Transport properties of quantum-classical systems

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Correlation function expressions for calculating transport coefficients for quantum-classical systems are derived. The results are obtained by starting with quantum transport coefficient expressions and replacing the quantum time evolution with quantum-classical Liouville evolution, while retaining the full quantum equilibrium structure through the spectral density function. The method provides a variety of routes for simulating transport coefficients of mixed quantum-classical systems, composed of a quantum subsystem and a classical bath, by selecting different but equivalent time evolution schemes of any operator or the spectral density. The structure of the spectral density is examined for a single harmonic oscillator where exact analytical results can be obtained. The utility of the formulation is illustrated by considering the rate constant of an activated quantum transfer process that can be described by a many-body bath reaction coordinate. © *2005 American Institute of Physics*. [DOI: 10.1063/1.1925268]

I. INTRODUCTION

Transport properties, such as diffusion and viscosity coefficients or rate constants, are some of the most basic quantities that are used to characterize the dynamical behavior systems. For equilibrium systems statistical mechanics provides well-defined expressions for transport coefficients in terms of time integrals of flux–flux correlation functions.[1] The evaluation of these correlation function expressions entails sampling over an equilibrium ensemble of initial conditions and time evolution of dynamical variables or operators. While such calculations are routinely carried out for classical many-body systems, their evaluation for quantum-mechanical systems is a very challenging problem. Part of the difficulty stems from the fact that no methods exist for solving the time-dependent quantum equations of motion for a large condensed phase system; thus, in contrast to classical systems, direct calculations of transport properties by quantum molecular dynamics are rarely attempted.[2]

In some instances a full quantum-mechanical treatment is unnecessary. In many applications the quantum character of certain degrees of freedom (termed the subsystem) must be accounted for, while the remainder of the system (bath) with which they interact may be approximated by classical mechanics.[3–6] For example, a decomposition of this type is appropriate for a subsystem composed of light particles, like electrons or protons, interacting with a solvent of heavy molecules. Thus, transport properties, such as quantum-particle diffusion coefficients, rate coefficients of proton or electron transfer processes and vibrational relaxation rate coefficients in the condensed phase, may be computed in a mixed quantum-classical framework.

Assuming the dynamics is described by the quantum-classical Liouville equation,[7–12] the linear response theory yields expressions for transport coefficients[6,13] the evaluation of which entails carrying out quantum-classical evolution of operators and sampling over the quantum-classical equilibrium density. More general expressions for time correlation functions have been derived by taking the quantum-classical limit of the quantum correlation function.[14] The evaluation of these correlation functions involves forward and backward quantum-classical time evolution of the operators and sampling based on the spectral density that retains the full quantum equilibrium structure. The structure of the propagator in this correlation function expression is reminiscent of that in the forward-backward influence functional technique,[15] and it may be possible to employ similar approximations to the propagator in a quantum-classical context. Linearization methods have also been used to incorporate nonadiabatic effects in the evaluation of time correlation functions.[16–19]

In this article we construct general quantum-classical expressions for transport properties, starting from a full quantum treatment of the entire many-body system. The transport coefficient formulas again retain the full quantum equilibrium structure of the system and entail carrying out quantum-classical Liouville evolution of operators but allow much more flexibility in how the quantum-classical limit is taken. The resulting expressions are flexible enough to be applicable to a variety of transport properties, including the calculation of the rate constants of activated nonadiabatic reactions.

In Sec. II we derive a number of general expressions for quantum transport coefficients in terms of Wigner transforms. These expressions provide a convenient separation of the quantum equilibrium structure in the spectral density function from the time evolution of operators. While formally exact, the results in this section do not provide a computationally tractable route to the evaluation of transport properties because of the instabilities inherent in the simulations of the Wigner-transformed expressions. The spectral density function plays a central role in this formulation. To

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examine its structure, in Sec. III we consider a single harmonic oscillator in thermal equilibrium for which this function can be analytically determined. In Sec. IV we employ the results of Ref. 14 to take the quantum-classical limit of the evolution equation for the spectral density and use this expression to obtain computationally useful expressions for the transport coefficients. The results are illustrated by deriving expressions that can be used to simulate the rates of activated nonadiabatic chemical reactions. The conclusions of the study are given in Sec. V.

II. QUANTUM TRANSPORT COEFFICIENTS

For a quantum-mechanical system in thermal equilibrium a transport coefficient λ_{AB} may be determined from the time integral of a flux–flux correlation function,[1]

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

where $\hat{j}_A = \dot{\hat{A}} = (i/\hbar)[\hat{H}, \hat{A}]$ is the flux of $\hat{A}$, with an analogous expression for $\hat{j}_B$, $[\cdot,\cdot]$ 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 simulations it is often convenient to consider the time-dependent transport coefficient defined as the finite time integral of the flux–flux correlation function,

$$\lambda_{AB}(t) = \int_0^t dt' \langle \hat{j}_A; \hat{j}_B(t') \rangle = \langle \hat{A}; \hat{B}(t) \rangle = \frac{1}{\beta} \left\langle \frac{i}{\hbar} [\hat{B}(t), \hat{A}] \right\rangle, \tag{2}$$

where we assumed $[\hat{B}, \hat{A}] = 0$.[20] The transport coefficient may then be obtained from the plateau value of $\lambda_{AB}(t)$.[21]

A. General expressions for $\lambda_{AB}(t)$

We first establish some general relations for the transport coefficients that will prove useful in the subsequent reduction to the quantum-classical limit. Writing the second equality in Eq. (2) in detail and inserting arbitrary time variables t_1 and t_2, we can write the transport coefficient $\lambda_{AB}(t)$ as

$$\begin{aligned} \lambda_{AB}(t) &= \frac{1}{\beta Z_Q} \int_0^\beta d\lambda \, \mathrm{Tr} (\dot{\hat{A}}(-i\hbar\lambda) \hat{B}(t) e^{-\beta \hat{H}}) \\ &= \frac{1}{\beta Z_Q} \int_0^\beta d\lambda \, \mathrm{Tr} (\dot{\hat{A}}(t_1 - i\hbar\lambda) \\ &\quad \times e^{(i/\hbar)\hat{H}t'} \hat{B}(t_2) e^{-(i/\hbar)\hat{H}t'} e^{-\beta \hat{H}}), \end{aligned} \tag{3}$$

where $t' \equiv t + t_1 - t_2$. To insert the times t_1 and t_2, we used the fact that the time evolution of an operator $\hat{O}$ is given by $\hat{O}(t) = e^{(i/\hbar)\hat{H}t} \hat{O} e^{-(i/\hbar)\hat{H}t}$.

