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Nonadiabatic quantum molecular dynamics with detailed balance

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We present an approach for carrying out nonadiabatic molecular dynamics simulations of systems in which nonadiabatic transitions arise from the coupling between the classical atomic motions and a quasicontinuum of electronic quantum states. Such conditions occur in many research areas, including chemistry at metal surfaces, radiation damage of materials, and warm-dense-matter physics. The classical atomic motions are governed by stochastic Langevin-like equations, while the quantum electron dynamics is described by a master equation for the populations of the electronic states. These working equations are obtained from a first-principles derivation. Remarkably, unlike the widely used Ehrenfest and surface-hopping methods, the approach naturally satisfies the principle of detailed balance at equilibrium and therefore can describe the evolution to thermal equilibrium from an arbitrary initial state. A practical algorithm is cast in the form of the widely used fewest-switches surface-hopping algorithm but with switching probabilities that are not specified *ad hoc* like in the standard algorithm but are instead derived.

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I. INTRODUCTION

Mixed quantum-classical dynamics methods are extensively used for simulating systems in many areas of the physical and chemical sciences [1]. These methods give a classical treatment to atomic motions while retaining a detailed quantum-mechanical description of electrons. This considerably reduces the formidable computational cost entailed by a complete quantum-mechanical description. The development of mixed quantum-classical dynamics methods beyond the Born-Oppenheimer approximation, by which electrons follow adiabatically the classical atomic motions, has been a topic of continuous research interest for several decades [2]. In general, atomic motions can induce transitions between electronic states, which, in turn, can alter the forces acting on the classical particles. Such nonadiabatic effects are ubiquitous and diverse [2], and the self-consistent incorporation of feedback between the quantum and classical degrees of freedom is highly nontrivial [3,4]. A well-known difficulty is to ensure that the principle of detailed balance, according to which transitions between any two states take place with equal frequency in either direction at equilibrium, is satisfied [2,5]. Failure to satisfy detailed balance introduces a bias and systematically skews the dynamics away from thermal equilibrium.

In this paper, we present an approach for carrying out nonadiabatic quantum-classical molecular dynamics simulations of systems in which nonadiabatic transitions arise from interactions between the motion of the classical degrees of freedom and a quasicontinuum of quantum states. Unlike the popular Ehrenfest method and Tully's trajectory surface-hopping method [5,6], this scheme naturally satisfies detailed balance. The atomic motions are governed by stochastic Langevin-like equations, while the electron dynamics is described by a master equation for the populations of the electronic states. The scheme can thus properly describe the irreversible evolution of an isolated system from an arbitrary initial state to a state of thermal equilibrium. At equilibrium, the transition rates between electronic states satisfy the detailed balance relations, while the nonadiabatic forces acting on the ions satisfy the fluctuation-dissipation relation.

There exists a large number of systems in which nonadiabatic effects can arise as a consequence of the coupling between the atomic motions and a quasicontinuum of electronic states [2]. The situation, which differs from the more commonly discussed case of a handful of strongly coupled energy levels, is in clear conflict with the Born-Oppenheimer criterion that the states be widely separated in energy. Here excitations of arbitrarily low energy are available to couple with the classical motions. Such couplings are known to significantly affect dynamical processes such as adsorption, dissociation, and catalytic reaction at metal surfaces [7,8]. In solids, atomic diffusion of impurities in metals [9] and the radiation damage processes induced by energetic particles [10,11] involve important nonadiabatic couplings with host electrons. In warm dense matter [12], not only is there a quasicontinuous density of electronic states at the Fermi level, but the volume of available, unoccupied states can be large since electrons are partially degenerate. Nonadiabatic couplings could potentially affect dynamical ionic properties even at equilibrium; without doubt, nonadiabatic couplings must be accounted for to calculate quantities of current experimental interest, such as temperature equilibration rates [13,14]. The list is not limited to bulk systems, as finite systems can also display a dense manifold of electronic states [15] (see [2] for an extensive list).

Our scheme results from a fairly long mathematical derivation. To ease the presentation, in Sec. II, we first outline the scheme, enumerate its salient properties, and propose an

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algorithm. We then proceed in Sec. III with the complete derivation. For readers who plan to skip the proofs given in Sec. III, we remark that, unlike other derivations of mixed quantum-classical schemes such as that of Ehrenfest, ours does not treat from the outset the atomic positions and momenta as classical parameters in the equations of electrons; this is indeed known to be at the origin of the breakdown of detailed balance [16,17]. Instead, it ensures that the canonical commutation relations of atomic variables in these equations are satisfied.

II. OUTLINE OF THE SCHEME

A. The scheme

Definitions and assumptions. Following standard notations, let r designate the three-dimensional Cartesian positions of electrons (mass m) and R denote the atomic positions (mass M) [18]. Below, N denotes the total number of atoms, and $R = \{R_\alpha\}_{\alpha=1,\dots,3N}$ denotes the set of all atomic positions. The total Hamiltonian describing the system is

$$\hat{H}(r, R) = -\frac{\hbar^2}{2M}\nabla_R^2 + \hat{H}_e(r, R), \tag{1}$$

where $\hat{H}_e(r, R)$ is the electronic Hamiltonian for fixed atomic position and $\nabla_R = \partial/\partial R$. For simplicity of exposition, we assume that there is no external time-dependent potential acting on the system; we consider situations in which the system is either in thermal equilibrium or initially excited and then let to freely evolve and relax. We also assume that $m \ll M$ and that the atomic velocities are large enough that the atomic de Broglie wavelengths are smaller than the characteristic variation length scales of interactions; thus, the atomic motions can be described by classical-like trajectories. If at time t the atomic positions are $R(t)$, we define the basis of adiabatic wave functions $|i(R(t))\rangle$ as the eigenfunctions of $\hat{H}_e(r, R(t))$ [1], i.e.,

$$\hat{H}_e(r, R(t))|i(R(t))\rangle = \epsilon_i(R(t))|i(R(t))\rangle. \tag{2}$$

From now on, we often omit writing explicitly the dependence on $R(t)$ of the adiabatic basis and related quantities in order to avoid cluttering the mathematical expressions. We define the nonadiabatic couplings $d_{ij} = \langle i|\nabla_R|j\rangle = -d_{ji}^*$ and $f_{ij} = \langle i| - \nabla_R \hat{H}_e(r, R(t))|j\rangle = \epsilon_{ij} d_{ij}$ with $\epsilon_{ij} = \epsilon_i - \epsilon_j$ [1].

As discussed above, we consider physical systems in which the electronic energy states $\epsilon_i(R)$ form a continuum or a manifold of infinitesimally separated electronic excitations. A large number of electronic states implies the existence of a short timescale τ_c (discussed below) arising from the rapid fluctuations of coherences $\rho_{ij}(t) = \mathrm{Tr}[\hat{\rho}(t)|i\rangle\langle j|]$ with $i \neq j$ (with $\hat{\rho}$ being the total density operator of the system), which, in turn, affect the atomic motions in the form of a rapidly fluctuating force. In our scheme, coherences are not treated explicitly; their influence is treated statistically and is responsible for the stochastic nature of the classical atomic motions discussed below. Instead, our approach describes the evolution of the atomic positions $R(t)$ and of the electronic populations $P_i(t) = \mathrm{Tr}[\hat{\rho}(t)|i\rangle\langle i|]$ on a timescale coarse-grained over τ_c.

