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Nonadiabatic quantum-classical reaction rates with quantum equilibrium structure

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Time correlation function expressions for quantum reaction-rate coefficients are computed in a quantum-classical limit. This form for the correlation function retains the full quantum equilibrium structure of the system in the spectral density function but approximates the time evolution of the operator by quantum-classical Liouville dynamics. Approximate analytical expressions for the spectral density function, which incorporate quantum effects in the many-body environment and reaction coordinate, are derived. The results of numerical simulations of the reaction rate are presented for a reaction model in which a two-level system is coupled to a bistable oscillator which is, in turn, coupled to a bath of harmonic oscillators. The nonadiabatic quantum-classical dynamics is simulated in terms of an ensemble of surface-hopping trajectories and the effects of the quantum equilibrium structure on the reaction rate are discussed. © *2005 American Institute of Physics*. [DOI: 10.1063/1.2110140]

I. INTRODUCTION

A variety of chemical reactions in complex and condensed phase systems, such as proton and electron transfers and photoinduced processes involving several electronic states, have an essential quantum-mechanical character that must be taken into account when constructing theoretical descriptions of the reaction rate.[1] The calculation of the rates and the elucidation of the mechanisms of such reactions present challenges for theory and simulation because of the large number of degrees of freedom that such systems possess. Various approaches have been devised to simulate such many-body quantum reactive systems. These include influence functional methods,[2,3] path-integral methods,[4] mode coupling theories,[5,6] techniques based on the initial value representation,[7–12] mapping Hamiltonian methods,[13,14] surface-hopping schemes,[15–19] nonadiabatic statistical methods,[20] multiconfiguration time-dependent Hartree with self-consistent hybrid methods,[21–23] and methods based on the quantum-classical Liouville equation.[24–29]

In reactions where the dynamics of only a few degrees of freedom need to be treated quantum mechanically, and the dynamics of the remainder can be approximated by classical mechanics, approaches based on quantum-classical equations of motion are appropriate. The quantum-classical Liouville equation specifies the time evolution of two coupled subsystems which, in the absence of coupling, evolve according to quantum and classical mechanics, respectively. Based on the linear-response theory carried out in the context of this quantum-classical framework,[30] expressions for reaction-rate coefficients have been derived and computed for model systems and proton transfer reactions.[31–34] An alternate approach to the calculation of quantum transport properties was described recently.[35,36] The starting point of this approach is the full quantum-mechanical expression for a transport property; however, the evolution of dynamical variables is carried out in the quantum-classical limit. This scheme has the advantage that the full quantum-mechanical equilibrium structure of the system, described by the spectral density function, is retained; only the quantum-mechanical time evolution is replaced by quantum-classical time evolution. The calculation of quantum equilibrium structure, although a difficult problem, is far more tractable than that of the quantum time evolution of a large many-body system. Expressions for the reaction-rate coefficient have been derived in this more general context.[36]

In this paper we show how the general expressions for quantum rate coefficients derived from the quantum-classical limit of quantum time correlation functions can be analyzed and simulated to yield the reaction rate. In Sec. II we summarize these transport coefficient expressions and cast them in a form that is suitable for our simulations. In Sec. III we specialize these expressions for the calculation of a class of nonadiabatic reaction rates and derive a number of approximate analytical expressions for the spectral density function that incorporate the quantum equilibrium structure of the reaction coordinate and the bath. Section IV presents the results of numerical simulations of the reaction rate for a two-level reactive system model for a variety of system parameters. We compare the results obtained when the reaction coordinate and bath are treated quantum mechanically with calculations that treat these degrees of freedom classically in the sampling of initial conditions. The nonadiabatic dynamics is carried out using a surface-hopping scheme that simulates the quantum-classical Liouville equation.[37] The concluding remarks of the study are given in Sec. V.

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II. GENERAL EXPRESSIONS FOR TRANSPORT PROPERTIES

The general expression for a time-dependent transport coefficient $\lambda_{AB}(t)$ is given by the flux-flux correlation function

$$\lambda_{AB}(t) = \langle \dot{\hat{A}} ; \hat{B}(t) \rangle = \frac{1}{\beta} \left\langle \frac{i}{\hbar} [\hat{B}(t), \hat{A}] \right\rangle, \tag{1}$$

where $[\cdot,\cdot]$ is the commutator and the angular brackets $\langle \hat{A} ; \hat{B} \rangle = (1/\beta)\int_0^\beta d\lambda \langle e^{\lambda \hat{H}} \hat{A} e^{-\lambda \hat{H}} \hat{B} \rangle$ denote a Kubo-transformed correlation function, with $\beta = (k_B T)^{-1}$. The equilibrium quantum canonical average is $\langle \cdots \rangle = Z_Q^{-1} \, \mathrm{Tr} \cdots e^{-\beta \hat{H}}$, where Z_Q is the partition function. In Ref. 36 we derived various equivalent expressions for transport coefficients involving the spectral density and quantum-classical dynamics. Since these expressions form the starting point of the calculations presented in this paper, in this section we give the expression that is most convenient for our calculations and establish useful symmetry properties involving the spectral density function.

Equation (1) can be written in the following equivalent form by introducing Wigner transforms that double the phase-space dimension:[36]

$$\lambda_{AB}(t) = \int d\mathcal{X} d\mathcal{X}' B_W(\mathcal{X},t) (iL_W(\mathcal{X}')(A)_W(\mathcal{X}')) \bar{W}(\mathcal{X}',\mathcal{X},0), \tag{2}$$

where $\mathcal{X} \equiv (\mathcal{R},\mathcal{P})$. The Wigner transform is defined by

$$O_W(\mathcal{X},t) = \int d\mathcal{Z} e^{(i/\hbar)\mathcal{P}\cdot\mathcal{Z}} \left\langle \mathcal{R} - \frac{\mathcal{Z}}{2} \middle| \hat{O}(t) \middle| \mathcal{R} + \frac{\mathcal{Z}}{2} \right\rangle. \tag{3}$$

The quantum Liouville operator in Wigner-transformed form is $iL_W = (2/\hbar) H_W(\mathcal{X}) \sin(\hbar \Lambda/2)$, where Λ is the negative of the Poisson bracket operator. The spectral density function is[38,39]

$$\begin{aligned} W(\mathcal{X}',\mathcal{X},t) = \frac{1}{(2\pi\hbar)^{2\nu} Z_Q} \int & d\mathcal{Z} d\mathcal{Z}' \, e^{-(i/\hbar)(\mathcal{P}\cdot\mathcal{Z} + \mathcal{P}'\cdot\mathcal{Z}')} \\ & \times \left\langle \mathcal{R} + \frac{\mathcal{Z}}{2} \middle| e^{-\beta \hat{H} - (i/\hbar)\hat{H}t} \middle| \mathcal{R}' - \frac{\mathcal{Z}'}{2} \right\rangle \\ & \times \left\langle \mathcal{R}' + \frac{\mathcal{Z}'}{2} \middle| e^{(i/\hbar)\hat{H}t} \middle| \mathcal{R} - \frac{\mathcal{Z}}{2} \right\rangle, \end{aligned} \tag{4}$$

where $\bar{W}(\mathcal{X}',\mathcal{X},0) = (1/\beta)\int_0^\beta d\lambda W(\mathcal{X}',\mathcal{X},i\hbar\lambda)$, and ν denotes the coordinate space dimension.

