Calculation of Molecular Properties Using Relativistic Real-Time TDDFT

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The development and the scope of applications of relativistic real-time time-dependent density functional theory (RT-TDDFT) as implemented in quantum chemistry computer program ReSpect is presented.

The defining feature of RT-TDDFT is direct stepwise propagation of one-electron density matrix in time and on-the-fly evaluation of molecular properties. In contrast to the more widespread response theory approach, RT-TDDFT allows to access spectra in various regions, including near-resonant frequencies, from a single run, and does not require the evaluation of response kernels. The presented relativistic implementation is based on two Hamiltonians. First is the four-component Dirac–Coulomb Hamiltonian in the basis of restricted kinetically balanced Gaussian type functions exploiting the noncollinear Kramers unrestricted formalism. Second is the two-component quasirelativistic X2C Hamiltonian, obtained from the original four-component Hamiltonian by a decoupling transformation formulated entirely in matrix algebra. The former represents the fully relativistic description while the latter achieves 7-fold acceleration practically without the loss of accuracy and is thus well suited for treatment of larger molecules.

The molecular properties calculated with relativistic RT-TDDFT include the electron absorption spectra from UV/Vis \[1\] to X-ray \[2\] regions, circular dichroism spectra \[3\] as well as molecular hyperpolarizabilities \[4\]. The considered systems range from smaller benchmark systems to lanthanide compounds and heavy metal complexes.

References