Time-Domain Ab Initio Modeling of Photoinduced Dynamics at Nanoscale Interfaces

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Abstract

Nonequilibrium processes involving electronic and vibrational degrees of freedom in nanoscale materials are under active experimental investigation. Corresponding theoretical studies are much scarcer. The review starts with the basics of time-dependent density functional theory, recent developments in nonadiabatic molecular dynamics, and the fusion of the two techniques. Ab initio simulations of this kind allow us to directly mimic a great variety of time-resolved experiments performed with pump-probe laser spectroscopies. The focus is on the ultrafast photoinduced charge and exciton dynamics at interfaces formed by two complementary materials. We consider purely inorganic materials, inorganic-organic hybrids, and all organic interfaces, involving bulk semiconductors, metallic and semiconducting nanoclusters, graphene, carbon nanotubes, fullerenes, polymers, molecular crystals, molecules, and solvent. The detailed atomistic insights available from time-domain ab initio studies provide a unique description and a comprehensive understanding of the competition between electron transfer, thermal relaxation, energy transfer, and charge recombination processes. These advances now make it possible to directly guide the development of organic and hybrid solar cells, as well as photocatalytic, electronic, spintronic, and other devices relying on complex interfacial dynamics.
1. INTRODUCTION

Interfacial electron transfer processes (1) are fundamental to many areas of research, including photovoltaics (2, 3), photocatalysis (4, 5), photosynthesis (6, 7), photochemistry (8, 9), electrolysis (10, 11), molecular electronics (12, 13), and spintronics (14, 15). As shown in Figure 1, efficient electron transfer at nanoscale interfaces needs to compete with thermal relaxation, energy transfer, charge recombination, and other dynamical processes, which ultimately determine the overall device efficiency. Numerous efforts have been devoted to exploring the nonequilibrium nature and mechanisms of these dynamical processes. Time-resolved experiments, such as transient absorption spectroscopy (16, 17) and optical second harmonic generation techniques (18–20), have been widely used to obtain the timescale for each dynamical channel. On the theoretical side, nonadiabatic molecular dynamics (NAMD) provides the most popular and reliable solution (21, 22). Over the past few decades, a suite of NAMD simulation approaches has been developed and implemented, aimed at modeling the dynamical events in the time domain and at the atomistic level of detail (23–29), as they occur in experiment and nature.

This review covers the basics of the theory underlying various NAMD strategies available in literature. We present the standard approaches, including mean-field (MF) (30–32), fewest-switches surface hopping (FSSH) (21, 33), and quantized Hamiltonian dynamics (QHD) (34, 35). Tully’s FSSH approach has retained its popularity owing to its appealing simplicity, ease of implementation, and computational efficiency (22, 36, 37). Because of its great success, FSSH has

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**Figure 1**

Photoinduced processes competing with electron transfer between a donor and an acceptor, including thermal relaxation, energy transfer, and charge recombination. The energy levels of the donor (acceptor) are shown as red (blue) solid horizontal lines. The electron and hole are represented by solid and open circles, respectively.
attracted a lot of attention, and various situations requiring improvements have been identified. When high density of states (DOS) come into play, in particular in nanoscale materials, standard FSSH encounters the so-called trivial, or unavoidable, crossing problem (38–41). It can be overcome with several modern developments, including self-consistent fewest-switches surface hopping (SC-FSSH) (42) and adaptive flexible surface hopping (FSH) (43, 44). In addition, FSSH lacks the capability of describing the superexchange mechanism of population transfer, which can be well captured by the global flux surface-hopping (GFSH) (45) and second-quantized surface-hopping (SQUASH) (46) methods developed recently. Decoherence is another issue that needs to be considered for proper descriptions of slow transitions between states separated by significant energy gaps (47–49). Decoherence can be taken into account by the stochastic mean-field (SMF) (50), decoherence-induced surface-hopping (DISH) (51), and coherence penalty functional (CPF) (52) methods.

Ab initio density functional theory (DFT) provides a rigorous and efficient means for describing the electronic structure of systems comprising most chemical elements. In recent years, time-dependent density functional theory (TDDFT) has been extensively combined with NAMD and applied to a broad range of inorganic and organic systems undergoing charge separation, electron and energy transfer, energy relaxation, charge recombination, chemical reactions, and other nonequilibrium processes (23–29). Inorganic materials generally exhibit strong bonding and high electrical conductivity. Their large dielectric constants result in strong electric field screening and reduced Coulomb binding between electrons and holes (53). In contrast, organic systems are generally loosely packed with small charge mobility due to weak electron-electron coupling and strong electron-phonon interactions (54–57). Small dielectric constants result in strong Coulombic binding of electron-hole pairs, and excitons tend to be localized (58–60). The fundamentally different properties of organic and inorganic materials are described by either chemistry or physics, which differ in concepts and language: compare the terms orbitals, electron correlation, and vibrations, used by chemists, with the terms band structure, excitons, and phonons, employed by physicists. Thus, significant challenges arise for a unified description of organic and inorganic components, and their hybrids.

The state-of-the-art simulation tool combining TDDFT and NAMD generates a detailed time-domain atomistic representation of the interfacial charge and exciton dynamics that are fundamental to a wide variety of applications. Studies performed by the Prezhdo group on quantum dots (QDs) and interfaces involving TiO$_2$ have been reviewed previously (23–29). The current review focuses on interfaces formed by two complementary materials, including purely inorganic interfaces, organic-inorganic hybrids, and all organic systems (see Figure 2). Only work published in 2010 or later is included.

A functional interface for photovoltaic or photocatalytic applications typically comprises a photon absorber and an electron acceptor. Different absorber-acceptor combinations exhibit distinct features. Exemplifying inorganic interfaces, we use an ab initio time-domain simulation to show that hot electrons can be extracted from QDs prior to relaxation (61), that electron-hole recombination can be minimized by tuning QD size and bridge length (62), that the mechanism of electron injection from a CdSe nanoparticle into nanoscale TiO$_2$ depends on the dimensionality of the latter (63), and that plasmon-driven charge separation on TiO$_2$ sensitized with plasmonic nanoparticles has a 50% chance of already occurring during light absorption (64). Considering organic-inorganic hybrids, we reveal why graphene, a metal, can be used as a TiO$_2$ sensitizer (65); that atomic defects can be both detrimental and beneficial for charge separation (66); how a long, insulating bridge can accelerate electron transfer (67); that nanoscale materials exhibit a new, Auger-assisted type of electron transfer (68); that dimensionality is inverted when a QD and conjugated polymer form a heterojunction (69); and that the low efficiency of photocatalytic
Inorganic interfaces, organic-inorganic hybrids, and organic systems discussed in the review: (a) a PbSe quantum dot (QD) on a TiO₂ surface, (b) CdSe QD attached to either a TiO₂ QD or TiO₂ nanobelt, (c) Au₂₃₀ cluster on a TiO₂ surface, (d) graphene on TiO₂, (e) RhB molecule interacting with a PbS QD, (f) C₆₀ bound to a CdSe QD, (g) CdX QD interacting with a Y molecule (X = S, Se, and Te; Y = AQ, MV₂⁺, and MB⁺), (h) P3HT on a CdS QD, (i) GaN-H₂O interface, (j) pentacene-C₆₀ composite, and (k) a P3HT–carbon nanotube system.

Water splitting by GaN results from unfavorable competition between charge relaxation and transfer (70). Finally, for organic interfaces, we demonstrate that optically dark states govern the rates and yields of singlet fission and charge transfer at a pentacene/C₆₀ interface (71) and illustrate how the asymmetry of electron and hole transfer at a polymer/nanotube interface can be used to optimize solar cell performance (72). The mechanisms of all processes involved in the photo-initiated dynamics are established, the key electronic states and phonon modes are characterized, and the interplay between the productive and unfavorable channels of photoinduced electron and energy flow is described. The reviewed time-domain ab initio simulations provide important insights into the fundamental chemical physics of electron transfer and related processes on the nanoscale and generate valuable guidelines for the design and improvement of photovoltaic and photocatalytic devices.

