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Following Photoexcited Structural Dynamics across Potential Energy Surfaces in Solids

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First-principles simulations of excited-state dynamics in solids have become an important avenue for understanding charge transfer, carrier relaxation, and electron–hole recombination. Nonadiabatic molecular dynamics (NAMD) provides a widely used framework for investigating these processes at the atomic level [1–9]. Many solid-state NAMD calculations employ the classical path approximation (CPA), in which electronic dynamics is propagated along prescribed nuclear trajectories without allowing electronic transitions to modify nuclear motion. This approximation becomes inadequate when photoexcitation drives substantial structural changes, as in photoinduced phase transitions, surface photochemistry, and polaron self-trapping. Such processes call for a description in which nuclear motion responds to the evolving electronic state and transitions between potential energy surfaces (PESs). Although established in molecular simulations, implementing this feedback efficiently in periodic solids remains challenging.

In the work by Gao *et al.* [10], they developed a delta self-consistent field (ΔSCF)-based on-the-fly surface hopping method for solids, using a single Slater determinant to represent the electron–hole excited state. Taking rutile TiO_2 as a prototypical example, they captured the complete dynamics of photoexcited polarons, from formation and migration to recombination and lattice recovery. The simulations resolve distinct structural dynamics on the excited- and ground-state PESs: following photoexcitation, carriers self-trap into polarons and migrate between lattice sites on the excited-state PES; electron–hole recombination then returns the system to the ground-state PES, where the lattice recovers from the polaron-induced distortion on a timescale of approximately 10 fs.

Beyond accounting for the feedback of the electronic state on lattice motion, on-the-fly surface hopping also substantially changes the predicted electron–hole recombination lifetime. Unlike NAMD within the CPA, the nonadiabatic couplings in this approach are calculated using two distinct sets of orbitals, one for the ground state and the other for the excited state. Even at the same nuclear geometry, the independently optimized ground- and excited-state orbitals differ

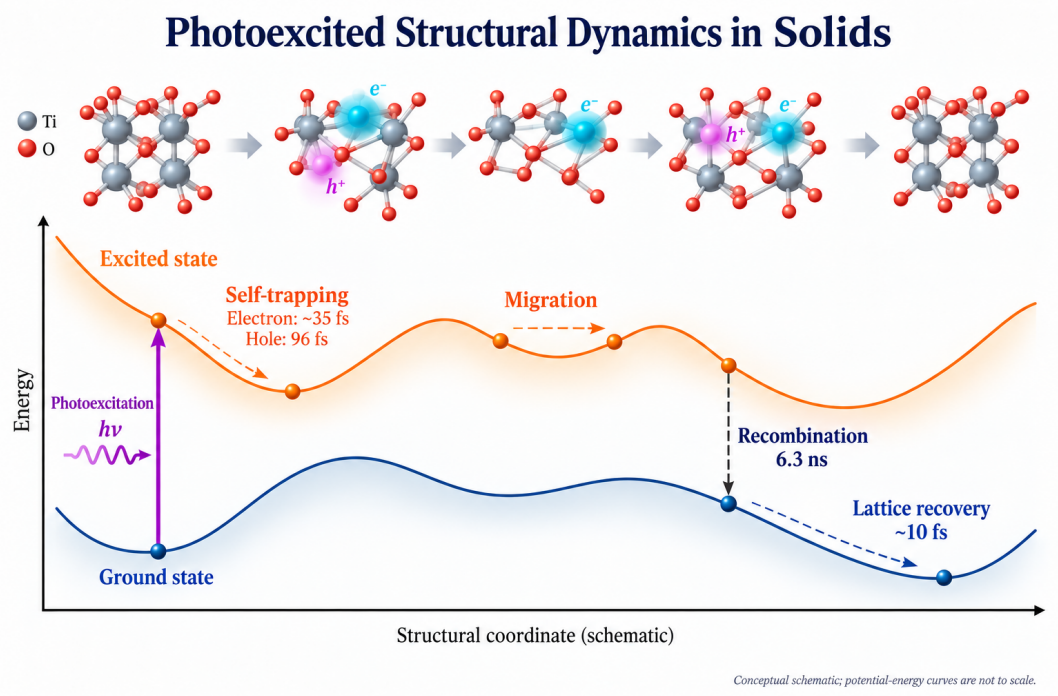

Fig. 1. Photoexcited polaron dynamics in rutile TiO_2. Schematic illustration of the coupled electronic and lattice dynamics following photoexcitation, including electron and hole polaron formation through self-trapping, polaron migration, electron–hole recombination, and subsequent lattice recovery. These processes are depicted on the excited- and ground-state PESs, highlighting their distinct timescales from femtoseconds to nanoseconds.

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substantially. This orbital reorganization reduces the average nonadiabatic coupling from 1.5 meV in the CPA treatment to 0.2 meV in on-the-fly surface hopping, a reduction of nearly an order of magnitude. Consequently, the electron–hole recombination lifetime increases from 38 ps to 6.3 ns, approximately two orders of magnitude.

Most notably, this work provides a computationally tractable on-the-fly surface hopping method for solids that may also find important applications in large molecules and clusters, particularly when the relevant electronic states are sufficiently separated and can be reliably tracked within ΔSCF. This framework opens opportunities to study defect-mediated electron–hole recombination, selected photoinduced phase transitions, and surface photocatalytic processes. With further development to incorporate spin–orbit coupling, it could also be extended to triplet–singlet transitions. Such an extension could have important applications in systems such as nitrogen-vacancy centers in diamond.

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