the reference configuration (column 12), obtained from the working directory of the calculation with the `GNUPLOT` package and the command `set logscale y; plot 'FCIQMCStats' u 1:5 w l, '' u 1:12 w l`.
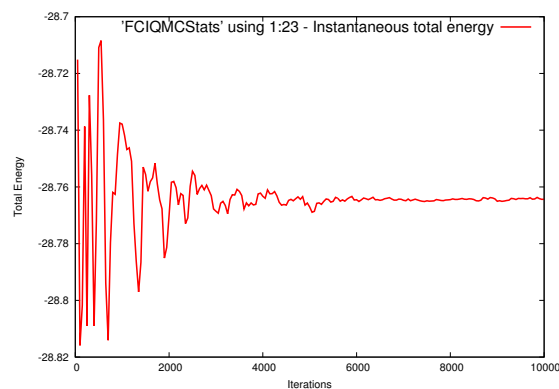
Figure 2: Instantaneous total energy estimate from column 23 of the **FCIQMCStats** file.

28.7   FCIQMC error analysis

Since the FCIQMC method is a stochastic simulation, care must be taken in order to obtain reliable energy averages and consequent errorbars. This can be difficult to automate reliably since a knowledge of the equilibration time is required for accurate estimates, as well as requiring serial correlation between the instantaneous estimates to be removed. This is traditionally done using a blocking analysis of the contributions to the energy. An attempt is made to estimate these and provide an automatic error analysis at the end of each FCIQMC calculation, which is then stored in the internal variable `FCIQMC_ERR`. This may often be good enough, however for production results it is recommended to provide some information manually to increase the accuracy and confidence in these errorbars. This can be done with the `REBLOCKSHIFT` and `REBLOCKPROJE` options.

If these options are present, then the FCIQMC calculation will be skipped, and the **FCIQMCStats** file from the previous calculation will be read back in to perform a blocking analysis. The values that these options take indicate the equilibration time in iterations that is to be given to the shift and projected energy estimates respectively before blocking to obtain accurate averaged energies and errors. These equilibration times can be estimated by plotting iteration against shift (columns 1:2 from the **FCIQMCStats** file) for the `REBLOCKSHIFT` value, and iterations against numerator and denominator (columns 1:24 and 1:25) for the `REBLOCKPROJE` value. It

may be important to consider the equilibration time for both of these columns for the projected energy estimate and give the maximum equilibration time, since the covariance between the quantities in the ratio is needed for an accurate error estimate.

Once these equilibration times have been provided and MOLPRO rerun in the same working directory with these options, a more accurate estimate of the averaged energies and errors will be provided. In addition, files called **Blocks_num**, **Blocks_denom**, **Blocks_proje** and **Blocks_shift** will be created. By plotting these files, an estimate for whether the random errors are reliable or not can be found, by checking whether the central limit theorem holds when the data is divided up into 'blocks' of different length. If column 1 (the number of resummed blocks) is plotted against column 3 (the estimated error between these blocks), with errorbars on the estimated error given in column 4, then a plateau should be observable as the number of blocks decreases. If the error increases continually as the number of blocks decreases, this is a sign that the serial correlation in the data may not have been removed yet, and continued running is advised. A log scale on the x-axis is recommended to observe the full range of block lengths. An example of one of these blocking graphs is shown in Fig. 3. If an incorrect number of blocks is automatically assumed for the plateau height, a more accurate final error can be found for the correct number of blocks in the relevant blocking file (**Blocks_proje** or **Blocks_shift**). For the projected energy, the minimum number of blocks should be calculated from the **Blocks_num** and **Blocks_denom** files, before the final error read from the corresponding number of blocks in the **Blocks_proje** file. Note that if the reference configuration changed during the initial run, this is not considered if the blocking is performed manually, and so the correlation energy obtained from manual reblocking will need to be added to previous changed reference energy.
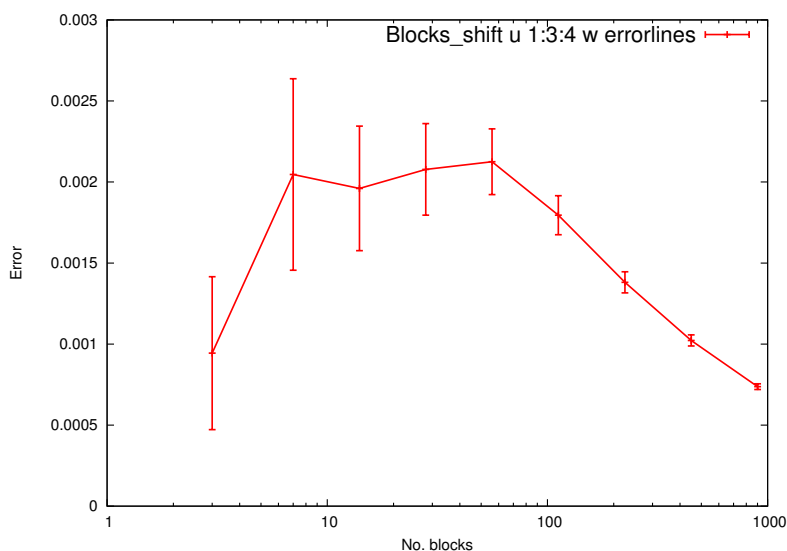
Figure 3: Example of well-converged blocking analysis, with plateau present. This would indicate an error of 0.002 Hartrees in the shift.

28.8   Examples

Examples: Closed-shell ground-state calculations for N_2 (results from one MPI process):

```
***, Nitrogen RHF FCIQMC calulation starting from MP2 distribution
if(.not.modul_neci) then
skipped
end if
memory,10,m
basis=cc-pvdz
geom={n1;n2,n1,1.0}
hf
{fciqmc,iterations=5930,spin=even,targetwalkers=100000, \
startmp1=20000,proje-changeref=10,writepopsfile=0,interval=10}
!{fciqmc,reblockshift=1200,reblockproje=1200}
```

> http://www.molpro.net/info/current/examples/nn_fciqmc.com

This yields

```
RESULTS FOR STATE 1.1
=====================

 Current reference energy                               -104.125525474439
 Projected correlation energy                             -0.200494452975
 Estimated error in Projected correlation energy           0.000267794947
 Shift correlation energy                                 -0.200119481250
 Estimated error in shift correlation energy               0.003568889015

 Projected and shift energy estimates agree within errorbars: EDiff =      0.00037497

 Total projected energy         -104.32601993 +/-    0.267795E-03
 Total shift energy             -104.32564496 +/-    0.356889E-02
 !FCIQMC STATE 1.1 ENERGY            -104.326019927414
 !FCIQMC STATE 1.1 FCIQMC_ERR            0.000267794947
```

To redo the error analysis, we can run again in the same directory, with the input line changed to include `fciqmc,reblockshift=1200,reblockproje=1200`, set to approximate equilibrated iterations, which returns

```
RESULTS FOR STATE 1.1
=====================

 Current reference energy                               -104.125525474439
 Projected correlation energy                             -0.200551071781
 Estimated error in Projected correlation energy           0.000257264982
 Shift correlation energy                                 -0.198657872098
 Estimated error in shift correlation energy               0.003792051242

 Projected and shift energy estimates agree within errorbars: EDiff =      0.00189320

 Total projected energy         -104.32607655 +/-    0.257265E-03
 Total shift energy             -104.32418335 +/-    0.379205E-02
 !FCIQMC STATE 1.1 ENERGY            -104.326076546221
 !FCIQMC STATE 1.1 FCIQMC_ERR            0.000257264982
```

High spin UHF calculations on atomic Nitrogen, including core correlation, and comparison to FCI (one MPI process):

```
***, High spin UHF basis iFCIQMC calculation on nitrogen atom, including core correlation
if(.not.modul_neci) then
skipped
end if
memory,50,m
geom={n}
basis=vdz
{uhf;wf,7,8,3}
{fciqmc,iterations=16000,targetwalkers=50000,proje-changeref=10,     \
writepopsfile=0,interval=10,memoryfacwalkers=2.0,memoryfacspawned=0.7;core}
{fci;core}
```

   http://www.molpro.net/info/current/examples/n_uhf_fciqmc.com

This returns

```
RESULTS FOR STATE 1.8
=====================

 Current reference energy                          -54.391114562126
 Projected correlation energy                       -0.089063298446
 Estimated error in Projected correlation energy     0.000031993101
 Shift correlation energy                           -0.088986058082
 Estimated error in shift correlation energy         0.000239973111

 Projected and shift energy estimates agree within errorbars: EDiff =      0.00007724

 Total projected energy          -54.48017786 +/-    0.319931E-04
 Total shift energy              -54.48010062 +/-    0.239973E-03
 !FCIQMC STATE 1.8 ENERGY              -54.480177860572
 !FCIQMC STATE 1.8 FCIQMC_ERR           0.000031993101

RESULTS FOR STATE 1.8
=====================

 Correlation energy                  -0.089000492121
 !FCI STATE 1.8 Energy                -54.480115054246
```

Excited spin state calculations of Be_2 using the SPIN option. With spin=odd set, it will converge to the lowest odd *S* spin state (one MPI process):

```
***, FCIQMC calculation on the lowest odd spin state of Be_2
if(.not.modul_neci) then
skipped
end if
geom={Be1;Be2,Be1,2.0}
basis=cc-pvdz
{hf;wf,8,1,0}
{fciqmc,iterations=18410,spin=odd,targetwalkers=100000, \
proje-changeref=10,writepopsfile=0,memoryfacwalkers=1.4,memoryfacspawned=0.3}
```

                              http:
 //www.molpro.net/info/current/examples/be2_highspin_fciqmc.com

This returns

```
RESULTS FOR STATE 1.1
=====================

 Current reference energy                              -28.418109510728
 Projected correlation energy                           -0.145376051508
 Estimated error in Projected correlation energy         0.000214957903
 Shift correlation energy                               -0.145621476634
 Estimated error in shift correlation energy             0.000167618454


 Projected and shift energy estimates agree within errorbars: EDiff =      0.00024543

 Total projected energy          -28.56348556 +/-    0.214958E-03
 Total shift energy              -28.56373099 +/-    0.167618E-03
 !FCIQMC STATE 1.1 ENERGY              -28.563730987362
 !FCIQMC STATE 1.1 FCIQMC_ERR            0.000167618454
```

which agrees with the fifth state (no symmetry) obtained with FCI:

```
RESULTS FOR STATE 5.1
=====================

 !FCI STATE 5.1 Energy              -28.563629184909
```

29   The DMRG program of the Chan group (BLOCK)

An interface exists to use the DMRG BLOCK program of the Chan group within Molpro. The source code of BLOCK can alternatively be obtained from WEBSITE. The parallel version is fully supportedunder MOLPRO. To use BLOCK in parallel, the flag

```
--no-helper-server
```

should be included on the MOLPROcommand line.

29.1   Installing BLOCK

MOLPROfetches a copy of the most recent stable BLOCK code, and compiles it. For this, the

```
--enable-Block
```

flag must be called when running `./configure\verb`.

29.2   Running BLOCK

29.2.1   Directives

The BLOCK program is invoked by the command

BLOCK, *options*
directives

The available options are summarized in Table 15. For more detailed descriptions, please refer to the BLOCK manual at WEBSITE.

To run a DMRG calculation with default settings, first specify the orbitals to correlate (the active space), using the CORE, OCC, and ORBITAL directives, similar to other correlated methods in MOLPRO. Then specify the maximum number of renormalized states to keep with MAXM. This runs a DMRG calculation with the default sweep schedule and a default orbital ordering. The default orbital ordering is determined by using the Fiedler vector method.

There may be times when one wants finer control of the DMRG calculation. In such cases, it is possible to specify the sweep schedule manually. A sweep schedule is set by directives, for example,

```
schedule, 0 50   1.0e-6 1e-06
schedule, 4 150  1e-6 1e-6
schedule, 6 200  1e-6  1e-6
schedule, 8 500  1e-8  0.0
```

Column 1 is the sweep number at which to change the parameters of the calculation, column 2 is the number of renormalized states, column 3 is the tolerance of the Davidson diagonalization, and column 4 is the noise to be added to the density matrix.

For finer control of the orbital ordering, we also provide a genetic algorithm minimization method of a weighted exchange matrix. The genetic algorithm usually provides a sensible orbital ordering, although it can take a long time for large numbers of orbitals.

To control the orbital ordering manually use the reorder directive with the indices of the reordered orbitals,

```
reorder, 3, 2, 6, 1, 5, 4
```

If one wishes to use the `Molpro` storage order (*i.e.* no reorder), add the following option: reorderorb=0.

To set non-default weights in state-averaged calculations, use the `weights` directive,

```
weights, 0.3, 0.7
```

29.2.2   Restarting calculations

The `BLOCK` program periodically checkpoints the calculation. To restart a DMRG calculation from a saved checkpoint, use the following command,

```
restart, FCIDUMP=dumpfile_name, SCRATCH=dir_name
```

where *dumpfile_name* and *dir_name*, are the name of the orbitals file and scratch directory, respectively.

Table 15: Full options for BLOCK

Option	Alias	Default value[a]	Meaning
MAXM		500	Maximum size of blocks; must always be specified
FIEDLER		1	Default ordering optimization
GAOPT		0	Orbital ordering optimization
REORDERORB		1	If 0, turn off all orbital ordering
MAXITER		30	Maximum no. of sweep iterations
SWEEP_TOL		1E-09	Sets the final DMRG tolerance
ONEDOT		0	One-dot sweeps only
TWODOT		0	Two-dot sweeps only
ONEPDM		0	Calculates the 1-PDM
TWOPDM		0	Calculates the 2-PDM
DRYRUN		0	Writes FCIDUMP and DMRG input file only
RESTART		0	DMRG restart
FCIDUMP		NA	For restart only. Specify name of dump file
SCRATCH		NA	For restart only. Specify name of the scratch directory
IRREP		1	Irreducible representation of state
NROOTS		1	Number of roots in state-averaged calculation
OUTPUTLEVEL		0	Set to -1 for more verbose molpro output, 1 for full output
NELEC		-1	Number of electrons
TWODOT_TO_ONEDOT		-1	Switch from two-dot to one-dot

a) -1 means default value taken from `BLOCK`

Examples:

Closed-shell ground-state calculations for sto-3g($10e^-$, $7o$) H_2O using default parameters.

```
angstrom
geomtyp=xyz
geometry={
O         .000000        .000000        .000000
H        0.700000        .000000       0.700000
H       -0.700000        .000000       0.700000
}
basis=sto-3g
{rhf}
{dmrg, maxm=50
core, 0, 0, 0, 0
occ,  4, 2, 1, 0
}
```

          http://www.molpro.net/info/current/examples/h2o_dmrg.com


```
 METHOD                E
 HF               -74.961135
 DMRG (M=50)      -75.017832
 FCI (comparison) -75.017832
```


Closed-shell ground-state calculations for the localized π-active space ($8e^-$, $8o$) of octatetraene in minimal basis using default parameters.

```
symmetry, nosym
geomtyp = xyz
angstrom
geometry = {
 C       2.35401      -6.07788      -0.00000
 C       3.40526      -5.24546      -0.00000
 C       3.28692      -3.88730      -0.00000
 C       4.33880      -3.04529      -0.00000
 C       4.21017      -1.68428      -0.00000
 C       5.26204      -0.84227      -0.00000
 C       5.14370       0.51589      -0.00000
 C       6.19495       1.34830      -0.00000
 H       1.42023      -5.73687      -0.00000
 H       2.49445      -7.06217      -0.00000
 H       4.31219      -5.65764      -0.00000
 H       2.36872      -3.49894      -0.00000
 H       5.25770      -3.43408      -0.00000
 H       3.29126      -1.29550      -0.00000
 H       6.18025      -1.23064      -0.00000
 H       4.23677       0.92806      -0.00000
 H       7.12873       1.00730      -0.00000
 H       6.05451       2.33259      -0.00000
}
basis=sto-3g
{rhf}
{locali, pipek, locmethod=3
thresh, 1d-12, 1e-5
core, 25
occ, 33
save, 2102.2
}
{dmrg, maxm=250
orbital, 2102.2
core, 25
occ, 33
}
```

                                   http:
  //www.molpro.net/info/current/examples/octatetraene_dmrg.com


```
 METHOD              E
 HF               -304.80229195
 DMRG             -304.97074163
 FCI (comparison) -304.97074163
```

An example of a non-default orbital ordering and non-default scheduling for the localized π-active space ($18e^-$, $18o$) of tetracene in minimal basis.

```
angstrom
symmetry, nosym
geomtyp = xyz
geometry = {
 C        5.7789901801      -1.5248905095        0.0000000000
 C        7.0401293170      -2.2085591442        0.0000000000
 C        8.2184825553      -1.5143631833        0.0000000000
 C        8.2184829496      -0.0829976070        0.0000000000
 C        7.0401299670       0.6111988751        0.0000000000
 C        5.7789904096      -0.0724690829        0.0000000000
 C        4.5632188446       0.6081247534        0.0000000000
 C        3.3272486621      -0.0722677743        0.0000000000
 C        3.3272486617      -1.5250913599        0.0000000000
 C        4.5632186002      -2.2054838807        0.0000000000
 H        7.0387315422      -3.2964281036        0.0000000000
 H        9.1661920542      -2.0465927646        0.0000000000
 H        9.1661927656       0.4492313275        0.0000000000
 H        7.0387324522       1.6990678777        0.0000000000
 H        4.5629588592       1.6967700679        0.0000000000
 H        4.5629585552      -3.2941290592        0.0000000000
 C        2.0912785157       0.6081247584        0.0000000000
 C        2.0912787599      -2.2054838850        0.0000000000
 C        0.8755071337      -1.5248905103        0.0000000000
 C        0.8755069045      -0.0724690822        0.0000000000
 H        2.0915384850       1.6967700763        0.0000000000
 H        2.0915387880      -3.2941290672        0.0000000000
 C       -0.3856326333       0.6111988735        0.0000000000
 C       -1.5639856245      -0.0829976283        0.0000000000
 C       -1.5639852310      -1.5143631626        0.0000000000
 C       -0.3856319836      -2.2085591425        0.0000000000
 H       -0.3842351293       1.6990678801        0.0000000000
 H       -2.5116954264       0.4492313184        0.0000000000
 H       -2.5116947162      -2.0465927555        0.0000000000
 H       -0.3842342185      -3.2964281058        0.0000000000
}
basis=sto-3g
{rhf}
{merge
orbital, 2100.2
move
rotate, 54.1, 48.1, 90
rotate, 52.1, 46.1, 90
rotate, 70.1, 69.1, 90
save, 2100.2
}
{rhf
maxit, 1}
{locali, pipek, locmethod=3
thresh, 1d-12, 1e-5
core, 51
occ, 69
save, 2102.2
}

{dmrg, maxiter=8, outputlevel=1
orbital, 2102.2
core, 51
occ, 69
reorder, 9,8,13,17,7,10,15,6,5,11,14,4,3,18,16,12,2,1
schedule,  0,  100, 1e-05, 1e-04
schedule,  4,  250, 1e-05, 1e-04
}
```

 http://www.molpro.net/info/current/examples/tetracene_dmrg.com

```
METHOD                  E
HF                 -680.245827
DMRG (M=100)       -680.349299
DMRG (M=250)       -680.578887
```

30 AB INITIO MULTIPLE SPAWNING DYNAMICS

AIMS is a multi-state first-principles dynamics program written by
Benjamin G. Levine, Joshua D. Coe, Aaron M. Virshup, Hongli Tao, Christian R. Evenhuis,
William J. Glover, Toshifumi Mori, Michal Ben-Nun and Todd J. Martinez.

Bibliography:

B. G. Levine, J. D. Coe, A. M. Virshup and T. J. Martinez, Chem. Phys. 347, 3 (2008).
M. Ben-Nun and T. J. Martinez, Chem. Phys. Lett. 298 57 (1998).

All publications resulting from use of this program must acknowledge the above. See also:

B. G. Levine and T. J. Martinez, J. Phys. Chem. A 113, 12815 (2009).
T. J. Martinez, Acc. Chem. Res. 39, 119 (2006).

The AIMS module implements the Ab Initio Multiple Spawning method to perform dynamics calculations on multiple electronic states. Although the program was designed for non-adiabatic dynamics with CASSCF wavefunctions, it can be used quite generally for first principles molecular dynamics, provided that nuclear gradients are available.

AIMS provides a description of a time-evolving molecular wavepacket with a multi-configurational, product gaussian function basis. To allow the size of the basis set to remain small while describing the wavepacket dynamics, the centers of the full-dimensional gaussian functions follow classical trajectories while their widths are kept fixed (the frozen Gaussian approximation). When these classical trajectories encounter regions of large non-adiabatic coupling to another electronic state, new basis functions are *spawned* on the coupled state and the Time Dependent Schrödinger Equation is solved in order to describe population transfer between the electronic states. In this way, the description of the wavepacket can be systematically improved by increasing the number of initial trajectory basis functions, while reducing the coupling threshold at which trajectories spawned. Alternatively, spawning can be disabled, and the method will reduce to traditional first-principles classical molecular dynamics when a single trajectory basis function is used.

30.1 Compilation

AIMS is compiled as a component of Molpro; however, it requires a fortran 2003 compiler and is disabled unless the preprocessor variable MOLPRO_f2003 is defined, which depends on the version of your compiler.

30.2 Structure of the input

The AIMS program is controlled by the Molpro input deck and a number of external text files:

30.2.1 Molpro input deck

The AIMS program is invoked by the command AIMS. The details of the electronic structure are defined in specifically named procedures. At a minimum, for first principles dynamics, AIMS requires the following structure to the input deck:

```
SYMMETRY, nosym
ORIENT, noorient
GEOMTYP=xyz
GEOMETRY={
```
Initial atom specifications. Must match ordering of Geometry.dat, but need not be the same geometry
```
}
```

`BASIS=`{*Basis specifications.*}

```
MPINIT={
```
Electronic structure routines for initial wavefunction
```
}
```

```
MPCALC={
```
Electronic structure routines for dynamics calculations. At a minimum, must include:
```
ener(1)=energy(1)
ener(2)=energy(2) etc
force
}
```

`AIMS,` *dir*

where

dir   (string) Relative directory to AIMS input files. (Default is working directory).

Note: the above is appropriate only for first-principles dynamics (without spawning). CASSCF spawning calculations require additional procedures and a specific structure to the MPINIT and MPCALC procedures. See the examples in section 30.5.

30.2.2   Control.dat

Control.dat is a fortran NAMELIST file storing the main parameters (in au) of an AIMS simulation. At the end of the file, one can optionally specify user-defined atom types (see below).

Table 16: Initialization

Parameter	Options (Default)	Description
Required parameters:		
NumStates	Integer	Number of electronic states.
InitState	Integer	Initial electronic state.
NumParticles	Integer	Number of atoms.
Common parameters:		
IMethod	0	First principles dynamics (No NACV).
	(1)	CASSCF dynamics, with NACV.
IRestart	(0)/1	Restart the calculation when set to 1.
RestartTime	Real (-100.0)	Time from which to restart in Checkpoint.txt
		If disabled, use Last_Bundle.txt.
IRndSeed	Integer (0)	Initial condition random number seed.
InitialCond	('NoSample')	Read initial conditions from Geometry.dat.
	'Wigner'	Sample from the Wigner distribution of harmonic
		normal modes in Frequencies.dat.
	'Quasiclassical'	As above, for the Quasiclassical distribution.
	'Boltzmann'	As above, for the Boltzmann distribution.
Temperature	Real (0.0)	Temperature (Kelvin) of the initial conditions.
Expert parameters:		
InitBright	Logical (.false.)	Select optically brightest of InitState
		and IDark as initial state.
InitDark	Logical (.false.)	As above, but for darkest state.
IDark	Integer (-1)	See above.
InitGap	Real (0.0)	Select initial ground-excited energy gap
		to within $\pm 0.5 \times$ InitGapWidth.
InitGapWidth	Real (0.0)	See above.
IRestartTraj	Integer array (0)	Subset of trajectories to restart from. Can
		restart a single dead trajectory.
NumInitBasis	Integer (1)	Number of initial coupled basis functions.
FirstGauss	Logical (.false.)	Place the first basis function at the
		molecular origin (that of Geometry.dat),
		with zero momentum.
MirrorBasis	Logical (.false.)	Mirror the initial basis on another
		electronic state, MirrorState.
MirrorState	Integer (1)	See above.
EnergyAdjust	Logical (.false.)	Adjust momenta of mirrored basis (along
		NACV) to match original basis energy.
SharpEnergy	Logical (.false.)	Adjust momenta of all initial basis functions
		to match first basis function energy.

Table 17: Integration and numerics

Parameter	Options (Default)	Description
Required parameters:		
TimeStep	Real	Simulation timestep.
SimulationTime	Real	Simulation length.
Common parameters:		
ExShift	Real (0.0)	Apply a shift of +ExShift to diagonals of Hamiltonian to improve amplitude/phase propagation. Good choice is average potential energy of ground and excited states.
CoupTimeStep	Real (TimeStep/4)	Timestep to use in regions of large nonadiabatic coupling.
Expert parameters:		
TimeStepRejection	Logical (.true.)	Enables adaptive time-stepping when encountering integration problems.
MinTimeStep	Real (CoupTimeStep/4)	Minimum timestep to use when adaptive time-stepping.
DieOnMinStep	Logical (.true.)	Stop calculation if minimum timestep is reached.
EnergyStepCons	Real (0.005)	Allowed violation of classical energy conservation before timestep is rejected.
NormCons	Real (0.25)	Permitted deviation in Norm from beginning of simulation.
RejectAllStateFlip	Logical (.true.)	Reject a timestep if any two electronic states flip. If .false. then only reject if state is coupled to occupied state.
OlapThresh	Real (0.001)	Threshold overlap between two trajectories below which matrix elements not calculated.
RegThresh	Real (0.0001)	Threshold to regularize the overlap matrix before inversion.
Constrain	Logical (.false.)	Apply geometric contraints? If yes, supply Constraints.dat

Table 18: Spawning

Parameter	Options (Default)	Description
Common parameters:		
CSThresh	Real (0.1)	Threshold Coupling, above which to spawn.
PopToSpawn	Real (0.1)	Minimum population a trajectory must have before it can spawn.
OMax	Real (0.8)	Prevent spawning if overlap of spawned trajectory with existing basis greater than Omax.
MaxTraj	Real (100)	Maximum number of allowed trajectories. Above which, spawning is disabled.
IgnoreState	Integer (0)	Stop dynamics of trajectories on IgnoreState if not coupled for at least DecoherenceTime. Choose 1 if only interested in excited states.
MaxEDiff	Real (0.03)	Energy gap threshold for calculating nonadiabatic couplings, above which, coupling taken to be zero.
Expert parameters:		
DecoherenceTime	Real (200.0)	See above.
SpawnCoupV	Logical (.false.)	Use Coup.velocity as criterion for spawning rather than Coupling magnitude alone.
EShellOnly	Logical (.true.)	Require spawned trajetories to have same classical energy as parent by adjusting momentum along NACV.

Table 19: Output

Parameter	Options (Default)	Description
Common parameters:		
zAllText	Logical (.false.)	Write all output files?
zEDatFile	Logical (.true.)	Write Energy file?
zNDatFile	Logical (.true.)	Write Population file?
zTrajFile	Logical (.false.)	Write Trajectory files?
zAmpFile	Logical (.false.)	Write Amplitude files?
zPotEnFile	Logical (.false.)	Write Potential Energy files?
zXYZ	Logical (.false.)	Write XYZ Geometry files?
zCoupFile	Logical (.false.)	Write Coupling files?
zChargeFile	Logical (.false.)	Write Charge files?
zDipoleFile	Logical (.false.)	Write Dipole files?
zTDipoleFile	Logical (.false.)	Write Transition Dipole files?
zQMRRFile	Logical (.false.)	Write $\langle r^2 \rangle$ quadrupole moment files?
zCIVecFile	Logical (.false.)	Write CI Vector files? (Not recommended for large CI)
zCorrfile	Logical (.false.)	Write Correlation function file?
zBundMatFile	Logical (.false.)	Write Matrices (H, S, etc)?
WriteMolden	Logical (.false.)	Write Molden files?
MoldenStep	Integer (200)	How often (every number of timesteps) Molden files are written.
RestartStep	Integer (4)	How often (every number of timesteps) Restart files are written.
Expert parameters:		
NStepToPrint	Integer (1)	How often (every number of timesteps) output files are written.
WriteEveryStep	Logical (.true.)	Write output every timestep, including subtimesteps of adaptive propagation. Overrides NStepToPrint.
NBonds	Integer (0)	Number of bond lengths to print. Define IBond below.
IBond(2,NBonds)	Integer (0)	List of atom indices that are bonded. See NBonds above.
NAngles	Integer (0)	Number of bond angles to print. Define IAngle below.
IAngle(3,NAngles)	Integer (0)	List of atom indices that define bond angles.
NDihedrals	Integer (0)	Number of dihedral angles to print. Define IDihedral below.
IDihedral(4,NDihedrals)	Integer (0)	List of atom indices that define dihedral angles.
NPyrams	Integer (0)	Number of pyramidalization angles to print.[2] Define IPyram below.
IPyram(4,NPyrams)	Integer (0)	List of atom indices that define pyramidalization angles.

User-defined atom types

AIMS recognizes the atoms H, C, N, O, S, F, Cl and assigns appropriate masses and gaussian width parameters for these atoms. If you wish to modify these defaults, or if your system contains other atoms, you can define custom atom types at the end of Control.dat. The format is (in atomic units):

```
n
AtomName(1) AtomicNumber(1) AtomicMass(1) GaussianWidth(1)
:
AtomName(n) AtomicNumber(n) AtomicMass(n) GaussianWidth(n)
```

30.2.3 Geometry.dat

Geometry.dat contains the molecular geometry that will be used in the generation of initial conditions. Optionally, the momenta can also be specified, which is useful if
`InitialCond='NoSample'`:

```
UNITS=ANG or UNITS=BOHR
natom
AtomName(1)     x(1)        y(1)        z(1)
:
AtomName(natom) x(natom)    y(natom)    z(natom)
Momenta:
AtomName(1)     px(1)       py(1)       pz(1)
:
AtomName(natom) px(natom)   py(natom)   pz(natom)
```

---

[2]For definition, see J. Phys. Chem. A 113, 12815 (2009)

30.2.4   FrequenciesMP.dat

FrequenciesMP.dat contains the normal-mode frequencies and displacements of the molecule in its initial geometry and electronic state (usually the ground state). This information is used in the generation of initial conditions. If `InitialCond`$\neq$`'NoSample'` then either this file, Hessian.dat or Frequencies.dat (Sections 30.2.5 and 30.2.6 respectively) must be present. The format of FrequenciesMP.dat follows the Molpro output of a Frequencies calculation:

```
6
                              1 A        2 A        3 A        4 A        5 A
Wavenumbers [cm-1]         1116.71    1725.49    1728.47    3435.76    3566.01
Intensities [km/mol]        157.34      17.93      16.24       1.67       0.53
Intensities [relative]      100.00      11.40      10.32       1.06       0.33
          GX1             -0.10597   -0.00088   -0.00021   -0.03801   -0.00009
          GY1              0.00067   -0.05838   -0.02628   -0.00017   -0.07554
          GZ1              0.00004    0.02639   -0.05807    0.00078    0.00226
          GX2              0.49134   -0.14946    0.19728    0.17300   -0.07729
          GY2              0.03972    0.54519    0.46553   -0.12339    0.02439
          GZ2             -0.19161    0.21763   -0.00782    0.51879   -0.19043
          GX3              0.49290   -0.09010   -0.22955    0.17771   -0.20720
          GY3              0.13665    0.43154   -0.28739   -0.39612    0.35792
          GZ3              0.13722   -0.52910    0.11024   -0.37702    0.36169
          GX4              0.48838    0.25184    0.03520    0.17755    0.28570
          GY4             -0.18573   -0.16545    0.18702    0.52182    0.66736
          GZ4              0.05376   -0.05521    0.70450   -0.15258   -0.20268


                              6 A
Wavenumbers [cm-1]         3570.66
Intensities [km/mol]          0.61
Intensities [relative]        0.39
          GX1             -0.00060
          GY1             -0.00245
          GZ1             -0.07574
          GX2              0.28798
          GY2             -0.16745
          GZ2              0.68133
          GX3             -0.20790
          GY3              0.37733
          GZ3              0.33817
          GX4             -0.07175
          GY4             -0.17584
          GZ4              0.03308
```

```
http://www.molpro.net/info/current/examples/FrequenciesMP.dat
```

Note: Only the real, non-zero frequencies should be included in this file (i.e. those corresponding to vibrations). The first line of the file must be the number of frequencies. See section 47 for details on how to perform a normal-mode frequencies calculation in Molpro.

30.2.5   Hessian.dat

As an alternative to FrequenciesMP.dat, AIMS can generate the normal mode frequencies after reading in the Hessian from Hessian.dat. The format of this file is:

```
natom
Hess(1,1) Hess(2,1) ... Hess(3*natom,3*natom)
```

Note: the Hessian should not be mass weighted. It is permissible to have carriage returns in the list of Hessian components.

30.2.6   Frequencies.dat

As an alternative to FrequenciesMP.dat and Hessian.dat, AIMS can read in normal-mode frequencies and vectors in AIMS format in Frequencies.dat. The format of this file is:

```
natom    nmodes
freq(1) freq(2) ... freq(nmodes)
modevec(1,1) modevec(2,1) ... modevec(3*natom,nmodes)
```

Note: Frequencies must be in cm^{-1}, but normal mode vectors can be mass scaled or not- AIMS will detect. Also, it is permissible to have carriage returns in the list of frequencies and mode vectors. This file is generated by AIMS if either FrequenciesMP.dat or Hessian.dat is used initially.

30.2.7   Constraints.dat

If `Constraint=.true.` then Constraints.dat must be supplied. This is a fortran NAMELIST file that defines the geometric constraints in the system. These constraints are enforced with the RATTLE algorithm. The parameters contained in this file are:

Table 20: Constraint parameters

Parameter	Options (Default)	Description
NumBonds	Integer (0)	Number of bond lengths to constrain Define IBondPtcles below.
IBondPtcles(2,NumBonds)	Integer (0)	List of atom indices that are bonded. See NumBonds above.
NumAngles	Integer (0)	Number of bond angles to constrain. Define IAnglePtcles below.
IAnglePtcles(3,NumAngles)	Integer (0)	List of atom indices that define bond angles.
NComAtoms	Integer (0)	Number of atoms that define the center-of-mass constraint. Define ICOMPtcles below.
ICOMPtcles(NComAtoms)	Integer (0)	List of atom indices that define the center of mass.
Toler	Real (1E-4)	Rattle tolerance
MaxIts	Integer (10000)	Maximum number of Rattle iterations

Note, a maximum of 1000 constraints is allowed.

30.3   Running a CASSCF spawning calculation

This section gives an overview of how to set up and run a CASSCF ab initio multiple spawning calculation.

1) The first step is to create a molpro input deck that controls how the CASSCF electronic structure calculations are performed. AIMS requires a fairly complicated structure to the molpro deck and it is highly recommended that you use the ethylene CASSCF example as a starting point (section 30.5). Control.dat should then be modified for your system and desired simulation parameters (section 30.2.2).

2) Next, the initial conditions should be defined. This involves providing an initial geometry in Geometry.dat (section 30.2.3) and normal-mode frequencies and displacements in FrequenciesMP.dat (section 30.2.4), which will be used to generate a phase-space distribution that the initial conditions sample. Alternatively, one can also provide momenta in Geometry.dat and set `InitialCond='NoSample'` in Control.dat, and directly specify the initial conditions.

3) The AIMS calculation is then initiated by running molpro on the input deck, in the usual fashion. In order to sample different initial conditions, multiple AIMS simulations should be run with different values of the random number seed `IRndSeed` (or different Geometry.dat files) - each of these should be run in a unique directory.

30.4   Output

Beyond the regular molpro output, which contains the electronic structure output, AIMS writes to a number of text files, depending on the output parameters in Control.dat (section 30.2.2). All values are given in atomic units unless otherwise specified. Electronic properties of a trajectory are evaluated at the center geometry of the trajectory basis function.

FMS.out	Current progress of simulation and any warning/error messages.
E.dat	Wavepacket energies. QM energies are expectation values of the quantum operators, including coherences between the trajectory basis functions. CL energies are averages of the trajectories' classical energies, weighted by the amplitude norm of each trajectory.
N.dat	Electronic populations, the sum of which should be conserved.
TrajDump.i	Dynamic variables for trajectory i.
Amp.i	Amplitudes of trajectory i. Note: since the product Gaussian basis is non-orthogonal, the amplitude norms do not necessarily sum to 1.
PotEn.i	Electronic energies for trajectory i. The last column displays the total classical energy of the trajectory, which should be conserved.
positions.i.xyz	Snapshots of trajectory i's center geometry in XYZ format (Angstrom).
Coup.i	Nonadiabatic couplings of each state to the occupied state for trajectory i. The first nstate columns contain the magnitude of coupling vectors and the last nstate columns contain the projection of the coupling onto the velocity vector.
Charge.i	Partial atomic charges corresponding to the occupied electronic state of trajectory i. The molpro input deck must contain a Mulliken population analysis directive in the `MPCALC` procedure.
Dipole.i	Dipole moments of each electronic state for trajectory i.
TDip.i	Transition dipoles from ground to excited states for trajectory i.
QMRR.i	Isotropic quadrupole moment $\langle r^2 \rangle$ of each electronic state for trajectory i. The molpro input deck must contain `EXPEC,QMRR`.
CIVec.i	CI Vectors for each state of trajectory i.
CFxn.dat	The overlap correlation function $\langle \Psi(t) | \Psi(0) \rangle$.
H.dat	Hamiltonian matrix.
S.dat	Overlap matrix. Note: the overlap between trajectories on different states is zero, but is displayed here as if they were on the same state.
SDot.dat	The time derivative of the Overlap matrix.
i.j.molf	Molden file for trajectory i at time j.
Checkpoint.txt	Restart file with history.
Last_Bundle.txt	Restart file for the last written timestep.
Spawn.log	Details of successful spawns.

| FailSpawn.log | Details of unsuccessful spawns. |
| Spawn.i | XYZ file of geometry where trajectory i was spawned. |

30.5 Examples

The following two examples show how AIMS can be run in either single-state first-principle molecular dynamics mode, or multi-state spawning mode. The parameters found in these input files were chosen for illustrative purposes and are not necessarily appropriate for your system of interest. It is recommended the literature be consulted before performing AIMS simulations.

Ethylene Hartree-Fock First-Principles Molecular Dynamics

See examples/aims_ethyl_HF

Ethylene CASSCF Spawning Dynamics

See examples/aims_ethyl_CASSCF

31 SMILES

SMILES is a package for molecular integrals with Slater functions implemented by J. Fernandez Rico, R. Lopez, G. Ramirez, I. Ema, D. Zorrilla and K.Ishida. It combines several techniques for the evaluation of the different types of integrals, a summary of which can be found in J. Fernandez Rico, R. Lopez, G. Ramirez, I. Ema, J. Comput. Chem., 25, 1987-1994 (2004) and J. Fernandez Rico, I. Ema, R. Lopez, G. Ramirez and K. Ishida, *SMILES: A package for molecular calculations with STO* in Recent Advances in Computational Chemistry. Molecular Integrals over Stater Orbitals, Telhat Ozdogan and Maria Belen Ruiz eds., ISBN ...

This code is not included in binary versions of Molpro, and by default the code is not included when building from source code; one should use the `--enable-slater` configure option to enable compilation of the code.

The SMILES module is invoked by the `intyp='SLATER'` card. Name for ancillary files generated by the package can be supplied by `SLFILES=`*filename*. Default name is 'slscratch'.

Three-center two-electron integrals of types $(AB|AC)$ and $(AB|CD)$ are computed by means of Gaussian expansions (STO-nG). The default length of the expansions is 9 (STO-9G). However, integrals obtained with STO-9G expansions may have not sufficient accuracy for post-HF calculations, specially with high quality basis sets. In these cases, the length of the expansions can be changed setting the variable `NGSSTO=` *number of gaussians*. Though a maximum of `NGSSTO=30` is allowed, the lengths of the expansions actually available in the package depend on the (n,l) quantum numbers. If an expansion not included is required, the program takes the largest currently available.

Program limitations: In the current version, a maximum of 511 basis functions is allowed, and contracted functions cannot be used.

31.1 INTERNAL BASIS SETS

The following internal basis sets are available.

Table 21: Internal basis sets in SMILES

Basis set	Atoms			
	H-He	Li-Be	B-Ne	Na-Ar
VB1	[3,1]	[5,1]	[5,3,1]	—
CVB1	[3,1]	[6,2]	[6,4,1]	—
FVB1	[3,2,1]	[5,3,1,1]	[5,4,2,1]	—
ZVB1	[3,1]	[4,3,1]	[4,3,1]	[6,5,1]
VB2	[4,2,1]	[6,2,1]	[6,4,2,1]	—
CVB2	[4,2,1]	[7,3,2]	[7,5,3,1]	—
ZVB2	[4,2,1]	[5,4,2,1]	[5,4,2,1]	[7,6,2,1]
VB3	[5,3,2,1]	[7,3,2,1]	[7,5,3,2,1]	—
CVB3	[5,3,2,1]	[8,4,3,2]	[8,6,4,3,1]	—
ZVB3	[5,3,2,1]	[6,5,3,2,1]	[6,5,3,2,1]	[8,7,3,2,1]

31.2 EXTERNAL BASIS SETS

External basis sets can be supplied in a file that must be located in the working directory. Each record will contain the following data (free format):

I N L EXP NG

where:

I: atom type index (integer)
N: principal quantum number (integer)
L: angular quantum number (integer)
EXP: exponent (double precision)
NG: number of gaussians for the $(AB|AC)$ and $(AB|CB)$ integrals (integer)

Atom type index is used to establish the correspondence between the basis functions and the centers (atoms). All records having the same value of I will define the basis set for all the atoms of the corresponding type.

Example:

For a calculation on the CO_2 molecule with the following geometry data:

```
Geometry={
    3

C1, 0.000000000000E+00, 0.000000000000E+00, 0.000000000000E+00
O2, 0.000000000000E+00, 0.000000000000E+00,-0.117963799946E+01
O3, 0.000000000000E+00, 0.000000000000E+00, 0.117963799946E+01
}
```

Clementi and Roetti's Single Zeta basis set could be supplied in an external file like:

```
1   1   0        5.67263   12
1   2   0        1.60833   12
1   2   1        1.56788   12
2   1   0        7.65781   12
2   2   0        2.24588   12
2   2   1        2.22662   12
```

The first three records define the basis set for atoms of the first type (carbon in this example), and the following three, the basis set for atoms of the second type (oxygen).

NG is mandatory even in case of diatomics, though gaussian expansions will not be used, the value of NG being irrelevant in this case.

31.3 Example

Example using internal basis set for H_2O.

```
memory,20,m

if(.not.modul_slater) then
exit
end if

geomtyp=zmat
geometry={
o;h1,o,r;h2,o,r,h1,theta
}
r=0.96 ang
theta=102

intyp='SLATER'
basis=VB1

hf
ccsd(t)
multi
mrci
```

http://www.molpro.net/info/current/examples/slater.com

32 LOCAL CORRELATION TREATMENTS

32.1 Introduction

The local correlation program of MOLPRO can currently perform closed-shell LMP2, LMP3, LMP4(SDTQ), LCISD, LDCSD, LQCISD(T), and LCCSD(T) calculations. For large molecules, all methods scale linearly with molecular size, provided very distant pairs are neglected, and the integral-direct algorithms are used.

Much higher efficiency is achieved by using density fitting (DF) approximations to compute the integrals. Density fitting is available for all local methods up to LCCSD(T), as well as for analytical LMP2 gradients. Only iterative triples methods like LCCSDT-1b can currently not be done with density fitting.

The errors introduced by DF are negligible, and the use of the DF methods is highly recommended. Linear scaling can be obtained in DF-LMP2 using the `LOCFIT` option (see Ref. 11); in DF-LCCSD(T), the most important parts also scale linearly, but some transformation steps scale quadratically.

Energy gradients are available for LMP2, DF-LMP2, DF-SCS-LMP2, and LQCISD (in the latter case only for `LOCAL=1`, i.e. the local calculation is simulated using the canonical program, and savings only result from the reduced number of pairs).

Local explicitly correlated methods (DF-LMP2-R12 and DF-LMP2-F12 are described in section 35.

Before using these methods, it is strongly recommended to read the literature in order to understand the basic concepts and approximations. A recent review [1] and Ref. [2] may be suitable for an introduction.

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Review:
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[4] M. Schütz, *Low-order scaling local electron correlation methods. III. Linear scaling local perturbative triples correction (T)*, J. Chem. Phys. **113**, 9986 (2000).
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[8] G. Hetzer, P. Pulay, H.-J. Werner, *Multipole approximation of distant pair energies in local MP2 calculations*, Chem. Phys. Lett. **290**, 143 (1998).

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LMP2 Gradients and geometry optimization:
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second-order Møller-Plesset perturbation theory using density fitting approximations, J. Chem. Phys. **121**, 737 (2004).

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[24] O. Masur, D. Usvyat and M. Schütz *Efficient and accurate treatment of weak pairs in local CCSD(T) calculations*, J. Chem. Phys., **139**, 164116 (2013).
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32.2 Getting started

The local correlation treatment is switched on by preceding the command name by an `L`, i.e., by using the `LMP2`, `LMP3`, `LMP4`, `LQCISD`, `LCCSD`, `LDCSD`, or `LCISD` commands.

The `LQCISD` and `LCCSD` commands can be appended by a specification for the perturbative treatment of triple excitations (e.g., `LCCSD(T0)`):

`(T)`	Use the default triples method. Currently this is T0.
`(T0)`	Non-iterative local triples. This is the fastest triples option. It is usually sufficiently accurate and recommended to be used in most cases.
`(T1)`	T0 plus one perturbative update of the triples amplitudes. If the accuracy of T0 is insufficient (very rarely the case!), this can be used to improve the accuracy. The computational cost is at least twice as large as for T0. In contrast to T0, the triples amplitudes must be stored on disk, which can be a bottleneck in calculations for large molecules. Also the memory requirements are substantially larger than for T0.
`(T1C)`	As T1, but a caching algorithm is used which avoids the simultaneous storage of all triples amplitudes on disk (as is the case for `(T1)` or `(TF)`). Hence, T1C requires less disk space but more CPU-time than T1. The more disk space is made available for the caching algorithm (using the T1DISK option on the local card, see below), the less CPU time is used.

(TF)	Full iterative triples calculation. With full domains and without weak pair approximations this gives the same result as a canonical (T) calculation. Typically, 3-5 iterations are needed, and therefore the computational effort is 2-3 times larger than for (T1). The disk and memory requirements are the same as for T1. The T0 energy is also computed and printed. `TFULL` and `FULL` are aliases for `TF`.
(TA)	As TF, but the T1 energy is also computed. Since the first iteration is different for T1, the convergence of the triples iterations is slightly different with TF and TA (TF being somewhat faster in most cases). `TALL` and `ALL` are aliases for `TA`.

Density fitting can be invoked by prepending the command name by `DF-`, e.g. `DF-LMP2`, `DF-LCCSD(T0)` etc. In density fitting calculations an additional auxiliary basis set is needed. Details about choosing such basis sets and other options for density fitting are described in sections 32.10 and 15.

The general input for local coupled LMP2 or coupled cluster calculations is:

`LMP2`,*options*	Local MP2 calculation
`LCCSD`,*options*	Local CCSD calculation
`LDCSD`,*options*	Local DCSD calculation
`LCCSD(T0)`,*options*	Local CCSD(T0) calculation

The same options as on the command line can also be given on subsequent `LOCAL` and `MULTP` directives. Instead of using the `MULTP` directive, the `MULTP` option on the command line can also be used.

In the following, we will first give a summary of all options and directives. These will be described in more detail in the subsequent sections. For new users it is recommended to read section 32.9 at the end of this chapter before starting calculations.

32.3 Summary of options

Many options can be specified on the command line. For all options appropriate default values are set, and so these options must usually be modified only for special purposes. For convenience and historical reasons, alias names are available for various options, which often correspond to the variable name used in the program. Table 22 summarizes the options, aliases and default values. In the following, the parameters will be described in more detail.

Table 22: Summary of `local` (*multp*) options and their default values

Parameter	Alias	Default value	Meaning
General Parameters:			
LOCAL		4	determines which program to use.
MULTP		0	turns on multipole approximations for distant pairs.
SAVEDOM	SAVE	0	specifies record for saving domain info.
RESTDOM	START	0	specifies record for reading domain info.
LOCORB		0	activates or deactivates orbital localization.
LOC_METHOD			specifies which localization method to use.
CANONICAL		0	allows to use canonical virtual orbitals (for testing).
PMDEL	CPLDEL	0	discards contributions of diffuse functions in PM localization.
SAVORB	SAVLOC	0	specifies record for saving local orbitals.
DOMONLY		0	if 1, only domains are made.
			if 2, only orbital domains are made.
Parameters to define domains:			
THRBP	DOMSEL	0.98	Boughton-Pulay selection criterion for orbital domains.
NPASEL		0	charge used in the NPA selection criterion for orbital domains.
CHGMIN		0.01	determines the minimum allowed atomic charge in domains.
CHGMINH		0.03	as CHGMIN, but used for H-atoms (default 0.03).
CHGMAX		0.40	If the atomic charge is larger than this value,
			the atom is always included in the domain.
MAXANG	MAXL	99	angular momentum restriction for BP domain selection
MAXBP		0	determines how atoms are ranked in BP procedure.
MULLIKEN	LOCMUL	0	determines the method to determine atomic charges.
MERGEDOM		0	merges overlapping domains.
DELCOR	IDLCOR	2	delete projected core AOs up to certain shell.
DELBAS	IBASO	0	determines how to remove redundancies.
Distance criteria for domain extensions:			
REXT		0	criterion for all pair domains.
REXTS		0	criterion for strong pair domains.
REXTC		0	criterion for strong and close pair domains.
REXTW		0	criterion for strong, close, and weak pair domains.
Connectivity criteria for domain extensions:			
IEXT		0	criterion for all pair domains.
IEXTS		0	criterion for strong pair domains.
IEXTC		0	criterion for strong and close pair domains.
IEXTW		0	criterion for strong, close, and weak pair domains.
Parameters to select pair classes:			
USE_DIST		1	determines if distance of connectivity criteria are used.
RCLOSE	CLOSEP	1	distance criterion for selection of weak pairs.
RWEAK	WEAKP	3	distance criterion for selection of weak pairs.
RDIST	DISTP	8	distance criterion for selection of distant pairs.
RVDIST	VERYD	15	distance criterion for selection of very distant pairs.
ICLOSE		1	connectivity criterion for selection of weak pairs.
IWEAK		2	connectivity criterion for selection of weak pairs.
IDIST		5	connectivity criterion for selection of distant pairs.
IVDIST		8	connectivity criterion for selection of very distant pairs.
CHGMIN_PAIRS	CHGMINP	0.20	determines minimum charge of atoms used for pair
			classification.
KEEPCL		0	determines if close pairs are included in LCCSD.

Parameter	Alias	Default value	Meaning
Parameter for multipole treatment of exchange operators:			
DSTMLT		3	multipole expansion level for distant pairs
Parameters for energy partitioning:			
IEPART		0	If nonzero: do energy partitioning.
EPART		3.0	cutoff parameter for determining individual monomers.
Parameters for redundancy check using DELBAS=1 *(not recommended)*			
TYPECHECK	TYPECHK	1	activates basis function type restrictions.
DELSHL	IDLSHL	1	determines if whole shells are to be deleted.
DELEIG	IDLEIG	1	determines how to select redundant functions.
DELCMIN	CDELMIN	0.1	parameter for use with DELEIG=1
Parameters for choosing operator domains in LCCSD			
OPDOM	IOPDOM	5	determines how operator domains are determined for LCCSD
RMAXJ		8	distance criterion for J-operator list.
RMAXK		8	distance criterion for K-operator list.
RMAXL		15	distance criterion for L-operator list.
RMAX3X		5	distance criterion for 3-ext integral list.
RDOMJ		0	distance criterion for K-operator domains.
RDOMK		8	distance criterion for J-operator domains.
IMAXJ		5	connectivity criterion for J-operator list.
IMAXK		5	connectivity criterion for K-operator list.
IMAXL		8	connectivity criterion for L-operator list.
IMAX3X		3	connectivity criterion for 3-ext integral list.
IDOMJ		0	connectivity criterion for K-operator domains.
IDOMK		5	connectivity criterion for J-operator domains.
Miscellaneous options:			
SKIPDIST	SKIPD	3	determines at which stage weak and distant pairs are eliminated
ASYDOM	JITERM	0	parameter for use of asymmetric domains
LOCSING	LOCSNG	0	determines virtual space used for singles
PIPEKAO	LOCAO	0	activates AO localization criterion
NONORM		2	determines whether projected functions are normalized
LMP2ALGO	MP2ALGO	3	if nonzero, use low-order scaling method in LMP22 iterations
OLDDEF		0	allows to revert to older defaults
T1DISK		10	maximum disk space (in GByte) for T1 caching algorithm
Thresholds:			
THRBP		0.98	Threshold Boughton-Pulay method.
THRPIP		1.d-12	Threshold for Pipek-Mezey localization.
THRORB		1.d-6	Threshold for eliminating projected orbitals with small norm.
THRLOC		1.d-6	Threshold for eliminating redundant projected orbitals.
THRCOR		1.d-1	Threshold for eliminating projected core orbitals.
THRMP2		1.d-8	Threshold for neglecting small fock matrix elements in the LMP2 iteration.

32.4 Summary of directives

The same standard directives as in the canonical programs, e.g., `OCC`, `CLOSED`, `CORE`, `WF`, `ORBITAL` are also valid in the local methods. In addition, there are some directives which only apply to local calculations:

`LOCAL`	Invokes local methods and allows to specify the same options as on the command line.
`MULTP`	As `LOCAL`, but multipole approximations are used for distant pairs.
`DOMAIN`	Define domains manually (not recommended).
`MERGEDOM`	Allows to merge domains
`REGION`	Allows to select regions of a molecule to be treated at a certain level of theory.
`ENEPART`	Analysis of pair energies.
`SAVE`	Save domains and LCCSD amplitudes.
`START`	Restart with domains and LCCSD amplitudes from a previous calculation.

32.5 General Options

`LOCAL=`*local*	Determines which method is used: `LOCAL=0`: Conventional (non-local) calculation. `LOCAL=1`: Local method is simulated using canonical MOs. The local basis is used only at an intermediate stage to update the amplitudes in each iteration (only for testing). `LOCAL=2`: Calculation is done in local basis, but without using local blocking (i.e. full matrices are used). This is the most expensive method and only for testing. `LOCAL=3`: Fully local calculation (obsolete). `LOCAL=4`: Fully local calculation (default). This is the fastest method for large molecules with many weak pairs and requires minimum memory.
`LOCORB=`*option*	If this option is given and *option*> 0, the orbitals are localized using the Pipek-Mezey technique. If this option is not given or *option*$=0$ (default), the orbitals are localized unless localized orbitals are found in the orbital record (cf. `ORBITAL` directive and `LOCALI` command). In the latter case, the most recent localized orbitals are used. Setting *option*$=-1$ switches the localization off. If *option*> 1 the localized orbitals are printed. Note: Boys localization can only be performed using the `LOCALI` command. The program will use the Boys orbitals if they are found in the orbital record and the `LOCORB` option is absent or *option*≤ 0.
`LOC_METHOD=`*method*	This option allows to select between Pipek-Mezey (*method*$=$PM) or Natural Orbitals (*method*$=$NBO) localization. If Pipek-Mezey orbitals are requested, the default Boughton-Pulay domain selection will be used. When *method*$=$NBO, the domain selection will be based on the NPA charges, with `NPASEL`$=0.03$ (by default). In both cases, the domain selection parameter can be explicitly given (cf. `DOMSEL` and

	NPASEL options) in order to use another domain criterion. If localized orbitals are found in the orbital record, but the type does not coincide, the orbitals are again localized according to *method* and used in the calculation.
SAVORB=*record*	Allows the localized and projected orbitals to be saved in *record=name.ifil* for later use (e.g. plotting). The two orbital sets are stored in the same dump record and can be restored at later stages using ORBITAL,*record*,[TYPE=]LOCAL or ORBITAL,*record*,[TYPE=]PROJECTED, respectively.
DOMONLY=*value*	If *value* > 0 only domains are made, but no energy is computed. This can be used to check and save the domains for later use.
DSTMLT=*level*	Determines the expansion level of the multipole expansion of distant pairs (e.g. 1 means dipole approximation, 2 quadrupole approximation and so on). The default for MULTP is 3.
INTERACT	Automatically determine individual molecules in a calculation and set appropriate pair lists for computing interaction energies. See section 32.9.8 for more details.

Parameters for energy partitioning:

IEPART=*value*	enables/disables energy partitioning. *iepart=0*: Energy partitioning is disabled. *iepart=1*: Energy partitioning is enabled. *iepart=2*: Energy partitioning is enabled. Additionally, a list of all pair energies and their components is printed.
EPART=*cutoff*	Cutoff parameter to determine individual monomers in a cluster (i.e. centre groups). Should be somewhat larger than the largest intramolecular bond length (given in a.u.).

Miscellaneous options:

SKIPDIST=*skipdist*	Test-parameter. Its value should only affect the efficiency but not influence the results. *skipdist=-1*: Weak and distant pairs are set to zero after MP2 but are not eliminated from the pair list and not skipped in any loop. *skipdist=0*: No pairs are deleted from pair list, but weak and distant pairs are skipped in the loops were appropriate. *skipdist=1*: Very distant pairs are neglected from the beginning. Distant pairs are eliminated after MP2. *skipdist=2*: As skipdist=1, but also weak pairs are eliminated after MP2. *skipdist=3*: As skipdist=2, but distant pairs are eliminated from the operator list in case of LMP2 with multipole approximations for distant pairs. This is the default.
ASYDOM=*jiterm*	Experimental test parameter. Enables the use of asymmetric domains for distant pairs. The asymmetric domain approximation supplements the multipole approximation for distant pairs, as it suppresses the treatment of configurations for which no integrals can be computed by multipole expansion. This leads to computational savings and improved numerical stability. *jiterm=0*: Disable asymmetric domains. *jiterm=-1*: Enable asymmetric domains (default).

jiterm=-2: Enable a variation of the asymmetric domain formalism: Exchange operators will initially be projected to the asymmetric domain instead of simply packed.

LOCSING=*locsing*	If *locsing.ne.0*, the single excitations use the full space, i.e., they are not treated locally. This is only works for LOCAL=1.
MAXANG=*lmax*	The purpose of this experimental option is to reduce the basis set sensitivity of the Boughton-Pulay (BP) method for domain selection. Only basis functions with angular momentum up to *lmax-1* are included when computing the overlap of the approximate and exact orbitals. For example, MAXANG=2 means to omit all contributions of *d*, *f* and higher angular momentum functions. To obtain reasonable domains, the value of THRBP must often be reduced (to 0.97 or so). This option should only be used with care!
PIPEKAO=*option*	If *option*$\geq$ 0, the orbitals are localized my maximizing the coefficients of basis functions of a given type at a given atom. Normally, this is only useful to uniquely define degenerate orbitals in atoms. For instance, when this option is used to localize the orbitals for a dimer like $(Ar)_2$ at a very long distance, clean *s*, p_x, p_y, and p_z atomic orbitals will be obtained. It is not recommended to use this option for molecular calculations!
NONORM=*value*	Determines if projected functions are normalized (not recommended). *value*=-1: projected orbitals are normalized before redundancy check. *value*=0: projected orbitals are normalized after redundancy check (default). *value*=1: projected orbitals are normalized in redundancy check, afterwards unnormalized. *value*=2: projected orbitals are never normalized (default in gradient calculations).
LMP2ALGO=*value*	If nonzero, use low-order scaling method in LMP2 iterations. Values can be 1, 2, or 3, and 3 is usually fastest if large basis sets are used.
OLDDEF=*value*	For compatibility with older versions: if nonzero, revert to old defaults. Options set before this may be overwritten.

Thresholds:

THRPIP=*thresh*	Threshold for Pipek-Mezey localization. The localization is assumed to be converged if all 2×2 rotation angles are smaller than *thresh*. The default is $1.d-12$. It can also be modified globally using GTHRESH, LOCALI=*thresh*.
THRORB=*thresh*	Threshold for eliminating functions from pair domains whose norm is smaller than *thresh* after projecting out the occupied space. The default is *throrb=1.d-6*.
THRLOC=*thresh*	Threshold for eliminating redundant basis functions from pair domains. For each eigenvalue of $\tilde{\mathbf{S}}^{ij} < thresh$ one function is deleted. The default is 1.d-6. The method used for deleting functions depends on the parameters IDLEIG and IBASO.
THRMP2=*thresh*	Threshold for neglecting small fock matrix couplings in the LMP2 iterations (default 1.d-8). Specifying a larger threshold speeds up the iterations but may lead to small errors in the energy. In the initial iterations, a larger threshold is chosen automatically. It is gradually reduced to the specified final value during the iterations.

THRCOR=*thresh*   Threshold for deleting projected core orbitals. The functions are only deleted if their norm is smaller than *thresh* (default 0.1)

The thresholds can also be specified on the THRESH directive.

32.6 Options for selection of domains

The following sections describe the most important options which affect the domains.

32.6.1 Standard domains

Standard domains are always determined first. They are used to define strong, close, weak, and distant pairs. More accurate results can be obtained with extended domains, as described in section 32.6.2.

THRBP=*value*   Threshold for selecting the atoms contributing to orbital domains using the method of Boughton and Pulay (BP). As many atoms as needed to fulfill the BP criterion are included in a domain. The order in which atoms are considered depends on the parameter MAXBP, see below. The default is THRBP=0.98. THRBP=1.0 includes all atoms into each orbital domain, i.e., leads to full domains. If no pairs are neglected, this should yield the canonical MP2 energy.

The criterion is somewhat basis dependent. See section 32.9.4 for recommended values of this threshold.

CHGMIN=*value*   determines the minimum allowed Mulliken (or Löwdin) charge for an atom (except H) in a domain, i.e., atoms with a smaller (absolute) charge are not included, even if the THRBP criterion is not fulfilled (default 0.01).

CHGMINH=*value*   as CHGMIN, but used for H-atoms (default 0.03).

CHGMAX=*value*   If the atomic charge is larger than this value, the atom is included, independent of any ranking.

MAXBP=*maxbp*   If *maxbp=1*, the atoms are ranked according to their contribution to the Boughton-Pulay overlap. If *maxbp=0* (default), the atoms are ranked according to atomic charges. In both cases atoms with charges greater than CHGMAX are always included, and atoms with the same charges are added as groups.

MULLIKEN=*option*   Determines the method to determine atomic charges. MULLIKEN=0 (default): squares of diagonal elements of $\mathbf{S}^{\frac{1}{2}}\mathbf{C}$ are used (Löwdin charges); MULLIKEN=1: Mulliken gross charges are used. The first choice is less basis set dependent and more reliable with diffuse basis sets.

MERGEDOM=*number*   If *number* is greater than zero, all orbital domains containing *number* or more atoms in common are merged (*number=1* is treated as *number=2*, default 0). This is particularly useful for geometry optimizations of conjugated or aromatic systems like, e.g., benzene. In the latter case, MERGEDOM=1 causes the generation of full π-domains, i.e., the domains for all three π-orbitals comprise all carbon basis functions. Note that the merged domains are generated after the above

print of orbital domains, and information about merged domains is printed separately. See section 32.9.7 for further discussion of geometry optimizations.

There are some other options which should normally not be modified:

DELBAS=*ibaso*   This parameter determines the method for eliminating redundant functions of pair domains.
ibaso=0: The space of normalized eigenvectors of $\tilde{\mathbf{S}}^{ij}$, which correspond to small eigenvalues, is eliminated (default). Any other value is not recommended and not further documented.

DELCOR=*nshell*   Activates elimination of basis functions corresponding to core orbitals. If *nshell=1*, only 1*s*-functions are eliminated from projected space. If *nshell=2* (default) 1*s* functions on first-row atoms, and 1*s*, 2*s*, and 2*p*-functions are eliminated on second-row atoms. Nothing is eliminated on H or He atoms. If effective core potentials are used, nothing is deleted at the corresponding atom. Also, functions are only deleted if the norm of the projected function is below THRCOR (default 0.1)

32.6.2   Extended domains

There are two alternative modes for domain extensions: either *distance criteria* REXT, REXTS, REXTC, or REXTW can be used. These are in Bohr and refer to the minimum distance between any atom in a standard orbital domain $[ij]$ and another atom. If an atom is found within the given distance, all PAOs at this atom are added to the domain $[ij]$. Alternatively, *connectivity criteria* IEXT, IEXTS, IEXTC, or IEXTW can be used. These refer to the number of bonds between any atom contained in the standard domain $[ij]$ and another atom. The advantage of distance criteria is that they select also atoms within the given radius which are not connected to the present domain by bonds. On the other hand, the connectivity criteria are independent of different bond lengths, e.g., for first and second-row atoms. Only one of the two possibilities can be used, i.e., they are mutually exclusive.

REXT=*value*   Distance criterion for extension of all pair domains.

REXTS=*value*   Distance criterion for extension of strong pair domains.

REXTC=*value*   Distance criterion for extension of strong and close pair domains.

REXTW=*value*   Distance criterion for extension of strong, close, and weak pair domains.

IEXT=*value*   Connectivity criterion for extension of all pair domains.

IEXTS=*value*   Connectivity criterion for extension of strong pair domains.

IEXTC=*value*   Connectivity criterion for extension of strong and close pair domains.

IEXTW=*value*   Connectivity criterion for extension of strong, close, and weak pair domains.

By default, domains are not extended, i.e., the default values of all parameters listed above are zero. Note that the pair classes are determined on the basis of the standard domains, and therefore domain extensions have no effect on the pair lists.

Also note that the computational effort increases with the fourth power of the domain sizes and can therefore increase quite dramatically when extending domains. This does not affect the linear scaling behaviour in the asymptotic limit.

32.6.3 Manually Defining orbital domains (`DOMAIN`)

It is possible to define the domains "by hand", using the `DOMAIN` directive:

`DOMAIN`,*orbital*,*atom1*, *atom2* . . .

where *orbital* has the form `iorb.isym`, e.g., 3.1 for the third orbital in symmetry 1, and *atomi* are the atomic labels as given in the Z-matrix geometry input, or, alternatively, the Z-matrix row numbers. All basis functions centred at the given atoms are included into the domain. For instance

`DOMAIN,3.1,C1,C2`

defines a domain for a bicentric bond between the carbon atoms `C1` and `C2`. The `DOMAIN` directive must be given after any `OCC`, `CLOSED`, or `CORE` directives. Note that the order of the localized orbitals depends on the localization procedure, and could even change as function of geometry, and therefore manual `DOMAIN` input should be used with great care. The domains of all orbitals which are not explicitly defined using `DOMAIN` directive are determined automatically as usual.

32.7 Options for selection of pair classes

There are two alternative modes for defining the pair classes: either *distance criteria* `RCLOSE`, `RWEAK`, `RDIST`, `RVDIST` can be used. These are in Bohr and refer for a given orbital pair (ij) to the minimum distance $R^{(ij)}$ between any atom in the standard orbital domains $[i]$ and any atom in the standard orbital domains $[j]$. Alternatively, the *connectivity criteria* `ICLOSE`, `IWEAK`, `IDIST`, `IVDIST` can be used. These refer to the minimum number of bonds between any atom contained in the standard domain $[i]$ and any atom contained in the standard domain $[j]$ The advantage of using connectivity criteria is the independence of the bond lengths, while the advantage of distance criteria (default) is that they are also effective in non-bonding situations. Only one of the two possibilities can be used, i.e., they are mutually exclusive. The use of distance criteria is the default. Using connectivity criteria for pair selection requires to set the option `USE_DIST=0`.

`USE_DIST`	(default 1) If nonzero, use distance criteria, otherwise connectivity criteria.
`CHGMIN_PAIRS`	Only atoms in the primary domains are considered for the pair classification if the atomic Löwdin charge is larger than `CHGMIN_PAIRS` (default value 0.2). This criterion was introduced in order to reduce the dependence of the pair selection on localization tails.
`RCLOSE`	(default 1) Strong pairs are defined by $0 \le R^{(ij)} <$ `RCLOSE`. Close pairs are defined by `RCLOSE` $\le R^{(ij)} <$ `RWEAK`.
`RWEAK`	(default 3) Weak pairs are defined by `RWEAK` $\le R^{(ij)} <$ `RDIST`.
`RDIST`	(default 8) Distant pairs are defined by `RDIST` $\le R^{(ij)} <$ `RVDIST`.
`RVDIST`	(default 15) Very distant pairs for which $R^{(ij)} \ge$ `RVDIST` are neglected.

ICLOSE	(default 1) Strong pairs are separated by less that `ICLOSE` bonds. Close orbital pairs are separated by at least `ICLOSE` bonds but less than `IWEAK` bonds.
IWEAK	(default 2) Weak orbital pairs are separated by at least `IWEAK` bonds but less than `IDIST` bonds.
IDIST	(default 5) Distant orbital pairs are separated by at least `IDIST` bonds but less than `IVDIST` bonds.
IVDIST	(default 8) Very distant orbital pairs (neglected) are separated by at least `IVDIST` bonds.
KEEPCL	(default 0) If `KEEPCL=1`, the LMP2 amplitudes of close pairs are included in the computation of the strong pair LCCSD residuals. If `KEEPCL=2` all close pairs are fully included in the LCCSD (this does not affect the triples list). This option is not yet implemented as efficiently as it could, and can therefore lead to a significant increase of the CPU time.

Setting `RCLOSE` or `RWEAK` to zero means that all pairs up to the corresponding class are treated as strong pairs (`RWEAK=0` implies `RCLOSE=0`). For instance, `RCLOSE=0` means that strong and close pairs are fully included in the LCCSD (in this case `KEEPCL=1` has no effect). Note, however, that setting `RCLOSE=0` increases the length of the triples list. Setting `RDIST=0` means that all distant pairs are treated as weak pairs. This does not affect `RWEAK` and `RCLOSE` and has no effect unless multipole approximations are used for distant pairs. Setting `RVDIST=0` means that no very distant pairs are neglected. Again, this has no effect on the other distance parameters.

32.8 Directives

32.8.1 The `LOCAL` directive

The `LOCAL` directive can be used to specify options for local calculations. If this directive is inside the command block of a local calculation, the options are used only for the current calculation, and this is entirely equivalent as if they were specified on the command line. The `LOCAL` directive can also be given outside a command block, and in this case the options are used for all subsequent local correlation calculations in the same input.

Example:

```
DF-LMP2,THRBP=0.985
```

is equivalent to

```
{DF-LMP2
LOCAL,THRBP=0.985}
```

In the following example the `LOCAL` directive is global and acts on all subsequent local calculations, i.e. both calculations will use `THRBP=0.985`

```
LOCAL,THRBP=0.985
DF-LMP2          !local MP2 calculation
OPTG            !geometry optimization using the DF-LMP2 energy
DF-LCCSD(T)     !local coupled cluster at the optimized structure.
```

32.8.2   The `MULTP` **directive**

The `MULTP` directive turns on the multipole approximations for distant pairs, as described in Ref. [8]. Further options can be given as described above for the `LOCAL` directive.

`LOCAL,MULTP,`*options*

is equivalent to

`MULTP,`*options*

The level of the multipole approximation can be chosen using option `DSTMLT` (default 3) (1 means dipole approximation, 2 quadrupole approximation and so on).

The multipole approximation reduces the computational cost of LMP2 calculations for very large molecules, but leads to some additional errors, see Ref. [8]. It is normally not recommended to be used in coupled-cluster calculations and should never be used for computing intermolecular forces. It can also not be used in geometry optimizations or gradient calculations.

32.8.3   **Saving the wavefunction** (`SAVE`)

The wavefunction can be saved for later restart using

`SAVE,`*record*

where *record* has the usual form, e.g., 4000.2 means record 4000 on file 2. If this directive is given, the domain information as well as the amplitudes are saved (for MPn the amplitudes are not saved). If just the domain information should be stored, the `SAVE` option on the `LOCAL` directive must be used (cf. section 32.3).

32.8.4   **Restarting a calculation** (`START`)

Local CCSD, DCSD or QCISD calculations can be restarted using

`START,`*record*

The record given must have been saved in a previous local calculation using the `SAVE` directive (otherwise this directive is ignored). If the `START` directive is given, the domain information as well as the amplitudes of the previous calculation are used for restart. It is possible, for instance, to start a local CCSD calculation with the amplitudes previously saved for a local QCISD calculation (but of course it is not possible to use a record saved for a non-local CCSD or QCISD calculation). If it is intended only to use the domain information but not the amplitudes for a restart, the `START` option on the command line or `LOCAL` directive must be used (cf. section 32.3).

32.8.5   **Correlating subsets of electrons** (`REGION`)

In large molecules, it may be sufficient to correlate only the electrons in the vicinity of an *active group*, and to treat the rest of the molecule at the SCF level. This approach can even be extended, different correlation levels may be used for different sections of the system. The `REGION` directive allows the specification of a subset of atoms:

`REGION,METHOD=`*method*`,[DEFAULT=`*default_method*`], [TYPE=INCLUSIVE|EXCLUSIVE],` *atom1*, *atom2* . . .

The orbitals located at these atoms will be treated at the level specified in *method*. The remaining orbitals will be treated as defined in *default*. If not given by the user, the latter option will be set to `HF`.

The orbital selection can be done in two ways. If *type* is set to `INCLUSIVE`, any orbital containing one of the atoms in its domain centre list will be included. If type is set to `EXCLUSIVE`, the program will only add orbitals whose domains are exclusively covered by the given atoms. Any local correlation treatment can be given as *method*, with the restriction that only `MP2` and `HF` can be used as *default_method*. Up to two `REGION` directives may be included in a single calculation, ordered according to the correlation level (*method*) specified for the region. The highest level region should be given last.

It is advisable to check the region orbital list and the orbital domains printed by the program. The use of regions may significantly reduce the computation time, and, provided the active atoms are sensibly chosen, may give still sufficiently accurate results for the *active group*, e.g. bond lengths and bond angles.

32.8.6 Domain Merging (`MERGEDOM`)

The restriction of the virtual space in local calculations may result in discontinuities for reaction path calculations due to changes of the geometry dependent domains. This may be avoided by the use of a `MERGEDOM` directive

`MERGEDOM,[NEIGHBOUR=`*value*`],[CENTERS=[`*atom1, atom2*`. . . ]], [RECORD=. . .],CHECK`

This directive provides augmented domains, which can be saved (using option or directive `SAVE`, see section 32.8.3) for later use in reaction paths or in single point calculations (in cases where the orbital domain description is unbalanced). The use of the *neighbour* option works in the same way as the local option `MERGEDOM`, with *value* specifying the number of coincident centres. If the *centres* option is used, an atom list should be given (enclosed by square brackets). The domains of all orbitals located exclusively at these atoms will be merged, and the resulting merged domains will be used for all these orbitals.

One may also give a *record* number from a previously saved local calculation. The domain list contained in the record will be matched to the current one, and orbital domains augmented (merged) to include both sets. This domain definition should then be adequate for calculations on both points (and all those in between). This procedure can be repeated to include more geometries. In this way domains can be defined that are appropriate for a whole range of geometries (e.g. a reaction path), and if these domains are used in all calculations a strictly smooth potential energy surface is obtained.

32.8.7 Energy partitioning for molecular cluster calculations (`ENEPART`)

The local character of occupied and virtual orbitals in the local correlation treatment also offers the appealing possibility to decompose the intermolecular interaction energy of molecular clusters into individual contributions of different excitation classes. This allows to distinguish between intramolecular-, dispersive-, and ionic components of the correlation contribution to the interaction energy (cf. M. Schütz, G. Rauhut and H.J. Werner, J. Phys. Chem. **102**, 5197 (1998)). The energy partitioning algorithm is activated either by supplying the `ENEPART` directive:

`ENEPART,[`*epart*`],[`*iepart*`]`

or by giving the parameters as options on the command line.

The *epart* parameter determines the cutoff distance for (intramolecular) bond lengths (in a.u., default 3 a.u.) and is used to automatically determine the individual monomer subunits of the cluster. The *iepart* parameter enables the energy partitioning, if set to a value larger than zero (default 1). Additionally, if iepart is set to 2, a list of all intermolecular pair energies and their components is printed.

The output section produced by the energy partitioning algorithm will look similar to the following example:

```
energy partitioning enabled !
centre groups formed for cutoff [au] = 3.00
 1    :O1  H11 H12
 2    :O2  H21 H22
energy partitioning relative to centre groups:
intramolecular correlation:     -.43752663
exchange dispersion       :      .00000037
dispersion energy         :     -.00022425
ionic contributions       :     -.00007637
```

The centre groups correspond to the individual monomers determined for *epart=3*. In the present example, two water monomers were found. The correlation energy is partitioned into the four components shown above. The exchange dispersion, dispersion and ionic components reflect directly the related intermolecular components of the complex, while the intramolecular correlation contribution to the interaction energy has to be determined by a super-molecular calculation, i.e. by subtracting the (two) corresponding monomer correlation energies from the intramolecular correlation component of the complex given in the output.

Alternatively, the following form can be used:

ENEPART,RMAX=[*r1,r2,r3,...*]

and the program will then print the energy contributions of all pairs in the ranges between the given distances (in bohr, enclosed by square brackets, e.g., `enepart,rmax=[0,3,5,7,9,11]`). A second list in which the contributions are given as a function of the number of bonds between the pair domains will also be printed.

32.9   Doing it right

The local correlation methods in MOLPRO employ localized molecular orbitals (LMOs). Pipek-Mezey localization is recommended, but Boys localization is also possible. The virtual orbital space is spanned by non-orthogonal projected atomic orbitals (PAOs). The local character of this basis makes it possible to introduce two distinct approximations: first, excitations are restricted to *domains*, which are subspaces of (PAOs) that are spatially close to the orbitals from which the electrons are being excited. Secondly, the orbital pairs are classified according to their importance (based on distance or connectivity criteria), and only *strong pairs* are treated at the highest level (e.g. CCSD). The remaining *weak* and *distant* pairs are treated at the LMP2 level, and *very distant* pairs are neglected. These approximations lead to linear scaling of the computational resources as a function of the molecular size.

Naturally, such approximation can introduce some errors, and therefore the user has to be more careful than with standard black box methods. On the other hand, the low-order scaling makes it possible to treat much larger systems at high levels of theory than it was possible so far.

This section summarizes some important points to remember when performing local correlation calculations.

32.9.1 Basis sets

For numerical reasons, it is useful to eliminate projected core orbitals, since these may have a very small norm. By default, projected core orbitals are eliminated if their norm is smaller than 0.1 (this behaviour can be changed using the `DELCOR` and `THRCOR` options). For local calculations we recommend the use of generally contracted basis sets, e.g., the correlation consistent cc-pVnZ sets of Dunning and coworkers. For these basis sets the core basis functions are uniquely defined, and will always be eliminated if the defaults for `DELCOR` and `THRCOR` are used.

The correlation consistent basis sets are also recommended for all density fitting calculations, since optimized fitting basis sets are available for each basis.

32.9.2 Symmetry and Orientation

1. Turn off symmetry! Otherwise, you won't get appropriately localized orbitals (local orbitals will tend to be symmetry equivalent instead of symmetry adapted). Symmetry can be used only if all atoms are symmetry unique. This allows the local treatment of planar molecules in C_s symmetry. But note that neither the multipole program nor the density fitting programs support symmetry at all, so choose always C_1 symmetry for DF-calculations or with the `MULTP` option.

To turn off symmetry, specify `NOSYM` as the first line of your geometry input, e.g.

```
geometry={
  nosym
  O1
  H1,O1,roh
  H2,O1,roh,h1,hoh
}
```

Alternatively, add

```
SET,ZSYMEL=NOSYM
```

before the geometry block.

2. Use NOORIENT! We recommend to use the `NOORIENT` option in the geometry input, to avoid unintended rotations of the molecule when the geometry changes. This is particularly important for geometry optimizations and for domain restarts in calculations of interaction energies (see section 32.9.8).

32.9.3 Localization

By default, Pipek-Mezey localization is used and performed automatically in the beginning of a local correlation calculation. Thus

```
df-hf        !Hartree-Fock with density fitting
df-lmp2      !LMP2 using the Pipek-Mezey LMOs
```

is equivalent to

```
df-hf        !Hartree-Fock with density fitting
locali,pipek !Orbital localization using the Pipek-Mezey criterion
df-lmp2      !LMP2 using the Pipek-Mezey LMOs
```

Boys localization can be used as well, but in this case the localization must be done beforehand, e.g.

```
df-hf          !Hartree-Fock with density fitting
locali,boys    !Orbital localization using the Boys criterion
df-lmp2        !LMP2 using the Boys LMOs
```

Poor localization is sometimes an intrinsic problem, in particular for strongly conjugated systems or when diffuse basis sets are used. This is caused by localization tails due to the overlapping diffuse functions. The problem is particularly frequent in calculations of systems with short bonds, e.g., aromatic molecules. It can be avoided using directive

PIPEK,DELETE=n

with $n = 1$ or 2. This means that the contributions of the n most diffuse basis functions of each angular momentum type are ignored in the localization. This often yields much better localized orbitals when diffuse basis sets are used. For aug-cc-pVTZ, $n = 2$ has been found to work very well, while for aug-cc-pVDZ $n=1$

In rare cases it might also happen that the localization procedure does not converge. It is them possible to choose a second-order Newton-Raphson localization scheme, using the directive

PIPEK,METHOD=2,[DELETE=n]

Alternatively (recommended) one can use

PIPEK,METHOD=3,[DELETE=n]

which first performs a few standard Pipek-Mezey iterations and the invokes the second-order localization scheme. This then usually converges very quickly.

32.9.4   Orbital domains

The orbital domains are determined automatically using the procedure of Boughton and Pulay, J. Comput. Chem., **14**, 736 (1993) and J. Chem. Phys. **104**, 6286 (1996). For higher accuracy the domains can be extended, and in this way the canonical result can be systematically approached (cf. Ref. [1] and section 32.6.2). Details are described in section 32.6.

In most cases, the domain selection is uncritical for saturated molecules. Nevertheless, in particular for delocalized systems, it is recommended always to check the orbital domains, which are printed in the beginning of each local calculation. For such checking, the option DOMONLY=1 can be used to stop the calculation after the domain generation. The orbital domains consist of all basis functions for a subset of atoms. These atoms are selected so that the domain spans the corresponding localized orbital with a preset accuracy (alterable with option THRBP). A typical domain output, here for water, looks like this:

```
 Orbital domains

    Orb.    Atom     Charge        Crit.
    2.1     1 O1      1.17          0.00
            3 H2      0.84          1.00
    3.1     1 O1      2.02          1.00
    4.1     1 O1      1.96          1.00
    5.1     1 O1      1.17          0.00
            2 H1      0.84          1.00
```

This tells you that the domains for orbitals 2.1 and 5.1 comprise the basis functions of the oxygen atom and and one hydrogen atom, while the domains for orbitals 3.1 and 4.1 consist

of the basis function on oxygen only. The latter ones correspond to the oxygen lone pairs, the former to the two OH bonds, and so this is exactly what one would expect. For each domain of AOs, corresponding projected atomic orbitals (PAOs) are generated, which span subspaces of the virtual space and into which excitations are made. Options which affect the domain selection are described in section 32.6. Improper domains can result from poorly localized orbitals (see section 32.9.3 or a forgotten `NOSYM` directive. This does not only negatively affect performance and memory requirements, but can also lead to unexpected results.

The default for the selection criterion `THRBP` is 0.98. This works usually well for small basis sets like cc-pVDZ. For larger basis sets like cc-pVTZ we recommend to use a slightly larger value of 0.985 to ensure that enough atoms are included in each domain. For cc-pVQZ recommend `THRBP=0.990` is recommended. In cases of doubt, compare the domains you get with a smaller basis (e.g., cc-pVDZ).

The choice of domains usually has only a weak effect on near-equilibrium properties like equilibrium geometries and harmonic vibrational frequencies. More critical are energy differences like reaction energies or barrier heights. In cases where the electronic structure strongly changes, e.g., when the number of double bonds changes, it is recommended to compare DF-LMP2 and DF-MP2 results before performing expensive LCCSD(T) calculations. More balanced results and smooth potentials can be obtained using the `MERGEDOM` directive, see section 32.8.6.

32.9.5 Freezing domains

In order to obtain smooth potential energy surfaces, domains must be frozen. The domain information can be stored using the `SAVE` option and recovered using the `START` option. Alternatively, the `SAVE` and `START` can be used, see section 32.8.3. In the latter case, also the CCSD amplitudes are saved/restarted. Freezing domains is particularly important in calculations of intermolecular interactions, see section 32.9.8. Domains that are appropriate for larger ranges of geometries, such as reaction pathways, can be generated using the `MERGEDOM` directive, section 32.8.6. The domains are automatically frozen in geometry optimizations and frequency calculations, see section 32.9.7. Note, however, that this automatic procedure only works if a single local calculation is involved in the optimization. In case of optimizations with counterpoise correction the domains for the complex and each monomer must be frozen individually in different records using the `SAVE` and `START` directives.

32.9.6 Pair Classes

The *strong*, *close*, *weak* and *distant* pairs are selected using distance or connectivity criteria as described in more detail in section 32.7. *Strong* pairs are treated by CCSD, all other pairs by LMP2. In triples calculations, all orbital triples (ijk) are included for which (ij), (ik), and (jk) are *close pairs*. In addition, one of these pairs is restricted to be strong. The triples energy depends on the strong and close pair amplitudes. The close pair amplitudes are taken from the LMP2 calculation. Thus, increasing the distance or connectivity criteria for close and weak pairs will lead to more accurate triples energies. While for near equilibrium properties like geometries and harmonic vibrational frequencies the default values are normally appropriate, larger distance criteria are sometimes needed when computing energy differences, in particular barrier heights. In cases of doubt, `RWEAK` should first be increased until convergence is reached, and then `RCLOSE` can be varied as well. Such tests can be performed with small basis sets like cc-pVDZ, and the optimized values then be used in the final calculations with large basis sets.

32.9.7 Gradients and frequency calculations

Geometry optimizations [15-17] and numerical frequency calculations [18-20] can be performed using analytical energy gradients [15-17] for local MP2. LMP2 geometry optimizations are particularly attractive for weakly bound systems, since virtually BSSE free structures are obtained (see section 32.9.8 and Refs. [21-23]). For reasons of efficiency it is strongly advisable to use the DF-LMP2 Gradient [17] for all geometry optimizations. Setting `SCSGRD=1` on the `DF-LMP2` command or `DFIT` directive activates the gradient with respect to Grimmes SCS scaled MP2 energy functional (see also section DFIT). Analytical energy gradients are not yet available for the multipole approximation of distant pairs, and therefore `MULTP` cannot be used in geometry optimizations or frequency calculations.

In geometry optimizations, the domains are allowed to vary in the initial optimization steps. When the stepsize drops below a certain threshold (default 0.01) the domains are automatically frozen. In numerical Hessian or frequency calculations the domains are also frozen. It is therefore not necessary to include `SAVE` and `START` options.

Particular care must be taken in optimizations of highly symmetric aromatic systems, like, e.g., benzene. In D_{6h} symmetry, the localization of the π-orbitals is not unique, i.e., the localized orbitals can be rotated around the C_6 axis without changing the localization criterion. This redundancy is lost if the symmetry is slightly distorted, which can lead to sudden changes of the localized orbitals. If now the domains are kept fixed using the `SAVE` and `START` options, a large error in the energy might result. On the other hand, if the domains are not kept fixed, their size and quality might change during the optimization, again leading to spurious energy changes and divergence of the optimization.

The best way to avoid this problem is to use the `MERGEDOM=1` option (see section 32.6). If this option is given, the domains for the π orbitals will comprise the basis functions of all six carbon atoms, and the energy will be invariant with respect to unitary transformations among the three π orbitals. Note that this problem does not occur if the symmetry of the aromatic system is lowered by a substituent.

Redundant orbital rotations can also lead to convergence difficulties of the `Pipek-Mezey` localization. This can be overcome by using

`PIPEK,METHOD=2`

or

`PIPEK,METHOD=3`

With `METHOD=2`, the second derivatives of the localization criterion with respect to the orbital rotations is computed and diagonalized, and rotations corresponding to zero eigenvalues are eliminated. This method converges quadratically. With `METHOD=3` first a few iterations with the standard Pipek-Mezey method are performed, then the second-order method is invoked. This appears to be the most robust and accurate localization method.

Finally, we note that the LMP2 gradients are quite sensitive to the accuracy of the SCF convergence (as is also the case for MP2). If very accurate structures are required, or if numerical frequencies are computed from the gradients, the default SCF accuracy might be insufficient. We recommend in such cases to add an `ACCU,14` directive (possibly even `ACCU,16`) after the `HF` command. Indicative of insufficient SCF accuracy are small positive energy changes near the end of the geometry optimization.

32.9.8 Intermolecular interactions

Local methods are particularly useful for the calculation of weak intermolecular interactions since the basis set superposition error (BSSE) is largely reduced [1,13,14] and counterpoise corrections are usually not necessary (provided the BSSE of the underlying Hartree-Fock is small). However, one must be careful to define the domains properly and to include all intermolecular pairs at the highest computational level. A convenient way to define appropriate domains and pair lists is to use the option `INTERACT=1`. If this option is given, individual molecules are identified automatically and all intermolecular pairs are automatically treated as strong pairs and included in the LCCSD. Similarly, appropriate triples lists are generated for LCCSD(T) calculations. It is required that all orbital domains are located on individual molecules. Note however that the inclusion of the intermolecular pairs strongly increases the number of strong pairs and triples, and therefore high-level calculations can become very expensive.

For calculations of interaction potentials of weakly interacting systems, the domains of the subsystems should be determined at a very large distance and saved using the `SAVE=`*record* option on the `LOCAL` or `MULTP` directive, or the `SAVE` directive (see section 32.8.3). If the asymptotic energy is not needed it is sufficient to do this initial calculation using option `DOMONLY=1`). These domains should then be reused in the subsequent calculations at all other intermolecular distances by using the `START=`*record* option or the `START` directive (see section 32.8.4). Only in this way the basis set superposition error is minimized and normally negligible (of course, this does not affect the BSSE for the SCF, and therefore the basis set should be sufficiently large to make the SCF BSSE negligible).

Usually, diffuse basis functions are important for obtaining accurate intermolecular interactions. When diffuse basis sets are used, it may happen that the Pipek-Mezey localization does not yield well localized orbitals. This problem can in most cases be overcome by using the directive

`PIPEK,DELETE=`*n*

as described in section 32.9.3

A final warning concerns local density fitting (see sections 32.10 and 15): local fitting must not be used in counterpoise calculations, since no fitting functions would be present on the dummy atoms and this can lead to large errors.

For examples and discussions of these aspects see Refs. [21-23]

32.9.9 Efficient and accurate treatment of close pairs in local CCSD(T)

As discussed above, efficient LCCSD(T) calculations employ a hierarchical tretament of the LMO pairs, which are distinguished into the pair classes *strong*, *close*, *weak*, and *very distant*. Only the strong pairs are actually treated at the full coupled cluster level, while for close and weak pairs only LMP2 is used (and very distant pairs are omitted altogether). Consequently, *intermolecular pairs* in bigger molecules or clusters, which are usually not strong, are only treated at the LMP2 level, which is often poor (since van der Waals interactions are only captured at the lowest level of perturbation theory) and compromises the otherwise high accuracy of coupled cluster like LCCSD(T). By setting the keyword `how_treatclswk` on the `local` card appropriately, it is possible to treat the close pairs at a higher level than LMP2, *i.e.,*

`how_treatclswk=1`   local MP2

`how_treatclswk=2`   direct local RPA

`how_treatclswk=3`   local ring-CCD3

```
how_treatclswk=4    local ring-CCD
```

```
how_treatclswk=5    local CCD[S]-R⁻⁶
```

These methods for close pairs are discussed in detail in Refs. [24-25]. The philosophy is to include all diagrams with R^{-6} decay behavior up to a certain order of perturbation theory. *E.g.*, LringCCD3 denotes local ring CCD up to third-order diagrams, and LCCD[S]-R^{-6} is full local CCD with a perturbative singles correction, yet omitting all diagrams with decay behavior quicker than R^{-6} (like ladder diagrams). As shown in Ref. [25], the LCCD[S]-R^{-6} provides excellent intermolecular interaction energies, virtually indistinguishable from LCCSD, at a much lower cost (mainly due to the omission of ladders). We therefore recommend to use either LringCCD3 or LCCD[S]-R^{-6}. Note that it is essential to couple strong and close pairs in such calculations, *i.e.*, to set `keepcls=1` (*vide supra*). As an example, the input segment to set all intermolecular pairs to close and treat them at the level of LCCD[S]-R^{-6} is

```
local,keepcls=1,interact=1,interpair=1,how_treatclswk=5
```

See also the input example `h2o_dimer_lccsdhybrids.com`.

32.10   Density-fitted LMP2 (`DF-LMP2`), LDCSD (`DF-LDCSD`), and coupled cluster (`DF-LCCSD(T0)`)

Density-fitting LMP2, LDCSD and LCCSD calculations can be performed by adding the prefix `DF-` to the command name. The input is as follows:

`DF-LMP2,[`*options*`]`
`DF-LCCSD(T),[`*options*`]`

Options for density fitting can be mixed with any options for `LOCAL`. Options for density fitting can also be given on a `DFIT` directive (see section 15).

The most important options for density fitting in local methods are

`BASIS_MP2=`*string*	Fitting basis set used in LMP2 and in LCCSD for integrals with up to 2 external orbitals. If a correlation consistent basis set is used (e.g. cc-pVTZ) the corresponding fitting basis for MP2 us used by default (cc-pVTZ/MP2FIT). Otherwise the fitting basis set must be defined in a preceding basis block (see section 11).
`BASIS_CCSD=`*string*	Fitting basis set used in LCCSD for integrals over 3- and 4-external orbitals. The default is `BASIS_MP2` and this is usually sufficient. However, the accurate approximation of 4-external integrals in LCCSD requires larger fitting basis sets than LMP2. Therefore, in order to minimize fitting errors, it is recommended to use the next larger fitting basis, e.g., `BASIS_CCSD=VQZ` for orbital basis `VTZ`.
`LOCFIT=`*value*:	If `LOCFIT=1` local fitting is enabled. This is necessary to achieve linear scaling in DF-LMP2 (see Refs. [11-14]). The errors introduced by local fitting are usually very small, but there are some exceptions. For instance, `LOCFIT=1` must not be used in counterpoise calculations, see section 32.9.8) Note that for small molecules `LOCFIT=1` can be more expensive than `LOCFIT=0`.

For further details and options for density fitting see section 15.

33 PNO-LMP2 and PNO-LMP2-F12

In this section local correlation methods that use pair natural orbitals (PNOs) are described. This program is entirely distinct from the older PAO-based methods that were described in the previous section. It is designed for parallel execution, and disk I/O is avoided as much as possible. This means that more memory is required than in other programs. However, the data are distributed over all computing cores, and the memory requirement per core is inversely linear in the number of cores used. Therefore, it is normally not recommended to use these programs on a single core. Depending on the molecular size, parallelization works well up to 100-200 cores using multiple nodes, provided a fast network (Infiniband or similar) is available.

Appropriate default values are set which normally yield results that are close to the canonical ones. In particular, sub-kJ/mol accuracy of relative energies is usually achieved with PNO-LMP2-F12 (relative to MP2-F12).

Currently the PNO program of MOLPRO can perform closed-shell PNO-LMP2 and PNO-LMP2-F12 calculations. We strongly recommend that the user reads the following references for the concepts and local approximations used in the PNO program.

[1] H.-J. Werner, G. Knizia, C. Krause, and M. Schwilk, *Scalable Electron Correlation Methods. I.: PNO-LMP2 with Linear Scaling in the Molecular Size and Near-Inverse-Linear Scaling in the Number of Processors*, J. Chem. Theory Comput., **11**, 484 (2015).

[2] Q. Ma and H.-J. Werner, *Scalable Electron Correlation Methods. 2. Parallel PNO-LMP2-F12 with Near Linear Scaling in the Molecular Size*, J. Chem. Theory Comput., DOI: 10.1021/acs.jctc.5b00843 (2015).

[3] M. Schwilk, D. Usvyat, and H.-J. Werner, *Communication: Improved pair approximations in local coupled-cluster methods*, J. Chem. Phys., **142**, 121102 (2015).

The point group symmetry support of the PNO-LMP2 method is described in

[3] C. Köppl and H.-J. Werner, *On the use of Abelian point group symmetry in density-fitted local MP2 using various types of virtual orbitals*, J. Chem. Phys., **142**, 164108 (2015).

More references on the correlation methods, including some reviews suitable for an introduction, are listed in Sec. 32.

The PNO program is currently under active development. More features, including a PNO-LCCSD method, and performance improvements, will be available in future releases.

33.1 Getting started

The program is invoked using

`PNO-LMP2,options`

or, for the explicitly correlated variants

`PNO-LMP2-F12,options`

Available options are described in later sections of this manual. An example input file can be found in `examples/h2odimer_pno_lmp2_f12.com`.

33.2   Fundamental options

In this section we describe the parameters most relevant to the accuracy and performance of the PNO program. We note that our team has carefully selected the default options through benchmark calculations, and the options only need to be modified for special cases.

Options for **PAO/OSV/PNO generation**:

THRNPA=*value*	Charge threshold for selection of primary PAO domains when using IBOs or NBOs (default 0.2).
IEXT=*value*	Domain extension using connectivity. *value* corresponds to the number of bonds by which the primary domains are extended. The default is IEXT=2.
REXT=*value*	Domain extension using distance. *value* is the radius in a_0 from any atom in the primary domain. IEXT and REXT can be combined. If both are given all atoms are included that are selected by one or the other criterion. The default is REXT=5.
THROSV=*threshold*	OSV selection threshold based on occupation numbers (default 1.d-9).
THRPNO=*threshold*	PNO selection threshold based on the energy criterion (default 0.998). If *thresh* is smaller than 0.1 it refers to the natural occupation numbers, otherwise it refers to the fraction of OSV pair energies to be recovered. It is also possible to specify 3 values for strong+close, weak, and distant pairs as THRPNO=[*thrstrong, thrweak, thrdist*].
THRPNO_OCC=*threshold*	PNO selection threshold based on occupation numbers (default 1.d-8). If THRPNO is also given, a PNO is selected only when both criteria are fulfilled.

Options for **F12 calculations**:

BB_F12	(logical). If true use the local and parallel F12 energy routines (default .true.). Otherwise F12 routines relying on hard disk I/O (and therefore shall be run on a single computer node) will be used. This option shall only be set false if problems (such as insufficient memory available) arise from the parallel F12 routines.
BB_F12_PNO=*value*	If BB_F12_PNO=0, both OSV- and PNO-LMP2-F12 energy will be computed; If BB_F12_PNO=1, only PNO-LMP2-F12 energy will be computed; If BB_F12_PNO=2, only OSV-LMP2-F12 correction will be computed and the resulting energy will be set to PNO-LMP2 energy plus OSV-LMP2-F12 correction (default 1).
THRF12=*threshold*	LMP2 pair energy threshold for selecting pairs for which F12 corrections are computed. The default value is 1.d-4.

Options for **domain approximations and orbital screening**:

LOCFIT=0	Disables local fitting (default is LOCFIT=1).
IDFDOM=*value*	Fitting domain extension using connectivity. The default is 3.
RDFDOM=*value*	Fitting domain extension using distances in a_0. The default is 7. If both IDFDOM and RDFDOM are given, the DF functions at a center will be included when either criterion is fulfilled.

LOCRI=0 — Disables local RI (default is LOCRI=1).

IRIDOM=*value* — RI domain extension using connectivity. The default is 3.

RRIDOM=*value* — RI domain extension using distances in a_0. The default is 7. If both IRIDOM and RRIDOM are given, the RI basis functions at a center will be included when either criterion is fulfilled.

FITLMO=*threshold* — In the PNO program LMOs are truncated if the square sum of the coefficients at one center is smaller than *threshold* (default 1.d-6). The remaining LMO coefficients are fitted to the original LMO.

