

# PROGRESS IN THE THEORY OF MIXED QUANTUM-CLASSICAL DYNAMICS

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■ **Abstract** Quantum-classical Liouville dynamics can be used to study the properties of open quantum systems that are coupled to bath or environmental degrees of freedom whose dynamics can be approximated by classical equations of motion. In contrast to many open quantum system approaches, quantum-classical dynamics provides a detailed description of the bath molecules. Such a description is especially appropriate for the study of quantum rate processes, such as proton and electron transport, where the detailed dynamics of the bath has a strong influence on the quantum rate. The quantum-classical Liouville equation can also serve as a starting point for the derivation of reduced descriptions where all or some of the bath degrees of freedom are projected out. Quantum-classical Liouville dynamics can be simulated in terms of an ensemble of surface-hopping trajectories whose character differs from that in other surface-hopping schemes. The results of studies of proton transfer in condensed phase and reactive dynamics in a dissipative environment are presented to illustrate applications of the formalism.

## 1. INTRODUCTION

Chemical and biological systems are often large and have a complex structure so that the investigation of their dynamical properties poses challenges for theory and simulation. A complete description of their dynamics must be based on quantum-mechanical time evolution equations, such as the Schrödinger equation for the wave function or the quantum-mechanical Liouville equation for the density matrix,  $\hat{\rho}(t)$ ,

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

Here  $\hat{H}$  is the Hamiltonian and the brackets signify the commutator. The construction of the solutions of either of these equations for a large many-body system is an intractable problem.

To circumvent this problem, it is often possible to focus attention on some relevant portion of a large quantum-mechanical system (quantum subsystem) that interacts with the remainder of the system (environment or bath). The subsystem of interest is then an open quantum system and the challenge is to construct evolution equations for quantum systems that communicate with the environment. This has been a long-standing problem, and there is a large literature dealing with descriptions of open quantum systems (1, 2).

Many treatments of open quantum systems are based on evolution equations for the quantum subsystem density matrix where the explicit dependence on bath degrees of freedom is eliminated. Examples of such equations include the Lindblad equation (3–5) and quantum master equations (6, 7). Although formulations of this type have a considerable domain of applicability, they are not appropriate for some applications: for example, proton or electron transfer in a condensed phase environment. The motion of a proton or electron must be treated quantum mechanically, and the transfer reaction depends strongly on the detailed dynamics of neighboring solvent molecules. Consequently, approaches that do not fully account for specific aspects of solvent dynamics may fail to capture important effects in these transfer reactions. If large numbers of neighboring solvent molecules are treated quantum mechanically, we are again faced with a difficult quantum-dynamical problem.

Here I adopt a different point of view and treat the environmental degrees of freedom explicitly but using classical mechanics. A description of this type is appropriate, for example, if the characteristic masses of the particles constituting the environment are much heavier than those of the quantum subsystem. This is the case for the proton- or electron-transfer processes mentioned above. Such considerations have motivated the construction of schemes to carry out mixed quantum-classical dynamics. Adiabatic dynamics, where the evolution of the classical variables occurs on a single adiabatic surface determined from the solution of the Schrödinger equation for the quantum subsystem in the field of the classical bath, has been used to study proton-transfer reactions (8–11). Mean-field methods and surface-hopping schemes that account for nonadiabatic transitions among quantum states induced by coupling to the classical environment are also in wide use (10, 12, 13). Other approaches to studying quantum dynamics that do not fall into the category of quantum-classical dynamics but employ other approximations to the quantum equations of motion include forward-backward semiclassical dynamics (14), the initial value representation (15), the mapping Hamiltonian (16), and mode coupling methods (17), to name a few such techniques.

Below I describe how it is possible to formulate the problem of nonadiabatic dynamics in terms of a quantum-classical Liouville equation, which has a status similar to that of the quantum Liouville equation for the entire system (18). Therefore, a very detailed description of how the quantum degrees of freedom interact with the environment is possible. In some circumstances, it is useful to represent a portion of the classical environment using a stochastic description, and I also consider how such a reduction of the quantum-classical evolution equations can be achieved. In analogy with the treatments of open quantum systems, one may

also consider the projection of the quantum-classical Liouville equation onto the quantum subspace. Because the coupling terms between the quantum subsystem and classical bath are specified in terms of classical bath correlation functions, these equations are useful in applications where details of the bath dynamics are unimportant. I show how the quantum-classical Liouville equation can be derived and how its solution can be constructed in terms of an ensemble of surface-hopping trajectories. I then consider applications to nonadiabatic chemical reactions, including proton-transfer reactions in the condensed phase.

## 2. QUANTUM-CLASSICAL LIOUVILLE EQUATION

We suppose that the system can be partitioned into two subsystems: the quantum subsystem of interest and the bath or environment. We are now faced with the task of reducing the full quantum-mechanical description of such a composite system to a mixed quantum-classical description where the bath dynamics is treated classically but the quantum character of the subsystem of interest is retained. A mixed quantum-classical description should be applicable if the subsystem is composed of light particles whereas the bath contains heavy particles.

It is difficult to combine the fundamentally different descriptions of nature provided by quantum and classical mechanics. A quantum system is described in terms of Hilbert space operators whereas a classical system is described in terms of phase-space positions and momenta. Path integral methods have been used to investigate this limit (19, 20). The Wigner representation of quantum mechanics provides a way to introduce a phase-space-like description of a quantum-mechanical system (21–23). However, we wish to retain a Hilbert space representation of the subsystem, so we introduce a partial Wigner representation only over the bath degrees of freedom. We then make use of the disparity between the masses of the subsystem and bath particles to find quantum-classical evolution equations (24).

To carry out this program explicitly, we suppose that the subsystem and bath particles have light  $m$  and heavy  $M$  masses ( $M \gg m$ ) and coordinate and momentum operators  $(\hat{q}, \hat{p})$  and  $(\hat{Q}, \hat{P})$ , respectively. The quantum mechanical Hamiltonian operator is given by  $\hat{H} = \hat{P}^2/2M + \hat{p}^2/2m + \hat{V}(\hat{q}, \hat{Q})$ . The partial Wigner transform of density matrix is

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

The subscript W refers to this partial Wigner transform and  $N$  is the coordinate space dimension of the bath. Taking the partial Wigner transform of the quantum Liouville equation, we obtain

$$\frac{\partial \hat{\rho}_W(R, P, t)}{\partial t} = -i(\hat{H}_W e^{\hat{i}\Lambda/2i} \hat{\rho}_W(t) - \hat{\rho}_W(t) e^{\hat{i}\Lambda/2i} \hat{H}_W). \quad 3.$$

Here we used the rule for the Wigner transform of a product of operators (22)  $(\hat{A}\hat{B})_W = \hat{A}_W e^{\hbar\Lambda/2i} \hat{B}_W$ , where the partial Wigner transform of an operator  $\hat{A}$  is

$$\hat{A}_W(R, P) = \int dz e^{iP \cdot z/\hbar} \left\langle R - \frac{z}{2} \left| \hat{A} \left| R + \frac{z}{2} \right. \right. \right\rangle. \quad 4.$$

The operator  $\Lambda$  is the negative of the Poisson bracket operator,  $\Lambda = \overleftarrow{\nabla}_P \cdot \overrightarrow{\nabla}_R - \overleftarrow{\nabla}_R \cdot \overrightarrow{\nabla}_P$ , and the direction of an arrow indicates the direction in which the operator acts.

To take the quantum-classical limit of Equation 1, we scale the variables so that the momenta of the heavy particles have the same magnitude as those of the light particles,  $\mu P$ , where  $\mu = (m/M)^{1/2}$ , and measure all distances in length units appropriate for the quantum subsystem (24). The reduction to a quantum-classical system can also be justified by arguments based on decoherence (25). Letting energy be measured in terms of the 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  $P_M = (M\epsilon_0)^{1/2}$ . In the scaled units  $\hat{q}' = \hat{q}/\lambda_m$ ,  $R' = R/\lambda_m$ ,  $\hat{p}' = \hat{p}/p_m$ ,  $P' = P/P_M$ , and  $t' = t/t_0$ , we have

$$\begin{aligned} \frac{\partial \hat{\rho}'_W(R', P', t)}{\partial t'} &= -i(\hat{H}'_W e^{\mu\Lambda'/2i} \hat{\rho}'_W(t') - \hat{\rho}'_W(t') e^{\mu\Lambda'/2i} \hat{H}'_W) \\ &\approx -i\left(\hat{H}'_W \left(1 + \frac{\mu\Lambda'}{2i}\right) \hat{\rho}'_W(t') - \hat{\rho}'_W(t') \left(1 + \frac{\mu\Lambda'}{2i}\right) \hat{H}'_W\right). \end{aligned} \quad 5.$$

To obtain the second approximate equality, we expanded the right-hand side to first order in the small parameter  $\mu = (m/M)^{1/2}$ . Returning to unscaled units, we have the quantum-classical Liouville equation,

$$\begin{aligned} \frac{\partial \hat{\rho}_W(R, P, t)}{\partial t} &= -\frac{i}{\hbar}[\hat{H}_W, \hat{\rho}_W(t)] + \frac{1}{2}(\{\hat{H}_W, \hat{\rho}_W(t)\} - \{\hat{\rho}_W(t), \hat{H}_W\}) \\ &= -(\hat{H}_W, \hat{\rho}_W(t)) = -i\hat{\mathcal{L}}\hat{\rho}_W(t), \end{aligned} \quad 6.$$

which gives the time evolution of the density matrix  $\hat{\rho}_W(R, P, t)$  (24, 26–32). Here  $[\cdot, \cdot]$  is again the commutator and  $\{\cdot, \cdot\}$  is the Poisson bracket. The Hamiltonian of the system is  $\hat{H}_W(R, P) = P^2/2M + \hat{p}^2/2m + \hat{V}_W(\hat{q}, R)$  and consists of the sum of the kinetic energy of the classical particles,  $P^2/2M$ , the kinetic energy operator for the quantum degrees of freedom,  $\hat{p}^2/2m$ , and the total potential energy operator,  $\hat{V}_W(\hat{q}, R)$ , of the system. The last two equalities in Equation 6 define the quantum-classical bracket and quantum-classical Liouville operator (24, 33). In Equation 6, the coupling between the quantum subsystem and bath appears in both terms in the quantum-classical Liouville operator. The quantum character manifests itself in the Poisson bracket terms because the quantum operators do not commute and their order must be respected.

Using a similar procedure, we may derive the equation of motion for an observable,  $\hat{A}_W(R, P, t)$  (24):

$$\frac{d\hat{A}_W(R, P, t)}{dt} = (\hat{H}_W, \hat{A}_W(t)) = i\hat{\mathcal{L}}\hat{A}_W(t), \quad 7.$$

which is the quantum-classical analog of the Heisenberg equation of motion. This equation manifestly conserves energy.

The quantum-classical Liouville equation may be expressed in any convenient basis. In particular, the adiabatic basis vectors,  $|\alpha; R\rangle$ , are given by the solutions of  $\hat{h}_W|\alpha; R\rangle = E_\alpha(R)|\alpha; R\rangle$ , where  $\hat{h}_W = \frac{\hat{p}^2}{2m} + \hat{V}_W(\hat{q}, R)$ . We take an Eulerian view of the dynamics so that the adiabatic basis vectors are parameterized by the time-independent values of the bath coordinates  $R$ . In this basis, the Liouville operator has matrix elements (24)

$$\begin{aligned} i\mathcal{L}_{\alpha\alpha',\beta\beta'} &= (i\omega_{\alpha\alpha'} + iL_{\alpha\alpha'})\delta_{\alpha\beta}\delta_{\alpha'\beta'} - J_{\alpha\alpha',\beta\beta'} \\ &\equiv iL_{\alpha\alpha'}^0\delta_{\alpha\beta}\delta_{\alpha'\beta'} - J_{\alpha\alpha',\beta\beta'}, \end{aligned} \quad 8.$$

where  $\omega_{\alpha\alpha'}(R) = (E_\alpha(R) - E_{\alpha'}(R))/\hbar$  is a frequency determined by the difference in energies of adiabatic states, and  $iL_{\alpha\alpha'}$  is the Liouville operator for classical evolution under the mean of the Hellmann-Feynman forces for adiabatic states  $\alpha$  and  $\alpha'$ ,

$$iL_{\alpha\alpha'} = \frac{P}{M} \cdot \frac{\partial}{\partial R} + \frac{1}{2}(F_W^\alpha + F_W^{\alpha'}) \cdot \frac{\partial}{\partial P}, \quad 9.$$

where  $F_W^\alpha = -\langle\alpha; R|\frac{\partial\hat{V}_W(\hat{q},R)}{\partial R}|\alpha; R\rangle$  is the Hellmann-Feynman force for state  $\alpha$ . The operator  $J_{\alpha\alpha',\beta\beta'}$  accounts for nonadiabatic transitions and corresponding changes of the bath momentum. It is given by

$$\begin{aligned} J_{\alpha\alpha',\beta\beta'} &= -\frac{P}{M} \cdot d_{\alpha\beta} \left(1 + \frac{1}{2}S_{\alpha\beta} \cdot \frac{\partial}{\partial P}\right) \delta_{\alpha'\beta'} \\ &\quad - \frac{P}{M} \cdot d_{\alpha'\beta'}^* \left(1 + \frac{1}{2}S_{\alpha'\beta'}^* \cdot \frac{\partial}{\partial P}\right) \delta_{\alpha\beta}, \end{aligned} \quad 10.$$

where  $d_{\alpha\beta} = \langle\alpha; R|\nabla_R|\beta; R\rangle$  is the nonadiabatic coupling matrix element and  $S_{\alpha\beta} = \Delta E_{\alpha\beta}\hat{d}_{\alpha\beta}(\frac{P}{M} \cdot \hat{d}_{\alpha\beta})^{-1}$  with  $\Delta E_{\alpha\beta}(R) = E_\alpha(R) - E_\beta(R)$ .