We partition the entire quantum system into a subsystem plus bath so that the Hamiltonian is the sum of the kinetic energy operators of the subsystem and bath and the potential energy of the entire system, $\hat{H} = \hat{P}^2/2M + \hat{p}^2/2m + \hat{V}(\hat{q}, \hat{Q})$, where lowercase and uppercase symbols refer to the subsystem and bath, respectively. In Sec. IV we shall show how the transport coefficients for a system partitioned in this way can be evaluated in the quantum-classical limit. For the present, however, it is convenient to first take a Wigner transform [22] over all degrees of freedom, subsystem plus bath, and later single out the subsystem and bath degrees of freedom for different treatments. Introducing a coordinate representation $\{\mathcal{Q}\} = \{q\}\{Q\}$ of the operators in Eq. (3) (calligraphic symbols are used to denote variables for the entire system), making a change of variables, $\mathcal{Q}_1 = \mathcal{R}_1 - \mathcal{Z}_1/2$, $\mathcal{Q}_2 = \mathcal{R}_1 + \mathcal{Z}_1/2$, etc., and then expressing the matrix elements in terms of the Wigner transforms of the operators, we have

$$\begin{aligned} \lambda_{AB}(t) = \frac{1}{\beta} \int_0^\beta d\lambda \int d\mathcal{X}_1 d\mathcal{X}_2 (\dot{A})_W(\mathcal{X}_1, t_1) B_W(\mathcal{X}_2, t_2) \\ \times \frac{1}{(2\pi\hbar)^{2\nu} Z_Q} \int d\mathcal{Z}_1 d\mathcal{Z}_2 e^{-(i/\hbar)(\mathcal{P}\cdot\mathcal{Z}_1 + \mathcal{P}_2 \cdot \mathcal{Z}_2)} \\ \times \left\langle \mathcal{R}_1 + \frac{\mathcal{Z}_1}{2} \middle| e^{(i/\hbar)\hat{H}(t' + i\hbar\lambda)} \middle| \mathcal{R}_2 - \frac{\mathcal{Z}_2}{2} \right\rangle \\ \times \left\langle \mathcal{R}_2 + \frac{\mathcal{Z}_2}{2} \middle| e^{-\beta\hat{H} - i/\hbar \hat{H}(t' + i\hbar\lambda)} \middle| \mathcal{R}_1 - \frac{\mathcal{Z}_1}{2} \right\rangle. \end{aligned} \tag{4}$$

In writing this equation we used the fact that the matrix element of the operator $\hat{O}(t)$ can be expressed in terms of its Wigner transform $O_W(\mathcal{X}, t)$ as

$$\begin{aligned} &\left\langle \mathcal{R} - \frac{\mathcal{Z}}{2} \middle| \hat{O}(t) \middle| \mathcal{R} + \frac{\mathcal{Z}}{2} \right\rangle \\ &\quad = \frac{1}{(2\pi\hbar)^\nu} \int d\mathcal{P} e^{-(i/\hbar)\mathcal{P}\cdot\mathcal{Z}} O_W(\mathcal{X}, t), \end{aligned} \tag{5}$$

where ν is the coordinate-space dimension and the Wigner transform is defined by

$$O_W(\mathcal{X}, t) = \int d\mathcal{Z} e^{(i/\hbar)\mathcal{P}\cdot\mathcal{Z}} \left\langle \mathcal{R} - \frac{\mathcal{Z}}{2} \middle| \hat{O}(t) \middle| \mathcal{R} + \frac{\mathcal{Z}}{2} \right\rangle. \tag{6}$$

We use the notation $\mathcal{R} = (r, R)$, $\mathcal{P} = (p, P)$ and $\mathcal{X} = (r, R, p, P)$ where again the lowercase symbols refer to the subsystem and the uppercase symbols refer to the bath

We define the spectral density by

$$\begin{aligned} W(\mathcal{X}_1, \mathcal{X}_2, t) = \frac{1}{(2\pi\hbar)^{2\nu} Z_Q} \int d\mathcal{Z}_1 d\mathcal{Z}_2 e^{-i/\hbar(\mathcal{P}\cdot\mathcal{Z}_1 + \mathcal{P}_2\cdot\mathcal{Z}_2)} \\ \times \left\langle \mathcal{R}_1 + \frac{\mathcal{Z}_1}{2} \middle| e^{(i/\hbar)\hat{H}t} \middle| \mathcal{R}_2 - \frac{\mathcal{Z}_2}{2} \right\rangle \\ \times \left\langle \mathcal{R}_2 + \frac{\mathcal{Z}_2}{2} \middle| e^{-\beta\hat{H} - (i/\hbar)\hat{H}t} \middle| \mathcal{R}_1 - \frac{\mathcal{Z}_1}{2} \right\rangle, \end{aligned} \tag{7}$$

which satisfies the following relations:

$$W(\mathcal{X}_1, \mathcal{X}_2, t)^* = W(\mathcal{X}_2, \mathcal{X}_1, -t), \tag{8}$$

$$W(\mathcal{X}_1, \mathcal{X}_2, t - i\beta\hbar) = W(\mathcal{X}_1, \mathcal{X}_2, t)^*. \tag{9}$$

The last equality may be written as

$$\tilde{W}(\mathcal{X}_1,\mathcal{X}_2,-\omega)=e^{-\beta\hbar\omega}\tilde{W}(\mathcal{X}_1,\mathcal{X}_2,\omega), \tag{10}$$

where the Fourier transform is defined as $\tilde{f}(\omega)=\int_{-\infty}^{\infty}dt e^{i\omega t}f(t)$. If we let

$$\overline{W}(\mathcal{X}_1,\mathcal{X}_2,t)=\frac{1}{\beta}\int_0^\beta d\lambda W(\mathcal{X}_1,\mathcal{X}_2,t+i\hbar\lambda), \tag{11}$$

we can write the transport coefficient as

$$\lambda_{AB}(t)=\int d\mathcal{X}_1 d\mathcal{X}_2(\dot{A})_W(\mathcal{X}_1,t_1)B_W(\mathcal{X}_2,t_2) \times\overline{W}(\mathcal{X}_1,\mathcal{X}_2,t+t_1-t_2). \tag{12}$$

Equation (12) involves the quantity $(\dot{A})_W(\mathcal{X}_1,t_1)$ which is not easy to compute. Starting with the Heisenberg equation of motion, $\dot{\hat{A}}=(i/\hbar)[\hat{H},\hat{A}]$, and taking its Wigner transform we have,

$$\begin{aligned}\frac{d}{dt}A_W(\mathcal{X}_1,t_1)&=\frac{i}{\hbar}(H_W(\mathcal{X}_1)e^{(\hbar\Lambda_1/2i)}A_W(\mathcal{X}_1,t_1) \\ &\quad -A_W(\mathcal{X}_1,t_1\ e^{(\hbar\Lambda_1/2i)}H_W(\mathcal{X}_1)) \\ &=\frac{2}{\hbar}H_W(\mathcal{X}_1)\sin\left(\frac{\hbar\Lambda_1}{2}\right)A_W(\mathcal{X}_1,t_1) \\ &\equiv iL_W(\mathcal{X}_1)A_W(\mathcal{X}_1,t_1).\end{aligned} \tag{13}$$