FITPAO=*threshold* — In the PNO program PAOs at one center are truncated when none of the PAOs at the center has a square sum of coefficients greater than *threshold* (default 1.d-6). The remaining PAO coefficients are fitted to the original PAOs.

BB_F12_THRVAL=*value* — The MP2 pair energy threshold in determining the LMO domains $[ij]_{\mathrm{LMO}}$ used in the F12 strong orthogonality projector (default 1.d-4). This option only applies to the selection of the valence occupied orbitals in the LMO domains.

ICOREDOM_F12=*value*, RCOREDOM_F12=*value* — The connectivity and distance (in a_0) criteria in determining the LMO domains $[ij]_{\mathrm{LMO}}$ used in the F12 strong orthogonality projector (defaults are 2 and 5.0, respectively). This option only applies to the selection of the core orbitals in the LMO domains.

Options for **symmetry**:

LOCSYM=1 — Use point group symmetry (default is LOCSYM=0). Note that the PNO-LMP2-F12 program does not support point group symmetry.

33.3 Advanced options

In this section we list some advanced options to the PNO program. These options exist for technical or historical reasons and we do not recommend modifying the default values in general.

The following options are available for the **orbital localization**:

LOC_METHOD=*method* — Localization method. *method* can be IBO (intrinsic bond orbitals, default), PM (Pipek-Mezey), or NBO (natural bond orbitals). IBO is strongly recommended, as it is most efficient and stable. The PNO-LMP2-F12 method only supports IBO presently.

IBTYPE=*value* — Projector type for generation of intrinsic atomic orbitals. *value* can be 1 or 2 (default).

IBOEXP=*value* — Exponent used in the PM-like localization functional. *value* can be 2 or 4 (default).

Options for **PAO domain selection**:

THRBP=*value* — Boughton-Pulay completeness criterion for selection of primary PAO domains when using PM.

Options for **OSV generation**:

OSV_AMPL=PAO|CAN|OPT Amplitudes to used to generate OSVs. PAO (default) means to use semi-canonical amplitudes in the PAO domains; CAN means semi-canonical in the full virtual space; OPT means fully optimized LMP2 amplitudes in the full virtual space.

Options for **PNO generation**:

PNO_AMPL=OSV|OSV(OPT)|PAO|PAO(OPT) Amplitudes to used to generate PNOs. OSV (default) means to use semi-canonical (non-iterative) OSV amplitudes; PAO means semi-canonical (non-iterative) PAO amplitudes; if (OPT) is appended the amplitudes are iteratively optimized (can be expensive with OSV(OPT) and very expensive with PAO(OPT)!

PNO_DIAG (logical). If true, use PNO domain selection criterion also for diagonal pairs. Otherwise OSV domains are used for diagonal pairs. If PNO_DIAG=true the threshold THROSV only affects the distant pair multipole treatment.

The PNO program devides basis functions to blocks for integral screening. The following options are available for defining the **block sizes**. A smaller block size encourages more efficient integral screening and improves the parallel efficient, while a larger block size improves the performance of matrix operations and reduces the bookkeeping cost.

BB_BLOCKS_AO=*value* Target blocking size in the AO basis (default 32).

BB_BLOCKS_DF_F12=*value* Target blocking size in the DF basis for the F12 calculations (default 32). The option does not affect PNO-LMP2 calculations.

BB_BLOCKS_RI=*value* Target blocking size in the RI basis for the F12 calculations (default 128).

In addition, the following options control the **integral screening thresholds**:

BB_THRESH=*value* Block screening threshold (default 1.d-5).

BB_RADIUS=*value* Block screening radius (default 4).

The following options controls some **technical details** of the PNO program.

BLOCKING (logical) If true use the blocked density fitting routines when possible (default).

BB_F12_CACHE=*value* Whether a local cache is used in combination with globalarrays (GA). Default value is 1, i.e., loading from GA is buffered.

33.4 Technical issues

For large molecules, we recommend using the density-fitted Hartree–Fock program (DF-HF) for the proceeding Hartree–Fock calculation. Presently the program is not well parallelized over multiple computer nodes. We therefore suggest running DF-HF calculations separately and using the save option to dump the molecular orbitals to disk for the electron correlation calculations. A parallel local density-fitted Hartree–Fock program is being developed and will be available in the near future.

The PNO program stores large data structure in distributed memory through the `globalarrays` toolkit. The toolkit has memory allocation mechanisms independent of `Molpro`. When running the PNO program, one should not allocate all available physical memory to `Molpro` using the `memory` command in an input file, so that the `globalarrays` toolkit could allocate sufficient memory when needed. In some cases it is helpful to pass the `-G [ga_mem]` option in the molpro command line. This allows the allocation of `ga_mem` megawords of memory for `globalarrays` at the beginning of execution. Without doing this, `globalarrays` may crash when the distributed data structure gets large, most likely due to an upstream bug. The total amount of memory used by `molpro` and `globalarrays` on a node, in MB, can be estimated from $n_{\text{core}}(8M_{\text{molpro}} + 1000) + 8M_{\text{GA}}/n_{\text{node}}$, where n_{core} is the number of cores per node, n_{node} is the number of nodes, M_{molpro} is the memory set by the `memory` command in the input file, and M_{GA} is the memory set with the `-G` option. The total amount of memory used shall not exceed available memory on a node, otherwise runtime errors due to insufficient memory are likely.

34 LOCAL METHODS FOR EXCITED STATES

34.1 Local CC2 and ADC(2)

Bibliography:
General local CC2 for excited states:
[1] D. Kats, T. Korona and M. Schütz, *Local CC2 electronic excitation energies for large molecules with density fitting*, J. Chem. Phys. **125**, 104106 (2006).
[2] D. Kats, T. Korona and M. Schütz, *Transition strengths and first-order properties of excited states from local coupled cluster CC2 response theory with density fitting*, J. Chem. Phys. **127**, 064107 (2007).
Laplace transformed local CC2 for excited states:
[3] D. Kats and M. Schütz, *A multistate local coupled cluster CC2 response method based on the Laplace transform*, J. Chem. Phys. **131**, 124117 (2009).
[4] D. Kats and M. Schütz, *Local Time-Dependent Coupled Cluster Response for Properties of Excited States in Large Molecules*, Z. Phys. Chem. **224**, 601 (2010).
[5] K. Freundorfer, D. Kats, T. Korona and M. Schütz, *Local CC2 response method for triplet states based on Laplace transform: Excitation energies and first-order properties*, J. Chem. Phys. **133**, 244110 (2010).
[6] K. Ledermüller, D.Kats and M. Schütz, *Local CC2 response method based on the Laplace transform: Orbital-relaxed first-order properties for excited states*, J. Chem. Phys. **139**, 084111 (2013).
Analytical nuclear gradients for ground and excited states:
7] K. Ledermüller and M. Schütz, *Local CC2 response method based on the Laplace transform: Analytic energy gradients for ground and excited states*, J. Chem. Phys. **140**, 164113 (2014).
8] M. Schütz, *Oscillator strengths, first-order properties, and nuclear gradients for local ADC(2)*, J. Chem. Phys. **142**, 214103 (2015).
Previous work on local methods for excited states (LEOM-CCSD):
[9] T. Korona and H.-J. Werner *Local treatment of electron excitations in the EOM-CCSD method*, J. Chem. Phys. **118**, 3006 (2003).

All publications resulting from use of this program must acknowledge Ref. [3] (calculations of singlet states) and [5] (calculations of triplet states and properties).

The command `LT-DF-LCC2` calls the Laplace transformed LCC2 program, and `LT-DF-LADC(2)` calls LADC(2). The excited states of interest should be specified on the `EOM` card.

34.2 Options for `EOM`

see also section 25.1.

In the case of LT-DF-LCC2/ADC(2) multistate calculations are possible, and it is recommended to calculate more states as needed.

The parameters on the `EOM` card:

`EOM,-n.1,` `key1=`*value1*`,` `key2=`*value2*`,...`

where *n.1* is the last state of interest, e.g., with `EOM,-5.1` the four lowest excited states will be calculated. The following keywords `key` are possible:

`SINGLET=`*ising* If set to 1, singlet states will be calculated (default).

`TRIPLET=`*itrip* If set to 1, triplet states will be calculated (not implemented for ADC(2)).

`EXFILE=`*record.ifil* Record for converged CIS eigenvectors (default 6100.2).

`SAVE=`*record.ifil* Record for save of restart information.

`SAVET=`*record.ifil* Record for restart information for triplet states (if calculated together with singlet states).

`START=`*record.ifil* Record for restart of previous calculation.

`STARTT=`*record.ifil* Record for restart of previous calculation (if calculated together with singlet states).

`NSRCH4ST=`*nst* In the first *nst* iterations in the Davidson diagonalisation the excited state domains are determined for each basis vector in the Davidson subspace ("search for states") (default 7).

`THRLCH=`*thrlch* threshold for the Davidson procedure. If smaller than zero, the Davidson procedure is skipped and DIIS is started directly instead (possible only for restart, `SAVE` and `START` have to be identical).

`THRLCD=`*thrlcd* threshold for DIIS.

`ADC2=`*adc2* if = 1, do ADC(2) calculation instead of CC2.

`LTGS=`*ltgs* if = 1, use LT-DF-LMP2 for the ground state.

Default local approximations are defined according to procedure described in Ref. [3] (Laplace domains).

`INTFRAC=`*fracint* Rough criterion for specifying eom-domains from laplace-transformed integrals (default 0.8).

`INTEXC=`*excint* Criterion for specifying important orbitals from laplace-transformed integrals (default 0.999).

`REALFRAC=`*fracreal* Exact criterion for specifying eom-domains from laplace-transformed integrals (default 0.98).

`FULLFRAC=`*fracfull* Check for all orbital domains (complete sum over all orbitals) (default 0.95).

To switch to local aproximations calculated according to Ref. [9] (Boughton-Pulay procedure for excited states), set `INTFRAC` to zero.

Occupied orbital pair lists are calculated from important orbitals (Refs. [1,5]).

EWEAKPAIR=*ewpair* Distance criterion for excited state orbital pairs definition (default 5).

ALLSTRONG=*allstr* Different possibilities for excited state orbital pairs:

> 0: $[ij] \leq ewpair$, $[im] \leq ewpair$, $[mn] \leq ewpair$;
> 1: $\forall [ij]$, $\forall [im]$, $[mn] \leq ewpair$;
> 2: $\forall [ij]$, $[im] \leq ewpair$, $[mn] \leq ewpair$ (default);
> where i, j are important orbitals and m, n non-important. More detailed see Ref.
> [1].

One can try to improve the convergence of iterative procedures by changing following parameters

PRECOND=*prec* Type of preconditioner in LT-DF-LCC2/ADC(2) and DF-CIS:

> 0: canonical orbital energies;
> 3: solving linear equations including diagonal part of $(H - F)^{\text{CIS}}$ with MINRES
> (default).

HSCAL=*hscl* Scaling factor for diagonal part of $(H - F)^{\text{CIS}}$ matrix in the case of linear equations preconditioner (default 0.7).

Properties are also activated on the EOM card:

PROPES=*prop* States for which properties (dipole moments) should be calculated, e.g., PROPES=-3.1+5.1-8.1
> $\implies$ 2.1 3.1 5.1 6.1 7.1 8.1 15.1

TRANES=*tran* States for which transition moments should be calculated, syntax like for properties. Is not implemented for ADC(2) and for triplet states.

DENSAVE=*rec.ifil* Record, where densities calculated for states *prop* can be saved (for printing, see 34.4)

Note that ADC(2) transition moments require second-order ground-state singles and doubles amplitudes [see e.g. G. Wälz, D. Kats, D. Usvyat, T. Korona and M. Schütz, Phys. Rev. A **86**, 052519 (2012); ADC(2) is equivalent to TD-UCC[2]-H]. This is done by carrying out a partial local MP4 calculation, with second-order doubles restricted to strong pairs. For ADC(2) excitation energies or first-order properties just the first-order LMP2 amplitudes are required. Strong, close, and weak pairs actually all enter the subsequent excited state calculations.

By default, orbital un-relaxed properties are computed. In order to calculate also orbital relaxed properties the option ORBREL on the LOCAL card should be set to 1, *i.e.*,

LOCAL,ORBREL=1

This also applies to the calculation of nuclear gradients. Options concerning nuclear gradients, which are also activated on the EOM card, are

GSONLY=0 or 1 1: only ground state gradient is calculated

GRADSTATE=*gradstate* Excited state for which the gradient is to be calculated, e.g., GRADSTATE=2.1; must be combined with GSONLY=0

GRADDIIS=0 or 1 0: DIIS after Davidson diagonalization is switched off for all states except *gradstate*

NOFOLLOWGRAD=0 or 1 0: tries to follow a state in a geometry optimization after crossing on the basis of the overlap with eigenvector of previuous geometry; 1: calculate gradient of state number *gradstate* regardless of crossing

`ONLYTOTZLM`=0 or 1 1: only total, rather than ground- and excited state Lagrange multipliers
for orbital variations are computed. Hence, only one set of CPL and CPHF equations need to be solved rather than two. However, orbital relaxed properties are then not available.

34.3 Parameters on `LAPLACE` card

`NPOINTS`   Number of quadrature points (default (for CC2) 3).

`NPOINTS_CC2S` Number of quadrature points in CC2 in "search for states" (default 1).

`DISTRF`   Type of distribution function in functional for determination of Laplace points:
0: integral with f_x=1;
4: sum of distributions f_x (default).

`NULLPOINT` If larger than zero, use also a Laplace-point with t=0. In case of CC2 is always zero.

34.4 Print options

Setting `GPRINT,CIVECTOR`=1 prints the ten largest canonical contributions from singles vectors in each iteration.

For `EOMPRINT` card:

`LOCEOM` ≥ 0: print eom domain informations

`POPUL` ≤ 0: dont print population analysis

The densities saved with `DENSAVE` can be written into a cube file. Corresponding commands in `CUBE` module 38.7 are

`DENSITY`,*rec.ifil*,`cc2` Creates a cube file from the ground state density saved on record *rec.ifil*.

`DENSITY`,*rec.ifil*,`full`,`state`=*st.1* Creates a cube file from the excited state density of state *st.1*.

`DENSITY`,*rec.ifil*,`diff`,`state`=*st.1* Creates a cube file from the difference density (`full` - `cc2`) for state *st.1*.

34.5 Examples

Example 1:

```
***,The five lowest singlet excited states of water molecule
memory,64,m
gdirect
symmetry,nosym;orient,noorient
geometry={
o ,,  0.000,  0.000,  0.119
h1,,  1.423,  0.000, -0.947
h2,, -1.423,  0.000, -0.947 }
basis={
default,vdz
set,mp2fit
default,vdz/mp2fit
set,jkfit
```

```
default,vdz/jkfit }
hf
{lt-df-lcc2                         !ground state CC2
eom,-6.1                            !five lowest states
eomprint,popul=-1,loceom=-1 }   !minimize the output
```

The excitation energies (in eV) stand after the calculation in array `OMEGAF_S` for singlet states and in `OMEGAF_T` for triplet states.

Example 2:

```
***,The five lowest triplet excited states and properties
memory,64,m
gdirect
symmetry,nosym;orient,noorient
geometry={
o ,,  0.000,  0.000,  0.119
h1,,  1.423,  0.000, -0.947
h2,, -1.423,  0.000, -0.947 }
basis={
default,vdz
set,mp2fit
default,vdz/mp2fit
set,jkfit
default,vdz/jkfit }
hf
{lt-df-lcc2                         !ground state CC2
!five lowest triplet states, dipole moments for four lowest, density saved:
eom,-6.1,triplet=1,singlet=0,propes=-5.1,densave=5000.2
eomprint,popul=-1,loceom=-1 }    !minimize the output
!ground state density, file h2o0_density.cube:
{cube,h2o0,,80,80,80
density,5000.2,cc2 }
!difference excited state density, file h2o1_density.cube:
{cube,h2o1,,80,80,80
density,5000.2,diff,state=2.1 }
```

In order to set up an input for a geometry optimization of an excited state we recommend to use the input examples `furan_opt_ltdflcc2lr.com` (for local CC2) and `furan_opt_ltdflucc2lr.com` (for local ADC(2) aka TD-LUCC[2]-H) as templates. Provided that second-order methods like CC2 or ADC(2) are appropriate for the state to be optimized, it is recommended to use local ADC(2) rather than local CC2, since the former is considerably faster. Even if a local CC2 optimized geometry of an excited state is required, it is wise to preoptimize with local ADC(2). For a comparison of the performance of these two methods in geometry optimizations we refer to Ref. [8].

35   EXPLICITLY CORRELATED METHODS

Explicitly correlated calculations provide a dramatic improvement of the basis set convergence of MP2, CCSD, CASPT2, and MRCI correlation energies. Such calculations can be performed using the commands of the form

command, *options*

where *command* can be one of the following:

MP2-F12   Closed-shell canonical MP2-F12. By default, the fixed amplitude ansatz (`FIX`, see
           below) is used, but other ansätze are also possible. The F12-corrections is com-

puted using density fitting, and then added to the MP2 correlation energy obtained without density fitting.

DF-MP2-F12 As MP2-F12, but the DF-MP2 correlation energy is used. This is less expensive than MP2-F12.

DF-LMP2-F12 Closed-shell DF-MP2-F12 with localized orbitals. Any method and ansatz as described in J. Chem. Phys. **126**, 164102 (2007) can be used (cf. secions 35.2,35.7).

DF-RMP2-F12 Spin-restricted open-shell DF-RMP2-F12 using ansatz 3C. Any method as described in J. Chem. Phys. **128**, 154103 (2008) can be used (cf. sections 35.2,35.7).

CCSD-F12 Closed-shell CCSD-F12 approximations as described in J. Chem. Phys. **127**, 221106 (2007). By default, the fixed amplitude ansatz is used and the CCSD-F12A and CCSD-F12B energies are computed. Optionally, the command can be appended by A or B, and then only the corresponding energy is computed. For more details see section 35.10.

CCSD-F12c Closed-shell CCSD(F12*) approximation as proposed by Hättig, Tew and Köhn. In Molpro this is denoted f12c. As compared to CCSD-F12a/b it requires additional computational effort. Since in some parts the implementation is brute-force without paging algorithms, large memory may be required. In most cases there is no gain in accuracy as compared to f12b and therefore the use of this method is normally not recommended. Currently CCSD-F12c is not available for open-shell cases.

CCSD(T)-F12 Same as CCSD-F12, but perturbative triples are added.

CCSD(T)-F12c Same as CCSD-F12c, but perturbative triples are added.

UCCSD-F12 Open-shell unrestricted UCCSD-F12 approximations as described by G. Knizia, T. B. Adler, and H.-J. Werner, J. Chem. Phys. **130**, 054104 (2009). Restricted open-shell Hartree-Fock (RHF) orbitals are used. Optionally, the command can be appended by A or B, and then only the corresponding energy is computed. For more details see section 35.10.

UCCSD(T)-F12 Same as UCCSD-F12, but perturbative triples are added.

RCCSD(T)-F12 Similar to UCCSD(T)-F12, but the partially spin-adapted scheme is used.

DCSD-F12 Closed-shell CCSD-F12 approximations applied to DCSD method, see CCSD-F12 for more details.

UDCSD-F12 Open-shell unrestricted CCSD-F12 approximations applied to DCSD method, see UCCSD-F12 for more details.

RDCSD-F12 Open-shell partially spin-adapted CCSD-F12 approximations applied to DCSD method.

RS2-F12 CASPT2-F12 method as described in J. Chem. Phys. **133**, 141103 (2010).

MRCI-F12 MRCI-F12 method as described in J. Chem. Phys. **134**, 034113 (2011), J. Chem. Phys. **134**, 184104 (2011), and Mol. Phys. **111**, 607 (2013).

Published work arising from these methods should cite the following:

F. R. Manby, J. Chem. Phys. **119**, 4607 (2003)
(for the density fitting approximations in linear R12 methods)

A. J. May and F. R. Manby, J. Chem. Phys. **121**, 4479 (2004)
(for the frozen geminal expansions)

H.-J. Werner and F. R. Manby, J. Chem. Phys. **124**, 054114 (2006);
F. R. Manby, H.-J. Werner, T. B. Adler and A. J. May, J. Chem. Phys. **124**, 094103 (2006);
H.-J. Werner, T. B. Adler, and F. R. Manby, J. Chem. Phys. **126**, 164102 (2007)
(for all other closed-shell MP2-F12 methods).

G. Knizia and H.-J. Werner, J. Chem. Phys. **128**, 154103 (2008)
(for all open-shell F12 calculations).

T. B. Adler, G. Knizia and H.-J. Werner, J. Chem. Phys. **127**, 221106 (2007)
(for CCSD(T)-F12).

G. Knizia,T. B. Adler, and H.-J. Werner, J. Chem. Phys. **130**, 054104 (2009)
(for CCSD(T)-F12 and UCCSD(T)-F12 calculations).

T. B. Adler and H.-J. Werner, J. Chem. Phys. **130**, 241101 (2009)
(for LCCSD-F12).

K.A. Peterson, T. B. Adler, and H.-J. Werner, J. Chem. Phys. **128**, 084102 (2008)
(for the VnZ-F12 basis sets)

K. E. Yousaf and K. A. Peterson, J. Chem. Phys. **129**, 184108 (2009)
(for the VnZ-F12/OPTRI basis sets)

K. E. Yousaf and K. A. Peterson, Chem. Phys. Lett., **476**, 303 (2009)
(for the AVnZ/OPTRI basis sets)

H.-J. Werner, G. Knizia, and F. R. Manby (Mol. Phys. **109**, 407 (2011);
Kirk A. Peterson , C. Krause, H. Stoll, J. G. Hill, and H.-J. Werner, Mol. Phys. **109**, 2607 (2011)
(for calculations with multiple geminal exponents).

H.-J. Werner, J. Chem. Phys. **129**, 101103 (2008);
T. B. Adler, F. R. Manby, and H.-J. Werner, J. Chem. Phys. **130**, 054106 (2009);
T. B. Adler and H.-J. Werner, J. Chem. Phys. **130**, 241101 (2009);
T. B. Adler and H.-H. Werner, J. Chem. Phys. **135**, 144117 (2011)
(for all local local F12 calculations)

T. Shiozaki and H.-J. Werner, J. Chem. Phys. **133**, 141103 (2010);
T. Shiozaki, G. Knizia, and H.-J. Werner, J. Chem. Phys. **134**, 034113 (2011);
T. Shiozaki and H.-J. Werner, J. Chem. Phys. **134**, 184104 (2011);
T. Shiozaki and H.-J. Werner, Mol. Phys. **111**, 607 (2013)
(for all explicitly correlated multireference calculations).

D. Kats, D. Kreplin, H.-J. Werner, F. R. Manby, J. Chem. Phys. **142**, 064111 (2015)
(for DCSD-F12, RDCSD-F12, and UDCSD-F12 calculations).

In the following, we briefly summarize the ansätze and approximations that can be used in single-reference treatments. For more details and further references to related work of other authors see H.-J. Werner, T. B. Adler, and F. R. Manby, *General orbital invarient MP2-F12 theory*, J. Chem. Phys. **126**, 164102 (2007) (in the following denoted **I**). More information about MRCI-F12 calculations are given in section 20.8

35.1 Reference functions

The MP2-F12, CCSD-F12, and UCCSD-F12 methods must use conventional (non-density fitted) spin-restricted Hartree-Fock reference functions (HF or RHF). DF-HF cannot be used for these methods. This restriction is necessary to ensure that the Fock matrix is diagonal and consistent with the integrals used in these methods. For DF-MP2-F12, DF-LMP2-F12, and

DF-RMP2-F12 either HF or DF-HF reference functions can be used.

Currently, only finite dipole fields can be applied, other perturbations are not yet supported. ECPs can be used, but this is still experimental and not extensively benchmarked. The Douglas-Kroll-Hess or eXact-2-Component Hamiltonians cannot currently be used in combination with F12 methods.

35.2 Wave function Ansätze

The so called "ansatz" determines the definition of the explicitly correlated wave function. This is to be distinguished from the various approximations that can be used to approximate the Hamiltonian matrix elements. Generally, we use ansatz **3** (cf. **I**), for which the projector has the form

$$\hat{Q}_{12} \quad = \quad (1 - \hat{o}_1)(1 - \hat{o}_2)(1 - \hat{v}_1\hat{v}_2),$$

where $\hat{o}_i$ is a one-electron projector for electron i onto the occupied space, and $\hat{v}_i$ projects onto the virtual orbital space. In the case that domain approximations are used in local explicitly correlated wave functions, the operators $\hat{v}$ are replaced by operators $\hat{d}^{ij}$ that project just onto the domain for the orbital pair ij.

In MOLPRO the following wave function ansätze can be used:

35.2.1 The *general ansatz*

The conventional external pair functions are augmented by terms of the form

$$|u_{ijp}^{\text{F12}}\rangle \quad = \quad \sum_{p\,=\pm 1} \sum_{kl} T_{kl}^{ijp}\hat{Q}_{12}\hat{F}_{12}|kl\rangle$$

This ansatz is orbital invariant (i.e., the same results are obtained with canonical or localized orbitals), but it often suffers from geminal basis set superposition errors. Furthermore, singularities may occur in the zeroth-order Hamiltonian, in particular for larger systems. Therefore, this ansatz is normally not recommended.

35.2.2 The *diagonal ansatz* (D)

The sum over kl in equation (59) is restricted to ij. This ansatz is not orbital invariant and size consistent only when localized orbitals are used. However, geminal basis set superposition errors are absent and therefore the results are often more accurate than with the general ansatz.

35.2.3 The *fixed amplitude ansatz* (FIX)

The diagonal ansatz is used and the amplitudes of the explicitly correlated configurations are determined by the wavefunction cusp conditions, i.e.

$$T_{ij}^{ij,1} \quad = \quad \frac{1}{2}$$
$$T_{ij}^{ij,-1} \quad = \quad \frac{1}{4}$$

This ansatz is orbital invariant, size consistent and free of GBSSE.

35.3 RI Approximations

Various approximations such as A, B, C, HY1, HY2 exist for the matrix elements of the first-order Hamiltonian (see **I**). They differ in the way the RI approximations are made. In the limit of a complete RI basis, approximations B and C are identical and yield the exact result for a given wave function ansatz. We generally recommend approximation C, which is simpler and more efficient than approximation B. Normally, the union of the AO and RI basis sets is used to approximate the resolution of the identity (CABS approach). In the hybrid approximations (HY1, HY2, HX) only the AO basis is used in some less important terms. Together with the recommended approximation C, HY1 or HY2 can be used; HY2 is more accurate, HY1 more efficient. In most cases, approximation 3C(HY1) provides an excellent compromise between accuracy and efficiency. In approximation A, all terms involving exchange operators are neglected. This approximation is used along with local approximations in our low-order scaling LMP2-F12/3*A(loc) method that can be applied to large molecules (cf. section 35.11)

If the extended Brillouin condition (EBC, see **I**) is assumed, the explicitly correlated and conventional amplitude equations decouple and can be solved independently. These approximations are denoted by a star, e.g. **3***C.

35.4 Basis sets

In MOLPRO the F12 integrals can only be computed using density fitting (DF) approximations. The many electron integrals are approximated by resolutions of the identity (RI) expansions. Thus, F12 calculations require three different basis sets: the orbital (AO) basis, the DF basis, and the RI basis.

We recommend as AO basis sets the augmented correlation consistent basis sets (denoted AVnZ) or the specially optimized correlation consistent F12 basis sets (denoted VnZ-F12, cf. K.A. Peterson and H.-J. Werner, J. Chem. Phys. **128**, 084102 (2008)). Normally, triples zeta basis sets (AVTZ or VTZ-F12) yield excellent results that are close to the basis set limit. Diffuse basis functions are rather essential both for the HF and MP2-F12 energies, and therefore the standard VTZ sets are not recommended. If the AVnZ or VnZ-F12 orbital basis sets are used, suitable density fitting (DF) basis and resolution of the identity (RI) basis sets are automatically chosen. For the AVnZ orbital basis sets, AVnZ/MP2FIT amd VnZ/JKFIT basis sets are used by default for the DF and RI, respectively. The associated optimized CABS basis set of Peterson et al. can be chosen by specifying `RI_BASIS=OPTRI`. For the VnZ-F12 orbital basis, the associated CABS (OPTRI) basis sets are used by default. Other basis sets can be chosen using the `DF_BASIS`, `DF_BASIS_EXCH` and `RI_BASIS` options (cf. section 35.6). See section 15 for more details about density fitting.

This is an example for using multiple basis sets for density fitting and resolution of the identity

```
***,h2o
geom={o;
      h1,o,r;
      h2,o,r,h1,theta}
r=0.97 ang
theta=104

basis={
default,avtz
set,df
default,avtz/mp2fit    !density fitting basis
set,jk
default,avtz/jkfit     !density fitting basis for Fock and exchange matrices
set,ri
default,avtz/optri     !ri cabs basis
}
hf
ccsd(t)-f12,df_basis=df,df_basis_exch=jk,ri_basis=ri
```

```
 http://www.molpro.net/info/current/examples/h2o_basissets1.com
```

The following two examples yield identical results:

```
***,h2o
geom={o;
      h1,o,r;
      h2,o,r,h1,theta}
r=0.97 ang
theta=104

basis={
default,avtz
set,df,context=mp2fit
default,avtz           !density fitting basis
set,jk,context=jkfit
default,avtz           !density fitting basis for Fock and exchange matrices
set,ri,context=optri
default,avtz           !ri cabs basis
}
hf
ccsd(t)-f12,df_basis=df,df_basis_exch=jk,ri_basis=ri
```

```
 http://www.molpro.net/info/current/examples/h2o_basissets2.com
```

```
***,h2o
geom={o;
      h1,o,r;
      h2,o,r,h1,theta}
r=0.97 ang
theta=104

basis=avtz
hf
ccsd(t)-f12,df_basis=avtz/mp2fit,df_basis_exch=avtz/jkfit,ri_basis=avtz/optri
```

```
 http://www.molpro.net/info/current/examples/h2o_basissets3.com
```

In the latter example the specifications MP2FIT and JKFIT could be omitted, i.e. the input

```
ccsd(t)-f12,df_basis=avtz,df_basis_exch=vtz,ri_basis=optri
```

would be equivalent. In fact, since default density fitting basis sets are used

```
ccsd(t)-f12,ri_basis=optri
```

would be sufficient. Note, however, that without the specification OPTRI the avtz/jkfit basis set would be used for the RI. For example,

```
basis=avtz
hf
ccsd(t)-f12
```

is equivalent to

```
basis=avtz
hf
ccsd(t)-f12,df_basis=avtz/mp2fit,df_basis_exch=vtz/jkfit,ri_basis=vtz/jkfit
```

If the VnZ-F12 basis sets are used, the OPTRI sets are used by default, i.e.,

```
basis=vtz-f12
hf
ccsd(t)-f12
```

is equivalent to

```
basis=vtz-f12
hf
ccsd(t)-f12,df_basis=avtz/mp2fit,df_basis_exch=vtz/jkfit,\\
ri_basis=vtz-f12/optri
```

35.5 Symmetry

Symmetry cannot be used in DF-LMP2-F12 calculations. However, in MP2-F12, DF-MP2-F12, DF-RMP2-F12, CCSD(T)-F12 and UCCSD(T)-F12 calculations Abelian symmetry can be used as usual; in these cases the preceding DF-MP2-F12 calculations will be automatically performed without symmetry, and the integrals that are necessary for subsequent CCSD-F12 or UCCSD-F12 calculations will be transformed to the symmetry adapted basis. This is fully automatic and transparent to the user. Note, however, that the prefix DF- turns off symmetry automatically, and if you want to use symmetry in the HF calculations preceding the DF-MP2-F12 or DF-MP2-F12 calculations the symmetry elements (or AUTO) must be specified using the SYMMETRY directive (setting SYMMETRY,AUTO works fine).

35.6 Options

There are many options available, but these are hardly needed. Normally, when standard orbital basis sets such as aug-cc-PVTZ or VTZ-F12 are used, appropriate defaults are used and no further options are needed. A typical input simply reads

```
basis=vtz-f12
hf
ccsd(t)-f12
```

We recommend to specify options only when necessary and when it is well understood what they mean!

Options for canonical and local versions:

DF_BASIS=*basis* Select the basis for density fitting (see section 15 for details). *basis* can either refer to a set name defined in the basis block, or to a default MP2 fitting basis (e.g., DF_BASIS=VTZ generates the VTZ/MP2FIT basis). By default, the MP2FIT basis that corresponds to the orbital basis is used.

DF_BASIS_EXCH=*basis* Select the density fitting basis for computing the exchange and Fock operators. By default, the JKFIT basis sets which correspond to the orbital basis are used.

RI_BASIS=*basis* Select the basis for the resolution of the identity (RI). This can refer to a default basis set or a set name defined in a basis block. For F12 methods the Hartree-Fock JKFIT basis sets perform well for the RI, despite having been optimized for other purposes. These sets are used by default for the AVnZ orbital basis sets. The basis type can be appended to the basis name after a slash, e.g. RI_BASIS=AVQZ/JKFIT would use the specified JKFIT set, or RI_BASIS=AVQZ/OPTRI would use the optimized CABS basis sets of Peterson et al. These are recommended for the AVnZ and VnZ-F12 basis sets and used by default for the latter ones. Note that each OPTRI basis is associated to a specific orbital basis. Therefore, the name of the OPTRI basis must either be the same as that of the orbital basis, or be omitted, e.g., RI_BASIS=OPTRI selects automatically the correct set for the current orbital basis.

In case of R12-methods (which are not recommended to be used), the RI basis should be chosen to be a large uncontracted AO basis (at least AVQZ). Contraction/uncontraction can be forced appending (CONTRACT) or (UNCONTRACT) to the basis name, e.g., RI_BASIS=AVQZ(UNCONTRACT)/ORBITAL. If other options are given in parenthesis, these can be separated by commas, e.g., RI_BASIS=AVQZ(f/d,UNCONTRACT)/ORBITAL. Alternative forms, which should work as well, are RI_BASIS=AVQZ(f/d)(UNCONTRACT)/ORBITAL or RI_BASIS=AVQZ(f/d)/ORBITAL(UNCONTRACT). Note that the CONTRACT/UNCONTRACT option cannot be used with basis set names previously defined in a basis block.

CONTEXT=*context* Can be used to change the default type for the RI basis, e.g. CONTEXT=OPTRI will use the OPTRI basis sets that correspond to the VnZ-F12 or AVnZ basis sets.

ANSATZ=*ansatz* Select the explicitly correlated ansatz *ansatz* methods. See section 35.7 for the possibilities and further details.

GEM_BASIS Basis set name for geminal expansion; atom labels are ignored. This can either be OPTFULL (full nonlinear fit of the geminal expansion), EVEN (even tempered fit), or refer to a set name defined in a previous BASIS block. Default is OPTFULL.

GEM_TYPE Frozen geminal type: LINEAR or SLATER, default is SLATER.

GEM_NUMBER Number of Gaussian geminal functions (default 6).

GEM_CENTRE Centre of even tempered geminal exponents, if GEM_BASIS=EVEN (default 1.0).

GEM_RATIO Ratio of even tempered geminal exponents, if GEM_BASIS=EVEN (default 3.0).

GEM_BETA Exponent for Slater-type frozen geminal, or parameter for weight function in other frozen geminal models (default 1.0 a_0^{-1}). It is possible to specify extra exponents for core-core and core-valence correlation. If two values are given (in square brackets), the first is used for valence pairs, the second for core-core (cc) and core-

valence (cv) pairs. If three values are given, the first is used for vv, the second for cv, and the third for cc correlation.

GEM_OMEGA Exponent for weighting function (default -1, which means a value derived from GEM_BETA).

GEM_MOM Exponent for r in omega fitting (default 0).

GEM_M Exponent for r in weighting function (default 0).

GEM_MAXIT Max. number of iterations in geminal optimization (default 200).

GEM_PRINT Print parameter for geminal optimization (default 0).

GEM_DEBUG Debug option for geminal optimization (default 0).

GEM_ACC Convergence threshold for geminal line search (default 0.001).

GEM_FAC Scaling factor for exponents in geminal optimization (default 1.0).

GEM_METHOD Geminal optimization method (augmented Hessian (AH) or Newton-Raphson (NR), default AH).

GEM_TRUST Trust ratio in AH geminal optimization (default 0.4).

GEM_SHIFT Hessian shift in AH geminal optimization (default 0).

GEM_NUMERICAL Flags numerical integration in geminal optimization (default 0).

GEM_PLOT Geminal plot file (default blank).

GEM_OPT_FULL If nonzero (default), fit each geminal independently to Gaussians (if several exponents are used). If zero, the first exponent is fitted, unless GEM_BETA_OPT is specified.

GEM_BETA_OPT Exponent used to fit the Gaussian expansion.

SIM_MULTGEM Only for calculation with multiple exponents: if nonzero, loop externally over integral program for different exponents. This is implied automatically if each geminal is fitted independently. If the same Gaussian exponents are used for each Slater exponent, SIM_MULTGEM=0 can be used (default). In this case the integral program handles the general contractions (slightly faster).

PRINT=*ipri* Select output level:

ipri=0	Standard output
ipri=1	Standard output plus more detailed information about integral evaluations.
ipri=2	Debugging output

THRBINV Threshold below which non-physical eigenvalues are projected from approximate B matrices

THRAOF12 Threshold for integral screening contribution.

35.7 Choosing the ansatz and the level of approximation

The Ansatz can be chosen using the ANSATZ option and/or by options on the command line.

3A	Ansatz 3A;
3*A	Ansatz 3A with EBC approximation
3B	Ansatz 3B
3*B	Ansatz 3B with EBC approximation

`3C`	Ansatz 3C
`3*C`	Ansatz 3C with EBC approximation

The ansatz can be further detailed by appending options in parenthesis, e.g.

`ANSATZ=3B(D)`

These options can be one of

`D`	Use diagonal ansatz
`FIX`	Use diagonal ansatz with fixed amplitudes (orbital invariant)
`FIXC`	Use diagonal ansatz with fixed amplitudes and canonical orbitals
`DX`	Use diagonal ansatz and assume X-matrix to be diagonal (only for Ansatz 3A)
`GBC`	Use GBC approximation (only for 3B, default in 3A)
`EBC`	Use EBC approximation (same as *)
`HX1`	Use HX1 approximation (only for 3B).
`HY1`	Use HY1 approximation (only for 3B and 3C).
`HY2`	Use HY2 approximation (only for 3B and 3C).
`HY`	Default hybrid approximation. HX1 and HY2 approximation in 3B, HY2 in 3C.
`NOZ`	Neglect Z terms (only for 3B and 3C).
`NOX`	Neglect X terms (only for 3A and 3B).

Several options separated by commas can be given. For instance

`ANSATZ=3C(FIX,HY1)`

uses the diagonal ansatz 3C(D) with fixed coefficients and the hybrid (HY1) approximation.

Alternatively or in addition, the following options can be given on the command line:

`DIAG=1`	Use diagonal ansatz.
`DIAGX=1`	Use diagonal ansatz and assume X-matrix to be diagonal.
`GBC=1`	Use GBC approximation (only for 3B, default in 3A).
`EBC=1`	Use EBC approximation (same as *).
`HYPRID=n`	Use HYn approximation.
`HYPRIDX=1`	Use HX1 approximation.
`NOZ=1`	Neglect Z terms (only 3B and 3C).
`NOX=1`	Neglect X terms (only 3A and 3B).
`FIX=1`	Use diagonal ansatz with fixed coefficient approximation (orbital invariant).
`FIX=2`	Use diagonal ansatz with fixed coefficient approximation. Evaluate only first order energy expression, not the Hylleraas functional. Very fast but less accurate and reliable!
`FIXCAN=1`	Use diagonal ansatz with fixed coefficient approximation and canonical orbitals. A non-iterative method is used to evaluate the energy. This is equivalent to `FIX=1,CANONICAL=1` and is most efficient.
`FIXCAN=-1`	As `FIXCAN=1`, but equations are solved iteratively (test purpose only).

CABS=1   Use CABS (default). If `CABS=0` is given, CABS is disabled. However, if `RI_BASIS=OPTRI`, the orbital and OPTRI basis sets are automatically merged, and then exactly the same results as with `CABS=1` are obtained.

ORTHO_CABS=1 Construct CABS basis from orthogonal MOs and ABS basis rather than AO and RI basis.

THRABS=*thrabs* Threshold for smallest eigenvalue of S in auxiliary ABS (only used with `ORTHO_CABS=1`; default=THRCABS).

THRCABS=*thrcabs* Threshold for smallest eigenvalue of S in CABS (default 1.d-8).

THRCABS_REL=*thrcabs_rel* Relative CABS threshold (default 1.d-9). The actual threshold is `max(thrcabs,eigmax*thrcabs_rel`, where `eigmax` is the largest eigenvalue of the overlap matrix.

PRINT=*level* Print parameter. `PRINT=1` give information about all computed integrals and the iterations.

DEBUG=*level* Can be used to obtain extended debug print.

SOLVE=0   Use a most efficient pair-specific fully iterative method (default).

SOLVE=1   Use simple fully iterative method.

SOLVE=2   Use pair specific iterative method (more expensive).

SOLVE=3   Use pair specific non iterative method (most expensive, only with canonical orbitals).

CANONICAL=1 Use canonical orbitals and full domains.

DOMSEL=1 Use full domains and localized orbitals (unless `CANONICAL=1` is given).

SCALE_TRIP=1 Scale triples energy as explained in section 35.10.

SINGLES   If set to one, include CABS singles correction (default=1)

CORE_SINGLES If set to one, include CABS singles correction for core orbitals (default=0)

EXTGEN   For open-shell systems: If 1 (default,recommended), include all occupied valence orbital pairs for *mn* in T_{mn}^{ij}, independent of spin (as described in J. Chem. Phys. 130, 054104 (2009), section II.E). If 0, use only pairs mn where the spins of *i* and *m*, and *j* and *n* are equal.

For instance

```
ANSATZ=3C,fix=1,hybrid=1,canonical=1
```

implies a canonical 3C calculation with diagonal ansatz 3C, using fixed coefficient and hynrid approximations. The combination of the options `fix=1` and `canonical=1` implies a non-iterative calculation of the energy and is recommended. The above is equivalent to all of the following:

```
ANSATZ=3C(FIXC,HY1)
ANSATZ=3C(D,FIXC,HY1)
ANSATZ=3C(D,HY1,FIX),canonical=1
```

Note that the HF convergence threshold should be rather strict to obtain accurate results (use `ACCU,14` in the HF).

Numerous further options are for specialist use only and not described here. See `explicit.registry` for a full list.

35.8 CABS Singles correction

By default, the perturbative CABS singles correction as described in J. Chem. Phys. **127**, 221106 (2007) and J. Chem. Phys. **128**, 154103 (2008) is included in the reference energy of all MP2-F12 and CCSD-F12 calculations (closed and open-shell, except for LMP2-F12/3*A(loc), which is done with a different program). The corrected reference energy is stored in variable `ENERGR`, so that `ENERGY-ENERGR` are the total correlation energies. For the setting of other variables by the F12 programs see section 35.12.

The singles correction can be turned off by option `SINGLES=0`, e.g.

`MP2-F12,SINGLES=0`

The contribution of core orbitals to the singles energy is not included by default, but can be turned on by option `CORE_SINGLES`, e.g.

`MP2-F12,CORE_SINGLES=1`

However, we do not recommended the use of core singles, because they depend sensitively on the CABS basis construction and do not offer significant improvements in relative energies.

35.9 Pair specific geminal exponents

Different Slater exponents can be used for core-core, core-valence and valence-valence pairs as described in H.-J. Werner, G. Knizia, and F. R. Manby (Mol. Phys. 2010, DOI: 10.1080/00268976.2010.526641). The exponents are specified using the `GEM_BETA` option, e.g., `GEM_BETA=[1.0, 1.7, 2.5]` (see options, section 35.6). The three values are used for vv, cv, cc pairs, respectively. In most cases, core pairs can be defined by using the `CORE` directive: all orbitals that are not core and do not belong to the default valence shell are then treated as core. If part of the default valence shell is to be taken as core (e.g., the 3d shell in first-row transition metals), the core can be defined via the `PRCORE` variable, e.g., `prcore=[4,2,2,1,4,2,2,1]` for Cu_2. This variable must then be defined before the F12 calculation that should use it. The following example shows calculation for Br_2, in which the $3d$ shell is treated as core.

```
memory,32,m
gthresh,energy=1.d-8
geometry={br;br,br,rmin}

rmin=2.281 ANG

basis={
ecp,Br,ecp10mdf
sp,Br,aug-cc-pVTZ-PP;c;
d,Br,338.996,103.217,42.3638,18.4356,8.37254,3.80222,1.68677,0.677520
c,1.8,0.001524,0.015673,0.072400,0.186303,0.323881,0.374534,0.257418,0.068051
d,Br,2.9173,0.6300,0.2228
f,Br,1.4417

set,dfmp
s,Br,40.9778,22.0940,14.1569,6.30933,3.49893,2.07145,1.22411,0.706125,0.421245,0.235424,0.1334
p,Br,31.5779,17.7012,10.3673,5.56829,3.34725,1.86205,1.12814,0.520803,0.290648,0.155863
d,Br,35.4419,14.4095,7.13728,4.02429,2.19901,1.18121,0.537101,0.320289,0.151982
f,Br,16.6283,7.92639,3.69263,1.89967,1.02171,0.418748
g,Br,58.3022,21.9356,7.85160,5.60937,2.04334,1.37529
h,Br,7.51453,3.15089

set,ri
s,Br,18.7563,9.07737,4.87021,2.00555,0.900841,0.080149
p,Br,26.0294,17.4402,5.55778,3.70554,2.47230,1.18351,0.511543,0.177391
d,Br,15.9542,11.4584,8.89027,1.44361,0.945611,0.334128
f,Br,42.4889,15.5186,10.3279,6.36172,2.80704,0.961178,0.415934
g,Br,24.3260,9.29525,3.78033,1.65385,0.919948
h,Br,18.4810,7.54637,2.84990,0.966374
i,Br,11.4466
}

explicit,ri_basis=ri,df_basis=dfmp,df_basis_exch=def2-qzvpp/jkfit

hf;accu,16
i=1
{mp2-f12,gem_beta=[1.25];core,2,1,1,,2,1,1}
emp2f12(i)=energy-energr
ef12_vv(i)=energ_vv
ef12_cv(i)=energ_cv
ef12_cc(i)=energ_cc
$beta(i)='[1.25]'
i=i+1
{mp2-f12,gem_beta=[0.8,1.7];core,2,1,1,,2,1,1}
emp2f12(i)=energy-energr
ef12_vv(i)=energ_vv
ef12_cv(i)=energ_cv
ef12_cc(i)=energ_cc
$beta(i)='[0.8,1.7]'

i=i+1
{mp2-f12,gem_beta=[0.8,1.7,2.2];core,2,1,1,,2,1,1}
emp2f12(i)=energy-energr
ef12_vv(i)=energ_vv
ef12_cv(i)=energ_cv
ef12_cc(i)=energ_cc
$beta(i)='[0.8,1.7,2.2]'

table,beta,ef12_cc,ef12_cv,ef12_vv,emp2f12
Title,Results for Br2, basis vdz-f12
```

http://www.molpro.net/info/current/examples/br2_f12_multgem.com

35.10 CCSD(T)-F12

The CCSD-F12 and UCCSD-F12 programs first do DF-MP2-F12/3C(FIX) (closed-shell) or DF-RMP2-F12/3C(FIX) (open-shell) calculations, and then perform the CCSD-F12 (UCCSD-F12) without density fitting. By default, the CCSD-F12A and CCSD-F12B energies are both computed. A specific method can be requested by appending A or B to the -F12 suffix. Furthermore, instead of the 3C(FIX) ansatz, different ansätze (e.g. 3C) can be used. In this case the amplitudes of the explicitly correlated terms are determined in the MP2-F12 calculation and kept fixed in the CCSD-F12.

It should be noted that these methods involve approximations and do not yield the exact CCSD-F12 energies. Preliminary experience has shown that the CCSD-F12A method slightly overestimates the correlation energies, while CCSD-F12B underestimates them. For AVDZ or AVTZ basis sets, CCSD-F12A usually gives very good results, but for larger basis sets it may overestimate the basis set limit and converge from below to the limit. Thus, convergence may not be monotonic, and extrapolation of the correlation energies should not be attempted. CCSD-F12B usually converges monotonically from below to the limit and gives best results for AVQZ and larger basis sets. Thus, we currently recommend CCSD-F12A for AVDZ and AVTZ basis sets, and CCSD-F12B for larger basis sets (rarely needed).

The perturbative triples correction can be invoked by using CCSD(T)-F12 or UCCSD(T)-F12. There is no direct F12 correction to the triples, and therefore the basis set error of the triples is not affected by the F12 (small changes of the triples energy arise from the fact that the doubles amplitudes are affected by the F12 terms). In many cases, a simple and pragmatic improvement of the triples energy can be obtained by scaling the triples energy contribution as

$$\Delta E_{(T*)} \quad = \quad \Delta E_{(T)} * E_{corr}^{MP2-F12} / E_{corr}^{MP2}$$

This can be done automatically by setting option `SCALE_TRIP=1`, i.e.

```
CCSD(T)-F12,SCALE_TRIP=1
```

35.11 DF-LMP2-F12 calculations with local approximations

Local variants of the DF-MP2-F12 and CCSD(T)-F12 methods are invoked by the commands `DF-LMP2-F12`, `DF-LCCSD-F12`, `DF-LCCSD(T)-F12` with ansatz 3*A(LOC) [for DF-LCCSD-F12 fixed amplitudes are used, i.e., the default is 3*A(LOC,FIX)]. These calculations are performed with a different program than non-local calculations. The (LOC) option implies that the LMP2 calculation with domain approximations is performed, and by default a local projector as first described in H.-J. Werner, J. Chem. Phys. **129**, 101103 (2008) is used [see also T. B. Adler, F. R. Manby, and H.-J. Werner, J. Chem. Phys. **130**, 054106 (2009); T. B. Adler and H.-J. Werner, J. Chem. Phys. **130**, 241101 (2009); T. B. Adler and H.-H. Werner, J. Chem. Phys. **135**, 144117 (2011)]
This yields very similar restults as the corresponding canonical methods at much lower cost [3] and the method can be applied to quite large molecules.

Special options for these local variants are (local RI works only with ansatz 3*A):

PAIRS   Specifies which pairs to be treated by R12 or F12
           (STRONG|CLOSE|WEAK|ALL; pairs up to the given level are included). The

---

[3] ANSATZ=3*A(LOC,FIX) is exactly equivalent to ANSATZ=3*A(FIX,NOX),PROJF=2,CABS=0,SINGLES=0, but if the latter options are used the non-local program is used to compute the F12 correction and local approximations are only simulated. CABS singles can then be included by omitting the SINGLES=0 option.

default is `ALL`. Note that even with `ALL` very distant pairs are neglected if these are neglected in the LMP2 as well.

USEVRT   If zero, the $1 - pp + po + op - p'o - op'$ form of the projector is used, and local RI approximations apply to p and p'. If set to 1, the $1 + oo - vv - p'o - op'$ form of the projector is used; any local RI approximation then applies only to the RI contribution p'.

USEPAO   If `USEPAO=1` use pair-specific local projectors instead of vv. This is the default if either the ansatz contains '(LOC)' or if domain approximations are made in the LMP2 (i.e., `DOMSEL<1` is explicitly specified). Otherwise the default is `USEPAO=0`. `USEPAO=1` automatically implies `USEVRT=1`, i.e. local RI approximations only affect the RI contributions p'. Furthermore, if `USEPAO=1` is specified and `DOMSEL` is not given, default domains are assumed in the LMP2. If `USEPAO=0`, full domains (`DOMSEL=1`) will be used.

FULLAO   if `USEVRT=0` and `FULLAO=1`, local RI approximations only apply to the RI contributions p'. This should give the same results as `USEVRT=1` (only applies if `USEPAO=0`).

DEBUG   Parameter for debug print

LOCFIT_F12   If set to one, use local fitting. Default is no local fitting (`LOCFIT_F12=0`)

LOCFIT_R12   Alias for `LOCFIT_F12`. Local fitting is not recommended in R12 calculations.

FITDOM   Determine how the base fitting domains are determined (only applies if `LOCFIT_F12=1`):
0: Fitdomains based on united operator domains;
1: Fitdomains based in orbital domains (default);
2: Fitdomains based on united pair domains using strong pairs;
3: Fitdomains based on united pair domains using strong, close and weak pairs.
Note: This is the only option implemented in the DF-LMP2 program. Therefore, the DF-LMP2 and DF-LMP2-F12 programs might give slightly different results if default values are used.

RDOMAUX   Distance criterion for density fitting domain extensions in case of local fitting. The default depends on `FITDOM`.

IDOMAUX   Connectivity criterion for density fitting domain extensions in case of local fitting.

RAODOM   Distance criterion for RI domain extensions. Zero means full RI basis (default). If `USEPAO=1` or `USEVRT=1` or `FULLAO=1` a value of 5 bohr is recommended. In other cases the local RI domains must be very large (`RAODOM>12`) and the use of local RI approximations is not recommended.

IAODOM   Connectivity criterion for RI domain extensions. Zero means full RI basis (default). Values greater or equal to 2 should lead to sufficiently accurate results, provided the local projector (`USEPAO=1`) is used.

THRAO   Screening threshold for coulomb integrals in the AO or RI basis.

THRAOF12 Screening threshold for F12 integrals.

THRMO   Screening threshold for half transformed integrals.

THRPROD   Product screening threshold in the first half transformation.

NOMP2   If set to 1, only the F12 calculation is performed, and the LMP2 is skipped. This is sometimes useful if full domains are used, since the iterative LMP2 then causes a big overhead and needs a lot of memory. It is then more efficient to do the a DF-MP2 calculation separately and compute the total energy as the sum of the DF-MP2 energy and the F12 energy

PROJF   Values greater than 0 invoke the local projector. `PROJF=1` project vv parts only (this is formally the most accurate case but only possible with the canonical program [`ANSATZ=3*A(FIX,NOX)`], `PROJF=2` project vv and vo parts (default). This is unavoidable if the local program is used [`ANSATZ=3*A(LOC)`].

MODOMC   If > 0, core contributions are neglected in the projector. This is a necessary approximation in order to compute the LCCSD-F12 coupling terms efficiently (implementation not yet finished). Setting `MODOMC=0` avoids the approximation. Note that the results in J. Chem. Phys. **135**, 144117 (2011) have been obtained using `MODOMC=0`.

Further options for density fitting are described in section 15, and further options to choose the ansatz in section 35.7.

Typical inputs for calculations with local approximations are:

```
!parameters for local density fitting:
DFIT,LOCFIT_F12=1,FITDOM_MP2=1,IDOMAUX_MP2=3,DSCREEN=1
!LMP2-F12(loc) with local RI:
{DF-LMP2-F12,ANSATZ=3*A(LOC),DOMSEL=0.985,RAODOM=5,PAIRS=WEAK}
```

This would perform a local MP2 with a Boughton-Pulay domain completeness criterion of 0.985. In the F12 part, distant pairs are not included (`PAIRS=WEAK`) and the local projector is used (`USEPAO=1`, default). Local density fitting and local RI approximations are used.

A corresponding non-local calculation (still using localized orbitals and the diagonal ansatz) would be

```
{DF-LMP2-F12,ANSATZ=3*A(LOC),DOMSEL=1.0,USEVRT=1,NOMP2=1}
ecorr_F12=ef12

{DF-MP2}
ecorr_MP2=energy-energr          !mp2 correlation energy
ecorr_MP2_F12=ecorr_MP2+ecorr_F12  !total correlation energy
```

Note: The use of local DF and RI domains is still experimental and should be use with care!

35.12 Variables set by the F12 programs

The following variables are set by the F12 programs:

ENERGR   Reference energy. This includes the perturbative CABS singles correction if computed.

ENERGY   Total energy of the requested method (including the F12 and singles corrections). `ENERGY(1)` and `ENERGY(2)` hold the F12A and F12B values, respectively (if both are computed).

ENERGC   Total CCSD-F12 energies in ccsd-f12 or uccsd-f12 calculations. `ENERGC(1)` and `ENERGC(2)` hold the F12A and F12B values, respectively (if both are computed). The difference of `ENERGY` and `ENERGC` is the triples energy contribution.

ENERGT   Triples energy contribution. This is a vector. The corresponding methods are stored in `METHODT` (strings).

EMP2   Total MP2 energy (excluding F12 correction, but including the singles correction).

EMP2_SCS Total SCS-MP2 energy (excluding F12 correction, but including the singles correction).

EMP2_SING Singlet MP2 correlation energy (excluding F12 correction).

EMP2_TRIP Triplet MP2 correlation energy (excluding F12 correction).

EMP2_STRONG Strong pair contribution to the LMP2 correlation energy (where applicable).

EMP2_CLOSE Close pair contribution to the LMP2 correlation energy (where applicable).

EMP2_WEAK Weak pair contribution to the LMP2 correlation energy (where applicable).

EMP2_DIST Distant pair F12 contribution to the LMP2-F12 correlation energy (where applicable).

EF12   F12 contribution to the MP2-F12 correlation energy for the requested ansatz.

EF12S   F12 contribution to the MP2-F12 correlation energy using EBC approximation for the requested ansatz.

EF12D   F12 contribution to the MP2-F12 correlation energy using EBC approximation and diagonal (DX) approximation for the requested ansatz.

EF12_SING Singlet F12 contribution to the MP2-F12 correlation energy for the requested ansatz.

EF12_TRIP Triplet F12 contribution to the MP2-F12 correlation energy for the requested ansatz.

EF12_STRONG Strong pair F12 contribution to the LMP2-F12 correlation energy (where applicable).

EF12_CLOSE Close pair F12 contribution to the LMP2-F12 correlation energy (where applicable).

EF12_WEAK Weak pair F12 contribution to the LMP2-F12 correlation energy (where applicable).

EF12_DIST Distant pair F12 contribution to the LMP2-F12 correlation energy (where applicable).

EF12_SCS F12 contribution to the MP2-F12 correlation energy for the requested ansatz.

EF12_SINGLES Total CABS singles contribution (in closed-shell case equal to EF12_RHFRELAX).

EF12_RHFRELAX CABS singles correction of the reference energy (only the spin-free contribution is used).

ANSATZ   The requested ansatz (string variable)

Variables corresponding to EF12_* exist also for EF12S_* and EF12D_*.

In case of doubt or problems, try in a test calculation

SHOW,ENERG*,EMP2*,EF12*

This should show all relevant variables that exist. Note that system variables are internally stored with an underscore as a prefix, and this may be shown by the SHOW command. The variables can be accessed with or without underscore (but if the user defines a variable with the same name then the underscore is needed to access the system variable and not the user variable).

36   THE FULL CI PROGRAM

This module is the determinant full CI program, as described in

P.J. Knowles and N.C. Handy, Chem. Phys. Letters 111 (1984) 315,
P.J. Knowles and N.C. Handy, Comp. Phys. Commun. 54 (1989) 75.

Published work resulting from the use of this program should cite these references.

The program in normal use finds the lowest eigenvector of the complete CI hamiltonian matrix; more sophisticated use is possible, but not documented here. The program is interfaced to free standing versions such as supplied in the CPC program library by use of the DUMP option.

The program is called with the command FCI.

36.1   Defining the orbitals

ORBIT,*name.file*;

name.file specifies the record from which orbitals are read. The default is the set of orbitals from the last SCF, MCSCF or CI calculation.

36.2   Occupied orbitals

OCC,$n_1,n_2,\ldots,n_8$;

n_i specifies numbers of occupied orbitals (including CORE) in irreducible representation number *i*. If not given, the default is the complete basis set.

36.3   Frozen-core orbitals

CORE,$n_1,n_2,\ldots,n_8$;

n_i is the number of frozen-core orbitals in irrep number *i*. These orbitals are doubly occupied in all configurations, i.e., not correlated. If no CORE card is given, the program uses the same core orbitals as the last CI calculation; if there was none, then the atomic inner shells are taken as core. To avoid this behaviour and correlate all electrons, specify

CORE

36.4   Defining the state symmetry

The number of electrons and the total symmetry of the wavefunction are specified on the WF card:

WF,*elec,sym,spin*

where

elec:	is the number of electrons
sym:	is the number of the irreducible representation
spin:	defines the spin symmetry, *spin*= 2S (singlet=0, doublet=1, triplet=2, etc.)

36.5 Density matrix

The 1-electron density matrix can be computed with

`DM`,*record.file*

and then subsequently used to calculate one-electron properties using the `PROP` program.

36.6 Excited states

`STATE`,*value*;

Specifies the number of states to be sought (default 1).

36.7 Convergence threshold

`THR`,*value*;

Convergence threshold (default 10^{-5}). If changes in the normalised wavefunction become less than this value, then the iterative eigenvector solver terminates.

36.8 Printing options

`PRINT`,*code,value*;

Print options. Generally, the value determines how much intermediate information is printed. *value*=-1 means no print (default for all codes). if *value* is omitted, it is taken as zero, which is usually appropriate. Specification of higher values will generate more output. The following codes are allowed:

`ORBITAL`   Print molecular orbitals

`INTEGRAL` Print integrals

`TIMING`   Print extra timing information

`DIAGONAL` Print diagonal elements of Hamiltonian

`HAMILTONIAN` Print much intermediate information

36.9 Interface to other programs

`DUMP`;

causes the FCI diagonalization to be bypassed, with input information and transformed integrals being written to a formatted file FCIDUMP. The format is as described in Comp. Phys. Commun. 54 (1989) 75, and in an external program should be accessed using the FCIdump class or module available from https://bitbucket.org/pjknowles/fcidump.

37 SYMMETRY-ADAPTED INTERMOLECULAR PERTURBATION THEORY

37.1 Introduction

The SAPT (symmetry-adapted intermolecular perturbation theory) program calculates the total interaction energy between closed-shell molecules as a sum of individual first and second order interaction terms, namely electrostatic $E_{pol}^{(1)}$, induction $E_{ind}^{(2)}$ and dispersion $E_{disp}^{(2)}$ accompanied by their respective exchange counterparts ($E_{exch}^{(1)}$, $E_{exch-ind}^{(2)}$ and $E_{exch-disp}^{(2)}$). The latter ones arise due to electron exchange between the monomers when the molecules are close to each other and are sometimes denoted as Pauli repulsion. Since all above terms are accessible through density matrices and static and dynamic density-density response functions of the monomers, in principle (see section 37.4) no calculation of the dimer wave function is required. Therefore SAPT is free from the basis set superposition error which occurs in the supermolecular approach.

References:

General Symmetry-adapted perturbation theory and many-body SAPT:
[1] B. Jeziorski, R. Moszynski and K. Szalewicz, Chem. Rev. **94**, 1887. (1994).

DFT-SAPT:
[2] G. Jansen and A. Heßelmann, J. Phys. Chem. A **105**, 646 (2001).
[3] A. Heßelmann and G. Jansen, Chem. Phys. Lett. **357**, 464 (2002).
[4] A. Heßelmann and G. Jansen, Chem. Phys. Lett. **362**, 319 (2002).
[5] A. Heßelmann and G. Jansen, Chem. Phys. Lett. **367**, 778 (2003).
[6] A. Heßelmann and G. Jansen, Phys. Chem. Chem. Phys. **5**, 5010 (2003).

Density fitting DFT-SAPT (DF-DFT-SAPT):
[7] A. Heßelmann, G. Jansen and M. Schütz, J. Chem. Phys. **122**, 014103 (2005).

Density fitting DFT-SAPT for arbitrary monomer basis sets (DFSAPT):
[8] A. Heßelmann and T. Korona, J. Chem. Phys. **141**, 094107 (2014).

(See also:
K. Szalewicz, K. Patkowski and B. Jeziorski, Struct. Bond **116**, 43 (2005)
K. Szalewicz, WIREs Comput. Mol. Sci. **2**, 254 (2011)
and references therein for a related approach to DFT-SAPT termed SAPT(DFT))

37.2 First example

A typical input for SAPT has the following form:

```
r=5.6
geometry={nosym; he1; he2,he1,r}
basis=avqz

!wf records
ca=2101.2
cb=2102.2

!monomer A
dummy,he2
{hf; save,$ca}
```

```
sapt;monomerA

!monomer B
dummy,he1
{hf; start,atdens; save,$cb}
sapt;monomerB

!interaction contributions
sapt;intermol,ca=$ca,cb=$cb
```

Here the `sapt;monomerA/B` store some informations about the two monomers which are needed in the subsequent SAPT calculation invoked by `sapt;intermol`. The individual interaction energy terms are stored (in millihartree) in distinct variables and may be collected in arrays for producing potential energy surfaces. For example the input

```
geometry={nosym; he1; he2,he1,r}
basis=avtz

!wf records
ca=2101.2
cb=2102.2

!distances
dist=[4.5,5.0,5.5,5.6,6.0,6.5,7.0]

do i=1,#dist
   r=dist(i)

   !monomer A
   dummy,he2
   {hf; save,$ca}
   sapt;monomerA

   !monomer B
   dummy,he1
   {hf; start,atdens; save,$cb}
   sapt;monomerB

   !interaction contributions
   sapt;intermol,ca=$ca,cb=$cb

   elst(i)=E1pol;  exch(i)=E1ex
   ind(i)=E2ind;   exind(i)=E2exind
   disp(i)=E2disp; exdisp(i)=E2exdisp
   etot(i)=E12tot

   data,truncate,$ca
enddo

{table,dist,elst,exch,ind,exind,disp,exdisp,etot
ftyp,d,d,d,d,d,d,d,d,d
plot}
```

yields the plot
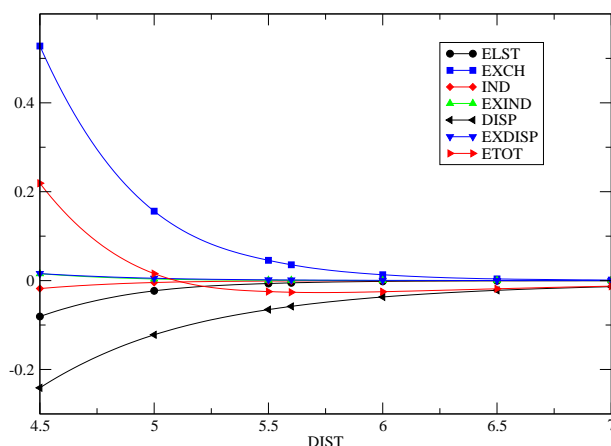
Currently SAPT only accepts single-determinant wave functions for the monomers, i.e. from Hartree-Fock or Kohn-Sham DFT (see next section) calculations. This means that if Hartree-Fock wave functions are used for monomer, the following quantity is obtained (zero in superscript denotes that no intramonomer correlation is accounted for) [1].

$$E_{\text{SAPT}} = E_{\text{pol}}^{(10)} + E_{\text{exch}}^{(10)} + E_{\text{ind,resp.}}^{(20)} + E_{\text{exch-ind,resp.}}^{(20)} + E_{\text{disp}}^{(20)} + E_{\text{exch-disp}}^{(20)}$$

No point group symmetry can be exploited in a SAPT calculation.

37.3 DFT-SAPT

It is of crucial importance to account for the *intra*molecular correlation effects of the individual SAPT terms since Hartree-Fock theory often yields poor first- and second-order electrostatic properties. While this can be done using many-body perturbation theory [1] (in a double perturbation theory ansatz) a more efficient way is to use static and time-dependent DFT theory. This variant of SAPT, termed as DFT-SAPT [2-6], has in contrast to Hartree-Fock-SAPT the appealing feature that the polarisation terms ($E_{\text{pol}}^{(1)}$, $E_{\text{ind}}^{(2)}$, $E_{\text{disp}}^{(2)}$) are potentially exact, i.e. they come out exactly if the exact exchange-correlation (xc) potential and the exact (frequency-dependent) xc response kernel of the monomers were known. On the other hand, this does not hold for the exchange terms since Kohn-Sham theory can at best give a good approximation to the exact density matrix of a many-body system. It has been shown [6] that this is indeed the the case and therefore DFT-SAPT has the potential to produce highly accurate interaction energies comparable to high-level supermolecular many-body perturbation or coupled cluster theory. However, in order to achieve this accuracy, it is of crucial importance to correct the wrong asymptotic behaviour of the xc potential in current DFT functionals [3-5]. This can be done by using e.g.:

```
{ks,lda; asymp,<shift>}
```

which activates the gradient-regulated asymptotic correction approach of Grüning *et al.* (J. Chem. Phys. **114**, 652 (2001)) for the respective monomer calculation. The user has to supply a `shift` parameter (Δ_{xc}) for the bulk potential which should approximate the difference between the HOMO energy ($\varepsilon_{\text{HOMO}}$) obtained from the respective standard Kohn-Sham calculation and the (negative) ionisation potential of the monomer (IP):

$$\Delta_{\text{xc}} = \varepsilon_{\text{HOMO}} - (-\text{IP}) \tag{59}$$

This method accounts for the derivative discontinuity of the exact xc-potential and that is missing in approximate ones. Note that this needs to be done only once for each system. (See also section 37.7.2 for an explicit example).

Concerning the more technical parameters in the DFT monomer calculations it is recommended to use lower convergence thresholds and larger intergration grids compared to standard Kohn-Sham calculations.

37.4 High order terms

It has been found that third and higher-order terms become quite important if one or both monomers are polar. As no higher than second-order terms are currently implemented in SAPT, one may use a non-correlated estimation of those terms by using supermolecular Hartree-Fock (see e.g. [7]). This can be done by adapting the following template:

```
!dimer
hf
edm=energy

!monomer A
dummy,<monomer2>
{hf; save,$ca}
ema=energy
sapt;monomerA

!monomer B
dummy,<monomer1>
{hf; start,atdens; save,$cb}
emb=energy
sapt;monomerB

!interaction contributions
sapt,sapt_level=2;intermol,ca=$ca,cb=$cb

esup=(edm-ema-emb)*1000. mH
dHF=esup-e1pol-e1ex-e2ind-e2exind
```

which stores the resulting δ(HF) term in `dHF`.

37.5 Density fitting

In order to be able to study interactions between extended monomers one can use density fitting to approximate the integrals in SAPT [7]. For this one may use the input:

```
{sapt;intermol,ca=$ca,cb=$cb,fitlevel=3
dfit,basis_coul=jkfit,basis_exch=jkfit,basis_mp2=mp2fit,cfit_scf=3}
```

with in the basis section defined `jkfit` and `mp2fit` fitting basis sets (see section 15).

Currently only the ALDA xc-kernel is implemented for the case SAPT_LEVEL=3 and SAPT_FITLEVEL=3. This means that a corresponding SAPT calculation would be uncompatible with hybrid-DFT monomer orbitals/orbital energies. Therefore it is recommended to use nonhybrid functionals in the case the dispersion/exchange-dispersion energy terms are requested in a DF-DFT-SAPT run. Another possibility is to localise the xc-potential via, e.g., the OEP method (see also example in section 37.7.3).

37.6 SAPT with ECP's

If effective core potentials (ECP's) are used in the monomer calculations, it is important to add the δ(HF) term to the SAPT interaction energy (see K. Patkowski, K. Szalewicz, *J. Chem. Phys.* **127** (2007) 164103). For examples for the calculation of δ(HF) see sections 37.4 and 37.7.

37.7 Examples

37.7.1 HF-SAPT calculation of the H_2O dimer using the δ(HF) correction

```
gthresh,energy=1.d-8,orbital=1.d-8,grid=1.d-8
symmetry,nosym
orient,noorient
GEOMETRY={
1,O1,,0.00000000,0.00000000,0.00000000
2,H1,,0.00000000,0.00000000,1.83606000
3,H2,,1.77604000,0.00000000,-0.4656040
4,O2,,-0.6605540,0.00000000,5.54064000
5,H3,,-1.6582100,-1.4536300,6.05324000
6,H4,,-1.6582100,1.45363000,6.05324000
}
basis=avdz

!sapt files
ca=2101.2
cb=2102.2

!dimer
hf
edm=energy

!monomer A
dummy,o2,h3,h4
{hf; save,$ca}
ema=energy
{sapt;monomerA}

!monomer B
dummy,o1,h1,h2
{hf; start,atdens; save,$cb}
emb=energy
{sapt;monomerB}

!interaction contributions
{sapt,SAPT_LEVEL=3;intermol,ca=$ca,cb=$cb,icpks=1}

!HF supermolecular interaction energy and delta(HF) contribution
eint_hf=(edm-ema-emb)*1000 mH
delta_hf=eint_hf-e1pol-e1ex-e2ind-e2exind

!add E2disp + E2exch-disp to HF interaction energy
eint_sapt=eint_hf+e2disp+e2exdisp
```

http:
//www.molpro.net/info/current/examples/h2odimer_sapt_hf.com

37.7.2   DFT-SAPT calculation of the NeAr dimer using the δ(HF) correction

```
gthresh,energy=1.d-8,orbital=1.d-8,grid=1.d-8
symmetry,nosym
orient,noorient
geometry={
Ne,,0.0,0.0,0.0
Ar,,0.0,0.0,6.5}
basis=avtz

!=========delta(HF) contribution for higher order interaction terms====
!sapt files
ca=2101.2
cb=2102.2

!dimer
hf
edm=energy

!monomer A
dummy,ar
{hf; save,$ca}
ema=energy
{sapt;monomerA}

!monomer B
dummy,ne
{hf; start,atdens; save,$cb}
emb=energy
{sapt;monomerB}

!interaction contributions
{sapt,SAPT_LEVEL=2;intermol,ca=$ca,cb=$cb,icpks=1}

!calculate high-order terms by subtracting 1st+2nd order energies
eint_hf=(edm-ema-emb)*1000 mH
delta_hf=eint_hf-e1pol-e1ex-e2ind-e2exind


!=========DFT-SAPT at second order intermol. perturbation theory====
!sapt files
ca=2103.2
cb=2104.2

!shifts for asymptotic correction to xc potential
eps_homo_pbe0_ar=-0.440936      !HOMO(Ar)/PBE0 functional
eps_homo_pbe0_ne=-0.589207      !HOMO(Ne)/PBE0
ip_ar=0.5792                    !exp. ionisation potential
ip_ne=0.7925                    !exp. ionisation potential
shift_ar=ip_ar+eps_homo_pbe0_ar !shift for bulk xc potential (Ar)
shift_ne=ip_ne+eps_homo_pbe0_ne !shift for bulk xc potential (Ne)

!monomer A
dummy,ar
{ks,pbe0; asymp,shift_ne; save,$ca}
{sapt;monomerA}

!monomer B
dummy,ne
{ks,pbe0; start,atdens; asymp,shift_ar; save,$cb}
{sapt;monomerB}

!interaction contributions
{sapt;intermol,ca=$ca,cb=$cb,icpks=0}

!add high-order approximation to obtain the total interaction energy
eint_dftsapt=e12tot+delta_hf
```

http://www.molpro.net/info/current/examples/near_sapt_acdft.com

Ar,

37.7.3 DF-DFT-SAPT calculation of the NeAr dimer using the δ(HF) correction

```
gdirect; gthresh,energy=1.d-8,orbital=1.d-8,grid=1.d-8
symmetry,nosym
orient,noorient
geometry={
Ne,,0.0,0.0,0.0
Ar,,0.0,0.0,6.5}
basis={
set,orbital; default,avtz         !for orbitals
set,jkfit;   default,avtz/jkfit   !for JK integrals
set,mp2fit;  default,avtz/mp2fit  !for E2disp/E2exch-disp
set,dflhf;   default,avtz/jkfit   !for LHF
}

!=========delta(HF) contribution for higher order interaction terms====
ca=2101.2; cb=2102.2 !sapt files

!dimer
{df-hf,basis=jkfit,locorb=0}
edm=energy

!monomer A
dummy,ar
{df-hf,basis=jkfit,locorb=0; save,$ca}
ema=energy
{sapt;monomerA}

!monomer B
dummy,ne
{df-hf,basis=jkfit,locorb=0; save,$cb}
emb=energy
{sapt;monomerB}

!interaction contributions
{sapt,SAPT_LEVEL=2;intermol,ca=$ca,cb=$cb,icpks=1,fitlevel=3
dfit,basis_coul=jkfit,basis_exch=jkfit,cfit_scf=3}

!calculate high-order terms by subtracting 1st+2nd order energies
eint_hf=(edm-ema-emb)*1000 mH
delta_hf=eint_hf-e1pol-e1ex-e2ind-e2exind

!=========DFT-SAPT at second order intermol. perturbation theory====
ca=2103.2; cb=2104.2 !sapt files;

!shifts for asymptotic correction to xc potential
eps_homo_pbe0_ar=-0.440936      !HOMO(Ar)/PBE0 functional
eps_homo_pbe0_ne=-0.589207      !HOMO(Ne)/PBE0
ip_ar=0.5792                    !exp. ionisation potential
ip_ne=0.7925                    !exp. ionisation potential
shift_ar=ip_ar+eps_homo_pbe0_ar !shift for bulk xc potential (Ar)
shift_ne=ip_ne+eps_homo_pbe0_ne !shift for bulk xc potential (Ne)

!monomer A, perform LPBE0AC calculation
dummy,ar
{df-ks,pbex,pw91c,lhf; dftfac,0.75,1.0,0.25; asymp,shift_ne; save,$ca}
{sapt;monomerA}

!monomer B, perform LPBE0AC calculation
dummy,ne
{df-ks,pbex,pw91c,lhf; dftfac,0.75,1.0,0.25; start,atdens; asymp,shift_ar; save,$cb}
{sapt;monomerB}

!interaction contributions
{sapt,SAPT_LEVEL=3;intermol,ca=$ca,cb=$cb,icpks=0,fitlevel=3,nlexfac=0.0
dfit,basis_coul=jkfit,basis_exch=jkfit,cfit_scf=3}

!add high-order approximation to obtain the total interaction energy
eint_dftsapt=e12tot+delta_hf

Ar,,0.0,0.0,6.5
```

37.8 Options

SAPT_LEVEL Set to 1 for first-order terms ($E_{\text{pol}}^{(1)}$ and $E_{\text{exch}}^{(1)}$), to 2 for additional second order (exchange-)induction terms ($E_{\text{ind}}^{(2)}$ and $E_{\text{exch}-\text{ind}}^{(2)}$) and 3 for all first- and second-order terms (including then also $E_{\text{disp}}^{(2)}$ and $E_{\text{exch}-\text{disp}}^{(2)}$) (default 3)

SAPT_FITLEVEL Level of density fitting approximations in SAPT which can have values 0 to 3 (default 0)

SAPT_ICPKS Switch between iterative (=1) and non-iterative (=0) solution of coupled-perturbed Kohn-Sham equations (default 0)

SAPT_CPKSTHR Threshold for density matrix convergency in the coupled-perturbed Kohn-Sham program (default 1.d-6).

SAPT_CPKMAXIT Maximum number of iterations in the coupled-perturbed Kohn-Sham program (default 50).

SAPT_FROZENA Number of frozen electrons in the response calculations for monomer A (default 0)

The following parameters are of importance if SAPT_FITLEVEL>0:

SAPT_NFRQ_DISP Number of frequencies for the Casimir-Polder integration (default 12)

SAPT_NORM_DISP Norm for the density fitting which can be either COULOMB or NATURAL (default COULOMB)

SAPT_DISP_N4 Can speedup the calculation of the dispersion energy by N^4 scaling (default 1)

THR_XCKERN Density threshold for the xc kernel matrix elements (default 1.d-8)

FIT_XCKERN Fit both sides of the xc kernel (default 0)

SAPT_DISK If 0 write all dimer amplitudes to file, if 1 write 3-index response propagators to file and if 2 write 3-index response propagators compressed to file. The latter two variants save disk space but need more CPU time to compute $E_{\text{exch}-\text{disp}}^{(2)}$ (default 0)

COMPRESS_THR If SAPT_DISK=2 this value determines the compression cutoff (default 1d-12)

UNCOUPLED If SAPT_DISK>0 calculate also uncoupled (exchange-)dispersion energies (default false)

THRAO Threshold for AO 3-index integrals (default 1.d-12)

THRMO Threshold for MO 3-index integrals (default 1.d-8)

THROV Threshold for AO 2-index integrals (default 1.d-10)

THRPROD Product threshold for first half transformation (default 1.d-8)

THRSW Threshold for Schwarz screening (default 1.d-5)

C6 Calculate dispersion coefficients for the two monomers (Note that the full dimer basis set is used in each case and that a closer distance of the monomers can perturb the result).

XCKERN_NBLOCK number of grid points treated together as a block for $(\text{aux}|f_{\text{xc}}|\text{occ}\times\text{virt})$ integrals (default 128)

CFAC factor for VWN correlation in ALDA xc-kernel (default 1.d0)

The last threshold values for the 2- and 3-index integrals should not be set higher in density fitting calculations as this can cause lower accuracies in the interaction terms. In addition SAPT knows the following subcommands:

MONOMERA Stores informations (like number of electrons, etc.) about previous monomer A calculation

MONOMERB See above

INTERMOL Starts the SAPT calculation

INTERMOL may have the following subkeywords:

CA   Record number of wave function for monomer A (always needed)

CB   Record number of wave function for monomer B (always needed)

SAPTLEVEL See above

FITLEVEL See above

ICPKS   See above

FROZA   See above

FROZB   See above

NLEXFAC   Amount of nonlocal exact exchange in hybrid DFT-SAPT calculations

CPKSTHR   Threshold for density matrix convergency in the coupled-perturbed Kohn-Sham program.

CPKSMAXIT Maximum number of iterations in the coupled-perturbed Kohn-Sham program.

37.9 DFSAPT: a density-fitting DFT-SAPT program for arbitrary monomer basis sets

DFSAPT is an alternative density-fitting DFT-SAPT program which works with arbitrary monomer basis sets and which can be used for extended dimer systems of about 800 electrons, see Ref.[8].

For a standard DFSAPT calculation using a dimer centered basis set the Molpro input file looks very similar to a corresponding DF-DFT-SAPT claculation, see example `h2o_2-dfsapt.com` (section 37.9.1). There are, however, two important points to be taken care of:

important #1 Set `oldnorm=1` before any call to the DFSAPT program.

important #2 Add numbers to atom labels in the geometry blocks. These have to have a subsequent ordering, see examples 37.9.1-37.9.4.

A corresponding calculation, in which the water monomers are calculated in their own local basis set (monomer centered basis set calculation) is presented in example `h2o_2-mc-dfsapt.com` (section 37.9.2). Note, however, that very large basis sets are required to converge the individual interaction energy contributions. In order to improve the basis set convergence, additional midbond functions can be added as is exemplified in example `h2o_2-mcplus-dfsapt.com` (section 37.9.3). Here the def2-TZVP basis functions for the Neon atom were positioned in between the O$\cdots$H hydrogen bridge.

A complete (DCBS) DFSAPT calculation with additional δ(HF) correction and using the PBE0AC(BRJ) xc potential (with automatic asymptotic correction) is shown in section 37.9.4.

Note that in contrast to the DFT-SAPT/DF-DFT-SAPT programs the exchange-dispersion energy is not calculated on the coupled level. Instead, the coupled $E_{exch-disp}^{(2)}$ energies are estimated by scaling the uncoupled ones with a factor which has been obtained from a linear fit to exact results, see Ref.[8].

The following list shows all options which can be used with the DFSAPT program:

E1P   Calculate $E_{pol}^{(1)}$ (default: `1`).

E1X   Calculate $E_{exch}^{(1)}$ (default: `1`).

E2I   Calculate $E_{ind}^{(2)}$ (default: `0`).

E2XI   Calculate $E_{exch-ind}^{(2)}$ (default: `0`).

E2D   Calculate $E_{disp}^{(2)}$ (default: `0`).

E2XD   Calculate $E_{exch-disp}^{(2)}$ (default: `0`).

ALL   Calculate all SAPT contributions (up to 2nd order) (default: `0`).

AUXBAS   Auxiliary basis set (default: `MP2FIT`).

NFREQ   Number of frequencies for computing the monomer response matrices (default: `10`).

GRIDTHR   Threshold for grid accuracy (default: `1d-10`).

THRKERN   Threshold for density in xc kernel calculation (default: `1d-12`).

PRINT   Print flag (default: `0`).

W0   Value effects Gauss-Legendre quadrature for computing the response function (see Amos,Handy,Knowles,Rice,Stone,*J. Phys.Chem.* **89** (1985) 2186) (default: `2d0`)

FEXX   Exact exchange factor in response calculations (default: `0d0`).

FXC   Exchange-correlation factor in response calculations (default: `0d0`).

FCOUL   Coulomb contribution factor in response calculations (default: `1d0`).

XFAC   Exchange factor in XC kernel (default: `1d0`).

CFAC   Correlation factor in XC kernel (default: `1d0`).

AUXMAX   Maximum block size of auxiliary function space for three-index integrals of the type (aux|orb.orb) (default: `50`).

MOMAX   Maximum block size of orbital function space for three-index integrals of the type (orb|orb.aux) (default: `50`).

FXCSING   Singularity correction for XC kernel matrix (default: `0`)

THRDUM   Threshold for density calculated at dummy function gridpoints (which can serve as a singularity correction for the calculation of the XC kernel matrix) (default: `1d-4`).

COMP   Write 3-index integrals compressed to disk (to save disk space) (default: `0`).

THRC   Threshold for 3-index integral calculations (integrals which are smaller than the given threshold are not written to disk) (default: `1d-10`).

MINB   Minimal bytelength for integral comression (default: `1`).

MODE   Switch for alternative DFSAPT driver which can use integral compression (to be evoked by `MODE=2`) (default: `1`).

FXCFIT   Use density fitting for computation of XC contributions in CPKS calculation (default: `0`).

CPKS   Switch for different CPKS solvers (default: `1`).

CDIRECT   Use integral direct algorithm for computing the (exact) exchange contributions in CPKS calculations, otherwise intergrals of the type (aux|vir.vir) are written to disk (default: `0`).

MAXIT   Maximum number of iterations in CPKS (default: `60`).

THRCG   Threshold for CG/GMRES solver in CPKS calculations (default: `1d-8`).

NSYSOLVE Switch for BiCG (`NSYSOLVE=1`) or GMRES (`NSYSOLVE=2`) solver in CPKS calculations (default: `2`).

NSUB   Subspace size in GMRES solver (default: `50`).

T678   Switch for 3 different computation modes for $E^{(2)}_{exch-disp}$. `T678=3` is recommended for the calculation of large systems but requires more disk space to store intermediate quantities (default: `1`).

37.9.1 DFSAPT calculation of the water dimer using a DCBS basis set

```
***,h2o-dimer DCBS
gthresh,energy=1.d-8,orbital=1.d-8,grid=1.d-8
oldnorm=1

ca=2101.2
cb=2102.2

basis={
set,orbital
default,def2-tzvpp
default,def2-tzvpp/jkfit
set,mp2fit
default,def2-tzvpp/mp2fit
}

symmetry,nosym
angstrom
geometry={
 1,O1,,  -1.551007,  -0.114520,   0.000000
 2,H2,,  -1.934259,   0.762503,   0.000000
 3,H3,,  -0.599677,   0.040712,   0.000000
 4,O4,,   1.350625,   0.111469,   0.000000
 5,H5,,   1.680398,  -0.373741,  -0.758561
 6,H6,,   1.680398,  -0.373741,   0.758561
}

dummy,4,5,6
{ks,pbe; save,$ca}
monomerA,orb=$ca,core=1

dummy,1,2,3
{ks,pbe; start,atdens; save,$cb}
monomerB,orb=$cb,core=1

{grid; gridthr,1d-8}
dfsapt,all=1,fcoul=1.0,fxc=1.0
```

  http://www.molpro.net/info/current/examples/h2o_2-dfsapt.com

37.9.2 DFSAPT calculation of the water dimer using an MCBS basis set

```
***,h2o-dimer MCBS
gthresh,energy=1.d-8,orbital=1.d-8,grid=1.d-8
oldnorm=1

ca=2101.2
cb=2102.2

symmetry,nosym
angstrom
noorient
geometry={
 1,O1,,  -1.551007,  -0.114520,   0.000000
 2,H2,,  -1.934259,   0.762503,   0.000000
 3,H3,,  -0.599677,   0.040712,   0.000000
}
basis={
set,orbital
default,def2-tzvpp
}

{ks,pbe; save,$ca}
monomerA,orb=$ca,core=1


symmetry,nosym
angstrom
noorient
geometry={
 4,O4,,   1.350625,   0.111469,   0.000000
 5,H5,,   1.680398,  -0.373741,  -0.758561
 6,H6,,   1.680398,  -0.373741,   0.758561
}

{ks,pbe; start,atdens; save,$cb}
monomerB,orb=$cb,core=1


symmetry,nosym
angstrom
noorient
geometry={
 1,O1,,  -1.551007,  -0.114520,   0.000000
 2,H2,,  -1.934259,   0.762503,   0.000000
 3,H3,,  -0.599677,   0.040712,   0.000000
 4,O4,,   1.350625,   0.111469,   0.000000
 5,H5,,   1.680398,  -0.373741,  -0.758561
 6,H6,,   1.680398,  -0.373741,   0.758561
}

basis={
set,orbital
default,def2-tzvpp
set,jkfit
default,def2-tzvpp/jkfit
set,mp2fit
default,def2-tzvpp/mp2fit
}

{grid; gridthr,1d-8}
dfsapt,all=1,fcoul=1.0,fxc=1.0
```

http://www.molpro.net/info/current/examples/h2o_2-mc-dfsapt.com

37.9.3 DFSAPT calculation of the water dimer using an MC+BS basis set

```
***,h2o-dimer MC+BS
gthresh,energy=1.d-8,orbital=1.d-8,grid=1.d-8
oldnorm=1
ca=2101.2
cb=2102.2
basis={
set,orbital
default,def2-tzvpp
}

symmetry,nosym
angstrom
noorient
geometry={
 1,O1,,  -1.551007,  -0.114520,   0.000000
 2,H2,,  -1.934259,   0.762503,   0.000000
 3,H3,,  -0.599677,   0.040712,   0.000000
 4,Ne7,,  0.375474,   0.076091,   0.000000
}
dummy,ne7
{ks,pbe; save,$ca}
monomerA,orb=$ca,core=1


symmetry,nosym
angstrom
noorient
geometry={
 4,O4,,   1.350625,   0.111469,   0.000000
 5,H5,,   1.680398,  -0.373741,  -0.758561
 6,H6,,   1.680398,  -0.373741,   0.758561
 7,Ne7,,  0.375474,   0.076091,   0.000000
}
dummy,ne7
{ks,pbe; start,atdens; save,$cb}
monomerB,orb=$cb,core=1

symmetry,nosym
angstrom
noorient
geometry={
 1,O1,,  -1.551007,  -0.114520,   0.000000
 2,H2,,  -1.934259,   0.762503,   0.000000
 3,H3,,  -0.599677,   0.040712,   0.000000
 4,O4,,   1.350625,   0.111469,   0.000000
 5,H5,,   1.680398,  -0.373741,  -0.758561
 6,H6,,   1.680398,  -0.373741,   0.758561
 7,Ne7,,  0.375474,   0.076091,   0.000000
}
basis={
set,orbital
default,def2-tzvpp
set,jkfit
default,def2-tzvpp/jkfit
set,mp2fit
default,def2-tzvpp/mp2fit
}

dummy,ne7
{grid; gridthr,1d-8}
dfsapt,all=1,fcoul=1.0,fxc=1.0
```

http:
//www.molpro.net/info/current/examples/h2o_2-mcplus-dfsapt.com

37.9.4 DFSAPT calculation of the water dimer with additional δ(HF) correction

```
gdirect
gthresh,energy=1d-8,orbital=1d-7,grid=1d-8

symmetry,nosym
angstrom
geometry={
 1,O1,,  -1.551007,  -0.114520,   0.000000
 2,H2,,  -1.934259,   0.762503,   0.000000
 3,H3,,  -0.599677,   0.040712,   0.000000
 4,O4,,   1.350625,   0.111469,   0.000000
 5,H5,,   1.680398,  -0.373741,  -0.758561
 6,H6,,   1.680398,  -0.373741,   0.758561
}
basis={
set,orbital
default,avdz
set,jkfit
default,avdz/jkfit
set,mp2fit
default,avdz/mp2fit
}
oldnorm=1

ca=2110.2
cb=2120.2
nkerna=1
nkernb=1

{df-hf,basis=jkfit; save,2100.2}
edm_hf=energy

dummy,4,5,6
{df-hf,basis=jkfit; save,$ca; start,atdens}
ema_hf=energy
monomerA,orb=$ca,core=$nkerna

dummy,1,2,3
{df-hf,basis=jkfit; save,$cb; start,atdens}
emb_hf=energy
monomerB,orb=$cb,core=$nkernb

{grid; gridthr,1d-6}
{dfsapt,e1p=1,e1x=1,e2i=1,e2xi=1,auxbas='jkfit',fexx=1.0,fcoul=1.0,mode=1,cdirect=1,thrcg=1d-6}
{grid; gridthr,1d-8}

eint_hf=(edm_hf-ema_hf-emb_hf)*1000e0 mH
delta_hf=eint_hf-e12tot

dummy,4,5,6
lxgamma=1.15
{df-ks,lxbecke,pbex,pbec,basis=jkfit; dftfac,0.25,0.75,1.0; asymp,0d0; save,$ca; start,atdens}
monomerA,orb=$ca,core=$nkerna

dummy,1,2,3
lxgamma=1.15
{df-ks,lxbecke,pbex,pbec,basis=jkfit; dftfac,0.25,0.75,1.0; asymp,0d0; save,$cb; start,atdens}
monomerB,orb=$cb,core=$nkernb

{grid; gridthr,1d-6}
{dfsapt,all=1,auxbas='mp2fit',fxc=1.0,fcoul=1.0,mode=1,cpks=2,fxcfit=1,fxcsing=1,t678=3}
eint_sapt=e12tot+delta_hf
```

http://www.molpro.net/info/current/examples/h2o_2-dfsapt2.com

37.10   SAPT(CCSD)

SAPT with monomers described on the CCSD level is available for small complexes. In SAPT(CCSD) monomer density matrices and density-density matrix response functions from expectation-value CCSD theory are utilized. A high cost of SAPT(CCSD) results from the necessity of calculation of the CCSD response functions. Cumulant contributions from two-electron density matrices for $E_{\mathrm{exch}}^{(1)}$ and $E_{\mathrm{exch-ind}}^{(2)}$ are also available. The calculations can be performed for dimer-centered or monomer-centered-plus basis sets (the latter for all components but $E_{\mathrm{exch-disp}}^{(2)}$). $E_{\mathrm{disp}}^{(2)}$ and $E_{\mathrm{exch-disp}}^{(2)}$ are usually calculated from density-fitted response functions in order to reduce the CPU time (from $\mathscr{O}(\mathscr{N}^8)$ to $\mathscr{O}(\mathscr{N}^7)$, where $\mathscr{N}$ is the molecular size). Some input examples can be found in the Molpro `testjobs` directory (note that $E_{\mathrm{disp}}^{(2)}$ and $E_{\mathrm{exch-disp}}^{(2)}$ are calculated separately from other SAPT components). It is important to note that SAPT(CCSD) and DFT-SAPT from Chapter 37.1 are completely different codes.

References:

Review of SAPT(CCSD):
[1] T. Korona, in *Recent Progress in Coupled Cluster Methods*, Eds. P. Čársky, J. Paldus, J. Pittner, Springer-Verlag (2010), *Coupled cluster treatment of intramonomer correlation effects in intermolecular interactions*, p. 267

[2] T. Korona, M. Przybytek, B. Jeziorski, Mol. Phys. **104**, 2303 (2006)
[3] T. Korona, B. Jeziorski, J. Chem. Phys. **125**, 184109 (2006)
[4] T. Korona, B. Jeziorski, J. Chem. Phys. **128**, 144107 (2008)
[5] T. Korona, J. Chem. Phys. **128**, 224104 (2008)
[6] T. Korona, Phys. Chem. Chem. Phys. **10**, 5698 (2008)
[7] T. Korona, Phys. Chem. Chem. Phys. **10**, 6509 (2008)
[8] T. Korona, J. Chem. Theory Comput. **5**, 2663 (2009)

38   PROPERTIES AND EXPECTATION VALUES

38.1   The property program

The property program allows the evaluation of one-electron operators and expectation values. Normally, the operators are computed automatically when using the global `GEXPEC` directive (see section 6.13) or the `EXPEC` or `TRAN` commands in the SCF, MCSCF, and CI programs. The explicit use of the property program is only necessary in the rare case that the user is interested in an orbital analysis of the properties.

38.1.1   Calling the property program (`PROPERTY`)

`PROPERTY`

invokes the property program.

38.1.2   Expectation values (`DENSITY`)

`DENSITY` [,*record.file*] [,*specifications*]

If this card is present, the density matrix will be read from record *record.file* and property expectation values will be calculated. If the specification *record.file* is omitted, the last dump record is used. Density matrices for specific states can be selected using *specifications*, as explained in section 4.11. Note that the density matrices are stored in the same record as the orbitals.

38.1.3   Orbital analysis (`ORBITAL`)

`ORBITAL` [,*record.file*] [,*specifications*]

If this card is present, the orbitals are read from record *record.file* and an orbital analysis of the expectation values is printed (the density matrix must also be provided!). If *record.file* is omitted, the last dump record is used. This is only meaningful for diagonal density matrices (SCF or natural orbitals). Natural orbitals for specific states can be selected using *specifications*, as explained in section 4.11.

38.1.4   Specification of one-electron operators

The required operators are specified by code words. Optionally, the geometry or the nuclear centre at which the operator is computed can be specified.

For each operator, an input card of the following form is required:

code,centre,x,y,z,,factor

code specifies the property. The available operators are given in section 6.13.

The other parameters have the following meaning:

centre	row number of Z–matrix or atomic symbol defining the centre at which property shall be calculated; if *centre*$\neq 0$ you need not read in coordinates.
x,y,z	cartesian coordinates of the point (only if *centre*=0).
factor	the operator is multiplied by this factor. The default is *factor*=1 except for `REL`. In this cases proper factors for relativistic corrections are used unless *factor* is given. The two commas before factor are needed to preserve compatibility with `Molpro96`.

38.1.5   Printing options

`PRINT`,*print*

This card is used to control output, mainly for debugging purposes.

print$= 0$	no test output (default)
print> 0	operators are printed.

38.1.6   Examples

The following example computes the dipole quadrupole moments of water and prints an orbital analysis. By default, the origin is at the centre of mass, and this is taken as origin for the quadrupole moments.

```
***,h2o properties
geometry={o;h1,o,r;h2,o,r,h1,theta}   !Z-matrix geometry input
r=1 ang                               !bond length
theta=104                             !bond angle
hf                                    !do scf calculation
property                              !call property program
orbital                               !read scf orbitals
density                               !read scf density matrix
dm                                    !compute dipole moments and print orbital contributions
qm                                    !compute quadrupole moments and print orbital contributi
{multi;wf;state,2;dm                  !do full-valence CASSCF
natorb,state=1.1                      !compute natural orbitals for state 1.1
natorb,state=2.1}                     !compute natural orbitals for state 2.1

{property                             !call property program
orbital,state=1.1                     !read casscf natural orbitals for state 1.1
density,state=1.1                     !read casscf density matrix for state 1.1
dm                                    !compute dipole moments and print orbital contributions
qm}                                    !compute quadrupole moments and print orbital contribut

{property                             !call property program
orbital,state=2.1                     !read casscf natural orbitals for state 2.1
density,state=2.1                     !read casscf density matrix for state 2.1
dm                                    !compute dipole moments and print orbital contributions
qm}                                   !compute quadrupole moments and print orbital contributi
```

> http://www.molpro.net/info/current/examples/h2o_property.com

Alternatively, the dipole and quadrupole moments can be computed directly in the SCF and MCSCF programs, but in this case no orbital contributions are printed:

```
***,h2o properties
geometry={o;h1,o,r;h2,o,r,h1,theta}   !Z-matrix geometry input
r=1 ang                               !bond length
theta=104                             !bond angle
gexpec,dm,qm                          !global request of dipole and quadrupole moments
hf                                    !do scf calculation
{multi;wf;state,2                     !do full-valence CASSCF
natorb,state=1.1                      !compute natural orbitals for state 1.1
natorb,state=2.1}                     !compute natural orbitals for state 2.1
```

> http://www.molpro.net/info/current/examples/h2o_gexpec1.com

38.2 Distributed multipole analysis

Any density matrix can be analysed using the distributed multipole analysis described by Stone, Chem. Phys. Letters (1981), 83, 233. The multipole moments arising from the overlap of each pair of primitives are calculated with respect to the overlap centre, and then shifted to the nearest of a number of *multipole sites*. By default these comprise all atoms specified in the integral input. However the list of multipole sites can be modified by deleting and/or adding sites, and also by restricting the rank of multipole which may be transferred to any given site. The atomic charges are stored in the MOLPRO variable ATCHARGE. The i'th element in ATCHARGE corresponds to the i'th row of the Z-matrix input.