2. SIMULATION APPROACHES

2.1. Time-Domain Density Functional Theory

The wave function, which determines all observable properties through the calculation of expectation values, is the central concept of quantum mechanics (73). However, it is still a forbidding task to find out the true many-electron wave function for large systems. The Hohenberg-Kohn
theorems have shown that the desired properties of any system under the influence of a static external potential can be obtained directly from the electron density, which is a function of only three coordinates (74). This many-electron problem can be further reduced approximately to a tractable picture of noninteracting electrons moving in an effective potential, resulting in the Kohn-Sham (KS) framework of DFT (75). With proper choices of exchange-correlation (XC) functionals, DFT finds an increasingly broad application in physics, chemistry, biology, and materials science for the atomistic interpretation and prediction of complex system behavior (76).

When the external perturbation, including electromagnetic field and vibrational motions, evolves in time, the Runge-Gross theorem has shown that the three-dimensional (3D) electron density is also sufficient to describe the time-dependent response of the system (77). The resulting density is also sufficient to describe the time-dependent response of the system (77). The resulting

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

where \( N_e \) is the total number of electrons, and \( r \) expresses the assembly of \( 3N_e \) electronic coordinates. The time-dependent variational principle can be applied to the KS energy (78),

\[ E = \sum_{i=1}^{N_e} \langle \psi_i | K(r) | \psi_i \rangle + \sum_{i=1}^{N_e} \langle \psi_i | V(r; R) | \psi_i \rangle + \frac{e^2}{2} \int \int \rho(r) \rho(r') d^3r d^3r' + E_{xc}(\rho(r)), \]  

where \( K(r) \) is the kinetic energy operator of noninteracting electrons, \( V(r; R) \) is the electron-nuclear attraction that relies on both electronic coordinates \( r \) and nuclear coordinates \( R \), and \( E_{xc}(\rho) \) is the XC functional taking into account the many-body interactions. The result is a system of coupled single-particle KS equations of motion (EOM) (78–80),

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

where the Hamiltonian \( H(r; R, \psi) \) is a functional of the overall density and, therefore, all occupied KS orbitals.

The adiabatic KS basis can be viewed as a numerical tool for solving the time-dependent Kohn-Sham (TDKS) equations given in Equation 3 (81). Expansion of the TDKS orbitals in the adiabatic KS basis, \( \{\tilde{\psi}_i(r; R)\} \),

\[ \psi_i(r, t) = \sum_{j=1}^{N_e} c_{ij}(t) |\tilde{\psi}_j(r; R)|, \]  

yields a set of EOM for the expansion coefficients (21),

\[ i\hbar \frac{\partial c_{ij}(t)}{\partial t} = \sum_{k} c_{ik}(t) \delta_{ik} \delta_{jk} + d_{jk} \cdot \ddot{R}, \]  

where \( \delta_{ik} \) is the corresponding energy of the adiabatic KS state, \( \tilde{\psi}_j(r; R) \). The last term in Equation 5 is the nonadiabatic coupling (NAC) (82–86),

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

which arises from the dependence of the adiabatic KS orbitals on the nuclear coordinates \( R \) (87). Solving the TDKS equations in the adiabatic KS basis shifts the computational effort to the highly optimized step of solving the time-independent DFT problem (88).
Slater determinants formed from single-electron KS orbitals can be viewed as an approximation to the many-electron adiabatic states (88). A state basis is needed to perform NAMD, as discussed in the next subsection. The NACs between the Slater determinants are nonzero only if the determinants differ by one orbital. As a result, the propagation involves very sparse matrices, allowing the use of large many-electron basis sets. At the level of the TDKS equations, the adiabatic KS representation makes no approximations and can be viewed as a particular choice of basis set. It carries a number of advantages associated with the fact that adiabatic KS orbitals are routinely computed by most electronic structure codes. The KS representation of excited states assumes that the error made in the calculation of the potential energy surface (PES) due to the missing TDDFT correction is constant in time, and therefore, it is independent of the structural changes. Thus, the adiabatic KS states can be viewed as a zeroth order to the linear response time-dependent density functional theory (LR-TDDFT) adiabatic states (89). In practice, the KS excitation is generally the leading term in the expression for the excitations calculated with LR-TDDFT (90). The agreement between the KS and LR-TDDFT descriptions is better for pure DFT functionals than for hybrid functionals. Larger systems with a greater number of electrons exhibit better agreement as well. The errors introduced with the KS description of electronic excitations should be compared with other approximations, such as those involved in the choice of the DFT functional and in the classical description of vibrational motions, neglecting zero-point energy contributions to the NAC and decoherence in the electronic subsystem induced by quantum vibrations (81).

2.2. Nonadiabatic Molecular Dynamics

NAMD provides a generalization of ordinary molecular dynamics (MD) to include transitions between electronic states. This is achieved in a self-consistent way: The nuclear motions drive the electronic evolution, for instance, by TDDFT, and the electronic evolution influences the classical nuclear dynamics (33). The latter can be carried out in an MF manner, leading to the Ehrenfest approximation (30). Correlations between the dynamics of nuclei and the electron can be built in using surface-hopping (SH) techniques (21). Typically, NAMD is performed in the adiabatic basis (91, 92). Adiabatic states are readily available from electronic structure calculations, and they give better results with SH approaches. In the following subsections, we discuss in detail various NAMD methods. Table 1 gives a brief description for each method, followed by advantages, weaknesses, and suggested applications.

2.2.1. Classical path and Ehrenfest approximations, quantized Hamilton dynamics. The classical path approximation (CPA) (93) provides a particularly simple solution to the quantum back-reaction problem, that is, the influence of the electronic evolution on the classical nuclei. CPA assumes that the classical trajectory is independent of electronic dynamics, whereas the electronic dynamics still depends on the classical coordinates. CPA is appropriate if electron-phonon interactions are much weaker than electron-electron couplings (94), or if the energy of the nuclei is sufficiently greater than that of the electrons, such that the electron–nuclear energy exchange does not affect the nuclear evolution appreciably. CPA is also valid if the PESs that are associated with different electronic states differ only slightly, in comparison, for instance, with the amplitude of nuclear fluctuations due to thermal or zero-point energy.

The Ehrenfest approximation is another attractive choice for NAMD simulations owing to its straightforward and rigorous foundations (30–32). There, the force applied on the classical particles is based on the gradient of the expectation value of the Hamiltonian acting on the time-evolving wave function. If the energy flow between electronic and nuclear subsystems is
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<th>Advantages</th>
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<td>Classical path approximation</td>
<td>No influence of electronic evolution on the dynamics of classical nuclei</td>
<td>Precomputed nuclear trajectory, allowing multiple realizations of electronic evolution</td>
<td>Feedback from electrons to nuclei is lost</td>
<td>High-energy processes</td>
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<td>Mean-field approximation</td>
<td>Average force from all electronic states on classical nuclei</td>
<td>Rigorous, simple, improvement on CPA</td>
<td>Cannot capture strong electron-nuclear correlations and thermodynamic equilibrium; overcoherent</td>
<td>Short-time dynamics in most cases; systems with high density of electronic states</td>
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<td>Quantized Hamilton dynamics</td>
<td>Hierarchy of equations for quantum descriptions of both electrons and nuclei</td>
<td>Convergence to exact result; quantum effects captured with minimal number of classical-like variables</td>
<td>Higher orders involve complicated closures and nonlinear equations</td>
<td>Quantitative short-time and qualitative long-time description of quantum effects</td>
</tr>
<tr>
<td>Fewest-switches surface hopping</td>
<td>Most popular surface-hopping algorithm minimizing the number of hops</td>
<td>Simple, efficient; strong electron-nuclear correlations captured; leads to thermodynamic equilibrium</td>
<td>Ad hoc and overcoherent; no superexchange; trivial crossing problem in extended systems</td>
<td>Most common method; corrections/modifications can be introduced as needed</td>
</tr>
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<td>Flexible surface hopping</td>
<td>FSSH with self-adjusted system size for surface hopping</td>
<td>Same as FSSH but trivial crossing problem also solved</td>
<td>Requires parameter to enlarge or shrink system size</td>
<td>FSSH for extended systems</td>
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<td>Self-consistent fewest-switches</td>
<td>FSSH with self-consistent surface-hopping probabilities</td>
<td>Same as FSSH but trivial crossing problem also solved</td>
<td>Overcoherent</td>
<td>Parameter-free FSSH for extended systems if wave-function evolution is accurately known</td>
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<td>Global flux surface hopping</td>
<td>FSSH generalized while minimizing number of hops</td>
<td>Same as FSSH but also superexchange described and trivial crossing problem solved</td>
<td>Overcoherent</td>
<td>Replacement for FSSH</td>
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<td>Second-quantized surface hopping</td>
<td>FSSH generalized to entangled trajectories</td>
<td>Quantum effects captured; simple implementation</td>
<td>Becomes expensive if many trajectories are entangled; requires energy partition scheme</td>
<td>FSSH with quantum effects</td>
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<tr>
<td>Stochastic mean field (SMF)</td>
<td>Stochastic modification of the Schrödinger equation that incorporates quantum decoherence and branching</td>
<td>Decoherence rigorously included; ad hoc branching eliminated; hop rejection much less pronounced</td>
<td>Requires decoherence time parameter; potential energy surface fluctuates every time step</td>
<td>DISH based on well-known Schrödinger equation for open systems</td>
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<td>Decoherence-induced surface hopping (DISH)</td>
<td>Surface hopping at decoherence events</td>
<td>Decoherence naturally implemented to give branching; standard potential energy surfaces</td>
<td>Requires decoherence time parameter</td>
<td>Replacement for FSSH when decoherence is essential</td>
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<td>Coherence penalty functional (CPF)</td>
<td>Introduced functional to penalize the development of coherence</td>
<td>Classical representation for both electrons and nuclei; general implementation of decoherence</td>
<td>Decoherence functional is not unique</td>
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<td>Classical path approximation for FSSH (CPA-FSSH) and DISH (CPA-DISH)</td>
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<td>Electron and energy transfer processes in nanoscale materials</td>
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insignificant, the Ehrenfest approach is sufficient. At the Ehrenfest level, NAMD is independent of the chosen electronic basis. The adiabatic representation is equivalent to spatial and plane-wave grids (79, 95) or a localized atomic basis (96). When electron-nuclear correlations are important, nuclear trajectories branch depending on the electronic state. Then, trajectory SH needs to be adopted (21, 33, 91).

