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Trajectory Surface Hopping in the Time-Dependent Kohn-Sham Approach for Electron-Nuclear Dynamics

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The mean-field treatment of electron-nuclear interaction results in many qualitative breakdowns in the time-dependent Kohn-Sham (TDKS) density functional theory. Examples include current-induced heating in nanoelectronics, charge dynamics in quantum dots and carbon nanotubes, and relaxation of biological chromophores. The problem is resolved by the trajectory surface-hopping TDKS approach, which is illustrated by the photoinduced electron injection from a molecular chromophore into TiO_2, and the excited-state relaxation of the green fluorescent protein chromophore.

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Density functional theory (DFT) is a versatile and computationally efficient tool for investigation of molecular and solid state structures, reaction pathways, thermochemistry, dipole moments, spectroscopic response, and many other properties [1,2]. Recent advancements in DFT have focussed on time-dependent (TD) phenomena. Developed as an extension of the Hohenberg-Kohn-Sham theory [3] for arbitrary TD systems by Runge and Gross [4], TDDFT allows for the description of excited-state properties and spectra, as well as the development of novel nonadiabatic (NA) functionals and *ab initio* studies of NA molecular dynamics in real time [2]. Although a fully quantum TDDFT for electronic and nuclear motion has been proposed and applied to simple systems [5], the majority of TDDFT applications treat nuclei classically [1,2,6–10]. Modeling the interaction between the quantum and classical subsystems—the so-called "quantum-backreaction" problem—has been the subject of active discussions [11–16].

The quantum-classical mean-field or Ehrenfest method is the most common scheme for treating backreaction and has been extensively analyzed. It is known to fail in numerous situations, such as molecular and atomic scattering, nonradiative electron-nuclear relaxation, and current-induced heating in molecular electronics [17–19]. Electron-nuclear correlations and state-specific nuclear dynamics, necessary to accurately describe such processes, are impossible to model in a mean-field regime. Several alternatives to Ehrenfest dynamics have been suggested [13–17,19,20]. The fewest-switches surface-hopping (FSSH) method [17] is one of the most popular approaches, since it captures the essential physics—including detailed balance [17(c)]—while remaining computationally simple.

The current Letter develops FSSH for DFT with the Kohn-Sham (KS) representation of the electron density, greatly expanding the range of TDDFT applications. The FSSH-TDKS approach is ideal for extending the description of quantum dots and carbon nanotubes from time-independent geometric and electronic structure studies [21,22] to real-time modeling of experimentally observed photoexcitation dynamics [23,24]. The Ehrenfest-TDKS dynamics cannot accurately describe such phenomena, since it excludes electron-nuclear correlations and does not satisfy detailed balance [17–19]. The recently developed restricted open-shell KS theory [10], while well suited for low-lying excited states, would be difficult to apply to these systems since they involve many states and high-energy excitations. FSSH-TDKS is illustrated below with two examples: the photoinduced electron injection from a molecular chromophore into a TiO_2 surface [25,26] and the nonradiative relaxation of the green fluorescent protein (GFP) chromophore [9,27–29]. Compared to traditional TDKS, FSSH-TDKS predicts a different electron injection mechanism in the TiO_2 system and a much faster GFP relaxation, agreeing with experiment [25,29].

The electron density in the KS representation of DFT [3(b)] is written as $\rho(x,t) = \sum_{p=1}^{N_e} |\varphi_p(x,t)|^2$, where N_e is the number of electrons and the $\varphi_p(x,t)$ are single-electron KS orbitals. The evolution of the $\varphi_p(x,t)$ is determined by application of the TD variational principle to the KS energy:

$$E\{\varphi_p\} = \sum_{p=1}^{N_e} \langle \varphi_p | K | \varphi_p \rangle + \sum_{p=1}^{N_e} \langle \varphi_p | V | \varphi_p \rangle + \frac{e^2}{2} \times \iint \frac{\rho(x',t)\rho(x,t)}{|x-x'|} d^3x d^3x' + E_{xc}\{\rho\}. \qquad (1)$$

The right-hand side of Eq. (1) gives the kinetic energy of noninteracting electrons, the electron-nuclear attraction, the Coulomb repulsion of density $\rho(x,t)$, and the exchange-correlation energy functional that accounts for the residual many-body interactions. Application of the variational principle leads to a system of single-particle equations [1,2,6–9]:

$$i\hbar \frac{\partial \varphi_p(x,t)}{\partial t} = H(\varphi(x,t))\varphi_p(x,t), \qquad p = 1, \dots, N_e, \qquad (2)$$

where the Hamiltonian H depends on the KS orbitals.