Options may appear in any order, except DENSITY, which must be first if given.

The present version does not allow generally contracted AO basis sets.

38.2.1 Calling the DMA program (`DMA`)

`DMA;`

This command initializes the DMA program.

38.2.2 Specifying the density matrix (`DENSITY`)

`DENSITY,`*record.file* [,*specifications*]

The density matrix to be analysed is that found in record *record* on file *file*. If omitted, *record.file* defaults to current orbital record. If specified, `DENSITY` must appear first in the input. Density matrices for specific states can be selected using *specifications*, as explained in section 4.11.

38.2.3 Linear molecules (`LINEAR`, `GENERAL`)

`GENERAL;`

(default) invokes the normal program, which copes with any geometry.

`LINEAR`

invokes a faster program which can be used when all the atoms are arranged parallel to the *z*-axis and only the $m = 0$ components of the multipoles are required.

38.2.4 Maximum rank of multipoles (`LIMIT`)

`LIMIT,`*name,lmax*;

lmax is the highest rank of multipole that is to be calculated by the program. Default (and maximum) is 10 for the general program and 20 for the linear one. If *name* is specified, the limit applies only to multipole site *name*.

38.2.5 Omitting nuclear contributions (`NONUCLEAR`)

`NONUCLEAR`

The nuclear contributions to properties are not to be evaluated.

38.2.6 Specification of multipole sites (`ADD`, `DELETE`)

`ADD,`*name,x,y,z,lmax,radius*;

Add a new site at (*x*, *y*, *z*) with the *name* specified. The multipole rank is limited to *lmax* if a value is specified, otherwise the value of lmax specified by the `LIMIT` directive is used. No account is taken of symmetry; every site in a symmetry-equivalent set must be specified explicitly. The *radius* of the site may also be specified (default 1.0).

`DELETE,`*name*

Delete all atoms with the *name* given from consideration as a multipole site. Note that original atoms from the integral program have names $1, 2, 3, \ldots$ as printed in integral output. `DELETE,ALL` deletes all atoms and gives the multipoles with respect to the origin only.

38.2.7 Defining the radius of multipole sites (`RADIUS`)

`RADIUS`,*name,r*;

Assign radius *r* to all sites with the *name* given. The program moves multipoles at an overlap centre *P* to the site *S* for which the value of $|P - S|/r(S)$ is smallest. In the absence of a `RADIUS` directive, all sites are given radius 1.

38.2.8 Notes and references

The multipoles produced by this analysis are given in their spherical harmonic definitions. Explicit formulae for translating between the cartesian and spherical harmonic definitions of the multipole moments are given in, *Explicit formulae for the electrostatic energy, forces and torques between a pair of molecules of arbitrary symmetry*, S. L. Price, A. J. Stone, and M. Alderton, Molec. Phys., 52, 987 (1984).

For examples of the use of `DMA` analysis see, Price and Stone, Chem. Phys. Lett., 98, 419 (1983); Buckingham and Fowler, J. Chem. Phys., 79, 6426 (1983).

38.2.9 Examples

The following input calculates SCF multipole moments for water.

```
***,h2o distributed multipole analysis
geometry={o;h1,o,r;h2,o,r,h1,theta}    !Z-matrix geometry input
r=1 ang                                !bond length
theta=104                              !bond angle
basis=6-311g**
hf                                     !do scf calculation
{dma;limit,,4}                         !results for total multipoles are
```

http://www.molpro.net/info/current/examples/h2o_dma.com

38.3 Mulliken population analysis

38.3.1 Calling the population analysis program (`POP`)

`POP`;

Invokes Mulliken analysis program, which analyses any density matrix into its contributions from s,p,d,f... basis functions on each atom. The density matrix is taken from the last dump record, unless overridden with the `DENSITY` card. The subcommands may be abbreviated by the first four characters. The atomic charges are stored in the MOLPRO variable `ATCHARGE`. The i'th element in `ATCHARGE` corresponds to the i'th row of the Z-matrix input.

38.3.2 Defining the density matrix (`DENSITY`)

`DENSITY`,*record.file* [,*specifications*]

Take density matrix to be analysed from record *record* on file *file*. Density matrices for specific states can be selected using *specifications*, as explained in section 4.11. Note that the density matrices are stored in the same record as the orbitals.

38.3.3   Populations of basis functions (`INDIVIDUAL`)

`INDIVIDUAL;`

38.3.4   Example

```
***,h2o population analysis
geometry={o;h1,o,r;h2,o,r,h1,theta}    !Z-matrix geometry input
r=1 ang                                !bond length
theta=104                              !bond angle
basis=6-311g**
hf                                     !do scf calculation
pop;                                   !Mulliken population analysis using mcscf density
individual                             !give occupations of individual basis functions
```

> `http://www.molpro.net/info/current/examples/h2o_pop.com`

If specified, the Mulliken populations of each individual basis function are printed.

38.4   Natural Bond Orbital Analysis

38.4.1   Calling the Natural Bond Orbital analysis program (`NBO`)

`NBO,[WITH_CORE=`*core_option*`],[LEVEL=`*level*`],[KEEP_WBI=`*wbi_option*`];`

The Natural Bond Orbital Analysis of Weinhold and coworkers (J. Chem. Phys. 83 (1985) 735, J. Chem. Phys. 83 (1985) 1736 and J. Chem. Phys. 78 (1983) 4066) can be called by the use of the `NBO` card. It reads from a density or orbital record, and performs the necessary transformations to Natural Atomic Orbitals (NAO), Natural Bond Orbitals (NBO) and Natural Localized Molecular Orbitals (NLMO). The latter can also be saved to a record and later used in local correlation treatments (cf. Section 32). By default, the full orbital space is used. The core orbitals can, however, be left out of the procedure if *core_option*=0.

One can choose to truncate the transformation series (e.g., only compute the NAO orbitals), with help of the `LEVEL` keyword. If *level*=1, only the NAO transformation will be carried out. For *level*=2 the NBO transformation is performed, and for 3 the NLMO (default).

Sometimes, the NBO procedure will not converge due to a bad ordering on the 2-center bond search. The first run is based on the Wiberg bond index, but the algorithm switches to the atom ordering on the subsequent runs. This can be avoided by the use of the option `KEEP_WBI`. If *wbi_option*=1, the Wiberg bond index is used in all iterations.

38.4.2   Saving the NLMO orbitals (`SAVE`)

`SAVE,`*record.file*`;`

The NLMO orbitals are saved in the specified *record*, together with the NPA charges.

38.5   Finite field calculations

Dipole moments, quadrupole moments etc. and the corresponding polarizabilities can be obtained as energy derivatives by the finite difference approximation. This is most easily done

with the `DIP`, `QUAD`, or `FIELD` commands. An error will result if the added perturbation is not totally symmetric (symmetry 1). Note that the orbitals must be recomputed before performing a correlation calculation.

38.5.1 Dipole fields (`DIP`)

`DIP`,*xfield,yfield,zfield*;
`DIP+`,*xfield,yfield,zfield*;

Add a finite dipole field to the one electron Hamiltonian and the core energy. The field strength is given by *xfield,yfield,zfield*. `DIP+` adds to any existing field, otherwise any previous field is removed.

38.5.2 Quadrupole fields (`QUAD`)

`QUAD`,*xxfield,yyfield,zzfield,xyfield,xzfield,yzfield*;
`QUAD+`,*xxfield,yyfield,zzfield,xyfield,xzfield,yzfield*;

Exactly as the `DIP` command, but adds a quadrupole field.

38.5.3 General fields (`FIELD`)

`FIELD`,*oper1,fac1, oper2,fac2,* ... ;
`FIELD+`,*oper1,fac1, oper2,fac2,* ... ;

Adds one-electron operators *oper1*, *oper2*, ... with the corresponding factors *fac1*, *fac2*, ... to the one-electron hamiltonian. The available operators are given in section 6.13. An error will result if the added perturbation is not totally symmetric (symmetry 1).

`FIELD+` adds to any existing field, otherwise any previous field is removed.

Note that `FIELD` does currently not modify core polarization potentials (CPP). If CPPs are present, only `DIP` and `QUAD` should be used.

38.5.4 Examples

The first examples shows various possibilities to add perturbations to the one-electron hamiltonian.

```
***,H2O finite fields
memory,4,m
R     =    0.96488518 ANG
THETA =  101.90140469
geometry={H1
          O,H1,R;
          H2,O,R,H1,THETA}
{hf;wf,10,1}              !scf without field


f=0.05

dip,,,f                   !add dipole (z) field to h0
hf                        !do scf with modified h0

field,dmz,f               !add dipole (z) field to H0
                          !same result as previous example
hf                        !do scf with modified h0

quad,,,f                  !add quadrupole (qmzz) field to h0
hf                        !do scf with modified h0

field,qmzz,f              !add quadrupole (qmzz) field to h0;
                          !same result as previous example
hf                        !do scf with modified h0

field,zz,f,xx,-0.5*f,yy,-0.5*f
                          !add general field; same result as quad above
hf                        !do scf with modified h0

field,zz,f            !same as before with separate field commands
field+,xx,-0.5*f
field+,yy,-0.5*f
hf                        !do scf with modified h0

field                     !remove field
hf                        !scf without field
```

        http://www.molpro.net/info/current/examples/field.com

The second example shows how to compute dipole moments and polarizabilities using finite
fields.

```
***,H2O finite field calculations

r=1.85,theta=104                        !set geometry parameters
geometry={O;                            !z-matrix input
          H1,O,r;
          H2,O,r,H1,theta}
basis=avtz                              !define default basis
field=[0,0.005,-0.005]                  !define finite field strengths
$method=[hf,mp4,ccsd(t),casscf,mrci]

k=0
do i=1,#field                           !loop over fields
  dip,,,field(i)                        !add finite field to H
  do m=1,#method                        !loop over methods
    k=k+1
    $method(m)                          !calculate energy
    e(k)=energy                         !save energy
  enddo
enddo

k=0
n=#method
do m=1,#method
  k=k+1
  energ(m)=e(k)
  dipmz(m)=(e(k+n)-e(k+2*n))/(field(2)-field(3))   !dipole moment as first energy derivative
  dpolz(m)=(e(k+n)+e(k+2*n)-2*e(k))/((field(2)-field(1))*(field(3)-field(1)))  !polarizability
enddo

table,method,energ,dipmz,dpolz
title,results for H2O, r=$R, theta=$theta, basis=$basis
---
```

http://www.molpro.net/info/current/examples/h2o_field.com

38.6 Relativistic corrections

Relativistic corrections may be calculated within the Cowan-Griffin approach by computing expectation values of the mass-velocity and 1-electron Darwin integrals; these should be generated using the property integral program with keyword REL The expectation values can be computed within the SCF, MCSCF and CI programs in the usual way using the EXPECT command, again with the keyword REL. The mass-velocity and Darwin terms, and their sum are subsequently available through the MOLPRO variables MASSV, DARW and EREL respectively.

38.6.1 Example

```
***,ar2
geometry={ar1;ar2,ar1,r}    !geometry definition
r=2.5 ang                   !bond distance
{hf;                        !non-relativisitic scf calculation
expec,rel,darwin,massv}     !compute relativistic correction using Cowan-Griffin operator
e_nrel=energy               !save non-relativistic energy in variable enrel
show,massv,darwin,erel      !show individual contribution and their sum

dkroll=1                    !use douglas-kroll one-electron integrals
hf;                         !relativistic scf calculation
e_dk=energy                 !save relativistic scf energy in variable e_dk.
show,massv,darwin,erel      !show mass-velocity and darwin contributions and their sum
show,e_dk-e_nrel            !show relativistic correction using Douglas-Kroll
```

38.7 CUBE — dump density or orbital values

CUBE,*filename,iflag,n_1,n_2,n_3*

calls a module which dumps the values of various properties on a spatial parallelopipedal grid to an external file. The purpose is to allow plotting of orbitals, densities and other quantities by external programs. The format of the file is intended to be the same as that produced by other programs.

filename   is the unix path name of the file to be written, and its specification is mandatory.

iflag   If *iflag* is negative (default), a formatted file will be written, otherwise unformatted fortran i/o will be used.

n_1,n_2,n_3 specify the number of grid points in each of three dimensions. If not specified, sensible defaults are chosen.

By default, the last density computed is evaluated on the grid, and written to *filename*. This behaviour can be modified by one or more of the following subcommands.

38.7.1 STEP — setting the point spacing

STEP,[*stepx*],[*stepy*], [*stepz*]

stepx,stepy, stepz specify the point spacing in each of three axis directions. By default, the value of *stepx,stepy, stepz* is determined by the number of grid points, the Bragg radii of the atoms, and some related parameters.

38.7.2 DENSITY — source of density

DENSITY,[*density-source*]
GRADIENT,[*density-source*]
LAPLACIAN,[*density-source*]

Compute the density and, optionally, its gradient and laplacian. *<density-source>* may be a record number containing the required density, and may contain further qualification, such as set number, in the usual way. By default, the last computed density is taken.

38.7.3   ORBITAL — source of orbitals

ORBITAL,[*orbital-list*],[RECORD=*orbital-source*]

<*orbital-list*> is a list of one or more orbital numbers of the form *number.symmetry* or keywords chosen from HOMO, LUMO, OCC (all occupied orbitals), ALL. If nothing is specified, the default is HOMO. <*orbital-source*> may be a record number containing the required density, and may contain further qualification, such as set number, in the usual way. By default, the last computed orbitals are taken.

Note that the CUBE file format precludes simultaneous orbital and density dumps, but that this may be achieved in the GOPENMOL format (see 38.8).

38.7.4   AXIS — direction of grid axes

AXIS,*x,y,z*

x,y,z specify the unnormalised direction cosines of one of the three axes defining the grid. Up to three AXIS commands can be given, but none is required. Axes need not be orthogonal. By default, the first axis is the cartesian *x*, the second is orthogonal to the first and to the cartesian *z*, and the third is orthogonal to the first two.

38.7.5   BRAGG — spatial extent of grid

Based on the direction of the coordinate axes, a parallelopiped (in the usual case of orthogonal axes, a cuboid) is constructed to contain the molecule completely. The atoms are assumed to be spherical, with an extent proportional to their Bragg radii, and the constant of proportionality can be changed from the default value using

BRAGG,*scale*

After the parallelopiped has been constructed, the grid is laid out with equal spacing to cover it using the number of points specified on the CUBE command.

38.7.6   ORIGIN — centroid of grid

ORIGIN,*x,y,z*

x,y,z specify the centroid of the grid. It is usually not necessary to use this option, since the default should suffice for most purposes.

38.7.7   TITLE — user defined title

TITLE,*title*

Set a user defined title in the cube file.

38.7.8   DESCRIPTION — user defined description

DESCRIPTION,*description*

Set a user defined description in the cube file.

38.7.9   Format of cube file

The formatted cube file contains the following records

`(A)`	job title.
`(A)`	brief description of the file contents.
`(I5,3F12.6)`	number of atoms, coordinates of grid origin (bohr).
`(I5,3F12.6)`	number of grid points n_1, step vector for first grid dimension.
`(I5,3F12.6)`	number of grid points n_2, step vector for second grid dimension.
`(I5,3F12.6)`	number of grid points n_3, step vector for third grid dimension.
`(I5,4F12.6)`	atomic number, charge and coordinates; one such record for each atom.
`(6E13.5)`	$n_1 \times n_2$ records of length n_3 containing the values of the density or orbital at each grid point. With default choice of the axes, the inner loop will be over n_3 points along the cartesian z axis, and the outer loop over n_1 points along the cartesian x axis.

In the case of a number of orbitals m, the record length is $m \times n_3$, with the data for a single grid point grouped together. In the case of the density gradient, there is first a record of length n_3 containing the density, then one of length $3n_3$ containing the gradient, with the three cartesian components contiguous. For the laplacian, there is a further record of length n_3.

38.8   GOPENMOL — calculate grids for visualization in gOpenMol

`GOPENMOL`,*filename,iflag,n_1,n_2,n_3*

The syntax and sub-options are exactly the same as for CUBE, except that the files produced are in a format that can be used directly in the gOpenMol visualization program. The following should be noted.

- Only the base name (up to the last '.') in *filename* is used, and is appended by different suffices to create several different files:

.crd	A CHARMm CRD-format file containing the coordinates is always produced, and may be used in the invocation of gOpenMol:
	`rungOpenMol −i`*filename*`.crd`
`_density.plt`	If `DENSITY` is given, then the file *filename*`_density.plt` is produced and contains the density grid in gOpenMol internal format.
`_orbital_`*number.symmetry*`.plt`	If `ORBITAL` is given, then for each orbital *number.symmetry* specified, the file *filename*`_orbital_`*number.symmetry*`.plt` is produced and contains the orbital grid in gOpenMol internal format.

- The default is not to produce any orbitals or densities, and so only the atomic coordinates are dumped.

- The default is to use unformatted binary files, and this should not normally be changed.

- The `ORIGIN` and `AXIS` commands should not be used.

- If

  ```
  INTERACT
  ```

  is given in the input, when all the grids have been calculated, an attempt is made to start gOpenMol by executing the Unix command `rungOpenMol`. If `rungOpenMol` is not in `$PATH`, then nothing happens. Otherwise, gOpenMol should start and display the molecule. Any `.plt` files produced can be added to the display by following the `Plot;Contour` menu item. The name of the Unix command may be changed from the default `rungOpenMol` by specifying it as the first argument to the `INTERACT` directive. By default, gOpenMol is not started, and this is equivalent to giving the command `BATCH`.

39 RELATIVISTIC CORRECTIONS

There are three ways in MOLPRO to take into account scalar relativistic effects:

1. Use the Douglas-Kroll-Hess or eXact-2-Component (X2C) relativistic one-electron integrals.

2. Compute a perturbational correction using the Cowan-Griffin operator (see section 6.13).

3. Use relativistic effective core potentials (see section 12).

39.1 Using the Douglas–Kroll–Hess or eXact-2-Component Hamiltonians

For all-electron calculations, the prefered way is to use either the Douglas–Kroll–Hess (DKH) or eXact-2-Component (X2C) Hamiltonians, the former of which is available up to (in principle) arbitrary order in MOLPRO. DKH is activated by setting any of

```
SET,DKROLL=1
SET,DKHO=n,  (n = 2,...,99),
SET,DKHP=m,  (m = 1,...,5)
```

or for X2C by setting

```
SET,DKHO=101
```

somewhere in the input before the first energy calculation.

Alternatively, these values can be given as options on the `INT` command:

```
INT,[DKROLL=1],DKHO=n,DKHP=m.
```

or

```
INT,DKHO=101
```

The DKH option `DKROLL` is available for compatibility with earlier versions of MOLPRO. If only `DKROLL=1` is given, the default for `DKHO` is 2. Setting `DKROLL=0` disables DKH and X2C, independently of the setting of `DKHO`. DKH is also disabled by setting `DKHO=0`, unless `DKROLL=1` is set. In order to avoid confusion, it is recommended only to use `DKHO` and never set `DKROLL`.

The value of `DKHP` specifies the parametrization for the DKH treatment (it has no effect for X2C):

DKHP=1: Optimum parametrization (OPT, default)

DKHP=2: Exponential parametrization (EXP)

DKHP=3: Square-root parametrization (SQR)

DKHP=4: McWeeny parametrization (MCW)

DKHP=5: Cayley parametrization (CAY)

Example:

```
SET,DKHO=8  !  DKH order = 8
SET,DKHP=2  !  choose exponential parametrization for unitary transformations (recommended)
```

Up to fourth order (DKHO=4) the DKH Hamiltonian is independent of the chosen parametrization. Higher-order DKH Hamiltonians depend slightly on the chosen paramterization of the unitary transformations applied in order to decouple the Dirac Hamiltonian.

For details on the infinite-order DKH Hamiltonians see

M. Reiher, A. Wolf, JCP **121**, 2037–2047 (2004),
M. Reiher, A. Wolf, JCP **121**, 10945–10956 (2004).

For details on the different parametrizations of the unitary transformations see
A. Wolf, M. Reiher, B. A. Hess, JCP **117**, 9215–9226 (2002).

The current implementation is the polynomial-cost algorithm by Peng and Hirao: D. Peng, K. Hirao, JCP 130, 044102 (2009).

A detailed comparison of the capabilities of this implementation as well as the current implementation of the X2C approach is provided in:

D. Peng, M. Reiher, TCA 131, 1081 (2012).

39.2 Example for computing relativistic corrections

```
***,ar2
geometry={ar1;ar2,ar1,r}      !geometry definition
r=2.5 ang                     !bond distance
{hf;                          !non-relativisitic scf calculation
expec,rel,darwin,massv}       !compute relativistic correction using Cowan-Griffin operator
e_nrel=energy                 !save non-relativistic energy in variable enrel
show,massv,darwin,erel        !show individual contribution and their sum

dkroll=1                      !use douglas-kroll one-electron integrals
hf;                           !relativistic scf calculation
e_dk=energy                   !save relativistic scf energy in variable e_dk.
show,massv,darwin,erel        !show mass-velocity and darwin contributions and their sum
show,e_dk-e_nrel              !show relativistic correction using Douglas-Kroll
```

> http://www.molpro.net/info/current/examples/ar2_rel.com

40 DIABATIC ORBITALS

In order to construct diabatic states, it is necessary to determine the mixing of the diabatic states in the adiabatic wavefunctions. In principle, this mixing can be obtained by integration of the non-adiabatic coupling matrix elements. Often, it is much easier to use an approximate

method, in which the mixing is determined by inspection of the CI coefficients of the MCSCF or CI wavefunctions. This method is applicable only if the orbital mixing is negligible. For CASSCF wavefunctions this can be achieved by maximizing the overlap of the active orbitals with those of a reference geometry, at which the wavefunctions are assumed to be diabatic (e.g. for symmetry reasons). The orbital overlap is maximized using using the new DIAB command in the MCSCF program.

This procedure works as follows: first, the orbitals are determined at the reference geometry. Then, the calculations are performed at displaced geometries, and the "diabatic" active orbitals, which have maximum overlap with the active orbitals at the reference geometry, are obtained by adding a DIAB directive to the input:

Old form (Molpro96, obsolete):

DIAB,*orbref, orbsav, orb1,orb2,pri*

New form:

DIAB,*orbref* [,TYPE=*orbtype*] [,STATE=*state*] [,SPIN=*spin*] [,*MS2=ms2*] [,SAVE=*orbsav*] [,ORB1=*orb1*, ORB2=*orb2*] [,*PRINT=pri*]

Here *orbref* is the record holding the orbitals of the reference geometry, and *orbsav* is the record on which the new orbitals are stored. If *orbsav* is not given (recommended!) the new orbitals are stored in the default dump record (2140.2) or the one given on the ORBITAL directive (see section 19.5.4). In contrast to earlier versions of MOLPRO it is possible that *orbref* and *orbsav* are the same. The specifications TYPE, STATE, SPIN can be used to select specific sets of reference orbitals, as described in section 4.11. *orb1, orb2* is a pair of orbitals for which the overlap is to be maximized. These orbitals are specified in the form *number.sym*, e.g. 3.1 means the third orbital in symmetry 1. If *orb1, orb2* are not given, the overlap of all active orbitals is maximized. *pri* is a print parameter. If this is set to 1, the transformation angles for each orbital are printed for each jacobi iteration.

Using the defaults described above, the following input is sufficient in most cases:

DIAB,*orbref*

Using Molpro98 is is not necessary any more to give any GEOM and DISPL cards. The displacements and overlap matrices are computed automatically (the geometries are stored in the dump records, along with the orbitals).

The diabatic orbitals have the property that the sum of orbital and overlap contributions in the non-adiabatic coupling matrix elements become approximately zero, such that the adiabatic mixing occurs only through changes of the CI coefficients. This allows to determine the mixing angle directly from the CI coefficients, either in a simple way as described for instance in J. Chem. Phys. **89**, 3139 (1988), or in a more advanced manner as described by Pacher, Cederbaum, and Köppel in J. Chem. Phys. **89**, 7367 (1988).

Below we present an example for the first two excited states of H_2S, which have B_1 and A_2 symmetry in C_{2v}, and A'' symmetry in C_S. We first perform a reference calculation in C_{2v} symmetry, and then determine the diabatic orbitals for displaced geometries in C_S symmetry. Each subsequent calculation uses the previous orbitals as reference. One could also use the orbitals of the C_{2v} calculation as reference for all other calculations. In this case one would have to take out the second-last input card, which sets reforb=2141.2.

```
***,H2S diabatic A" states

basis=VDZ                                 !use cc-pVDZ basis set
symmetry,x,planeyz                        !use Cs symmetry & fix orientation of the molecule
orient,noorient                           !dont allow automatic reorientation
geometry={s;h1,s,r1;h2,s,r2,h1,theta}     !Z-matrix geometry input

gprint,orbitals,civector                  !global print options

text,reference calculation for C2V
theta=92.12,r1=2.3,r2=2.3                  !reference geometry

{hf;occ,7,2;wf,18,1}                       !scf calculation for ground state

{multi;occ,9,2;closed,4,1;                 !define active and inactive spaces
wf,18,2;state,2;                           !two A" states (1B1 and 1A2 in C2v)
orbital,2140.2}                            !save orbitals to 2140.2
reforb=2140.2

text,calculations at displaced geometries

rd=[2.4,2.5,2.6]                           !define a range of bond distances

do i=1,#rd                                 !loop over displaced geometries

r2=rd(i)                                   !set r2 to current distance

{multi;occ,9,2;closed,4,1;                 !same wavefunction definition as at reference geom.
wf,18,2;state,2;
orbital,2141.2                             !save new orbitals to record
diab,reforb}                               !compute diabatic orbitals using reference orbitals
                                           !stored on record reforb
reforb=2141.2                              !set variable reforb to the new orbitals.
enddo
```

      http://www.molpro.net/info/current/examples/h2s_diab.com

41   NON ADIABATIC COUPLING MATRIX ELEMENTS

Non-adiabatic coupling matrix elements can be computed by finite differences for MCSCF or
CI wavefunctions using the DDR program. For state-averaged MCSCF wavefunctions, they can
also computed analytically (cf. section 19.9.2).

Note that present numerical procedure has been much simplified relative to Molpro96. No
GEOM and DISPL input cards are needed any more, and the three necessary calculations can be
done in any order.

41.1   The DDR procedure

In order to compute the coupling matrix elements by finite differences, one has to compute and
store the wavefunctions at two (first-order algorithm) or three (second-order algorithm) slightly
displaced geometries. The order of these calculations is arbitrary.

The typical strategy is as follows:

1.) Compute the wavefunction at the reference geometry. The wavefunctions for both states
have to be stored using the SAVE command of the CI program. If the matrix elements are
computed for MCSCF wavefunctions, it is necessary to recompute the wavefunction with the CI

program, using the `NOEXC` option. The transition density matrix is stored using the `DM` directive of the CI program.

2.) Compute the wavefunctions at the (positively) displaced geometry and store the CI wavefunction in a second record.

3.) If the second-order (three-point) method is used, step (2) is repeated at a (negatively) displaced geometry.

4.) Compute the transition density matrices between the states at the reference geometry and the displaced geometr(ies). This is done with the `TRANS` directive of the CI program.

5.) Finally, the `DDR` program is used to assemble the matrix element. Using the first-order two-point method, only a single input line is needed:

`DDR`, *dr, orb1, orb2, trdm2*

where *dr* is the geometry increment used as denominator in the finite difference method, *orb1* is the record holding the orbitals of the reference geometry, *orb2* is the record holding the orbitals of the displaced geometry, and *trdm2* is the record holding the transition density matrix computed from the CI-vectors at *R* and *R+DR*.

If central differences (three points) are used, the input is as follows:

`DDR`,*2*dr*
`ORBITAL`,*orb1,orb2,orb3*
`DENSITY`,*trdm1,trdm2,trdm3*

where *dr, orb1, orb2* are as above, and *orb3* is the record holding the orbitals at the negatively displaced geometry.

trdm1, trdm2, trdm3 are the records holding the transition densities $\gamma(R|R)$, $\gamma(R|R+DR)$, and $\gamma(R|R-DR)$, respectively.

If more than two states are computed simultaneously, the transition density matrices for all pairs of states will be stored in the same record. In that case, and also when there are just two states whose spatial symmetry is not 1, it is necessary to specify for which states the coupling is to be computed using the `STATE` directive:

`STATE`,*state$_1$, state$_2$*

where *state$_i$* is of the form *istate.isym* (the symmetries of both states must be the same, and it is therefore sufficient to specify the symmetry of the first state).

As an example the input for first-order and second-order calculations is given below. The calculation is repeated for a range of geometries, and at the end of the calculation the results are printed using the `TABLE` command.

In the calculation shown, the "diabatic" CASSCF orbitals are generated in the two CASSCF calculations at the displaced geometries by maximizing the overlap with the orbitals at the reference geometry. This is optional, and (within the numerical accuacy) does not influence the final results. However, the relative contributions of the orbital, overlap and CI contributions to the NACME are modified. If diabatic orbitals are used, which change as little as possible as function of geometry, the sum of overlap and orbital contribution is minimized, and to a very good approximation the NACME could be obtained from the CI-vectors alone.

```
***,lif non-adiabatic coupling
memory,1,m

basis,f=avdz,li=vdz           !define basis
r=[10.0,10.5,11.0,11.5,12.0]  !define bond distances
dr=0.01                       !define increment
geometry={li;f,li,rlif}       !define geometry

rlif=3                        !first calculation at R=3
{hf;occ,4,1,1}                !SCF
{multi;closed,3;              !CASSCF, 3 inactive orbitals
wf,12,1;state,2;              !Two 1A1 states
orbital,2140.2}               !dump orbitals to record 2140.2

do i=1,#r                     !loop over geometries
rlif=r(i)                     !set bond distance
{multi;closed,3;              !CASSCF, 3 inactive orbitals
wf,12,1;state,2;              !Two 1A1 states
orbital,2140.2}               !Overwrite previous orbitals by present ones

{ci;state,2;noexc;            !CI for 2 states, no excitations
save,6000.2;                  !save wavefunction to record 6000.2
dm,8000.2}                    !save (transition) densities to record 8000.2

rlif=r(i)+dr                  !increment bond distance by dr

{multi;closed,3;              !same CASSCF as above
wf,12,1;state,2;              !Two 1A1 states
start,2140.2;                 !start with orbitals from reference geometry
orbital,2141.2;               !save orbitals to record 2141.2
diab,2140.2}                  !generate diabatic orbitals by maximizing the
                              !overlap with the orbitals at the reference geometry

{ci;state,2;noexc;save,6001.2}   !CI for 2 states, wavefunction saved to record 6001.2

{ci;trans,6000.2,6001.2;      !Compute overlap and transition density <R|R+DR>
dm,8100.2}                    !Save transition density to record 8100.2

rlif=r(i)-dr                  !repeat at r-dr

{multi;closed,3;              !same CASSCF as above
wf,12,1;state,2;              !Two 1A1 states
start,2140.2;                 !start with orbitals from reference geometry
orbital,2142.2;               !save orbitals to record 2142.2
diab,2140.2}                  !generate diabatic orbitals by maximizing the
                              !overlap with the orbitals at the reference geometry

{ci;state,2;noexc;save,6002.2}   !CI for 2 states, wavefunction saved to record 6002.2

{ci;trans,6000.2,6002.2;      !Compute overlap and transition density <R|R-DR>
dm,8200.2}                    !Save transition density to record 8200.2

{ddr,dr,2140.2,2141.2,8100.2}  !compute NACME using 2-point formula (forward difference)
nacme1p(i)=nacme              !store result in variable nacme1p
{ddr,-dr,2140.2,2142.2,8200.2}  !compute NACME using 2-point formula (backward difference)
nacme1m(i)=nacme              !store result in variable nacme1m

{ddr,2*dr                     !compute NACME using 3-point formula
orbital,2140.2,2141.2,2142.2;  !orbital records for R, R+DR, R-DR
density,8000.2,8100.2,8200.2}  !transition density records for R, R+DR, R-DR
nacme2(i)=nacme               !store result in variable nacme2

end do                        !end of loop over differend bond distances

nacmeav=(nacme1p+nacme1m)*0.5  !average the two results forward and backward differences
table,r,nacme1p,nacme1m,nacmeav,nacme2   !print a table with results
title,Non-adiabatic couplings for LiF     !title for table
```

http://www.molpro.net/info/current/examples/lif_nacme.com

This calculation produces the following table:

```
Non-adiabatic couplings for LiF

      R       NACME1P        NACME1M        NACMEAV         NACME2
    10.0    -0.22828936    -0.22328949    -0.22578942    -0.22578942
    10.5    -0.51777034    -0.50728914    -0.51252974    -0.51252974
    11.0     0.76672943     0.76125391     0.76399167     0.76399167
    11.5     0.42565202     0.42750263     0.42657733     0.42657733
    12.0     0.19199878     0.19246799     0.19223338     0.19223338
```

Note that the sign changes because of a phase change of one of the wavefunctions. In order to keep track of the sign, one has to inspect both the orbitals and the ci-vectors.

42 QUASI-DIABATIZATION

The DDR procedure can also be used to generate quasi-diabatic states and energies for MRCI wavefucntions (CASSCF case can be treated as special case using the `NOEXC` directive in the MRCI). The quasi-diabatic states have the propery that they change as little as possible relative to a reference geometry; with other words, the overlap between the states at the current geometry with those at a reference geometry is maximized by performing a unitary transformation among the given states. Preferably, the adiabatic and diabatic states should be identical at the reference geometry, e.g., due to symmetry. For instance, in the examples given below for the $^1B_1$ and $^1A_2$ states of H_2S, C_{2v} geomtries are used as reference, and at these geometries the states are unmixed due to their different symmetry. At the displaced geometries the molecular symmetry is reduced to C_S. Both states now belong to the $^1A''$ irreducible representation and are strongly mixed. For a description and application of the procedure described below, see D. Simah, B. Hartke, and H.-J. Werner, J. Chem. Phys. **111**, 4523 (1999).

This diabatization can be done automatically and requires two steps: first, the active orbitals of a CASSCF calculation are rotated to maximize the overlap with the orbitals at the reference geometry. This is achieved using the `DIAB` procedure described in section 19.5.9. Secondly, the `DDR` procedure can be used to find the transformation among the CI vectors.

The following input is required:

DDR   calls the DDR procedure.

ORBITAL,*orb1, orb2 orb1* and *orb2* are the (diabatic) orbitals at the current and reference geometry, respectively.

DENSITY,*trdm1,trdm2 trdm1* are the transition densities computed at the current geometry, *trdm2* are transition densities computed using the wavefunctions of the current (bra) and reference (ket) geometries.

MIXING,*state1, state2, . . .*   The given states are included in the diabatization.

ENERGY,*e1, e2, . . .*   Adiabatic energies of the states. If this input card is present, the Hamiltonian in the basis of the diabatic states is computed and printed. Alternatively, the energies can be passed to `DDR` using the Molpro variable `EADIA`.

The results are printed and stored in the following Molpro variables, provided the `ENERGY` directive or the `EADIA` variable is found:

Results including the first-order orbital correction:

SMAT   The first *nstate* × *nstate* elements contain the state overlap matrix (bra index rans
           fastest).

UMAT   The first *nstate* × *nstate* elements contain the transformation matrix.

HDIA   The first *nstate* · (*nstate* + 1)/2 elements contain the lower triangle of the diabatic
           hamiltonian.

MIXANG   Non-adiabatic mixing angle in degree. This is available only in the two-state case.

The corresponding results obtained from the CI-vectors only (without orbital correction) are
stored in the variables [SMATCI], UMATCI, HDIACI, and MIXANGCI.

The way it works is most easily demonstrated for some examples. In the following input, the
wavefunction is first computed at the C_{2v} reference geometry, and then at displaced geometries.

```
***,h2s Diabatization
memory,3,m

gprint,orbitals,civector

symmetry,x
orient,noorient             !noorient should always be used for diabatization
geometry={
        s;
        h1,s,r1;
        h2,s,r2,h1,theta}

basis=avdz                  !This basis is too small for real application

r1=2.5                      !Reference geometry
theta=[92]

r=[2.50,2.55,2.60]          !Displaced geometries

reforb=2140.2               !Orbital dumprecord at reference geometry
refci=6000.2                !MRCI record at reference geometry
savci=6100.2                !MRCI record at displaced geometries

text,compute wavefunction at reference geometry (C2v)
r2=r1

{hf;occ,9,2;wf,18,2,4;
orbital,2100.2}

{multi;occ,9,2;closed,4,1;
wf,18,2;state,2;            !1B1 and 1A2 states
natorb,reforb               !Save reference orbitals on reforb
noextra}                    !Dont use extra symmetries

{ci;occ,9,2;closed,4,1;      !MRCI at reference geometry
wf,18,2,0;state,2;          !1B1 and 1A2 states
orbital,reforb              !Use orbitals from previous CASSCF
save,refci}                 !Save MRCI wavefunction

Text,Displaced geometries

do i=1,#r                   !Loop over different r values
data,truncate,savci+1       !truncate dumpfile after reference
r2=r(i)                     !Set current r2

{multi;occ,9,2;closed,4,1;
wf,18,2,0;state,2;          !Wavefunction definition
start,reforb               !Starting orbitals
orbital,3140.2;            !Dump record for orbitals
diab,reforb                !Generate diabatic orbitals relative to reference geometry
noextra}                    !Dont use extra symmetries

{ci;occ,9,2;closed,4,1;
wf,18,2,0;state,2;          !1B1 and 1A2 states
orbital,diabatic           !Use diabatic orbitals
save,savci}                 !Save MRCI for displaced geometries

e1(i)=energy(1)             !Save adiabatic energies
e2(i)=energy(2)

{ci;trans,savci,savci        !Compute transition densities at R2
dm,7000.2}                  !Save transition densities on this record
{ci;trans,savci,refci;       !Compute transition densities between R2 and R1
dm,7100.2}                  !Save transition densities on this record

{ddr
density,7000.2,7100.2       !Densities for <R2||R2> and <R2||R1>
orbital,3140.2,2140.2       !Orbitals for <R2||R2> and <R2||R1>
energy,e1(i),e2(i)          !Adiabatic energies
mixing,1.2,2.2}             !Compute mixing angle and diabatic energies
```

This calculation produces the following results:

```
Diabatic energies for H2S, obtained from CI-vectors

      R         E1              E2              H11CI           H22CI           H21CI           MIXCI
    2.50  -398.64296319   -398.63384782   -398.64296319   -398.63384782    0.00000000        0.00
    2.55  -398.64572746   -398.63666636   -398.64509901   -398.63729481   -0.00230207       15.27
    2.60  -398.64911752   -398.63771802   -398.64662578   -398.64020976   -0.00471125       27.87

Diabatic energies for H2S, obtained from CI-vectors and orbital correction

      R         E1              E2              H11             H22             H21            MIXTOT
    2.50  -398.64296319   -398.63384782   -398.64296319   -398.63384782    0.00000000        0.00
    2.55  -398.64572746   -398.63666636   -398.64509941   -398.63729441   -0.00230139       15.26
    2.60  -398.64911752   -398.63771802   -398.64662526   -398.64021027   -0.00471160       27.88
```

The results in the first table are obtained from the CI-contribution to the state-overlap matrix only, while the ones in the second table include a first-order correction for the orbitals. In this case, both results are almost identical, since the `DIAB` procedure has been used to minimize the change of the active orbitals. This is the recommended procedure. If simply natural orbitals are used without orbital diabatization, the following results are obtained from the otherwise unchanged calculation:

```
Diabatic energies for H2S, obtained from CI-vectors

      R         E1              E2              H11CI           H22CI           H21CI           MIXCI
    2.50  -398.64296319   -398.63384782   -398.64296319   -398.63384782    0.00000000        0.00
    2.55  -398.64572742   -398.63666630   -398.64475612   -398.63763760   -0.00280315       19.11
    2.60  -398.64911746   -398.63771803   -398.64521031   -398.64162518   -0.00541050       35.83

Diabatic energies for H2S, obtained from CI-vectors and orbital correction

      R         E1              E2              H11             H22             H21            MIXTOT
    2.50  -398.64296319   -398.63384782   -398.64296319   -398.63384782    0.00000000        0.00
    2.55  -398.64572742   -398.63666630   -398.64509146   -398.63730226   -0.00231474       15.36
    2.60  -398.64911746   -398.63771803   -398.64648358   -398.64035190   -0.00480493       28.73
```

It is seen that the mixing obtained from the CI vectors only is now very different and meaningless, since the orbitals change significantly as function of geometry. However, the second calculations, which accounts for this change approximately, still gives results in quite good agreement with the calculation involving diabatic orbitals.

The final examples shows a more complicated input, which also computes the non-adiabatic coupling matrix elements. In a two-state model, the NACME should equal the first derivative of the mixing angle. In the example, the NACME is computed using the 3-point `DDR` method (NACMECI), and also by finite difference of the mixing angle (DCHI).

```
***,h2s Diabatization and NACME calculation
memory,3,m

gprint,orbitals,civector

symmetry,x
orient,noorient           !noorient should always be used for diabatization
geometry={
        s;
        h1,s,r1;
        h2,s,r2,h1,theta}

basis=avdz                !This basis is too small for real application

r1=2.5                    !Reference geometry
theta=[92]

r=[2.55,2.60]             !Displaced geometries
dr=[0,0.01,-0.01]         !Samll displacements for finite difference NACME calculation

reforb1=2140.2            !Orbital dumprecord at reference geometry
refci=6000.2              !MRCI record at reference geometry
savci=6100.2              !MRCI record at displaced geometries

text,compute wavefunction at reference geometry (C2v)
r2=r1

{hf;occ,9,2;wf,18,2,4;orbital,2100.2}

{multi;occ,9,2;closed,4,1;
wf,18,2;state,2;          !1B1 and 1A2 states
natorb,reforb1            !Save reference orbitals on reforb1
noextra}                  !Dont use extra symmetries

{ci;occ,9,2;closed,4,1;    !MRCI at reference geometry
wf,18,2,0;state,2;        !1B1 and 1A2 states
orbital,reforb1           !Use orbitals from previous CASSCF
save,refci}               !Save MRCI wavefunction

Text,Displaced geometries

do i=1,#r                 !Loop over different r values
data,truncate,savci+1     !truncate dumpfile after reference
reforb=reforb1

do j=1,3                  !Loop over small displacements for NACME
r2=r(i)+dr(j)             !Set current r2

{multi;occ,9,2;closed,4,1;
wf,18,2,0;state,2;        !Wavefunction definition
start,reforb              !Starting orbitals
orbital,3140.2+j;         !Dumprecord for orbitals
diab,reforb               !Generate diabatic orbitals relative to reference geometry
noextra}                  !Dont use extra symmetries

reforb=3141.2             !Use orbitals for j=1 as reference for j=2,3

{ci;occ,9,2;closed,4,1;
wf,18,2,0;state,2;
orbital,diabatic          !Use diabatic orbitals
save,savci+j}             !Save MRCI for displaced geometries

eadia=energy              !Save adiabatic energies for use in ddr
if(j.eq.1) then
e1(i)=energy(1)           !Save adiabatic energies for table printing
e2(i)=energy(2)
end if

{ci;trans,savci+j,savci+j;  !Compute transition densities at R2+DR(j)
dm,7000.2+j}              !Save transition densities on this record
{ci;trans,savci+j,refci;    !Compute transition densities between R2+DR(j) and R1
```

The calculation produces the following table

```
Mixing angles and non-adiabatic coupling matrix elements for H2S

      R           MIXCI          MIXTOT           DCHI          NACMECI
     2.55         15.2694         15.2644         -5.2226         -5.2365
     2.60         27.8740         27.8772         -3.4702         -3.4794


Diabatic energies for H2S, obtained from CI-vectors

      R      E1              E2              H11CI           H22CI           H21CI
     2.55 -398.64572746 -398.63666636 -398.64509901 -398.63729481  -0.00230207
     2.60 -398.64911752 -398.63771802 -398.64662578 -398.64020976  -0.00471125


Diabatic energies for H2S, obtained from CI-vectors and orbital correction

      R      E1              E2              H11             H22             H21
     2.55 -398.64572746 -398.63666636 -398.64509941 -398.63729441  -0.00230139
     2.60 -398.64911752 -398.63771802 -398.64662526 -398.64021027  -0.00471160
```

As expected the coupling matrix elements obtained from the 3-point DDR calculation (NACMECI) and by differentiating the mixing angle (DCHI) are in close agreement.

43   THE VB PROGRAM CASVB

> *CASVB* is a general program for valence bond calculations
> written by T. Thorsteinsson and D. L. Cooper (1996–2005).

This program can be used in two basic modes:

a) variational optimization of quite general types of nonorthogonal MCSCF or modern valence bond wavefunctions

b) representation of CASSCF wavefunctions in modern valence form, using overlap- (*relatively inexpensive*) or energy-based criteria.

Bibliography:

T. Thorsteinsson, D. L. Cooper, J. Gerratt, P. B. Karadakov and M. Raimondi, Theor. Chim. Acta **93**, 343–66 (1996).
T. Thorsteinsson and D. L. Cooper, in *Quantum Systems in Chemistry and Physics. Volume 1: Basic problems and models systems*, eds. A. Hernández-Laguna, J. Maruani, R. McWeeny, and S. Wilson (Kluwer, Dordrecht, 2000); pp 303–26. [Please contact David L. Cooper if you have problems accessing this key reference]

All publications resulting from use of this program should acknowledge relevant publications. There is a more complete bibliography at http://www.liv.ac.uk/ dlc/CASVB.html

43.1   Structure of the input

All *CASVB* sub-commands may be abbreviated by four letters. The general input structure can be summarized as follows:

a) For generating representations of CASSCF wavefunctions, the program is invoked by the command `CASVB`. For variational optimization of wavefunctions it is normally invoked inside *MULTI* by the sub-command `VB` (see 19.10).

b) Definition of the CASSCF wavefunction (not generally required).

c) Definition of the valence bond wavefunction.

d) Recovery and/or storage of orbitals and vectors.

e) Manual input of starting guess (optional).

g) Optimization control.

f) Definition of molecular symmetry and possible constraints on the VB wavefunction.

h) Wavefunction analysis.

i) Further general options.

Items a) and b) should precede everything else in the input; apart from this, commands may come in any order.

43.2 Defining the CASSCF wavefunction

CASVB is interfaced with the determinant part of *MULTI* (i.e., CONFIG,CSF; must *not* be specified). When this program is run prior to *CASVB*, the CI vector must dumped using one of the directives SAVE, NATORB, CANONICAL, or LOCALI (see section 19.5.5). The three latter are recommended.

43.2.1 The VBDUMP directive

VBDUMP[,*vbdump*];

If present, the VBDUMP card must occur first in the *CASVB* input. It is *not* required for variational calculations.

Note that in the majority of cases (*e.g.*, if a *CASVB* run occurs immediately after *MULTI*, or for variational calculations), explicit specification of dump records with *vbdump* is not required.

Wavefunction definitions may be restored here using VBDUMP cards (see also Section 19.8.6). The default record name (*vbdump*) is 4299.2. If a VBDUMP card is not present and record 4299.2 does not exist, then *CASVB* will attempt to generate the wavefunction information automatically based on the latest MCSCF calculation (however, STATE and WEIGHT information will not be restored in such a case).

43.3 Other wavefunction directives

The definitions of the CASSCF wavefunction may also be specified manually using some or all of the directives:

OCC	Occupied orbitals.
CLOSED	Closed-shell orbitals.
FROZEN	Frozen-core orbitals.
WF	Wavefunction card.
STATE	Number of states for this wavefunction symmetry.
WEIGHT	Weights of states.

For the exact definition of these cards see sections 19.2 and 19.3. These commands may also be used to modify the values defined in VBDUMP. The information given on these cards should correspond to the CI vector saved in the CASSCF calculation. The cards, and their ordering, should therefore coincide with those used in *MULTI*, except for the WEIGHT cards which may differ. At present, the VB wavefunction must correspond to a well-defined number of electrons and total spin. Other states may be present, but an error condition will occur if non-zero weights are specified for wavefunction symmetries with varying values of *elec* or *spin*.

43.4 Defining the valence bond wavefunction

43.4.1 Specifying orbital configurations

The number of core and active orbitals (*mcore*, *mact*), active electrons (*Nact*), and the value of the total spin will be identical to that defined for the CASSCF wavefunction. The spatial VB

configurations are defined in terms of the active orbitals only, and may be specified using one or more CON cards (note that the RESTRICT and SELECT keywords are not used in *CASVB*):

CON,$n_1,n_2,n_3,n_4,\ldots$;

The configurations can be specified by occupation numbers, exactly as in *MULTI* (see section 19.4.3), so that n_i is the occupation of the *i*th valence bond orbital. Alternatively a list of *Nact* orbital numbers (in any order) may be provided – the program determines which definition applies. The two cards CON,1,0,1,2; and CON,1,3,4,4; are thus equivalent.

If no configurations are specified the single covalent configuration $\phi_1\phi_2\cdots\phi_{Nact}$ is assumed.

43.4.2   Selecting the spin basis

SPINBASIS,*key*;

key may be chosen from KOTANI (default), RUMER, PROJECT or LTRUMER, specifying the basis of spin eigenfunctions used in the definition of valence bond structures. PROJECT refers to spin functions generated using a spin projection operator, LTRUMER to Rumer functions with the so-called "leading term" phase convention.

43.5   Recovering CASSCF CI vector and VB wavefunction

The appropriate MOLPRO records may be specified explicitly using the START directive (an alternative is the *vbdump* mechanism described in section 43.2.1):

START,*ci,vb,orb,trnint*;

ci: record name for the CASSCF CI vector. The CI vector must have been dumped previously using either of the SAVE, NATORB, CANONICAL, or LOCALI directives (see section 19.5.5). A default value for *ci* is determined from the most recent *vbdump* record(s).

Note that if the *ci* record is not found, only an energy-based optimization of the VB wavefunction can be carried out.

vb: record name for the valence bond orbitals and structure coefficients, as saved by a previous CASVB calculation. If the VB wavefunction was previously saved in the AO basis the orbitals will be projected onto the present active space (note that it is necessary to specify a record name for the molecular orbitals (*orb* below) for this to be possible).

orb: record name for the molecular orbitals defining the CASSCF wavefunction. This information is necessary if one wants to output the valence bond orbitals in the atomic orbital basis.

trnint: record name for the transformed CASSCF integrals. These are required for the energy-based criteria (i.e., if CRIT,ENERGY is specified), and can be saved inside *MULTI* by the TRNINT sub-command (see 19.8.7). The default record name, both here and in *MULTI*, is 1900.1.

43.6   Saving the VB wavefunction

SAVE,*vb,civb*;

vb: record name for VB wavefunction (default is first available record after 3200.2), i.e., orbitals and structure coefficients.

civb: record name for valence bond full CI vector defined in terms of the CASSCF MOs (default is 3300.2). Saving this vector is necessary for the calculation of further properties, geometry optimization, etc.

It is normally advisable to use records on file 2 for *vb* and *civb*.

43.7   Specifying a guess

GUESS;*key-1,...*;*key-2,...*;*...*

The GUESS keyword initiates the input of a guess for the valence bond orbitals and structure coefficients. *key-i* can be either ORB, STRUC or READ. These keywords modify the guess provided by the program, or specified by the START directive. It is thus possible to modify individual orbitals in a previous solution to construct the starting guess.

43.7.1   Orbital guess

ORB,*i*, c_1, c_2,... c_{mact};

Specifies a starting guess for valence bond orbital number *i*. The guess is specified in terms of the *mact* active MOs defining the CASSCF wavefunction. (Note that the definition of these MOs will depend on how the CI vector was dumped – i.e. which of the SAVE, NATORB, CANONICAL, or LOCALI directives was used (see section 19.5.5). Use of one of the three latter keywords is recommended.)

43.7.2   Guess for structure coefficients

STRUC,c_1, c_2,... c_{NVB};

Specifies a starting guess for the *NVB* structure coefficients. If this card is not provided, and no guess specified by START, the perfect-pairing mode of spin coupling is assumed for the spatial configuration having the least number of doubly occupied orbitals. Note that the definition of structures depends on the value of SPINBASIS. Doubly occupied orbitals occur first in all configurations, and the spin eigenfunctions are based on the singly occupied orbitals being in ascending order.

43.7.3   Read orbitals or structure coefficients

The READ keyword can take one of the following forms:

READ,ORB,*iorb1*[,TO,*iorb2*] [,AS,*jorb1*[,TO,*jorb2*]] [,FROM,*record*];

READ,STRUC,*istruc1*[,TO,*istruc2*] [,AS,*jstruc1*[,TO,*jstruc2*]] [,FROM,*record*];

READ,ALL [,FROM,*record*];

In this way a subset of orbitals and/or structure coefficients may be picked out from a previous calculation. Renumbering of orbitals or structures can be done using the "AS" construct as outlined above. If the VB wavefunction was previously saved in the AO basis, the orbitals will be projected onto the present active space (note that it is necessary to specify a record name for the molecular orbitals (*orb* in the START commmand) for this to be possible).

Default for *record* is the *vb* record name specified in keyword START (if applicable).

43.8 Permuting orbitals

ORBPERM,$i_1,\ldots,i_{mact}$;

Permutes the orbitals in the valence bond wavefunction and changes their phases according to $\phi'_j = \text{sign}(i_j)\phi_{\text{abs}(i_j)}$. The guess may be further modified using the GUESS keyword. Also the structure coefficients will be transformed according to the given permutation (note that the configuration list must be closed under the orbital permutation for this to be possible).

43.9 Optimization control

43.9.1 Optimization criterion

CRIT,*method*;

Specifies the criterion for the optimization. *method* can be OVERLAP or ENERGY (OVERLAP is default). The former maximizes the normalized overlap with the CASSCF wavefunction:

$$\max\left(\frac{\langle\Psi_{CAS}|\Psi_{VB}\rangle}{(\langle\Psi_{VB}|\Psi_{VB}\rangle)^{1/2}}\right)$$

and the latter simply minimizes the energy:

$$\min\left(\frac{\langle\Psi_{VB}|\hat{H}|\Psi_{VB}\rangle}{\langle\Psi_{VB}|\Psi_{VB}\rangle}\right).$$

43.9.2 Number of iterations

MAXITER,N_{iter};

Specifies the maximum number of iterations in the second order optimizations. Default is N_{iter}=50.

43.9.3 CASSCF-projected structure coefficients

(NO)CASPROJ;

With this keyword the structure coefficients are picked from the transformed CASSCF CI vector, leaving only the orbital variational parameters. For further details see the bibliography. This option may be useful to aid convergence.

43.9.4 Saddle-point optimization

SADDLE,*n*;

Defines optimization onto an nth-order saddle point. See also T. Thorsteinsson and D. L. Cooper, Int. J. Quant. Chem. **70**, 637–50 (1998).

43.9.5   Defining several optimizations

More than one optimization may be performed in the same *CASVB* deck, by the use of OPTIM keywords:

OPTIM[;...;FINOPTIM];

The subcommands may be any optimization declarations defined in this section, as well as any symmetry or constraints specifications described in section 43.10. Commands given as arguments to OPTIM will be particular to this optimization step, whereas commands specified outside will act as default definitions for all subsequent OPTIM keywords.

If only one optimization step is required, the OPTIM keyword need not be specified.

When only a machine-generated guess is available, *CASVB* will attempt to define a sequence of optimization steps chosen such as to maximize the likelihood of successful convergence and to minimize CPU usage. To override this behaviour, simply specify one or more OPTIM cards.

43.9.6   Multi-step optimization

A loop over two or more optimization steps may be specified using:

ALTERN,*Niter*;...;FINALTER

With this specification the program will repeat the enclosed optimization steps until either all optimizations have converged, or the maximum iteration count, *Niter*, has been reached.

43.10   Point group symmetry and constraints

The problems associated with symmetry-adapting valence bond wavefunctions are considered, for example, in: T. Thorsteinsson, D. L. Cooper, J. Gerratt and M. Raimondi, Theor. Chim. Acta **95**, 131 (1997).

43.10.1   Symmetry operations

SYMELM,*label*,*sign*;

Initiates the definition of a symmetry operation referred to by *label* (any three characters). *sign* can be + or −; it specifies whether the total wavefunction is symmetric or antisymmetric under this operation, respectively. A value for *sign* is not always necessary but, if provided, constraints will be put on the structure coefficients to ensure that the wavefunction has the correct overall symmetry (note that the configuration list must be closed under the orbital permutation induced by *label* for this to be possible).

The operator is defined in terms of its action on the active MOs as specified by one or more of the keywords IRREPS, COEFFS, or TRANS (any other keyword will terminate the definition of this symmetry operator). If no further keyword is supplied, the identity is assumed for *label*. The alternative format SYMELM,*label*,*sign*;*key-1*,...;*key-2*,...;... may also be used.

43.10.2   The IRREPS keyword

IRREPS,i_1, i_2,...;

The list i_1, i_2,... specifies which irreducible representations (as defined in the CASSCF wavefunction) are antisymmetric with respect to the *label* operation. If an irreducible representation is not otherwise specified it is assumed to be symmetric under the symmetry operation.

43.10.3 The COEFFS keyword

COEFFS,i_1, i_2,...;

The list i_1, i_2,... specifies which individual CASSCF MOs are antisymmetric with respect to the *label* operation. If an MO is not otherwise specified, it is assumed to be symmetric under the symmetry operation. This specification may be useful if, for example, the molecule possesses symmetry higher than that exploited in the CASSCF calculation.

43.10.4 The TRANS keyword

TRANS,n_{dim}, i_1, ... $i_{n_{dim}}$, c_{11}, c_{12}, ... $c_{n_{dim}n_{dim}}$;

Specifies a general $n_{dim} \times n_{dim}$ transformation involving the MOs i_1, ... $i_{n_{dim}}$, specified by the c coefficients. This may be useful for systems with a two- or three-dimensional irreducible representation, or if localized orbitals define the CASSCF wavefunction. Note that the specified transformation must always be orthogonal.

43.10.5 Symmetry relations between orbitals

In general, for a VB wavefunction to be symmetry-pure, the orbitals must form a representation (not necessarily irreducible) of the symmetry group. Relations between orbitals under the symmetry operations defined by SYMELM may be specified according to:

ORBREL,i_1, i_2, *label1, label2*,...;

Orbital i_1 is related to orbital i_2 by the sequence of operations defined by the *label* specifications (defined previously using SYMELM). The operators operate right to left. Note that i_1 and i_2 may coincide. Only the minimum number of relations required to define all the orbitals should be provided; an error exit will occur if redundant ORBREL specifications are found.

43.10.6 The SYMPROJ keyword

As an alternative to incorporating constraints, one may also ensure correct symmetry of the wavefunction by use of a projection operator:

(NO)SYMPROJ[,*irrep*$_1$,*irrep*$_2$,...];

The effect of this keyword is to set to zero coefficients in unwanted irreducible representations. For this purpose the symmetry group defined for the CASSCF wavefunction is used (always a subgroup of D_{2h}). The list of irreps in the command specifies which components of the wavefunction should be kept. If no irreducible representations are given, the current wavefunction symmetry is assumed. In a state-averaged calculation, all irreps are retained for which a non-zero weight has been specified in the wavefunction definition. The SYMPROJ keyword may also be used in combination with constraints.

43.10.7   Freezing orbitals in the optimization

FIXORB,i_1, i_2,...;

This command freezes the orbitals specified in the list i_1, i_2,... to that of the starting guess. Alternatively the special keywords ALL or NONE may be used. These orbitals are eliminated from the optimization procedure, but will still be normalized and symmetry-adapted according to any ORBREL keywords given.

43.10.8   Freezing structure coefficients in the optimization

FIXSTRUC,i_1, i_2,...;

Freezes the coefficients for structures i_1, i_2,... . Alternatively the special keywords ALL or NONE may be used. The structures are eliminated from the optimization procedure, but may still be affected by normalization or any symmetry keywords present.

43.10.9   Deleting structures from the optimization

DELSTRUC,i_1, i_2,...,[ALL],[NONE];

Deletes the specified structures from the wavefunction. The special keywords ALL or NONE may be used. A structure coefficient may already be zero by symmetry (as defined by SYMELM and ORBREL), in which case deleting it has no effect.

43.10.10   Orthogonality constraints

ORTHCON;*key-1*,...;*key-2*,...;...

The ORTHCON keyword initiates the input of orthogonality constraints between pairs of valence bond orbitals. The sub-keywords *key-i* can be one of ORTH, PAIRS, GROUP, STRONG or FULL as described below. Orthogonality constraints should be used with discretion. Note that orthogonality constraints for an orbital generated from another by symmetry operations (using the ORBREL keyword) cannot in general be satisfied.

ORTH,i_1, i_2, ...;

Specifies a list of orbitals to be orthogonalized. All overlaps between pairs of orbitals in the list are set to zero.

PAIRS,i_1, i_2, ...;

Specifies a simple list of orthogonalization pairs. Orbital i_1 is made orthogonal to i_2, i_3 to i_4, etc.

GROUP,*label*,i_1, i_2, ...;

Defines an orbital group to be used with the ORTH or PAIRS keyword. The group is referred to by *label* which can be any three characters beginning with a letter a–z. Labels defining different groups can be used together or in combination with orbital numbers in ORTH or PAIRS. i_1, i_2, ... specifies the list of orbitals in the group. Thus the combination GROUP,AZZ,1,2; GROUP,BZZ,3,4; ORTH,AZZ,BZZ; will orthogonalize the pairs of orbitals 1-3, 1-4, 2-3 and 2-4.

STRONG;

This keyword is short-hand for strong orthogonality. The only allowed non-zero overlaps are between pairs of orbitals $(2n-1, 2n)$.

```
FULL;
```

This keyword is short-hand for full orthogonality. This is mainly likely to be useful for testing purposes.

43.11 Wavefunction analysis

43.11.1 Spin correlation analysis

```
(NO)SCORR;
```

With this option, expectation values of the spin operators $(\hat{s}_\mu + \hat{s}_\nu)^2$ are evaluated for all pairs of μ and ν. Default is NOSCORR. The procedure is described by: G. Raos, J. Gerratt, D. L. Cooper and M. Raimondi, Chem. Phys. **186**, 233–250 (1994); ibid, 251–273 (1994); D. L. Cooper, R. Ponec, T. Thorsteinsson and G. Raos, Int. J. Quant. Chem. **57**, 501–518 (1996).

At present this analysis is only implemented for spin-coupled wavefunctions.

43.11.2 Printing weights of the valence bond structures

For further details regarding the calculation of weights in CASVB, see T. Thorsteinsson and D. L. Cooper, J. Math. Chem. **23**, 105-26 (1998).

```
VBWEIGHTS,key1,key2,...
```

Calculates and outputs weights of the structures in the valence bond wavefunction Ψ_{VB}. *key* specifies the definition of nonorthogonal weights to be used, and can be one of:

CHIRGWIN   Evaluates Chirgwin-Coulson weights (see: B. H. Chirgwin and C. A. Coulson, Proc. Roy. Soc. Lond. **A201**, 196 (1950)).

LOWDIN   Performs a symmetric orthogonalization of the structures and outputs the corresponding weights.

INVERSE   Outputs "inverse overlap populations" as in G. A. Gallup and J. M. Norbeck, Chem. Phys. Lett. **21**, 495–500 (1973).

ALL   All of the above.

NONE   Suspends calculation of structure weights.

The commands LOWDIN and INVERSE require the overlap matrix between valence bond structures, and some computational overhead is thus involved.

43.11.3 Printing weights of the CASSCF wavefunction in the VB basis

For further details regarding the calculation of weights in *CASVB*, see T. Thorsteinsson and D. L. Cooper, J. Math. Chem. **23**, 105-26 (1998).

```
CIWEIGHTS,key1,key2,...[,N_conf];
```

Prints weights of the CASSCF wavefunction transformed to the basis of nonorthogonal VB structures. For the *key* options see VBWEIGHTS above. Note that the evaluation of inverse overlap weights involves an extensive computational overhead for large active spaces. Weights are

given for the total CASSCF wavefunction, as well as the orthogonal complement to Ψ_{VB}. The default for the number of configurations requested, N_{conf}, is 10. If $N_{\text{conf}}=-1$ all configurations are included.

43.12 Controlling the amount of output

PRINT,i_1, i_2,... ;

Each number specifies the level of output required at various stages of the execution, according to the following convention:

-1   No output except serious, or fatal, error messages.

0   Minimal output.

1   Standard level of output.

2   Extra output.

The areas for which output can be controlled are:

i_1 Print of input parameters, wavefunction definitions, etc.

i_2 Print of information associated with symmetry constraints.

i_3 General convergence progress.

i_4 Progress of the 2nd order optimization procedure.

i_5 Print of converged solution and analysis.

i_6 Progress of variational optimization.

i_7 Usage of record numbers on file 2.

For all, the default output level is +1. If $i_5 \geq 2$ VB orbitals will be printed in the AO basis (provided that the definition of MOs is available); such output may be especially useful for plotting of orbitals.

43.13 Further facilities

Calculations can also be performed for various types of direct product wavefunctions and/or with strictly localized orbitals. Details are available from the authors. These facilities will be documented in a later release.

43.14 Service mode

SERVICE;
This keyword takes precedence over any others previously defined to *CASVB*. It provides simple facilities for retrieving orbital coefficients and VB structure coefficients. It should not be used during a run of *CASVB* that has been invoked from inside *MULTI*.

START,*record.file*;
Coefficients are taken from *record.file*. The default value is *2100.2*.

WRITE,*iwrite*;
Vectors in the symmetry orbital basis are written to channel *iabs(iwrite)*. The default action is

to write these vectors to the standard output. If *iwrite* is negative, then the vectors are instead written to a binary file as a single record.

SPECIAL,*idim1,idim2,idim3,idim4*;

If present, this keyword must come last. The program attempts to retrieve from *record.file* a vector of length *idim1*idim2+idim3*, after first skipping *idim4* elements. The vector is written according to the setting of *iwrite*. (Default *idim* values are zero.)

43.15 Examples

```
***, ch2                         ! A1 singlet state
geometry={angstrom
c
h1,c,1.117
h2,c,1.117,h1,102.4}
int
hf
{multi;occ,4,1,2;closed,1       ! 6 in 6 CASSCF
natorb,,ci,save=3500.2;vbdump}
{casvb                           ! Overlap-based VB using
save,3200.2}                     ! the spin-coupled wavefunction
{casvb                           ! Energy-based VB calculation
start,,3200.2;save,3220.2
crit,energy}
{multi;occ,4,1,2;closed,1       ! Fully variational VB calculation
{vb;start,,3220.2;save,3240.2;print,,,,,2}}
---


***,n2s2 (model a)               ! Variational calculation for N2S2.
v=2.210137753 bohr
geometry={ n, -v, 0, 0;          ! NOTE: other choices of active space
           n, +v, 0, 0;          ! give alternative (competing) models.
           s, 0, -v, 0;
           s, 0, +v, 0}
basis=VTZ
hf
{multi; occ,7,4,5,2,4,2,2,0; closed,7,4,5,2,1,0,1,0; natorb,,ci,save=3500.2}
{multi; occ,7,4,5,2,4,2,2,0; closed,7,4,5,2,1,0,1,0;
{vb; start,3500.2; scorr}}
---


***, lih                         ! Fully-variational VB calculation
r=2.8 bohr                       ! and geometry optimization.
geometry={li;h,li,r}
basis={
s,1,921.300000,138.700000,31.940000,9.353000,3.158000,1.157000;
c,1.6,0.001367,0.010425,0.049859,0.160701,0.344604,0.425197;
s,1,0.444600,0.076660,0.028640;
p,1,1.488000,0.266700,0.072010,0.023700;
c,1.2,0.038770,0.236257;
s,2,13.36,2.013,0.4538,.1233;
c,1.2,0.032828,0.231204}
hf
{multi; occ,4,0,0,0; closed,0,0,0,0; natorb,,ci,save=3500.2}
{multi; occ,4,0,0,0; closed,0,0,0,0;
{vb; start,3500.2}}
optg
---
```

44 SPIN-ORBIT-COUPLING

44.1 Introduction

Spin-orbit matrix elements and eigenstates can be computed using either the Breit-Pauli (BP) operator or spin-orbit pseudopotentials (ECPs). The *state-interacting* method is employed, which means that the spin-orbit eigenstates are obtained by diagonalizing $\hat{H}_{el} + \hat{H}_{SO}$ in a basis of eigenfunctions of $\hat{H}_{el}$. The full Breit-Pauli SO-operator can be used only for MCSCF wavefunctions. For MRCI wavefunctions, the full BP operator is used for computing the matrix elements between *internal configurations* (no electrons in external orbitals), while for contributions of external configurations a mean-field one-electron fock operator is employed. The error caused by this approximation is usually smaller than 1 cm^{-1}.

The program allows either the computation of individual spin-orbit matrix elements for a given pair of states, or the automatic setting-up and diagonalization of the whole matrix for a given set of electronic states. In the latter case, matrix elements over one-electron operators are also computed and transformed to the spin-orbit eigenstates (by default, the dipole matrix elements are computed; other operators can be specified on the GEXPEC or EXPEC cards, see section 6.13). Since it may be often sufficient to compute the spin-orbit matrix elements in a smaller basis than the energies, it is possible to replace the energy eigenvalues by precomputed values, which are passed to the spin-orbit program by the MOLPRO variable HLSDIAG.

44.2 Calculation of SO integrals

The one-and two-electron spin-orbit integrals over the BP Hamiltonian can be precomputed and stored on disk using the command

LSINT [,X] [,Y] [,Z] [,ONECENTER] [;TWOINT,*twoint*;] [;PREFAC,*prefac*;]

X, Y, and Z specify the components to be computed. If none of these is given, all three are evaluated. The advantage of precomputing the integrals is that they can then be used in any number of subsequent SO calculations, but this may require a large amount of disk space (note that there are 6 times as many integrals as in an energy calculation). If the LSINT card is not given, the integrals are computed whenever needed. The keyword ONECENTER activates the one-center approximation for one- and two- electron spin-orbit integrals. This can reduce drastically the computing time for large molecules. TWOINT and PREFAC can be used to control the accuracy of spin-orbit integrals. These thresholds are similar to TWOINT and PREFAC for standard integrals. The default value for PREFAC is TWOINT/100, and the default value for TWOINT is 10^{-7}. In the case when no integrals are precomputed, these thresholds can be specified as options for HLSMAT or TRANLS cards, see below.

The input for spin-orbit ECPs is described in section 12. Of course, in ECP-LS calculations the LSINT card is not needed.

44.3 Calculation of individual SO matrix elements

Individual spin-orbit matrix elements can be computed within the MRCI program using

TRANLS,*record1.file, record2.file, bra2ms, ket2ms, lsop*;

where

record1.file   Record holding the bra-wavefunction.

record2.file   Record holding the ket-wavefunction. Both records must have been generated using the `SAVE` directive of the MRCI program.

bra2ms $2 \times M_S$ value of the bra-wavefunction.

ket2ms $2 \times M_S$ value of the ket-wavefunction.

lsop   Cartesian component of the Spin-orbit Hamiltonian.
This can be one of LSX, LSY, or LSZ in all electron calculations, and ECPLSX, ECPLSY, or ECPLSZ in ECP calculations. Starting from the MOLPRO version 2008.1, more types are available which control the approximation level. These are described in section 44.4.

Since the spin-orbit program is part of the MRCI program, the `TRANLS` card must be preceded by a `[MR]CI` card. For the case that the matrix elements are computed for MCSCF wavefunctions, one has to recompute and save the CI-vectors using the MRCI program (see chapter 20), using the `NOEXC` directive to avoid inclusion of any further excitations out of the MCSCF reference function. If in the MRCI step several states of the same symmetry are computed simultaneously using the `STATE` directive, the matrix elements are computed for all these states. Note that the `OCC` and `CLOSED` cards must be the same for all states used in a `TRANLS` calculation.

The selection rules for the M_S values are $\Delta M_S = \pm 1$ for the `LSX` and `LSY` operators, and $\Delta M_S = 0$ for the `LSZ` operator. Note that $2M_S$ has to be specified, and so the selection rules applying to the difference of the input values are 0 or 2.

In all-electron SO calculations the value of the calculated spin-orbit matrix element is saved (in atomic units) in the MOLPRO variables `TRLSX`, `TRLSY` and `TRLSZ` for the x, y, and z components respectively. For ECP-LS calculations the variables `TRECPLSX`, `TRECPLSY`, and `TRECPLSZ` are used. Note that for imaginary matrix elements (i.e., for the x and z components of the SO Hamiltonian) the matrix elements are imaginary and the stored real values have to be multiplied by i. If matrix elements for several states are computed, all values are stored in the respective variable-arrays with the bra-states running fastest.

44.4   Approximations used in calculating spin-orbit integrals and matrix elements

Recently, more sophisticated approximations were introduced to simplify spin-orbit calculations for larger molecules. These are controlled by specifying the spin-orbit operator type *lsop* as follows (we omit suffixes X, Y, Z which specify the component):

LS   Standard spin-orbit calculations.

ALS   The one-center approximation is used for one- and two-electron spin-orbit integrals.

FLS   The effective Fock-matrix approximation is used for the internal part too.

AFLS|AMFI   The one-center approximation is used for one- and two-electron spin-orbit integrals, and the effective Fock-matrix approximation for the internal part.

ECPLS   Effective core potentials are used for all atoms at which they are defined; contributions of all other atoms are neglected (see below).

In case that the effective Fock matrix is used for all contributions, and no spin-orbit integrals are pre-calculated and stored on disk (i.e., the `LSINT` command is not given), the Fock matrices are evaluated in direct mode and no integrals are stored on disk. When this is combined with

the one-center approximation (AMFI), the computing and I/O times are drastically reduced, and this makes spin-orbit calculations quite fast even for larger molecules.

Also, the treatment of ECP-type of spin-orbit interaction has been changed and now allows for treating both ECP and non-ECP atoms in one calculation. Thus, in molecules containing both heavy and light atoms, the heavy atoms can be described using ECPs and the light atoms using all-electron basis sets. If the operator type is `LS`, `ALS`, `FLS`, or `AFLS`, then for the atoms having an ECP spin-orbit operator defined in the basis input the ECP operator is used, while the full BP-operator is used for all other atoms (couplings are neglected). Both one-center and AMFI approximations can be used in this case. If, on the other hand, one specifies the operator type as `ECPLS`, then the behavior is the same as in the previous versions, i.e., only the ECP contributions are considered and the contributions from all other atoms are neglected.

44.5 Calculation and diagonalization of the entire SO-matrix

`HLSMAT`,*type*, *record1, record2, record3, ...*

Computes the entire SO matrix and diagonalizes it using all states which are contained in the records *record1, record2, record3, ...* All records must have been generated using the `SAVE` directive of the MRCI program. *type* may be either `LS` for Breit-Pauli calculations, or `ECP` for ECP-LS calculations. By default, the eigenvalues and dipole transition matrix elements between the ground and excited states are printed.

As with the `TRANLS` card, the `HLSMAT` is recognized only by the MRCI program and must be preceded by a `CI` card. Also, the `OCC` and `CLOSED` cards must be the same for all states used in a `HLSMAT` calculation.

44.6 Modifying the unperturbed energies

Often it may be sufficient to compute the spin-orbit matrix elements in a smaller basis or at a lower computational level than the energies. It is therefore possible to replace the energy eigenvalues by precomputed values, which are passed to the spin-orbit program by the MOLPRO variable `HLSDIAG`. The energy values in `HLSDIAG` must be in exactly the same order as the states in the records given on the `HLSMAT` card. Before any spin-orbit calculation, the variable `HLSDIAG` must either be undefined or cleared (then the original energies are used), or must contain exactly the number of energies as the number of states treated in the subsequent spin-orbit calculation (use `CLEAR,HLSDIAG` to clear any previous values in the variable). It is the user's responsibility that the order of the energies in `HLSDIAG` is correct!

44.6.1 Print Options for spin-orbit calculations

`PRINT`,*option$_1$=value$_1$, option$_2$=value$_2$,...*

where option can be

HLS   HLS=-1 only the SO energies and transition matrix elements between ground and excited states are printed (default).
         HLS$\geq$ 0: The SO matrix is printed.
         HLS$\geq$ 1: The property matrices are printed.
         HLS$\geq$ 2: The individual matrix elements are printed (same as `OPTION,MATEL`).
         HLS$\geq$ 3: Debugging information is printed.

VLS   VLS=-1: No print of eigenvectors (default).

                    VLS$\geq$ 0: The eigenvectors are printed.

44.6.2 Options for spin-orbit calculations

Some options can be set using the OPTION directive (in any order)

OPTIONS [,WIGNER=*value*] [,HLSTRANS=*value*] [,MATEL=*value*]

where

WIGNER   This option determines whether the Wigner-Eckart theorem should be used when the SO matrix is determined. WIGNER=1 (default) uses the theorem, WIGNER=0 calculates each SO matrix element individually. This option is needed for test purposes only.

HLSTRANS   This option determines whether a SO matrix calculation should be performed in the not spin-symmetry adapted basis set (HLSTRANS=0), in the spin-symmetry adapted basis set (HLSTRANS=1, default) or with both basis sets (HLSTRANS=2). At present, symmetry adaption can only be performed for triplet states, where the following notation is used to indicate the symmetry adapted spin functions: $|S,M_S\rangle_+ = \frac{1}{\sqrt{2}}(|S,M_S\rangle + |S,-M_S\rangle)$, $|S,M_S\rangle_- = \frac{1}{\sqrt{2}}(|S,M_S\rangle - |S,-M_S\rangle)$. If only singlet and triplet states are considered, the spin-orbit matrix is blocked according to double-group symmetry and the eigenvalues for each each block are printed separately. In all other cases the HLSTRANS option is ignored.

MATEL   If the entire SO matrix is calculated using HLSMAT, the individual matrix elements are normally not shown. When the option MATEL=1 is given, the individual matrix elements and the contributions of the internal and external configuration classes are printed.

44.7   Examples

44.7.1   SO calculation for the S-atom using the BP operator

```
***,SO calculation for the S-atom
geometry={s}
basis={spd,s,vtz}                                        !use uncontracted basis

{rhf;occ,3,2,2,,2;wf,16,4,2}                              !rhf for 3P state

{multi                                                    !casscf
wf,16,4,2;wf,16,6,2;wf,16,7,2;wf,16,1,0;state,3;          !1D and 1S states
wf,16,4,0;wf,16,6,0;wf,16,7,0}                            !3P states

{ci;wf,16,1,0;save,3010.1;state,3;noexc}                  !save casscf wavefunctions using mrci
{ci;wf,16,4,0;save,3040.1;noexc}
{ci;wf,16,6,0;save,3060.1;noexc}
{ci;wf,16,7,0;save,3070.1;noexc}
{ci;wf,16,4,2;save,3042.1;noexc}
{ci;wf,16,6,2;save,3062.1;noexc}
{ci;wf,16,7,2;save,3072.1;noexc}

{ci;wf,16,1,0;save,4010.1;state,3}                        !mrci calculations for 1D, 1S states
ed=energy(1)                                              !save energy for 1D state in variable ed
es=energy(3)                                              !save energy for 1S state in variable es
{ci;wf,16,4,2;save,4042.1}                                !mrci calculations for 3P states
ep=energy                                                 !save energy for 3P state in variable ep
{ci;wf,16,6,2;save,4062.1}                                !mrci calculations for 3P states
{ci;wf,16,7,2;save,4072.1}                                !mrci calculations for 3P states
text,only triplet states, casscf

lsint                                                     !compute so integrals

text,3P states, casscf
{ci;hlsmat,ls,3042.1,3062.1,3072.1}                       !Only triplet states, casscf

text,3P states, mrci
{ci;hlsmat,ls,4042.1,4062.1,4072.1}                       !Only triplet states, mrci

text,3P, 1D, 1S states, casscf
{ci;hlsmat,ls,3010.1,3040.1,3060.1,3070.1,3042.1,3062.1,3072.1}       !All states, casscf

text,only triplet states, use mrci energies and casscf SO-matrix elements
hlsdiag=[ed,ed,es,ed,ed,ed,ep,ep,ep]            !set variable hlsdiag to mrci energies
{ci;hlsmat,ls,3010.1,3040.1,3060.1,3070.1,3042.1,3062.1,3072.1}
```

http://www.molpro.net/info/current/examples/s_so.com

44.7.2   SO calculation for the I-atom using ECPs

```
***,I
memory,5,M;
gprint,orbitals,civector,basis;
gthresh,energy=1.d-8,coeff=1.d-8;
geometry={I};

basis={
!
! Iodine-ECP (Dirac-Fock) with SO-coupling
!
ecp,I,46,4,3;
1; 2,   1.00000000,       0.00000000;                                        ! lokal term = 0
2; 2,   3.50642001,      83.09814545; 2,   1.74736492,       5.06370919;     ! s-terme
4; 2,   2.99860773, 1/3* 81.88444526; 2,   3.01690894, 2/3* 83.41280402;     ! p-terms with wei
   2,   1.59415934, 1/3*  2.32392477; 2,   1.19802939, 2/3*  2.72079843;
4; 2,   1.03813792, 2/5*  6.40131754; 2,   1.01158599, 3/5*  6.21328827;     ! d-terms with wei
   2,   2.04193864, 2/5* 19.11604172; 2,   1.99631017, 3/5* 19.08465909;
4; 2,   2.64971585,-3/7* 24.79106489; 2,   2.75335574,-4/7* 24.98147319;     ! f-terms with wei
   2,   0.49970082,-3/7*  0.27936581; 2,   0.79638982,-4/7*  0.70184261;
4; 2,   2.99860773,-2/3* 81.88444526; 2,   3.01690894, 2/3* 83.41280402;     ! ECP-SO for p-ter
   2,   1.59415934,-2/3*  2.32392477; 2,   1.19802939, 2/3*  2.72079843;
4; 2,   1.03813792,-2/5*  6.40131754; 2,   1.01158599, 2/5*  6.21328827;     ! ECP-SO for d-ter
   2,   2.04193864,-2/5* 19.11604172; 2,   1.99631017, 2/5* 19.08465909;
4; 2,   2.64971585, 2/7* 24.79106489; 2,   2.75335574,-2/7* 24.98147319;     ! ECP-SO for f-ter
   2,   0.49970082, 2/7*  0.27936581; 2,   0.79638982,-2/7*  0.70184261;
!
! Iodine-basis
!
s,I,0.2027624,0.4080619,0.8212297,1.6527350,3.3261500;
c,1.5,-0.4782372,-0.5811680,0.2617769,0.4444120,-0.1596560;
s,I,0.05,0.1007509;
p,I,0.2027624,0.4080619,0.8212297,1.6527350,3.3261500;
c,1.5,0.4251859,0.2995618,0.0303167,-0.2064228,0.0450858;
p,I,0.05,0.1007509,0.01;  ! diffuse p-Funktion wegen evt. neg. Part.Ldg
d,I,0.2,0.4;
f,I,0.3;
}


{hf;occ,1,1,1,,1;wf,7,5,1}       !scf for 2Pz
{multi;occ,1,1,1,,1;             !casscf with minmal active space
wf,7,2,1;wf,7,3,1;wf,7,5,1}      !average 2P states
{ci;wf,7,2,1;noexc;save,5000.2}  !save casscf vector for 2Px state
{ci;wf,7,3,1;noexc;save,5100.2}  !save casscf vector for 2Py state
{ci;wf,7,5,1;noexc;save,5200.2}  !save casscf vector for 2Pz state
{ci;wf,7,2,1;save,6000.2}        !mrci for 2Px state
{ci;wf,7,3,1;save,6100.2}        !mrci for 2Py state
{ci;wf,7,5,1;save,6200.2}        !mrci for 2Pz state

{multi;occ,1,2,2,,2              !casscf with larger active space
wf,7,2,1;wf,7,3,1;wf,7,5,1}      !average 2P states
{ci;wf,7,2,1;noexc;save,5010.2}
{ci;wf,7,3,1;noexc;save,5110.2}
{ci;wf,7,5,1;noexc;save,5210.2}
{ci;wf,7,2,1;save,6010.2}
{ci;wf,7,3,1;save,6110.2}
{ci;wf,7,5,1;save,6210.2}

text,casscf,  occ,1,1,1,,1
{ci;hlsmat,ecp,5000.2,5100.2,5200.2}   !do spin-orbit calculations
text,casscf,  occ,1,2,2,,2
{ci;hlsmat,ecp,5010.2,5110.2,5210.2}

text,mrci, occ,1,1,1,,1
{ci;hlsmat,ecp,6000.2,6100.2,6200.2}
text,mrci, occ,1,2,2,,2
{ci;hlsmat,ecp,6010.2,6110.2,6210.2}
```

45   ENERGY GRADIENTS

45.1   Analytical energy gradients

MOLPRO uses different gradient programs:

The CADPAC gradient program is based on the CADPAC integral routines by R. D. Amos. Currently, this program works for closed shell SCF, high spin RHF, and (state averaged) MCSCF. In the MCSCF case the wavefunction must either be fully optimized, or frozen core orbitals must be taken from a closed-shell SCF calculation (but this does not work in the case of state-averaged MCSCF). Note that CADPAC does not work with generally contracted basis functions.

The ALASKA gradient program is based on the SEWARD integral routines by R. Lindh. It allows the calculation of gradients of generally contracted basis functions for closed shell SCF, open shell RHF, UHF, RKS, UKS, MCSCF, MP2, LMP2, DF-LMP2, QCISD, QCISD(T), CCSD, DCSD and RS2 (CASPT2). Gradients for state averaged MCSCF wave functions can be evaluated using the RS2 gradient program, see section 45.1.5. For details about CASPT2 gradients, see section 21.7.

The AIC density fitting integral program written by G. Knizia computes two- and three-index integrals and integral derivatives. This program is used for computing gradients for the DF-MP2, DF-LMP2, state averaged DF-MCSCF, and DF-CASPT2 methods.

By default, the program uses ALASKA gradients whenever possible. However, it is possible to force the use of a particular gradient program by defining the variable `GRADTYP` before calling the gradient program:

```
GRADTYP=ALASKA
GRADTYP=CADPAC
```

The gradient program is called using the `FORCE` command:

```
FORCE
```

Normally, the `FORCE` command is not needed, since geometry optimizations should be performed using the `OPTG` procedure. An exception is the optimization of counterpoise corrected energies, which requires several force calculations (cf. section 46.4.7).

If no further data cards are given, the default is to evaluate the gradient for the last optimized wavefunction. In this case no further input is needed for ordinary gradient cases (the program remembers the records on which the wavefunction information is stored). An exception is the unusual case that several different `CPMCSCF` calculations have been formed in a previous MC-SCF calculation. In this case the `SAMC` directive must be used to select the desired record. If analytical gradients are not available for the last wavefunction, the gradient is computed numerically. For more details regarding numerical energy gradients see section 45.2.

45.1.1   Adding gradients (`ADD`)

`ADD`,*factor*,[`NOCHECK`];

If this card is present, the current gradient and energy are added to the previous ones using the given factor. This is useful for the optimization of counterpoise corrected energies (cf. 46.4.7). By default, the program will stop with an error message unless `NOORIENT` has been specified in the geometry input. This behaviour can be disabled by the `NOCHECK` option. This option should only be given if all gradients which are added are evaluated at exactly the same nuclear geometry; otherwise wrong results could result due to unintended rotations of the system.

45.1.2 Scaling gradients (`SCALE`)

`SCALE`,*factor*;

If this card is present, the current gradient and energy are scaled by the give factor. This is sometimes useful for the optimization of counterpoise corrected energies (cf. 46.4.7).

45.1.3 Defining the orbitals for SCF gradients (`ORBITAL`)

`ORBITAL`,*record.file*;

In the SCF case, *record.file* specifies the location of the orbitals, which are used for constructing density matrices, etc. This card is only needed if the SCF for which the gradient is to be computed was not the most recent energy calculation.

For MCSCF wavefunctions, the `ORBITAL` card is not needed, because the location of the orbitals is stored in the MCSCF dump record.

45.1.4 MCSCF gradients (`MCSCF`)

`MCSCF`,*record.file*;

Triggers code for MCSCF gradient. *record.file* specifies the location of information dumped from the MCSCF program, using a `SAVE,GRD=`*recmc.filmc* card. This card is not needed if the `FORCE` command appears directly after the corresponding MCSCF input, since the program automatically remembers where the MCSCF information was stored. The same is true if `OPTG` is used.

45.1.5 State-averaged MCSCF gradients with SEWARD

SA-MCSCF gradients can be computed using segmented or generally contracted basis sets using SEWARD and the RS2 gradient program. The `NOEXC` directive has to be used in the `RS2` input, but no `CPMCSCF` card is required in `MULTI`. The RS2 gradient program does the CP-MCSCF automatically.

Example: compute SA-CASSCF gradients for $^2\Pi$ and $^2\Sigma^+$ state of OH.

```
geometry={o;h,o,r}
r=1.83
{multi;wf,9,2,1;wf,9,3,1;wf,9,1,1}      !state averaged casscf for X(2PI) and A(2SIGMA)
{rs2;noexc;wf,9,1,1}                     !compute A(2SIGMA) energy
forces                                   !energy gradient for A(2SIGMA) state
{rs2;noexc;wf,9,2,1}                     !compute A(2PI) energy
forces                                   !energy gradient for A(2PI) state
```

  http://www.molpro.net/info/current/examples/oh_samcforce.com

Without the `NOEXC` directive, the RS2 (CASPT2) gradient would be evaluated, using the state-averaged orbitals.

45.1.6 State-averaged MCSCF gradients with CADPAC

Normally, no further input is required for computing gradients for state-averaged MCSCF when CADPAC is used. Note, however, that a `CPMCSCF,GRAD,`*state* directive is required in the SA-MCSCF calculation (see Section 19.9). The gradients are then computed automatically for the *state* specified on the `CPMCSCF` card. The same is true for difference gradients (`CPMCSCF,DGRAD,`*state1, state2*) and non-adiabatic coupling matrix elements (`CPMCSCF,NACM,`*state1, state2*). It is possible to do several coupled-perturbed MCSCF calculations one after each other in the same MCSCF. In this case `FORCE` would use the last solution by default. The information from the CPMCSCF is passed to the FORCE program in a certain records (default 5101.1, 5102.1, ...). If several CPMCSCF calculations are performed in the same MCSCF, several such records may be present, and a particular one can be accessed in the `FORCE` program using the `SAMC` directive:

`SAMC,`*record.*

An alias for `SAMC` is `CPMC`. For compatibility with earlier versions one can also use

`NACM,`*record*

for non-adiabatic couplings or

`DEMC,`*record*

for difference gradients.

Example:

```
multi;
....
state,3
cpmcscf,nacm,1.1,2.1,save=5101.1    !do cpmcscf for coupling of states 1.1 - 2.1
cpmcscf,nacm,1.1,3.1,save=5102.1    !do cpmcscf for coupling of states 1.1 - 3.1
cpmcscf,nacm,2.1,3.1,save=5103.1    !do cpmcscf for coupling of states 2.1 - 3.1

force;samc,5101.1;                  !compute NACME for states 1.1 - 2.1
force;samc,5102.1;                  !compute NACME for states 1.1 - 3.1
force;samc,5103.1;                  !compute NACME for states 2.1 - 3.1
```

45.1.7 Non-adiabatic coupling matrix elements (NACM)

see Section 45.1.6.

45.1.8 Difference gradients for SA-MCSCF (DEMC)

see Section 45.1.6.

45.1.9 Example

```
***, Calculate Gradients for Water
alpha=104 degree          !set geometry parameters
r=1 ang
geometry={O;              !define z-matrix
        H1,o,r;
        H2,o,r,H1,alpha}
basis=vdz                 !basis set
hf                        !do scf
forces                    !compute gradient for SCF
mp2                       !mp2 calculation
forces                    !mp2 gradients
multi                     !casscf calculation
forces                    !casscf gradient
```

http://www.molpro.net/info/current/examples/h2o_forces.com

45.2 Numerical gradients

It is possible to compute gradients by finite differences using

FORCE,NUMERICAL,*options*

Numerical gradients are computed automatically if no analytical gradients are available for the
last energy calculation. By default, no further input are needed, and the gradient will be com-
puted for the last energy calculation. The following options can be given on the FORCE com-
mand or on subsequent directives (see subsequent sections):

STARTCMD=*command* The input between *command* and the current FORCE command defines
the energy calculation for which the gradient is computed. This input section is
executed for each displacement.

PROC=*procname* specifies a procedure to be executed for each displacement. This must define a
complete energy calculation and must not contain gradient or Hessian calculations.

VARIABLE=*varname* Compute the gradient of the value of variable *varname*. This implies
numerical gradients. The variable must be set in the corresponding energy calcu-
lation.

COORD=ZMAT|CART|3N coordinates with respect to which the gradient is evaluated. See
section 45.2.1 for more information.

DISPLACE=ZMAT|SYM|UNIQUE|CART
Displacement coordinates to be used for numerical gradient. The default is ZMAT
if the geometry is given as a zmatrix which depends on variables, and SYM (sym-
metrical displacement coordinates) otherwise. See section 45.2.1 for more infor-
mation.

SYMMETRY=AUTO|NOSYM Symmetry to be used in wavefunction calculations of numerical
gradients. This option is only relevant if DISPLACE=UNIQUE|CART. If AUTO
is given, the maximum possible symmetry is used for each displacement. This
implies that the energy is independent of the symmetry used. Note that this often
not the case in MRCI or CASPT2 calculations. The option can also not be used in
local correlation calculations.

AUTO   (logical). Same as SYMMETRY=AUTO

ZMAT   (logical). Same as COORD=ZMAT

OPT3N   (logical). Same as `COORD=3N`

RSTEP=*rstep* Step length for distances in numerical gradient calculations (in bohr). The default is 0.01.

DSTEP=*dstep* Step length for symmetrical displacements (in bohr). The default is 0.01.

ASTEP=*astep* Step length for angles in numerical gradient calculations (in degree). The default is 1.

CENTRAL   (logical). Use 2-point central formula; needs $2M$ energy calculations for M degrees of freedom.

FORWARD   (logical). Use forward gradients (needs only $M+1$ energy calculations, but less accurate)

FOURPOINT   (logical). Use 4-point formula for accurate numerical gradient; needs $4M$ energy calculations.

NUMERICAL   (logical). Force the use of numerical gradients, even if gradients are available.

VARSAV   (logical). Save gradient in variables `GRADX`, `GRADY`, `GRADZ`.

Example

```
hf
ccsd(t)
forces,numerical
```

The program will then automatically repeat `HF` and `CCSD(T)` at as many geometries as needed for evaluating the gradient. This is equivalent to

```
hf
ccsd(t)
forces,numerical,startcmd=hf
```

or, using a procedure

```
forces,numerical,proc=runccsdt
...
runccsdt={
hf
ccsd(t)}
```

45.2.1 Choice of coordinates (`COORD`)

By default, the numerical gradients are computed relative to all variables on which the z-matrix depends. If the z-matrix depends on no variables or on $3N$ variables, the gradient is computed for all $3N$ coordinates and symmetrical displacement coordinates are used to evaluate the gradient. This yields the minimum computational effort.

These defaults can be modified using the `COORD` directive:

COORD,*coord_type*,[*displacement_type*]

where *coord_type* can be one of the following:

ZMAT   Compute the numerical gradients for all variables on which the geometry depends (default).

`3N` or `CART` Compute the gradients for all 3*N* nuclear coordinates. This is the default if the z-matrix does not depend on variables or if the `xyz` input format is used. If this option is used and the original geometry is given in z-matrix form, the z-matrix is lost.

The specification of *displacement_type* is optional and only affects the numerical calculation of the gradient for 3*N* coordinates. It can also be given using

`DISPLACE,`*displacement_type*

displacement_type can be one of the following:

`SYM`   Use symmetrical displacements. This yields the minimum number of displacements and always preserves the symmetry of the wavefunction. This is the default and only recommended option.

`CART`   Displacements are generated for all 3*N* Cartesian coordinates. This is normally not recommended, since in cases in which molecular symmetry is present it generates far more displacements than needed. Also, the wavefunction symmetry is not preserved, and the calculation must be done in C1 symmetry.

`UNIQUE`   As `CART`, but symmetry-equivalent displacements are eliminated. Not recommended either.

45.2.2 Numerical derivatives of a variable

Numerical derivatives of the value of a variable can be computed using

`VARIABLE,`*name*

The default is to compute the gradient of the current energy.

45.2.3 Step-sizes for numerical gradients

By default, the numerical step sizes are 0.01 bohr for distances or Cartesian coordinates, and 1 degree for angles. These defaults can be changed using

`RSTEP,`*dr*
`ASTEP,`*da*

where *dr* is the displacement for distances (or Cartesian coordinates) in bohr, and *da* is the displacement for angles in degree. The value of `RSTEP` is used for symmetrical displacements. The step sizes for individual variables can be modified using

`VARSTEP,`*varname=value,...*

where the *value* must be in atomic units for distances and in degree for angles.

45.2.4 Active and inactive coordinates

By default, numerical gradients are computed with respect to all variables on which the Z-matrix depends, or for all 3*N* coordinates if there are no variables or `XYZ` inputstyle is used. One can define subsets of active variables using

`ACTIVE,`*variables*

If this card is present, all variables which are not specified are inactive. Alternatively,

`INACTIVE,`*variables*

In this case all variables that are not given are active.

45.3 Saving the gradient in a variables

If the directive

`VARSAV`

is given, the gradient is saved in variables `GRADX`, `GRADY`, `GRADZ`. `GRADX(n)` is the derivative with respect to *x* for the *n*-th atom. The atoms are in the order as printed. This order can be different from the order in the input z-matrix, since the centres are reordered so that all atoms of the same type follow each other.

46 GEOMETRY OPTIMIZATION (OPTG)

Automatic geometry optimization is invoked using the `OPTG` command. The `OPT` command available in previous MOLPRO versions is no longer needed and not available any more.

`OPTG[,` *key1=value, key2=value,......*`]`

The `OPTG` command can be used to perform automatic geometry optimizations for all kinds of wavefunctions. For minimum searches, it is usually sufficient to give just the `OPTG` command without further options or directives, but many options are available which are described in the following sections.

Various optimization methods can be selected as described in section 46.2.1. MOLPRO allows minimization (i.e. search for equilibrium geometries), transition state optimization (i.e. search for saddle points on energy surfaces), and reaction path following. The standard algorithms are based on the *rational function* approach and the *geometry DIIS* approach. Also available is the *quadratic steepest descent following* method of Sun and Ruedenberg (see J. Sun and K. Ruedenberg, *J. Chem. Phys.* **99**, 5257 (1993)). This method is often advantageous in Transition State searches. For a detailed discussion of the various minimization algorithms see F. Eckert, P. Pulay and H.-J. Werner, *J. Comp. Chem* **18**, 1473 (1997). Reaction path following is described in F. Eckert and H.-J. Werner, *Theor. Chem. Acc.* **100**, 21, (1998). Please refer to the references section for citations of the analytic gradient methods.

When analytical gradients are available for the optimized energy these will be used. See section 45.1 for a list of methods with analytical gradients. Otherwise the gradient will be computed numerically from finite energy differences. Normally, the last computed ground-state energy is used. But the `VARIABLE` directive or option can be used to optimize, e.g., Davidson corrected energies, excited states, or counterpoise corrected energies.

By default the program repeats in each geometry optimization step those commands in the input that are needed to compute the last energy. For example, for MP2 gradients the commands HF and MP2 are needed. The MP2 gradients will then be computed automatically. It is also possible to define procedures for the energy calculation, or to specify the first command from which the input should be repeated in each step (see section 46.1.1). The section of the input which is needed for the geometry optimization must not modify variables that are used in the geometry definition (changes of such variables are ignored, and a warning message is printed).

46.1   Options

Most parameters can be given as options on the `OPTG` command line, as described in this section. Alternatively, directives can be used, which will be described in section 46.2.

46.1.1   Options to select the wavefunction and energy to be optimized

By default, the last computed energy is optimized, and all commands on which the last energy calculation depends are automatically executed. For certain purposes, e.g., optimization of counter-poise corrected energies or Davidson corrected energies, the following options can be used to alter the default behaviour.

