Exploring Molecular Photophysical and Photochemical Properties Using Linear Response Time-Dependent Density Functional Theory with Classical Embedding

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Time-dependent density functional theory (TDDFT) based approaches have been developed in recent years to model the excited-state properties and transition processes of the molecules in gas-phase and in a condensed medium such as in solution and protein microenvironment or near semiconductor and metal surfaces. In the latter case, usually classical embedding models have been adopted to account for the molecular environmental effects, leading to the multi-scale approaches of TDDFT/PCM and TDDFT/MM, where a molecular system of interest is designated as the quantum mechanical region and treated with TDDFT, while the environment is usually described using either a polarizable continuum model (PCM) or a (non-polarizable or polarizable) molecular mechanics (MM) force fields. In this talk, I will present my group's recent works on the analytic energy derivatives for plasmon-enhanced Raman spectra and the first-order derivative couplings between the ground and excited states as well as between two excited states for the description of nonadiabatic phenomena within the theoretical framework of TDDFT/MM and TDDFT/PCM, respectively. The analytic implementation has been validated by the comparison of the analytical and finite-difference results, and reproducing experimental or other calculated results.

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