Time-dependent excited-state molecular dynamics

Yulun Han, Landon Johnson, Sameer Colbert, David Graupner, Aaron Forde, Dmitri Kilin

Department of Chemistry and Biochemistry, North Dakota State University, Fargo ND 58102

Open quantum system concept is used for practical exploration of excited state dynamics in molecules and nanostructures in the limits of electromagnetic radiation of low- and mid- intensity. Modeling of low-intensity excitations predicts radiative and nonradiative dissipation of electronic excitation energy and allows to assess efficiency of photoluminescence and charge transfer in semiconductor nanostructures. In contrast, modeling of mid-intensity laser field opens an opportunity to facilitate additional processes in molecular systems, such as chemical reactions with substantial activation energy, not available in conventional chemistry. A DFT based time-dependent excited-state molecular dynamics (TDESMD) approach offers a compromise in numeric expense / accuracy balance in modeling photoinduced chemical reactions. The TDESMD combines concepts of Rabi oscillations and trajectory surface hopping. The leading order process is represented by the molecule undergoing cyclic excitations and de-excitations. During excitation cycles, the nuclear kinetic energy is accumulated to overcome the reaction barriers. The dynamical formation of multiple products is observed in TDESMD trajectories. A recent update to TDESMD approach considers intermediates and transition states in non-singlet configurations, for the pathways including fragments and radicals. Applications of TDESMD include photofragmentation of gas-phase metal-organic complexes and small organic molecules as well as photopolymerization of inorganic monomers and photo-adsorption of functional groups to single wall carbon nanotubes, leading to formation of IR-emitting covalent defects. Similar methods were used to explore photo-desorption of ligands from surface of lead-halide perovskite nanostructures.

Supported by NSF CHE-1944921 and DOE DE-SC0021287