Electromagnetic radiation in first-principles electron dynamics: an equation story

Electron dynamics simulations of atomic and molecular systems ignore in most cases an important phenomenon: radiative dissipation. Spontaneous emission, or the radiative decay of an excited electronic state, is typically absent from quantum dynamics modelling. As a consequence, the energy absorbed during the excitation of a molecule at zero temperature will remain in the system in the form of undamped dipole oscillations, indefinitely in time. We have addressed this problem starting from the idea that the electromagnetic radiation of the charge density can be approximated as the power dissipated by a classical dipole. This strategy leads to a semiclassical equation of motion that reproduces radiative emission in a simple way, providing a first-principles formalism that quantitatively captures decay rates, natural broadening, and absorption intensities [1]. The implementation of this theory in real time TDDFT simulations produces accurate excitation lifetimes for atomic species. Furthermore, its application to the description of cooperative emission in H_2 arrays predicts superradiant and subradiant behavior, unveiling the relation between spatial configuration and decoherence and how the fine-tuning of a pulse can accumulate or release optical energy in molecular assemblies [2].

[1] *Phys. Rev. Lett.* 126, 087401 (2021).
[2] *J. Phys. Chem. Lett.* 13, 11601 (2022).