These equations are solved explicitly, in contrast to the perturbative linear-response TDDFT used to obtain the electronic excitation energies [2]. Within the local density approximation [3(b)], the exchange-correlation energy depends on density, $E_{xc} = \int \rho\epsilon(\rho)dx^3$.

In the generalized gradient approximation E_{xc} depends on both density and its gradient, and the Hamiltonian is written as

$$H = -\frac{\hbar^2}{2m_e}\nabla^2 + V_N(x) + e^2\int\frac{\rho(x')}{|x-x'|}d^3x' + V_{xc}\{\rho, \nabla\rho\}. \tag{3}$$

In the HF approximation V_{xc} is orbital dependent. The KS energy (1) may be expressed as $E = \langle\varphi_a\varphi_b\cdots\varphi_p|H|\varphi_a\varphi_b\cdots\varphi_p\rangle$, the expectation value of the Hamiltonian in the basis of Slater determinants (SD) formed with TD KS orbitals [3(b)]. The single-electron density is obtained from the many-electron SD density matrix by the trace over $N_e - 1$ electrons.

$$\rho(x_1, t) = N_e \operatorname{Tr}_{x_2,\ldots,x_{N_e}}|\varphi_a(x_1, t)\varphi_b(x_2, t)\cdots \times \varphi_p(x_{N_e}, t)\rangle\langle\varphi_a(x_1, t)\varphi_b(x_2, t)\cdots\varphi_p(x_{N_e}, t)|. \tag{4}$$

The time-dependence in TDDFT for electron-nuclear dynamics is due to ionic motion; thus $V_N(x) \equiv V_N(x; \mathbf{R}(t))$ depends on time through the nuclear trajectory $\mathbf{R}(t)$. The additional time dependence of the electron density due to an external electric field such as a laser excitation or an electric current is not considered here, but can be added if necessary [6]. The prescription for $\mathbf{R}(t)$ constitutes the quantum-backreaction problem.

The mean-field or Ehrenfest approximation follows when the classical variables couple to the expectation value of the quantum force operator [18] $M\ddot{\mathbf{R}} = -\langle\varphi_a\varphi_b\cdots\varphi_p|\nabla_{\mathbf{R}}H|\varphi_a\varphi_b\cdots\varphi_p\rangle$. The gradient $\nabla_{\mathbf{R}}$ is applied directly to the Hamiltonian according to the TD Hellmann-Feynman theorem [18]. The Ehrenfest method requires modification when electron-nuclear correlations and detailed balance must be taken into account [17–19]. Inclusion of "quantum fluctuation variables" in the mean-field formalism alleviates some problems [19,20], but a more radical improvement is provided by the trajectory SH schemes [14,15,17,18], in which the nuclear trajectory $\mathbf{R}(t)$ responds to electronic forces by stochastically "hopping" between electronic states. The fewest-switches scheme employed here is designed to minimize the number of hops.

Analytical and numerical arguments have indicated that FSSH should be performed in the adiabatic representation, in which the electronic states that define the quantum force are the electronic eigenstates for the current nuclear configuration [14,17,18]. The single-electron adiabatic KS orbitals and the many-electron SDs formed from these orbitals are the eigenstates of the KS Hamiltonian (3). Expanding the time-dependent $\varphi_p(x, t)$ in the adiabatic KS orbitals $\tilde{\varphi}_k(x; R)$, we obtain $\varphi_p(x, t) = \sum_k^{N_e} c_{pk}(t)|\tilde{\varphi}_k(x; R)\rangle$, and the TDKS Eq. (2) transforms to an equation in the coefficients

$$i\hbar\frac{\partial}{\partial t}c_{pk}(t) = \sum_m^{N_e} c_{pm}(t)(\epsilon_m\delta_{km} + \mathbf{d}_{km}\cdot\dot{\mathbf{R}}). \tag{5}$$

The NA coupling

$$\mathbf{d}_{km}\cdot\dot{\mathbf{R}} = -i\hbar\langle\tilde{\varphi}_k(x; R)|\nabla_{\mathbf{R}}|\tilde{\varphi}_m(x; R)\rangle\cdot\dot{\mathbf{R}} = -i\hbar\langle\tilde{\varphi}_k|\frac{\partial}{\partial t}|\tilde{\varphi}_m\rangle \tag{6}$$

arises from the dependence of the adiabatic KS orbitals on the nuclear trajectory. Similarly, the time-evolving SD $|\varphi_a\varphi_b\cdots\varphi_p\rangle$ evolves into a superposition of adiabatic SDs,

$$|\varphi_a\varphi_b\cdots\varphi_p\rangle = \sum_{j\neq k\neq\cdots\neq l}^{N_e} C_{j\cdots l}(t)|\tilde{\varphi}_j\tilde{\varphi}_k\cdots\tilde{\varphi}_l\rangle, \tag{7}$$

with the many-electron coefficients $C_{j\cdots l}(t) = c_{aj}(t)c_{bk}(t)\cdots c_{pl}(t)$ expressed in terms of the single-electron coefficients. The evolution of $C_{j\cdots l}$ follows from Eq. (5):

$$i\hbar\frac{\partial}{\partial t}C_{q\cdots v}(t) = \sum_{a\cdots p}^{N_e} C_{a\cdots p}(t)[E_{q\cdots v}\delta_{aq}\cdots\delta_{pv} + \mathbf{D}_{a\cdots p;q\cdots r}\cdot\dot{\mathbf{R}}]. \tag{8}$$