Here, the Wigner-transformed Hamiltonian is $H_W(\mathcal{X})=\mathcal{P}^2/2M+V_W(\mathcal{R})$ and Λ is the negative of the Poisson-bracket operator,

$$\Lambda=\vec{\nabla}_{\mathcal{P}}\cdot\vec{\nabla}_{\mathcal{R}}-\vec{\nabla}_{\mathcal{R}}\cdot\vec{\nabla}_{\mathcal{P}}, \tag{14}$$

where the direction of an arrow indicates the direction in which the operator acts. To obtain this equation we used the relation $(\hat{A}\hat{B})_W=\hat{A}_W(\mathcal{X})e^{(\hbar\Lambda/2i)}\hat{B}_W(\mathcal{X})$ for the Wigner transform of a product of operators.[22]

Using the properties of the phase-space derivatives of the Wigner-transformed Hamiltonian and integration by parts, one may establish that

$$\begin{aligned}&\int d\mathcal{X}(iL_W(\mathcal{X})A_W(\mathcal{X},t))G(\mathcal{X}) \\ &\quad=-\int d\mathcal{X}\ A_W(\mathcal{X},t))iL_W(\mathcal{X})G(\mathcal{X}),\end{aligned} \tag{15}$$

for any function $G(\mathcal{X})$. Making use of this result, it follows that the transport coefficient can be cast in the form

$$\begin{aligned}\lambda_{AB}(t)&=-\int d\mathcal{X}_1 d\mathcal{X}_2 A_W(\mathcal{X}_1,t_1)B_W(\mathcal{X}_2,t_2) \\ &\quad\times iL_W(\mathcal{X}_1)\overline{W}(\mathcal{X}_1,\mathcal{X}_2,t+t_1-t_2) \\ &\equiv-\int d\mathcal{X}_1 d\mathcal{X}_2 A_W(\mathcal{X}_1,t_1)B_W(\mathcal{X}_2,t_2) \\ &\quad\times\frac{\partial}{\partial t}\overline{W}(\mathcal{X}_1,\mathcal{X}_2,t+t_1-t_2),\end{aligned} \tag{16}$$

where we have written the evolution equation for $\overline{W}$ as

$$\frac{\partial}{\partial t}\overline{W}(\mathcal{X}_1,\mathcal{X}_2,t)=iL_W(\mathcal{X}_1)\overline{W}(\mathcal{X}_1,\mathcal{X}_2,t). \tag{17}$$

Equivalent forms of the evolution equation can be derived as follows: Taking complex conjugates on both side of Eq. (17) gives

$$\frac{\partial}{\partial t}\overline{W}(\mathcal{X}_2,\mathcal{X}_1,-t)=iL_W(\mathcal{X}_1)\overline{W}(\mathcal{X}_2,\mathcal{X}_1,-t), \tag{18}$$

where we used the relations $iL_W^*=iL_W$ and Eq. (6). If we then exchange variables $\mathcal{X}_1\leftrightarrow\mathcal{X}_2$ and $t\leftrightarrow -t$, we get

$$\frac{\partial}{\partial t}\overline{W}(\mathcal{X}_1,\mathcal{X}_2,t)=-iL_W(\mathcal{X}_2)\overline{W}(\mathcal{X}_1,\mathcal{X}_2,t). \tag{19}$$

An alternative proof of these expressions is given in Appendix A. From these results it also follows that[23]

$$\frac{\partial}{\partial t}\overline{W}(\mathcal{X}_1,\mathcal{X}_2,t)=\tfrac{1}{2}(iL_W(\mathcal{X}_1)-iL_W(\mathcal{X}_2))\overline{W}(\mathcal{X}_1,\mathcal{X}_2,t). \tag{20}$$

From the last equality in Eq. (2), the transport coefficient can be written in a form involving the commutator of $\hat{A}$ and $\hat{B}(t)$. Performing a set of manipulations similar to those used above, we may show that $\lambda_{AB}(t)$ is also given by,

$$\begin{aligned}\lambda_{AB}(t)&=\frac{i}{\hbar\beta}\int d\mathcal{X}_1 d\mathcal{X}_2 A_W(\mathcal{X}_1,t_1)B_W(\mathcal{X}_2,t_2) \\ &\quad\times[W(\mathcal{X}_1,\mathcal{X}_2,t-i\hbar\beta+t_1-t_2) \\ &\quad-W(\mathcal{X}_1,\mathcal{X}_2,t+t_1-t_2)].\end{aligned} \tag{21}$$

Comparing this result with Eq. (16), we have

$$\begin{aligned}\frac{\partial}{\partial t}\overline{W}(\mathcal{X}_1,\mathcal{X}_2,t)&=-\frac{i}{\hbar\beta}[W(\mathcal{X}_1,\mathcal{X}_2,t-i\hbar\beta)-W(\mathcal{X}_1,\mathcal{X}_2,t)] \\ &=-\frac{2}{\hbar\beta}\mathrm{Im}W(\mathcal{X}_1,\mathcal{X}_2,t),\end{aligned} \tag{22}$$

where Im stands for the imaginary part, and we used Eq. (9). Thus, we have

$$\begin{aligned}\lambda_{AB}(t)&=\frac{2}{\hbar\beta}\int d\mathcal{X}_1 d\mathcal{X}_2 A_W(\mathcal{X}_1,t_1)B_W(\mathcal{X}_2,t_2) \\ &\quad\times\mathrm{Im}W(\mathcal{X}_1,\mathcal{X}_2,t+t_1-t_2).\end{aligned} \tag{23}$$

We may choose the times t_1 and t_2 to yield various forms for the correlation functions. For example, setting $t_1=0$ and $t_2=t$, Eq. (16) reduces to

$$\begin{aligned}\lambda_{AB}(t)&=-\int d\mathcal{X}_1 d\mathcal{X}_2 A_W(\mathcal{X}_1)B_W(\mathcal{X}_2,t) \\ &\quad\times iL_W(\mathcal{X}_1)\overline{W}(\mathcal{X}_1,\mathcal{X}_2,0) \\ &=\int d\mathcal{X}_1 d\mathcal{X}_2(iL_W(\mathcal{X}_1)A_W(\mathcal{X}_1))B_W(\mathcal{X}_2,t) \\ &\quad\times\overline{W}(\mathcal{X}_1,\mathcal{X}_2,0).\end{aligned} \tag{24}$$

Finally, we observe that the initial value of W,

$$W(\mathcal{X}_1,\mathcal{X}_2,0) = e^{-(2i/\hbar)\mathcal{P}_2\cdot(\mathcal{R}_2-\mathcal{R}_1)} \times \frac{1}{Z_Q(\sqrt{2}\pi\hbar)^{2\nu}} \int d\mathcal{Z} e^{-(i/\hbar)(\mathcal{P}_1-\mathcal{P}_2)\cdot\mathcal{Z}} \times \left\langle 2\mathcal{R}_2 - \mathcal{R}_1 - \frac{\mathcal{Z}}{2} \middle| e^{-\beta\hat{H}} \middle| \mathcal{R}_1 - \frac{\mathcal{Z}}{2} \right\rangle, \quad (25)$$

involves only a single propagator, while $\overline{W}$ defined in Eq. (11), which appears in the transport coefficient expression, still involves two imaginary time propagators.

