Nonadiabatic MD with Time-Domain Density Functional Theory

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Modeling of non-equilibrium excited state processes in nanoscale systems create new challenges to time-domain density functional theory (TDDFT) and nonadiabatic molecular dynamics (NAMD). Examples include proper treatment of quantum coherence, transition from coherent to hopping transport in long-range charge and energy transfer, super-exchange, and many-particle Auger-type processes. Motivated by these challenges, our group developed several new NAMD techniques and implemented them within TDDFT. Decoherence-induced surface hopping (DISH) incorporates decoherence effects in a way that naturally achieves trajectory branching. Coherence penalty functional (CPF) uses DFT-like ideas to introduce decoherence into the Ehrenfest method. Self-consistent fewest-switches surface hopping (SC-FSSH) provides a simple solution to the trivial (or “unavoided”) crossings in FSSH. Global flux surface hopping (GFSH) generalizes FSSH to treat super-exchange. Second quantized surface hopping (SQUASH) utilizes second quantization and generalizes FSSH to include both super-exchange and decoherence effects. We will introduce the key ideas underlying these NAMD-TDDFT approaches, and illustrate their utility with applications to excited state dynamics in nanoscale materials.

Excited state dynamics at nanoscale interfaces for solar light harvesting

Photo-induced processes at interfaces are key to photovoltaic and photo-catalytic applications. They require understanding of dynamical response of novel materials on atomic and nanometer scales. Our non-adiabatic molecular dynamics techniques, implemented within time-dependent density functional theory, allow us to model such non-equilibrium response in real time. The talk will focus on photo-initiated charge and energy transfer at interfaces involving several classes of nanoscale materials. Examples include TiO_2 sensitized with organic molecules, water, semiconductor quantum dots, graphene and perovskites, a GaN/water interface, carbon nanotube bundles, mixtures of C_{60} with inorganic particles, etc. Photoinduced charge separation across such interfaces creates many challenges due to stark differences between molecular and periodic, and organic and inorganic systems. Our simulations provide a unifying description of quantum dynamics on nanoscale, characterize the rates and branching ratios of competing processes, resolve debated issues, and generate theoretical guidelines for development of novel systems for solar energy harvesting.