PUSHING THE BOUNDARIES OF SPECTROSCOPIC SIMULATIONS WITH REAL TIME PROPAGATION

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Real-time time-dependent density functional theory (RT-TDDFT) has become a widely used tool for the simulation of optical response. Apart from its favorable scaling and its capacity to resolve the whole frequency dependent linear response functions in one go, RT-TDDFT provides a non-perturbative framework to apply finite electro-magnetic fields, mimicking actual experiments.

In this contribution the versatility of RT-TDDFT is illustrated by showcasing its ability to simulate UV-VIS absorption, electric circular dichroism (ECD), (resonance) Raman and (resonance) Raman optical activity (ROA) spectra [1], the latter two within the short time approximation. For the formulation of the spectroscopic response tensors a unified formalism in terms of linear response propagators is applied, allowing insights into how the perturbation and response operators are distinguishable in the practical real-time linear response protocol. Special emphasis is on the choices of gauge, specifically length-, velocity- and symmetric gauges, and the coupling of the electro-magnetic fields to the non-local part of pseudo potentials, a proper handling of which proves to be vital for an adequate description of the chiral spectroscopic responses, ECD and ROA [2]. For UV-VIS absorption and Raman spectroscopy results for non-periodic and periodic simulation cells are presented, drawing on the velocity gauge and the modern theory of polarization. The results were obtained with a modified development version of the CP2K package.

These developments allow applications beyond single molecules, e. g. the study of liquids and interfaces [3].

[1] J. Mattiat, S. Luber, *J. Chem. Phys.* **151**, 234110, (2019)
[2] J. Mattiat, S. Luber, *J. Chem. Theory Comput.* **18**, 9, 5513–5526, (2022)
[3] J. Mattiat, S. Luber, *J. Chem. Theory Comput.* **17**, 1, 344–356 (2021)