The transport coefficient is real for the Hermitian operators $\hat{A}$ and $\hat{B}$ and the function $\bar{W}(\mathcal{X}',\mathcal{X},t)$ is real. The spectral density $W(\mathcal{X}',\mathcal{X},t)$ satisfies the symmetry relation

$$W(\mathcal{X}',\mathcal{X},t + i\hbar\lambda)^* = W(\mathcal{X}',\mathcal{X},t + i\hbar(\beta - \lambda)). \tag{5}$$

Using this expression, we can write $\bar{W}(\mathcal{X}',\mathcal{X},0)$ as

$$\bar{W}(\mathcal{X}',\mathcal{X},0) = \frac{2}{\beta} \int_0^{\beta/2} d\lambda \, \mathrm{Re} \, W(\mathcal{X}',\mathcal{X},i\hbar\lambda). \tag{6}$$

Note that $W(\mathcal{X}',\mathcal{X},t + i\hbar\lambda)$ is real only for $\lambda = \beta/2$; namely,

$$W\left(\mathcal{X}',\mathcal{X},t + \frac{i\hbar\beta}{2}\right)^* = W\left(\mathcal{X}',\mathcal{X},t + \frac{i\hbar\beta}{2}\right). \tag{7}$$

This is also the first-order term when $\bar{W}$ is expanded in terms of β,

$$\bar{W}(\mathcal{X}',\mathcal{X},0) = W\left(\mathcal{X}',\mathcal{X},\frac{i\hbar\beta}{2}\right) + \mathcal{O}(\beta^2). \tag{8}$$

This high-temperature approximation is often appropriate in many applications.

It is convenient to write the expression for the transport coefficient as

$$\lambda_{AB}(t) = \int d\mathcal{X} B_W(\mathcal{X},t) \bar{W}_A(\mathcal{X},0), \tag{9}$$

by combining the factor involving the time-independent operator $\hat{A}_W$ and $\bar{W}$ to define

$$\bar{W}_A(\mathcal{X},0) \equiv \int d\mathcal{X}' (iL_W(\mathcal{X}')(A)_W(\mathcal{X}')) \bar{W}(\mathcal{X}',\mathcal{X},0), \tag{10}$$

which depends on only one of the two phase spaces. The relations in Eqs. (5)–(8) also hold for $W_A(\mathcal{X},t)$.

The time evolution of the operator $\hat{B}_W$ in Eq. (9) is given by the quantum Liouville operator iL_W defined above. Expanding the sine operator as power series in $\hbar$ and keeping only the first term, we obtain the classical Liouville operator, $iL_{\mathrm{cl}} = H_W \Lambda = \{, H_W\}$. If the time evolution of $\hat{B}_W$ is carried out in this approximation, the transport coefficient is given by

$$\lambda_{AB}(t) \approx \int d\mathcal{X} B_W(\mathcal{X}_{\mathrm{cl}}(t)) \bar{W}_A(\mathcal{X},0). \tag{11}$$

This formula can be used to compute transport coefficients approximately by carrying out classical evolution combined with a full quantum description of the equilibrium structure. As we shall show below, this formula reduces to one form of the rate coefficient formula using the initial value representation.[7]

A. Quantum-classical limit

Instead of carrying out the time evolution of the many-body system exactly using a full quantum description, or approximately using classical mechanics, we have shown that one may retain the full equilibrium structure in $\bar{W}$ but evolve the operator using quantum-classical dynamics.[35,36] The Wigner phase-space set of coordinates $\mathcal{X}$ is partitioned into two sets corresponding to the subsystem and bath $\mathcal{X}=(x,X)$ and the quantum-classical limit is taken. When the quantum subsystem is expressed in an adiabatic basis, the transport coefficient formula takes the form[36]

$$\begin{aligned}\lambda_{AB}(t) &= \sum_{\alpha_1,\alpha_1',\alpha,\alpha'} \int dX dX' B_W^{\alpha\alpha'}(X,t)(i\mathcal{L}(X') \\ &\quad \times A_W(X'))^{\alpha_1\alpha_1'}\bar{W}^{\alpha_1'\alpha_1\alpha'\alpha}(X',X,0) \\ &= \sum_{\alpha,\alpha'} \int dX B_W^{\alpha\alpha'}(X,t)\bar{W}_A^{\alpha'\alpha}(X,0).\end{aligned} \tag{12}$$

The spectral density function W_A, with the subsystem expressed in the adiabatic basis, is

$$\begin{aligned}W_A^{\alpha'\alpha}(X,t) = \sum_{\alpha_1\alpha_1'} \int dX'(i\mathcal{L}(X')(A)_W(X'))^{\alpha_1\alpha_1'} \frac{1}{(2\pi\hbar)^{2\nu}Z_Q} \int dZdZ' e^{-(i/\hbar)(P\cdot Z+P'\cdot Z')} < \alpha';R\left|\left\langle R+\frac{Z}{2}\right| e^{-(i/\hbar)\hat{H}t-\beta\hat{H}}\right| R' \\ -\frac{Z'}{2}\Big\rangle|\alpha_1;R' > \; < \alpha_1';R'\left|\left\langle R'+\frac{Z'}{2}\right| e^{(i/\hbar)\hat{H}t}\right| R-\frac{Z}{2}\Big\rangle|\alpha;R>.\end{aligned} \tag{13}$$

Here, $A_W^{\alpha_1\alpha_1'}(X')=\langle\alpha_1;R'|\hat{A}_W(X')|\alpha_1';R'\rangle$ and $\hat{A}_W(X')$ is the partial Wigner transform of $\hat{A}$, defined as in Eq. (3), but with the transform taken only over the bath degrees of freedom. The partial Wigner transform of the Hamiltonian is $\hat{H}_W = P^2/2M+\hat{p}^2/2m+\hat{V}_W(\hat{q},R)\equiv P^2/2M+\hat{h}_W(R)$, where $\hat{h}_W(R)$ is the Hamiltonian for the subsystem in the presence of fixed particles of the bath. The adiabatic eigenstates are the solutions of the eigenvalue problem $\hat{h}_W(R)|\alpha;R\rangle=E_\alpha(R)|\alpha;R\rangle$.

In the quantum-classical limit, $B_W^{\alpha'\alpha}(X,t)$ satisfies the following quantum-classical evolution equation:[27]

$$\frac{d}{dt}B_W^{\alpha'\alpha}(X,t) = \sum_{\beta\beta'} i\mathcal{L}_{\alpha'\alpha,\beta'\beta}(X)B_W^{\beta'\beta}(X,t). \tag{14}$$

The quantum-classical Liouville operator in the adiabatic basis $i\mathcal{L}$ is given by[27] $i\mathcal{L}_{\alpha\alpha',\beta\beta'}(X)=[i\omega_{\alpha\alpha'}(R) + iL_{\alpha\alpha'}(X)]\delta_{\alpha\beta}\delta_{\alpha'\beta'}-J_{\alpha\alpha',\beta\beta'}(X)$, where the classical evolution operator is defined as

$$iL_{\alpha\alpha'} = \frac{P}{M}\frac{\partial}{\partial R} + \frac{1}{2}[F_W^{\alpha}(R) + F_W^{\alpha'}(R)]\frac{\partial}{\partial P}, \tag{15}$$

with

$$\begin{aligned}J_{\alpha\alpha',\beta\beta'}(X) &= -\frac{P}{M}d_{\alpha\beta}\left[1+\frac{1}{2}S_{\alpha\beta}(R)\frac{\partial}{\partial P}\right]\delta_{\alpha'\beta'} \\ &\quad -\frac{P}{M}d^*_{\alpha'\beta'}\left[1+\frac{1}{2}S^*_{\alpha'\beta'}(R)\frac{\partial}{\partial P}\right]\delta_{\alpha\beta}.\end{aligned} \tag{16}$$

Here the frequency $\omega_{\alpha\alpha'}(R)\equiv[E_\alpha(R)-E_{\alpha'}(R)]/\hbar$, the Hellmann-Feynman force $F_W^{\alpha}=-\langle\alpha;R|\partial\hat{V}_W(\hat{q},R)/\partial\hat{R}|\alpha;R\rangle$, the nonadiabatic coupling matrix element is $d_{\alpha\beta} = \langle\alpha;R|\nabla_R|\beta;R\rangle$, and $S_{\alpha\beta}=(E_\alpha-E_\beta)d_{\alpha\beta}[(P/M)d_{\alpha\beta}]^{-1}$.