As shown in Section 5, one may construct solutions of the quantum-classical Liouville equation in terms of an ensemble of surface-hopping trajectories.

## 2.1. Equilibrium Density

The quantum-canonical equilibrium density matrix,  $\hat{\rho}_Q = Z_Q e^{-\beta\hat{H}}$ , is a stationary solution of the quantum Liouville equation (Equation 1). Similarly, the quantum-classical canonical equilibrium density matrix,  $\hat{\rho}_{We}(R, P)$ , is stationary under quantum-classical dynamics,  $i\hat{\mathcal{L}}\hat{\rho}_{We} = 0$ . Although it is difficult to find a general analytical solution for the quantum-classical canonical equilibrium density matrix, a solution can be found by writing  $\hat{\rho}_{We}$  as a power series in the small parameter  $\mu = (m/M)^{1/2}$ . In unscaled variables, we have  $\rho_{We}^{\alpha\alpha'} = \rho_{We}^{(0)\alpha}\delta_{\alpha\alpha'} - i\hbar f_{We}^{\alpha\alpha'} + \dots$

where  $\rho_{\text{We}}^\alpha = Z_0^{-1} e^{-\beta H_{\text{W}}^\alpha}$  with  $Z_0 = \sum_\alpha \int dRdP e^{-\beta H_{\text{W}}^\alpha}$  and  $f_{\text{We}}^{\alpha\alpha'}$  is a known function (33). To first order in  $\mu$ , the quantum and quantum-classical stationary densities are identical. The stationary density enters in the derivations of reduced quantum-classical equations of motion and in the calculation of transport properties in the quantum-classical limit.

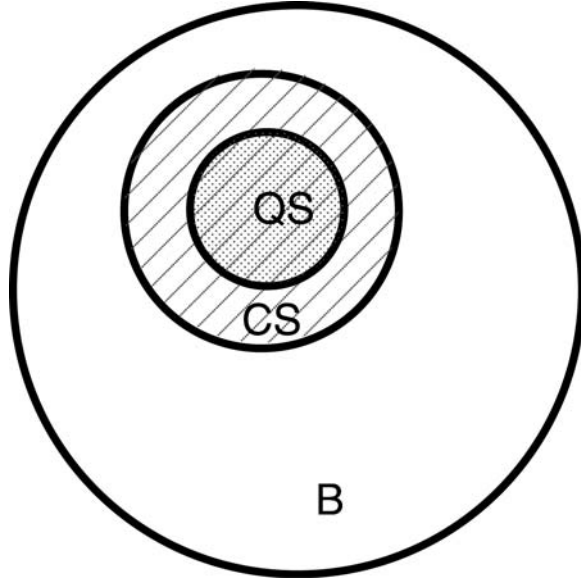
### 3. DISSIPATIVE QUANTUM-CLASSICAL DYNAMICS

The quantum-classical Liouville equation describes the dynamics of the entire system, although the bath, in isolation from the subsystem, obeys classical mechanics. The dynamics is deterministic and conservative. The advantages of such a complete description of the environment have been noted earlier, namely, that the effects of detailed local solvent or bath particle motions on the quantum subsystem dynamics are taken into account. One may also envisage situations where a detailed treatment of all bath degrees of freedom is unnecessary; for example, we can imagine that the quantum degrees of freedom may be coupled directly to a certain number of bath variables whose dynamics must be considered in full detail. However, these important bath variables may themselves be coupled to a much larger set of bath variables whose detailed dynamics is not of interest. This indirectly coupled set of bath variables acts like a dissipative heat bath on the quantum subsystem and directly coupled classical bath variables. Proton- and electron-transfer reactions in biosystems fall into this category because the transfer event is strongly influenced by motions of the neighboring molecular groups, which are, in turn, embedded in a bath of solvent molecules.

An equation of motion can be derived to describe such situations by starting with the quantum-classical Liouville equation for the entire system and projecting out the effects of those bath degrees of freedom that are not of interest (34). We shall show that this procedure yields dissipative equations of motion where the irrelevant part of the classical bath is described by a Fokker-Planck operator.

To carry out this program, the entire classical bath is partitioned into two subsystems with phase-space coordinates denoted by  $(R', P')$  and  $(R'', P'')$ , respectively, so that  $(R, P) = (R', R'', P', P'') = (R', P')(R'', P'')$ . The  $(R', P')$  classical subsystem is coupled directly to the quantum subsystem and the irrelevant  $(R'', P'')$  classical subsystem couples only to the  $(R', P')$  classical subsystem. (The primed variables introduced here should not be confused with the dimensionless variables in the previous section.) The partially Wigner-transformed Hamiltonian can be written in terms of contributions from the different subsystems and the coupling between them:

$$\begin{aligned} \hat{H}_{\text{W}}(R, P) &= \frac{P'^2}{2M} + \frac{\hat{p}^2}{2m} + \hat{V}'_{\text{W}}(\hat{q}, R') + \frac{P''^2}{2M} + V_{\text{B}}(R'') + V_{\text{CB}}(R', R'') \\ &\equiv \hat{H}'_{\text{W}}(R', P') + H_0(R', R'', P''), \end{aligned} \quad 11.$$



**Figure 1** Schematic diagram showing the partition of the system into a quantum subsystem (QS), a classical subsystem (CS) directly coupled to the quantum subsystem, and a large classical bath (B) directly coupled to the classical subsystem.

where  $\hat{H}'_W(R', P') = P'^2/2M + \hat{p}^2/2m + \hat{V}'_W(\hat{q}, R')$  is the Hamiltonian of the mixed quantum-classical subsystem (quantum subsystem and directly coupled classical bath variables) and  $H_0(R', R'', P'') = H''_B(R'', P'') + V_{CB}(R', R'')$  is the Hamiltonian of the irrelevant variables of the classical bath,  $H''_B(R'', P'') = P''^2/2M + V_B(R'')$ , in the potential field  $V_{CB}(R', R'')$  of the fixed particles in the classical bath subsystem that are directly coupled to the quantum subsystem. This partition of the system is shown schematically in Figure 1.

If the decomposition of the Hamiltonian given in Equation 11 is substituted into Equation 6, the quantum-classical Liouville operator for the entire system may be written as  $i\hat{\mathcal{L}} = i\hat{\mathcal{L}}' + i\mathcal{L}_0$ . We use the following notation: If a quantity depends only on  $(R', P')$  or  $(R'', P'')$ , it will have a prime or double prime, respectively. If a quantity depends on both types of classical phase-space coordinates, it will not have a prime.

An evolution equation for the reduced density matrix for the quantum-classical subsystem,

$$\hat{\rho}'_W(t) \equiv \hat{\rho}'_W(R', P', t) = \int dR'' dP'' \hat{\rho}_W(R, P, t), \quad 12.$$

can be obtained by using projection operator methods. Consider the projection operator  $\mathcal{P}$  acting on any mixed quantum-classical operator  $\hat{f}_W(R, P)$

defined by (35–37)

$$\mathcal{P}\hat{f}_W(R, P) = \frac{1}{2} \left( \hat{\rho}_{ce} \left( \int dR'' dP'' \hat{f}_W \right) + \left( \int dR'' dP'' \hat{f}_W \right) \hat{\rho}_{ce}^\dagger \right). \quad 13.$$

The density operator  $\hat{\rho}_{ce}$  is defined in the following way: The canonical equilibrium density matrix for the entire system, i.e., the mixed quantum-classical subsystem plus the bath,  $\hat{\rho}_{We}$ , is defined above. We let  $\hat{\rho}_{ce}(R, P) = \hat{\rho}_{We}(R, P)(\hat{\rho}'_c)^{-1}(R', P')$ , where  $\hat{\rho}'_c(R', P') = \int dR'' dP'' \hat{\rho}_{We}(R, P)$ . Its adjoint is  $\hat{\rho}_{ce}^\dagger = (\hat{\rho}'_c)^{-1} \hat{\rho}_{We}$ .

To derive a dissipative equation for the mixed quantum-classical evolution, we note that

$$\int dR'' dP'' \mathcal{P}\hat{\rho}_W(R, P, t) = \hat{\rho}'_W(R', P', t) \quad 14.$$

and apply projection operator algebra (38, 39) to obtain

$$\frac{\partial \hat{\rho}'_W(t)}{\partial t} = -i\hat{\mathcal{L}}'\hat{\rho}'_W - \mathcal{F} \cdot \frac{\partial}{\partial P'} \hat{\rho}'_W + \zeta(R') : \frac{\partial}{\partial P'} \left( \frac{P'}{M} + k_B T \frac{\partial}{\partial P'} \right) \hat{\rho}'_W(t). \quad 15.$$

The effects of the irrelevant bath degrees of freedom on the mixed quantum-classical subsystem are accounted for by the Fokker-Planck-like operator, which depends on the fixed particle friction tensor,  $\zeta(R)$ , as well as through the mean force  $\mathcal{F}$  defined by  $\mathcal{F} = -\langle \partial V_{CB} / \partial R' \rangle_0$ , where the average is over a canonical equilibrium distribution involving the Hamiltonian  $H_0$ . If the dependence of the friction tensor on the bath coordinates is neglected, we obtain a simpler form of the dissipative quantum-classical Liouville equation,

$$\frac{\partial \hat{\rho}'_W(t)}{\partial t} = -i\hat{\mathcal{L}}'\hat{\rho}'_W - \mathcal{F} \cdot \frac{\partial}{\partial P'} \hat{\rho}'_W - i\mathcal{L}'_{FP} \hat{\rho}'_W(t) \equiv -i\mathcal{L}^{K'} \hat{\rho}'_W(t), \quad 16.$$

where  $\mathcal{L}'_{FP}$  is the Fokker-Planck operator,  $-i\mathcal{L}'_{FP} = \zeta \partial / \partial P' \cdot (P'/M + k_B T \partial / \partial P')$ . Dropping the primes and expressing the evolution operator in the adiabatic basis, we have

$$i\mathcal{L}^{K}_{\alpha\alpha'\beta\beta'} = (i\omega_{\alpha\alpha'}(R) + iL^{K}_{\alpha\alpha'}) \delta_{\alpha\beta} \delta_{\alpha'\beta'} - J_{\alpha\alpha'\beta\beta'}, \quad 17.$$

where we have defined the Kramers operator as

$$i\mathcal{L}^{K}_{\alpha\alpha'} = \left[ \frac{P}{M} \frac{\partial}{\partial R} + \frac{1}{2} \left( \mathcal{F}_W^\alpha + \mathcal{F}_W^{\alpha'} \right) \cdot \frac{\partial}{\partial P} - \zeta \frac{\partial}{\partial P} \left( \frac{P}{M} + k_B T \frac{\partial}{\partial P} \right) \right], \quad 18.$$

and  $\mathcal{F}_W^\alpha = -\partial \mathcal{V}_W^\alpha / \partial R$  denotes the effective Hellmann-Feynman force acting on the relevant variables.

