

## Mixed quantum-classical dynamics

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Mixed quantum-classical equations of motion are derived for a quantum subsystem of light (mass  $m$ ) particles coupled to a classical bath of massive (mass  $M$ ) particles. The equation of motion follows from a partial Wigner transform over the bath degrees of freedom of the Liouville equation for the full quantum system, followed by an expansion in the small parameter  $\mu = (m/M)^{1/2}$  in analogy with the theory of Brownian motion. The resulting mixed quantum-classical Liouville equation accounts for the coupled evolution of the subsystem and bath. The quantum subsystem is represented in an adiabatic (or other) basis and the series solution of the Liouville equation leads to a representation of the dynamics in an ensemble of surface-hopping trajectories. A generalized Pauli master equation for the evolution of the diagonal elements of the density matrix is derived by projection operator methods and its structure is analyzed in terms of surface-hopping trajectories.  
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### I. INTRODUCTION

One is often interested in the dynamics of a light quantum particle or set of quantum degrees of freedom interacting with more massive particles.<sup>1</sup> Examples include electron and proton transfer or diffusion processes in condensed phase systems, or vibrational motions of molecules in liquids. In such circumstances it is not feasible to attempt a full quantum solution of the Schrödinger equation for the thousands of degrees of freedom of the system. Consequently one is led to consider the dynamics of a quantum subsystem coupled to a classical bath.

The nature of the equations of motion describing such a mixed quantum-classical system is unclear since the coupling to the quantum subsystem endows the classical bath with unusual properties. For example, by a stationary phase analysis of the equations of motion Pechukas demonstrated that the variational principle leading to the evolution equations is not Lagrangian in character and the equations of motion do not possess unique solutions as a consequence of the coupling to the quantum degrees of freedom.<sup>2</sup>

The most common methods for treating these mixed quantum-classical systems utilize surface-hopping schemes involving various approximations to the dynamics. Once one goes beyond a description based on adiabatic dynamics where the evolution takes place on a single potential energy surface, a number of different methods have been suggested for devising trajectories of the classical bath that account for transitions among the quantum states of the subsystem.<sup>3-6</sup> These methods are based on assumptions concerning the nature of the mixed quantum-classical dynamics. Approximate schemes based on the evolution of the quantum density matrix coupled to a classical bath<sup>7</sup> and on the use of generalized Hellmann-Feynman forces<sup>8</sup> have been constructed. Studies of the density matrix evolution for two-level systems in a

semiclassical limit have been used to explore mixed quantum-classical dynamics in terms of classical trajectories.<sup>9</sup> Also, multistate quantum Fokker-Planck equations have formed the basis of investigations of nonadiabatic dynamics.<sup>10</sup>

In this article we present a formulation of this problem that yields a set of evolution equations for the mixed quantum-classical system. The method utilizes a partial Wigner representation<sup>11</sup> of the bath degrees of freedom while retaining the operator character of the quantum subsystem. The mixed quantum-classical limit is obtained by an expansion in a small parameter  $\mu = (m/M)^{1/2} \ll 1$ , where  $m$  and  $M$  are the masses of the quantum and "classical" particles, respectively. This expansion of the equations of motion is analogous to that utilized in the classical theory of Brownian motion. The derivation of the equation of motion for the density matrix is presented in Sec. II. The representation of the evolution equation in an adiabatic basis is given in Sec. III. Section IV shows how the time evolution of the density matrix may be computed in terms of an ensemble of surface-hopping trajectories. Both exact and approximate representations in such trajectories are described. Section V presents a derivation of the Pauli master equation for a mixed quantum-classical system. The equation for the density matrix is cast in the form of a generalized master equation for the diagonal elements. An analysis of this master equation yields further insight into the dynamics in terms of surface-hopping trajectories. The conclusions of the study are given in Sec. VI.

### II. EVOLUTION EQUATION FOR DENSITY MATRIX

Consider a quantum system composed of an  $n$ -particle subsystem and an  $N$ -particle bath with coordinate operators

$\hat{q}$  and  $\hat{Q}$  and particle masses of  $m$  and  $M$ , respectively. The evolution of the density matrix  $\hat{\rho}(t)$  for this system is given by the quantum Liouville equation

$$\frac{\partial \hat{\rho}}{\partial t} = -\frac{i}{\hbar} [\hat{H}, \hat{\rho}], \quad (1)$$

where the Hamiltonian operator is

$$\hat{H} = \frac{\hat{P}^2}{2M} + \frac{\hat{p}^2}{2m} + \hat{V}(\hat{q}, \hat{Q}). \quad (2)$$

The momentum operators are  $\hat{p}$  and  $\hat{P}$  while the total potential energy  $\hat{V}(\hat{q}, \hat{Q})$  may be written as  $\hat{V}(\hat{q}, \hat{Q}) = \hat{V}_s(\hat{q}) + \hat{V}_b(\hat{Q}) + \hat{V}_c(\hat{q}, \hat{Q})$ , where the subscripts  $s$ ,  $b$ , and  $c$  refer to the (quantum) subsystem, bath and coupling, respectively, but we shall rarely need this decomposition. The hats refer to abstract operators; when the hat is omitted the symbols will refer to the coordinate representation of these quantities. In addition, symbols such as  $\hat{q}$  or  $\hat{Q}$  will stand for vectors of operators,  $\hat{q} = (\hat{q}_1, \hat{q}_2, \dots, \hat{q}_{3n})$ , or  $\hat{Q} = (\hat{Q}_1, \hat{Q}_2, \dots, \hat{Q}_{3N})$ , corresponding to the different particles in the system under consideration.

Since we are interested in the limit where the bath degrees of freedom are treated classically in a sense described below, it is convenient to first perform a partial Wigner transformation with respect to the  $Q$  bath coordinates, retaining the operator character that exists because of the  $q$  coordinate operators. So we consider the quantum Liouville equation in the  $\{Q\}$  representation, where  $\hat{\rho}(Q, Q', t) = \langle Q | \hat{\rho}(t) | Q' \rangle$ . We have

$$\frac{\partial \hat{\rho}(Q, Q', t)}{\partial t} = -\frac{i}{\hbar} \int dQ'' (\langle Q | \hat{H} | Q'' \rangle \hat{\rho}(Q'', Q', t) - \hat{\rho}(Q, Q'', t) \langle Q'' | \hat{H} | Q' \rangle), \quad (3)$$

where

$$\langle Q | \hat{H} | Q' \rangle = \frac{-\hbar^2}{2M} \frac{\partial^2}{\partial Q^2} \delta(Q - Q') + \left( \frac{\hat{p}^2}{2m} + \hat{V}(\hat{q}, Q) \right) \delta(Q - Q'). \quad (4)$$

The partial Wigner transforms are defined as follows:<sup>11</sup>

$$\hat{\rho}_W(R, P) = (2\pi\hbar)^{-3N} \int dz e^{iP \cdot z/\hbar} \left\langle R - \frac{z}{2} \left| \hat{\rho} \right| R + \frac{z}{2} \right\rangle, \quad (5)$$

and for an operator  $\hat{A}$

$$\begin{aligned} \hat{A}_W(R, P) &= \int dz e^{iP \cdot z/\hbar} \left\langle R - \frac{z}{2} \left| \hat{A} \right| R + \frac{z}{2} \right\rangle \\ &= \int dz e^{-iP \cdot z/\hbar} \left\langle R + \frac{z}{2} \left| \hat{A} \right| R - \frac{z}{2} \right\rangle. \end{aligned} \quad (6)$$

We shall need the partial Wigner transform of a product of operators. It is<sup>12</sup>

$$(\hat{A}\hat{B})_W(R, P) = \hat{A}_W(R, P) e^{\hbar\Lambda/2i} \hat{B}_W(R, P), \quad (7)$$

where the Poisson bracket operator  $\Lambda$  is defined as

$$\Lambda = \vec{\nabla}_P \cdot \vec{\nabla}_R - \vec{\nabla}_R \cdot \vec{\nabla}_P, \quad (8)$$

and the direction of an arrow indicates the direction in which the operator acts.