The Wigner representation results obtained in this section involved no approximations and are as difficult to solve for a many-body quantum system as the original expressions for the transport coefficients. However, as we shall see in Sec. IV, they form a convenient starting point for approximations leading to quantum-classical limit expressions.

III. SPECTRAL DENSITY FOR A HARMONIC OSCILLATOR

The spectral density W plays a central role in the expressions for the transport coefficients and its calculation is a difficult task, even at $t=0$. Consequently, it is instructive to examine its structure for a single harmonic oscillator where a complete analytical solution may be obtained.

For a single harmonic oscillator, the system Hamiltonian is given by $\hat{H}=(1/2)m\omega^2(\hat{p}'^2+\hat{q}^2)$, where m and ω denote mass and frequency, respectively, and we have rescaled the momentum operator as $\hat{p}' \equiv \hat{p}/(m\omega)$. The propagator for this Hamiltonian is well known[24] and is given by

$$\langle q|e^{-\beta\hat{H}}|q'\rangle = \left(\frac{a}{2\pi\sinh\beta\hbar\omega}\right)^{1/2} \exp\left[-\frac{a}{2}\{(q^2+q'^2)\times\coth\beta\hbar\omega - 2qq'\,\mathrm{csch}\,\beta\hbar\omega\}\right], \quad (26)$$

with $a=m\omega/\hbar$. Substituting Eq. (26) into Eq. (7) specialized to the single harmonic oscillator and integrating over z_1 and z_2, we obtain

$$W(x_1,x_2,t) = \left(\frac{a}{\pi}\right)^2 \exp[-a\{(r_1^2+r_2^2+p_1'^2+p_2'^2)c_1 + (r_1r_2+p_1'p_2')c_2(t) + (r_1p_2'-p_1'r_2)c_3(t)\}], \quad (27)$$

where $x=(r,p)$ and

$$c_1 = \coth(\beta\hbar\omega/2),$$
$$c_2(t) = -2(c_1\cos\omega t + i\sin\omega t), \quad (28)$$
$$c_3(t) = 2(c_1\sin\omega t - i\cos\omega t).$$

From this explicit expression for $W(x_1,x_2,t)$ one can easily see that the relations in Eqs. (8) and (9) are satisfied.

The initial value of W is

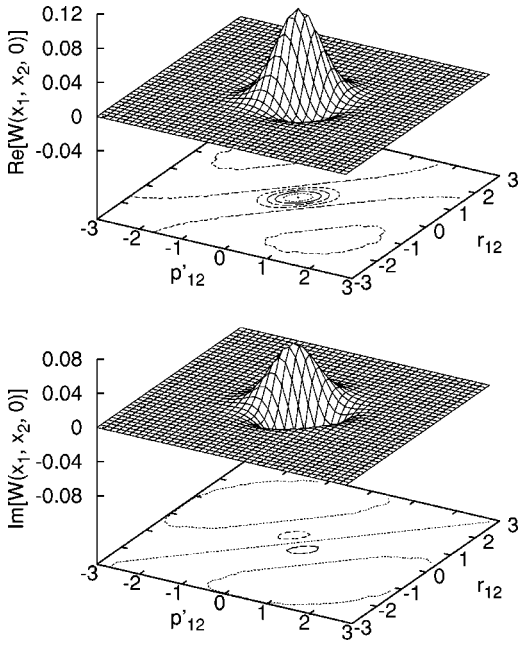

FIG. 1. Real (upper panel) and imaginary (lower) parts of $W(x_1,x_2,0)$ as a function of r_{12} and p'_{12} for $r_c=p'_c=1$ and $\beta\hbar\omega=1$. Results are reported in terms of the dimensionless units $(m\omega/\hbar)^{1/2}r$ and $(m\omega/\hbar)^{1/2}p'$.

$$W(x_1,x_2,0) = \left(\frac{a}{\pi}\right)^2 \exp[-a\{((r_1-r_2)^2+(p_1'-p_r'^2)^2)c_1 - 2i(r_1p_2'-p_1'r_2)\}]. \quad (29)$$

The phase factor couples the position and momentum variables in the two x_1 and x_2 phase spaces. If we define $x_{12}=x_1-x_2$ and $x_c=(x_1+x_2)/2$, with a similar change of variables for the momenta, Eq. (29) can be written as

$$W(x_1,x_2,0) = \left(\frac{a}{\pi}\right)^2 \exp[-a\{(r_{12}^2+p_{12}'^2)c_1 - 2i(p_c'r_{12}-r_cp_{12}')\}], \quad (30)$$

where now the phase factor couples the relative and center of mass positions and momenta. In Fig. 1, we plot $W(x_1,x_2,0)$ versus r_{12} and p'_{12} for $\beta\hbar\omega=1$ and $r_c=p'_c=1$.

The fact that $W(x_1,x_2,0)$ is symmetric with respect to the plane $p'_{12}=-r_{12}$ for $p'_c=r_c=1$ is evident in the figure. The real part of W contains a Gaussian function that is sharply peaked around $r_{12}=p'_{12}=0$ and the imaginary part of W is small in the vicinity of the origin. When r_{12} and p'_{12} are small, we can represent the function in a multipole expansion and keep only the first order term to get

$$W(x_1,x_2,0) \approx \frac{a}{\pi c_1}\exp\left[-\frac{a}{c_1}(p_c'^2+r_c^2)\right]\delta(x_{12}) \equiv \rho_{We}(x_c)\,\delta(x_{12}). \quad (31)$$

In this case W reduces to the Wigner-transformed equilibrium density matrix ρ_{We} for the center of mass variables of two phase spaces. This result is also expected to hold for general potentials. For other values of p'_c and r_c, we find that the peak rotates around the origin, maintaining its shape.

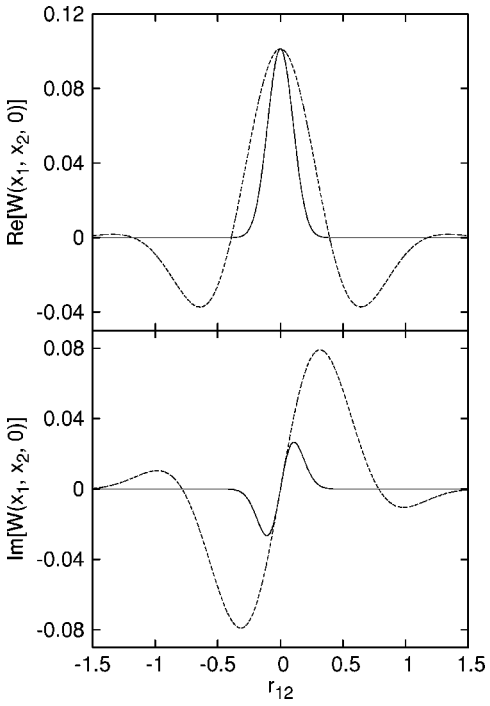

FIG. 2. Plots of the real (upper panel) and imaginary (lower) parts of W versus (dimensionless) r_{12} along the line $p'_{12}=-r_{12}$ for $\beta\hbar\omega=0.1$ (solid lines) and $\beta\hbar\omega=10$ (dashed lines).