The evolution equation for a dynamical variable has the form of Equation 7 and, expressed in an adiabatic basis, involves the backward operator

$$i\mathcal{L}^{KB}_{\alpha\alpha'\beta\beta'} = (i\omega_{\alpha\alpha'}(R) + iL^{KB}_{\alpha\alpha'}) \delta_{\alpha\beta} \delta_{\alpha'\beta'} - J_{\alpha\alpha'\beta\beta'}, \quad 19.$$

where the backward Kramers operator is defined as

$$iL_{\alpha\alpha'}^{\text{KB}} = \left[ \frac{P}{M} \frac{\partial}{\partial R} + \frac{1}{2} (\mathcal{F}_W^\alpha + \mathcal{F}_W^{\alpha'}) \cdot \frac{\partial}{\partial P} - \zeta \left( \frac{P}{M} - k_B T \frac{\partial}{\partial P} \right) \frac{\partial}{\partial P} \right]. \quad 20.$$

Thus, we see that the evolution equations have a similar structure for both deterministic and dissipative baths, except that the Fokker-Planck evolution operator replaces the Newtonian evolution operator in the quantum-classical Liouville operator. Simulation methods and applications using this equation are described below.

#### 4. QUANTUM SUBSYSTEM DYNAMICS

Many descriptions of open quantum systems focus entirely on the dynamics of the quantum subsystem where any detailed reference to bath degrees of freedom has been eliminated completely (1, 2).

A system composed of a quantum particle immersed in a thermal bath of harmonic oscillators has been studied often as a simple model of an open quantum system. This system can be treated in full detail using influence functional methods (40–47). In more general contexts, equations of motion for the reduced density matrix of the quantum system obtained by tracing over all bath degrees of freedom take the form of quantum master equations (2, 45), Redfield equations (6), and the Lindblad equation (3). In this section, we derive the form of the equation of motion for the reduced density matrix of a quantum-classical system by projecting out all classical bath degrees of freedom (35).

The reduced density matrix  $\hat{\rho}_Q(t)$  for the quantum subsystem, where the bath phase-space variables are integrated out, is given by

$$\hat{\rho}_Q(t) = \int dR dP \hat{\rho}_W(R, P, t). \quad 21.$$

The approach we take is very similar to that in the previous section, except now the projection operator  $\mathcal{P}$  is chosen to project out the effects of all bath variables (35),

$$\mathcal{P} \hat{f}_W(R, P) = \frac{1}{2} \left( \hat{\rho}_b \left( \int dR dP \hat{f}_W \right) + \left( \int dR dP \hat{f}_W \right) \hat{\rho}_b^\dagger \right). \quad 22.$$

The equilibrium distribution  $\hat{\rho}_b(R, P)$  and its adjoint are defined as  $\hat{\rho}_b(R, P) = \hat{\rho}_{\text{We}}(R, P) \hat{\rho}_s^{-1}$  and  $\hat{\rho}_b^\dagger(R, P) = \hat{\rho}_s^{-1} \hat{\rho}_{\text{We}}(R, P)$  where  $\hat{\rho}_s = \int dR dP \hat{\rho}_{\text{We}}(R, P)$ . Here  $\hat{\rho}_s$  is the equilibrium density matrix for the quantum subsystem in equilibrium with the classical bath and  $\hat{\rho}_s^{-1}$  is its inverse. The densities are normalized so that  $\int dR dP \hat{\rho}_b(R, P) = 1$ .

The interaction potential energy operator between the quantum subsystem and bath may be written as the sum of products of  $\hat{A} = \{\hat{A}_j\}$  and  $B(R) = \{B_j(R)\}$ ,

subsystem operators and bath functions, respectively, as

$$\hat{V}_c(\hat{q}, R) = \sum_j \hat{A}_j B_j(R) \equiv \hat{A} \cdot B(R). \quad 23.$$

Employing this form of the potential energy operator, using projection operator techniques (38), (39), taking the weak coupling limit where  $\hat{\rho}_b$  may be replaced by the canonical equilibrium density for the bath in isolation from the quantum subsystem, and making a Markovian approximation on the memory kernels in the generalized Langevin equation, we obtain (35)

$$\begin{aligned} \frac{\partial \hat{\rho}_Q(t)}{\partial t} = & -\frac{i}{\hbar} [\hat{h}_s + \hat{A} \cdot \langle B \rangle_B, \hat{\rho}_Q(t)] + \left(\frac{i}{\hbar}\right)^2 \gamma_B : [\hat{A}, [\hat{A}, \hat{\rho}_Q(t)]] \\ & - \frac{i}{\hbar} \gamma'_B : \left[ \hat{A}, \frac{1}{2} (\hat{A} \hat{\rho}_Q(t) + \hat{\rho}_Q(t) \hat{A}) \right]. \end{aligned} \quad 24.$$

In this equation, the parameters  $\gamma_B$  and  $\gamma'_B$  are defined in terms of classical bath correlation functions,

$$\gamma_B = \int_0^\infty dt \langle \delta B(t) \delta B \rangle_B, \quad \gamma'_B = \int_0^\infty dt \langle \{\delta B(t), \delta B\} \rangle_B, \quad 25.$$

where  $\delta B = B - \langle B \rangle_B$  and the angular brackets signify an average over the bath. This equation has the same form as the Lindblad equation (3) but now the parameters are completely specified in terms of well-defined classical bath correlation functions.

## 5. SIMULATION OF QUANTUM-CLASSICAL EVOLUTION EQUATIONS

Having discussed the basis for the quantum-classical Liouville equation and its dissipative analog where part of the bath is treated stochastically, we now turn our attention to simulation methods for solving these evolution equations. Various schemes have been proposed for the solution of the quantum-classical Liouville equation (31, 48–52). Below we describe a method that represents the solution in an ensemble of surface-hopping trajectories (53). Quantum-classical Liouville dynamics may then be contrasted with the dynamics generated by other surface-hopping schemes (12, 13, 54–58).

Before describing the simulation algorithm, we must consider the nature of the operator  $J$  that is responsible for both quantum transitions and associated momentum changes in the bath. It is difficult to evaluate the action of this operator on phase-space functions because of the contribution involving derivatives with respect to bath particle momenta. In the simulation algorithms described below, we employ the momentum-jump approximation (18, 24, 59, 60). We use the fact that  $\frac{1}{2} S_{\alpha\beta} \cdot \frac{\partial}{\partial P} = \Delta E_{\alpha\beta} \partial / \partial (\bar{P} \cdot \hat{d}_{\alpha\beta})^2$ , where  $\Delta E_{\alpha\beta} = E_\alpha - E_\beta$ ,  $\bar{P} = P / \sqrt{M}$ , and

$\tilde{d}_{\alpha\beta} \equiv \hat{d}_{\alpha\beta}/\sqrt{M}$ . Here we use the notation  $\hat{d}_{\alpha\beta}/\sqrt{M} = \hat{d}_{\alpha\beta}^T M^{-1/2}$  and  $\bar{P} \cdot \tilde{d}_{\alpha\beta} = \bar{P}^T \hat{d}_{\alpha\beta} = \sum_j \bar{P}_j \tilde{d}_{\alpha\beta}^j$ , where  $T$  stands for the transpose,  $M^{-1/2}$  is a diagonal matrix of the inverse square root of the masses, and the sum on  $j$  runs over all bath particle coordinates.

Using this notation, the action of the operator  $J$  on any function  $f(P)$  of the bath momenta can be written in the momentum-jump approximation as

$$\left(1 + \Delta E_{\alpha\beta} \frac{\partial}{\partial(\bar{P} \cdot \tilde{d}_{\alpha\beta})}\right) f(P) \approx \exp(\Delta E_{\alpha\beta}) \partial/\partial(\bar{P} \cdot \tilde{d}_{\alpha\beta})^2 f(P) = f(P + \Delta P), \tag{26}$$

where

$$\Delta P = \sqrt{M} \tilde{d}_{\alpha\beta} \left[ \text{sgn}(\bar{P} \cdot \tilde{d}_{\alpha\beta}) \times \sqrt{(\bar{P} \cdot \tilde{d}_{\alpha\beta})^2 + \Delta E_{\alpha\beta}} - (\bar{P} \cdot \tilde{d}_{\alpha\beta}) \right]. \tag{27}$$

The use of this approximation leads to a representation of the dynamics in terms of energy-conserving trajectories.

### 5.1. Quantum-Classical Liouville Equation

The quantum-classical Liouville equation for an operator  $\hat{A}_W(R, P, t)$  is given in Equation 7. Its formal solution is  $\hat{A}_W(t) = \exp(i\hat{\mathcal{L}}t)\hat{A}_W(0)$ . To simulate the time evolution, we must construct an algorithm for the action of the quantum-classical propagator on an operator. The propagator,  $\exp(i\hat{\mathcal{L}}t)$ , can be decomposed into a composition of propagators in time segments of arbitrary length. The evolution of a dynamical variable over any time interval can then be obtained by the successive application of evolution operators in the small time segments (53).

Suppose we are interested in determining the time evolution over a time interval  $(0, t)$ . We first divide this interval into  $N$  segments such that the  $j$ th segment has length  $\Delta t_j = t_j - t_{j-1} = \Delta t$ . This interval may be chosen to be either equal to the molecular dynamics simulation time step or integer multiple of the time step. We may then write the propagator in the adiabatic basis as

$$(e^{i\hat{\mathcal{L}}t})_{\alpha_0\alpha'_0, \alpha_N\alpha'_N} = \sum_{(\alpha_1\alpha'_1)\dots(\alpha_{N-1}\alpha'_{N-1})} \prod_{j=1}^N (e^{i\hat{\mathcal{L}}(t_j-t_{j-1})})_{\alpha_{j-1}\alpha'_{j-1}, \alpha_j\alpha'_j}, \tag{28}$$

where  $(\alpha_0\alpha'_0) \equiv (\alpha\alpha')$ . Using this expression for the propagator, we have

$$A_W^{\alpha\alpha'}(R, P, t) = \sum_{(\alpha_1\alpha'_1)\dots(\alpha_N\alpha'_N)} \left[ \prod_{j=1}^N (e^{i\hat{\mathcal{L}}(t_j-t_{j-1})})_{\alpha_{j-1}\alpha'_{j-1}, \alpha_j\alpha'_j} \right] A_W^{\alpha_N\alpha'_N}(R, P). \tag{29}$$

Given this form of a time-dependent observable, the simulation algorithm exploits the structure of the propagator in the short-time segments.

The quantum-classical Liouville operator is decomposed into diagonal  $i\mathcal{L}^0$  and off-diagonal  $J$  parts in Equation 8. Using this decomposition and taking the time

interval  $\Delta t$  to be small enough, we can approximate the propagator in an interval by

$$\begin{aligned} (e^{i\hat{L}(t_j-t_{j-1})})_{\alpha_{j-1}\alpha'_{j-1},\alpha_j\alpha'_j} &\approx e^{i\mathcal{L}^0_{\alpha_{j-1}\alpha'_{j-1}}\Delta t} (\delta_{\alpha_j\alpha'_j,\alpha_{j-1}\alpha'_{j-1}} - \Delta t J_{\alpha_{j-1}\alpha'_{j-1},\alpha_j\alpha'_j}) \\ &= \mathcal{W}_{\alpha_{j-1}\alpha'_{j-1}}(t_{j-1}, t_j) e^{iL_{\alpha_{j-1}\alpha'_{j-1}}\Delta t} \\ &\quad \times (\delta_{\alpha_j\alpha'_j,\alpha_{j-1}\alpha'_{j-1}} - \Delta t J_{\alpha_{j-1}\alpha'_{j-1},\alpha_j\alpha'_j}), \end{aligned} \quad 30.$$

where  $\mathcal{W}_{\alpha_{j-1}\alpha'_{j-1}}(t_{j-1}, t_j) = e^{i\omega_{\alpha_{j-1}\alpha'_{j-1}}(t_j-t_{j-1})}$  is the phase factor associated with time segment  $(t_j, t_{j-1})$ . At the end of each time segment, the system either may remain in the same pair of adiabatic states or make a transition to a new pair of states. More specifically, for an initial pair of quantum states,  $(\alpha_0\alpha'_0)$ , the phase point  $(R, P)$  is evolved for a time  $\Delta t$  to a new value  $(R_{\Delta t}, P_{\Delta t})$  using the classical propagator  $e^{iL_{\alpha_0\alpha'_0}\Delta t}$  and the phase factor  $\mathcal{W}_{\alpha_0\alpha'_0}$  is computed. With probability  $1/2$ , one chooses whether the transition  $\alpha_0 \rightarrow \alpha_1$  or  $\alpha'_0 \rightarrow \alpha'_1$  occurs. The states  $\alpha_1$  and  $\alpha'_1$  are chosen uniformly from the set of allowed final states; the weight  $w_{\alpha_0\alpha'_0,\alpha_1\alpha'_1}$  associated with the final state is the number of allowed final states. Once  $(\alpha_1\alpha'_1)$  or  $(\alpha_0\alpha'_0)$  is chosen, the nonadiabatic coupling matrix element  $d_{\alpha_0\alpha_1}$  (or  $d_{\alpha'_0\alpha'_1}$ ) is computed at  $R_{\Delta t}$  and the probability,  $\pi$ , of a nonadiabatic transition is given by

$$\pi = \left| \frac{P_{\Delta t}}{M} \cdot d_{\alpha_0\alpha_1}(R_{\Delta t}) \right| \Delta t \left( 1 + \left| \frac{P_{\Delta t}}{M} \cdot d_{\alpha_0\alpha_1}(R_{\Delta t}) \right| \Delta t \right)^{-1}. \quad 31.$$