`STARTCMD=`*command*	Specifies a start command. In each geometry optimization step all input beginning with *command* to the current `OPTG` is processed. This input must not include numerical gradient or Hessian calculations. If numerical gradients are needed, these will be computed for the final energy (or specified variable) by `OPTG`. It is assumed that these commands have been executed before entering the `OPTG` program.
`PROC=`*procname*	specifies a procedure to be executed in each geometry optimization step. This must define a complete energy calculation (orbital optimization and correlation treatment), and must not include numerical gradient of Hessian calculations (numerical gradients will be computed automatically for the optimized energy or variable). However, the procedure can include the calculation of analytical gradients, for instance for counter-poise corrected optimizations in which a linear combination of several gradient calculations is needed.
`VARIABLE=`*varname*	Optimize the value of variable *varname*. This implies numerical gradients.

46.1.2   Options for optimization methods

`METHOD=RF|AH|DIIS|QSD|QSDPATH|SRMIN|SRTRANS|STSTEEP`	
	Optimization method to be used. See section 46.2.1 for details.
`ROOT=1`|`2`	Minimum search (1, default) or transition state search (2).
`DIRECTION`|`IDIR=`*idir*	Determines initial step length and direction in reaction path following, see section 46.2.16.
`STPTOL=`*value*	For reaction path following, see section 46.2.16.
`SLMAX=`*value*	For reaction path following, see section 46.2.16.
`STEPMAX=`*value*	Max step length in one optimization step. This also affects the step length in reaction path following. For more detailed specifications see section 46.2.12.
`TRUST=`*value*	Trust ratio for Augmented Hessian method (default 0.5).
`AHMAX=`*value*	Maximum step size allowed in the Augmented Hessian procedure. This refers to the scaled parameter space (default 0.5).
`CUT=`*value*	Threshold for orthonormalization used in conjugate gradient update of Hessian (default 1.d-3).
`ROTATE`	(logical). If .true., the Cartesian coordinates are transformed to minimize rotations (default=.true.)

46.1.3 Options to modify convergence criteria

The standard MOLPRO convergency criterion requires the maximum component of the gradient to be less then $3 \cdot 10^{-4}$ [a.u.] and the maximum energy change to be less than $1 \cdot 10^{-6}$ [H] *or* the maximum component of the gradient to be less then $3 \cdot 10^{-4}$ [a.u.] and the maximum component of the step to be less then $3 \cdot 10^{-4}$ [a.u.].

It is also possible to use the convergency criterion of the Gaussian program package. It is somewhat weaker than the MOLPRO criterion and requires the maximum component of the gradient to be less then $4.5 \cdot 10^{-4}$ [a.u.] and the root mean square (RMS) of the gradient to be less then $3 \cdot 10^{-4}$ [a.u.] as well as the maximum component of the optimization step to be less then 0.0018 [a.u.] and the RMS of the optimization step to be less then 0.0012 [a.u.].

MAXIT=*maxit*	maximum number of optimization cycles. The default is 50.
GRADIENT=*thrgrad*	required accuracy of the optimized gradient. The default is $3 \cdot 10^{-4}$.
ENERGY=*threnerg*	required accuracy of the optimized energy. The default is $1 \cdot 10^{-6}$.
STEP=*thrstep*	convergence threshold for the geometry optimization step. The default is $3 \cdot 10^{-4}$.
BAKER	(logical). Use Baker's convergency criteria (see J. Baker, *J. Comp. Chem.* **14**,1085 (1993)).
GAUSSIAN	(logical). Use Gaussian convergency criteria.
SRMS=*thrsrms*	sets (for Gaussian convergency criterion) the required accuracy of the RMS of the optimization step. The default is 0.0012.
GRMS=*thrgrms*	sets (for Gaussian convergency criterion) the required accuracy of the RMS of the gradient. The default is $3 \cdot 10^{-4}$.
FREEZE=*thrfreez*	Freeze DFT grid and domains in local calculations if the step length is smaller than *thrfreez* (default 0.01).

Note: The defaults for the convergence parameters can also be changed by using a global GTHRESH directive, i.e.

GTHRESH, OPTSTEP=*step*, OPTGRAD=*grad*, ENERGY=*energy*;

46.1.4 Options to specify the optimization space

If the geometry is given as Z-matrix, the default is to optimize the variables on which the Z-matrix depends. In case of xyz input, always all 3N coordinates are optimized, even if the xyz input depends on fewer variables. If Cartesian z-matrix input is used, optimization in full space is only enforced if automatic orientation is requested using the MASS, or CHARGE options on the ORIENT directive. See *opt_space* in section 46.2.2 for details.

SPACE=ZMAT|3N	Specifies the coordinates to be used in the optimization. Z-matrix optimization is only possible if the geometry is given as Z-matrix.
OPT3N|3N	(logical). Same as SPACE=3N
ZMAT	(logical). Same as SPACE=ZMAT

46.1.5   Options to specify the optimization coordinates

These options specify the coordinates in which the optimization takes place. The default is to use local normal coordinates. See *opt_coord* in section 46.2.2 for details.

```
COORD=NORMAL|NONORMAL|BMAT
```

NORMAL	(logical). Same as `COORD=NORMAL`.
NONORMAL	(logical). Same as `COORD=NONORMAL`.
BMAT	(logical). Same as `COORD=BMAT`.

46.1.6   Options for numerical gradients

Numerical gradients can be computed with respect to variables on which the Z-matrix depends or with respect to Cartesian coordinates. In the latter case, it is most efficient to use symmetrical displacement coordinates. These do not change the symmetry of the molecule and the number of displacements is minimal. Alternatively (mainly for testing purpose) the gradients can be computed using symmetry unique Cartesian displacements or all 3N Cartesian displacements. In these cases the symmetry of the molecule can be reduced by the displacements and using such displacements is normally not recommended.

```
DISPLACE=ZMAT|SYMM|UNIQUE|CART
```
Displacement coordinates to be used for numerical gradient. The default is `ZMAT` if the geometry is given as a zmatrix which depends on variables, and `SYMM` (symmetrical displacement coordinates) otherwise. The use of `UNIQUE` or `CART` is not recommended.

`SYMMETRY=AUTO|NOSYM` Symmetry to be used in wavefunction calculations of numerical gradients. This option is only relevant if `DISPLACE=UNIQUE|CART`. If `AUTO` is given, the maximum possible symmetry is used for each displacement. This implies that the energy is independent of the symmetry used. Note that this often not the case in MRCI or CASPT2 calculations. The option can also not be used in local correlation calculations.

AUTO	(logical). Same as `SYMMETRY=AUTO`
NOSYM	(logical). Same as `SYMMETRY=NOSYM`
RSTEP=*rstep*	Step length for distances in numerical gradient calculations (in bohr). The default is 0.01.
DSTEP=*dstep*	Step length for symmetrical displacements (in bohr). The default is 0.01.
ASTEP=*astep*	Step length for angles in numerical gradient calculations (in degree). The default is 1.
FOURPOINT	(logical). Use 4-point formula for accurate numerical gradient.
NUMERICAL	(logical). Force the use of numerical gradients, even if gradients are available.

In special cases the energy calculations may require several steps with different occupations and/or symmetries. In this case the `FORCEINP` directive must be given (see section 46.1.8).

46.1.7 Options for computing Hessians

By default, an approximate Hessian (model Hessian) is used. Optionally, a Hessian can be computed in the optimization or read from a previous Hessian or frequency calculation.

NUMHESS=*hstep*	If given, a numerical Hessian is computed in each *hstep'th* iteration. If *hstep=0* or not given, only an initial Hessian is computed.
HESSREC=*record*	Read initial Hessian from the given record. If *record* is not given or zero, the last computed Hessian is used.
READHESS	(logical). Same as HESSREC=0.
HESSPROC=*procname*	specifies a procedure to be used for computing the Hessian. This procedure must be define a complete energy calculation (orbital optimization and correlation treatment). A different method can be used than for the optimized energy, but the basis must not be redefined in this procedure. For instance, an MP2 Hessian can be used for CCSD(T) optimizations, or a CASPT2 Hessian for MRCI optimizations. By default, the same procedure is used for the Hessian as for the optimized energy. Note: If a hessian procedure is used and two or more optimizations are done after each other in the same input, the complete energy calculation (including orbital optimization) must be defined before each optg command or in the optg procedure.
HESSVAR=*varname*	Compute Hessian for variable *varname*. This implies numerical calculation of the Hessian from energies. The default is to use the same variable as for the energy and gradient.
HESSCENT	Use central gradient differences for computing Hessian (only effective if gradients are available)
HESSFORW	Use forward gradient differences for computing Hessian (only effective if gradients are available). This effectively computes the Hessian at a slightly displaced geometry, but needs only half the number of displacements. This is the default.
UPDATE=BFGS|IBFGS|CGRD|PMS|POWELL|MS|NONE	
	Hessian update method to be used. See section 46.2.9 for details.
MAXUPD=*maxupd*	Max number of Hessian updates. The count is reset to zero each time a Hessian is computed.
NUMDIAG	If true, replace diagonal elements of model hessian by diagonal numerical hessian (if available). This sometimes improves convergence, but since it may lead to symmetry breaking it is no the default.

Note that there are restrictions for computing Hessians for multireference methods (MCSCF, MRCI, ACPF,AQCC,RS2). For these methods the symmetry must not change by any displacements, since this could change the occupations and states and may lead to non-contiguous potential energy surfaces. One of the following three options can be used in these cases:

- Use no symmetry from the beginning (NOSYM).

- Use symmetric displacement coordinates. This is the default if the optimization is done in 3N cartesian coordinates. One can use OPTG,DISPLACE=SYMM to force the use of symmetrical displacements (this creates 3N cartesian coordinates if a Z-matrix is used in the geometry input).

- Use a Z-matrix with the restriction that no variable in the Z-matrix may change the symmetry. For example, `geometry={O;H1,O,r;H2,O,r,H1,theta}` would work, but `geometry={O;H1,O,r1;H2,O,r2,H1,thetai}` would not work. In this case the program prints a warning message. If an incorrect Z-matrix is used and the symmetry changes, the program will crash.

46.1.8 Miscellaneous options:

VARSAVE	Save Cartesian gradients in variables GRADX, GRADY, GRADZ.
NONUC	Do not compute gradients at lattice points.
DEBUG	Set debug print options.
PRINT=*iprint*	Print option for optimization.
SAVEXYZ[=*file*]	Save the optimized coordinates in an xyz-file. One file is written for each step. The filename is *file_nn*.xyz, where *nn* is the iteration number. For the final geometry, *_nn* is omitted. If filename is not given, *file* is taken to be the root name of the input, i.e. test.inp creates test_1.xyz in the first iteration and test.xyz for the converged geometry. By default, the xyz information is written to the log file in each step.
SAVEACT[=*file*]	Save optimized variables in each step. The file name is *file*.act. If *file* is not given the root name of the input is used. The file can be read later using the READVAR command or copied into new input.
SAVEGRD[=*file*]	Write in each step the Cartesian coordinates and gradients. The file name is *file*.grd. If file is not given, the root name of the input appended by .grd is used.
APPEND	(logical). If given, existing SAVEACT and/or SAVEGRD files are appended.
REWIND	(logical). If given, the SAVEACT and/or SAVEGRD files are rewound at each step, i.e. only the last geometry or gradient is saved, previous values are overwritten.
FORCEINP	(logical) Disables the mechanism that freezes the occupations during geometry optimizations. If this option is given, the occupations and wave function definitions given in the input for the energy calculations are strictly obeyed.

46.2 Directives for OPTG

An alternative way to specify options is to use directives, as described in this section. In some cases this allows more detailed specifications than with the options on the OPTG command. In particular, directives ACTIVE or INACTICE can be used to define the optimization space in more detail.

46.2.1 Selecting the optimization method (METHOD)

METHOD,*key*;

key defines the optimization method.

For *minimization* the following options are valid for *key*:

`RF`	Rational Function method (default).
`AH`	Augmented Hessian method. This is similar to `RF` algorithm but uses a more sophisticated step restriction algorithm.
`DIIS`	Pulay's Geometry DIIS method. As an an additional option you may add the number of geometries to be used in GDIIS interpolation (default 5) and the interpolation type (i.e. the subspace in which the GDIIS interpolation is made. `METHOD,DIIS`, *number*, *type* *type* may be `GRAD` interpolation using the gradients (default), working good for rigid molecules, `STEP` interpolation using Quasi-Newton steps which could be advantageous in dealing with very floppy molecules, `ENER` interpolation using energies, which is an intermediate between the above two.
`QSD`	Quadratic steepest descent method of Sun and Ruedenberg.
`SRMIN`	Old version of `QSD`.

For *transition state* searches (invoked with the `ROOT` option, see section 46.2.11) *key* can be

`RF`	Rational Function method (default).
`DIIS`	Pulay's Geometry DIIS method (see above).
`QSD`	Quadratic Steepest Descent Transition State search using the image Hessian method (see J. Sun and K. Ruedenberg, *J. Chem. Phys.* **101**, 2157 (1994)) The use of this option is recommended for transition state searches – especially in complicated cases. The optimization step is checked and the Hessian is recalculated when approaching a troublesome region of the PES. Thus **this method is somewhat safer (and often faster) in reaching convergence than the RF or DIIS method**. The Hessian recalculation safeguard may be turned off using the `METHOD,QSD,NOHESS` input card.
`SRTRANS`	Old version of `QSD`.

For *reaction path following* the input *key* is

`QSDPATH`	Quadratic Steepest Descent reaction path following. This methods determines reaction paths (intrinsic reaction coordinates, IRCs) by following the exact steepest descent lines of subsequent quadratic approximations to the potential energy surface. The Hessian matrix is calculated numerically at the first optimization step and subsequently updated by Powell or BFGS update. If a given arc length of the steepest descent lines is exceeded, the Hessian is recalculated numerically (see `OPTION` section 46.2.16). For details see J. Sun and K. Ruedenberg, *J. Chem. Phys.* **99**, 5269 (1993) It is also possible to recalculate the Hessian after each *m* steps using the `NUMHES`,*m* command (see section 46.2.7). If the Hessian matrix is recalculated in every optimization step (`NUMHES`,1) a algorithm different to the one with updated Hessians is used, which is very accurate. Using the `PRINT,OPT` card, this algorithm prints in every optimization step a *reaction path point r* which is different from the point where the energy and the gradient is calculated but closer to the real reaction path (for further

details of the algorithm see J. Sun and K. Ruedenberg, *J. Chem. Phys.* **99**, 5257 (1993)). For further input options of the QSD reaction path following see `OPTION` section 46.2.16.

SRSTEEP	Old Version of `QSDPATH`.

46.2.2 Optimization coordinates (`COORD`)

It is possible to use various coordinate types and algorithms for the optimization. This can be controlled by additional subcommands as described in this and the following subsections.

`COORD,[`*opt_space*`],[`*opt_coord*`],[NOROT]`

These options choose the optimization space and the coordinate system in which the optimization takes place.

opt_space defines the parameters to be optimized. By default, if the geometry input is given in Z-matrix format, all variables on which the Z-matrix depends are optimized. Subsets of the variables on which the Z-matrix depends can be chosen using the `ACTIVE` or `INACTIVE` subdirectives. If the Z-matrix depends on no variables or `xyz` input is used, all 3*N* cartesian coordinates are optimized.

opt_space can be one of the following:

ZMAT	Optimize all variables on which the Z-matrix depends (default if the geometry is given as Z-matrix).
3N	Optimize all 3*N* cartesian coordinates (default if the Z-matrix depends on no variables, or if xyz-input is used). Z-Matrix input coordinates will be destroyed if 3N is used..

opt_coord determines the coordinates in which the optimization takes place. By default, local normal coordinates are used. Optionally cartesian coordinates or natural internal coordinates can be used.

opt_coord can be one of the following:

NORMAL	Optimization in local normal coordinates. This is default if the Model Hessian is used to approximate the Hessian.
NONORM	Don't use local normal coordinates.
BMAT[=*filename*]	Use Pulay's *natural internal coordinates*, see G. Fogarasi, X. Zhou, P. W. Taylor and P. Pulay *J. Am. Chem. Soc.* **114**, 8191 (1992); P. Pulay, G. Fogarasi, F. Pang, J. E. Boggs *J. Am. Chem. Soc.* **101**, 2550 (1979)). Optionally, the created coordinates as well as additional informations about this optimization are written to the specified file. These coordinates resemble in part the valence coordinates used by vibrational spectroscopist, and have the advantage of decreasing coupling between different modes. This often increases the speed of convergence. The use of this option is highly recommended, especially in minimization of large organic molecules with rings. Nevertheless you should keep in mind that these coordinates are constructed automatically, and there exist exotic bond structures which might not be treated properly (e.g. weakly bonded species as in transition state optimizations). In such a case, if the `BMAT` optimization converges slowly or leads to symmetry-breaking errors, you should try another optimization method and/or cartesian or Z-Matrix coordinates.

If the option [`NOROT`] is given, the cartesian coordinates are not transformed to minimize rotations.

46.2.3 Displacement coordinates (`DISPLACE`)

`DISPLACE`,*displacement_type*

see section 45.2.1 for details.

46.2.4 Defining active geometry parameters (`ACTIVE`)

`ACTIVE`,*param*;

Declares variable name *param* to be active in the optimization. By default, initially all variables on which the geometry depends are active; inclusion of an `ACTIVE` card makes all parameters inactive unless explicitly declared active (see also `INACTIVE`).

46.2.5 Defining inactive geometry parameters (`INACTIVE`)

`INACTIVE`,*param*;

Declares variable name *param* to be inactive in the optimization. If any `ACTIVE` card appears in the input, this card is ignored! (see also `ACTIVE`)

46.2.6 Hessian approximations (`HESSIAN`)

By default, the MOLPRO geometry optimization utilizes a force field approximation to the hessian ("Model Hessian", see R. Lindh, A. Bernhardsson, G. Karlström and P. Malmqvist *Chem. Phys. Lett.* **241**, 423 (1995)), which speeds up convergence significantly. The Model Hessian is parameterized for the elements up to the third row. Alternatively, the model Hessian of Schlegel can be used, or the Hessian can be computed numerically (see also section 46.2.7).

`HESSIAN`,*options*

where *options* can be

`MODEL`	Use Lindh's Model Hessian in optimization (default).
`MODEL=SCHLEGEL`	Use Schlegel's Model Hessian.
`MODEL=VDW`	Add vdW terms to Lindh's Model Hessian.
`SCHLEGEL`	same as `MODEL=SCHLEGEL`.
`VDW`	same as `MODEL=VDW`.
`NOMODEL`	Don't use Model Hessian approximation to the hessian.
`NUMERICAL=`*hstep*	Recompute Hessian after *hstep* iterations. This disables the use of a model hessian. If *hstep*=0, the Hessian is only computed in the first iteration. Default parameters are used for computing the numerical Hessian, unless modified using options as described for the `NUMHESS` directive, see Sect. 46.2.7. Any option valid for the `NUMHESS` directive may also follow the `NUMERICAL` option on the `HESSIAN` directive.

READ | RECORD | HESSREC=*record* Read Hessian from given *record*. If *record* is not given or zero, the last computed hessian will be read. See section 46.2.7 for more details about numerical Hessians.

UPDATE=*type*   Method used for hessian update. See section 46.2.9 for possibilities and details.

MAXUPD=*maxupd*   Max number of hessian updates. The count is reset to zero each time a hessian is computed.

If the Model Hessian is disabled (NOMODEL) and no Hessian is read or computed, the initial hessian is assumed to be diagonal, with values 1 hartree*bohr**(-2) for all lengths, 1 hartree*radian**(-2) for all angles. Additional matrix elements of the hessian can be defined using the HESSELEM directive, see section 46.2.8.

In transition state searches the Hessian is evaluated numerically in the first iteration by default. Alternatively, if READ is specified, a previously computed hessian is used.

46.2.7 Numerical Hessian (NUMHESS)

NUMHESS,*options*

or

NUMHESS,*hstep,options*

If this directive is present a numerical Hessian is computed using finite differences. If analytical gradients are available, one can use forward gradient differences (needs one gradient calculation for each coordinate) or central differences (more accurate, needs two gradient calculations for each coordinate). For transition state optimizations it is usually sufficient to use forward differences. If analytical gradients are not available for the optimized method, the energy is differentiated twice. In this case only central differences are possible.

The following options can be given:

HSTEP=*hstep*   *hstep*=-1: Don't calculate numerical hessian (default for minimization);
                     hstep=0 Calculate numerical hessian only once at the start of the optimization (default for transition state searches).
                     hstep=*n* Calculate numerical hessian after each *n* optimization steps. This is useful for difficult transition state optimizations (e.g. if the eigenvalue structure of the hessian changes during the optimization).

FORWARD   Use forward differences (default).

CENTRAL   Use the more accurate central differences.

RSTEP=*rstep*   Step length for distances (in bohr). The default is 0.01.

ASTEP=*astep*   Step length for angles (in degree). The default is 0.5 or 1 for angles below and above 90 degree, respectively.

DSTEP=*dstep*   Step length for symmetrical displacements (in bohr). The default is 0.01.

VARIABLE=*varname*   Use given variable for numerical calculation of the Hessian. Note that this disables the use of gradients, and Hessian evaluation can be very expensive.

PROCEDURE=*procname* Procedure to be used for computing Hessian. This procedure must be define a complete energy calculation (orbital optimization and correlation treatment). A different method can be used than for the optimized energy. For instance, an MP2 hessian can be used for CCSD(T) optimizations, or a CASPT2 hessian for MRCI optimizations. By default, the same procedure is used for the hessian as for the optimized energy.

DISPLACE=*type* *type* can be one of the following:

SYMM Use symmetric displacement coordinates (default). This is the only recommended option.

CART Use $3N$ cartesian displacements (not recommended). This requires many more energy calculations than necessary and does not preserve the molecular symmetry.

UNIQUE Use symmetry-unique cartesian displacements (not recommended)

Note that the displacement type for gradient and hessian must be the same.

CALC=*icalc* *icalc*=0: Recalculate the complete Hessian matrix numerically after each *hstep* optimization steps (default).
icalc=1 (currently disabled): Recalculate selected Hessian matrix elements if the relative deviation of this element before and after update (see UPDATE, section 46.2.9) is larger than *thresh*. If *thresh* is not specified, a default value of *thresh* = 0.05 (i.e. a maximum deviation of 5%) is used.
icalc=2 (currently disabled): Recalculate complete Hessian matrix if the RMS deviation of the Hessian matrix before and after update is larger than *thresh*. If *thresh* is not specified a default value of *thresh* = 0.5 *a.u.* is used.

THRESH=*thresh* Threshold for partial or dynamical update of hessian, see above

46.2.8 Hessian elements (HESSELEM)

HESSELEM,*value*, *active1*,*active2*,...

sets the starting value for hessian matrix element between active variables *active1*, *active2* to *value*. If *active2* is omitted it defaults to *active1* (diagonal element). As many HESSELEM directives as needed may be given.

46.2.9 Hessian update (UPDATE)

UPDATE,[TYPE=]*type*,MAXUPD=*maxupd*

This directive chooses the update type and limits the number of points used for the hessian update to *maxupd*. The default number of steps used in hessian update procedures is 5. If there are symmetry constraint in the coordinates of the optimization, the default number may be lower than five.

In minimizations *type* may be

BFGS Use BFGS update of hessian (default).

IBFGS	Use BFGS update of the inverse hessian.
CGRD	Use Conjugate Gradient update (see also `CUT,TRUST`).
NONE	Don't do any update.

In transition state optimizations *type* may be

PMS	Combined Powell/Murtagh-Sargent update of hessian (default).
POWELL	Use Powell's update of the hessian.
MS	Use update procedure of Murtagh and Sargent.
NONE	Don't do any update.

46.2.10 Numerical gradients (`NUMERICAL`)

`NUMERICAL`,*options*,*active*$_1$=*step*$_1$, *active*$_2$=*step*$_2$ ...;

With this directive the gradients are computed by finite differences. *step*$_i$ is the increment for the active geometry parameter *active*$_i$. For active parameters which are not specified, the default values are used. By default, the increment is 0.01 bohr for bond distances and 0.5 or 1 degree for angles less than or greater than 90 degrees, respectively. These defaults can be modified by specifying `RSTEP` or `ASTEP`. `DSTEP` is the length of symmetrical displacements, which are used if the optimization is performed in 3N coordinates.

For each active variable, two energy calculations are necessary in each geometry optimization step – so numerical optimizations may be expensive! In optimizations of 3N coordinates symmetrical displacement coordinates are normally used to minimize the number of energy calculations. (see section 45.2.1).

For optimization of special energies see `VARIABLE` section 46.2.17.

The following options can be given:

`RSTEP`=*rstep*	Step length for distances (in bohr). The default is 0.01.
`ASTEP`=*astep*	Step length for angles (in degree). The default is 0.5 or 1 for angles below and above 90 degree, respectively.
`DSTEP`=*dstep*	Step length for symmetrical displacements (in bohr). The default is 0.01.
`CENTRAL`	Use central differences for gradient (default)
`FORWARD`	Use forward differences (not recommended for gradient).
`FOURPOINT`	Use four-point formula for very accurate numerical gradients.
`PROCEDURE`=*procname*	Use given procedure for numerical calculation of the gradient. This procedure must define a complete energy calculation (orbital optimization and correlation treatment).
`VARIABLE`=*varname*	Use given variable for numerical calculation of the gradient.
`DISPLACE`=*type*	The displacement type. Note that the displacement type for gradient and hessian must be the same. *type* can be one of the following:
	`SYMM` Use symmetric displacement coordinates (default). This is the only recommended option.

| CART | Use 3*N* cartesian displacements (not recommended). This requires many more energy calculations than necessary and does not preserve the molecular symmetry. |
| UNIQUE | Use symmetry-unique cartesian displacements (not recommended) |

46.2.11 Transition state (saddle point) optimization (`ROOT`)

`ROOT`,*root*

Specifies the eigenvector of the hessian to be followed.

root=1   specifies a minimization (default).

root=2   specifies a transition state (saddle point) optimization.

In the present implementation a saddle point search is possible with the rational function method (`METHOD,RF`), the geometry DIIS method (`METHOD,DIIS`) and the quadratic steepest descent method of Sun and Ruedenberg (`METHOD,SRTRANS`).

Note that convergence is usually much more difficult to achieve than for minimizations. In particular, a good starting geometry and a good approximation to the hessian is needed. The latter is achieved by evaluating the hessian numerically (see section 46.2.7) or using a precomputed hessian (see section 46.2.6).

46.2.12 Setting a maximum step size (`STEP`)

`STEP`,*steplength,drmax,damax,drmax1,damax1*

steplength is the initial step length in the scaled parameter space (default 0.3). In the AH-method this is dynamically adjusted, and can have a maximum value *ahmax* (see `TRUST`).

drmax is the initial max change of distances (in bohr, default 0.3). In the AH-method this is dynamically adjusted up to a maximum value of *drmax1* (default 0.5 bohr).

damax is the initial max change of angles (in degree, default 2). In the AH-method this is dynamically adjusted up to a maximum value of *damax1* (default 10 degrees).

46.2.13 Redefining the trust ratio (`TRUST`)

`TRUST`,*ratio,ahmax*

ratio determines the radius around the current minimum in which points are used to update the Hessian with the conjugate gradient method (default 0.5; see also `UPDATE`).

ahmax is the maximum step size allowed in the Augmented Hessian procedure. This refers to the scaled parameter space (default 0.5). The initial step size is *stepmx* (see `STEP` card).

46.2.14 Setting a cut parameter (`CUT`)

`CUT`,*threshold*

Specifies a threshold for ortho-normalization used in conjugate gradient update of hessian (default 1.d-3; see also `UPDATE`).

46.2.15   Line searching (`LINESEARCH`)

`LINESEARCH`,*iflag*,*thrlmin*,*thrlmax*

Interpolate the geometry of the stationary point (minimum or saddle point) by a quartic polynomial between the current and the previous geometry. If *iflag*=0 or no *iflag* is set, the next optimization step will be taken from the interpolated geometry using the interpolated energy and gradient. If *iflag*=1 the energy and gradient will be recalculated at the interpolated geometry before taking the new optimization step. Note though, that the additional effort of recalculating the energy and gradient is usually not met by the increase of the convergence rate of the optimization. *thrlmin* and *thrlmax* are min and max thresholds for the recalculation of the energy and the gradient in case *iflag*=1. I.e. the recalculation just takes place if the interpolated geometry isn't too close to the actual geometry *thrlmin* and isn't too remote from the actual geometry *thrlmax*. Default values are *thrlmin*=0.001 and *thrlmax*=0.05 in the scaled parameter space of the optimization.

46.2.16   Reaction path following options (`OPTION`)

`OPTION`,*key=param*;

where *key* can be

IDIR	If starting at a transition state (or near a transition state) determine where to take the first step. If `IDIR=0` is chosen, the first step will be towards the transition state. This is the default. If `IDIR=1` is given in the input the first optimization step will be along the "transition vector" i.e. the hessian eigenvector to the smallest eigenvalue which points down towards the minimum. If using a larger `IDIR` parameter, the first step will be larger; if using a negative value, the first step will be in the opposite direction.
STPTOL	If using an updated hessian matrix, this parameter determines what update to take. If the step size between two subsequent points on which the steepest decent lines are puzzled together is smaller than *stptol* (i.e. if we are close to a minimum) the BFGS update is used, otherwise it is Powell update. The default value of *stptol* is $1.d - 6$. Note that the stepsize is also affected by the `STEPMAX` option.
SLMAX	This option is only valid with the old version of the reaction path following algorithm (i.e. `METHOD, SRSTEEP`). In this algorithm *slmax* determines the frequency of the recalculation of the numerical hessian. If the total step size of the last steps exceeds *slmax* the hessian will be recalculated, otherwise it will be updated. By default *slmax* is two times the maximum step size of the optimization step *steplength* (see `STEP` section 46.2.12). If you are using `METHOD,QSD`, the `SLMAX` option is obsolete and the `NUMHES` command (see above) should be used instead.

These options can also be given on the `OPTG` command line.

46.2.17   Optimizing energy variables (`VARIABLE`)

`VARIABLE`,*name*;

Defines a variable *name* which holds the energy value to be optimized in using finite differences. By default, this is `ENERGY(1)` as set by the most recent program. Other variables which can be used are

`ENERGY(`*i*`)`	holds last energy for state *i*.
`ENERGR(`*i*`)`	holds last reference energy for state *i*.
`ENERGD(`*i*`)`	holds last Davidson corrected energy for state *i*.
`ENERGP(`*i*`)`	holds last Pople corrected energy for state *i*.
`ENERGC`	holds CCSD (QCI, BCCD) energy in CCSD(T) [QCI(T), BCCD(T)] calculations (single state optimization).
`ENERGT(1)`	holds CCSD(T) energy in CCSD(T) calculations (single state)
`ENERGT(2)`	holds CCSD[T] energy in CCSD(T) calculations (single state).
`ENERGT(3)`	holds CCSD-T energy in CCSD(T) calculations (single state).

These variables are set automatically by the CI and/or CCSD programs. It is the user's responsibility to use the correct variable name; an error exit occurs if the specified variable has not been defined by the last program or the user.

Note: The use of the `VARIABLE` option triggers `NUMERICAL`, so optimization can be very inefficient!

46.2.18 Printing options (`PRINT`)

`PRINT`,*code=level,*... ;

Enables printing options. Usually level should be omitted or 0; values of *level* > 0 produce output useful only for debugging. *code* can be

`HESSIAN`	prints the updated hessian matrix. Note that its diagonal elements are printed anyway.
`HISTORY`	prints the complete set of previous geometries, gradients and energies.
`GRADIENT`	prints extended gradient information
`OPT`	prints detailed information about the optimization process (mainly for debugging).

Several print options can be specified with one `PRINT` command.

46.2.19 Conical Intersection optimization (`CONICAL`)

To optimize a conical intersection between two electronic states having the same spin, three vectors must be evaluated at SA-CPMCSCF level:

1) Non-Adiabatic Derivative Coupling (DC).

2) Gradient of the lower state (LSG).

3) Gradient of the upper state (USG).

This requires three different `CPMCSCF` directives in the MULTI input:

`CPMCSCF,` `NACM`, S_i, S_j, `ACCU=`*1.0d-7*, `record=`*record1.file*
`CPMCSCF,` `GRAD`, S_i, `SPIN=`*Spin of state S_i*, `ACCU=`*1.0d-7*, `record=`*record2.file*
`CPMCSCF,` `GRAD`, S_j, `SPIN=`*Spin of state S_j*, `ACCU=`*1.0d-7*, `record=`*record3.file*

where S_i,S_j are the electronic states in the usual format *istate.istsym*, and *record[n].file* specifies the name and the file number where CPMCSCF solutions should be stored. Parameter `SPIN` is half of the value in the `WF` card used to define the electronic state.

Things to remember:

i) Specify always three different *record.file* on the `CPMCSCF` directives.

ii) Evaluate the CPMCSCF for USG always last.

iii) Skip the DC evaluation if the conical intersection involves states with different spin (e.g., a Singlet/Triplet crossing) because the coupling is then zero.

Three sets of `FORCE` commands (only two for Singlet/Triplet intersection) follow the `MULTI` input. They will be like:

`FORCE`
`SAMC,`*record[n].file*
`CONICAL,`*record4.file*[`,NODC`]

where *record.file* is one of the records containing CPMCSCF info and *record4.file* points to a free record used for internal storage by the CONICAL code. *record4.file* must be the same on all the `CONICAL` directives. Furthermore, the present implementation works properly only if *file=1* on the `CONICAL` directive. The optional keyword `NODC` must be used in case of different spins (e.g., S/T crossing) when DC is not needed.

The actual optimization is performed using `OPTG,STARTCMD=MULTI` The example below optimizes the conical intersection in *LiH$_2$* (ground and excited states are both doublets).

```
***, LiH2

basis=sto-3g
print,orbitals,civector

symmetry,x              !use only molecular plane. Both states must be in the same symmetry.
geometry={
        Li;
        h1,Li,r;
        h2,Li,r,h1,theta}

r=3.0
theta=35

{hf;wf,4,1,0}

{multi;occ,6,1;wf,5,1,1;state,2                        !state averaged casscf
CPMCSCF,NACM,1.1,2.1,accu=1.0d-7,record=5100.1         !cpmcscf for non-adiabatic couplings
CPMCSCF,GRAD,1.1,spin=0.5,accu=1.0d-7,record=5101.1    !gradient for state 1
CPMCSCF,GRAD,2.1,spin=0.5,accu=1.0d-7,record=5102.1}   !gradient for state 2

{Force
SAMC,5100.1               !compute coupling matrix element
CONICAL,6100.1}           !save information for optimization of conical intersection

{Force
SAMC,5101.1               !compute gradient for state 1
CONICAL,6100.1}           !save information for optimization of conical intersection

{Force
SAMC,5102.1               !compute gradient for state 2
CONICAL,6100.1}           !save information for optimization of conical intersection

optg,startcmd=multi       !find conical intersection
```

  http://www.molpro.net/info/current/examples/lih2_D0D1.com

This second example optimizes the singlet-triplet intersection in *LiH*$_2$(+) (ground state is Singlet, excited state is Triplet).

```
***, LiH2

basis=sto-3g

symmetry,nosym
geometry={
        Li;
        H1,Li,r;
        H2,Li,r,H1,theta}

r=3.7
theta=160

{hf;wf,4,1,0}

{multi;
 occ,7;
 wf,4,1,0;   !singlet state
 wf,4,1,2;   !triplet state
 CPMCSCF,GRAD,1.1,spin=0,accu=1.0d-7,record=5101.1   !cpmcscf for gradient of singlet state
 CPMCSCF,GRAD,1.1,spin=1,accu=1.0d-7,record=5100.1   !cpmcscf for gradient of triplet state
}

{Force
 SAMC,5101.1                 !state averaged gradient for singlet state
 CONICAL,6100.1,NODC}        !save information for OPTCONICAL

{Force
 SAMC,5100.1                 !state averaged gradient for triplet state
 CONICAL,6100.1,NODC}        !save information for OPTCONICAL

optg,startcmd=multi,gradient=1.d-6  !find singlet-triplet crossing point
```

   http://www.molpro.net/info/current/examples/lih2+_S0T0.com

46.3 Using the `SLAPAF` program for geometry optimization

It is optionally possible to use the `SLAPAF` program written by Roland Lindh for geometry optimizations. This is done by prepending the optimization method with 'SL'. The following methods are supported:

SLRF	Use the rational function approximation;
SLNR	Use the Newton-Raphson method;
SLC1	Use the C1-DIIS method;
SLC2	Use the C2-DIIS method.

When using DIIS methods (`SLC1` or `SLC2`), the DIIS parameters are specified in the same way as in standard molpro optimizer.

There are some differences when using the `SLAPAF` program:

1) It is not possible to use Z-matrix coordinates in the optimization.

2) Instead, one can explicitly define internal coordinates to be varied or fixed.

3) Additional constraints can be imposed on the converged geometry in a flexible way.

46.3.1 Defining constraints

Constraints and internal coordinates (see below) can be linear combinations of bonds, angles etc. The latter, called here primitive internal coordinates, can be specified before the constraints definition, or directly inside. The general definition of a primitive coordinate is:

PRIMITIVE,[NAME=]*symbolic name*, *explicit definition;*

or

PRIM,[NAME=]*symbolic name*, *explicit definition;*

Here *symbolic name* is the name given to the primitive coordinate (if omitted, it will be generated automatically). This name is needed for further reference of this primitive coordinate.

explicit definition has the form:

type,atoms

type can be one of the following:

BOND	Bond length, defined by 2 atoms.
ANGLE	Bond angle, defined by 3 atoms (angle 1–2–3).
DIHEDRAL	Dihedral angle, defined by 4 atoms (angle between the planes formed by atoms 1,2,3 and 2,3,4, respectively).
OUTOFPLANE	Out-of-plane angle, defined by 4 atoms (angle between the plane formed by atoms 2,3,4 and the bond 1–4).
DISSOC	A dissociation coordinate, defined by two groups of atoms (Not permitted with constraints).
CARTESIAN	Cartesian coordinates of an atom.

For all types except DISSOC and CARTESIAN, atoms are given as:

ATOMS=[*a1,a2,a3,...*]

where the number of atoms required varies with *type* as specified above, and the atomic names *a1,a2,a3,...* can be either atomic tag names from the Z-matrix input, or integers corresponding to Z-matrix rows. Note that the square brackets are required here and do not indicate optional input.

For DISSOC the specification is as follows:

DISSOC,GROUP1=[*a1,a2,...*],GROUP2=[*b1,b2,...*];

The corresponding internal coordinate is the distance between the centres of mass of the two groups.

For CARTESIAN the definition is

CARTESIAN, *I, atom;*

where *I* can be one of X,Y,Z or 1,2,3 and *atom* can be a z-matrix atom name or an integer referring to the z-matrix row.

With this definition, the constraints are defined as

CONSTRAINT,[VALUE=]*value*,[*unit*],[[FACTOR=]*fac*,*prim*,[[FACTOR=]*fac*],*prim*,...;

where *value* is the value imposed to the constraint, and *prim* is either the name of the primitive defined before this constraint, or an explicit definition; and *fac* is a factor of the corresponding primitive in the constraint. If *fac* is omitted it is taken to be 1.

If *value* is specified in `Angstrom` or `Radian`, *unit* must be given.

Examples for H_2O in C_s symmetry:

Constraining the bond angle to 100 degrees:

`constraint,100,deg,angle,atoms=[h1,o,h2];`

which is equivalent to

`primitive,a1,angle,atoms=[h1,o,h2];`

`constraint,100,a1;`

Keeping the two OH distances equal:

`constraint,0,bond,atoms=[h1,o],-1.,bond,atoms=[h2,o];`

which is equivalent to

`primitive,b1,bond,atoms=[h1,o];`

`primitive,b2,bond,atoms=[h2,o];`

`constraint,0,b1,-1.,b2;`

46.3.2 Defining internal coordinates

By default `SLAPAF` optimizes in force-constant weighted normal coordinates that are determined automatically. However, the user can define his own coordinates. The definition of internal coordinates, similar to constraints, is based on primitive coordinates. The input is:

`INTERNAL`,[[NAME=]*name*],[[FACTOR=]*fac*],*prim*,[[FACTOR=]*fac*],*prim*,...;

`FIX`, [[NAME=]*name*],[[FACTOR=]*fac*],*prim*,[[FACTOR=]*fac*],*prim*,...;

Internal coordinates that are specified using `INTERNAL` are varied and those using `FIX` are fixed to their initial values.

An important point for the definition of internal coordinates is that their total number must be equal to the number of degrees of freedom of the molecule . Otherwise an error message is generated. Only symmetry independent coordinates need to be given.

46.3.3 Additional options for SLAPAF

Some options can be passed to the SLAPAF program. Options are specified with SLOPT sub-directive:

`{opt;method=slnr;{slopt;opt1;opt2,`*par1,par2*`;opt3;...}}`

The available options are

`CART`	Use eigenvectors of the approximate Hessian, expressed in cartesian coordinates, as the definition of internal coordinates;
`NOMA`	Don't impose any restrictions on the step size;

UORD	Order the gradients and displacement vectors according to Schlegel prior to the update of the Hessian. Default is no reordering;
HWRS	Use force field weighted internal coordinates (default);
RS-P	Activate RS-P-RFO as default for transition state search; default is RS-I-RFO;
NOHW	Use unweighted internal coordinates;
PRBM	Print B-matrix;
RTHR,*Thra,Thrb,Thrt*	Thresholds for redundant coordinate selection for bonds, bends and torsions, respectively. Default 0.2, 0.2, 0.2
MODE,*index*	Hessian vector index for mode following when calculating transition states.
FIND	Enable unconstrained optimization for constrained cases, when looking for transition states (see MOLCAS manual).
GNRM,*thr*	Threshold for FIND, default 0.2 (see MOLCAS manual).

For more information, please consult the MOLCAS manual.

46.4 Examples

46.4.1 Simple HF optimization using Z-matrix

```
***, Allene geometry optimization using Z-Matrix
memory,1,m
basis=sto-3g

rcc=1.32 ang
rch=1.08 ang
acc=120  degree
Geometry={C1                          !Z-matrix input
          C2,c1,rcc
          Q1,c1,rcc,c2,45
          C3,c2,rcc,c1,180,q1,0
          h1,c1,rch,c2,acc,q1,0
          h2,c1,rch,c2,acc,h1,180
          h3,c3,rch,c2,acc,h1,90
          h4,c3,rch,c2,acc,h2,90}
hf
optg,saveact='allene.act',savexyz='allene.xyz' !default optimization using model hessian.
                                        !Save optimized variables in file allene.act
                                        !Save optimized geometry in xyz style in in fi
```

http://www.molpro.net/info/current/examples/allene_optscf.com

46.4.2   Optimization using natural internal coordinates (BMAT)

```
***, Allene geometry optimization using natural internal coordinates
memory,1,m
basis=sto-3g

rcc=1.32 ang
rch=1.08 ang
acc=120  degree
symmetry,nosym
Geometry={C1;                          !Z-matrix input
          C2,c1,rcc
          Q1,c1,rcc,c2,45
          C3,c2,rcc,c1,180,q1,0
          h1,c1,rch,c2,acc,q1,0
          h2,c1,rch,c2,acc,h1,180
          h3,c3,rch,c2,acc,h1,90
          h4,c3,rch,c2,acc,h2,90}
hf;
optg               !default optimization using model hessian
coord,bmat         !use natural internal coordinates

optg,coord=bmat    !same as above
```

http://www.molpro.net/info/current/examples/allene_opt_bmat.com

46.4.3   MP2 optimization using a procedure

```
***, Allene geometry optimization using Z-Matrix
memory,2,m
basis=vdz

rcc=1.32 ang
rch=1.08 ang
acc=120  degree
Geometry={C1                           !Z-matrix input
        C2,c1,rcc
        Q1,c1,rcc,c2,45
        C3,c2,rcc,c1,180,q1,0
        h1,c1,rch,c2,acc,q1,0
        h2,c1,rch,c2,acc,h1,180
        h3,c3,rch,c2,acc,h1,90
        h4,c3,rch,c2,acc,h2,90}

optg,procedure=runmp2     !use procedure optmp2

runmp2={hf;mp2}           !procedure definition
```

http://www.molpro.net/info/current/examples/allene_optmp2.com

46.4.4 Optimization using geometry DIIS

```
***, CAFFEINE cartesian coordinates (XYZ format)
memory,1,m
basis=sto-3g
geomtyp=xyz
geometry={
24
          CAFFEINE CARTESIAN COORDINATES
C          0.8423320060       -0.3654865620        0.0000000000
C         -0.2841017540       -1.1961236000        0.0000000000
N          2.0294818880       -1.1042264700        0.0000000000
N          0.0774743850       -2.5357317920        0.0000000000
N         -1.6472646000       -0.6177952290        0.0000000000
C          1.4531962870       -2.3678913120        0.0000000000
C          0.6373131870        1.1735112670        0.0000000000
C         -1.7812691930        0.7688916330        0.0000000000
N         -0.6771444680        1.6306355000        0.0000000000
O          1.6106752160        1.9349693060        0.0000000000
O         -2.9202890400        1.2510058880        0.0000000000
C         -0.9202462430        3.1094501020        0.0000000000
C         -2.8623938560       -1.4824503660        0.0000000000
C          3.4552156930       -0.6811094280        0.0000000000
H          2.0878150460       -3.2451913360        0.0000000000
H         -1.4989252090        3.4222116470       -0.8897886280
H         -1.4989252090        3.4222116470        0.8897886280
H          0.0071905670        3.7148499490        0.0000000000
H         -3.4903070930       -1.2888938190       -0.8907763360
H         -3.4903070930       -1.2888938190        0.8907763360
H         -2.6289534570       -2.5638654230        0.0000000000
H          4.1360211370       -1.5529079440        0.0000000000
H          3.6817059520       -0.0685850980        0.8931597470
H          3.6817059520       -0.0685850980       -0.8931597470
}

hf
optg,savexyz=caffeine.xyz    !save optimized geometry in file caffeine.xyz
coord,bmat                   !Optimization in natural internal coordinates
method,diis                  !Optimization method: Geometry DIIS

optg,coord=bmat,method=diis,savexyz=caffeine.xyz   !same as above
```

<div align="center">

http:
//www.molpro.net/info/current/examples/caffeine_opt_diis.com

</div>

46.4.5 Transition state of the HCN – HNC isomerization

The first example shows how to do a MP2 transition state optimization. The initial Hessian is taken from a previous HF frequency calculation.

```
***, HCN <--> NHC Isomerization - Transition State Optimization and Frequencies

l1=1.18268242 ang
l2=1.40745082 ang
a1=55.05153416 degree

basis=3-21G

symmetry,nosym
geometry={
        C
        N,1,l1
        H,2,l2,1,a1}

hf                        ! HF-SCF

frequencies,analytical    ! Vibrational frequencies for HF-SCF (analytical Hessian)

mp2                       ! MP2

optg,root=2,method=rf,readhess     ! Transition State Search using Rational Function Optimizer

frequencies               ! Vibrational frequencies for MP2 (numerical Hessian)
---
```

  http://www.molpro.net/info/current/examples/hcn_mp2_ts.com

The second example shows how to do a CCSD(T) optimization with an MP2 hessian. Note
that currently the CCSD(T) gradient is computed numerically using finite energy differences,
and this can take long time for larger molecules. The calculation of the MP2 hessian finite
differences of analytical gradients.

```
***, HCN <--> NHC Transition State Optimization and Frequencies

rcn=1.18 ang
rnh=1.40 ang
alpha=55 degree

basis=vtz

geometry={
        C
        N,1,rcn
        H,2,rnh,1,alpha}

hf
ccsd(t)
optg,root=2,hessproc=runmp2  !Transition state optimization for ccsd(t) using mp2 hessian
frequencies                  !CCSD(T) frequencies (using numerical second derivatives)

runmp2={hf;mp2}    !procedure definition
---
```

  http://www.molpro.net/info/current/examples/hcn_ccsd_ts.com

The last example shows how to do a MRCI+Q (MRCI with Davidson correction) optimization
with an CASPT2 hessian. As for CCSD(T), the MRCI+Q gradient as computed numerically,
while the CASPT2 hessian is obtained using finite differences of analytical CASPT2 gradients.

```
***, HCN <-> NHC Isomerization - Transition State Optimization and Frequencies
print,orbitals,civector
rcn=1.18 ang
rnh=1.40 ang
alpha=55 degree

basis=vtz

geometry={
        C
        N,1,rcn
        H,2,rnh,1,alpha}

closed,4      ! global setting for casscf inactive space

hf            ! HF-SCF
multi         ! CASSCF
mrci          ! MRCI
optg,root=2,variable=energd,hessproc=runrs2    !optimize mrci+q transition state and caspt2 for

runrs2={multi;rs2}       !procedure definition for caspt2
---
```

   http://www.molpro.net/info/current/examples/hcn_mrci_ts.com

46.4.6   Reaction path of the HCN – HNC isomerization

The following input first optimizes the transition state, and then performs reaction path calculations in both directions. The results are plotted.

```
***, HCN <---> NHC Isomerization Reaction Path
memory,1,m
basis=3-21G

rcn=1.18282 ang        ! Starting geometry is transition state
rnh=1.40745 ang
alpha=55.05 degree

symmetry,x             ! Cs Symmetry
geometry={
          C
          N,1,rcn
          H,2,rnh,1,alpha}

int
rhf
optg,root=2,saveact=hcn_ts,rewind                  ! Find and store the TS
{optg,method=qsdpath,dir=1, numhess=5,hesscentral,saveact=hcn_path}          ! find IRC in pos

readvar,hcn_ts.act                                 ! Reset geometry to TS
{optg,method=qsdpath,dir=-1,numhess=5,hesscentral,saveact=hcn_path,append} !find IRC in negat

readvar,hcn_path.act

alpha=alpha*pi/180     !convert angle to radian

table,irc,rcn,rnh,alpha,e_opt    !tabulate results

{table,irc,e_opt               !plot energy profile as function of irc
 plot,file='hcn_eopt.plot'}

{table,irc,rcn,rnh,alpha       !plot distances and angle as function of irc
 plot,file='hcn_dist.plot'}
```

http:
 //www.molpro.net/info/current/examples/hcn_isomerization.com

This produces the plots
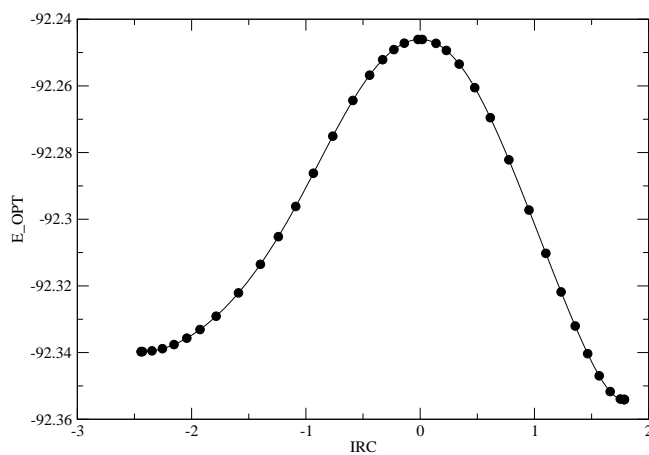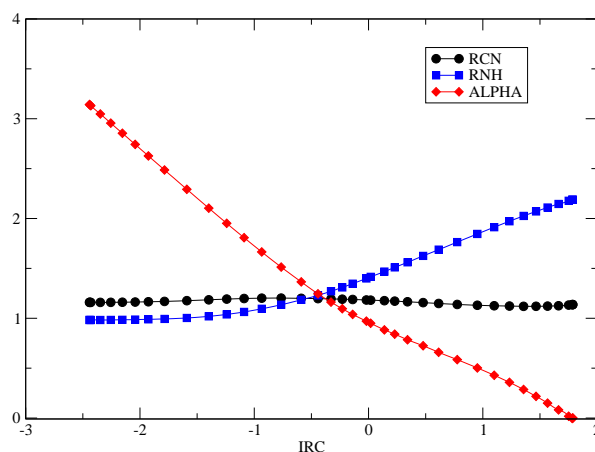
46.4.7 Optimizing counterpoise corrected energies

Geometry optimization of counterpoise corrected energies is possible by performing for the total system as well as for each individual fragment separate FORCE calculations. The gradients and energies are added using the ADD directive. This requires that NOORIENT has been specified in the geometry input, in order to avoid errors due to unintended rotation of the system. This default can be disabled using the NOCHECK option, see ADD above.

The way a counterpoise corrected geometry optimization works is shown in the following example. Note that the total counterpoise corrected energy must be optimized, not just the interaction energy, since the interaction energy depends on the monomer geometries and has a different minimum than the total energy. The interaction energy could be optimized, however, if the monomer geometries were frozen. In any case, the last calculation before calling OPTG must be the calculation of the total system at the current geometry (in the example below the dimer calculation), since otherwise the optimizer gets confused.

```
***,HF dimer MP2/CP optimization with relaxed monomers

basis=avtz
gthresh,energy=1.d-8

! INITIAL VALUES OF GEOMETRY VARIABLES

RFF=     5.3
R1=      1.76
R2 =     1.75
THETA1 = 7.0
THETA2 = 111

symmetry,x
orient,noorient
geometry={
     f1
     f2  f1  rff
     h1  f1  r1   f2  theta1
     h2  f2  r2   f1  theta2  h1  180.}

label:

text, CALCULATION AT LARGE SEPARATION

rff_save=rff            !save current rff distance
rff=1000                !dimer calculation at large separation

text, HF1

dummy,f2,h2;            !second hf is now dummy
{hf;accu,16}            !scf for first monomer
mp2;                    !mp2 for first monomer
ehf1inf=energy          !save mp2 energy in variable
forces;                 !compute mp2 gradient for first monomer

text, HF2

dummy,f1,h1;            !first hf is now dummy
{hf;accu,16}            !scf for second monomer
mp2;                    !mp2 for second monomer
ehf2inf=energy          !save mp2 energy in variable
forces;                 !compute mp2 gradient for second monomer
add,1                   !add to previous gradient
einf=ehf1inf+ehf2inf    !total energy of unrelaxed momomers

rff=rff_save            !reset HF - HF distance to current value

text, CP calculation for HF1 MONOMER

dummy,f2,h2;            !second hf is now dummy
{hf;accu,16}            !scf for first monomer
mp2;                    !mp2 for first monomer
ehf1=energy             !save mp2 energy in variable
forces;                 !compute mp2 gradient for first monomer
add,-1                  !subtract from previous gradient

text, CP calculation for HF2 MONOMER

dummy,f1,h1;            !first hf is now dummy
{hf;accu,16}            !scf for second monomer
mp2;                    !mp2 for second monomer
ehf2=energy             !save mp2 energy in variable
forces;                 !compute mp2 gradient for first monomer
add,-1                  !subtract from previous gradient

text, DIMER CALCULATION
dummy                   !reset dummies
{hf;accu,16}            !scf for dimer
mp2;                    !mp2 for dimer
edimer=energy           !save mp2 energy in variable
```

The next example shows how the same calculations can be done using numerical gradients. In this case, first the total counter-poise corrected energy is formed and then optimized. Note that the `ADD` command does not work for numerical gradients.

```
***,HF dimer MP2/CP optimization with relaxed monomers

basis=avtz
gthresh,energy=1.d-8

! INITIAL VALUES OF GEOMETRY VARIABLES

RFF=      5.3
R1=       1.76
R2 =      1.75
THETA1 =  7.0
THETA2 = 111

symmetry,x
orient,noorient
geometry={
      f1
      f2  f1  rff
      h1  f1  r1   f2  theta1
      h2  f2  r2   f1  theta2  h1  180.}

label:

text, CALCULATION AT LARGE SEPARATION

rff_save=rff            !save current rff distance
rff=1000                !dimer calculation at large separation

text, HF1

dummy,f2,h2;            !second hf is now dummy
{hf;accu,16}            !scf for first monomer
mp2;                    !mp2 for first monomer
ehf1inf=energy          !save mp2 energy in variable

text, HF2

dummy,f1,h1;            !first hf is now dummy
{hf;accu,16}            !scf for second monomer
mp2;                    !mp2 for second monomer
ehf2inf=energy          !save mp2 energy in variable
einf=ehf1inf+ehf2inf    !total energy of unrelaxed momomers

rff=rff_save            !reset HF - HF distance to current value

text, CP calculation for HF1 MONOMER

dummy,f2,h2;            !second hf is now dummy
{hf;accu,16}            !scf for first monomer
mp2;                    !mp2 for first monomer
ehf1=energy             !save mp2 energy in variable

text, CP calculation for HF2 MONOMER

dummy,f1,h1;            !first hf is now dummy
{hf;accu,16}            !scf for second monomer
mp2;                    !mp2 for second monomer
ehf2=energy             !save mp2 energy in variable

text, DIMER CALCULATION
dummy                   !reset dummies
{hf;accu,16}            !scf for dimer
mp2;                    !mp2 for dimer
edimer=energy           !save mp2 energy in variable
etot=edimer-ehf2-ehf1+ehf1inf+ehf2inf  !total BSSE corrected energy

optg,numerical,variable=etot,gradient=1.d-4,startcmd=label:   !optimize geometry


text, compute optimized monomer energy
```

In the last example the monomer structures are kept fixed, and the interaction energy is optimized.

```
***,HF dimer MP2/CP optimization without monomer relaxation

basis=avtz
gthresh,energy=1.d-8

! INITIAL VALUES OF GEOMETRY VARIABLES

RFF=      5.3
THETA1 =  7
THETA2 = 111

symmetry,x
orient,noorient
geometry={
      f1
      f2  f1  rff
      h1  f1  1.74764059  f2  theta1
      h2  f2  1.74764059  f1  theta2  h1  180.}   !using fixed HF distances of isolated HF

label:

text, CP calculation for HF1 MONOMER

dummy,f2,h2;             !second hf is now dummy
{hf;accu,16}             !scf for first monomer
mp2;                     !mp2 for first monomer
ehf1=energy              !save mp2 energy in variable
forces;                  !compute mp2 gradient for first monomer
scale,-1                 !multiply gradient by -1

text, CP calculation for HF2 MONOMER

dummy,f1,h1;             !first hf is now dummy
{hf;accu,16}             !scf for second monomer
mp2;                     !mp2 for second monomer
ehf2=energy              !save mp2 energy in variable
forces;                  !compute mp2 gradient for first monomer
add,-1                   !subtract from previous gradient

text, DIMER CALCULATION
dummy                    !reset dummies
{hf;accu,16}             !scf for dimer
mp2;                     !mp2 for dimer
edimer=energy            !save mp2 energy in variable
forces;                  !compute mp2 gradient for dimer
add,1                    !add to previous gradient

optg,gradient=1.d-5,startcmd=label:   !find next energy

text,optimized geometry parameters
show,rhf,rff,theta1,theta2

text,computed interaction energies
de=(edimer-ehf1-ehf2)*tocm     !CPC corrected interaction energy with fixed monomers
```

http://www.molpro.net/info/current/examples/hfdimer_cpcopt2.com

47 HARMONIC VIBRATIONAL FREQUENCIES (`FREQUENCIES`)

`FREQUENCIES`,*options*,

Calculate harmonic vibrational frequencies and normal modes. For the calculation of anharmonic vibrational frequencies see sections 52 to 55. The hessian is calculated analytically or numerically by finite differences in 3N cartesian coordinates (Z-Matrix coordinates will be destroyed on entry). If analytic gradients are available these are differentiated once to build the hessian, otherwise the energy is differentiated twice. If for the wavefunction method dipole moments are available, the dipole derivatives and the IR intensities are also calculated. Note that numerical hessians cannot be computed when dummy atoms holding basis functions are present. To get reasonable results it is necessary to do a geometry optimization before using the frequency calculation.

47.1 Options

The following *options* are available:

`ANALYTICAL`	Use analytical second derivatives of the energy. At present, analytical second derivatives are only possible for closed shell Hartree-Fock (HF) and MCSCF wavefunctions without symmetry. It is not yet possible to calculate IR-intensities analytically. Note that, due to technical reasons, the analytical MCSCF second derivatives have to be computed in the MCSCF-program using e.g. `multi; cpmcscf,hess` (see `MULTI`) before they can be used in `FREQUENCIES`. If analytical MCSCF second derivatives have been computed using `multi; cpmcscf,hess`, `FREQUENCIES` will use them by default.
`CENTRAL`	Use central differences/high quality force constants (default).
`NUMERICAL`	Differentiate the energy twice, using central differences.
`FORWARD`	Use forward differences/low quality force constants (only effective if gradients are available).
`SYMM=AUTO|NO`	During the numerical calculation of the hessian, the symmetry of the molecule may be lowered. Giving `SYMM=AUTO` the program uses the maximum possible symmetry of the molecular wavefunction in each energy/gradient calculation, and this option therefore minimizes the computational effort. With `SYMM=NO` no symmetry is used during the frequency calculation (default). For single reference calculations like HF, MP2, CCSD, RCCSD the `AUTO` option can be safely used and is recommended. However, the `AUTO` option cannot be used for multireference methods (MCSCF/MRCI/ACPF/AQCC/RS2). If given, the option is disabled in these cases. For these methods frequency calculations are only possible without symmetry. Symmetry is turned off atomically if the state symmetry is 1. Note that this may fail if there are lower states in other symmetries. Use of `RESTRICT`, `SELECT`, `REF`, `PROJECT`, `LOCAL`, state-averaged MCSCF will lead on errors unless the calculation is performed in C_1 symmetry In such cases the whole calculation must be done without symmetry.
`AUTO`	Same as `SYMM=AUTO`, see above.
`NOAUTO|NOSYM`	Same as `SYMM=NO`, see above.

HESSREC|SAVE=*record* Save hessian to *record*. By default the hessian is saved on record 5300.2.

FREQREC=*record* Save frequencies and normal modes to *record* (default 5400.2) This information is used, e.g., by the VSCF/VCI program.

TASKREC=*record* Save task information in numerical hessian calculation to the given record. This information is required for a restart of a numerical hessian calculation. By default, the information is saved on record 5500.2.

READ Read hessian from default hessian record.

READ|START=*record* Use hessian from previously saved on *record*. If the hessian has been computed for the current method and geometry already, it is used by default.

RESTART Attempt to restart a previous numerical frequency/hessian calculation using default task record.

RESTART=*record* Attempt to restart a previous numerical frequency/hessian calculation using task record *record*.

LOW=*value* Threshold for printing low frequencies in cm^{-1}. If this option is given, frequencies below the given value are not printed. By default, all frequencies are printed.

STEP=*value* Determines the step size of the numerical differentiation of the energy or the gradient. The default step size is 0.01 a.u.

MAXTASK=*value* Stop the calculation if the number of tasks is exceeded (the calculation can be restarted later).

MAXCPU=*value* Stop the calculation if the given CPU-time (in sec) exceeded (the calculation can be restarted later).

NEW Recompute hessian, even if a hessian is already available.

PROJECT Project rotations and translations out of the hessian (default).

NOPROJECT Don't project rotations and translations out of the hessian.

PRINT=*value* Print option. If *value* is greater or equal to zero, the hessian and other information is printed (default -1).

DEBUG Print Debug information, same as PRINT=1.

SCALE=*value* Scaling factor for frequencies. The scaled frequencies are used to compute the ZPE and thermodynamic properties.

For compatibility with older MOLPRO versions many of the options can also be set using directives, as described in the following sections.

47.2 Printing options (PRINT)

PRINT,*options*

This directive can be used to control the output:

The following *options* can be given:

HESSIAN Print the force constant matrix (hessian) i.e. the second derivative matrix of the energy and the mass weighted hessian matrix.

LOW	Print low vibrational frequencies (i.e. the 5 or 6 frequencies belonging to rotations and translations) and their normal modes (default; LOW=-1 suppresses the print).
LOW=*value*	Threshold for printing low vibrations in cm^{-1} (default 150). If a value > 0 is given, frequencies below this value are not printed.

47.3   Saving the hessian and other information (SAVE)

SAVE,*options*

The following *options* can be given:

hessian=*record*	Save hessian to *record* (same effect as option HESSREC). By default the hessian is saved on record 5300.2.
FREQ=*record*	Save frequencies and normal modes to *record* (same effect as option FREQREC). By default the frequencies are saved on record 5400.2.
TASK=*record*	Save task information for possible restart of hessian calculation to *record* (same effect as option TASKREC). By default the frequencies are saved on record 5500.2.

47.4   Restarting a hessian/Frequency calculation (START)

START,*options*

The following options can be given:

HESSIAN=*record*	Read hessian from record *record* (same effect as option READHESS).
TASK=*record*	Read task information from record *record* and restart numerical hessian calculation (same effect as option RESTART).

47.5   Coordinates for numerical hessian calculations (COORD)

COORD,*type*

type can be one of the following:

UNIQUE	Use symmetry-unique displacements in the numerical calculation of the hessian (default).
3N	Don't use symmetry-unique displacements (not recommended).

47.6   Stepsizes for numerical hessian calculations (STEP)

[STEP,*rstep*]

determines the step size of the numerical differentiation of the energy or the gradient. The default step size is *rstep*=0.01 a.u.

47.7 Numerical hessian using energy variables (VARIABLE)

VARIABLE,*name*;

Defines a variable *name* which holds the energy value to be used for computing the hessian using finite differences. By default, this is ENERGY(1) as set by the most recent program. For other other variables which can be used see section 46.2.17. Note that numerical hessians cannot be computed when dummy atoms holding basis functions are present.

47.8 Thermodynamical properties (THERMO)

It is also possible to calculate the thermodynamical properties of the molecule. Since MOLPRO can only handle Abelian point groups it is necessary to give the point group of the molecule in the input file:

THERMO,[SYM=*pointgroup*],[TEMP=*value*], [PRESS=*value*], [TMIN=*value*, TMAX=*value*, TSTEP=*value*]

pointgroup has to be the Schoenflies Symbol (e.g. C3v for ammonia; linear molecules have to be C*v or D*h respectively). If no point group is given, the point group is determined automatically, but only Abelian groups (D2H and subgroups) are recognized. If the molecule has higher symmetry this may eventually cause deviations in the rotational entropy.

The temperature (in K), pressure (in atm) or a range of temperatures (in K) can be given as options.

If no temperature or pressure is specified the zero-point vibrational energy and the enthalpy $H(T) - H(0)$ [kJ/mol], heat capacity C_v [J/mol K] and entropy S [J/mol K] are calculated for standard temperature and pressure ($T = 298.150$ [K], $p = 1$ [atm]).

The FREQUENCIES program sets the variable ZPE containing the zero-point-energy of the harmonic vibrations in atomic units. If the THERMO option is used, the variables HTOTAL and GTOTAL, containing the enthalpy and the free enthalpy of the system in atomic units, are also set.

47.9   Examples

```
***,formaldehyde freqency calculation
memory,8,m

basis=vdz
gthresh,energy=1.d-8

geomtyp=xyz
symmetry,nosym
geometry={
   4
FORMALDEHYDE
C         0.0000000000        0.0000000000       -0.5265526741
O         0.0000000000        0.0000000000        0.6555124750
H         0.0000000000       -0.9325664988       -1.1133424527
H         0.0000000000        0.9325664988       -1.1133424527
}

hf;accu,14
optg;coord,3n;

{frequencies,analytic
thermo,sym=c2v
print,thermo}

mp2
optg;coord,3n
{frequencies
thermo,sym=c2v
print,thermo}
```

    http://www.molpro.net/info/current/examples/form_freq.com

```
***, Phosphorous-pentafluoride Vibrational Frequencies
memory,1,m
basis=3-21G

geomtyp=xyz         ! use cartesian coordinates xmol style
symmetry,nosym      ! don't use symmetry
geometry={          ! geometry input
6
  PF5
  P       0.00000        0.00000        0.00000
  F       0.00000        1.11100       -1.12400
  F       0.00000       -1.52800       -0.40100
  F       0.00000        0.41700        1.52500
  F      -1.60400        0.00000        0.00000
  F       1.60400        0.00000        0.00000}

rhf
optg               ! optimize geometry

frequencies        ! calculate vibrational frequencies
print,low          ! print frequencies+modes of zero frequencies
thermo,sym=d3h     ! calculate thermodynamical properties
temp,200,400,50    ! temperature range 200 - 400 [K]
---
```

    http://www.molpro.net/info/current/examples/pf5_freq.com

48 CHEMICAL SHIELDINGS, MAGNETIZABILITY, AND ROTATIONAL g-TENSOR

Bibliography:

[1] S. Loibl, F.R. Manby, M. Schütz, *Density fitted, local Hartree-Fock treatment of NMR chemical shifts using London atomic orbitals*, Mol. Phys. **108**, 477 (2010).

[2] S. Loibl and M. Schütz, *NMR shielding tensors for density fitted local second-order Møller-Plesset perturbation theory using gauge including atomic orbitals*, J. Chem. Phys. **137**, 084107 (2012).

[3] S. Loibl and M. Schütz, *Magnetizability and rotational g tensors for density fitted local second-order Møller-Plesset perturbation theory using gauge-including atomic orbitals*, J. Chem. Phys. **141**, 024108 (2014).

All publications resulting from use of this program must acknowledge the above.

The command `nmrshld` invokes the calculation of NMR chemical shielding tensors at the level of (local) density-fitted HF (GIAO-DF-HF) or local density-fitted MP2 (GIAO-DF-LMP2). Note: Chemical shieldings at the level of MP2 are only implemented for DF-LMP2.

For the calculation of the chemical shieldling tensor a preceding DF-HF, respectively, DF-LMP2 calculation is required. Symmetry has to be set to `nosym`. For the GIAO-DF-HF code one can use canonical orbitals from the DF-HF run or localized orbitals (recommended).
Example:

```
***,Chemical shielding tensors for water molecule
symmetry,nosym
GEOMETRY={    !geometry input
h1;o,h1,r1;h2,o,r2,h1,theta}
r1=0.9583 ang
r2=0.9583 ang
theta=104.2
basis={       !specify basis
default,cc-pVDZ
set,mp2fit
default,vdz/mp2fit
set,jkfit
default,vdz/jkfit
}
df-hf,df_basis=jkfit
df-lmp2,df_basis=mp2fit
nmrshld;comp      !invoke calculations of shieldings, print the components
```

The shielding calculation returns the chemical shielding tensors σ and a summary of the chemical shifts (i.e. the arithmetic mean of the diagonal elements) for each nucleus in the order they were specified in the geometry input. The directive `comp` additionally prints the diamagnetic and paramagnetic contributions (for further information see R. Ditchfield, Mol. Phys. 27(4), 789 (1974)) for all shielding tensors.

Additionally, the calculation of magnetizabilities and rotational *g* tensors has been implemented: the command `magprop` invokes the calculation of magnetizabilities and chemical shielding tensors. The directive `comp` can be specified. The command `magnetiz` invokes a pure magnetizability calculation. Note that a pure magnetizability calculation takes nearly as long as a chemical shielding calculation and hence does not provide any advantage in comparison to `magprop`. See also the input examples `gly1_mag.com` and `h2o_mag.com`.

If one is interested in the calculation of rotational *g* tensors the molecule has to be aligned in the

principal axis system with the command `orient,mass`. Otherwise, the results are meaningless.

49 MINIMIZATION OF FUNCTIONS

The minimization of general functions of one or more variables can be carried out using the command:

`MINIMIZE,` *func, x_1* [, x_2, x_3, ...]

where *func* represents a function of up to 50 variables x_1, x_2, ... Two different optimization methods can be selected as described below which do or do not use numerical derivative information.

The optimization method, as well as finer control over *func*, can be chosen using the `METHOD` directive

`METHOD,` *key* [, *key1=value, key2=value, ...*]

where *key* defines the optimization method. Valid options for *key* are:

`BFGS`	Broyden-Fletcher-Goldfarb-Shanno conjugate gradient method, which uses numerical gradients (default)
`SIMPLEX`	Downhill simplex method, which uses only function evaluations

Options to these methods, *key1, key2, ...*, are:

`VARSCALE=`*vscale*	Optimization in space of scaled variables. *vscale=0* no scaling (not recommended) *vscale=1* optimization in the space of ln(x) *vscale=2* optimization in space of initial value scaling, e.g., x_1/x_{1i} (default)
`THRESH=`*thresh*	Required accuracy of either the gradient (BFGS) or parameters (SIMPLEX). The default is $1 \cdot 10^{-4}$ for BFGS and $1 \cdot 10^{-2}$ for SIMPLEX. Note that previously this pertained to the function value in the Simplex case.
`VSTEP=`*epsd*	Step size for numerical gradients (BFGS) or initial SIMPLEX vertices
`PROC=`*procname*	Specifies the procedure to be executed in each optimization step. This defines a complete function evaluation (if needed, numerical gradients will be evaluated using this procedure as well)
`STARTCMD=`*command*	Specifies a start command. In each optimization step all input beginning with *command* to the current `MINIMIZE` is processed.

Miscellaneous directives (separated by semicolons or line breaks)

`MAXIT,`*maxit*	maximum number of optimization cycles. The default is 30 for BFGS and 100 for SIMPLEX.

49.1   Examples

49.1.1   Geometry optimization

```
***, Simple geometry optimization

basis=vdz

geometry={
O
H 1 r
H 1 r 2 theta}

r=1.8
theta=104

hf
mp2

{minimize,energy,r,theta}
---
```

   http://www.molpro.net/info/current/examples/min_optgeo.com

49.1.2   Basis function optimizations

```
***, Optimization of 2 d functions

geometry={Ne}

dexp=[2.0,1.0]

basis={
sp,Ne,vdz;c;
d,Ne,dexp(1),dexp(2)
}

hf
mp2
eval=energy

minimize,eval,dexp(1),dexp(2)
---
```

http://www.molpro.net/info/current/examples/basisopt_simple.com

```
***, Optimization of 2 d functions

geometry={Ne}

dexp=[2.0,1.0]

{minimize,eval,dexp(1),dexp(2)
method,bfgs,varscale=1,thresh=1e-5,proc=optd}


proc optd

basis={
sp,Ne,vdz;c;
d,Ne,dexp(1),dexp(2)
}

hf
mp2
eval=energy

endproc
```

  http://www.molpro.net/info/current/examples/basisopt_proc.com


```
***, MP2 optimization of core-valence cc-pCVDZ functions

geometry={Ne}

sexp=20.
pexp=30.

{minimize,ecv,sexp,pexp
method,bfgs,varscale=1,thresh=1e-5,proc=myopt}


proc myopt

basis={
spd,Ne,vdz;c;
s,Ne,sexp
p,Ne,pexp
}

hf
{mp2;core,1}
eval=energy

{mp2;core,0}
eall=energy

ecv=eall-eval

endproc
```

  http://www.molpro.net/info/current/examples/basisopt_cv.com

50 INSTANTONS

Instantons can be located within the ring-polymer formalism using the INSTANTON command:
INSTANTON[, *key1=value*, *key2=value*, . . .]

These instantons can be used to compute either the thermal reaction rate or the tunnelling splitting between degenerate potential wells. The behaviour can be controlled with the `splitting` option. It is a good idea to turn symmetry off (using `nosym`) during the calculation as the ring-polymer beads do not necessarily share the same symmetry operations as the transition state or well minima.

50.1 Thermal reaction rates

Quantum rate calculations proceed via an instanton which is equivalent to the transition state on the ring-polymer surface. These stationary points are computed using a quasi-Newton saddle-point search with Powell's Hessian update. Because of the known symmetry of the final geometry (that the ring polymer folds back on itself), only half of the beads need be specified.

The geometry of the transition state should be specified with the `geometry` keyword, and the classical TST rate through this point is compared with the rate computed from the instanton. The action of the instanton, its fluctuations and rotations are printed to the output file. MOLPRO computes the tunnelling factor which is the ratio of these rates and the rate itself can be calculated if the reactant partition function is known. It is necessary to converge the results in the large-*N* limit.

References for the ring-polymer instanton method are:

- J. O. Richardson and S. C. Althorpe. "Ring-polymer molecular dynamics rate-theory in the deep-tunneling regime: Connection with semiclassical instanton theory." *J. Chem. Phys.* **131**, 214106 (2009).

50.2 Tunnelling splittings

Instantons used to compute tunnelling splittings are local minima on the ring-polymer surface. They are located using the limited-memory Broyden-Fletcher-Goldfarb-Shanno (L-BFGS) method. All publications describing work using this method should quote at least one of these references:

- J. Nocedal. "Updating quasi-Newton matrices with limited storage". *Math. Comput.* **35**, 773 (1980).

- D. C. Liu and J. Nocedal. "On the limited memory BFGS method for large scale optimization". *Math. Program.* **45**, 503 (1989).

The geometry of the well minimum should be specified with the `geometry` keyword. The action of the instanton, its fluctuations and the fluctuations about the well minimum are printed to the output file. MOLPRO computes the tunnelling-matrix element which can be used to construct the tunnelling-splitting pattern for a molecular cluster with two or more degenerate wells as described in the latter of the two references. It is necessary to converge the results in the limit that $\beta \to \infty$ and $\beta/N \to 0$.

References for the ring-polymer instanton method are:

- J. O. Richardson and S. C. Althorpe. "Ring-polymer instanton method for calculating tunneling splittings." *J. Chem. Phys.* **134**, 054109 (2011).

- J. O. Richardson, S. C. Althorpe and D. J. Wales. "Instanton calculations of tunneling splittings for water dimer and trimer." *J. Chem. Phys.* **135**, 124109 (2011).

50.3   Input file

An input file should be supplied in `xyz` format containing the Cartesian coordinates (in Ångstroms) of the beads used to initialize the instanton optimization. A rate calculation requires $N/2$ beads, whereas a tunnelling-splitting calculation requires N. The first line contains the number of atoms in the system and the second has two numbers: N, the number of beads, and T, temperature in Kelvin (for the case of a rate calculation) or β, the reciprocal temperature in atomic units (for the case of a tunnelling-splittings calculation). These two lines appear before the coordinates of each bead which are given one atom per line including the element symbol.

50.4   Procedures

A few procedures must be defined. `beadpot` defines the method for computing the potential energy of a single bead geometry. `beadgrad` gives the method for computing the gradient for a bead using the `force` command. `beadfreq1`, `beadfreq2` and `beadfreq3` define methods for computing frequencies of the transition state/well minimum, of the initial (pre-optimized) ring-polymer beads and of the final (optimized) beads. Because the procedure `beadfreq1` is only called once directly after `beadpot`, it is not necessary to recalculate the wavefunction in this case. For the tunnelling-splitting calculations, `beadfreq2` is not used as the L-BFGS optimization proceeds without a Hessian.

50.5   Options

SPLITTING	runs the tunnelling splitting calculation instead of a rate calculation. The default is False.
INPUT=*filename*	file containing initial instanton geometry in format described in section 50.3. The default is initial.xyz.
OUTPUT=*filename*	file containing final instanton geometry in format described in section 50.3. The default is final.xyz.
REACTANT=*value*	value of potential (in E_h) of reactant states used to scale the instanton action in a rate calculation only. The default is 0.
MAXIT=*integer*	maximum number of optimization cycles. The default is 50.
GRADIENT=*value*	required accuracy of the optimized ring-polymer gradient. The default is $3 \cdot 10^{-4}$.
STEPMAX=*value*	maximum allowed step (in bohr) in the quasi-Newton instanton optimization. Attempted steps larger than this are scaled down. The default is $0 \cdot 3\, a_0$.
MSAVE=*integer*	number of gradients saved from previous iterations used in the L-BFGS optimization. The default is 3.
READ	Reads initial (pre-optimized) Hessian from file `$TMPDIR/instanton.hess`, which is automatically created from the final geometry of the previous run, instead of calling `beadfreq2`. The default is False.
READ	Uses a banded-matrix eigensolver in the quasi-Newton optimization. The default is False.

50.6 Parallelization

The ring-polymer instanton approach is naturally parallelized by computing the energies and gradients of each bead on separate processors. It is necessary to run MOLPRO with the `--mppx` flag and it is recommended for the number of processors used to be a factor of the number of beads.

50.7 Examples

Here we give an example for calculating the rate of the $H + H_2 \rightarrow H_2 + H$ reaction at 250 K using MRCI. The MOLPRO input file is

```
***, H + H2 instanton
if(NPROC_MPP.gt.1) then
skipped
endif

proc beadpot={
hf
casscf
mrci
}

proc beadgrad={
beadpot
force,numerical,dstep=1e-4
}

proc beadfreq1={
frequencies
}
proc beadfreq2={
beadpot
frequencies,forward
}
proc beadfreq3={
beadpot
frequencies,print=0
}

nosym

geometry={ ! optimized geometry at transition state
    3
 MRCI/VDZ   ENERGY=-1.64651538 ! comment line
 H         -0.9401271688        0.0000000000        0.0000000000
 H          0.0033328462        0.0000000000        0.0000000000
 H          0.9467943226        0.0000000000        0.0000000000
}

mass,isotope,print
basis=vdz

instanton, input='instanton_initial.xyz', \\
   output='instanton_final.xyz', reactant=-1.66295138342, \\
   save='instanton_ts.dat', hessfile='instanton.hess'
!table,action,perm,rotratio,fluctratio,tunfac
text, $action    $perm    $rotratio    $fluctratio    $tunfac
```

   http://www.molpro.net/info/current/examples/instanton.com

and an initial 16-bead half ring-polymer geometry is given in `instanton_initial.xyz`, which can be found in the examples directory.

An example calculation of the tunnelling splitting in the HO_2 cluster using UHF is provided by the input files

```
***, hydroperoxyl HO2 splitting instanton
if(NPROC_MPP.gt.1) then
skipped
endif
FILE,2,ho2inst.wfu,new

proc beadpot={
uhf
}

proc beadgrad={
beadpot
force
}

proc beadfreq1={
frequencies
}
proc beadfreq3={
beadpot
frequencies
}

geometry={ ! optimized geometry at well minimum
    3
 UHF-SCF002/VDZ  ENERGY=-150.16631226 ! comment line
H 0.904294157899999895 0.919502897200000113 0
O 0.681281911699999965 -0.00702956160000003938 0
O -0.683576069499999939 0.00706386439999998061 0
}

mass,isotope,print
basis=vdz

instanton, splitting, input='splitting_initial.xyz', \\
   output='splitting_final.xyz', maxit=200
table,action,fluctratio,tunsplit*1e9
```

> http://www.molpro.net/info/current/examples/splitting.com

where an initial 32-bead linear-polymer geometry is given in `splitting_initial.xyz`, which can be found in the examples directory.

In both examples, data is saved to a `.wfu` file. If another instanton calculation at a different temperature or with a different number of beads is run, some information can be recovered by using `frequencies,read=5300.2` in `beadfreq1`.

51 BASIS SET EXTRAPOLATION

Basis set extrapolation can be carried out for correlation consistent basis sets using

```
EXTRAPOLATE,BASIS=basislist,options
```

where basislist is a list of at least two basis sets separated by colons, e.g. AVTZ:AVQZ:AV5Z. Some extrapolation types need three or more basis sets, others only two. The default is to use n^{-3} extrapolation of the correlation energies, and in this case two subsequent basis sets and the corresponding energies are needed. The default is not to extrapolate the reference (HF) energies; the value obtained with the largest basis set is taken as reference energy for the CBS estimate. However, extrapolation of the reference is also possible by specifying the METHOD_R option.

The simplest way to perform extraplations for standard methods like MP2 or CCSD(T) is to use, e.g.

```
***,H2O
memory,32,m
gthresh,energy=1.d-8

r =   0.9572 ang, theta =  104.52
geometry={O;
          H1,O,r;
          H2,O,r,H1,theta}

basis=avtz
hf
ccsd(t)
extrapolate,basis=avqz:av5z

table,basissets,energr,energy-energr,energy
head,basis,ehf,ecorr,etot
```

This will perform the first calculation with AVTZ basis, and then compute the estimated basis set limit using the AVQZ and AV5Z basis sets. The correlation energy obtained in the calculation that is performed immediately before the extrapolate command will be extrapolated (in this case the CCSD(T) energy), and the necessary sequence of calculations [here HF;CCSD(T)] will be automatically carried out.

The resulting energies are returned in variables ENERGR (reference energies), ENERGY (total energies), and ENERGD (Davidson corrected energy if available); the corresponding basis sets are returned in variable BASISSETS. The results can be printed, e.g., in a table as shown above, or used otherwise. The above input produces the table

```
BASIS       EHF           ECORR          ETOT
AVQZ    -76.06600082  -0.29758099  -76.36358181
AV5Z    -76.06732050  -0.30297495  -76.37029545
CBS     -76.06732050  -0.30863418  -76.37595468
```

The extrapolated total energy is also returned in variable ECBS (ECBSD for Davidson corrected energy if available).

In order to extrapolate the HF energy as well (using exponential extrapolation), three energies are needed. One can modify the input as follows:

```
extrapolate,basis=avtz:avqz:av5z,method_r=ex1,npc=2
```

method_r determines the method for extrapolating the reference energy (in this case a single exponential); npc=2 means that only the last two energies should be used to extrapolate the correlation energy (by default, a least square fit to all given energies is used). This yields

```
BASIS           EREF              ECORR             ETOT
AVTZ          -76.06061330      -0.28167606      -76.34228936
AVQZ          -76.06600082      -0.29758099      -76.36358180
AV5Z          -76.06732050      -0.30297495      -76.37029545
CBS           -76.06774863      -0.30863419      -76.37638283
```

Rather than using the default procedure as above, one can also specify a procedure used to carry out the energy calculation, e.g.

```
extrapolate,basis=avtz:avqz:av5z,proc=runccsd, method_r=ex1,npc=2}

procedure runccsd
hf
ccsd(t)
endproc
```

Alternatively, the energies can be provided via variables EREF, ECORR, ETOT etc. These must be vectors, holding as many values as basis sets are given.

51.1   Options

The possible options and extrapolation methods are:

BASIS=*basissets*	Specify as set of correlation consistent basis sets, separated by colons.
PROC=*procname*	Specify a procedure to run the energy calculations
STARTCMD=*command*	Start command for the energy calculations: the sequence of commands from STARTCMD and the current EXTRAPOLATE is run. STARTCMD must come before the extrapolate command in the input.
METHOD=*key*	Specifies a keyword to define the extrapolation function, see section 51.2.
METHOD_C=*key*	Specifies a keyword to define the extrapolation function for the correlation energy, see section 51.2.
METHOD_R=*key*	Specifies a keyword to define the extrapolation function for the reference energy, see section 51.2.
VARIABLE=*name*	Specifies a variable name; this variable should contain the energies to be extrapolated.
ETOT=*variable*	Provide the total energies in *variable* (a vector with the same number of energies as basis sets are given) If only ETOT but not EREF is given, the total energy is extrapolated.
EREF=*variable*	Provide the reference energies to be extrapolated in *variable* (a vector with the same number of energies as basis sets are given)
ECORR=*variable*	Provide the correlation energies to be extrapolated in *variable* (a vector with the same number of energies as basis sets are given)
ECORRD=*variable*	Provide the Davidson corrected correlation energies to be extrapolated in *variable* (a vector with the same number of energies as basis sets are given). If both ECORR and ECORRD are given, both will be extrapolated.
MINB=*number*	First basis set to be used for extrapolation (default 1)

MAXB=*number*	Last basis set to be used for extrapolation (default number of basis sets)
NPR=*number*	If given, the last NPR values are used for extrapolating the reference energy. NPR must be smaller or equal to the number of basis sets.
NPC=*number*	If given, the last NPC values are used for extrapolating the reference energy. NPC must be smaller or equal to the number of basis sets.
XR=*array*	Provide a vector of exponents to be used for defining the extrapolation functional for the reference energy when using the LX functional.
XC=*array*	Provide a vector of exponents to be used for defining the extrapolation functional for the correlation energy when using the LX functional.
PR=*array*	Provide the constant p to be used for defining the extrapolation functional for the reference energy.
PC=*array*	Provide the constant p to be used for defining the extrapolation functional for the correlation energy.

51.2 Extrapolation functionals

The extrapolation functional is chosen by a keyword with the METHOD, METHOD_R, and/or METHOD_C options. The default functional is L3. In the following, n is the cardinal number of the basis set (e.g., 2 for VDZ, 3 for VTZ etc), and x is an arbitrary number. p is a constant given either by the PR or PC options (default $p = 0$). X is a number or a vector given either by the XR or XC options (only for LX; nx is the number of elements provided in X). A, B, A_i are the fitting coefficients that are optioized by least-squares fits.

Lx	$E_n = E_{\text{CBS}} + A \cdot (n + p)^{-x}$
LHx	$E_n = E_{\text{CBS}} + A \cdot (n + \frac{1}{2})^{-x}$
LX	$E_n = E_{\text{CBS}} + \sum_{i=1}^{nx} A_i \cdot (n + p)^{-x(i)}$
EX1	$E_n = E_{\text{CBS}} + A \cdot \exp(-C \cdot n)$
EX2	$E_n = E_{\text{CBS}} + A \cdot \exp(-(n-1)) + B \cdot \exp(-(n-1)^2)$
KM	Two-point formula for extrapolating the HF reference energy, as proposed by A. Karton and J. M. L. Martin, Theor. Chem. Acc. **115**, 330 (2006): $E_{\text{HF,n}} = E_{\text{HF,CBS}} + A(n+1) \cdot \exp(-9\sqrt{n})$. Use METHOD_R=KM for this.

The following example shows various possibilities for extrapolation:

```
***,h2o
memory,32,m

gthresh,energy=1.d-9
basis=avtz

r =   0.9572 ang, theta =  104.52
geometry={!nosym
         O;
         H1,O,r;
         H2,O,r,H1,theta}

hf
{ccsd(t)}
text,compute energies, extrapolate reference energy using EX1 and correlation energy using L3
extrapolate,basis=avtz:avqz:av5z,method_c=l3,method_r=ex1,npc=2

ehf=energr(1:3)
etot=energy(1:3)

text,extrapolate total energy using EX2
extrapolate,basis=avtz:avqz:av5z,etot=etot,method=ex2

text,extrapolate reference energy by EX1 and correlation energy by EX2
extrapolate,basis=avtz:avqz:av5z,etot=etot,method_c=ex2,eref=ehf,method_r=ex1

text,extrapolate reference energy by EX1 and correlation energy by LH3
extrapolate,basis=avtz:avqz:av5z,etot=etot,method_c=LH3,eref=ehf,method_r=ex1,npc=2

text,extrapolate reference energy by EX1 and correlation energy by LX
extrapolate,basis=avtz:avqz:av5z,etot=etot,method_c=LX,eref=ehf,method_r=ex1,xc=[3,4],pc=0.5
```

http:
//www.molpro.net/info/current/examples/h2o_extrapolate_ccsd.com

The second example shows extrapolations of MRCI energies. In this case both the MRCI and
the MRCI+Q energies are extrapolated.

```
***,h2o
memory,32,m

gthresh,energy=1.d-9
basis=avtz

r =   0.9572 ang, theta =  104.52
geometry={
        O;
        H1,O,r;
        H2,O,r,H1,theta}

hf
multi
mrci
text,Compute energies, extrapolate reference energy using EX1 and correlation energy using L3;
text,The Davidson corrected energy is also extraplated
extrapolate,basis=avtz:avqz:av5z,method_c=l3,method_r=ex1,npc=2

emc=energr
ecorr_mrci=energy-emc
ecorr_mrciq=energd-emc

text,Extrapolate reference energy by EX1 and correlation energy by LH3
text,The Davidson corrected energy is also extraplated
extrapolate,basis=avtz:avqz:av5z,ecorr=ecorr_mrci,ecorrd=ecorr_mrciq,method_c=LH3,eref=emc,met
```

http:
//www.molpro.net/info/current/examples/h2o_extrapolate_mrci.com

51.3   Geometry optimization using extrapolated energies

Geometry optimizations are possible by using numerical gradients obtained from extrapolated energies. Analytical energy gradients cannot be used.

The following possibilities exist:

1.) If OPTG directly follows the EXTRAPOLATE command, the extrapolated energy is optimized automatically (only variable settings may occur between EXTRAPOLATE and OPTG).

Examples:

Extrapolating the energy for the last command:

```
geometry={o;h1,o,r;h2,o,r,h1,theta}
theta=102
r=0.96 ang
basis=vtz

hf
ccsd(t)
extrapolate,basis=vtz:vqz

optg
```

http:
//www.molpro.net/info/current/examples/h2o_extrapol_opt1.com

Extrapolating the energy computed in a procedure:

```
geometry={o;h1,o,r;h2,o,r,h1,theta}
theta=102
r=0.96 ang

proc ccsdt
hf
ccsd(t)
endproc

extrapolate,basis=vtz:vqz,proc=ccsdt

optg
```

http:
//www.molpro.net/info/current/examples/h2o_extrapol_opt2.com

Note that this is not possible if EXTRAPOLATE gets the input energies from variables.

2.) Using a procedure for the extrapolation:

By default, variable `ECBS` is optimized, but other variables (e.g. `ECBSD`) can be specified using the `VARIABLE` option on the `OPTG` command.

```
geometry={o;h1,o,r;h2,o,r,h1,theta}
theta=102
r=0.96 ang
basis=vtz

proc cbs34
hf
ccsd(t)
extrapolate,basis=vtz:vqz
endproc

optg,variable=ecbs,proc=cbs34
```

```
geometry={o;h1,o,r;h2,o,r,h1,theta}
theta=102
r=0.96 ang

proc cbs34
basis=vtz
hf
ccsd(t)
eref(1)=energr
ecc(1)=energy

basis=vqz
hf
ccsd(t)
eref(2)=energr
ecc(2)=energy
extrapolate,basis=vtz:vqz,eref=eref,etot=ecc
endproc

optg,variable=ecbs,proc=cbs34
```

51.4 Harmonic vibrational frequencies using extrapolated energies

This is possible by defining the extrapolation in a procedure:

```
geometry={o;h1,o,r;h2,o,r,h1,theta}
theta=102
r=0.96 ang
basis=vtz

proc cbs34
hf
ccsd(t)
extrapolate,basis=vtz:vqz
endproc

optg,variable=ecbs,proc=cbs34
freq,variable=ecbs,proc=cbs34
```

http:
//www.molpro.net/info/current/examples/h2o_extrapol_freq.com

52 POTENTIAL ENERGY SURFACES (SURF)

SURF,Start1D=label,options

The SURF program allows for the calculation of the potential energy surface around a reference structure as required for the calculation of anharmonic frequencies (see the VSCF and VCI programs). The reference structure is supposed to be a (local) minimum or a transition state of a double-minimum potential. The potential is represented by energy grid points rather than an analytical representation. Within the SURF program the potential energy surface is expanded in terms of normal coordinates, linear combination of normal coordinates or localized normal coordinates. Consequently, a harmonic frequency calculation needs to be performed first. The potential will then be represented by a multi-mode expansion, i.e. a hierarchical scheme given by

$$V(q_1,\ldots,q_{3N-6}) = \sum_i V_i(q_i) + \sum_{i<j} V_{ij}(q_i,q_j) + \sum_{i<j<k} V_{ijk}(q_i,q_j,q_k) + \ldots \tag{60}$$

with

$$V_i(q_i) = V_i^0(q_i) - V(0) \tag{61}$$

$$V_{ij}(q_i,q_j) = V_{ij}^0(q_i,q_j) - \sum_{r \in \{i,j\}} V_r(q_r) - V(0) \tag{62}$$

$$V_{ijk}(q_i,q_j,q_k) = V_{ijk}^0(q_i,q_j,q_k) - \sum_{\substack{r,s \in \{i,j,k\} \\ r>s}} V_{rs}(q_r,q_s) - \sum_{r \in \{i,j,k\}} V_r(q_r) - V(0) \tag{63}$$

$$V_{ijkl}(q_i,q_j,q_k,q_l) = \ldots \tag{64}$$

where q_i denotes the coordinates. This expansion needs to be terminated after an *n*-body contribution as controlled by the keyword NDIM. The SURF program is fully parallelized in a sense that the calculation of different grid points is send to different processors (embarassingly parallel MPPX scheme). The START1D keyword is mandatory and defines the label where to jump in the input in order to do an electronic structure calculation which is terminated by the SURF command. This way the quality of the potential energy surface is defined. For example, the input for the calculation of a CCSD surface looks like:

```
label1
hf
ccsd
surf,start1D=label1
```

The SURF program is based on an iterative algorithm, i.e. grid points will be added automatically to the grid representation of the potential until a convergence threshold will be met. This guarantees a well-balanced description of the different terms in the expansion of the potential and simultaneously minimizes the number of *ab initio* calculations for a representation of the potential. For further details see:

G. Rauhut, *Efficient Calculation of Potential Energy Surfaces for the Generation of Vibrational Wave Functions*, J. Chem. Phys. **121**, 9313 (2004).

T. Hrenar, H.-J. Werner, G. Rauhut *Accurate Calculation of Anharmonic Vibrational Frequencies of Medium Sized Molecules Using Local Coupled Cluster Methods*, J. Chem. Phys. **126**, 134108 (2007).

52.1 Options

The following *options* are available:

NDIM=*n*   The keyword NDIM=*n* terminates the expansion of the PES after the *n*-body term. Currently, at most 4-body terms can be included, but the default is set to 3. Please note, when you use NDIM=4 as a keyword for the SURF program, you need to pass this information to the VSCF and VCI programs also. Otherwise these programs will neglect the 4-body terms.

NGRID=*n*   Based on a coarse grid of *ab initio* points a fine grid will be generated from automated interpolation techniques. The keyword NGRID=*n* determines the number of equidistant grid points in one dimension. NGRID=*n* has to be an even number. The default is currently set to 16. Note that the number of grid points also controls the extension of the *n*-dimensional potential energy surfaces (see keyword SCALE) and thus influences many internal thresholds which are optimized to the default value of NGRID. The number of grid points also determines the number of basis functions in the grid-based VSCF program. At present the maximum grid size is 36.

Grid points	14	16	18	20
Surface extension	4.30	4.69	5.05	5.39

VAR1D=*variable*   The SURF program reads the energy of electronic structure calculations from the internal MOLPRO variables, e.g. ENERGY, EMP2, ... The internal variable is specified by the keyword VAR1D. Within the example shown above, VAR1D=ENERGY would read the CCSD energy, while VAR1D=EMP2 would read the MP2 energy, which is a byproduct of the CCSD calculation. The default for the VAR1D keyword is the internal variable ENERGY.

SYM=*variable*   Symmetry within electronic structure calculations can be exploited by the keyword SYM=Auto. Usually this leads to significant time savings. By default this symmetry recognition is switched off as certain calculations may cause some trouble (e.g. local correlation methods). Symmetry in electronic structure calculations may not be mistaken by the symmetry of the mode-coupling terms (see keyword MPG).

MPG=*n*   Symmetry of the normal modes is recognized by the program automatically. Only Abelian point groups can be handled at the moment. Symmetry of the modes will be determined even if the NOSYM keyword is used in the electronic structure calculations. In certain cases numerical noise can be very high and thus prohibits a correct determination of the symmetry labels. Symmetry can be switched off by using MPG=1.

SCALE=*value*   The extension of the potential energy surfaces is determined from Gauss-Hermite quadrature points. Using a fine grid NGRID=16 the surface stretches out to the NGRID/2th Gauss-Hermite point, i.e. 4.69, in each direction (see keyword NGRID). As these values are fairly large within the calculation of fundamental modes, a scaling factor, SCALE=*f*, has been introduced. A default scaling of 0.75 is used. Increasing the size of the surfaces usually requires the calculation of

further *ab initio* points as the surface interpolation is more stable for surfaces of limited size.

THRFIT=*value* The iterative algorithm for generating potential energy surfaces is based on a successive increase of interpolation points. The iterations are terminated once the interpolation of two subsequent iteration steps became stable. The convergence threshold can be changed by the keyword THRFIT=f. There is currently just one control variable for the different 1D, 2D, 3D, and 4D iterations. The 4 thresholds are different but depend on each other. Consequently, changing the default value (THRFIT=4.0d-2) will change all thresholds simultaneously which keeps the calculation balanced.

FIT1D=*n* The maximum order of the polynomials used for fitting within the iterative interpolation scheme can be controlled by the keywords FIT1D, FIT2D, FIT3D, FIT4D. The default is given by 8. However in certain cases higher values may be necessary, but require an appropriate number of coarse grid points, which can be controlled by MIN1D etc.

