Nonadiabatic charge dynamics in novel solar cell materials

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The review describes recent research into the nonequilibrium phenomena in nanoscale materials, with focus on charge separation and recombination, that form the basis for photovoltaic and photocatalytic devices. Nonadiabatic molecular dynamics combined with *ab initio* real-time time-dependent density functional theory enable us to model time-resolved laser experiments at the atomistic level, emphasizing realistic aspects of the materials, such as defects, dopants, boundaries, chemical bonding, etc. A variety of systems have been considered, including bulk semiconductors sensitized by semiconducting/metalllic nanoparticles and graphene, nanocrystal/molecule junctions, polymer interfaces with carbon nanotubes and nanoclusters, van der Waals heterojunctions, black phosphorus, and hybrid organic–inorganic perovskites. The detailed atomistic knowledge obtained from the explicit time-domain modeling generates comprehensive understanding of electron-vibrational dynamics in complex multicomponent systems, provides critical insights into quantum mechanical transport of energy and charge, and leads to valuable guidelines for improvement of solar-to-electric power conversion in photovoltaic and photocatalytic applications and for efficient performance of transport devices. © 2017 John Wiley & Sons, Ltd

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INTRODUCTION

Solar power is attractive due to the abundance of sunlight. It has enormous potential to supply society with the energy needed for production of alternative fuels. Development of efficient tools for conversion of sunlight to electricity by photo-induced charge separation, to hydrogen by splitting water, and to methane and other hydrocarbons by carbon dioxide reduction through photovoltaic or photocatalytic reactions is a major pathway for enabling a green and energy efficient economy. Improved strategies for design of cost effective solar cells rely on fundamental scientific breakthroughs in light harvesting and novel photo-conversion concepts rooted in high performance materials. Charge excitation, separation, relaxation, and recombination across interfaces of two distinct materials constitute the most important and fundamental dynamical processes in photovoltaics and photocatalysis, Figure 1. The competition between these dynamics channels determines the overall solar cell conversion efficiency. Theoretical description of nonequilibrium electron behavior in these systems is difficult. The challenge often resides in contrasting characteristics of the two interface components, e.g., localized verdus delocalized electronic states, high photo-induced low frequency phonon modes, soft organic versus hard inorganics materials, well-ordered versus disordered phases, and so on. Disparate sets of theories to describe these materials have been developed within different disciplines, including chemistry, physics, biology, and engineering.¹,² Additional complications arise due to a variety of imperfections and realistic aspects of interface due to chemical bonding, local and extended defects, impurities, dopants, substrates, interactions with water, air and other surrounding media, etc.

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FIGURE 1 | Electronic energy levels involved in the photo-induced nonequilibrium processes in a type-II donor-acceptor heterojunction. Absorption of a photon $\nu$ by either electron donor or electron acceptor leads to charge separation $\circ$ due to electron or hole transfer, respectively. Competing with the separation, the electron and hole can undergo recombination $\otimes$ or relaxation $\oslash$ inside either material. Following the separation, the charges can recombine at the interface $\otimes$.

Density functional theory (DFT)$^3$ provides a powerful and rigorous tool for describing geometric, electronic, and optical properties of most of inorganic and organic materials, and their hybrids. Photo-induced nonequilibrium processes occurs on ultrafast time scales, and electron-vibrational interactions are nonnegligible. The traditional Born-Oppenheimer approximation breaks down, because coupling between potential surfaces opens channels for system to change electronic states, leading to nonadiabatic (NA) transitions. In recent years, nonadiabatic molecular dynamics (NAMD)$^4,5$ has been developed, implemented with real-time time-dependent density functional theory (TDDFT),$^6-8$ and applied to a broad spectrum of photovoltaic and photocatalytic systems involving various dynamics phenomena, such as charge separation, energy transfer, elastic and inelastic electron-electron and electron-phonon scattering, Auger-type processes, energy relaxation, and electron-hole recombination.$^1,9-19$ Inorganic three-dimensional (3D) bulk materials often exhibit large dielectric constants that can screen Coulomb interaction between electrons and holes, facilitating photo-induced charge separation to free electrons and holes.$^{20}$ Owing to quantum confinement, one- (1D) and two-dimensional (2D) systems show particularly strong correlation, compared with their 3D parent systems. Electron-hole Coulomb attraction increases on the surface,$^{21}$ and photo-induced charge separation into free electrons and holes becomes more difficult. Similarity, low dielectric constants of organic materials result in bound electron-hole pairs, so-called excitons that tend to be localized.$^{22-24}$ Solar cells made by these materials may display diverse performance subject to bound or unbound electron-hole pairs arising from the significantly different properties of organic and inorganic materials. The unique capabilities of TDDFT combined with NAMD enable us to mimic the time-resolved experiments in real-time and at the atomistic level of detail, and to address the mechanisms for charge separation, recombination, and other competing processes.

The present review introduces briefly the computational methodologies underlying the time-domain ab initio calculations of the photo-induced dynamics in nanoscale materials and interfaces, and then discusses charge separation and recombination in a variety of systems.$^{25-38}$ In particular, focusing on charge separation, we show that metallic graphene can be used as a light harvester,$^25$ and that the photoexcited hot electron can be extracted from PbSe QDs into TiO$_2$ before cooling.$^{26}$ We demonstrate that photoexcitation of a plasmon band in metallic nanoparticles adsorbed on TiO$_2$ leads with high probability to immediate charge separation,$^{27}$ and that acceptor dimensionality determines the electron transfer (ET) mechanism across CdSe QD/TiO$_2$ interfaces.$^{28}$ We illustrate that defects can help charge separation in a QD/molecule system,$^{29}$ and that asymmetric dynamics of electron and hole transfer at a polymer/carbon nanotube interface can be utilized to improve solar cell efficiency.$^{30}$ We show that atomistic description is needed to understand electron and hole transfer dynamics in a polymer/QD hybrid,$^{31}$ and that quantum coherence facilitates charge separation at a MoS$_2$/MoSe$_2$ van der Waals heterojunction.$^{32}$

Focusing on charge recombination, we show how grain boundaries (GBs) accelerate electron-hole recombination in perovskite CH$_3$NH$_3$PbI$_3$ (MAPbI$_3$),$^{33}$ and how humidity can have both positive and negative influence on perovskite MAPbI$_3$ excited state properties.$^{34}$ We demonstrate how dopants can be used to control electron-hole recombination across a MAPbI$_3$/TiO$_2$ interface,$^{35}$ and how defects slow down electron-hole recombination in black phosphorus (BP).$^{36}$ We discuss suppression of charge recombination in a BP/MoS$_2$ van der Waals heterojunction,$^{37}$ and dependence of electron-hole recombination at a QD/bulk TiO$_2$ interface on QD size and bridge length.$^{38}$ We establish the mechanisms of the photo-initiated charge separation and recombination, characterize the key electronic states.
and vibrational modes, and explore the interplay between the productive and counter-productive channels of photogenerated electron and energy flow. The time-domain ab initio NAMD simulations generate a detailed atomistic description of the interfacial charge dynamics in real time, and provide valuable insights for a broad range of applications, including photovoltaics,\textsuperscript{39,40} photocatalysis,\textsuperscript{41,42} and transport devices.\textsuperscript{43–46}

### THEORETICAL METHODOLOGIES

#### Time-Dependent Kohn-Sham Theory for Electron-Nuclear Dynamics

The interfacial ET dynamics including NA effects\textsuperscript{47} are described by real-time TDDFT\textsuperscript{6,7} within the Kohn-Sham (KS) approach.\textsuperscript{3} The electron density at a time \( t \), \( \rho(r, t) \), is expressed by the sum of the overall densities of the occupied single-electron KS orbital,

\[
\rho(r, t) = \sum_{i=1}^{N_e} |\psi_i(r, t)|^2
\]  

(1)

where \( i = 1, 2, \ldots, N_e \), and \( N_e \) is the number of electrons. The evolution of the electron density is determined by the time-dependent variational principle applied to the KS energy\textsuperscript{48}:

\[
E\{\psi_i\} = \sum_{p=1}^{N_p} \langle \phi_p | K(r) | \phi_i \rangle + \sum_{p=1}^{N_p} \langle \phi_p | V(r; R) | \phi_i \rangle + \frac{e^2}{2} \int \frac{\rho(r', t) \rho(r, t)}{|r - r'|} d^3r'd^3r' + E_{XC}\{\rho\}
\]  

(2)

Here, the first, second, third, and fourth term on the right-hand side represent the kinetic energy of noninteracting electrons, the electron-nuclear attraction, the electron-electron Coulomb repulsion, and the exchange-correlation energy functional, respectively. With proper selection of exchange-correlation functionals, DFT is capable of describing various properties of complex systems in the scope of physics, chemistry, biology, and material sciences. Application of the time-dependent variational principle to Eq. (2) gives a set of single-particle equations for the evolution of KS orbitals\textsuperscript{5,48,49}

\[
i\hbar \frac{\partial \psi_i(r, t)}{\partial t} = H(r, R, t) \psi_i(r, t)
\]  

(3)

These single-particle equations are coupled because the Hamiltonian \( H(r, R, t) \) depends on the overall electron density. The electron-vibrational coupling enters the Hamiltonian through the external potential created by the atoms.