If the transition is rejected, then

$$A_W^{\alpha_0\alpha'_0}(R, P, \Delta t) = \mathcal{W}_{\alpha_0\alpha'_0}(\Delta t) A_W^{\alpha_0\alpha'_0}(R_{\Delta t}, P_{\Delta t}) \frac{1}{1-\pi}. \quad 32.$$

If the transition is accepted, then, using the momentum-jump approximation, we translate the momentum  $P_{\Delta t}$  to  $\tilde{P}_{\Delta t} = P_{\Delta t} + \Delta P$  where  $\Delta P$  is defined in Equation 27. We then write

$$\begin{aligned} A_W^{\alpha_0\alpha'_0}(R, P, \Delta t) &= \mathcal{W}_{\alpha_0\alpha'_0}(\Delta t) A_W^{\alpha_1\alpha'_1}(R_{\Delta t}, \tilde{P}_{\Delta t}) \Delta t \\ &\quad \times \frac{P_{\Delta t}}{M} \cdot d_{\alpha_0\alpha_1}(R_{\Delta t}) \frac{1}{\pi} w_{\alpha_0\alpha'_0,\alpha_1\alpha'_1}. \end{aligned} \quad 33.$$

From Equation 27, we see that if  $\Delta E_{\alpha\beta} < 0$  (an upward transition from  $\alpha \rightarrow \beta$ ) and  $(\tilde{P} \cdot \tilde{d}_{\alpha\beta})^2 \leq |\Delta E_{\alpha\beta}|$  so that there is insufficient kinetic energy from both momenta along  $\tilde{d}_{\alpha\beta}$  for the quantum transition to occur, the argument of the square root is negative leading to imaginary momentum changes. In this case, the quantum transition does not occur and the trajectory is continued adiabatically.

The total energy of the system is conserved along a quantum-classical surface-hopping trajectory when the momentum-jump approximation is used, even if the transition is to a pair of coherently coupled surfaces.

## 5.2. Dissipative Quantum-Classical Liouville Equation

The algorithm for simulating the dissipative quantum-classical Liouville equation is similar to that described above, except that one must evolve the system stochastically between quantum transitions (61).

The time evolution under the backward Kramers operator  $iL_{\alpha\alpha'}^{\text{KB}}$  in Equation 20 can be replaced by an average over realizations of stochastic Langevin dynamics where the time evolution of the classical trajectory segments is determined by the Langevin equations of motion,

$$\dot{R} = \frac{P}{M}, \quad \dot{P} = -\frac{\zeta}{M}P + \frac{1}{2}(\mathcal{F}_W^\alpha + \mathcal{F}_W^{\alpha'}) + \xi(t). \quad 34.$$

Here  $\xi(t)$  is a Gaussian white noise process with the properties  $\langle \xi(t) \rangle = 0$  and  $\langle \xi(t)\xi(t') \rangle = 2k_B T \zeta \delta(t - t')$ . The Langevin equations can be written in Liouville form (62, 63) by defining a time-dependent Liouville operator

$$iL_{\alpha\alpha'}^L(t) = \frac{P}{M} \frac{\partial}{\partial R} + \left( -\frac{\zeta}{M}P + \frac{1}{2}(\mathcal{F}_W^\alpha + \mathcal{F}_W^{\alpha'}) + \xi(t) \right) \frac{\partial}{\partial P}. \quad 35.$$

The time evolution over an interval  $(0, t)$  is given by the time-ordered propagator

$$U_{\alpha\alpha'}^L(t, t_0) = \mathcal{T} \exp \left[ \int_{t_0}^t dt' iL_{\alpha\alpha'}^L(t') \right]. \quad 36.$$

As a result, we may define the time-dependent quantum-classical Langevin-Liouville operator

$$i\mathcal{L}_{\alpha\alpha'\beta\beta'}^L(t) = (i\omega_{\alpha\alpha'}(R) + iL_{\alpha\alpha'}^L(t)) \delta_{\alpha\beta} \delta_{\alpha'\beta'} - J_{\alpha\alpha'\beta\beta'} \quad 37.$$

and the propagator

$$U_{\alpha\alpha'\beta\beta'}^L(t, t_0) = \left( \mathcal{T} \exp \left[ \int_{t_0}^t dt' i\mathcal{L}^L(t') \right] \right)_{\alpha\alpha'\beta\beta'}. \quad 38.$$

We may now again use the sequential short-time propagation method to simulate the dynamics; however, now the time-ordered nature of the evolution operator must be taken into account. Suzuki's form (64) for a time-ordered exponential and a Trotter factorization may be used to simulate the dynamics (61).

## 6. TRANSPORT PROPERTIES

Given the quantum-classical Liouville equation and its various reduced forms, and an algorithm for simulating quantum-classical evolution, our next task is to formulate expressions for transport properties as these are the typical quantities of interest.

The quantum-mechanical forms of the correlation function expressions for transport coefficients are well-known and may be derived using linear response

theory (65) or projection operator techniques (39, 66). In linear response theory, an external force  $F(t)$  that couples to an operator  $\hat{A}^\dagger$  is applied to the system from the distant past where the system is assumed to be in thermal equilibrium. The response of the system to the external force may be determined by computing the average value of an operator  $\hat{C}$  using the density matrix at time  $t$ , evaluated to linear order in the external force,

$$\overline{C(t)} = \text{Tr} \hat{C} \hat{\rho}(t) = \int_{-\infty}^t dt' \phi_{CA}(t-t') F(t'), \quad 39.$$

where the response function is given by

$$\phi_{CA}(t) = -\left\langle \frac{i}{\hbar} [\hat{A}^\dagger, \hat{C}(t)] \right\rangle_Q = \int_0^\beta d\lambda \text{Tr} \hat{A} \dot{\hat{A}}^\dagger(-i\hbar\lambda) \hat{C}(t) \hat{\rho}_e^Q, \quad 40.$$

and the angle brackets denote a quantum canonical equilibrium average,  $\langle \dots \rangle_Q = \text{Tr} \dots \hat{\rho}_e^Q$ . If we choose  $\hat{C} = \hat{B} \equiv \hat{j}_B$ , the flux corresponding to the operator  $\hat{B}$ , the response has the form of a macroscopic law and the response function is proportional to the flux autocorrelation function

$$\phi_{BA}(t) = \left\langle \frac{i}{\hbar} [\hat{j}_B(t), \hat{A}^\dagger] \right\rangle_Q = \int_0^\beta d\lambda \text{Tr} \hat{j}_A^\dagger(-i\hbar\lambda) \hat{j}_B(t) \hat{\rho}_e^Q \equiv \beta \langle \hat{j}_A^\dagger; \hat{j}_B(t) \rangle_Q. \quad 41.$$

The last equality defines the Kubo transformed correlation function. A transport property  $\lambda_{AB}$  in quantum mechanics is proportional to the time integral of the flux autocorrelation function,

$$\lambda_{AB} = \int_0^\infty dt \langle \hat{j}_A; \hat{j}_B(t) \rangle_Q = \frac{1}{\beta} \int_0^\infty dt \left\langle \frac{i}{\hbar} [\hat{j}_B(t), \hat{A}^\dagger] \right\rangle_Q. \quad 42.$$

We now consider how to evaluate transport properties for quantum-classical systems. Two approaches will be considered. First, we start with the quantum mechanical expressions for transport coefficients and take the quantum-classical limit of the time evolution while retaining the full quantum nature of the equilibrium structure. In the second approach, we carry out a linear response derivation based on the quantum-classical Liouville equation.

## 6.1. Quantum-Classical Limit of Quantum Correlation Functions

We take as a starting point the quantum-mechanical expression for a transport coefficient and consider a limit where the dynamics is approximated by quantum-classical dynamics (67, 68). The advantage of this approach is that the full quantum equilibrium structure can be retained but at the price of a more difficult sampling problem. We now outline how this program can be carried out.

The quantum-mechanical expression for a transport property is given in Equation 42, and its generalization to a time-dependent transport coefficient, defined as

the finite time integral of the flux-flux correlation function, is

$$\lambda_{AB}(t) = \int_0^t dt' \langle \hat{J}_A; \hat{J}_B(t') \rangle_Q = \langle \dot{\hat{A}}; \hat{B}(t) \rangle = \frac{1}{\beta} \left\langle \frac{i}{\hbar} [\hat{B}(t), \hat{A}] \right\rangle_Q. \quad 43.$$

In simulations, it is convenient to obtain the transport coefficient from the plateau value of  $\lambda_{AB}(t)$ . Writing the second equality in Equation 43 in detail and inserting arbitrary time variables  $t_1$  and  $t_2$ , we can write the transport coefficient  $\lambda_{AB}(t)$  as

$$\begin{aligned} \lambda_{AB}(t) &= \frac{1}{\beta Z_Q} \int_0^\beta d\lambda \operatorname{Tr}(\hat{A} (-i\hbar\lambda) \hat{B}(t) e^{-\beta\hat{H}}) \\ &= \frac{1}{\beta Z_Q} \int_0^\beta d\lambda \operatorname{Tr}(\hat{A}(t_1 - i\hbar\lambda) e^{\frac{i}{\hbar}\hat{H}t'} \hat{B}(t_2) e^{-\frac{i}{\hbar}\hat{H}t'} e^{-\beta\hat{H}}), \end{aligned} \quad 44.$$

where  $t' \equiv t + t_1 - t_2$ . Introducing a coordinate representation  $\{Q\} = \{q\}\{Q\}$  of the operators in Equation 44 (calligraphic symbols are used to denote variables for the entire system, subsystem plus bath), making a change of variables,  $Q_1 = \mathcal{R}_1 - \mathcal{Z}_1/2$ ,  $Q_2 = \mathcal{R}_1 + \mathcal{Z}_1/2$ , etc., and then expressing the matrix elements in terms of the Wigner transforms of the operators, we have (68)

$$\begin{aligned} \lambda_{AB}(t) &= \frac{1}{\beta} \int_0^\beta d\lambda \int d\mathcal{X}_1 d\mathcal{X}_2 (\dot{A})_W(\mathcal{X}_1, t_1) B_W(\mathcal{X}_2, t_2) \frac{1}{(2\pi\hbar)^{2\nu} Z_Q} \\ &\quad \times \int d\mathcal{Z}_1 d\mathcal{Z}_2 e^{-\frac{i}{\hbar}(\mathcal{P}_1 \cdot \mathcal{Z}_1 + \mathcal{P}_2 \cdot \mathcal{Z}_2)} \left\langle \mathcal{R}_1 + \frac{\mathcal{Z}_1}{2} \left| e^{\frac{i}{\hbar}\hat{H}(t'+i\hbar\lambda)} \right| \mathcal{R}_2 - \frac{\mathcal{Z}_2}{2} \right\rangle \\ &\quad \times \left\langle \mathcal{R}_2 + \frac{\mathcal{Z}_2}{2} \left| e^{-\beta\hat{H} - \frac{i}{\hbar}\hat{H}(t'+i\hbar\lambda)} \right| \mathcal{R}_1 - \frac{\mathcal{Z}_1}{2} \right\rangle. \end{aligned} \quad 45.$$

Here we used the fact that the matrix element of an operator  $\hat{A}(t)$  can be expressed in terms of its Wigner transform  $A_W(\mathcal{X}, t)$  as

$$\left\langle \mathcal{R} - \frac{\mathcal{Z}}{2} \left| \hat{A}(t) \right| \mathcal{R} + \frac{\mathcal{Z}}{2} \right\rangle = \frac{1}{(2\pi\hbar)^\nu} \int d\mathcal{P} e^{-\frac{i}{\hbar}\mathcal{P} \cdot \mathcal{Z}} A_W(\mathcal{X}, t), \quad 46.$$

where  $\nu$  is the coordinate space dimension and the Wigner transform is defined by

$$A_W(\mathcal{X}, t) = \int d\mathcal{Z} e^{\frac{i}{\hbar}\mathcal{P} \cdot \mathcal{Z}} \left\langle \mathcal{R} - \frac{\mathcal{Z}}{2} \left| \hat{A}(t) \right| \mathcal{R} + \frac{\mathcal{Z}}{2} \right\rangle. \quad 47.$$