Taking the partial Wigner transform of the evolution equation [Eq. (3)] we find

$$\begin{aligned} \frac{\partial \hat{\rho}_W(R, P, t)}{\partial t} &= -\frac{i}{\hbar} ((\hat{H}\hat{\rho})_W - (\hat{\rho}\hat{H})_W) \\ &= -\frac{i}{\hbar} (\hat{H}_W(R, P) e^{\hbar\Lambda/2i} \hat{\rho}_W(R, P, t) \\ &\quad - \hat{\rho}_W(R, P, t) e^{\hbar\Lambda/2i} \hat{H}_W(R, P)). \end{aligned} \quad (9)$$

Here

$$\hat{H}_W(R, P) = \frac{P^2}{2M} + \frac{\hat{p}^2}{2m} + \hat{V}_W(\hat{q}, R). \quad (10)$$

We are interested in the limit where the masses of the bath particles are much larger than those of the subsystem,  $M \gg m$ . In order to take this limit of the equations of motion it is useful to follow a procedure familiar from the classical theory of Brownian motion<sup>13</sup> and first scale the variables so that the momenta of the heavy particles are of the same order of magnitude as those of the light particles:  $\mu P$ , where  $\mu = (m/M)^{1/2}$ . In order to cast the equation of motion into a form that makes the small  $\mu$  limit transparent, it is convenient to also measure all distances in length units appropriate for the quantum subsystem. Letting energy be measured in terms of the arbitrary energy unit  $\epsilon_0$ , time in units of  $t_0 = \hbar/\epsilon_0$  and length in units of  $\lambda_m = (\hbar^2/m\epsilon_0)^{1/2}$ , the momentum units are selected to be  $p_m = (m\lambda_m/t_0) = (m\epsilon_0)^{1/2}$  and  $P_M = (M\epsilon_0)^{1/2}$ . Using these units we introduce the dimensionless variables

$$\hat{q}' = \hat{q}/\lambda_m, \quad R' = R/\lambda_m, \quad (11)$$

$$\hat{p}' = \hat{p}/p_m, \quad P' = P/P_M. \quad (12)$$

In terms of these scaled variables, the scaled time  $t' = t/(\hbar/\epsilon_0)$ , and scaled Hamiltonian,  $\hat{H} = \epsilon_0 \hat{H}'(\hat{p}', P', \hat{q}', R')$ , we may rewrite the equation of motion in a dimensionless form that makes the  $\mu$  dependence explicit.

Carrying out this scaling, the density matrix equation [Eq. (9)] in *dimensionless* variables is

$$\begin{aligned} \frac{\partial \hat{\rho}'_W(R', P', t')}{\partial t'} &= -i (\hat{H}'_W(R', P') e^{\mu\Lambda'/2i} \hat{\rho}'_W(R', P', t') \\ &\quad - \hat{\rho}'_W(R', P', t') e^{\mu\Lambda'/2i} \hat{H}'_W(R', P')). \end{aligned} \quad (13)$$

Note  $\Lambda = \mu\Lambda'/\hbar$ . To obtain a description of a quantum subsystem composed of light particles coupled to a heavy bath we expand in  $\mu$  and keep only linear terms. The evolution equation becomes

$$\begin{aligned} \frac{\partial \hat{\rho}'_W(R', P', t')}{\partial t'} &= -i[\hat{H}'_W(R', P'), \hat{\rho}'_W(R', P', t')] \\ &+ \frac{\mu}{2}(\{\hat{H}'_W(R', P'), \hat{\rho}'_W(R', P', t')\} \\ &- \{\hat{\rho}'_W(R', P', t'), \hat{H}'_W(R', P')\}), \end{aligned} \quad (14)$$

where the Poisson bracket is

$$\{\hat{A}(R, P), \hat{B}(R, P)\} = \frac{\partial \hat{A}}{\partial R} \cdot \frac{\partial \hat{B}}{\partial P} - \frac{\partial \hat{A}}{\partial P} \cdot \frac{\partial \hat{B}}{\partial R}, \quad (15)$$

and the order of the quantum operator is preserved. Returning to *unscaled* variables we finally obtain

$$\begin{aligned} \frac{\partial \hat{\rho}_W(R, P, t)}{\partial t} &= -\frac{i}{\hbar}[\hat{H}_W(R, P), \hat{\rho}_W(R, P, t)] \\ &+ \frac{1}{2}(\{\hat{H}_W(R, P), \hat{\rho}_W(R, P, t)\} \\ &- \{\hat{\rho}_W(R, P, t), \hat{H}_W(R, P)\}). \end{aligned} \quad (16)$$

We shall refer to this equation as the Liouville equation for the mixed quantum-classical system. It will form the basis of the subsequent calculations in this paper.

The heavy mass limit considered above may be interpreted in the following fashion: Suppose the characteristic energy  $\epsilon_0$  is taken to be the thermal energy  $k_B T$  as is appropriate for condensed phase systems. Then  $\lambda_m$  is the thermal wavelength of the mass  $m$  particles. The thermal wavelength of the heavy particles is shorter by  $(m/M)^{1/2}$ . Since, in scaled units, the dimensionless velocities of the light and heavy particles are comparable, in a fixed scaled time interval the scaled distances for light and heavy particles are the same. Thus, the scaling focuses on the length scale determined by the light particles and on this scale the heavy particles exhibit many de Broglie oscillations. Formally, one may arrive at the same result by simply expanding  $\exp(\hbar\Lambda/2i)$  in powers of  $\hbar$ , but while this type of expansion may have meaning for the entire system its application to the bath alone requires additional justification. The mass expansion makes the precise nature of our mixed quantum-classical limit clear. We note that if one assumes there is no subsystem then the resulting bath evolution equation is exactly that for a classical system of particles with mass  $M$ , justifying the terminology.

The terms on the right hand side of this equation reflect both the quantum and ‘‘classical’’ aspects of the density matrix: The first term is the commutator of  $\hat{\rho}_W$  with  $\hat{H}_W$ , analogous to that in the evolution of a pure quantum system, while the second term contains Poisson brackets involving these quantities, maintaining the fact that  $\hat{\rho}_W$  does not commute with  $\hat{H}_W$ .

The density matrix is still an abstract quantity in the subsystem degrees of freedom and in order to analyze its structure in more detail it is useful to consider its representation in some basis.

### III. REPRESENTATION IN ADIABATIC BASIS

A convenient basis in which to represent the quantum evolution is the basis of adiabatic states defined by

$$\hat{h}_W(R)|\alpha;R\rangle = E_\alpha(R)|\alpha;R\rangle, \quad (17)$$

where the Hamiltonian for the system with fixed values of the bath coordinates is

$$\hat{h}_W(R) = \frac{\hat{p}^2}{2m} + \hat{V}_W(\hat{q}, R). \quad (18)$$

Note that the Wigner transformed Hamiltonian is just the sum of the classical kinetic energy of the bath plus  $\hat{h}_W(R)$ ,

$$\hat{H}_W(R, P) = \frac{P^2}{2M} + \hat{h}_W(R). \quad (19)$$

Taking matrix elements of Eq. (16) and letting  $\rho_W^{\alpha\alpha'}(R, P) = \langle\alpha;R|\hat{\rho}_W(R, P)|\alpha';R\rangle$ , we obtain

$$\begin{aligned} \frac{\partial \rho_W^{\alpha\alpha'}(R, P, t)}{\partial t} &= -i\omega_{\alpha\alpha'}(R)\rho_W^{\alpha\alpha'}(R, P, t) \\ &+ \frac{1}{2}\langle\alpha;R|\{\hat{H}_W(R, P), \hat{\rho}_W(R, P, t)\}|\alpha';R\rangle \\ &- \frac{1}{2}\langle\alpha;R|\{\hat{\rho}_W(R, P, t), \hat{H}_W(R, P)\}|\alpha';R\rangle. \end{aligned} \quad (20)$$

Making use of the fact that

$$\begin{aligned} \langle\alpha;R|\frac{\partial \hat{\rho}_W}{\partial R}|\alpha';R\rangle &= \frac{\partial \rho_W^{\alpha\alpha'}}{\partial R} - \sum_{\alpha''}(\rho_W^{\alpha\alpha''}d_{\alpha''\alpha'} - d_{\alpha\alpha''}\rho_W^{\alpha''\alpha'}), \end{aligned} \quad (21)$$

with the nonadiabatic coupling matrix element given by

$$d_{\alpha\alpha'} = \langle\alpha;R|\frac{\partial}{\partial R}|\alpha';R\rangle, \quad (22)$$

we obtain the adiabatic representation of the equation of motion for the mixed quantum-classical system

$$\begin{aligned} \frac{\partial \rho_W^{\alpha\alpha'}(R, P, t)}{\partial t} &= -i\omega_{\alpha\alpha'}(R)\rho_W^{\alpha\alpha'}(R, P, t) \\ &+ \sum_{\alpha''} \frac{P}{M} \cdot (\rho_W^{\alpha\alpha''}d_{\alpha''\alpha'} - d_{\alpha\alpha''}\rho_W^{\alpha''\alpha'}) - \frac{P}{M} \cdot \frac{\partial \rho_W^{\alpha\alpha'}}{\partial R} \\ &- \frac{1}{2} \sum_{\alpha''} \left( F_W^{\alpha\alpha''} \cdot \frac{\partial \rho_W^{\alpha''\alpha'}}{\partial P} + \frac{\partial \rho_W^{\alpha\alpha''}}{\partial P} \cdot F_W^{\alpha''\alpha'} \right). \end{aligned} \quad (23)$$

Here  $\omega_{\alpha\alpha'}(R) = (E_\alpha(R) - E_{\alpha'}(R))/\hbar$  and the ‘‘force’’  $F_W^{\alpha\alpha'}$  has the definition  $F_W^{\alpha\alpha'} = -\langle\alpha;R|[\partial\hat{V}_W(\hat{q}, R)/\partial R]|\alpha';R\rangle = -\langle\alpha;R|[\partial\hat{H}_W(R)/\partial R]|\alpha';R\rangle$ .

