Divergence of Perturbation Theory in Noncovalent Interactions

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Abstract

Noncovalent interactions (NIs) play a large role in structural biology and supramolecular chemistry. The prediction of NIs remains an outstanding computational challenge. Couple-cluster singles, doubles, and perturbative triples (CCSD(T)) has been the method to predict NIs. However, CCSD(T) is limited to the computation of small molecules which has limited the understanding of NIs to small complexes of up to ~ 50 atoms. Electronic structure methods were developed based on small molecules with the underlying assumptions that these methods may be scaled up to larger ones without deterioration in accuracy. Perturbation theory has been the common approach to predict NIs. The efficient second-order Møller-Plesset perturbation theroy (MP2) has been shown to be accurate for small complexes based on the S22 benchmark. In this work, we demonstrated that the accuracy of MP2 severely deteriorates as the system size grows and it is indicative of the limitations of perturbation theory for NIs.

The first step to accurately compute NIs requires methods to account for London dispersion interactions, which can account up to 200% of the interaction energies. RPA, which is based on the interactions between virtual ground-state density fluctuations, presents itself as an accurate way to describe NIs. It correctly captures three- and higher-body dispersion effects due to inclusion of polarization and screening. New numerical results of the S66, L7, S30L, and ROT34 test sets for RPA illustrate the importance of higher-body dispersion effects. This material is based upon work supported by the National Science Foundation under CHE-1800431