In order to illustrate the quantum effects more clearly, $W(x_1,x_2,0)$ is plotted in Fig. 2 for $\beta\hbar\omega=0.1$ and $\beta\hbar\omega=10$, corresponding to small and large quantum character, respectively.

As the value of $\beta\hbar\omega$ becomes larger, negative values of the real and imaginary parts of the W function become significant. For $\beta=0$, W is proportional to a delta function as in Eq. (31).

A. Equation of motion for *W*

The general form of the equation of motion for $\overline{W}(t)$, and hence $W(t)$, was given in Eqs. (17), (19), and (20). For a harmonic oscillator the operator $\sin(\hbar\Lambda/2)$ can be replaced by the first term in its expansion, so that

$$\frac{\partial}{\partial t}W(x_1,x_2,t)=\{W(x_1,x_2,t),H_W(x_1)\},$$

$$=\{H_W(x_2),W(x_1,x_2,t)\}, \tag{32}$$

where $\{\cdot,\}$ denotes the Poisson bracket; thus, $W(t)$ evolves through the classical equations of motion. This is not surprising since the quantum and classical evolution of p and r are the same for a single harmonic oscillator and quantum effects enter through the initial condition in the Wigner representation. We may verify that these equations of motion also follow directly from the analytical solutions by differentiation with respect to time. In particular, noting that $\partial c_2/\partial(\omega t)=c_3$ and $\partial c_3/\partial(\omega t)=-c_2$, we can easily confirm the above equations of motion.

Finally, we observe that using the explicit expressions for the time evolution of the position and momentum, $r(t)=r\cos\omega t+p'\sin\omega t$ and $p'(t)=p'\cos\omega t-r\sin\omega t$, respectively, we can rewrite Eq. (27) as $W(x_1,x_2,t)=W(x_1(t),x_2,0)$. In more general situations it is not possible to obtain such a simple form involving the phase-space coordinates at time t.

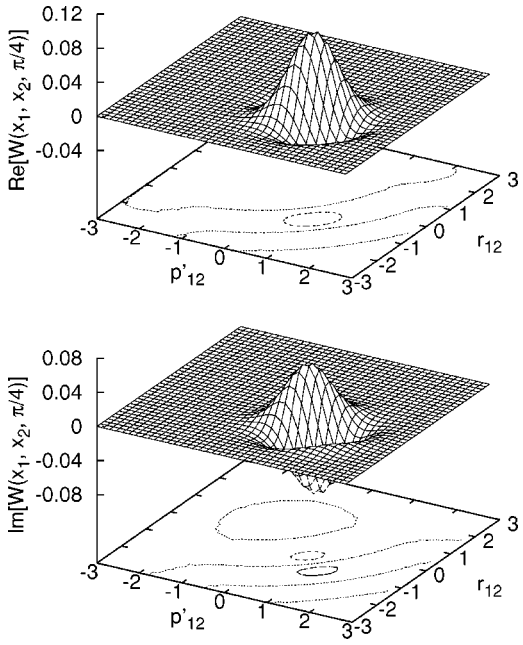

FIG. 3. Real (upper panel) and imaginary (lower panel) parts of $W(x_1,x_2,t)$ for $\omega t=\pi/4$.

In Fig. 3, we plot $W(x_1,x_2,t)$ at $\omega t=\pi/4$ with the other parameters, the same as in Fig. 1. Comparing this figure with Fig. 1, one can see that the peak moves along the line $p'_{12}=-r_{12}$ with little change in its shape. Figure 4 shows plots W versus r_{12} with $p'_{12}=-r_{12}$ for three different time values. The

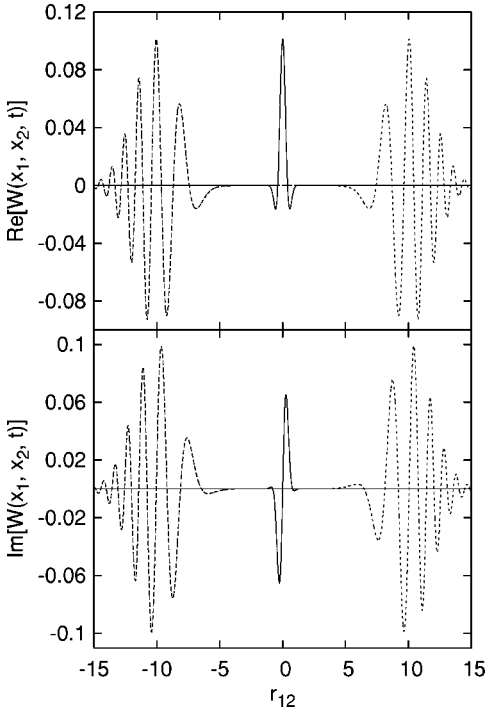

FIG. 4. Plot of $W(x_1,x_2,t)$ function vs r_{12} for $\omega t=0$ (solid line), $\omega t=7\pi/8$ (long dashed line) and $\omega t=9\pi/8$ (short dashed line).

dynamics is periodic, as expected with strongly oscillatory behavior for long times. It is of interest to note that when $\omega t=\pi$ the W function depends on the difference variables only through the phase factor,

$$W\left(x_1,x_2,\frac{\pi}{\omega}\right)=\left(\frac{a}{\pi}\right)^2\exp[-a\{(r_c^2+p_c'^2)4c_1 + 2i(p_c'r_{12}-r_cp_{12}')\}]. \tag{33}$$

For the harmonic oscillator it is also possible to obtain analytical expressions for general quantum correlation functions, and these results are given in Appendix B.

IV. QUANTUM-CLASSICAL SYSTEMS

In this section we show how to take the quantum-classical limit of the general expressions for the transport coefficients given in Sec. II. As discussed earlier, the general equations in the Wigner-transformed representation are intractable as they stand, except for very simple harmonic systems, since they are equivalent to a full quantum mechanical treatment of the system plus bath. By taking the quantum-classical limit of these expressions we can obtain transport coefficient expressions that are amenable to solution using surface-hopping methods. The computation of the initial value of W is still a challenging problem but far less formidable than the solution of the time-dependent Schrödinger or von Neumann equation for the entire quantum system since it involves only imaginary time propagators.