Equation (23) shows that the density matrix evolution consists of two types of contribution: The first two terms on the right-hand-side (r.h.s.) of Eq. (23) account for the quantum evolution of the density matrix, while the third and fourth terms account for the evolution of the ‘‘classical’’ degrees of freedom of the density matrix. Assuming that the trajectory  $\{R(t)\}$  is given one may consider the evolution of the quantum subsystem described by the state vector  $|\Psi[t;R(t)]\rangle$  which is a functional of  $\{R(t)\}$  and a regular function of  $t$ . Expanding the state vector  $|\Psi[t;R(t)]\rangle$  in terms of the instantaneous adiabatic states as

$$|\Psi[t;R(t)]\rangle = \sum_{\alpha} c_{\alpha}(t)|\alpha;R(t)\rangle, \quad (24)$$

one finds the well-known evolution equations for the coefficients  $c_{\alpha}(t)$ . The time evolution of the density matrix elements in this basis,  $\rho^{\alpha\alpha'}(t) = c_{\alpha}^{*}(t)c_{\alpha'}(t)$ , is given by the first two terms on the r.h.s. of Eq. (23); however, the evolution prescribed by Eq. (23) is different in character: It describes the density matrix evolution at the fixed time-independent phase point  $(R,P)$  due both to quantum transitions and bath evolution. The adiabatic states used to express the density matrix in Eq. (23) are determined at this phase point.

In order to write these equations in compact form we can introduce the (super)operator  $\mathcal{L}_{\alpha\alpha',\beta\beta'}$  defined as

$$\begin{aligned} -i\mathcal{L}_{\alpha\alpha',\beta\beta'} &= -i\omega_{\alpha\alpha'}(R)\delta_{\alpha\beta}\delta_{\alpha'\beta'} + \frac{P}{M} \cdot (\delta_{\alpha\beta}d_{\beta'\alpha'} - d_{\alpha\beta}\delta_{\alpha'\beta'}) \\ &\quad - \frac{P}{M} \cdot \frac{\partial}{\partial R}\delta_{\alpha\beta}\delta_{\alpha'\beta'} - \frac{1}{2}(\delta_{\alpha'\beta'}F_W^{\alpha\beta} + \delta_{\alpha\beta}F_W^{\beta'\alpha'}) \cdot \frac{\partial}{\partial P}. \end{aligned} \quad (25)$$

Using this expression for the mixed quantum-classical Liouville operator, the equation of motion for the density matrix becomes

$$\frac{\partial \rho_W^{\alpha\alpha'}(R,P,t)}{\partial t} = \sum_{\beta\beta'} -i\mathcal{L}_{\alpha\alpha',\beta\beta'}\rho_W^{\beta\beta'}(R,P,t), \quad (26)$$

or, using a formal notation

$$\frac{\partial \rho_W(R,P,t)}{\partial t} = -i\mathcal{L}\rho_W(R,P,t), \quad (27)$$

where  $\rho_W$  is understood to be a matrix and  $\mathcal{L}$  a superoperator.

Of course, one may use any convenient basis to represent the quantum degrees of freedom in Eq. (16). The expression for the mixed quantum-classical Liouville operator in the quantum subsystem basis is given in the Appendix.

Starting with the Heisenberg equation of motion for an operator and repeating the analysis described above one may obtain the evolution equation for the partial Wigner transform of an operator  $\hat{A}$  given in Eq. (6). Again, using a formal notation analogous to that in Eq. (27), in the adiabatic basis the result takes the expected form

$$\frac{dA_W(t)}{dt} = i\mathcal{L}A_W(t), \quad (28)$$

where  $i\mathcal{L}$  is defined in Eq. (25). A similar expression applies for the representation in the subsystem basis. If the operator  $\hat{A}$  is taken to be the Hamiltonian, the commutator and Poisson bracket form of the evolution equation [Eq. (16)] from which Eq. (28) was obtained makes the conservation of the total energy manifest. We now return to the discussion of the formal properties of the  $\mathcal{L}$  operator.

We may rewrite the mixed quantum-classical Liouville operator in a form that makes its structure more apparent. The classical evolution part can be cast into a form involving Hellmann–Feynman evolution and off-diagonal force elements as

$$\begin{aligned} \frac{P}{M} \cdot \frac{\partial}{\partial R}\delta_{\alpha\beta}\delta_{\alpha'\beta'} + \frac{1}{2}(\delta_{\alpha'\beta'}F_W^{\alpha\beta} + \delta_{\alpha\beta}F_W^{\beta'\alpha'}) \cdot \frac{\partial}{\partial P} \\ = iL_{\alpha\alpha'}\delta_{\alpha\beta}\delta_{\alpha'\beta'} + \frac{1}{2}(\delta_{\alpha'\beta'}F_W^{\alpha\beta} + \delta_{\alpha\beta}F_W^{\beta'\alpha'}) \\ - (F_W^{\alpha} + F_W^{\alpha'})\delta_{\alpha\beta}\delta_{\alpha'\beta'} \cdot \frac{\partial}{\partial P}, \end{aligned} \quad (29)$$

The first term on the r.h.s. is a classical evolution operator containing the mean of the Hellmann–Feynman forces for states  $\alpha$  and  $\alpha'$

$$iL_{\alpha\alpha'} = \frac{P}{M} \cdot \frac{\partial}{\partial R} + \frac{1}{2}(F_W^{\alpha} + F_W^{\alpha'}) \cdot \frac{\partial}{\partial P}. \quad (30)$$

We note that if  $\alpha = \alpha'$  then

$$iL_{\alpha\alpha} = \frac{P}{M} \cdot \frac{\partial}{\partial R} + F_W^{\alpha} \cdot \frac{\partial}{\partial P} \equiv iL_{\alpha}, \quad (31)$$

is the standard classical evolution operator with the Hellmann–Feynman force for state  $\alpha$ . The second term on the r.h.s. of Eq. (29) contributes only if  $\alpha \neq \beta$  or  $\alpha' \neq \beta'$  and involves only off-diagonal Hellmann–Feynman forces.

Using Eq. (29), collecting terms in Eq. (25) proportional to the unit operator  $\delta_{\alpha\beta}\delta_{\alpha'\beta'}$  and combining the classical off-diagonal force terms with the terms involving the non-adiabatic coupling matrix elements, we may write the mixed quantum-classical Liouville operator as

$$-i\mathcal{L}_{\alpha\alpha',\beta\beta'} = (-i\omega_{\alpha\alpha'} - iL_{\alpha\alpha'})\delta_{\alpha\beta}\delta_{\alpha'\beta'} + J_{\alpha\alpha',\beta\beta'}, \quad (32)$$

where

$$\begin{aligned} J_{\alpha\alpha',\beta\beta'} = -\frac{P}{M} \cdot d_{\alpha\beta} \left( 1 + \frac{1}{2}S_{\alpha\beta} \cdot \frac{\partial}{\partial P} \right) \delta_{\alpha'\beta'} \\ - \frac{P}{M} \cdot d_{\alpha'\beta'}^* \left( 1 + \frac{1}{2}S_{\alpha'\beta'}^* \cdot \frac{\partial}{\partial P} \right) \delta_{\alpha\beta}, \end{aligned} \quad (33)$$

and the quantity  $S_{\alpha\beta}$  is defined as

$$\begin{aligned} S_{\alpha\beta} = (F_W^{\alpha\beta} - F_W^{\alpha}\delta_{\alpha\beta}) \left( \frac{P}{M} \cdot d_{\alpha\beta} \right)^{-1} \\ = (E_{\alpha} - E_{\beta})d_{\alpha\beta} \left( \frac{P}{M} \cdot d_{\alpha\beta} \right)^{-1}, \end{aligned} \quad (34)$$

where we have used the fact that

$$F_W^{\alpha\beta} = F_W^\alpha \delta_{\alpha\beta} + (E_\alpha - E_\beta) d_{\alpha\beta}. \quad (35)$$

In the discussion that follows we shall show that the second term in Eq. (32) is responsible for the momentum transfer to and from the bath that accompanies quantum transitions. We note that the quantity  $S_{\alpha\beta}$  has appeared in Tully's theory<sup>3</sup> of nonadiabatic surface-hopping dynamics as the momentum jump that the bath particles experience when a quantum transition occurs. We shall make this interpretation explicit below.

