ACCURATE INTERMOLECULAR INTERACTIONS AT DRAMATICALLY REDUCED COST AND A MANY-BODY ENERGY DECOMPOSITION SCHEME FOR XPol+SAPT

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An efficient, monomer-based electronic structure method is introduced for computing non-covalent interactions in molecular and ionic clusters. It builds upon our "explicit polarization" (XPol) with pairwise-additive symmetry-adapted perturbation theory (SAPT) using the Kohn-Sham (KS) version of SAPT, but replaces the problematic and expensive sum-over-states dispersion terms with empirical potentials. This modification reduces the scaling from $O(N^5)$ to $O(N^3)$ and also facilitates the use of Kohn-Sham density functional theory (KS-DFT) as a low-cost means to capture intramolecular electron correlation. Accurate binding energies are obtained for benchmark databases of dimer binding energies, and potential energy curves are also captured accurately, for a variety of challenging systems. As compared to traditional DFT-SAPT or SAPT(DFT) methods, it removes the limitation to dimers and extends SAPT-based methodology to many-body systems. For many-body systems such as water clusters and halide–water cluster anions, the new method is superior to established density-functional methods for non-covalent interactions. We suggest that using different asymptotic corrections for different monomers is necessary to get good binding energies in general, as DFT-SAPT or SAPT(DFT), especially for hydrogen-bonded complexes. We also introduce a decomposition scheme for the interaction energy that extends traditional SAPT energy decomposition analysis to systems containing more than two monomers, and we find that the various energy components (electrostatic, exchange, induction, and dispersion) are in very good agreement with high-level SAPT benchmarks for dimers. For $(\mathrm{H_2O})_6$, the many-body contribution to the interaction energy agrees well with that obtained from traditional Kitaura-Morokuma energy decomposition analysis.