It should be noted that $\bar{W}_A^{\alpha'\alpha}(X,t)$ is not real and satisfies the following symmetry relations:

$$\bar{W}_A^{\alpha'\alpha}(X,t)^* = \bar{W}_A^{\alpha\alpha'}(X,t), \tag{17}$$

$$W_A^{\alpha'\alpha}(X,t+i\hbar\lambda)^* = W_A^{\alpha\alpha'}(X,t+i\hbar(\beta-\lambda)). \tag{18}$$

It follows that

$$\{\bar{W}_A^{\alpha'\alpha}(X,t) + \bar{W}_A^{\alpha\alpha'}(X,t)\}^* = \bar{W}_A^{\alpha'\alpha}(X,t) + \bar{W}_A^{\alpha\alpha'}(X,t), \tag{19}$$

and

$$\begin{aligned}&\{W_A^{\alpha'\alpha}(X,t+i\hbar\lambda) + W_A^{\alpha\alpha'}(X,t+i\hbar\lambda)\}^* \\ &\quad = W_A^{\alpha'\alpha}(X,t+i\hbar(\beta-\lambda)) + W_A^{\alpha\alpha'}(X,t+i\hbar(\beta-\lambda)).\end{aligned} \tag{20}$$

Using these properties, we may write $\lambda_{AB}(t)$ as

$$\lambda_{AB}(t) = \sum_{\alpha}\sum_{\alpha'\geqslant\alpha}(2-\delta_{\alpha'\alpha})\int dX\,\mathrm{Re}[B_W^{\alpha\alpha'}(X,t)\bar{W}_A^{\alpha'\alpha}(X,0)]. \tag{21}$$

This transport coefficient expression involves quantum-classical evolution of the operator but retains the full quantum equilibrium structure of the system. We now specialize this expression to the reaction-rate coefficient.

III. NONADIABATIC REACTION RATE

The general expressions in the previous section can be applied easily to the calculation of the thermal reaction rate for the interconversion $A \rightleftharpoons B$ between metastable A and B states. Letting $\hat{A}_W=-\hat{N}_A$ and $\hat{B}_W=\hat{N}_B$ in Eq. (21), where $\hat{N}_A$ and $\hat{N}_B$ are the species operators for the A and B metastable states, the rate coefficient can be written as

$$k_{AB}(t) = \frac{1}{n_A^{\text{eq}}} \sum_{\alpha} \sum_{\alpha' \geqslant \alpha} (2 - \delta_{\alpha'\alpha}) \int dX \times \text{Re}[N_B^{\alpha\alpha'}(X,t) \bar{W}_A^{\alpha'\alpha}(X,0)]. \tag{22}$$

This formula for the rate coefficient can be further simplified if we make use of the approximate expression for $\bar{W}$ in Eq. (8) to obtain

$$k_{AB}(t) = \frac{1}{n_A^{\text{eq}}} \sum_{\alpha} \sum_{\alpha' \geqslant \alpha} (2 - \delta_{\alpha'\alpha}) \times \int dX \times \text{Re}\left[N_B^{\alpha\alpha'}(X,t) W_A^{\alpha'\alpha}\left(X, \frac{i\hbar\beta}{2}\right)\right]. \tag{23}$$

A few remarks about the nature of the approximation in Eq. (8) are in order. The reaction rate is independent of λ for open reactive systems[40,41] or if absorbing boundaries are introduced to prevent escape from the metastable states once they are reached from the barrier top or, more rigorously, by formulating the rate coefficient expressions using projected dynamics.[42] Such an approximation will be valid if there is a large time scale separation between that for the interconversion rate process and other microscopic relaxation times in the system. Thus, although this approximation gives rise to some differences in the short-time behavior of the time-dependent rate coefficient, for long times, given reactive time scale separation, the rate coefficient extracted from the plateau value of $k_{AB}(t)$ should be given accurately. Note also that $W_A(X, i\hbar\beta/2)$ is real, which makes the calculation of the initial distribution a somewhat simpler problem.

To illustrate the application of this formula, here, we consider a class of systems where a subsystem ($\mathcal{S}$) with Hamiltonian $\hat{H}_s(\hat{p},\hat{q})$ is directly coupled to a subset ($\mathcal{N}$) of the degrees of freedom with Hamiltonian $\hat{H}_n(\hat{P}_0,\hat{R}_0)$. These special degrees of freedom are, in turn, coupled to the large number of remaining degrees of freedom which constitute a bath ($\mathcal{B}$) with Hamiltonian $\hat{H}_b(\hat{P}_b,\hat{R}_b)$. The total Hamiltonian of the system may then be written as $\hat{H}=\hat{H}_s+\hat{H}_n+\hat{V}_{sn}+\hat{H}_b+\hat{V}_{nb}\equiv\hat{H}_{sn}+\hat{H}_{b(n)}$, where $\hat{V}_{sn}$ and $\hat{V}_{nb}$ are the coupling potentials. Here we defined $\hat{H}_{sn}=\hat{H}_s+\hat{H}_n+\hat{V}_{sn}$ as the Hamiltonian for the coupled $\mathcal{S}$ and $\mathcal{N}$ subsystems and $\hat{H}_{b(n)}=\hat{H}_b+\hat{V}_{nb}\equiv\hat{P}_b^2/2M+V_{b(n)}$ as that for the bath $\mathcal{B}$ in the field of the coordinates of the $\mathcal{N}$ subsystem. Hamiltonians of this type are encountered in condensed phase systems where reactive degrees of freedom are coupled to nearby molecular groups that directly influence the reaction dynamics; these local molecular groups are coupled to the remainder of the condensed phase system that has a less direct effect on the reaction dynamics.

