

Perturbation theory of intermolecular interactions based on density-functional description of monomers

Krzysztof Szalewicz, Alston J. Misquitta, and Bogumil Jeziorski

University of Delaware

Symmetry-adapted perturbation theory (SAPT) provides not only a conceptual basis for understanding intermolecular interactions but also an efficient computational framework for accurate predictions of interaction energies [1, 2]. The pair interactions and three-body nonadditive interactions of arbitrary closed-shell molecules can now be computed using the program SAPT2002 [3]. This approach has provided some of the most accurate intermolecular potentials for various dimers and trimers, as confirmed by comparisons of the computed spectra with experiment. In particular, the water dimer and trimer spectra agreed with experiment very well [4] and the predictions of the SAPT potential are competitive to those provided by empirical potentials fitted to the spectra. Simulations of liquid water with SAPT potentials [5, 6] provided the first quantitative determination of the role that the three-body effects play in this system.

Investigations of ultracold molecules put stringent requirements on the accuracy of potentials needed to model the systems. To meet these requirements, one would have to use very large basis sets, which may be not practical since calculations employing SAPT (or any other electronic structure method that includes correlation effects at a level adequate for describing intermolecular interactions) require relatively significant computer resources. A solution to this difficulty could be a SAPT approach utilizing density-functional theory (DFT) description of monomers. Such a method, now called SAPT(DFT), has been first proposed by Williams and Chabalowski [7] and later developed by us [8, 9] and independently by Hesselmann and Jansen [10]. The method does not rely on asymptotic expansions and therefore is applicable for all separations between the interacting molecules.

It is well known that DFT applied in the supermolecular way fails to describe an important part of the van der Waals forces, the dispersion interaction. In fact, we have shown [8] that supermolecular DFT calculations lead to large errors also in other interaction energy components (the electrostatic, induction, and exchange interactions) due to an incorrect behavior of electron densities at distances from nuclei that are relevant for intermolecular interactions. The SAPT(DFT) approach avoids these problems by using DFT only to describe each monomer, but calculating the interaction energies from expressions beyond DFT. In addition, the wrong long-range behavior of monomer densities is fixed by applying an asymptotic correction to the exchange-correlation potential of DFT. SAPT(DFT) calculations require only a small fraction of computer resources used by the regular SAPT and converge much faster in the size of the basis sets. Moreover, although initially SAPT(DFT) was expected to be a method providing medium quality results for very large molecules, it turned out that at least in some cases the accuracy of SAPT(DFT) surpasses that which can be reached with the currently programmed regular SAPT and reasonable size basis sets. Our most recent results for several dimers show that in all cases when there were significant discrepancies between the results from the two approaches, these were resolved in favor of SAPT(DFT), i.e., were resulting from theory level truncations and basis set incompleteness in the regular SAPT calculations.

[1] B. Jeziorski, R. Moszynski, and K. Szalewicz, *Chem. Rev.* **94**, 1887 (1994).

[2] B. Jeziorski and K. Szalewicz, in *Handbook of Molecular Physics and Quantum Chemistry*, edited by S. Wilson, Wiley, 2002, Vol. 3, Part 2, Chap. 9, p. 232.

[3] *SAPT2002: An Ab Initio Program for Many-Body Symmetry-Adapted Perturbation Theory Calculations*

lations of Intermolecular Interaction Energies by R. Bukowski *et al.*, University of Delaware and University of Warsaw: <http://www.physics.udel.edu/~szalewic/SAPT/SAPT.html>.

- [4] G. C. Groenenboom, E. M. Mas, R. Bukowski, K. Szalewicz, P. E. S. Wormer, and A. van der Avoird, *Phys. Rev. Lett.* **84**, 4072 (2000).
- [5] E. M. Mas, R. Bukowski, and K. Szalewicz, *J. Chem. Phys.* **118**, 4386 (2003).
- [6] E. M. Mas, R. Bukowski, and K. Szalewicz, *J. Chem. Phys.* **118**, 4404 (2003).
- [7] H.L. Williams and C.F. Chabalowski, *J. Phys. Chem. A* **105**, 646 (2001).
- [8] A.J. Misquitta and K. Szalewicz, *Chem. Phys. Lett.* **357**, 301 (2002).
- [9] A.J. Misquitta, B. Jeziorski, and K. Szalewicz, *Phys. Rev. Lett.* **91**, 033201 (2003).
- [10] A. Hesselmann and G. Jansen, *Chem. Phys. Lett.* **357**, 464 (2002); *ibid.* **362**, 319 (2002); *ibid.* **367**, 778 (2003).