The adiabatic KS basis can be viewed as a numerical tool for solving the time-dependent Kohn-Sham (TD-KS) equations given in Eq. (3).\textsuperscript{5} Expansion of the TD-KS orbitals in adiabatic KS basis, \( \psi_i(r, R(t)) \), which is calculated for the current atomic positions \( R \),

\[
\psi_i(r, t) = \sum_{i=1}^{N_e} c_i(t) |\tilde{\psi}_i(r, R(t))\rangle
\]  

(4)

and insertion of Eq. (4) into Eq. (3), lead to a set of equations describing the evolution of the expansion coefficients:

\[
i\hbar \frac{\partial \tilde{c}_i(t)}{\partial t} = \sum_{k} c_i(t) \left( \tilde{\varepsilon}_k \delta_{jk} + d_{jk} \tilde{R} \right)
\]  

(5)

Here, \( \tilde{\varepsilon}_k \) is the energy of the adiabatic state \( k \), and \( d_{jk} \cdot \tilde{R} \) is the NA coupling between orbital \( j \) and \( k \), which is generated by atomic motions. The NA coupling can be calculated numerically as the overlap of orbitals \( j \) and \( k \) at sequential time steps\textsuperscript{50}

\[
d_{jk} \cdot \tilde{R} = -i\hbar \langle \tilde{\psi}_j(r, R(t)) | \nabla_R | \tilde{\psi}_k(r, R(t)) \rangle
\]

\[
\tilde{R} = -i\hbar \langle \tilde{\psi}_j(r, R(t)) | \frac{\partial}{\partial t} | \tilde{\psi}_k(r, R(t)) \rangle \approx
\]

\[
-\frac{i\hbar}{2\Delta t} \left( \langle \phi_j(t) | \phi_k(t + \Delta t) \rangle - \langle \phi_j(t + \Delta t) | \phi_k(t) \rangle \right)
\]  

(6)

This approximation converts the majority of the computational efforts from solving the TD-KS equations into solving the time-independent DFT problem,\textsuperscript{4} whose numerical solution has been extensively developed. This step greatly reduces the computational cost and allows applications to large-scale condensed-phase systems. The scheme can be easily implemented into most modern electronic structure codes, such as VASP\textsuperscript{51,52} Quantum Espresso (QE),\textsuperscript{53} DFTB+,\textsuperscript{54} GAMES,\textsuperscript{55} etc. In the plane-wave based quantum chemistry codes (VASP, QE), all electronic states are expressed as superpositions of plane-waves in the momentum k-space. Therefore, the numerical derivative involved in the computation of the NA couplings, Eq. (6), is also performed in the k-space. The many-particle generalization of the above KS formulation is presented in Pyxaid.\textsuperscript{56,57}

The simulations discussed below employ periodic boundary conditions. If the system is not
periodic in a given direction, we have added a vacuum layer to eliminate the spurious interactions between the periodic images. To achieve this goal, we have performed test calculations to choose a sufficiently large vacuum depth.

NA Molecular Dynamics
Nuclear motions drive NA transitions between electronic states. In turn, the electronic evolution influences dynamics of the classical nuclei. The latter influence can be described in a mean-field way, if electron-nuclear correlations are not strong, leading to the Ehrenfest approximation. If correlations between nuclei and electrons cannot be ignored, one requires more sophisticated models. Surface hopping (SH) has emerged as a technique capable of describing state-specific back-reaction of electrons onto the nuclei, providing a solution to the trajectory branching problem.

The use of population fluxes between electronic states rather than populations themselves, for determining SH probabilities, lead to a very popular SH approach, known as fewest switches surface hopping (FSSH). FSSH minimizes the number of surface hops and increases the computational efficiency. In addition to introducing electron-nuclear correlations, FSSH also leads to thermodynamic equilibrium in the long-time limit. This property is particularly important in studying relaxation processes. Considering charge separation, Charge Separation Section, only the photo-induced ET from the PbSe QD into TiO₂ has been investigated using the Ehrenfest approximation, while all other systems have been studied by the FSSH approach.

Studies of charge recombination processes require more advanced NAMD techniques, in particular those including quantum decoherence effects. NA coupling induces transitions between electronic states, and the transitions occur through formation of coherent superpositions between the states. In a fully quantum description of electron-nuclear dynamics, quantum mechanical nuclei induce loss of coherence in such superpositions. The decoherence effect is absent in the Ehrenfest and FSSH approaches, which treat nuclei classically. In order to account for the coherence loss, one can introduce semiclassical corrections to FSSH, or use decoherence-induced SH (DISH).

Classical Path and Ehrenfest Approximations
The classical path approximation (CPA) achieves substantial computational savings by assuming that the nuclear trajectory of the system remains unaffected by the electronic dynamics, while the electronic dynamics still depends on the nuclear evolution. Under the CPA, one can use a single trajectory, typically computed in the ground electronic state at a finite temperature, and obtain an ensemble of NA evolutions based on this trajectory. The CPA is valid if electron-electron couplings are much stronger than electron-phonon interactions, or if the kinetic energy of nuclei is significantly greater than the amount of energy exchanged during NA transitions. The CPA operates if electron-nuclear energy exchange does not result in significant structural changes. The situation is often satisfied in condensed-phase systems, such as inorganic and organic crystals and interfaces, in which nuclei undergo thermal fluctuations around equilibrium positions, and the energy deposited by electrons is rapidly dissipated among all vibrational degrees of freedom. The CPA can be combined with FSSH and other SH schemes.

In constructing a CPA approximation one needs to consider how strongly the change in the forces on nuclei due to electronic excitation affects the nuclear dynamics. In all systems under investigation, the nuclear dynamics is rather simple, involving anharmonic vibrations around equilibrium positions. This is a thermal effect arising at a finite, typically ambient temperature. No bond breaking, isomerization and other types of chemical transformations are involved. Further, the systems under investigation are rather large, containing hundreds or even thousands of electrons. Promotion of a single electron to an excited state by absorption of light induces minor changes in the electronic density. This is further supported by the fact that in most cases the electronic states are delocalized over many atoms, and an excitation of a single electron converts to excitation of a small fraction of electron per atom/bond. In several instances we tested the CPA approximation by comparing the difference in the excited and ground state geometries to the thermally induced fluctuations of atomic coordinates in the ground state. The ground state thermal fluctuations were larger than the geometry changes upon photoexcitation.

We find that typically, NA coupling is generated by vibrational modes with frequencies 100 cm⁻¹ and above 1 picoseconds corresponds to the period of a 33 cm⁻¹ mode. By running the dynamics for several picoseconds, we ensure that all relevant motions are properly sampled in the systems considered in this review.

The Ehrenfest approximation introduces correlation between quantum electrons and classical nuclei in a mean-field way. The nuclei evolve on a
single average potential energy surface. Ehrenfest MD cannot achieve the Boltzmann equilibrium populations of the quantum subsystem at a finite temperature, because the mean-filed approximation mistreats the transfer of energy from the quantum to the classical subsystem. Since all productive processes in solar energy harvesting compete with energy losses to heat, the ability to model thermal equilibrium is very important. Tully’s FSSH is needed to describe the coupled electron-nuclei dynamics, because FSSH satisfies approximately the detailed balance between transitions upward and downward in energy.

**Fewest-Switches Surface Hopping**

Tully’s FSSH is the most popular SH strategies. In the applications of this mixed quantum-classical dynamics scheme discussed in this review, the nuclei are treated classically and the electrons are described quantum mechanically. Classical particles move along a single adiabatic potential energy surface, and the electronic wave function associated with each classical trajectory is propagated according to the electronic time-dependent Schrödinger equation with the classical nuclear positions treated as parameters. In turn, the evolution of the electronic wave function affects the nuclei, by inducing hop from the current adiabatic state to another state. The scheme minimizes the number of surface hops by determining a SH probability based on population fluxes, rather than populations themselves. FSSH provides a prescription for the back-reaction of electrons onto the nuclei, both allowing for branching between alternative reaction pathways and satisfying detailed balance between transitions upward and downward in energy.

The time dependent probability of hopping between states \( i \) and \( j \) within a time step \( \delta t \) is given by:

\[
g_{ij}(t, \Delta t) = \max \left\{ 0, \frac{b_{ij} \delta t}{a_{ij}} \right\}
\]

where

\[
a_{ij} = c_i(t)c_j(t)
\]

and

\[
b_{ij} = -2 \Re \left( a^*_j d_i \cdot \mathbf{R} \right)
\]

If the calculated \( g_{ij} \) is negative, the hopping probability is set to zero; a hop from state \( j \) to state \( i \) is allowed to take place only when the electronic occupation of state \( j \) decreases and the occupation of state \( i \) increases. To converse the total electron-nuclear energy after a hop, the nuclear velocities are rescaled along the direction of the NA coupling. If a NA transition to a higher energy electronic state is predicted by Eq. (7) and the kinetic energy available in the nuclear coordinates along the direction of NA coupling is insufficient to accommodate the increase in the electronic energy, then the hop is rejected. The velocity rescaling and hop rejection maintains the detailed balance between transitions upward and downward in energy, ensuring that in the long-time limit the energy is fully and properly equilibrated between the electronic and vibrational subsystems.

Straightforward application of FSSH to large, nanoscale systems at the \textit{ab initio} level is computationally challenging, since FSSH involves averaging over many excited state trajectories. A simplification can be made if the energy exchanged between the electronic and nuclear subsystems during a hop is rapidly distributed among all nuclear modes, such that the energy distribution is approximately Boltzmann before another hop is attempted. This approximation can be made if the energy involved in the hop exchange is small amounts of energy, as in the case of intraband charge relaxation, or if hops are infrequent, as with transitions across large energy gaps, e.g., during electron-hole recombination. If the energy distribution among the nuclear modes is Boltzmann, the probability that the mode along the direction of the NA coupling has a given amount of energy is equal to the Boltzmann factor for that energy. In such situations, hop rejection amounts to multiplying the probability for transitions upward in energy by the Boltzmann factor. Combined with the CPA, discussed in Classical Path and Ehrenfest Approximations Section, this leads to the CPA-FSSH approach. CPA-FSSH is much more computationally efficient than the original FSSH. It uses only one nuclear trajectory in the ground electronic state to generate canonically averaged NAMD results, while FSSH requires an ensemble of excited state trajectories. By avoiding the need to compute electronic excited state energies and forces, and by requiring only one trajectory, CPA-FSSH is capable of describing NA dynamics in large-scale condensed-phase and nanoscale systems.

