Calculation of Molecular Properties Using Relativistic Real-Time TDDFT

Lukas Konecny[a], Marius Kadek[a], Mehboob Alam[b], Kenneth Ruud[a] and Michal Repisky[a]

[a] *Hylleraas Centre for Quantum Molecular Sciences, UiT The Arctic University of Norway, Tromsø, Norway* [b] *IIT Bhilai, Raipur, India*
lukas.konecny@uit.no

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

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