Dispersion energy

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Dispersion energy results from long-range correlations of motions of electrons from different monomers. This quantity is precisely defined in symmetry-adapted perturbation theory (SAPT) [1]. Approximate but very accurate values of dispersion energies can be calculated using monomers described at the coupled-cluster level with single and double excitations (CCSD) [2]. Fairly accurate values can also be obtained at a small fraction of the costs of the CCSD-based calculations if monomers are described by density-functional theory (DFT), a method denoted as SAPT(DFT) [3, 4], The dispersion energy in SAPT(DFT) is computed from Kohn-Sham density-density response functions which involve virtual orbitals. Such calculations can be done for dimers containing couple hundreds of atoms [5]. There have been several expressions for dispersion energies proposed in literature that depend only on ground-state densities, often called nonlocal density functionals, the best known is the vdW-DF method [6]. Comparisons with SAPT dispersion energies show that these methods recover dispersion energies with relatively large errors. Such errors are actually larger than the errors of the total interaction energies computed by adding vdW-DF-type dispersion energies to the DFT interaction energies. This somewhat baffling finding results from the fact that virtually all vdW-DF-type methods are adjusted to reproduce total interaction energies near minima. A new nonlocal functional which gives dispersion energies in good agreement with SAPT at all intermolecular separations will be presented. These dispersion energies can be used with the dispersionless density functional [7].

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