$E_{q\cdots v} = \langle\tilde{\varphi}_q\cdots\tilde{\varphi}_v|H|\tilde{\varphi}_q\cdots\tilde{\varphi}_v\rangle$ is the many-electron eigenenergy, and the many-electron NA coupling

$$\mathbf{D}_{a\cdots p;q\cdots r}\cdot\dot{\mathbf{R}} = -i\hbar\langle\tilde{\varphi}_a\tilde{\varphi}_b\cdots\tilde{\varphi}_p|\frac{\partial}{\partial t}|\tilde{\varphi}_q\tilde{\varphi}_r\cdots\tilde{\varphi}_v\rangle \tag{9}$$

is nonzero only if the determinants are different in a single KS orbital.

The FSSH algorithm is described in detail in Ref. [17(a)]. As in the Ehrenfest-TDKS approach, the electronic system is initially described by a single SD that evolves into a superposition of the adiabatic SDs [Eq. (7)]. Between hops, the nuclear trajectory propagates adiabatically, $M\ddot{\mathbf{R}} = -\langle\tilde{\varphi}_a\tilde{\varphi}_b\cdots\tilde{\varphi}_p|\nabla_{\mathbf{R}}H|\tilde{\varphi}_a\tilde{\varphi}_b\cdots\tilde{\varphi}_p\rangle$, rather than in the mean field as before. The probability that the nuclear trajectory hops to another adiabatic state during time interval dt is

$$d\mathrm{P}_{a\cdots p;q\cdots r} = \frac{B_{a\cdots p;q\cdots r}}{A_{a\cdots p;a\cdots p}}dt, \tag{10}$$

where

$$B_{a\cdots p;q\cdots r} = -2\,\mathrm{Re}(A^*_{a\cdots p;q\cdots r}\mathbf{D}_{a\cdots p;q\cdots r}\cdot\dot{\mathbf{R}}); \quad A_{a\cdots p;q\cdots r} = C_{a\cdots p}C^*_{q\cdots r}. \tag{11}$$

If the calculated $dP_{a\cdots p;q\cdots r}$ is negative, the hopping probability is set to zero. This feature of the FSSH approach minimizes the number of hops: a hop from state $a\cdots p$ to state $q\cdots r$ can occur only when the electronic occupation of state $a\cdots p$ decreases and the occupation of state $q\cdots r$ increases. After the hop, the nuclear trajectory continues adiabatically in the new state $q\cdots r$. To conserve the total electron-nuclear energy after a hop, the nuclear velocities are rescaled [17(a),17(b)] along the direction of the electronic component of the NA coupling $\mathbf{D}_{a\cdots p;q\cdots r}$. If a NA transition to a higher-energy electronic state is predicted by Eq. (10), and the kinetic energy available in the nuclear coordinates along the direction of the NA coupling is insufficient to accommodate the increase in the electronic energy, the hop is rejected. The velocity rescaling and hop rejection result in a detailed balance between upward and downward transitions [17(c)].

We have implemented FSSH-TDKS with the VASP package [30] and have applied it to the nonradiative relaxation of the GFP chromophore and the photoinduced electron injection from the alizarin chromophore into a TiO_2 surface. The simulations were performed with the exchange-correlation functional in the generalized gradient approximation due to Perdew and Wang [31] and a converged plane-wave basis. A 1 fs nuclear and a 10^{-3} fs electronic time step were used. The data shown in the figures were converged by averaging over ensembles of initial conditions representing the photoexcitations at room temperature. Additional simulation details will be reported elsewhere. The FSSH results are compared with the traditional Ehrenfest-TDKS theory.

The naturally occurring GFP protects the chromophore [Fig. 1] that emits green light. The solvated chromophore is nonradiatively quenched in less than 1 ps and does not fluoresce [29]. The mechanism of the fluorescence quenching is under active investigation [9,27–29]. Ehrenfest-TDKS greatly underestimates the quenching rate, while FSSH-TDKS gives good agreement with experiment [29]. FSSH-TDKS is able to describe the state-specific electron-nuclear dynamics that involves correlated nuclear motions on the excited and ground electronic states, followed by rapid dissipation of energy deposited along the NA coupling vector into other vibrational modes.

