Benchmarking study of the sTD-DFT and XsTD-DFT methods to compute first hyperpolarizabilities

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Simplified time-dependent density functional theory (sTD-DFT) and its eXact integral version (XsTD-DFT) are methods that have been developed to quickly compute electronic spectra, and linear and quadratic responses of large systems.[1],[2],[3] A specific application that is gaining interest is their use to evaluate first hyperpolarizabilities (β) in biological structures since it may prompt the design of new and improved second-harmonic imaging microscopy (SHIM) biotags.[4] However, a comprehensive benchmarking study of their performance in computing β was not carried out.

In this poster, I present a benchmarking study of the (X)sTD-DFT methods with respect to TD-DFT and CCSD(T) references. We analyzed the performance of these methods to compute β on a molecular set of more than 50 medium-sized push-pull π-conjugated systems. We studied several families of functionals and, in the first term, we analyzed the capability of (X)sTD-DFT methods to reproduce standard TD-DFT results. Working with relatively small systems allowed us to spell out which are the error sources of the results between both formalism and the quantum-physical terms to improve. We also compared CCSD(T) reference data and TD-DFT results to guide us on the new density functionals to parameterize for (X)sTD-DFT in the next stage of research.

References

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