Consistent Second Order Treatment of Spin-Orbit Coupling and Dynamic Correlation in Quasi-Degenerate N-electron Valence Perturbation Theory

Rajat S. Majumder, Alexander Y. Sokolov
Department of Chemistry and Biochemistry,
The Ohio State University, Columbus, OH, 43210

Spin-orbit interactions play a major role in understanding the magnetic properties of matter and describing the hyperfine structure of molecules and atoms. Accurate theoretical treatment of these effects has garnered significant interest, especially in modelling single-molecule magnets and molecular spintronic devices. Though significant progress has been made in simulating the spin-orbit interactions of molecular systems, accurate and efficient description of several electronic states with spin-orbit coupling (SOC) for transition metal systems and rare earth elements remains an active area of research. In this poster, I will present the first complete second-order spin-orbit coupling implementation in partially contracted quasi-degenerate N-electron Valence perturbation theory (QD-NEVPT2) using the Douglas—Kroll—Hess (DKH) type and Breit—Pauli (BP) Hamiltonians. In our implementation, the dynamical correlation and spin-orbit coupling effects are treated equally through second order in perturbation. We will demonstrate the capabilities of our new implementation for small open shell molecules and atoms with substantial spin-orbit coupling and compare our results with variational SOC methods. We will also present results on heavy element molecules where SOC dominates over correlation effects.