If we define the spectral density by

$$\begin{aligned} W(\mathcal{X}_1, \mathcal{X}_2, t) &= \frac{1}{(2\pi\hbar)^{2\nu} Z_Q} \int d\mathcal{Z}_1 d\mathcal{Z}_2 e^{-\frac{i}{\hbar}(\mathcal{P}_1 \cdot \mathcal{Z}_1 + \mathcal{P}_2 \cdot \mathcal{Z}_2)} \\ &\quad \times \left\langle \mathcal{R}_1 + \frac{\mathcal{Z}_1}{2} \left| e^{\frac{i}{\hbar}\hat{H}t} \right| \mathcal{R}_2 - \frac{\mathcal{Z}_2}{2} \right\rangle \left\langle \mathcal{R}_2 + \frac{\mathcal{Z}_2}{2} \left| e^{-\beta\hat{H} - \frac{i}{\hbar}\hat{H}t} \right| \mathcal{R}_1 - \frac{\mathcal{Z}_1}{2} \right\rangle, \end{aligned} \quad 48.$$

we can write the transport coefficient as

$$\lambda_{AB}(t) = \int d\mathcal{X}_1 d\mathcal{X}_2 (\dot{A})_W(\mathcal{X}_1, t_1) B_W(\mathcal{X}_2, t_2) \overline{W}(\mathcal{X}_1, \mathcal{X}_2, t + t_1 - t_2), \quad 49.$$

where

$$\overline{W}(\mathcal{X}_1, \mathcal{X}_2, t) = \frac{1}{\beta} \int_0^\beta d\lambda W(\mathcal{X}_1, \mathcal{X}_2, t + i\hbar\lambda). \quad 50.$$

To take the quantum-classical limit of this general expression for the transport coefficient, we partition the system into a subsystem and bath and use the notation  $\mathcal{R} = (r, R)$ ,  $\mathcal{P} = (p, P)$ , and  $\mathcal{X} = (r, R, p, P)$ , where the lowercase symbols refer to the subsystem and the uppercase symbols refer to the bath. To make a connection with surface-hopping representations of the quantum-classical Liouville equation (24), we first observe that  $A_W(\mathcal{X}_1)$  can be written as

$$A_W(\mathcal{X}_1) = \int dz_1 e^{\frac{i}{\hbar} p_1 \cdot z_1} \left\langle r_1 - \frac{z_1}{2} | \hat{A}_W(X_1) | r_1 + \frac{z_1}{2} \right\rangle, \quad 51.$$

where  $\hat{A}_W(X_1)$  is the partial Wigner transform of  $\hat{A}$ , defined in Equation 47, but with the transform taken only over the bath degrees of freedom. We may now express the subsystem operators in the adiabatic basis to obtain

$$A_W(\mathcal{X}_1) = \sum_{\alpha_1 \alpha'_1} \int dz_1 e^{\frac{i}{\hbar} p_1 \cdot z_1} \left\langle r_1 - \frac{z_1}{2} | \alpha_1; R_1 \right\rangle A_W^{\alpha_1 \alpha'_1}(X_1) \left\langle \alpha'_1; R_1 | r_1 + \frac{z_1}{2} \right\rangle, \quad 52.$$

where  $A_W^{\alpha_1 \alpha'_1}(X_1) = \langle \alpha_1; R_1 | \hat{A}_W(X_1) | \alpha'_1; R_1 \hbar \rangle$ . Inserting this expression, and its analog for  $B_W(\mathcal{X}_2)$ , into Equation 45 for  $t_1 = t_2 = 0$  we have

$$\lambda_{AB}(t) = - \sum_{\alpha_1, \alpha'_1, \alpha_2, \alpha'_2} \int \prod_{i=1}^2 dX_i A_W^{\alpha_1 \alpha'_1}(X_1) B_W^{\alpha_2 \alpha'_2}(X_2) \frac{\partial}{\partial t} \overline{W}^{\alpha'_1 \alpha_1 \alpha'_2 \alpha_2}(X_1, X_2, t), \quad 53.$$

where the matrix elements of  $W$  are given by

$$\begin{aligned} W^{\alpha'_1 \alpha_1 \alpha'_2 \alpha_2}(X_1, X_2, t) &= \int \prod_{i=1}^2 dZ_i e^{-\frac{i}{\hbar}(P_1 \cdot Z_1 + P_2 \cdot Z_2)} \frac{1}{Z_Q} \frac{1}{(2\pi\hbar)^{2\nu_h}} \\ &\times \langle \alpha'_1; R_1 | \left\langle R_1 + \frac{Z_1}{2} | e^{\frac{i}{\hbar} \hat{H} t} | R_2 - \frac{Z_2}{2} \right\rangle | \alpha_2; R_2 \rangle \\ &\times \langle \alpha'_2; R_2 | \left\langle R_2 + \frac{Z_2}{2} | e^{-\frac{i}{\hbar} \hat{H} t''} | R_1 - \frac{Z_1}{2} \right\rangle | \alpha_1; R_1 \rangle, \quad 54. \end{aligned}$$

with  $t'' = t - i\beta\hbar$ .

The quantum-classical limit of the transport coefficient is obtained by evaluating the evolution equation for the matrix elements of  $\overline{W}$  in the quantum-classical limit. This limit was taken in Reference (67), and the result is

$$\begin{aligned} & \frac{\partial}{\partial t} \overline{W}^{\alpha'_1 \alpha_1 \alpha'_2 \alpha_2}(X_1, X_2, t) \\ &= \frac{1}{2} \sum_{\beta'_1 \beta_1 \beta'_2 \beta_2} (i \mathcal{L}_{\alpha'_1 \alpha_1, \beta'_1 \beta_1}(X_1) \delta_{\alpha'_2 \beta'_2} \delta_{\alpha_2 \beta_2} - i \mathcal{L}_{\alpha'_2 \alpha_2, \beta'_2 \beta_2}(X_2) \delta_{\alpha'_1 \beta'_1} \delta_{\alpha_1 \beta_1}) \\ & \quad \times \overline{W}^{\beta'_1 \beta_1 \beta'_2 \beta_2}(X_1, X_2, t). \end{aligned} \tag{55}$$

We can also write the following equivalent forms of the evolution equation (68):

$$\begin{aligned} \frac{\partial}{\partial t} \overline{W}^{\alpha'_1 \alpha_1 \alpha'_2 \alpha_2}(X_1, X_2, t) &= \sum_{\beta'_1 \beta_1} i \mathcal{L}_{\alpha'_1 \alpha_1, \beta'_1 \beta_1}(X_1) \overline{W}^{\beta'_1 \beta_1 \alpha'_2 \alpha_2}(X_1, X_2, t) \\ &= - \sum_{\beta'_2 \beta_2} i \mathcal{L}_{\alpha'_2 \alpha_2, \beta'_2 \beta_2}(X_2) \overline{W}^{\alpha'_1 \alpha_1 \beta'_2 \beta_2}(X_1, X_2, t). \end{aligned} \tag{56}$$

We use the first equality in Equation 56, insert this into Equation 53, and move the evolution operator  $i \mathcal{L}(X_1)$  onto the  $A_W(X_1)$  dynamical variable. Next, we use the second equality in Equation 56 and formally solve the equation to obtain  $\overline{W}(X_1, X_2, t) = e^{-i \mathcal{L}(X_2)t} \overline{W}(X_1, X_2, 0)$ . Finally we substitute this form for  $\overline{W}(X_1, X_2, t)$  into Equation 53 and move the evolution operator to the dynamical variable  $B_W(X_2)$ . In the adiabatic basis, the action of the propagator  $e^{-i \mathcal{L}(X_2)t}$  on  $\hat{B}_W(X_2)$  is

$$B_W^{\alpha_2 \alpha'_2}(X_2, t) = \sum_{\beta_2 \beta'_2} (e^{-i \mathcal{L}(X_2)t})_{\alpha_2 \alpha'_2, \beta_2 \beta'_2} B_W^{\beta_2 \beta'_2}(X_2). \tag{57}$$

The result of these operations is

$$\begin{aligned} \lambda_{AB}(t) &= \sum_{\alpha_1, \alpha'_1, \alpha_2, \alpha'_2} \int \prod_{i=1}^2 dX_i (i \mathcal{L}(X_1) A_W(X_1))^{\alpha_1 \alpha'_1} \\ & \quad \times B_W^{\alpha_2 \alpha'_2}(X_2, t) \overline{W}^{\alpha'_1 \alpha_1 \alpha'_2 \alpha_2}(X_1, X_2, 0). \end{aligned} \tag{58}$$

This equation can serve as the basis for the computation of transport properties for quantum-classical systems. Note that full quantum effects are described by the initial value of  $\overline{W}$ .

These results may be immediately applied to the calculation of the reaction rate for the interconversion  $A \rightleftharpoons B$  between metastable A and B states. Letting the A and B species operators be denoted by  $\hat{N}_A$  and  $\hat{N}_B$ , Equation 58, specialized to the time-dependent rate constant for the reaction, is given by (68)

$$\begin{aligned} k_{AB}(t) &= \frac{1}{n_A^{\text{eq}}} \sum_{\alpha_1, \alpha'_1, \alpha_2, \alpha'_2} \int \prod_{i=1}^2 dX_i (i \mathcal{L}(X_1) N_A(X_1))^{\alpha_1 \alpha'_1} \\ & \quad \times N_B^{\alpha_2 \alpha'_2}(X_2, t) \overline{W}^{\alpha'_1 \alpha_1 \alpha'_2 \alpha_2}(X_1, X_2, 0). \end{aligned} \tag{59}$$

## 6.2. Quantum-Classical Linear Response Theory

Another route to the computation of transport properties is to derive expressions for transport properties using linear response theory within a quantum-classical dynamical framework (18, 33). In analogy with quantum-mechanical linear response theory (65), we assume that the mixed quantum-classical system is subjected to a time-dependent external force  $F(t)$  that couples to the observable  $\hat{A}_W^\dagger$  and is applied from the distant past where the system is in equilibrium. The partially Wigner-transformed Hamiltonian of the system in the presence of the external force is  $\hat{\mathbf{H}}_W(t) = \hat{H}_W - \hat{A}_W^\dagger F(t)$ , and the evolution equation for the density matrix takes the form

$$\frac{\partial \hat{\rho}_W(t)}{\partial t} = -(i\hat{\mathcal{L}} - i\hat{\mathcal{L}}_A F(t))\hat{\rho}_W(t), \quad 60.$$

where  $i\hat{\mathcal{L}}_A$  has a structure analogous to  $i\hat{\mathcal{L}}$  with  $\hat{A}_W^\dagger$  replacing  $\hat{H}_W$ ,  $i\hat{\mathcal{L}}_A = (\hat{A}_W^\dagger, \cdot)$ . The formal solution of this equation is found by integrating from  $t_0$  to  $t$ ,

$$\hat{\rho}_W(t) = e^{-i\hat{\mathcal{L}}(t-t_0)}\hat{\rho}_W(t_0) + \int_{t_0}^t dt' e^{-i\hat{\mathcal{L}}(t-t')} i\hat{\mathcal{L}}_A \hat{\rho}_W(t') F(t'). \quad 61.$$

Choosing  $\hat{\rho}_W(t_0)$  to be the equilibrium density matrix,  $\hat{\rho}_{We}$ , defined to be invariant under quantum-classical dynamics,  $i\hat{\mathcal{L}}\hat{\rho}_{We} = 0$ , the first term on the right-hand side of Equation 61 coincides with  $\hat{\rho}_{We}$  and is independent of  $t_0$ . We can now assume that the system with Hamiltonian  $\hat{H}_W$  is in thermal equilibrium from  $t = -\infty$  up to  $t_0$ . With this boundary condition, to first order in the external force, Equation 61 yields

$$\hat{\rho}_W(t) = \hat{\rho}_{We} + \int_{-\infty}^t dt' e^{-i\hat{\mathcal{L}}(t-t')} i\hat{\mathcal{L}}_A \hat{\rho}_{We} F(t'). \quad 62.$$

The nonequilibrium average value of any operator  $\hat{C}_W$  over the density matrix  $\hat{\rho}_W(t)$ ,  $\overline{C_W(t)} = \text{Tr}' \int dRdP \hat{C}_W \hat{\rho}_W(t)$  may be computed to determine the response of the system to the external force. The response function,

$$\phi_{CA}(t) = -\langle (\hat{A}_W^\dagger, \hat{C}_W(t)) \rangle, \quad 63.$$

has the same structure as that for a fully quantum-mechanical system in Equation 40 except that the average is taken over the quantum-classical equilibrium density, and the quantum bracket and quantum evolution are replaced by their quantum-classical analogs.

