

# Pervasive Divergence of Many-Body Perturbation Theory for Dispersion Interactions

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Recent benchmark calculations for supramolecular complexes with 4-206 atoms have shown that *relative* errors in binding energies from second-order Møller-Plesset (MP2) many-body perturbation theory (MBPT) increase systematically with the system size at a rate of approximately 1‰ per valence electron [1]. To analyze these unexpected results, an asymptotic adiabatic connection symmetry-adapted perturbation theory (AC-SAPT) is presented which uses monomers at full coupling. Using the fluctuation–dissipation theorem, we obtain a nonperturbative “screened second-order” expression for the dispersion energy in terms of monomer quantities which is exact for non-overlapping subsystems and free of induction terms; a first-order random phase approximation (RPA) [2] like approximation to the Hartree, exchange, and correlation kernel recovers the macroscopic Lifshitz limit [3]. Explicit expressions for the convergence radius of the AC-SAPT series are derived within RPA and MBPT and numerically evaluated. Whereas the AC-SAPT expansion is always convergent for nondegenerate monomers when RPA is used, 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.

## References

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- [3] J. F. Dobson, T. Gould, *J. Phys: Cond. Mat.* **24** (2012), 073201.