Working equations of the scheme. Each atomic position R_α satisfies the stochastic equation

$$M\ddot{R}_\alpha(t) = F_\alpha^{BO}(t) - M\sum_{\beta=1}^{3N}\gamma_{\alpha,\beta}\dot{R}_\beta(t) + \xi_\alpha(t), \tag{3}$$

with initial conditions $R_\alpha(0)$ and $\dot{R}_\alpha(0)$ at initial time $t = 0$. In these equations, dropping the time variable,

$$F_\alpha^{BO} = -\sum_i P_i f_{ii}^\alpha \tag{4}$$

is the adiabatic Born-Oppenheimer force defined with respect to the adiabatic states (2) at time t, i.e., the average over all states i of the forces $-f_{ii}^\alpha$ weighted by the occupation number P_i. The remaining two terms result from the nonadiabatic couplings: a sum of friction forces $-M\sum_{\beta=1}^{3N}\gamma_{\alpha,\beta}\dot{R}_\beta(t)$ with friction coefficients

$$\gamma_{\alpha,\beta} = -\frac{\pi}{M}\sum_{i\neq j}\frac{P_i - P_j}{\epsilon_{ij}} f_{ij}^\alpha f_{ji}^\beta \mathcal{L}(\epsilon_{ij}, \Gamma_{ij}), \tag{5}$$

which describes the systematic effect of nonadiabatic transitions on the atomic motions and damps the velocities over a characteristic time $T_\gamma = 1/\gamma$, and a δ-correlated Gaussian random force $\xi_\alpha(t)$ satisfying [19]

$$\langle\langle\xi_\alpha(t)\rangle\rangle = 0, \quad \langle\langle\xi_\alpha(t)\xi_\beta(t')\rangle\rangle = B_{\alpha,\beta}\delta(t - t'), \tag{6}$$

with

$$B_{\alpha,\beta} = \pi\sum_{i\neq j}(P_i + P_j) f_{ij}^\alpha f_{ji}^\beta \mathcal{L}(\epsilon_{ij}, \Gamma_{ij}), \tag{7}$$

which describes the fluctuations of nonadiabatic forces around their average values and varies over a short timescale of the order of τ_c (see below). The Lorentzian

$$\mathcal{L}(\epsilon_{ij}, \Gamma_{ij}) = \frac{1}{\pi}\frac{\hbar^2\Gamma_{ij}}{(\epsilon_{ij})^2 + (\hbar\Gamma_{ij})^2} \tag{8}$$

describes the energy conservation, corrected by the broadening of the transition due to the finite lifetime of the coherence between states i and j [recall that $\mathcal{L}(\epsilon, \Gamma) \sim \delta(\epsilon/\hbar)$ as $\Gamma \to 0$]. The inverse lifetime Γ_{ij} is found from the self-consistency equation,

$$\Gamma_{in} = \frac{2\hbar^2}{M|d_{in}\cdot V|^2}\sum_{j\neq j'}\frac{|d_{in}\cdot f_{j'j}|^2\Gamma_{jj'}P_j}{(\epsilon_{jj'})^2 + (\hbar\Gamma_{jj'})^2}, \tag{9}$$

where $V(t) = \dot{R}(t)$ are the atomic velocities [20].

We thus recover that the effect of nonadiabatic couplings is analogous to that of collisions undergone by a heavy Brownian particle immersed in a fluid of light particles. In the latter, the Brownian motion appears erratic over a timescale τ_c of several successive collisions, while a much longer timescale $T_\gamma = 1/\gamma$, or, equivalently, a significant number of collisions, is required to move appreciably the Brownian particle from its inertial motion. In our case, τ_c and T_γ can be identified as follows. For simplicity of notation, consider the case of a system at thermal equilibrium at temperature T and one atomic degree of freedom. The friction coefficients (5) are then given by the Green-Kubo formula (13) below in terms of the time correlation functions of the adiabatic forces. In the presence of a quasicontinuum of state, it is easily seen that these correlations decay very rapidly with time: $\langle \delta\hat{F}(t)\delta\hat{F}(0)\rangle \approx \langle \delta\hat{F}^2\rangle e^{-t/\tau_c}$, where τ_c is the correlation time of the nonadiabatic force; this implies $T_\gamma = 1/\gamma = M^2 v_{th}^2/\langle \delta\hat{F}^2\rangle \tau_c$, with the thermal velocity $v_{th} = \sqrt{k_B T/M}$. The time $T_\gamma \gg \tau_c$ characterizes the time necessary for the cumulative effect of nonadiabatic electron-ion interactions to damp the atomic velocities. The condition $\tau_c \ll T_\gamma$ on which our treatment relies writes $\sqrt{\langle \delta\hat{F}^2\rangle}\, \tau_c/M v_{th} \ll 1$. It expresses that the evolution due to nonadiabatic couplings has a very weak effect during the correlation time τ_c, in analogy with the weak effect of individual collisions on a classical Brownian particle.

In the past, several mathematical derivations of Eqs. (3)–(7) were published at different levels of mathematical rigor [21–25]. These works, however, treated the electronic subsystem as a reservoir; that is, they assumed that the electronic subsystem is not modified by its coupling with atoms and remains in a steady state. The present work goes beyond this limitation and, as described below, gives an explicit treatment of the modifications of the state of electrons resulting from the nonadiabatic couplings between the electronic and atomic degrees of freedom. In the equilibrium limit, the present results are in perfect agreement with previous works.

Our approach describes the electronic dynamics in terms of the evolution of populations of adiabatic states according to the master equation

$$\frac{dP_i}{dt} = \sum_a \{W_{ia}P_a - W_{ai}P_i\}. \tag{10}$$

The first sum describes both the gain of state i due to nonadiabatic transitions induced by the atomic motions from other states a and the loss due to nonadiabatic transitions from i into other states a. The corresponding transition rates are

$$W_{ia} = 2\pi|d_{ia}\cdot V|^2\, e^{-\frac{\epsilon_{ai}d_{ia}^2}{2M[d_{ia}\cdot V]^2}}\, \mathcal{L}(\epsilon_{ia},\Gamma_{ia}). \tag{11}$$

The term $2\pi|d_{ia}\cdot V|^2\mathcal{L}$ is similar to the expression that one would obtain with a Fermi's golden rule calculation by treating the atomic subsystem as an external disturbance on the electronic subsystem. The exponential term $e^{-\frac{\epsilon_{ai}d_{ia}^2}{2M|d_{ia}\cdot V|^2}}$ results from the careful treatment of the quantum commutation relations of atomic variables in the equation of evolution of electronic populations; when the atomic positions are treated purely classically from the outset, as in the Ehrenfest method, this term equals unity. As we shall discuss below, with this term, the rates (11) satisfy the principle of detailed balance.

