

Enabling Open-Shell X-ray Absorption Spectroscopy Calculations within Relativistic Damped-Response TDDFT

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The damped response time-dependent density functional theory (DR-TDDFT), also known as the complex polarization propagator approach, is a perturbational method used as an alternative to standard eigenvalue TDDFT. Its main advantage lies in its superior performance for high-energy spectroscopic regions and for systems with a high density of electronic states. However, direct solution of the response equations is computationally impractical because of the large dimensionality of the matrices involved, leading to prohibitive computational cost and memory requirements. Consequently, iterative solution strategies are essential and have been developed for both relativistic and non-relativistic formulations.

Within the relativistic framework, the iterative solver exploits time-reversal symmetry and Hermiticity, and is therefore restricted to closed-shell systems [1,2]. In particular, the method relies on the presence of Kramers pair structure, which is intrinsic to closed-shell molecules. This project generalizes the relativistic iterative DR-TDDFT solver to handle any symmetry accessible within TDDFT. The resulting implementation is applied to the calculation of X-ray absorption spectra (XAS) of open-shell doublet and triplet systems, followed by a critical assessment of its performance and of the chemical insight that can be extracted from the computed spectra.

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References

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