Instead of the Schrödinger representation, correlated electron-nuclear dynamics can also be studied within the Heisenberg representation. By treating quantum mechanically not only the electron creation and annihilation operators, but also the nuclear position and momentum variables, one can achieve the time derivative of the expectation value for any system observable of interest from the Heisenberg equation. In this QHD method, there exists an interesting phenomenon: The original operators become coupled to higher-order operators, resulting in a hierarchy of equations (34, 35, 97–99). Different levels of approximations to the quantum dynamics are achieved through termination of the chain with a closure that expresses the expectation values of the higher-order operators in terms of products of the expectations of the lower-order operators. In particular, it was found that the first-order QHD coincides with the Ehrenfest theory (35). Simple extensions to higher-order QHD can efficiently represent quantum nuclear effects, such as phonon zero-point energy, tunneling, and loss of coherence in the electronic subsystem caused by phonons.

2.2.2. Fewest-switches surface hopping, self-consistent fewest-switches surface hopping, and adaptive flexible surface hopping. Among all SH strategies, Tully’s (21) FSSH is the most widely used approach. It minimizes the number of surface hops by prescribing an SH probability based on population fluxes, rather than the populations themselves. The NACs are used, along with the wave function amplitudes, to determine the FSSH probabilities. The time-dependent probability of hopping between states $i$ and $j$ within a time step $\Delta t$ reads (21)

$$g_{ij}(t, \Delta t) = \max \left\{ 0, -\frac{b_{ij}}{a_{ii}(t)} \right\},$$

(7)

where

$$b_{ij} = -2\text{Re}(a_{ij}^\ast \mathbf{d}_{ij} \cdot \mathbf{R}).$$

(8)

$$a_{ij} = \epsilon_i \epsilon_j^\ast.$$

(9)

A ground state nuclear trajectory can be used to sample initial conditions to create ensemble averages for the excited state dynamics.

SH studies on weakly interacting or large-scale systems severely suffer from the trivial crossing problem, arising from the high density of adiabatic PESs (38–41). Around the trivial crossing point, the NAC becomes a delta function, and FSSH probabilities cannot be computed accurately in numerical simulations with a finite time step. The SC-FSSH technique (42) provides a straightforward solution to the problem by introducing a self-consistency test to the standard FSSH procedure. The sum of all FSSH probabilities from the active state $i$ to other states $j$ satisfies (42)

$$g_{\text{tot}} = a_{ii}(t) - a_{ii}(t + \Delta t)$$

$$a_{ii}(t).$$

(10)

If we calculate the energy differences between the active adiabatic state $i$ and all other adiabatic states, and find the adiabatic state $k$ that gives the smallest energy difference, we identify the main source of the trivial crossing. Then, we can correct the error by computing the SH probability...
corresponding to the trivial crossing, \( g_{ik} \), using the simple expression

\[
g_{ik} = g_{k\alpha} - \sum_{j \neq k} g_{ij}.
\]  

(11)

With the Holstein Hamiltonian as an example, SC-FSSH allows us to reduce the simulation time 10,000-fold to achieve the FSSH accuracy already in a five-state system (42).

Because an electron is delocalized over a finite space, and electron-phonon interactions are generally local (100–102), only a limited number of nuclear degrees of freedom are strongly coupled to the electron dynamics. Thereby, one can treat a small portion of the nuclei surrounding the electron in an SH manner and the rest of the nuclei simply at the MD level (43). As both the central position and extension of the electron may change in time, this should be done in a flexible way by adding and/or removing neighboring nuclear degrees of freedom to/from the SH subsystem at any time step. In this aspect, the problematic trivial crossings are avoided because all adiabatic states are spatially close. The computational cost is also largely reduced because only a very small Hamiltonian matrix is diagonalized to get all important PESs. A flexible time-step technique, which ensures the smoothness of all time-dependent adiabatic states, enables us to describe SH accurately with a relative large time step. This FSH algorithm (43, 44) based on a minimum subsystem implementing SH and a maximum time step for SH dynamics can recover all charge transport regimes described by existing theories (103–105) and can be easily extended to more complex Hamiltonians.

2.2.3. Global flux surface hopping and second-quantized surface hopping. Superexchange is a class of dynamical processes (106) in which two electronic states are coupled indirectly through an intermediate state, typically with higher energy. Common to nanoscale systems, Auger-type electron-hole energy exchange and multi-exciton (ME) generation and annihilation (107–109) are multiparticle reactions, which also proceed with intermediate states. Transitions into high-energy intermediate states violate energy conservation and are forbidden in SH. Because FSSH allows transitions only between states that are directly coupled, it mistreats quantum processes involving the superexchange mechanism. GFSH solves this problem while remaining close to FSSH in other instances. Rather than using the FSSH state-to-state flux given by Equation 7, the GFSH method (45) considers the gross population flow between states. The SH probabilities are expressed as

\[
g_{ij} = \frac{\Delta a_{ij}}{a_{ii}} \frac{\Delta a_{jj}}{a_{jj}} \sum_k \frac{\Delta a_{ik}}{\Delta a_{kk}} (\text{if } \Delta a_{ii} < 0, \Delta a_{jj} > 0, \text{and } \Delta a_{kk} < 0).
\]  

(12)

No other type of state switching is allowed. Similar to FSSH, GFSH uses a flux of populations rather than their absolute values, and therefore, it also minimizes the number of hops. Just like FSSH, GFSH fulfills the internal consistency: The changes in the state populations according to the SH rules (Equations 7 and 12) agree with the changes produced by solving the Schrödinger equation. Numerical calculation shows that GFSH captures the superexchange mechanism and Auger-type population transfer. GFSH can replace FSSH, although further tests are needed (45).

The problem of superexchange can be related to the quality of the nuclear wave-function representation in the approximate semiclassical schemes. In particular, FSSH utilizes a set of uncorrelated trajectories to describe a nuclear wave packet. The approximation breaks down when nuclear quantum effects become important. The SQUASH method has been developed to overcome this limitation of the FSSH method (46). The approach is based on two key ideas. First, one describes dynamics in terms of coupled \( N \)-particle states that entangle \( N \) semiclassical
trajectories. In contrast, the standard FSSH formulation uses only one-particle states, each of which is associated with an independent trajectory. Second, SQUASH allows energy exchange via entangled trajectories. This is achieved by imposing energy conservation on a set of $N$ coupled trajectories, rather than on each individual trajectory. The resulting SQUASH technique achieves high accuracy as demonstrated on a three-state model of superexchange. The energy exchange in the set of entangled trajectories provides a natural mechanism for tunneling and superexchange, and can be used to capture decoherence effects.

