Non-Adiabatic Molecular Dynamics Methods for Materials Discovery
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The direct conversion of sunlight to chemical energy by photocatalysis underlies solar fuel generation, efficient energy storage, and artificial photosynthesis. However, as opposed to ground-state reactions, mechanistic details of excited state processes in real materials have remained elusive, because short-lived excited state species are exceedingly difficult to characterize both experimentally and theoretically. For example, the rate-limiting step of the photooxidation of water on TiO_2 nanoparticles was still under debate when this project started [1]. The leading cause of losses in TiO_2 photocatalysts and other light driven materials are non-adiabatic transitions that convert excitation energy into heat. Such non-adiabatic radiationless transitions between electronic states are notoriously hard to control and proceed through "dark", experimentally elusive conical intersections (CIs).

The work performed under this project led to significant methodological improvements enabling the study of non-adiabatic photocatalytic processes in molecular materials using non-adiabatic molecular dynamics (NAMD) simulations with hybrid time-dependent density functional theory (TDDFT) and Tully's fewest switches surface hopping algorithm [2,3]. Our recently developed non-orthonormal Krylov space algorithm speeds up TDDFT simulations by up to a factor of five [4], and a new broken-symmetry algorithm makes both simulations of homolytic and heterolytic bond dissociations possible using TDDFT [5]. These improvements extend the applicability of TDDFT in NAMD simulations of real materials and photochemical reactions that cannot be tackled by existing methodology.

The newly developed methods were validated by simulations of acetaldehyde photodissociation reaction [5], which reproduced experimental branching ratios and kinetic energy probability distributions (KEPDs) from molecular beam experiment at a semiquantitative level. While the branching ratios are relatively insensitive to non-adiabatic effects, the reaction mechanisms and the experimental KEPDs are explained only by non-adiabatic simulations. This demonstrates that the strong correlation between nuclear and electronic motion due to non-adiabatic effects cannot be neglected even in simple photodissociation reactions.

The improved efficiency of our nonorthonormal Krylov space methods [4] enabled us to perform the first unconstrained NAMD simulations of the photooxidation of water on TiO_2 nanoparticles [1]. In these simulations, we identified a novel photooxidation mechanism involving the S_1 potential energy surface (PES) close to the S_1-S_0 CI see Fig. 1. The simulations show that unbound water is directly oxidized by the nanoparticles, yielding mobile hydroxyl radicals in agreement with the recent experiments. The calculations also revealed an important reason for the relatively low activity of undoped TiO_2 photocatalysts: Exciton binding and proximity of the particle-hole pair are required for lowering the oxidation reaction barrier, but also greatly enhance nonradiative exciton decay. These results may be valuable for future developments of more efficient photocatalysts.

Since transitions between adiabatic electronic states result from derivative couplings, and thus simulations involving more than two excited states require couplings between all pairs of excited states. We showed that derivative couplings between two TDDFT excited states (state-to-state) can be obtained from the quadratic response function [6]. However, implementation of the state-to-state couplings also uncovered severe defects in the analytical structure of the quadratic response function within TDDFT: spurious poles in the quadratic response function give rise to unphysical divergences in state-to-state properties whenever the energy difference between the two states, Ω_{mn}, matches *any other* excitation energy from the ground state [7,8]. We further showed that these divergences are not limited to TDDFT, but affect state-to-state properties from any response theory based on a nonlinear effective Hamiltonian, including response theories based on multiconfigurational self-consistent field and coupled cluster approaches.

We also developed an efficient method for simulating vibronic absorption spectra that includes Dushinsky rotation and avoids the explosion of computational cost limiting brute-force Franck-Condon approaches. The

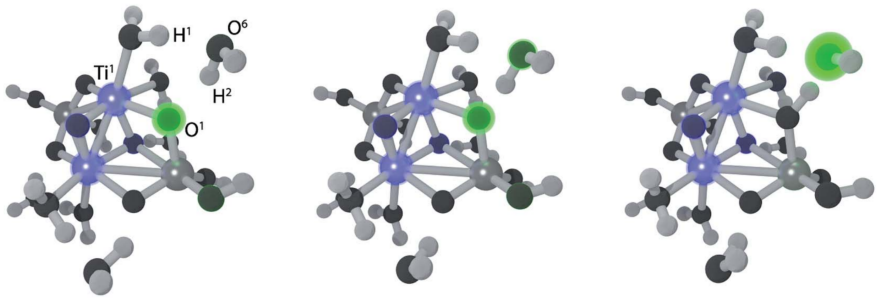

Figure 1: Snapshots from a NAMD trajectory at 200 fs (left), 213 fs (middle) and 218 fs (right) showing electron-proton transfer between water and TiO_2 nanoparticle. Blue and green colors indicate negative and positive computed excitonic (electron-hole pair) charges, respectively. Reproduced from [1] - Published by The Royal Society of Chemistry.

method was applied simulate the ultraviolet-visible spectrum of the black absorber 7,7,8,8-tetracyanoquinodimethane anion ($TCNQ^-$) [9]. Simple Gaussian broadening of vertical electronic excitations produces only one single band in the visible region, failing catastrophically. However, inclusion of vibronic effects produces nearly quantitative agreement with the experimental spectrum of $TCNQ^-$. These results underline the significance of vibronic effects in predicting the absorption spectra of molecules with large degrees of vibrational freedom.

Further applications performed during this project involved luciferin-derived bioluminescent probes [10], charge-transfer processes in transition-metal complexes with non-innocent ligands [11], and photoinduced activation of lanthanide complexes [12, 13].

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