B. Salient properties

We now discuss the key properties of the scheme.

(i) *Equilibrium limit, detailed balance, and fluctuation-dissipation relation.* Given a temperature T, the classical and quantum Boltzmann distributions $f_{eq}(R,V) = \exp\{-\frac{1}{k_BT}[\frac{MV^2}{2} + \phi_{B0}(R)]\}/\mathcal{Z}_{cl}$ and $P_i^{eq}(R) = e^{-\epsilon_i(R))/k_BT}/\mathcal{Z}_q$, with partition functions $\mathcal{Z}_{cl} = \iint dR dV f_{eq}(R,V)$ and $\mathcal{Z}_q = \sum_i e^{-\epsilon_i(R)/k_BT}$ and BO potential $\phi_{BO} = -k_BT\ln\mathcal{Z}_q$, constitute an equilibrium solution of the dynamics governed by Eqs. (3)–(10). Indeed, Eqs. (5) and (7) with $P_i = P_i^{eq}$ give the celebrated fluctuation-dissipation relation

$$\langle\langle \xi_\alpha(t)\xi_\beta(t')\rangle\rangle = 2Mk_BT\gamma_{\alpha,\beta}\delta(t-t'), \tag{12}$$

with

$$\gamma_{\alpha,\beta} = \frac{1}{2Mk_BT}\mathrm{Re}\int_{-\infty}^{\infty}\langle \delta F_\alpha(t)\delta F_\beta(0)\rangle dt, \tag{13}$$

where $\delta F_\alpha = F_\alpha - F_\alpha^0$, with the electron-ion force $F_\alpha = \partial\hat{H}_e(r,R)/\partial R_\alpha$ and its diagonal part F_α^0 in the adiabatic basis. Equation (3) reduces to the traditional Langevin equation, which is known to yield the stationary distribution function $f_{eq}(R,V)$ [26]. This in turn implies $\widetilde{V_\alpha V_\beta} \equiv \iint dRdV V_\alpha V_\beta f_{eq}(R,V) = k_BT/M\delta_{\alpha\beta}$, which, when used in Eq. (11), yields

$$\widetilde{W_{ia}}P_i^{eq} = \widetilde{W_{ai}}P_a^{eq} \quad \forall i,a. \tag{14}$$

Indeed, Eq. (11) implies

$$\widetilde{W_{ia}} = \frac{2\pi k_BT}{M}d_{ia}d_{ia}^* e^{-\frac{\epsilon_{ia}}{2k_BT}}\mathcal{L}(\epsilon_{ia},\Gamma_{ia}). \tag{15}$$

This is obtained using $\exp(x) \approx 1 + x \approx$ for $|x| < 1$ and the small magnitude of the exponent in Eq. (11). Equation (14) is nothing but the detailed balance conditions, which say that the rates of the forward and backward nonadiabatic transitions between any pair of adiabatic electronic states, weighted by the probabilities of the initial and final states, are equal to each other. With this relation, the right-hand side of the master equations (10) vanishes, and the quantum Boltzmann distribution P_i^{eq} is stationary.

(ii) *Conservation properties.* The Langevin equation implies the conservation over time of the number of classical particles and of the average momentum. Similarly, the master equation implies the conservation of the normalization $\sum_i P_i$ over time. As proved in Sec. III E, the scheme conserves the total energy $E(t) = \frac{M}{2}\sum_{\alpha=1}^{3N}V_\alpha(t)^2 + \sum_i P_i(t)\epsilon_i(t)$ is conserved in the sense $\frac{d}{dt}\langle\langle E(t)\rangle\rangle = 0$.

(iii) *Relation to other schemes.* The scheme reduces to the Born-Oppenheimer approximation when all terms related to nonadiabatic couplings are dropped, which amounts to setting γ, ξ, and $\{W_{ia}\}$ to zero in Eqs. (3) and (10). When in our mathematical derivation the atomic degrees of freedom are treated classically, as is the case, e.g., in the Ehrenfest method, the transition rates (11) become $\widetilde{W_{ia}} = 2\pi\frac{k_BT}{M}d_{ia}d_{ia}^*\mathcal{L}(\epsilon_{ia},\Gamma_{ia})$ (i.e., the exponential term disappears). In this case, $W_{ia} = W_{ai}$ is satisfied, which violates the expected detailed balance relations (14). Finally, we shall see that our scheme can advantageously be cast in the form of the widely used fewest-switches surface-hopping method proposed by Tully [3], but with switching probabilities that are not specified *ad hoc* and are instead derived.

C. An algorithm

Different algorithms can be envisioned to integrate the set of coupled equations (3) and (10). Here we find it interesting to introduce an algorithm that is closely related to the popular "fewest-switches" surface-hopping method of Tully [3]. Below we assume that we have a practical way of generating all of the matrix elements d_{ij}. For convenience, we closely follow Tully's original presentation (see steps 1 through 4 on p. 1065 of [3]) and adapt it to our purpose. The algorithm propagates an ensemble of trajectories $(R(t), V(t), P_i(t))$. Each trajectory moves on a weighted average potential energy surface, weighted by the occupation probabilities P_i, interrupted only by the possibility of sudden stochastic switches between electronic states. Practically, the dynamics proceeds as follows:

(1) Initial conditions $\{R_\alpha(0), V_\alpha(0), P_i(0)\}$ at time $t = 0$ are assigned consistent with the physical conditions to be simulated (e.g., a thermal ensemble).

(2) The classical equation of motion $M\ddot{R}_\alpha = F_\alpha^{BO}$ is integrated over a small time interval δt.

(3) The population P_i of each state i is then updated as follows. A uniform random number ξ_i, $0 < \xi_i < 1$, is selected to determine whether a switch to any state j will be invoked. A switch between a state i and a state j occurs if $W_{ij}\delta t < \xi_i < W_{i,(j+1)}\delta t$. In the notations of Tully (see Eq. (19) in [3]), the switching probabilities in accordance with our scheme are $g_{ij} = W_{ij}\delta t$, which differ from the original *ad hoc* prescription. Note that the effective width of the "δ" function $\mathcal{L}(\epsilon_{ia}, \Gamma_{ia})$ in the expression for the rate in Eq. (11) is calculated on the fly according to Eq. (54).

(4) If a switch between a state i and a state j has occurred, an adjustment ΔV of atomic velocities V must be made as follows in order to conserve energy:

$$\frac{MV^2}{2} + \epsilon_i = \frac{M(V + \Delta V^i)^2}{2} + \epsilon_j. \tag{16}$$

Taking the distribution of states into account, the velocity V must be adjusted to $V + \sum_i P_i \Delta V_i$. As in [3], the adjustment ΔV is made in the direction of the nonadiabatic coupling d_{ij} (here we assume that we work with real-valued eigenstates $|i\rangle$, as can always be done in the absence of magnetic fields). After the velocity adjustments have been made (if needed), return to step 2. We observe that an advantage of this algorithm is that it does not necessitate the direct calculation of the coefficients $\gamma_{\alpha,\beta}$ and $B_{\alpha,\beta}$ and requires only the calculation of the nonadiabatic couplings d_{ij} needed to evaluate the switching probabilities W_{ia} and the adjustments ΔV^i. We refer the reader to the extensive literature on the calculation of nonadiabatic couplings d_{ij}; for example, for widely used independent particle formulations such as density functional theory, see [27,28] and references therein.

