

Symmetry-adapted perturbation theory

Krzysztof Szalewicz

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

Intermolecular forces determine properties of condensed phases and of biological systems. These properties can be predicted provided the intermolecular interaction potentials (force fields) are known. With recent progress in electronic structure methods, potentials computed from first principles are surpassing the previously used empirical potentials in terms of quality of predictions. The most natural approach to intermolecular interaction is perturbation theory starting from noninteracting monomers. To obtain properly behaving potentials, one has to impose permutational symmetry on the wave functions to satisfy Pauli's exclusion principle. This procedure results in the so-called symmetry-adapted perturbation theory (SAPT) of intermolecular interactions [1, 2]. Some fundamental developments of SAPT are due to Adams and coworkers [3–8]. SAPT became a powerful computational tool, enabling generation of pair potentials for fairly large systems, with monomers containing 20 or more atoms. The treatment of such large systems became possible due to the development of SAPT based on density-functional theory (DFT) description of monomers [SAPT(DFT)] [9–11]. This method gives results comparable to those of the coupled-cluster approach with single, double, and noniterative triple excitations at a much lower computational cost. Interaction energies for systems as large as the dimer of perylene, containing 64 atoms, have been computed using SAPT(DFT). The intermolecular potentials developed using SAPT have been used to set thermophysical standards [12], interpret spectra of clusters [13, 14], and to predict the structure of molecular crystals [15]. An important emerging application of SAPT(DFT) are investigations of interactions of biomolecules.

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