FSSH can be viewed as a master equation, in which the rates of NA transitions are defined in a nonperturbative, non-Markovian way, based on the evolution of the electronic wave function. FSSH keeps track of populations of different states. The CPA-FSSH dynamics is still NA in the electronic subsystem because the electronic wave function evolves into a superposition of many states due to NA
coupling. The electronic populations change because of NA transitions, even though the nuclear trajectory remains pre-determined based on CPA. In particular, one can solve the Schrödinger equation once in CPA-FSSH, and then use the solution to compute the hopping probabilities that are used repeatedly to sample many stochastic realizations of the hopping.

The following perspective article discusses recent progress in SH.

### Decoherence-corrected Surface Hopping and DISH

Electronic degrees of freedom undergo decoherence due to coupling to a bath of quantum vibrations. FSSH and the Ehrenfest approach are over-coherent, because the vibrations are classical. The problem is not important if loss of coherence between a pair of electronic states is slower than the quantum transition between the states. Then, decoherence can be ignored. This condition is satisfied for charge separation, if it involves multiple rapid hops between closely spaced electronic states, for instance, during ET across an interface between two semiconductors. In contrast, electron-hole recombination involves transitions across large energy gaps. Tully’s FSSH is, in principle, valid in this case. However, a decoherence correction is required, because decoherence is much faster than the quantum transition. For instance, electron-hole recombination in semiconductors takes pico- to nanoseconds, while coherence is lost on a femtosecond time scale. Therefore, all simulations for electron-hole recombination across large energy gaps are performed with decoherence corrections. FSSH can be corrected for decoherence by collapsing the time-evolving wavefunction \( \langle \psi(r, t) | \psi_{\text{ad}}(r, R(t)) \rangle \), Eq. (4), on the decoherence time scale. The collapse times are determined by a sequence of random numbers sampled from the Poisson distribution with the characteristic time determined by the decoherence time.

The decoherence time is equivalent to the pure-dephasing in the optical response theory. It can be computed using the linear response formalism, with or without the cumulant approximation. The inverse of the pure-dephasing/decoherence time determines the homogeneous optical linewidth, which can be measured experimentally. In several cases, we have compared the computed decoherence times to the experimental single-particle linewidths and found excellent agreement.

Loss of quantum coherence provides the physical mechanism for trajectory branching. The stochastic mean field method and later DISH are based on this idea. By combining the computational simplicity of quantum-classical NAMD with a formal treatment of quantum decoherence, DISH requires quantum transitions between surfaces to occur during decoherence events. The transition probabilities are computed according to the standard quantum mechanical rules. On the one hand, DISH can be viewed as a SH approach to quantum dynamics in dissipative environments. On the other hand, DISH unifies decoherence, NA transitions and trajectory branching within a single framework, providing a nonphenomenological description of quantum transitions in condensed-phase systems.

Our scheme for evaluating the decoherence time is based on the optical response theory and has no adjustable or phenomenological parameters. The decoherence time is computed as the pure-dephasing time of the optical response function, based on the fluctuations of the energy gap between the two states forming a coherent superposition. The input to the calculation comes from the same ab initio trajectory used to perform NAMD. The obtained decoherence time can be tested directly by comparison with single-particle (homogeneous) optical linewidths detectable experimentally. Such tests have been performed on a number of nanoscale materials, showing good agreement in both absolute values and trends, including size dependence, temperature dependence, etc.

A variety of schemes for estimating quantum coherence times have been proposed for NAMD simulations. Several years after the appearance of Tully’s FSSH algorithm, Rossky and co-workers explicitly pointed out that the FSSH algorithm requires a decoherence correction, and proposed the frozen Gaussian approximation. Prezhdo and co-workers proposed a method to estimate the decoherence rate in gas phase. Schwartz et al. derived a decoherence rate expression for use in the mean-field with stochastic decoherence method. Prezhdo and co-workers suggested to compute the decoherence time for NAMD simulations using the optical response theory, providing a parameter-free method that can be calibrated directly against optical experiments. More recently, Subotnik and coworkers developed a scheme to compute the decoherence rate to solve the overcoherence problem in Tully’s FSSH. With the notable exception of the optical response theory, the majority of the techniques have been tested against small models, and it remains to be seen whether they can provide accurate estimates of decoherence times in large condensed-phase and nanoscale systems, including dependence on system size, temperature, density,
Electron Transfer Mechanisms

Photo-induced ET can proceed by adiabatic, NA, and direct mechanisms. By direct ET we imply that the photoexcited state is shared by the donor and acceptor materials, such that part of an electron is transferred during photoexcitation. This mechanism requires strong donor-acceptor coupling. Direct electron injection implies that positive and negative charges are created at the energy of the absorbed photon, significantly reducing energy losses to heat. Adiabatic ET also operates in a strong donor-acceptor interaction regime. It proceeds by a change in localization of the adiabatic photoexcited state from donor to acceptor, induced by atomic motions. NA ET does not require strong donor-acceptor interaction and, thereby, occurs in a broader range of systems. To undergo a NA ET, the photoexcited electron has to hop from a donor to an acceptor state, causing a change in the state occupations. NA ET can be ultrafast in the presence of a high density of acceptor states. As the distance between the donor and acceptor species increases and the donor-acceptor coupling decreases, direct and adiabatic ET mechanisms become insignificant, and ET proceeds by the NA mechanism, showing exponential dependence on the distance. Nonradiative transitions across large energy gaps, for instance, electron-hole recombination in semiconductors, always proceed by the NA mechanism, because the initial and final states cannot be brought into resonance by a nuclear motion. The adiabatic and NA mechanisms represent opposite, strong and weak coupling limits. The corresponding rates are described by different analytic formulas and exhibit different dependence on system properties. Therefore, establishing the ET mechanism if of both fundamental and practical importance for improvement of photovoltaic and photocatalytic device efficiencies.

PHOTOEXCITATION DYNAMICS

The discussion of the photo-induced charge and energy transfer dynamics in a broad spectrum of systems is divided into two subsections. The first subsection focuses on the photo-induced charge separation and intraband electron-vibrational energy relaxation. The second subsection describes electron-hole recombination, and nonradiative electron-vibrational relaxation across a bandgap. The processes discussed in Charge Separation Section are fast, typically sub-picosecond. They occur via dense (quasi-) continuum manifolds of states and are simulated using FSSH described in Fewest-Switches Surface Hopping Section. The dynamics involving transitions across substantial energy gaps require decoherence corrections, Decoherence-Corrected Surface Hopping and Decoherence-Induced Surface Hopping Section, and occur on timescales ranging from tens of picoseconds to nanoseconds.

Charge Separation

Charge separation is at the heart of photovoltaic and photocatalytic cells, because only free electrons and holes can generate photocurrent. Typically, charge separation occurs at an interface composed by two complementary materials via either electron or hole transfer. The complex interplay of donor-acceptor and electron-phonon interactions determines ET mechanisms, including the adiabatic, NA, and direct mechanisms described by different mathematical expressions. This section presents recent ab initio NAMD simulations of photo-induced ET at interfaces formed between inorganic and/or organic materials. We observe a variety of ET scenarios for electron injection into periodic and nanoscale TiO₂ from graphene, PbSe QD, metallic gold nanoparticle, and CdSe QD. We show that both electron and energy transfer from graphene into TiO₂ are consistently faster than energy relaxation, rationalizing why metallic graphene can act as a chromophore. We demonstrate that hot electrons can be efficiently extracted from a PbSe QD into TiO₂, in a process forms the basis for QD sensitized solar cells. We argue that a charge-separated state can be generated instantaneously at the Au₂₀/TiO₂ interface upon absorption of light resonant with the plasmon band of the gold particle. The instantaneous charge separation greatly enhances the photon-to-electron conversion efficiency. We demonstrate
how TiO$_2$ dimensionality determines the mechanisms of ET from a CdSe QD into TiO$_2$.\textsuperscript{28} We argue that defects on a QD surface are helpful rather than detrimental for fast ET from a QD to a molecule.\textsuperscript{29} We rationalize the origin of a significant asymmetry in the dynamics of electron and hole transfer in a polymer/CNT hybrid, and argue that the asymmetry means to optimize solar cells performance.\textsuperscript{30} We demonstrate that an atomistic description of nonequilibrium dynamics in a polymer/QD composite changes qualitatively the expectation made based on simple models.\textsuperscript{31} We propose that quantum coherence facilitates charge delocalization and separation, resolving the question of how ultrafast charge separation is possible at a MoS$_2$/MoSe$_2$ junction despite a small driving force and weak donor-acceptor coupling.\textsuperscript{32}

**Charge Separation Across Graphene-TiO$_2$ Interface Is Faster than Energy Losses**

Hybrid graphene/TiO$_2$ composites show great potential for photovoltaic and photocatalytic applications due to the excellent properties of both graphene and TiO$_2$.\textsuperscript{97,98} The combined systems show activity under visible-light irradiation and harvest a larger fraction of the solar-radiation wavelengths than many other nanostructured materials, producing greater fluxes of photoexcited electrons. The electrons can create electricity directly in photovoltaic solar cells or drive photochemical reactions, such as water-splitting for hydrogen production and CO$_2$ reduction into methane and other hydrocarbon fuels. However, graphene is a metal and has a continuous manifold of states near the Fermi energy. Therefore, the photogenerated electron and hole can rapidly relax by coupling to phonons and recombine, greatly reducing the photon-to-charge conversion yield. Unexpectedly, recent experiment demonstrated that ultrafast ET takes place in hybrid graphene/TiO$_2$ composites, and that this system generates significant photocurrents.\textsuperscript{99} A microscopic rationalization of why graphene, being a metal, can be used as a light harvester for solar energy conversion remained unclear.

