

Transition-Potential Coupled Cluster

Megan Simons, Devin Matthews

Southern Methodist University, Department of Chemistry, Dallas, TX 75275

X-ray absorption spectroscopy (XAS) has been used for many years by experimental chemists to study electronic and molecular structure, but theoretical calculations can often assist in interpreting spectra as well as predicting spectra of unknown compounds. Theoretical chemists have predominately used density functional theory (DFT) methods for XAS. Techniques such as Transition-Potential DFT (TP-DFT) and Δ Kohn-Sham improve on TD-DFT, but the systematic improvability of equation-of-motion coupled cluster (EOMCC) methods provides a significant motivation for applying EOM-CC to XAS. However, the large orbital relaxation energy is challenging for a purely linear response method due to the nature of the core hole, and absolute errors of 1–5 eV remain at the CCSD level.

Here, we suggest a “Transition-Potential Coupled Cluster” method in analogy to TP-DFT, in hopes of reducing the orbital relaxation error. In TP-CC, we use reference orbitals from a TP-DFT calculation with 1/2 electron (total) in the core orbitals. The orbitals are then reoccupied a la QRHF and used in a normal CC calculation. The TP-DFT calculations were performed in psi4 using the psixas plugin and then exported to CFOUR format. A development version of CFOUR was then used to calculate the core-valence separated equation-of-motion coupled cluster singles and doubles (CVS-EOM-CCSD) excitation energies, as well as ionization energies. TP-CC and vanilla CVS-EOM-CCSD calculations are compared to the excitation energies calculated using CVS-EOM-CCSDT, which served as a benchmark. The calculations were run using a small test set of various molecules: C₂H₄, HCN, H₂O, NH₃, and CO. Calculations with 1/2 or 1/4 core holes and either a TP- or XTP-DFT reference were performed (the latter places the partially ionized electrons in the LUMO). There seems to be some promise with 1/2 electron and 1/4 electron transition potential calculations, but more investigation is needed into convergence issues and potential systematic errors.