Photoionization and Photodetachment Spectra From Equation-of-Motion Coupled-Cluster Dyson Orbitals

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Photoionization and photodetachment spectroscopy experiments are powerful techniques for probing the electronic structure of molecules and ions, but are difficult to interpret without the help of theory. The modeling of photoionization/photodetachment spectra requires calculating the wavefunctions of the initial (ground or excited state) N-electron system, the final N-1-electron system, as well as the final wavefunction of the ejected photoelectron. All the necessary information related to the N and N-1 electron wavefunctions is embodied in a Dyson orbital. Dyson orbitals can be computed from equation-of-motion coupled-cluster (EOM-CC) wavefunctions. EOM-CC Dyson orbitals include correlation and orbital relaxation effects missing in Koopmans' framework, and different flavors of EOM-CC can be used to describe photoionization in strongly correlated systems such as diradicals, triradicals, and electronically excited states. We show that it is possible to reproduce experimental photodetachment spectra of anions as well as photoionization spectra of atoms and molecules using EOM-CC Dyson orbitals with a relatively simple treatment of the photoelectron wave function; namely, using plane waves for the case of photodetachment from anions, Coulomb waves for photoionization from atoms, and Coulomb waves with a partial (effective) charge smaller than unity in the case of molecules.

Reference: Gozem, S.; Gunina, A.O.; Ichino, T.; Osborn, D.L.; Stanton, J.F.; Krylov, A.I. Photoelectron wave function in photoionization: Plane wave or Coulomb wave? *J. Phys. Chem. Lett.* **2015***, 6,* 4532–4540.