The linear response theory described above can be used to derive an expression for the reaction rate by considering the quantum-classical system subject to external time-dependent affinities that couple to microscopic variables that characterize the chemical species (69). For the interconversion between metastable A and B states,  $A \rightleftharpoons B$ , considered above, expression for the time-dependent rate coefficient is (69)

$$k_{AB}(t) = -\frac{1}{\beta n_A^{\text{eq}}} \sum_{\alpha\alpha'} \int dX N_B^{\alpha\alpha'}(X, t) (\hat{N}_A, \hat{\rho}_{W_e})_{\alpha\alpha'}, \quad 64.$$

where we again express the result using the adiabatic basis.

## 7. NONADIABATIC REACTION RATES

The determination of the mechanisms and the computation of the rates of chemical reactions are important parts of many problems in chemical and biochemical systems. If the reaction involves quantum degrees of freedom, the calculation of the reaction rate is very difficult. We now show how the quantum-classical Liouville formulation can be used to compute quantum-mechanical reaction rates.

The general expressions for the rate constants of a reaction  $A \rightleftharpoons B$  given above can serve as the starting points for the computation of the reaction rate. Although these general formulae allow one to compute the rate for any choice of reaction coordinate, below, for illustration, we consider systems where the reaction coordinate of the quantum rate process can be expressed as a function of the classical bath coordinates. Specifically, we let  $\xi(R)$  be the reaction coordinate and define A and B species variables as  $\hat{N}_B = \theta(\xi^\ddagger - \xi(R))$  and  $\hat{N}_A = \theta(\xi(R) - \xi^\ddagger)$ , where  $\xi^\ddagger$  is the location of the free energy barrier top along the  $\xi$  coordinate and  $\theta$  is the Heaviside step function.

Starting with Equation 59 and the explicit expression for the species variable in the adiabatic basis, we have

$$(i\mathcal{L}(X_1)N_A(X_1))^{\alpha_1\alpha'_1} = \frac{P_1}{M} \cdot \nabla_{R_1}\xi(R_1)\delta(\xi(R_1) - \xi^\ddagger)\delta_{\alpha_1\alpha'_1}. \quad 65.$$

The time-dependent rate coefficient may then be written as

$$k_{AB}(t) = \frac{1}{n_A^{\text{eq}}} \sum_{\alpha_1, \alpha_2, \alpha'_2} \int \prod_{i=1}^2 dX_i \delta(\xi(R_1) - \xi^\ddagger) \\ \times \frac{P_1}{M} \cdot (\nabla_{R_1}\xi(R_1))N_B^{\alpha_2\alpha'_2}(X_2, t)\overline{W}^{\alpha'_1\alpha_1\alpha'_2\alpha_2}(X_1, X_2, 0). \quad 66.$$

The high-temperature, classical-bath limit expression for  $\overline{W}$  is (67)

$$\overline{W}^{\alpha'_1\alpha_1\alpha'_2\alpha_2}(X_1, X_2, 0) = \frac{\exp(\beta(E_{\alpha'_1}(R_1) - E_{\alpha'_2}(R_1))) - 1}{\beta(E_{\alpha'_1}(R_1) - E_{\alpha'_2}(R_1))} \\ \times \rho_e^{\alpha'_1}(X_1)\delta_{\alpha'_1\alpha_2}\delta_{\alpha'_2\alpha_1}\delta(R_{12})\delta(P_{12}), \quad 67.$$

where  $\rho_e^\alpha(X_1) = Z_Q^{-1}e^{-\beta(\frac{p^2}{2M} + E_\alpha(R_1))}$  and  $Z_Q \approx \sum_\alpha \int dR dP \exp(-\beta(\frac{p^2}{2M} + E_\alpha(R)))$ . Using this expression, the time-dependent rate coefficient can be written in the

simple form,

$$k_{AB}(t) = \frac{1}{n_A^{\text{eq}}} \sum_{\alpha} \int dX \delta(\xi(R) - \xi^{\ddagger}) \times \frac{P}{M} \cdot (\nabla_R \xi(R)) N_B^{\alpha\alpha'}(X_1, t) \rho_c^{\alpha}(X). \quad 68.$$

Similarly, if we consider Equation 64 obtained from quantum-classical linear response theory and use the fact that

$$(\hat{N}_A, \hat{\rho}_{\text{We}})_{\alpha\alpha'} = -\delta(\xi(R) - \xi^{\ddagger}) \frac{\partial \xi(R)}{\partial R} \cdot \frac{\partial \rho_{\text{We}}^{\alpha\alpha'}}{\partial P}, \quad 69.$$

the time-dependent rate coefficient takes the form

$$k_{AB}(t) = \frac{1}{\beta n_A^{\text{eq}}} \sum_{\alpha\alpha'} \int dX N_B^{\alpha\alpha'}(X, t) \delta(\xi(R) - \xi^{\ddagger}) \frac{\partial \xi(R)}{\partial R} \cdot \frac{\partial \rho_{\text{We}}^{\alpha\alpha'}}{\partial P}. \quad 70.$$

If the quantum-classical equilibrium density matrix is approximated by  $\rho_{\text{We}}^{\alpha\alpha'}(X) \approx \rho_{\text{We}}^{\alpha}(X) \delta_{\alpha\alpha'}$ , we recover Equation 68.

## 7.1. Proton Transfer

Proton-transfer reactions in the condensed phase and in biochemical systems are an important class of reactions (70, 71) that pose challenges for simulation methods. In order to determine the rates and even the mechanisms of such reactions, the quantum-mechanical nature of the proton must be taken into account. Because the condensed phase environment or large biomolecule in which the proton-transfer reaction takes place may usually be treated classically to a good approximation, this type of reaction lies in the class of systems that can be treated using quantum-classical Liouville dynamics.

As an example, consider the computation of the rate of a proton-transfer reaction ( $AH-B \rightleftharpoons A^- - H^+B$ ) that takes place in a linear hydrogen-bonded complex ( $AHB$ ) dissolved in a polar solvent. A model for this type of reaction was constructed by Azzouz & Borgis (9) to mimic the proton transfer taking place in a phenol-trimethylamine complex in a liquid-state methyl chloride solvent. It has been studied using a number of different approaches (10, 72–76). Below we summarize the results for this model obtained using quantum-classical Liouville dynamics (60).

The interconversion between the covalent  $AH-B$  and ionic  $A^- - H^+B$  forms of the complex is strongly affected by the solvation structure of the surrounding polar molecules. Consequently, a convenient way to monitor the progress of the reaction is through the value of the solvent polarization,  $\xi(R) = \Delta E(R)$  (77–79),

$$\Delta E(R) = \sum_{i,a} z_a e \left( \frac{1}{|R_i^a - s|} - \frac{1}{|R_i^a - s'|} \right), \quad 71.$$

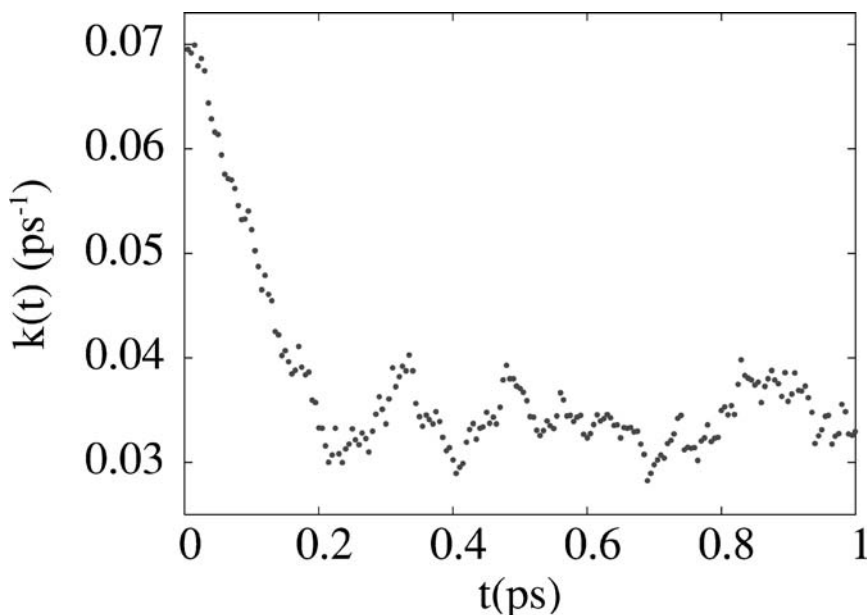
which is the difference between the solvent electrical potentials at points  $s$  and  $s'$ . Here  $z_a e$  is the charge on atom  $a$ , and the points  $s$  and  $s'$  correspond to the mean positions of the proton in the covalent and ionic forms of the complex. The sums run over all solvent molecules  $i$  and atoms  $a$ . Because this reaction coordinate depends only on the solvent positions, we may use Equation 68 to estimate the proton-transfer rate.

Equation 68 provides a well-defined formula involving sampling from the barrier top and can be used to calculate the time-dependent rate coefficient  $k_{AB}(t)$  using blue moon sampling methods (80). In addition to sampling from the barrier top, quantum-classical time evolution of  $N_B^{\alpha\alpha'}(R, P, t)$  using the methods discussed in Section 5 must be carried out to determine the reaction rate.

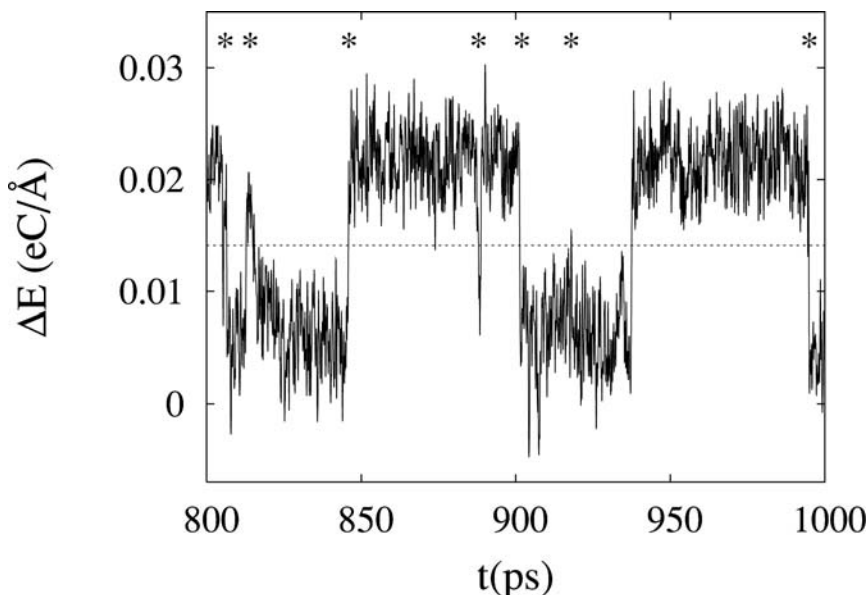
The proton-transfer relaxation rate can be determined from the plateau value of the time-dependent rate coefficient,  $k(t) = k_{AB}(t) + k_{BA}(t)$ . A plot of  $k(t)$  versus time was obtained from an average over 16,000 trajectories. From the plateau value of  $k(t)$  shown in Figure 2, a value of  $k = 0.035 \text{ ps}^{-1}$  is obtained (60).

The adiabatic rate constant can be computed in a similar manner. It decays more slowly to its plateau value ( $k_{\text{ad}} \approx 0.046 \text{ ps}^{-1}$ ). Nonadiabatic effects lower the proton-transfer rate.

It is interesting to examine the nature of the nonadiabatic quantum-classical dynamics that underlies this rate constant calculation. Figure 3 shows the evolution of the solvent polarization  $\Delta E(t)$  in a long nonadiabatic trajectory.



**Figure 2** Time-dependent rate coefficient versus time computed using nonadiabatic quantum-classical Liouville dynamics.



**Figure 3** A sample stochastic nonadiabatic trajectory is illustrated using a plot of  $\Delta E$  as a function of time. The dotted line indicates the position of the barrier top and the asterisks indicate points where nonadiabatic transitions occur.

