Connecting Kohn-Sham density functional theory with wave-function-based symmetry-adapted perturbation theory

Krzysztof Szalewicz

Department of Physics and Astronomy,
University of Delaware, Newark, Delaware 19716

Symmetry-adapted perturbation theory (SAPT) [1, 2] is a method of computing intermolecular interaction energies starting from isolated monomers as zeroth-order approximation. The regular SAPT starts from antisymmetrized products of monomers' Hartree-Fock (HF) determinants and is a triple perturbation expansion: in powers of the intermolecular perturbation operator V and of the Møller-Plesset potentials of monomers, W_A and W_B. The latter expansion is analogous to many-body perturbation theory of electron correlation and leads to similar scalings with system size. In the early 2000s, Williams and Chabalowski [3] proposed to replace the HF determinants by Kohn-Sham (KS) ones and omit all powers of W_C. While this original idea does not work well, future improvements resulted in a theory, called SAPT based on DFT description of monomers [SAPT(DFT)], which gives interaction energies as accurate as those from regular SAPT with N^7 scaling, but scales as only N^5 (see Refs. 4–6 for the final version of this method). SAPT(DFT) can be applied to dimers containing about two hundreds of atoms and gives interaction energies for such systems with uncertainties competitive with any method applicable to systems of such sizes [7]. This performance has strong physical grounding.

SAPT interaction energy is a sum of physical components and one of these components is the dispersion energy. This quantity computed from SAPT can be used in various ways to investigate and cure problems of DFT in recovering dispersion energies. First, SAPT dispersion energies can be used in the so-called DFT plus dispersion (DFT+D) approaches, as done in Ref. 8, see also Ref. 9. Insights from SAPT have been used to construct a new nonlocal functional [10] which reproduces dispersion energies better than any published functional of this type. Finally, SAPT dispersion energies can be used to evaluate quality of various published dispersion expressions [11].

---

[1] B. Jeziorski, R. Moszyński, and K. Szalewicz, Chem. Rev. **94**, 1887 (1994).
[2] K. Szalewicz, Wiley Interdisc. Rev.–Comp. Mol. Sci. **2**, 254 (2012).
[3] H. L. Williams and C. F. Chabalowski, J. Phys. Chem. A **105**, 646 (2001).
[4] A. J. Misquitta and K. Szalewicz, J. Chem. Phys. **122**, 214109 (2005).
[5] A. J. Misquitta, R. Podeszwa, B. Jeziorski, and K. Szalewicz, J. Chem. Phys. **123**, 214103 (2005).
[6] A. Hesselmann, G. Jansen, and M. Schütz, J. Chem. Phys. **122**, 014103 (2005).
[7] J. Garcia and K. Szalewicz, J. Chem. Theory Comput. (2020), manuscript in preparation.
[8] K. Pernal, R. Podeszwa, K. Patkowski, and K. Szalewicz, Phys. Rev. Lett. **103**, 263201 (2009).
[9] M. Shahbaz and K. Szalewicz, Phys. Rev. Lett. **121**, 113402 (2018).
[10] M. Shahbaz and K. Szalewicz, Phys. Rev. Lett. **122**, 213001 (2019).
[11] M. Shahbaz and K. Szalewicz, Theor. Chem. Acc. **138**, 25 (2019).