2.2.4. Stochastic mean-field, decoherence-induced surface-hopping, and coherence penalty functional theories. The SMF method (50) to NAMD bridges the gap between mixed quantum-classical and fully quantum descriptions. With the presence of additional terms in the Schrödinger equation that result from the system-environment interaction, SMF accounts for the quantum features of the environment with the Lindblad approach (110). In the simplest form, the quantum environment, such as a set of harmonic oscillators linearly coupled to the system, is described by Markovian diffusion terms in the Schrödinger equation (50). The SMF method simultaneously resolves the two major drawbacks of NAMD: Decoherence effects within the quantum subsystem due to interactions with the environment are rigorously included, and branching of NAMD trajectories is achieved. Decoherence provides the physical mechanism for the trajectory branching. Hop rejection due to violation of energy conservation disappears in the SMF approach.

The quantum mechanical wave packet of the whole system, including both electrons and nuclei, splits into uncorrelated branches and loses coherence over time. The resulting decoherence can be viewed as an environment-induced destruction of superpositioned quantum states of the microscopic system (111, 112). Drawing from the methodology of stochastic Schrödinger and master equations (113–115), the DISH method (51) was proposed. By combining the computational simplicity of quantum-classical NAMD with a formal treatment of quantum decoherence, DISH provides a straightforward and physically justified trajectory SH scheme, in which quantum transitions between surfaces occur only during decoherence events. The transition probabilities are computed according to the standard quantum mechanical rules. On one hand, DISH can be viewed as an SH approach to quantum dynamics in dissipative environments. And, on the other hand, DISH unifies decoherence and nonadiabatic transitions, providing a nonphenomenological account of quantum transitions in condensed-phase systems. DISH extends the feasibility of quantum-classical simulations to large quantum systems in macroscopic environments.

The CPF method (52) is another approach to incorporate decoherence effects into NAMD simulations. The method is based on a simple idea of dynamically penalizing the development of coherences during the evolution of quantum degrees of freedom. The methodology is formulated on the grounds of the Ehrenfest method for semiclassical dynamics. Decoherence effects are introduced via an additional term in the classically mapped Hamiltonian, thus preserving the overall Hamiltonian structure of the EOM. The CPF is analogous to XC functionals in DFT. It provides an effective way of introducing dynamical correlation effects, such as decoherence, on top of the Ehrenfest approach. The CPF methodology has a certain relation to QHD, and the method can be enhanced by allowing some of the variables entering the penalty functional to depend on time. A simple form for the penalty functional has been proposed, and good results have been demonstrated (52). The dependence of the penalty functional on coherences can be rather arbitrary, in principle, and other functional forms may prove more accurate, more general, or both. It is straightforward to combine the CPF scheme with FSSH and related approaches discussed above, in which SH probabilities can include decoherence effects through the modified time-dependent Schrödinger equation.
2.3. User-Friendly Implementation: The PYXAID Program

The PYXAID (PYthon eXtension for Ab Initio Dynamics) program has been developed as an open-source, flexible, and computationally efficient implementation of the NAMD methodology in the framework of KS DFT for large-scale condensed matter systems (93, 116). It carries out a number of basic and more advanced functionalities, including standard FSSH, the decoherence corrections via DISH, the use of ME basis configurations of the TDKS equations, and the direct simulation of photoexcitation via explicit light-matter interaction. Advanced integration techniques with Trotter factorization (117) of the evolution operator for solving the time-dependent Schrödinger equation lead to a significant speedup of the calculations and provide more stable solutions. The CPA approximation (93) achieves additional and considerable computational savings and makes it possible to study photoinduced dynamics at the ab initio level in systems comprising hundreds of atoms and involving thousands of electronic states. The first PYXAID paper describes the CPA for FSSH and DISH (93). The software is interfaced with QUANTUM ESPRESSO (118), which is used as an efficient driver for ab initio electronic structure and MD calculations. The key features of the PYXAID program have been demonstrated by studying the electron-nuclear dynamics in a variety of systems. PYXAID is organized as a Python extension module and can be easily combined with other Python-driven modules, enhancing user-friendliness and flexibility of the software. In addition to QUANTUM ESPRESSO, PYXAID has been interfaced with VASP and semiempirical electronic structure codes. The source and additional information are available on the PYXAID website (http://gdriv.es/pyxaid). The program is released under the GNU General Public License.

3. INORGANIC INTERFACES

Inorganic materials (e.g., colloidal QDs, noble metal nanoparticles, and TiO2) exhibit high charge carrier conductivity and excellent photostability. Photoinduced electron transfer at the interfaces between these inorganic components is essential for various photovoltaic and photocatalytic applications. Electron transfer occurs by two basic mechanisms (61): Adiabatic electron transfer results from a vibrational motion driving the electronic subsystem over a transition state, and nonadiabatic electron transfer occurs by a quantum transition between electron donor and acceptor states. Adiabatic electron transfer relies on strong donor-acceptor coupling, whereas nonadiabatic electron transfer operates in the weak-coupling regime. The nonadiabatic electron transfer rate is enhanced by the high density of acceptor states. The adiabatic and nonadiabatic mechanisms are described by different mathematical expressions [e.g., an Arrhenius expression and Fermi’s golden rule (55), respectively]. The complex interplay of donor-acceptor and electron-phonon interactions creates a broad spectrum of electron injection scenarios. This section describes recent atomistic studies on real-time photoinduced electron transfer at interfaces of bulk and nanoscale TiO2 with semiconducting and metallic nanoparticles. We analyze in detail why hot electrons can be extracted efficiently from PbSe QDs into TiO2, how TiO2 dimensionality determines the mechanism of electron transfer from CdSe QDs, and why charge separation can be achieved instantaneously at the interface between a gold particle and TiO2.

3.1. Extraction of Hot Electrons from a PbSe Quantum Dot into a TiO2 Slab

In recent years, QDs have been extensively employed as chromophores for TiO2 sensitization producing quantum dot–sensitized solar cells (QDSCs) (119). QDs are excellent light absorbers due to their large intrinsic dipole moments, high extinction coefficients, and good photostability.
They have size-dependent band gaps and thus can be easily tuned to absorb light at any wavelength of the solar spectrum. QDs provide opportunities for increasing solar cell voltage by rapid extraction of hot charge carriers and enhancing current using the additional energy available at the blue end of the solar spectrum via the generation of multiple electron-hole pairs (120). Because of these advantages, QDSCs become promising candidates to harvest sunlight for solar-to-electrical energy conservation.

Photoinduced electron transfer is key for QDSC efficiency. As a representative example, the nanoscale system comprising a PbSe QD adsorbed on a rutile TiO$_2$ (111) surface has been investigated (61). In line with recent time-resolved experiments (19, 20), the computational result directly mimics the observation that the ultrafast interfacial electron transfer in the PbSe-TiO$_2$ system successfully competes with energy losses due to electron-phonon relaxation inside the PbSe subsystem. The electron transfer is found to proceed primarily by the adiabatic mechanism (see Supplemental Figure 1; follow the Supplemental Material link from the Annual Reviews home page at http://www.annualreviews.org) because of the strong coupling between PbSe and TiO$_2$. Owing to the large size and high rigidity of QDs, the electron donor density is spread over the whole QD, whereas the acceptor density is distributed nearly uniformly across the TiO$_2$ slab. The optical phonons available in the PbSe-TiO$_2$ system are of the same order of magnitude of thermal energies because QDs comprise heavy elements. These vibrations, in particular polar Pb-Se and Ti-O stretches, promote electron transfer because they can rapidly shift the electronic density between the donor and acceptor species. Low-frequency modes of TiO$_2$ and PbSe surfaces create an inhomogeneous distribution of initial conditions for electron transfer. The nonadiabatic transfer component is nearly an order of magnitude slower than the adiabatic electron transfer.

3.2. Minimizing Electron-Hole Recombination on TiO$_2$ Sensitized with PbSe Quantum Dots

Despite the rapid interfacial charge separation, the final yields of the light-induced processes in QDSCs are limited by electron-hole recombination that also occurs at the interface. Minimizing charge recombination can largely enhance the photon-to-electron conversion efficiency.

