Cost-effective approaches for relativistic electron-correlated calculations

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Four-component methodologies based on the no-pair Dirac-Coulomb (DC) Hamiltonian [1] offer the possibility for a rigorous treatment of relativistic effects in quantum chemistry. Unfortunately, DC-based correlation methods such as the DC coupled-cluster (CC) approaches are at least one order of magnitude more expensive than corresponding nonrelativistic schemes due to spin-symmetry breaking. Moreover, scalar-relativistic effects often dominate the relativistic corrections; spin-orbit (SO) effects are mainly responsible for level splitting and related phenomena. [3]

In this work a cost-effective scheme is presented which consists of a high-level spin-free Dirac-Coulomb (SFDC) calculation [4, 5] augmented by an approximate treatment of SO effects via perturbation theory. [6] In the latter, we treat the difference between the DC and SFDC Hamiltonian as the perturbation, and the second-order SO energy correction is computed as a second derivative of the SFDC energy at the Hartree-Fock level. The efficacy of the proposed scheme is demonstrated in benchmark calculations of energies and electrical properties for a set of diatomic molecules. We also report a first chemical application of the suggested approach to various gold-containing compounds.

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