

Symmetry-Adapted Perturbation Theory Based on Multiconfigurational Wave Function Description of Monomers

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We present a formulation of the multiconfigurational (MC) wave function symmetry-adapted perturbation theory (SAPT). The method is applicable to noncovalent interactions between monomers which require a multiconfigurational description, in particular when the interacting system is strongly correlated or in an electronically excited state. SAPT(MC) is based on one- and two-particle reduced density matrices of the monomers and assumes the single-exchange approximation for the exchange energy contributions. Second-order terms are expressed through response properties from extended random phase approximation (ERPA). The dispersion components of SAPT(MC) have been introduced in our previous works [1,2]. SAPT(MC) is applied either with generalized valence bond perfect pairing (GVB) or with complete active space self-consistent field (CASSCF) treatment of the monomers. We discuss two model multireference systems: the $\text{H}_2 \cdots \text{H}_2$ dimer in out-of-equilibrium geometries and interaction between the argon atom and excited state of ethylene. Using the $\text{C}_2\text{H}_4^* \cdots \text{Ar}$ complex as an example, we examine second-order terms arising from negative transitions in the linear response function of an excited monomer. We demonstrate that the negative-transition terms must be accounted for to ensure qualitative prediction of induction and dispersion energies and develop a procedure allowing for their computation. Factors limiting the accuracy of SAPT(MC) are discussed in comparison with other second-order SAPT schemes on a data set of small single-reference dimers.

[1] M. Hapka, M. Przybytek, K. Pernal, *J. Chem. Theory Comput.* 2019, 15, 1016-1027.

[2] M. Hapka, M. Przybytek, K. Pernal, *J. Chem. Theory Comput.* 2019, 15, 6712-6723.