Dispersion-only approximation for long-range RPA correlation contributions to DFT intermolecular interaction energies

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Dispersion interactions can be included in DFT calculations in a range-separated framework by standard correlation methods from perturbation or coupled-cluster theory. One appealing possibility is the random-phase approximation (RPA), which is based on the interaction of mono-excitations. When employed for fragmented molecular systems, a classification of occupied and virtual orbitals on monomers[1] allows us to identify dispersion-type coupled mono-excitations contributing to inter-fragment interaction energies. A first study[2] pointed out that the combination of localized orbitals and range-separated DFT provides an appropriate framework for this approximation, too crude in a standard correlation calculation context based on a Hartree-Fock reference.

We apply the approach to a larger variety of systems, in order to assess the applicability in different contexts, ranging from highly ionic interactions to charge transfer complexes. The efficiency and potential gains of the approximations will be discussed.

[1] P. Reinhardt, J.-P. Piquemal, A. Savin, *J.Comp.Theor.Chem.*, 4:2020-2029, 2008.

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