MIN1D=*n* The minimum number of coarse grid points can be controlled by the keywords MIN1D, MIN2D, MIN3D, MIN4D. These 4 keywords determine the minimum number of *ab initio* calculations in one dimension for each 1D, 2D, 3D and 4D surface. The defaults are currently MIN1D=4, MIN2D=4, MIN3D=4, MIN4D=4. Presently, values larger than 24 are not supported.

MAX1D=*n* The maximum number of coarse grid points can be controlled by the keywords MAX1D, MAX2D, MAX3D, MAX4D. These 4 keywords determine the maximum number of *ab initio* calculations in one dimension for each 1D, 2D, 3D and 4D surface. The defaults are currently MAX1D=24, MAX2D=16, MAX3D=10, MAX4D=8. Presently, values larger than 24 are not supported.

EXT12D=*value* Outer regions of the potential energy surfaces may be determined by extrapolation rather than interpolation schemes. By default extrapolation is switched off, i.e. Ext12D=1.0 and Ext34D=1.0. However, an extrapolation of 10% in case of the 1D and 2D contributions to the potential (Ext12D=0.9) and of 20% in case of the 3D and 4D terms (Ext34D=0.8) may be useful as it usually stabilizes the fitting procedure.

SKIP3D=*value* As the number of 3D and 4D surfaces can increase very rapidly, there exists the possibility to neglect unimportant 3D and 4D surfaces by the keywords SKIP3D and SKIP4D. The criterion for the prescreening of the 3D surfaces is based on the 2D terms and likewise for the 4D terms the 3D surfaces are used. The neglect of 3D surfaces automatically leads to the neglect of 4D surfaces, as the latter depend on the previous ones. By default prescreening is switched on, but can be switched off by SKIP3D=0.0 and SKIP4D=0.0.

VRC=*n* Once the keyword VRC=1 is provided, the SURF program will also compute the vibrational-rotational coupling surfaces and thus increases the number of degrees of freedom to 3N-3. Vibrational-rotational coupling surfaces can only be used within the PESTRANS program (see below), but will be neglected in any VSCF or VCI calculations.

BATCH3D=*n*   After calculating a number of grid points within the iterative interpolation scheme the convergence of the individual surfaces will be checked and, if provided by the keyword DUMP, dumped to disk. This leads typically to 3-5 iterations and thus the same number of restart points within the calculation of the 1D, 2D, ... surfaces. As the number of 3D and 4D terms can be very large this is not sufficient in these cases. Therefore, the lists of 3D and 4D terms is cut into batches which will be processed subsequently. BATCH3D and BATCH4D control the number of 3D and 4D surfaces within each batch. By default BATCH3D is set to 30 times the number of processors and BATCH4D to 10 times the number of processors. Accordingly the number of restart points is increased. Smaller values for BATCH3D and BATCH4D, e.g. BATCH3D=20, increase the number of restart points on cost of the efficiency of the parallelization.

SADDLE=*n*   Standard SURF calculations expect the reference structure to be a (local) minimum on the PES, i.e. SADDLE=0 (default). Alternatively, one may start the PES generation from a transition state, which is recommended for the calculation of double-minimum potentials. This situation is not recognized automatically and thus requires the keyword SADDLE=1.

TYPE=*variable*   TYPE=QFF calls a macro, which modifies the parameters of the SURF program in order to compute a quartic force field in the most efficient manner. This implies a reduction of the size of the coupling surfaces and a limitation of the maximum number of points for the *n*D-terms. It should be used for VPT2 calculations. TYPE=ZPVE calls a macro, which changes the defaults for several parameters of the SURF, VSCF and VCI programs. It is meant for the quick and efficient calculation of zero point vibrational energies on cost of some accuracy. For example, the expansion of the potential will be truncated after the 2D terms. As a consequence the output of course is reduced to the presentation of the vibrational ground state only. TYPE=FULL (default) performs a standard calculation as needed for VSCF or VCI calculations.

USEMRCC=*n*   Once the MRCC program of M. Kallay is used for determining individual grid points, the option USEMRCC=1 needs to be set, which is needed to ensure proper communication between MOLPRO and MRCC. Default: USEMRCC=0.

DELLOG=*n*   For large molecules or in the case of modelling the 3D and 4D terms, the .log-file may become huge. First of all the .log-file can be directed to scratch within the electronic structure program, i.e. logfile, scratch. The option DELLOG=1 always truncates the .log-file in a way that it contains only the very last energy calculation. Default: DELLOG=0.

INFO=*n*   INFO=1 provides a list of the values of all relevant program parameters (options). Default: INFO=0.

PLOT=*n*   PLOT=*n* plots all *n*D surfaces and a corresponding GNUPLOT script in a separate subdirectory (plots1) in the *home*-directory in order to allow for visualization of the computed *n*D surfaces. E.g. the command "gnuplot plotV1D.gnu" in the plots1 directory produces .eps files for all 1D surfaces. Default: PLOT=0.

The following example shows the input of a calculation which computes energy and dipole surfaces at the MP2/cc-pVTZ level and subsequently determines the anharmonic frequencies at the VSCF and VCI levels. Hartree-Fock calculations will not be restarted and the .log-file is directed to the scratch directory as defined by the $TMPDIR variable.

```
memory,20,m
orient,mass
geometry={
   3
Water
O          0.0675762564      0.0000000000     -1.3259214590
H         -0.4362118830     -0.7612267436     -1.7014971211
H         -0.4362118830      0.7612267436     -1.7014971211
}

mass,iso
basis=vdz
logfile,scratch

hf
mp2
optg
frequencies,symm=auto

label1
{hf
 start,atden}
{mp2
 cphf,1}

{surf,start1D=label1,sym=auto
 intensity,dipole=2}
vscf,combi=1
vci,combi=1
```

52.2 Multi-level calculations

`VMULT`,*options*

The level of the electronic structure calculations can be changed for the different *i*-body terms in the expansion of the potential. As a consequence, the keywords `START2D`, `START3D`, `VAR2D` and `VAR3D` exist in full analogy to the keywords `START1D` and `VAR1D` in standard calculations (see above). The number always represents the level of the expansion term. Such calculations are termed multi-level calculations. There does *not* exist a corresponding set of keywords for the 4-body terms. 4-body terms will always use the variables specified for the 3-body terms.

`MULTI`=*n*   The keywords `START1D`, `START2D`, `START3D` in combination with the commands `VAR1D`, `VAR2D` and `VAR3D` allow for the calculation of multi-level potential energy surfaces. This would imply in principle that the 1D term of the potential needs to be computed at all three levels and the 2D term at two computational levels. As certain low level results are a byproducts of more sophisticated methods (e.g. the HF energy is a byproduct of an MP2 calculation or the MP2 energy is a byproduct of a CCSD(T) calculation) the computational overhead can be avoided by the `MULTI` option.

`MULTI`=1: This is the default and most expensive choice. The 1D potential will be computed at all 3 levels of theory. Likewise, the 2D

potential will be calculated at 2 levels explicitly. An example would be:

```
1D: CCSD(T)/cc-pVTZ
2D: MP4(SDQ)/cc-pVTZ
3D: MP2/cc-pVDZ

{SURF,Start1D=label1
 VMULT,Start2D=label2,Start3D=label3,Multi=1}
```

MULTI=2: All information is provided by the preceding calculations and thus no part of the potential has to be computed twice. Examples:

```
1D: CCSD(T)/cc-pVTZ
2D: CCSD(T)/cc-pVTZ
3D: MP2/cc-pVTZ

{SURF,Start1D=label1
 VMULT,Start2D=label1,Start3D=label2
 VMULT,Var3D=EMP2,Multi=2}


1D: CCSD(T)/cc-pVTZ
2D: MP2/cc-pVTZ
3D: MP2/cc-pVTZ

{SURF,Start1D=label1
 VMULT,Start2D=label2,Start3D=label2
 VMULT,Var2D=EMP2,Var3D=EMP2,Multi=2}
```

MULTI=3: The 2D potential provides all information for the 3D part while there is no connection between 1D and 2D. Consequently, the 1D contributions need to be computed twice (at the 1D and 2D levels) while all other terms will be computed just once. Examples:

```
1D: CCSD(T)/cc-pVTZ
2D: MP4(SDQ)/cc-pVTZ
3D: MP2/cc-pVTZ

{SURF,Start1D=label1
 VMULT,Start2D=label2,Start3D=label3
 VMULT,Var3D=EMP2,Multi=3}


1D: CCSD(T)/cc-pVTZ
2D: MP4(SDQ)/cc-pVTZ
3D: MP4(SDQ)/cc-pVTZ

{SURF,Start1D=label1
 VMULT,Start2D=label2,Start3D=label2,Multi=3}
```

MULTI=4: The 1D calculation provides all information for the 2D potential but does not so for the 3D part. Hence, the 1D contribution and the 2D contributions need to be computed twice. Examples:

```
1D: CCSD(T)/cc-pVTZ
2D: CCSD(T)/cc-pVTZ
3D: MP4(SDQ)/cc-pVTZ

{SURF,Start1D=label1
 VMULT,Start2D=label1,Start3D=label2,Multi=4}
```

```
                      1D: CCSD(T)/cc-pVTZ
                      2D: MP2/cc-pVTZ
                      3D: MP2/cc-pVDZ

                      {SURF,Start1D=label1
                       VMULT,Start2D=label2,Start3D=label3
                       VMULT,Var2D=EMP2,Multi=4}
```

In 2D and 4D calculations (i.e. `NDIM=2,4`) the `VMULT` command can be used as well. In 4D calculations the last level must always be identical to the 3D level. In 2D the meaning of `MULTI=1` and `MULTI=3` is the same. Likewise, `MULTI=2` and `MULTI=4` are the same in case of 2D calculations.

START2D=*label* `START2D` and `START3D` define labels in the input stream in order to compute the 2D and 3D terms at different levels of electronic structure theory than the 1D terms. The use of the `START2D` and `START3D` commands usually requests the use of `GOTO` commands in the input.

VAR2D=*variable* The keywords `VAR2D` and `VAR3D` are defined in full analogy to the `VAR1D` option. They specify the internal variable (e.g. ENERGY, EMP2, CCSD, ...) to be read out for a given grid point.

The following example shows a 1D:CCSD(T)/cc-pVTZ; 2D:MP4(SDQ)/cc-pVTZ and 3D:MP2/cc-pVTZ multi-level calculation. As the MP2 energy is a byproduct of the CCSD(T) and MP4(SDQ) calculations only the 1D grid points will be computed twice (at the CCSD(T) and MP4(SDQ) levels). The 1D and 2D energies will be obtained from the internal variable ENERGY while the 3D energies make use of the EMP2 variable.

```
memory,50,m
orient,mass
geometry={
6
Ethene
C         0.0000000000      0.0000000000     -0.6685890718
C         0.0000000000      0.0000000000      0.6685890718
H         0.0000000000     -0.9240027061     -1.2338497710
H         0.0000000000      0.9240027061     -1.2338497710
H         0.0000000000      0.9240027061      1.2338497710
H         0.0000000000     -0.9240027061      1.2338497710
}

mass,iso
basis=vtz
logfile,scratch

hf
ccsd(t)
optg
freq,symm=auto

label1
hf
ccsd(t)
goto,label4

label2
{hf
 start,atden}
{mp4
 notripl}
```

```
goto,label4

label3
{hf
 start,atden}
mp2

label4
{surf,start1D=label1,sym=auto
 vmult,start2D=label2,start3D=label3,Var3D=EMP2,Multi=3}
vscf
vci
```

52.3   Special options for Intensities

`INTENSITY`,*options*

The `INTENSITY` directive of the `SURF` program provides the option to alter the electronic structure methods for calculating the dipole surfaces. It also allows to define the VARDIPnD[X,Y,Z] variables separately. n describes the dimension of the coupling surface and can be chosen to be 1 - 4.

Dipole surfaces can be computed for all those methods for which analytical gradients are available in MOLPRO. For all methods except Hartree-Fock this requires the keyword `CPHF,1` after the keyword for the electronic structure method. In multi-level schemes for which the variables `VAR1D`, `VAR2D` and `VAR3D` are set individually, the VARDIPnD[X,Y,Z] variables have to be set accordingly. Symmetry is currently only implemented for the 1D, 2D and 3D dipole surfaces. For 4D terms symmetry will automatically switched off at the moment. The determination of dipole surfaces beyond Hartree-Fock quality effectively doubles the computation time for surface calculations.

`DIPOLE`=n	Allows to switch between the different dipole surface calculations. `DIPOLE`=0 switches of all dipole calculations. `DIPOLE`=1 (this is the default) computes the dipole surfaces at the Hartree Fock level of theory, and therefore does not increase the computation time of electronic structure theory. `DIPOLE`=2 switches on the dipole surfaces at the full level of theory therefore `CPHF,1` is required, this effectively doubles the computation time for surface calculations.
`NDIMDIP`=n	This denotes the term after which the n-body expansion of the dipole surfaces is truncated. The default is set to 3. Note that `NDIMDIP` has to be lower or equal to `NDIM`.
`VARDIP1DX`=*variable*	Variable which is used for the x direction of the dipole moment for 1D surfaces.
`VARDIP1DY`=*variable*	Variable which is used for the y direction of the dipole moment for 1D surfaces.
`VARDIP1DZ`=*variable*	Variable which is used for the z direction of the dipole moment for 1D surfaces.
`POLAR`=n	By default (`POLAR`=0) Raman intensities will not be computed. `POLAR`=1 switches the calculation of polarizability tensor surfaces on. Note that currently only Hartree-Fock polarizabilities are supported, which requires the `POLARI` keyword in the Hartree-Fock program.

NDIMPOL=*n*   This variable denotes the term after which the *n*-body expansion of the polarizability tensor surfaces is truncated. The default is set to 2. Note that NDIMPOL has to be lower or equal to NDIM and must be smaller than 4.

VARPOL1DXX=*variable*   Variable which is used for the *xx* component of the polarizability tensor for 1D surfaces.

VARPOL1DYY=*variable*   Variable which is used for the *yy* component of the polarizability tensor for 1D surfaces.

VARPOL1DZZ=*variable*   Variable which is used for the *zz* component of the polarizability tensor for 1D surfaces.

VARPOL1DXY=*variable*   Variable which is used for the *xy* component of the polarizability tensor for 1D surfaces.

VARPOL1DXZ=*variable*   Variable which is used for the *xz* component of the polarizability tensor for 1D surfaces.

VARPOL1DYZ=*variable*   Variable which is used for the *yz* component of the polarizability tensor for 1D surfaces.

The higher order terms VARDIP*n*D[X,Y,Z] and VARPOL*n*D[XX,...,YZ] can be defined the same way. An example for a calculation, which provides both, infrared and Raman intensities, is given below.

```
label1
{hf
 start,atden
 polari}

{surf,start1D=label1,ndim=3,info=1
 intensity,polar=1,ndimpol=3
 scalnm,auto=on }

vscf,polar=1,ndimpol=3,info=1
vci,version=4,polar=1,ndimpol=3,info=1
```

52.4 Error correction schemes

ALT ER,*options*

The ALTER directive of the SURF program allows to provide error correction schemes for individual single point calculations. For example, in case that the Hartree Fock calculation for a certain grid point did not converge and the ORBITAL directive in the subsequent electron correlation calculation uses the IGNORE_ERROR option, an alternative calculation scheme can be provided, e.g. MCSCF in contrast to RHF. In the case of *multi level* calculations the ALT2D and ALT3D options can be set according to the START2D and START3D options. Note that the energy variable has to be the same in the original method and the alternative.

ALT1D=*label*   Alternative procedure to calculate the 1D single points.

ALT2D=*label*   Alternative procedure to calculate the 2D single points.

ALT3D=*label*   Alternative procedure to calculate the 3D single points.

Note that DFT calculations often still converge when RHF calculations already fail to do so.

52.5 Restart capabilities

`DISK`,*options*

As `SURF` calculations are very demanding it is highly recommended to dump the grid representation of the potential to disk. This allows for convenient restarts for subsequent vibrational structure calculations. In contrast to previous Molpro releases, the current version supports only restarts from external ASCII-files - due to many new options. Note, that restarts can also be performed for incomplete potentials. An open-access database of high-level potential files is available at http://http://pes-database.theochem.uni-stuttgart.de/surfaces. Potential files have their own version number and start with version 3.0 for the current Molpro release. Older potential file versions may not support the full capabilities of the current Molpro release.

`WHERE`=*value*	In combination with the keywords `DUMP` and `EXTERN` for an external restart file, the keyword `WHERE` specifies the path for the external ASCII file. Two options are available, `WHERE=home` and `WHERE=scr`. As the external files can be huge for `SURF` calculations, they will be stored on the scratch disk given by the MOLPRO variable `$TMPDIR` by default.
`DUMP`=*file name*	The potential can be dumped into an external ASCII-file which can be used for restarting. Its name must be provided as the argument of the `DUMP` keyword, e.g. `DUMP='formaldehyde.pot'`. The ASCII-file provides the interface to other programs and offers the possibility for controlled storage and modification of the computed potentials. Dipole and polarizability surfaces will also be dumped if available.
`EXTERN`=*file name*	In principle, `SURF` calculations should be restartable at any point of a truncated calculation. However, since only fully converged difference potentials will be stored in the ASCII file (`DUMP`), this is not the case. As a consequence, `SURF` calculations can be restarted from dump-files once a batch of surfaces has been dumped. Since the generation of the 2D or 3D surfaces usually requires about 2 to 3 batches, there are about 6-10 restart points for surface calculation including 3D potentials (see also the keywords `BATCH3D` and `BATCH4D` of the `SURF` program). Restarting from the ASCII dump-file is possible for any type of `VMULT` calculation. Harmonic frequencies should not be recalculated for restarts.
`SAVE`=*record*	Once a complete surface has been generated, a record can be specified, where to dump the potential in the temporary binary files. Once this keyword is not provided explicitly, the potential will be dumped in record 5600.2

52.6 Linear combinations of normal coordinates

`LINCOMB`,*options*

The `LINCOMB` directive allows for the calculation of linear combinations of normal coordinates for the expansion of the potential. This is realized by 2x2 Jacobi rotations. At most 3N-6/2 rotations can be provided in the input. Using an angle of 45° between the degenerate modes of non-Abelian molecules avoids symmetry breaking in the subsequent `VSCF` and `VCI` calculations.

NM1=*n*, NM2=*m*	Denotes the normal coordinates to be rotated.
ANGLE=*value*	Rotation angle in degree.
LOCAL=*value*	LOCAL=1 localizes the normal coordinates of the CH-stretchings. Note that this destroys symmetry of these modes. Usually localization has strong impact on subsequent VSCF calculations. LOCAL=2 localizes the normal coordinates of a molecular cluster to the contributing entities. This localization scheme localizes within the individual irreps, which usually leads to a very faint localization. Switching symmetry off by MPG=1 in the SURF program leads to a much stronger localization. LOCAL=3 is a combination of LOCAL=1 and LOCAL=2.

52.7 Scaling of individual coordinates

SCALNM,*options*

The SCALE option of the SURF program enables a modifaction of the extension of all difference potentials by a common factor. In contrast to that the SCALNM directive allows for the scaling with respect to the individual normal coordinates. This is the recommended choice for potentials dominated by quartic rather than quadratic terms. At most 3N-6 individual scale factors and shift parameters can be provided. In particular the AUTO option was found to be very helpful in practical applications.

MODE=*n*	Denotes the normal coordinate to be scaled or shifted.
SFAC=*value*	Scaling factor for mode MODE. The default is 1.0.
SHIFT=*n*	Allows to shift the potential with respect to the specified coordinate by *n* or -*n* grid points, respectively. Default: SHIFT=0.
AUTO=*on / off*	AUTO=*on* switches on an automatic scaling procedure of the potential in order to determine meaningful elongations and SHIFT values with respect to all coordinates, i.e. for each normal mode an optimized scaling parameter SFAC and SHIFT parameter will be determined. Usually this results in an increased number of 1D grid points. The AUTO keyword intrinsically depends on the thresholds and parameters, which can be controlled by the keywords THRSHIFT, ITMAX, LEVMAX, DENSMAX, and DENSMIN.
ITMAX=*n*	Specifies the maximum number of iterations within the automatic scaling of the potentials (see Keyword AUTO).
THRSHIFT=*value*	Threshold controlling the automated shifting of potentials as obtained from the state densities on the lhs and rhs of the potentials. The default is given as THRSHIFT=0.05.
LEVMAX=*n*	Maximum number of vibrational states to be included for controlling the automated scaling and shifting procedure. The default is set to 5.
DENSMAX=*value*	Threshold for the maximum vibrational density on the edges of the potential needed for the automated upscaling of the potentials (see keyword AUTO).
DENSMIN=*value*	Threshold for the minimum vibrational density on the edges of the potential needed for the automated downscaling of the potentials (see keyword AUTO).

52.8 Deleting individual surfaces

DELETE,*surface labels*

The DELETE directive allows to eliminate individual surfaces within the multi-mode expansion of the potential. Unlike the SKIP3D and SKIP4D keywords, this directive can only be used once a calculation is restarted from a completed potential energy surface calculation. This directive is meant for studying the impact of individual surfaces or to eliminate troublesome surfaces, which failed to converge in the iterative fitting procedure.

DELETE,*i,j*   deletes the 2D surface *ij*
DELETE,*i,j,k*   deletes the 3D surface *ijk*
DELETE,*i,j,k,l* deletes the 4D surface *ijkl*

52.9 Modeling of high-order *n*-body terms

REPAR,*options*

Within the framework of multi-level calculations (see the directive VMULT), 3D and 4D terms can be modeled. The modeling scheme is based on a reparametrization of the semiempirical AM1 method. Consequently, in the input stream the energy variable to be read in must refer to a semiempirical calculation. After the 2D terms the program optimizes the semiempirical parameters in order to represent the 1D and 2D surfaces best.

RMS1D=*value*   The keywords RMS1D and RMS2D specify the threshold for terminating the 1D and 2D iterations in the local optimization of the semiempirical parameters. The defaults are given by RMS1D=1.d-6 and RMS2D=1.d-6.

ITMAX1D=*n*   The maximum number of iterations in the local optimization of the semiempirical parameters can be controlled by ITMAX1D and ITMAX2D. The defaults are ITMAX1D=100 and ITMAX2D=150.

The following example shows the input for a surface calculation in which the 3D terms will be modeled.

```
memory,20,m
orient,mass
geometry={
   3
Water
O        0.0675762564       0.0000000000      -1.3259214590
H       -0.4362118830      -0.7612267436      -1.7014971211
H       -0.4362118830       0.7612267436      -1.7014971211
}

hf
mp2
optg
freq

label1
abinitio
basis=vdz
int
rhf
```

```
mp2
goto,label4

label2
semi,am1
int
rhf

label4
{surf,start1D=label1
 vmult,start2D=label1,start3D=label2,multi=4
 repar}
vscf
vci
```

52.10 Quality Check

CHECK,*options*

The CHECK directive of the SURF program allows for a quality check of a completed surface. This routine simply computes the exact *ab initio* energies at randomly selected grid points and compares these values with the interpolated ones, which will be used subsequently for the determination of the wavefunction. This program is fully parallelized.

LEVEL=*n*	Denotes the level to be checked, i.e. 1 corresponds to 1D, etc. Note, levels below *n* will not be checked automatically.
POINTS=*value*	Determines the number of grid points in one dimension to be checked. The default is set to 4.

52.11 Grid Computing

GRIDCOMP,*options*

The GRIDCOMP directive of the SURF program allows to interface MOLPRO with a grid computing client such as SEGL. It is also possible to use the grid computing interface without any grid computing client by using the two scripts (CREATE_SUBMIT and COLLECT) being supplied in the directory "src/vscf/". The charge of the molecule as well as some other general commands are transferred to the individual grid point command files, which are printed out in the subdirectory POINTS. If there are any doubts whether the specified command is transferred to the single point or not, the command should be given within the definition of the electronic structure calculations.

MEMORY=*n*	Denotes the amount of memory (in MW) which is needed in each single point calculation. The default is given by 100 MW.
MAXFILE=*n*	Defines the maximum number of files produced in a single run of the grid computing interface. Default: MAXFILE=100000.
FREEZE=*n*	Determines to which permanent file some relevant orbital information has been saved. This is necessary when using the i explicitly correlated or local methods. Default: FREEZE=0.
FRNAME=*value*	The name of the permanent file, which should be used in each single point.

```
memory,50,m
orient,mass
geometry={
6
Ethene
C           0.0000000000        0.0000000000        -0.6685890718
C           0.0000000000        0.0000000000         0.6685890718
H           0.0000000000       -0.9240027061        -1.2338497710
H           0.0000000000        0.9240027061        -1.2338497710
H           0.0000000000        0.9240027061         1.2338497710
H           0.0000000000       -0.9240027061         1.2338497710
}

mass,iso
basis=vtz
logfile,scratch

hf
ccsd(t)
optg
freq,symm=auto

label1
hf
ccsd(t)
goto,label4

label2
{hf
 start,atden}
{mp4
 notripl}
goto,label4

label3
{hf
 start,atden}
mp2

label4
{surf,start1D=label1,sym=auto
 gridcomp,memory=10
 vmult,start2D=label2,start3D=label3,Var3D=EMP2,Multi=3}
vscf
vci
```

To generate a potential energy surface with the grid computing interface, follow these steps:

- Run a Molpro calculation on the master control file (see the example above) to generate the control files for the individual single points.

- Calculate the energies for all generated control files in the POINTS subdirectory

- Collect the results and start with point 1 until no more new .com files are produced.

The results of the point calculations should be collected as listed below:

```
grep -h '*** 1D Surf ilev=1' *.out >> results1Dilev-1
grep -h '*** 1D Surf ilev=2' *.out >> results1Dilev-2
grep -h '*** 1D Surf ilev=3' *.out >> results1Dilev-3
grep -h '*** 2D Surf ilev=2' *.out >> results2Dilev-2
grep -h '*** 2D Surf ilev=3' *.out >> results2Dilev-3
```

```
grep -h '*** 3D Surf' *.out >>results3D
grep -h '*** 4D Surf' *.out >>results4D
```

To reduce the calculation time of the first step, the restart procedure can be used.

52.12 Recommendations

It is recommended to

- use the ORIENT,MASS keyword in order to rotate the molecule into standard orientation. This is necessary for a full exploitation of symmetry within the generation of the potential energy surface.

- use the MASS,ISO keyword to use the most available isotopes.

- use multi-level schemes in combination with symmetry and a parallelized MOLPRO version (MPPX) in order to speed up the calculations. Explicitly correlated methods are preferable over conventional approaches.

- reduce the quality of the normal coordinates. If you do not require extremely high accuracy, it is sufficient to compute the normal coordinates (i.e. the harmonic frequencies) at the DFT level rather than the CCSD(T) level. This saves a lot of computer time and the deviations are usually not larger than 1 or 2 wavenumbers in the subsequent VSCF and VCI calculations.

52.13 Standard Problems

- Problem: The SURF calculation crashes with an error message like

  ```
  ?ERROR IN VIRTORB: INCORRECT NUMBER OF ORB...

  ERROR EXIT
  CURRENT STACK:     MAIN
  ```

  Solution: The program has problems in the symmetry conversion when restarting a Hartree-Fock calculation from the reference calculation at the equilibrium geometry. You need to start the Hartree-Fock calculations independently by using the keywords start,atden.

- Problem: In parallel calculations (MPPX) the CPU-time of a SURF calculation differs considerably from the real-time (wallclock time).

  Solution: There may be two reasons for this: (1) Usually a SURF calculation spends a significant amount of the total time in the Hartree-Fock program and the 2-electron integrals program. As the integrals are stored on disk, 2 processes on the same machine may write on disk at the same time and thus the calculation time depends to some extend on the disk controller. It is more efficient to stripe several disks and to use several controllers. This problem can be circumvented by distributing the job over several machines, but limiting the number of processors for each machine to 1. (2) The integrals program buffers the integrals. Parallel jobs may require too much memory (factor of 2 plus the

shared memory) and thus the integrals buffering will be inefficient. Try to reduce the memory as much as you can. It might be advantageous to separate the memory demanding VCI calculation from the SURF calculation.

53 PES TRANSFORMATIONS

Once a potential energy surface (PES) has been generated by the `SURF` program, it can be transformed to different representations. The first possibility is a representation by polynomials, i.e. the `POLY` program. The representation by grid points may be altered by the `VGRID` program, which includes a grid to grid transformation. Finally the `PESTRANS` program offers a transformation of the PES for vibrational structure calculations of isotopologues or Franck-Condon factors.

53.1 Polynomial representations (`POLY`)

`POLY`,*options*

The `POLY` program allows for the transformation of the potential energy surface and property surfaces from a grid representation to a polynomial representation. Once a polynomial representation has been chosen, the corresponding VSCF, VCI or VMP2 programs need to be selected (see below). The `POLY` program is fully parallelized in terms of the `MPPX` scheme. An example for the use of the `POLY` program can be found in chapter 55.1.3.

The following *options* are available:

`NDIM=`*n*	The keyword `NDIM=`*n* terminates the transformation after the *n*D terms within the *n*-mode expansion of the surfaces. The default is set to 3. The transformation of the 4D terms can be very time consuming.
`NDIMDIP=`*n*	Term after which the *n*-body expansions of the dipole surfaces are truncated. The default is set to 3. Note that `NDIMDIP` has to be lower or equal than `NDIM`.
`NDIMPOL=`*n*	Term after which the *n*-body expansions of the polarizability tensor surfaces are truncated. The default is 0. `NDIMPOL` has to be lower or equal than `NDIM` and must be smaller than 4.
`NGRID=`*n*	Once the value of the `NGRID=`*n* keyword for controlling the number of grid points has been changed in the `SURF` program, this information will be passed to the `POLY` program automatically.
`AUTOPOL=`*n*	`AUTOPOL=1` (default) determines the optimal parameters for `PMAX` and `PSUM` in an iterative procedure. In combination with `AUTOPOL=1` the `PMAX` and `PSUM` keywords specify the maximum values within the automated determination of these parameters.
`PMAX=`*n*	This keyword controls the order of the polynomial to be determined in the fitting procedure. The default is set to 8. The definition of this keyword changes in combination with the `AUTOPOL` keyword (see above).
`PSUM=`*n*	In multidimensional fitting the maximum order of the polynomial is not given by `PMAX` times the dimension, but rather by `PSUM`. The default is set to 24. This reduces the computational cost for fitting tremendously. However, for accurate calculations `PMAX=12` and `PSUM=30` are recommended. The definition of this keyword changes in combination with `AUTOPOL` keyword (see above).

TYPE=*variable*	Once polynomials have been generated, the expansion of the potential can be restricted to the harmonic approximation or a semi-quartic force field, i.e. `TYPE=`*HARM* or `TYPE==`*QFF*.
DIPOLE=*n*	In case that dipole surfaces have been computed, they need to be transformed to a polynomial representation as well. This can be accomplished by `DIPOLE=1` and will be set by default, if dipole surfaces are available. `DIPOLE=0` excludes existing dipole surfaces from the transformation.
POLAR=*n*	Once set to one this keyword switches the transformation of the polarizability tensor surfaces on. The default is `POLAR=0`.
VAM=*n*	The Watson correction term, i.e. `VAM=1`, is absorbed in the potential by default. Once the polynomials to be generated should exclude this correction, this needs to be specified by `VAM=0`. Any other values, i.e. 2 or 3, will be ignored.
DELAUTO=*value*	In order to delete troublesome 2D, 3D or 4D surfaces from the multimode expansion of the potential, the `DELAUTO` keyword sets all coefficients of the polynomial expansion of these surfaces to zero. The threshold passed to the `DELAUTO` keyword corresponds to the χ^2 value of the least squares fitting procedure. It acts on both, the energy and the dipole surfaces. The default is set to 9.d99, i.e. all surfaces with χ^2 values below this threshold will not be affected.
SOLVER=*n*	By default, `SOLVER=1`, an LU decomposition will be used within the fitting procedure. Alternatively, a Cholesky decomposition is available, which sometimes leads to more stable solutions (`SOLVER=2`).
NVARC=*n*	For the calculation of vibrationally averaged rotational constants μ-tensor surfaces will be generated and transformed to polynomials up to 2nd order (default). The order can be changed by the integer passed to the `NVARC` keyword. This transformation can also be extended within the `VSCF` program.
VRC=*n*	Once vibrational-rotational coupling surfaces have been computed in the `SURF` program, these couplings can be considered (`VRC=1`) or excluded (`VRC=0`, default) in the `POLY` program.
SHOW=*n*	The coefficients of the polynomial representation can be printed. In order to identify quartic potentials, it is recommended to use `SHOW=1`. Higher values will lead to a very long output file.
START=*record*	This keyword controls the record, from which the potential shall be read. The default is 5600.2. This keyword usually is only needed within the calculation of vibronic spectra.
SAVE=*record*	Specification of the record, where to dump the polynomials. The default is 5750.2. This keyword usually is only needed within the calculation of vibronic spectra.
INFO=*n*	`INFO=1` provides a list of the values of all relevant program parameters (options).

53.1.1 Plotting of 3D surfaces

LEVELCURVES,*options*

The `LEVELCURVES` directive within the `POLY` program allows to plot isosurfaces for the sum of the corresponding 1D, 2D, and 3D surfaces. This enables the visual control of the potential including the 3D terms. Datafiles for the gnuplot program and associated input files will be provided in individual subdirectories.

The following *options* are available:

`ENERGY=`*value*	If this keyword isn't used, the energy value for the isosurface will be determined by the program automatically. The value determined this way is the lowest energy of the outer surfaces of the 3D cube. If a specific value is provided for `ENERGY`, the corresponding 3D level surface will be plotted.
`ESTEP=`*value*	Once several isosurfaces shall be plotted for a given 3D potential, the energy difference between two isosurfaces can be specified by `ESTEP=value`. The first isosurface, that will be plotted, corresponds to the level energy of the stepwidth itself. In all subsequent isosurfaces the energy will be increased by the value of the stepwidth `ESTEP`, until the final energy as defined by the `ENERGY` keyword is obtained. As a consequence, a series of isosurfaces will be produced, which is different for each 3D potential.
`DUMP=`*path*	`DUMP=path` provides the path of the subdirectory, in which the datafiles for the isosurfaces will be dumped.
`MODE=`*n*	In order to restrict the generation of isosurfaces to individual triples of modes, the `MODE` keyword can be used. For example, `LEVELCURVES,MODE=5,MODE=3,MODE=2` generates the isosurface for the 3D potential V_{532}. The ordering of the modes is insignificant. Once isosurfaces for different triples shall be plotted, the directive `LEVELCURVES` needs to be provided several times.

53.2 Grid to grid transformations (`VGRID`)

`VGRID,`*options*

For certain applications a finer grid may be needed than generated by the `SURF` program. In order to avoid the recalculation of the entire PES the `VGRID` program offers the possibility of a grid to grid transformation. The transformation of polarizability tensor surfaces is not yet supported.

The following *options* are available:

`NGRID=`*n*	This keyword provides the number of grid points as generated by the `SURF` program, i.e. this is the *old* number of grid points.
`NEWGRID=`*n*	Determines the number of grid points to be used in all subsequent programs. Note that in the subsequent programs the variable `NGRID` controls the number of grid points. The keyword `NEWGRID` exists only within the `VGRID` program.
`NDIM=`*n*	Specifies the maximum order of the PES expansion, which shall be transformed. Default: `NDIM=3`.

DIPOLE=*n*	In case that dipole surfaces have been computed, these may be transformed to a finer or coarser grid as well. This transformation can be switched off by `DIPOLE=0`.
NDIMDIP=*n*	Specifies the maximum order of the dipole surfaces, which shall be transformed. *n* must be equal or smaller than the corresponding value of `NDIM`.
INFO=*n*	`INFO=1` provides a list of the values of all relevant program parameters (options).

53.3   Transformation of the coordinate system (`PESTRANS`)

`PESTRANS`,*options*

The `PESTRANS` program allows to change the coordinate system being used within the representation of the potential by a Duschinsky-like transformation. This allows for the transformation of PESs as needed for the calculation of the vibrational spectra of isotopologues or Franck-Condon factors including Duschinsky rotations. For further details see:

P. Meier, D. Oschetzki, R. Berger, G. Rauhut, *Transformation of potential energy surfaces for estimating isotopic shifts in anharmonic vibrational frequency calculations*, J. Chem. Phys. **140**, 184111 (2014).

The following *options* are available:

ECKART=*n*	By default the Eckart transformation matrix needed within the `PESTRANS` program will be computed explicitly. `ECKART=0` replaces the Eckart transformation matrix by a unit matrix.
UMAT=*n*	As needed for Franck-Condon calculations, `UMAT=1` defines the linear combinations of the displacement vectors due to Duschinsky rotations, which influences the selection of states in subsequent VCI calculations. The default, `UMAT=0`, switches off this feature.
VRC=*n*	Once vibrational-rotational coupling surfaces have been computed in the `SURF` program, these couplings can be considered (`VRC=1`) or excluded (`VRC=0`, default) in the `PESTRANS` program. The inclusion of these terms usually increases the accuracy of the transformation.
CUT=*n*	`CUT=0` (default) transforms all surfaces as requested by the input. `CUT=1` neglects the generation of vibrational-rotational coupling surfaces for the new potential. `CUT=2` neglects rotational-rotational coupling surfaces within the transformation and thus also for the new potential.
THRQ=*value*	Elements in the displacement vectors below this threshold (default `THRQ=`10^{-8}) will be neglected within the transformation.
THRMATS=*value*	Threshold controlling the analysis of the **S**-matrix indicating the accuracy of the transformation (default: `THRMATS=0.3`).

Most keywords and directives of the `SURF` program can also be used in the `PESTRANS` program (i.e. `NDIM`, `SCALE`, `INFO`, `INTENSITY`, `SCALNM`, `DISK`, `LINCOMB`), while specific ones had to be excluded (i.e. `NGRID`, etc.).

53.3.1   Definition of atomic masses

`MASS`,*options*

Once the `PESTRANS` program will be used for the calculation of isotopologues, the atomic masses of the individual atoms can be specified by this directive. Note, the use of the `MASS` directive here differs from that in the electronic structure code as it requests the running number of the atoms in the geometry definition.

`MASS`,*n*,*value*   The *n*th atom is supposed to have the mass *value*.

53.3.2   Reading of 2nd Hessian

`DISK`,*options*

Within Franck-Condon calculations information about the geometry and the Hessian of the 2nd system (belonging to the 2nd electronic state) is needed. This can be realized by the `DISK` directive, which thus differs from the directive of the same name within the `SURF` program. The options of this directive are the same as for the directive of the `SURF` program.

`EXTERN`=*file name*   Specifies the name of the ASCII restart file (see the `SURF` program) belonging to the 2nd system, which includes the 2nd coordinate system.

The following example shows a calculation for water including vibrational-rotational coupling surfaces, the corresponding VSCF and VCI calculations a subsequent transformation of the potential to doubly deuterated water.

```
memory,100,m
gthresh,optgrad=1.d-7,twoint=1.d-14,prefac=1.d-16
geometry={
O   ,,    0.0000000000  ,    0.0000000000  ,     0.1241819425
H   ,,    0.0000000000  ,   -1.4320403835  ,    -0.9855926792
H   ,,    0.0000000000  ,    1.4320403835  ,    -0.9855926792
}

basis=vtz-f12

hf
optg
ccsd(t)-f12
freq,symm=auto

label1
{hf
start,atden}
ccsd(t)-f12

{surf,start1D=label1,sym=auto,vrc=1,ndim=4
 scalnm,auto=on
 disk,where=home,dump='h2o.pot'}

vscf
vci
poly,vam=0,vrc=1,ndim=4
```

```
{pestrans,vrc=1,ndim=4
 mass,2,2.0141017778d0
 mass,3,2.0141017778d0
 scalnm,auto=on
 disk,where=home,dump='d2o.pot'}
vscf
vci
```

54   VIBRATIONAL SCF PROGRAMS

54.1   The VSCF program (`VSCF`)

`VSCF`,*options*

The `VSCF` program is exclusively based on the Watson Hamiltonian

$$\hat{H} = \frac{1}{2}\sum_{\alpha\beta}(\hat{J}_\alpha - \hat{\pi}_\alpha)\mu_{\alpha\beta}(\hat{J}_\beta - \hat{\pi}_\beta) - \frac{1}{8}\sum_\alpha \mu_{\alpha\alpha} - \frac{1}{2}\sum_i \frac{\partial^2}{\partial q_i^2} + V(q_1,\ldots,q_{3N-6}) \qquad (65)$$

in which the potential energy surfaces, $V(q_1,\ldots,q_{3N-6})$, are provided by the `SURF` module. The Watson correction term and the 0D term of the vibrational angular momentum terms are by default (`VAM=2`) included. Within the grid-based version of the program the one-dimensional Schrödinger equation is solved by the DVR procedure of Hamilton and Light. Note that, the number of basis functions (distributed Gaussians) is determined by the grid points of the potential and cannot be increased without changing the PES grid representation. In contrast to that the number of basis functions can be modified without restrictions in the polynomial based version. In all cases the basis is fixed to distributed Gaussians (DG). As VSCF calculations are extremely fast, these calculations cannot be restarted. For details see:

G. Rauhut, T. Hrenar, *A Combined Variational and Perturbational Study on the Vibrational Spectrum of P_2F_4*, Chem. Phys. **346**, 160 (2008).

The anharmonic frequencies and intensities calculated by the `VSCF` program can be used to plot an IR spectrum, using the `PUT` command (see subsection 10.3) with the *style* `IRSPEC`.

The following *options* are available:

`TYPE=`*variable*	VSCF solutions can be obtained using a potential in grid representation, i.e. `TYPE=GRID`, or in a polynomial representation, `TYPE=POLY`. In the latter case the `POLY` program needs to be called prior to the `VSCF` program in order to transform the potential.
`SADDLE=`*n*	By default, i.e. `SADDLE=0`, the `VSCF` program assumes, that the reference point of the potential belongs to a local minimum. Once the PES calculation has been started from a transition state, this information must be provided to `VSCF` program by using `SADDLE=1`. Currently, the `VSCF` program can only handle symmetrical double-minimum potentials.
`VAM=`*n*	The 0D terms of the vibrational angular momentum terms, i.e. $\frac{1}{2}\sum_{\alpha\beta}\hat{\pi}_\alpha\mu_{\alpha\beta}\hat{\pi}_\beta$, and the Watson correction term are by default (`VAM=2`) included. `VAM=1` adds the Watson correction term (see eq. 65) as a pseudo-potential like contribution to the fine grid of the potential. `VAM=2` allows for the calculation of the integrals of the `VAM` operator using the approximation that the μ tensor is given as the inverse of the moment of inertia tensor at equilibrium geometry.i When using `VAM=4` the expansion of the effective moment of inertia tensor will be truncated after the 1D terms (rather than the 0D term in case of `VAM=2`). Note that values higher than 2 are only active for

non-linear molecules. `VAM=5` truncates the series after the 2D term. In almost all cases `VAM=2` is fully sufficient. Vibrational angular momentum terms are accounted for in a perturbational manner and do not affect the wavefunction.

MUPLOT=*n*   Plots all μ-tensor surfaces up to *n*D and a corresponding GNUPLOT script in a separate subdirectory (`plots`). This option works only in combination with `TYPE=POLY`. The `VAM` option has to be set accordingly.

COMBI=*n*   By default the `VSCF` program calculates the fundamental modes of the molecule only. However, choosing `COMBI=n` allows for the calculation of the vibrational overtones and combination bands. The value of *n* controls the excitation level, i.e. the number of states to be computed increases very rapidly for large values of *n*. Therefore, by default the upper limit is set to 5000 cm^{-1}, but this cutoff can be changed by the option `UBOUND`. See also the `VIBSTATE` program (section 54.3) for even more possibilities of defining vibrational states.

USERMODE=*n*   Once vibrational states have been defined with the `VIBSTATE` program (section 54.3), the VSCF program can be forced to compute just these states by the option `USERMODE=1`. Note that the vibrational ground state will always be computed and needs not to be specified explicitly.

UBOUND=*n*   Once overtones and combination bands shall be computed, the upper energy limit is controlled by the keyword `UBOND`, i.e. states, for which the harmonic estimate is larger than *n*, will not be computed. the default is set to *n*=5000 cm^{-1}.

SOLVER=*n*   For solving the one-dimensional Schrödinger equation within a grid representation two different algorithms can be used. The default, i.e. `SOLVER=1`, calls the discrete variable representation (DVR) as proposed by Hamilton and Light. Alternatively, the collocation algorithm of Young and Peet can be used (`SOLVER=2`).

GUESS=*n*   The initial guess for the VSCF programs is by default generated from the uncoupled one-dimensional potentials, i.e. `GUESS=1`. Alternatively, one may start within the calculation of excited vibrational states from the solution of the vibrational ground state, `GUESS=2`.

BASIS=*n*   `BASIS=1` (default) defines a mode-specific basis of distributed Gaussians, which is the recommended choice. However, for certain applications a mode-independent basis (`BASIS=2`) can be used as well. Very often this leads to worse results for torsional modes. `BASIS=3` distributes the Gaussians in a way, that the overlap integral between two functions is always the same (controlled by `THRBASOVLP`. This guarantees that an increasing number of basis functions will always lead to an improvement.

THRBASOVLP=*value*   Overlap between two Gaussian basis functions, once `BASIS=3` has been chosen. The default is 0.75.

ORTHO=*n*   Determines the type of orthogonalization within the VSCF program. `ORTHO=1` invokes a symmetrical orthogonalization, `ORTHO=2` a canonical one and `ORTHO=3` uses a canonical one together with an elimination of linear dependencies (see also keyword `THRLINDEP`. The deafult is `ORTHO=1`.

THRLINDEP=*value*	Threshold for eliminating linear dependencies in the VSCF procedure (see keyword BASIS=3). The default is THRLINDEP=1e-8.
THERMO=*n*	THERMO=1 allows for the improved calculation of thermodynamical quantities (compare the THERMO keyword in combination with a harmonic frequency calculation). However, the approach used here is an approximation: While the harmonic approximation is still retained in the equation for the partition functions, the actual values of the frequencies entering into these functions are the anharmonic values derived from the VSCF calculation. Default: THERMO=0.
DIPOLE=*n*	DIPOLE=1 allows for the calculation of infrared intensities. Calculation of infrared intensities requires the calculation of dipole surfaces within the SURF program. By default the intensities will be computed on the basis of Hartree-Fock dipole surfaces.
POLAR=*n*	POLAR=*1* allows to compute Raman intensities in addition to infrared intensities, but of course requires polarizability tensor surfaces from the SURF program. By default Raman intensities are switched off.
NDIM=*n*	The expansion of the potential in the VSCF calculation can differ from the expansion in the SURF calculation. However, only values less or equal to the one used in the surface calculation can be used.
NDIMDIP=*n*	Term after which the *n*-body expansions of the dipole surfaces are truncated. The default is set to 3. Note that NDIMDIP has to be lower or equal to NDIM.
NDIMPOL=*n*	Term after which the *n*-body expansions of the polarizability tensor surfaces are truncated. The default is set to 0. Note that NDIMPOL has to be lower or equal to NDIM and must be smaller than 4.
NBAS=*n*	The number of basis functions (distributed Gaussians) to be used for solving the VSCF equations can be controlled by NBAS=*n*. The default is NBAS=20. This option is only active once a polynomial representation of the potential has been chosen, see the option TYPE=POLY and the POLY program.
NVARC=*n*	By default the expansion of the μ-tensor for calculating the vibrationally averaged rotational constants is truncated after the 2nd order terms, i.e. NVARC=2. This may be altered by the NVARC keyword.
PRINT=*n*	This option provides an extended output. PRINT=1 prints the vibrationally averaged rotational constants for all computed states and the associated vibration-rotation constants α. PRINT=2 prints the effective 1D polynomials in case that the potential is represented in terms of polynomials, see the option TYPE=POLY and the POLY program. In addition the generalized VSCF property integrals, i.e. $\langle VSCF|q_i^r|VSCF\rangle$ are printed. These integrals allow for the calculation of arbitrary vibrationally averaged properties once the property surfaces are available. Default: PRINT=0.
STARTSURF=*record*	Surface information shall be read from the specified record. This must correspond to the record, to which the potential has been dumped in the SURF program. This option is only of importance within the calculation of vibronic spectra.
START=*record*	Polynomial and other information shall be read from the specified record. This must be the same record, to which the polynomials have

been dumped in the `POLY` program. This option is only of importance within the calculation of vibronic spectra.

SAVE=*record*   This specifies the record, where to dump the VSCF information. Usually this is the same record as specified in the `START` option. Note that the VSCF information is currently stored in the same record as the polynomial information.

INFO=*n*   `INFO=1` provides a list of the values of all relevant program parameters (options).

The following input example for a grid based calculation of anharmonic frequencies and intensities on the `VSCF` level (1) optimizes the geometry of water, (2) computes the harmonic frequencies,(3) generates a potential energy surface around the equilibrium structure and (4) computes the nuclear wave function and the infrared intensities at the `VSCF` level. Vibrational angular momentum terms (`VAM`) are included. Note, that it is recommended to perform a `VCI` calculation after a `VSCF` calculation. The details of the `VCI` input are described in the next chapter 55.1.

```
memory,20,m
basis=vdz
orient,mass
geometry={
    3
Water
O          0.0675762564      0.0000000000     -1.3259214590
H         -0.4362118830     -0.7612267436     -1.7014971211
H         -0.4362118830      0.7612267436     -1.7014971211
}

mass,iso

hf
mp2
optg                                     !(1) optimizes the geometry
frequencies,symm=auto                    !(2) compute harmonic frequencies

label1
{hf
start,atden}
{mp2
cphf,1}

{surf,start1D=label1,sym=auto            !(3) generate potential energy surface
 intensity,dipole=2}
vscf                                     !(4) do a VSCF calculation
put,irspec,irspec.gnu                    !writes a gnuplot file to plot an IR
                                         !spectrum of the VSCF calculation
```

54.2 The VMCSCF program (`VMCSCF`)

`VMCSCF`,*options*

The `VMCSCF` program is still under development and has not yet been fully optimized with respect to speed and efficiency. It is strongly recommended to run a VSCF calculation prior to the VMCSCF calculation and thus to use VSCF modals as an initial guess. By default configuration-selective VMCSCF calculations will be performed. The polynomial based VMCSCF calculation is significantly faster than the grid-based version and should be used whenever possible. For details see:

S. Heislbetz, G. Rauhut, *Vibrational multiconfiguration self-consistent field theory: Implementation and test calculations*, J. Chem. Phys. **132** (2010) 124102.

S. Heislbetz, F. Pfeiffer, G. Rauhut, *Configuration selection within vibrational multiconfiguration self-consistent field theory: Application to bridged lithium compounds*, J. Chem. Phys. **134** (2011) 204108.

The following *options* are available:

NACT=*n*	Is the number of active modals for each mode. The smallest meaningful value for NACT is 3, which is the current default. Configurations will only be generated within this space. Note that there is no equivalent in the VMCSCF program to the closed and core orbitals in electronic structure theory.
NVIRT=*n*	Is the number of modals on top of the number of active modals. The default is NVIRT=3. The virtual modals are needed for the modal rotations. Modals above the virtual modals are entirely neglected.
ROT=*n*	Specifies, if only active-virtual modal rotations shall be considered (ROT=0, default) or if active-active modal rotations shall be considered as well (ROT=1). Formally one would need active-active modal rotations for configuration-selective VMCSCF calculations, but the effects are usually extremely small.
CALCANGLE=*n*	The procedure how to determine the rotational angles between the modals within the Jacobi rotations can be specified by this keyword. CALCANGLE=1 uses the standard quadratic procedure, which is the current default. CALCANGLE=2 uses a cubic equation instead. CALCANGLE=3 switches to a full numerical determination of the rotational angle.
USERMODE=*n*	Once vibrational states have been defined with the VIBSTATE program (section 54.3), the VMCSCF program can be forced to compute just these states by the option USERMODE=1. Note that the vibrational ground state will always be computed and needs not to be specified explicitly.
VERSION=*n*	By default configuration-selective VMCSCF calculations will be performed (VERSION=3). Note that the selection is always performed prior to the VMCSCF iterations but not within them. The selection of configurations can be switched off by (VERSION=4).
CITYPE=*n*	Defines the maximum number of simultaneous excitations within the configurations generated from modals of the active space, i.e. Singles, Doubles, Triples, ... The maximum excitation level is limited to CITYPE=6, the default is set to 4.
REF=*n*	REF=0 specifies ground-state based VMCSCF calculations, i.e. the initial guess of the VMCSCF calculation is given by the VSCF wave function of the vibrational ground state. In contrast to that, REF=1 allows for a state-specific initial guess (default).
GSMODALS=*n*	By default all VMCSCF calculations are based on state-specific VSCF modals, GSMODALS=0. GSMODALS=1 uses the modals of the VSCF ground-state for all VMCSCF calculations.

MAXMAC=*n*	Controls the maximum number of macroiterations of the VMCSCF program. The default is 25.
THRMAC=*value*	Controls the convergence threshold for the macroiterations of the VM-CSCF program. The default is 1.d-2.
MAXMIC=*n*	Controls the maximum number of microiterations of the VMCSCF program. The default is 50.
THRMIC=*value*	Controls the convergence threshold for the microiterations of the VM-CSCF program. The default is 1.d-5.
PRINT=*n*	Provides additional information within the VMCSCF iterations, once a value larger than 0 (default) is used.
SAVE=*record*	Specifies the record and file, on which the VMCSCF wave function shall be stored. The default is 5950.2.
SAVEVSCF=*n*	Once set to 1, this option allows to store the VMCSCF modals in the record of the VSCF modals (which will be overwritten). This allows for VCI calculations with VMCSCF modals.

Besides these VMCSCF specific keywords, a number of option can be used, which are identical with those provided for the VCI program. These keywords are `NDIM`, `VAM`, `TYPE`, `NBAS`, `DIPOLE`, `NDIMDIP`, `COMBI`, `INFO`, `MPG`, `DIAG`, `CONT`, `THRSEL`, `THRCF`, `ANALYZE`.

54.2.1 Explicit definition of active spaces

`NACT`,*options*

Within the VMCSCF program the active space can be specified in a general manner (keword `NACT`), which means that the same number of active modals for each mode will be used. Alternatively, one may use the `NACT` directive. This allows to specify active spaces for the individual modes. Typically such definition refer to just one vibrational state and thus the program should be used within the `USERMODE` mode.

MODE(n)=*m*	The number of active modals for mode *n* is set to *m*. This always includes the vibrational ground state. In order to resolve Fermi resonances, one would need to choose *m* at least to be 3, which corresponds to the modals 0, 1 and 2.

54.3 The VIBSTATE program (`VIBSTATE`)

`VIBSTATE`,*options*

The `VIBSTATE` program allows to specify the occupation number vectors for individual vibrational states to be calculated in the following vibrational SCF and vibration correlation programs. Within the input stream, the `VIBSTATE` program needs to be called prior to the first call of the VSCF program. Note that, the `VIBSTATE` program needs only to be called, if a limited number of states shall be computed. On the contrary, the `COMBI` keyword within the `VSCF` and `VCI` programs generate large lists of vibrational states, which may result in significant computational effort. The `VIBSTATE` program necessarily requests the `VSTATE` directive to be called as described below. If only those vibrational states shall be computed, which are defined by the `VIBSTATE` program, all subsequent programs need to call the `USERMODE` option.

54.3.1 Definition of vibrational states

VSTATE,*options*

This directive specifies the occupation number vector of the vibrational state to be calculated.

MODE(n)=*m*   The *n*th mode of the moecule is supposed to have the quantum number *m*. If several modes are excited, the option can be repeated accordingly, e.g. VSTATE,MODE(1)=3,MODE(3)=2,MODE(6)=2. All other modes are not excited and thus have the quantum number 0.

55 VIBRATION CORRELATION PROGRAMS

55.1 The VCI program (`VCI`)

`VCI`,*options*

`VCI` calculations account for vibration correlation effects and use potential energy surfaces as generated from the `SURF` program and a basis of `VSCF` modals. All `VCI` calculations will be performed state-specific, i.e. for each vibrational mode an individual `VCI` calculation will be performed. As `VCI` calculations may require substantial computer resources, these calculations can be rather expensive. Currently, two different `VCI` programs (configuration selective and conventional) are available (see below). Moreover, VCI calculations can be performed using the grid-based version of the program or within a polynomial representation. The latter is significantly faster and is thus recommended. The different versions of the configuration selection `VCI` program and the underlying configuration selection scheme are described in detail in:

M. Neff, G. Rauhut, *Toward large scale vibrational configuration interaction calculations*, J. Chem. Phys. **131**, 124129 (2009).
M. Neff, T. Hrenar, D. Oschetzki, G. Rauhut, *Convergence of vibrational angular momentum terms within the Watson Hamiltonian*, J. Chem. Phys. **134**, 064105 (2011).

The anharmonic frequencies and intensities calculated by the `VCI` program can be used to plot an IR spectrum, using the `PUT` command (see subsection 10.3) with the *style* `IRSPEC`.

55.1.1 Options

The following *options* are available:

`TYPE`=*variable*	VCI solutions can be obtained using a potential in grid representation, i.e. `TYPE=GRID` (default), or in a polynomial representation, `TYPE=POLY`. In the latter case the `POLY` program needs to be called prior to the `VSCF` and `VCI` programs in order to transform the potential.
`SADDLE`=*n*	By default, i.e. `SADDLE=0`, the `VCI` program assumes, that the reference point of the potential belongs to a local minimum. Once the PES calculation has been started from a transition state, this information must be provided to `VCI` program by using `SADDLE=1`. Currently, the `VCI` program can only handle symmetrical double-minimum potentials.
`VERSION`=*n*	Both, the grid-based and the polynomial-based versions of the `VCI` programs offer 2 different kinds of `VCI` implementations: `VERSION=3` (which is the default) is a configuration selective and most efficient `VCI` program. `VERSION=4` is a conventional `VCI` program without configuration selection. It is thus computationally extremely demanding.
`CITYPE`=*n*	`CITYPE` defines the maximum number of simultaneous excitations, i.e. Singles, Doubles, Triples, ... and thus determines the kind of calculations, i.e. VCISD, VCISDT, ... The default is `CITYPE=4` (VCISDTQ), which appears to be a fair compromise between accuracy and computational speed. The maximum excitation level is currently limited to `CITYPE=6`.

LEVEX=*n*

LEVEX determines the level of excitation within one mode, i.e. $0 \rightarrow 1$, $0 \rightarrow 2$, $0 \rightarrow 3$, ... The default is LEVEX=5, which was found to be sufficient for many applications.

CIMAX=*value*

CIMAX is the maximum excitation level corresponding to CITYPE and LEVEX. In principle, a triple configuration $(1^4 2^4 3^4)$ would contribute to the VCI space. However, CIMAX=7 restricts this to $(1^4 2^3)$, $(1^3 2^3 3^1)$, $(1^3 2^2 3^2)$,.... The default is CIMAX=9, which needs to be extended for certain applications.

THRSEL=*value*

THRSEL controls the determination of the iterative configuration selection scheme. By default the wavefunction is considered to be converged once energy changes drop below THRSEL=0.05 cm^{-1}.

THRCF=*value*

THRCF is the threshold for selecting individual configurations. The default is given by THRCF=10^{-9}.

CONT=*n*

Within the evaluation of the VCI integrals contraction schemes are used to reduce the computational effort. In the polynomial based VCI program values 0, 1 and 2 are supported, while in the grid based version only the options 0 and 1 exist. Memory demands and CPU speed-ups increase with increasing values. The default is set to 1. On machines with limited memory a value of 0 is recommended for this keyword.

VAM=*n*

VAM=0: switches off all vibrational angular momentum terms and the Watson correction term.

VAM=1: adds the Watson correction term (see eq. 65) as a pseudo-potential like contribution to the fine grid of the potential.

VAM=2: (default) the 0D terms of the vibrational angular momentum terms, i.e. $\frac{1}{2} \sum_{\alpha\beta} \hat{\pi}_\alpha \mu_{\alpha\beta} \hat{\pi}_\beta$, and the Watson correction term are included. The VAM-terms will be added to the diagonal elements of the VCI-matrix only. This approximations works rather well for many applications.

VAM=3: again, the μ tensor is given as the inverse of the moment of inertia tensor at equilibrium geometry, but is added to all elements of the VCI matrix.

VAM=4: extends the constant μ-tensor (0D) by 1D terms and is added to all elements of the VCI matrix. A prescreening technique is used for the 1D terms, in which the convergence of the VAM operator will be checked for each VCI matrix element.

VAM=5: includes 0D, 1D and 2D terms of the μ-tensor, which are added to all elements of the VCI matrix. Prescreening is used for the 1D and 2D terms.

VAM=6: includes 0D and 1D terms of the μ-tensor without prescreening.

VAM=7: includes 0D, 1D and 2D terms of the μ-tensor, which are added to all elements of the VCI matrix. Prescreening is used for the 2D terms only.

VAM=8: includes 0D, 1D and 2D terms of the μ-tensor without any prescreening.

Note that the 1D and 2D corrections increase the computational cost considerably and are only available for non-linear molecules.

COMBI=*n*

By default the VSCF program calculates the fundamental modes of the molecule only. However, choosing COMBI=*n* allows for the calcula-

tion of the vibrational overtones and combination bands. The value of n controls the excitation level, i.e. the number of states to be computed increases very rapidly for large values of n. Therefore, by default the upper limit is set to 5000 cm^{-1}, but this cutoff can be changed by the option `UBOUND`.

USERMODE=*n* Once vibrational states have been defined with the `VIBSTATE` program (section 54.3), the VCI program can be forced to compute just these states by the option `USERMODE=1`. Note that the vibrational ground state will always be computed and needs not to be specified explicitly.

UBOUND=*n* Once overtones and combination bands shall be computed, the upper energy limit is controlled by the keyword `UBOND`, i.e. states, for which the harmonic estimate is larger than n, will not be computed. the default is set to n=5000 cm^{-1}.

BASIS=*n* `BASIS=1` (default) defines a mode-specific basis of distributed Gaussians, which is the recommended choice. However, for certain applications a mode-independent basis (`BASIS=2`) can be used as well. Very often this leads to worse results for torsional modes. `BASIS=3` distributes the Gaussians in a way, that the overlap integral between two functions is always the same (controlled by `THRBASOVLP`. This guarantees that an increasing number of basis functions will always lead to an improvement.

THRBASOVLP=*value* Overlap between two Gaussian basis functions, once `BASIS=3` has been chosen. The default is 0.75.

THERMO=*n* `THERMO=1` allows for the improved calculation of thermodynamical quantities (compare the `THERMO` keyword in combination with a harmonic frequency calculation). However, the approach used here is an approximation: While the harmonic approximation is still retained in the equation for the partition functions, the actual values of the frequencies entering into these functions are the anharmonic values derived from the VCI calculation. Default: `THERMO=0`.

DIPOLE=*n* `DIPOLE=1` (default) allows for the calculation of infrared intensities. Calculation of infrared intensities requires the calculation of dipole surfaces within the `SURF` program. By default the intensities will be computed on the basis of Hartree-Fock dipole surfaces.

POLAR=*n* `POLAR=1` allows to compute Raman intensities in addition to infrared intensities, but of course requires polarizability tensor surfaces from the `SURF` program. By default Raman intensities are switched off.

NDIM=*n* The expansion of the potential in the VCI calculation can differ from the expansion in the `SURF` calculation. However, only values less or equal to the one used in the surface calculation can be used. Default: `NDIM=3`.

NDIMDIP=*n* Term after which the n-body expansions of the dipole surfaces are truncated. The default is set to 3. Note that `NDIMDIP` has to be lower or equal to `NDIM`.

NDIMPOL=*n* Term after which the n-body expansions of the polarizability tensor surfaces are truncated. The default is set to 0. Note that `NDIMPOL` has to be lower or equal to `NDIM` and must be samller than 4.

MPG=*n*	By default the symmetry of the molecule will be recognized automatically within the VCI calculations. MPG=1 switches symmetry off.
NBAS=*n*	The number of basis functions (distributed Gaussians) to be used for obtaining the VCI solutions can be controlled by NBAS=*value*. The number of basis functions must be identical to the number used in the VSCF program. The default is NBAS=20. This option is only active once a polynomial representation of the potential has been chosen, see the option TYPE=POLY and the POLY program.
REFERENCE=*n*	This keyword specifies the reference for the definition of the configurations. By default, REFERENCE=0 the reference for all state-specific calculations is the vibrational ground-state configuration. This leads to a violation of the Brillouin condition, but often to also to faster convergence. REFERENCE=1 uses the VSCF configuration as reference for generating all excited configurations. This is the proper way of doing it, but usually requests higher excitation levels.
GSMODALS=*n*	By default all VCI calculations will be done state-specifically, GSMODALS=0, i.e. the modals refer to the individual VSCF solutions. GSMODALS=1 uses the modals of the VSCF ground-state for all VCI calculations. This still requests an individual VCI calculation for each vibrational state (in contrast to just one VCI calculations from which all solutions will be retrieved) and thus the final VCI wave functions may not be strictly orthogonal to each other once the VCI space is incomplete.
DIAG=*n*	In the polynomial configuration selective VCI program different diagonalization schemes can be used. DIAG=CON specifies a conventional non-iterative diagonalization as used in the grid-based versions. DIAG=JAC is the default and uses a Jacobi-Davidson scheme. DIAG=HJD denotes a disk-based Jacobi-Davidson algorithm.
ANALYZE=*value*	In case of resonances or strongly mixed states in general (i.e. low VCI coefficients) a multi-state analysis can be performed, which prints major contributions of the VCI-vectors for all states in a certain window around the state of interest. Typically a window between 10 and 20% (i.e. ANALYZE=0.1 or ANALYZE=0.2) provides all the information needed. As this analyses requires a conventional diagonalization (see DIAG), the CPU time may increase significantly.
NVARC=*n*	By default the expansion of the μ-tensor for calculating the vibrationally averaged rotational constants is truncated after the 2nd order terms, i.e. NVARC=2. This may be altered by the NVARC keyword.
PRINT=*n*	This option provides an extended output. PRINT=1 prints the vibrationally averaged rotational constants for all computed states and the associated vibration-rotation constants α. PRINT=2 prints the effective 1D polynomials in case that the potential is represented in terms of polynomials, see the option TYPE=POLY and the POLY program. In addition the generalized VSCF property integrals, i.e. $\langle VSCF | q_i^r | VSCF \rangle$ are printed. These integrals allow for the calculation of arbitrary vibrationally averaged properties once the property surfaces are available. Default: PRINT=0.
START=*record*	This card specifies the record from where to read the VSCF information. As the VSCF information usually is stored in the same record as

the polynomials, it is usually defined in the `POLY` program. This option is only of importance within the calculation of vibronic spectra.

`SAVE=`*record* This keyword specifies the record where to dump the VCI information. This option is only of importance within the calculation of vibronic spectra.

`EXPORT=`*variable* If *variable* is set to *FCON*, important VCI information will be passed to the Franck-Condon calculation. Within Franck-Condon calculations this option *has to be* used.

`INFO=`*n* `INFO=1` provides a list of the values of all relevant program parameters (options).

55.1.2 Explicit definition of the correlation space

`LEVEX,`*options*

Within the VCI program the correlation space can be specified in a general manner (keword `LEVEX`), which means that the same number of modals for each mode will be used. Alternatively, one may use the `LEVEX` directive. This allows to specify the correlation spaces for the individual modes.

`MODE(n)=`*m* The number of correlating modals for mode *n* is set to *m*.

55.1.3 Examples

The following input example for a grid based calculation of anharmonic frequencies and intensities (1) optimizes the geometry of water, (2) computes the harmonic frequencies, (3) generates a potential energy surface around the equilibrium structure, (4) computes the vibrational wave function and the infrared intensities at the `VSCF` level, and finally (5) a `VCI` calculation will be performed. Vibrational angular momentum terms (`VAM`) are included even for the non-diagonal elements of the VCI matrix.

```
memory,20,m
basis=vdz
orient,mass
geometry={
   3
Water
O          0.0675762564      0.0000000000     -1.3259214590
H         -0.4362118830     -0.7612267436     -1.7014971211
H         -0.4362118830      0.7612267436     -1.7014971211
}

mass,iso

hf
mp2
optg                                   !(1) optimizes the geometry
frequencies,symm=auto                  !(2) compute harmonic frequencies

label1
{hf
start,atden}
{mp2
```

```
cphf,1}

{surf,start1D=label1,sym=auto          !(3) generate potential energy surface
 intensity,dipole=2}
vscf                                   !(4) do a VSCF calculation
vci,vam=3                              !(5) do a VCI calculation
put,irspec,irspec.gnu                  !writes a gnuplot file to plot an IR
                                       !spectrum of the last VCI calculation
```

The following input example for a polynomial based calculation of anharmonic frequencies
and intensities (1) optimizes the geometry of water, (2) computes the harmonic frequencies,(3)
generates a potential energy surface around the equilibrium structure, (4) converts the potential
energy surface into a polynomial representation (5) computes the nuclear wave function and the
infrared intensities at the VSCF level, and finally (6) performs a VCI calculation. Vibrational
angular momentum terms (VAM) are included even for the non-diagonal elements of the VCI
matrix.

```
memory,20,m
basis=vdz
orient,mass
geometry={
    3
Water
O          0.0675762564      0.0000000000      -1.3259214590
H         -0.4362118830     -0.7612267436      -1.7014971211
H         -0.4362118830      0.7612267436      -1.7014971211
}

mass,iso

hf
mp2
optg                                   !(1) optimizes the geometry
frequencies,symm=auto                  !(2) compute harmonic frequencies

label1
{hf
start,atden}
{mp2
cphf,1}

{surf,start1D=label1,sym=auto          !(3) generate potential energy surface
 intensity,dipole=2}
poly,dipole=1                          !(4) converts potential energy surface
                                       !    to a polynomial representation
vscf,type=poly                         !(5) do a VSCF calculation
vci,type=poly,vam=3                    !(6) do a VCI calculation
put,irspec,irspec.gnu                  !writes a gnuplot file to plot an IR
                                       !spectrum of the last VCI calculation
```

55.2   The vibrational MP2 program(VMP2)

VMP2,*options*

The VMP2 program allows to perform 2nd order vibrational Møller-Plesset calcula-
tions. The program has been implemented in a grid-based and a polynomial-based ver-
sion. Most of the keywords as described for the VCI program are also valid for
the VMP2 program, i.e. TYPE, CITYPE, LEVEX, CIMAX, NGRID, NDIM, NBAS,
VAM, COMBI, THERMO, DIPOLE, MPG and INFO.

```
memory,20,m
basis=vdz
orient,mass
geomtyp=xyz
geometry={
   3
Water
O         0.0675762564        0.0000000000       -1.3259214590
H        -0.4362118830       -0.7612267436       -1.7014971211
H        -0.4362118830        0.7612267436       -1.7014971211
}

hf
mp2
optg
{frequencies,symm=auto
print,low=50}

label1
{hf
start,atden}
{mp2
cphf,1}

{surf,start1D=label1,sym=auto
intensity,dipole=2}
poly,pmp=1,dipole=1,show=1
vscf,type=poly,pmp=2,dipole=1
vmp2,type=poly,pmp=3,dipole=1
```

http://www.molpro.net/info/current/examples/vmp2.com

55.3   The vibrational multi-reference CI program (`VMRCI`)

`VMRCI`,*options*

The vibrational multi-reference CI program requests a preceding VMCSCF calculation and ac-
counts for correlation effects on top of those considered in the VMCSCF run. Note, in all
VMRCI calculations, configurations being considered within the active space of the underlying
VMCSCF calculation, will be relaxed. Configurations to be generated for the VMRCI correla-
tion space refer to *all* reference configurations and thus the VMRCI correlation space increases
significantly faster than the VCI space. Once parameters have been altered with respect to
the defaults in the VMCSCF program, e.g. `NGRID`, the same settings must be used within the
`VMRCI program`. Further details are described in:

F. Pfeiffer, G. Rauhut, *Multi-reference vibration correlation methods*, J. Chem. Phys. **140**,
064110 (2014).

55.3.1   Options

The following *options* are available:

VSCFMODALS=*n*   Instead of using VMCSCF modals (default), VSCF modals will be
                        used (once a VSCF calculation has been performed prior to the VM-
                        CSCF calculation), i.e. `VSCFMODALS=1`.

Most of the keywords as described for the `VCI` program are also valid for the `VMRCI` program, i.e. `TYPE, CITYPE, LEVEX, CIMAX, NDIM, NBAS, DIAG, VAM, COMBI, DIPOLE, CONT, ANALYZE, MPG` and `INFO`.

55.3.2 Explicit definition of the correlation space

`LEVEX,`*options*

Within the VMRCI program the correlation space can be specified in a general manner (keword `LEVEX`), which means that the same number of modals for each mode will be used. Alternatively, one may use the `LEVEX` directive. This allows to specify the correlation spaces for the individual modes.

`MODE(n)=`*m*   The number of correlating modals for mode *n* is set to *m*.

56 VIBRATIONAL PERTURBATION THEORY (`VPT2`)

`VPT2`,*options*

The `VPT2` program is based on force constants, which are retrieved from the polynomial coefficients as generated by the `POLY` program. Therefore, each `VPT2` calculation requests a call of the `POLY` program prior to the `VPT2` call. As the `VPT2` program relies on a quartic force field (QFF), one may use the option `TYPE=QFF` in the `SURF` program. This will lead to tremendous time savings as the size of the potential energy surface is significantly reduced. However, this is an option and the force constants can be retrieved from any potential provided by the `SURF` program. Note, the option `QFF=1` in the `POLY` program has no impact on `VPT2` calculations, but on `VSCF` and `VCI` calculations. The current VPT2 implementation is limited to asymmetric top molecules. For further details see:

R. Ramakrishnan, G. Rauhut, *Semi-quartic force fields retrieved from multi-mode expansions: Accuracy, scaling behavior and approximations*, J. Chem. Phys. **142** (2015) 154118.

56.1 Options

The following *options* are available:

`PRINT=`*n*	`PRINT=0` (default) prints the anharmonic vibrational frequencies and the most important vibrational constants.
	`PRINT=1` prints in addition the force constants as retrieved from the polynomial coefficients.
	`PRINT=2` prints the force constants and an analysis of the detected resonances.
`INFO=`*n*	`INFO=1` provides a list of the values of all relevant program parameters.

56.1.1 Example

The following example shows an input for water, for which a semi-quartic force field will be generated at the MP2/cc-pVDZ level.

```
memory,20,m
basis=vdz
orient,mass
geometry={
   3
Water
O         0.0675762564      0.0000000000     -1.3259214590
H        -0.4362118830     -0.7612267436     -1.7014971211
H        -0.4362118830      0.7612267436     -1.7014971211
}

mass,iso

hf
mp2
optg                                    !(1) optimizes the geometry
```

```
frequencies,symm=auto                    !(2) compute harmonic frequencies

label1
{hf
start,atden}
mp2

surf,start1D=label1,type=qff,sym=auto    !(3) generate a QFF
poly,vam=0                               !(4) transform the PES to polynomials
vpt2                                     !(5) do a VPT2 calculation
```

57 FRANCK-CONDON FACTORS (FCON)

FCON,*options*

The FCON program allows for the calculation of Franck-Condon factors based on potential energy surfaces obtained from the SURF program and vibrational wavefunctions as provided by the VSCF or VCI programs. Duschinsky effects may or may not be included. These can either be applied to the vibrational wavefunction (of the vibrational ground state) or the potential by using the PESTRANS program. The latter possibility is the recommended one as it is significantly faster. The FCON program including Duschinsky rotations can only be used with analytical representations of the potential energy surfaces. A prescreening of the Franck-Condon factors without Duschinsky effects at the VSCF level is used to reduce the computational effort for correlated levels, e.g. VCI. Note that, Franck-Condon factors at the uncorrelated VSCF level including Duschinsky effects are usually of fairly poor quality. As the calculation of Franck-Condon factors often involves very high quantum numbers for the vibrational states of the final electronic state, very high excitation levels must be enabled in the VCI calculations, i.e. see keyword LEVEX. As a consequence, the SCALE parameter in SURF calculations needs to be modified in most applications.

57.1 Options

The following *options* are available:

WF=*type*	Defines the type of the wavefunction. WF=VSCF specifies state-specific VSCF wavefunctions for both levels, while WF=VCI denotes state-specific VCI wavefunctions. Alternatively, one may use WF=VSCFG for ground-state based VSCF wavefunctions and WF=VCIG for ground-state based VCI wavefunctions. The default is WF=VCI.
THRPRINT=*value*	This keyword defines the smallest value of a Franck-Condon factor to be printed in the output. The default is set to 1.0d-99, i.e. this threshold usually is inactive.
THRFCFSPEC=*value*	This threshold controls, if a Franck-Condon factor will be considered within the plotting of the spectrum. See the PUT command and the IRSPEC style. The default is 1.0d-6.
THRFCF=*value*	The sum of all Franck-Condon factors is 1.0d0 by definition. However, this value is hard to reach by sum over states approaches. Therefore, it can be lowered by this keyword.
THRDELTA=*value*	The δ-criterion is a threshold, which allows for the prescreening of overlap integrals within the evaluation of the Franck-Condon factors prior to their evaluation. The default is set to 1.0d-8.
THRSKIPBAS=*value*	Basis functions in the outer regions of the potentials may be skipped within the calculation of Franck-Condon factors. In particular within the approach of Doktorov, the CPU time depends strongly on the number of basis functions. This keyword allows to skip such basis functions and is given as the overlap integral of the modal. The default is 0.999999d0.
THRSEL=*value*	This threshold controls, if a Franck-Condon factor shall be selected and thus be considered in all subsequent calculations or not. The default is 1.0d-5.

THRVCIMIN=*value*	Within the calculation of Franck-Condon factors based on VCI wavefunctions, the leading VCI coefficient should be largest in order to correspond to the state of interest. The default is set to 0.01d0, which of course means that this keyword essentially is inactive.
THRSUMSEL=*value*	This threshold controls the sum of the selected Franck-Condon factors, which must formally be 1.0d0. The default is set to 0.999999d0.
MAXSEL=*n*	MAXSEL=n determines the maximum number of Franck-Condon factors to be selected. By default *n* is set to 100.
SEL=*n*	This option switches the selection of Franck-Condon factors based on VSCF calculation on (SEL=1) or off (SEL=0, default).
DUSCH=*n*	This keyword controls the Duschinsky transformation. DUSCH=0 entirely neglects the Duschinsky transformation - including the shift-vector. DUSCH=1 switches the Duschinsky transformation on and the algorithm of Doktorov will be used. Note that this option is only limited to 3-atomic systems. DUSCH=3 neglects the Duschinsky rotation, but includes the shift-vector. This is the default option as the Duschinsky rotation can be passed to the PESTRANS program, which is much more efficient.
ECKART=*n*	ECKART=1 (default) determines the Eckart transformation matrix as described in the literature. ECKART=0 approximates the Eckart transformation matrix by a unit matrix, which is meaningless unless for debugging purposes or for some very special tests.

Some of the keywords as described for the VCI program are also valid for the FCON program, i.e. CITYPE, LEVEX, CIMAX, DIPOLE, NDIM, NBAS, NGRID, BASIS and INFO.

57.1.1 Information Handling

DISK,*options*

As the Franck-Condon program requests the information of two sets of potentials and wave functions, the information handling is controlled by an extra directive. All the record provided here must refer to the defaults or the explicitly given records in the preceding POLY, VSCF and VCI calculations.

SURF1=*record*	Specifies the record from where to read the potential information for the final PES.
SURF2=*record*	Specifies the record from where to read the potential information for the initial PES.
VSCF1=*record*	Specifies the record from where to read the VSCF information for the final wave function.
VSCF2=*record*	Specifies the record from where to read the VSCF information for the initial wave function.
VCI1=*record*	Specifies the record from where to read the VCI information for the final wave function.
VCI2=*record*	Specifies the record from where to read the VCI information for the initial wave function.

The following example shows the input for a calculation of Franck-Condon factors at the VCI
level. The selection of important Franck-Condon factors will be done at the VSCF level without
Duschinsky rotation.

```
memory,20,m
basis=vdz
orient,mass
geometry={
    3
Water
O        0.0675762564       0.0000000000      -1.3259214590
H       -0.4362118830      -0.7612267436      -1.7014971211
H       -0.4362118830       0.7612267436      -1.7014971211
}

label1
hf

{surf,start1D=label1,sym=auto          ! reads the PES of the final electronic
 disk,where=home,extern='final.pot'}    ! state from 'final.pot'

poly
vscf,type=poly                          ! saves VSCF wavefunction in record 5750.2
vci,type=poly,export=fcon               ! saves  VCI wavefunction in record 5800.2

{surf,start1D=label1,sym=auto          ! reads the PES of the initial electronic
 disk,where=home,save=5601.2,extern='initial.pot'}   ! state from 'initial.pot'

poly,save=5751.2
vscf,type=poly,save=5751.2

{fcon,wf=vscfg,sel=1                     ! selection of the FCFs based on a VSCF calc.
 disk,surf1=5600.2,surf2=5601.2}

poly,start=5601.2,save=5751.2,vam=0      ! it is important to switch off VAM terms
                                         ! for pestrans
{pestrans,umat=1                         ! rotate the PES of initial.pot in the
                                         ! coordinates of final.pot
 disk,where=home,save=5601.2             ! umat=1 save the Duschinsky matrix in the
 disk,extern='final.pot'}                ! U-matrix for the VCI program, the extern file
                                         ! provides the hessian of the other system

poly,start=5600.2,save=5750.2
vscf,type=poly,save=5750.2,             ! saves VSCF wavefunction in record 5750.2
vci,type=poly,export=fcon,save=5800.2   ! saves  VCI wavefunction in record 5800.2

poly,start=5601.2,save=5751.2
vscf,type=poly,save=5751.2,             ! saves VSCF wavefunction in record 5751.2
vci,type=poly,export=fcon,save=5801.2   ! saves  VCI wavefunction in record 5801.2

{fcon                                    ! calculate the selected FCFs
 disk,surf1=5600.2,surf2=5601.2          ! disk directive is not necessary here,
 disk,vscf1=5750.2,vscf2=5751.2          ! but one can see the standard values this way
 disk,vci1=5800.2,vci2=5801.2}           ! 1 correspond to the final state;
                                         ! 2 correspond to the initial state

put,irspec,h2o_pe.gnu                    ! generate a GNU file with the PE spectrum
```

58   THE COSMO MODEL

The Conductor-like Screening Model (COSMO) (A. Klamt and G. Schüürmann, J. Chem. Soc. Perkin Trans. II 799-805 (1993)) is currently available for HF (RHF,UHF) and DFT (RKS,UKS) energy calculations and the corresponding gradients.

The COSMO model is invoked by the COSMO card:

COSMO[,*option*$_1$=*value*$_1$, *option*$_2$=*value*$_2$,...]

where option can be

NPPA	size of the underlying basis grid. The value must satisfy: $value = 10 \times 3^k \times 4^l + 2$ (default = 1082; type integer).
NSPA	number of segments for non hydrogen atoms. The value must satisfy: $values = 10 \times 3^k \times 4^l + 2$ (default = 92; type integer).
CAVITY	the intersection seams of the molecular surface are closed (1) or open (0) (default = 1; type integer).
EPSILON	dielectric permittivity (default = -1.d0, which means $\varepsilon = \infty$; type real)
DISEX	distance criteria for the **A**-matrix setup. Short range interactions (segment centre distances ¡ DISEX $\times$ mean atomic diameter) are calculated using the underlying basis grid. Long range interactions are calculated via the segment centres (default = 10.d0; type float).
ROUTF	factor used for outer cavity construction. The radii of the outer cavity are defined as: $r_i^{out} = r_i + ROUTF \times RSOLV$ (default = 0.85d0; type float)
PHSRAN	phase offset of coordinate randomization (default = 0.d0; type float)
AMPRAN	amplitude factor of coordinate randomization (default = 1.0d-5; type float)
RSOLV	additional radius for cavity construction (default = -1d0, the optimized H radius is used; type float).
MAXNPS	maximal number of surface segments (default = -1, will be estimated; type integer).

It is recommended to change the default values for problematic cases only.

By default the program uses optimized radii if existent and $1.17 \times$ vdW radius else. The optimized radii [Å] are: H=1.30, C=2.00, N=1.83, O=1.72, F=1.72, S=2.16, Cl=2.05, Br=2.16, I=2.32. Own proposals can be given directly subsequent to the cosmo card:

RAD,*symbol, radius*

where the *radius* has to be given in Å.

Example:
```
cosmo
rad,O,1.72
rad,H,1.3
```

Output file:
The COSMO output file will be written after every converged SCF calculation. The segment charges and potentials are corrected by the outlying charge correction. For the total charges and energies corrected and uncorrected values are given. The normal output file contains uncorrected values only. It is recommended to use the corrected values from the output file.

Optimizations:
It is recommended to use optimizer that operates with gradients exclusively. Line search techniques that use energies tends to fail, because of the energy discontinuities which may occur due to a reorganization of the segments after a geometry step. For the same reasons numerical gradients are not recommended.

58.1   BASIC THEORY

COSMO is a continuum solvation model, in which the solvent is represented as a dielectric continuum of permittivity ε. The solute molecule is placed in a cavity inside the continuum. The response of the continuum due to the charge distribution of the solute is described by the generation of a screening charge distribution on the cavity surface. This charge distribution can be calculated by solving the boundary equation of vanishing electrostatic potential on the surface of a conductor. After a discretization of the cavity surface into sufficiently small segments, the vector of the screening charges on the surface segments is

$$\mathbf{q}^* = -\mathbf{A}^{-1}\Phi$$

where Φ is the vector of the potential due to the solute charge distribution on the segments, and $\mathbf{A}$ is the interaction matrix of the screening charges on the segments. This solution is exact for an electric conductor. For finite dielectrics the true dielectric screening charges can be approximated very well by scaling the charge density of a conductor with $f(\varepsilon)$.

$$\mathbf{q} = f(\varepsilon)\mathbf{q}^*; \quad f(\varepsilon) = (\varepsilon - 1)/(\varepsilon + 0.5)$$

In every SCF step the screening charges $\mathbf{q}$ have to be generated from the potential Φ, and then added to the Hamiltonian as external point charges. The total energy of the system is

$$E_{tot} = E_0 + E_{diel}; \quad E_{diel} = \frac{1}{2}\Phi\mathbf{q}$$

where E_0 is the bare self-energy of the system and E_{diel} the dielectric energy.

Cavity construction:
First a surface of mutually excluding spheres of radius $R_i + rsolv$ is constructed, where the R_i are the radii of the atoms, defined as element specific radii and *rsolv* is some radius representing a typical maximum curvature of a solvent molecular surface. *rsolv* should not be misinterpreted as a mean solvent radius, nor modified for different solvents. Every atomic sphere is represented by an underlying basis grid of `nppa` points per full atom. Basis grid points which intersect a sphere of a different atom are neglected. In a second step the remainder of the basis grid points are projected to the surface defined by the radii R_i. As a third step of the cavity construction the remaining basis grid points are gathered to segments, which are the areas of constant screening charges in the numerical solution. Finally, the intersection seams between the atoms are filled with additional segments.
Now the A-matrix can be set up. The matrix elements will be calculated from the basis grid points of the segments for close and medium segment distances (governed by the `disex` value), or using the segment centres for large segment distances.

Outlying charge correction:
The non vanishing electron density outside the cavity causes an error that can be corrected by the outlying charge correction. This correction uses the potential on the so called outer surface (defined by the radii $R_i + \text{rsolv} \times \text{routf}$) to estimate a correction term for the screening charges and the energies (A. Klamt and V. Jonas, J. Chem. Phys., 105, 9972-9981(1996)). The correction will be performed once at the end of a converged SCF calculation. All corrected values can be found in the COSMO output file.

59 QM/MM INTERFACES

The MOLPRO program package can be used in combination with other software to perform hybrid Quantum Mechanics/Molecular Mechanics (QM/MM) calculations. Through the use of point charges, electrostatic embedding can be used for both energy and gradient runs. In particular, lattices of point charges can be included in an external file, gradients with respect to charge positions can be computed, as described in section 10.5. Gradients with respect to QM nuclear positions can be computed (and include the effect of the MM charges) as usual using the FORCE command (section 45).

Although MOLPRO itself does not offer any interface to force field programs, the coupling is supplied by other commercial and non-commercial software. The following is a list of QM/MM software which allow the use of MOLPRO.

59.1 Chemshell

The Chemshell computational chemistry environment (http://www.chemshell.org) offers an interface to many well known force field software (CHARMM, GROMOS, GULP,...). The program supports several geometry optimization algorithms; a molecular dynamics driver for *NVE*, *NVT* and *NPT* ensembles; Monte Carlo; and many other utilities.

The Chemshell Manual can be found at the following website:

http://www.cse.scitech.ac.uk/ccg/software/chemshell/manual/

Instructions on the use of Molpro are available therein. Also concerning the Chemshell environment, a free Graphical User Interface (GUI) has been released. The CCP1GUI facilitates the input for hybrid calculations, allows visualisation of molecular structures and includes molecule editing tools:

http://www.cse.scitech.ac.uk/ccg/software/ccp1gui/

60 PERIODIC-BOUNDARY CONDITIONS

Periodic-boundary conditions are indicated by use of the PBC command. It can take the following options and directive

- LATT_TYPE The shape of the unit cell. CUBIC: cubic unit cell, HEXAG: hexagonal unit cell, PARAP: a parallelpiped shaped cell

- BOXSIZE For cubic unit cells this specifies the length of the side of the cube in Angstroms.

- HEXWIDTH, HEXHEIGHT For hexagonal unit cells this specifies the width and height of the cell in Angstroms.

- VEC A directive which should be followed by 3 numbers to specify a lattice vector. When specifying lattice vectors like this, there are usually 3 instances of such a directive and the vectors will be checked that they conform to the specified LATT_TYPE. This is the only way to specify lattice vectors for LATT_TYPE=PARAP. The program will not error if less than 3 vectors have been given, as in principle 1 or 2 dimensional periodicity could be desired, although this has not been implemented.

To define parallelpiped lattice vectors, something like the following would be used

```
{PBC,LATT\_TYPE='PARAP'
VEC,1.0,0.0,0.0
VEC,0.0,1.5,1.5
VEC,0.0,0.0,1.5
}
```

61 MANY-BODY EXPANSION

61.1 Compilation

To run `MBE` for large systems, the default maximum number of atoms must be increased. This can be done via configure. The maximum number that can be entered here is 1000. To increase this further the configure script must be modified. The default number of records should also be increased. This should typically be about 4 times the number of monomers in the system, as multipoles, polarizabilities and density-fitting information are held separate records for each monomer. To compile for parallel execution the MPPX parallel mode should be chosen.

61.2 Units

All lengths in the input file should be given in Angstroms.

61.3 Incremental Monte-Carlo

- `LMAX_M` Angular momentum of multipoles to be used

- `LMAX_P` Angular momentum of polarizabilities to be used

- `PRINT` Level of information to output

- `IMCDUMP` At end of a calculation dump various levels of information: $>= 1$ dumps properties and one-body energies, $>= 2$ dumps all two-body energies, $>= 3$ all three-body energies

- `MAXLEV` Maximum level of MBE. Default is to include dimers (=2). For IMC maximum is trimers. For a manybody analysis can go up to 5.

- `CUTOFF` Distance within which to do QM calculations. For 3 body calculations, all dimer separations must be within this distance.

- `THRDENOV` Distance within which to calculate the overlap for damping. By default the same as `CUTOFF`.

- `MC` Do a Monte-Carlo simulation if 1 (Default 0)

- `MCMAX` Maximum number of MC steps to perform

- `MCTEMP` Temperature of a MC simulation

- `NPT` Do a NPT simulation

- `PRESSURE` Pressure for a NPT MC simulation

- `PRFREQ` How often to print output during a MC simulation

- `RESFREQ` How often to save restart information (may not work!)

- `ENG_PROC` Name of energy procedure for all levels (if the same is to be used for all)

- `ENG_PROC1` Name of energy procedure for monomers

- `ENG_PROC2` Name of energy procedure for dimers

- `ENG_PROC3` Name of energy procedure for trimers

- `PROP_PROC` Name of property procedure

- `RESTART` If we are doing a restart (may not work)

- `DAMPING` Use damping (Tang-Toennies with empirical factor of 1.94 by default)

- `DAMPFAC` Empirical factor to use in damping function

- `DF_SET` Density-fitting set to use in damping. Density damping is only switched on if this is specified

- `DF_CON`   Optional specification of `CONTEXT` for `DF_SET`, e.g. `JKFIT` or `MP2FIT`. `JKFIT` by default

- `DFMAXL`   Optional specification of maximum angular momentum functions to use in `DF_SET`

- `DENREC`   Location where density has been stored for calculating distributed multipoles

- `GEOM_LOC`   Location where geometry output from MC should be stored

- `ANALYSE`   Only do analysis and no calculation

- `RDF_TYPES`   Type of RDFs to calculate

- `RDF_VOL`   Volume for non-periodic RDF

- `RDF_NBIN`   Number of bins for RDF

- `RDF_DBIN`   Width of bin

- `RDF_EQ`   Number of equilibration steps to ignore when calculating RDF

- `MANYBODY`   Just do a many-body analysis. =1 does normal many-body analysis and =2 does full counterpoise corrected.

- `SCALTYPE`   Scale box before starting calculation. =A for side of box in Angstroms, =B for side of box in Bohr, =N for number density, =D for density in kg/m3

- `SCALE`   Size of scaled box in whatever type has been specified in `SCALTYPE`

- `DTRANS`   Initial size of translational move in Angstrom

- `DROT`   Initial size of rotational move in degrees

- `DSTR`   Initial size of bond stretch in Angstrom

- `DBEND`   Initial size of bond angle bend in degrees

- `DBOX`   Initial size of box move in Angstroms (for NPT simulations)

- `DINTRA`   Bias for intramolecular moves (this plus `DRIGID` will be equal to one. `DINTRA` takes priority, if both specified)

- `DRIGID`   Bias for rigid-body moves (this plus `DINTRA` will be equal to one. `DINTRA` takes priority, if both specified)

- `DVOL`   Bias for volume moves versus molecular moves in NPT simulations

- `TARGINT`   Acceptance/rejection ratio target for intramolecular moves

- `TARGRIG`   Acceptance/rejection ratio target for rigid-body moves

- `TARGVOL`   Acceptance/rejection ratio target for volume moves in NPT simulations

- `MONFILE`   File to specify connectivity of system which overrides automatic connectivity subroutine. Should not be used with MC simulations, but OK for energy.

- `CHGFILE`   File to specify if any of the monomers are charged.

- `ANISODISP`   Are we using anisotropic dispersion integrals

- `DISPFILE`   File to specify dispersion coefficients or integrals, bohr for isotropic and anisotropic

- `INDMETH`   Method to use for self-consistent induction calculation. =0 don't iterate, =1 iterate and use Ewald only on first iteration for PBC, =2 iterate and use Ewald at every step for PBC, =3 use Lanczos algorithm which uses Ewald on first iteration only.

- `ITNUM`   Starting value for the iteration number.

- `NBODY`   Include n-body energy (default =1)

- `CLASSICAL`   Include classical energies (default =1)

- `SWITCH`   Use a switching function. =0 no switching, =1 quintic splines switching, (=2 GAP switching)

- `PROPFILE` File which contains multipoles and polarizabilities when doing a MaxLev=0 calculation, i.e. no QM calculations being done

- `DFPROC` Name of density-fitting procedure when only model being used and properties being input. Done only once for each type of monomer

- `EXCH_K` Factor by which to multiply the overlap to give the exchange energy

- `MANYBODY` Do a many-body analysis on the system. =1 do normal MBE, =2 do MBE in basis of cluster, i.e. properly counterpoise-corrected

- `DMAMON` Do a distributed multipole analysis on the whole system and also output the multipoles at the centres-of-mass of each monomer, due to contributions from that monomer only. Should be comparable to induced multipoles.

- `CLOSEST` =*N* Output the closest *N* molecules (possibly within minimum image convention if PBC being used) to a molecule chosen at random. Useful for creating clusters

- `SUPERCELL` Output a supercell specified as a string 'na:nb:nc' using the PBC specifications, e.g. `SUPERCELL='1:1:1'` creates an array of 8 of the original cells in a 'cubic' arrangement

- `SUPERFILE` File to which the supercell geometry is output

61.4 `EWALD` **directive**

- `GAMMA` Exponent of screening gaussian in Ewald summation

- `KCUT` Cutoff radius for radius of k-vectors

- `RCUT` Cutoff radius for real-space ewald

- `LCUT` Cutoff for angular momentum in multipolar Ewald. Higher-order terms probably convergent in real-space radius

- `EPS` Permittivity to use for surface term in Ewald

61.5 **Examples**

61.5.1 **Obtaining TDHF and UCHF dispersion coefficients**

The example below demonstrates how to get T. Korona's CC-SAPT program to output TDHF and UCHF dispersion coefficients. The UCHF coefficients are the relevant ones for an MP2 calculation. This example gives dispersion coefficients for water-water, ammonia-ammonia and water-ammonia. To use them in a calculation all of the integrals listed in the output for a given interaction should be put into a file in exactly the format they are output, i.e. four indices and an integral. This can then be read by the `MBE` program.

```
memory,100,m
if(NPROC_MPP.gt.1) then
skipped
end if

gthresh,energy=1.d-10
! don't use symmetry - can mess things up
symmetry,nosym
geometry={
H
O 1 R
H 2 R 1 A
}
R=0.966443838 Angstrom
A=103.84335748 Degree

gexpec,nspmlt3
ileden=0
iledenp=0

! first call just sets up CCSAPT program
dispgg=15
set,CC_NORM_MAX=50
basis=sto-3g
hf;maxit,0
{ccsd,check=0
polari,nspmlt3
orbital,ignore_error=1;maxit,3
cprop,ccsapt=3}

! now calculate the dispersion integrals for water

basis=avdz
hf;save,scfa

tdhf=tdhfa
tdhfdisp=tdhfdispa
{ccsd,check=0
polari,nspmlt3
orbital,ignore_error=1;maxit,3
cprop,ccsapt=5,dispcoef=dispgg,dispomega=0.3}


! calculate dispersion integrals for ammonia and mixed coefficient for NH3-H2O

symmetry,nosym
geometry={
  N
  X1     N      RX
  H1     N      RNH        X1      DUMB
  H2     N      RNH        X1      DUMB      H1     DIHE       0
  H3     N      RNH        X1      DUMB      H1     -DIHE      0
}
RX= 1.02 Angstrom
RNH= 1.02071411 Angstrom
DIHE= 120. Degree
DUMB= 112.48619220 Degree
ileden=0
iledenp=0
gexpec,nspmlt3

dispgg=15
set,CC_NORM_MAX=50
basis=sto-3g
hf;maxit,0
{ccsd,check=0
polari,nspmlt3
orbital,ignore_error=1;maxit,3
cprop,ccsapt=3}

basis=avdz
```

There are testjobs already present which show how to calculate dispersion coefficients using CC-SAPT. These should be modified to use the spherical harmonic multipole operators on the `EXPEC` and `POLARI` cards to produce the required integrals.

