Perturbation-adapted Perturbation Theory

Peter J. Knowles

Cardiff University

KnowlesPJ@Cardiff.ac.uk

A new general approach is introduced[1] for defining an optimum zero-order Hamiltonian for Rayleigh-Schrödinger perturbation theory. Instead of taking the operator directly from a model problem, it is constructed to be a best fit to the exact Hamiltonian within any desired functional form. When applied to many-body perturbation theory for electrons, strongly improved convergence is observed in cases where the conventional Fock Hamiltonian leads to divergence or slow convergence. This alternative to Møller-Plesset perturbation theory is explored, comparing its performance to that of Møller-Plesset for thermochemistry, reaction barrier heights, non-covalent interactions and the breaking of covalent bonds.

(1) Knowles, P. J. *J. Chem. Phys.* **2022**, *156*, 011101.

(2) Surján, P. R.; Kohalmi, D.; Szabados, Á. *J. Chem. Phys.* **2022**, *156*, 116102.