Relativistic Coupled Cluster with Completely Renormalized and Perturbative Triples Corrections and Spin-Orbit Coupling

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We have implemented noniterative triples corrections to the coupled-cluster with singles and doubles (CCSD) energetics within the exact two-component (X2C) relativistic framework using the CCSD(T) and completely renormalized (CR) CC(2,3) formalisms. The efficacy of these approaches is showcased by performing all-electron correlated calculations of the ground-state potential energy curves of copper, silver, and gold dimers along with selected spectroscopic constants. We demonstrate that for these test systems, the X2C framework is necessary to recover the correct shape of the potential energy curves. Furthermore, correlation effects due to triply excited clusters change the dissociation energies by about 0.1–0.2 eV or about 4–7% for these dimers. We also use these test systems to show the need for high-quality basis sets for correlated X2C calculations, especially those that include core correlations.