In order to establish the mechanisms and time scales of ET, energy relaxation and energy transfer processes, NAMD simulations were carried out on a periodically repeated hybrid graphene/TiO$_2$ system.\textsuperscript{25} The simulations demonstrated that the photoinduced ET was several times faster than the electron-phonon energy relaxation, demonstrating that the charge separation was efficient even in the presence of the relaxation. At room temperature, thermal fluctuations created possibilities for chemical bonding between carbon atoms and bridging oxygen atoms, strengthening the graphene/TiO$_2$ donor-acceptor interaction, increasing the NA electron-phonon coupling, favoring photoexcited states that were delocalized significantly between the two sub-systems, Figure 2. The ultrafast electron injection from graphene into TiO$_2$ occurred primarily by the NA mechanism. The injection was driven by both the low frequency out-of-plane graphene motions, and the high frequency C-C bond stretching and bending vibrations. The out-of-plane distortions perturb the $\pi\pi^*$-electron conjugation, and modulate the graphene/TiO$_2$ separation and interaction. The high-frequency phonons generate large electron-phonon coupling because they are fast and create large nuclear velocities, $\text{d}R/\text{d}t$, that enter the NA coupling matrix element, Eq. (6). This finding was supported by the Fourier transforms of both energy and localization of the photoexcited states, shown in Figure 7 in Ref 25. The energy coupled primarily to the high and intermediate frequency motions of the graphene sheet, including the C–C stretch at around 1600 cm$^{-1}$ and carbon bond bending in the 400–800 cm$^{-1}$ frequency range. The evolution occurred by rapid NA transitions down the manifold of delocalized states, resulting in simultaneous ET, energy transfer and electron-vibrational energy relaxation. Importantly, the simulations indicated that both ET and energy transfer from graphene into the TiO$_2$ slab were consistently faster than the energy relaxation, regardless of the excitation energy, Figure 2. This finding provided a rational explanation for the high solar-to-electric energy conversion efficiencies of graphene/TiO$_2$ photovoltaic cells reported experimentally.\textsuperscript{99} The calculations demonstrated that graphene/TiO$_2$ composites can form the basis for photovoltaic and photocatalytic devices with visible-light activity.

**Hot Electron Injection from PbSe Quantum Dots into TiO$_2$**

Compared to molecular chromophores, QDs show size-dependent bandgap, and thus, their absorption can be tuned to harvest light at many wavelengths of the solar spectrum. QDs are excellent light absorbers due to large intrinsic dipole moments, high extinction coefficients, and good photostability. QDs have the potential to increase the maximum attainable thermodynamic efficiency of solar photon conversion by utilizing photogenerated hot charge carriers to produce higher photovoltages and photocurrents using the additional energy available at the blue end of the solar spectrum via hot electron extraction and generation of multiple electron-hole pairs.\textsuperscript{100} Because of these advantages, QD sensitized-TiO$_2$ solar cells\textsuperscript{101}
have become promising candidates to replace the current generation solar cells.

Motivated by the experiments,\textsuperscript{102,103} electron injection from PbSe QD into rutile TiO\textsubscript{2} (110) surface was investigated to explore its mechanism and time scale. The simulations supported the experimental observation that the ultrafast ET into TiO\textsubscript{2} from PbSe QDs successfully competes with phonon-induced electronic energy losses inside the PbSe sub-system. The tail of the donor wave function leaks from the QD into the TiO\textsubscript{2}, while the acceptor density is spread uniformly across the TiO\textsubscript{2} slab, leading to significant interaction between the PbSe QD and TiO\textsubscript{2}, Figure 3. As a result, the ultrafast ET operates primarily by the adiabatic mechanism, Figure 3. The ET is promoted by high frequency optical vibrations, particularly Pb-Se and Ti-O polar stretches, because these modes can rapidly modulate the donor-acceptor state energies and coupling. Low frequency vibrations of TiO\textsubscript{2} and PbSe generate an inhomogeneous distribution of initial conditions for the photoinduced ET. The weak NA transfer component is nearly an order of magnitude slower than the adiabatic ET. The obtained total ET time scale showed excellent agreement with the available experimental data and rationalized the mechanism underlying the hot electron injection.\textsuperscript{102}

**Instantaneous Charge Separation in TiO\textsubscript{2} Sensitized with Plasmonic Nanoparticles**

Compared to the excellent electronic and optical properties of semiconducting QD, metallic nanoparticles...
carry additional advantages. In particular, the exciting optical physics of metal nanoparticles arises from the coherent oscillation of the conduction band electrons induced by the electromagnetic field. The collective excitations, known as plasmons, are responsible for large light extinction coefficients and strong local electro-magnetic fields, which could be used to enhance light harvesting. Combined with prominent catalytic properties of metal clusters, photoexcitation of the plasmon band in metallic nanoparticles adsorbed on a TiO$_2$ surface leads to a number of important photovoltaic and photocatalytic processes, and attracts intense attention.

A representative Au$_{20}$ nanoparticle absorbed on a TiO$_2$ surface was systemically investigated using the NAMD calculations, and the photo-induced charge separation dynamics was explored. The simulations showed that the excited electron density created at the plasmon energy is significantly delocalized onto TiO$_2$, and thus, the excitation is shared by both subsystems. This situation leads to charge separation at the interface, occurring instantaneously upon photoexcitation of the plasmon band with a 50% probability, bypassing the intermediate step of electron-hole thermalization inside the gold nanoparticle. This novel mechanism of charge separation alters the traditional multistep processes, Figure 4, significantly reducing energy losses. In the remaining 50% of the scenarios, excitation at the plasmon energy generates electron-hole pairs in the metal, and the electron is transferred to the TiO$_2$ surface on a sub-100 femtoseconds time scale. The ET proceeds primarily by the NA mechanism, due to a relatively weak donor-acceptor coupling and a high density of TiO$_2$ acceptor states. The ET is primarily driven by low-frequency acoustic modes of Au$_{20}$, which alter the shape and size of the nanoparticle and the surface plasmon wave function.

**FIGURE 3** | Charge densities of (a) donor and (b) acceptor states at a PbSe QD-TiO$_2$ interface. (c) Photo-induced ET dynamics from the PbSe QD into the TiO$_2$ slab. The solid black, dashed blue, and dotted red lines represent the total, adiabatic, and NA ET, respectively. The open circles are exponential fits with the time scales shown in the figure. Adapted from Ref 26. *J Am Chem Soc* **133**, 19240 (2011). Copyright 2011 American Chemical Society.

**FIGURE 4** | Left-panel: Schematic diagram of the mechanisms of photo-induced ET from a plasmonic nanoparticle into a bulk acceptor. Left-top: The traditional view assumes that a surface plasmon breaks into electron-hole pairs, after which an electron is injected into the acceptor. Left-bottom: Photoexcitation resonant with the plasmon energy creates an excited state with the electronic wavefunction extended into the acceptor. Right-panel: The excited state is delocalized significantly onto TiO$_2$, leading to instantaneous charge separation upon photoexcitation at the plasmon energy. Adapted from Ref 27. *J Am Chem Soc* **136**, 4343 (2014). Copyright 2014 American Chemical Society.
is also influenced by the high-frequency dipolar Ti-O bond vibrations via electrostatic interaction. The electron-phonon energy relaxation parallels the injection and is slightly slower. Driven by entropy due to the high density of bulk TiO$_2$ states, the electron overcomes attraction to the hole and moves further into TiO$_2$ bulk. If the electron remains trapped at the TiO$_2$ surface, it recombines with the hole on a picosecond time scale exclusively by the NA mechanism due to of the large energy gap between the initial and final states in present system. The obtained ET and recombination time scales agreed well with the available time-resolved experimental data. The delocalized state observed in the study established a novel concept for plasmonic photo-sensitization of wide bandgap semiconductors, leading to efficient conversion of photons to charge carriers and to hybrid materials with a wide variety of applications, including photovoltaics and visible-light photocatalysis. The theoretical finding was corroborated experimentally.

**Acceptor Dimensionality Affects Electron Transfer Mechanism in Quantum Dot Sensitized TiO$_2$**

Generally, transfer of the photoexcited electron from donor to acceptor can proceed by either adiabatic or NA mechanism, as determined by the strength of the donor-acceptor coupling. The ET mechanisms carry different implications for the variation of the interface conductance and solar cell voltage with system properties. Adiabatic ET requires strong donor-acceptor interaction. It can take place near the edge of semiconductor conduction band, potentially avoiding energy losses to heat. NA ET does not require strong donor-acceptor interaction and, therefore, occurs in a broader range of systems. NA ET cannot be efficient near the semiconductor conduction band edge, because it requires a high density of acceptor states. Given a wide variety of nanoscale materials available for solar energy applications, one may ask oneself, whether material's dimensionality, which greatly affects the density of states, would also influence the ET mechanism. Highly ordered 1D nanostructures, e.g., nanotubes, nanowires, and nanorods, have received considerable attention as solar materials. They provide significant improvement in the charge transport and photoconversion efficiency compared to 0D QDs. In addition to the differences in the densities of states between the 1D and 0D systems, donor-acceptor interactions may also vary with the shape of semiconductor nanostructures, affecting the photo-induced ET mechanisms.