Depending on the system under investigation, it may be convenient to define the metastable states in terms of degrees of freedom of the quantum subsystem, classical bath, or both. In systems of the type under consideration here, it is often possible to characterize the progress of the quantum reaction in terms of a reaction coordinate that depends on the coordinates of the R_0 subsystem. The A and B species operators may be defined as $\hat{N}_A=\theta(-R_0)$ and $\hat{N}_B=\theta(R_0)$, where θ is the Heaviside step function and the dividing surface has been taken to lie at $R_0^{\ddagger}=0$. A more complex version of this kind of reaction coordinate is the solvent polarization, a nonlinear function of the solvent coordinates, that can be used to monitor the progress of a proton transfer process in the condensed phase.[34]

For this choice of species variable, $W_A^{\alpha'\alpha}(X, i\hbar\beta/2)$ can be simplified by taking advantage of the fact that integrations over all X' coordinates, with the exception of X_0', can be performed to obtain

$$W_A^{\alpha'\alpha}\left(X, \frac{i\hbar\beta}{2}\right) = \frac{1}{(2\pi\hbar)^{\nu+1} Z_Q} \int dX_0' \left\{ \delta(R_0') \frac{P_0'}{M_0} \right\} \times \int dZ dZ_0' e^{-(i/\hbar)(P\cdot Z + P_0'\cdot Z_0')} \langle \alpha' ; R_0 | \times \left\langle R + \frac{Z}{2} \right| e^{-(\beta/2)\hat{H}} \left| R_0' - \frac{Z_0'}{2} \right\rangle \times \left\langle R_0' + \frac{Z_0'}{2} \right| e^{-(\beta/2)\hat{H}} \left| R - \frac{Z}{2} \right\rangle | \alpha ; R_0 \rangle. \tag{24}$$

Furthermore, in view of the fact that the flux of the A species gives rise to a delta function in R_0, the integration over X_0' can be easily performed to get

$$W_A^{\alpha'\alpha}\left(X, \frac{i\hbar\beta}{2}\right) = \frac{1}{(2\pi\hbar)^{\nu} Z_Q} \frac{i\hbar}{M_0} \int dZ dZ_0' \delta'(Z_0') e^{-(i/\hbar)P\cdot Z} \times \langle \alpha' ; R_0 | \left\langle R + \frac{Z}{2} \right| e^{-(\beta/2)\hat{H}} \left| -\frac{Z_0'}{2} \right\rangle \times \left\langle \frac{Z_0'}{2} \right| e^{-(\beta/2)\hat{H}} \left| R - \frac{Z}{2} \right\rangle | \alpha ; R_0 \rangle. \tag{25}$$

In this equation the adiabatic eigenstates depend only on R_0 since the $\mathcal{S}$ subsystem couples directly only to the coordinates R_0.

In order to use Eq. (23) to compute the rate, we need to carry out quantum-classical evolution of $N_B^{\alpha\alpha'}(X,t)$, as given by Eq. (14), and sample from an initial quantum distribution with weights determined by $W_A^{\alpha'\alpha}(X, i\hbar\beta/2)$. The imaginary time propagators in $W_A^{\alpha'\alpha}(X, i\hbar\beta/2)$ can, in principle, be computed using quantum path integral methods[4] or through the use of approximations, such as linearization methods.[13,14,43,44] Below we show how one may construct approximate analytical expressions for this quantity that are useful in carrying out the numerical computations in the next section.

A. Parabolic barrier region treated explicitly

In activated rate processes a knowledge of the dynamics in the barrier region is crucial for the calculation of the rate constant. In most circumstances the potential is locally parabolic in the barrier region and such harmonic barrier approximations have been employed frequently in the study of quantum and classical reaction rates.[9,45–49] Here we show how the local harmonic character of the barrier along the reaction coordinate R_0 can be exploited to construct an approximate form for $W_A^{\alpha'\alpha}(X,i\hbar\beta/2)$.

We assume that the imaginary time propagator may be written as $\exp(-\beta\hat{H}/2)\approx\exp(-\beta\hat{H}_{sn}/2)\exp(-\beta\hat{H}_{b(n)}/2)$, so that expression (25) for $W_A^{\alpha'\alpha}(X,i\hbar\beta/2)$ is given by

$$W_A^{\alpha'\alpha}\left(X,\frac{i\hbar\beta}{2}\right)=\frac{1}{Z_Q}\frac{i}{2\pi M_0}\int dZ_0dZ_0'\delta'(Z_0')e^{-(i/\hbar)P_0\cdot Z_0}\times\langle\alpha';R_0|\left\langle R_0+\frac{Z_0}{2}\right|e^{-(\beta/2)\hat{H}_{sn}}\left|-\frac{Z_0'}{2}\right\rangle\times\left\langle\frac{Z_0'}{2}\right|e^{-(\beta/2)\hat{H}_{sn}}\left|R_0-\frac{Z_0}{2}\right\rangle\times|\alpha;R_0\rangle\rho_b(P_b,R_b;R_0), \tag{26}$$

where $\rho_b(P_b,R_b;R_0)$ is proportional to the Wigner transform of the canonical equilibrium density matrix for the bath in the field of the R_0 coordinates

$$\rho_b(P_b,R_b;R_0)=\frac{1}{(2\pi\hbar)^{\nu-1}}\int dZ_be^{-(i/\hbar)P_b\cdot Z_b}\times\left\langle R_b+\frac{Z_b}{2}\right|e^{-\beta\hat{H}_{b(n)}}\left|R_b-\frac{Z_b}{2}\right\rangle. \tag{27}$$

Next, we single out the barrier region around $R_0=0$ for special consideration. Separating the potential energy in the $\hat{H}_n$ Hamiltonian into harmonic and remainder terms, $\hat{V}_n(\hat{R}_0)=-(1/2)M_0\omega^{\ddagger 2}R_0^2+\delta\hat{V}_n(\hat{R}_0)$, with $\omega^{\ddagger}$ the frequency at the barrier top, we can write $\hat{H}_n=\hat{H}_{h0}+\delta\hat{V}_n(\hat{R}_0)$. The Hamiltonian $\hat{H}_{sn}$ then takes the form $\hat{H}_{sn}=\hat{H}_{h0}+\hat{h}_{sn}$, where $\hat{h}_{sn}=\hat{H}_s+\hat{V}_{sn}+\delta\hat{V}_n(\hat{R}_0)$ is the Hamiltonian of $\mathcal{S}$ in the field of the fixed coordinates of the $\mathcal{N}$ subsystem with the harmonic part of the potential removed. The eigenstates of $\hat{h}_{sn}$ are $|\alpha;R_0\rangle$ as above but the eigenvalues, denoted by $\varepsilon_\alpha(R_0)$, are related to the $E_\alpha(R_0)$ introduced earlier by $E_\alpha(R_0)=\varepsilon_\alpha(R_0)-(1/2)M_0\omega^{\ddagger 2}R_0^2$. Taking $\exp(-\beta\hat{H}_{sn}/2)\approx\exp(-\beta\hat{H}_{h0}/2)\exp(-\beta\hat{h}_{sn}/2)$, the matrix elements in Eq. (26) can be written as

$$\langle\alpha';R_0|\left\langle R_0+\frac{Z_0}{2}\right|e^{-(\beta/2)\hat{H}_{sn}}\left|-\frac{Z_0'}{2}\right\rangle\left\langle\frac{Z_0'}{2}\right|e^{-(\beta/2)\hat{H}_{sn}}\left|R_0-\frac{Z_0}{2}\right\rangle|\alpha;R_0\rangle=\int dR_0'dR_0''\langle\alpha';R_0|\left\langle R_0+\frac{Z_0}{2}\right|e^{-(\beta/2)\hat{h}_{sn}}|R_0'\rangle\times\langle R_0'|e^{-(\beta/2)\hat{H}_{h0}}\left|-\frac{Z_0'}{2}\right\rangle\left\langle\frac{Z_0'}{2}\right|e^{-(\beta/2)\hat{H}_{h0}}|R_0''\rangle\langle R_0''|e^{-(\beta/2)\hat{h}_{sn}}\left|R_0-\frac{Z_0}{2}\right\rangle|\alpha;R_0\rangle=\left\langle R_0+\frac{Z_0}{2}\right|e^{-(\beta/2)\hat{H}_{h0}}\left|-\frac{Z_0'}{2}\right\rangle\times\left\langle\frac{Z_0'}{2}\right|e^{-(\beta/2)\hat{H}_{h0}}\left|R_0-\frac{Z_0}{2}\right\rangle\langle\alpha';R_0|e^{-(\beta/2)\hat{h}_{sn}[R_0+(Z_0/2)]}e^{-(\beta/2)\hat{h}_{sn}[R_0-(Z_0/2)]}|\alpha;R_0\rangle. \tag{28}$$

