

# A New Hybrid DFT Functional: Accurate Description of Excited States, Charge-transfer States, and van der Waals Interactions

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Density functional theory (DFT) has advanced to one of the most popular theoretical approaches to calculate molecular properties. The first-order molecular properties (energies, geometries, frequencies, dipole moments, etc) are well predicted by local GGA functionals. However, DFT fails to describe induced or response properties. Although the valence-excited states can be well described by time-dependent DFT (TDDFT), TDDFT significantly underestimates the Rydberg and charge transfer (CT) excitation energies. The computed oscillator strengths have substantial errors. Also DFT fails to describe van der Waals interactions. This failure has been attributed to the wrong long-range behavior of the standard exchange-correlation functionals.

Recently we have proposed a long-range exchange correction scheme for GGA functional. In the scheme, the two-electron operator,  $1/r_{12}$ , is separated into the short-range and long-range parts by using the standard error function *erf* such that

$$\frac{1}{r_{12}} = \frac{1 - \text{erf}(\mu r_{12})}{r_{12}} + \frac{\text{erf}(\mu r_{12})}{r_{12}}$$

where  $r_{12} = |\mathbf{r}_1 - \mathbf{r}_2|$  for coordinate vectors of electrons,  $\mathbf{r}_1$  and  $\mathbf{r}_2$ , and  $\mu$  is a parameter that determines the ratio of these parts. The long-range exchange interaction is described by the Hartree-Fock exchange integral and the short-range part is replaced by the GGA exchange functional.

The present long-range corrected functional has been successfully applied to the various molecular properties. It remedies the underestimation of Rydberg excitation energies and reproduces the correct asymptotic behavior of the CT excitation energies. The van der Waals interactions can be described accurately by the present scheme with combining Andersson's potential.