**Ab initio** time-domain simulations of photoinjection of electrons from an excited CdSe QD to a quasi-0D TiO$_2$ QD and a 1D TiO$_2$ nanobelt (NB) were performed to investigate the influence of acceptor TiO$_2$ dimensionality on the ET mechanisms. The calculations showed that the adiabatic mechanism operates in the CdSe/TiO$_2$ QD system due to strong donor-acceptor coupling (cf. Figure 5) arising from the covalent bonding between the donor and acceptor species, and low density of acceptor states. In contrast, the NA mechanism dominates ET in the CdSe/TiO$_2$ NB system, because the donor-acceptor coupling is weak due to lack of chemical bonding, while the density of the NB acceptor state is high, and multiple phonons can accommodate changes in the electronic energy. The CdSe adsorbant breaks the symmetry of delocalized band-type states of the TiO$_2$ NB, creating localized acceptor states. The symmetry breaking relaxes the donor-acceptor and NA electron-phonon coupling selection rules, and generates additional ET channels. Both mechanisms can give efficient and ultrafast injection.

The studied demonstrated that it is feasible to modulate the mechanism of the photo-induced ET by changing the acceptor dimensionality. This ability can be used to improve solar-to-electron conversion efficiency in nanoscale solar cells. For instance, adiabatic ET into the conduction band edge of a TiO$_2$ QD minimizes energy and voltage losses associated
with injection high into the conduction band. At the same time, some current will be lost due to a high probability of electron trapping on QD surfaces. In contrast, NA injection into extended TiO$_2$ acceptors will facilitate high currents, while leading to some energy and voltage losses, since NA injection becomes efficient at energies above the conduction band edge.

**Defects Assist Electron Transfer from a Quantum Dot into a Molecule**

Semiconductor surfaces, especially those encountered in nanoscale systems, exhibit a variety of defects associated with edges, steps, nonstoichiometric atomic vacancies, etc. These defects strongly influence optical and photovoltaic properties of nanomaterials due to formation of states inside the fundamental bandgap. For instance, defects often lead to rapid electron-phonon energy losses arising from decreased electronic energy gaps and increased electron-phonon NA coupling. Generally, the NA electron-phonon coupling is stronger for small/localized systems because it depends on the sensitivity of wave functions to nuclear motion: If wave functions are delocalized, they are less sensitive to system geometry than if they are localized. We observe this phenomenon systematically in many systems: the NA coupling grows because defects create localized states. In addition, defects break symmetry and give rise to new vibrational modes that couple to the electronic subsystem and enhance the NA coupling. Even though defects accelerate electron-phonon relaxation, they are not always detrimental. For instance, defect sites are often responsible for catalytic properties of a material. Therefore, it is important to investigate the role that defect states may play in photo-induced charge separation. Such study was performed with the focus on a QD/molecule interface.

Motivated by experiments, ET from a PbS QD to the rhodamine B (RhB) molecule and subsequent electron return from RhB to the QD was investigated by *ab initio* NAMD simulations. The simulations supported the experimental observation that charge separation was faster than recombination, even though the donor-acceptor energy gap was smaller for the recombination, Figure 6. The NA coupling in the ideal system without defects was twice stronger for charge separation than recombination. The computed electron-hole recombination time obtained for the ideal system agreed very well with the experiment data. However, the charge separation time was significantly underestimated. Repeating the simulations with a sulfur vacancy, which commonly exists on PbS QD surfaces, revealed that the vacancy accelerated the charge separation, improving agreement with experiment. The improvement was rationalized by two factors. First, the sulfur vacancy created a gap state below the PbS QD conduction band. Second, the wave function of the electronic state associated with the sulfur vacancy extended onto the adsorbed molecule, increasing the donor-acceptor interaction. The decreased donor-acceptor energy gap and the increased coupling accelerated the charge separation process, Figure 6.

Both charge separation and recombination occurred by the NA mechanism due to wide energy gaps.
gaps. Phonon modes created the NA coupling and accommodated the excess energy released during the quantum transitions. The NA electron-phonon coupling was created predominantly by the high-frequency vibrations arising from the molecule, because it is composed of lighter atoms than the QD. In contrast, the donor-acceptor coupling between the QD and the molecule was determined by the QD properties. The QD wave function leaks onto the adsorbed molecular subsystem, creating the needed wave function overlap between the donor and the acceptor species. The counterintuitive conclusion that defects are benign rather than detrimental to solar cells performance provided a new design principle for optimization of solar cell efficiency via defects engineering.

**Asymmetry between Electron and Hole Transfer at a Polymer/Carbon Nanotube Heterojunction**

Organic photovoltaics possess significant potential for low-cost, scalable solar power conversion. To achieve high photon-to-electricity conversion efficiency, the electron-hole pairs photogenerated in organic materials must overcome the Coulomb attraction and separate. However, low dielectric constants of organic matter result in poor interaction screening, giving rise to strongly bound electron-hole pairs. By combining organic conjugated polymers with other carbon materials, such as fullerenes and carbon nanotubes (CNT), one can form bulk heterojunctions that facilitate the charge separation via increased driving force.

The photo-induced charge separation and energy relaxation across an interface formed by poly (3-hexylthiophene) (P3HT) and a CNT was investigated by combining TDDFT with NAMD. Photoexcitation of P3HT lead to a 100 femtoseconds ET, followed by a loss of 0.6 eV energy within 0.5 picoseconds. The obtained ET time scale agreed well with the experimental data. By considering the complementary photoexcitation of the CNT, it was found that excited CNT transferred the hole to P3HT. The hole transfer took nearly 2 picoseconds, more than an order of magnitude longer than the ET, but was accompanied by a loss of only 0.3 eV of energy, twice less than the ET. The electron and hole transfer dynamics at the P3HT/CNT heterojunction showed a strong asymmetry. The transfer of both electron and hole was promoted primarily by the high-frequency C-C stretching of the polymer and CNT. Additionally, the electron coupled to lower frequency radial breathing modes of CNT and P3HT torsional motions, which provided additional ET channels. The ET proceeded faster than the hole transfer due to a higher density of acceptor states (Figure 7), and a stronger donor-acceptor and electron-phonon NA couplings.

Used as a light harvester, P3HT produces faster charge separation but leads to larger energy losses, and cannot harvest light in the red region of the solar spectrum. In contrast, CNT absorbs a broader range of photons, reduces energy losses, but gives less efficient charge separation. On the one hand, one can harvest a broader range of solar spectrum, and reduce energy and voltage losses by increasing the CNT concentration in a P3HT/CNT mixture. On the other hand, one can achieve better charge separation and higher currents by increasing the P3HT concentration. The reported results provided a comprehensive description of the charge and energy transfer dynamics in the organic photovoltaic materials and suggested novel design principles for photovoltaic and photocatalytic devices.

**Ultrafast Electron and Hole Transfer Dynamics in a Quantum Dot/Polymer Hybrid**

Compared to CNT, QDs have higher dielectric constants and show smaller Coulomb interactions between charge carriers. Electron-hole pairs generated in QDs by photoexcitation can efficiently dissociate into free carriers. In addition, QDs improve light absorption due to large absorption cross...
sections and bandgaps that can be easily tuned for harvesting the entire solar spectrum. Hot-carrier generation and carrier multiplication provide opportunities to improve conversion efficiencies of QD solar cells, by reducing the loss of high-energy carriers. Polymers offer the advantages of solution processing and straightforward chemical synthesis. The disadvantages of polymers include inefficient charge separation due to strong Coulomb coupling between photorexited carriers. Utilization of the combined advantages of inorganic QD materials and organic polymers paves new ways to enhance solar cell performance and make QD/polymer systems an attractive alternative to the traditional cells.

Owing to formation of a type-II heterojunction between P3HT and CdS QDs, photoexcitation of P3HT leads to ET, while photoexcitation of CdS QD results in hole transfer. Simple models postulate that quasi-0D QDs exhibit atom-like electronic structure, and 1D polymers form continuous bands. However, atomistic calculations provide an alternative description. Electronic states in polymers are molecule-like: finite in size and discrete in energy. QDs show high, bulk-like densities of states, because they are composed of many atoms. Ab initio NAMD calculations on the photo-induced electron and hole dynamics in the CdS QD/P3HT system show that an atomistic description is necessary to understand the time-resolved experimental data.120

Both electron and hole transfers across the CdS QD/P3HT interface proceed within sub-picosecond time scale, showing good agreement with experiment.120 The donor-acceptor coupling is similar for both processes. High frequency modes involved in the hole transfer offsets the low density of acceptor states, balancing the rates of the electron and hole injection. Symmetric electron and hole dynamics is important for solar cells applications because it eliminates channels for energy losses. The interfacial charge separation is ultrafast due to strong donor-acceptor coupling, arising from delocalization of the photoexcited states between the two subsystems, Figure 8. The ET from P3HT is somewhat faster than the hole transfer from the QD, due to a significantly higher density of acceptor states. Since QDs have high densities of states, the ET dynamics is exponential. In comparison, hole transfer is highly nonexponential due to relaxation through a low density of states in P3HT.