#### IV. TRAJECTORY DESCRIPTION OF THE DENSITY MATRIX

The evolution equation for the density matrix can form the basis for an understanding of the nature of mixed quantum-classical dynamics and provide the starting point for approximations to the complete evolution. In this section we consider the structure of the time-dependent mixed quantum-classical density matrix and show how its evolution may be determined from an ensemble of surface-hopping trajectories.

Since  $R$  and  $P$  are independent of time we may formally solve Eq. (27) to obtain

$$\rho_W^{\alpha\alpha'}(R, P, t) = \sum_{\beta\beta'} (e^{-i\mathcal{L}t})_{\alpha\alpha', \beta\beta'} \rho_0^{\beta\beta'}(R, P), \quad (36)$$

where  $\rho_0^{\beta\beta'}(R, P) = \rho_W^{\beta\beta'}(R, P, 0)$ . Using the form of the Liouville operator  $i\mathcal{L}_{\alpha\alpha', \beta\beta'}$  in Eq. (32), we may write the evolution operator as

$$\begin{aligned} (e^{-i\mathcal{L}t})_{\alpha\alpha', \beta\beta'} &= e^{-(i\omega_{\alpha\alpha'} + iL_{\alpha\alpha'})t} \delta_{\alpha\beta} \delta_{\alpha'\beta'} \\ &+ \sum_{\mu\mu'} \int_0^t dt' e^{-(i\omega_{\alpha\alpha'} + iL_{\alpha\alpha'})(t-t')} \\ &\times J_{\alpha\alpha' \mu\mu'}(e^{-i\mathcal{L}t'})_{\mu\mu', \beta\beta'}. \end{aligned} \quad (37)$$

Substitution of this expression into Eq. (36) yields the result

$$\begin{aligned} \rho_W^{\alpha\alpha'}(R, P, t) &= e^{-(i\omega_{\alpha\alpha'} + iL_{\alpha\alpha'})t} \rho_0^{\alpha\alpha'}(R, P) \\ &+ \sum_{\beta\beta'} \int_0^t dt' e^{-(i\omega_{\alpha\alpha'} + iL_{\alpha\alpha'})(t-t')} \\ &\times J_{\alpha\alpha' \beta\beta'} \rho_W^{\beta\beta'}(R, P, t'). \end{aligned} \quad (38)$$

Iterating this formula we obtain the following expression for the density matrix at time  $t$ :

$$\begin{aligned} \rho_W^{\alpha\alpha'}(R, P, t) &= e^{-(i\omega_{\alpha\alpha'} + iL_{\alpha\alpha'})t} \rho_0^{\alpha\alpha'}(R, P) + \sum_{\beta\beta'} \int_0^t dt' e^{-(i\omega_{\alpha\alpha'} + iL_{\alpha\alpha'})(t-t')} J_{\alpha\alpha' \beta\beta'} e^{-(i\omega_{\beta\beta'} + iL_{\beta\beta'})t'} \rho_0^{\beta\beta'}(R, P) \\ &+ \sum_{\beta\beta'} \sum_{\mu\mu'} \int_0^t dt' \int_0^{t'} dt'' e^{-(i\omega_{\alpha\alpha'} + iL_{\alpha\alpha'})(t-t')} J_{\alpha\alpha' \mu\mu'} e^{-(i\omega_{\mu\mu'} + iL_{\mu\mu'})(t'-t'')} J_{\mu\mu', \beta\beta'} e^{-(i\omega_{\beta\beta'} + iL_{\beta\beta'})t''} \rho_0^{\beta\beta'}(R, P) \\ &+ \dots \end{aligned} \quad (39)$$

This equation expresses  $\rho_W^{\alpha\alpha'}(R, P, t)$  in terms of a sequence of trajectory segments whose evolution is determined by  $\exp[-(i\omega_{\alpha\alpha'} + iL_{\alpha\alpha'})t]$  involving the frequencies and mean Hellmann–Feynman forces of the two adiabatic states  $\alpha$  and  $\alpha'$ . These trajectory segments are interspersed with quantum transition and bath momentum change events described by  $J_{\alpha\alpha', \beta\beta'}$ .

The action of  $\exp[-(i\omega_{\alpha\alpha'} + iL_{\alpha\alpha'})(t-t_1)]$  on any function  $f_{\alpha\alpha'}(R, P)$  may be computed explicitly in terms of time-reversed trajectories starting at the phase point  $(R, P)$  at time  $t$  and terminating at another phase point at time  $t=t_1$  ( $t_1 < t$ ). In particular we let

$$\tilde{R}_{t_1, \alpha\alpha'} = e^{-iL_{\alpha\alpha'}(t-t_1)} R, \quad (40)$$

$$\tilde{P}_{t_1, \alpha\alpha'} = e^{-iL_{\alpha\alpha'}(t-t_1)} P,$$

be the time-reversed trajectory that starts at  $(R, P)$  at time  $t$  and ends at  $(\tilde{R}_{t_1, \alpha\alpha'}, \tilde{P}_{t_1, \alpha\alpha'})$  at time  $t=t_1$ . Making repeated use of the analog of the identity in Eq. (37) we find

$$\begin{aligned} &e^{-(i\omega_{\alpha\alpha'} + iL_{\alpha\alpha'})(t-t_1)} f_{\alpha\alpha'}(R, P) \\ &= e^{-i\int_{t_1}^t d\tau \omega_{\alpha\alpha'}(\tilde{R}_{\tau, \alpha\alpha'})} f_{\alpha\alpha'}(\tilde{R}_{t_1, \alpha\alpha'}, \tilde{P}_{t_1, \alpha\alpha'}) \\ &\equiv W_{\alpha\alpha'}(t, t_1) f_{\alpha\alpha'}(\tilde{R}_{t_1, \alpha\alpha'}, \tilde{P}_{t_1, \alpha\alpha'}). \end{aligned} \quad (41)$$

This general expression can be used in the computations below to simplify the evolution in terms of trajectory segments.

#### A. Approximate surface-hopping trajectories

The actions of the operators  $J_{\alpha\alpha', \beta\beta'}$  that determine both the quantum transitions and changes in the bath momentum are difficult to compute in general since one must calculate momentum derivatives of the functions appearing to their right. However, if one assumes that the  $S_{\alpha\beta}$  are sufficiently small then the operators specifying the momentum changes in the bath may be approximated by momentum translation operators

$$\left(1 + \frac{1}{2} S_{\alpha\beta} \cdot \frac{\partial}{\partial P}\right) \approx e^{(1/2) S_{\alpha\beta} \cdot \partial / \partial P}, \quad (42)$$

whose effect on any function of the momentum  $f(P)$  is to increment the momentum by  $\frac{1}{2} S_{\alpha\beta}$

$$e^{(1/2)S_{\alpha\beta} \cdot \partial/(\partial P)} f(P) = f(P + \frac{1}{2}S_{\alpha\beta}). \quad (43)$$

In this momentum-jump approximation we may write

$$J_{\alpha\alpha',\beta\beta'} \approx -\frac{P}{M} \cdot d_{\alpha\beta} e^{(1/2)S_{\alpha\beta} \cdot \partial/(\partial P)} \delta_{\alpha'\beta'} - \frac{P}{M} \cdot d_{\alpha'\beta'}^* e^{(1/2)S_{\alpha'\beta'}^* \cdot \partial/(\partial P)} \delta_{\alpha\beta}. \quad (44)$$

Using this form for  $J_{\alpha\alpha',\beta\beta'}$  the series solution for the density matrix can be represented as sequence of surface-hopping trajectories. We shall now make the trajectory description explicit.

