

Extended Symmetry-Adapted Perturbation Theory

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Abstract

Extended symmetry-adapted perturbation theory (XSAPT)¹ is a hybrid quantum chemistry approach for computing noncovalent interaction energies, combining a density functional theory (DFT) description of the monomers with elements of traditional SAPT. The “extended” version of the theory goes beyond the conventional dimer SAPT approach by

- substituting more accurate treatments of dispersion in place of second-order perturbation theory,^{2,3} and
- incorporating many-body polarization via self-consistent charge embedding.⁴

The result of these modifications is a cubic-scaling method⁵ that is faster and more scalable than DFT for large systems, yet achieves an accuracy of < 1 kcal/mol versus complete-basis CCSD(T) benchmarks for small dimers (*e.g.*, S66 data set),⁶ and ~ 1 kcal/mol for large dispersion-bound complexes (*e.g.*, L7 data set).^{1,5} The method is systematically improvable insofar as SAPT provides a separable energy decomposition framework wherein individual terms may be swapped out for better-performing alternatives. Moreover, XSAPT extends conventional SAPT’s energy decomposition analysis to many-body systems. We have recently used this family of methods to explore the basic molecular physics of π - π interactions,^{7,8} and to upend some “conventional wisdom” regarding the role of electrostatics in non-bonded interactions.⁹ This talk will describe the XSAPT framework, illustrate some performance benchmarks, and describe some prototypical applications.

References

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