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While scalar-relativistic core-valence separated equation-of-motion coupled-cluster [1] methods can provide quantitative description of core ionization energies [2,3], the necessity of including higher excitations (full triples and quadruples) limits the applicability to small molecules. Here we explore the use of delta-coupled-cluster (Δ CC) methods as an efficient alternative that is applicable to larger molecules. The Δ CC methods perform CC calculations separately for the neutral and core ionized states and thus fully account for the orbital relaxation induced by the core hole in the core ionized state. The convergence difficulty in Δ CC equations [4] is solved by adapting the generic idea of core-valence separation (CVS) [5] to Δ CC. In benchmark calculations of chemical shifts for the core ionization energies for second-row elements, Δ CCSD(T) is shown to be as accurate as EOM-CCSDTQ, which is by far a more expensive method. It is also shown that the errors introduced by CVS within Δ CC for the absolute values of core ionization energies is around 0.5 eV and should be taken care of when aiming at high-accuracy calculations of the absolute values.

References

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