RELATIVISTIC DELTA-COUPLED-CLUSTER CALCULATIONS OF K-EDGE CORE-IONIZATION ENERGIES FOR THIRD-ROW ELEMENTS

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Core-valance separated delta-coupled-cluster (CVS-ΔCC) with spin-free exact two-component theory in its one-electron variant (SFX2C-1e) has been shown to provide quantitative description of core-ionization energies for second-row elements [1]. Here we extend the applicability of CVS-ΔCC calculations to K-edge core-ionization energies for third-row elements. We develop a revised CVS scheme to make it applicable in larger basis sets. Basis-sets effects have been demonstrated to be important. The use of uncontracted cc-pCVTZ basis sets for target atom and cc-pVTZ sets for the other atoms appears to be an efficient and accurate approach (cc-pCVTZ-unc*). High-level relativistic (HLR) corrections beyond the SFX2C-1e, including two-electron picture change, spin-orbit coupling, Breit interaction and QED effects have been taken into account and shown to play an important role. SFX2C-1e CVS-ΔCCSD(T)/cc-pCVTZ-unc* calculations augmented with high-level relativistic corrections can provide highly accurate K-edge core-ionization energies of third-row elements with deviation of less than 0.5 eV from experimental values.

Reference

[1] Zheng, Cheng, J. Chem. Theory Comput. **15**, 4945–4955 (2019).