Towards Accurate Description of Intermolecular Induction

Humahuti Dihingia[1], Bartosz Tyrcha[1],
Konrad Patkowski[2], Piotr S. Żuchowski[1], Alston J. Misquitta[3]

[1]*Faculty of Physics, Astronomy and Informatics, Nicolaus Copernicus University in Toruń, Grudziądzka 5, 87-100,Poland*
[2]*Department of Chemistry and Biochemistry, Auburn University, Auburn, Alabama 36849, USA*
[3]*School of Physical and Chemical Sciences, Queen Mary University of London, Mile End Road, E1 4NS, United Kingdom*
humahuti@umk.pl

A key feature of Symmetry-Adapted Perturbation Theory (SAPT)[1] is the composition of the interaction energy in terms of physically significant terms such as: electrostatics, exchange, induction and dispersion. Among these, the induction energy plays a significant role, specially for strongly bonded systems. However, the induction terms in perturbation theory diverge and the lowest order terms do not recover the total induction. The missing higher order induction can be incorporated with delta-HF correction, resulting into a hybrid theory[2]. While the delta-HF correction is important for H-bonded systems, but it is also known to overbind dispersion-dominated complexes. Therefore, it would be ideal to recover the induction effect in a consistent theory. One such approach is Pauli-Blockade[3,4] method, which offers a variational framework for infinite-order induction. However, because of the orthogonalization step and subsequent loss of monomer identity, this theory is not useful for further SAPT-like development.

In this work, we explore intermolecular interactions through a potentially infinite-order induction, dispersion-free and many-body variational approach termed as Symmetry-Adapted Relaxation Theory, which is motivated by Pauli-Blockade but maintains monomer identity, therefore retaining SAPT-like character. Our methodology formulated in second quantization, is implemented using Psi4NumPy[5], a Python-based interface for the computational chemistry software Psi4. We report the agreement between interaction energy computed using our approach and supermolecular Hartree-Fock energy, demonstrating that variationally relaxed monomers effectively capture induction effects to infinite-order in the interaction operator.

References:

[1] Jeziorski B., Moszynski R. and Szalewicz K., Perturbation theory approach to intermolecular potential energy surfaces of van der Waals complexes, Chemical Reviews,(1994)
[2] Patkowski K., Szalewicz K. and Jeziorski B., Orbital relaxation and the third-order induction energy in symmetry-adapted perturbation theory, Theor Chem Acc (2010)
[3] Gutowski M.,Piela L., Interpretation of the Hartree-Fock interaction energy between closed shell systems, Mol. Phys. 64 (1988)
[4] Rajchel Ł., Żuchowski P. S., Szczęśniak M. M. and Chałasiński G., Interpretation of the Hartree-Fock interaction energy between closed shell systems, Phys. Rev. Lett. 104 (2010)
[5] Psi4NumPy: An Interactive Quantum Chemistry Programming Environment for Reference Implementations and Rapid Development, J. Chem. Theory Comput. (2018)