While both ET from P3HT and hole transfer from the QD can occur on similar, sub-picosecond timescales, the electron-hole recombination is very different inside the two materials and at the interface. The stronger electron-hole and charge-phonon coupling are responsible for the electron-hole recombination inside organic P3HT proceeding several orders of magnitude faster than in the inorganic QD. Since the excitation inside the QD is long-lived, the hole transfer into P3HT can occur over a broad range of time scales, from sub-picosecond to nanosecond. In contrast, transfer of short-lived electron inside the P3HT always occurs within one picosecond. Otherwise, the electron recombines with the hole. The simulations demonstrated the importance of an atomistic description of the photo-induced charge and energy transfer dynamics in the hybrid nanoscale QD/polymer interface. Such atomistic modeling generates a fundamental understanding of the dynamics and suggests valuable guidelines for design of photovoltaic and photocatalytic devices.

**Quantum Coherence Facilitates Charge Separation at a MoS2/MoS2 van der Waals Heterojunction**

Two-dimensional transition metal dichalcogenides (MX2, M = Mo, W; X = S, Se) have received broad interest in optoelectronic and photovoltaics applications.121 To achieve efficient light-to-current conversion, electron-hole pairs generated by adsorbed photons must dissociate into free charges. Because of low dielectric constants, the Coulomb interaction is poorly screened in the 2D MX2 materials, leading to exciton binding energies between charges in MX2...
that often exceeds the charge transfer driving force.\textsuperscript{122–124} Thereby, one expects inefficient charge separation at a MX\textsubscript{2} heterojunction. Experiments defy the expectation and demonstrate efficient charge separation at MX\textsubscript{2} heterojunctions via photo-induced electron and/or hole transfer.\textsuperscript{125} The contradiction between the expectation and the experimental data raises questions regarding the mechanism of the photo-induced charge separation across interfaces between 2D transition metal dichalcogenides.

\textit{Ab initio} NAMD simulations were performed to investigate the photo-induced charge separation at a MoS\textsubscript{2}/MoSe\textsubscript{2} heterojunction.\textsuperscript{32} The simulations showed that quantum coherence at the interface, facilitated by significant delocalization of photoexcited states between the donor and acceptor materials, helps to overcome the electron-hole pair interaction and leads to efficient charge separation. The delocalization is larger for electron than hole, resulting in longer coherence and faster transfer. In addition to longer coherence, the ET is faster than the hole transfer due to stronger NA coupling, higher density of acceptor states, and interaction with higher frequency vibrational modes, Figure 9. The obtained sub-picosecond time scales for the electron and hole transfers are in excellent with the available experimental observations.\textsuperscript{125} The charge transfers are promoted primarily by the out-of-plane Mo-S and Mo-Se modes of the acceptors, because they influence the relative energies and localizations of the donor and acceptor states, and create the NA couplings.

The slower relaxation of the photogenerated hot hole suggests possibility of long-range band-like transport. Charge separation at the MoS\textsubscript{2}/MoSe\textsubscript{2} heterojunction reduces the electron-hole recombination rate, compared to the corresponding rates in isolated MoS\textsubscript{2} and MoSe\textsubscript{2}, favoring long-lived charge separation. Rapid charge transfer, combined with long electron-hole recombination times, demonstrates that MoS\textsubscript{2}/MoSe\textsubscript{2} and similar metal dichalcogenides van der Waals heterojunctions constitute appealing candidates for photovoltaics and electronics applications. The quantum dynamics simulations revealed hitherto unexpected details regarding the mechanism of the photo-induced charge separation at 2D transition metal dichalcogenides interfaces, rationalizing the discrepancy between the initial expectation and experiment. The provided insights can lead to novel design principles for operation of ultrathin devices under far-from-equilibrium conditions.

\textbf{FIGURE 9} | (a) Projected density of states (PDOS) of the MoS\textsubscript{2} and MoSe\textsubscript{2} monolayers in the MoS\textsubscript{2}/MoSe\textsubscript{2} heterojunction. The driving force for the charge separation is determined by the donor-acceptor band edge energy offsets. (b) Charge densities of the donor and acceptor states for the electron and hole transfer. Both electron and hole donor states are significantly delocalized between MoSe\textsubscript{2} and MoS\textsubscript{2}, forming coherent superpositions between the two materials. The electron acceptor state is slightly delocalized onto the donor, due to a small donor-acceptor energy offset in this case, part a. In the contrary, the hole acceptor state is fully localized on the MoSe\textsubscript{2} monolayer, because the donor-acceptor energy offset is large. The vertical arrows between parts (a) and (b) relate the donor and acceptor orbital densities to the energies. Compare with Figures 7 and 8. Adapted from Ref 32. \textit{Nano Lett} 16, 1996 (2016). Copyright 2016 American Chemical Society.

\textbf{Charge Recombination}

Electron-hole recombination is another factor that determines solar cell performance, in addition to charge separation. The recombination constitutes a major pathway for charge and energy losses. To achieve high photon-to-electron conversion efficiency, one needs to minimize nonradiative electron-hole recombination. We show why a grain boundary accelerates charge recombination in the CH\textsubscript{3}NH\textsubscript{3}PbI\textsubscript{3} (MAPbI\textsubscript{3}) perovskite, and why chlorine passivation of the boundary extends the excited-state lifetime.\textsuperscript{33} We demonstrate that moderate humidity delays electron-hole recombination in MAPbI\textsubscript{3} and that heavy humidity accelerates the recombination.\textsuperscript{34} We analyze in detail how dopants control electron-hole recombination at a MAPbI\textsubscript{3}/TiO\textsubscript{2} interface and suggest a route to suppress the charge and energy losses via a rational choice of dopants.\textsuperscript{35} We show how QD size and donor-acceptor separation can be used to minimize electron-hole recombination in a PbSe QD/TiO\textsubscript{2} composite.\textsuperscript{38} Finally, we rationalize why defects delay electron-hole recombination in MBP,\textsuperscript{36} and how the recombination is slowed down in the BP/MoS\textsubscript{2} van der Waals heterojunction.\textsuperscript{37}
Grain Boundary Accelerates Charge Recombination in the CH$_3$NH$_3$PbI$_3$ Perovskite

Hybrid organic–inorganic perovskite solar cells have attracted great attention due to the high power conversion efficiencies reaching $126\%$ and exceeding $127\%$. The remarkable performance stems from large carrier lifetimes and long carrier diffusion lengths. In particular, the bandgap of MAPbI$_3$ is suitable to harvest both visible and near-infrared parts of the solar spectrum. However, GBs unavoidably exist in perovskite samples obtained from low-temperature thermal evaporation and solution-based processing methods, affects the excited state lifetime and solar cell performance. First-principles calculations have suggested that MAPbI$_3$ GBs are benign. However, experiments contradict the prediction and show that GBs notably degrade the film optoelectronic properties.

*Ab initio* NAMD combined with TDDFT showed that GBs notably accelerate the electron-hole recombination in the MAPbI$_3$ perovskite relative to the pristine system. At the same time, boundary doping with Cl notably reduced the recombination rate, Figure 10. The presented analysis established detailed mechanisms for these effects. The increased recombination rate can be rationalized at the atomic level by changes in the NA electron-phonon coupling, the bandgap, and the phonon-induced loss of coherence in the electronic subsystem. First, GBs enhance the electron-vibrational NA coupling by localizing and contributing to the electron and hole wave functions and by creating additional phonon modes that couple to the electronic subsystem. Second, GBs decrease the MAPbI$_3$ bandgap, reducing the number of vibrational quanta required to accommodate the electronic energy loss. Third, the phonon-induced decoherence time remains largely unchanged rather than decreased, as one may expect based on the stronger NA electron-phonon interaction. Additionally, replacing iodines by chlorines at the GBs pushes the highest occupied molecular orbital density away from the boundary, restoring the NA coupling close to the value for the pristine MAPbI$_3$. At the same time, chlorine dopants introduce higher-frequency modes and increase fluctuation of the electronic energy gap, accelerating loss of electronic coherence. Both factors compete successfully with the bandgap reduction, relative to pristine MAPbI$_3$, and help to extend the excited-state lifetime. The study highlighted the importance of electron-vibrational interactions and quantum coherence in the excited-state dynamics of perovskite-based materials. The simulations agreed well with experiment, established how GBs and chlorine dopants affect electron-hole recombination in perovskite solar cells, and suggested a valuable route to optimization of solar-to-electric power conversion through rational GB passivation.

**Moderate Humidity Delays Electron-hole Recombination at the CH$_3$NH$_3$PbI$_3$ Surface**

Disparate experimental data give rise to debates regarding the effects of humidity on efficiencies of perovskite solar cells. Both positive and negative influences of exposure to moisture on the solar cells performance were reported. Macroscopically, it was suggested that moisture influences crystalline grain size. The microscopic mechanism responsible for degradation or improvement of performance of perovskite solar cells subject to humidity remains largely unclear.

