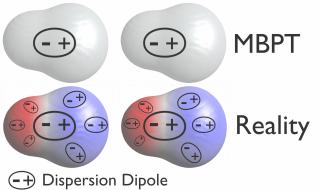


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## View Abstract

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<b>PRESNTATION TYPE:</b> Poster Preferred : Consider for Sci-Mix
<b>TITLE:</b> Divergence of many-body perturbation theory in noncovalent interactions
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<b>ABSTRACT BODY:</b> <p><b>Abstract:</b> 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 show that the accuracy of the second-order Møller-Plesset MBPT severely deteriorates as the system size grows with an error rate of approximately 0.1% per valence electron. To analyze these unexpected results, an asymptotic adiabatic connection symmetry-adapted perturbation theory (AC-SAPT) is presented which uses monomers at full coupling. A nonperturbative "screened second-order" expression for the dispersion energy in terms of monomer quantities is derived using the fluctuation-dissipation theorem. Explicit expressions for the convergence radius of the AC-SAPT series are derived within the random phase approximation (RPA) and MBPT. Expansion of the AC-SAPT series within RPA for nondegenerate monomers is shown to always be convergent whereas, it is found to spuriously diverge for second-order MBPT, except for the smallest and least polarizable monomers. I will argue that the divergence of MBPT for presumably "weak" dispersion interactions is caused by missing or incomplete "electrodynamic" screening of the Coulomb interaction due to induced particle-hole pairs between electrons in different monomers, leaving the effective interaction too strong for AC-SAPT to converge within MBPT even in moderately polarizable molecules with a few tens of atoms. Conclusions for electronic structure theory and computational practice will be discussed.</p>


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