Spin-Orbit Symmetry Breaking and Restoring in Kramers-Unrestricted Multireference Approaches

Xiaosong Li, Andrew J. Jenkins, Hongbin Liu, Hang Hu

Department of Chemistry, University of Washington, Seattle, WA, 98195
xsli@uw.edu

The accurate description of the electronic structure of transition metals, heavy-elements, and their compounds can be complicated by both the large number of close-lying states that often have multi-configurational nature in addition to significant relativistic effects. In order to address these challenges we present a Kramers-unrestricted relativistic two-component complete-active-space self-consistent field method (CASSCF) and a multireference configuration interaction (MRCI) that includes scalar relativistic effects and one-electron spin-orbit coupling during the self-consistent wave function optimization procedure. These relativistic effects are included via an "exact two-component" transformation of the solution of the one-electron modified Dirac equation. This approach is variational in nature, allowing the orbitals to be affected by the spin-orbit coupling; a requirement for accurate description of atomic spin-orbit splittings. The ability to restore spin-orbit symmetry/degeneracy in Kramers-unrestricted multireference approaches will be discussed. The qualitative behavior of the methods is highlighted by an example of spin-orbit splitting – the sodium '*d*-line'. The correct spin-orbit splitting structure is restored by optimizing the orbitals using state averaging or using a large active space. The methods are also tests with benchmark calculations of the ground and excited state spin-orbit splitting of lower *p*- and *d*-block elements, as well as some heavy-elements, compared to experiments. The formulation developed in this work is for the general Kramers-unrestricted case, and could be extended to include magnetic field effects in the future, where time-reversal symmetry is no longer preserved.

References

1. A. Jenkins, H. Liu, J. Kasper, M. Frisch, X. Li, "Variational Relativistic Two-Component Complete Active Space Self-Consistent Field Method," *J. Chem. Theory Comput.* **15** (2019), 15, 2974.