*Ab initio* NAMD combined with TDDFT were performed to investigate the influence of different levels of humidity on nonradiative electron-hole recombination at the MAPbI$_3$ (001) surface with a varying number of adsorbed water molecules. The study demonstrated that moderate humidity extends the excited-state lifetime, while heavy humidity reduces the lifetime, in agreement with experiments. Small amounts of water perturb the surface layer, localize the photoexcited electron on the surface,

**FIGURE 10** | Electron-hole recombination dynamics in the MAPbI$_3$ perovskite, the perovskite with the $\Sigma_5$ (012) grain boundary (GB), and Cl-doped GB. The $\Sigma_5$ (012) GB system shows faster decay compared to pristine MAPbI$_3$, due to larger nonadiabatic coupling and longer coherence time. In contrast, the Cl-doped GB system slowest decay, stemming from smaller nonadiabatic coupling and shorter coherence time. The black solid and dashed lines represent electron-hole recombination in pristine MAPbI$_3$ with the theoretical and experimental bandgaps, respectively. Adapted from Ref 33. *J Am Chem Soc* **138**, 3884 (2016). Copyright 2016 American Chemical Society.
while creating no trap states, and decouple the electron from the hole. The overlap of the electron and hole wave functions decreases, and the quantum coherence time decreases as well. Both factors reduce the electron-hole recombination and extend excited-state lifetime. In large amounts, water aggregates on the perovskite surface, forming a continuous hydrogen bonded network. The perovskite-water interaction is weaker than water–water interaction. Therefore, a continuous water layer creates a smaller perturbation to the perovskite surface than isolated water molecules, and has little effect on charge localization. At the same time, by contributing high frequency polar vibrations, water molecules increase the NA coupling and accelerate the electron-hole recombination. The obtained electron-hole recombination timescales show good agreement with the available experimental data. \cite{133,134} Figure 11. The simulations revealed the microscopic effects of humidity on the excited-state lifetime of the MAPbI$_3$ perovskite, rationalized the conflicting experimental results, and advanced our understanding of excited-state dynamics in perovskite solar cells. The short-range chemical and long-range electrostatic mechanisms of perovskite-water interaction provide means of control over charge localization and recombination. The study suggests that different solvents can have different effects on the electron-hole recombination, depending on the relative strength of the solvent-solvent and solvent-perovskite interactions.

**Dopants Affect Electron-hole Recombination at the CH$_3$NH$_3$PbI$_3$/TiO$_2$ Interface**

Dopants often modulate electronic properties of host materials and affect excited state lifetimes in solar cell systems. Experiments showed that nonradiative electron-hole recombination in solar cells composed of TiO$_2$ sensitized with MAPbI$_3$ reduces when iodides are substituted with chlorines or bromines. In contrast, the recombination increase when lead is replaced with tin. \cite{126,135,136} Generally, lighter and faster atoms should increase electron-vibrational NA coupling and energy losses to heat. Since the dopants are lighter than the atoms they replace, one expects \textit{a priori} that all three dopants should accelerate the recombination.

In order to establish the fundamental mechanisms of the energy losses and to propose practical means for controlling the interfacial electron-hole recombination, \textit{ab initio} NAMD simulations were conducted on pristine and doped MAPbI$_3$(100)/TiO$_2$ anatase (001) interfaces. \cite{35} The study showed that doping by substitution of iodine with chlorine or bromine reduces charge recombination, while replacing lead with tin accelerates the recombination, Figure 12. The unexpected behavior of chlorine and bromine can be attributed to three factors. First, the Pb-Cl and Pb-Br bonds are shorter than the Pb-I bond. As a result, Cl and Br atoms are farther away from the TiO$_2$ surface, decreasing the donor-acceptor coupling. In contrast, the coupling is increased with...
Pb atoms are replaced by Sn. Second, Cl and Br reduce the NA electron-vibrational coupling, because they contribute little to the electron and hole wave functions, and push the charges away from the interface. Sn increases the NA coupling because it does contribute to the hole wave function and it is lighter than Pb. Third, higher frequency modes introduced by Cl and Br shorten quantum coherence, thereby decreasing the transition rate. In comparison, Sn leaves the coherence time largely unchanged. The recombination occurs due to coupling of the electronic degrees of freedom to low-frequency bending and stretching modes of I-Pb bonds in perovskite and acoustic modes in TiO₂. The study shows good agreement with the time-resolved experimental data and contributes to the detailed understanding of electronic and vibrational dynamics in perovskites. The generated insights into design of higher efficiency solar cells range from fundamental scientific principles, such as the role of quantum coherence, to practical guidelines, such as specific suggestions for rational choice of dopants.

**Defects Reduce Charge Recombination in Monolayer Black Phosphorus**

In recent years, 2D BP has been receiving intense attention in the area of optoelectronics and solar energy conversion, because of its layer-dependent direct bandgap and high charge mobility. Particularly, monolayer black phosphors (MBP) has a suitable bandgap, varying in the range from 1.0 eV to 2.0 eV depending on the type of measurement, enabling this material to harvest visible light up to the near-infrared region in the solar spectrum. Minimizing charge recombination can lower energy losses to heat, potentially enhancing solar power conversion efficiency. Time-resolved experiments showed multiple excited-state lifetimes in BP, ranging from one hundred picoseconds to nanoseconds. A mechanistic understanding of the source of variation in the electron-hole recombination rate was needed.

TDDFT combined with *ab initio* NAMD were used to investigate the nonradiative electron-hole recombination in MBP with and without the divacancy (DV). The simulations showed that nonradiative electron-hole recombination in ideal MBP completed within 100 picoseconds, while phosphorus DV substantially reduced the recombination rate, with the time scale on the order of 1.6 nanoseconds, Figure 13. The obtained time scales showed excellent agreement with the available pump-probe time-resolved experiments. The reduced NA electron-phonon coupling and increased bandgap in MBP-DV rationalized slower recombination in this material. Both factors compete successfully with the slower loss of quantum coherence in the MBP-DV system. The simulations demonstrated that reduced NA coupling in MBP containing defects arises from diminishing overlap between electron and hole wave functions, Figure 13, whereas the slower loss of quantum coherence is due to the reduced mobility of phosphorus atoms. The recombination in ideal MBP occurred exclusively due to coupling of the electronic subsystem to the 450 cm⁻¹ vibrational mode, whereas the recombination in MBP-DV was driven by a broad range of vibrational modes. The simulations suggested that vacancy defects can play an important role in the rational design of BP materials for minimizing nonradiative energy losses in optoelectronic and photovoltaic applications.

**Suppression of Electron-hole Recombination at the BP/MoS₂ van der Waals Heterojunction**

Similar to 2D transition-metal dichalcogenides MX₂ (M =Mo, W; X = S, Se), the large exciton binding energy of BP prevents photexcited electron-hole pairs from dissociating into free electrons and holes, limiting photon-to-electron conversion efficiencies. Experiment showed that stacking BP with MoS₂ increases the driving force for ET and helps charge separation at the interface. Motivated by
this experimental finding, one wonders how the electron-hole recombination occurs across the BP/MoS$_2$ interface compared to the BP bilayer, both of which are bound by van der Waals interactions.

BP bilayer and BP/MoS$_2$ heterojunction were systematically investigated, using the state-of-the-art methodology combining TDDFT with NAMD, in order to characterize the nonradiative electron-hole recombination dynamics. The simulations showed that replacing a BP layer by a MoS$_2$ monolayer notably suppresses the recombination relative to bilayer BP. First, the BP/MoS$_2$ heterojunction decreases the NA electron-vibrational coupling by reducing the overlap between the electron and hole wave functions. Second, the BP/MoS$_2$ heterojunction increases the bandgap compared to bilayer BP. Both factors prevail the slower loss of quantum coherence in the heterojunction, suppressing electron-hole recombination. The obtained time scale showed good agreement with the time-resolved experimental data, Figure 14. The simulations suggested that stacking BP with a choice of 2D materials can extend excited state lifetime, and thereby, reduce the nonradiative energy loss during electron-hole recombination. The time-domain ab initio simulations provided valuable insights assisting in rational design of novel van der Waals photovoltaic solar cells based on BP and related materials.

**Minimizing Electron-hole Recombination in Quantum Dot Sensitized TiO$_2$**

To achieve high solar power conversion efficiencies, one requires fast injection of hot electrons from a light absorber into a semiconductor, and slow electron-hole recombination and energy loss to heat. The later processes occur by coupling to vibrational modes. Experiments reported that scattering of photoexcited electrons in PbSe QDs occurs faster than electron cooling. As a result, hot electrons can be extracted faster than they lose energy to phonons. In addition to rapid interfacial charge separation, the overall conversion efficiencies of QD solar cells also depend on electron-hole recombination across the interface between the QDs and semiconductor acceptor of photogenerated electrons. Because rapid charge recombination decreases solar cell current and hence efficiency, it is particularly important to understand how the recombination can be slowed down.

Time-domain atomistic simulation combined with analytic theory were applied to study in detail the mechanism of the charge recombination at the PbSe QD/TiO$_2$ interface and to develop guidelines for minimizing charge losses. It was found that the recombination occurs due to coupling of the electronic subsystem to high-frequency polar optical modes, in particular, the high-frequency optically active Raman mode of TiO$_2$. The inelastic electron-phonon scattering leading to electron-hole recombination occurred on a picosecond timescale in the system under investigation, in agreement with time-resolved laser experiments. The elastic scattering, characterizing the lifetime of the coherent quantum-mechanical superpositions between the donor and acceptor states, required 40 femtoseconds. The donor and acceptor states were localized on TiO$_2$ and QD respectively, reducing the overlap of the wave functions of the initial and final electronic states, and decreasing the NA electron-vibrational coupling. In comparison, the photo-induced charge separation in the same system started from a QD state that is delocalized onto TiO$_2$ and was significantly faster than the charge recombination due to strong NA electron-vibrational couplings.

Model simulations suggested that charge recombination can be suppressed exponentially by using either larger QDs or longer bridges between QD and TiO$_2$, Figure 15. The main effect arises due to reduced overlap of the donor and acceptor wave function rather than changes in the donor-acceptor energy gap. The former factor determines the magnitude of the NA coupling, which governs the recombination rate. The study indicated that one can achieve efficient charge separation while reducing charge losses via variation in QD size or ligand length, providing rational principles for optimizing solar cell design and increasing efficiency of conversion of solar energy to electricity.