That this algorithm achieves a numerical solution of the scheme (3)–(10) can be seen as follows. Let $K(t) \equiv M\sum_i P_i(t)\Delta V^i(t)/\delta t$ denote the force change on the atoms described in step 4. The force $K(t)$ is a stochastic quantity, which results from the random switches between electronic states governed by the random numbers ξ_i. Let $\langle\cdots\rangle_\xi$ denote the average with respect to the uniform random numbers ξ_i used in step 3. The energy conservation constraint (16) gives

$$\Delta V^i = -\frac{\epsilon_{ij}}{M d_{ij}\cdot V}\left[1 + \frac{\epsilon_{ij}}{2M}\frac{d_{ij}d_{ij}}{|d_{ij}\cdot V|^2}\right]d_{ij} + O((\epsilon_{ij}/MV^2)^3).$$

With this expression, we find by straightforward algebra that $K(t)$ has the following statistical properties: with $\delta K_\alpha = K_\alpha - \langle K_\alpha\rangle_\xi$,

$$\langle K_\alpha(t)\rangle_\xi = M\sum_{\beta=1}^{3N}\gamma_{\alpha,\beta}V_\beta(t), \tag{17a}$$

$$\langle \delta K_\alpha(t)\rangle_\xi = 0, \tag{17b}$$

$$\langle \delta K_\alpha(t)\,\delta K_\alpha(t')\rangle_\xi = B_{\alpha,\beta}\delta(t - t'). \tag{17c}$$

These properties hold provided δt is small enough that $W_{ij}\delta t \ll 1$, which is consistent with the primary motivation of Tully's fewest-switches method that the electronic populations change with the minimum number of hops [3]. The relations (17) justify the proposed algorithm as the sudden stochastic switches and associated velocity "kicks" reproduce, on average over the trajectories, the effect of the friction and random forces in the Langevin equation (3); indeed, $\langle K_\alpha(t)\rangle_\xi$ equals the friction force in Eq. (3), while $\delta K_\alpha(t)$ has the same statistical properties as the stochastic force $\xi_\alpha(t)$ given in Eq. (6).

III. MATHEMATICAL DERIVATION AND PROOFS

A. Effective Hamiltonian

As remarked in the Introduction, in order for a mixed quantum-classical scheme to satisfy the principle of detailed balance, it is essential to ensure that the canonical commutation relations of atomic variables be respected [16,17]. This is not the case in the Ehrenfest method, for the atomic positions are treated classically in the equations of electrons. Instead, our derivation treats the atomic variables quantum mechanically before proceeding to the reductions leading to equations of evolution of the averaged atomic positions (3) and electronic populations (10). We assume that the *total* wave function of the system can be written

$$\Psi(r, R, t) = \phi(r, R, t; R_0(t)), \tag{18}$$

where the slow variations are carried by the parametric function $R_0(t)$ that is self-consistently set to equal the average atomic trajectory

$$R_0(t) = \iint R\,|\Psi(r, R, t)|^2 dr\,dR. \tag{19}$$

The ansatz (18) recognizes that, as a consequence of the large atom-to-electron mass ratio and of the quasicontinuum of the density of electronic states, one can identify two well-separated timescales in the system: the slow, adiabatic timescale T_γ of the classical atomic motion described by Eq. (19) and the fast timescale $\tau_c \ll T_\gamma$ that characterizes the fluctuations of the interactions between electrons and atoms. The ansatz (18) nevertheless retains the quantum character of atomic variables R. However, in order to account for the nearly classical character of ions, we assume that the dependence on R of ϕ is strongly peaked around the averaged position $R_0(t)$, i.e.,

$$\langle\Psi(t)|[\hat{R} - R_0(t)]^2|\Psi(t)\rangle \ll R_0(t)^2. \tag{20}$$

An illustrative example of a wave function like Eq. (18) is the product of an electronic wave function times a Gaussian wave packet narrowly centered around $R_0(t)$ and of average momentum $M\dot{R}_0(t)$. Extension to a statistical ensemble of states $\hat{\rho}$, e.g., a canonical ensemble, is straightforward and will be considered below.

The equations of motion for the atomic positions R_0 and electronic state populations outlined in Sec. II are obtained by considering the propagation in time of the state Ψ on an intermediate timescale $\tau_c \ll t \ll T_\gamma$ over which the electronic coherences vary (oscillate) widely, while the adiabatic atomic positions do not move appreciably. Substituting Eq. (18) in the Schrödinger equation $i\hbar\frac{\partial}{\partial t}\Psi = \hat{H}\Psi$, we obtain the evolution equation of ϕ over the fast timescale,

$$i\hbar\frac{\partial\phi}{\partial t} = \frac{\hat{P}^2}{2M}\phi + \hat{H}_e(\hat{r},\hat{R})\phi - i\hbar\dot{R}_0(t)\frac{\partial\phi}{\partial R_0(t)}. \tag{21}$$

The assumption (20) of spatially localized atomic positions atomic positions allows one to approximate $\hat{H}\phi$ by the Taylor expansion,

$$\hat{H}_e(\hat{r},\hat{R})\phi \approx \hat{H}_e(\hat{r},R_0(t))\phi + (\hat{R}-R_0(t))\frac{\partial H_e}{\partial R}(\hat{r},R_0(t))\phi, \tag{22}$$

so that Eq. (21) can be rewritten as the effective Schrödinger equation

$$i\hbar\frac{\partial}{\partial t}\phi = \hat{H}_{\text{eff}}\phi, \tag{23}$$

with the effective Hamiltonian [29]

$$\hat{H}_{\text{eff}} = \frac{\hat{P}^2}{2M} + \sum_n \epsilon_n|n\rangle\langle n| - i\hbar\sum_{n,m}\dot{R}_0(t)\cdot d_{nm}|n\rangle\langle m| + \sum_{n,m} f_{nm}[\hat{R}-R_0(t)]|n\rangle\langle m|. \tag{24}$$

Here we conveniently express the effective Hamiltonian in the orthonormal basis of adiabatic wave functions $|n[R_0(t)]\rangle$ defined above by Eq. (2) for $R(t) = R_0(t)$. Below we shall often omit writing explicitly the dependence on $R_0(t)$ of the adiabatic basis and related quantities. Our scheme is obtained by considering the dynamics of R_0 and of the electronic state populations that result from the effective Hamiltonian (24).