61.5.2 Many-body analysis of water hexamer

This example performs a many-body analysis of the water hexamer up to 3-body contributions. The routines go up to a maximum of 5-body contributions. By specifying `MANYBODY=2` a full counterpoise corrected many-body analysis would be done.

```
PROC mbeeng
{df-hf;start,atden}
{df-lmp2,interact=1
enepart}
ENDPROC

! input ensemble geometry
memory,20,m
symmetry,nosym
orient,noorient
geomtyp=xyz
geometry={
   18
 DF-LMP2/AVDZ   ENERGY=-457.63602408
 O        -2.1233226309       -1.7688858791        0.1524109399
 H        -2.4367986815       -2.2103390376        0.9513842141
 H        -1.2045230633       -2.0982518768        0.0330050109
 O         2.5947061994       -0.9537736740        0.1422730545
 H         2.4193021370        0.0068583194        0.0266664332
 H         3.1418238405       -1.0061708640        0.9356521604
 O        -2.5946186870        0.9534257806       -0.1546242536
 H        -3.1315700574        1.0016502753       -0.9551345770
 H        -2.4201260402       -0.0065436988       -0.0322861934
 O         2.1219816165        1.7703156035       -0.1450981681
 H         1.2027719526        2.0987725437       -0.0263944582
 H         2.4388614383        2.2190153349       -0.9386745371
 O        -0.4725613825        2.7226532886        0.1512286611
 H        -0.7014891628        3.2160843341        0.9484803611
 H        -1.2168653397        2.0916787132        0.0293211623
 O         0.4703934181       -2.7233099281       -0.1463373783
 H         0.6968166194       -3.2213522313       -0.9414479081
 H         1.2152177361       -2.0918266148       -0.0304245102
 }
basis,avdz
{mbe,manybody=1,maxlev=3}
```

> http://www.molpro.net/info/current/examples/water6_mbe.com

61.5.3 Two-body-plus-polarization treatment of water hexamer

This demonstrates a many-body evaluation of the energy of the cluster using the long-range model for well-separated dimers and the polarization model for many-body (beyond two-body) effects. Two procedures are defined, one for the energy and one for the properties. Properties up to quadrupoles (`LMAX_M=2`, `LMAX_P=2`) are used. `MBEENG` and `MBEPROP` are the default names for these procedures and hence do not need to be specified on the input line. `MAXLEV=2` indicates that up to dimers should be calculated using `MBEENG` and within `CUTOFF=4.5` (in Angstroms). Isotropic dispersion coefficients of Wormer *et al.* are used by default for water.

```
PROC mbeeng    !default procedure name
hf
ENDPROC

PROC mbeprop   !default procedure name
hf
polarizability,nspmlt2
ENDPROC

! input ensemble geometry
memory,10,m
symmetry,nosym
orient,noorient
geomtyp=xyz
geometry={
   18
 Water hexamer
 O       -2.1233226309     -1.7688858791      0.1524109399
 H       -2.4367986815     -2.2103390376      0.9513842141
 H       -1.2045230633     -2.0982518768      0.0330050109
 O        2.5947061994     -0.9537736740      0.1422730545
 H        2.4193021370      0.0068583194      0.0266664332
 H        3.1418238405     -1.0061708640      0.9356521604
 O       -2.5946186870      0.9534257806     -0.1546242536
 H       -3.1315700574      1.0016502753     -0.9551345770
 H       -2.4201260402     -0.0065436988     -0.0322861934
 O        2.1219816165      1.7703156035     -0.1450981681
 H        1.2027719526      2.0987725437     -0.0263944582
 H        2.4388614383      2.2190153349     -0.9386745371
 O       -0.4725613825      2.7226532886      0.1512286611
 H       -0.7014891628      3.2160843341      0.9484803611
 H       -1.2168653397      2.0916787132      0.0293211623
 O        0.4703934181     -2.7233099281     -0.1463373783
 H        0.6968166194     -3.2213522313     -0.9414479081
 H        1.2152177361     -2.0918266148     -0.0304245102
}
basis,avdz
{mbe,maxlev=2,cutoff=4.5,lmax_m=2,lmax_p=2}
```

```
  http://www.molpro.net/info/current/examples/water6_mbe2.com
```

61.5.4 Three-body-plus-polarization treatment of water hexamer

Same as previous but with `MAXLEV=3` so that trimers are also calculated using `MBEENG`. Note that `SWITCH=0` has been used as no 3-body switching function has been implemented and 'unswitched' 3-body energies should not be mixed with 'switched' 2-body ones.

```
PROC mbeeng    !default procedure name
hf
ENDPROC

PROC mbeprop    !default procedure name
hf
polarizability,nspmlt2
ENDPROC

! input ensemble geometry
memory,10,m
symmetry,nosym
orient,noorient
geomtyp=xyz
geometry={
   18
 Water hexamer
 O        -2.1233226309       -1.7688858791        0.1524109399
 H        -2.4367986815       -2.2103390376        0.9513842141
 H        -1.2045230633       -2.0982518768        0.0330050109
 O         2.5947061994       -0.9537736740        0.1422730545
 H         2.4193021370        0.0068583194        0.0266664332
 H         3.1418238405       -1.0061708640        0.9356521604
 O        -2.5946186870        0.9534257806       -0.1546242536
 H        -3.1315700574        1.0016502753       -0.9551345770
 H        -2.4201260402       -0.0065436988       -0.0322861934
 O         2.1219816165        1.7703156035       -0.1450981681
 H         1.2027719526        2.0987725437       -0.0263944582
 H         2.4388614383        2.2190153349       -0.9386745371
 O        -0.4725613825        2.7226532886        0.1512286611
 H        -0.7014891628        3.2160843341        0.9484803611
 H        -1.2168653397        2.0916787132        0.0293211623
 O         0.4703934181       -2.7233099281       -0.1463373783
 H         0.6968166194       -3.2213522313       -0.9414479081
 H         1.2152177361       -2.0918266148       -0.0304245102
}
basis,avdz
{mbe,maxlev=3,cutoff=4.5,lmax_m=2,lmax_p=2,switch=0}
```

    http://www.molpro.net/info/current/examples/water6_mbe3.com

.

61.5.5 Specifying isotropic dispersion coefficients

Similar to the example in Subsection 61.5.3, but here we are specifying the isotropic dispersion coefficients which should be used. The `DISPFILE` variable specifies the file where these should be found. It should be a list of the relevant interactions and the C_6, C_8 and C_{10} coefficients. For example
`OH2:OH2 46.0 800.0 10000.0`

where molecules should be listed by elements of decreasing atomic mass. If a charged species is being used, the charge should be included in parentheses, e.g. `F(-1)`. The file may contain interactions not relevant to the system under consideration, so a library of dispersion coefficients may be built up. The input file is

```
PROC mbeeng    !default procedure name
hf
ENDPROC

PROC mbeprop    !default procedure name
hf
polarizability,nspmlt2
ENDPROC

! input ensemble geometry
memory,10,m
symmetry,nosym
orient,noorient
geomtyp=xyz
geometry={
   18
 Water hexamer
 O        -2.1233226309      -1.7688858791       0.1524109399
 H        -2.4367986815      -2.2103390376       0.9513842141
 H        -1.2045230633      -2.0982518768       0.0330050109
 O         2.5947061994      -0.9537736740       0.1422730545
 H         2.4193021370       0.0068583194       0.0266664332
 H         3.1418238405      -1.0061708640       0.9356521604
 O        -2.5946186870       0.9534257806      -0.1546242536
 H        -3.1315700574       1.0016502753      -0.9551345770
 H        -2.4201260402      -0.0065436988      -0.0322861934
 O         2.1219816165       1.7703156035      -0.1450981681
 H         1.2027719526       2.0987725437      -0.0263944582
 H         2.4388614383       2.2190153349      -0.9386745371
 O        -0.4725613825       2.7226532886       0.1512286611
 H        -0.7014891628       3.2160843341       0.9484803611
 H        -1.2168653397       2.0916787132       0.0293211623
 O         0.4703934181      -2.7233099281      -0.1463373783
 H         0.6968166194      -3.2213522313      -0.9414479081
 H         1.2152177361      -2.0918266148      -0.0304245102
}
basis,avdz
{mbe,maxlev=2,cutoff=4.5,mc=0,lmax_m=2,lmax_p=2,anisodisp=0,dispfile='disp_iso.inp'}
```

> http://www.molpro.net/info/current/examples/water6_iso.com

and the required dispersion file is:

```
OH2:OH2 40.196  496.889  8263.5
```

> http://www.molpro.net/info/current/examples/disp_iso.inp

61.5.6 Specifying anisotropic dispersion coefficients

Again this is controlled by the DISPFILE variable, but the file now has a different format. For each type of interaction three filenames should be specified. The first should contain the dispersion integrals and the second two the reference geometries at which they were calculated, e.g.

```
 OH2:OH2 h2oh2odisp.dat  h2o.xyz  h2o.xyz
```

The geometries should be given in standard XYZ format. The input file is:

```
PROC mbeeng    !default procedure name
hf
ENDPROC

PROC mbeprop    !default procedure name
hf
polarizability,nspmlt2
ENDPROC

! input ensemble geometry
memory,10,m
symmetry,nosym
orient,noorient
geomtyp=xyz
geometry={
   18
 Water hexamer
 O        -2.1233226309     -1.7688858791      0.1524109399
 H        -2.4367986815     -2.2103390376      0.9513842141
 H        -1.2045230633     -2.0982518768      0.0330050109
 O         2.5947061994     -0.9537736740      0.1422730545
 H         2.4193021370      0.0068583194      0.0266664332
 H         3.1418238405     -1.0061708640      0.9356521604
 O        -2.5946186870      0.9534257806     -0.1546242536
 H        -3.1315700574      1.0016502753     -0.9551345770
 H        -2.4201260402     -0.0065436988     -0.0322861934
 O         2.1219816165      1.7703156035     -0.1450981681
 H         1.2027719526      2.0987725437     -0.0263944582
 H         2.4388614383      2.2190153349     -0.9386745371
 O        -0.4725613825      2.7226532886      0.1512286611
 H        -0.7014891628      3.2160843341      0.9484803611
 H        -1.2168653397      2.0916787132      0.0293211623
 O         0.4703934181     -2.7233099281     -0.1463373783
 H         0.6968166194     -3.2213522313     -0.9414479081
 H         1.2152177361     -2.0918266148     -0.0304245102
}
basis,avdz
{mbe,maxlev=2,cutoff=4.5,mc=0,lmax_m=2,lmax_p=2,anisodisp=1,dispfile='disp.inp'}
```

http://www.molpro.net/info/current/examples/water6_aniso.com

The additional files that are required are: `disp.inp`, `h2o_tip.xyz` and `h2o_tip_uchf.disp`, which can be found in the `examples` directory.

61.5.7   Using MP2 properties

As the example in Subsection 61.5.3 but using MP2 properties. We have now also specified different procedures for monomer and dimer energies. This is important for correlated energies as the specifying the correct number of core orbitals is important. The examples require auxiliary files `disp.inp`, `h2o_tip.xyz` and `h2o_tip_uchf.disp`, which can be found in the `examples` directory

```
PROC mbeeng1
core,1
{df-hf;start,atden}
{df-lmp2,interact=1
pipek,delete=1
enepart}
ENDPROC

PROC mbeeng2
core,2
{df-hf;start,atden}
{df-lmp2,interact=1
pipek,delete=1
enepart}
ENDPROC

PROC mbeprop
core,0
{hf;start,atden
polarizability,NSPMLT2}
{mp2;dm,11000.2}
ENDPROC

! input ensemble geometry
memory,10,m
symmetry,nosym
orient,noorient
geomtyp=xyz
geometry={
    18
 Water hexamer
  O        -2.1233226309      -1.7688858791       0.1524109399
  H        -2.4367986815      -2.2103390376       0.9513842141
  H        -1.2045230633      -2.0982518768       0.0330050109
  O         2.5947061994      -0.9537736740       0.1422730545
  H         2.4193021370       0.0068583194       0.0266664332
  H         3.1418238405      -1.0061708640       0.9356521604
  O        -2.5946186870       0.9534257806      -0.1546242536
  H        -3.1315700574       1.0016502753      -0.9551345770
  H        -2.4201260402      -0.0065436988      -0.0322861934
  O         2.1219816165       1.7703156035      -0.1450981681
  H         1.2027719526       2.0987725437      -0.0263944582
  H         2.4388614383       2.2190153349      -0.9386745371
  O        -0.4725613825       2.7226532886       0.1512286611
  H        -0.7014891628       3.2160843341       0.9484803611
  H        -1.2168653397       2.0916787132       0.0293211623
  O         0.4703934181      -2.7233099281      -0.1463373783
  H         0.6968166194      -3.2213522313      -0.9414479081
  H         1.2152177361      -2.0918266148      -0.0304245102
}
basis,avdz
{mbe,maxlev=2,cutoff=4.5,mc=0,lmax_m=2,lmax_p=2,eng_proc1='MBEENG1',eng_proc2='MBEENG2',anisod
```

   http://www.molpro.net/info/current/examples/water6_mp2.com

A second example is provided which produces more verbose output.

```
PROC MBEENG1
core,1
{df-hf;start,atden}
{df-lmp2,interact=1
pipek,delete=1
enepart}
ENDPROC

PROC MBEENG2
core,2
{df-hf;start,atden}
{df-lmp2,interact=1
pipek,delete=1
enepart}
ENDPROC

PROC MBEPROP
core,0
{hf;start,atden
polarizability,NSPMLT2}
{mp2;dm,11000.2}
ENDPROC

! input ensemble geometry
memory,10,m
symmetry,nosym
orient,noorient
geomtyp=xyz
geometry={
   18
 Water hexamer
 O        -2.1233226309        -1.7688858791         0.1524109399
 H        -2.4367986815        -2.2103390376         0.9513842141
 H        -1.2045230633        -2.0982518768         0.0330050109
 O         2.5947061994        -0.9537736740         0.1422730545
 H         2.4193021370         0.0068583194         0.0266664332
 H         3.1418238405        -1.0061708640         0.9356521604
 O        -2.5946186870         0.9534257806        -0.1546242536
 H        -3.1315700574         1.0016502753        -0.9551345770
 H        -2.4201260402        -0.0065436988        -0.0322861934
 O         2.1219816165         1.7703156035        -0.1450981681
 H         1.2027719526         2.0987725437        -0.0263944582
 H         2.4388614383         2.2190153349        -0.9386745371
 O        -0.4725613825         2.7226532886         0.1512286611
 H        -0.7014891628         3.2160843341         0.9484803611
 H        -1.2168653397         2.0916787132         0.0293211623
 O         0.4703934181        -2.7233099281        -0.1463373783
 H         0.6968166194        -3.2213522313        -0.9414479081
 H         1.2152177361        -2.0918266148        -0.0304245102
}
basis,avdz
{mbe,maxlev=2,cutoff=4.5,mc=0,lmax_m=2,lmax_p=2,eng_proc1='MBEENG1',eng_proc2='MBEENG2',anisod
```

61.5.8 Mixed water–ammonia cluster

A mixed cluster of 10 water molecules and two ammonia molecules. There is now anisotropic dispersion information listed for multiple interactions. The dispersion file `disp_h2o_nh3.inp` specifies monomer reference geometries (`h2o.xyz` and `nh3.xyz`) and UCHF dispersion coefficients in `h2o_nh3_uchf.dat`, `h2o_uchf.dat` and `nh3_uchf.dat`. The geometry is specified in `water10_ammonia2.xyz`.

The input file is below, and all other auxiliary files can be found in the `examples` directory.

```
memory,40,m

PROC MBEENG1
core,1
{df-hf;start,atden}
{df-lmp2,interact=1
pipek,delete=1
enepart}
ENDPROC

PROC MBEENG2
core,2
{df-hf;start,atden}
{df-lmp2,interact=1
pipek,delete=1
enepart}
ENDPROC

PROC MBEPROP
core,0
{hf;start,atden
polarizability,nspmlt3}
{mp2;dm,11000.2}
ENDPROC

symmetry,nosym
geomtyp=xyz
geom=water_ammonia_12.xyz
basis,avdz
{mbe,maxlev=2,cutoff=4.5,lmax_m=3,lmax_p=3,damping=1,df_set='CC-PVTZ(D/P)',dispfile='disp.inp'
```

http:
//www.molpro.net/info/current/examples/water10_ammonia2.com

61.5.9 Single calculation on 64 water molecules in periodic boundary conditions

The `PBC` command specifies that periodic boundary conditions should be invoked. The `ewald` directive is also present so that periodic electrostatic and induction energies are included. Without this directive everything would simply be done in the minimum image convention. Damping is used and since a fitting set has been specified using `DF_SET`, damping will be done using density overlap of monomers. The required auxiliary files for this example are:

- dispersion files: `disp.inp`, `h2o_tip.xyz` and `h2o_tip_uchf.disp`
- geometry: `water64.xyz`

all available in the `examples` directory. The input file is below.

```
if(NPROC_MPP.gt.1) then
skipped
end if

memory,20,m
! define the procedure to be run on the monomers

PROC MBEENG1
core,1
{df-hf;start,atden}
{df-lmp2,interact=1
pipek,delete=1
enepart}
ENDPROC

PROC MBEENG2
core,2
{df-hf;start,atden}
{df-lmp2,interact=1
pipek,delete=1
enepart}
ENDPROC

PROC MBEPROP
core,1
{hf;start,atden
polarizability,nspmlt2}
{mp2;dm,11000.2}
ENDPROC


! input ensemble geometry
symmetry,nosym
orient,noorient
geomtyp=xyz
geom=water64.xyz
basis=avdz
{pbc,latt_type='CUBIC',boxsize=12.4297299}
{mbe,maxlev=2,print=1,lmax_m=2,lmax_p=2,cutoff=4.5,damping=1,DF_SET='CC-PVTZ(D/P)',eng_proc1='
ewald}
```

   http://www.molpro.net/info/current/examples/water64_pbc.com

62   WF-in-DFT EMBEDDING

Embedding methods allow a system to be divided into two smaller subsystems, each of which can be treated using a different level of theory. For example, in WF-in-DFT embedding, a WF-level (e.g. HF, MP2, CCSD(T), CASSCF, etc.) calculation is performed on one subsystem, while a DFT-level calculation is performed on the other subsystem. The interactions between the two subsystems are calculated at the DFT level. The primary advantage of WF-in-DFT embedding is that it facilitates the application of an accurate, systematically improvable WF method to regions where such accuracy is required, while a more efficient DFT method is applied to the remainder of the system. The overall strategy for WF-in-DFT embedding is described as follows:

(1) A DFT calculation is performed on the full system.

(2) The system is partitioned into two subsystems, labeled the active subsystem and the frozen subsystem.

(3) The interaction potential between the two subsystems is calculated at the DFT level.

(4) A WF-level calculation is performed on the electrons in the active subsystem, embedded in the DFT-level interaction potential produced by the electrons in the frozen subsystem.

Note: WF-in-DFT embedding is not implemented with symmetry.

It is possible to replace the WF-level calculation on subsystem A with a DFT-level calculation, which corresponds to DFT-in-DFT embedding. Because the interaction potential between the subsystems is calculated at the DFT level, the result of a DFT-in-DFT embedding calculation is numerically identical to the results of a DFT calculation on the full system. Confirming that the DFT-in-DFT energy is numerically equivalent to the energy of a DFT calculation on the full system can thus be a useful sanity check. Similarly, it is possible to replace the DFT-level calculation with a HF-level calculation, which corresponds to WF-in-HF embedding.

Molpro implements the numerically exact projection-based WF-in-DFT embedding method for open and closed shell systems developed in the following papers:

F. R. Manby, M. Stella, J. D. Goodpaster, and T. F. Miller III, J. Chem. Theory Comput., 8, 2564 (2012)

T. A. Barnes, J. D. Goodpaster, F. R. Manby, and T. F. Miller III, J. Chem. Phys., 139, 024103 (2013)

J. D. Goodpaster, T. A. Barnes, F. R. Manby, and T. F. Miller III, J. Chem. Phys., 140, 18A507 (2014)

S. J. Bennie, M. Stella, T. F. Miller III and F. R. Manby, J. Chem. Phys., 143, 024105 (2015)

All publications resulting from the use of this method must acknowledge the above.

62.1 Getting Started

The DFT embedding program is called by the `EMBED,PROJ` directive. When using this directive, the user must specify which MOs are associated with the active subsystem. This can be most directly accomplished through the `ORBS` option:

- `ORBS=[orbital1,orbital2,orbital3...]`

  where *orbital1* is an integer indicating that MO number *orbital1* is associated with the active subsystem. The minimum input to run using the `ORBS` array is:

  ```
  {ks}
  {embed,proj,orbs=[orbital1]}
  {hf}
  {ccsd(t)}
  ```

The KS calculation is performed on the full system. The `EMBED,PROJ` directive indicates the beginning of an embedding calculation in which subsystem A corresponds to the single MO *orbital1*. The HF and CCSD(T) calculations are performed on subsystem A, embedded in a subsystem interaction potential calculated at the KS level.

Alternatively to setting the `ORBS` array, the user can instead specify the `ATOMS` card:

- `ATOMS,atom1,atom2,atom3...`

  where *atom1* is the name of an atom from the geometry specification. Any MO having a Mulliken population greater than `CHARGE_THRESHOLD` (see subsection 62.2) on one of the listed atoms is associated with subsystem A. The minimum input to run using the `ATOMS` card is:

  ```
  {ks}
  {embed,proj;atoms,atom1}
  {hf}
  {ccsd(t)}
  ```

CASSCF calculations can be used as the WF method, but some care must be taken for the specification of the active space. In particular, the `OCC`, `CLOSED`, and `FROZEN` cards must be specified, and they must correspond to the number of `OCC`, `CLOSED`, and `FROZEN` orbitals within the active subsystem:

{ks}

{embed,proj;atoms,*atom1,atom2,...*}

{hf}

{Multi

OCC

CLOSED

FROZEN}

62.2 Options

62.2.1 EMBED,PROJ Options

The following options may be specified on the EMBED,PROJ command line:

- `ORBS=`*[orbital1,orbital2,orbital3...]*

  The ORBS option is described in the section Getting Started (62.1).

- `ATOMS,`*atom1,atom2,atom3...*

  The ATOMS option is described in the section Getting Started (62.1).

- `MU=`value (default 1.d6)

  The value of the coefficient for the level shift used in the projection-based embedding calculations. The projection-based embedding method is in principle numerically exact in the limit of infinite `MU`, but in practice very large values of `MU` will lead to machine-precision errors. Typically, changing `MU` by 1-2 orders of magnitude relative to the default value should have only negligible impact on the energy.

- `CHARGE_THRESHOLD=`value (default 0.4)

  This option is only relevant if the `ATOMS` card is present. Any MO having a Mulliken population on an atom specified by the `ATOMS` card that is greater than `CHARGE_THRESHOLD` is associated with the active subsystem.

- `N_ORBITALS=`value (default none)

  If the `ATOMS` card is present, as an alternative to defining `CHARGE_THRESHOLD`, one can instead define `N_ORBITALS`. In this case, the `N_ORBITALS` MOs with the largest summed Mulliken population on the atoms specified by the `ATOMS` card are associated with the active system. This can be particularly useful for ensuring that the number of MOs in the active subsystem remains constant when calculating the potential energy surface of a reaction.

- `ORBITAL,[record],local`

  This card specifies the orbital record from which MOs corresponding to a HF-level or DFT-level calculation on the full system are read. These MOs should be localized prior to use by the embedding calculation, as shown in the following example:

  {ks;orbital,2200.2}

  {locali,pipek;orbital,2200.2;save,2300.2}

  {embed,proj;atoms,*atom1*;orbital,2300.2,local}

  {hf}

  {ccsd(t)}

  If this card is not present, the last calculated HF or DFT MOs are localized using the Pipek-Mezey algorithm and then employed by the embedding calculation. Thus the preceding example is equivalent to:

```
{ks}
{embed,proj;atoms,atom1}
{hf}
{ccsd(t)}
```

- PRINT=value (default 0)

  Level of output. The value print=0 gives standard output. The value print=1 prints the atoms and molecular orbitals in the active region as well as the active and frozen electrons. The value print=2 prints the same output as print=1 along with the localized molecular orbital composition.

- DIRECTA

  The DIRECTA option controls whether the calculation on the active subsystem is performed in integral-direct mode. By default, the calculation on the active subsystem is performed in integral-direct mode only if the DIRECT or GDIRECT directives have been used globally (see section 14.3). Setting DIRECTA=1 causes all calculations on the active subsystem to be performed in integral-direct mode, while setting DIRECTA=0 causes all calculations on the active subsystem to be performed without integral-direct mode, even if the DIRECT or GDIRECT directives have been previously used globally. Setting DIRECTA=0 is necessary when the calculation on the full system is performed using integral-direct mode and the calculation on the active subsystem is performed using a method for which integral-direct mode is not supported, such as CCSD(T). In this case, it is also necessary to use the FDIRECT directive instead of the DIRECT or GDIRECT directives, which forces Molpro to ignore potential method conflicts when enabling integral-direct mode.

  An example of this process is provided below:

```
FDIRECT
{ks}
{embed,proj,directa=0;atoms,atom1,atom2,...}
DIRECT=.false.
{hf}
{ccsd(t)}
```

- REMOVE

  The EMBED,PROJ command modifies the core Hamiltonian and orbital occupation such that subsequent calculations are performed only on the active subsystem. The EMBED,PROJ,REMOVE command is required to revert to full system calculations after the EMBED,PROJ command. An example is provided below:

```
{ks}
{embed,proj;atoms,atom1,atom2,...}
{hf}
{ccsd(t)}
{embed,proj,remove}
```

- SAVE_ORBITALS

  The SAVE_ORBITALS command is used in conjunction with REMOVE. If this card is present, orbitals that are generated on the active subsystem are not deleted when calling REMOVE. By default, REMOVE will delete all records and orbitals that were saved by the embedding code. To use the EMBED,PROJ code in input file loops, the SAVE_ORBITALS card must not be present.

62.2.2 SCF Options in Regards to WF-in-DFT Embedding

The following options may be specified in the SCF directive in regards to WF-in-DFT embedding.

- HF_COR=value (default 1)

  This option refers to the calculation of the first-order correction to the energy, described in the following paper:

F. R. Manby, M. Stella, J. D. Goodpaster, and T. F. Miller III, J. Chem. Theory Comput., 8, 2564 (2012)

The value `HF_COR=1` causes the first-order correction to be calculated and automatically added to the energy. The value `HF_COR=0` stops the first-order correction from being calculated.

`{ks}`

`{embed,proj;atoms,`*atom1,atom2,...*`}`

`{hf,hf_cor=0}`

`{ccsd(t)}`

62.3   Corrections to the non-additive exchange-correlation

Often the largest source of error in a WF-in-DFT calculation, relative to a WF calculation on the full system, results from evaluation of the exchange-correlation contributions to the embedding potential at the DFT level. This error can be largely removed by evaluating the exchange-correlation contributions to the embedding potential using MP2 theory. It is thus possible to calculate an MP2-level correction to the WF-in-DFT energies, as described in the following paper:

J. D. Goodpaster, T. A. Barnes, F. R. Manby, and T. F. Miller III, J. Chem. Phys. 140, 18A507 (2014)

The MP2 correction can be invoked by running the `EMBED,PROJ,MP2_CORR` command:

- `EMBED,PROJ,MP2_CORR`
  `{ks}`
  `{embed,proj;atoms,`*atom1,atom2,...*`}`
  `{hf}`
  `{ccsd(t)}`
  `{embed,proj,mp2_corr}`

By default, the program will calculate the MP2 correction using LMP2; however, any local method can be used. The program will search for a procedure named `PROC MP2_CORR` and will use any location correlation method specified there. For example, including the following procedure at the top of the input file:

`PROC MP2_CORR`

`{df-lmp2,THRBP=1;orbital,5300.2} !  Must be 5300.2`

`ENDPROC`

will calculate the MP2 correction with all pairs correlated using density fitting.
Similarly,

`PROC MP2_CORR`

`{df-lccsd,THRBP=0.99,throsv=1.d-4;orbital,5300.2} !  Must be 5300.2`

`ENDPROC`

will calculate the MP2 correction using the orbital-specific virtual LCCSD method.

62.4   Improved efficiency using basis set truncation

By default, the calculation on the active subsystem is performed using all basis functions employed by the calculation on the full system. The computational cost of a high-level WF calculation on even a small active subsystem can thus be prohibitively high if the full system is sufficiently large. This cost can be greatly reduced by performing the calculation on the active subsystem using only the basis functions that are most important for representation of the MOs associated with the active subsystem. Two methods are implemented to facilitate truncation of the active subsystem basis set, and these methods are described in the subsections below.

62.4.1   Atom-based method

In the atom-based method for truncating the active subsystem basis set, only basis functions that are centered on atoms near the active subsystem are included in the active subsystem basis set. This method is described more detail in:

T. A. Barnes, J. D. Goodpaster, F. R. Manby, and T. F. Miller III, J. Chem. Phys. 139, 024103 (2013)

This method can be invoked using the BATOMS card:

- `BATOMS,`*`atom1,atom2,atom3...`*

  where *`atom1`* is the name of an atom from the geometry specification, and the atoms are listed in the order in which they appear in the geometry specification. The calculation on the active subsystem is performed using only basis functions centered on atoms listed by the `BATOMS` card. The minimum input to run using the `BATOMS` card is:

  `{ks}`
  `{embed,proj;atoms,`*`atom1`*`;batoms,`*`atom1`*`}`
  `{hf}`
  `{ccsd(t)}`

Alternatively to using the `BATOMS` card, the user can instead specify the `BASECUT` option:

- `BASECUT=`*`value`*

  `{ks}`
  `{embed,proj,basecut=`*`value`*`;atoms,`*`atom1`*`}`
  `{hf}`
  `{ccsd(t)}`

  where *`value`* is a distance in Angstroms. The calculation on the active subsystem is performed using only basis functions centered on atoms within a distance `BASECUT` of an atom specified by the `ATOMS` card.

When employing basis set truncation, the embedding potential produced by the MOs in the frozen subsystem is only partially calculated using the numerically exact projection-based embedding method described in section 62. For MOs that have negligible Mulliken population on the basis functions that are employed in the calculation on the active subsystem, the non-additive kinetic energy contribution to embedding potential is calculated using the approximate Thomas-Fermi (TF) functional. Specifically, the TF functional is used for any MO in the frozen subsystem for which the sum of the absolute Mulliken populations on the atoms included by the `BATOMS` card or `BASECUT` option is less than the option `TAU` (default = 0.1). For closed-shell MOs, `TAU` should typically be in the range 0.0-2.0. Setting `TAU` to a value that is too close to zero can cause numerical artifacts that prevent convergence of the energy with respect to the value of the `MU` option (see subsection 62.1); as a result, it is recommended to perform all calculations with multiple values of `MU` to ensure that these numerical artifacts are not present.

62.4.2   Density threshold method

The density threshold truncation method is an alternative to the atom-based truncation method described in section 62.4.1. Its primary advantage is that it requires just one parameter to be adjusted for all types of molecular system and functions that are important in the long range are automatically kept. At its low truncation limit it produces the full basis embedding answer or at high truncation its limit is a result constructed from just the functions on the active embedding region. Application of this method involves slightly different input options:

- AOTRUNC

  The AOTRUNC option invokes the use of the density threshold method, and must always be be given when this method is used.

- DENKEEP=value (default 0.0)

  The DENKEEP option is the minimum gross Mulliken population that each basis function is compared against. Environment functions with a greater gross populations than this value are grouped (according to angular momentum partners i.e px, with py and pz) and are kept. Environment functions lower than DENKEEP are grouped and discarded from the post embedding calculation. Setting DENKEEP=0.0 is equivalent to the case in which the basis set is not truncated as all functions have a gross population greater than 0. For accurate type-in-type energies, DENKEEP should typically be no more than 0.001, although convergence with respect to this parameter slightly varies according to the system and degree of delocalisation.

  For example:

  {ks;orbital,2100.2}

  {ibba,bonds=1;orbital,2100.2;save,2300.2}

  {embed,proj,AOTRUNC,DENKEEP=0.001;orbital,2300.2,local}

  {hf}

  {ccsd(t)}

- STOREAO

  Enables the retention of selected functions along a geometry scan. This can be useful for basis set consistency for a dissociation reaction, which naturally would have fewer functions retained for a given threshold as the active and environment are separated. It is recommended that the calculations always go from associated to dissociated in order to benefit from this routine.

When using this method, the following should be taken into consideration:
(1) The accuracy of this truncation method is sensitive to the size of the basis set. For this reason, it is recommended to use at least a triple-zeta basis set.
(2) It is recommended to use Knizia's IBO localization method, which reduces the orbital tails.
(3) For accurate HF-in-HF and DFT-in-DFT results, it is recommended to use a value for DENKEEP of less than 0.0001. This is especially important when embedding across covalent bonds.
(4) The geometry must be in Cartesian coordinates.

All publications resulting from the use of this method must acknowledge the following:

S. J. Bennie, M. Stella, T. F. Miller III and F. R. Manby, J. Chem. Phys., 143, 024105 (2015).

62.5   Examples

62.5.1   Projection-Based Embedding

This example performs a HF-in-HF and CCSD(T)-in-HF calculation on methanol. The HF-in-HF energy is numerically identical to the HF energy of the full system. By replacing the initial HF calculation on the full system with a DFT calculation, it is possible to perform HF-in-DFT and CCSD(T)-in-DFT calculations.

```
!methanol
memory,100,m
symmetry,nosym ! Embedding is not implemented with symmetry

r1=2.648205499 ! Bohr
r2=1.780518852 ! Bohr
r3=2.064847045 ! Bohr
a1=110.61344
d1=0
d2=119.9573

{gthresh,grid=1e-12,orbital=1e-8,coeff=1e-7}

geometry= {C;
           O,C,r1;
           H1,O,r2,C,a1;
           H2,C,r3,O,a1,H1,d1;
           H3,C,r3,O,a1,H1,d2;
           H4,C,r3,O,a1,H1,-d2}

basis,6-31g

! Step 1: Perform a HF calculation on the full system.
{hf}

! Step 2: Perform orbital localization.
! Localized MOs are saved to record 3100.2
{locali,pipek;save,3100.2}

! Step 3: Call embedding code to generate the embedding potential. This requires:
! Specification of embedded MOs
! Location of localized orbitals
{embed,proj,orbs=[1,6,7,8,9]       ! The active subsystem corresponds to the indicated MOs
orbital,3100.2,local}              ! Use the localized MOs from record 3100.2

! Step 4: Now call HF again, but this time only subsystem A will be calculated.
! This corresponds to a HF-in-HF calculation.
{hf}

! Step 5: Now call CCSD(T). This will perform a CCSD(T)-in-HF calculation
{ccsd(t)}

! Step 6: Remove the projection operator from the core if addition calculations
! are given in the input after embedding.
{embed,proj,remove}
```

62.5.2 Embedded Multiconfigurational Calculations

This example performs an MCSCF-in-DFT calculation on butene.

```
!butene
memory,10,m
symmetry,nosym ! Embedding is not implemented with symmetry

{gthresh,grid=1e-12,orbital=1e-8,coeff=1e-7}

geometry={
C1,,           0.835432384 ,    0.049538050 ,   -1.305177530
C2,,          -0.187431703 ,   -1.125601622 ,    1.070665830
C3,,          -0.143380420 ,    0.687719249 ,    3.341106035
H1,,          -2.118667450 ,   -1.789600571 ,    0.735591607
H2,,           0.942690000 ,   -2.802115823 ,    1.537268881
H3,,          -0.860542916 ,   -0.240216354 ,    5.042940132
H4,,          -1.309266799 ,    2.354788168 ,    2.978399494
H5,,           1.778149207 ,    1.339614495 ,    3.742333311
C4,,          -0.440429873 ,    0.344384131 ,   -3.450328416
H6,,           2.782544497 ,    0.715697009 ,   -1.206788342
H7,,          -0.434433198 ,   -1.089606640 ,   -4.914726597
H8,,          -1.545390643 ,    2.035286250 ,   -3.818951212
} !Geometry is in Bohr

basis=6-31g*

! Step 1: Perform DFT on full system.
! Level shift added for improved convergence for this system.
!  The system is a butene where the double bond is twisted by 90 degrees.
{rks,b-lyp,shifta=-0.3}

! Step 2: Call embedding code and specify the atoms corresponding to the twisted double bond.
{embed,proj;atoms,C1,C4,H6,H7,H8}

! Step 3: Generate initial orbitals for MCSCF.
{rhf}

! Step 4: Perform MCSCF calculation.
! When performing an embedded MCSCF calculation, always specify the active space.
{mcscf;
config,csf;
OCC,9;
closed,7;
frozen,2;}

! Step 5: Add dynamic correlation
{mrci}

! Step 6: Remove the projection operator from the core if additional calculations
! are given in the input after embedding.
{embed,proj,remove}
```

   http://www.molpro.net/info/current/examples/embed_mrci.com

62.5.3   Atom-Based Truncation

This example performs an RCCSD(T)-in-B3LYP calculation on a water hexamer. The basis set used by
the calculation on the active subsystem is truncated using the atom-based method.

```
!water hexamer
memory,10,m
symmetry,nosym ! Embedding is not implemented with symmetry

{gthresh,grid=1e-12,orbital=1e-8,coeff=1e-7}

Geometry={
O1,,         30.135084563 , -74.799706380  ,  1.048420054
H1,,         28.921313473 , -75.753640128  ,  0.078612607
H2,,         31.789161840 , -75.151195440  ,  0.241884944
O2,,         34.670994180 , -75.109054547  , -1.258935544
H3,,         36.151405626 , -75.595470051  , -0.256813780
H4,,         34.965413510 , -73.329310483  , -1.617038645
O3,,         39.016608376 , -75.723971428  ,  1.713981595
H5,,         40.543885030 , -76.445468862  ,  1.027066149
H6,,         39.369987161 , -73.909078458  ,  1.857033863
O4,,         39.375845312 , -70.481115268  ,  1.713981595
H7,,         37.857450371 , -69.945566884  ,  0.797653397
H8,,         39.389451340 , -69.480883230  ,  3.238045714
O5,,         30.452369580 , -69.704059885  ,  1.057490739
H9,,         30.104659973 , -71.541440596  ,  1.112103824
H10,,        30.145478057 , -69.115599170  ,  2.755787607
O6,,         35.044970980 , -69.587463784  , -1.139504853
H11,,        34.987523306 , -68.420179956  , -2.539602939
H12,,        33.376531785 , -69.444222543  , -0.300466454
} !Geometry is in Bohr

basis,VDZ

! Step 1: Perform a B3LYP calculation on the full system.
{rks,B3LYP}

! Step 2: Perform orbital localization.
{locali,pipek;save,3101.2}

! Step 3: Call embedding code to generate the embedding potential.
! Truncation of the active subsystem basis set includes only atoms within 3.5 Angstroms.
! The active subsystem corresponds to the first water molecule.
{embed,proj,mu=1.d6,tau=0.1,basecut=3.5;atoms,O1,H1,H2;orbital,3101.2,local}

! Step 4: Peform a HF-in-B3LYP calculation.
{hf;noenest}

! Step 5: Perform an RCCSD(T)-in-B3LYP calculation.
{rccsd(t)}

! Step 6: Remove the projection operator from the core if additional calculations
! are given in the input after embedding.
{embed,proj,remove}
```

62.5.4   Density Threshold Truncation

This example performs a CCSD(T)-in-B3LYP calculation on a water dimer, using the density-threshold method with a DENKEEP of 0.001.

```
!water dimer
!memory,150,m

{gthresh,orbital=1e-8,coeff=1e-7}

geometry={
O1,,          2.872302451 , -0.739837226  ,  2.587473481
H11,,         1.114872273 , -1.362093804  ,  2.841067168
H12,,         3.830013761 , -1.316171569  ,  4.018958028
O2,,          1.378439935 ,  3.695314083  , -0.113721828
H21,,         2.070708975 ,  2.651580550  ,  1.227452707
H22,,         2.064068477 ,  2.891071211  , -1.605148488
} !Geometry is in Bohr

Basis,avtz

! Step 1: Perform a HF calculation on the full system
{hf}

! Step 2: Perform orbital localization.
{locali,pipek;save,3100.2}

! Step 3: Call embedding code to generate the embedding potential
! using truncation with the density threshold method.
{embed,proj,N_orbitals=5,Aotrunc,DENKEEP=0.0001;atoms,O1,H11,H12;orbital,3100.2,local}

! Step 4: Perform a HF-in-HF calculation
{hf;noenest;wf,10}

! Step 5: Perform a CCSD(T)-in-HF calculation
{ccsd(t);wf,10}

! Step 6: Remove the projection operator from the core if additional calculations
! are given in the input after embedding
{embed,proj,remove}
```

  http://www.molpro.net/info/current/examples/embed_trunc2.com

62.5.5 Open Shell System

This example performs a RCCSD(T)-in-LDA calculation on the methoxy radical.

```
!Methoxy Radical
memory,8,M
zsymel=nosym  ! Embedding is not implemented with symmetry

{gthresh,grid=1e-12,orbital=1e-8,coeff=1e-7}

Geometry={
O1,,          2.328578323 , -0.516253350 , -0.241152468
H1,,         -3.930899693 ,  0.818199944 ,  0.136592671
C1,,         -2.292181882 , -0.433746123 , -0.018359872
H2,,         -2.391620554 , -1.802771746 ,  1.530291417
C2,,          0.160581025 ,  1.056429748 ,  0.096479104
H3,,          0.284618712 ,  2.116540479 ,  1.878957579
H4,,          0.248705545 ,  2.426749515 , -1.444737877
H5,,         -2.407046505 , -1.464278195 , -1.802909809
}! Geometry is in Bohr

basis,6-31g

! Step 1: Perform a DFT calculation on the full system.
{ks,lda;wf,25,1,1}

! Step 2: Perform orbital localization.
{locali,pipek;save,3100.2}

! Step 3: Call embedding code to generate the embedding potential.
{embed,proj,mu=1d5;atoms,O1}

! Step 4: Now call HF, but this time only subsystem A will be calculated.
! This corresponds to a HF-in-LDA calculation.
{hf}

! Step 5: Now call CCSD(T). This will perform a RCCSD(T)-in-LDA calculation
{rccsd(t)}

! Step 6: Remove the projection operator from the core if addition calculations
! are given in the input after embedding.
{embed,proj,remove}
```

http://www.molpro.net/info/current/examples/embed_open.com

63   THE TDHF AND TDKS PROGRAMS

Real-time electronic dynamics using time-dependent Hartree-Fock and time-dependent Kohn-Sham theories can be performed using the commands TDHF and TDKS respectively, which have to be preceded by a HF and KS command. Unrestriced versions are available through TDUHF and TDUKS and should be preceded by UHF and UKS runs respectively. All methods require symmetry to be switched off. For details on the theory and methods see H. Eshuis, G. G. Balint-Kurti and F. R. Manby, *J. Chem. Phys.* **128**, 114113 (2008), and references therein. The commands take several options:

```
command,t=,dt=,ns=,ng=,grsize=,print=;
PULSE,options
```

The total propagation time (in au) is set by *t*; *dt* sets the timestep and *ns* the number of steps, where two of the three have to be provided. *ng* sets the number of grid points in one dimension (default = 0) and *grsize* the grid size in bohr (default = 10 bohr). Setting $ng > 2$ switches on the calculation of quantum currents (see below). The option *print* determines the level of output (0=normal output, 1=object linear

in matrices, 2=matrices as well, > 2 debug). The subcommand `PULSE` determines the envelope used, and takes several options depending on the envelope selected. Possibilities are:

> `NONE`: no pulse, no options
>
> `STEP,` $e_x, e_y, e_z,$ `length`
> a DC-field of strength e_q is applied in the qth direction for a total time *length* (in au)
>
> `DC,` e_x, e_y, e_z, α
> a DC-field of strength e_q is applied in the qth direction. The field is switched on exponentially with a rate determined by α.
>
> `TRAP,` $e_x, e_y, e_z, \omega, \alpha$
> an oscillating field of strength e_q is applied in the qth direction. The field oscillates with angular frequency ω. The envelope reaches e_q in one period of the field, stays constant for α periods and then decays to zero in one period.
>
> `CW,` e_x, e_y, e_z, ω
> an oscillating field of strength e_q is applied in the qth direction. The field oscillates with angular frequency ω. No envelope present.
>
> `CWSIN,` $e_x, e_y, e_z, \omega, \alpha$
> an oscillating field of strength e_q is applied in the qth direction. The field oscillates with angular frequency ω and is switched on using a $\sin^2$ envelope, where α determines how fast the field is switched on.
>
> `CWGAUSS,` $e_x, e_y, e_z, \omega, \alpha$
> like `CWSIN`, but with a Gaussian envelope

The finite pulses `TRAP` and `STEP` produce an absorption spectrum obtained from the time-dependent dipole moment sampled after the field is switched off. It is located in *($input).spec*, or in *molpro.spec* when running interactively, and contains of 4 columns, which contain energy (eV) and the absorption in the x, y, z direction respectively.

All runs produce a file *($input).dat* (or *molpro.dat*) which contains time-dependent properties, like the components of the field, components of the dipole moment, total energy, orbital occupation numbers, orbital energies and total number of electrons. The Molpro output file specifies the order of the data in the file. For very long runs the size of the file is restricted by printing only every twentieth set of data.

In case of an unrestricted run three files are produced: *($input).dat, ($input)a.dat, ($input)b.dat*. The first file contains the generic data about the field, total energy, dipole moments and the expectation value of the total spin operator. The other two files contain the orbital energies and occupation numbers for the α and β electrons respectively.

`TDKS` and `TDUKS` use the options provided by the `KS` and `UKS` comands. At the moment `TDKS`/`TDUKS` suffers from numerical instabilities when using strong fields. Divergence of the energy is observed, possibly due to the use of quadrature for the evaluation of the potential.

Quantum currents will be calculated when choosing $ng > 2$. A cubic grid will be computed of size *grsize* with a total of ng^3 gridpoints. The imaginary part of the density will be summed at every timestep and after the dynamics the total current will be evaluated at every gridpoint. The user can extract the required data from this array by printing out parts of it, or by integrating over point, but this requires actual coding, as this has not been implemented sufficiently neat. It is also straightforward to evaluate the currents at every timestep or at selected timesteps. This is not done automatically, because it slows down the dynamics considerably.

64   ORBITAL MERGING

Orbitals can be manipulated using the `MERGE` facility. For instance, this allows the construction of molecular orbitals from atomic orbitals, to merge and orthogonalize different orbital sets, or to perform 2×2 rotations between individual orbitals. Other orbital manipulations can be performed using the `LOCALI` program (see section 18) or the `MATROP` program (section 65).

The merge program is called using

MERGE [,*namout.file*]

All subcommands described in the following sections may be abbreviated by three characters. *namout.file* specifies the output data set (see also SAVE command). If *namout.file* is omitted and no SAVE card is present, the new orbitals are not saved. All output orbitals must be supplied via ORBITAL and ADD, MOVE, EXTRA, or PROJECT directives before they can be saved.

64.1   Defining the input orbitals (ORBITAL)

ORBITAL,*namin.file*,*specifications*

Reads an input orbital set from a dump record. *specifications* can be used to select specific orbital sets, as described in section 4.11. Subsets of these orbitals can be added to the output set by the ADD, MOVE, or EXTRA commands.

64.2   Moving orbitals to the output set (MOVE)

MOVE,*orb1.sym1*,*orb2.sym2*,*orb3.sym3*,*ioff*,*fac*,*istart*,*iend*

Moves orbitals *orb1.sym1* to *orb2.sym2* from the input set to the first vector of symmetry *sym3* in the output set which is undefined so far. The first *orb3-1* vectors in the output set are skipped regardless of whether they have been defined before or not. If *sym2* > *sym1*, *sym3* will run from *sym1* to *sym2* and the input for *sym3* has no effect. If *orb1.sym1* is negative, abs(*orb1*) is the maximum number of orbitals to be moved, starting with orbital *1.sym1*, up to *orb2.sym2*. If *orb2.sym2* is negative, abs(*orb2*) is the maximum number of vectors to be moved, starting at *orb1.isym1* up to the last orbital in symmetry *sym2*.

Orbitals from the input set which have already been moved or added to the output set are generally skipped. If *orb1* and *orb2* are zero, the whole input set is moved to the output set. In this case the input and output dimensions must be identical. If *orb1* is nonzero but *orb2* is zero, *orb2* is set to the last orbital in symmetry *sym2*. If *sym2=0*, *sym2* is set to *sym1*. *ioff* is an offset in the output vector, relative to the global offset set by OFFSET directive. *fac* has no effect for move. The elements *istart* to *iend* of the input vector are moved. If *istart=0* and *iend=0*, the whole input vector is moved.

The usage of the MOVE directive is most easily understood by looking at the examples given below. See also ADD and EXTRA commands.

64.3   Adding orbitals to the output set (ADD)

ADD,*orb1.sym1*,*orb2.sym2*,*orb3.sym3*,*ioff*,*fac*,*istart*,*iend*

This adds orbitals *orb1.sym1* to *orb2.sym2* to the output vectors, starting at *orb3.sym3*. The input vectors are scaled by the factor *fac*. If *fac=0*, *fac* is set to 1.0. For other details see MOVE command. Note, however, that the output vectors which have already been defined are not skipped as for MOVE.

See also MOVE and EXTRA commands.

64.4   Defining extra symmetries (EXTRA)

EXTRA,*exsym*,*orb1.sym1*,*orb2.sym2*,*orb3.sym3*,*ioff*,*fac*,*istart*,*iend*

Works exactly as MOVE, but only input vectors with extra symmetry *exsym* are considered. If *orb1.sym1* and *orb2.sym2* are zero, all input vectors are moved to the output set ordered according to increasing extra symmetries.

Examples:

`EXTRA,1,-4.1`	will move the next 4 orbitals in symmetry 1 which have extra symmetry 1. Orbitals which have been moved before are skipped.
`EXTRA,2,1.1`	will move all orbitals of symmetry 1 which have extra symmetry 2. Orbitals which have been moved before are skipped.
`EXTRA`	will move all orbitals (all symmetries) and order them according to extra symmetries.
`EXTRA,3,1.1,0.8`	Will move all orbitals which have extra symmetry 3 in all symmetries. Orbitals which have been moved before are skipped.

See also `ADD` and `MOVE` commands.

64.5   Defining offsets in the output set (`OFFSET`)

`OFFSET`,*iof$_1$*,*iof$_2$*,…,*iof$_8$*;

Sets offsets in the output vector for symmetries 1 to 8. In subsequent `MOVE` or `ADD` commands, the input vectors are moved to the locations *iof$_i$+1* in the output vectors. The offset for individual `ADD` or `MOVE` commands can be modified by the parameter *ioff* on these cards. This card should immediately follow the orbital directive to which it applies. Generally, this card is only needed if the dimensions of input and output vectors are not identical.

If the dimensions of the input orbital sets are smaller than the current basis dimension, the offsets are determined automatically in the following way: each time an orbital set is read in, the previous input orbital dimensions are added to the offsets. Hence, this works correctly if the orbital sets are given in the correct order and if the individual dimensions add up to the current total dimension. If this is not the case, the offsets should be specified on an `OFFSET` card which must follow the orbital directive.

64.6   Projecting orbitals (`PROJECT`)

`PROJECT`,*namin.file*

This command will read vectors from record *namin.file*. These vectors must have the same dimension as those of the current calculation. All orbitals defined so far by the `ORBITAL`, `MOVE`, and `ADD` directives are projected out of the input set. The projected orbitals are then orthonormalized and moved to the undefined output vectors. This should always yield a complete set of vectors.

64.7   Symmetric orthonormalization (`ORTH`)

`ORTH`,*n$_1$*,*n$_2$*,…,*n$_8$*

Symmetrically orthonormalizes the first *n$_i$* vectors in each symmetry *i*. These vectors must be supplied before by `ORBITAL` and `MOVE` or `ADD` directives.

64.8   Schmidt orthonormalization (`SCHMIDT`)

`SCHMIDT`,*n$_1$*,*n$_2$*,…,*n$_8$*

Schmidt orthonormalizes the first *n$_i$* vectors in each symmetry *i*. These vectors must be supplied before by `ORBITAL` and `MOVE` or `ADD` directives.

64.9   Rotating orbitals (`ROTATE`)

`ROTATE`,*iorb1.sym,iorb2,angle*

Will perform 2×2 rotation of orbitals *iorb1* and *iorb2* in symmetry *sym* by the specified *angle* (in degree). *angle=0* means to swap the orbitals (equivalent to *angle=90*) These vectors must be supplied before by `ORBITAL` and `MOVE` or `ADD` directives.

64.10   Initialization of a new output set (`INIT`)

`INIT`,*namout.file*

Will initialize a new output set. All previous vectors in the output set are lost unless they have been saved by a `SAVE` directive!

64.11   Saving the merged orbitals

`SAVE`,*namout.file*

Saves the current output set to record *namout.file*. The current output set must be complete and will be Schmidt orthonormalized before it is saved. If the `SAVE` directive is not supplied, the output vectors will be saved after all valid commands have been processed to the record specified on the `MERGE` card.

64.12   Printing options (`PRINT`)

`PRINT`,*iprint,ideb*

Specifies print options.

$iprint = 0$	no print
$iprint \geq 1$:	orthonormalized orbitals specified on `ORTH` card are printed.
$iprint \geq 2$:	orbitals are also printed before this orthonormalization.
$iprint \geq 3$:	all final vectors are printed.
$ideb \neq 0$:	the overlap matrices are printed at various stages.

64.13   Examples

64.13.1 H_2F

This example merges the orbitals of H_2 and F

```
***,example for merge
print,orbitals,basis
rh2=1.4
rhf=300.
basis=vdz
symmetry,x,y                              !use C2v symmetry
geometry={F}

text,F
{rhf;wf,9,1,1;occ,3,1,1;orbital,2130.2} !rhf for f-atom

text,H2
symmetry,x,y                              !use C2v symmetry
geometry={
        H1,
        H2,H1,rh2}

{hf;orbital,2100.2}                       !scf for h2
{multi;occ,2;orbital,2101.2}             !mcscf for h2

text,FH2
geometry={F;                              !linear geometry for F+H2
        H1,F,rhf
        H2,H1,rh2,F,180}

{merge
orbital,2130.2                            !rhf orbitals for F-atom
move,1.1,2.1,1.1                          !move orbitals 1.1, 2.1
move,3.1,0.4,4.1;                         !move all remaining, starting at 4.1
orbital,2100.2                            !hf orbitals for H2
move,1.1,0.4                              !move these to free positions
save,2131.2}                              !save merged orbitals

{rhf;occ,4,1,1;start,2131.2              !rhf for F+H2
orbital,2132.2}

{merge
orbital,2130.2                            !rhf orbitals for F-atom
move,1.1,2.1,1.1                          !move orbitals 1.1, 2.1
move,3.1,3.1,4.1;                         !move orbital 3.1 to 4.1
move,4.1,0.4,6.1                          !move all remaining, starting at 6.1
orbital,2101.2                            !mcscf orbitals for H2
move,1.1,0.4                              !move these to free positions
save,2141.2}                              !save merged orbitals

{multi;occ,5,1,1;start,2141.2}            !casscf for F+H2 using valence space
```

   http://www.molpro.net/info/current/examples/h2f_merge.com

64.13.2   NO

This example merges the SCF orbitals of N and O to get a full valence space for NO. In the simplest case
the atomic calculations are performed in the individual separate basis sets, but using the same symmetry
(C_{2v}) as the molecular calculation.

```
***,NO merge
r=2.1

symmetry,x,y
geometry={n}           !N-atom, c2v symmetry

{rhf;occ,3,1,1;        !rhf nitrogen
wf,7,4,3;              !4S state
orbital,2110.2}        !save orbitals to record 2110 on file 2

symmetry,x,y
geometry={o}

{rhf;occ,3,1,1;        !rhf for oxygen
wf,8,4,2               !3P state
orbital,2120.2}        !save orbitals to record 2120 on file 2

geometry={n;o,n,r}     ! NO molecule, c2v symmetry

{MERGE
ORBITAL,2110.2         ! read orbitals of N atom
MOVE,1.1,1.1           ! move 1s orbital to output vector 1.1
MOVE,2.1,2.1,3.1       ! move 2s orbital to output vector 3.1
MOVE,3.1,3.1,5.1       ! move 2pz orbital to output vector 5.1
MOVE,1.2,1.2           ! move 2px orbital to output vector 1.2
MOVE,1.3,1.3           ! move 2py orbital to output vector 1.3
MOVE,4.1,,7.1          ! move virtual orbitals of symmetry 1
MOVE,2.2,,3.2          ! move virtual orbitals of symmetry 2
MOVE,2.3,,3.3          ! move virtual orbitals of symmetry 2
MOVE,1.4               ! move virtual orbitals of symmetry 2
ORBITAL,2120.2         ! read orbitals of O atom
MOVE,1.1,0.4           ! move all oxygen orbitals into place
ROT,3.1,4.1,45;        ! rotate 2s orbitals to make bonding and antibonding
                       ! linear combinations
ROT,5.1,6.1,-45;       ! rotate 2pz orbitals to make bonding and antibonding
                       ! linear combinations
PRINT,1                ! set print option
ORTH,6,2,2             ! symmetrically orthonormalize the valence orbitals
                       ! the resulting orbitals are printed
save,2150.2}           ! save merged orbitals to record 2150.2

{multi;occ,6,2,2       ! perform full valence casscf for NO
wf,15,2,1              ! 2Pix state
wf,15,3,1              ! 2Piy state
start,2150.2}          ! start with merged orbitals
```

    http://www.molpro.net/info/current/examples/no_merge1.com

One can also do the atomic calculations in the total basis set, using dummy cards. In this case the procedure is more complicated, since the union of the two orbital spaces is over-complete. The calculation can be done as follows:

a) SCF for the total molecule, orbitals saved to 2100.2

b) SCF for the N atom with dummy basis on the O atom, orbitals saved on 2110.2

c) SCF for the O atom with dummy basis on the N atom, orbitals saved on 2120.2

d) Merge the atomic SCF orbitals. Finally, obtain the virtual orbitals by projecting the merge orbitals out of the SCF orbitals for NO.

```
***,NO merge
geometry={n;o,n,r}
r=2.1

{rhf;occ,5,2,1     !rhf for NO
wf,15,2,1          !2Pi state
orbital,2100.2}    !save orbitals to record 2100 on file 2

dummy,o            !oxygen is dummy
{rhf;occ,3,1,1;     !rhf nitrogen
wf,7,4,3;          !4S state
orbital,2110.2}    !save orbitals to record 2110 on file 2

dummy,n            !nitrogen is dummy
{rhf;occ,3,1,1;    !rhf for oxygen
wf,8,4,2           !3P state
orbital,2120.2}    !save orbitals to record 2120 on file 2

dummy              ! remove dummies
{MERGE              !call merge program

ORBITAL,2110.2     ! read orbitals of N atom
MOVE,1.1,1.1       ! move input vector 1.1 to output vector 1.1
MOVE,2.1,3.1,3.1   ! move input vectors 2.1,3.1 to output vectors
                   ! 3.1 and 4.1
MOVE,1.2,1.2       ! move input vector 1.2  to output vector 1.2
MOVE,1.3,1.3       ! move input vector 1.3  to output vector 1.3
ORBITAL,2120.2     ! read orbitals of O atom
MOVE,1.1,3.1       ! move input vectors 1.1 to 3.1 to output vectors
                   ! 2.1, 5.1, 6.1
MOVE,1.2,1.2       ! move input vector 1.2 to output vector 2.2
MOVE,1.3,1.3       ! move input vector 1.3 to output vector 2.3
ROT,3.1,5.1,45;    ! rotate 2s orbitals to make bonding and antibonding
                   ! linear combinations
ROT,4.1,6.1,-45;   ! rotate 2pz orbitals to make bonding and antibonding
                   ! linear combinations
PRINT,1            ! set print option
ORTH,6,2,2         ! symmetrically orthonormalize the valence orbitals
                   ! the resulting orbitals are printed
PROJ,2100.2        ! Project valence orbitals out of scf orbitals of the
                   ! molecule and add virtual orbital set.
SAVE,2150.2        ! save merged orbitals to record 2150 on file 2
}

{multi;occ,6,2,2   ! perform full valence casscf for NO
wf,15,2,1          ! 2Pi state
wf,15,3,1          ! 2Pi state
start,2150.2}      ! start with merged orbitals
```

http://www.molpro.net/info/current/examples/no_merge2.com

65 MATRIX OPERATIONS

MATROP;

MATROP performs simple matrix manipulations for matrices whose dimensions are those of the one particle basis set. To do so, first required matrices are loaded into memory using the LOAD command. To each matrix an internal *name* (an arbitrary user defined string) is assigned, by which it is referenced in further commands. After performing operations, the resulting matrices can be saved to a dump record using the SAVE directive. Numbers, e.g. traces or individual matrix elements, can be saved in variables.

code may be one of the following:

LOAD	Loads a matrix from a file
SAVE	Saves a matrix to a file
ADD	Adds matrices
TRACE	Forms the trace of a matrix or of the product of two matrices
MULT	Multiplies two matrices
TRAN	Transforms a matrix
DMO	Transforms density into MO basis
NATORB	Computes natural orbitals
DIAG	Diagonalizes a matrix
OPRD	Forms an outer product of two vectors
DENS	Forms a closed-shell density matrix
FOCK	Computes a closed-shell fock matrix
COUL	Computes a coulomb operator
EXCH	Computes an exchange operator
PRINT	Prints a matrix
PRID	Prints diagonal elements of a matrix
PRIO	Prints orbitals
PRIC	Prints the transpose of a matrix in scientific notation
ELEM	Assigns a matrix element to a variable
READ	Reads a square matrix from input
WRITE	Writes a square matrix to a file
SET	Assigns a value to a variable
ADDVEC	Adds a multiple of a column of one matrix to a column of a second matrix

Note that the file name appearing in above commands is converted to lower case on unix machines.

See the following subsections for explanations.

65.1 Calling the matrix facility (MATROP)

The program is called by the input card MATROP without further specifications.

MATROP

It can be followed by the following commands in any order, with the restriction that a maximum of 50 matrices can be handled. The first entry in each command line is a command keyword, followed by the name of the result matrix. If the specified result matrix *result* already exists, it is overwritten, otherwise a new matrix is created. All matrices needed in the operations must must have been loaded or defined before, unless otherwise stated.

If a backquote (') is appended to a name, the matrix is transposed.

65.2 Loading matrices (LOAD)

All matrices which are needed in any of the subsequent commands must first be loaded into memory using the LOAD command. Depending on the matrix type, the LOAD command has slightly different options. In all forms of LOAD *name* is an arbitrary string (up to 16 characters long) by which the loaded matrix is denoted in subsequent commands.

65.2.1 Loading orbitals

LOAD,*name*,ORB [,*record*] [,*specifications*]

loads an orbital coefficient matrix from the given dump record. If the record is not specified, the last dump record is used. Specific orbitals sets can be selected using the optional *specifications*, as explained in section 4.11. The keyword ORB needs not to be given if *name*=ORB.

65.2.2 Loading density matrices

LOAD,*name*,DEN [,*record*] [,*specifications*]

loads a density matrix from the given dump record. If the record is not given, the last dump record is used. Specific densities sets can be selected using the optional *specifications*, as explained in section 4.11. The keyword DEN needs not to be given if *name*=DEN.

Example,

load,trdm,dens,6000.2,stateb=1.1,statek=3.2

loads a transition density matrix that has previously been saved on record 6000.2. The bra state is the first state in symmetry 1, and ket is the third state in symmetry 2.

An equivalent input would be

load,trdm,dens,6000.2,stateb=1,statek=3,symb=1,symk=2

65.2.3 Loading the AO overlap matrix S

LOAD,*name*,S

loads the overlap matrix in the AO basis. The keyword S needs not to be given if *name*=S.

65.2.4 Loading $S^{-1/2}$

LOAD,*name*,SMH

loads $S^{-1/2}$, where S is the overlap matrix in the AO basis. The keyword SMH needs not to be given if *name*=SMH.

65.2.5 Loading the one-electron hamiltonian

LOAD,*name*,H0

LOAD,*name*,H01

loads the one-electron hamiltonian in the AO basis. H01 differs from H0 by the addition of perturbations, if present (see sections 38.5.1, 38.5.2). The keyword H0 (H01) needs not to be given if *name*=H0 (H01). The nuclear energy associated to H0 or H01 is internally stored.

65.2.6 Loading the kinetic or potential energy operators

LOAD,*name*,EKIN

LOAD,*name*,EPOT

loads the individual parts of the one-electron hamiltonian in the AO basis. EPOT is summed for all atoms. The nuclear energy is associated to EPOT and internally stored. The keyword EKIN (EPOT) needs not to be given if *name*=EKIN (EPOT).

65.2.7   Loading one-electron property operators

LOAD,*name*,OPER,*opname*,[*isym*],*x,y,z*

loads one-electron operator *opname*, where *opname* is a keyword specifying the operator (a component must be given). See section 6.13 for valid keys. *isym* is the total symmetry of the operator (default 1), and *x,y,z* is the origin of the operator. If the operator is not available yet in the operator record, it is automatically computed. The nuclear value is associated internally to *name* and also stored in variable OPNUC (this variable is overwritten for each operator which is loaded, but can be copied to another variable using the SET command. Note that the electronic part of dipole and quadrupole operators are multiplied by -1.

65.2.8   Loading matrices from plain records

LOAD,*name*,TRIANG,*record*,[*isym*]
LOAD,*name*,SQUARE,*record*,[*isym*]

Loads a triangular or square matrix from a plain record (not a dump record or operator record). If *isym* is not given, 1 is assumed.

65.3   Saving matrices (SAVE)

SAVE,*name*,*record* [,*type*]

At present, *type* can be DENSITY, ORBITALS, FOCK, H0, ORBEN, OPER, TRIANG, SQUARE, or VECTOR. If type is not given but known from LOAD or another command, this is assumed. Orbitals, density matrices, fock matrices, and orbital energies are saved to a dump record (the same one should normally be used for all these quantities). If *type* is H0, the one-electron hamiltonian is overwritten by the current matrix and the nuclear energy is modified according to the value associated to *name*. The nuclear energy is also stored in the variable ENUC. All other matrices can be saved in triangular or square form to plain records using the TRIANG and SQUARE options, respectively (for triangular storage, the matrix is symmetrized before being stored). Eigenvectors can be saved in plain records using the VECTOR option. Only one matrix or vector can be stored in each plain record.

One-electron operators can be stored in the operator record using

SAVE,*name*,OPER, [PARITY=*np*], [NUC=*opnuc*], CENTRE=*icen*],[COORD=[*x,y,z*]]

The user-defined operator *name* can can then be used on subsequent EXPEC or GEXPEC cards. $np = 1, 0, -1$ for symmetric, square, antisymmetric operators, respectively (default 1). If CENTRE is specified, the operator is assumed to have its origin at the given centre, where *icen* refers to the row number of the z-matrix input. The coordinates can also be specified explicitly using COORD. By default, the coordinates of the last read operator are assumed, or otherwise zero.

If NATURAL orbitals are generated and saved in a dump record, the occupation numbers are automatically stored as well. This is convenient for later use, e.g., in MOLDEN.

65.4   Adding matrices (ADD)

ADD,*result* [,*fac1*],*mat1* [,*fac2*],mat2,...

calculates *result = fac1 · mat1 + fac2 · mat2 + ...*

The strings *result*, *mat1*, *mat2* are internal names specifying the matrices. *mat1*, *mat2* must exist, otherwise an error occurs. If *result* does not exist, it is created.

The factors *fac1*, *fac2* are optional (may be variables). If not given, one is assumed.

The nuclear values associated to the individual matrices are added accordingly and the result is associated to *result*.

65.5   Trace of a matrix or the product of two matrices (`TRACE`)

`TRACE`,*variable, mat1,,*[*factor*]

Computes *variable = factor**tr(*mat1*).

`TRACE`,*variable, mat1, mat2,*[*factor*],[*facnuc*]

Computes *variable = factor**trace(*mat1 · mat2*) + facnuc*opnuc.

The result of the trace operation is stored in the MOLPRO variable *variable*, which can be used in subsequent operations.

If *factor* is not given, one is assumed. If *facnuc* is given, the nuclear contribution multiplied by facnuc is added. It is assumed that either *mat1* or *mat2* has a nuclear contribution. The default for *facnuc* is zero.

65.6   Setting variables (`SET`)

`SET`,*variable*,*value*

Assigns *value* to MOLPRO variable *variable*, where *value* can be an expression involving any number of variables or numbers. Indexing of *variable* is not possible, however.

65.7   Multiplying matrices (`MULT`)

`MULT`,*result, mat1, mat2,*[*fac1*],[*fac2*]

calculates *result = fac2 * result + fac1 * mat1 · mat2*

The strings *result* , *mat1* , *mat2* are the internal names of the matrices. If *fac1* is not given, *fac1=1* is assumed. If *fac2* is not given, *fac2=0* is assumed. If a backquote (') is appended to *mat1* or *mat2* the corresponding matrix is transposed before the operation. If a backquote is appended to *result*, the resulting matrix is transposed.

65.8   Transforming operators (`TRAN`)

`TRAN`,*result*, *Op*, *C*

calculates *result = C(T)*Op*C*. The strings *result*, *C*, and *Op* are the internal names of the matrices. If a backquote (') is appended to *C* or *Op* the corresponding matrix is transposed before the operation. Thus,

`TRAN`,*result*, *Op*, *C'*

computes *result = C*Op*C(T)*.

65.9   Transforming density matrices into the MO basis (`DMO`)

`DMO`,*result*, *D*, *C*

calculates *result = C(T)*S*D*S*C*. The strings *result*, *C*, and *D* are internal names.

65.10   Diagonalizing a matrix `DIAG`

`DIAG`,*eigvec*,*eigval*,*matrix* [,*iprint*]

Diagonalizes *matrix*. The eigenvectors and eigenvalues are stored internally with associated names *eigvec* and *eigval*, respectively (arbitrary strings of up to 16 characters). The if *iprint*.gt.0, the eigenvalues are printed. If *iprint.gt.1*, also the eigenvectors are printed.

65.11 Generating natural orbitals (`NATORB`)

`NATORB`,*name*,*dens*,*thresh*

computes natural orbitals for density matrix *dens*. Orbitals with occupation numbers greater or equal to *thresh* (default 1.d-4) are printed.

65.12 Forming an outer product of two vectors (`OPRD`)

`OPRD`,*result*,*matrix*,*orb1*,*orb2*,*factor*

Takes the column vectors *v1* and *v2* from *matrix* and adds their outer product to *result*. *v1* and *v2* must be given in the form *icol.isym*, e.g., 3.2 means the third vector in symmetry 2. The result is

$$result(a,b) = result(a,b) + factor * v1(a) * v2(b)$$

If *result* has not been used before, it is zeroed before performing the operation.

65.13 Combining matrix columns (`ADDVEC`)

`ADDVEC`,*result*,*orbr*,*source*,*orbs*,*factor*

Takes the column vector *orbs* from *source* and adds it to columnn *orbr* of *result*. *v1* and *v2* must be given in the form *icol.isym*, e.g., 3.2 means the third vector in symmetry 2.

65.14 Forming a closed-shell density matrix (`DENS`)

`DENS`,*density*,*orbitals*,*iocc*$_1$, *iocc*$_2$ ...

Forms a closed-shell density matrix *density* from the given *orbitals*. The number of occupied orbitals in each symmetry *i* must be provided in *iocc*$_i$.

65.15 Computing a fock matrix (`FOCK`)

`FOCK`,*f*,*d*

computes a closed shell fock matrix using density *d*. The result is stored in *f*.

65.16 Computing a coulomb operator (`COUL`)

`COUL`,*J*,*d*

computes a coulomb operator J(d) using density *d*.

65.17 Computing an exchange operator (`EXCH`)

`EXCH`,*K*,*d*

computes an exchange operator K(d) using density *d*.

65.18 Printing matrices (`PRINT`)

`PRINT`,*name*,[*ncol(1), ncol(2),...*]

prints matrix *name*. *ncol(isym)* is the number of columns to be printed for row symmetry *isym* (if not given, all columns are printed). For printing orbitals one can also use `ORB`.

65.19   Printing diagonal elements of a matrix (`PRID`)

`PRID`,*name* prints the diagonal elements of matrix *name*.

65.20   Printing orbitals (`PRIO`)

`PRIO`,*name*,$n_1, n_2, n_3, \ldots, n_8$

prints orbitals *name*. The first n_i orbitals are printed in symmetry *i*. If $n_i = 0$, all orbitals of that symmetry are printed.

65.21   Printing a matrix transpose in scientific notation(`PRIC`)

`PRIC`,*name*,[*ncol(1), ncol(2),...*]

prints the transpose of matrix *name* in scientific notation (comma delimited). *ncol(isym)* is the number of columns to be printed for row symmetry *isym* (if not given, all columns are printed). For printing orbitals one can also use `ORB`.

65.22   Assigning matrix elements to a variable (`ELEM`)

`ELEM`,*name*,*matrix*, *col*,*row*

assigns elements (col,row) of *matrix* to variable *name*. *col* and *row* must be given in the form *number.isym*, where *number* is the row or column number in symmetry *isym*. The product of the row and column symmetries must agree with the matrix symmetry.

65.23   Setting a matrix element to a variable (`POKE`)

`POKE`,*name*,*matrix*, *col*,*row*

sets elements (col,row) of *matrix* to variable *name*. *col* and *row* must be given in the form *number.isym*, where *number* is the row or column number in symmetry *isym*. The product of the row and column symmetries must agree with the matrix symmetry.

65.24   Reading a matrix from the input file (`READ`)

`READ`,*name*,[[TYPE=]*type*],[[SUBTYPE=]*subtype*],[[SYM=]*symmetry*], [FILE=*file*]
{ *values* }

Reads a square matrix (symmetry 1) from input or an ASCII file. The *values* can be in free format, but their total number must be correct. Comment lines starting with '#', '*', or '!' are skipped. If the data are given in input, the data block must be enclosed either by curley brackets or the first linbe must be `BEGIN_DATA` and the last line `END_DATA`. If a *filename* is specified as option, the data are read from this file. In this case, the `BEGIN_DATA`, `END_DATA` lines in the file are optional, and no data block must follow.

For compatibility with older versions, the data can also be included in the input using the `INCLUDE` command (see section 3.1). In this case, the include file must contain the `BEGIN_DATA` and `END_DATA` lines (this is autopmatically the case if the file has been written using the `MATROP,WRITE` directive).

type is a string which can be used to assign a matrix type. If appropriate, this should be any of the ones used in the `LOAD` command. In addition, `SUBTYPE` can be specified if necessary. This describes, e.g., the type of orbitals or density matrices (e.g., for natural orbitals *TYPE*=`ORB` and *SUBTYPE*=`NATURAL`). The matrix symmetry needs to be given only if it is not equal to 1.

65.25 Writing a matrix to an ASCII file (`WRITE`)

`WRITE,`*name*,[*filename* [*status*]]

Writes a matrix to an ASCII file. If *filename* is not given the matrix is written to the output file, otherwise to the specified file (*filename* is converted to lower case). If *filename*=`PUNCH` it is written to the current punch file.

If *status*=`NEW`, `ERASE` or em `REWIND`, a new file is written, otherwise as existing file is appended.

65.26 Examples

The following example shows various uses of the `MATROP` commands.

```
***,h2o matrop examples
geometry={o;h1,o,r;h2,o,r,h1,theta}   !Z-matrix geometry input
r=1 ang                               !bond length
theta=104                             !bond angle
hf                                    !do scf calculation
{multi
natorb
canonical}
{matrop
load,D_ao,DEN,2140.2                  !load mcscf density matrix
load,Cnat,ORB,2140.2,natural         !load mcscf natural orbitals
load,Ccan,ORB,2140.2,canonical       !load mcscf canonical orbitals
load,Dscf,DEN,2100.2                  !load scf density matrix
load,S                               !load overlap matrix

prio,Cnat,4,1,2                       !prints occupied casscf orbitals

elem,d11,Dscf,1.1,1.1                 !print element D(1,1)
elem,d21,Dscf,2.1,1.1                 !print element D(2,1)
elem,d12,Dscf,1.1,2.1                 !print element D(1,2)

tran,S_mo,s,Cnat                      !transform s into MO basis (same as above)
print,S_mo                           !print result - should be unit matrix

trace,Nao,S_mo                        !trace of S_MO = number of basis functions
trace,Nel,D_ao,S                      !form trace(DS) = number of electrons

mult,SC,S,Cnat                        !form SC=S*Cnat
tran,D_nat,D_ao,SC                    !transform density to natural MO (could also be done usi

prid,D_nat                           !print diagonal elements (occupation numbers)

dmo,D_can,D_ao,Ccan                  !transform D_ao to canonical MO basis. Same as above sim
add,D_neg,-1,D_can                   !multiply d_can by -1
diag,U,EIG,D_neg                     !diagonalizes density D_can
mult,Cnat1,Ccan,U                    !transforms canonical orbitals to natural orbitals
prio,Cnat1,4,1,2                     !prints new natural orbitals

natorb,Cnat2,D_ao                    !make natural orbitals using MCSCF density D_ao directly
prio,Cnat2,4,1,2                     !prints new natural orbitals (should be the same as abov

add,diffden,D_ao,-1,Dscf             !form mcscf-scf difference density
natorb,C_diff,diffden                !make natural orbitals for difference density

write,diffden,denfile                !write difference density to ASCII file denfile
save,C_diff,2500.2                   !store natural orbitals for difference density in dump r
}
```

http://www.molpro.net/info/current/examples/matrop.com

This second example adds a quadrupole field to H0. The result is exactly the same as using the QUAD command. H0 is overwritten by the modified one-electron matrix, and the nuclear energy is automatically changed appropriately. The subsequent SCF calculations use the modified one-electron operator.

Note that it is usually recommended to add fields with the D̂IP, QUAD, or FIELD commands.

```
memory,2,m
R    =    0.96488518 ANG
THETA= 101.90140469
geometry={H1
          O,H1,R;
          H2,O,R,H1,THETA}
{hf;wf,10,1}

field=0.05              !define field strength

{matrop
load,h0,h0              !load one-electron hamiltonian
load,xx,oper,xx         !load second moments
load,yy,oper,yy
load,zz,oper,zz
add,h01,h0,field,zz,-0.5*field,xx,-0.5*field,yy   !add second moments to h0 and store in h01
save,h01,1210.1,h0}    !save h0
hf                      !do scf with modified h0

{matrop
load,h0,h0              !load h0
load,qmzz,oper,qmzz     !load quadrupole moment qmzz
add,h01,h0,field,qmzz   !add quadrupole moment to h0  (same result as above with second moments
save,h01,1210.1,h0}    !save h0
hf                      !do scf with modified h0

quad,,,field            !add quadrupole field to h0
hf                      !do scf with modified h0 (same result as above with matrop)

field,zz,field,xx,-0.5*field,yy,-0.5*field   ! (add general field; same result as above)
hf                      !do scf with modified h0 (same result as above with matrop)

field,zz,field      !same as before with separate field commands
field+,xx,-0.5*field
field+,yy,-0.5*field
hf                      !do scf with modified h0 (same result as above with matrop)
```

    http://www.molpro.net/info/current/examples/matropfield.com

65.27 Exercise: SCF program

Write a closed-shell SCF program for H_2O using MATROP!

Hints:

First generate a starting orbital guess by finding the eigenvectors of *h0*. Store the orbitals in a record. Basis and geometry are defined in the usual way before the first call to MATROP.

Then use a MOLPRO DO loop and call MATROP for each iteration. Save the current energy in a variable (note that the nuclear energy is stored in variable ENUC). Also, compute the dipole moment in each iteration. At the end of the iteration perform a convergence test on the energy change using the IF command. This must be done outside MATROP just before the ENDDO. At this stage, you can also store the iteration numbers, energies, and dipole moments in arrays, and print these after reaching convergence using TABLE. For the following geometry and basis set

```
geometry={o;h1,o,r;h2,o,r,h1,theta}   !Z-matrix geometry input
```

```
r=1 ang                                    !bond length
theta=104                                  !bond angle
basis=vdz                                  !basis set
thresh=1.d-8                               !convergence threshold
```

the result could look as follows:

```
 SCF has converged in 24 iterations

    ITER        E              DIP
     1.0   -68.92227207    2.17407361
     2.0   -71.31376891   -5.06209922
     3.0   -73.73536433    2.10199751
     4.0   -74.64753557   -1.79658706
     5.0   -75.41652680    1.43669203
     6.0   -75.77903293    0.17616098
     7.0   -75.93094231    1.05644998
     8.0   -75.98812258    0.63401784
     9.0   -76.00939154    0.91637513
    10.0   -76.01708679    0.76319435
    11.0   -76.01988143    0.86107911
    12.0   -76.02088864    0.80513445
    13.0   -76.02125263    0.83990621
    14.0   -76.02138387    0.81956198
    15.0   -76.02143124    0.83202128
    16.0   -76.02144833    0.82464809
    17.0   -76.02145450    0.82912805
    18.0   -76.02145672    0.82646089
    19.0   -76.02145752    0.82807428
    20.0   -76.02145781    0.82711046
    21.0   -76.02145792    0.82769196
    22.0   -76.02145796    0.82734386
    23.0   -76.02145797    0.82755355
    24.0   -76.02145797    0.82742787
```

It does not converge terribly fast, but it works!

66   Post-processing of output and databases

66.1   Output

MOLPRO produces an output file that is in XML format with appropriate mark-up for all important results. This file, which has a `.xml` suffix, is normally filtered into a plain-text file (`.out` suffix) with all of the mark-up removed, for more convenient browsing. The XML file conforms strictly to a well-defined schema, and the the schema definition file `molpro-output.xsd` can be found in the main MOLPRO source or installation tree in the directory `lib/schema`. The principal elements of marked-up output are

jobstep	The results from one job step.
molecule	A container for data on a single molecule.
cml:molecule	Molecular geometry in the Chemical Markup Language (CML) format.
property	A computed property, for example an energy or dipole moment.
table	The output of MOLPRO's TABLE command in XHTML format.
basisSet	A self-contained description of the orbital basis set.
orbitals	A set of orbitals.
vibrations	Harmonic normal vibrational modes.
variables	MOLPRO's internal variables.
platform	Information about the computing system on which a job was run.

Not all of these elements are produced by default in the regular job transcript `.xml` file; some of them can result from using the `PUT,XML` to make a separate dump file.

`molpro-output` is understood by several post-processing programs, including Jmol (http://www.jmol.org) and its derivative molproView (http://www.molpro.net/molproView).

66.2   Databases

A facility is provided to store and interrogate sets of molecules, together with information about how they are to be combined in balanced chemical equations. This collection of information is referred to as a *database*, and can be generated completely manually, or partially by running appropriate MOLPRO calculations. Analysis of the database can give a summary of the energy changes associated with each described reaction, and two or more similar databases can be compared reaction by reaction, to give a statistical analysis of the differences between them.

All of the files associated with the database facility can be found in the directory `database` in the main MOLPRO source or installation tree.

66.2.1   Description and specification of databases

A database is an XML file conforming to the `molpro-database` schema, and consists one or more occurrences of each of the following two principal elements.

molecule	Information about a single molecular species in the `molpro-output` XML format. This will usually be the result of `PUT,XML` in a MOLPRO calculation, but can also be constructed directly from an external data source. The important quantities that are used are the geometry and energy, together with metadata such as the method and basis set, and other quantities such as spin and symmetry that might be useful for constructing a new MOLPRO job for the molecule.

reaction   A list of `species` specifications that point uniquely to one of the `molecule` nodes, together with information on how the species appears stoichimetrically in the reaction, and whether it is a special point such as a transition state. `species` specifications can also be given without either of these tags, allowing additional geometries, for example along a reaction coordinate or potential surface cut, to be included.

Normally, the `molecule` nodes will be in separate self-contained files that are then referenced in the main database file through the syntax of XInclude. There are three reasons for this. Firstly, these files can be produced directly by a MOLPRO calculation, with the rest of the database being constructed by hand. Secondly, they allow the possibility that the molecule files be replaced in the future by, for example, running all the molecule calculations again using a different method; in that case, the rest of the database, i.e. the reaction specifications, does not need to change. This supports the possibility of having several databases that have the same structure – specification of reactions – but different numerical data, and therefore being capable of numerical comparison. Thirdly, several databases can coexist in the same directory, and share some of the same molecule files. An example of this is a supplementary database that consists of a subset of the reactions contained in the main database.

The following is an example of a complete database of four reactions involving the species O, H_2, H_2O, H_2O_2 and CH_2O. Note that the association between the `species` and the `molpro-output:molecule` nodes is achieved through the use of InChI (http://www.iupac.org/home/publications/e-resources/inchi.html) tags, which `PUT,XML` will produce provided that OpenBabel (http://openbabel.org) is installed on the system. An alternative is through syntax such as

```
{PUT,XML,file.xml; index,73}
```

and the use of `<species index="73">` in the database file. Note that sometimes different species have the same InChI, and so the use of `index` is necessary to resolve ambiguities.

```
<?xml version="1.0"?>
<database xmlns="http://www.molpro.net/schema/molpro-database"
  xmlns:xi="http://www.w3.org/2001/XInclude">
    <xi:include href="h2o.xml" />
    <xi:include href="h2o2.xml"/>
    <xi:include href="h2.xml"/>
    <xi:include href="o2.xml"/>
    <xi:include href="co.xml"/>
    <xi:include href="h2co.xml"/>
    <xi:include href="h2cots.xml"/>
    <xi:include href="o.xml"/>
    <reaction title="insertion of O into H2">
      <species InChI="InChI=1S/H2O/h1H2" count="1"/>
      <species InChI="InChI=1S/O" count="-1"/>
      <species InChI="InChI=1S/2H2/h2*1H" count="-1"/>
    </reaction>
    <reaction title="H2O formation">
      <species InChI="InChI=1S/H2O/h1H2" count="1"/>
      <species InChI="InChI=1S/O2/c1-2" count="-0.5"/>
      <species InChI="InChI=1S/2H2/h2*1H" count="-1"/>
    </reaction>
    <reaction title="H2O2 formation">
      <species InChI="InChI=1S/H2O2/c1-2/h1-2H" count="1"/>
      <species InChI="InChI=1S/O2/c1-2" count="-1"/>
      <species InChI="InChI=1S/2H2/h2*1H" count="-1"/>
    </reaction>
    <reaction title="Formaldehyde dissociation">
      <species InChI="InChI=1S/CH2O/c1-2/h1H2" count="-1"/>
      <species InChI="InChI=1S/CO/c1-2" count="1"/>
      <species InChI="InChI=1S/2H2/h2*1H" count="1"/>
      <species InChI="InChI=1S/CHO.H/c1-2;/h1H;"
 transitionState="true"/>
    </reaction>
</database>
```

```
 http://www.molpro.net/info/current/examples/../database/sets/
                examples/reactions/reactions.xml
```

For full specification of the possible structure of a database, see the schema file
`lib/schema/molpro-database.xsd`.

The directory `database/utilities` contains several Python scripts that manipulate databases. For
convenience, they can be run through the script

molpro --database *script-name arguments* ...

so long as Python (version 3 preferred) is installed on the system. You need the lxml and requests package
included in your Python installation:

```
pip install lxml requests
```

(or `pip3` if you are using Python 3).

The script `validate` checks whether a database conforms to the schema, for example

```
cd Molpro  # assuming below that we are in Molpro source tree, but works from anywhere
bin/molpro --database validate \
 database/sets/examples/reactions/reactions.xml
```

66.2.2 Computation of new database data

The script `clone` takes an existing database, for which the file name should be provided as an argument,
and generates a set of MOLPRO jobs that will run the same method on each of the molecules, with the

end result that a new database is created. If the database master file is the only one in the directory that declares itself to belong to the `molpro-database` schema, then you can just give the directory name as the argument to this and other scripts instead. In addition, if the database master file has the suffix `.xml`, the suffix does not need to be specified. For the above example, this could be

```
cd Molpro  # assuming below that we are in Molpro source tree, but works from anywhere
bin/molpro --database clone \
 database/sets/examples/reactions
```

This will create a new directory `reactions.d` with the following contents.

```
original/          reactions.xml      runall/
procedures.molpro  run/

reactions.d/original:
co.xml      h2co.xml    h2o.xml     o.xml
h2.xml      h2cots.xml  h2o2.xml    o2.xml

reactions.d/run:
co.molpro       h2co.molpro   h2o.molpro      o.molpro
h2.molpro       h2cots.molpro h2o2.molpro     o2.molpro

reactions.d/runall:
reactions.molpro
```

The file `procedures.molpro` contains a procedure that will be run on every molecule, and it should be edited to use the desired methods. Then the calculations can be run, either via each of the individual MOLPRO input files in `run/`, or the single input file `reactions.molpro` in the directory `runall`. Once these jobs have completed, then the directory contains a complete database with the original reaction scheme but new data.

66.2.3 Analysis of databases

```
cd Molpro
bin/molpro --database analyse \
 database/sets/examples/reactions/reactions.xml
```

will analyse the database, and report the energy change for each described reaction. If two or more databases are given as arguments, the analysis will be done on each, and also on the difference between the first database and the second and any subsequent, including a statistical summary. For the example given above, one might say

```
cd Molpro/reactions.d
../bin/molpro --database analyse original .
```

`analyse` has a number of options that are described by running

```
molpro --database analyse --help
```

66.2.4 Library of databases

The directory `database/sets` contains several standard databases. Within each one is a description of its origin, contents and purpose. The scripts described above can take these databases as inputs, for example `database/sets/examples/reactions/reactions.xml`; as a shortcut, one could simply instead use `examples/reactions` which will find the system database irrespective of the current working directory.

67 PHYSICAL CONSTANTS

The values of fundamental physical constants are revised periodically by CODATA. Molpro uses the values from the latest revision. Some previous values are available, see the `lib/include/codata/` directory. To use these system include files, simply add for instance:

```
include,codata/molpro2006
```

to use the values from Molpro 2006.

A   Installation Guide

MOLPRO is distributed to licensees on a self-service basis using the world-wide web. Those entitled to the code should obtain it from https://www.molpro.net/download supplying the username and password given to them. The web pages contain both source code and binaries, although not everyone is entitled to source code, and binaries are not available for every platform.

Execution of MOLPRO, whether a supplied binary or built from source, requires a valid licence key. Note that the key consists of two components, namely a list of comma-separated key=value pairs, and a password string, and these are separated by '&'. In most cases the licence key will be automatically downloaded from the website when building or installing the software.

A.1   Installation of pre-built binaries

Binaries are given as self-extracting tar archives which are installed by running them on the command line. There are binaries tuned for several architectures. These also support parallel execution. The parallel binaries are built using GA with MPI.

The tar archives are fully relocatable, the location can be changed when running the script interactively, the default is `/usr/local`.

If the script finds a licence key which has been cached in `$HOME/.molpro/token` from a previous install then that key will be installed with the software. If the script cannot find a key or automatically download it from the molpro website then the script will prompt that this part of the install has failed. All files of Molpro are installed, but the user must then manually install the key with the library files in a file named `.token`, e.g.:
`/usr/local/molpro-`*mpptype-arch*`/lib/.token`

Other configuration options as described in section A.2.5 may also be specified in the script file:
`/usr/local/bin/molpro`

A.2   Installation from source files

A.2.1   Overview

There are usually four distinct stages in installing MOLPRO from source files:

Configuration	A shell script that allows specification of configuration options is run, and creates a configuration file that drives subsequent installation steps.
Compilation	The program is compiled and linked, and other miscellaneous utilities and files, including the default options file, are built. The essential resulting components are

1. The `molpro` shell script which launches the main executable. In serial case one can directly run the main executable.

2. The `molpro.exe` executable, which is the main program. For parallel computation, multiple copies of `molpro.exe` are started by a single instance of `molpro` shell script using the appropriate system utility, e.g. `mpirun`.

3. Machine-ready basis-set, and other utility, libraries.

Validation   A suite of self-checking test jobs is run to provide assurance that the code as built will run correctly.

Installation   The program can be run directly from the source tree in which it is built, but it is usually recommended to run the procedure that installs the essential components in standard system directories.

A.2.2 Prerequisites

The following are required or strongly recommended for installation from source code.

1. A Fortran 2003 compiler. On HPC systems the latest vendor-supplied compiler should be used. The program is regularly tested with recent versions of GNU and Intel Fortran compilers.

2. GNU *make*, freely available from http://www.fsf.org and mirrors. GNU *make* must be used; most system-standard makes do not work. In order to avoid the use of a wrong *make*, it may be useful to set an alias, e.g., `alias make='gmake -s'`. A recent version of GNU *make* is required, 3.80 or above.

3. Libxml2 library and header files.

4. About 10GB disk space (strongly system-dependent; more with large-blocksize file systems, and where binary files are large) during compilation. Typically 100Mb is needed for the finally installed program. Large calculations will require larger amounts of disk space.

5. One or more large scratch file systems, each containing a directory that users may write on. There are parts of the program in which demanding I/O is performed simultaneously on two different files, and it is therefore helpful to provide at least two filesystems on different physical disks if other solutions, such as striping, are not available. The directory names should be stored in the environment variables `$TMPDIR`, `$TMPDIR2`, `$TMPDIR3`,.... These variables should be set before the program is installed (preferably in `.profile` or `.cshrc`), since at some stages the installation procedures will check for them (cf. section A.2.5).

6. If the program is to be built for parallel execution then the Global Arrays toolkit or the MPI-2 library is needed. For building MOLPRO with the Global Arrays toolkit, we recommend the latest stable version (although earlier versions may also work). This is available from http://www.emsl.pnl.gov/docs/global and should be installed prior to compiling MOLPRO. For building MOLPRO with the MPI-2 library, we recommend to use the built-in MPI-2 library, which may have advantages of optimization on some platforms. If there is no built-in one on the platform, a fresh MPI-2 library (e.g.: MPICH2, see http://http://www.mpich.org/) should be installed prior to compiling MOLPRO. Many MPI-2 libraries, including Intel MPI, Bull MPI, MPICH2, and Open MPI, have been tested, and others untested could also work.

7. The source distribution of MOLPRO, which consists of a compressed tar archive with a file name of the form `molpro.2015.1.tar.gz`. The archive can be unpacked using `gunzip` and `tar`.

Fedora packages   To build using GNU compilers one should ensure the following packages are installed (via dnf):

gcc-c++	provides GNU C and C++ compiler,
gcc-gfortran	provides GNU Fortran compiler,
libxml2-devel	provides libxml2 library & headers,
make	provides GNU make.

Optionally one can choose to install:

blas-devel	provides a BLAS library,
lapack-devel	provides a LAPACK library,

which will be used instead of compiling the equivalent MOLPRO routines.

openSUSE packages   To build using GNU compilers one should ensure the following packages are installed (via YaST):

gcc-c++	provides GNU C and C++ compiler,
gcc-fortran	provides GNU Fortran compiler,
libxml2-devel	provides libxml2 library & headers,
make	provides GNU make.

Optionally one can choose to install:

blas	provides a BLAS library,
lapack	provides a LAPACK library,

which will be used instead of compiling the equivalent MOLPRO routines.

Ubuntu packages   To build using GNU compilers one should ensure the following packages are installed via (apt-get):

build-essential	provides GNU C++ compiler,
curl	provides curl for downloading patches,
gfortran	provides GNU Fortran compiler,
libxml2-dev	provides libxml2 library & headers,
openssh-server	provides ssh access to localhost.

Optionally one can choose to install:

libblas-dev	provides a BLAS library,
liblapack-dev	provides a LAPACK library,

which will be used instead of compiling the equivalent MOLPRO routines. Set up password-less ssh by running the following commands and not entering a password when prompted:

```
ssh-keygen -t rsa
cat ~/.ssh/id_rsa.pub >> ~/.ssh/authorized_keys
```

This must be done for each user account which will be running MOLPRO.

macOS   It is recommended to install and manage the additional compilers and utilities needed for building and running MOLPRO using the `Homebrew` system. Visit http://brew.sh, and copy the installation command into a terminal window. On an empty system, you will be prompted to install command line tools; do this first. Then accept all prompts from the Homebrew installation script.

The following will install all utilities that might be needed for building and running MOLPRO for development in serial; for production calculations in parallel, a binary can be downloaded.

```
brew install Caskroom/cask/xquartz homebrew/x11/grace \
  open-babel doxygen automake wget \
  Caskroom/cask/java homebrew/science/jmol
```

A.2.3   Configuration

Once the distribution has been unpacked, change to the `Molpro` directory that has been created. Having changed to the `Molpro` directory, you should check that the directory containing the Fortran compiler you want to use is in your PATH. Then run the command

```
./configure
```

which creates the file `CONFIG`. This file contains machine-dependent parameters, such as compiler options. Normally `CONFIG` will not need changing, but you should at the least examine it, and change any configuration parameters which you deem necessary. Any changes made to `CONFIG` will be lost next time `./configure` is invoked, so it is best to supply as many of these as possible via the command line.

The `configure` procedure may be given command line options, and, some commonly used options include:

1. In the case of building for parallel execution, the option `--enable-mpp` must be given on the command line. This enables both mpp and mppx parallelism; for the distinction between these two parallelism modes, please refer to the user manual, section 2. The option `--enable-mpp` must be set to the location of the Global Arrays library directory or the MPI-2 library include directory.

   For the case of using the Global Arrays toolkit, one example can be

   ```
   ./configure --enable-mpp=/usr/local/ga-install/lib
   ```

   If using a Global Arrays build with an MPI library the appropriate MPI executable should appear first in PATH when more than one is available.

   Queries regarding Global Arrays installations should be sent directly to the Global Arrays team, any Molpro related queries will assume a fully functional Global Arrays suite with all internal tests run successfully.

   For the case of using the MPI-2 library, one example can be

   ```
   ./configure --enable-mpp=/usr/local/mpich2-install/include
   ```

   and the directory should contain file mpi.h. Please ensure the built-in or freshly built MPI-2 library fully supports MPI-2 standard and works properly.

   For desktop or single node installations, there are a series of options prefixed with `auto` which build any prerequisites, and can be passed to `--enable-mpp`, eg.

   ```
   ./configure --enable-mpp=auto-ga-mpich
   ```

2. For good performance it is important to use appropriate BLAS libraries; in particular, a fast implementation of the matrix multiplication `dgemm` is very important for MOLPRO. Therefore you should use a system tuned BLAS library whenever available.

   MOLPRO will automatically detect the most appropriate BLAS library in many cases. In certain cases, in particular when the BLAS library is installed in a non-default location, configure should be directed to the appropriate directory with:

   ```
   ./configure --with-blas-path=/path/to/lib/dir
   ```

3. The Molpro installation directory can be given with `--prefix`.

A.2.4   Compilation and linking

After configuration, the remainder of the installation is accomplished using the GNU *make* command. Remember that the default *make* on many systems will not work, and that it is essential to use GNU *make* (cf. section A.2.2). Everything needed to make a functioning program together with all ancillary files is carried out by default simply by issuing the command

```
make
```

in the MOLPRO base directory. Most of the standard options for GNU *make* can be used safely; in particular, `-j` can be used to speed up compilation on a parallel machine. The program can then be accessed by making sure the `bin/` directory is included in the PATH and issuing the command `molpro`. If MPI library is used for building Global Arrays or building MOLPRO directly, please be aware that some MPI libraries use mpd daemons to launch parallel jobs. In this case, mpd daemons must already be running before `make`.

A.2.5   Adjusting the default environment for MOLPRO

The default running options for MOLPRO are stored in the script `bin/molpro`. After program installation, either using binary or from source files, this file should be reviewed and adjusted, if necessary, to make system wide changes.

A.2.6   Tuning

MOLPRO can be tuned for a particular system by running in the root directory the command

```
make tuning
```

This job automatically determines a number of tuning parameters and appends these to the file `bin/molpro`. Using these parameters, MOLPRO will select the best BLAS routines depending on the problem size. This job should run on an empty system. It may typically take 10 minutes, depending on the processor speed, and you should wait for completion of this run before doing the next steps.

A.2.7   Testing

At this stage, it is essential to check that the program has compiled correctly. The makefile target *test* (i.e., command `make test`) will do this using the full suite of test jobs, and although this takes a significantly long time, it should always be done when porting for the first time. A much faster test, which checks the main routes through the program, can be done using `make quicktest`. For parallel installation, it is highly desirable to perform this validation with more than one running process. This can be done conveniently through the `make` command line as, for example,

```
make MOLPRO_OPTIONS=-n2 test
```

If any test jobs fail, the cause must be investigated. If, after due efforts to fix problems of a local origin, the problem cannot be resolved, the developers of MOLPRO would appreciate receiving a report. There is a web-based mechanism at https://www.molpro.net/bugzilla at which as many details as possible should be filled in. It may also be helpful to attach a copy of the CONFIG file along with the failing output. Please note that the purpose of such bug reports is to help the developers improve the code, and not for providing advice on installation or running.

A.2.8   Installing the program for production

Although the program can be used in situ, it is usually convenient to copy only those files needed at run time into appropriate installation directories as specified at configuration time (see section A.2.3) and stored in the file CONFIG. To install the program in this way, do

```
make install
```

The complete source tree can then be archived and deleted. The overall effect of this is to create a shell script in the `INSTBIN` directory. The name should relate to the architecture, type of build, integer etc. Symbolic links relating to the type of build are then made, and finally providing that `INSTBIN/molpro` is not a file, a symbolic link is created to the new script. In some cases it is preferable to create a localized script in `INSTBIN/molpro` which will not be over written. The overall effect of this cascade of links is to provide, in the normal case, the commands `molpro` and one or both of `molpros` (serial) and `molprop` (parallel) for normal use, with the long names remaining available for explicit selection of particular variants.

