Equation of Motion Coupled-Cluster Theory with Spin-Orbit Coupling

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Abstract

Recently we developed a coupled-cluster approach (CC) with spin-orbit coupling (SOC) for closed-shell systems with SOC included in post-Hartee-Fock treatment. This SOC-CC approach is efficient due to the use of real spin orbitals and accurate due to a proper treatment of orbital relaxation and analytical first and second order derivates of this SOC-CC approach at the CCSD and CCSD(T) levels have also been developed. Both time-reversal symmetry and spatial symmetry for D_{2h} and its subgroups are exploited in the implementation [1]. In the present work, we report implementation of the equation of motion method based on this closed-shell SOC-CC approach for excitation energies, ionized states [2] as well as electron attachment [3]. Both ground and excited state energies for open-shell systems with one more or one less electron compared with the closed-shell reference state can thus be calculated. Analytical energy gradient for excited states and ionized states at EOMEE-CCSD and EOMIP-CCSD level have also been implemented, which enable geometry optimization, harmonic frequencies calculations for excited or ionized states with SOC. In addition, EPR g-tensors for ionized states can also be calculated.

Keywords:

Spin-orbit coupling; excitation energies; analytical energy gradient

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