A Systematic Study to Improve Core Ionization Energies using Douglas-Kroll-Hess Transformations and a Novel Direct ΔE_{SCF} Algorithm via Coupled-Cluster Theory

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Abstract

We explore the utility, in terms of accuracy and efficiency, of various direct and indirect Hartree-Fock and Coupled Cluster theories to compute the principal core ionization potentials (IP) of molecules. The following methods were used: ΔE_{SCF} , $\Delta E_{CCSD,relaxed}$, $\Delta E_{CCSD,nonrelaxed}$, and IP-EOM-CCSD. Since the dominant energetics are the relaxation processes of the remaining electrons in a core ionization, and this is adequately described using Hartree-Fock theory, a "Direct ΔE_{SCF} " algorithm was formulated to capture the relaxation energy to *infinite* order. This algorithm uses, and does not modify, the N-electron HF orbitals and converges extremely well, as opposed to performing a HF calculation on the cation. It is also general and can be used with any SCF method, including Kohn-Sham DFT. Relativistic effects were probed and incorporated using the Douglas-Kroll-Hess scalar-relativistic transformed Hamiltonian. Although unimportant for small molecules, the DKH transformation is necessary for highly stripped atoms, enabling an efficient route to study plasmas.