

Casimir-Polder size consistency: a case for RPA

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For years, quantum chemical approaches have aimed to accurately and efficiently predict non-covalent interactions (NIs) between atoms and molecules. These include dispersion interactions, π - π stacking, or hydrogen and halogen bonding that play an important role in structural biology and supramolecular chemistry. Here we assess the performance of the random phase approximation (RPA), which has evolved from a semi-analytical technique for model Hamiltonians to a powerful tool for ab initio electronic structure calculations in chemistry and materials science. The accuracy of RPA for weakly interacting systems from the L7, S66, and S30L benchmarks illustrates the critical importance of beyond the pairwise additivity of NIs in moderately large sized molecules with 100 - 200 atoms. Comparison to the second order Møller-Plesset perturbation theory (MP2) and semilocal density functional approximations (DFAs) with dispersion correction reveals that RPA performs better than MP2 and on par with dispersion corrected-DFAs.