

Density-Fitted Implementation of Open-Shell SAPT Energies and Validity of the S^2 Approximation

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Intermolecular interactions play an ubiquitous role in chemistry and biology, with representative examples including protein-ligand interactions, supramolecular assembly, pre-reactive complexes, etc. The theoretical decomposition of intermolecular interactions into physically meaningful terms enhances our understanding of such processes and helps us design more efficient chemical systems. Among the various existing decomposition schemes, Symmetry-Adapted Perturbation Theory (SAPT)[1] may be considered as the most successful, as it naturally decomposes the interaction energy into physical and intuitive terms such as electrostatics, exchange, induction and dispersion. Until recently, most SAPT implementations were restricted to closed-shell systems, precluding the analysis of interactions between high-spin radical systems or between a radical and a closed-shell molecule. In the present work, we implement the open-shell version of lowest-order SAPT energy terms, including $E_{elst}^{(10)}$, $E_{exch}^{(10)}$, $E_{ind,r}^{(20)}$, $E_{exch-ind,r}^{(20)}$, $E_{disp}^{(20)}$ and $E_{exch-disp}^{(20)}$ in the software PSI4.[2] All the energy terms make use of the efficient density fitting approximation, thereby allowing the study of large radical systems.

Moreover, the present open-shell implementation of SAPT allow us to assess the S^2 approximation to the full antisymmetrizing operator in the exchange energy for open-shell systems, thus complementing the existing literature on closed-shell systems.

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

[2] Turney, J. M.; Simmonett A. C.; Parrish R. M.; Hohenstein E. G.; Evangelista F.; Fermann J. T.; Mintz B. J.; Burns L. A.; Wilke J. J.; Abrams M. L.; Russ N. J.; Leininger M. L.; Janssen C. L.; Seidl E. T.; Allen W. D.; Schaefer H. F.; King R. A.; Valeev E. F.; Sherrill C. D.; Crawford T. D., *WIREs Comput. Mol. Sci.* **2012**, *2*, 556.