For normal single-variant installations, none of the above has to be worried about, and the `molpro` command will be available from directory `INSTBIN`.

During the install process the key from `$HOME/.molpro/token` is copied to `PREFIX/.token` so that the key will work for all users of the installed version.

A.2.9   Installation of documentation

The documentation is available on the web at http://www.molpro.net/info/users. It is also included with the source code. The PDF user's manual is found in the directory `Molpro/doc/manual.pdf`, with the HTML version in the directory `Molpro/doc/manual/index.html`. After `make install` the documentation is installed in the `doc` subdirectory of `PREFIX` specified in `CONFIG` file generated by the `configure` command. Numerous example input files are included in the manual, and can alternatively be seen in the directory `Molpro/examples`.

A.2.10   Simple building for single workstations Linux or Mac OS X

The following instructions are quick instructions for installing MOLPRO on a single-workstation Linux or Mac OS X system. The instructions assume GNU compilers have been installed (details of getting GNU compilers for common Linux distributions are contained in the prerequisites section), but these can be substituted with alternative compilers. For serial MOLPRO:

```
./configure CXX=g++ FC=gfortran
make
```

For parallel MOLPRO one can use:

```
./configure CXX=g++ FC=gfortran --enable-mpp=/path/to/ga-install/lib
make
```

if Global Arrays has already been built. There is a simpler option, providing the curl utility is installed, and the machine is connected to the internet:

```
./configure CXX=g++ FC=gfortran --enable-mpp=auto-ga-mpich
make
```

which will automatically download and install MPICH and Global Arrays.

A.2.11   Installation on a Cygwin system

On a Windows machine Cygwin should be installed. In addition to the default package list one should also install the packages listed in table 23. If undertaking development work table 24 contains a list of potentially useful packages.

With the above steps, configure can be run and the Molpro built in the normal way.

Package	Package Group	Reason
gcc-core	Devel	compiling C files
gcc-fortran	Devel	compiling Fortran files
gcc-g++	Devel	compiling C++ files
make	Devel	need GNU make
ca-certificates	Net	download boost
curl	Net	token download

Table 23: Cygwin requirments for user install

Package	Package Group	Reason
bison	Devel	bison
gdb	Devel	gdb
git	Devel	git
libxslt	Libs	xsltproc
openssh	Net	ssh
vim	Editors	vi

Table 24: Cygwin packages for developers

B Recent Changes

B.1 New features of MOLPRO2015.1

Molpro 2015 contains many improvements, bug-fixes and new features. Only the most important ones are listed in the following.

B.1.1 Projector-based wavefunction-in-DFT embedding

The WF-in-DFT impementation in Molpro [F. R. Manby et al., J. Chem. Theory Comput. **8**, 2564 (2012)] permits embedding of almost any ground-state wavefunction method in Molpro in an environment described by DFT.

B.1.2 Intrinsic bond-orbital analysis and orbital localization (IBO).

IBOs provide a reliable and efficient way to generate localized orbitals and to analyze wavefunctions, see G. Knizia, J. Chem. Theory Comput. **9**, 4834 (2013)

B.1.3 Interface to NBO6

Molpro 2015 supports NBO6 Natural Bond Orbital Analysis (NBO6) via an interface. NBO6 must be licensed separately.

B.1.4 Beyond LMP2 treatment of intermolecular pairs in local coupled cluster methods

Usually close (and weak) pairs are treated only at the LMP2 level in LCCSD(T) calculations. This not satisfying since LMP2 often treats van der Waals interactions poorly, hence compromising the high accuracy of the actual LCCSD(T) calculation. Fortunately, close pairs can now be treated in an inexpensive way at a level beyond LMP2, ranging from local direct RPA *via* ring CCD to LCCD[S]-R^{-6}. This is described in

O. Masur, D. Usvyat and M. Schütz, J. Chem. Phys., **139**, 164116 (2013);
M. Schütz, O. Masur and D. Usvyat, J. Chem. Phys., **140**, 244107 (2014).

B.1.5 Distinguishable cluster Approximation (DCSD and DCSD-F12)

This approximation yields improved results at the cost of CCSD. In particular, DCSD equilibrium structures are as accurate as for CCSD(T), see

D. Kats and F. R. Manby, J. Chem. Phys. **139**, 021102 (2013);
D. Kats, J. Chem. Phys. **141i**, 061101 (2014);
D. Kats, D. Kreplin, H.-J. Werner, F. R. Manby, J. Chem. Phys. **142**, 064111 (2015).

B.1.6 Analytical energy gradients

Analytical gradients are now available for DCSD. Analytical gradients for CCSD(T), as well as for MP2-F12, CCSD(T)-F12, and DCSD-F12 are under development and will be made available free of charge at a later stage.

B.1.7 Orbital relaxed properties and analytical nuclear gradients for excited states

Orbital relaxed properties, and analytical nuclear gradients for excited states are now available for local CC2 response and local ADC(2). This allows for geometry optimizations of excited states of large chromophores at these levels of theory. Furthermore, also local ADC(2) transition moments at the level of strict ADC(2) (which require second-order ground state singles and doubles) are available. For further reference see

K. Ledermüller, D.Kats and M. Schütz, J. Chem. Phys. **139**, 084111 (2013);
K. Ledermüller and M. Schütz, J. Chem. Phys. **140**, 164113 (2014);
M. Schütz, J. Chem. Phys. **142**, 214103 (2015).

B.1.8 PNO-LMP2 and PNO-LMP2-F12

New parallel linear scaling PNO-LMP2 and PNO-LMP2-F12 programs as described in

H.-J. Werner, G. Knizia, C. Krause, and M. Schwilk, J. Chem. Theory Comput., **11**, 484 (2015);
Q. Ma and H.-J. Werner, J. Chem. Theory Comput., DOI: 10.1021/acs.jctc.5b00843 (2015);
C. Köppl and H.-J. Werner, J. Chem. Phys., **142**, 164108 (2015).

are available in version 2015. PNO-LCCSD(T) is currently under development and will be made freely available to licensees of Molpro 2015 at a later stage.

B.1.9 Magnetizability and rotational g-tensor at DF-LMP2 level using GIAOs

The program for NMR chemical shifts has been extended to include also magnetizability and rotational g-tensor. This is described in

S. Loibl and M. Schütz, J. Chem. Phys., **141**, 024108 (2014).

B.1.10 Faster density fitting integral routines

DFT and F12 methods with density fitting are significantly speeded up using improved integration routines written by G. Knizia.

B.1.11 Vibrational perturbation theory: VPT2

A VPT2 program based on a semi-quartic force field (QFF) has been implemented, which allows for low-cost evaluations of anharmonic vibrational frequencies and associated vibrational constants. The determination of the QFF does not require analytical gradients (see the `SURF` program) and can thus been used in combination with any electronic structure method.

B.1.12   Vibrational multi-reference methods: VMCSCF, VMRCI

A suite of vibrational multi-reference methods is available now. Modals can be optimized at the VMC-SCF level [S. Heislbetz and G. Rauhut, J. Chem. Phys. **132**, 124102 (2012)] and correlation effects can be accounted for either variationally (VMRCI [F. Pfeiffer and G. Rauhut, J. Chem. Phys. **140**, 064110 (2014)].

B.1.13   Anharmonic Franck-Condon factors: FCON

A Franck-Condon program based on anharmonic vibrational wavefunctions has been implemented. Franck-Condon factors can either be computed by rotating the vibrational wavefunction or by transforming the potential energy surface in order to account for Duschinsky effects. This program, which allwos for the accurate calculation of photoelectron spectra (absorption and fluorescence) relies on the newly developed transformation program SURFTRANS [P. Meier and G. Rauhut, J. Chem. Phys. (2015)].

B.1.14   Transformation of multi-dimensional potential energy surfaces: PESTRANS

Multi-dimensional potential energy surfaces spanned in terms of normal coordinates - as computed with the SURF program - can now be rotated or transformed into an arbitrary set of normal coordinates. This allows for the efficient calculation of Franck-Condon factors or the calculation of vibrational spectra of isotopologues from just one potential energy surface [P. Meier, D. Oschetzki, R. Berger and G. Rauhut, J. Chem. Phys. **140**, 184111 (2014)].

B.1.15   Localized normal coordinates

Within the SURF program, multi-dimensional potential energy surfaces can now alternatively be spanned in terms of localized normal coordinates. Three localization schemes are offered: (a) localization of the CH-stretching modes only and (b) localization of all normal coordinates to the subunits in molecular cluster calculations or (c) both. All localization schemes are symmetry sensitive.

B.1.16   Calculation of arbitrary vibrational states: VIBSTATE

In the old Molpro release the calculation of vibrational states was limited to fundamentals, first vibrational overtones and simple combination bands. The new VIBSTATE program allows to specify arbitrary vibrational states, but the user must take care, that the parameters in the SURF program and the vibrational correlation programs are adjusted accordingly.

B.1.17   Raman scattering activities

Raman scattering activities can now be computed within all vibrational SCF and vibration correlation programs. As polarizabilities can only be determined at the Hartree-Fock level, the accuracy is currently still limited.

B.1.18   Reaction databases

A facility is provided to store and interrogate sets of molecules, together with information about how they are to be combined in balanced chemical equations. This database can be generated manually, or partially by running appropriate MOLPROcalculations. Analysis of the database can give a summary of the energy changes associated with each described reaction, and two or more similar databases can be compared reaction by reaction, to give a statistical analysis of the differences between them. Several common databases are included.

B.1.19 New density-fitting DFT-SAPT program

A new DFT-SAPT program has been implemented in Molpro which can be used in conjunction with monomer-centered (MCBS), monomer-centered plus (MC+BS) or dimer-centered (DCBS) basis sets. Even in DCBS mode fairly large complexes with about 800 electrons can be studied with this program, see A. Heßelmann and T. Korona. J. Chem. Phys. **141**, 094107 (2014).

B.2 New features of MOLPRO2012.1

A summary of the features in Molpro can be found in a recent review: H.-J. Werner, P. J. Knowles, G. Knizia, F. R. Manby, and M. Schütz, *Molpro – a general purpose quantum chemistry program package*, WIRES Comput. Mol. Sci. **2**, 242 (2012), doi:10.1002/wcms.82.

The new features of MOLPRO version 2012.1 include the following.

B.2.1 Quasi-variational coupled-cluster theory

This modification of standard CCSD is capable of robustly describing chemical bond breaking with a single Hartree-Fock reference determinant (see J. B. Robinson and P. J. Knowles, J. Chem. Phys. **136**, 054114 (2012), doi:10.1063/1.3680560). It is implemented for closed-shell systems, with either the Brueckner condition or energy optimisation for the determination of orbitals. Triple excitations can be included perturbatively, `BQVCCD(T)` or `OQVCCD(T)` (J. B. Robinson and P. J. Knowles, Phys. Chem. Chem. Phys. **14**, 6729-6732 (2012), doi:10.1039/C2CP40698E; J. Chem. Theor. Comput. **8**, 2653-2660 (2012), doi:10.1021/ct300416b).

B.2.2 A new internally contracted MRCI code: MRCIC

A new internally contracted MRCI code [see K. R. Shamasundar, G. Knizia, and H.-J. Werner, *A new internally contracted multi-reference configuration interaction (MRCI) method*, J. Chem. Phys. **135**, 054101 (2011)] is now available. As compared to the old MRCI code it has the following advantages: (i) inactive orbitals (correlated in MRCI but closed-shell in the reference function) are treated explicitly, i.e., no density matrices and coupling coefficients need to be computed that involve these orbitals. Thus, in principle any number of inactive orbitals can be correlated, without the previously existing limitation to 32 correlated orbitals. Furthermore, additional configuration spaces are internally contracted (as in the RS2C code), resulting in a much improved efficiency, particularly for cases with many inactive orbitals. Currently, the method is implemented only for single-state calculations, but an extension to multi-state cases is under development and will be provided in the near future.

B.2.3 Explicitly correlated multireference theories: RS2-F12, MRCI-F12

Explicitly correlated multireference theories (CASPT2-F12, MRCI-F12) as described in T. Shiozaki and H.-J. Werner, *Communication: Second-order multireference perturbation theory with explicit correlation: CASPT2-F12*, J. Chem. Phys. **133**, 141103 (2010); T. Shiozaki, G. Knizia, and H.-J. Werner, *Explicitly correlated multireference configuration interaction: MRCI-F12*, J. Chem. Phys. **134**, 034113 (2011); T. Shiozaki and H.-J. Werner, *Explicitly correlated multireference configuration interaction with multiple reference functions: Avoided crossings and conical intersections*, J. Chem. Phys. **134**, 184104 (2011) lead to much improved convergence of the correlation energies with the basis set size. Explicitly correlated version of the RS2C and MRCIC codes are not yet available but will be made available as soon as possible.

A review of the explicitly correlated multireference methods can be found in T. Shiozaki and H.-J. Werner, Mol. Phys. **111**, 607 (2013).

B.2.4 Extended multi-state CASPT2

Extended multistate CASPT2 (XMS-CASPT2) [see T. Shiozaki, W. Győrffy, P. Celani, and H.-J. Werner, *Communication: The extended multi-state CASPT2 method: Energy and nuclear gradients*, J. Chem. Phys. **135**, 081106 (2011)] provides a better description of near degenerate situations and avoided crossings. Currently this option is available only with the RS2 code, not for RS2C.

B.2.5 Density fitted CASSCF and CASPT2

CASSCF and CASPT2 as well as the corresponding analytical gradient theories are now available with density fitting (DF-CASSCF, DF-RS2). See details in W. Győrffy, T. Shiozaki, G. Knizia, and H.-J. Werner, *Analytical energy gradients for second-order multireference perturbation theory using density fitting*, J. Chem. Phys. **138**, 104104 (2013).

B.2.6 Extensions of explicitly correlated coupled-cluster methods

The (F12*) approximation proposed by Hättig et al. [J. Chem. Phys. **132**, 231102 (2010)] has been implemented for closed-shell cases (in Molpro, this is denoted F12c). Other recent work (partly already included in Molpro2010.1) is described in H.-J. Werner, G. Knizia, and F. R. Manby, *Explicitly correlated coupled-cluster methods with pair-specific geminals*, Mol. Phys. **109**, 407 (2011); K. A. Peterson, C. Krause, H. Stoll, J. G. Hill, and H.-J. Werner, *Application of explicitly correlated coupled-cluster methods to molecules containing post-3d main group elements*, Mol. Phys. **109**, 2607 (2011) for alternative approximations.

Further basis sets of K. A. Peterson and J.G. Hill for explicitly correlated methods have been included. In particular these include the aug-cc-pVnZ-PP/OptRI and aug-cc-pwCVnZ-PP/OptRI sets for the group 11 and 12 transition metals. A full set of F12 basis sets for the *p*-block elements Ga-Rn will be added in the very near future. For recent work on molecules containing transition metals see D. H. Bross, J. G. Hill, H.-J. Werner, and Kirk A. Peterson, *Explicitly correlated composite thermochemistry of transition metal species*, J. Chem. Phys. **139**, 094302 (2013).

B.2.7 Density fitted local coupled-cluster methods: DF-LCCSD(T), DF-LUCCSD(T), DF-LRPA

The local coupled cluster methods have been further improved. See H.-J. Werner and M. Schütz, *An efficient local coupled-cluster method for accurate thermochemistry of large systems*, J. Chem. Phys. **135**, 144116 (2011) for a description of the current implementation. An open-shell implementation [DF-LUCCSD(T)] is now also available (Y. Liu and H.-J. Werner, to be published.) Furthermore, the direct random phase approximation (RPA) has been implemented as a local method and using density fitting. Direct RPA can be considered as a CCD method reduced to only ring diagrams. In contrast tp MP2 it also contains higher-order diagrams which e.g. cover Axilrod-Teller terms in intermolecular calculations. It is therefore especially attractive to replace in LCC calculations the LMP2 method for weak pairs by LRPA. This is now possible in our LCC code (O. Masur and M. Schütz, to be published.)

B.2.8 Local coupled-cluster methods with orbital-specific virtual orbitals: OSV-LCCSD(T)

Local coupled cluster methods can optionally use orbital specific virtual orbitals (OSVs), see J. Yang, G. K. L. Chan, F. R. Manby, M. Schütz, and H.-J. Werner, *The orbital-specific virtual local coupled-cluster singles and doubles method: OSV-LCCSD*, J. Chem. Phys. **136**, 144105 (2012). The main advantage of this method is that the accuracy of the domain approximation can be controlled by a single parameter. Further developments that also use pair-natural orbitals (PNOs) as descibed in C. Krause and H.-J. Werner, *Perspective: Comparison of explicitly correlated local coupled-cluster methods with various choices of virtual orbitals*, Phys. Chem. Chem. Phys. **14**, 7591-7604 (2012) are in progress. A preliminary parallel PNO-LMP2-F12 method is already available.

B.2.9   Explicitly correlated local MP2 and CC methods: DF-LMP2-F12, DF-LCCSD(T)-F12

The explicitly correlated coupled cluster methods as described in H.-J. Werner, *Eliminating the domain error in local explicitly correlated second-order Møller-Plesset perturbation theory*, J. Chem. Phys. **129**, 101103 (2008); T. B. Adler, F. R. Manby, and H.-J. Werner, *Local explicitly correlated second-order perturbation theory for the accurate treatment of large molecules*, J. Chem. Phys. **130**, 054106 (2009); T. B. Adler and H.-J. Werner, *Local explicitly correlated coupled-cluster methods: Efficient removal of the basis set incompleteness and domain errors*, J. Chem. Phys. **130**, 241101 (2009); T. B. Adler and H.-J. Werner, *An explicitly correlated local coupled-cluster method for calculations of large molecules close to the basis set limit*, J. Chem. Phys. **135**, 144117 (2011) are available for closed-shell cases (an open-shell implementation will follow soon). In these methods the errors of the local domain approximation are eliminated to a large extend, and the same accuracy as with the corresponding canonical methods can be achieved, even for molecules with 50-100 atoms.

B.2.10   Improved DFT with density fitting

The efficiency of density functional theory has been much improved. In particular, the density fitting (DF-RKS, DF-UKS) codes for analytical energy gradients are now very much faster, due to a new integral code (adaptive integral core, AIC) written by G. Knizia. Some benchmarks can be found in H.-J. Werner, P. J. Knowles, G. Knizia, F. R. Manby, and M. Schütz, *Molpro – a general purpose quantum chemistry program package*, WIRES Comput. Mol. Sci. **2**, 242 (2012).

B.2.11   Additional density functionals

A large number of additional density functionals has been added, including PBE0, PBEREV, M05, M05-2X, M06, M06-2X, M06-L, M06-HF, M08-HX, M08-SO, M11-L, SOGGA, SOGGA11, SOGGA11-X. (M11 is currently not available, but will likely be added in the near future).

B.2.12   Additional gradient theories: CCSD, DF-MP2, DF-CASSCF, DF-RS2

New analytical gradient codes are now available for DF-MP2, DF-CASSCF, DF-RS2 (including MS and XMS options, also without density fitting), and for CCSD.

B.2.13   Local methods for excited states

First-order properties of excited states via time-dependent Local CC2 linear response theory and ADC(2) are now also available for triplet states. This is described in K. Freundorfer, D. Kats, T. Korona, and M. Schütz, *Local CC2 response method for triplet states based on Laplace transform: Excitation energies and first-order properties*, J. Chem. Phys. **133**, 244110 (2010);

B.2.14   NMR shielding tensors at DF-LMP2 level using GIAOs

An efficient method for calculating NMR shielding tensors at the local MP2 level has been implemented. Gauge including atomic orbitals (GIAOs) are used to eliminate the gauge origin dependence. Density fitting is employed to factorize the relevant electron repulsion integrals and their derivatives w.r. to the magnetic field. So far, the method has been already applied to systems with more than 2500 contracted basis functions and 300 correlated electrons. Relevant publications are S. Loibl, F. R. Manby, and M. Schütz, *Density fitted, local Hartree-Fock treatment of NMR chemical shifts using London atomic orbitals*, Mol. Phys., **108**, 477 (2010), and S. Loibl and M. Schütz, *NMR shielding tensors for density fitted local second-order Møller-Plesset perturbation theory using gauge including atomic orbitals*, J. Chem. Phys., **137**, 084107 (2012).

B.2.15   SAPT(CCSD)

Symmetry-adapted perturbation theory of intermolecular interactions with monomers described in the CCSD level.

B.2.16   Improved SCF algorithms for high-spin open-shell systems

For open-shell systems, RHF and RKS now use a two-step diagonalization process by default: Here the beta orbitals are found by a second diagonalization in the subspace of occupied alpha orbitals. This process usually leads to more stable convergence in difficult cases, compared to the standard diagonalization of a single open-shell Fock matrix (the latter behavior is recovered by {rhf,algo=0}). An additional section with suggestions for dealing with difficult cases has been added to be manual under "The SCF program". Additionally, various limitations of the SCF program have been lifted. In particular, {rhf; maxit,1} now always works, and just calculates a Fock matrix and energy from the input orbitals, without updating said orbitals.

B.2.17   FCIQMC: Stochastic Full CI

The FCIQMC program exists through an interface to the `NECI` codebase, which is actively developed in the group of A. Alavi, and has been integrated in to the MOLPRO code. The FCIQMC method is a recently introduced stochastic method which can calculate in principle FCI-quality energies for small to medium-sized molecules. See G. H. Booth, A. J. W. Thom, and A. Alavi, J. Chem. Phys. **131**, 054106 (2009); D. M. Cleland, G. H. Booth, and A. Alavi, J. Chem. Phys. **134**, 024112 (2011); G. H. Booth, D. M. Cleland, A. J. W. Thom, and A. Alavi, J. Chem. Phys. **135**, 084104 (2011).

B.2.18   Ab Initio Multiple Spawning Dynamics

The AIMS module implements the Ab Initio Multiple Spawning method to perform dynamics calculations on multiple electronic states. It can also be used quite generally for first principles molecular dynamics on a single electronic surface, provided that nuclear gradients are available. Currently, non-adiabatic dynamics is limited to CASSCF wavefunctions; however, MS-CASPT2 non-adiabatic dynamics (with an implementation of analytical MS-CASPT2 non-adiabatic couplings) will be provided in the very near future. See M. Ben-Nun and T. J. Martinez, Chem. Phys. Lett. **298**, 57 (1998); B. G. Levine, J. D. Coe, A. M. Virshup and T. J. Martinez, Chem. Phys. **347**, 3 (2008); T. Mori, W. J. Glover, M. S. Schuurman and T. J. Martinez, J. Phys. Chem. A **116**, 2808 (2012).

B.2.19   Updated def2 basis sets

The partially augmented Turbomole basis sets def2-SVPD, def2-TZVPD, and def2-QZVPPD (Rappoport, Furche: J. Chem. Phys. 133, 134105 (2010)) have been added to the library. Additionally, the recently developed dhf- variants of the def2- basis sets have been included (dhf-SVP, dhf-TZVPP, ..., Weigend, Baldes: J. Chem. Phys. 133, 174102 (2010)); these are reoptimized versions for the more modern MDF effective core potentials (most elements used MDF ECPs already in def2- and are unchanged). Short names like TZVPP (without prefix) now refer to dhf- basis sets.

B.2.20   Parallel builds merged

The MPP and MPPX builds of Molpro have been merged and the decision to run in MPP or MPPX mode made a run-time option. To build parallel Molpro the `-mpp` flag to configure should be used; the `-mppx` flag is no longer required or valid. When running parallel Molpro, the `--mpp` option (default) can be used to specify MPP mode, and the `--mppx` option for MPPX mode.

B.2.21 Auto-build options for parallel configuration

New options for configuring parallel Molpro to run on a single node or workstation have been implemented. These options (see manual) are prefixed with `-auto`, and in conjunction with `-mpp` configure will download, build and install a variety of different prerequisites for parallel Molpro.

B.3 New features of MOLPRO2010.1

The functionality is essentially the same as in 2009.1, but many bug fixes and small improvements have been added. Please note the following major changes, in particular of the default RI basis sets in explicitly correlated methods as described below.

B.3.1 AIC density fitting integral program

A faster integral program for density fitting, written by Gerald Knizia, has been added. In particular this speeds up the integral evaluation in F12 calculations by up to a factor of about 10 (depending on the basis set). This program is now used by default, but can be disabled by setting

```
dfit,aic=0
```

in the beginning of the input.

B.3.2 Pair specific geminal exponents in explicitly correlated methods

Different exponents for the Slater-type geminals can be used for valence-valence, core-valence, and core-core pairs. See manual for details.

B.3.3 Change of defaults in explicitly correlated methods

For explicitly correlated F12 calculations that use the VnZ-F12 orbital basis sets (OBS), it is now the default to use the corresponding VnZ-F12/OPTRI basis sets to construct the complementary auxiliary orbital basis (CABS). In case that CABS is not used (e.g., in LMP2-F12), the OBS and OPTRI sets are merged automatically. This yields exactly the same results as would be obtained with the CABS approach. In order to use the default RI sets of 2009.1, please specify option RI_BASIS=JKFIT on the command line, or

```
explicit,ri_basis=jkfit
```

For compatibility reasons, it is still the default to use the JKFIT sets as RI basis for the AVnZ orbital basis sets. In order to use the corresponding OPTRI sets (where available) please specify option RI_BASIS=OPTRI.

B.3.4 New basis sets in the Molpro library

A number of new basis sets have been added to the Molpro library since version 2009.1. The references for these sets can be found in the headers of the respective libmol files.

Li, Be, Na, Mg:	a) New official versions of the correlation consistent basis sets for these elements have been added, both non-relativistic and those contracted for Douglas-Kroll relativistic calculations. Specifically these are:
	cc-pVnZ (n=D-5) cc-pwCVnZ (n=D-5) aug-cc-pVnZ (n=D-5) aug-cc-pwCVnZ (n=D-5)
	and the above with a -DK extension. The older cc-pVnZ basis sets for these elements can still be accessed via the keywords vdz-old, etc.

b) New basis sets, including RI and MP2 auxiliary sets, have been added for F12 explicit correlation calculations:

cc-pVnZ-F12 (n=D-Q) cc-pCVnZ-F12 (n=D-Q)

The optimized CABS auxiliary sets have the same name but with a /OptRI context

For MP2 and CCSD auxiliary sets, the cc-pVnZ/MP2FIT sets of Hättig can be used, but a new cc-pV5Z/MP2FIT set has been added that is optimal for the new cc-pV5Z basis set; new aug-cc-pVnZ/MP2FIT (n=D-5) sets have been added as well. The original cc-pV5Z/MP2FIT sets of Hättig have been renamed v5z-old/mp2fit.

Cu-Zn, Y-Cd, Hf-Hg:
a) While the aug-cc-pVnZ-PP (n=D-5) and cc-pwCVnZ-PP (n=D-5) sets were already available, the combination aug-cc-pwCVnZ-PP was not yet defined. These have now been added for these elements.

b) Triple-zeta DK sets have been included now for all of these elements. Unless otherwise noted, these were optimized for 2nd-order DKH. In the cases of Hf-Hg, sets contracted for 3rd-order DKH are also now included:

cc-pVTZ-DK cc-pwCVTZ-DK aug-cc-pVTZ-DK aug-cc-pwCVTZ-DK

and the above with -DK replaced by -DK3 for DKH3 calculations in the case of Hf-Hg.

H-He, B-Ne, Al-Ar, Ga-Kr:
a) A variety of DK contracted basis sets have been added for these elements:

aug-cc-pVnZ-DK (n=D-5) cc-pCVnZ-DK (n=D-5) cc-pwCVnZ-DK (n=D-5) aug-cc-pCVnZ-DK (n=D-5) aug-cc-pwCVnZ-DK (n=D-5)

b) Official cc-pCV6Z and aug-cc-pCV6Z are now also available for Al-Ar

c) For explicitly correlated calculations, the core-valence sets have been added:

cc-pCVnZ-F12 (n=D-Q) for B-Ne, Al-Ar cc-pCVnZ-F12/OptRI (n=D-Q) for B-Ne, Al-Ar

d) cc-pVnZ-F12/OptRI (n=D-Q) as also been added for He

Turbomole def2 basis sets:
The complete Turbomole def2 basis set family has been added to the Molpro basis library (for all elements H to Rn, except Lanthanides). The def2-orbital basis sets can now be accessed as SV(P), SVP, TZVP, TZVPP, QZVP and QZVPP. In this nomenclature SVP, TZVPP, and QZVPP correspond to valence double-zeta (VDZ), valence triple-zeta (VTZ) and valence quadruple-zeta (VQZ) basis sets, respectively.

Auxiliary density fitting basis sets for all elements are available as well (e.g., TZVPP/JFIT, TZVPP/JKFIT, TZVPP/MP2FIT) and are chosen automatically in density-fitted calculations. Supposedly, the JKFIT sets are universal and also applicable in combination with the AVnZ basis sets. Initial results indicate that they also work well with the cc-pVnZ-PP and aug-cc-pVnZ-PP series of basis sets.

The orbital basis sets can also be accessed in singly and doubly augmented versions (carrying A or DA prefixes, respectively, e.g., ASVP, DASVP), and the auxiliary fitting sets in singly augmented versions (e.g., ATZVPP/MP2FIT).

The old Turbomole basis sets have been renamed; if required, they can be accessed with a def1-prefix (e..g, def1-SVP, def1-TZVPP, etc.).

B.3.5 Improved support for MPI implementation of parallelism

The *ppidd* harness that manages interprocess communication has been improved. The performance of the implementation based on pure MPI, as an alternative to use of the Global Arrays toolkit, is considerably improved, through the use of dedicated helper processes that service one-sided remote memory accesses.

B.3.6   Change of the order of states and the defaults for computing the Davidson correction in multi-state MRCI

The previous way to compute the Davidson correction in multi-state MRCI could lead to non-continuous cluster corrected energies. This is now avoided by ordering the MRCI eigenstates according to increasing energy (previously they were ordered according to maximum overlap with the reference wavefunctions). Furthermore, additional options for computing the Davidson correction in multi-state calculations are added (for details see manual). The old behavior can be recovered using options SWAP,ROTREF=-1.

B.3.7   IPEA shift for CASPT2

A variant of the IPEA shift of G. Ghigo, B. O. Roos, and P.A. Malmqvist, Chem. Phys. Lett. **396**, 142 (2004) has been added. The implementation is not exactly identical to the one in MOLCAS, since in our program the singly external configurations are not (RS2) or only partially (RS2C) contracted. The shift is invoked by giving option `IPEA`=*shift* on the `RS2` or `RS2C` commands; the recommended value for *shift* is 0.25. For details of the implementation see manual.

B.3.8   Karton-Martin extrapolation of HF energies

The two-point formula for extrapolating the HF reference energy, as proposed by A. Karton and J. M. L. Martin, Theor. Chem. Acc. **115**, 330 (2006) has been added: $E_{\text{HF},n} = E_{\text{HF,CBS}} + A(n+1) \cdot \exp(-9\sqrt{n})$. Use `METHOD_R=KM` for this.

B.4   New features of MOLPRO2009.1

B.4.1   Basis set updates

Correlation consistent basis sets for Li, Be, Na, and Mg have been updated to their official versions as reported in Prascher et al., Theor. Chem. Acc. (2010). These now also include core-valence, diffuse augmented, and Douglas-Kroll relativistically contracted versions. The previous sets are still available but have been renamed vdz-old, vtz-old, etc.

B.4.2   Explicitly correlated calculations

Due to new findings, the default behavior of the F12 programs was changed in the following points:

1. For open-shell systems the default wave function ansatz for was modified. This affects RMP2-F12 and open-shell CCSD-F12 calculations. The new default generally improves open-shell treatments and leads to more consistent behavior. The previous behavior can be restored by

   `explicit,extgen=0`

   (for more details see manual).

2. The procedure for the construction of complementary auxiliary basis sets (CABS) and the thresholds were changed. This affects all non-local F12 calculations. The previous behavior can be restored by

   `explicit,ortho_cabs=0,thrcabs=1-7,thrcabs_rel=1e-8`

3. In numeric frequency calculations, the freezing of auxiliary basis sets was improved. This can affect calculations where many redundant functions are deleted.

4. Pair energies for the explicitly correlated methods can be printed using

   `print,pairs`

   If inner-shell orbitals are correlated, the cc, cv, and vv contributions to the correlation energies are also printed.

B.4.3 Improvements to the Hartree-Fock program

The atomic density guess in Hartree-Fock has been improved and extended. Guess basis sets are now available for most atoms and for all pseudopotentials. Most pseudopotentials have been linked to the appropriate basis sets, so that it is sufficient to specify, e.g.

```
basis=vtz-pp
```

which will select the correlation consistent triple zeta basis sets and the associated (small core) pseudopotential. Similarly, it is mostly sufficient to specify the basis set for other pseudopotential/basis set combinations.

If the wavefunction symmetry is not given in the Hartree-Fock input and not known from a previous calculation, the HF program attempts to determine it automatically from the aufbau pricniple (previously, symmetry 1 was assumed in all cases). For example,

```
geometry={n};
{hf;wf,spin=3}
```

automatically finds that the wavefunction symmetry is 8.

B.4.4 Changes to geometry input

1. Rationalisation of options for molecular geometry. It is now illegal to specify symmetry and orientation options (eg x;noorient;angstrom) inside a geometry block, which now contains just the geometry specification (Z-matrix or XYZ). Options have to be specified using the new ORIENT and SYMMETRY commands, and/or existing commands such ANGSTROM. This change will, unfortunately, render many inputs incompatible with 2008.1 and earlier versions of Molpro, but has been introduced to allow correct and clean parsing of geometries containing, for example, yttrium atoms, which previously conflicted with the Y symmetry option.

2. Simplification of geometry input. The program now detects automatically whether the geometry is specified as a Z-matrix, or using cartesian coordinates, and so there is no need any more to set the geomtyp variable. The standard XYZ format is still accepted for cartesian coordinates, but the first two lines (number of atoms, and a comment) can be omitted if desired.

B.4.5 MPI-2 parallel implementation

The program now can be built from the source files with the Global Arrays toolkit or the MPI-2 library for parallel execution.

B.5 New features of MOLPRO2008.1

The new features of MOLPRO version 2008.1 include the following.

1. Efficient closed-shell and open-shell MP2-F12 and CCSD(T)-F12 methods which dramatically improve the basis set convergence, as described in J. Chem. Phys. 126, 164102 (2007); ibid. 127, 221106 (2007); ibid. 128, 154103 (2008).

2. Natural bond order (NBO) and natural population analysis (NPA) as described in Mol. Phys. 105, 2753 (2007) and references therein.

3. Correlation regions within a localized molecular orbital approach as described in J. Chem. Phys. 128, 144106 (2008).

4. Automated calculation of anharmonic vibrational frequencies and zero-point energies using VCI methods as described in J. Chem. Phys. 126, 134108 (2007) and references therein.

5. Coupling of DFT and coupled cluster methods as described in Phys. Chem. Chem. Phys. 10, 3353 (2008) and references therein.

6. Enhanced connections to other programs, including graphical display of output and 3-dimensional structures.

7. Support for latest operating systems and compilers, including Mac OS X.

B.6   New features of MOLPRO2006.1

Features and enhancements in MOLPRO version 2006.1 most notably included efficient density fitting methods, explicitly correlated methods, local coupled cluster methods, and several new gradient programs: following:

1. More consistent input language and input pre-checking.

2. More flexible basis input, allowing to handle multiple basis sets

3. New more efficient density functional implementation, additional density functionals.

4. Low-order scaling local coupled cluster methods with perturbative treatment of triples excitations (LCCSD(T) and variants like LQCISD(T))

5. Efficient density fitting (DF) programs for Hartree-Fock (DF-HF), Density functional Kohn-Sham theory (DF-KS), Second-order Møller-Plesset perturbation theory (DF-MP2), as well as for all local methods (DF-LMP2, DF-LMP4, DF-LQCISD(T), DF-LCCSD(T))

6. Analytical QCISD(T) gradients

7. Analytical MRPT2 (CASPT2) and MS-CASPT2 gradients, using state averaged MCSCF reference functions

8. Analytical DF-HF, DF-KS, DF-LMP2, and DF-SCS-LMP2 gradients

9. Explicitly correlated methods with density fitting: DF-MP2-R12/2A', DF-MP2-F12/2A' as well as the local variants DF-LMP2-R12/2*A(loc) and DF-LMP2-F12/2*A(loc).

10. Coupling of multi-reference perturbation theory and configuration interaction (CIPT2)

11. DFT-SAPT

12. Transition moments and transition Hamiltonian between CASSCF and MRCI wavefunctions with different orbitals.

13. A new spin-orbit integral program for generally contracted basis sets.

14. Douglas-Kroll-Hess Hamiltonian up to arbitrary order.

15. Improved procedures for geometry optimization and numerical Hessian calculations, including constrained optimization.

16. Improved facilities to treat large lattices of point charges for QM/MM calculations, including lattice gradients (see section 59) .

17. An interface to the MRCC program of M. Kallay, allowing coupled-cluster calculations with arbitrary excitation level.

18. Automatic *embarrassingly parallel* computation of numerical gradients and Hessians (`mppx Version`).

19. Additional parallel codes, e.g. DF-HF, DF-KS, DF-LCCSD(T) (partly, including triples).

20. Additional output formats for tables (XHTML, LaTeX, Maple, Mathematica, Matlab and comma-separated variables), orbitals and basis sets (XML), and an optional well-formed XML output stream with important results marked up.

B.7   New features of MOLPRO2002.6

Relative to version 2002.1, there are the following changes and additions:

1. Support for IA-64 Linux systems (HP and NEC) and HP-UX 11.22 for IA-64 (Itanium2).

2. Support for NEC-SX systems.

3. Support for IBM-power4 systems.

4. Modified handling of Molpro system variables. The SET command has changed (see sections 8 and 8.4) .

5. The total charge of the molecule can be specified in a variable CHARGE or on the WF card (see section 4.9) .

6. Improved numerical geometry optimization using symmetrical displacement coordinates (see sections 45.2 and 46) .

7. Improved numerical frequency calculations using the symmetry (AUTO option (see section 47) .

B.8   New features of MOLPRO2002

Relative to version 2000.1, there are the following principal changes and additions:

1. Modules direct and local are now included in the base version. This means that integral-direct procedures as described in

   M. Schütz, R. Lindh, and H.-J. Werner, Mol. Phys. 96, 719 (1999),

   linear-scaling local MP2, as described in

   G. Hetzer, P. Pulay, and H.-J. Werner, Chem. Phys. Lett. 290, 143 (1998),
   M. Schütz, G. Hetzer, and H.-J. Werner, J. Chem. Phys. **111**, 5691 (1999),
   G. Hetzer, M. Schütz, H. Stoll, and H.-J. Werner, J. Chem. Phys. **113**, 9443 (2000),

   as well as LMP2 gradients as described in

   A. El Azhary, G. Rauhut, P. Pulay, and H.-J. Werner, J. Chem. Phys. **108**, 5185 (1998)

   are now available without special license. The linear scaling LCCSD(T) methods as described in

   M. Schütz and H.-J. Werner, J. Chem. Phys. **114**, 661 (2001),
   M. Schütz and H.-J. Werner, Chem. Phys. Lett. **318**, 370 (2000),
   M. Schütz, J. Chem. Phys. **113**, 9986 (2000)

   will be made available at a later stage.

2. QCISD gradients as described in Phys. Chem. Chem. Phys. **3**, 4853 (2001) are now available.

3. Additional and more flexible options for computing numerical gradients and performing geometry optimizations.

4. A large number of additional density functionals have been added, together with support for the automated functional implementer described in Comp. Phys. Commun. **136** 310–318 (2001).

5. Multipole moments of arbitrary order can be computed.

6. Further modules have been parallelized, in particular the CCSD(T) and direct LMP2 codes. The parallel running procedures have been improved. The parallel version is available as an optional module.

7. The basis set library has been extended.

8. Some subtle changes in the basis set input: it is not possible any more that several one-line basis input cards with definitions for individual atoms follow each other. Each new basis card supercedes previous ones. Either all specifications must be given on *one* BASIS card, or a basis input block must be used. BASIS,NAME is now entirely equivalent to BASIS=NAME, i.e. a global default basis set is defined and the variable BASIS is set in both cases.

9. Pseudopotential energy calculations can now be performed with up to *i*-functions, gradients with up to *h*-functions.

10. Many internal changes have been made to make MOLPRO more modular and stable. Support has been added for recent operating systems on Compaq, HP, SGI, SUN, and Linux. The patching system has been improved.

B.9   Features that were new in MOLPRO2000

Relative to version 98.1, there are the following principal changes and additions:

1. There was a fundamental error in the derivation of the spin-restricted open-shell coupled-cluster equations in J. Chem. Phys. 99, 5129 (1993) that is also reflected in the RCCSD code in MOLPRO version 98.1 and earlier. This error has now been corrected, and an erratum has been published in J. Chem. Phys. **112**, 3106 (2000). Fortunately, the numerical implications of the error were small, and it is not anticipated that any computed properties will have been significantly in error.

2. There was a programming error in the transformation of gradients from Cartesian to internal coordinates, which in some cases resulted in slow convergence of geometry optimizations. The error is now fixed.

3. Vibrational frequencies formerly by default used average atomic masses, rather than those of the most common isotopes, which is now the default behaviour.

4. MCSCF second derivatives (author Riccardo Tarroni) added (preliminary version, only without symmetry). Frequency and geometry optimization programs are modified so that they can use the analytic Hessian.

5. New internally contracted multi-reference second-order perturbation theory code (author Paolo Celani) through command `RS2C`, as described in P. Celani and H.-J. Werner, J. Chem. Phys. **112**, 5546 (2000).

6. EOM-CCSD for excited states (author Tatiana Korona).

7. QCISD dipole moments as true analytical energy derivatives (author Guntram Rauhut).

8. Linear scaling (CPU and memory) LMP2 as described by G. Hetzer, P. Pulay, and H.-J. Werner, Chem. Phys. Lett. 290, 143 (1998).
   M. Schütz, G. Hetzer, and H.-J. Werner, J. Chem. Phys. **111**, 5691 (1999).

9. Improved handling of basis and geometry records. 98.1 and 99.1 dump files can be restarted, but in case of problems with restarting old files, add `RESTART,NOGEOM` immediately after the `file` card. Also, if there are unjustified messages coming up in very large cases about "ORBITALS CORRESPOND TO DIFFERENT GEOMETRY" try `ORBITAL,record,NOCHECK`. (This can happen for cases with more than 100 atoms, since the old version was limited to 100).

10. Reorganization and generalization of basis input. Increased basis library.

11. Counterpoise geometry optimizations.

12. Improved running procedures for MPP machines. Parallel direct scf and scf gradients are working. These features are only available with the MPP module, which is not yet being distributed.

13. Important bugfixes for DFT grids, CCSD with paging, finite field calculations without core orbitals, spin-orbit coupling.

14. Many other internal changes.

As an additional service to the MOLPRO community, an electronic mailing list has been set up to provide a forum for open discussion on all aspects of installing and using MOLPRO. The mailing list is intended as the primary means of disseminating hints and tips on how to use Molpro effectively. It is not a means of raising queries directly with the authors of the program. For clearly demonstrable program errors, reports should continue to be sent to molpro@molpro.net; however, 'how-to' questions sent there will merely be redirected to this mailing list.

In order to subscribe to the list, send mail to molpro-user-request@molpro.net containing the text `subscribe`; for help, send mail containing the text `help`.

Messages can be sent to the list (molpro-user@molpro.net), but this can be done only by subscribers. Previous postings can be viewed in the archive at http://www.molpro.net/molpro-user/archive irrespective of whether or not you subscribe to the list. Experienced Molpro users are encouraged to post responses to queries raised. Please do contribute to make this resource mutually useful.

B.10   Facilities that were new in MOLPRO98

MOLPRO98 has the full functionality of MOLPRO96, but in order to make the code more modular and easier to use and maintain, a number of structural changes have been made. In particular, the number of different records has been significantly reduced. The information for a given wavefunction type, like orbitals, density matrices, fock matrices, occupation numbers and other information, is now stored in a single dump record. Even different orbital types, e.g., canonical, natural, or localized orbitals, are stored in the same record, and the user can subsequently access individual sets by keywords on the ORBITAL directive. New facilities allow the use of starting orbitals computed with different basis sets and/or different symmetries for SCF or MCSCF calculations. The default starting guess for SCF calculations has been much improved, which is most useful in calculations for large molecules. The use of special procedures for computing non-adiabatic couplings or diabatization of orbitals has been significantly simplified. We hope that these changes make the program easier to use and reduce the probability of input errors. However, in order to use the new facilities efficiently, even experienced MOLPRO users should read the sections *RECORDS* and *SELECTING ORBITALS AND DENSITY MATRICES* in the manual. It is likely that standard MOLPRO96 inputs still work, but changes may be required in more special cases involving particular records for orbitals, density matrices, or operators.

All one-electron operators needed to compute expectation values and transition quantities are now stored in a single record. Operators for which expectation values are requested can be selected globally for all programs of a given run using the global GEXPEC directive, or for a specific program using the EXPEC directive. All operators are computed automatically when needed, and the user does not have to give input for this any more. See section *ONE-ELECTRON OPERATORES AND EXPECTATION VALUES* of the manual for details.

Due to the changed structure of dump and operator records, the utility program MATROP has a new input syntax. MOLPRO96 inputs for MATROP do not work any more.

In addition to these organizational changes, a number of new programs have been added. Analytic energy gradients can now be evaluated for MP2 and DFT wavefunctions, and harmonic vibrational frequencies, intensities, and thermodynamic quantities can be computed automatically using finite differences of analytical gradients. Geometry optimization has been further improved, and new facilities for reaction path following have been added.

An interface to the graphics program MOLDEN has been added, which allows to visualize molecular structures, orbitals, electron densities, or vibrations.

Integral-direct calculations, in which the two-electron integrals in the AO basis are never stored on disk but always recomputed when needed, are now available for all kinds of wavefunctions, with the exception of perturbative triple excitations in MP4 and CCSD(T) calculations. This allows the use of significantly larger basis sets than was possible before. The direct option can be selected globally using the GDIRECT command, or for a specific program using the DIRECT directive. See section *INTEGRAL DIRECT METHODS* in the manual for details. Note that the DIRECT module is optional and not part of the basic MOLPRO distribution.

Local electron correlation methods have been further improved. In combination with the integral-direct modules, which implement efficient prescreening techniques, the scaling of the computational cost with molecular size is dramatically reduced, approaching now quadratic or even linear scaling for MP2 and higher correlation methods. This makes possible to perform correlated calculations for much larger molecules than were previously feasible. However, since these methods are subject of active current research and still under intense development, we decided not to include them in the current MOLPRO release. They will be optionally available in one of the next releases.

C Density functional descriptions

C.1 `B86`: $\mathbf{X}\alpha\beta\gamma$

Divergence free semiempirical gradient-corrected exchange energy functional. $\lambda = \gamma$ in ref.

$$g = -\frac{c\,(\rho\,(s))^{4/3}\,\left(1 + \beta\,(\chi\,(s))^2\right)}{1 + \lambda\,(\chi\,(s))^2}, \tag{66}$$

$$G = -\frac{c\,(\rho\,(s))^{4/3}\,\left(1 + \beta\,(\chi\,(s))^2\right)}{1 + \lambda\,(\chi\,(s))^2}, \tag{67}$$

$$c = 3/8\,\sqrt[3]{3}\,4^{2/3}\,\sqrt[3]{\pi^{-1}}, \tag{68}$$

$$\beta = 0.0076, \tag{69}$$

$$\lambda = 0.004. \tag{70}$$

C.2 `B86MGC`: $\mathbf{X}\alpha\beta\gamma$ with Modified Gradient Correction

B86 with modified gradient correction for large density gradients.

$$
\begin{aligned}
g = {}& -c\,(\rho\,(s))^{4/3} \\
& -\frac{\beta\,(\chi\,(s))^2\,(\rho\,(s))^{4/3}}{(1 + \lambda\,(\chi\,(s))^2)^{4/5}},
\end{aligned} \tag{71}
$$

$$
\begin{aligned}
G = {}& -c\,(\rho\,(s))^{4/3} \\
& -\frac{\beta\,(\chi\,(s))^2\,(\rho\,(s))^{4/3}}{(1 + \lambda\,(\chi\,(s))^2)^{4/5}},
\end{aligned} \tag{72}
$$

$$c = 3/8\,\sqrt[3]{3}\,4^{2/3}\,\sqrt[3]{\pi^{-1}}, \tag{73}$$

$$\beta = 0.00375, \tag{74}$$

$$\lambda = 0.007. \tag{75}$$

C.3 `B86R`: $\mathbf{X}\alpha\beta\gamma$ Re-optimised

Re-optimised β of B86 used in part 3 of Becke's 1997 paper.

$$g = -\frac{c\,(\rho\,(s))^{4/3}\,\left(1 + \beta\,(\chi\,(s))^2\right)}{1 + \lambda\,(\chi\,(s))^2}, \tag{76}$$

$$G = -\frac{c\,(\rho\,(s))^{4/3}\,\left(1 + \beta\,(\chi\,(s))^2\right)}{1 + \lambda\,(\chi\,(s))^2}, \tag{77}$$

$$c = 3/8\,\sqrt[3]{3}\,4^{2/3}\,\sqrt[3]{\pi^{-1}}, \tag{78}$$

$$\beta = 0.00787, \tag{79}$$

$$\lambda = 0.004. \tag{80}$$

C.4 `B88`: Becke 1988 Exchange Functional

$$G = -\left(\rho\left(s\right)\right)^{4/3}\left(c \right. \tag{81}$$

$$\left. + \frac{\beta\left(\chi\left(s\right)\right)^2}{1 + 6\beta\,\chi\left(s\right)\,arcsinh\left(\chi\left(s\right)\right)}\right),$$

$$g = -\left(\rho\left(s\right)\right)^{4/3}\left(c \right. \tag{82}$$

$$\left. + \frac{\beta\left(\chi\left(s\right)\right)^2}{1 + 6\beta\,\chi\left(s\right)\,arcsinh\left(\chi\left(s\right)\right)}\right),$$

$$c = 3/8\,\sqrt[3]{3}\,4^{2/3}\,\sqrt[3]{\pi^{-1}}, \tag{83}$$

$$\beta = 0.0042. \tag{84}$$

C.5 `B88C`: Becke 1988 Correlation Functional

Correlation functional depending on B86MGC exchange functional with empirical atomic parameters, t and u. The exchange functional that is used in conjunction with B88C should replace B86MGC here.

$$f = -0.8\,\rho\left(a\right)\rho\left(b\right)q^2\left(1 \right. \tag{85}$$

$$\left. - \frac{\ln\left(1 + q\right)}{q}\right),$$

$$q = t\left(x \right. \tag{86}$$

$$\left. + y\right),$$

$$x = 0.5\left(c\,\sqrt[3]{\rho\left(a\right)} \right. \tag{87}$$

$$\left. + \frac{\beta\left(\chi\left(a\right)\right)^2\,\sqrt[3]{\rho\left(a\right)}}{\left(1 + \lambda\left(\chi\left(a\right)\right)^2\right)^{4/5}}\right)^{-1},$$

$$y = 0.5\left(c\,\sqrt[3]{\rho\left(b\right)} \right. \tag{88}$$

$$\left. + \frac{\beta\left(\chi\left(b\right)\right)^2\,\sqrt[3]{\rho\left(b\right)}}{\left(1 + \lambda\left(\chi\left(b\right)\right)^2\right)^{4/5}}\right)^{-1},$$

$$t = 0.63, \tag{89}$$

$$g = -0.01\,\rho\left(s\right)dz^4\left(1 \right. \tag{90}$$

$$\left. - 2\,\frac{\ln\left(1 + 1/2\,z\right)}{z}\right),$$

$$z = 2\,ur, \tag{91}$$

$$r = 0.5\,\rho\left(s\right)\left(c\left(\rho\left(s\right)\right)^{4/3} \right. \tag{92}$$

$$\left. + \frac{\beta\left(\chi\left(s\right)\right)^2\left(\rho\left(s\right)\right)^{4/3}}{\left(1 + \lambda\left(\chi\left(s\right)\right)^2\right)^{4/5}}\right)^{-1},$$

$$u = 0.96, \tag{93}$$

$$d = \tau(s) \\ - 1/4 \frac{\sigma(ss)}{\rho(s)}, \tag{94}$$

$$G = -0.01 \rho(s) dz^4 \left(1 \right. \tag{95}$$
$$\left. - 2 \frac{\ln(1 + 1/2z)}{z} \right),$$

$$c = 3/8 \sqrt[3]{3} 4^{2/3} \sqrt[3]{\pi^{-1}}, \tag{96}$$

$$\beta = 0.00375, \tag{97}$$

$$\lambda = 0.007. \tag{98}$$

C.6   `B95`: Becke 1995 Correlation Functional

tau dependent Dynamical correlation functional.

$$T = [0.031091, 0.015545, 0.016887], \tag{99}$$

$$U = [0.21370, 0.20548, 0.11125], \tag{100}$$

$$V = [7.5957, 14.1189, 10.357], \tag{101}$$

$$W = [3.5876, 6.1977, 3.6231], \tag{102}$$

$$X = [1.6382, 3.3662, 0.88026], \tag{103}$$

$$Y = [0.49294, 0.62517, 0.49671], \tag{104}$$

$$P = [1, 1, 1], \tag{105}$$

$$f = \frac{E}{1 + l((\chi(a))^2 + (\chi(b))^2)}, \tag{106}$$

$$g = \frac{F \varepsilon(\rho(s), 0)}{H(1 + v(\chi(s))^2)^2}, \tag{107}$$

$$G = \frac{F \varepsilon(\rho(s), 0)}{H(1 + v(\chi(s))^2)^2}, \tag{108}$$

$$E = \varepsilon(\rho(a), \rho(b)) \\ - \varepsilon(\rho(a), 0) \\ - \varepsilon(\rho(b), 0), \tag{109}$$

$$l = 0.0031, \tag{110}$$

$$F = \tau(s) \tag{111}$$
$$- 1/4 \frac{\sigma(ss)}{\rho(s)},$$

$$H = 3/5\, 6^{2/3}\left(\pi^2\right)^{2/3}\left(\rho(s)\right)^{5/3}, \tag{112}$$

$$v = 0.038, \tag{113}$$

$$\varepsilon(\alpha,\beta) \tag{114}$$
$$= (\alpha$$
$$+ \beta)\left(e\left(r(\alpha,\beta),T_1,U_1,V_1,W_1,X_1,Y_1,P_1\right)\right.$$
$$- \frac{e\left(r(\alpha,\beta),T_3,U_3,V_3,W_3,X_3,Y_3,P_3\right)\omega\left(\zeta(\alpha,\beta)\right)\left(1-(\zeta(\alpha,\beta))^4\right)}{c}$$
$$+ \left(e\left(r(\alpha,\beta),T_2,U_2,V_2,W_2,X_2,Y_2,P_2\right)\right.$$
$$\left.- e\left(r(\alpha,\beta),T_1,U_1,V_1,W_1,X_1,Y_1,P_1\right)\right)\omega\left(\zeta(\alpha,\beta)\right)\left(\zeta(\alpha,\beta)\right)^4 \Bigg),$$

$$r(\alpha,\beta) \tag{115}$$
$$= 1/4 \sqrt[3]{3}\, 4^{2/3}\, \sqrt[3]{\frac{1}{\pi(\alpha+\beta)}},$$

$$\zeta(\alpha,\beta) \tag{116}$$
$$= \frac{\alpha - \beta}{\alpha + \beta},$$

$$\omega(z) \tag{117}$$
$$= \frac{(1+z)^{4/3} + (1-z)^{4/3} - 2}{2\sqrt[3]{2} - 2},$$

$$e(r,t,u,v,w,x,y,p) \tag{118}$$
$$=$$
$$-2t\,(1$$
$$+ ur)\ln\left(1\right.$$
$$\left.+ 1/2\, \frac{1}{t\left(v\sqrt{r} + wr + xr^{3/2} + yr^{p+1}\right)}\right),$$

$$c = 1.709921. \tag{119}$$

C.7 B97DF: Density functional part of B97

This functional needs to be mixed with 0.1943*exact exchange.

$$T = [0.031091, 0.015545, 0.016887], \tag{120}$$

$$U = [0.21370, 0.20548, 0.11125], \tag{121}$$

$$V = [7.5957, 14.1189, 10.357], \tag{122}$$

$$W = [3.5876, 6.1977, 3.6231], \tag{123}$$

$$X = [1.6382, 3.3662, 0.88026], \tag{124}$$

$$Y = [0.49294, 0.62517, 0.49671], \tag{125}$$

$$P = [1, 1, 1], \tag{126}$$

$$A = [0.9454, 0.7471, \tag{127}$$
$$-4.5961],$$

$$B = [0.1737, 2.3487, \tag{128}$$
$$-2.4868],$$

$$C = [0.8094, 0.5073, 0.7481], \tag{129}$$

$$\lambda = [0.006, 0.2, 0.004], \tag{130}$$

$$d = 1/2 \, (\chi(a))^2 \tag{131}$$
$$+ \, 1/2 \, (\chi(b))^2,$$

$$f = (\varepsilon(\rho(a), \rho(b)) \tag{132}$$
$$- \, \varepsilon(\rho(a), 0)$$
$$- \, \varepsilon(\rho(b), 0)) \, \big(A_0$$
$$+ A_1 \, \eta(d, \lambda_1)$$
$$+ A_2 \, (\eta(d, \lambda_1))^2 \big),$$

$$\eta(\theta, \mu) \tag{133}$$
$$= \frac{\mu \, \theta}{1 + \mu \, \theta},$$

$$g = \varepsilon(\rho(s), 0) \, \big(B_0 \tag{134}$$
$$+ B_1 \, \eta \big((\chi(s))^2, \lambda_2\big)$$
$$+ B_2 \, \big(\eta \big((\chi(s))^2, \lambda_2\big)\big)^2\big)$$
$$- \, 3/8 \, \sqrt[3]{3} 4^{2/3} \sqrt[3]{\pi^{-1}} \, (\rho(s))^{4/3} \, \big(C_0$$
$$+ C_1 \, \eta \big((\chi(s))^2, \lambda_3\big)$$
$$+ C_2 \, \big(\eta \big((\chi(s))^2, \lambda_3\big)\big)^2\big),$$

$$G = \varepsilon(\rho(s), 0) \, \big(B_0 \tag{135}$$
$$+ B_1 \, \eta \big((\chi(s))^2, \lambda_2\big)$$
$$+ B_2 \, \big(\eta \big((\chi(s))^2, \lambda_2\big)\big)^2\big)$$
$$- \, 3/8 \, \sqrt[3]{3} 4^{2/3} \sqrt[3]{\pi^{-1}} \, (\rho(s))^{4/3} \, \big(C_0$$
$$+ C_1 \, \eta \big((\chi(s))^2, \lambda_3\big)$$
$$+ C_2 \, \big(\eta \big((\chi(s))^2, \lambda_3\big)\big)^2\big),$$

$$\varepsilon(\alpha, \beta) \tag{136}$$
$$= (\alpha$$
$$+ \beta) \left(e(r(\alpha, \beta), T_1, U_1, V_1, W_1, X_1, Y_1, P_1) \right.$$
$$- \frac{e(r(\alpha, \beta), T_3, U_3, V_3, W_3, X_3, Y_3, P_3) \, \omega(\zeta(\alpha, \beta)) \, (1 - (\zeta(\alpha, \beta))^4)}{c}$$
$$+ (e(r(\alpha, \beta), T_2, U_2, V_2, W_2, X_2, Y_2, P_2)$$
$$\left. - e(r(\alpha, \beta), T_1, U_1, V_1, W_1, X_1, Y_1, P_1)) \, \omega(\zeta(\alpha, \beta)) \, (\zeta(\alpha, \beta))^4 \right),$$

$$r(\alpha,\beta)$$
$$= 1/4\,\sqrt[3]{3}\,4^{2/3}\,\sqrt[3]{\dfrac{1}{\pi\,(\alpha+\beta)}}, \tag{137}$$

$$\zeta(\alpha,\beta)$$
$$= \dfrac{\alpha-\beta}{\alpha+\beta}, \tag{138}$$

$$\omega(z)$$
$$= \dfrac{(1+z)^{4/3}+(1-z)^{4/3}-2}{2\sqrt[3]{2}-2}, \tag{139}$$

$$e(r,t,u,v,w,x,y,p)$$
$$=$$
$$-2t\,(1$$
$$+\,ur)\ln\left(1\right.$$
$$\left.+\,1/2\,\dfrac{1}{t\left(v\sqrt{r}+wr+xr^{3/2}+yr^{p+1}\right)}\right), \tag{140}$$

$$c = 1.709921. \tag{141}$$

C.8   `B97RDF`: Density functional part of B97 Re-parameterized by Hamprecht et al

Re-parameterization of the B97 functional in a self-consistent procedure by Hamprecht et al. This functional needs to be mixed with 0.21*exact exchange.

$$T = [0.031091, 0.015545, 0.016887], \tag{142}$$

$$U = [0.21370, 0.20548, 0.11125], \tag{143}$$

$$V = [7.5957, 14.1189, 10.357], \tag{144}$$

$$W = [3.5876, 6.1977, 3.6231], \tag{145}$$

$$X = [1.6382, 3.3662, 0.88026], \tag{146}$$

$$Y = [0.49294, 0.62517, 0.49671], \tag{147}$$

$$P = [1, 1, 1], \tag{148}$$

$$A = [0.955689, 0.788552, \tag{149}$$
$$-5.47869],$$

$$B = [0.0820011, 2.71681, \tag{150}$$
$$-2.87103],$$

$$C = [0.789518, 0.573805, 0.660975], \tag{151}$$

$$\lambda = [0.006, 0.2, 0.004], \tag{152}$$

$$d = 1/2\,(\chi\,(a))^2 \tag{153}$$
$$+ 1/2\,(\chi\,(b))^2,$$

$$f = (\varepsilon\,(\rho\,(a),\rho\,(b)) \tag{154}$$
$$-\,\varepsilon\,(\rho\,(a),0)$$
$$-\,\varepsilon\,(\rho\,(b),0))\,\big(A_0$$
$$+ A_1\,\eta\,(d,\lambda_1)$$
$$+ A_2\,(\eta\,(d,\lambda_1))^2\big),$$

$$\eta\,(\theta,\mu) \tag{155}$$
$$= \frac{\mu\,\theta}{1 + \mu\,\theta},$$

$$g = \varepsilon\,(\rho\,(s),0)\,\big(B_0 \tag{156}$$
$$+ B_1\,\eta\,((\chi\,(s))^2,\lambda_2)$$
$$+ B_2\,(\eta\,((\chi\,(s))^2,\lambda_2))^2\big)$$
$$-\,3/8\,\sqrt[3]{3}\,4^{2/3}\,\sqrt[3]{\pi^{-1}}\,(\rho\,(s))^{4/3}\,\big(C_0$$
$$+ C_1\,\eta\,((\chi\,(s))^2,\lambda_3)$$
$$+ C_2\,(\eta\,((\chi\,(s))^2,\lambda_3))^2\big),$$

$$G = \varepsilon\,(\rho\,(s),0)\,\big(B_0 \tag{157}$$
$$+ B_1\,\eta\,((\chi\,(s))^2,\lambda_2)$$
$$+ B_2\,(\eta\,((\chi\,(s))^2,\lambda_2))^2\big)$$
$$-\,3/8\,\sqrt[3]{3}\,4^{2/3}\,\sqrt[3]{\pi^{-1}}\,(\rho\,(s))^{4/3}\,\big(C_0$$
$$+ C_1\,\eta\,((\chi\,(s))^2,\lambda_3)$$
$$+ C_2\,(\eta\,((\chi\,(s))^2,\lambda_3))^2\big),$$

$$\varepsilon\,(\alpha,\beta) \tag{158}$$
$$= (\alpha$$
$$+ \beta)\left(e\,(r\,(\alpha,\beta),T_1,U_1,V_1,W_1,X_1,Y_1,P_1)\right.$$
$$-\,\frac{e\,(r\,(\alpha,\beta),T_3,U_3,V_3,W_3,X_3,Y_3,P_3)\,\omega\,(\zeta\,(\alpha,\beta))\,\big(1 - (\zeta\,(\alpha,\beta))^4\big)}{c}$$
$$+ (e\,(r\,(\alpha,\beta),T_2,U_2,V_2,W_2,X_2,Y_2,P_2)$$
$$\left.-\,e\,(r\,(\alpha,\beta),T_1,U_1,V_1,W_1,X_1,Y_1,P_1))\,\omega\,(\zeta\,(\alpha,\beta))\,(\zeta\,(\alpha,\beta))^4\right),$$

$$r\,(\alpha,\beta) \tag{159}$$
$$= 1/4\,\sqrt[3]{3}\,4^{2/3}\,\sqrt[3]{\frac{1}{\pi\,(\alpha + \beta)}},$$

$$\zeta\,(\alpha,\beta) \tag{160}$$
$$= \frac{\alpha - \beta}{\alpha + \beta},$$

$$\omega\,(z) \tag{161}$$
$$= \frac{(1 + z)^{4/3} + (1 - z)^{4/3} - 2}{2\,\sqrt[3]{2} - 2},$$

$$e\left(r,t,u,v,w,x,y,p\right)$$
$$=$$
$$-2t\left(1\right.$$
$$\left.+ur\right)\ln\left(1\right.$$
$$\left.+1/2\,\frac{1}{t\left(v\sqrt{r}+wr+xr^{3/2}+yr^{p+1}\right)}\right),$$

(162)

$$c = 1.709921.$$

(163)

C.9   BR: Becke-Roussel Exchange Functional

A. D. Becke and M. R. Roussel,Phys. Rev. A 39, 3761 (1989)

$$K = \frac{1}{2}\sum_{s}\rho_{s}U_{s},$$

(164)

where

$$U_s = -(1-e^{-x}-xe^{-x}/2)/b,$$

(165)

$$b = \frac{x^3 e^{-x}}{8\pi\rho_s}$$

(166)

and x is defined by the nonlinear equation

$$\frac{xe^{-2x/3}}{x-2} = \frac{2\pi^{2/3}\rho_s^{5/3}}{3Q_s},$$

(167)

where

$$Q_s = (\upsilon_s - 2\gamma D_s)/6,$$

(168)

$$D_s = \tau_s - \frac{\sigma_{ss}}{4\rho_s}$$

(169)

and

$$\gamma = 1.$$

(170)

C.10   BRUEG: Becke-Roussel Exchange Functional — Uniform Electron Gas Limit

A. D. Becke and M. R. Roussel,Phys. Rev. A 39, 3761 (1989)

As for BR but with $\gamma = 0.8$.

C.11 `BW`: Becke-Wigner Exchange-Correlation Functional

Hybrid exchange-correlation functional comprimising Becke's 1998 exchange and Wigner's spin-polarised correlation functionals.

$$\alpha = -3/8 \sqrt[3]{3} 4^{2/3} \sqrt[3]{\pi^{-1}}, \tag{171}$$

$$g = \alpha \, (\rho \, (s))^{4/3} \\ - \frac{\beta \, (\rho \, (s))^{4/3} \, (\chi \, (s))^2}{1 + 6 \beta \, \chi \, (s) \, arcsinh \, (\chi \, (s))}, \tag{172}$$

$$G = \alpha \, (\rho \, (s))^{4/3} \\ - \frac{\beta \, (\rho \, (s))^{4/3} \, (\chi \, (s))^2}{1 + 6 \beta \, \chi \, (s) \, arcsinh \, (\chi \, (s))}, \tag{173}$$

$$f = -4 c \rho \, (a) \, \rho \, (b) \, \rho^{-1} \left(1 \right. \tag{174}$$
$$\left. + \frac{d}{\sqrt[3]{\rho}} \right)^{-1},$$

$$\beta = 0.0042, \tag{175}$$

$$c = 0.04918, \tag{176}$$

$$d = 0.349. \tag{177}$$

C.12 `CS1`: Colle-Salvetti correlation functional

R. Colle and O. Salvetti, Theor. Chim. Acta 37, 329 (1974); C. Lee, W. Yang and R. G. Parr, Phys. Rev. B 37, 785(1988)

`CS1` is formally identical to `CS2`, except for a reformulation in which the terms involving υ are eliminated by integration by parts. This makes the functional more economical to evaluate. In the limit of exact quadrature, `CS1` and `CS2` are identical, but small numerical differences appear with finite integration grids.

C.13 `CS2`: Colle-Salvetti correlation functional

R. Colle and O. Salvetti, Theor. Chim. Acta 37, 329 (1974); C. Lee, W. Yang and R. G. Parr, Phys. Rev. B 37, 785(1988)

`CS2` is defined through

$$K = -a \left(\frac{\rho + 2b\rho^{-5/3} \left[\rho_\alpha t_\alpha + \rho_\beta t_\beta - \rho t_W \right] e^{-c\rho^{-1/3}}}{1 + d\rho^{-1/3}} \right) \tag{178}$$

where

$$t_\alpha = \frac{\tau_\alpha}{2} - \frac{\upsilon_\alpha}{8} \tag{179}$$

$$t_\beta = \frac{\tau_\beta}{2} - \frac{\upsilon_\beta}{8} \tag{180}$$

$$t_W = \frac{1}{8} \frac{\sigma}{\rho} - \frac{1}{2} \upsilon \tag{181}$$

and the constants are $a = 0.04918, b = 0.132, c = 0.2533, d = 0.349$.

C.14 `DIRAC`: Slater-Dirac Exchange Energy

Automatically generated Slater-Dirac exchange.

$$g = -c\left(\rho\left(s\right)\right)^{4/3},$$ (182)

$$c = 3/8\sqrt[3]{3}4^{2/3}\sqrt[3]{\pi^{-1}}.$$ (183)

C.15 `ECERF`: Short-range LDA correlation functional

Local-density approximation of correlation energy
for short-range interelectronic interaction $\mathrm{erf}(\mu r_{21})/r_{12}$,
S. Paziani, S. Moroni, P. Gori-Giorgi, and G. B. Bachelet, Phys. Rev. B 73, 155111 (2006).

$$\varepsilon_c^{\mathrm{SR}}(r_s,\zeta,\mu) = \varepsilon_c^{\mathrm{PW92}}(r_s,\zeta) - \frac{[\phi_2(\zeta)]^3 Q\left(\frac{\mu\sqrt{r_s}}{\phi_2(\zeta)}\right) + a_1\mu^3 + a_2\mu^4 + a_3\mu^5 + a_4\mu^6 + a_5\mu^8}{(1+b_0^2\mu^2)^4},$$ (184)

where

$$Q(x) = \frac{2\ln(2)-2}{\pi^2}\ln\left(\frac{1+ax+bx^2+cx^3}{1+ax+dx^2}\right),$$ (185)

with $a = 5.84605$, $c = 3.91744$, $d = 3.44851$, and $b = d - 3\pi\alpha/(4\ln(2)-4)$. The parameters $a_i(r_s,\zeta)$ are given by

$$
\begin{aligned}
a_1 &= 4b_0^6 C_3 + b_0^8 C_5,\\
a_2 &= 4b_0^6 C_2 + b_0^8 C_4 + 6b_0^4\varepsilon_c^{\mathrm{PW92}},\\
a_3 &= b_0^8 C_3,\\
a_4 &= b_0^8 C_2 + 4b_0^6\varepsilon_c^{\mathrm{PW92}},\\
a_5 &= b_0^8\varepsilon_c^{\mathrm{PW92}},
\end{aligned}
$$

with

$$
\begin{aligned}
C_2 &= -\frac{3(1-\zeta^2)g_c(0,r_s,\zeta=0)}{8r_s^3}\\
C_3 &= -(1-\zeta^2)\frac{g(0,r_s,\zeta=0)}{\sqrt{2\pi}r_s^3}\\
C_4 &= -\frac{9c_4(r_s,\zeta)}{64r_s^3}\\
C_5 &= -\frac{9c_5(r_s,\zeta)}{40\sqrt{2\pi}r_s^3}\\
c_4(r_s,\zeta) &= \left(\frac{1+\zeta}{2}\right)^2 g''\left(0,r_s\left(\frac{2}{1+\zeta}\right)^{1/3},\zeta=1\right) + \left(\frac{1-\zeta}{2}\right)^2 \times\\
&\quad g''\left(0,r_s\left(\frac{2}{1-\zeta}\right)^{1/3},\zeta=1\right) + (1-\zeta^2)D_2(r_s) - \frac{\phi_8(\zeta)}{5\alpha^2 r_s^2}\\
c_5(r_s,\zeta) &= \left(\frac{1+\zeta}{2}\right)^2 g''\left(0,r_s\left(\frac{2}{1+\zeta}\right)^{1/3},\zeta=1\right) + \left(\frac{1-\zeta}{2}\right)^2 \times\\
&\quad g''\left(0,r_s\left(\frac{2}{1-\zeta}\right)^{1/3},\zeta=1\right) + (1-\zeta^2)D_3(r_s),
\end{aligned}
$$ (186)

and

$$b_0(r_s) = 0.784949 \, r_s \tag{187}$$

$$g''(0, r_s, \zeta = 1) = \frac{2^{5/3}}{5 \, \alpha^2 \, r_s^2} \frac{1 - 0.02267 r_s}{(1 + 0.4319 r_s + 0.04 r_s^2)} \tag{188}$$

$$D_2(r_s) = \frac{e^{-0.547 r_s}}{r_s^2} \left(-0.388 r_s + 0.676 r_s^2 \right) \tag{189}$$

$$D_3(r_s) = \frac{e^{-0.31 r_s}}{r_s^3} \left(-4.95 r_s + r_s^2 \right). \tag{190}$$

Finally, $\varepsilon_c^{\mathrm{PW92}}(r_s, \zeta)$ is the Perdew-Wang parametrization of the correlation energy of the standard uniform electron gas [J.P. Perdew and Y. Wang, Phys. Rev. B 45, 13244 (1992)], and

$$g(0, r_s, \zeta = 0) = \frac{1}{2}(1 - B r_s + C r_s^2 + D r_s^3 + E r_s^4) \, e^{-d r_s}, \tag{191}$$

is the on-top pair-distribution function of the standard jellium model [P. Gori-Giorgi and J.P. Perdew, Phys. Rev. B 64, 155102 (2001)], where $B = -0.0207$, $C = 0.08193$, $D = -0.01277$, $E = 0.001859$, $d = 0.7524$. The correlation part of the on-top pair-distribution function is $g_c(0, r_s, \zeta = 0) = g(0, r_s, \zeta = 0) - \frac{1}{2}$.

C.16 ECERFPBE**: Range-Separated Correlation Functional**

Toulouse-Colonna-Savin range-separated correlation functional based on PBE, see J. Toulouse et al., J. Chem. Phys. 122, 014110 (2005).

C.17 EXACT**: Exact Exchange Functional**

Hartree-Fock exact exchange functional can be used to construct hybrid exchange-correlation functional.

C.18 EXERF**: Short-range LDA correlation functional**

Local-density approximation of exchange energy
for short-range interelectronic interaction $\mathrm{erf}(\mu r_{12})/r_{12}$,
A. Savin, in Recent Developments and Applications of Modern Density Functional Theory, edited by J.M. Seminario (Elsevier, Amsterdam, 1996).

$$\varepsilon_x^{\mathrm{SR}}(r_s, \zeta, \mu) = \frac{3}{4\pi} \frac{\phi_4(\zeta)}{\alpha r_s} - \frac{1}{2}(1+\zeta)^{4/3} f_x \left(r_s, \mu(1+\zeta)^{-1/3} \right) + \frac{1}{2}(1-\zeta)^{4/3} f_x \left(r_s, \mu(1-\zeta)^{-1/3} \right) \tag{192}$$

with

$$\phi_n(\zeta) = \frac{1}{2} \left[(1+\zeta)^{n/3} + (1-\zeta)^{n/3} \right], \tag{193}$$

$$f_x(r_s, \mu) = -\frac{\mu}{\pi} \left[(2y - 4y^3) \, e^{-1/4y^2} - 3y + 4y^3 + \sqrt{\pi} \, \mathrm{erf}\left(\frac{1}{2y} \right) \right], \qquad y = \frac{\mu \, \alpha \, r_s}{2}, \tag{194}$$

and $\alpha = (4/9\pi)^{1/3}$.

C.19   `EXERFPBE`: Range-Separated Exchange Functional

Toulouse-Colonna-Savin range-separated exchange functional based on PBE, see J. Toulouse et al., J. Chem. Phys. 122, 014110 (2005).

C.20   `G96`: Gill's 1996 Gradient Corrected Exchange Functional

$$\alpha = -3/8 \sqrt[3]{3} 4^{2/3} \sqrt[3]{\pi^{-1}}, \tag{195}$$

$$g = (\rho(s))^{4/3} \left(\alpha \right. \tag{196}$$
$$\left. - \frac{1}{137} (\chi(s))^{3/2} \right), $$

$$G = (\rho(s))^{4/3} \left(\alpha \right. \tag{197}$$
$$\left. - \frac{1}{137} (\chi(s))^{3/2} \right). $$

C.21   `HCTH120`: Handy least squares fitted functional

$$T = [0.031091, 0.015545, 0.016887], \tag{198}$$

$$U = [0.21370, 0.20548, 0.11125], \tag{199}$$

$$V = [7.5957, 14.1189, 10.357], \tag{200}$$

$$W = [3.5876, 6.1977, 3.6231], \tag{201}$$

$$X = [1.6382, 3.3662, 0.88026], \tag{202}$$

$$Y = [0.49294, 0.62517, 0.49671], \tag{203}$$

$$P = [1, 1, 1], \tag{204}$$

$$A = [0.51473, 6.9298, \tag{205}$$
$$-24.707, 23.110,$$
$$-11.323],$$

$$B = [0.48951, \tag{206}$$
$$-0.2607, 0.4329,$$
$$-1.9925, 2.4853],$$

$$C = [1.09163, \tag{207}$$
$$-0.7472, 5.0783,$$
$$-4.1075, 1.1717],$$

$$\lambda = [0.006, 0.2, 0.004], \tag{208}$$

$$d = 1/2 (\chi(a))^2 \tag{209}$$
$$+ 1/2 (\chi(b))^2,$$

$$f = (\varepsilon(\rho(a),\rho(b)) \tag{210}$$
$$- \varepsilon(\rho(a),0)$$
$$- \varepsilon(\rho(b),0))\,(A_0$$
$$+ A_1\,\eta(d,\lambda_1)$$
$$+ A_2\,(\eta(d,\lambda_1))^2$$
$$+ A_3\,(\eta(d,\lambda_1))^3$$
$$+ A_4\,(\eta(d,\lambda_1))^4),$$

$$\eta(\theta,\mu) \tag{211}$$
$$= \frac{\mu\,\theta}{1+\mu\,\theta},$$

$$g = \varepsilon(\rho(s),0)\,(B_0 \tag{212}$$
$$+ B_1\,\eta((\chi(s))^2,\lambda_2)$$
$$+ B_2\,(\eta((\chi(s))^2,\lambda_2))^2$$
$$+ B_3\,(\eta((\chi(s))^2,\lambda_2))^3$$
$$+ B_4\,(\eta((\chi(s))^2,\lambda_2))^4)$$
$$- 3/8\,\sqrt[3]{3}\,4^{2/3}\,\sqrt[3]{\pi^{-1}}\,(\rho(s))^{4/3}\,(C_0$$
$$+ C_1\,\eta((\chi(s))^2,\lambda_3)$$
$$+ C_2\,(\eta((\chi(s))^2,\lambda_3))^2$$
$$+ C_3\,(\eta((\chi(s))^2,\lambda_3))^3$$
$$+ C_4\,(\eta((\chi(s))^2,\lambda_3))^4),$$

$$\varepsilon(\alpha,\beta) \tag{213}$$
$$= (\alpha$$
$$+ \beta)\left(e(r(\alpha,\beta),T_1,U_1,V_1,W_1,X_1,Y_1,P_1) \right.$$
$$- \frac{e(r(\alpha,\beta),T_3,U_3,V_3,W_3,X_3,Y_3,P_3)\,\omega(\zeta(\alpha,\beta))\,(1-(\zeta(\alpha,\beta))^4)}{c}$$
$$+ (e(r(\alpha,\beta),T_2,U_2,V_2,W_2,X_2,Y_2,P_2)$$
$$\left. - e(r(\alpha,\beta),T_1,U_1,V_1,W_1,X_1,Y_1,P_1))\,\omega(\zeta(\alpha,\beta))\,(\zeta(\alpha,\beta))^4 \right),$$

$$r(\alpha,\beta) \tag{214}$$
$$= 1/4\,\sqrt[3]{3}\,4^{2/3}\,\sqrt[3]{\frac{1}{\pi(\alpha+\beta)}},$$

$$\zeta(\alpha,\beta) \tag{215}$$
$$= \frac{\alpha-\beta}{\alpha+\beta},$$

$$\omega(z) \tag{216}$$
$$= \frac{(1+z)^{4/3}+(1-z)^{4/3}-2}{2\sqrt[3]{2}-2},$$

$$e(r,t,u,v,w,x,y,p)$$
$$=$$
$$-2t\,(1$$

$$+ur)\ln\left(1\right.$$

$$\left.+\,1/2\,\frac{1}{t\left(v\sqrt{r}+wr+xr^{3/2}+yr^{p+1}\right)}\right), \tag{217}$$

$$c = 1.709921. \tag{218}$$

C.22 `HCTH147`: Handy least squares fitted functional

$$T = [0.031091, 0.015545, 0.016887], \tag{219}$$

$$U = [0.21370, 0.20548, 0.11125], \tag{220}$$

$$V = [7.5957, 14.1189, 10.357], \tag{221}$$

$$W = [3.5876, 6.1977, 3.6231], \tag{222}$$

$$X = [1.6382, 3.3662, 0.88026], \tag{223}$$

$$Y = [0.49294, 0.62517, 0.49671], \tag{224}$$

$$P = [1, 1, 1], \tag{225}$$

$$A = [0.542352, 7.01464, \tag{226}$$
$$-28.3822, 35.0329,$$
$$-20.4284],$$

$$B = [0.562576, \tag{227}$$
$$-0.0171436,$$
$$-1.30636, 1.05747, 0.885429],$$

$$C = [1.09025, \tag{228}$$
$$-0.799194, 5.57212,$$
$$-5.86760, 3.04544],$$

$$\lambda = [0.006, 0.2, 0.004], \tag{229}$$

$$d = 1/2\,(\chi(a))^2 \tag{230}$$
$$+\,1/2\,(\chi(b))^2,$$

$$f = (\varepsilon(\rho(a), \rho(b)) \tag{231}$$
$$-\,\varepsilon(\rho(a), 0)$$
$$-\,\varepsilon(\rho(b), 0))\,(A_0$$
$$+\,A_1\,\eta(d, \lambda_1)$$
$$+\,A_2\,(\eta(d, \lambda_1))^2$$
$$+\,A_3\,(\eta(d, \lambda_1))^3$$
$$+\,A_4\,(\eta(d, \lambda_1))^4\,),$$

$$\eta\left(\theta,\mu\right) \tag{232}$$
$$= \frac{\mu\,\theta}{1+\mu\,\theta},$$

$$g = \varepsilon\left(\rho\left(s\right),0\right)\big(B_0 \tag{233}$$
$$+ B_1\eta\left(\left(\chi\left(s\right)\right)^2,\lambda_2\right)$$
$$+ B_2\left(\eta\left(\left(\chi\left(s\right)\right)^2,\lambda_2\right)\right)^2$$
$$+ B_3\left(\eta\left(\left(\chi\left(s\right)\right)^2,\lambda_2\right)\right)^3$$
$$+ B_4\left(\eta\left(\left(\chi\left(s\right)\right)^2,\lambda_2\right)\right)^4\big)$$
$$- 3/8\,\sqrt[3]{3}\,4^{2/3}\,\sqrt[3]{\pi^{-1}}\left(\rho\left(s\right)\right)^{4/3}\big(C_0$$
$$+ C_1\eta\left(\left(\chi\left(s\right)\right)^2,\lambda_3\right)$$
$$+ C_2\left(\eta\left(\left(\chi\left(s\right)\right)^2,\lambda_3\right)\right)^2$$
$$+ C_3\left(\eta\left(\left(\chi\left(s\right)\right)^2,\lambda_3\right)\right)^3$$
$$+ C_4\left(\eta\left(\left(\chi\left(s\right)\right)^2,\lambda_3\right)\right)^4\big),$$

$$\varepsilon\left(\alpha,\beta\right) \tag{234}$$
$$= \big(\alpha$$
$$+ \beta\big)\left(e\left(r\left(\alpha,\beta\right),T_1,U_1,V_1,W_1,X_1,Y_1,P_1\right)\right.$$
$$+ \frac{e\left(r\left(\alpha,\beta\right),T_3,U_3,V_3,W_3,X_3,Y_3,P_3\right)\omega\left(\zeta\left(\alpha,\beta\right)\right)\left(1-\left(\zeta\left(\alpha,\beta\right)\right)^4\right)}{c}$$
$$+ \left(e\left(r\left(\alpha,\beta\right),T_2,U_2,V_2,W_2,X_2,Y_2,P_2\right)\right.$$
$$\left.\left. - e\left(r\left(\alpha,\beta\right),T_1,U_1,V_1,W_1,X_1,Y_1,P_1\right)\right)\omega\left(\zeta\left(\alpha,\beta\right)\right)\left(\zeta\left(\alpha,\beta\right)\right)^4\right),$$

$$r\left(\alpha,\beta\right) \tag{235}$$
$$= 1/4\,\sqrt[3]{3}\,4^{2/3}\,\sqrt[3]{\frac{1}{\pi\left(\alpha+\beta\right)}},$$

$$\zeta\left(\alpha,\beta\right) \tag{236}$$
$$= \frac{\alpha-\beta}{\alpha+\beta},$$

$$\omega\left(z\right) \tag{237}$$
$$= \frac{\left(1+z\right)^{4/3}+\left(1-z\right)^{4/3}-2}{2\,\sqrt[3]{2}-2},$$

$$e\left(r,t,u,v,w,x,y,p\right) \tag{238}$$
$$=$$
$$-2t\left(1\right.$$
$$+ ur)\ln\left(1\right.$$
$$\left.\left. + 1/2\,\frac{1}{t\left(v\sqrt{r}+wr+xr^{3/2}+yr^{p+1}\right)}\right),\right.$$

$$c = 1.709921. \tag{239}$$

C.23 `HCTH93`: **Handy least squares fitted functional**

$$T = [0.031091, 0.015545, 0.016887], \tag{240}$$

$$U = [0.21370, 0.20548, 0.11125], \tag{241}$$

$$V = [7.5957, 14.1189, 10.357], \tag{242}$$

$$W = [3.5876, 6.1977, 3.6231], \tag{243}$$

$$X = [1.6382, 3.3662, 0.88026], \tag{244}$$

$$Y = [0.49294, 0.62517, 0.49671], \tag{245}$$

$$P = [1, 1, 1], \tag{246}$$

$$A = [0.72997, 3.35287, \tag{247}$$
$$-11.543, 8.08564,$$
$$-4.47857],$$

$$B = [0.222601, \tag{248}$$
$$-0.0338622,$$
$$-0.012517,$$
$$-0.802496, 1.55396],$$

$$C = [1.0932, \tag{249}$$
$$-0.744056, 5.5992,$$
$$-6.78549, 4.49357],$$

$$\lambda = [0.006, 0.2, 0.004], \tag{250}$$

$$d = 1/2 \, (\chi\,(a))^2 \tag{251}$$
$$+ 1/2 \, (\chi\,(b))^2,$$

$$f = (\varepsilon\,(\rho\,(a), \rho\,(b)) \tag{252}$$
$$- \varepsilon\,(\rho\,(a), 0)$$
$$- \varepsilon\,(\rho\,(b), 0))\,(A_0$$
$$+ A_1 \eta\,(d, \lambda_1)$$
$$+ A_2\,(\eta\,(d, \lambda_1))^2$$
$$+ A_3\,(\eta\,(d, \lambda_1))^3$$
$$+ A_4\,(\eta\,(d, \lambda_1))^4),$$

$$\eta\,(\theta, \mu) \tag{253}$$
$$= \frac{\mu\,\theta}{1 + \mu\,\theta},$$

$$g = \varepsilon\left(\rho\left(s\right),0\right)\left(B_0 \right.$$
$$+ B_1 \eta\left(\left(\chi\left(s\right)\right)^2, \lambda_2\right) \tag{254}$$

$$+ B_2 \left(\eta\left(\left(\chi\left(s\right)\right)^2, \lambda_2\right)\right)^2$$
$$+ B_3 \left(\eta\left(\left(\chi\left(s\right)\right)^2, \lambda_2\right)\right)^3$$
$$+ B_4 \left(\eta\left(\left(\chi\left(s\right)\right)^2, \lambda_2\right)\right)^4\Big)$$
$$- 3/8 \sqrt[3]{3} 4^{2/3} \sqrt[3]{\pi^{-1}} \left(\rho\left(s\right)\right)^{4/3} \left(C_0\right.$$

$$+ C_1 \eta\left(\left(\chi\left(s\right)\right)^2, \lambda_3\right)$$

$$+ C_2 \left(\eta\left(\left(\chi\left(s\right)\right)^2, \lambda_3\right)\right)^2$$
$$+ C_3 \left(\eta\left(\left(\chi\left(s\right)\right)^2, \lambda_3\right)\right)^3$$
$$+ C_4 \left(\eta\left(\left(\chi\left(s\right)\right)^2, \lambda_3\right)\right)^4\Big),$$

$$\varepsilon\left(\alpha,\beta\right)$$
$$= \left(\alpha \right. \tag{255}$$

$$+ \beta\right)\left(e\left(r\left(\alpha,\beta\right), T_1, U_1, V_1, W_1, X_1, Y_1, P_1\right)\right.$$

$$- \frac{e\left(r\left(\alpha,\beta\right), T_3, U_3, V_3, W_3, X_3, Y_3, P_3\right) \omega\left(\zeta\left(\alpha,\beta\right)\right)\left(1 - \left(\zeta\left(\alpha,\beta\right)\right)^4\right)}{c}$$
$$+ \left(e\left(r\left(\alpha,\beta\right), T_2, U_2, V_2, W_2, X_2, Y_2, P_2\right)\right.$$
$$\left. - e\left(r\left(\alpha,\beta\right), T_1, U_1, V_1, W_1, X_1, Y_1, P_1\right)\right) \omega\left(\zeta\left(\alpha,\beta\right)\right)\left(\zeta\left(\alpha,\beta\right)\right)^4\right),$$

$$r\left(\alpha,\beta\right)$$
$$= 1/4 \sqrt[3]{3} 4^{2/3} \sqrt[3]{\frac{1}{\pi\left(\alpha+\beta\right)}}, \tag{256}$$

$$\zeta\left(\alpha,\beta\right)$$
$$= \frac{\alpha - \beta}{\alpha + \beta}, \tag{257}$$

$$\omega\left(z\right)$$
$$= \frac{\left(1+z\right)^{4/3} + \left(1-z\right)^{4/3} - 2}{2\sqrt[3]{2} - 2}, \tag{258}$$

$$e\left(r, t, u, v, w, x, y, p\right)$$
$$= \tag{259}$$
$$-2t\left(1\right.$$

$$+ ur\right)\ln\left(1\right.$$

$$+ 1/2 \frac{1}{t\left(v\sqrt{r} + wr + xr^{3/2} + yr^{p+1}\right)}\bigg),$$

$$c = 1.709921. \tag{260}$$

C.24   `HJSWPBEX`: Meta GGA Correlation Functional

Henderson-Janesko-Scuseria range-separated exchange functional based on a model of an exchange hole derived by a constraint-satisfaction technique, see T. M. Henderson et al., J. Chem. Phys. 128, 194105 (2008).