B. Initial conditions and statistical averaging

It will be convenient to describe the electron dynamics in terms of the electron density matrix $\hat{\rho}_e(r;R_0(t))$,

$$\langle r|\hat{\rho}_e(t;R_0(t))|r'\rangle = \int dR\,\phi(r,R,t;R_0(t))\phi^*(r',R,t;R_0(t)),$$

and to expand the latter in terms of the adiabatic basis functions

$$\hat{\rho}_e(t;R_0(t)) = \sum_{i,j} c_{ji}(t)|i[R_0(t)]\rangle\langle j[R_0(t)]|. \tag{25}$$

For convenience, we introduce the notation (dropping dependencies)

$$\hat{c}_{ij} = |i\rangle\langle j|,$$

so that $\hat{\rho}_e = \sum_{i,j} c_{ji}\hat{c}_{ij}$. The coefficient c_{ij} in the expansion (25) is given by

$$c_{ij} = \langle j|\hat{\rho}_e|i\rangle = \text{Tr}[\hat{\rho}_e\hat{c}_{ij}] = \langle\Psi|\hat{c}_{ij}|\Psi\rangle. \tag{26}$$

The diagonal elements c_{ii} are the electronic state populations, and the off-diagonal elements c_{ij} define the coherences. Our scheme outlined in Sec. II describes the dynamics of the complete system in terms of the evolution of the averaged position $R_0(t)$ and of the populations c_{ii}. The temporal evolution of initial coherences c_{ij} to the next time step is not treated explicitly. Indeed, as we shall see below, coherences fluctuate rapidly on a timescale smaller than the adiabatic time. In the presence of a quasicontinuum of states, it is legitimate to neglect their influence on the evolution of the quantum population: this is the basis of the so-called secular approximation. The remaining effect of coherences is on the atomic motions in the form of a rapidly fluctuating force that depends on only the initial values of coherences $\rho_{ij}(t)$. Here our lack of knowledge of the initial coherences is treated statistically: we assume that they are of the form $c_{ij}(0)e^{i(\phi_i-\phi_j)}$, where the phase factor ϕ_i is uniformly distributed in the interval $[0,2\pi]$. If $\langle\langle\cdots\rangle\rangle$ denotes the average of all phases $\{\phi_i\}$,

$$\langle\langle c_{ij}(0)\rangle\rangle = \langle\langle c_{ii}(0)\rangle\rangle\delta_{ij},$$
$$\langle\langle c_{ij}(0)c_{kl}(0)\rangle\rangle = \langle\langle c_{ii}(0)\rangle\rangle\delta_{i,l}\delta_{j,k}.$$

C. Evolution of atomic positions

On the fast timescale, the effective Hamiltonian (24) yields

$$\frac{d\hat{R}}{dt} = \frac{\hat{P}}{M}, \quad M\frac{d^2\hat{R}}{dt^2} = \frac{d\hat{P}}{dt} = -\sum_{i,j} f_{ij}\hat{c}_{ij}. \tag{27}$$

Tracing over the total quantum state, Eq. (27) gives the equation of motion of R_0,

$$M\frac{d^2R_0}{dt^2} = -\sum_{i,j} f_{ij}c_{ij}(t). \tag{28}$$

The forces driving $R_0(t)$ are found by determining the temporal evolution of c_{ij}. The latter are obtained by integrating the evolution equations for $\hat{c}_{ij}$ over the fast timescale driven by the effective Hamiltonian (24),

$$\begin{aligned} i\hbar\frac{d\hat{c}_{ij}}{dt} &= [\hat{c}_{ij},\hat{H}_{\text{eff}}] \\ &= -\epsilon_{ij}\hat{c}_{ij} - i\hbar\sum_n(\dot{R}_0\cdot d_{jn}\hat{c}_{in} - \dot{R}_0\cdot d_{ni}\hat{c}_{nj}) \\ &\quad + \sum_n(f_{jn}\hat{X}_{in} - f_{ni}\hat{X}_{nj}), \end{aligned} \tag{29}$$

where we defined $\hat{X}_{ij} = [\hat{R}-R_0(t)]|i\rangle\langle j|$. Averaging Eq. (29) as in Eq. (26) to obtain the equation satisfied by c_{ij} and integrating over time, we find

$$\begin{aligned} c_{ij}(t) = e^{i\epsilon_{ij}t/\hbar}c_{ij}(0) - \dot{R}_0(t)\int_0^t dt' e^{i\epsilon_{ij}(t-t')/\hbar} \\ \times\sum_n[d_{jn}c_{in}(t') - d_{ni}c_{nj}(t')]. \end{aligned} \tag{30}$$

In deriving Eq. (30), we have neglected the last term in Eq. (29) since its contribution to the nonadiabatic forces on the classical atoms is completely negligible. As we will see in the next section, this is justified because the relevant states n in Eq. (29) satisfy the condition $3Nk_BT \gg \epsilon_{in},\epsilon_{jn}$.

Substituting the solution (30) in Eq. (28), the force driving the motion of R_0 is conveniently split into three parts, such as

$$M\frac{d^2R_0}{dt^2} = F^{BO}(t) + F^{\text{friction}}(t) + \xi(t). \tag{31}$$

The first term

$$F^{BO}(t) = -\sum_i c_{ii}(t) f_{ii} = -\sum_i c_{ii}\frac{\partial\epsilon_i}{\partial R_0}$$

is the traditional Born-Oppenheimer force. The remaining two terms originate from the off-diagonal elements $c_{ij}(t)$, $i \neq j$ and are given by

$$F^{\text{friction}}(t) = \sum_{i,j\neq i} f_{ij}\dot{R}_0 \int_0^t dt' e^{\epsilon_{ij}(t-t')/\hbar} \times \sum_n [d_{jn}c_{in}(t') - d_{ni}c_{nj}(t')] \tag{32}$$

and

$$\xi(t) = -\sum_{i,j\neq i} f_{ij}e^{i\epsilon_{ij}t/\hbar}c_{ij}(0).$$

They correspond, respectively, to the friction force and noise term of Eq. (3) that we discussed in Sec. II. Indeed,

$$F^{\text{friction}}(t) \simeq \sum_{i,j\neq i} f_{ij}\dot{R}_0 d_{ji}\int_0^t dt' e^{\epsilon_{ij}(t-t')/\hbar}[c_{ii}(t') - c_{jj}(t')] \tag{33}$$

$$\simeq \sum_{i,j\neq i} f_{ij}[c_{ii}(t) - c_{jj}(t)]\dot{R}_0\cdot d_{ji}\int_0^t dt' e^{\epsilon_{ij}(t-t')/\hbar} \tag{34}$$

$$\simeq \pi\sum_{i,j\neq i} f_{ij}[c_{ii}(t) - c_{jj}(t)]\dot{R}_0\cdot d_{ji}\delta(\epsilon_{ij}/\hbar) \tag{35}$$

$$= -M\overleftrightarrow{\gamma}\cdot\dot{R}_0(t), \tag{36}$$

where we defined the matrix $\overleftrightarrow{\gamma}$ of friction coefficients