Since each action of the approximate form of  $J_{\alpha\alpha',\beta\beta'}$  induces a quantum transition and a corresponding momentum jump in the bath, we also need a trajectory notation that accounts for these changes. Suppose we have arrived at the phase point  $(\tilde{R}_{t_1,\alpha\alpha'}, \tilde{P}_{t_1,\alpha\alpha'})$  at time  $t_1$  by the evolution specified by Eq. (40). At time  $t_1$  a quantum transition  $\alpha \rightarrow \beta$  occurs, accompanied by a momentum jump of  $S_{\alpha\beta}/2$  in the bath,  $\tilde{P}_{t_1,\alpha\alpha'} \rightarrow \tilde{P}_{t_1,\alpha\alpha'} + S_{\alpha\beta}/2$ , as a result of the action of the first term in Eq. (44). Let the phase point at time  $t_2$

obtained from time-reversed evolution under  $\exp[-iL_{\beta\alpha'}(t_1 - t_2)]$ , given the position and momenta at time  $t_1$ ,  $(\tilde{R}_{t_1,\alpha\alpha'}, \tilde{P}_{t_1,\alpha\alpha'} + S_{\alpha\beta}/2)$ , be denoted by

$$\begin{aligned} \tilde{R}_{t_2,\beta\alpha'}^{t_1,\alpha\alpha'} &= e^{-iL_{\beta\alpha'}(t_1-t_2)} \tilde{R}_{t_1,\alpha\alpha'}, \\ \tilde{P}_{t_2,\beta\alpha'}^{t_1,\alpha\alpha'} &= e^{-iL_{\beta\alpha'}(t_1-t_2)} (\tilde{P}_{t_1,\alpha\alpha'} + S_{\alpha\beta}/2). \end{aligned} \quad (45)$$

Similarly, the second term in Eq. (44) is responsible for the transition  $\alpha' \rightarrow \beta'$  and a bath momentum jump of  $\tilde{P}_{t_1,\alpha\alpha'} \rightarrow \tilde{P}_{t_1,\alpha\alpha'} + S_{\alpha'\beta'}^*/2$ . The state at time  $t_2$  after time-reversed evolution under  $\exp[-iL_{\alpha\beta'}(t_1 - t_2)]$  is

$$\begin{aligned} \tilde{R}_{t_2,\alpha\beta'}^{t_1,\alpha\alpha'} &= e^{-iL_{\alpha\beta'}(t_1-t_2)} \tilde{R}_{t_1,\alpha\alpha'}, \\ \tilde{P}_{t_2,\alpha\beta'}^{t_1,\alpha\alpha'} &= e^{-iL_{\alpha\beta'}(t_1-t_2)} (\tilde{P}_{t_1,\alpha\alpha'} + S_{\alpha'\beta'}^*/2). \end{aligned} \quad (46)$$

Making use of the trajectory notation in Eqs. (40)–(46), along with Eq. (41), we may write Eq. (38) in the momentum-jump approximation as

$$\begin{aligned} \rho_W^{\alpha\alpha'}(R, P, t) &= W_{\alpha\alpha'}(t, 0) \rho_0^{\alpha\alpha'}(\tilde{R}_{0,\alpha\alpha'}, \tilde{P}_{0,\alpha\alpha'}) - \int_0^t dt' W_{\alpha\alpha'}(t, t') \left[ \sum_{\beta} \frac{\tilde{P}_{t_1,\alpha\alpha'}}{M} \cdot d_{\alpha\beta}(\tilde{R}_{t',\alpha\alpha'}) \rho_W^{\beta\alpha'}(\tilde{R}_{t',\alpha\alpha'}, \tilde{P}_{t',\alpha\alpha'} \right. \\ &\quad \left. + \frac{1}{2}S_{\alpha\beta}, t') + \sum_{\beta'} \frac{\tilde{P}_{t_1,\alpha\alpha'}}{M} \cdot d_{\alpha'\beta'}^*(\tilde{R}_{t',\alpha\alpha'}) \rho_W^{\alpha\beta'}(\tilde{R}_{t',\alpha\alpha'}, \tilde{P}_{t',\alpha\alpha'} + \frac{1}{2}S_{\alpha'\beta'}^*, t') \right]. \end{aligned} \quad (47)$$

The solution of this equation may be obtained by iteration and the first two terms of the series are given in terms of trajectory segments as

$$\begin{aligned} \rho_W^{\alpha\alpha'}(R, P, t) &= W_{\alpha\alpha'}(t, 0) \rho_0^{\alpha\alpha'}(\tilde{R}_{0,\alpha\alpha'}, \tilde{P}_{0,\alpha\alpha'}) - \int_0^t dt' W_{\alpha\alpha'}(t, t') \left[ \sum_{\beta} \frac{\tilde{P}_{t_1,\alpha\alpha'}}{M} \cdot d_{\alpha\beta}(\tilde{R}_{t',\alpha\alpha'}) W_{\beta\alpha'}^{\alpha\alpha'}(t', 0) \right. \\ &\quad \left. \times \rho_0^{\beta\alpha'}(\tilde{R}_{0,\beta\alpha'}, \tilde{P}_{0,\beta\alpha'}) + \sum_{\beta'} \frac{\tilde{P}_{t_1,\alpha\alpha'}}{M} \cdot d_{\alpha'\beta'}^*(\tilde{R}_{t',\alpha\alpha'}) W_{\alpha\beta'}^{\alpha\alpha'}(t', 0) \rho_0^{\alpha\beta'}(\tilde{R}_{0,\alpha\beta'}, \tilde{P}_{0,\alpha\beta'}) \right] + \dots \end{aligned} \quad (48)$$

Here phase factors like  $W_{\beta\beta'}^{\alpha\alpha'}(t_1, t_2)$  have a definition analogous to Eq. (41) except that the coordinate at time  $t_1$  is obtained from evolution under the  $(\alpha\alpha')$  Hellmann–Feynman force

$$W_{\beta\beta'}^{\alpha\alpha'}(t_1, t_2) = e^{-i \int_{t_1}^{t_2} d\tau \omega_{\beta\beta'}(\tilde{R}_{\tau,\beta\beta'}^{\alpha\alpha'})}. \quad (49)$$

Subject to the momentum-jump approximation (44), Eq. (48) provides a full description of the time-evolved density matrix in terms of an integral equation containing easily computed classical trajectories. Integral equations like Eq. (48) which involve the sum over an infinite number of iterations can be conveniently solved by hybrid molecular dynamics (MD)—“grand canonical” Monte Carlo (MC) methods. The first step in such a solution is to rewrite Eq. (48) as a probabilistic expression giving the density matrix at time  $t$

as an expected value over a series of Bernoulli extractions (fixing the order of the iteration to be considered). Then one samples by an ad hoc probabilistic procedure the quantum transitions and the times at which they occur while the trajectory segments appearing in Eq. (48) are simply computed by using standard MD techniques. The quantities appearing in the integral equation are in general not positive definite; however, Filinov<sup>14</sup> has shown how to extract positive definite expressions from those kernels. For example, in the case of the quantum transitions, the probabilistic weights are proportional to  $|(P/M) \cdot d_{\alpha\beta}(R)|$ . The entire procedure has been clearly reconstructed in Bonella *et al.*<sup>15</sup>

## B. Exact surface-hopping trajectories

At the cost of introducing singular kernels in the integral equation one may give an exact representation of the solution

of the density matrix in terms of surface-hopping trajectories. To do this we make use of the following identity for the transition terms  $J_{\alpha\alpha',\beta\beta'}(R,P)$ :

$$\begin{aligned} & \sum_{\beta\beta'} J_{\alpha\alpha',\beta\beta'}(R,P) f_{\beta\beta'}(P) \\ &= \int dS \left[ - \sum_{\beta} \frac{P}{M} \cdot d_{\alpha\beta}(R) \left( 1 + \frac{1}{2} S_{\alpha\beta} \cdot \frac{\partial}{\partial S} \right) \right. \\ & \quad \times \delta(S) f_{\beta\alpha'}(P-S) - \sum_{\beta'} \frac{P}{M} \cdot d_{\alpha'\beta'}^*(R) \\ & \quad \left. \times \left( 1 + \frac{1}{2} S_{\alpha'\beta'}^* \cdot \frac{\partial}{\partial S} \right) \delta(S) f_{\alpha\beta'}(P-S) \right], \end{aligned} \quad (50)$$

where  $f_{\alpha\alpha'}(P)$  is an arbitrary function. If we let

$$\mathcal{G}_{\alpha\beta}(R,P,S) = - \frac{P}{M} \cdot d_{\alpha\beta}(R) \left( 1 + \frac{1}{2} S_{\alpha\beta} \cdot \frac{\partial}{\partial S} \right) \delta(S), \quad (51)$$

$$\mathcal{G}_{\alpha'\beta'}^*(R,P,S) = - \frac{P}{M} \cdot d_{\alpha'\beta'}^*(R) \left( 1 + \frac{1}{2} S_{\alpha'\beta'}^* \cdot \frac{\partial}{\partial S} \right) \delta(S), \quad (52)$$

we may write Eq. (38) for the density matrix elements as

$$\begin{aligned} \rho_W^{\alpha\alpha'}(R,P,t) &= W_{\alpha\alpha'}(t,0) \rho_0^{\alpha\alpha'}(\tilde{R}_{0,\alpha\alpha'}, \tilde{P}_{0,\alpha\alpha'}) + \int_0^t dt' W_{\alpha\alpha'}(t,t') \int dS \left[ \sum_{\beta} \mathcal{G}_{\alpha\beta}(\tilde{R}_{t',\alpha\alpha'}, \tilde{P}_{t',\alpha\alpha'}, S) \right. \\ & \quad \left. \times \rho_W^{\beta\alpha'}(\tilde{R}_{t',\alpha\alpha'}, \tilde{P}_{t',\alpha\alpha'} - S, t') + \sum_{\beta'} \mathcal{G}_{\alpha'\beta'}^*(\tilde{R}_{t',\alpha\alpha'}, \tilde{P}_{t',\alpha\alpha'}, S) \rho_W^{\alpha\beta'}(\tilde{R}_{t',\alpha\alpha'}, \tilde{P}_{t',\alpha\alpha'} - S, t') \right]. \end{aligned} \quad (53)$$