Ab initio NAMD has been combined with analytic theory to investigate charge recombination at the PbSe QD-TiO$_2$ interface (62). The time-domain atomistic simulation directly mimics the laser experiment (20) and generates important details of the recombination mechanism. The simulations indicate that the recombination is largely promoted by a high-frequency optical Raman-active mode of TiO$_2$. Lower-frequency optical modes contribute to a lesser extent. The elastic electron-phonon scattering takes 40 fs, which is an order of magnitude shorter than the picosecond timescale of inelastic scattering. The simulated electron-hole recombination timescale agrees well with the experimental observation (20). The donor and acceptor states are strongly localized on the corresponding materials. This contrasts with the photoinduced charge separation in the same system, which starts from a QD state that is delocalized onto TiO$_2$ and which is significantly faster than the charge recombination. Counter to expectations, the PbSe-TiO$_2$ bonding strengthens at an elevated temperature because thermal fluctuations create additional bonding opportunities.

An analytic theory extends the simulation results to larger QDs and longer QD-TiO$_2$ bridges. It shows that the electron-hole recombination rate can be suppressed exponentially by increasing either the ligand bridge length or the QD size (see Supplemental Figure 2). Changes in both donor-acceptor coupling and the energy gap lead to exponential dependence, with the coupling providing a more significant contribution. By varying the QD size and/or ligands, one can reduce charge losses while still maintaining efficient charge separation, providing design principles for optimizing solar cells.
3.3. Dimensionality of TiO₂ Determines Photoinduced Electron Transfer Mechanism from CdSe Quantum Dots

The dependence of electron transfer efficiency on the system properties is very different for the adiabatic and nonadiabatic electron transfer mechanisms. The adiabatic mechanism requires strong donor-acceptor coupling, and therefore, it is quite sensitive to the binding mode, and the presence and length of a bridge. In contrast, the nonadiabatic mechanism operates if the donor-acceptor coupling is weak and requires a high density of acceptor states and the availability of phonon modes to accommodate changes in the electronic energy during nonadiabatic transitions. As a result, the efficiency of nonadiabatic electron transfer depends on the photoexcitation energy and acceptor size. Highly ordered 1D nanostructures (e.g., nanotubes, nanowires, and nanorods) have recently received considerable attention as solar materials (121–123). They provide a significant improvement in the charge transport and photoconversion efficiency compared to 0D QDs. The photoinjection mechanism of electrons across QD-TiO₂ interfaces may vary with the shape of the semiconductor nanostructure.

The role of TiO₂ dimensionality on the mechanism of photoinduced interfacial electron transfer from CdSe QDs into nanoscale TiO₂ has been studied (63). A quasi-0D TiO₂ QD and 1D TiO₂ nanobelt have been considered. As shown in Supplemental Figure 3, the adiabatic mechanism operates in the TiO₂ QD system because of the strong chemical binding between CdSe and TiO₂, arising from unsaturated chemical bonds on the QD surface. The density of acceptor states in the TiO₂ QD is low, inhibiting the nonadiabatic mechanism. In contrast, the injection into a TiO₂ nanobelt is nonadiabatic because the donor-acceptor coupling is weak, the acceptor state density 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 TiO₂ nanobelt, creating localized acceptor states. It also relaxes donor-acceptor and nonadiabatic coupling selection rules and generates more electron transfer channels. Both mechanisms can give efficient and ultrafast injection. However, the fundamental principles leading to efficient charge separation strongly depend on the type of nanoscale material.

3.4. Instantaneous Charge Separation on a TiO₂ Surface Sensitized with Plasmonic Nanoparticles

Solar cells based on semiconductor sensitization with metal nanoparticles have also attracted significant attention because of the unique electronic and optical properties of metallic clusters (124). The exciting optical physics of metal nanoparticles arises from the resonant interaction of conduction band electrons and the electromagnetic field (125). The collective excitations, usually known as plasmons, are responsible for the specific light extinction and high local fields. In addition, the prominent catalytic properties of gold nanoparticles on well-ordered metal oxide substrates stimulate extensive research activities. These systems combine the light-harvesting ability of semiconductor nanocrystals with the catalytic activity of small metal particles, showing great promise in photocatalysis, such as light-driven hydrogen production (126).

An Au₂₀ nanoparticle absorbed on a TiO₂ surface has been carefully studied (64). The interaction between gold and TiO₂ is noncovalent at both low and room temperatures. Ab initio simulations show that the photogenerated plasmon-like state is highly delocalized onto TiO₂ (i.e., it is shared by the whole system) (see Figure 3). Because of this, the interfacial charge separation occurs instantaneously upon photoexcitation of the plasmon band with a high probability (<50%), bypassing the intermediate step of electron-hole thermalization inside the Au₂₀ nanoparticle. In the remaining 50% of the scenarios, the plasmon excitation generates electron-hole pairs in gold,
Figure 3

Charge densities of (a) a plasmon state, (b) a TiO$_2$ acceptor state, and (c) the Fermi energy state of the Au$_{20}$-TiO$_2$ system. The excited state is delocalized significantly onto TiO$_2$, leading to instantaneous charge separation upon photoexcitation at the plasmon energy. Entropy drives the electron into the TiO$_2$ bulk, exemplified by the TiO$_2$ acceptor state. Following electron-vibrational relaxation, the electron can recombine with the hole, residing in the Fermi energy state, on a picosecond timescale. Figure adapted with permission from Reference 64. Copyright 2014 American Chemical Society.

and the electron is transferred to the TiO$_2$ surface on a sub-100-fs timescale. Electron-phonon energy relaxation paralleling electron injection is somewhat slower. Driven by entropy due to the high density of bulk TiO$_2$ states, the electron overcomes the Coulombic electron-hole attraction and delocalizes further into TiO$_2$ bulk. Structural defects in the TiO$_2$ surface can trap the injected electron near the gold nanoparticle, leading to a picosecond timescale of electron-hole recombination. Electrons that have diffused into bulk TiO$_2$ can find their way back to the surface and recombine with the hole on a much longer timescale.

The electron injection occurs primarily by the nonadiabatic mechanism due to a relatively weak donor-acceptor coupling and a high density of TiO$_2$ acceptor states. The recombination proceeds exclusively by the nonadiabatic mechanism because of the large energy gap between the initial and final states in this case. The obtained electron transfer and recombination timescales show excellent agreement with the time-resolved experimental data (17). The strong optical response of the surface plasmon, rapid charge separation, and a significantly slower electron-hole recombination provide the fundamental basis for utilization of plasmon-sensitized TiO$_2$ as an excellent photovoltaic material and a visible-light photocatalyst.

4. ORGANIC/INORGANIC HYBRIDS

Organic/inorganic nanocomposites find multiple applications in photovoltaic, photocatalytic, and transport devices. Similar to metal nanocrystals, graphene has no band gap and exhibits ultrahigh charge mobility (127, 128). Efficient photoinduced charge separation needs to compete with energy losses due to rapid electron-hole annihilation inside metallic graphene. In contrast, bulk semiconductors, QDs, molecules, and polymers possess band gaps; thus charge recombination can be restrained. Besides electricity, solar energy can be converted to chemical energy, for instance, by water splitting assisted by inorganic photocatalysts. In this section, we describe recent work concerning graphene-TiO$_2$, QD-molecule, QD-polymer, and GaN-H$_2$O interfaces. We show that both electron and energy transfer from graphene to the TiO$_2$ surface are consistently
faster than energy relaxation and that defects are essential rather than detrimental for fast electron transfer from QDs to molecules. We rationalize a counterintuitive result that, along an insulating bridge, can enhance photoinduced charge separation. We also introduce a new type of electron transfer mechanism, Auger-assisted electron transfer, that eliminates the electron transfer rate reduction in the Marcus inverted regime. Because Auger-type processes are generic to nanoscale materials, Auger-assisted electron transfer should be very common in these systems. We find that 1D poly(3-hexylthiophene) (P3HT) behaves as a 0D molecule, whereas a 0D QD acts as a 3D bulk material in the P3HT/QD interaction region. The inverted dimensionally restores symmetric electron-hole dynamics, creating favorable conditions for current generation in solar cells. Finally, we discuss photocatalytic water oxidation on a semiconductor surface and formulate a set of design rules for improving water splitting.