$$\gamma_{\alpha\beta} = -\frac{\pi\hbar}{M}\sum_{i,j\neq i}\frac{f_{ij}^{\alpha}f_{ji}^{\beta}}{\epsilon_{ij}}(c_{ii} - c_{jj})\delta(\epsilon_{ij}),$$

with $\alpha,\beta = 1,\dots,3N$. In deriving Eq. (36), we have performed the following standard steps. First, in going from Eq. (32) to Eq. (33), we have used the secular approximation. The approximation consists of neglecting the off-diagonal terms $i \neq n$ (and $j \neq n$) in Eq. (33) that, unlike the diagonal terms, oscillate rapidly at frequency $\epsilon_{in}/\hbar$ [see Eq. (30)], and their overall contribution nearly cancels out as they interfere destructively for large enough finite times t. The cancellation is most effective for a denser density of states. Second, in going from Eq. (33) to Eq. (34), we have replaced $c_{ii}(t')$ and $c_{jj}(t')$ by the values $c_{ii}(t)$ and $c_{jj}(t)$ at time t. Indeed, in the contribution $\int_0^t dt'[\sum_{j\neq i} f_{ij}(\dot{R}_0\cdot d_{ji})e^{\epsilon_{ij}(t-t')/\hbar}]c_{ii}(t')$ [with similar notation for the term involving $c_{jj}(t')$], the only values of $c_{ii}(t')$ to contribute significantly to the integral are those which correspond to t' very close to t since the sum in the square brackets practically interferes destructively for a quasicontinuum of states as soon as $t - t' \gg \hbar/\Delta$, where Δ is the energy "width" of $F(\epsilon_i) = \sum_{j\neq i} f_{ij}(\dot{R}_0\cdot d_{ji})e^{\epsilon_{ij}(t-t')/\hbar}$, i.e., the order of magnitude of the variation in ϵ_i needed for $F(\epsilon_i)$ to change significantly. Last, in going from Eq. (34) to Eq. (35), we have used

$$\int_0^t dt' e^{i\epsilon_{in}(t-t')/\hbar} = e^{i\epsilon_{in}t/2}\frac{\sin(\epsilon_{in}t/2)}{\epsilon_{in}/2} \approx \pi\hbar\delta(\epsilon_{in}) + i\hbar\mathcal{P}\frac{1}{\epsilon_{in}} \tag{37}$$

at large enough t. Note that it is not necessary to let t approach infinity in order to use (37) in Eq. (34), but it suffices for $\hbar/t$ to be smaller than the energy width of $F(\epsilon_i)$ discussed above. As for the term $\xi(t)$, it corresponds to a δ-correlated Gaussian random force characterized by the relations (6). Indeed, the properties (6) imply

$$\begin{aligned}\langle\langle\xi_\alpha(t)\xi_\beta(t')\rangle\rangle &= \sum_{a,b}{}'\sum_{k,l}{}' f_{ab}^{\alpha}f_{kl}^{\beta}e^{i(\epsilon_{ab}t+\epsilon_{kl}t')/\hbar}\langle\langle c_{ab}(0)c_{kl}(0)\rangle\rangle \\ &= \sum_{a,b}{}' f_{ab}^{\alpha}f_{ba}^{\beta}e^{i\epsilon_{ab}(t-t')/\hbar}c_{aa}(0) \\ &\approx B_{\alpha,\beta}\delta(t-t'),\end{aligned} \tag{38}$$

with

$$\begin{aligned}B_{\alpha,\beta} &= \int d(t-t')\sum_{a,b}{}' f_{ab}^{\alpha}f_{ba}^{\beta}e^{i\epsilon_{ab}(t-t')/\hbar}c_{aa}(0) \\ &= \pi\sum_{i\neq j}(P_i + P_j)f_{ij}^{\alpha}f_{ji}^{\beta}\delta(\epsilon_{ij}/\hbar).\end{aligned}$$

More generally, Eq. (38) can be written as $\langle\langle\xi_\alpha(t)\xi_\beta(t')\rangle\rangle = B_{\alpha,\beta}g(t-t')$, where $g(t)$ is an even, normalized function of width τ_c. If, as assumed here, the atomic motions are integrated over time steps $\delta t > \tau_c$, g can be approximated by a delta function as in Eq. (38).

D. Evolution of electronic populations

We consider again the evolution equations (29) of the operators $\hat{c}_{ij}$ over the fast timescale governed by the effective Hamiltonian. In order to get the rate equations for the electronic populations $\langle\hat{c}_{ii}\rangle$ we iterate Eqs. (29). That is, we formally solve Eqs. (29) for operators $\hat{c}_{ij}(t)$,

$$\hat{c}_{ij}(t) = \hat{c}_{ij}(0)\,e^{-i\epsilon_{ij}t/\hbar} + \int_0^t dt'\,e^{i\epsilon_{ij}(t-t')/\hbar} \times \sum_n [d_{jn}\hat{V}_{in}(t') - d_{ni}\hat{V}_{jn}^{\dagger}(t')], \tag{39}$$

where

$$\hat{V}_{in} = i\dot{R}_0\hat{c}_{in} + (1/\hbar)\epsilon_{ij}\hat{c}_{in}\,\delta\hat{R},$$

$\delta\hat{R} = \hat{R} - R_0(t)$, and the dagger stands for Hermitian conjugation, and we substitute these expressions back into Eqs. (29). In doing so we should keep in mind that the order of operators $\delta\hat{R}$ and $\hat{c}_{in}$ matters. While these operators commute at the same time, they do not commute when taken at different t due to the noncommutativity between $\delta\hat{R}$ and $\hat{P}$. Then, applying the same approximations as we did in deriving equations of motion for the ions in the previous section, i.e., dropping the rapidly oscillating terms as well as the terms linear in $\delta\hat{R}$ (which average to zero), we arrive at the following equation of motion for the electronic populations $c_{ii} = \langle \hat{c}_{ii} \rangle$:

$$\frac{dc_{ii}}{dt} = \sum_{n \neq i} (W_{in} c_{nn} - W_{ni} c_{ii}) + \langle \eta_i(t) \rangle, \tag{40}$$

with the rates

$$\begin{aligned} W_{in} = \sum_{\alpha,\beta} d_{in}^{\alpha} d_{in}^{\beta} \int_0^t dt' \{ & 2\mathrm{Re}[\dot{R}_{0\alpha}(t)\dot{R}_{0\beta}(t')\, e^{i\epsilon_{in}(t-t')/\hbar}] \\ & + (\epsilon_{in})^2 [\langle \delta\hat{R}_\alpha(t)\delta\hat{R}_\beta(t')\rangle e^{i\epsilon_{in}(t-t')/\hbar} \\ & + \langle \delta\hat{R}_\beta(t')\delta\hat{R}_\alpha(t)\rangle e^{i\epsilon_{in}(t'-t)/\hbar}]\} \end{aligned} \tag{41}$$

and the noise terms

$$\begin{aligned} \eta_i(t) = \sum_n \{ & d_{in}[i\dot{R}_0 + (1/\hbar)\epsilon_{in}\, \delta\hat{R}]\hat{c}_{in}(0)\, e^{-i\epsilon_{in} t/\hbar} \\ & - d_{ni}[i\dot{R}_0 + (1/\hbar)\epsilon_{ni}\, \delta\hat{R}]\hat{c}_{in}(0)\, e^{i\epsilon_{in} t/\hbar}\}. \end{aligned} \tag{42}$$

