Divergence of Many-Body Perturbation Theory in Noncovalent Interactions

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Abstract

Many-body perturbation theory (MBPT) has been the method of choice to predict noncovalent interactions (NIs). The assumption that "weak" closed-shell interactions between distant electron pairs are accurately captured by MBPT is implicit in many applications as well as theoretical approaches such as local correlation methods. However, recent benchmark calculations for supramolecular complexes with $4 - 206$ atoms revealed large errors in NI energies of supramolecular complexes obtained from MBPT. Noncovalent interactions (NIs) play a large role in structural biology and supramolecular chemistry. The prediction of NIs remains an outstanding computational challenge. Many-body perturbation theory (MBPT) has been the approach to predict NIs such as the efficient second-order Møller-Plesset perturbation theory (MP2) which is accurate for small complexes based on the S66 benchmark. However, recent reports revealed large errors in NI energies of supramolecular complexes obtained from MBPT. Prompted by these errors, we compare the performance of MP2, spin-scaled MP2, dispersion-corrected semilocal density functional approximations (DFAs), and the post-Kohn–Sham random phase approximation (RPA) for predicting binding energies of complexes within the S66, L7, and S30L benchmarks. Numerical results demonstrated that the accuracy of MP2 severely deteriorates as the system size grows with an error rate of 0.1% per electron. Whereas, empirical dispersion-corrected DFAs and RPA errors remain virtually constant.

To analyze these results, the asymptotic adiabatic connection symmetry-adapted perturbation theory (AC-SAPT) is developed which uses monomers at full coupling whose ground-state density is constrained to the ground-state density of the complex. Taylor series expansion of AC-SAPT interaction energies with respect to the coupling strength integrand is shown to be convergent for nondegenerate monomers when RPA is used, while it spuriously diverges for second-order MBPT. Based on the analysis and numerical results, MBPT for NIs may safely be replaced with non-perturbative approaches such as RPA or coupled cluster methods.