4.1. Efficient Photoinduced Charge Separation Across the Graphene~TiO$_2$ Interface

Many experimental efforts are currently focusing on the synthesis of hybrid graphene-TiO$_2$ nanocomposites for photovoltaic and photocatalytic applications (129, 130). Graphene’s advantages include a high surface area for interfacial contact, excellent charge conductivity, and outstanding mechanical properties. Graphene can harvest a larger fraction of the solar spectrum than can many other nanostructured materials. The obtained electrons can produce electricity or drive a water-splitting reaction to generate hydrogen. However, because graphene is a metal, the photogenerated electrons and holes may rapidly relax through the continuous manifold of states and annihilate. Therefore, one wonders whether graphene can be used at all as a chromophore for solar power conversion.

A representative hybrid graphene-TiO$_2$ system has been constructed (65). At ambient temperatures, the interfacial oxygen atoms disrupt the π-electron system of graphene. This makes graphene locally semiconducting and strengthens graphene-TiO$_2$ bonding. The electron and energy transfer in graphene-TiO$_2$ composites can proceed in both directions, depending on the energy of the excited electron. Once the electron relaxes to the bottom of the TiO$_2$ conduction band, it can move back onto graphene, as graphene has energy levels within the TiO$_2$ band gap. The back-transfer process competes with the electron delocalization into bulk TiO$_2$ that is driven by entropy, related to the TiO$_2$ DOS.

The timescales for the photoinduced interfacial electron transfer, energy relaxation, and energy transfer can be obtained using NAMD. It has been established that the photoinduced electron transfer occurs faster than the electron-phonon energy relaxation (i.e., charge separation is efficient in the presence of electron-phonon relaxation). The ultrafast electron injection occurs because of the strong donor-acceptor coupling, favoring the photoexcitation of states that are delocalized significantly between the two subsystems (see Supplemental Figure 4a). Injection is promoted by both out-of-plane graphene motions, which modulate the graphene-TiO$_2$ distance and interaction, and high-frequency carbon bond stretching and bending vibrations, which generate large nonadiabatic coupling. The subsequent evolution occurs by rapid nonadiabatic transitions down the manifold of delocalized states, resulting in simultaneous electron transfer, energy transfer, and electron-vibrational energy relaxation. The simulation shows that both electron transfer and energy transfer from graphene to the TiO$_2$ surface are consistently faster than the relaxation, regardless of the excitation energy (see Supplemental Figure 4b,c), rationalizing the high direct light-to-current conversion efficiencies of graphene-TiO$_2$ solar cells reported experimentally (131). Thereby, graphene-TiO$_2$ composites can form the basis for photovoltaic and photocatalytic devices.
4.2. Defects Are Needed for Fast Photoinduced Electron Transfer from a Quantum Dot to a Molecule

The surfaces of most optically active QDs are metal rich because metal atoms can successfully reconstruct nanocrystal surfaces, eliminating unsaturated chemical bonds and other defects (132). As a result, QD surfaces are missing the complementary elements, for instance, sulfur atoms in CdS QDs. Sulfur vacancies create states below the conduction band (133). Defects are considered detrimental in many applications. For instance, they lead to QD blinking due to charge trapping and rapid electron-phonon energy losses due to decreased electronic energy gaps and increased electron-phonon coupling. Surface defects can have a positive effect on the photoinduced charge separation, thereby improving solar energy conversion efficiencies (66).

Electron transfer from a PbS QD to the rhodamine B molecule and subsequent electron return from rhodamine B to the QD has been investigated in detail (66). Both charge separation and recombination are nonadiabatic processes, driven by nuclear vibrational motions. The nonadiabatic electron-phonon coupling is created predominantly by motions of the molecule because it comprises lighter atoms and is more labile than the QD. In contrast, the donor-acceptor coupling between the QD and molecule arises from the QD because its wave function is more delocalized and leaks onto the adsorbed molecular species, generating the required overlap between the donor and acceptor wave functions. Although the donor-acceptor energy gap is smaller for the recombination, the NAMD simulation supports the experimental observation (134) that charge separation is faster than recombination, rationalizing this fact by a twice-stronger nonadiabatic coupling for the forward than the backward electron transfer reaction. The computed electron-hole recombination timescale obtained for the system without defects agrees very well with experiment (134). However, the charge separation timescale is notably overestimated. Repeating the simulation by including a sulfur vacancy has improved agreement between theory and experiment. The missing sulfur creates unsaturated chemical bonds on lead atoms, which form the PbS conduction band. As a result, the QD lowest unoccupied molecular orbital (LUMO) is lowered in energy, decreasing the donor-acceptor energy gap. In addition, the unsaturated bonds extend the LUMO density onto the adsorbed molecule, increasing the donor-acceptor coupling. The combination of a decreased energy gap and an increased nonadiabatic coupling accelerates the charge separation (see Figure 4). The counterintuitive conclusion that defects are helpful rather than harmful to sunlight harvesting and utilization brings a novel perspective to QD synthesis for photovoltaic and photocatalytic applications.

4.3. An Insulating Bridge Greatly Enhances Photoinduced Electron Transfer in Quantum Dot–Fullerene Nanocomposites

Bang & Kamat (135) prepared fullerene-QD solar cells by placing a blend of CdSe QDs and C60 on an optically transparent electrode. By functionalizing C60 with a thiol compound, they covalently linked it to the QD and investigated the photoinduced electron transfer from the QD to C60 using time-resolved transient absorption spectroscopy. The covalent linking provided a significant improvement in the charge separation and photoconversion efficiency compared with the previous work utilizing a mechanical blend.

To rationalize the experimental findings, investigators have used NAMD combined with TDDFT to characterize photoinduced electron transfer in two kinds of architectures, including a mechanical mixture of C60 and CdSe QD, as well as covalently linked composites (67). The calculations demonstrated that a covalent bridge connecting the QD to C60 is particularly important to ensure ultrafast transmission of the excited electron from the QD photon harvester to the C60 electron acceptor (see Supplemental Figure 5). Despite the close proximity of the
Figure 4
Energy levels and timescales involved in charge separation and recombination processes in the PbS quantum dot (QD)–rhodamine B (RhB) system. The geometries of the QD and RhB are shown next to their corresponding levels. Figure adapted with permission from Reference 66. Copyright 2013 American Chemical Society. Abbreviations: HOMO, highest occupied molecular orbital; LUMO, lowest unoccupied molecular orbital.

donor and acceptor species provided by direct van der Waals contact, it leads to a notably weaker QD-C60 interaction than a lengthy and insulating molecular bridge. Additionally, it was found that the electron transfer rate in a nonbonded mixture can be tuned by C60 doping with lithium. The calculated electron transfer times are in good agreement with experiment (135). The electron transfer rate in the QD-bridge-C60 system is enhanced owing to the following three factors. (a) Most importantly, the bridge increases the nonadiabatic coupling by providing high-frequency vibrational modes. The electron-vibrational interaction is critical to the electron transfer because significant amounts of the electronic energy have to be deposited into vibrational modes. (b) By allowing the QD wave function to extend onto the bridge and effectively increasing the QD size, the bridge lowers the QD band gap and consequently the donor-acceptor energy gap. (c) Long-range correlations between the atomic motions of the donor and acceptor species created by the bridge decrease the phonon-induced pure-dephasing rate and prolong quantum coherence during the nonadiabatic transition. This study highlights an often-overlooked design principle for enhancing photoinduced charge separation in nanoscale light-harvesting materials.

4.4. Auger-Assisted Electron Transfer from Photoexcited Quantum Dots to Molecular Acceptors

Traditionally in chemistry, electron transfer processes are understood in terms of the Marcus theory (136). Because of strong electron-nuclear interaction in molecules, intermolecular electron transfer is accompanied by a large rearrangement of the nuclear configuration. The Marcus theory describes the well-known dependence of the electron transfer rate on the donor-acceptor energy gap, including the normal, barrierless, and inverted regimes. In bulk inorganic semiconductors, electron transfer requires little change in nuclear configuration due to weak electron-phonon coupling (137), and charge carriers are regarded as quasi-free particles. Both electron-hole and
electron-phonon interactions in nanoscale materials fall between those in molecules and bulk. The choice of an appropriate model for describing photoinduced electron transfer on the nanoscale remains an area of active research.