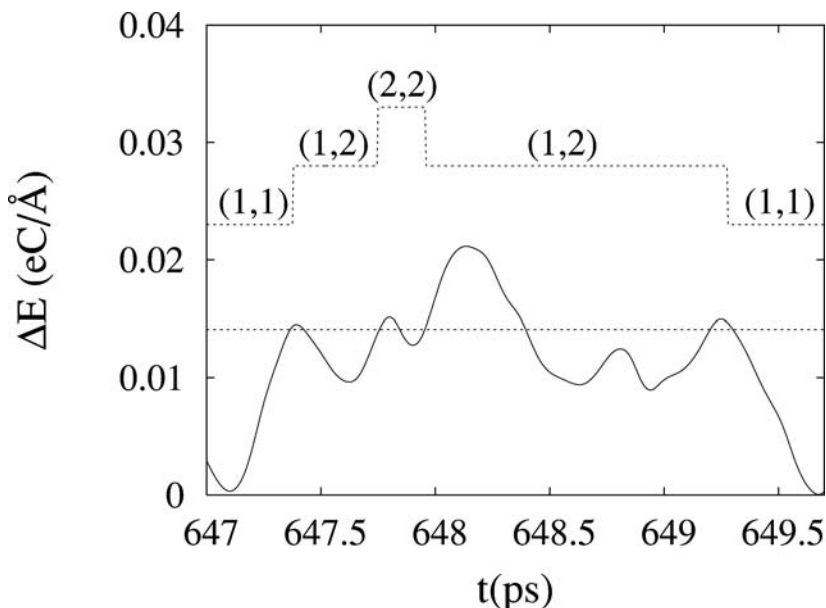
We observe that nonadiabatic transitions occur when  $\Delta E(t)$  is near the top of the barrier. This is expected because the nonadiabatic coupling matrix element is strongly peaked in this region. Not all reactive events are accompanied by nonadiabatic transitions, although nonadiabatic events are frequent.

Some crossings of the dividing surface, which are associated with nonadiabatic transitions, are immediately followed by recrossings (Figure 4).

Such nonadiabatic transitions give rise to increased recrossing of the barrier top and reduce the reaction rate. When the system makes a transition to the so-called coherent-state (1,2) or the excited-state (2,2) surface, it does not remain there long (tenths to a few picoseconds), but it returns to the ground-state (1,1) surface where it spends the majority of its time. Transitions from the ground- to the coherent-state surface and back are more frequent than transitions to and from the first excited-state surface and back. The coherent-state surface plays an important role in this rate process and this feature is different from other surface-hopping schemes that involve only propagation on single adiabatic surfaces.

## 7.2. Reactive Dynamics in a Dissipative Bath

Using the formalism discussed in Section 3, we show here how the rate constant may be computed for a quantum-classical system in contact with a dissipative bath described by stochastic dynamics. We consider a quantum two-level system, which is directly coupled to a classical quartic oscillator; this quartic oscillator is



**Figure 4** A detailed examination of a sequence of nonadiabatic transitions is presented as a plot of  $\Delta E$  as a function of time. The dotted line indicates the position of the barrier top, and the quantum state is indicated in the upper part of the figure.

in turn coupled to a dissipative bath. The Hamiltonian of the model is

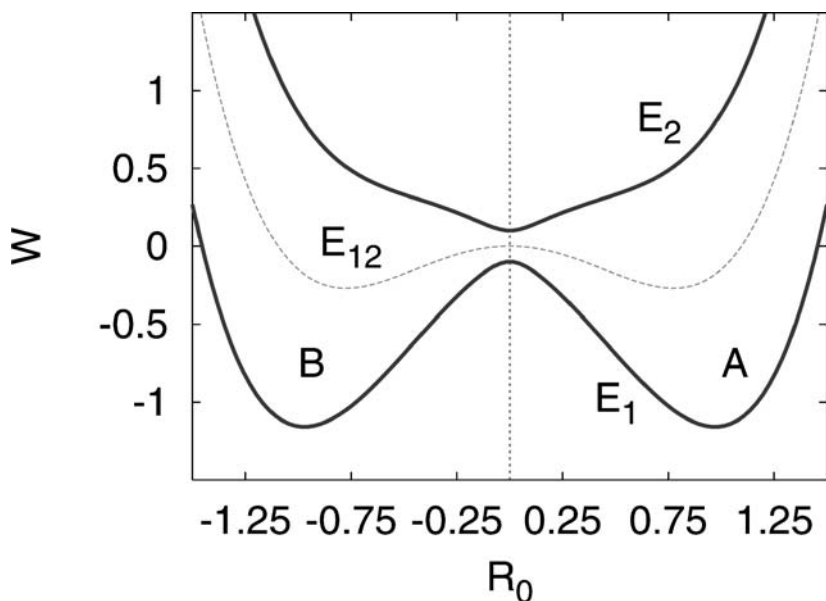
$$\hat{H}_W(R_0, P_0) = \frac{P_0^2}{2M_0} + V_q(R_0) - \hbar\Omega\hat{\sigma}_x - \hbar\gamma_0 R_0\hat{\sigma}_z \equiv \frac{P_0^2}{2M_0} + \hat{h}_W(R_0), \quad 72.$$

where  $V_q(R_0) = \frac{a}{4}R_0^4 - \frac{b}{2}R_0^2$ , and  $\hat{\sigma}_x$  and  $\hat{\sigma}_z$  are the Pauli matrices. The potential energy can be interpreted as free energy because the bath degrees of freedom have been projected out and their effects are accounted by the frictional and random forces discussed in Section 3. The evolutions of the density matrix and a dynamical variable are specified by the dissipative quantum-classical forward (Equation 17) and backward (Equation 19) Liouville operators, respectively.

The adiabatic energies  $E_{1,2}(R_0) = V_b(R_0) \mp \sqrt{\Omega^2 + \gamma^2(R_0)}$  are obtained as the eigenvalues of the Hamiltonian  $\hat{h}_W(R_0)$  with fixed values of the classical coordinate  $R_0$ . These adiabatic energies are plotted as a function of  $R_0$  in Figure 5.

The ground-state energy has a double-well structure giving rise to metastable A and B states. The excited adiabatic state has single minimum with an avoided crossing with the ground-state curve near the barrier top. The mean of these two curves figures prominently in the reactive dynamics as discussed for the proton-transfer problem.

We again take as species variables quantum-classical operators,  $\hat{N}_A = \theta(R_0)$  and  $\hat{N}_B = \theta(-R_0)$ , for species A and B, respectively, where  $\theta(R_0)$  is a Heaviside function.



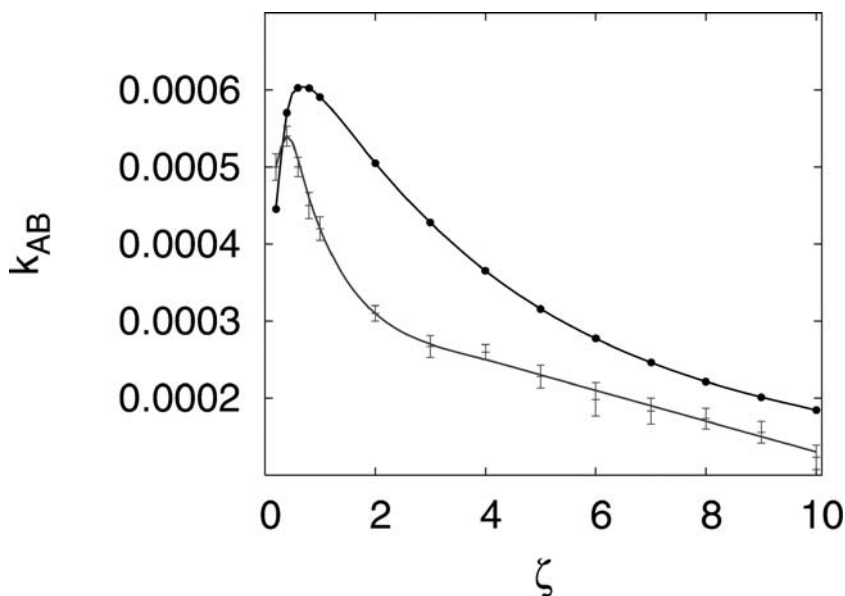
**Figure 5** Adiabatic free energy curves versus the reaction coordinate  $R_0$ . The heavy solid lines are the ground- and excited-state free energy curves, whereas the dashed line depicts the mean of these curves.

We may now directly use Equation 68 to compute the rate, taking  $\xi(R) = R_0$  and  $\xi_{\ddagger} = 0$  and using dissipative quantum-classical Liouville dynamics to evolve the species variable. The model is characterized by the parameters in the Hamiltonian and the friction constant  $\zeta$  that account for the bath dissipation. Figure 6 shows the time-dependent rate coefficients for both adiabatic and nonadiabatic dynamics including up to two quantum transitions per trajectory for  $\Omega = 0.1$ ,  $a = 3$ ,  $b = 1.8$ , and  $\gamma_0 = 1$  (the dimensionless units introduced in Reference 57) as a function of the friction.

Again, nonadiabatic effects tend to lower the rate. Both adiabatic and nonadiabatic dynamics show qualitatively similar behavior as a function of the friction, including the turnover at small values of the friction.

## 8. CONCLUSIONS

The quantum-classical Liouville equation describes the dynamics of quantum degrees of freedom interacting with a classical environment. The quantum degrees of freedom constitute an open quantum system; thus, the equation can be applied to the study of a large class of physical systems where interaction with the environment leads to decoherence and dissipation in the quantum system. The approach differs from many standard treatments of open quantum systems in that the environmental degrees of freedom are treated in detail, albeit at the level of classical



**Figure 6** Adiabatic rate constants (*black circles*) as function of friction constant  $\zeta$ . Nonadiabatic rate constants are depicted by small dots with error bars. The continuous lines are provided as guides.

mechanics. It should be noted, however, that while the environmental phase-space coordinates evolve by the classical equations of motion in the absence of coupling to the quantum subsystem, the dynamics of the combined system does not admit a Newtonian description. I have shown that it is also possible to take the full description provided by the quantum-classical Liouville equation for the density matrix,  $\hat{\rho}(R, P, t)$ , which is an operator in Hilbert space and a function of the classical phase space  $(R, P)$ , and project out all or a portion of the bath degrees of freedom to derive reduced equations akin to the Fokker-Planck or Lindblad equations. In this reduction, explicit expressions for the coupling terms are obtained in terms of classical bath correlation functions.

The quantum-classical Liouville equation should prove useful in the exploration of large, complex systems, such as condensed phase or biochemical systems, where only a few light-mass degrees of freedom need to be treated quantum mechanically, but they interact with a large many-body bath of heavy particles. In many rate processes of interest, such as electron transfer or proton transfer discussed in the text, the local polar solvent motions are responsible for the distinguishing features of the reaction mechanism. As a result, it is essential that the dynamics of these environmental degrees of freedom be treated in detail. Open quantum system equations of motion that trace out all bath details cannot capture important aspects of such dynamics.

Many different mixed quantum-classical methods for dynamics have been developed, and especially important methods in this class are surface-hopping

schemes. The solutions of the quantum-classical Liouville equation can also be cast in the form of surface-hopping trajectories. However, the nature of the trajectories and the manner in which the trajectories are assembled to compute the value of an observable differ from other surface-hopping schemes. Using an adiabatic basis to represent the quantum degrees of freedom, the trajectories that contribute to the evolution of the density matrix elements (or matrix elements of an observable) evolve either on single adiabatic surfaces or on a superposition of two surfaces, for diagonal and off-diagonal contributions, respectively. When a transition from a diagonal state to an off-diagonal state occurs, a coherence is created in the system and the trajectory contribution carries a phase factor that accounts for this coherence. Transitions from coherently coupled states to diagonal states destroy this coherence. The value of the observable or density matrix results from a weighted average over all such trajectories.

The observables of interest are often correlation functions that yield transport properties such as the diffusion and rate coefficients. I have shown how one may start with the quantum transport expressions and take the limit where the dynamics is described quantum-classically, while retaining the full equilibrium structure of the system. The challenge is then to determine ways to effectively sample from this initial distribution. Expressions for transport properties can also be derived in a quantum-classical framework using linear response theory. Perhaps the biggest challenge facing approaches based on the quantum-classical Liouville equation is the development of robust algorithms that allow the dynamics to be accurately simulated for long times. The hybrid Monte Carlo–molecular dynamics approach discussed above cannot be used to simulate the long-time dynamics of the system because of the accumulation of Monte Carlo weights along the trajectory. It is possible that an analysis of decoherence in this quantum-classical framework may provide the basis for the development of new algorithms. There are challenges for both theory and simulation in this field that will make it an interesting area of research for some time.

