Simplified methods for the (non)linear optics of large systems: applications to fluorescent proteins and introducing the “less" simplified time-dependent density functional theory (lsTD-DFT)

In a first part, we present an all-atom quantum mechanical methodology to evaluate the second harmonic generation and the two-photon absorption of the fluorescent proteins iLOV and bacteriorhodopsin.[1,2] This is now possible because of two recent implementations: the tight-binding GFN2-xTB method to optimize geometries and a related version of the simplified time-dependent density functional theory (sTD-DFT-xTB) to evaluate quadratic response functions. Excellent agreements are provided with respect to experiment.

In a second part, we introduce the “less" simplified time-dependent density functional theory (lsTD-DFT), an “ab initio” alternative to the sTD-DFT method, for which semi-empirical two-electron integrals are replaced by exact one- and two-center atomic orbital (AO) two-electron integrals, restoring its AO dependence. With this new parameter-free simplified method, we benchmarked its performance when evaluating excited state and (non)linear response properties, including ultra-violet/visible absorption, circular dichroism, optical rotation, first hyperpolarizability, and two-photon absorption.

[1] Pierre Beaujean, Benoît Champagne, Stefan Grimme, and Marc de Wergifosse *J. Phys. Chem. Lett.* 2021, 12, 39, 9684–9690.
[2] Marc de Wergifosse, Pierre Beaujean, and Stefan Grimme *J. Phys. Chem. A* 2022, submitted.