To make connection with surface-hopping representations of the quantum-classical Liouville equation,[7] we first observe that $A_W(\mathcal{X}_1)$ can be written as

$$A_W(\mathcal{X}_1)=\int dz_1 e^{(i/\hbar)p_1\cdot z_1}\left\langle r_1-\frac{z_1}{2}\left|\hat{A}_W(X_1)\right|r_1+\frac{z_1}{2}\right\rangle, \tag{34}$$

where $\hat{A}_W(X_1)$ is the *partial* Wigner transform of $\hat{A}$, defined as in Eq. (6), 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, $\hat{h}_W(R)|\alpha;R\rangle=E_\alpha(R)|\alpha;R\rangle$. We may now express the subsystem operators in the adiabatic basis to obtain

$$A_W(\mathcal{X}_1)=\sum_{\alpha_1\alpha_1'}\int dz_1 e^{(i/\hbar)p_1\cdot z_1}\left\langle r_1-\frac{z_1}{2}|\alpha_1;R_1\right\rangle \times A_W^{\alpha_1\alpha_1'}(X_1)\left\langle\alpha_1';R_1|r_1+\frac{z_1}{2}\right\rangle, \tag{35}$$

where $A_W^{\alpha_1\alpha_1'}(X_1)=\langle\alpha_1;R_1|\hat{A}_W(X_1)|\alpha_1';R_1\rangle$.

Inserting this expression and its analog for $B_W(\mathcal{X}_2)$ into Eq. (16) for $t_1=t_2=0$, we have

$$\lambda_{AB}(t)=-\sum_{\alpha_1,\alpha_1',\alpha_2,\alpha_2'}\int\prod_{i=1}^{2}dX_iA_W^{\alpha_1\alpha_1'}(X_1)B_W^{\alpha_2\alpha_2'}(X_2) \times\frac{\partial}{\partial t}\overline{W}^{\alpha_1'\alpha_1\alpha_2'\alpha_2}(X_1,X_2,t), \tag{36}$$

where the matrix elements of W are given by

$$\begin{aligned}W^{\alpha_1'\alpha_1\alpha_2'\alpha_2}(X_1,X_2,t)&=\int\prod_{i=1}^{2}dZ_ie^{-(i/\hbar)(P_1\cdot Z_1+P_2\cdot Z_2)}\\&\times\langle\alpha_1';R_1|\left\langle R_1+\frac{Z_1}{2}\left|e^{(i/\hbar)\hat{H}t}\right|R_2-\frac{Z_2}{2}\right\rangle|\alpha_2;R_2\rangle\\&\times\langle\alpha_2';R_2|\left\langle R_2+\frac{Z_2}{2}\left|e^{-(i/\hbar)\hat{H}t''}\right|R_1-\frac{Z_1}{2}\right\rangle|\alpha_1;R_1\rangle\\&\times\frac{1}{Z_Q}\frac{1}{(2\pi\hbar)^{2\nu_\hbar}},\end{aligned} \tag{37}$$

with $t''=t-i\beta\hbar$. From the definition in Eq. (37) one may show that these matrix elements satisfy the symmetry properties,

$$\begin{aligned}W^{\alpha_1'\alpha_1\alpha_2'\alpha_2}(X_1,X_2,t)^*&=W^{\alpha_2\alpha_2'\alpha_1\alpha_1'}(X_2,X_1,-t),\\W^{\alpha_1'\alpha_1\alpha_2'\alpha_2}(X_1,X_2,t-i\hbar\beta)&=W^{\alpha_1\alpha_1'\alpha_2\alpha_2'}(X_1,X_2,t)^*,\end{aligned} \tag{38}$$

which are the analogs of Eqs. (8) and (9).

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 Ref. 14 and the result was found to be[25]

$$\begin{aligned}\frac{\partial}{\partial t}\overline{W}^{\alpha_1'\alpha_1\alpha_2'\alpha_2}(X_1,X_2,t)&=\frac{1}{2}\sum_{\beta_1'\beta_1\beta_2'\beta_2}(i\mathcal{L}_{\alpha_1'\alpha_1,\beta_1'\beta_1}(X_1)\\&\times\delta_{\alpha_2'\beta_2'}\delta_{\alpha_2\beta_2}-i\mathcal{L}_{\alpha_2'\alpha_2,\beta_2'\beta_2}(X_2)\delta_{\alpha_1'\beta_1'}\delta_{\alpha_1\beta_1})\\&\times\overline{W}^{\beta_1'\beta_1\beta_2'\beta_2}(X_1,X_2,t),\end{aligned} \tag{39}$$

which has the same structure as Eq. (20). The quantum- classical Liouville operator in the adiabatic basis $i\mathcal{L}$ is given by[7]

$$i\mathcal{L}_{\alpha\alpha',\beta\beta'}(X)=[i\omega_{\alpha\alpha'}(R)+iL_{\alpha\alpha'}(X)]\delta_{\alpha\beta}\delta_{a'\beta'} - J_{\alpha\alpha',\beta\beta'}(X), \tag{40}$$

where the classical evolution operator is defined as

$$iL_{\alpha\alpha'}=\frac{P}{M}\frac{\partial}{\partial R}+\frac{1}{2}[F_W^{\alpha}(R)+F_W^{\alpha'}(R)]\frac{\partial}{\partial P}, \tag{41}$$

with

$$J_{\alpha\alpha',\beta\beta'}(X) = -\frac{P}{M} d_{\alpha\beta}\left[1+\frac{1}{2}S_{\alpha\beta}(R)\frac{\partial}{\partial P}\right]\delta_{\alpha'\beta'} - \frac{P}{M} d^{*}_{\alpha'\beta'}\left[1+\frac{1}{2}S^{*}_{\alpha'\beta'}(R)\frac{\partial}{\partial P}\right]\delta_{\alpha\beta}. \quad (42)$$

Here the frequency $\omega_{\alpha\alpha'}(R) \equiv [E_\alpha(R) - E_{\alpha'}(R)]/\hbar$, the Hellmann–Feynman force $F^\alpha_W = -\langle \alpha;R|\partial \hat{V}_W(\hat{q},R)/\partial \hat{R}|\alpha;R\rangle$, the nonadiabatic coupling matrix element is $d_{\alpha\beta} = \langle \alpha;R|\nabla_R|\beta;R\rangle$, and $S_{\alpha\beta} = (E_\alpha - E_\beta) d_{\alpha\beta}[(P/M) d_{\alpha\beta}]^{-1}$. In view of Eqs. (17) and (19) we can also write the following equivalent forms of the evolution equation:

$$\frac{\partial}{\partial t}\overline{W}^{\alpha_1'\alpha_1\alpha_2'\alpha_2}(X_1,X_2,t) = \sum_{\beta_1'\beta_1} i\mathcal{L}_{\alpha_1'\alpha_1,\beta_1'\beta_1}(X_1)\overline{W}^{\beta_1'\beta_1\alpha_2'\alpha_2}(X_1,X_2,t) = -\sum_{\beta_2'\beta_2} i\mathcal{L}_{\alpha_2'\alpha_2,\beta_2'\beta_2}(X_2)\overline{W}^{\alpha_1'\alpha_1\beta_2'\beta_2}(X_1,X_2,t). \quad (43)$$

The derivation of these expressions follows directly from taking the quantum-classical limits of Eqs. (17) and (19) and expressing them in an adiabatic basis.

