Relativistic iterative linear damped response TDDFT solver for predicting X-ray absorption spectra of open-shell molecules

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The damped response time-dependent DFT method (DR-TDDFT), or also known as the complex polarization propagator approach is a perturbational method used as an alternative to standard eigenvalue TDDFT. The method provides better applicability in systems with high density of states or in high-frequency domains. The size of the systems commonly computed are too large for direct calculations to be viable, which only leaves iterative approaches as a practical solution. Iterative solvers exist for both non-relativistic and relativistic frameworks. In the non-relativistic picture, the solvers can be used to compute systems with any multiplicity, as long as it can be treated with a single determinant, due to the nature of the DFT method. In the relativistic domain, the present iterative subspace solver considers hermicity and time reversal symmetry [1,2], and is applicable only to closed-shell singlet configuration systems. Methods for treatment of open-shell systems require the separation of time-symmetric general terms into symmetric and antisymmetric parts, which provides a new layer of complexity. The goal of this project is to extend the scope of the DR-TDDFT methodology by developing the formalism that allows the inclusion of open-shell systems in the relativistic domain, include it in the ReSpect software package, and assess the performance by comparing the results with experimental data.

References

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