Because of quantum confinement, semiconductor QDs exhibit atomic-like discrete electronic levels and corresponding excitonic transitions that can be widely tuned by QD size (138). Such size-dependent energetics provides an ideal platform for testing theoretical models for describing electron transfer from excitonic nanomaterials. With regard to this aspect, photoinduced electron transfer from CdS, CdSe, and CdTe QDs to three molecular acceptors, anthraquinone, methyl viologen, and methylene blue, has been systematically studied (68). The observed electron transfer rates increase with decreasing QD size, regardless of QD compositions and acceptor redox potentials, showing a lack of the Marcus inverted regime over a broad range of donor-acceptor energy gaps, from 0 to 1.3 eV (see Supplemental Figure 6). The unexpected driving force dependence has been accounted for by the recently proposed Auger-assisted electron transfer model (68), in which the electron transfer is coupled to the excitation of the hole, circumventing the unfavorable Franck-Condon overlap in the Marcus inverted regime. This model is supported by computational studies on a realistic QD-acceptor complex.

The photoinduced electron transfer from QDs is fundamentally different from those in molecular chromophores and bulk semiconductors. Supplemental Figure 6 shows the time evolution of the energies of various parts of the system along a representative trajectory. The energy lost by the electron during the transfer is gained at the initial stage exclusively by the hole rather than by the phonons, confirming the proposed Auger-assisted electron transfer mechanism. Because Auger-type processes occur in most nanomaterials exhibiting quantum confinement, the Auger-assisted electron transfer model proposed for CdX QDs should be generally applicable to exciton dissociation in other nanomaterials, including nanotubes, nanowires, quantum wells, and graphene.

4.5. Inverted Dimensionality Restores Electron-Hole Symmetry in a Quantum Dot–Polymer Hybrid

Hybrid photovoltaic cells based on inorganic QDs and polymers possess significant potential for low-cost and scalable solar power conversion. Polymers harvest solar light and donate electrons in organic solar cells. Polymer-based solar cells offer the advantages of solution processing and straightforward chemical synthesis. At the same time, Coulomb interactions between charge carriers are strong because of low dielectric constants, giving rise to strongly bound electron-hole pairs rather than to free charge carriers (139). This drawback significantly reduces the power conversion efficiency of polymer-based solar cells.

Compared to fullerenes, which are used as electron acceptors in traditional organic solar cells, colloidal QDs exhibit better morphological stability and higher electron mobilities. In addition, QDs improve light harvesting because of their large absorption cross sections, easily tunable over the entire solar spectrum. The electron-phonon relaxation dynamics in QDs have attracted intense attention. Hot-carrier generation and carrier multiplication provide opportunities to improve the conversion efficiencies of QDSCs by reducing the loss of high-energy carriers. Using the advantages of both organic polymer and inorganic QD materials provides new ways to enhance solar cell performance.

NAMD combined with TDDFT has been employed to investigate the photoinduced electron and hole dynamics in a heterojunction formed by P3HT and a CdS QD. QDs are viewed as quasi-0D materials, whereas polymers are 1D. Simple models predict discrete energy levels in QDs and continuous bands in polymers. However, the atomistic calculations present a different picture. Generally, QDs exhibit discrete levels only close to the band gap. Indeed, Figure 5 shows that
the CdS QD LUMO is separated from LUMO $+1$ by approximately 0.5 eV. At higher energies relevant for the charge separation dynamics, the QD spectrum is continuous. The polymer indeed exhibits a band-like electronic structure. At the same time, the DOS of the polymer is much lower than that of the QD. In the local interaction QD-P3HT region involved in the photoinduced charge separation, and at the relevant energy range, P3HT behaves as a molecule, while the QD is nearly bulk-like. The inversion of the dimensionally, relative to the common expectation, helps to balance the electron and hole injection rates. Such balance is essential for a solar device; otherwise, one of the charges will present a bottleneck to the photoinduced dynamics. The driving force for the hole transfer from the QD to P3HT is larger, but the density of P3HT acceptor states is small (Figure 5). In comparison, the driving force for the electron transfer from P3HT to the QD is small, but the density of QD acceptor states is large. The leveling of the two factors produces electron and hole injection times on a timescale of several hundred femtoseconds, in agreement with experiment (140).

4.6. Positive Charge Dynamics During Photocatalytic Water Splitting on a GaN(10-10) Surface

Photocatalytic water splitting is a promising avenue to sustainable, clean energy and fuel production. Since the discovery of water splitting on TiO$_2$ electrodes by Fujishima & Honda (141), significant progress has been made in the experimental characterization and preparation of various
Thermal activation

Hole relaxation

~50 fs

h+

h+h+

N-H deprotonation

>1 ps

>50 ps

Hole migration

~50 fs

Proton transfer

~1.5 ps

~0.5 ps

O-H deprotonation: water splitting

Figure 6

(a) Electron spin density of the photogenerated hole in the GaN-water system at 0.22 eV below the valence band edge. The black parallelogram indicates the simulation cell. (b) Kinetic scheme of the hole and proton migration processes involved in the initial stages of photocatalytic water oxidation. Figure adapted with permission from Reference 70. Copyright 2013 American Chemical Society.

photocatalytic materials, as well as in the theoretical description of the underlying processes and their mechanisms (142, 143). Nonetheless, the fundamental understanding is far from complete. One of the manifestations of the lack of comprehensive knowledge is a relatively small quantum yield of this reaction achieved with the currently available materials. The search for efficient and cheap catalytic materials has led scientists to explore a large variety of semiconductor photocatalysts. In recent studies, Domen and colleagues (144) have shown that GaN can be used for water splitting under ultraviolet light irradiation, although with a relatively small yield. The yield increases in a GaN:ZnO solid solution and especially in the presence of a cocatalyst.

A comprehensive kinetic model of the processes taking place during the initial stages of the photoinduced water oxidation reaction on the GaN(10-10) surface has been constructed based on NAMD calculations (see Figure 6) (70). The quantum dynamics of hole relaxation, mediated by coupling to nuclear vibrations, the hole transfer from GaN to water, and the ensuing proton-transfer events have been characterized. The calculations show that the hole loses its excess energy within 100 fs and localizes primarily on the nitrogen atoms of the GaN surface, initiating a sequence of proton-transfer events from the surface N-H group to the nearby OH groups and bulk water molecules. During the energy relaxation, the hole transiently populates the oxygen species, making water oxidation possible from both kinetic and thermodynamics points of view. The relaxation kinetics of the hole determines its dwelling time on the surface hydroxyl groups. This time is approximately 50 fs and is too short in general to initiate the nuclear rearrangements required for the water oxidation reaction, contributing to the low efficiency of water splitting on pure GaN. This atomistic study strongly indicates that an efficient material for water oxidation should favor hole localization on surface hydroxyl groups. Lacking in pure GaN, this feature can be achieved with composite materials, such as oxide cocatalysts, oxinitride substrates, and their chemically modified derivatives.

In the absence of a hole, water molecules are completely dissociated, occupying all available gallium and nitrogen surface sites. The situation is qualitatively different for the charged surface, in which some protons dissociate from surface N-H groups and migrate near the surface. The result

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is a hydroxonium cation and a free, uncapped nitrogen site. The proton moves further between the hydroxonium and the adjacent chemisorbed hydroxyl groups or, with a smaller probability, diffuses into bulk water. The free energy barriers for the proton transfer along the GaN surface are calculated to be 2.16 and 0.64 kcal/mol, depending on the direction of the proton transfer among the asymmetric surface sites. The characteristic time of the proton-transfer reaction starting from the most stable configuration of the charged surface is estimated to be 1.6 ps. Both the free energy barriers and the transfer rates are in good agreement with the available experimental and theoretical studies (144).

5. ORGANIC SYSTEMS

Organic systems, including small molecules and polymers, exhibit both advantages and disadvantages compared to inorganic compounds. Organic molecules are extremely diverse, providing an essentially unlimited availability of raw materials. They are mechanically flexible and lightweight. They can be mass produced at a low cost. At the same time, electrons and holes are strongly bound inside organic matter, making photoinduced charge separation challenging. The opposite process, the radiative recombination of injected charges, occurs more readily, giving rise to light-emitting diodes. Electron-phonon interaction is also strong in organic materials, generating polarons with large effective masses and low mobilities. Charge and exciton dynamics at organic interfaces are of great importance for solar energy and electronics applications. In the following, we present a comprehensive kinetics at a pentacene-C₆₀ interface, exhibiting a fundamentally interesting and practically important phenomenon known as singlet fission (SF). SF allows one to convert one photon into two electron-hole pairs, thereby increasing the photoinduced current. We also analyze the origin of significant asymmetry between electron and hole transfer in a polymer-carbon nanotube (CNT) composite and propose how this asymmetry can be utilized to tune photovoltaic performance.

