NEW METHODS FOR CORE-HOLE SPECTROSCOPY BASED ON COUPLED CLUSTER

<u>MEGAN SIMONS</u>, DEVIN A. MATTHEWS, *Department of Chemistry, Southern Methodist University, Dallas, TX, USA*.

Equation-of-Motion Coupled cluster (EOM-CC) is a preferred method for high-precision electronic spectroscopy due to its size-extensivity and implicit inclusion of higher-order excitation effects in the electronic wavefunction. The accuracy of the EOM-CC wave function can be controlled by truncating the cluster operator, T, and/or excitation operator, R, at increasing levels of excitation. Within core-hole calculations (XPS, XAS/NEXAFS, XES, and RIXS), the inclusion of triple excitations, in concert with the core-valence separation (CVS), is critical in order to accurately treat orbital relaxation effects; however, including triple excitations unavoidably leads to high computational cost. Instead, we propose two alternative approaches: first, in Transition-Potential Coupled Cluster (TP-CCSD), orbital relaxation is explicitly included in the reference orbitals through the use of a fractional-occupation SCF calculation followed by CVS-EOM-CCSD. Second, the CVS-STEOMEE-CCSD+cT method extends the similarity-transformed EOM-CC approach of Nooijen with triple excitations, but only for the inexpensive core ionization potentials. We benchmark both methods for first-row K-edge vertical ionization and excitation energies of 14 small molecules, compared to the accurate but extremely expensive CVS-EOMEE-CCSDT method, as well as select comparisons to experimental gas-phase XAS. We find that both methods are effective in treating the orbital relaxation of core-hole states, with absolute energy errors below 0.5 eV and relative errors for peak positions typically below 0.3 eV. Both methods are also computationally efficient: TP-CCSD has the same computational cost as the less-accurate CVS-EOM-CCSD method, while CVS-STEOMEE-CCSD+cT is only marginally more expensive for a small number of excitations. For large numbers of excited states, the STEOM-based approach may be significantly faster.