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## LITERATURE CITED

1. Davis EB. 1976. *Quantum Theory of Open Systems*. London: Academic
2. Weiss U. 1999. *Quantum Dissipative Systems*. Singapore: World Sci.
3. Lindblad G. 1976. On the generators of quantum dynamical semigroups. *Commun. Math. Phys.* 48:119–30
4. Gorini V, Kossakowski A, Sudarshan

- ECG. 1976. Completely positive dynamical semigroups of  $N$ -level systems. *J. Math. Phys.* 17:821–25
5. Alicki R, Lendi K. 1987. Quantum dynamical semigroups and applications. In *Lecture Notes in Physics*, Vol. 286. Berlin: Springer-Verlag
6. Redfield A. 1965. In *Advances in Magnetic Resonance*, ed. J Waugh, Vol 1. New York: Academic
7. Blum K. 1981. *Density Matrix Theory and Applications*. New York: Plenum
8. Laria D, Ciccotti G, Ferrario M, Kapral R. 1992. Molecular-dynamics study of adiabatic proton-transfer reactions in solution. *J. Chem. Phys.* 97:378–88
9. Azzouz H, Borgis D. 1993. A quantum molecular-dynamics study of proton-transfer reactions along asymmetrical H bonds in solution. *J. Chem. Phys.* 98:7361–74
10. Hammes-Schiffer S, Tully JC. 1994. Proton transfer in solution: Molecular dynamics with quantum transitions. *J. Chem. Phys.* 101:4657–67
11. Consta S, Kapral R. 1995. Dynamics of proton transfer in mesoscopic clusters. *J. Chem. Phys.* 104:4581–90
12. Tully JC. 1990. Molecular dynamics with electronic transitions. *J. Chem. Phys.* 93:1061–71
13. Tully JC. 1998. Mixed quantum-classical dynamics: mean-field and surface-hopping. In *Classical and Quantum Dynamics in Condensed Phase Simulations*, ed. BJ Berne, G Ciccotti, DF Coker, pp. 489–514. Singapore: World Sci.
14. Thompson K, Makri N. 1998. Rigorous forward-backward semiclassical formulation of many-body dynamics. *Phys. Rev. E* 59:R4729–32
15. Thoss M, Wang H, Miller WH. 2001. Generalized forward-backward initial value representation for the calculation of correlation functions in complex systems. *J. Chem. Phys.* 114:9220–35
16. Bonella S, Coker D. 2005. LAND-map, a linearized approach to nonadiabatic dynamics using the mapping formalism. *J. Chem. Phys.* 122:194102–13
17. Rabani E, Reichman D. 2004. A fully self-consistent treatment of collective fluctuations in quantum liquids. *J. Chem. Phys.* 120:1458–65
18. Kapral R, Ciccotti G. 2002. A statistical mechanical theory of quantum dynamics in classical environments. In *Bridging Time Scales: Molecular Simulations for the Next Decade*, ed. P Nielaba, M Mareschal, G Ciccotti, 605:445–72. Berlin: Springer-Verlag
19. Pechukas P. 1969. Time-dependent semiclassical scattering theory. I. Potential scattering. *Phys. Rev.* 181:166–74
20. Pechukas P. 1969. Time-dependent semiclassical scattering theory. II. Atomic collisions. *Phys. Rev.* 181:174–85
21. Wigner E. 1932. On the quantum correction for thermodynamic equilibrium. *Phys. Rev.* 40:749–59
22. Imre K, Özizmir E, Rosenbaum M, Zwiefel PF. 1967. Wigner method in quantum statistical mechanics. *J. Math. Phys.* 8:1097–108
23. Hillery M, O’Connell RF, Scully MO, Wigner EP. 1984. Distribution functions in physics: Fundamentals. *Phys. Rep.* 106:121–67
24. Kapral R, Ciccotti G. 1999. Mixed quantum-classical dynamics. *J. Chem. Phys.* 110:8919–29
25. Shiokawa K, Kapral R. 2002. Emergence of quantum-classical dynamics in an open quantum environment. *J. Chem. Phys.* 117:7852–63
26. Aleksandrov IV. 1981. The statistical dynamics of a system consisting of a classical and a quantum subsystem. *Z. Naturforsch. Teil A* 36:902–8
27. Gerasimenko VI. 1982. Dynamical equations of quantum-classical systems. *Theor. Math. Phys.* 50:49–55
28. Boucher W, Traschen J. 1988. Semiclassical physics and quantum fluctuations. *Phys. Rev. D* 37: 3522–32
29. Zhang WY, Balescu R. 1988. Statistical

- mechanics of a spin-polarized plasma. *J. Plasma Phys.* 40:199–213
30. Martens CC, Fang JY. 1996. Semiclassical-limit molecular dynamics on multiple electronic surfaces. *J. Chem. Phys.* 106:4918–30
  31. Horenko I, Salzmann C, Schmidt B, Schütte C. 2002. Quantum-classical Liouville approach to molecular dynamics: Surface hopping Gaussian phase-space packets. *J. Chem. Phys.* 117:11075–88
  32. Shi Q, Geva E. 2004. A derivation of the mixed quantum-classical Liouville equation from the influence functional formalism. *J. Chem. Phys.* 121:3393–404
  33. Nielsen S, Kapral R, Ciccotti G. 2001. Statistical mechanics of quantum-classical systems. *J. Chem. Phys.* 115:5805–15
  34. Kapral R. 2001. Quantum-classical dynamics in a classical bath. *J. Phys. Chem. A* 105:2885–89
  35. Toutounji M, Kapral R. 2001. Subsystem dynamics in mixed quantum-classical systems. *Chem. Phys.* 268:79–89
  36. Romero-Rochin V, Oppenheim I. 1989. Relaxation properties of two-level systems in condensed phases. *Physica A* 155:52–72
  37. Romero-Rochin V, Orsky A, Oppenheim I. 1989. Theory of spin-relaxation processes. *Physica A* 156:244–59
  38. Nakajima S. 1958. On quantum theory of transport phenomena. *Prog. Theor. Phys.* 20:948–59
  39. Zwanzig R. 1961. Statistical mechanics of irreversibility. In *Lectures in Theoretical Physics*, ed. WE Brittin, BW Downs, J Downs, 3:106–41. New York: Interscience
  40. Caldeira AO, Leggett AJ. 1983. Path integral approach to quantum Brownian motion. *Physica A* 121:587–616
  41. Hakim V, Ambegaokar V. 1985. Quantum theory of a free particle interacting with a linearly dissipative environment. *Phys. Rev. A* 32:423–34
  42. Grabert H, Schramm P, Ingold GL. 1988. Quantum Brownian motion: The functional integral approach. *Phys. Rep.* 168:115–207
  43. Unruh WG, Zurek WH. 1989. Reduction of a wave packet in quantum Brownian motion. *Phys. Rev. D* 40:1071–94
  44. Anastopoulos C, Halliwell JJ. 1995. Generalized uncertainty relations and long-time limits for quantum Brownian motion models. *Phys. Rev. D* 51:6870–85
  45. Hu BL, Paz JP, Zhang Y. 1992. Quantum Brownian motion in a general environment: Exact master equation with nonlocal dissipation and colored noise. *Phys. Rev. D* 45:2843–61
  46. Thompson K, Makri N. 1999. Influence functionals with semiclassical propagators in combined forwardbackward time. *J. Chem. Phys.* 110:1343–53
  47. Makri N. 1999. The linear response approximation and its lowest order corrections: An influence functional approach. *J. Phys. Chem. B* 103:2823–29
  48. Donoso A, Martens CC. 1998. Simulation of coherent nonadiabatic dynamics using classical trajectories. *J. Phys. Chem. A* 102:4291–300
  49. Wan CC, Schofield J. 2000. Mixed quantum-classical molecular dynamics: Aspects of the multithreads algorithm. *J. Chem. Phys.* 113:704754
  50. Wan CC, Schofield J. 2002. Solutions of mixed quantum-classical dynamics in multiple dimensions using classical trajectories. *J. Chem. Phys.* 116:494–506
  51. Santer M, Manthe U, Stock G. 2001. Quantum-classical Liouville description of multidimensional nonadiabatic molecular dynamics. *J. Chem. Phys.* 114:2001–12
  52. Horenko I, Weiser M, Schmidt B, Schütte C. 2004. Fully adaptive propagation of the quantum-classical Liouville equation. *J. Chem. Phys.* 120:8913–23
  53. MacKernan D, Ciccotti G, Kapral R. 2002. Sequential short-time propagation of quantum-classical dynamics. *J. Phys. Condens. Matter* 14:9069–76
  54. Tully JC. 1991. Nonadiabatic molecular dynamics. *Int. J. Quantum Chem.* 25:299–309
  55. Xiao L, Coker DF. 1994. The influence of nonadiabatic rotational transitions on the

- line shapes of the rotational Raman spectrum of H<sub>2</sub> in liquid argon. *J. Chem. Phys.* 100:8646–55
56. Mei HS, Coker DF. 1996. Quantum molecular dynamics studies of H<sub>2</sub> transport in water. *J. Chem. Phys.* 104:4755–67
57. Webster F, Rossky PJ, Friesner RA. 1991. Nonadiabatic processes in condensed matter: Semi-classical theory and implementation. *Comput. Phys. Commun.* 63:494–522
58. Webster F, Wang ET, Rossky PJ, Friesner RA. 1994. Stationary-phase surface hopping for nonadiabatic dynamics: Two-state systems. *J. Chem. Phys.* 100:4835–47
59. Sergi A, MacKernan D, Ciccotti G, Kapral R. 2003. Simulating quantum dynamics in classical environments. *Theor. Chem. Acc.* 110:49–58
60. Hanna G, Kapral R. 2005. Quantum-classical Liouville dynamics of nonadiabatic proton transfer. *J. Chem. Phys.* 122:244505–11
61. Sergi A, Kapral R. 2003. Non-adiabatic reaction rates for dissipative quantum-classical systems. *J. Chem. Phys.* 119:12776–83
62. Tuckerman M, Berne BJ, Martyna GJ. 1992. Reversible multiple time scale molecular dynamics. *J. Chem. Phys.* 97:1990–2001
63. Sergi A, Ferrario M, Costa D. 1999. Reversible integrators for basic extended system molecular dynamics. *Mol. Phys.* 97:825–32
64. Suzuki M. 1993. General decomposition theory of ordered exponentials. *Proc. Jpn. Acad. B* 69:161–66
65. Kubo R. 1957. Statistical-mechanical theory of irreversible processes. I. General theory and simple applications to magnetic and conduction problems. *J. Phys. Soc. Jpn.* 12:570–86
66. Mori H. 1965. Transport, collective motion, and Brownian motion. *Prog. Theor. Phys.* 33:423–55
67. Sergi A, Kapral R. 2004. Quantum-classical limit of quantum correlation functions. *J. Chem. Phys.* 121:7565–76
68. Kim H, Kapral R. 2005. Transport properties of quantum-classical systems. *J. Chem. Phys.* 122:214105
69. Sergi A, Kapral R. 2003. Quantum-classical dynamics of nonadiabatic chemical reactions. *J. Chem. Phys.* 118:8566–75
70. Bell RP. 1973. *The Proton in Chemistry*. London: Chapman & Hall
71. Kornyshev AA, Tosi M, Ulstrup J, eds. 1997. *Electron and Ion Transfer in Condensed Media*. Singapore: World Sci.
72. McRae RP, Schenter GK, Garrett BC, Svetlicic Z, Truhlar DG. 2001. Variational transition state theory evaluation of the rate constant for proton transfer in a polar solvent. *J. Chem. Phys.* 115:8460–80
73. Antoniou D, Schwartz SD. 1999. A molecular dynamics quantum Kramers study of proton transfer in solution. *J. Chem. Phys.* 110:465–72
74. Antoniou D, Schwartz SD. 1999. Quantum proton transfer with spatially dependent friction: Phenol–amine in methyl chloride. *J. Chem. Phys.* 110:7359–64
75. Kim SY, Hammes-Schiffer S. 2003. Molecular dynamics with quantum transitions for proton transfer: Quantum treatment of hydrogen and donor-acceptor motions. *J. Chem. Phys.* 119:4389–98
76. Yamamoto T, Miller WH. 2005. Path integral evaluation of the quantum instanton rate constant for proton transfer in a polar solvent. *J. Chem. Phys.* 122:044106
77. Marcus RA, Sutin N. 1985. Electron transfers in chemistry and biology. *Biochim. Biophys. Acta* 811:265–322
78. Warshel A. 1982. Dynamics of reactions in polar solvents. Semiclassical trajectory studies of electron-transfer and proton-transfer reactions. *J. Phys. Chem.* 86:2218–24
79. Kiefer PM, Hynes JT. 2004. Adiabatic and nonadiabatic proton transfer rate constants in solution. *Solid State Ion.* 168:219–24
80. Carter EA, Ciccotti G, Hynes JT, Kapral R. 1989. Constrained reaction coordinate dynamics for the simulation of rare events. *Chem. Phys. Lett.* 156:472–77



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