

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

Ariana Beste¹, Álvaro Vázquez-Mayagoitia², J. Vincent Ortiz³

¹Joint Institute for Computational Sciences, University of Tennessee, Oak Ridge, TN 37831

²Argonne Leadership Computing Facility, Argonne National Laboratory, Argonne, IL 60439

³Department of Chemistry and Biochemistry, Auburn University, Auburn, AL 36849

A direct method (D- Δ MBPT(2)) to calculate second-order ionization potentials and excitation energies is developed. The Δ MBPT(2) method is defined as the correlated extension of the Δ HF 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- Δ MBPT(2) applicable not only to single excited but also higher excited states. We show the relationship of the D- Δ MBPT(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- Δ MBPT(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 Δ MBPT(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 Δ MBPT(2) values. Most importantly, we conclude that relaxation beyond the Hartree Fock level is significant.

This research was conducted at the Center for Nanophase Materials Sciences, which is sponsored at Oak Ridge National Laboratory by the Scientific User Facilities Division, Office of Basic Energy Sciences, U.S. Department of Energy. This research was supported by an allocation of advanced computing resources provided by the National Science Foundation. The computations were performed on Kraken at the National Institute for Computational Sciences (<http://www.nics.tennessee.edu/>). One of the authors (JVO) acknowledges support from the National Science Foundation to Auburn University through grant CHE-0809199.