Efficient Nonadiabatic Excited-State Molecular Dynamics Simulations for Large Molecules

Tammie Nelson

Theoretical Division, T-1, MS-B214, Los Alamos National Laboratory Los Alamos, NM

The simulation of photochemical and photophysical processes governed by nonadiabatic (NA) dynamics in polyatomic molecules is one of the main driving forces in the field of molecular excitonics. Over the years, we have developed a nonadiabatic excited-state molecular dynamics (NA- ESMD) framework using the fewest switches surface hopping algorithm to go beyond the Born-Oppenheimer approximation and allow NA dynamics on several coupled potential energy surfaces to be followed after light absorption. Extended molecular systems are particularly challenging to model as they often contain hundreds of atoms and have large densities of excited states participating in the NA dynamics. In this talk, I will discuss several recently developed NA-ESMD methods that allow system size limitations to be overcome. With these advances, we can now model systems with hundreds of atoms on ∼10 ps time scales exhibiting complex processes such as energy transfer, exciton localization/delocalization, and/or charge separation as well as photochemical reactions involving bond breaking and formation. Here, we have applied these techniques to model the relaxation dynamics in linear and circular oligomers and dendrimers relevant to light harvesting and photovoltaic applications, as well as in the development of optically active energetic materials.