Mixed quantum-classical dynamics using collective electronic variables: A better alternative to electronic friction theories

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An accurate description of nonadiabatic dynamics of molecular species on metallic surfaces poses a serious computational challenge associated with a multitude of closely-spaced electronic states. We propose a mixed quantum-classical scheme that addresses this challenge by introducing collective electronic variables. These variables are defined through analytic block-diagonalization applied to the time-dependent Hamiltonian governing the electronic dynamics. We compare our scheme with the Ehrenfest approach and with a full-memory electronic friction model on a one-dimensional “adatom + atomic chain” model. Our simulations demonstrate that collective-mode dynamics with only few (2–3) electronic variables is robust and can describe a variety of situations: from a chemisorbed atom on an insulator to an atom on a metallic surface. Our molecular model also reveals that the friction approach is prone to unpredictable and catastrophic failures.

First-principles nonadiabatic simulations of large molecular systems, such as biomolecules, molecular aggregates and crystals are now routinely possible with the aid of mixed quantum-classical (MQC) methods, which treat nuclei classically whereas electrons quantum-mechanically. Computational efficiency of MQC methods hinges upon a large spacing between electronic states. Only a small subset of strongly coupled states needs to be considered and their explicit propagation poses no computational difficulty. The situation becomes more complicated for nonadiabatic dynamics on metallic and semiconductor surfaces. Tracing a plethora of electronic states is computationally intensive. Even in the simplest MQC Ehrenfest method, a representation chosen for the electronic wave function cannot contain fewer variables than the number of accessible states, and hence, hundreds or even thousands of electronic degrees of freedom (DOF) must be considered for molecular dynamics on a metallic surface. Computing this number of excited states and nonadiabatic couplings may not be a daunting task per se. For example, within the independent-particle approximation, like the Kohn–Sham density functional theory, the excitation frequencies are only orbital energy differences, and the nonadiabatic couplings can be computed from derivatives of the corresponding orbitals. A challenge, therefore, is how to avoid solving the time-dependent Schrödinger equation for all electronic variables.

This problem has already received some attention. An effective electronic picture has been proposed by Shenvi et al. for the fewest-switches surface hopping (FSSH) method. A metallic continuum was discretized through a Gaussian quadrature, whose nodes and weights were derived from a molecule-metal coupling (hybridization) function. Several dozens of states were sufficient for converged dynamics at a sub-picosecond timescale. Despite all the merits, this approach requires prior knowledge of the hybridization function, which has to be deduced from the Newns–Anderson model Hamiltonian, making this approach unsuitable for on-the-fly simulations.

More traditional approach to systems with a dense electronic spectrum is to eliminate the explicit electronic dynamics entirely. Typically, the electronic subsystem is described as a bath of harmonic oscillators. However, realistic electron-nuclear couplings do not allow for analytic integration of the electronic equations of motion (EOM), and further simplifications become inevitable. These usually involve the constant-coupling approximation, which leads to the Markovian limit, and an assumption that the density of states around the Fermi level is smooth. Several such electronic friction theories have been presented over the years. All of them were capable to capture experimental trends when applied to selected realistic systems.

Surprisingly, none of these frictional theories have been scrutinized on models where the Ehrenfest method can be used to gauge the adequacy of introduced dynamical approximations. To the best of our knowledge, only Ref. 14 made a direct comparison of the Head-Gordon and Tully friction model with the FSSH-style dynamics. Authors point out that the friction model predicts somewhat faster relaxation at short times ($t < 150$ fs) as compared to its surface-hopping counterpart. There are other indications that friction models may exaggerate nuclear energy dissipation: for example, Refs. 26 and 27 report the divergence of the friction coefficient (“infinite stopping power”) for the H on Cu(111) system. However, it is not clear to what level of approximation these issues must be attributed.