Using the representation of $\hat{h}_{sn}$ in the adiabatic basis, $e^{-(\beta/2)\hat{h}_{sn}(R_0)}=\sum_\alpha|\alpha;R_0\rangle e^{-(\beta/2)\varepsilon_\alpha(R_0)}\langle\alpha;R_0|$, we obtain

$$\langle\alpha';R_0|e^{-(\beta/2)\hat{h}_{sn}[R_0+(Z_0/2)]}e^{-(\beta/2)\hat{h}_{sn}[R_0-(Z_0/2)]}|\alpha;R_0\rangle=\sum_{\alpha_1,\alpha_2}e^{-(\beta/2)\{\varepsilon_{\alpha_2}[R_0+(Z_0/2)]+\varepsilon_{\alpha_1}[R_0-(Z_0/2)]\}}\times\left\langle\alpha';R_0|\alpha_2;R_0+\frac{Z_0}{2}\right\rangle\left\langle\alpha_2;R_0+\frac{Z_0}{2}|\alpha_1;R_0-\frac{Z_0}{2}\right\rangle\times\left\langle\alpha_1;R_0-\frac{Z_0}{2}|\alpha;R_0\right\rangle. \tag{29}$$

Expressing the matrix elements in a Taylor series in Z_0

$$\left\langle\alpha';R_0|\alpha_2;R_0+\frac{Z_0}{2}\right\rangle=\delta_{\alpha'\alpha_2}+\frac{Z_0}{2}d_{\alpha'\alpha_2}+\cdots \tag{30}$$

and retaining up to the first-order terms in Z_0 we find

$$\langle\alpha';R_0|e^{-(\beta/2)\hat{h}_{sn}[R_0+(Z_0/2)]}e^{-(\beta/2)\hat{h}_{sn}[R_0-(Z_0/2)]}|\alpha;R_0\rangle=e^{-\beta\varepsilon_\alpha(R_0)}\left[\delta_{\alpha\alpha'}+\frac{Z_0}{2}O_{\alpha'\alpha}(R_0)d_{\alpha'\alpha}(R_0)+\cdots\right], \tag{31}$$

where

$$O_{\alpha'\alpha}(R_0)=[1-e^{-(\beta/2)\varepsilon_{\alpha'\alpha}(R_0)}]^2, \tag{32}$$

with $\varepsilon_{\alpha'\alpha}=\varepsilon_{\alpha'}-\varepsilon_\alpha$.

Finally, using the well-known expression for the matrix elements of the harmonic-oscillator imaginary time propagator,

$$\langle R_0|e^{-(\beta/2)\hat{H}_{h0}}|R_0'\rangle=\sqrt{\frac{2aM_0u}{\pi\sin u}}\exp\left[-aM_0u\left\{-(R_0+R_0')^2\tan\frac{u}{2}+(R_0-R_0')^2\cot\frac{u}{2}\right\}\right], \tag{33}$$

where $u\equiv\beta\hbar\omega^{\ddagger}/2$ and $a=(2\beta\hbar^2)^{-1}$, and carrying out the integrations over Z_0 and Z_0', we have

$$W_A^{\alpha'\alpha}\left(X,\frac{i\hbar\beta}{2}\right)=\frac{1}{2\pi\hbar Z_Q}\frac{1}{\cos^2 u}\sqrt{\frac{2M_0u'}{\beta\hbar^2\pi}}e^{-(2M_0u'/\beta\hbar^2)R_0^2}\times\frac{P_0}{M_0}e^{-(\beta P_0^2/2M_0u')}F_{\alpha'\alpha}(R_0)\rho_b(P_b,R_b;R_0),\tag{34}$$

where $u'\equiv u\cot u$ and

$$F_{\alpha'\alpha}(R_0)=e^{-\beta\varepsilon_\alpha(R_0)}\left(\delta_{\alpha'\alpha}+\frac{1}{2}\left(1-\frac{\beta P_0^2}{M_0u'}\right)\frac{i\hbar}{P_0}d_{\alpha'\alpha}O_{\alpha'\alpha}\right).\tag{35}$$

The off-diagonal contribution is imaginary and the imaginary part of $N_B^{\alpha\alpha'}(X,t)$ contributes to the rate. Note that $\mathrm{Im}\{N_B^{\alpha\alpha'}(X,t)W_A^{\alpha'\alpha}(X,i\hbar\beta/2)+N_B^{\alpha'\alpha}(X,t)W_A^{\alpha\alpha'}(X,i\hbar\beta/2)\}=0$. The exact expression for $W_A^{\alpha'\alpha}$ also satisfies this relation.

B. Initial value representation

It is interesting to consider a limiting case where the subsystem $\mathcal{S}$ is absent and $\mathcal{N}$ is a double-well oscillator. In this case we can suppress the quantum indices $F_{\alpha'\alpha}=e^{-\beta V_n(0)}$ and Eq. (34) reduces to

$$W_A\left(X,\frac{i\hbar\beta}{2}\right)=\frac{1}{Z_Q}\frac{\omega^{\ddagger}e^{-\beta V_n(0)}}{2\pi\sin 2u}\sqrt{\frac{2M_0u'}{\beta\hbar^2\pi}}e^{-(2M_0u'/\beta\hbar^2)R_0^2}\times\frac{\beta P_0}{M_0u'}e^{-(\beta P_0^2/2M_0u')}\rho_b(P_b,R_b;R_0).\tag{36}$$

If quantum-classical evolution is approximated by classical evolution, the rate coefficient is given by

$$k_{AB}(t)=\frac{1}{n_A^{\mathrm{eq}}}\int dXN_B(X_{\mathrm{cl}}(t))W_A\left(X,\frac{i\hbar\beta}{2}\right).\tag{37}$$

This is the expression for the rate coefficient obtained by Wang *et al.*[7] using the initial value representation. This formula can also be obtained directly from Eq. (11) by specializing it to the reaction rate for a double-well oscillator coupled to a harmonic bath. More accurate treatments using the initial value representation that are not restricted to classical evolution have been implemented.[8,9,11]

We have derived Eq. (37), or the more general Eq. (11), from the classical limit of the quantum Liouville operator. It has been noted previously[43,50–52] that Eq. (37) can be obtained without invoking semiclassical approximation by linearizing the exact path-integral expression.

