

On perturbative correction to spin-projected Hartree-Fock

Takashi Tsuchimochi and Seiichiro L. Ten-no

Graduate School of System Informatics, Kobe University, Japan

Computationally practical multiconfiguration wave functions are necessary for describing large multi-reference systems. Spin-projected Hartree-Fock is a very compact single-reference ansatz that automatically generates a multiconfiguration wave function. However, dynamical correlation is indispensable to obtain quantitative accuracy. For this purpose, we have developed second-order perturbation theory with spin-projected Hartree-Fock being a zeroth-order state. The first-order wave function is represented by a linear combination of particle-hole excited configurations followed by spin-projection. The generalized Fock operator is used to construct a spin-free zeroth-order Hamiltonian. To avoid the intruder state problem, we adopt the level-shift techniques frequently used in other multi-reference perturbation theories. The method is applied to transition metal complexes for computing spin gaps as well as the potential energy curve of the chromium dimer.