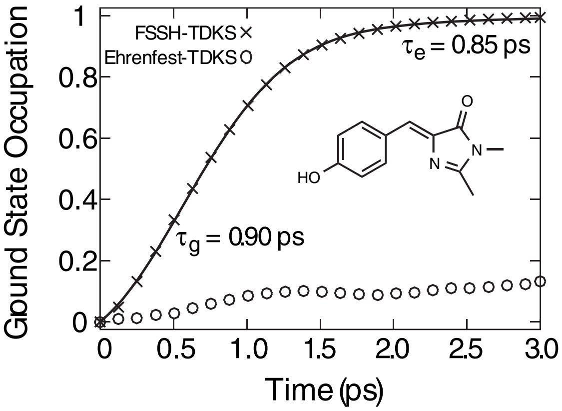

FIG. 1. Ground state recovery in neutral GFP chromophore calculated by FSSH-TDKS (crosses) and traditional Ehrenfest-TDKS (circles). The FSSH-TDKS results are well described by a Gaussian plus an exponential. (See text for details.)

The photoinduced electron injection from alizarin into TiO_2 is the primary step of the photovoltaic Grätzel cell [26] and has been shown experimentally [25] to occur on a sub-10 fs time scale. The mechanism of the injection is a subject of debate, since the adiabatic and NA mechanisms have different implications for solar cell design and are described with different analytic theories [32]. Both Ehrenfest-TDKS and FSSH-TDKS reproduce the sub-10 fs adiabatic injection time [Fig. 2]. The NA mechanism differs in the two models, facilitating injection in the traditional model and creating a back transfer in FSSH-TDKS. The back transfer is a consequence of detailed balance and is the major mechanism that decreases solar cell efficiency [25,26,32].

FSSH is one of many alternatives [13–20] to Ehrenfest dynamics. One of the most popular approaches due to its simplicity and accuracy, FSSH nevertheless has several drawbacks, including the so-called frustrated hopping re-

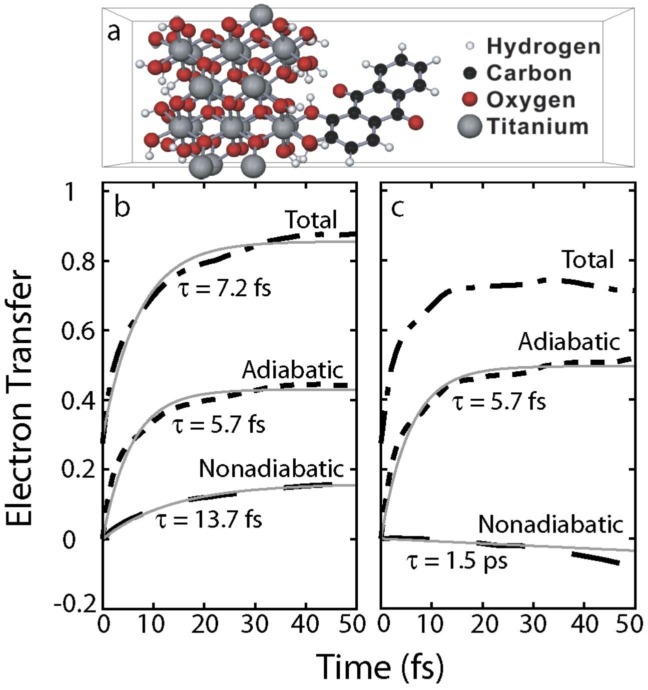

FIG. 2 (color online). (a) Simulation cell for the alizarin-TiO_2 system. (b)–(c) Electron transfer in alizarin-TiO_2 calculated by traditional Ehrenfest-TDKS (b) and FSSH-TDDFT (c). Nonadiabatic, adiabatic, and total electron transfer profiles are shown for each method. All fits are single exponential. The nonadiabatic data in (c) were fit with a first-order Taylor expansion of the exponential for the first 30 fs to model the short-time behavior. (See text for details.)

lated to quantum tunneling [33,34] and improper treatment of the electronic state decoherence [15,34,35]. Remedies to these and other problems have been proposed, and the reader is referred to the extensive literature on quantum-classical and semiclassical dynamics, including, but by no means limited to, the references cited here [11–20,33–35].

In summary, we have reported an improved version of TDDFT for electron-nuclear dynamics that explicitly includes electron-nuclear correlations and satisfies detailed balance. The method has been applied to the nonradiative relaxation of the GFP chromophore and solar cell electron transfer. In agreement with experiment, FSSH-TDKS captures the essential physics that traditional TDKS misses in both cases. This new approach greatly extends the utility of TDDFT for electron-nuclear dynamics.

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