New Implementation of Spin-orbit Coupling Calculation on Multi-configuration Electron Correlation Theory

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Abstract

For treating both relativistic effect and electron correlation, the spin-free exact two-component and spin-dependent first-order Douglas-Kroll-Hess (sf-X2C-so-DKH1) Hamiltonian and the state-interaction (SI) method are combined to calculate the spin-orbit coupling (SOC) on multi-configuration electron correlation theory. Here, SOC is evaluated via SI among the spin-free states from the complete active space self-consistent field (CASSCF) calculation, and the dynamic electron correlation could be reckoned via the high-level multi-reference electron correlation method. Work equations to evaluate SOC matrix elements over spin-adapted Gelfand states in the framework of the graphic unitary group approach (GUGA) are presented. Benchmark calculations have verified the validity of the present implementation. As a pilot application, the internally contracted MRCI (icMRCI) with the inclusion of SOC calculation produces the reasonable equilibrium bond length and the harmonic vibrational frequency of the ground state of AuO, as well as the transition energy of $X\^2\Pi_{3/2} \leftarrow \^2\Pi_{1/2}$.

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