C. Barrier region not treated explicitly

Instead of singling out the harmonic part of the potential in the barrier region, one may simply write the Hamiltonian $\hat{H}_{sn}$ as $\hat{H}_{sn}=\hat{P}_0^2/2M_0+\hat{h}_0$. Then, approximating the propagator in Eq. (26) as $e^{\beta\hat{H}_{sn}/2}\approx e^{\beta\hat{P}_0^2/4M_0}e^{\beta\hat{h}_0/2}$ and carrying out a series of calculations similar to those outlined above, we obtain

$$W_A^{\alpha'\alpha}\left(X,\frac{i\hbar\beta}{2}\right)=\frac{1}{2\pi\hbar Z_Q}\sqrt{\frac{2M_0}{\beta\hbar^2\pi}}e^{-(2M_0/\beta\hbar^2)R_0^2}\times\frac{P_0}{M_0}e^{-(\beta P_0^2/2M_0)}\mathcal{F}_{\alpha'\alpha}(R_0)\rho_b(P_b,R_b;R_0),\tag{38}$$

where $\mathcal{F}_{\alpha'\alpha}$ has a definition similar to that of $F_{\alpha'\alpha}$ but with $\varepsilon_\alpha(R_0)$ replaced by $E_\alpha(R_0)$, the full adiabatic energy of the $\mathcal{S}$ subsystem in the field of the R_0 coordinates,

$$\mathcal{F}_{\alpha'\alpha}(R_0)=e^{-\beta E_\alpha(R_0)}\left(\delta_{\alpha'\alpha}+\frac{1}{2}\left(1-\frac{\beta P_0^2}{M_0}\right)\frac{i\hbar}{P_0}d_{\alpha'\alpha}\mathcal{O}_{\alpha'\alpha}\right).\tag{39}$$

Here $\mathcal{O}_{\alpha'\alpha}$ has a definition analogous to that of $O_{\alpha'\alpha}$ with $\varepsilon_\alpha(R_0)$ replaced by $E_\alpha(R_0)$. In Eq. (38) the nature of the barrier potential, harmonic or not, is accounted for in the adiabatic energies.

D. Classical treatment of R_0 and bath coordinates

Noting that $\lim_{\beta\to 0}\sqrt{(2M_0/\beta\hbar^2\pi)}e^{-(2M_0/\beta\hbar)^2R_0^2}=\delta(R_0)$ and using the classical limit form of Eq. (27), $\rho_b^{\mathrm{cl}}(P_b,R_b;R_0)=e^{-\beta H_{b(n)}}$, Eq. (38) reduces to

$$\begin{aligned}W_A^{\alpha'\alpha}\left(X,\frac{i\hbar\beta}{2}\right)&=\frac{1}{2\pi\hbar Z_Q}\left\{\delta(R_0)\frac{P_0}{M_0}\right\}e^{-\beta P_0^2/2M_0}\mathcal{F}_{\alpha'\alpha}(R_0)\\&\quad\times\rho_b^{\mathrm{cl}}(P_b,R_b{:}R_0)\\&=\frac{1}{(2\pi\hbar)^{\nu}Z_Q}\delta(R_0)\frac{P_0}{M_0}e^{-\beta H_\alpha(R,P)}\\&\quad\times\left(\delta_{\alpha'\alpha}+\frac{1}{2}\left(1-\frac{\beta P_0^2}{M_0}\right)\frac{i\hbar}{P_0}d_{\alpha'\alpha}\mathcal{O}_{\alpha'\alpha}\right),\end{aligned}\tag{40}$$

where $H_\alpha(R,P)=P^2/2M+E_\alpha(R)$. This result may be substituted into Eq. (23) to obtain an expression for the rate coefficient. Keeping the diagonal contribution to $W_A^{\alpha'\alpha}$ (the dominant contribution as we show below) we find

$$k_{AB}(t)=\frac{1}{n_A^{\mathrm{eq}}(2\pi\hbar)^{\nu}Z_Q}\sum_\alpha\int dXN_B^{\alpha\alpha}(X,t)\times\left\{\delta(R_0)\frac{P_0}{M_0}\right\}e^{-\beta H_\alpha(R,P)}.\tag{41}$$

This result agrees with that obtained earlier using quantum-classical linear-response theory. In the classical limit, the partition function can be obtained as $Z_Q\approx(1/2\pi\hbar)^{\nu}\Sigma_\alpha\int dX\exp[-\beta H_\alpha(X)]$.

The corresponding transition state value can be obtained from the $t=0$ value of this expression. We have

$$k_{AB}^{TST} = \frac{1}{\sqrt{2\pi M_0 \beta}} \frac{\sum_\alpha e^{-\beta W_\alpha(0)}}{\sum_\alpha \int dR_0 \theta(-R_0) e^{-\beta W_\alpha(0)}}, \tag{42}$$

where $W_\alpha(R_0)$ is the potential of mean force defined by $P_u e^{-\beta W_\alpha(R_0)} = \int dR_b e^{-\beta E_\alpha(R)} / \Sigma_\alpha \int dR e^{-\beta E_\alpha(R)}$ with P_u the uniform probability density of R_0.[34]

IV. NONADIABATIC SIMULATION RESULTS

As a specific example of the type of system discussed in general terms above, we consider a two-level system coupled to a quartic bistable oscillator which is in turn coupled to a heat bath of independent harmonic oscillators. The Hamiltonian operator, expressed in a diabatic basis $\{|\uparrow\rangle, |\downarrow\rangle\}$, is[31,32]

$$\mathbf{H} = \begin{pmatrix} V_n(R_0) + \hbar\gamma_0 R_0 & -\hbar\Omega \\ -\hbar\Omega & V_n(R_0) - \hbar\gamma_0 R_0 \end{pmatrix} + \left(\frac{P_0^2}{2M_0} + \sum_{j=1}^{\nu-1} \frac{P_j^2}{2M_j} + \frac{M_j\omega_j^2}{2}\left(R_j - \frac{c_j}{M_j\omega_j^2} R_0 \right)^2 \right) \mathbf{I}. \tag{43}$$

The coupling to the two-level system is given by $\hbar\gamma(R_0) = -\hbar\gamma_0 R_0$. The nonlinear quartic oscillator $V_n(R_0) = -M_0 \omega^{\ddagger 2} R_0^2/2 + AR_0^4/4$ is bilinearly coupled to $\nu-1$ independent one-dimensional harmonic oscillators. The bilinear coupling is characterized by an Ohmic spectral density $J(\omega) = \pi \Sigma c_j^2/(2M_j\omega_j)\delta(\omega-\omega_j)$, where $c_j = (\xi\hbar\Delta\omega M_j)^{1/2}\omega_j$, $\omega_j = -\omega_c \ln(1 - j\Delta\omega/\omega_c)$ and $\Delta\omega = \omega_c/(\nu-1)(1-e^{-\omega_{\max}/\omega_c})$ with ω_c the cut-off frequency.[3]

The adiabatic states are obtained by the diagonalization of the two-level system Hamiltonian in Eq. (43) and are given by

$$|1;R_0\rangle = \frac{1}{\mathcal{N}}[(1+G)|\uparrow\rangle + (1-G)|\downarrow\rangle]$$

$$|2;R_0\rangle = \frac{1}{\mathcal{N}}[-(1-G)|\uparrow\rangle + (1+G)|\downarrow\rangle], \tag{44}$$

where $\mathcal{N}(R_0) = \sqrt{2(1+G^2(R_0))}$ with $G(R_0) = (\gamma_0 R_0)^{-1}[-\Omega + \sqrt{\Omega^2 + \gamma_0^2 R_0^2}]$. The corresponding adiabatic energies are

$$E_\alpha(R) = -\frac{1}{2}M_0\omega^{\ddagger 2}R_0^2 + \frac{1}{4}AR_0^4 \mp \hbar\sqrt{\Omega^2 + \gamma_0^2 R_0^2} + \sum_{j=1}^{\nu-1} \frac{1}{2} M_j \omega_j^2 \left(R_j - \frac{c_j}{M_j\omega_j^2} R_0 \right)^2, \tag{45}$$

where the sign is minus for the ground state and plus for the excited state. In the notation of the previous section, we have $\varepsilon_\alpha(R) = (1/4)AR_0^4 \mp \hbar\sqrt{\Omega^2 + \gamma_0^2 R_0^2}$ and $V_{b(n)}(R) = \Sigma_{j=1}^{\nu-1}(1/2)M_j\omega_j^2[R_j - (c_j/M_j\omega_j^2)R_0]^2$ for the two-level Hamiltonian.

