Geometrical Derivatives and EPR G-tensor Based on Equation of Motion Coupled- Cluster Theory with Spin-Orbit Coupling

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Recently we developed a coupled-cluster approach (CC) for closed-shell systems with SOC included in post-Hartee-Fock treatment. Total energy, analytical first and second order derivates of this SOC-CC approach at the CCSD and CCSD(T) levels have been developed. Both time-reversal symmetry and spatial symmetry for D_{2h} and its subgroups are exploited[1] in the implementation. In addition, the equation of motion method based on this SOC-CC approach for excitation energies, ionized states[2] as well as electron attachment[3] is also developed.

Analytical energy gradient of this EOM-CCSD approach for excited, ionized or electron attached states with SOC has been implemented, which facilitates geometry optimization, harmonic frequencies calculations. In the implementation, a Lagrangian is introduced to avoid calculating first order derivatives of the eigenvectors and cluster operator. In addition, EPR g-tensor for open-shell molecules with one unpaired electron has also been calculated as a first order derivative of total energy based on EOMIP-CCSD and EOMEA-CCSD with SOC with respect to external magnetic field. To achieve high efficiency, a proper combination of different spin cases is introduced in the Lagrangian to restore time-reversal symmetry. We present equilibrium structures and harmonic frequencies of CH_2ClI^+, AuH_2 based on EOMIP-CCSD as well as those of UO_2^+ with EOMEA-CCSD. Furthermore, EPR g-tensors of some diatomic molecules are also presented.

[1] Z. Tu, D. Yang, F. Wang and J. Guo, *J. Chem. Phys.* 135, 034115, 2011.
[2] Z. Tu, F. Wang and X. Li, *J. Chem. Phys.* 136, 174102, 2012.
[3] D. Yang, F. Wang and J. Guo, *Chem. Phys. Lett.*, 531, 236, 2012.