![Figure 14](image-url) | Decay of populations of the first excited state in bilayer black phosphorus (BP) and at the BP/MoS$_2$ interface. BP/MoS$_2$ shows slower decay because of electron-hole separation across the interface. Adapted from Ref 37. J Phys Chem Lett 7, 1830 (2016). Copyright 2016 American Chemical Society.
CONCLUSIONS AND OUTLOOK

The review has summarized the recent theoretical studies of nonequilibrium quantum processes that occur at various nanoscale interfaces. Based on a combination of TDDFT with NAMD, the calculations mimic time-resolved experiments directly, in real time and at the atomistic level of detail. Real-time modeling of electron-vibrational dynamics is particularly valuable for understanding the charge separation and recombination at interfaces, because these processes are fundamental to photovoltaic, photocatalytic, and transport applications. Charge separation via interfacial injection of electrons and holes from photoexcited sensitizer donors into acceptor substrates constitutes the initial and key step of solar energy utilization, since free charge carriers are required to achieve a photovoltaic response and to drive photochemical reactions. Low dielectric constants in novel materials with reduced dimensionality, such as 2D transition metal dichalcogenides and BP, 1D polymers, and CNT, and quasi zero-dimensional semiconducting and metallic clusters, enhance Coulomb interactions between electrons and holes relative to the parent bulk materials. Reduced dimensionality also creates additional possibilities for introduction of defects, dopants, boundaries, surfaces and other imperfections that affect systems’ response to photoexcitation. Therefore, atomistic exploration of the interfacial charge separation and recombination mechanisms becomes a prerequisite to understanding the nonequilibrium phenomena and generating important guidelines for improvement of solar power conversion efficiency.

Many additional processes, such as nonradiative relaxation and electron-hole recombination, compete with photo-induced charge separation and influence photon conversion efficiencies. Usually, in a great variety of systems, electron injection occurs faster or on a similar timescale, compared to energy relaxation. The situation ensures that the relaxation does not present a major pathway for charge and energy losses, if the system maintains a large energy gap. This condition is satisfied in inorganic semiconductors, organic crystals, and their hybrids. Transport of photo-generating charges to collecting electrodes, or chemically active sites and catalysis occurs on a longer timescale. Charge transport competes with charge trapping and recombination. As a result, the power conversion efficiency is significantly affected by interfacial trapping and recombination of electrons and holes; and therefore, the efficiency can be dramatically increased by reducing the recombination rate.

The charge and energy transfer processes can be investigated by ab initio NAMD only with relatively small systems, involving hundreds of atoms, and on timescales of tens of picoseconds, depending on the approximations used. In order to perform larger-scale simulations, one needs to develop methods that reduce the computational cost for electronic structure calculations and in particular, for calculation of reliable NA couplings, which are more sensitive to wave function accuracy than energies. Linear scaling KS-DFT brings such framework, and enabling description of thousands of atoms at the quantum-mechanical level. The efficiency is achieved by employing algorithms with a cost that grows linearly with system size. Time-dependent linear-scaling KS-DFT implementation of NAMD will allow one to handle larger, more realistic and more complex systems, and longer time-scales, providing the desired capacity for addressing a much broader range of important experimental problems. Employing the single electron orbital framework and the CPA will be particularly useful for achieving the linear scaling.

More advanced methods, such as the GW theory and its various approximations (GW_0, G_0W_0) provide better description of excitation energies, increase the energy gaps relative to GGA DFT. At the same time, GW is significantly more computationally expensive than KS-DFT with a GGA functional. The Bethe-Salpeter theory describes electron-hole interactions (excitonic effects). It is even more expensive...
than GW. Unfortunately, both approaches cannot be used in time-domain simulations on nanoscale systems involving electron-phonon interactions, because calculations of this type are very computationally demanding. In the present calculations on systems composed by two different materials we made sure that the relative energy alignment was correct, based on the corresponding experiments. The rate of charge recombination, in particular, depends on the energy gap, NA coupling, and decoherence time. The recombination rate is approximately linear in the energy gap, according to energy gap law.\(^{147}\) According to Fermi’s golden rule, the rate is proportional to the NA coupling squared, and depends significantly on the decoherence time, which enters the rate expression in the form of the Franck-Condon factor.\(^{64,69}\) Thus, the dependence on the energy gap is weakest among the three factors. If needed, the absolute value of the energy gap can be corrected by applying either the ‘scissor’ operator or the DFT+U method,\(^{148}\) to match the experimental values.

Alternatively, one can employ semiempirical electronic structure methodologies. Recently, Prezhdo and co-workers implemented NAMD within tight-binding DFT (DFTB).\(^{54}\) Tretiak and co-workers employed the semiempirical AM1 Hamiltonian and the configuration interaction singles (CIS) description of electronic excitations. They investigated the electron and energy relaxation dynamics in extended conjugated molecules involving multiple coupled electronic excited states by the NA excited state molecular dynamics technique that combines the FSSH algorithm with ‘on the fly’ analytic calculations of excited-state energies, gradients and NA couplings.\(^{149-152}\)

The CPA approximation provides significant computational savings in NAMD simulations of systems, in which excited and ground state dynamics is similar, in particular, compared to the extent of thermal fluctuations of atoms. Batista and coworkers employed the CPA when investigating the dynamics of electron injection from the higher excited states of catechol into TiO\(_2\), using a combination of \textit{ab initio} and extended Hückel approaches.\(^{153,154}\) They employed ground state \textit{ab initio} DFT to obtain nuclear configurations for the Hückel calculations. At the same time, the CPA cannot be used processes in which nuclear dynamics depends strongly on the electronic states, for example, photo-induced chemical reactions involving bond breaking and formation. Coupling real-time TDDFT with Ehrenfest MD provides means to achieve this goal. Kaxiras et al. studied the electron and hole injection into TiO\(_2\) from several dye molecules using local-basis real-time TDDFT in combination with Ehrenfest dynamics.\(^{155,156}\) In this approach, the TDKS equations for electrons and the Newton’s equation for nuclei are solved simultaneously, and the nuclear forces are obtained by averaging over the manifold of adiabatic electronic states according to the state populations. Real-time excited state trajectories are generated self-consistently with propagation of the many-electron density. Rigorous for short times, the original Ehrenfest method can be corrected for the thermal equilibrium\(^{157}\) and decoherence\(^{96}\) effects. A computationally efficient description of excited state trajectories can be achieved with the delta self-consistent filed (\textit{ΔSCF}) method, in which one or more electrons are promoted into higher energy KS orbitals. For example, the restricted open-shell KS description of the lowest energy excited state was implemented within NAMD by Doltsinis and Marx.\(^{158}\) \textit{ΔSCF} description of higher energy excited states can encounter convergence problems, because occupied higher energy orbitals tend to cross with unoccupied lower energy orbitals during the SCF optimization. Linear response TDDFT description of excited states was used by Rothlisberger and coworkers.\(^{159}\)

Tully’s FSSH and Ehrenfest approaches neglect decoherence and other quantum nuclear effects. The importance of quantum coherence in charge and energy transport has been demonstrated in a number of biological\(^{160,161}\) and nanoscale\(^{162,163}\) systems. Several methods for describing decoherence effects in NAMD are available, including semiclassical corrections to FSSH,\(^{61,63,82}\) stochastic mean field,\(^{70}\) DISH,\(^{62}\) coherence penalty functional for adding decoherence to Ehrenfest dynamics,\(^{2,96}\) the Ehrenfest with stochastic decoherence method,\(^{81}\) and coherence switching with decay of mixing.\(^{164}\) The DISH and coherence penalty functional methods have been adapted for the CPA approximation and implemented in the PYXIAI software.\(^{57}\)

Several groups investigated photo-induced ET dynamics employing fully quantum dynamical approaches rather than quantum-classical SH, with a quantum description of nuclear motion. Examples include the multi-layer multi-configuration time-dependent Hartree (ML-MCTDH) method\(^{165-167}\) and the hierarchy equations-of-motion (HEOM) approach.\(^{168,169}\) A quantum description of nuclear motion necessarily invokes high computational cost, and therefore, it is hard to apply to large condensed-phase systems.

Auger-type processes are ubiquitous in nanoscale materials, because these materials exhibit both significant electron-hole interactions and high
densities of states. Previously, we studied Auger-type processes using the Ehrenfest and global flux SH methods. The former describes Auger-type phenomena and short-time dynamics, but mistreats electron-vibrational relaxation and approach to thermodynamics equilibrium. The latter captures both Auger processes and long-time electron-phonon interactions. Still, the enormous number of excited states involved in Auger processes presents a significant challenge, motivating the use stochastic electronic structure methods and sparse matrix techniques to propagating the Schrödinger equation. Simultaneous inclusion of NA effects and explicit Coulomb interactions between single-particle KS states is desirable.

It has been established recently that straightforward application of FSSH excludes superexchange effects, including important pathways of Auger-type dynamics. Superexchange is captured at the Ehrenfest level, and can be recovered within the SH description by using global flux SH and second quantized SH, or by performing SH simulations in Liouville rather than Hilbert space. The following perspective article discusses recent progress in SH.

Charge and exciton diffusion involve large distances and long periods of time, generating additional challenges for NAMD. During such simulations one runs into the trivial (or ‘unavoided’) crossing problem that can lead to jumps across unphysically large distances. Solutions of the trivial crossing issue include the self-consistent SH, flexible SH and diabatization techniques. Long timescales are accessible with NA transition state theories.

Significant progress has been achieved in developing photovoltaic and photocatalytic cells for solar energy harvesting. Improvement of pump-probe time-resolved laser techniques, combined with structural, electrical and mechanical probes, leads to discovery of new physical and chemical phenomena, generating additional challenges for theory to accurately model the behavior of complex systems. Novel theoretical frameworks and tools are waiting to be developed suitable for investigating highly nonequilibrium carrier and energy transfer dynamics, in order to provide insights and design principles for improvement of photovoltaic, photocatalytic, and transport devices.

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