A new size extensive multireference perturbation theory

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Abstract: A new multireference perturbation series is derived based on the Reighley-Schrödinger perturbation theory. It is orbitally invariant. Its computational cost is comparable to the single reference Møller–Plesset perturbation theory. It is demonstrated numerically that the present multireference second and third order energies are size extensive by two types of super-molecules composed of H_2 and BH monomers. Spectroscopic constants of $F_2(X^1\Sigma_g^+)$, $Cl_2(X^1\Sigma_g^+)$, $C_2^-(X^2\Sigma_g^+)$, $B_2(X^3\Sigma_g^-)$ and $C_2^+(X^4\Sigma_g^-)$ as well as the ground state energies of H_2O, NH_2 and CH_2 at three bond lengths have been calculated with the second multireference perturbation theory. The dissociation behaviors of CH_4 and HF have also been investigated. Comparisons with other approximate theoretical models as well as the experimental data have been carried out to show their relative performances.

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