In this Letter we carefully assess the friction approximation and propose a computationally superior scheme that employs a superadiabatic-like transformation. This transformation introduces approximate dynamical decoupling of electronic DOF and allows us to reduce the number of retained electronic variables to only few. With the new formalism we aim at the description of systems with a dense but potentially highly non-uniform electronic
where $\mathbf{R} \equiv \{R_\alpha\}$ is a collection of nuclear classical DOF, a dot stands for the full time derivative, $\langle \Psi | \hat{H}_e | \Psi \rangle$ is a time-dependent electronic wave function, and $\hat{H}_e$ is the electronic Hamiltonian which operates on electronic variables and is a parametric function of $\mathbf{R}$. In the interaction picture $\langle \Psi |$ is \(^2\):

$$\langle \Psi | = \sum_j c_j(t) e^{-i\phi_j(t)} | \Phi_j(\mathbf{R}(t)) \rangle,$$

where $\phi_j(t) = \hbar^{-1} \int_0^t E_j(\mathbf{R}(t')) dt'$ are dynamical phases, $\langle E_j(\mathbf{R}(t)) \rangle$ and $\langle | \Phi_j(\mathbf{R}(t)) \rangle$ are adiabatic potential energy surfaces (PESs) and wave functions, respectively, $\hat{H}_e | \Phi_j(\mathbf{R}(t)) \rangle = E_j(\mathbf{R}(t)) | \Phi_j(\mathbf{R}(t)) \rangle$, and $\{c_j(t)\}$ are complex time-dependent coefficients. Using the electronic time-dependent Schrödinger equation projected onto $\{ | \Phi_j(\mathbf{R}(t)) \rangle \}$, one can derive the electronic EOM:

$$\dot{c}_k = -\sum_{j,k} c_{j} e^{i\phi_{kj}} \tau_{kj},$$

where $\tau_{kj}(t) = \langle \hat{\Phi}_k(\mathbf{R}(t)) | \hat{\dot{\Phi}}_j(\mathbf{R}(t)) \rangle$ are the time-derivative nonadiabatic couplings. Conservation of $W$, $\dot{W} = 0$, gives the nuclear EOM:

$$M_\alpha \ddot{R}_\alpha + \sum_k |c_k(t)|^2 \frac{\partial E_k}{\partial R_\alpha} = \sum_{k,j} c_k^* c_j e^{i\phi_{kj}} f^a_{kj},$$

where $f^a_{kj}(t) = -\langle \hat{\Phi}_k | \hat{\partial}_{R_\alpha} \hat{H}_e | \Phi_j \rangle$ are nonadiabatic forces along the trajectory and $\phi_{kj}(t) = \phi_k(t) - \phi_j(t)$.

Two approximations are used for deriving friction theories: 1) the average force $-\sum_k |c_k(t)|^2 \partial E_k / \partial R_\alpha$ is replaced with a derivative of the ground-state PES, $-\partial E_0 / \partial R_\alpha$, in Eq. (4), and 2) all excited-excited couplings $\tau_{kj}$ are considered to be insignificant. These approximations are justified by accounting a predominant role of the ground state and low population of the excited states. They result in the simplified Ehrenfest equations

$$\dot{c} = -\mathbf{T} c, \quad T_{kj} = \delta_{0k} \delta_{0j} \tau_{kj} e^{i\phi_{kj}},$$

$$M_\alpha \ddot{R}_\alpha + \frac{\partial E_0}{\partial R_\alpha} = \sum_{k,j} c_k^* c_j e^{i\phi_{kj}} f^a_{kj},$$

To obtain a microscopic frictional theory we follow Head-Gordon and Tully. Note, however, that, in accordance with the original work, two additional approximations have been adopted: 1) the adiabatic excitation frequencies are position-independent: $\hbar \omega_{k0}(\mathbf{R}) = E_k(\mathbf{R}) - E_0(\mathbf{R}) = \text{const}_k$, 2) the ground electronic state is weakly coupled to the excited ones, which translates into the condition $|c_0(t)|^2 = 1$. Under these assumptions the electronic dynamics can be integrated out, and Eqs. (5) and (6) are converted into

$$M_\alpha \ddot{R}_\alpha + \frac{\partial E_0}{\partial R_\alpha} = \sum_{\beta} \int_0^t \mathcal{D}^{\alpha\beta}(t, t') \dot{R}_\beta(t') dt' + \mathcal{R}^\alpha(t),$$

where $\mathcal{D}^{\alpha\beta}(t, t') = -\frac{2\hbar}{\omega_{k0}} \sum_{k > 0} |f^\alpha_{k0}(t)|^2 f^\beta_{k0}(t') \cos(\omega_{k0}(t' - t))/\omega_{k0}$ is the friction kernel, and $\mathcal{R}^\alpha(t)$ represents a random force associated with generally unknown initial conditions for the electronic subsystem. In what follows we omit this term as for a pure initial electronic state it is zero. We integrate the Langevin equation (7) exactly; details of the integration scheme can be found in Supplementary Information (SI). It is the most accurate frictional approach possible because of the absolute minimum number of introduced approximations. Any other models with additional approximations can only be more accurate due to fortuitous cancellation of errors.