One may use the different forms of the quantum-classical evolution equation given above to derive different but equivalent expressions for the transport coefficient in the quantum-classical limit. For example, a particularly useful expression for the evaluation of chemical reaction rates when the observable is a function of only the classical bath coordinates is obtained as follows: We use the first equality in Eq. (43), insert this into Eq. (36), 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 Eq. (43) 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 Eq. (36) 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

$$B_W^{\alpha_2\alpha_2'}(X_2,t) = \sum_{\beta_2\beta_2'} (e^{-i\mathcal{L}(X_2)t})_{\alpha_2\alpha_2',\beta_2\beta_2'} B_W^{\beta_2\beta_2'}(X_2). \quad (44)$$

The result of these operations is

$$\lambda_{AB}(t) = \sum_{\alpha_1,\alpha_1',\alpha_2,\alpha_2'} \int \prod_{i=1}^{2} dX_i (i\mathcal{L}(X_1)A_W(X_1))^{\alpha_1\alpha_1'} \times B_W^{\alpha_2\alpha_2'}(X_2,t)\overline{W}^{\alpha_1'\alpha_1\alpha_2'\alpha_2}(X_1,X_2,0), \quad (45)$$

which is the quantum-classical analog of Eq. (24). This equation can serve as the basis for the computation of transport properties for quantum-classical systems. Comparing with Eq. (12), we see that the Wigner transform of $\dot{\hat{A}}$ is replaced by its analog for a quantum-classical system and the time evolution of the dynamical variable is given by quantum-classical Liouville evolution. Full quantum effects are described by the initial value of $\overline{W}$. A number of other equivalent forms may be derived by using combinations of the various forms of the evolution equation for $\overline{W}$ given in Eqs. (39) and (43).

A. Reaction rate coefficient

As an illustration of the utility of this transport coefficient expression, consider the calculation of the reaction rate for the interconversion $A \rightleftharpoons B$ between metastable A and B states. We suppose that the reaction can be characterized by a scalar reaction coordinate $\xi(R)$ which is a function of the classical bath coordinates. The A and B species operators may then be defined as $\hat{N}_A = \theta(\xi^\ddagger - \xi(R))$ and $\hat{N}_B = \theta(\xi(R) - \xi^\ddagger)$ where $\xi^\ddagger$ is the location of the free-energy barrier top along the ξ coordinate and θ is the Heaviside step function. An example of such a many-body reaction coordinate is the solvent polarization that may be used to characterize proton or electron transfer processes in polar solvents. Although the rate process is intrinsically quantum in character, this reaction coordinate involves only the classical bath degrees of freedom.

Equation (45), specialized to the time-dependent rate constant for the reaction, is given by

$$k_{AB}(t) = \frac{-1}{n_A^{\mathrm{eq}}} \sum_{\alpha_1,\alpha_1',\alpha_2,\alpha_2'} \int \prod_{i=1}^{2} dX_i (i\mathcal{L}(X_1)N_A(X_1))^{\alpha_1\alpha_1'} \times N_B^{\alpha_2\alpha_2'}(X_2,t)\overline{W}^{\alpha_1'\alpha_1\alpha_2'\alpha_2}(X_1,X_2,0). \quad (46)$$

Using the fact that

$$(i\mathcal{L}(X_1)N_A(X_1))^{\alpha_1\alpha_1'} = -\frac{P_1}{M}\nabla_{R_1}\xi(R_1)\delta(\xi(R_1)-\xi^\ddagger)\delta_{\alpha_1\alpha_1'}, \quad (47)$$

the rate coefficient takes the form

$$k_{AB}(t) = \frac{1}{n_A^{\mathrm{eq}}} \sum_{\alpha_1,\alpha_2,\alpha_2'} \int \prod_{i=1}^{2} dX_i \delta(\xi(R_1)-\xi^\ddagger) \times \frac{P_1}{M}(\nabla_{R_1}\xi(R_1))N_B^{\alpha_2\alpha_2'}(X_2,t) \times \overline{W}^{\alpha_1\alpha_1\alpha_2'\alpha_2}(X_1,X_2,0). \quad (48)$$

The evaluation of the rate constant then entails being able to evolve the B species variable using quantum-classical Liouville surface-hopping dynamics[26] and sampling from a weight function determined by $\overline{W}(X_1,X_2,0)$, where the delta function restricts $\xi(R_1)$ at the barrier top.

If $\overline{W}$ is approximated by its value in the high-temperature, classical-bath limit[14]

$$\overline{W}^{\alpha_1'\alpha_1\alpha_2'\alpha_2}(X_1,X_2,0) = \frac{e^{\beta(E_{\alpha_1'}(R_1)-E_{\alpha_2'}(R_1))}-1}{\beta(E_{\alpha_1'}(R_1)-E_{\alpha_2'}(R_1))} \times \frac{1}{Z_Q} e^{-\beta((P_1^2/2M)+E_{\alpha_1'}(R_1))} \delta_{\alpha_1'\alpha_2}\delta_{\alpha_2'\alpha_1}\delta(R_{12})\delta(P_{12}), \tag{49}$$

where

$$Z_Q \approx \sum_\alpha \int dR dP e^{-\beta((P^2/2M)+E_\alpha(R))}, \tag{50}$$

the time-dependent rate coefficient can be written in the simple form,

$$k_{AB}(t) = \frac{1}{n_A^{\mathrm{eq}}} \sum_{\alpha_1} \int dX_1 \delta(\xi(R_1)-\xi^\ddagger) \times \frac{P_1}{M}(\nabla_{R_1}\xi(R_1)) N_B^{\alpha_1\alpha_1}(X_1,t)\rho_{We}^{\alpha_1}(X_1). \tag{51}$$

Here $\rho_{We}^{\alpha_1}(X_1)=Z_Q^{-1}\exp[-\beta(P_1^2/2M+E_{\alpha_1}(R_1))]$ is the equilibrium distribution. This equation is amenable to calculation using rare event sampling methods since the delta function confines the initial value of the reaction coordinate to the barrier top. As above, the evolution of the species variable $N_B^{\alpha_1\alpha_1}(X_1,t)$ is to be carried out using quantum-classical Liouville surface-hopping dynamics. This result is the same as that derived using linear response theory based on the quantum-classical Liouville equation when the diagonal part of the equilibrium quantum-classical density is used in the rate coefficient expression.[27] Equation (48) provides a more general expression for the reaction rate that incorporates bath quantum effects in the equilibrium structure. The focus then shifts to the derivation of more accurate analytical expressions for $\overline{W}^{\alpha_1'\alpha_1\alpha_2'\alpha_2}(X_1,X_2,0)$ or the construction of simulation methods to calculate this quantity.