In Fig. 1, we plot free-energy profiles for two parameter sets. While the ground and excited states are similar to each other for small values of γ_0, their shapes differ for larger γ_0 values. Since the anharmonicity of the reaction coordinate potential increases with increasing γ_0, the explicit treatment of the barrier region in the parabolic approximation is useful only for small γ_0 values. When the ground and excited states have different structures in the barrier region, we can utilize the form given in Eq. (38).

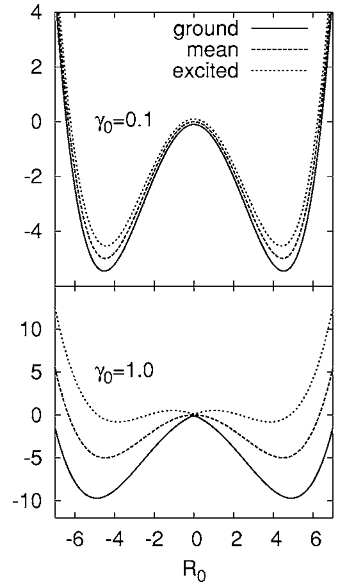

FIG. 1. Free-energy profiles for the ground and excited states. The mean of these two states is also plotted. Parameter values: $\gamma_0=0.1$ (upper), $\gamma_0=1$ (lower), $A=0.05$, $\omega^\ddagger=0.1$, and $\Omega=0.1$.

For small γ_0 where the ground and excited potential surfaces are nearly parallel, the partition function for the reactant state $n_A^{\mathrm{eq}} Z_Q$ can be approximated by that for the mean surface and is given by

$$(n_A^{\mathrm{eq}} Z_Q)^{-1} \approx e^{\beta V_r} \sinh(\beta\hbar\omega_r/2) \prod_{j=1} 2\sinh(\beta\hbar\omega_j/2), \tag{46}$$

with ω_r the well frequency and V_r the bare potential at the bottom of the well. Using the high-temperature form for Eq. (46) in the formula (42) for k_{AB}^{TST} we obtain

$$k_{AB}^{TST} \approx \frac{\omega_r}{2\pi} \frac{e^{\beta V_r}(e^{-\beta\hbar\Omega} + e^{\beta\hbar\Omega})}{2}, \tag{47}$$

which will be used to scale the results presented in the figures. When the coupling between the two-level system and the quartic oscillator is negligible, the value of Ω vanishes and k_{AB}^{TST} becomes the well-known value of $\omega_r e^{\beta V_r}/2\pi$. For the current symmetric oscillator, and for the parameter range under investigation, $\omega_r \approx \sqrt{2}\omega^\ddagger$. Using these results, the transmission coefficient $\kappa_{AB}(t) = k_{AB}(t)/k_{AB}^{TST}$ takes the form

$$\kappa_{AB}(t) = \sum_\alpha \sum_{\alpha' \geqslant \alpha} (2 - \delta_{\alpha'\alpha}) \int dX \, \mathrm{Re}[N_B^{\alpha\alpha'}(X,t) w^{\alpha'\alpha}(X)], \tag{48}$$

where

$$w^{\alpha'\alpha}(X)=\frac{2u}{\sin 2u}\frac{\sinh u_r}{u_r}\frac{P_0}{M_0}\sqrt{\frac{\pi M_0\beta}{2u'}}\frac{F_{\alpha'\alpha}(R_0)}{\sum_\alpha e^{-\beta\varepsilon_\alpha(0)}}$$
$$\times G_a\left(R_0;\frac{2M_0u'}{\beta\hbar^2}\right)G_a\left(P_0;\frac{\beta}{2M_0u'}\right)$$
$$\times\prod_{j=1} G_a\left(R_j-\frac{c_jR_0}{M_j\omega_j^2};\frac{\beta}{2u''_j}M_j\omega_j^2\right)G_a\left(P_j;\frac{\beta}{2M_ju''_j}\right), \tag{49}$$

and the Gaussian function G_a is defined by $G_a(x;b) = \sqrt{b/\pi}\exp(-bx^2)$ while $u''_j=u_j\coth u_j$ with $u_j=\beta\hbar\omega_j/2$. We label results obtained using this formula that treats the reaction coordinate and bath quantum mechanically as QRB.

The limit where the reaction coordinate and bath are treated classically can be obtained by using Eq. (40) for $W_A^{\alpha'\alpha}$. The diagonal contribution in this limit is

$$w_{crb}^{\alpha'\alpha}(X)=\frac{P_0}{M_0}\sqrt{\frac{\pi M_0\beta}{2}}\delta(R_0)\frac{e^{-\beta E_\alpha(0)}}{\sum_\alpha e^{-\beta E_\alpha(0)}}\delta_{\alpha'\alpha}$$
$$\times G_a\left(P_0;\frac{\beta}{2M_0}\right)\prod_{j=1} G_a\left(R_j;\frac{\beta}{2}M_j\omega_j^2\right)G_a\left(P_j;\frac{\beta}{2M_j}\right). \tag{50}$$

When this expression is used to compute the rate coefficient, we obtain the diagonal contribution to the rate obtained earlier using quantum-classical linear-response theory.[31] Results obtained using this formula that treats the reaction coordinate and bath classically are labeled as CRB.

A. Numerical results

Dimensionless units with time scaled by the cut-off frequency ω_c are used in the calculations described below.[31] In particular, $t\leftarrow t\omega_c$, $R_0\leftarrow\sqrt{M_0\omega_c/\hbar}R_0$, $\beta\leftarrow\beta\hbar\omega_c$. We set $A=0.05$ and $\omega^{\ddagger}=1$ and the bare barrier height of the $V_n(R_0)$ potential is 5 in these dimensionless units. The number of bath harmonic oscillators is $N_b=100$ so that $\nu=101$. We have taken $\omega_{\max}=3$.

The simulation scheme for carrying out quantum-classical molecular dynamics has been described in detail earlier[31,33,34,37] and only a few comments on the method are needed here. The initial distribution of X is sampled from weights determined from Eq. (49) using Gaussian random numbers with corresponding mean deviations. The constant energy quantum-classical trajectories are constructed using the sequential short-time propagation algorithm.[37] The total time of the calculation is divided into a fixed number of time slices. The most natural choice for the length of the time slice is the molecular-dynamics simulation time step, which is $dt=0.01$. The phase-space coordinates are propagated adiabatically within a time step and the phase factor is computed if the evolution is on the mean of two adiabatic surfaces. At the end of each time step, the probabilities of acceptance or rejection of a quantum transition are determined.