**Two collective mode (2CM) model:** As an alternative to the frictional model we propose a different treatment of the simplified Ehrenfest equations (5) and (6). The $\mathbf{T}$ matrix in Eq. (5) can be block-diagonalized analytically. Block-diagonalization of $\mathbf{T}$ gives $\mathbf{Z} = \mathbf{U}^{-1} \mathbf{T} \mathbf{U}$, where $\mathbf{Z}$ defines a canonical form of the interaction matrix, and $\mathbf{U} = \mathbf{U}(\tau_{ij}, \phi_{ij})^{\dagger}$. The only non-zero block of $\mathbf{Z}$ is the upper-left corner, $\mathbf{Z}_{2 \times 2} = -\sigma_e g_z$, where $\sigma_e$ is the Pauli matrix and $\mathbf{g} = (\sum_{k=1}^n \tau_{k0}^2)^{1/2}$. Thus, $\mathbf{Z}$ acts non-trivially only within a two-dimensional subspace of transformed electronic variables $\mathbf{d} = \mathbf{U}^{-1} \mathbf{c}$, where it couples only $d_0$ and $d_1$. We denote this two-dimensional subspace as the interaction space. $d_0$ coincides with the probability amplitude of the ground adiabatic state $c_0$ and will be used to track the ground state population evolution. The remaining variables $\{d_1\}_{i=2,3,4}$ define the spectator space.

The transformation matrix $\mathbf{U}$ is time-dependent, therefore, the electronic EOM in new variables, $\dot{\mathbf{d}} = -\left(\mathbf{U}^{-1} \dot{\mathbf{U}} + \mathbf{Z}\right) \mathbf{d}$, acquire a new nonadiabatic term $\mathbf{N} = \mathbf{U}^{-1} \dot{\mathbf{U}}$. $\mathbf{N}$ has a quite involved explicit form, but its $2 \times 2$ upper block is quite simple. Therefore, we introduce our first approximate 2CM method by restricting the electronic dynamics to the interaction space only

$$\begin{pmatrix} d_0 \\ d_1 \end{pmatrix} = \begin{pmatrix} 0 & -z \\ z & w_{11} \end{pmatrix} \begin{pmatrix} d_0 \\ d_1 \end{pmatrix},$$

where $w_{11} = z^{-2} \sum_{k=1}^n \omega_{k0}^2 t_{k0}^2$ is the collective frequency, which originated from $\mathbf{N}$. The nonadiabatic force matrix $\{f^\alpha_{kj}(t)\}_{k,j \geq 0}$, projected onto the interaction space, $\{\mathbf{U} \mathbf{f}^\alpha_{kj} \}_{2 \times 2}$, has only one non-zero element, $f^\alpha_{10} = z^{-1} \sum_{k \geq 0} f^\alpha_{k0} \tau_{k0}$. Using this projection we re-write the nuclear Ehrenfest EOM (6) as

$$M_\alpha \ddot{R}_\alpha + \frac{\partial E_0}{\partial R_\alpha} = (d_0^\alpha d_1 + d_1^\alpha d_0) f^\alpha_{10}.$$
Three collective mode (3CM) model: The 2CM model treats all the original electronic DOF in a democratic fashion in the collective frequency $\tilde{\omega}_1$ and coupling $z$. For a chemisorbed species on a surface, however, one coupling, which corresponds to molecular binding, can be appreciably larger than others. Interaction-space variables in this case may be biased toward a description of that particular electronic DOF, and the 2CM dynamics will miss contributions from weakly-coupled states. One needs, therefore, a procedure to select the most important DOF from the spectator space. The spectator space interacts with $(d_0, d_1)$-space only through the matrix $N$. In the presence of one dominant coupling, without restricting generality we can take it as $\tau_{10}$, $k > 1$ and their time derivatives $\dot{\tau}_k$ are small. Therefore, the matrix $N$ can be simplified by neglecting $\dot{\tau}_k$ and off-diagonal quadratic terms $p_k\tau_k$:

$$N \approx N^{(\alpha)} = i \text{diag} \{ \tilde{w}_{11}, \tilde{w}_{22}, \ldots \} - i \begin{pmatrix} 0 & 0 & 0 \\ 0 & 0 & \pi \\ 0 & \pi & 0 \end{pmatrix},$$