5.1. Singlet Fission and Charge Transfer at the Pentacene-C₆₀ Interface

The generation of two electron-hole pairs per single absorbed photon is known in organic systems as SF (145–147). SF is interesting from a fundamental point of view because simple selection rules forbid the excitation of two electrons by one photon. SF holds promise for the development of solar cells with enhanced photon-to-electron yields, and therefore, it is of substantial applied interest as well. The efficiency of photovoltaic devices based on this principle is determined by complex dynamics involving key electronic states coupled to particular nuclear motions. Extensive experimental and theoretical studies are dedicated to this topic, generating multiple opinions on the nature of such states and motions, their properties, and mechanisms of the competing processes, including electron-phonon relaxation, SF, and charge separation (145, 146). Using NAMD, one can identify the most important steps involved in SF and subsequent charge separation, and build a comprehensive kinetic scheme that is consistent with the existing experimental and theoretical results. The model helps to resolve controversies regarding the nature and importance of intermediate states, energy-level alignment, SF mechanism, and timescales of quantum dynamics.

A minimalistic atomistic model has been constructed to describe a pentacene/C₆₀ interface (71). The simulation has demonstrated that SF competes with the traditional photoinduced electron transfer between pentacene and C₆₀ layers. Efficient SF relies on the presence of intermediate dark states. These configurations can be viewed as either independent states or components of the ME and triplet pair (TT) states arising due to electron correlation. Several pentacene-pentacene and pentacene-fullerene charge transfer states should be taken into account, including the lowest-energy charge transfer state (CT₀) and excited charge transfer states (CT₁ and CT₂). Having
ME and charge transfer character, these states play critical roles in the dynamics and should be considered explicitly when explaining the entire process from photoexcitation to the final charge separation.

The relative energies of the states involved in the photoinduced dynamics should be carefully aligned with respect to each other. Assigning the energy of the CT0 state at approximately 0.5 eV according to experiment (148) produces a consistent quantum dynamical scheme. An interesting way of controlling the SF efficiency can be suggested based on the energy alignment. If CT2 is designed to have energy larger than that of the TT state, triplet production can be maximized. After dissociation of the TT state, each triplet can access states of the CT0 type, provided that their energy is lower than the energy of the TT state. Then, the generation of two electron-hole pairs will be maximized. The S1 and ME states involved in the SF process are rather weakly coupled. Direct nonadiabatic transitions between these states are suppressed, although not forbidden. Because the S1 and TT states are also weakly coupled, the triplet production originates only from the ME state, which is populated during photoexcitation (see Figure 7). Generally, photoexcitation creates a superposition of the S1 and ME configurations. To maximize the SF yield, one should design systems and utilize photoexcitation conditions under which the contribution of the ME configurations is maximized. One can also consider designing electromagnetic fields to directionally pump S1 into the ME or TT state. The reported analysis enhances our understanding of the complex quantum dynamics in nanoscale materials capable of the SF and charge transfer processes.

5.2. Asymmetric Electron and Hole Transfer at a P3HT–Carbon Nanotube Heterojunction

Bulk heterojunction organic photovoltaics have been demonstrated as low-cost alternatives to silicon-based solar cells, offering a long-term solution for clean, renewable energy (149). To achieve high photon-to-charge conversion efficiency, the electron-hole pair generated by photon absorption in organic photovoltaic systems must overcome the Coulomb attraction, which often results in voltage loss. The low dielectric constant of organic conjugated materials results in significant Coulomb interactions between charge carriers and gives rise to a strongly bound electron-hole pair, rather than to free charge carriers.
By applying the unique methodologies combining TDDFT and NAMD, one can investigate the photoinduced electron and hole dynamics and energy relaxation across an interface formed by P3HT and a single-walled CNT (72). As shown in Supplemental Figure 7, photoexcitation of the polymer leads to a 100-fs electron transfer, in agreement with experiment (150), followed by an energy loss of 0.6 eV within 0.5 ps. Photoexcitation of the CNT leads to hole transfer, which requires nearly 2 ps, but loses only 0.3 eV of energy. The electron transfer is an order of magnitude faster than the hole transfer, establishing that the electron and hole dynamics are highly asymmetric in CNT/P3HT composite materials. The strong disparity arises from the differences in the localization of the photoexcited donor states, the densities of the acceptor states, the strength of the donor-acceptor interaction, and the phonon modes involved. The hole-vibrational relaxation is promoted primarily by the high-frequency C–C stretching modes, with the electron relaxation additionally involving low-frequency CNT and P3HT motions. Used as a chromophore, 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, and reduces energy losses, but gives less efficient charge separation.

The complementary properties of P3HT and CNT can be utilized to improve the performance of solar cells by simultaneously optimizing light harvesting, charge separation, and energy relaxation, which affect photovoltaic yield, current, and voltage. By increasing the CNT concentration, one can harvest a broader range of the solar spectrum and reduce energy and voltage losses. By increasing the P3HT concentration, one achieves better charge separation and higher currents. The reported simulations provide a comprehensive description of the charge and energy transfer dynamics in the hybrid nanoscale material and suggest novel design principles for photovoltaic and photocatalytic devices.

6. CONCLUSIONS AND OUTLOOK

The amount of solar energy reaching the Earth’s surface is approximately 7,000 times more than our current global consumption, and thereby solar energy conversion is currently the most promising tool to solve the energy problem. If we could use a larger fraction of the solar energy, we could reduce our dependence on fossil fuels. A massive array of materials has been designed and applied in photovoltaic and photocatalytic devices. Because of the substantial difference in the origin and nature of the explored materials, ab initio atomistic simulations are especially valuable for investigating the charge and exciton dynamics at photovoltaic and photocatalytic interfaces.

The combination of TDDFT and NAMD has provided a unique, practical, and universal theoretical tool to study various nonequilibrium processes in a broad spectrum of systems. Above we summarize recent efforts in both methodological developments and realistic applications. The timescales for electron and energy transfer, thermal relaxation, and charge recombination in systems consisting of two complementary inorganic or organic materials have been obtained and compared extensively with experimental observations. The branching between the alternative dynamical processes governs the global efficiency of various devices and determines efficiency bottlenecks. Thorough understanding of the mechanisms underlying each dynamical channel provides useful guidelines for improving the performance of devices for solar energy conversion. The issues and processes occurring at photovoltaic and photocatalytic interfaces bear close resemblance to those encountered in electronic, spintronic, and other types of transport processes.

An atomistic simulation of nonequilibrium processes in molecular, nanoscale, and condensed matter systems relies on an accurate description of the electronic structure and a reliable representation of the electron-vibrational dynamics. These needs motivate further developments in the field. More robust and simultaneously efficient XC DFT functionals are required for the
proper description of long-range electron transfer, multiply excited states, bond breaking, and other situations that take the system far from the ground state equilibrium. To perform large-scale simulations, the computational cost for electronic structure calculations should be reduced. Significant efforts are devoted to the density-functional tight-binding (DFTB) method (151), which parameterizes the key DFT quantities, such as pseudo-atomic orbitals, matrix elements, and short-range repulsions. DFTB can significantly reduce the computational complexity, while maintaining reasonable accuracy (152). Implementing time-dependent DFTB can greatly extend the scope of NAMD applications. Most NAMD applications still neglect decoherence (47–49) and other quantum nuclear effects, which are important for many dynamical processes and deserve serious consideration. With rare exceptions, semiclassical NAMD algorithms capable of capturing these effects have been applied only to model or small systems. Further simplifying approximations and implementations of such schemes are clearly needed. NAMD simulations performed explicitly in the time domain can be coupled to kinetic descriptions to explore longer timescales. NAMD techniques have clearly demonstrated the ability to resolve a wide range of problems and questions arising in systems perturbed far from equilibrium. As demonstrated in this review, in particular, they satisfy the impending demand of mechanism exploration and material design for more efficient utilization of solar energy.

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### Errata

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