Direct ΔMBPT(2) method for ionization potentials and excitation energies using fractional occupation numbers

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A direct method (D-ΔMBPT(2)) to calculate second-order ionization potentials and excitation energies is developed. The ΔMBPT(2) method is defined as the correlated extension of the ΔHF method. Energy differences are obtained by integrating the energy derivative with respect to occupation numbers over the appropriate parameter range. This is made possible by writing the second-order energy as a function of the occupation numbers. Relaxation effects are fully included at the SCF level. This is in contrast to linear response theory, which makes the D-ΔMBPT(2) applicable not only to single excited but also higher excited states. We show the relationship of the D-ΔMBPT(2) method for ionization potentials and electron affinities to a second-order approximation of the effective Fock-space coupled-cluster Hamiltonian and a second-order electron propagator method. We also discuss the connection between the D-ΔMBPT(2) method for excitation energies and the CIS-MP2 method. Finally, as a proof of principle, we apply our method to calculate ionization potentials and excitation energies of some small molecules. For ionization potentials, the ΔMBPT(2) results compare well to the second-order solution of the Dyson equation. For excitation energies, the deviation from EOM-CCSD increases when correlation becomes more important. When using the numerical integration technique, we encounter difficulties that prevented us from reaching the ΔMBPT(2) values. Most importantly, we conclude that relaxation beyond the Hartree Fock level is significant.