(10)

where $\tilde{w}_{kk} = w_{k0} - \tau_{k0}^2\omega_{k1}/z^2$, $k > 1$ and $\pi = (\pi_2, \ldots)$ with $\pi_k = \tau_{k1}^2\omega_{k1}/z^2$. In the interaction representation for $N^{(\alpha)}$, the diagonal matrix of collective frequencies [the first term in Eq. (10)] is transferred to the corresponding dynamical phases. This reveals the structure of $N^{(\alpha)}$, which is similar to that of the matrix $T$ [cf. Eq. (5)] with only zero first row and column. Thus, we repeat the block-diagonalizing transformation and separate one additional mode from the spectator space to obtain a new 3CM model with the following EOM:

$$M_{\alpha} \ddot{R}_\alpha + \frac{\partial E_0}{\partial R_\alpha} = \mathbf{d}^\dagger \begin{pmatrix} 0 & \tilde{f}_{j0} & \tilde{f}_{k0} \\ \tilde{f}_{j0} & 0 & 0 \\ \tilde{f}_{k0} & 0 & 0 \end{pmatrix} \mathbf{d},$$

(11)

$$\mathbf{d} = \begin{pmatrix} 0 & -z & 0 \\ z & i\tilde{w}_{11} & -i\tilde{z} \\ 0 & -i\tilde{z} & i\tilde{w}_{22} \end{pmatrix},$$

(12)

where $\mathbf{d} = (d_0, d_1, d_2)$ are new collective electronic variables, $\tilde{z} = (\sum_{k=2} \pi_k^2)^{1/2}$, $\tilde{w}_{22} = \tilde{z}^{-2} \sum_{k=2} \tilde{w}_{kk} \pi_k^2$, and $\tilde{f}_{k0} = \tilde{z}^{-1} \sum_{k=2} (f_{k0} - \tau_{k0}^2) \pi_k$.

Recursive nature of the procedure should be apparent now. One can proceed by separating more modes from the spectator space to obtain higher-level collective-mode models. The appearance of combination frequencies [e.g. $\omega_{k1} = (E_k - E_1)/\hbar$] warrants, however, that neglecting the excited-excited couplings, which are dynamical partners of these frequencies, is no longer justified. Moreover, the transformed forces $\tilde{f}_{k0} = 0$, $k \geq 3$, and hence, higher collective modes do not contribute to the nuclear dynamics directly, although they are still coupled in the electronic space. That is, the 3CM model constitutes a natural stopping point for the collective-mode transformation.

Molecular model: We assess different nonadiabatic approaches on a model with several electronic and a single nuclear DOF. The model is intended to represent an atom chemisorbed on a one-dimensional chain of atoms modelling the surface. We parametrize the electronic Hamiltonian $\hat{H}_e$ in the diabatic representation as $\hat{H}_e = \sum_{i<j} |\phi_i\rangle V_{ij}(R) \langle \phi_j|$, where $V_{ij}(R)$ are either constants for $i \neq j$ or harmonic potentials (all definitions are detailed in SI). All electronic states are organized in nine layers, so that the off-diagonal couplings are large for states in different layers and small for states within the same layer. Diagonalization of $\hat{H}_e$ determines the adiabatic potentials $\{E_k(R)\}$, nonadiabatic couplings $\{\tau_{kj}(R)\}$ and forces $\{f_{kj}(R)\}$. The resulting adiabatic PESs in a multiple-state-per-layer case are sketched in Fig. 1. $\tau_{kj}$ and $f_{kj}$ are set to zero once both $k, j \geq 1$ simultaneously. The nuclear kinetic energy is $T_N = M \vec{R}^2/2$ with $M = 2000 m_e$, multiplied by the identity matrix of the appropriate dimension.

