The self-consistent Maxwell-TDDFT method and its implementation in the new framework of the Octopus code

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In the realm of quantum chemistry and materials science, the dipole approximation (DA) is by far the most widely used treatment of light-matter coupling, owing to the typically long wavelength of external electromagnetic radiation. However, when shorter wavelengths are considered (e.g. core-level spectroscopy), or when the induced electromagnetic fields are strong (e.g. nanoplasmonic systems), a description beyond DA is needed. However, such theoretical treatment to properly account for the self-induced fields is challenging.

In this work, we show an efficient fully ab initio approach to couple electrons, nuclei and photons, by self-consistently coupling Maxwell's equations with time-dependent density functional theory (TDDFT) using the Pauli full minimal coupling Hamiltonian [1]. This method is based on a rigorous density-functional reformulation of the non-relativistic Pauli-Fierz Hamiltonian of quantum electrodynamics, taking the mean-field approximation for the nuclei (Ehrenfest) and photons (Maxwell), and accounting for the full spatial and time dependence of the electromagnetic fields in the so-called full minimal coupling Hamiltonian. By simulation of light-driven molecular systems, the emergent features of such a full minimal coupling will be ilustrated for molecules and nanoplasmonic dimers.

The Maxwell-TDDFT method has been recently implemented in the Octopus package [2] using the new multisystem framework, designed to couple an arbitrary number of electronic, electromagnetic and classical systems, with different time steps, box shapes and grid spacings. This framework also allows driving external codes from Octopus, allowing the exchange of quantities during the time propagation, as was implemented for time-dependent density functional tight-binding (TDDFTB) simulations by linking Octopus with the DFTB+ code [3,4]. Future possibilities enabled by such coupling will be discussed.

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