Spectroscopy with RT-TDDFT

J. Mattiat[a] and S. Luber[a]

[a] *Department of Chemistry, University of Zurich, Zurich, Switzerland*
johann.mattiat@chem.uzh.ch

Time dependent density functional theory (TDDFT) is the work horse of theoretical spectroscopy due to its reasonable compromise between accuracy and computational cost. Complementary to linear response TDDFT (LR-TDDFT), like Sternheimer's or Casida's approach, a direct numerical integration of the time dependent Kohn-Sham equations is also viable for the calculation of spectroscopic properties. Distinct features of the real time TDDFT (RT-TDDFT) approach are an advantageous scaling for larger molecules, response beyond the standard linear response and the complete spectral range from just one simulation run.
Since the electronic response of the system to a perturbation is tracked in real time, a range of linear response functions can be calculated straightforwardly, giving access to purely electronic responses, such as UV/VIS and Xray absorption spectra, as well as electro-magnetic responses, such as electronic circular dichroism (ECD) spectra. These applications of RT-TDDFT are discussed with respect to gauge invariance and origin dependence also in the presence of non-local potentials [1].
Moreover RT-TDDFT has been be extended to the calculation of Raman spectra [2] in a short time approximation, using a Placzek type expansion of the electric-dipole electric-dipole polarizability [3,4]. This approach allows the simulation of full excitation profiles, including non-resonance as well as resonance Raman spectra [5]. In the resonance case Heller's excited state gradient approximation [6] is recovered from the RT-TDDFT calculations using Padé approximants [7].

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