Critical Assessment of Coupled Cluster Methods for Computing Core Ionization Potentials of Small Molecules

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It is well known that in Canonical Hartree-Fock theory the orbital energies are approximations to ionization potentials (IPs) via Koopmans' Theorem. While these IPs are not chemically predictive, they do provide *qualitatively* correct ordering of the IPs in many instances. Although Koopmans' Theorem does not apply to Kohn-Sham (KS) orbitals, D.P. Chong has reported using Density Functional Theory (DFT) to obtain more accurate core and valence IPs by taking into account the relaxation of the orbitals after the removal of an electron.[1,2] The present work demonstrates Coupled Cluster (CC) Theory's accuracy for computing core IPs of the G2 test set. There are complications within equation of motion methods; in particular, convergence using Davidson Diagonalization for high-energy states can be difficult, especially for EE-EOM-CC Theory.

Our approach utilizes three schemes to evaluate the core IPs of the test set. First, we use the equation of motion method, IP-EOM-CCSD, to compute the core IPs. The second method we employ is $\Delta CCSD_{nonopt}$, whereby all occupied orbitals are optimized at the CCSD/aug-cc-pCVXZ (X=T, Q) level of theory, and then the energy is recalculated in the presence of a hole (an empty core orbital) with all other orbitals frozen. The difference of the two energies yields an approximate IP. Finally, we use the $\Delta CCSD_{opt}$ approach, similar to the $\Delta CCSD_{nonopt}$ method; however, the orbitals are reoptimized in the presence of the hole state to account for relaxation effects. $\Delta CCSD_{opt}$ exhibits occasional convergence sensitivity related to variational collapse of the wavefunction.

[1] D. P. Chong, J. Chem. Phys. **111** (21), 9485, (1999).
[2] D. P. Chong, J. Chem. Phys. **116** (5), 1760, (2002).