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Spin–orbit Coupling of TDDFT Amplitudes: Left or Right?

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The need for a fast and easy procedure to include spin–orbit coupling (SOC) effects in calculations of transition metal compounds led Wang and Ziegler to devise an approximate relativistic TDDFT formalism. [1] It employs scalar relativistic auxiliary many-electron wave functions (AMEWs), constructed from the eigenvectors in Casida's formulation of TDDFT, to calculate SOC matrix elements (SOCMEs). Similar approaches to compute interstate SOCMEs from AMEWs were subsequently developed by several groups including our own. [2] One problem that arises in the framework of full linear response TDDFT and that has been addressed by a few groups only is the appropriate choice of amplitudes employed for constructing the AMEWs: When hybrid functionals are used, the eigenvalue equation for determining the amplitudes is non-Hermitian and hence left and right eigenvectors are not equal. Matrix elements of real symmetric operators (such as the electric dipole operator μ) connecting an excited state with the singlet electronic ground state are formed with the right eigenvector whereas the left eigenvector is employed for matrix elements of antisymmetric imaginary operators (such as the angular momentum operator L). It therefore seems appropriate to use the left eigenvector of a triplet state for computing SOCMEs with the singlet ground state. [3] As discussed in this contribution, this choice entails complications, however, when phosphorescence rates are to be determined in the framework of quasi-degenerate perturbation theory. Moreover, there is no clear prescription for SOCMEs between excited-state AMEWs, which are needed for both, intersystem crossing and phosphorescence rates. Extensive benchmarking against reference data from multi-reference configuration interaction wavefunctions show that electric transition dipole moments are much more sensitive with respect to the choice of AMEWs than SOCMEs. [4] The Spoiler program developed in our laboratory therefore employs renormalized right TDDFT amplitudes in conjunction with quasi-degenerate perturbation theory, but offers users the freedom of choosing the amplitudes otherwise.

References

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