

Time-Domain Ab Initio Analysis of Excitation Dynamics in a Quantum Dot/Polymer Hybrid: Atomistic Description Rationalizes Experiment

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Time-Domain Density Functional Theory. The standard time-domain density functional theory (TDDFT)¹ relates electronic properties of a system to the electron density, expressed by the sum of the densities of the occupied time-dependent single-electron Kohn-Sham (KS) orbitals, $\varphi_p(\mathbf{r}, t)$,

$$\rho(\mathbf{r}, t) = \sum_{p=1}^{N_e} |\varphi_p(\mathbf{r}, t)|^2, \quad (1)$$

where N_e is the number of electrons. The evolution of $\varphi_p(\mathbf{r}, t)$ is determined by application of the time-dependent variational principle to the expectation value of the KS density functional. It gives a set of single-particle equations for the evolution of the KS orbitals:^{2, 3}

$$i\hbar \frac{\partial \varphi_p(\mathbf{r}, t)}{\partial t} = H(\mathbf{r}, \mathbf{R}, t) \varphi_p(\mathbf{r}, t); p = 1, 2, \dots, N_e \quad (2)$$

These single-electron equations are coupled, because the DFT Hamiltonian H depends on the overall electron density, eq 1. The electron-vibrational coupling enters the Hamiltonian through the external potential created by the nuclei. Expanding the time-dependent KS orbital $\varphi_p(\mathbf{r}, t)$ in the adiabatic KS orbital basis $\tilde{\varphi}_k(\mathbf{r}, \mathbf{R}(t))$

$$\varphi_p(\mathbf{r}, t) = \sum c_{pk}(t) \tilde{\varphi}_k(\mathbf{r}; \mathbf{R}(t)), \quad (3)$$

and inserting the expansion into eq 2, give the equation describing the evolution of the expansion coefficients:⁴

$$i\hbar \frac{\partial}{\partial t} c_{pk}(t) = \sum_{m=1}^{N_e} c_{pm}(t) (\varepsilon_m \delta_{km} + \mathbf{d}_{km} \cdot \dot{\mathbf{R}}) \quad (4)$$

The adiabatic KS orbitals are readily available from time-independent DFT calculations, which bear the majority of the computational effort in the current approach. The nonadiabatic coupling

$$\begin{aligned} \mathbf{d}_{km} \cdot \dot{\mathbf{R}} &= -i\hbar \langle \tilde{\varphi}_k | \nabla_{\mathbf{R}} | \tilde{\varphi}_m \rangle \cdot \frac{d\mathbf{R}}{dt} = -i\hbar \left\langle \tilde{\varphi}_k \left| \frac{\partial}{\partial t} \right| \tilde{\varphi}_m \right\rangle \\ &\approx -\frac{i\hbar}{2\Delta t} (\langle \tilde{\varphi}_k(t) | \tilde{\varphi}_m(t + \Delta t) \rangle - \langle \tilde{\varphi}_k(t + \Delta t) | \tilde{\varphi}_m(t) \rangle) \end{aligned} \quad (5)$$

arises from the dependence of the adiabatic KS orbitals on the atomic coordinates. It is calculated numerically as the overlap of orbitals at sequential steps⁵ using eq 5.

Fewest Switches Surface Hopping. FSSH is an algorithm for modeling dynamics of mixed quantum-classical systems.^{6, 7} The algorithm was implemented within TDKS theory in ref⁴, tested in ref⁸, and applied to a number of nanoscale systems.⁹⁻²⁰ FSSH provides a probability for hopping between quantum states based on the evolution of the expansion coefficients, eq 4. The probability of a transition from state k to another state m within the time interval δt is given in FSSH by⁶

$$dP_{km} = \frac{b_{km}}{a_{kk}} dt, \text{ where } b_{km} = -2\text{Re}(a_{km}^* \mathbf{d}_{km} \cdot \dot{\mathbf{R}}) a_{km} = c_k c_m^*. \quad (6)$$

If the calculated dP_{km} is negative, the hopping probability is set to zero; a hop from state k to state m can take place only when the electronic occupation of state k decreases and the occupation of state m increases. To conserve the total electron-nuclear energy after a hop, the original FSSH technique rescales the nuclear velocities along the direction of the nonadiabatic coupling. If a nonadiabatic transition to a higher energy electronic state is predicted by eq 6, but the kinetic energy available in the nuclear coordinates along the direction of the nonadiabatic coupling is insufficient to accommodate the increase in the electronic energy, the hop is rejected. The velocity rescaling and hop rejection give rise to the detailed balance between transitions upward and downward in energy.⁷ The assumption that the energy exchanged between the electronic and nuclear degrees of freedom during the hop is redistributed rapidly, gives Boltzmann distribution of energy among nuclear modes. Then, the velocity rescaling and hop rejection can be replaced by multiplying the probability (eq 6) for transitions upward in energy by the Boltzmann factor.^{21, 22} This simplification of the original FSSH technique gives great computational savings, allowing us to determine the time-dependent potential that drives multiple FSSH realizations of the dynamics of the electronic subsystem using a single MD trajectory.

Transitions across large energy gaps take long time and require a semiclassical decoherence correction to FSSH.²³⁻²⁵ This is because a purely classical description of nuclear motions keeps the electronic subsystem fully coherence, while a quantum nuclear bath leads to decoherence of superpositions of electronic states. A time-domain property, decoherence, or pure-dephasing, is equivalent to the Franck-Condon nuclear overlap factor in the energy domain.^{25, 26} An

infinitely long coherence time is equivalent to the unit Franck-Condon factor. The decoherence correction to FSSH was implemented within TDDFT,²⁷ and is employed here to study electron-hole recombination processes involving large energy gaps. Formulated at the wave-function level, decoherence leads to branching. Rather than a correction to FSSH, decoherence has been used as a physical mechanism of branching to formulate a variety of surface hopping techniques,²⁸⁻³³ starting from Ref.²⁸

Simulation Details. The geometry optimization, electronic structure, and adiabatic MD calculations are carried out with the Vienna ab initio simulation package (VASP).^{34, 35} The electron exchange and correlation interactions are treated with the Perdew-Burke-Ernzerhof (PBE) functional³⁶ and the interactions of the ionic cores with the valence electrons are described by the projector-augmented (PAW) approach.^{37, 38} The van der Waals long-range force is included by DFT-D2 method of Grimme to stabilize the system for geometry optimization and MD simulation.³⁹ After the geometry optimization at 0 K, repeated velocity rescaling is used to bring the temperature of the P3HT/QD system to 300 K, corresponding to the temperature in the experiment. Finally, trajectories for the nonadiabatic electron-vibrational dynamics are generated in the 4 ps microcanonical ensemble. The nuclear time-step for the equilibration and production runs is set to 1.0 fs. The electronic time-step for the nonadiabatic dynamics is 1.0 as. In the simulation, it is assumed that photoexcitation of either P3HT or the QD creates either an electron or a hole in the corresponding lowest unoccupied molecular orbital (LUMO) or highest occupied molecular orbital (HOMO), Figure 1 of main text. For simulation of electron-hole recombination in the pristine P3HT and QD, we repeat geometry optimization, adiabatic and nonadiabatic MD for the same P3HT and QD separately, using the same simulation cell.

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