This equation may be solved by iteration and expressed in terms of surface-hopping trajectories without approximation. To do this one introduces a trajectory definition analogous to that in Eq. (45)

$$\begin{aligned} \tilde{R}_{t_2,\beta\alpha'}^{t_1,\alpha\alpha'}(S) &= e^{-iL_{\beta\alpha'}(t_1-t_2)} \tilde{R}_{t_1,\alpha\alpha'}, \\ \tilde{P}_{t_2,\beta\alpha'}^{t_1,\alpha\alpha'}(S) &= e^{-iL_{\beta\alpha'}(t_1-t_2)} (\tilde{P}_{t_1,\alpha\alpha'} - S), \end{aligned} \quad (54)$$

which differs only in the nature of the momentum jump. The analog of Eq. (46) follows from an obvious change in notation. The iterated solution can be expressed again in these trajectory segments following the procedure outlined above. In this exact representation in surface-hopping trajectories the probabilities of quantum transitions and magnitudes of the momentum jumps must be sampled from suitable distributions determined by the kernels  $\mathcal{G}_{\alpha\beta}(R,P,S)$ , analogous to that discussed earlier for the approximate surface-hopping trajectories. The main difference is that the momentum jump  $S$  must also be sampled using a weight that depends on  $S_{\alpha\beta}/2$  rather than being precisely prescribed.<sup>16</sup>

## V. PAULI MASTER EQUATION

We now present a derivation of a generalized version of the Pauli master equation<sup>17-19</sup> for a mixed quantum-classical system. The generalized master equation provides a means to study the time evolution of the populations of the quantum states which is of interest in many applications. Thus, we focus our attention on the diagonal elements of the density matrix and derive an evolution equation for these diagonal

elements from the mixed quantum-classical Liouville equation [Eq. (27)]. This derivation will illustrate several other aspects of surface-hopping dynamics.

### A. General formulation

The Liouville equation for the mixed quantum-classical system describes the evolution of both the diagonal and off-diagonal elements of the density matrix. By making use of a projection operator that projects the dynamics onto the diagonal elements (populations) of the density matrix, we may derive a closed equation for the evolution of these populations at the expense of introducing memory into the evolution equation. The resulting equation for the evolution of the diagonal elements has the form of a generalized master equation where the transition matrix elements are replaced by a memory kernel.

To carry out this analysis we define the projection operator

$$\mathcal{P}_{\alpha\alpha',\beta\beta'} = \delta_{\alpha\alpha'} \delta_{\alpha\beta} \delta_{\alpha'\beta'}, \quad (55)$$

and its complement

$$\mathcal{Q}_{\alpha\alpha',\beta\beta'} = (1 - \delta_{\alpha\alpha'}) \delta_{\alpha\beta} \delta_{\alpha'\beta'}. \quad (56)$$

The superoperator  $\mathcal{P}$  projects any operator onto its diagonal part

$$(\mathcal{P}f)_{\alpha\alpha'} = \delta_{\alpha\alpha'} f_{\alpha\alpha}. \quad (57)$$

Now one is in a position to carry out the projection operator algebra<sup>19</sup> needed to reduce the mixed quantum-

classical Liouville equation for  $\rho_W$  to a generalized master equation. Acting with  $\mathcal{P}$  and  $\mathcal{Q}$  on Eq. (27) and formally solving for  $\mathcal{P}\rho_W$ , we obtain

$$\frac{\partial \mathcal{P}\rho_W(t)}{\partial t} = -i\mathcal{P}\mathcal{L}\mathcal{P}\rho_W(t) + \int_0^t dt' i\mathcal{P}\mathcal{L}e^{-i\mathcal{Q}\mathcal{L}\mathcal{Q}(t-t')} \times i\mathcal{Q}\mathcal{L}\mathcal{P}\rho_W(t') - i\mathcal{P}\mathcal{L}e^{-i\mathcal{Q}\mathcal{L}\mathcal{Q}t}\mathcal{Q}\rho_W(0). \quad (58)$$

The last term is an initial condition term which will vanish if the initial distribution is diagonal. For simplicity we shall assume that this is the case but if nondiagonal initial states are of interest it is a simple matter to retain these contributions in the development given below.

Here our focus will be on the evolution of the diagonal elements of the density matrix given a diagonal initial distribution. Of course, nonadiabatic coupling among the different quantum states will not preserve the initial diagonal distribution and it is the nature of the subsequent dynamics that we shall investigate.

Using the explicit expressions for  $\mathcal{P}$  and  $\mathcal{L}$  this equation may be written in the form of a generalized Pauli master equation

$$\frac{\partial \rho_W^\alpha(t)}{\partial t} = -iL_\alpha \rho_W^\alpha(t) + \int_0^t dt' \sum_\beta \mathcal{M}_{\alpha\beta}(t-t') \rho_W^\beta(t'), \quad (59)$$

where  $\rho_W^\alpha \equiv \rho_W^{\alpha\alpha}$  are the diagonal elements of the density matrix. The operator  $\mathcal{M}$  is defined by

$$\mathcal{M}_{\alpha\beta}(t) = \sum_{\nu\nu'} \sum_{\mu\mu'} J_{\alpha,\nu\nu'}(e^{-i\mathcal{Q}\mathcal{L}\mathcal{Q}t})_{\nu\nu',\mu\mu'} J_{\mu\mu',\beta}. \quad (60)$$

In this equation  $J_{\alpha,\nu\nu'} \equiv J_{\alpha\alpha,\nu\nu'}$  and  $J_{\mu\mu',\beta} \equiv J_{\mu\mu',\beta\beta}$ .

The generalized master equation [Eq. (59)] makes explicit the evolution through the standard Hamilton's equations of motion with the Hellmann–Feynman force  $F_W^\alpha$  through  $iL_\alpha$ . Changes in the quantum state are governed by the time-dependent transition operator  $\mathcal{M}_{\alpha\beta}(t)$  whose evolution is determined by the projected part of the Liouville operator. Thus, all of the off-diagonal evolution terms are separated from the diagonal evolution terms.

We may integrate the generalized master equation [Eq. (59)] formally to obtain

$$\rho_W^\alpha(R, P, t) = e^{-iL_\alpha t} \rho_0^\alpha(R, P) + \sum_\beta \int_0^t dt_1 \int_0^{t_1} dt' e^{-iL_\alpha(t-t_1)} \times \mathcal{M}_{\alpha\beta}(t_1-t') \rho_W^\beta(R, P, t'). \quad (61)$$

Equation (61) may now form the starting point for exact or approximate representations in terms of surface-hopping trajectories.

## B. Trajectory description

The evolution of  $\mathcal{M}_{\alpha\beta}(t)$  is given by the projected evolution operator

$$U_{\nu\nu',\mu\mu'}^P(t) = (e^{-i\mathcal{Q}\mathcal{L}\mathcal{Q}t})_{\nu\nu',\mu\mu'}, \quad (62)$$

which acts only on off-diagonal operators with  $\nu \neq \nu'$  and  $\mu \neq \mu'$  and thus determines the coherent evolution of the coupled quantum states. Since  $i\mathcal{Q}\mathcal{L}\mathcal{Q}$  contains the transition operators  $J_{\nu\nu',\mu\mu'}$ , again with  $\nu \neq \nu'$  and  $\mu \neq \mu'$ , the evolution specified by Eq. (62) includes all possible infinite sequences of quantum transitions starting with the coupled pair of states  $(\mu\mu')$  and ending with the coupled pair  $(\nu\nu')$ .

Although the computation of such evolution is complicated and requires the methods described in the previous section, we may give a compact form for the evolution in terms of trajectory segments assuming such evolution can be carried out. We now give an explicit representation in terms of surface-hopping trajectories using the momentum-jump approximation, Eq. (44). An exact representation in surface-hopping trajectories can also be given using the results in Sec. IV B.