The first contribution to the rates on the right-hand side of Eq. (41) is the dominating term associated with the classical motion of atoms. The second term is smaller but plays an important role. To see this, let's integrate this second term by parts (over t'). The boundary terms vanish: the $t' = t$ contribution exactly cancels, while $t' = 0$ contributions, $\langle \delta\hat{R}_\alpha(t)\delta\hat{R}_\beta(0)\rangle e^{i\epsilon_{in}t/\hbar}$ and $\langle \delta\hat{R}_\alpha(0)\delta\hat{R}_\beta(t)\rangle e^{-i\epsilon_{in}t/\hbar}$, vanish in the limit of sufficiently large t. The remaining term is

$$\begin{aligned} & i\left(d_{in}^{\alpha} d_{in}^{\beta} \epsilon_{in}/M\right) \int_0^t dt' [\langle \delta\hat{R}_\alpha(t)\delta\hat{P}_\beta(t')\rangle e^{i\epsilon_{in}(t-t')/\hbar} \\ & - \langle \delta\hat{P}_\beta(t')\delta\hat{R}_\alpha(t)\rangle e^{i\epsilon_{in}(t'-t)/\hbar}], \end{aligned} \tag{43}$$

where we have used $d\delta\hat{R}/dt = \delta\hat{P}/M$. Furthermore, since this term is small compared to the first "classical" term in Eq. (41), we can set $t = t'$ in the correlation functions $\langle \delta\hat{R}_\alpha(t)\delta\hat{P}_\beta(t')\rangle$, etc. Then, by virtue of the coordinate-momentum commutation relation $[\hat{P}_\alpha, \hat{R}_\beta] = i\hbar\, \delta_{\alpha\beta}$, the above expression is written as

$$\begin{aligned} & \left(d_{in}^{\alpha} d_{in}^{\alpha} \epsilon_{in}/M\right) \int_0^t dt' \{\hbar\, \mathrm{Re}[e^{i\epsilon_{in}(t-t')/\hbar}] \\ & + i\langle \{\delta\hat{R}_\alpha(t), \delta\hat{P}_\beta(t)\}\rangle\, \mathrm{Im}[e^{i\epsilon_{in}(t-t')/\hbar}]\}. \end{aligned} \tag{44}$$

The anticommutator $\{\delta\hat{R}_\alpha, \delta\hat{P}_\beta\}$, when averaged relative to a spatially localized atomic state, is small. For instance, for normalized Gaussian wave functions $\Psi(R) = e^{-(R-R_0)^2/2\sigma^2} e^{iP_0\cdot(R-R_0)/\hbar}/\pi^{1/4}\sqrt{\sigma}$ (written here in one dimension for simplicity), it is equal to zero. Also, its contribution, unlike that for the first term in Eq. (44), is imaginary, so it can contribute to only the renormalization of energy differences, e.g., ϵ_{in}, and not to the rates. Thus, we get

$$\begin{aligned} W_{in} = \sum_{\alpha,\beta} 2\, d_{in}^{\alpha} d_{in}^{\beta} \mathrm{Re}\Bigg\{ \int_0^t dt' \Bigg[& \dot{R}_{0\alpha}(t)\dot{R}_{0\beta}(t') \\ & + \delta_{\alpha\beta} \frac{\epsilon_{in}}{2M} \Bigg] e^{i\epsilon_{in}(t'-t)/\hbar} \Bigg\}. \end{aligned} \tag{45}$$

The $\dot{R}_{0\alpha}(t)\dot{R}_{0\beta}(t')$ term on the right-hand side of Eq. (45) can be transformed to

$$\dot{R}_{0\alpha}(t)\dot{R}_{0\beta}(t) - (t - t')B_{\alpha,\beta}/M^2, \tag{46}$$

where $B_{\alpha,\beta}$ is given by Eq. (38). Indeed, by writing

$$\dot{R}_{0\alpha}(t') = \dot{R}_{0\alpha}(t) + \int_t^{t'} \ddot{R}_{0\alpha}(t_1)\, dt_1$$

and taking into account that on the short timescale the classical atomic coordinate obeys $M\ddot{R}_{0\alpha} = \xi_\alpha(t)$, we can average $(1/M)\int_t^{t'} \dot{R}_{0\alpha}(t)\xi_\beta(t_1)\, dt_1$ over the white noise, obtaining the second term in Eq. (46). Furthermore, exponentiating $(t' - t)B_{\alpha,\beta}/M^2 + \epsilon_{in}/(2M)$, we obtain

$$\begin{aligned} W_{in} = \sum_{\alpha,\beta} & 2[d_{in} \cdot \dot{R}_0(t)]^2\, e^{\frac{\epsilon_{in} d_{in}^2}{2M[d_{in}\cdot \dot{R}_0(t)]^2}} \\ & \times \mathrm{Re}\left\{ \int_0^t dt'\, e^{(i\epsilon_{in}/\hbar - \Gamma_{in})(t'-t)} \right\}, \end{aligned} \tag{47}$$

where

$$\Gamma_{in} = \sum_{\alpha,\beta} d_{in}^{\alpha} d_{in}^{\beta} B_{\alpha,\beta}(t)/[M d_{in} \cdot \dot{R}_0(t)]^2. \tag{48}$$

We remark that the exponentiation of the perturbative calculation is done on the physical grounds that the exact rates should satisfy the detailed balance and that the linewidths of the transitions between states are finite.

Thus, we can write the rate as

$$W_{in} = 2\pi [d_{in} \cdot \dot{R}_0(t)]^2\, e^{\frac{\epsilon_{in} d_{in}^2}{2M[d_{in}\cdot \dot{R}_0(t)]^2}}\, \mathcal{L}(\epsilon_{in}, \Gamma_{in}), \tag{49}$$

with the δ function having finite width due to the noise induced by the electrons on the atomic motions.

The additive noise $\eta_i(t)$ in Eqs. (41) and (42) has zero average over the ensemble of initial conditions $\hat{c}_{in}(0)$, and it is δ correlated on the atomic timescale. A straightforward calculation analogous to the derivation of expression (49) leads to

$$\langle \eta_i(t)\eta_j(t')\rangle = \left[\sum_{n\neq i} (W_{in} + W_{ni}) \right] \delta_{ij}\, \delta(t - t'). \tag{50}$$

Equations (40) and (50) imply that the electronic dynamics is Markovian, with the electronic subsystem spontaneously "hopping" between states with gradually varying energies ϵ_i. Upon averaging the stochastic rate equations (41) over the noise configurations one obtains the master equation (10) with $P_i = \langle c_{ii} \rangle \equiv \langle\langle \hat{c}_{ii} \rangle\rangle$.