C.25   `LTA`: Local τ Approximation

LSDA exchange functional with density represented as a function of τ.

$$g = 1/2\,E\,(2\,\tau\,(s))\,, \tag{261}$$

$$E\,(\alpha)$$
$$= 1/9\,c5^{4/5}\sqrt[5]{9}\left(\frac{\alpha\,\sqrt[3]{3}}{(\pi^2)^{2/3}}\right)^{4/5}, \tag{262}$$

$$c = -3/4\,\sqrt[3]{3}\,\sqrt[3]{\pi^{-1}}, \tag{263}$$

$$G = 1/2\,E\,(2\,\tau\,(s))\,. \tag{264}$$

C.26   `LYP`: Lee, Yang and Parr Correlation Functional

C. Lee, W. Yang and R. G. Parr, Phys. Rev. B 37, 785(1988); B. Miehlich, A. Savin, H. Stoll and H. Preuss, Chem. Phys. Letters 157, 200 (1989).

$$f = -4A\rho\,(a)\,\rho\,(b)\left(1\right.$$
$$\left.+\frac{d}{\sqrt[3]{\rho}}\right)^{-1}\rho^{-1} \tag{265}$$
$$-\,AB\omega\left(\rho\,(a)\,\rho\,(b)\left(8\,2^{2/3}cf\,((\rho\,(a))^{8/3}\right.\right.$$
$$+\,(\rho\,(b))^{8/3})$$
$$+\left(\frac{47}{18}\right.$$
$$\left.-\,\frac{7}{18}\delta\right)\sigma$$
$$-\,(5/2$$
$$-\,1/18\,\delta)\,(\sigma\,(aa)$$
$$+\,\sigma\,(bb))$$
$$-\,1/9\,(\delta$$
$$-\,11)\left(\frac{\rho\,(a)\,\sigma\,(aa)}{\rho}\right.$$
$$\left.\left.+\frac{\rho\,(b)\,\sigma\,(bb)}{\rho}\right)\right)$$
$$-\,2/3\,\rho^2\sigma$$
$$+\,(2/3\,\rho^2$$
$$-\,(\rho\,(a))^2)\,\sigma\,(bb)$$
$$+\,(2/3\,\rho^2$$
$$\left.-\,(\rho\,(b))^2)\,\sigma\,(aa)\right),$$

$$\omega = e^{-\frac{c}{\sqrt[3]{\rho}}}\rho^{-11/3}\left(1\right. \tag{266}$$
$$\left.+\frac{d}{\sqrt[3]{\rho}}\right)^{-1},$$

$$\delta = \frac{c}{\sqrt[3]{\rho}} + d\frac{1}{\sqrt[3]{\rho}}\left(1 \right. \tag{267}$$

$$\left. + \frac{d}{\sqrt[3]{\rho}}\right)^{-1},$$

$$cf = 3/10\,3^{2/3}\left(\pi^2\right)^{2/3}, \tag{268}$$

$$A = 0.04918, \tag{269}$$

$$B = 0.132, \tag{270}$$

$$c = 0.2533, \tag{271}$$

$$d = 0.349. \tag{272}$$

C.27 `M052XC`: M05-2X Meta-GGA Correlation Functional

$$T = [0.031091, 0.015545, 0.016887], \tag{273}$$

$$U = [0.21370, 0.20548, 0.11125], \tag{274}$$

$$V = [7.5957, 14.1189, 10.357], \tag{275}$$

$$W = [3.5876, 6.1977, 3.6231], \tag{276}$$

$$X = [1.6382, 3.3662, 0.88026], \tag{277}$$

$$Y = [0.49294, 0.62517, 0.49671], \tag{278}$$

$$P = [1, 1, 1], \tag{279}$$

$$\varepsilon\,(\alpha, \beta)$$
$$= (\alpha \tag{280}$$

$$+ \beta)\left(e\,(r\,(\alpha, \beta)\,, T_1, U_1, V_1, W_1, X_1, Y_1, P_1) \right.$$

$$- \frac{e\,(r\,(\alpha, \beta)\,, T_3, U_3, V_3, W_3, X_3, Y_3, P_3)\,\omega\,(\zeta\,(\alpha, \beta))\left(1 - (\zeta\,(\alpha, \beta))^4\right)}{c}$$
$$+ (e\,(r\,(\alpha, \beta)\,, T_2, U_2, V_2, W_2, X_2, Y_2, P_2)$$
$$\left. - e\,(r\,(\alpha, \beta)\,, T_1, U_1, V_1, W_1, X_1, Y_1, P_1))\,\omega\,(\zeta\,(\alpha, \beta))\,(\zeta\,(\alpha, \beta))^4 \right),$$

$$r\,(\alpha, \beta)$$
$$= 1/4\,\sqrt[3]{3}\,4^{2/3}\,\sqrt[3]{\frac{1}{\pi\,(\alpha + \beta)}}, \tag{281}$$

$$\zeta\,(\alpha, \beta)$$
$$= \frac{\alpha - \beta}{\alpha + \beta}, \tag{282}$$

$$\omega(z)$$
$$= \frac{(1+z)^{4/3} + (1-z)^{4/3} - 2}{2\sqrt[3]{2} - 2},$$

(283)

$$e(r,t,u,v,w,x,y,p)$$
$$=$$
$$-2t(1$$

(284)

$$+ ur)\ln\left(1\right.$$
$$\left. + 1/2\,\frac{1}{t\left(v\sqrt{r} + wr + xr^{3/2} + yr^{p+1}\right)}\right),$$

$$c = 1.709921,$$

(285)

$$tausMFM = 1/2\,\tau(s),$$

(286)

$$ds = 2\,tausMFM - 1/4\,\frac{\sigma(ss)}{\rho(s)},$$

(287)

$$Gab(chia, chib)$$
$$= \sum_{i=0}^{n} cCab_i \left(\frac{yCab\left(chia^2 + chib^2\right)}{1 + yCab\left(chia^2 + chib^2\right)}\right)^i,$$

(288)

$$Gss(chis)$$
$$= \sum_{i=0}^{n} cCss_i \left(\frac{yCss\,chis^2}{1 + yCss\,chis^2}\right)^i,$$

(289)

$$n = 4,$$

(290)

$$cCab = [1.0, 1.09297,$$
$$-3.79171, 2.82810,$$
$$-10.58909],$$

(291)

$$cCss = [1.0,$$
$$-3.05430, 7.61854, 1.47665,$$
$$-11.92365],$$

(292)

$$yCab = 0.0031,$$

(293)

$$yCss = 0.06,$$

(294)

$$f = (\varepsilon(\rho(a), \rho(b))$$
$$- \varepsilon(\rho(a), 0)$$
$$- \varepsilon(\rho(b), 0))\,Gab(\chi(a), \chi(b)),$$

(295)

$$g = 1/2\,\frac{\varepsilon(\rho(s), 0)\,Gss(\chi(s))\,ds}{tausMFM},$$

(296)

$$G = 1/2\,\frac{\varepsilon(\rho(s), 0)\,Gss(\chi(s))\,ds}{tausMFM}.$$

(297)

C.28 `M052XX`: **M05-2X Meta-GGA Exchange Functional**

$$g = -3/4 \frac{\sqrt[3]{6}\sqrt[3]{\pi^2}\left(\rho\left(s\right)\right)^{4/3} F\left(S\right) Fs\left(ws\right)}{\pi}, \tag{298}$$

$$G = -3/4 \frac{\sqrt[3]{6}\sqrt[3]{\pi^2}\left(\rho\left(s\right)\right)^{4/3} F\left(S\right) Fs\left(ws\right)}{\pi}, \tag{299}$$

$$S = 1/12 \frac{\chi\left(s\right) 6^{2/3}}{\sqrt[3]{\pi^2}}, \tag{300}$$

$$F\left(S\right)$$
$$= 1$$
$$+ R$$
$$- R\left(1\right.$$
$$\left. + \frac{\mu S^2}{R}\right)^{-1}, \tag{301}$$

$$R = 0.804, \tag{302}$$

$$\mu = 1/3\,\delta\,\pi^2, \tag{303}$$

$$\delta = 0.066725, \tag{304}$$

$$n = 11, \tag{305}$$

$$A = [1.0,$$
$$-0.56833, \tag{306}$$
$$-1.30057, 5.50070, 9.06402,$$
$$-32.21075,$$
$$-23.73298, 70.22996, 29.88614,$$
$$-60.25778,$$
$$-13.22205, 15.23694],$$

$$Fs\left(ws\right)$$
$$= \sum_{i=0}^{n} A_i ws^i, \tag{307}$$

$$ws = \frac{ts - 1}{ts + 1}, \tag{308}$$

$$ts = \frac{tslsda}{tausMFM}, \tag{309}$$

$$tslsda = 3/10\,6^{2/3}\left(\pi^2\right)^{2/3}\left(\rho\left(s\right)\right)^{5/3}, \tag{310}$$

$$tausMFM = 1/2\,\tau\left(s\right). \tag{311}$$

C.29 M05C: **M05 Meta-GGA Correlation Functional**

$$T = [0.031091, 0.015545, 0.016887], \tag{312}$$

$$U = [0.21370, 0.20548, 0.11125], \tag{313}$$

$$V = [7.5957, 14.1189, 10.357], \tag{314}$$

$$W = [3.5876, 6.1977, 3.6231], \tag{315}$$

$$X = [1.6382, 3.3662, 0.88026], \tag{316}$$

$$Y = [0.49294, 0.62517, 0.49671], \tag{317}$$

$$P = [1, 1, 1], \tag{318}$$

$$
\begin{aligned}
\varepsilon(\alpha, \beta) \\
= (\alpha \\
+ \beta) \Bigg(e\left(r(\alpha, \beta), T_1, U_1, V_1, W_1, X_1, Y_1, P_1\right) \\
- \frac{e\left(r(\alpha, \beta), T_3, U_3, V_3, W_3, X_3, Y_3, P_3\right) \omega(\zeta(\alpha, \beta)) \left(1 - (\zeta(\alpha, \beta))^4\right)}{c} \\
+ (e\left(r(\alpha, \beta), T_2, U_2, V_2, W_2, X_2, Y_2, P_2\right) \\
- e\left(r(\alpha, \beta), T_1, U_1, V_1, W_1, X_1, Y_1, P_1\right)) \omega(\zeta(\alpha, \beta)) (\zeta(\alpha, \beta))^4 \Bigg),
\end{aligned}
\tag{319}
$$

$$
\begin{aligned}
r(\alpha, \beta) \\
= 1/4 \sqrt[3]{3} \, 4^{2/3} \sqrt[3]{\frac{1}{\pi(\alpha + \beta)}},
\end{aligned}
\tag{320}
$$

$$
\begin{aligned}
\zeta(\alpha, \beta) \\
= \frac{\alpha - \beta}{\alpha + \beta},
\end{aligned}
\tag{321}
$$

$$
\begin{aligned}
\omega(z) \\
= \frac{(1 + z)^{4/3} + (1 - z)^{4/3} - 2}{2 \sqrt[3]{2} - 2},
\end{aligned}
\tag{322}
$$

$$
\begin{aligned}
e(r, t, u, v, w, x, y, p) \\
= \\
-2t(1 \\
+ ur) \ln \Bigg(1 \\
+ 1/2 \frac{1}{t\left(v\sqrt{r} + wr + xr^{3/2} + yr^{p+1}\right)} \Bigg),
\end{aligned}
\tag{323}
$$

$$c = 1.709921, \tag{324}$$

$$tausMFM = 1/2\,\tau(s), \tag{325}$$

$$ds = 2\,tausMFM - 1/4\,\frac{\sigma\,(ss)}{\rho\,(s)}, \tag{326}$$

$$
\begin{aligned}
&Gab\,(chia, chib)\\
&\quad = \sum_{i=0}^{n} cCab_i \left(\frac{yCab\,\left(chia^2 + chib^2\right)}{1 + yCab\,\left(chia^2 + chib^2\right)} \right)^i,
\end{aligned}
\tag{327}
$$

$$
\begin{aligned}
&Gss\,(chis)\\
&\quad = \sum_{i=0}^{n} cCss_i \left(\frac{yCss\,chis^2}{1 + yCss\,chis^2} \right)^i,
\end{aligned}
\tag{328}
$$

$$n = 4, \tag{329}$$

$$
\begin{aligned}
cCab = [1.0, 3.78569,&\\
-14.15261,&\\
-7.46589, 17.94491],&
\end{aligned}
\tag{330}
$$

$$
\begin{aligned}
cCss = [1.0, 3.77344,&\\
-26.04463, 30.69913,&\\
-9.22695],&
\end{aligned}
\tag{331}
$$

$$yCab = 0.0031, \tag{332}$$

$$yCss = 0.06, \tag{333}$$

$$
\begin{aligned}
f = (&\varepsilon\,(\rho\,(a), \rho\,(b))\\
&- \varepsilon\,(\rho\,(a), 0)\\
&- \varepsilon\,(\rho\,(b), 0))\,Gab\,(\chi\,(a), \chi\,(b)),
\end{aligned}
\tag{334}
$$

$$g = 1/2\,\frac{\varepsilon\,(\rho\,(s), 0)\,Gss\,(\chi\,(s))\,ds}{tausMFM}, \tag{335}$$

$$G = 1/2\,\frac{\varepsilon\,(\rho\,(s), 0)\,Gss\,(\chi\,(s))\,ds}{tausMFM}. \tag{336}$$

C.30   M05X: M05 Meta-GGA Exchange Functional

$$g = -3/4\,\frac{\sqrt[3]{6}\,\sqrt[3]{\pi^2}\,(\rho\,(s))^{4/3}\,F\,(S)\,Fs\,(ws)}{\pi}, \tag{337}$$

$$G = -3/4\,\frac{\sqrt[3]{6}\,\sqrt[3]{\pi^2}\,(\rho\,(s))^{4/3}\,F\,(S)\,Fs\,(ws)}{\pi}, \tag{338}$$

$$S = 1/12\,\frac{\chi\,(s)\,6^{2/3}}{\sqrt[3]{\pi^2}}, \tag{339}$$

$$
\begin{aligned}
F\,(S)&\\
&= 1\\
&\quad + R\\
&\quad - R\left(1\right.\\
&\hspace{10em}\left.+ \frac{\mu\,S^2}{R}\right)^{-1},
\end{aligned}
\tag{340}
$$

$$R = 0.804, \tag{341}$$

$$\mu = 1/3\,\delta\,\pi^2, \tag{342}$$

$$\delta = 0.066725, \tag{343}$$

$$n = 11, \tag{344}$$

$$A = [1.0, 0.08151, \tag{345}$$
$$-0.43956,$$
$$-3.22422, 2.01819, 8.79431,$$
$$-0.00295, 9.82029,$$
$$-4.82351,$$
$$-48.17574, 3.64802, 34.02248],$$

$$Fs(ws) \tag{346}$$
$$= \sum_{i=0}^{n} A_i ws^i,$$

$$ws = \frac{ts - 1}{ts + 1}, \tag{347}$$

$$ts = \frac{tslsda}{tausMFM}, \tag{348}$$

$$tslsda = 3/10\,6^{2/3}\left(\pi^2\right)^{2/3}\left(\rho(s)\right)^{5/3}, \tag{349}$$

$$tausMFM = 1/2\,\tau(s). \tag{350}$$

C.31   `M062XC`: **M06-2X Meta-GGA Correlation Functional**

$$T = [0.031091, 0.015545, 0.016887], \tag{351}$$

$$U = [0.21370, 0.20548, 0.11125], \tag{352}$$

$$V = [7.5957, 14.1189, 10.357], \tag{353}$$

$$W = [3.5876, 6.1977, 3.6231], \tag{354}$$

$$X = [1.6382, 3.3662, 0.88026], \tag{355}$$

$$Y = [0.49294, 0.62517, 0.49671], \tag{356}$$

$$P = [1, 1, 1], \tag{357}$$

$$\varepsilon(\alpha, \beta) \tag{358}$$
$$= (\alpha$$
$$+ \beta)\left(e(r(\alpha,\beta), T_1, U_1, V_1, W_1, X_1, Y_1, P_1) \right.$$
$$- \frac{e(r(\alpha,\beta), T_3, U_3, V_3, W_3, X_3, Y_3, P_3)\,\omega(\zeta(\alpha,\beta))\left(1 - (\zeta(\alpha,\beta))^4\right)}{c}$$
$$+ (e(r(\alpha,\beta), T_2, U_2, V_2, W_2, X_2, Y_2, P_2)$$
$$\left. - e(r(\alpha,\beta), T_1, U_1, V_1, W_1, X_1, Y_1, P_1))\,\omega(\zeta(\alpha,\beta))\,(\zeta(\alpha,\beta))^4 \right),$$

$$r(\alpha,\beta)$$
$$= 1/4\,\sqrt[3]{3}\,4^{2/3}\,\sqrt[3]{\frac{1}{\pi\,(\alpha+\beta)}}, \tag{359}$$

$$\zeta(\alpha,\beta)$$
$$= \frac{\alpha-\beta}{\alpha+\beta}, \tag{360}$$

$$\omega(z)$$
$$= \frac{(1+z)^{4/3}+(1-z)^{4/3}-2}{2\sqrt[3]{2}-2}, \tag{361}$$

$$e(r,t,u,v,w,x,y,p)$$
$$=$$
$$-2t\,(1$$

$$+ur)\ln\left(1\right.$$
$$\left.+1/2\,\frac{1}{t\left(v\sqrt{r}+wr+xr^{3/2}+yr^{p+1}\right)}\right), \tag{362}$$

$$c = 1.709921, \tag{363}$$

$$Gab\,(chia,chib)$$
$$= \sum_{i=0}^{n} cCab_i\left(\frac{yCab\,(chia^2+chib^2)}{1+yCab\,(chia^2+chib^2)}\right)^i, \tag{364}$$

$$Gss\,(chis)$$
$$= \sum_{i=0}^{n} cCss_i\left(\frac{yCss\,chis^2}{1+yCss\,chis^2}\right)^i, \tag{365}$$

$$n = 4, \tag{366}$$

$$cCab = [0.8833596, 33.57972, \tag{367}$$
$$-70.43548, 49.78271,$$
$$-18.52891],$$

$$cCss = [0.3097855, \tag{368}$$
$$-5.528642, 13.47420,$$
$$-32.13623, 28.46742],$$

$$yCab = 0.0031, \tag{369}$$

$$yCss = 0.06, \tag{370}$$

$$x = \sqrt{(\chi(a))^2+(\chi(b))^2}, \tag{371}$$

$$tausMFM = 1/2\,\tau(s), \tag{372}$$

$$tauaMFM = 1/2\,\tau(a), \tag{373}$$

$$taubMFM = 1/2\,\tau\,(b)\,, \tag{374}$$

$$zs = 2\,\frac{tausMFM}{(\rho\,(s))^{5/3}} - cf\,, \tag{375}$$

$$z = 2\,\frac{tauaMFM}{(\rho\,(a))^{5/3}} + 2\,\frac{taubMFM}{(\rho\,(b))^{5/3}} - 2\,cf\,, \tag{376}$$

$$cf = 3/5\,6^{2/3}\left(\pi^2\right)^{2/3}\,, \tag{377}$$

$$ds = 1 - \frac{(\chi\,(s))^2}{4\,zs + 4\,cf}\,, \tag{378}$$

$$
\begin{aligned}
&h\,(x,z,d0,d1,d2,d3,d4,d5,\alpha)\\
&= \frac{d0}{\lambda\,(x,z,\alpha)}\\
&\quad + \frac{d1\,x^2 + d2\,z}{(\lambda\,(x,z,\alpha))^2}\\
&\quad + \frac{d3\,x^4 + d4\,x^2 z + d5\,z^2}{(\lambda\,(x,z,\alpha))^3}\,,
\end{aligned}
\tag{379}
$$

$$
\begin{aligned}
&\lambda\,(x,z,\alpha)\\
&= 1\\
&\quad + \alpha\,\big(x^2\\
&\qquad\qquad\qquad\qquad + z\big)\,,
\end{aligned}
\tag{380}
$$

$$
\begin{aligned}
dCab = [&0.1166404,\\
&-0.09120847,\\
&-0.06726189, 0.00006720580, 0.0008448011, 0.0]\,,
\end{aligned}
\tag{381}
$$

$$
\begin{aligned}
dCss = [&0.6902145, 0.09847204, 0.2214797,\\
&-0.001968264,\\
&-0.006775479, 0.0]\,,
\end{aligned}
\tag{382}
$$

$$aCab = 0.003050\,, \tag{383}$$

$$aCss = 0.005151\,, \tag{384}$$

$$
\begin{aligned}
f = (&\varepsilon\,(\rho\,(a),\rho\,(b))\\
&- \varepsilon\,(\rho\,(a),0)\\
&- \varepsilon\,(\rho\,(b),0))\,(Gab\,(\chi\,(a),\chi\,(b))\\
&+ h\,(x,z,dCab_0,dCab_1,dCab_2,dCab_3,dCab_4,dCab_5,aCab))\,,
\end{aligned}
\tag{385}
$$

$$
\begin{aligned}
g = \varepsilon\,(\rho\,(s),0)\,(&Gss\,(\chi\,(s))\\
&+ h\,(\chi\,(s),zs,dCss_0,dCss_1,dCss_2,dCss_3,dCss_4,dCss_5,aCss))\,ds\,,
\end{aligned}
\tag{386}
$$

$$
\begin{aligned}
G = \varepsilon\,(\rho\,(s),0)\,(&Gss\,(\chi\,(s))\\
&+ h\,(\chi\,(s),zs,dCss_0,dCss_1,dCss_2,dCss_3,dCss_4,dCss_5,aCss))\,ds\,.
\end{aligned}
\tag{387}
$$

C.32 `M062XX`: **M06-2X Meta-GGA Exchange Functional**

$$g = -3/4 \frac{\sqrt[3]{6}\sqrt[3]{\pi^2}\left(\rho\left(s\right)\right)^{4/3}F\left(S\right)Fs\left(ws\right)}{\pi}, \tag{388}$$

$$G = -3/4 \frac{\sqrt[3]{6}\sqrt[3]{\pi^2}\left(\rho\left(s\right)\right)^{4/3}F\left(S\right)Fs\left(ws\right)}{\pi}, \tag{389}$$

$$S = 1/12 \frac{\chi\left(s\right)6^{2/3}}{\sqrt[3]{\pi^2}}, \tag{390}$$

$$
\begin{aligned}
F\left(S\right) & \\
& = 1 \\
& \quad + R \\
& \quad - R\left(1\right. \\
& \qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad \left. + \frac{\mu S^2}{R}\right)^{-1},
\end{aligned}
\tag{391}
$$

$$R = 0.804, \tag{392}$$

$$\mu = 1/3\,\delta\,\pi^2, \tag{393}$$

$$\delta = 0.066725, \tag{394}$$

$$n = 11, \tag{395}$$

$$
\begin{aligned}
A = [\,0.4600000, & \\
& -0.2206052, \\
& -0.09431788, 2.164494, \\
& -2.556466, \\
& -14.22133, 15.55044, 35.98078, \\
& -27.22754, \\
& -39.24093, 15.22808, 15.22227\,],
\end{aligned}
\tag{396}
$$

$$
Fs\left(ws\right) = \sum_{i=0}^{n} A_i ws^i, \tag{397}
$$

$$ws = \frac{ts-1}{ts+1}, \tag{398}$$

$$ts = \frac{tslsda}{tausMFM}, \tag{399}$$

$$tslsda = 3/10\,6^{2/3}\left(\pi^2\right)^{2/3}\left(\rho\left(s\right)\right)^{5/3}, \tag{400}$$

$$tausMFM = 1/2\,\tau\left(s\right). \tag{401}$$

C.33 $\mathtt{M06C}$: **M06 Meta-GGA Correlation Functional**

$$T = [0.031091, 0.015545, 0.016887], \tag{402}$$

$$U = [0.21370, 0.20548, 0.11125], \tag{403}$$

$$V = [7.5957, 14.1189, 10.357], \tag{404}$$

$$W = [3.5876, 6.1977, 3.6231], \tag{405}$$

$$X = [1.6382, 3.3662, 0.88026], \tag{406}$$

$$Y = [0.49294, 0.62517, 0.49671], \tag{407}$$

$$P = [1, 1, 1], \tag{408}$$

$$\varepsilon(\alpha, \beta) \tag{409}$$
$$= (\alpha$$
$$+ \beta) \Bigg(e(r(\alpha,\beta), T_1, U_1, V_1, W_1, X_1, Y_1, P_1)$$
$$- \frac{e(r(\alpha,\beta), T_3, U_3, V_3, W_3, X_3, Y_3, P_3) \, \omega(\zeta(\alpha,\beta)) \left(1 - (\zeta(\alpha,\beta))^4\right)}{c}$$
$$+ (e(r(\alpha,\beta), T_2, U_2, V_2, W_2, X_2, Y_2, P_2)$$
$$- e(r(\alpha,\beta), T_1, U_1, V_1, W_1, X_1, Y_1, P_1)) \, \omega(\zeta(\alpha,\beta)) (\zeta(\alpha,\beta))^4 \Bigg),$$

$$r(\alpha, \beta) \tag{410}$$
$$= 1/4 \sqrt[3]{3} 4^{2/3} \sqrt[3]{\frac{1}{\pi(\alpha + \beta)}},$$

$$\zeta(\alpha, \beta) \tag{411}$$
$$= \frac{\alpha - \beta}{\alpha + \beta},$$

$$\omega(z) \tag{412}$$
$$= \frac{(1+z)^{4/3} + (1-z)^{4/3} - 2}{2\sqrt[3]{2} - 2},$$

$$e(r, t, u, v, w, x, y, p) \tag{413}$$
$$=$$
$$-2t(1$$
$$+ ur) \ln \Bigg(1$$
$$+ 1/2 \frac{1}{t\left(v\sqrt{r} + wr + xr^{3/2} + yr^{p+1}\right)} \Bigg),$$

$$c = 1.709921, \tag{414}$$

$$Gab(chia, chib) \tag{415}$$
$$= \sum_{i=0}^{n} cCab_i \left(\frac{yCab\left(chia^2 + chib^2\right)}{1 + yCab\left(chia^2 + chib^2\right)} \right)^i,$$

$$
Gss\,(chis)
$$
$$
= \sum_{i=0}^{n} cCss_i \left(\frac{yCss\,chis^2}{1 + yCss\,chis^2} \right)^i,
$$
(416)

$$
n = 4,
$$
(417)

$$
cCab = [3.741593, 218.7098,
$$
$$
-453.1252, 293.6479,
$$
$$
-62.87470],
$$
(418)

$$
cCss = [0.5094055,
$$
$$
-1.491085, 17.23922,
$$
$$
-38.59018, 28.45044],
$$
(419)

$$
yCab = 0.0031,
$$
(420)

$$
yCss = 0.06,
$$
(421)

$$
x = \sqrt{(\chi\,(a))^2 + (\chi\,(b))^2},
$$
(422)

$$
tausMFM = 1/2\,\tau\,(s),
$$
(423)

$$
tauaMFM = 1/2\,\tau\,(a),
$$
(424)

$$
taubMFM = 1/2\,\tau\,(b),
$$
(425)

$$
zs = 2\frac{tausMFM}{(\rho\,(s))^{5/3}} - cf,
$$
(426)

$$
z = 2\frac{tauaMFM}{(\rho\,(a))^{5/3}} + 2\frac{taubMFM}{(\rho\,(b))^{5/3}} - 2cf,
$$
(427)

$$
cf = 3/5\,6^{2/3}\left(\pi^2\right)^{2/3},
$$
(428)

$$
ds = 1 - \frac{(\chi\,(s))^2}{4\,zs + 4\,cf},
$$
(429)

$$
h\,(x, z, d0, d1, d2, d3, d4, d5, \alpha)
$$
$$
= \frac{d0}{\lambda\,(x, z, \alpha)}
$$
$$
+ \frac{d1\,x^2 + d2\,z}{(\lambda\,(x, z, \alpha))^2}
$$
$$
+ \frac{d3\,x^4 + d4\,x^2 z + d5\,z^2}{(\lambda\,(x, z, \alpha))^3},
$$
(430)

$$
\lambda\,(x, z, \alpha)
$$
$$
= 1
$$
$$
+ \alpha\,(x^2
$$
$$
+ z),
$$
(431)

$$dCab = [\tag{432}$$
$$-2.741539,$$
$$-0.6720113,$$
$$-0.07932688, 0.001918681,$$
$$-0.002032902, 0.0],$$

$$dCss = [0.4905945, \tag{433}$$
$$-0.1437348, 0.2357824, 0.001871015,$$
$$-0.003788963, 0.0],$$

$$aCab = 0.003050, \tag{434}$$

$$aCss = 0.005151, \tag{435}$$

$$f = (\varepsilon(\rho(a), \rho(b)) \tag{436}$$
$$- \varepsilon(\rho(a), 0)$$
$$- \varepsilon(\rho(b), 0))(Gab(\chi(a), \chi(b))$$
$$+ h(x, z, dCab_0, dCab_1, dCab_2, dCab_3, dCab_4, dCab_5, aCab)),$$

$$g = \varepsilon(\rho(s), 0)(Gss(\chi(s)) \tag{437}$$
$$+ h(\chi(s), zs, dCss_0, dCss_1, dCss_2, dCss_3, dCss_4, dCss_5, aCss)) ds,$$

$$G = \varepsilon(\rho(s), 0)(Gss(\chi(s)) \tag{438}$$
$$+ h(\chi(s), zs, dCss_0, dCss_1, dCss_2, dCss_3, dCss_4, dCss_5, aCss)) ds.$$

C.34 `M06HFC`: **M06-HF Meta-GGA Correlation Functional**

$$T = [0.031091, 0.015545, 0.016887], \tag{439}$$

$$U = [0.21370, 0.20548, 0.11125], \tag{440}$$

$$V = [7.5957, 14.1189, 10.357], \tag{441}$$

$$W = [3.5876, 6.1977, 3.6231], \tag{442}$$

$$X = [1.6382, 3.3662, 0.88026], \tag{443}$$

$$Y = [0.49294, 0.62517, 0.49671], \tag{444}$$

$$P = [1, 1, 1], \tag{445}$$

$$\varepsilon(\alpha, \beta) \tag{446}$$
$$= (\alpha$$
$$+ \beta)\left(e(r(\alpha, \beta), T_1, U_1, V_1, W_1, X_1, Y_1, P_1) \right.$$
$$- \frac{e(r(\alpha, \beta), T_3, U_3, V_3, W_3, X_3, Y_3, P_3)\, \omega(\zeta(\alpha, \beta))\, (1 - (\zeta(\alpha, \beta))^4)}{c}$$
$$+ (e(r(\alpha, \beta), T_2, U_2, V_2, W_2, X_2, Y_2, P_2)$$
$$\left. - e(r(\alpha, \beta), T_1, U_1, V_1, W_1, X_1, Y_1, P_1))\, \omega(\zeta(\alpha, \beta))\, (\zeta(\alpha, \beta))^4 \right),$$

$$r(\alpha, \beta)$$
$$= 1/4 \sqrt[3]{3} \, 4^{2/3} \sqrt[3]{\frac{1}{\pi (\alpha + \beta)}}, \tag{447}$$

$$\zeta(\alpha, \beta)$$
$$= \frac{\alpha - \beta}{\alpha + \beta}, \tag{448}$$

$$\omega(z)$$
$$= \frac{(1+z)^{4/3} + (1-z)^{4/3} - 2}{2\sqrt[3]{2} - 2}, \tag{449}$$

$$e(r, t, u, v, w, x, y, p)$$
$$=$$
$$-2t\left(1\right.$$

$$\left. + ur\right) \ln \left(1\right.$$
$$\left. + 1/2 \, \frac{1}{t\left(v\sqrt{r} + wr + xr^{3/2} + yr^{p+1}\right)}\right), \tag{450}$$

$$c = 1.709921, \tag{451}$$

$$Gab(chia, chib)$$
$$= \sum_{i=0}^{n} cCab_i \left(\frac{yCab\left(chia^2 + chib^2\right)}{1 + yCab\left(chia^2 + chib^2\right)}\right)^i, \tag{452}$$

$$Gss(chis)$$
$$= \sum_{i=0}^{n} cCss_i \left(\frac{yCss\, chis^2}{1 + yCss\, chis^2}\right)^i, \tag{453}$$

$$n = 4, \tag{454}$$

$$cCab = [1.674634, 57.32017, 59.55416, \tag{455}$$
$$-231.1007, 125.5199],$$

$$cCss = [0.1023254, \tag{456}$$
$$-2.453783, 29.13180,$$
$$-34.94358, 23.15955],$$

$$yCab = 0.0031, \tag{457}$$

$$yCss = 0.06, \tag{458}$$

$$x = \sqrt{(\chi(a))^2 + (\chi(b))^2}, \tag{459}$$

$$tausMFM = 1/2\,\tau(s), \tag{460}$$

$$tauaMFM = 1/2\,\tau(a), \tag{461}$$

$$taubMFM = 1/2\,\tau(b), \tag{462}$$

$$zs = 2\frac{tausMFM}{(\rho\,(s))^{5/3}} - cf, \tag{463}$$

$$z = 2\frac{tauaMFM}{(\rho\,(a))^{5/3}} + 2\frac{taubMFM}{(\rho\,(b))^{5/3}} - 2\,cf, \tag{464}$$

$$cf = 3/5\,6^{2/3}\left(\pi^2\right)^{2/3}, \tag{465}$$

$$ds = 1 - \frac{(\chi\,(s))^2}{4\,zs + 4\,cf}, \tag{466}$$

$$
\begin{aligned}
&h\,(x,z,d0,d1,d2,d3,d4,d5,\alpha) \\
&= \frac{d0}{\lambda\,(x,z,\alpha)} \\
&\quad + \frac{d1\,x^2 + d2\,z}{(\lambda\,(x,z,\alpha))^2} \\
&\quad + \frac{d3\,x^4 + d4\,x^2 z + d5\,z^2}{(\lambda\,(x,z,\alpha))^3},
\end{aligned}
\tag{467}
$$

$$
\begin{aligned}
&\lambda\,(x,z,\alpha) \\
&= 1 \\
&\quad + \alpha\,\big(x^2 \\
&\qquad\qquad\qquad\qquad + z\big),
\end{aligned}
\tag{468}
$$

$$
\begin{aligned}
dCab = [\quad & \\
& -0.6746338, \\
& -0.1534002, \\
& -0.09021521, \\
& -0.001292037, \\
& -0.0002352983, 0.0],
\end{aligned}
\tag{469}
$$

$$
\begin{aligned}
dCss = [0.8976746, \quad & \\
& -0.2345830, 0.2368173, \\
& -0.0009913890, \\
& -0.01146165, 0.0],
\end{aligned}
\tag{470}
$$

$$aCab = 0.003050, \tag{471}$$

$$aCss = 0.005151, \tag{472}$$

$$
\begin{aligned}
f = (&\varepsilon\,(\rho\,(a),\rho\,(b)) \\
&- \varepsilon\,(\rho\,(a),0) \\
&- \varepsilon\,(\rho\,(b),0))\,(Gab\,(\chi\,(a),\chi\,(b)) \\
&+ h\,(x,z,dCab_0,dCab_1,dCab_2,dCab_3,dCab_4,dCab_5,aCab)),
\end{aligned}
\tag{473}
$$

$$
\begin{aligned}
g = \varepsilon\,(\rho\,(s),0)\,(&Gss\,(\chi\,(s)) \\
&+ h\,(\chi\,(s),zs,dCss_0,dCss_1,dCss_2,dCss_3,dCss_4,dCss_5,aCss))\,ds,
\end{aligned}
\tag{474}
$$

$$
\begin{aligned}
G = \varepsilon\,(\rho\,(s),0)\,(&Gss\,(\chi\,(s)) \\
&+ h\,(\chi\,(s),zs,dCss_0,dCss_1,dCss_2,dCss_3,dCss_4,dCss_5,aCss))\,ds.
\end{aligned}
\tag{475}
$$

C.35   `M06HFX`: **M06-HF Meta-GGA Exchange Functional**

$$g = -3/4 \frac{\sqrt[3]{6}\sqrt[3]{\pi^2}\left(\rho\left(s\right)\right)^{4/3} F\left(S\right) Fs\left(ws\right)}{\pi} + eslsda\, h\left(\chi\left(s\right), zs\right), \tag{476}$$

$$G = -3/4 \frac{\sqrt[3]{6}\sqrt[3]{\pi^2}\left(\rho\left(s\right)\right)^{4/3} F\left(S\right) Fs\left(ws\right)}{\pi} + eslsda\, h\left(\chi\left(s\right), zs\right), \tag{477}$$

$$S = 1/12 \frac{\chi\left(s\right) 6^{2/3}}{\sqrt[3]{\pi^2}}, \tag{478}$$

$$
\begin{aligned}
F\left(S\right) \\
&= 1 \\
&\quad + R \\
&\quad - R\left(1\right. \\
&\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad \left. + \frac{\mu S^2}{R}\right)^{-1},
\end{aligned}
\tag{479}
$$

$$R = 0.804, \tag{480}$$

$$\mu = 1/3\,\delta\,\pi^2, \tag{481}$$

$$\delta = 0.066725, \tag{482}$$

$$n = 11, \tag{483}$$

$$
\begin{aligned}
A = [0.1179732, \\
&-1.066708, \\
-0.1462405&, 7.481848, 3.776679, \\
&-44.36118, \\
-18.30962&, 100.3903, 38.64360, \\
&-98.06018, \\
-25.57716&, 35.90404],
\end{aligned}
\tag{484}
$$

$$
\begin{aligned}
Fs\left(ws\right) \\
&= \sum_{i=0}^{n} A_i ws^i,
\end{aligned}
\tag{485}
$$

$$ws = \frac{ts - 1}{ts + 1}, \tag{486}$$

$$ts = \frac{tslsda}{tausMFM}, \tag{487}$$

$$tslsda = 3/10\,6^{2/3}\left(\pi^2\right)^{2/3}\left(\rho\left(s\right)\right)^{5/3}, \tag{488}$$

$$eslsda = -3/8\,\sqrt[3]{3}\,4^{2/3}\sqrt[3]{\pi^{-1}}\left(\rho\left(s\right)\right)^{4/3}, \tag{489}$$

$$
\begin{aligned}
d = [\\
&-0.1179732, \\
&-0.002500000, \\
-0.01180065&, 0.0, 0.0, 0.0],
\end{aligned}
\tag{490}
$$

$$\alpha = 0.001867, \tag{491}$$

$$zs = 2\,\frac{tausMFM}{\left(\rho\left(s\right)\right)^{5/3}} - cf, \tag{492}$$

$$
\begin{aligned}
&h\left(x,z\right)\\
&\quad = \frac{d_0}{\lambda\left(x,z,\alpha\right)}\\
&\qquad + \frac{d_1 x^2 + d_2 z}{\left(\lambda\left(x,z,\alpha\right)\right)^2}\\
&\qquad + \frac{d_3 x^4 + d_4 x^2 z + d_5 z^2}{\left(\lambda\left(x,z,\alpha\right)\right)^3},
\end{aligned}
\tag{493}
$$

$$
\begin{aligned}
&\lambda\left(x,z,\alpha\right)\\
&\quad = 1\\
&\qquad + \alpha\,\big(x^2\\
&\hspace{9cm} + z\big),
\end{aligned}
\tag{494}
$$

$$cf = 3/5\,6^{2/3}\left(\pi^2\right)^{2/3}, \tag{495}$$

$$tausMFM = 1/2\,\tau\left(s\right). \tag{496}$$

C.36   M06LC: **M06-L Meta-GGA Correlation Functional**

$$T = [0.031091, 0.015545, 0.016887], \tag{497}$$

$$U = [0.21370, 0.20548, 0.11125], \tag{498}$$

$$V = [7.5957, 14.1189, 10.357], \tag{499}$$

$$W = [3.5876, 6.1977, 3.6231], \tag{500}$$

$$X = [1.6382, 3.3662, 0.88026], \tag{501}$$

$$Y = [0.49294, 0.62517, 0.49671], \tag{502}$$

$$P = [1, 1, 1], \tag{503}$$

$$
\begin{aligned}
&\varepsilon\left(\alpha,\beta\right)\\
&\quad = (\alpha\\
&\hspace{5cm} + \beta)\left(e\left(r\left(\alpha,\beta\right), T_1, U_1, V_1, W_1, X_1, Y_1, P_1\right)\right.\\
&\quad - \frac{e\left(r\left(\alpha,\beta\right), T_3, U_3, V_3, W_3, X_3, Y_3, P_3\right)\omega\left(\zeta\left(\alpha,\beta\right)\right)\left(1 - \left(\zeta\left(\alpha,\beta\right)\right)^4\right)}{c}\\
&\quad + \left(e\left(r\left(\alpha,\beta\right), T_2, U_2, V_2, W_2, X_2, Y_2, P_2\right)\right.\\
&\quad \left.\left. - e\left(r\left(\alpha,\beta\right), T_1, U_1, V_1, W_1, X_1, Y_1, P_1\right)\right)\omega\left(\zeta\left(\alpha,\beta\right)\right)\left(\zeta\left(\alpha,\beta\right)\right)^4\right),
\end{aligned}
\tag{504}
$$

$$
\begin{aligned}
&r\left(\alpha,\beta\right)\\
&\quad = 1/4\,\sqrt[3]{3}\,4^{2/3}\,\sqrt[3]{\frac{1}{\pi\left(\alpha+\beta\right)}},
\end{aligned}
\tag{505}
$$

$$\zeta(\alpha,\beta)$$
$$= \frac{\alpha - \beta}{\alpha + \beta}, \tag{506}$$

$$\omega(z)$$
$$= \frac{(1+z)^{4/3} + (1-z)^{4/3} - 2}{2\sqrt[3]{2} - 2}, \tag{507}$$

$$e(r,t,u,v,w,x,y,p)$$
$$=$$
$$-2t(1$$

$$+ ur)\ln\left(1\right.$$
$$\left. + 1/2\,\frac{1}{t\left(v\sqrt{r} + wr + xr^{3/2} + yr^{p+1}\right)}\right), \tag{508}$$

$$c = 1.709921, \tag{509}$$

$$Gab(chia, chib)$$
$$= \sum_{i=0}^{n} cCab_i \left(\frac{yCab\left(chia^2 + chib^2\right)}{1 + yCab\left(chia^2 + chib^2\right)}\right)^i, \tag{510}$$

$$Gss(chis)$$
$$= \sum_{i=0}^{n} cCss_i \left(\frac{yCss\,chis^2}{1 + yCss\,chis^2}\right)^i, \tag{511}$$

$$n = 4, \tag{512}$$

$$cCab = [0.6042374, 177.6783, \tag{513}$$
$$-251.3252, 76.35173,$$
$$-12.55699],$$

$$cCss = [0.5349466, 0.5396620, \tag{514}$$
$$-31.61217, 51.49592,$$
$$-29.19613],$$

$$yCab = 0.0031, \tag{515}$$

$$yCss = 0.06, \tag{516}$$

$$x = \sqrt{(\chi(a))^2 + (\chi(b))^2}, \tag{517}$$

$$tausMFM = 1/2\,\tau(s), \tag{518}$$

$$tauaMFM = 1/2\,\tau(a), \tag{519}$$

$$taubMFM = 1/2\,\tau(b), \tag{520}$$

$$zs = 2\,\frac{tausMFM}{(\rho(s))^{5/3}} - cf, \tag{521}$$

$$z = 2\frac{tauaMFM}{(\rho(a))^{5/3}} + 2\frac{taubMFM}{(\rho(b))^{5/3}} - 2\,cf, \tag{522}$$

$$cf = 3/5\,6^{2/3}\left(\pi^2\right)^{2/3}, \tag{523}$$

$$ds = 1 - \frac{(\chi(s))^2}{4\,zs + 4\,cf}, \tag{524}$$

$$
\begin{aligned}
&h(x,z,d0,d1,d2,d3,d4,d5,\alpha) \\
&= \frac{d0}{\lambda(x,z,\alpha)} \\
&\quad + \frac{d1\,x^2 + d2\,z}{(\lambda(x,z,\alpha))^2} \\
&\quad + \frac{d3\,x^4 + d4\,x^2 z + d5\,z^2}{(\lambda(x,z,\alpha))^3},
\end{aligned} \tag{525}
$$

$$
\begin{aligned}
&\lambda(x,z,\alpha) \\
&= 1 \\
&\quad + \alpha\,(x^2 \\
&\hspace{10cm} + z),
\end{aligned} \tag{526}
$$

$$
\begin{aligned}
dCab = [0.3957626, \\
-0.5614546, 0.01403963, 0.0009831442, \\
-0.003577176, 0.0],
\end{aligned} \tag{527}
$$

$$
\begin{aligned}
dCss = [0.4650534, 0.1617589, 0.1833657, 0.0004692100, \\
-0.004990573, 0.0],
\end{aligned} \tag{528}
$$

$$aCab = 0.003050, \tag{529}$$

$$aCss = 0.005151, \tag{530}$$

$$
\begin{aligned}
f = (&\varepsilon(\rho(a),\rho(b)) \\
&- \varepsilon(\rho(a),0) \\
&- \varepsilon(\rho(b),0))\,(Gab(\chi(a),\chi(b)) \\
&+ h(x,z,dCab_0,dCab_1,dCab_2,dCab_3,dCab_4,dCab_5,aCab)),
\end{aligned} \tag{531}
$$

$$
\begin{aligned}
g = \varepsilon(\rho(s),0)\,(&Gss(\chi(s)) \\
&+ h(\chi(s),zs,dCss_0,dCss_1,dCss_2,dCss_3,dCss_4,dCss_5,aCss))\,ds,
\end{aligned} \tag{532}
$$

$$
\begin{aligned}
G = \varepsilon(\rho(s),0)\,(&Gss(\chi(s)) \\
&+ h(\chi(s),zs,dCss_0,dCss_1,dCss_2,dCss_3,dCss_4,dCss_5,aCss))\,ds.
\end{aligned} \tag{533}
$$

C.37   M06LX: M06-L Meta-GGA Exchange Functional

$$g = -3/4 \frac{\sqrt[3]{6}\sqrt[3]{\pi^2}(\rho(s))^{4/3}F(S)Fs(ws)}{\pi} + eslsdah(\chi(s),zs), \tag{534}$$

$$G = -3/4 \frac{\sqrt[3]{6}\sqrt[3]{\pi^2}(\rho(s))^{4/3}F(S)Fs(ws)}{\pi} + eslsdah(\chi(s),zs), \tag{535}$$

$$S = 1/12 \frac{\chi(s)6^{2/3}}{\sqrt[3]{\pi^2}}, \tag{536}$$

$$F(S) = 1 + R - R\left(1 + \frac{\mu S^2}{R}\right)^{-1}, \tag{537}$$

$$R = 0.804, \tag{538}$$

$$\mu = 1/3\,\delta\,\pi^2, \tag{539}$$

$$\delta = 0.066725, \tag{540}$$

$$n = 11, \tag{541}$$

$$A = [0.3987756, 0.2548219, 0.3923994, \tag{542}$$
$$-2.103655,$$
$$-6.302147, 10.97615, 30.97273,$$
$$-23.18489,$$
$$-56.73480, 21.60364, 34.21814,$$
$$-9.049762],$$

$$Fs(ws) = \sum_{i=0}^{n} A_i ws^i, \tag{543}$$

$$ws = \frac{ts-1}{ts+1}, \tag{544}$$

$$ts = \frac{tslsda}{tausMFM}, \tag{545}$$

$$tslsda = 3/10\,6^{2/3}\left(\pi^2\right)^{2/3}(\rho(s))^{5/3}, \tag{546}$$

$$eslsda = -3/8\sqrt[3]{3}4^{2/3}\sqrt[3]{\pi^{-1}}(\rho(s))^{4/3}, \tag{547}$$

$$d = [0.6012244, 0.004748822, \tag{548}$$
$$-0.008635108,$$
$$-0.000009308062, 0.00004482811, 0.0],$$

$$\alpha = 0.001867, \tag{549}$$

$$zs = 2\frac{tausMFM}{(\rho(s))^{5/3}} - cf, \tag{550}$$

$$h(x,z)$$
$$= \frac{d_0}{\lambda(x,z,\alpha)}$$
$$+ \frac{d_1 x^2 + d_2 z}{(\lambda(x,z,\alpha))^2}$$
$$+ \frac{d_3 x^4 + d_4 x^2 z + d_5 z^2}{(\lambda(x,z,\alpha))^3}, \tag{551}$$

$$\lambda(x,z,\alpha)$$
$$= 1$$
$$+ \alpha\left(x^2\right.$$
$$\left. + z\right), \tag{552}$$

$$cf = 3/5\,6^{2/3}\left(\pi^2\right)^{2/3}, \tag{553}$$

$$tausMFM = 1/2\,\tau(s). \tag{554}$$

C.38   M06X: **M06 Meta-GGA Exchange Functional**

$$g = -3/4\frac{\sqrt[3]{6}\sqrt[3]{\pi^2}(\rho(s))^{4/3}F(S)\,Fs(ws)}{\pi} + eslsdah(\chi(s),zs), \tag{555}$$

$$G = -3/4\frac{\sqrt[3]{6}\sqrt[3]{\pi^2}(\rho(s))^{4/3}F(S)\,Fs(ws)}{\pi} + eslsdah(\chi(s),zs), \tag{556}$$

$$S = 1/12\frac{\chi(s)\,6^{2/3}}{\sqrt[3]{\pi^2}}, \tag{557}$$

$$F(S)$$
$$= 1$$
$$+ R$$
$$- R\left(1\right.$$
$$\left. + \frac{\mu S^2}{R}\right)^{-1}, \tag{558}$$

$$R = 0.804, \tag{559}$$

$$\mu = 1/3\,\delta\,\pi^2, \tag{560}$$

$$\delta = 0.066725, \tag{561}$$

$$n = 11, \tag{562}$$

$$A = [0.5877943, \tag{563}$$
$$-0.1371776, 0.2682367,$$
$$-2.515898,$$
$$-2.978892, 8.710679, 16.88195,$$
$$-4.489724,$$
$$-32.99983,$$
$$-14.49050, 20.43747, 12.56504],$$

$$Fs(ws) \tag{564}$$
$$= \sum_{i=0}^{n} A_i ws^i,$$

$$ws = \frac{ts - 1}{ts + 1}, \tag{565}$$

$$ts = \frac{tslsda}{tausMFM}, \tag{566}$$

$$tslsda = 3/10\, 6^{2/3} \left(\pi^2\right)^{2/3} \left(\rho(s)\right)^{5/3}, \tag{567}$$

$$eslsda = -3/8 \sqrt[3]{3}\, 4^{2/3} \sqrt[3]{\pi^{-1}} \left(\rho(s)\right)^{4/3}, \tag{568}$$

$$d = [0.1422057, 0.0007370319, \tag{569}$$
$$-0.01601373, 0.0, 0.0, 0.0],$$

$$\alpha = 0.001867, \tag{570}$$

$$zs = 2\frac{tausMFM}{\left(\rho(s)\right)^{5/3}} - cf, \tag{571}$$

$$h(x,z) \tag{572}$$
$$= \frac{d_0}{\lambda(x,z,\alpha)}$$
$$+ \frac{d_1 x^2 + d_2 z}{\left(\lambda(x,z,\alpha)\right)^2}$$
$$+ \frac{d_3 x^4 + d_4 x^2 z + d_5 z^2}{\left(\lambda(x,z,\alpha)\right)^3},$$

$$\lambda(x,z,\alpha) \tag{573}$$
$$= 1$$
$$+ \alpha\left(x^2\right.$$
$$\left.+ z\right),$$

$$cf = 3/5\, 6^{2/3} \left(\pi^2\right)^{2/3}, \tag{574}$$

$$tausMFM = 1/2\, \tau(s). \tag{575}$$

C.39 `M12C`: Meta GGA Correlation Functional

Meta-GGA correlation functional based on first principles, see M. Modrzejewski et al., J. Chem. Phys. 137, 204121 (2012).

C.40 `MK00`: Exchange Functional for Accurate Virtual Orbital Energies

$$g = -3 \frac{\pi \left(\rho\left(s\right)\right)^3}{\tau\left(s\right) - 1/4\, \upsilon\left(s\right)}. \tag{576}$$

C.41 `MK00B`: Exchange Functional for Accurate Virtual Orbital Energies

MK00 with gradient correction of the form of B88X but with different empirical parameter.

$$g = -3 \frac{\pi \left(\rho\left(s\right)\right)^3}{\tau\left(s\right) - 1/4\, \upsilon\left(s\right)} - \frac{\beta \left(\rho\left(s\right)\right)^{4/3} \left(\chi\left(s\right)\right)^2}{1 + 6\beta\,\chi\left(s\right) arcsinh\left(\chi\left(s\right)\right)}, \tag{577}$$

$$\beta = 0.0016, \tag{578}$$

$$G = -3 \frac{\pi \left(\rho\left(s\right)\right)^3}{\tau\left(s\right) - 1/4\, \upsilon\left(s\right)} - \frac{\beta \left(\rho\left(s\right)\right)^{4/3} \left(\chi\left(s\right)\right)^2}{1 + 6\beta\,\chi\left(s\right) arcsinh\left(\chi\left(s\right)\right)}. \tag{579}$$

C.42 `P86`: .

Gradient correction to VWN.

$$f = \rho\,e + \frac{e^{-\Phi}C\left(r\right)\sigma}{d\rho^{4/3}}, \tag{580}$$

$$r = 1/4 \sqrt[3]{3}\, 4^{2/3} \sqrt[3]{\frac{1}{\pi\rho}}, \tag{581}$$

$$x = \sqrt{r}, \tag{582}$$

$$\zeta = \frac{\rho\left(a\right) - \rho\left(b\right)}{\rho}, \tag{583}$$

$$k = [0.0310907, 0.01554535, \tag{584}$$
$$-1/6\,\pi^{-2}],$$

$$l = [\tag{585}$$
$$-0.10498,$$
$$-0.325,$$
$$-0.0047584],$$

$$m = [3.72744, 7.06042, 1.13107], \tag{586}$$

$$n = [12.9352, 18.0578, 13.0045], \tag{587}$$

$$e = \Lambda + \omega y\,(1 \tag{588}$$
$$+ h\zeta^4),$$

$$y = \frac{9}{8}\,(1 \tag{589}$$
$$+ \zeta)^{4/3}$$
$$+ \frac{9}{8}\,(1$$
$$- \zeta)^{4/3}$$
$$- 9/4,$$

$$h = 4/9 \, \frac{\lambda - \Lambda}{\left(\sqrt[3]{2} - 1 \right) \omega} - 1, \tag{590}$$

$$\Lambda = q \left(k_1, l_1, m_1, n_1 \right), \tag{591}$$

$$\lambda = q \left(k_2, l_2, m_2, n_2 \right), \tag{592}$$

$$\omega = q \left(k_3, l_3, m_3, n_3 \right), \tag{593}$$

$$
\begin{aligned}
q \, &(A, p, c, d) \\
&= A \left(\ln \left(\frac{x^2}{X \left(x, c, d \right)} \right) \right. \\
&\quad + 2 \, c \arctan \left(\frac{Q \left(c, d \right)}{2x + c} \right) \left(Q \left(c, d \right) \right)^{-1} \\
&\quad - cp \left(\ln \left(\frac{\left(x - p \right)^2}{X \left(x, c, d \right)} \right) \right. \\
&\quad + 2 \, (c \\
&\qquad\qquad\qquad\qquad \left. \left. + 2p) \arctan \left(\frac{Q \left(c, d \right)}{2x + c} \right) \left(Q \left(c, d \right) \right)^{-1} \right) \left(X \left(p, c, d \right) \right)^{-1} \right),
\end{aligned}
\tag{594}
$$

$$
\begin{aligned}
Q \, &(c, d) \\
&= \sqrt{4d - c^2},
\end{aligned}
\tag{595}
$$

$$
\begin{aligned}
X \, &(i, c, d) \\
&= i^2 \\
&\quad + ci \\
&\quad + d,
\end{aligned}
\tag{596}
$$

$$\Phi = 0.007390075 \, \frac{z \sqrt{\sigma}}{C \left(r \right) \rho^{7/6}}, \tag{597}$$

$$d = \sqrt[3]{2} \sqrt{\left(1/2 + 1/2 \, \zeta \right)^{5/3} + \left(1/2 - 1/2 \, \zeta \right)^{5/3}}, \tag{598}$$

$$
\begin{aligned}
C \, &(r) \\
&= 0.001667 \\
&\quad + \frac{0.002568 + \alpha \, r + \beta \, r^2}{1 + \xi \, r + \delta \, r^2 + 10000 \, \beta \, r^3},
\end{aligned}
\tag{599}
$$

$$z = 0.11, \tag{600}$$

$$\alpha = 0.023266, \tag{601}$$

$$\beta = 0.000007389, \tag{602}$$

$$\xi = 8.723, \tag{603}$$

$$\delta = 0.472. \tag{604}$$

C.43   PBEC: **PBE Correlation Functional**

$$f = \rho \left(\varepsilon \left(\rho \left(a \right), \rho \left(b \right) \right) \right.$$
$$\left. + H \left(d, \rho \left(a \right), \rho \left(b \right) \right) \right), \tag{605}$$

$$G = \rho \left(\varepsilon \left(\rho \left(s \right), 0 \right) \right.$$
$$\left. + C \left(Q, \rho \left(s \right), 0 \right) \right), \tag{606}$$

$$d = 1/12 \, \frac{\sqrt{\sigma} 3^{5/6}}{u \left(\rho \left(a \right), \rho \left(b \right) \right) \sqrt[6]{\pi^{-1}} \rho^{7/6}}, \tag{607}$$

$$u \left(\alpha, \beta \right) \tag{608}$$
$$= 1/2 \, (1$$
$$+ \zeta \left(\alpha, \beta \right))^{2/3}$$
$$+ 1/2 \, (1$$
$$- \zeta \left(\alpha, \beta \right))^{2/3},$$

$$H \left(d, \alpha, \beta \right) \tag{609}$$
$$= 1/2 \, \left(u \left(\rho \left(a \right), \rho \left(b \right) \right) \right)^3 \lambda^2 \ln \left(1 \right.$$
$$\left. + 2 \, \frac{\iota \left(d^2 + A \left(\alpha, \beta \right) d^4 \right)}{\lambda \left(1 + A \left(\alpha, \beta \right) d^2 + \left(A \left(\alpha, \beta \right) \right)^2 d^4 \right)} \right) \iota^{-1},$$

$$A \left(\alpha, \beta \right) \tag{610}$$
$$= 2 \iota \lambda^{-1} \left(e^{-2 \frac{\iota \varepsilon \left(\alpha, \beta \right)}{\left(u \left(\rho \left(a \right), \rho \left(b \right) \right) \right)^3 \lambda^2}} \right.$$
$$\left. - 1 \right)^{-1},$$

$$\iota = 0.0716, \tag{611}$$

$$\lambda = \nu \kappa, \tag{612}$$

$$\nu = 16 \, \frac{\sqrt[3]{3} \sqrt[3]{\pi^2}}{\pi}, \tag{613}$$

$$\kappa = 0.004235, \tag{614}$$

$$Z = -0.001667, \tag{615}$$

$$\phi \left(r \right) \tag{616}$$
$$= \theta \left(r \right)$$
$$- Z,$$

$$\theta \left(r \right) \tag{617}$$
$$= \frac{1}{1000} \, \frac{2.568 + \Xi r + \Phi r^2}{1 + \Lambda r + \Upsilon r^2 + 10 \Phi r^3},$$

$$\Xi = 23.266, \tag{618}$$

$$\Phi = 0.007389, \tag{619}$$

$$\Lambda = 8.723, \tag{620}$$

$$\Upsilon = 0.472, \tag{621}$$

$$T = [0.031091, 0.015545, 0.016887], \tag{622}$$

$$U = [0.21370, 0.20548, 0.11125], \tag{623}$$

$$V = [7.5957, 14.1189, 10.357], \tag{624}$$

$$W = [3.5876, 6.1977, 3.6231], \tag{625}$$

$$X = [1.6382, 3.3662, 0.88026], \tag{626}$$

$$Y = [0.49294, 0.62517, 0.49671], \tag{627}$$

$$P = [1, 1, 1], \tag{628}$$

$$
\begin{aligned}
\varepsilon\left(\alpha,\beta\right) & \\
&= e\left(r\left(\alpha,\beta\right), T_1, U_1, V_1, W_1, X_1, Y_1, P_1\right) \\
&\quad - \frac{e\left(r\left(\alpha,\beta\right), T_3, U_3, V_3, W_3, X_3, Y_3, P_3\right)\omega\left(\zeta\left(\alpha,\beta\right)\right)\left(1-\left(\zeta\left(\alpha,\beta\right)\right)^4\right)}{c} \\
&\quad + \left(e\left(r\left(\alpha,\beta\right), T_2, U_2, V_2, W_2, X_2, Y_2, P_2\right)\right. \\
&\quad \left. - e\left(r\left(\alpha,\beta\right), T_1, U_1, V_1, W_1, X_1, Y_1, P_1\right)\right)\omega\left(\zeta\left(\alpha,\beta\right)\right)\left(\zeta\left(\alpha,\beta\right)\right)^4,
\end{aligned} \tag{629}
$$

$$
\begin{aligned}
r\left(\alpha,\beta\right) & \\
&= 1/4\,\sqrt[3]{3}\,4^{2/3}\,\sqrt[3]{\frac{1}{\pi\left(\alpha+\beta\right)}},
\end{aligned} \tag{630}
$$

$$
\begin{aligned}
\zeta\left(\alpha,\beta\right) & \\
&= \frac{\alpha-\beta}{\alpha+\beta},
\end{aligned} \tag{631}
$$

$$
\begin{aligned}
\omega\left(z\right) & \\
&= \frac{\left(1+z\right)^{4/3}+\left(1-z\right)^{4/3}-2}{2\sqrt[3]{2}-2},
\end{aligned} \tag{632}
$$

$$
\begin{aligned}
e\left(r,t,u,v,w,x,y,p\right) & \\
&= \\
&\quad -2t\left(1\right.
\end{aligned} \tag{633}
$$

$$
\left. + ur\right)\ln\left(1 + 1/2\,\frac{1}{t\left(v\sqrt{r}+wr+xr^{3/2}+yr^{p+1}\right)}\right),
$$

$$c = 1.709921, \tag{634}$$

$$
\begin{aligned}
C\left(d,\alpha,\beta\right) & \\
&= K\left(Q,\alpha,\beta\right) \\
&\quad + M\left(Q,\alpha,\beta\right),
\end{aligned} \tag{635}
$$

$$
\begin{aligned}
M\,(d,\alpha,\beta)\\
= 0.5\,\nu\,(\phi\,(r\,(\alpha,\beta))\\
-\,\kappa\\
-\,3/7\,Z)\,d^2 e^{-335.9789467\,\frac{3^{2/3}d^2}{\sqrt[3]{\pi^5\rho}}}\,,
\end{aligned}
\tag{636}
$$

$$
\begin{aligned}
K\,(d,\alpha,\beta)\\
= 0.2500000000\,\lambda^2 \ln\Bigg(1\\
+\,2\,\frac{\iota\,(d^2 + N\,(\alpha,\beta)\,d^4)}{\lambda\,(1 + N\,(\alpha,\beta)\,d^2 + (N\,(\alpha,\beta))^2 d^4)}\Bigg)\,\iota^{-1}\,,
\end{aligned}
\tag{637}
$$

$$
\begin{aligned}
N\,(\alpha,\beta)\\
= 2\,\iota\,\lambda^{-1}\Bigg(e^{-4\,\frac{\iota\,\varepsilon(\alpha,\beta)}{\lambda^2}}\\
-\,1\Bigg)^{-1}\,,
\end{aligned}
\tag{638}
$$

$$
Q = 1/12\,\frac{\sqrt{\sigma\,(ss)}\,\sqrt[3]{2}\,3^{5/6}}{\sqrt[6]{\pi^{-1}}\rho^{7/6}}\,.
\tag{639}
$$

C.44   PBESOLC: PBEsol Correlation Functional

C.45   PBESOLX: PBEsol Exchange Functional

C.46   PBEX: PBE Exchange Functional

$$
g = 1/2\,E\,(2\,\rho\,(s))\,,
\tag{640}
$$

$$
G = 1/2\,E\,(2\,\rho\,(s))\,,
\tag{641}
$$

$$
\begin{aligned}
E\,(n)\\
=\\
-3/4\,\frac{\sqrt[3]{3}\,\sqrt[3]{\pi^2}n^{4/3}F\,(S)}{\pi}\,,
\end{aligned}
\tag{642}
$$

$$
S = 1/12\,\frac{\chi\,(s)\,6^{2/3}}{\sqrt[3]{\pi^2}}\,,
\tag{643}
$$

$$
\begin{aligned}
F\,(S)\\
= 1\\
+\,R\\
-\,R\Bigg(1\\
+\,\frac{\mu\,S^2}{R}\Bigg)^{-1}\,,
\end{aligned}
\tag{644}
$$

$$
R = 0.804\,,
\tag{645}
$$

$$
\mu = 1/3\,\delta\,\pi^2\,,
\tag{646}
$$

$$
\delta = 0.066725\,.
\tag{647}
$$

C.47 `PBEXREV`: **Revised PBE Exchange Functional**

Changes the value of the constant R from the original PBEX functional

$$g = 1/2\,E\,(2\rho\,(s))\,, \tag{648}$$

$$G = 1/2\,E\,(2\rho\,(s))\,, \tag{649}$$

$$E\,(n)$$
$$= -3/4\,\frac{\sqrt[3]{3}\,\sqrt[3]{\pi^2}\,n^{4/3}\,F\,(S)}{\pi}\,, \tag{650}$$

$$S = 1/12\,\frac{\chi\,(s)\,6^{2/3}}{\sqrt[3]{\pi^2}}\,, \tag{651}$$

$$F\,(S)$$
$$= 1$$
$$+ R$$
$$- R\left(1\right.$$
$$\left. + \frac{\mu\,S^2}{R}\right)^{-1}\,, \tag{652}$$

$$R = 1.245\,, \tag{653}$$

$$\mu = 1/3\,\delta\,\pi^2\,, \tag{654}$$

$$\delta = 0.066725\,. \tag{655}$$

C.48 `PW86`: .

GGA Exchange Functional.

$$g = 1/2\,E\,(2\rho\,(s))\,, \tag{656}$$

$$E\,(n)$$
$$= -3/4\,\sqrt[3]{3}\,\sqrt[3]{\pi^{-1}}\,n^{4/3}\,F\,(S)\,, \tag{657}$$

$$F\,(S)$$
$$= \left(1\right.$$
$$+ 1.296\,S^2$$
$$+ 14\,S^4$$
$$\left. + 0.2\,S^6\right)^{1/15}\,, \tag{658}$$

$$S = 1/12\,\frac{\chi\,(s)\,6^{2/3}}{\sqrt[3]{\pi^2}}\,, \tag{659}$$

$$G = 1/2\,E\,(2\rho\,(s))\,. \tag{660}$$

C.49 `PW91C`: Perdew-Wang 1991 GGA Correlation Functional

$$f = \rho \left(\varepsilon \left(\rho \left(a \right), \rho \left(b \right) \right) \right. \tag{661}$$
$$\left. + H \left(d, \rho \left(a \right), \rho \left(b \right) \right) \right),$$

$$G = \rho \left(\varepsilon \left(\rho \left(s \right), 0 \right) \right. \tag{662}$$
$$\left. + C \left(Q, \rho \left(s \right), 0 \right) \right),$$

$$d = 1/12 \frac{\sqrt{\sigma} 3^{5/6}}{u \left(\rho \left(a \right), \rho \left(b \right) \right) \sqrt[6]{\pi^{-1}} \rho^{7/6}}, \tag{663}$$

$$u \left(\alpha, \beta \right) \tag{664}$$
$$= 1/2 \, (1$$
$$+ \zeta \left(\alpha, \beta \right))^{2/3}$$
$$+ 1/2 \, (1$$
$$- \zeta \left(\alpha, \beta \right))^{2/3},$$

$$H \left(d, \alpha, \beta \right) \tag{665}$$
$$= L \left(d, \alpha, \beta \right)$$
$$+ J \left(d, \alpha, \beta \right),$$

$$L \left(d, \alpha, \beta \right) \tag{666}$$
$$= 1/2 \left(u \left(\rho \left(a \right), \rho \left(b \right) \right) \right)^3 \lambda^2 \ln \left(1 \right.$$
$$\left. + 2 \frac{\iota \left(d^2 + A \left(\alpha, \beta \right) d^4 \right)}{\lambda \left(1 + A \left(\alpha, \beta \right) d^2 + \left(A \left(\alpha, \beta \right) \right)^2 d^4 \right)} \right) \iota^{-1},$$

$$J \left(d, \alpha, \beta \right) \tag{667}$$
$$= v \left(\phi \left(r \left(\alpha, \beta \right) \right) \right.$$
$$- \kappa$$
$$- 3/7 \, Z) \left(u \left(\rho \left(a \right), \rho \left(b \right) \right) \right)^3 d^2 e^{- \frac{400}{3} \frac{\left(u (\rho(a), \rho(b)) \right)^4 3^{2/3} d^2}{\sqrt[3]{\pi^5 \rho}}},$$

$$A \left(\alpha, \beta \right) \tag{668}$$
$$= 2 \iota \lambda^{-1} \left(e^{-2 \frac{\iota \varepsilon(\alpha, \beta)}{\left(u(\rho(a), \rho(b)) \right)^3 \lambda^2}} \right.$$
$$\left. - 1 \right)^{-1},$$

$$\iota = 0.09, \tag{669}$$

$$\lambda = v \kappa, \tag{670}$$

$$v = 16 \frac{\sqrt[3]{3} \sqrt[3]{\pi^2}}{\pi}, \tag{671}$$

$$\kappa = 0.004235, \tag{672}$$

$$Z = -0.001667, \tag{673}$$

$$\phi(r) \tag{674}$$
$$= \theta(r)$$
$$- Z,$$

$$\theta(r) \tag{675}$$
$$= \frac{1}{1000} \frac{2.568 + \Xi r + \Phi r^2}{1 + \Lambda r + \Upsilon r^2 + 10\Phi r^3},$$

$$\Xi = 23.266, \tag{676}$$

$$\Phi = 0.007389, \tag{677}$$

$$\Lambda = 8.723, \tag{678}$$

$$\Upsilon = 0.472, \tag{679}$$

$$T = [0.031091, 0.015545, 0.016887], \tag{680}$$

$$U = [0.21370, 0.20548, 0.11125], \tag{681}$$

$$V = [7.5957, 14.1189, 10.357], \tag{682}$$

$$W = [3.5876, 6.1977, 3.6231], \tag{683}$$

$$X = [1.6382, 3.3662, 0.88026], \tag{684}$$

$$Y = [0.49294, 0.62517, 0.49671], \tag{685}$$

$$P = [1, 1, 1], \tag{686}$$

$$\varepsilon(\alpha, \beta) \tag{687}$$
$$= e(r(\alpha, \beta), T_1, U_1, V_1, W_1, X_1, Y_1, P_1)$$
$$- \frac{e(r(\alpha, \beta), T_3, U_3, V_3, W_3, X_3, Y_3, P_3) \, \omega(\zeta(\alpha, \beta)) \left(1 - (\zeta(\alpha, \beta))^4\right)}{c}$$
$$+ (e(r(\alpha, \beta), T_2, U_2, V_2, W_2, X_2, Y_2, P_2)$$
$$- e(r(\alpha, \beta), T_1, U_1, V_1, W_1, X_1, Y_1, P_1)) \, \omega(\zeta(\alpha, \beta)) (\zeta(\alpha, \beta))^4,$$

$$r(\alpha, \beta) \tag{688}$$
$$= 1/4 \sqrt[3]{3} 4^{2/3} \sqrt[3]{\frac{1}{\pi(\alpha + \beta)}},$$

$$\zeta(\alpha, \beta) \tag{689}$$
$$= \frac{\alpha - \beta}{\alpha + \beta},$$

$$\omega(z) \tag{690}$$
$$= \frac{(1 + z)^{4/3} + (1 - z)^{4/3} - 2}{2\sqrt[3]{2} - 2},$$

$$e(r,t,u,v,w,x,y,p) \tag{691}$$
$$=$$
$$-2t\,(1$$

$$+ur)\ln\left(1\right.$$
$$\left.+1/2\,\frac{1}{t\,(v\sqrt{r}+wr+xr^{3/2}+yr^{p+1})}\right),$$

$$c = 1.709921, \tag{692}$$

$$C(d,\alpha,\beta) \tag{693}$$
$$= K(Q,\alpha,\beta)$$
$$+ M(Q,\alpha,\beta),$$

$$M(d,\alpha,\beta) \tag{694}$$
$$= 0.5\,v\,(\phi\,(r(\alpha,\beta)))$$
$$-\kappa$$
$$-3/7\,Z)\,d^2 e^{-335.9789467\,\frac{3^{2/3}d^2}{\sqrt[3]{\pi^5}\rho}},$$

$$K(d,\alpha,\beta) \tag{695}$$
$$= 0.2500000000\,\lambda^2 \ln\left(1\right.$$
$$\left.+2\,\frac{\iota\,(d^2+N(\alpha,\beta)\,d^4)}{\lambda\,(1+N(\alpha,\beta)\,d^2+(N(\alpha,\beta))^2 d^4)}\right)\iota^{-1},$$

$$N(\alpha,\beta) \tag{696}$$
$$= 2\,\iota\lambda^{-1}\left(e^{-4\,\frac{\iota\varepsilon(\alpha,\beta)}{\lambda^2}}\right.$$
$$\left.-1\right)^{-1},$$

$$Q = 1/12\,\frac{\sqrt{\sigma\,(ss)}\,\sqrt[3]{2}\,3^{5/6}}{\sqrt[6]{\pi^{-1}}\rho^{7/6}}. \tag{697}$$

C.50   `PW91X`: **Perdew-Wang 1991 GGA Exchange Functional**

$$g = 1/2\,E\,(2\rho\,(s)), \tag{698}$$

$$G = 1/2\,E\,(2\rho\,(s)), \tag{699}$$

$$E(n) \tag{700}$$
$$=$$
$$-3/4\,\frac{\sqrt[3]{3}\,\sqrt[3]{\pi^2}\,n^{4/3}F(S)}{\pi},$$

$$S = 1/12\,\frac{\chi\,(s)\,6^{2/3}}{\sqrt[3]{\pi^2}}, \tag{701}$$

$$F(S) \tag{702}$$
$$= \frac{1+0.19645\,S\text{arcsinh}\,(7.7956\,S) + \left(0.2743 - 0.1508\,e^{-100\,S^2}\right)S^2}{1+0.19645\,S\text{arcsinh}\,(7.7956\,S) + 0.004\,S^4}.$$

C.51 `PW92C`: Perdew-Wang 1992 GGA Correlation Functional

Electron-gas correlation energy.

$$T = [0.031091, 0.015545, 0.016887], \tag{703}$$

$$U = [0.21370, 0.20548, 0.11125], \tag{704}$$

$$V = [7.5957, 14.1189, 10.357], \tag{705}$$

$$W = [3.5876, 6.1977, 3.6231], \tag{706}$$

$$X = [1.6382, 3.3662, 0.88026], \tag{707}$$

$$Y = [0.49294, 0.62517, 0.49671], \tag{708}$$

$$P = [1, 1, 1], \tag{709}$$

$$f = \rho \, \varepsilon \left(\rho \left(a \right), \rho \left(b \right) \right), \tag{710}$$

$$
\begin{aligned}
\varepsilon \left(\alpha, \beta \right) \\
= e \left(r \left(\alpha, \beta \right), T_1, U_1, V_1, W_1, X_1, Y_1, P_1 \right) \\
- \frac{e \left(r \left(\alpha, \beta \right), T_3, U_3, V_3, W_3, X_3, Y_3, P_3 \right) \omega \left(\zeta \left(\alpha, \beta \right) \right) \left(1 - \left(\zeta \left(\alpha, \beta \right) \right)^4 \right)}{c} \\
+ \left(e \left(r \left(\alpha, \beta \right), T_2, U_2, V_2, W_2, X_2, Y_2, P_2 \right) \right. \\
\left. - e \left(r \left(\alpha, \beta \right), T_1, U_1, V_1, W_1, X_1, Y_1, P_1 \right) \right) \omega \left(\zeta \left(\alpha, \beta \right) \right) \left(\zeta \left(\alpha, \beta \right) \right)^4,
\end{aligned}
\tag{711}
$$

$$
\begin{aligned}
r \left(\alpha, \beta \right) \\
= 1/4 \, \sqrt[3]{3} 4^{2/3} \, \sqrt[3]{\frac{1}{\pi \left(\alpha + \beta \right)}},
\end{aligned}
\tag{712}
$$

$$
\begin{aligned}
\zeta \left(\alpha, \beta \right) \\
= \frac{\alpha - \beta}{\alpha + \beta},
\end{aligned}
\tag{713}
$$

$$
\begin{aligned}
\omega \left(z \right) \\
= \frac{\left(1 + z \right)^{4/3} + \left(1 - z \right)^{4/3} - 2}{2 \sqrt[3]{2} - 2},
\end{aligned}
\tag{714}
$$

$$
\begin{aligned}
e \left(r, t, u, v, w, x, y, p \right) \\
= \\
-2t \left(1 \right. \\
+ ur) \ln \left(1 \right. \\
\left. \left. + 1/2 \, \frac{1}{t \left(v \sqrt{r} + wr + xr^{3/2} + yr^{p+1} \right)} \right) \right),
\end{aligned}
\tag{715}
$$

$$c = 1.709921. \tag{716}$$

C.52 `STEST`: Test for number of electrons

$$g = \rho \left(s \right). \tag{717}$$

C.53 TFKE: Thomas-Fermi Kinetic Energy

Automatically generated Thomas-Fermi Kinetic Energy.

$$g = ctf \left(\rho \left(s \right) \right)^{5/3}, \tag{718}$$

$$ctf = 3/10 \, 2^{2/3} 3^{2/3} \left(\pi^2 \right)^{2/3}. \tag{719}$$

C.54 TH1: Tozer and Handy 1998

Density and gradient dependent first row exchange-correlation functional.

$$t = [7/6, 4/3, 3/2, 5/3, 4/3, 3/2, 5/3, \frac{11}{6}, 3/2, 5/3, \frac{11}{6}, 2, 3/2, 5/3, \frac{11}{6}, 2, 7/6, 4/3, 3/2, 5/3, 1], \tag{720}$$

$$u = [0,0,0,0,0,0,0,0,0,0,0,0,0,0,0,0,1,1,1,1,0], \tag{721}$$

$$v = [0,0,0,0,1,1,1,1,2,2,2,2,0,0,0,0,0,0,0,0,0], \tag{722}$$

$$w = [0,0,0,0,0,0,0,0,0,0,0,0,1,1,1,1,0,0,0,0,0], \tag{723}$$

$$\omega = [\tag{724}$$
$$-0.728255, 0.331699,$$
$$-1.02946, 0.235703,$$
$$-0.0876221, 0.140854, 0.0336982,$$
$$-0.0353615, 0.00497930,$$
$$-0.0645900, 0.0461795,$$
$$-0.00757191,$$
$$-0.00242717, 0.0428140,$$
$$-0.0744891, 0.0386577,$$
$$-0.352519, 2.19805,$$
$$-3.72927, 1.94441, 0.128877],$$

$$n = 21, \tag{725}$$

$$R_i = \left(\rho \left(a \right) \right)^{t_i} + \left(\rho \left(b \right) \right)^{t_i}, \tag{726}$$

$$S_i = \left(\frac{\rho \left(a \right) - \rho \left(b \right)}{\rho} \right)^{2u_i}, \tag{727}$$

$$X_i = 1/2 \frac{\left(\sqrt{\sigma \left(aa \right)} \right)^{v_i} + \left(\sqrt{\sigma \left(bb \right)} \right)^{v_i}}{\rho^{4/3 \, v_i}}, \tag{728}$$

$$Y_i = \left(\frac{\sigma \left(aa \right) + \sigma \left(bb \right) - 2 \sqrt{\sigma \left(aa \right)} \sqrt{\sigma \left(bb \right)}}{\rho^{8/3}} \right)^{w_i}, \tag{729}$$

$$f = \sum_{i=1}^{n} \omega_i R_i S_i X_i Y_i, \tag{730}$$

$$G = \sum_{i=1}^{n} 1/2 \, \omega_i \left(\rho \left(s \right) \right)^{t_i} \left(\sqrt{\sigma \left(ss \right)} \right)^{v_i} \left(\frac{\sigma \left(ss \right)}{\left(\rho \left(s \right) \right)^{8/3}} \right)^{w_i} \left(\left(\rho \left(s \right) \right)^{4/3 \, v_i} \right)^{-1}. \tag{731}$$

C.55 `TH2:`.

Density and gradient dependent first row exchange-correlation functional.

$$t = [\frac{13}{12}, 7/6, 4/3, 3/2, 5/3, \frac{17}{12}, 3/2, 5/3, \frac{11}{6}, 5/3, \frac{11}{6}, 2, 5/3, \frac{11}{6}, 2, 7/6, 4/3, 3/2, 5/3], \tag{732}$$

$$u = [0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 1, 1, 1, 1], \tag{733}$$

$$v = [0, 0, 0, 0, 0, 1, 1, 1, 1, 2, 2, 2, 0, 0, 0, 0, 0, 0, 0], \tag{734}$$

$$w = [0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 1, 1, 1, 0, 0, 0, 0], \tag{735}$$

$$\omega = [0.678831, \tag{736}$$
$$-1.75821, 1.27676,$$
$$-1.60789, 0.365610,$$
$$-0.181327, 0.146973, 0.147141,$$
$$-0.0716917,$$
$$-0.0407167, 0.0214625,$$
$$-0.000768156, 0.0310377,$$
$$-0.0720326, 0.0446562,$$
$$-0.266802, 1.50822,$$
$$-1.94515, 0.679078],$$

$$n = 19, \tag{737}$$

$$R_i = (\rho(a))^{t_i} + (\rho(b))^{t_i}, \tag{738}$$

$$S_i = \left(\frac{\rho(a) - \rho(b)}{\rho}\right)^{2u_i}, \tag{739}$$

$$X_i = 1/2 \, \frac{\left(\sqrt{\sigma(aa)}\right)^{v_i} + \left(\sqrt{\sigma(bb)}\right)^{v_i}}{\rho^{4/3 v_i}}, \tag{740}$$

$$Y_i = \left(\frac{\sigma(aa) + \sigma(bb) - 2\sqrt{\sigma(aa)}\sqrt{\sigma(bb)}}{\rho^{8/3}}\right)^{w_i}, \tag{741}$$

$$f = \sum_{i=1}^{n} \omega_i R_i S_i X_i Y_i, \tag{742}$$

$$G = \sum_{i=1}^{n} 1/2 \, \omega_i \, (\rho(s))^{t_i} \left(\sqrt{\sigma(ss)}\right)^{v_i} \left(\frac{\sigma(ss)}{(\rho(s))^{8/3}}\right)^{w_i} \left((\rho(s))^{4/3 v_i}\right)^{-1}. \tag{743}$$

C.56 `TH3:` .

Density and gradient dependent first and second row exchange-correlation functional.

$$t = [7/6, 4/3, 3/2, 5/3, \frac{17}{12}, 3/2, 5/3, \frac{11}{6}, 5/3, \frac{11}{6}, 2, 5/3, \frac{11}{6}, 2, 7/6, 4/3, 3/2, 5/3, \frac{13}{12}], \tag{744}$$

$$u = [0,0,0,0,0,0,0,0,0,0,0,0,0,0,1,1,1,1,0], \tag{745}$$

$$v = [0,0,0,0,1,1,1,1,2,2,2,0,0,0,0,0,0,0,0], \tag{746}$$

$$w = [0,0,0,0,0,0,0,0,0,0,0,1,1,1,0,0,0,0,0], \tag{747}$$

$$\omega = [\tag{748}$$
$$-0.142542,$$
$$-0.783603,$$
$$-0.188875, 0.0426830,$$
$$-0.304953, 0.430407,$$
$$-0.0997699, 0.00355789,$$
$$-0.0344374, 0.0192108,$$
$$-0.00230906, 0.0235189,$$
$$-0.0331157, 0.0121316, 0.441190,$$
$$-2.27167, 4.03051,$$
$$-2.28074, 0.0360204],$$

$$n = 19, \tag{749}$$

$$R_i = (\rho(a))^{t_i} + (\rho(b))^{t_i}, \tag{750}$$

$$S_i = \left(\frac{\rho(a) - \rho(b)}{\rho} \right)^{2u_i}, \tag{751}$$

$$X_i = 1/2 \frac{\left(\sqrt{\sigma(aa)} \right)^{v_i} + \left(\sqrt{\sigma(bb)} \right)^{v_i}}{\rho^{4/3 v_i}}, \tag{752}$$

$$Y_i = \left(\frac{\sigma(aa) + \sigma(bb) - 2\sqrt{\sigma(aa)}\sqrt{\sigma(bb)}}{\rho^{8/3}} \right)^{w_i}, \tag{753}$$

$$f = \sum_{i=1}^{n} \omega_i R_i S_i X_i Y_i, \tag{754}$$

$$G = \sum_{i=1}^{n} 1/2 \, \omega_i \, (\rho(s))^{t_i} \left(\sqrt{\sigma(ss)} \right)^{v_i} \left(\frac{\sigma(ss)}{(\rho(s))^{8/3}} \right)^{w_i} \left((\rho(s))^{4/3 v_i} \right)^{-1}. \tag{755}$$

C.57 TH4:.

Density an gradient dependent first and second row exchange-correlation functional.

$$t = [7/6, 4/3, 3/2, 5/3, \frac{17}{12}, 3/2, 5/3, \frac{11}{6}, 5/3, \frac{11}{6}, 2, 5/3, \frac{11}{6}, 2, 7/6, 4/3, 3/2, 5/3, \frac{13}{12}], \tag{756}$$

$$u = [0,0,0,0,0,0,0,0,0,0,0,0,0,0,1,1,1,1,0], \tag{757}$$

$$v = [0,0,0,0,1,1,1,1,2,2,2,0,0,0,0,0,0,0,0], \tag{758}$$

$$w = [0,0,0,0,0,0,0,0,0,0,0,1,1,1,0,0,0,0,0], \tag{759}$$

$$\omega = [0.0677353, \tag{760}$$
$$-1.06763,$$
$$-0.0419018, 0.0226313,$$
$$-0.222478, 0.283432,$$
$$-0.0165089,$$
$$-0.0167204,$$
$$-0.0332362, 0.0162254,$$
$$-0.000984119, 0.0376713,$$
$$-0.0653419, 0.0222835, 0.375782,$$
$$-1.90675, 3.22494,$$
$$-1.68698,$$
$$-0.0235810],$$

$$n = 19, \tag{761}$$

$$R_i = (\rho(a))^{t_i} \tag{762}$$
$$+ (\rho(b))^{t_i},$$

$$S_i = \left(\frac{\rho(a) - \rho(b)}{\rho}\right)^{2u_i}, \tag{763}$$

$$X_i = 1/2 \frac{\left(\sqrt{\sigma(aa)}\right)^{v_i} + \left(\sqrt{\sigma(bb)}\right)^{v_i}}{\rho^{4/3 v_i}}, \tag{764}$$

$$Y_i = \left(\frac{\sigma(aa) + \sigma(bb) - 2\sqrt{\sigma(aa)}\sqrt{\sigma(bb)}}{\rho^{8/3}}\right)^{w_i}, \tag{765}$$

$$f = \sum_{i=1}^{n} \omega_i R_i S_i X_i Y_i, \tag{766}$$

$$G = \sum_{i=1}^{n} 1/2\,\omega_i\,(\rho(s))^{t_i} \left(\sqrt{\sigma(ss)}\right)^{v_i} \left(\frac{\sigma(ss)}{(\rho(s))^{8/3}}\right)^{w_i} \left((\rho(s))^{4/3 v_i}\right)^{-1}. \tag{767}$$

C.58 THGFC:.

Density and gradient dependent first row exchange-correlation functional for closed shell systems. Total energies are improved by adding DN, where N is the number of electrons and $D = 0.1863$.

$$t = [7/6, 4/3, 3/2, 5/3, 4/3, 3/2, 5/3, \frac{11}{6}, 3/2, 5/3, \frac{11}{6}, 2], \tag{768}$$

$$v = [0, 0, 0, 0, 1, 1, 1, 1, 2, 2, 2, 2], \tag{769}$$

$$\omega = [\tag{770}$$
$$-0.864448, 0.565130,$$
$$-1.27306, 0.309681,$$
$$-0.287658, 0.588767,$$
$$-0.252700, 0.0223563, 0.0140131,$$
$$-0.0826608, 0.0556080,$$
$$-0.00936227],$$

$$n = 12, \tag{771}$$

$$R_i = (\rho(a))^{t_i} \tag{772}$$
$$+ (\rho(b))^{t_i},$$

$$X_i = 1/2 \frac{\left(\sqrt{\sigma(aa)}\right)^{v_i} + \left(\sqrt{\sigma(bb)}\right)^{v_i}}{\rho^{4/3 v_i}}, \tag{773}$$

$$f = \sum_{i=1}^{n} \omega_i R_i X_i, \tag{774}$$

$$G = \sum_{i=1}^{n} 1/2 \frac{\omega_i (\rho(s))^{t_i} \left(\sqrt{\sigma(ss)}\right)^{v_i}}{\rho^{4/3 v_i}}. \tag{775}$$

C.59 THGFCFO:.

Density and gradient dependent first row exchange-correlation functional. FCFO = FC + open shell fitting.

$$t = [7/6, 4/3, 3/2, 5/3, 4/3, 3/2, 5/3, \frac{11}{6}, 3/2, 5/3, \frac{11}{6}, 2, 3/2, 5/3, \frac{11}{6}, 2, 7/6, 4/3, 3/2, 5/3], \tag{776}$$

$$u = [0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 1, 1, 1, 1], \tag{777}$$

$$v = [0, 0, 0, 0, 1, 1, 1, 1, 2, 2, 2, 2, 0, 0, 0, 0, 0, 0, 0, 0], \tag{778}$$

$$w = [0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 1, 1, 1, 1, 0, 0, 0, 0], \tag{779}$$

$$\omega = [$$
$$\text{(780)}$$
$$-0.864448, 0.565130,$$
$$-1.27306, 0.309681,$$
$$-0.287658, 0.588767,$$
$$-0.252700, 0.0223563, 0.0140131,$$
$$-0.0826608, 0.0556080,$$
$$-0.00936227,$$
$$-0.00677146, 0.0515199,$$
$$-0.0874213, 0.0423827, 0.431940,$$
$$-0.691153,$$
$$-0.637866, 1.07565],$$

$$n = 20, \tag{781}$$

$$R_i = (\rho(a))^{t_i} \\ + (\rho(b))^{t_i}, \tag{782}$$

$$S_i = \left(\frac{\rho(a) - \rho(b)}{\rho}\right)^{2u_i}, \tag{783}$$

$$X_i = 1/2 \frac{\left(\sqrt{\sigma(aa)}\right)^{v_i} + \left(\sqrt{\sigma(bb)}\right)^{v_i}}{\rho^{4/3\,v_i}}, \tag{784}$$

$$Y_i = \left(\frac{\sigma(aa) + \sigma(bb) - 2\sqrt{\sigma(aa)}\sqrt{\sigma(bb)}}{\rho^{8/3}}\right)^{w_i}, \tag{785}$$

$$f = \sum_{i=1}^{n} \omega_i R_i S_i X_i Y_i, \tag{786}$$

$$G = \sum_{i=1}^{n} 1/2\,\omega_i\,(\rho(s))^{t_i}\left(\sqrt{\sigma(ss)}\right)^{v_i}\left(\frac{\sigma(ss)}{(\rho(s))^{8/3}}\right)^{w_i}\left((\rho(s))^{4/3\,v_i}\right)^{-1}. \tag{787}$$

C.60 `THGFCO:`.

Density and gradient dependent first row exchange-correlation functional.

$$t = [7/6, 4/3, 3/2, 5/3, 4/3, 3/2, 5/3, \frac{11}{6}, 3/2, 5/3, \frac{11}{6}, 2, 3/2, 5/3, \frac{11}{6}, 2, 7/6, 4/3, 3/2, 5/3], \tag{788}$$

$$u = [0,0,0,0,0,0,0,0,0,0,0,0,0,0,0,0,1,1,1,1], \tag{789}$$

$$v = [0,0,0,0,1,1,1,1,2,2,2,2,0,0,0,0,0,0,0,0], \tag{790}$$

$$w = [0,0,0,0,0,0,0,0,0,0,0,0,1,1,1,1,0,0,0,0], \tag{791}$$

$$\omega = [\tag{792}$$
$$-0.962998, 0.860233,$$
$$-1.54092, 0.381602,$$
$$-0.210208, 0.391496,$$
$$-0.107660,$$
$$-0.0105324, 0.00837384,$$
$$-0.0617859, 0.0383072,$$
$$-0.00526905,$$
$$-0.00381514, 0.0321541,$$
$$-0.0568280, 0.0288585, 0.368326,$$
$$-0.328799,$$
$$-1.22595, 1.36412],$$

$$n = 20, \tag{793}$$

$$R_i = (\rho(a))^{t_i} \tag{794}$$
$$+ (\rho(b))^{t_i},$$

$$S_i = \left(\frac{\rho(a) - \rho(b)}{\rho} \right)^{2u_i}, \tag{795}$$

$$X_i = 1/2 \frac{\left(\sqrt{\sigma(aa)} \right)^{v_i} + \left(\sqrt{\sigma(bb)} \right)^{v_i}}{\rho^{4/3 \, v_i}}, \tag{796}$$

$$Y_i = \left(\frac{\sigma(aa) + \sigma(bb) - 2 \sqrt{\sigma(aa)} \sqrt{\sigma(bb)}}{\rho^{8/3}} \right)^{w_i}, \tag{797}$$

$$f = \sum_{i=1}^{n} \omega_i R_i S_i X_i Y_i, \tag{798}$$

$$G = \sum_{i=1}^{n} 1/2 \, \omega_i \, (\rho(s))^{t_i} \left(\sqrt{\sigma(ss)} \right)^{v_i} \left(\frac{\sigma(ss)}{(\rho(s))^{8/3}} \right)^{w_i} \left((\rho(s))^{4/3 \, v_i} \right)^{-1}. \tag{799}$$

C.61   THGFL:.

Density dependent first row exchange-correlation functional for closed shell systems.

$$t = [7/6, 4/3, 3/2, 5/3], \tag{800}$$

$$\omega = [\tag{801}$$
$$-1.06141, 0.898203,$$
$$-1.34439, 0.302369],$$

$$n = 4, \tag{802}$$

$$R_i = (\rho(a))^{t_i} \tag{803}$$
$$+ (\rho(b))^{t_i},$$

$$f = \sum_{i=1}^{n} \omega_i R_i. \tag{804}$$

C.62 `TPSSC`**: TPSS Correlation Functional**

J. Tao, J. P. Perdew, V. N. Staroverov, and G. E. Scuseria, Phys. Rev. Lett. 91, 146401 (2003).

C.63 `TPSSX`**: TPSS Exchange Functional**

J. Tao, J. P. Perdew, V. N. Staroverov, and G. E. Scuseria, Phys. Rev. Lett. 91, 146401 (2003).

C.64 `VSXC`**: .**

$$p = [\tag{805}$$
$$-0.98, 0.3271, 0.7035],$$

$$q = [\tag{806}$$
$$-0.003557,$$
$$-0.03229, 0.007695],$$

$$r = [0.00625, \tag{807}$$
$$-0.02942, 0.05153],$$

$$t = [\tag{808}$$
$$-0.00002354, 0.002134, 0.00003394],$$

$$u = [\tag{809}$$
$$-0.0001283,$$
$$-0.005452,$$
$$-0.001269],$$

$$v = [0.0003575, 0.01578, 0.001296], \tag{810}$$

$$\alpha = [0.001867, 0.005151, 0.00305], \tag{811}$$

$$g = (\rho(s))^{4/3} F(\chi(s), zs, p_1, q_1, r_1, t_1, u_1, v_1, \alpha_1) \tag{812}$$
$$+ ds\varepsilon(\rho(s), 0) F(\chi(s), zs, p_2, q_2, r_2, t_2, u_2, v_2, \alpha_2),$$

$$G = (\rho(s))^{4/3} F(\chi(s), zs, p_1, q_1, r_1, t_1, u_1, v_1, \alpha_1) \tag{813}$$
$$+ ds\varepsilon(\rho(s), 0) F(\chi(s), zs, p_2, q_2, r_2, t_2, u_2, v_2, \alpha_2),$$

$$f = F(x, z, p_3, q_3, r_3, t_3, u_3, v_3, \alpha_3)(\varepsilon(\rho(a), \rho(b)) \tag{814}$$
$$- \varepsilon(\rho(a), 0)$$
$$- \varepsilon(\rho(b), 0)),$$

$$x = (\chi(a))^2 \tag{815}$$
$$+ (\chi(b))^2,$$

$$zs = \frac{\tau(s)}{(\rho(s))^{5/3}} - cf, \tag{816}$$

$$z = \frac{\tau(a)}{(\rho(a))^{5/3}} + \frac{\tau(b)}{(\rho(b))^{5/3}} - 2cf, \tag{817}$$

$$ds = 1 - \frac{(\chi(s))^2}{4zs + 4cf}, \tag{818}$$

$$
\begin{aligned}
F&(x,z,p,q,c,d,e,f,\alpha) \\
&= \frac{p}{\lambda(x,z,\alpha)} \\
&\quad + \frac{qx^2 + cz}{(\lambda(x,z,\alpha))^2} \\
&\quad + \frac{dx^4 + ex^2z + fz^2}{(\lambda(x,z,\alpha))^3},
\end{aligned}
\tag{819}
$$

$$
\begin{aligned}
\lambda&(x,z,\alpha) \\
&= 1 \\
&\quad + \alpha\,(x^2 \\
&\qquad\qquad\qquad\qquad\qquad + z),
\end{aligned}
\tag{820}
$$

$$cf = 3/5\,3^{2/3}\left(\pi^2\right)^{2/3}, \tag{821}$$

$$T = [0.031091, 0.015545, 0.016887], \tag{822}$$

$$U = [0.21370, 0.20548, 0.11125], \tag{823}$$

$$V = [7.5957, 14.1189, 10.357], \tag{824}$$

$$W = [3.5876, 6.1977, 3.6231], \tag{825}$$

$$X = [1.6382, 3.3662, 0.88026], \tag{826}$$

$$Y = [0.49294, 0.62517, 0.49671], \tag{827}$$

$$P = [1, 1, 1], \tag{828}$$

$$
\begin{aligned}
\varepsilon&(\alpha,\beta) \\
&= (\alpha \\
&\quad + \beta)\Bigg(e\,(l(\alpha,\beta), T_1, U_1, V_1, W_1, X_1, Y_1, P_1) \\
&\quad - \frac{e\,(l(\alpha,\beta), T_3, U_3, V_3, W_3, X_3, Y_3, P_3)\,\omega(\zeta(\alpha,\beta))\left(1 - (\zeta(\alpha,\beta))^4\right)}{c} \\
&\quad + (e\,(l(\alpha,\beta), T_2, U_2, V_2, W_2, X_2, Y_2, P_2) \\
&\quad - e\,(l(\alpha,\beta), T_1, U_1, V_1, W_1, X_1, Y_1, P_1))\,\omega(\zeta(\alpha,\beta))\,(\zeta(\alpha,\beta))^4\Bigg),
\end{aligned}
\tag{829}
$$

$$
\begin{aligned}
l&(\alpha,\beta) \\
&= 1/4\,\sqrt[3]{3}\,4^{2/3}\sqrt[3]{\frac{1}{\pi(\alpha+\beta)}},
\end{aligned}
\tag{830}
$$

$$
\begin{aligned}
\zeta&(\alpha,\beta) \\
&= \frac{\alpha - \beta}{\alpha + \beta},
\end{aligned}
\tag{831}
$$

$$\omega(z)$$
$$= \frac{(1+z)^{4/3} + (1-z)^{4/3} - 2}{2\sqrt[3]{2} - 2},$$

(832)

$$e(r,t,u,v,w,x,y,p)$$
$$=$$
$$-2t(1$$

(833)

$$+ur)\ln\left(1\right.$$
$$\left. + 1/2\,\frac{1}{t\left(v\sqrt{r} + wr + xr^{3/2} + yr^{p+1}\right)}\right),$$

$$c = 1.709921.$$

(834)

C.65   `VW`: von Weizsäcker kinetic energy

Automatically generated von Weizsäcker kinetic energy.

$$g = \frac{c\sigma(ss)}{\rho(s)},$$

(835)

$$G = \frac{c\sigma(ss)}{\rho(s)},$$

(836)

$$c = 1/8.$$

(837)

C.66   `VWN3`: Vosko-Wilk-Nusair (1980) III local correlation energy

VWN 1980(III) functional

$$x = 1/4\,\sqrt[6]{3}\,4^{5/6}\,\sqrt[6]{\frac{1}{\pi\rho}},$$

(838)

$$\zeta = \frac{\rho(a) - \rho(b)}{\rho},$$

(839)

$$f = \rho e,$$

(840)

$$k = [0.0310907, 0.01554535,$$
$$-1/6\,\pi^{-2}],$$

(841)

$$l = [$$
$$-0.409286,$$
$$-0.743294,$$
$$-0.228344],$$

(842)

$$m = [13.0720, 20.1231, 1.06835],$$

(843)

$$n = [42.7198, 101.578, 11.4813],$$

(844)

$$e = \Lambda + z(\lambda$$
$$-\Lambda),$$

(845)

$$y = \frac{9}{8} (1 \tag{846}$$

$$+ \zeta)^{4/3}$$

$$+ \frac{9}{8} (1$$

$$- \zeta)^{4/3}$$

$$- 9/4,$$

$$\Lambda = q(k_1, l_1, m_1, n_1), \tag{847}$$

$$\lambda = q(k_2, l_2, m_2, n_2), \tag{848}$$

$$q(A, p, c, d) \tag{849}$$
$$= A \left(\ln \left(\frac{x^2}{X(x,c,d)} \right) \right.$$
$$+ 2c \arctan \left(\frac{Q(c,d)}{2x+c} \right) (Q(c,d))^{-1}$$
$$- cp \left(\ln \left(\frac{(x-p)^2}{X(x,c,d)} \right) \right.$$
$$+ 2(c$$

$$\left. \left. + 2p) \arctan \left(\frac{Q(c,d)}{2x+c} \right) (Q(c,d))^{-1} \right) (X(p,c,d))^{-1} \right),$$

$$Q(c,d) \tag{850}$$
$$= \sqrt{4d - c^2},$$

$$X(i,c,d) \tag{851}$$
$$= i^2$$
$$+ ci$$
$$+ d,$$

$$z = 4 \frac{y}{9 \sqrt[3]{2} - 9}. \tag{852}$$

C.67   VWN5: **Vosko-Wilk-Nusair (1980) V local correlation energy**

VWN 1980(V) functional. The fitting parameters for $\Delta \varepsilon_c(r_s, \zeta)_V$ appear in the caption of table 7 in the reference.

$$x = 1/4 \sqrt[6]{3} 4^{5/6} \sqrt[6]{\frac{1}{\pi \rho}}, \tag{853}$$

$$\zeta = \frac{\rho(a) - \rho(b)}{\rho}, \tag{854}$$

$$f = \rho e, \tag{855}$$

$$k = [0.0310907, 0.01554535, \tag{856}$$
$$-1/6 \pi^{-2}],$$

$$l = [\tag{857}$$
$$-0.10498,$$
$$-0.325,$$
$$-0.0047584],$$

$$m = [3.72744, 7.06042, 1.13107], \tag{858}$$

$$n = [12.9352, 18.0578, 13.0045], \tag{859}$$

$$e = \Lambda + \alpha y \, (1 \tag{860}$$
$$+ h\zeta^4 \big) ,$$

$$y = \frac{9}{8} \, (1 \tag{861}$$
$$+ \zeta)^{4/3}$$

$$+ \frac{9}{8} \, (1$$
$$- \zeta)^{4/3}$$

$$- 9/4,$$

$$h = 4/9 \frac{\lambda - \Lambda}{\left(\sqrt[3]{2} - 1 \right) \alpha} - 1, \tag{862}$$

$$\Lambda = q \, (k_1, l_1, m_1, n_1), \tag{863}$$

$$\lambda = q \, (k_2, l_2, m_2, n_2), \tag{864}$$

$$\alpha = q \, (k_3, l_3, m_3, n_3), \tag{865}$$

$$q \, (A, p, c, d) \tag{866}$$
$$= A \left(\ln \left(\frac{x^2}{X \, (x, c, d)} \right) \right.$$
$$+ 2c \arctan \left(\frac{Q \, (c, d)}{2x + c} \right) (Q \, (c, d))^{-1}$$
$$- cp \left(\ln \left(\frac{(x - p)^2}{X \, (x, c, d)} \right) \right.$$
$$+ 2 \, (c$$
$$\left. + 2p) \arctan \left(\frac{Q \, (c, d)}{2x + c} \right) (Q \, (c, d))^{-1} \right) (X \, (p, c, d))^{-1} \bigg) ,$$

$$Q \, (c, d) \tag{867}$$
$$= \sqrt{4d - c^2},$$

$$X \, (i, c, d) \tag{868}$$
$$= i^2$$
$$+ ci$$
$$+ d.$$

C.68 `XC-M05`: M05 Meta-GGA Exchange-Correlation Functional

Here it means M05 exchange-correlation part which excludes HF exact exchange term. Y. Zhao, N. E. Schultz, and D. G. Truhlar, J. Chem. Phys. 123, 161103 (2005).

C.69 `XC-M05-2X`: M05-2X Meta-GGA Exchange-Correlation Functional

Here it means M05-2X exchange-correlation part which excludes HF exact exchange term. Y. Zhao, N. E. Schultz, and D. G. Truhlar, J. Chem. Theory Comput. 2, 364 (2006).

C.70 `XC-M06`: M06 Meta-GGA Exchange-Correlation Functional

Here it means M06 exchange-correlation part which excludes HF exact exchange term. Y. Zhao and D. G. Truhlar, Theor. Chem. Acc. 120, 215 (2008).

C.71 `XC-M06-2X`: M06-2X Meta-GGA Exchange-Correlation Functional

Here it means M06-2X exchange-correlation part which excludes HF exact exchange term. Y. Zhao and D. G. Truhlar, Theor. Chem. Acc. 120, 215 (2008).

C.72 `XC-M06-HF`: M06-HF Meta-GGA Exchange-Correlation Functional

Here it means M06-HF exchange-correlation part which excludes HF exact exchange term. Y. Zhao and D. G. Truhlar, J. Phys. Chem. A 110, 13126 (2006).

C.73 `XC-M06-L`: M06-L Meta-GGA Exchange-Correlation Functional

Y. Zhao and D. G. Truhlar, J. Chem. Phys. 125, 194101 (2006).

C.74 `XC-M08-HX`: M08-HX Meta-GGA Exchange-Correlation Functional

Here it means M08-HX exchange-correlation part which excludes HF exact exchange term. Y. Zhao and D. G. Truhlar, J. Chem. Theory Comput. 4, 1849 (2008).

C.75 `XC-M08-SO`: M08-SO Meta-GGA Exchange-Correlation Functional

Here it means M08-SO exchange-correlation part which excludes HF exact exchange term. Y. Zhao and D. G. Truhlar, J. Chem. Theory Comput. 4, 1849 (2008).

C.76 `XC-M11-L`: M11-L Exchange-Correlation Functional

R. Peverati and D. G. Truhlar, Journal of Physical Chemistry Letters 3, 117 (2012).

C.77 `XC-SOGGA`: SOGGA Exchange-Correlation Functional

Y. Zhao and D. G. Truhlar, J. Chem. Phys. 128, 184109 (2008).

C.78 `XC-SOGGA11`: SOGGA11 Exchange-Correlation Functional

R. Peverati, Y. Zhao and D. G. Truhlar, J. Phys. Chem. Lett. 2 (16), 1991 (2011).

C.79 `XC-SOGGA11-X`: SOGGA11-X Exchange-Correlation Functional

Here it means SOGGA11-X exchange-correlation part which excludes HF exact exchange term. R. Peverati and D. G. Truhlar, J. Chem. Phys. 135, 191102 (2011).

D   License information

The Molpro source code contains some external code which is listed in this section. Molpro binaries may, in some instances, contain compiled versions of this code also.

D.1   BLAS

Copies of some of the netlib BLAS routines are included in the Molpro source code. The source code is identical except for the addition of a revision control header, and renaming of the file suffix from .f to .fh. These routines are only used if the user does not provide an external BLAS library. In addition, as suggested in the comments, the STOP statement in subroutine XERBLA has been modified.

D.2   LAPACK

Copies of some of the netlib LAPACK routines are included in the Molpro source code. The source code is identical except for the addition of a revision control header, and renaming of the file suffix from .f to .fh. These routines are only used if the user does not provide an external LAPACK library. The license follows.

```
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