

New range separation ideas in DFT for intermolecular interactions

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Range separation technique has become a method of choice for seamless connection of different components of density functional. In this talk we will describe its application to two problems of vital importance in the field of intermolecular interactions. 1) Alignment of frontier orbitals via parameter tuning, via a global density dependent range-separation parameter derived from a model of the electron-hole distance [1]. 2) Separation of short-range semi-local correlation from the long-range dispersion to avoid double counting of dispersion terms in a dispersion-corrected DFT formalisms [2].

1. Quantum mechanical methods based on the density functional theory (DFT) offer a realistic possibility of first-principles design of organic donor-acceptor systems and engineered band-gap materials. This promise is contingent upon the ability of DFT to predict the one-particle states accurately. Unfortunately, approximate functionals fail to align the orbital energies with ionization potentials. We describe a new paradigm for achieving this alignment. In the proposed model, an average outer electron—exchange hole separation controls the onset of the orbital-dependent exchange in approximate range-separated functionals. The correct description of one-particle states is thus achieved without explicit electron removal or attachment. Extensive numerical tests show that the proposed method provides physically-sound orbital gaps and leads to excellent predictions of charge-transfer excitations and other properties critically depending on the tail of the electron density.

2. We present a physically motivated correlation functional belonging to the meta generalized gradient approximation (meta-GGA) rung, which can be supplemented with long-range dispersion corrections without introducing double-counting of correlation contributions. The functional is derived by the method of constraint satisfaction, starting from an analytical expression for a real-space spinresolved correlation hole. The model contains a position-dependent function that controls the range of the interelectron correlations described by the semilocal functional. With minimal empiricism, this function may be adjusted so that the correlation model blends with a specific dispersion correction describing long-range contributions. For a preliminary assessment, our functional has been combined with an atom-pairwise dispersion correction and full Hartree-Fock (HF)-like exchange. Despite the HF-exchange approximation, its predictions compare favorably with reference interaction energies in an extensive set of non-covalently bound dimers.

[1] Modrzejewski, M., Lesiuk, M., Rajchel, L., Szczeńsiak, M. M., Chałasiński, G. *J. Chem. Phys.*, 137:204121-10, 2012.

[2] Modrzejewski, M., Szczeńsiak, M. M., Chałasiński, G. submitted for publication
<http://arxiv.org/abs/1305.6869>.