E. Proof of energy conservation property

The total energy of the system at time t in the state $\phi(r, R, t; R_0(t))$ along a trajectory $R_0(t)$ is

$$E_{tot}(t) = \frac{M\dot{R}_0^2}{2} + \sum_i \epsilon_i P_i.$$

We will show that the ensemble-averaged energy $\langle\langle E_{tot}(t)\rangle\rangle$ is conserved over time, i.e.,

$$\frac{d\langle\langle E_{tot}(t)\rangle\rangle}{dt} = 0.$$

First, taking the dot product of the equation of motion (31) by the vector $\dot{R}_0(t)$ of atomic velocities, we obtain

$$\frac{M}{2}\frac{d}{dt}\dot{R}_0^2+\sum_i\frac{d\epsilon_i}{dt}P_i=2\pi\hbar{\sum_{i,j}}'P_i\frac{|\dot{R}_0\cdot f_{ij}|^2}{\epsilon_{ij}}\delta(\epsilon_{ij})+\dot{R}_0\cdot\xi. \tag{51}$$

Second, multiplying the rate equation (40) by the electronic energy ϵ_i and summing over all states i, we find

$$\sum_i\epsilon_i\frac{dP_i}{dt}=-2\pi\hbar{\sum_{ij}}'P_i\frac{|\dot{R}_0\cdot f_{ij}|^2}{\epsilon_{ij}}\delta(\epsilon_{ij})-\frac{1}{2M}{\sum_{ij}}'B_{ij}. \tag{52}$$

Summing the previous two equations yields

$$\frac{dE_{tot}}{dt}=-\frac{1}{2M}{\sum_{ij}}'B_{ij}+\dot{R}\cdot\xi.$$

This equation averages out to zero upon averaging over the initial phases to yield the desired result. Indeed, using the stochastic equation (31) and the property (38), we find

$$\langle\dot{R}(t)\cdot\xi(t)\rangle=\left\langle\int_0^t dt'\,\frac{\xi(t')}{M}\xi(t)\right\rangle=\frac{1}{2M}{\sum_{ij}}'B_{ij}$$

for $\tau_c \ll t \ll T_\gamma$.

F. Linewidth

The equations for the rates derived in this section, e.g., Eq. (49), contain a broadened δ function of the energy difference $\epsilon_{in}=\epsilon_i-\epsilon_n$ with the width given by Eq. (48). The latter equation contains the atomic noise correlator $B_{\alpha,\beta}$, which gradually varies with time due to the changing atomic positions in the course of the evolution. The instantaneous (on the timescale of atomic motions) value of $B_{\alpha,\beta}$ is given by Eq. (7), which, in turn, contains a sum over δ functions. In our derivation in Sec. III C the values for the width of the δ functions in Eq. (7) were not specified for two reasons: first, it cannot be easily derived within the framework of the calculation presented in this paper. Presumably, it can be carried out by analyzing the dynamics of higher correlators, $\langle\hat{R}\hat{c}_{ij}\rangle$, $\langle\hat{P}\hat{c}_{ij}\rangle$, etc., which lies beyond the scope of this calculation. Second, since the δ functions in Eqs. (5) and (7) are effectively under the integrations over the energies, their precise widths should not matter [unless the sums in Eqs. (5) and (7) contain a finite number of terms].

The energy conservation property derived in the previous section, however, dictates that the widths of the δ functions in Eqs. (5) and (7) and in Eq. (49) should be the same ([as was saliently implied in Eqs. (48) and (49), where we used the same Γ_{in} as in Eqs. (5), (7), (8)]. Indeed, had Γ_{in} in these expressions been different, the first terms on the right-hand sides of Eqs. (51) and (52) would not cancel each other in Eq. (53) (again, for a finite number of electronic states). Therefore, Eq. (48) can be rewritten as a self-consistency equation for determining Γ_{in}, e.g., Eq. (9).

The right-hand side of Eq. (9) can be easily estimated if we assume that the number of atomic degrees of freedom is large. Then the expression $(Md_{in}\cdot V)^2$ in Eq. (9) self-averages to give $M^2d_{in}^2\langle V_\alpha^2\rangle = Md_{in}^2T_i$, where T_i is the temperature of the atomic degrees of freedom. Furthermore, the sum over j, j', i.e., $B_{\alpha,\beta}$, by virtue of the fluctuation-dissipation theorem can be estimated to give $\sim 2M\gamma T_e\delta_{\alpha\beta}$, where γ is the typical atomic friction coefficient and T_e is the electronic temperature. Thus, we obtain

$$\Gamma\sim 2\,\frac{T_e}{T_i}\,\gamma, \tag{53}$$

so in the equilibrium, i.e., for $T_e\sim T_i$, the linewidths Γ_{in} are of the order of the atomic friction coefficient.

In the surface-hopping algorithm described in Sec. II C the values of Γ_{in} should be calculated on the fly, i.e., when the electronic subsystem is in a particular state i_0. In that case we should replace P_j in Eq. (9) by δ_{i_0j}, which leads to the following self-consistency equation for Γ_{i_0n}:

$$\Gamma_{i_0n}=\frac{2\hbar^2}{\left(Md_{i_0n}\cdot V\right)^2}\sum_{j\neq i_0}\frac{\left(d_{i_0n}f_{i_0j}\right)^2\Gamma_{i_0j}}{\left(\epsilon_{i_0j}\right)^2+\left(\hbar\Gamma_{i_0j}\right)^2}. \tag{54}$$

It should be pointed out that Γ evaluated according to Eqs. (9) and (54) are not the actual electronic linewidths. The latter should include effects related to the disorder caused by the randomness in atomic positions and thus the fluctuations in the energies ϵ_i of the electronic states. Such disorder effects can be accounted for by running a *bundle* of trajectories with different initial conditions (rather than a single trajectory). Averaging the fluctuations in ϵ_i over the ensemble of these trajectories will produce the linewidths of the order of τ_c^{-1} discussed in Sec. II A. These linewidths define the rate of decay of electronic correlations or coherences as well as the transport time. On the contrary, the partial widths Γ_{in} ($\Gamma\sim T_\gamma^{-1}$) are associated with the atomic jittering around a *single* trajectory and therefore define the linewidths for the transitions associated with this trajectory.

IV. SUMMARY

In summary, we have presented a scheme for carrying out nonadiabatic molecular dynamics simulations of systems where a quasicontinuum of electronic excitations of arbitrarily low energy is available to couple with the ionic motions. The scheme, which is derived from first principles and does not rely on *ad hoc* parameters, naturally satisfies the principle of detailed balance and therefore can properly describe nonequilibrium dynamics. A numerical algorithm was proposed in the form of the widely used fewest-switches surface-hopping algorithm but with switching probabilities that are not specified *ad hoc* like in the original algorithm but are instead derived. The present approach could greatly increase the number of processes amenable to realistic simulation by molecular dynamics in several research areas.

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