Development of analytical energy gradient for two-component relativistic time-dependent density functional theory

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Precise information on excited state potential energy surfaces is the most important prerequisite for a deeper understanding of photochemical reaction or the shape of absorption and luminescence spectra. In particular, the inclusion of spin–orbit coupling and other relativistic effect is crucial for a proper description of excited-state characters, relaxation dynamics, radiative and nonradiative decay pathways, as well as lifetimes and reactivity for systems containing heavy elements. The development and efficient implementation of an analytic gradient theory for reliable theoretical models incorporating electron correlation and relativistic effect has been awaited. two-component relativistic Time-dependent density functional theory with Spin-Orbit interaction method (SO-TDDFT) is becoming popular methodologies for computing excited states containing heavy elements because of its reasonable cost and relatively high accuracy

In this work, we have implemented the two-component relativistic TDDFT with Spin-Orbit interaction method and its analytical gradient in the NTChem programs. Our implementation is based on the derivation of the geometrical derivatives for nonrelativistic TDDFT presented by Furche and Ahlrichs. The noncollinear exchange-correlation potential presented by Wang et al. has been applied. The higher-order matrix elements of the noncollinear exchange-correlation kernel for the relaxed one-particle and two-particle density matrices have been derived and implemented into efficient computer codes with the aid of a newly-developed computerized symbolic algebra system. In addition, various DFT functionals including the recently proposed range-separated hybrid functionals are applicable to the calculations of excitation energy for spin-orbit coupled states.