The eXact integral simplified time-dependent density functional theory (XsTD-DFT) for global and range-separated hybrid density functionals

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In the framework of simplified quantum chemistry methods, we introduce the eXact integral simplified time-dependent density functional theory (XsTD-DFT). [1,2] This method is based on the simplified time-dependent density functional theory (sTD-DFT) where all semi-empirical two-electron integrals are replaced by exact one- and two-center atomic orbital (AO) two-electron integrals while all other approximations from sTD-DFT are kept. The performance of this new parameter-free XsTD-DFT method was benchmarked to evaluate excited state and (non)linear response properties, including ultra-violet/visible absorption, circular dichroism, optical rotation, first hyperpolarizability, and two-photon absorption.

For a set of 77 molecules, results from the XsTDA approach (or XsTD-DFT considering the Tamm-Dancoff approximation) were compared to corresponding TDA data. XsTDA/B3LYP excitation energies only deviate absolutely by 0.14 eV in average from those obtained from standard TDA while drastically cutting computational costs by a factor of 20 or more depending on the single energy threshold chosen. The absolute deviations of excitation energies with respect to the full scheme are decreasing when the system size is increasing, showing the suitability of XsTDA/XsTD-DFT to treat large systems. Comparing XsTDA and its predecessor sTDA, the new scheme globally improves excitation energies and oscillator strengths. Particularly, the XsTDA scheme can faithfully reproduce TDA results for charge transfer states, especially using range-separated hybrid density functionals.

Among the various results, TD-DFT first hyperpolarizability frequency dispersions for a set of push-pull π-conjugated molecules are faithfully reproduced by XsTD-DFT while the sTD-DFT method always provides red-shifted resonance energy positions. Excellent performance with respect to experiment is observed for the 2PA spectrum of the enhanced green fluorescent protein (eGFP). The generally excellent results with an accuracy similar to TD-DFT but at a fraction of its computational cost opens the way for a plethora of applications considering large systems as well as high throughput screening studies.

[1] M. de Wergifosse*, S. Grimme, *Journal of Physical Chemistry A*, **2021**, *125*, 3841–3851.
[2] S. Löffelsender, P. Beaujean, and M. de Wergifosse*, WIREs Comp. Mol. Sci., **2023**, 14, e1695.