First, we compare the QRB and CRB results for two temperatures in Fig. 2. For high temperatures ($\beta=0.1$), both the QRB and CRB results are indistinguishable, except at very short times. The CRB results for the rate constant are nonzero and equal to the transition state theory value of the rate constant at $t=0+$ as in classical theories of the reaction rate. The QRB results for the time dependent rate constant are zero at $t=0$, typical of quantum rate processes.[42] For the lower of the two temperatures, because of quantum effects which are included through initial distributions, one sees that the QRB results yield a larger rate constant than the CRB simulations. The quantum rate enhancement is similar to that seen in other studies.[4,7,53] In Fig. 3, the QRB transmission coefficients are plotted versus the Kondo parameter ξ and show the well-known turnover behavior.

In Fig. 4, the temperature dependence of the QRB and CRB transmission coefficients is shown. The QRB rate constant increases strongly with β while the CRB rate constant varies only weakly with β.

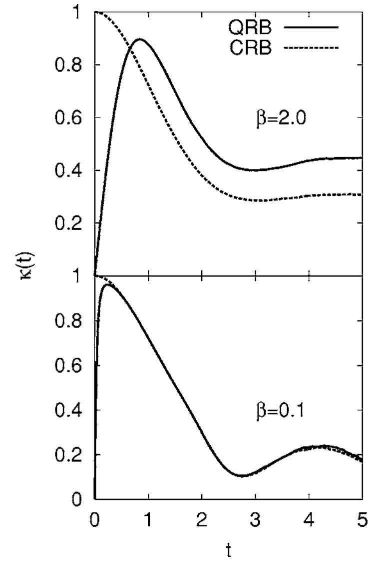

FIG. 2. Comparison of quantum-classical nonadiabatic dynamics for cases where the equilibrium structure of the reaction coordinate and bath is treated quantum mechanically (QRB) with those where the equilibrium structure of the reaction coordinate and bath is treated classically (CRB). Parameter values: $\beta=2$ (upper), $\beta=0.1$ (lower), $\gamma_0=0.1$, $\Omega=0.1$, and $\xi=3$.

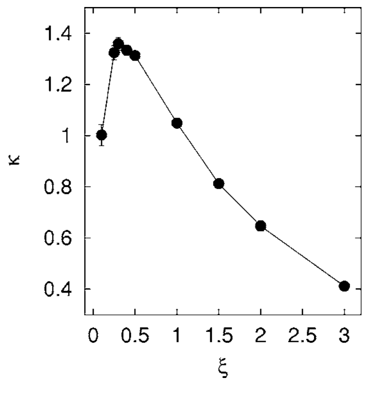

FIG. 3. QRB transmission coefficient vs ξ for $\beta=2$, $\gamma_0=0.1$, and $\Omega=0.1$.

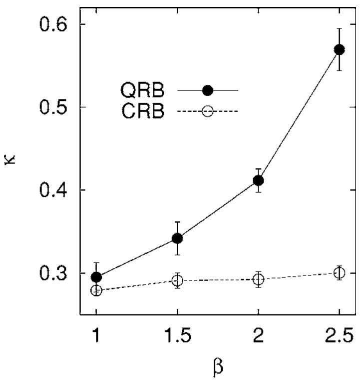

FIG. 4. Transmission coefficient vs β for $\gamma_0=0.1$, $\Omega=0.1$, and $\xi=3$.

In Figs. 5 and 6, we plot the QRB transmission coefficients versus γ_0 and Ω, respectively. In Fig. 5, adiabatic and nonadiabatic rate constants and the contributions to these quantities arising from the ground and excited states are compared. The adiabatic and nonadiabatic rate constants do not differ much for small values of γ_0. As γ_0 increases, nonadiabatic rates decrease while adiabatic rates increase. As seen in Fig. 1, the recrossing effect decreases for the steeper ground-state potential-energy surface with a larger value of γ_0 while it increases for the flatter excited-state surface. The increase of ground-state contributions to adiabatic rate constants is larger than the decrease of the excited-state contributions and the total rate increases with the value of γ_0 in the adiabatic limit. When the nonadiabatic transitions are allowed, this effect is reduced since ground- and excited-state contributions are not independent of each other. As a result, the ground-state contributions do not change much while the excited-state contributions decrease in a manner similar to those in the adiabatic limit; hence, the inclusion of nonadiabatic effects significantly reduces the rate constant with respect to that obtained using adiabatic dynamics.[31] In Fig. 6, we plot a graph similar to that in Fig. 5 but for various values of Ω. Unlike the variations seen as function of γ_0, the magnitude of Ω is found to have little effect on the rate constants. This can be understood from the fact that the shape of the free-energy profile does not depend strongly on the value of Ω.

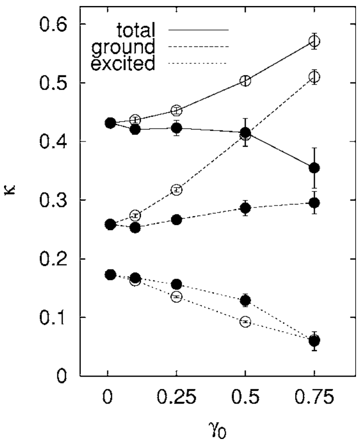

FIG. 5. QRB transmission coefficient vs γ_0 for $\beta=2$, $\Omega=0.1$, and $\xi=3$. Nonadiabatic (closed circles) and adiabatic (open circles) results are compared.

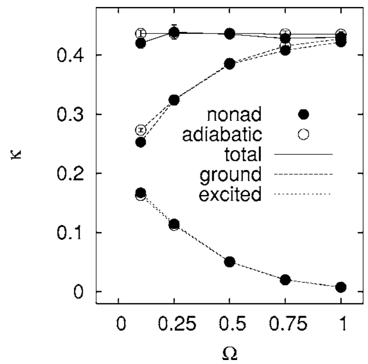

FIG. 6. QRB transmission coefficient vs Ω for $\beta=2$, $\gamma_0=0.1$, and $\xi=3$. Nonadiabatic (closed circles) and adiabatic (open circles) results are compared.

V. CONCLUSIONS

The results presented above show how nonadiabatic contributions to chemical reaction rates can be computed from time correlation function expressions that retain the quantum equilibrium structure of the system and employ a quantum-classical description of the dynamics. Thus, the computational method combines Liouville surface-hopping dynamics with sampling from quantum equilibrium initial conditions. As such, the method differs from conventional surface-hopping schemes[15] for reactive dynamics both in the nature of the time evolution of operators and in the way the trajectories are sampled to compute the reaction rate.

The simulation results reported above utilized various approximate analytical expressions for the spectral density function that describes the quantum equilibrium structure. In some circumstances, especially for low temperatures, effects arising from the quantum equilibrium structure lead to important modifications of the reaction rate. To treat more general and complex molecular-reacting systems one should resort to numerical schemes to compute the equilibrium structure, similar to those that have been employed in recent computations using the initial value representation.[54–56]

The general formulas for transport coefficients, and more specifically the reaction-rate coefficient, should be useful in a variety of contexts involving other choices for the reaction coordinate or operators different from the specific chemical species variables used in this study. The results should allow one to investigate nonadiabatic effects on a variety of quantum-chemical rate processes.

ACKNOWLEDGMENT

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