Density functional theory of van der Waals forces

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Symmetry-adapted perturbation theory (SAPT) has been shown to provide accurate intermolecular potentials which perform very well in numerous applications to spectroscopy and to simulation of bulk properties. The high accuracy of a SAPT treatment requires, however, that the effect of the intra-monomer electron correlation on the major components of the intermolecular potential (electrostatics, exchange, induction and dispersion) is properly included. In the conventional SAPT calculations this effect is accounted for by computationally costly expansion in powers of the monomer fluctuation potentials or by, even more costly, coupled-cluster iterative techniques. We show that by adopting the density functional theory (DFT) description of monomers, it is possible to include the intra-atomic correlation effects with very good accuracy and at a modest computational cost. Specifically, by evaluating the simplest zeroth-order SAPT expressions with the Kohn-Sham orbitals we effectively perform an infinite-order summation of SAPT expansion in powers of monomer fluctuation potentials and obtain very accurate values of the electrostatic and exchange energies. This accuracy is possible, however, only if the exchange correlation potential $V_{xc}(r)$ is asymptotically corrected at large r.

The dispersion part of the interaction energy is obtained from a generalized Casimir-Polder formula evaluated with density-density response functions of monomers computed using the time-dependent DFT theory. Employing the asymptotically corrected exchange correlation potentials for monomers is also essential in this case. The method recovers the dispersion energies of He, Ne or H_2O dimer to within 3% or better and leads to very accurate interaction potentials in the whole range of van der Waals minimum. For the benzene dimer the results are very close to those of the much more expensive CCSD(T) treatment. The method has been implemented using the density-fitting procedure, which leads to cubic dependence of the computational effort on the employed basis set size. Due to this favorable scaling the resulting computational procedure, referred to as SAPT(DFT), is applicable to much larger molecules than any method used thus far for calculating the van der Waals interaction energy at similar level of accuracy.