A Quantitative Description of Orbital Relaxation in Core Ionization Processes

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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 unrelaxed IPs are not chemically predictive, they do provide a *qualitatively* correct ordering of the IPs in many instances. Kohn-Sham orbital energies, on the other hand, can yield reasonably accurate *relaxed* vertical IPs[1,2] when compared to experiment. Much progress has been made in understanding this orbital relaxation using the Green's function formalism with the goal of helping spectroscopists decipher detailed ionization spectra.[3] The latter methods are practical only for smaller systems and therefore not widely applicable. There has, however, been a limited number of studies devoted to obtaining a non-empirical operator form for orbital relaxation that would be used at the self-consistent field (SCF) stage of a computation. The present work is an effort to formulate relaxation from first-principles. Our approach utilizes three schemes to evaluate the core IPs of the G2 test set with the purpose of separating relaxation and correlation from the SCF and post-SCF energies to better understand the two effects.

First, we use the equation of motion method, IP-EOM-CCSD, to compute the core IPs. There are complications within equation of motion methods; in particular, convergence using Davidson Diagonalization for high-energy states can be difficult. The second method we employ is $\Delta\text{CCSD}_{\text{nonopt}}$, where the energy difference between the N and the $N-1$ states yields the ionization energy, and the relaxation contributions should arise from $e^{\hat{T}_1}$ only. Finally, we use the $\Delta\text{CCSD}_{\text{opt}}$ approach, similar to the $\Delta\text{CCSD}_{\text{nonopt}}$ method; however, the SCF orbitals are reoptimized in the presence of the core-hole state to account for relaxation effects at the HF-SCF level. $\Delta\text{CCSD}_{\text{opt}}$ exhibits occasional convergence sensitivity related to the variational collapse of the wavefunction. The results help to elucidate the contributions solely from relaxation and provide a promising route to accurately determine ionization energies.

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[2] D. P. Chong, *J. Chem. Phys.* **116** (5), 1760, (2002).
[3] M. C. Bohm, *J. Phys. B.* **17**, 3103, (1984).