Substituting the explicit expression for the memory kernel (60) (using the momentum-jump approximation for the partial derivatives in  $J$ ) into the integrated form of the generalized master equation [Eq. (61)] yields the result

$$\begin{aligned} \rho_W^\alpha(R, P, t) = & e^{-iL_\alpha t} \rho_0^\alpha(R, P) + \sum_\beta \int_0^t dt_1 \int_0^{t_1} dt' e^{-iL_\alpha(t-t_1)} \left[ \sum_{\nu,\mu} \left( \frac{P}{M} \cdot d_{\alpha\nu}(R) e^{(1/2) S_{\alpha\nu} \cdot \nabla_P} \right) U_{\nu\alpha,\mu\beta}^P(t_1-t') \right. \\ & \times \left( \frac{P}{M} \cdot d_{\mu\beta}(R) e^{(1/2) S_{\mu\beta} \cdot \nabla_P} \right) + \sum_{\nu',\mu'} \left( \frac{P}{M} \cdot d_{\alpha\nu'}^*(R) e^{(1/2) S_{\alpha\nu'}^* \cdot \nabla_P} \right) U_{\alpha\nu',\beta\mu'}^P(t_1-t') \left( \frac{P}{M} \cdot d_{\mu'\beta}^*(R) e^{(1/2) S_{\mu'\beta}^* \cdot \nabla_P} \right) \\ & + \sum_{\nu,\mu'} \left( \frac{P}{M} \cdot d_{\alpha\nu}(R) e^{(1/2) S_{\alpha\nu} \cdot \nabla_P} \right) U_{\nu\alpha,\beta\mu'}^P(t_1-t') \left( \frac{P}{M} \cdot d_{\mu'\beta}^*(R) e^{(1/2) S_{\mu'\beta}^* \cdot \nabla_P} \right) \\ & \left. + \sum_{\nu',\mu} \left( \frac{P}{M} \cdot d_{\alpha\nu'}^*(R) e^{(1/2) S_{\alpha\nu'}^* \cdot \nabla_P} \right) U_{\alpha\nu',\mu\beta}^P(t_1-t') \left( \frac{P}{M} \cdot d_{\mu\beta}(R) e^{(1/2) S_{\mu\beta} \cdot \nabla_P} \right) \right] \rho_W^\beta(R, P, t'). \quad (63) \end{aligned}$$

The action of the projected mixed quantum-classical evolution operator on any function  $f_{\mu\mu'}(R, P)$  may be evaluated using the analog of the identity in Eq. (37)

$$\sum_{\mu\mu'} U_{\nu\nu',\mu\mu'}^P(t) f_{\mu\mu'}(R,P) = f_{\nu\nu'}^P(R,P,t) = W_{\nu\nu'}(t,0) f_{\nu\nu'}(\tilde{R}_{0,\nu\nu'}, \tilde{P}_{0,\nu\nu'}) + \sum_{\mu\mu'} \int_0^t dt' W_{\nu\nu'}(t,t') J_{\nu\nu',\mu\mu'}(\tilde{R}_{t',\nu\nu'}, \tilde{P}_{t',\nu\nu'}) f_{\mu\mu'}^P(\tilde{R}_{t',\nu\nu'}, \tilde{P}_{t',\nu\nu'}, t'). \tag{64}$$

Substitution of Eq. (64) into Eq. (63) followed by iteration will generate the ensemble of surface-hopping trajectories that yield the solution for the diagonal elements of the density matrix in this approximation. The surface-hopping trajectories consist of a concatenation of segments involving classical evolution on single adiabatic potential energy surfaces, and ‘‘coherent’’ evolution segments in the off-diagonal subspace.

Although the evolution equations for the density matrix conserve the total energy of the system by construction, it is interesting to examine energy conservation for the realizations of the mixed quantum-classical dynamics that are used to construct the full solution. As an illustration we consider the structure of the first-order terms obtained by iteration of Eq. (63). The first two terms in the iterated solution are

$$\begin{aligned} \rho_W^\alpha(R,P,t) = & \rho_0^\alpha(\tilde{R}_{0,\alpha}, \tilde{P}_{0,\alpha}) + \int_0^t dt_1 \int_0^{t_1} dt' \left[ \sum_\nu \left( \frac{\tilde{P}_{t_1,\alpha}}{M} \cdot d_{\alpha\nu}(\tilde{R}_{t_1,\alpha}) \right) W_{\nu\alpha}(t_1-t') \left( \frac{\tilde{P}_{t',\nu\alpha}}{M} \cdot d_{\nu\alpha}(\tilde{R}_{t',\nu\alpha}^{t_1,\alpha}) \right) \rho_0^\alpha(\tilde{R}_{0,\alpha}^{t',\nu\alpha}, \tilde{P}_{0,\alpha}^{t',\nu\alpha}) \right. \\ & + \sum_{\nu'} \left( \frac{\tilde{P}_{t_1,\alpha}}{M} \cdot d_{\alpha\nu'}^*(\tilde{R}_{t_1,\alpha}) \right) W_{\alpha\nu'}(t_1-t') \left( \frac{\tilde{P}_{t',\alpha\nu'}}{M} \cdot d_{\nu'\alpha}^*(\tilde{R}_{t',\alpha\nu'}^{t_1,\alpha}) \right) \rho_0^\alpha(\tilde{R}_{0,\alpha}^{t',\alpha\nu'}, \tilde{P}_{0,\alpha}^{t',\alpha\nu'}) \\ & + \left( \frac{\tilde{P}_{t_1,\alpha}}{M} \cdot d_{\alpha\beta}(\tilde{R}_{t_1,\alpha}) \right) W_{\beta\alpha}(t_1-t') \left( \frac{\tilde{P}_{t',\beta\alpha}}{M} \cdot d_{\alpha\beta}^*(\tilde{R}_{t',\beta\alpha}^{t_1,\alpha}) \right) \rho_0^\beta(\tilde{R}_{0,\beta}^{t',\beta\alpha}, \tilde{P}_{0,\beta}^{t',\beta\alpha}) + \left( \frac{\tilde{P}_{t_1,\alpha}}{M} \cdot d_{\alpha\beta}^*(\tilde{R}_{t_1,\alpha}) \right) \\ & \left. \times W_{\alpha\beta}(t_1-t') \left( \frac{\tilde{P}_{t',\alpha\beta}}{M} \cdot d_{\alpha\beta}(\tilde{R}_{t',\alpha\beta}^{t_1,\alpha}) \right) \rho_0^\beta(\tilde{R}_{0,\beta}^{t',\alpha\beta}, \tilde{P}_{0,\beta}^{t',\alpha\beta}) \right] + \dots \end{aligned} \tag{65}$$

Considering the integrand of the double integral on the right of Eq. (65), the first two terms in the square bracket represent processes where the system is in the diagonal state  $\alpha$  at time  $t$  and makes a transition to some intermediate state  $\nu$  (or  $\nu'$ ); the states  $\alpha$  and  $\nu$  (or  $\nu'$ ) evolve coherently until a transition from  $\nu$  (or  $\nu'$ ) to the diagonal state  $\alpha$  occurs. Focusing on the first such contribution, at time  $t_1 - \epsilon$ , just *prior* to the first momentum jump, the adiabatic energy is  $E_\alpha(\tilde{R}_{t_1,\alpha})$  and the bath has phase space coordinates  $(\tilde{R}_{t_1,\alpha}, \tilde{P}_{t_1,\alpha})$  so that the total energy is  $\tilde{P}_{t_1,\alpha}^2/2M + E_\alpha(\tilde{R}_{t_1,\alpha})$ .

At time  $t' + \epsilon$ , just *after* the second momentum jump, the adiabatic energy is  $E_\alpha(\tilde{R}_{t',\nu\alpha}^{t_1,\alpha})$ , the bath coordinates are  $(\tilde{R}_{t',\nu\alpha}^{t_1,\alpha}, \tilde{P}_{t',\nu\alpha}^{t_1,\alpha} + \frac{1}{2}S_{\nu\alpha})$  and the total energy is

$$\begin{aligned} & \frac{(\tilde{P}_{t',\nu\alpha}^{t_1,\alpha} + (1/2)S_{\nu\alpha})^2}{2M} + E_\alpha(\tilde{R}_{t',\nu\alpha}^{t_1,\alpha}) \\ & = \frac{(\tilde{P}_{t',\nu\alpha}^{t_1,\alpha})^2}{2M} + \frac{1}{2}(E_\nu(\tilde{R}_{t',\nu\alpha}^{t_1,\alpha}) + E_\alpha(\tilde{R}_{t',\nu\alpha}^{t_1,\alpha})) + \mathcal{O}(S_{\nu\alpha}^2), \end{aligned}$$

where we have used the definition of the momentum jump in Eq. (34). The quantity on the right is conserved under action of  $\exp[iL_{\nu\alpha}(t_1-t')]$  [cf. Eq. (30)] and its value at  $t = t_1 + \epsilon$  is

$$\begin{aligned} & \frac{(\tilde{P}_{t_1,\alpha} + (1/2)S_{\alpha\nu})^2}{2M} + \frac{1}{2}(E_\nu(\tilde{R}_{t_1,\alpha}) + E_\alpha(\tilde{R}_{t_1,\alpha})) \\ & = \frac{(\tilde{P}_{t_1,\alpha})^2}{2M} + E_\alpha(\tilde{R}_{t_1,\alpha}) + \mathcal{O}(S_{\alpha\nu}^2). \end{aligned}$$

We see that energy is conserved to  $\mathcal{O}(S_{\nu\alpha}^2)$  across the coherent evolution segment, including the momentum jumps at both ends, i.e., to the same order of validity as the momentum-jump approximation.