Results: We consider five dynamical approaches: the Ehrenfest [Eqs. (5) and (6)], the full-memory friction [Eq. (7)], 2CM [Eqs. (8) and (9)], 3CM [Eqs. (11) and (12)] models, and the Born-Oppenheimer approximation [Eq. (6) with the zero right hand side]. We start with a set of molecular parameters that correspond to weak nonadiabatic coupling between layers. The initial energy is taken to be low so that the nonadiabatic dynamics takes place within a ground-state layer (Fig. 1). The nonadiabatic effects are small overall: trajectory deviations from that of the Born-Oppenheimer approximation are fractions of bohr $(a_0)$ as compared to the total trajectory length of $50 a_0$ (Fig. 2).

With one state per layer—an insulator-like surface—both collective mode models work very well reproducing almost exactly the Ehrenfest dynamics. Despite the fact that this setup favors the friction approach as the elec-
Trajectory deviation, $a_0$

Time, $\times 10^3$ a.u.

FIG. 2. Trajectory dynamics in low-energy, weak-coupling regime. Top row (a,b): one state per layer. Middle row (c,d): 5 states per layer. Bottom row (e-f): 10 states per layer (see Fig. 1). The left column shows deviations of trajectories in different methods from that of the Born–Oppenheimer approximation, the right column displays ground-state weight $|c_0|^2(t)$ dynamics.

With more states per layer the ground state depletion becomes more pronounced (Figs. 2d and 2f). For 10 states per layer the ground-state weight drops to ca. 50%, and the 2CM model breaks down due to the large number of energetically accessible (albeit weakly-coupled) electronic states. On the other hand, the 3CM model displays rather accurate electronic and very accurate nuclear dynamics, as can be seen in Figs. 2f and 2c, respectively. The nuclear dynamics is accurate because all the PESs within a layer have almost identical profiles, and hence, the nucleus feels the same force, so that the electronic population within a layer needs to be accurate only on average. The friction model shows moderate deviations from the Ehrenfest model shown the superiority of the former. The employed friction model reflects a general ability of any friction model to reproduce nonadiabatic dynamics. Any additional approximations to it may improve results only by fortuitous cancellations of errors. The main drawback of the friction theory is insufficient energy back-flow from the electronic subsystem. That can cause nuclear reflection or trapping if certain and largely unpredictable resonance conditions are met. Our observation supports an idea that the similar failure reported in Refs. 26 and 27 is caused by the friction approach itself and is unrelated to the level of electronic structure theory.

In conclusion, we have derived a new MQC dynamical model that is fully ab initio: the collective variables are constructed on the fly from the nonadiabatic data available from electronic structure calculations. The electronic dynamics in our approach is unitary and, hence, properly accounts for electronic back-reaction and memory. Our numerical simulations show that the collective variable approach provides good and reliable description of nonadiabatic dynamics in a variety of situations. The 2CM variant is accurate for “an atom on an insulator-like surface” cases, whereas the 3CM model is applicable to metallic surfaces as well. One of the collective variables coincides with the ground-state amplitude, and can be used to draw a conclusion whether the nonadiabatic effects are important or not. Comparison of the collective-mode models with the full-memory ab initio electronic friction model show the superiority of the former. The employed friction model reflects a general ability of any friction model to reproduce nonadiabatic dynamics. Any additional approximations to it may improve results only by fortuitous cancellations of errors. The main drawback of the friction theory is insufficient energy back-flow from the electronic subsystem. That can cause nuclear reflection or trapping if certain and largely unpredictable resonance conditions are met. Our observation supports an idea that the similar failure reported in Refs. 26 and 27 is caused by the friction approach itself and is unrelated to the level of electronic structure theory.

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FIG. 3. Molecular model has 5 levels per layer, all other parameters detailed in SI.12 Panel a): Adiabatic and diabatic potentials (same as in Fig. 1). Horizontal lines labelled as ① and ② show two different initial energies. Trajectories for the setups ① and ② are on panels b) and c), respectively.

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35Explicit form of all matrices, parameters for the molecular models, and the details of numerical integration scheme are in the provided Supplementary Info file.