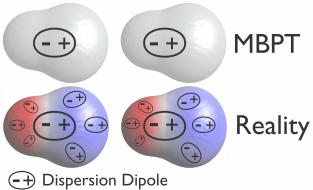


ACS

View Abstract

ABSTRACT SYMPOSIUM NAME: Sci-Mix
ABSTRACT SYMPOSIUM PROGRAM AREA NAME: COMP
CONTROL ID: 3400291
PRESNTATION TYPE: Poster Preferred : Consider for Sci-Mix
TITLE: Divergence of Many-Body Perturbation Theory in Noncovalent Interactions
AUTHORS (FIRST NAME, LAST NAME): Brian D. Nguyen ¹ , Guo P. Chen ¹ , Matthew M. Agee ¹ , Asbjörn Burow ¹ , Matthew P. Tang ¹ , Filipp U. Furche ¹
INSTITUTIONS (ALL): 1. Department of Chemistry, University California Irvine, Irvine, CA, United States.
ABSTRACT BODY: <p>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 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>
 <p>The diagram illustrates the difference between the MBPT model and the reality of dispersion interactions. The MBPT model, at the top, shows two separate, isolated monomers, each represented by a grey circle containing a dipole moment (indicated by a minus sign above a plus sign). Below this, the reality model shows two molecules composed of multiple atoms. Each atom is represented by a small circle with a dipole moment. The molecules are shown interacting, with arrows indicating electron movement between atoms, particularly between atoms of opposite charges (positive to negative and vice versa). A legend at the bottom left defines the symbol $\ominus\oplus$ as a Dispersion Dipole.</p>

ACS MAPS Environment. Copyright © 2020 American Chemical Society. All rights reserved.

[Terms of Use](#) | [Privacy](#) | [ACS Homepage](#)

© Clarivate Analytics | © ScholarOne, Inc., 2020. All Rights Reserved.

ScholarOne Abstracts and ScholarOne are registered trademarks of ScholarOne, Inc.

ScholarOne Abstracts Patents #7,257,767 and #7,263,655.

 [@ScholarOneNews](#) |  [System Requirements](#) |  [Privacy Statement](#) |  [Terms of Use](#)

Product version number 4.16.0 (Build 116). Build date Thu Dec 5 14:35:03 EST 2019. Server ip-10-236-29-249