The last two terms in the square bracket in Eq. (65) represent processes where the system is in the diagonal state  $\alpha$  at time  $t$  and ends in the diagonal state  $\beta \neq \alpha$  at time 0. Just prior to the first momentum jump at  $t_1 - \epsilon$  the adiabatic energy is  $E_\alpha(\tilde{R}_{t_1,\alpha})$ , the bath has phase space coordinates  $(\tilde{R}_{t_1,\alpha}, \tilde{P}_{t_1,\alpha})$  and the total energy is  $\tilde{P}_{t_1,\alpha}^2/2M + E_\alpha(\tilde{R}_{t_1,\alpha})$  as in the first case.

At time  $t' + \epsilon$  the adiabatic energy is  $E_\beta(\tilde{R}_{t',\beta\alpha}^{t_1,\alpha})$ , the bath coordinates are  $(\tilde{R}_{t',\beta\alpha}^{t_1,\alpha}, \tilde{P}_{t',\beta\alpha}^{t_1,\alpha} + \frac{1}{2}S_{\alpha\beta}^*)$  and the total energy is

$$\begin{aligned} & \frac{(\tilde{P}_{t',\beta\alpha}^{t_1,\alpha} + (1/2)S_{\alpha\beta}^*)^2}{2M} + E_\beta(\tilde{R}_{t',\beta\alpha}^{t_1,\alpha}) \\ & = \frac{(\tilde{P}_{t',\beta\alpha}^{t_1,\alpha})^2}{2M} + \frac{1}{2}(E_\beta(\tilde{R}_{t',\beta\alpha}^{t_1,\alpha}) + E_\alpha(\tilde{R}_{t',\beta\alpha}^{t_1,\alpha})) + \mathcal{O}(S_{\alpha\beta}^{*2}). \end{aligned}$$

The quantity on the right is conserved under action of  $\exp[-iL_{\beta\alpha}(t_1-t')]$  and its value at  $t=t_1+\epsilon$  is

$$\begin{aligned} & \frac{(\tilde{P}_{t_1,\alpha} + (1/2)S_{\alpha\beta})^2}{2M} + \frac{1}{2}(E_{\beta}(\tilde{R}_{t_1,\alpha}) + E_{\alpha}(\tilde{R}_{t_1,\alpha})) \\ &= \frac{(\tilde{P}_{t_1,\alpha})^2}{2M} + E_{\alpha}(\tilde{R}_{t_1,\alpha}) + \mathcal{O}(S_{\alpha\beta}^2). \end{aligned}$$

Once again energy is conserved only to  $\mathcal{O}(S_{\alpha\beta}^2)$ .

If one considers the exact surface-hopping algorithm described in Sec. IV B, the ensemble energy is conserved since no approximation to the evolution equation has been made; however, the structure of the realizations of the dynamics that contribute to the full solution remains to be analyzed.

As discussed above, the evolution of  $\mathcal{M}_{\alpha\beta}(t)$  is determined by the projected evolution operator that acts only on off-diagonal operators that reflect the coherence in the quantum system. The motions of the classical degrees of freedom and quantum transitions in this off-diagonal subspace will tend to damp the coherent quantum evolution of the coupled quantum states. Thus, one may use Eq. (61) as the starting point for decoherence approximations to the full memory kernel in order to circumvent the full computation in the off-diagonal space. Such decoherence in the context of surface-hopping dynamics has been discussed by Bittner and Rossky<sup>20</sup> and may find application in the present context.

## VI. CONCLUSIONS

The formulation presented here clarifies some aspects of the nature of mixed quantum-classical dynamics. The Liouville equation for the density matrix derived in the limit of  $\mu \ll 1$  explicitly describes the nature of the coupling between the quantum subsystem and classical bath. It specifies the evolution of both the quantum and classical degrees of freedom.

The representation of the solution for the density matrix in an ensemble of surface-hopping trajectories provides a precise, and in general exact, method for its computation using hybrid MD-MC techniques. The calculations also indicate how existing approximations, such as the momentum-jump approximation, may be incorporated into the theory to simplify the computations.

The generalized Pauli master equation specifies the evolution of the diagonal elements of the density matrix and the time dependence of the memory kernel in this equation is determined by the coherent evolution of the off-diagonal parts of the density matrix. The series solution of this equation yields a description of the dynamics in terms of surface hopping classical trajectories involving both incoherent and coherent segments separated by momentum jumps in the classical subsystem.

The formalism presented in this paper provides a framework for the study of nonadiabatic dynamics in mixed quantum-classical systems and may be extended to directly compute correlation functions of interest rather than the full density matrix.

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## APPENDIX: PROJECTION ONTO SUBSYSTEM BASIS

The adiabatic states depend on the bath coordinates. In some circumstances it is convenient to consider other bases that do not depend on these coordinates. For example, instead of projecting onto an adiabatic basis, we may also project onto the eigenstates of the subsystem Hamiltonian. Writing the potential energy in terms of its contributions from the subsystem, bath and interactions between the subsystem and bath, the Hamiltonian reads

$$\hat{H} = \frac{\hat{P}^2}{2M} + \frac{\hat{p}^2}{2m} + \hat{V}_s(\hat{q}) + \hat{V}_b(\hat{Q}) + \hat{V}_c(\hat{q}, \hat{Q}). \quad (\text{A1})$$

The eigenstates  $|\alpha\rangle$  of the subsystem Hamiltonian

$$\hat{h}_s = \frac{\hat{p}^2}{2m} + \hat{V}_s(\hat{q}), \quad (\text{A2})$$

$$\hat{h}_s|\alpha\rangle = \epsilon_{\alpha}|\alpha\rangle, \quad (\text{A3})$$

are independent of  $R$ .

Projecting Eq. (16) onto this basis we obtain

$$\begin{aligned} & \frac{\partial \rho_W^{\alpha\alpha'}(R, P, t)}{\partial t} \\ &= -i\tilde{\omega}_{\alpha\alpha'}\rho_W^{\alpha\alpha'}(R, P, t) \\ &+ \frac{i}{\hbar} \sum_{\alpha''} (\rho_W^{\alpha\alpha''} V_c^{\alpha''\alpha'} - V_c^{\alpha\alpha''} \rho_W^{\alpha''\alpha'}) \\ &- \left( \frac{P}{M} \frac{\partial}{\partial R} + F_b(R) \frac{\partial}{\partial P} \right) \rho_W^{\alpha\alpha'} \\ &+ \frac{1}{2} \sum_{\alpha''} \left( \frac{\partial V_c^{\alpha\alpha''}}{\partial R} \frac{\partial \rho_W^{\alpha''\alpha'}}{\partial P} + \frac{\partial \rho_W^{\alpha\alpha''}}{\partial P} \frac{\partial V_c^{\alpha''\alpha'}}{\partial R} \right), \quad (\text{A4}) \end{aligned}$$

where  $\tilde{\omega}_{\alpha\alpha'} = (\epsilon_{\alpha} - \epsilon_{\alpha'})/\hbar$  and  $V_c^{\alpha\alpha'} = \langle \alpha | \hat{V}_c | \alpha' \rangle$ . We may also write this in terms of a Liouville-type superoperator as

$$\frac{\partial \rho_W(R, P, t)}{\partial t} = -i\tilde{\mathcal{L}}\rho_W(R, P, t), \quad (\text{A5})$$

where

$$\begin{aligned} -i\tilde{\mathcal{L}}_{\alpha\alpha',\beta\beta'} &= -i\tilde{\omega}_{\alpha\alpha'}\delta_{\alpha\beta}\delta_{\alpha'\beta'} + \frac{i}{\hbar} (\delta_{\alpha\beta} V_c^{\beta\alpha'} - V_c^{\alpha\beta} \delta_{\alpha'\beta'}) \\ &- \left( \frac{P}{M} \frac{\partial}{\partial R} + F_b(R) \frac{\partial}{\partial P} \right) \delta_{\alpha\beta} \delta_{\alpha'\beta'} \\ &+ \frac{1}{2} \left( \delta_{\alpha'\beta'} \frac{\partial V_c^{\alpha\beta}}{\partial R} + \delta_{\alpha\beta} \frac{\partial V_c^{\beta\alpha'}}{\partial R} \right) \frac{\partial}{\partial P}, \quad (\text{A6}) \end{aligned}$$

and  $F_b(R) = -\partial V_b / \partial R$  is the bath force.

If these equations are specialized to a two-level system the results are the same as those obtained in Ref. 9 by replacing commutators by Poisson brackets and anti-commutators by products of operators.

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