Employing Eq. (51), quantum-classical dynamics was used previously to study reactive dynamics in a two-level quantum system coupled to a nonlinear oscillator, which in turn was coupled to a harmonic bath.[27] Making use of the new expression for the reaction rate in Eq. (48), along with an approximate form for $\overline{W}$ that incorporates quantum dispersion in the reaction coordinate, we have been able to obtain additional quantum effects on the nonadiabatic reaction rate that are outside the scope of quantum-classical treatments that neglect quantum effects in the equilibrium structure of the bath.[28]

V. CONCLUSION

The quantum-classical expressions for transport coefficients derived in this paper, such as Eq. (45), form the basis for algorithms that can be used to compute these quantities using surface-hopping methods. The expressions involve a doubling of the classical phase space with the quantum connectivity between two phase spaces accounted for by the spectral density W. The initial value of the spectral density depends on the quantum equilibrium structure of the subsystem as well as that of the bath. Its calculation is a difficult problem, but more tractable than the simulation of the full quantum time evolution of the entire system. The harmonic oscillator results provided insight into its structure, especially into the nature of the coupling of the two phase spaces.

Given the general expressions for the time evolution of $\overline{W}$ in Eqs. (39) and (43), one can place the time dependence on either operator or the spectral density function. This allows one to choose the most convenient strategy for the evaluation of a specific transport coefficient. One useful strategy for the calculation of the rates of activated chemical reactions is to evolve $\hat{B}_W(X_2)$ using quantum-classical evolution and average over the two phase spaces with a weight determined by the equilibrium spectral density function. In the limit of a high-temperature bath approximation for $\overline{W}(X_1,X_2,0)$ we showed that the resulting expression for the reaction rate can be related to that obtained earlier using linear response theory based on the quantum-classical Liouville equation.[27] The more general expressions obtained in this paper allow one to incorporate equilibrium quantum bath effects which are outside the scope of the quantum-classical linear response results, while still carrying out the dynamics using quantum-classical surface hopping schemes. Calculations of the reaction rate and other transport properties using this formalism will be given in the future work.

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APPENDIX A: ALTERNATIVE PROOF OF *W* EVOLUTION EQUATIONS

Another proof of Eqs. (17) and (19) is possible by direct differentiation of $W(\mathcal{X}_1,\mathcal{X}_2,t)$. The time derivative of Eq. (7) can be expressed as either

$$\frac{\partial}{\partial t}W(t) = \frac{1}{(2\pi\hbar)^{2\nu}Z_Q}\int d\mathcal{Z}_1 d\mathcal{Z}_2 e^{-(i/\hbar)(\mathcal{P}_1\cdot\mathcal{Z}_1+\mathcal{P}_2\cdot\mathcal{Z}_2)} \times \frac{i}{\hbar}\int ds\Bigg\{\left\langle \mathcal{R}_1+\frac{\mathcal{Z}_1}{2}\middle|\hat{H}\middle|s\right\rangle\left\langle s\middle|e^{(i/\hbar)\hat{H}t}\middle|\mathcal{R}_2-\frac{\mathcal{Z}_2}{2}\right\rangle \times\left\langle \mathcal{R}_2+\frac{\mathcal{Z}_2}{2}\middle|e^{-(i/\hbar)\hat{H}(t-i\hbar\beta)}\middle|\mathcal{R}_1-\frac{\mathcal{Z}_1}{2}\right\rangle - \left\langle \mathcal{R}_1+\frac{\mathcal{Z}_1}{2}\middle|e^{(i/\hbar)\hat{H}t}\middle|\mathcal{R}_2-\frac{\mathcal{Z}_2}{2}\right\rangle \times\left\langle \mathcal{R}_2+\frac{\mathcal{Z}_2}{2}\middle|e^{-(i/\hbar)\hat{H}(t-i\hbar\beta)}|s\rangle\langle s|\hat{H}\middle|\mathcal{R}_1-\frac{\mathcal{Z}_1}{2}\right\rangle\Bigg\} \tag{A1}$$

or

$$\frac{\partial}{\partial t}W(t)=\frac{1}{(2\pi\hbar)^{2\nu}Z_Q}\int d\mathcal{Z}_1 d\mathcal{Z}_2 e^{-(i/\hbar)(\mathcal{P}_1\cdot\mathcal{Z}_1+\mathcal{P}_2\cdot\mathcal{Z}_2)}$$
$$\times\frac{i}{\hbar}\int ds\left\{\left\langle\mathcal{R}_1+\frac{\mathcal{Z}_1}{2}\middle|e^{(i/\hbar)\hat{H}t}|s\rangle\langle s|\hat{H}\middle|\mathcal{R}_2-\frac{\mathcal{Z}_2}{2}\right\rangle\right.$$
$$\times\left\langle\mathcal{R}_2+\frac{\mathcal{Z}_2}{2}\middle|e^{-(i/\hbar)\hat{H}(t-i\hbar\beta)}\middle|\mathcal{R}_1-\frac{\mathcal{Z}_1}{2}\right\rangle$$
$$-\left\langle\mathcal{R}_1+\frac{\mathcal{Z}_1}{2}\middle|e^{(i/\hbar)\hat{H}t}\middle|\mathcal{R}_2-\frac{\mathcal{Z}_2}{2}\right\rangle$$
$$\left.\times\left\langle\mathcal{R}_2+\frac{\mathcal{Z}_2}{2}\middle|\hat{H}|s\rangle\langle s|e^{-(i/\hbar)\hat{H}(t-i\hbar\beta)}\middle|\mathcal{R}_1-\frac{\mathcal{Z}_1}{2}\right\rangle\right\}. \tag{A2}$$

We will prove that the former expression reduces to Eq. (17) and the latter reduces to Eq. (19). The matrix element $\langle s|\hat{H}|\mathcal{R}_i\pm\mathcal{Z}_i/2\rangle$ is equal to $\{(-\hbar^2/2\mathcal{M})(\partial^2/\partial s^2)+V(s)\}\times\delta(\mathcal{R}_i\pm\mathcal{Z}_i/2-s)$. We first examine the kinetic-energy part. Using this form of the matrix element and noting the general structure of the terms in Eqs. (A1) and (A2), we are led to consider integrals of the form,

$$\frac{-i\hbar}{2\mathcal{M}}\int ds e^{-(i/\hbar)\mathcal{P}_i\cdot\mathcal{Z}_i}\frac{\partial^2}{\partial s^2}\delta\left(\mathcal{R}_i\pm\frac{\mathcal{Z}_i}{2}-s\right)$$
$$\times f(s)g\left(\mathcal{R}_i\mp\frac{\mathcal{Z}_i}{2}\right)$$
$$=\frac{2i\hbar}{\mathcal{M}}e^{-(i/\hbar)\mathcal{P}_i\cdot\mathcal{Z}_i}\frac{\partial}{\partial\mathcal{Z}_i}f\left(\mathcal{R}_i\pm\frac{\mathcal{Z}_i}{2}\right)$$
$$\times\left\{\frac{\partial}{\partial\mathcal{Z}_i}-\frac{i\mathcal{P}_i}{\hbar}\right\}g\left(\mathcal{R}_i\mp\frac{\mathcal{Z}_i}{2}\right)$$
$$=e^{-(i/\hbar)\mathcal{P}_i\cdot\mathcal{Z}_i}\frac{\partial}{\partial\mathcal{R}_i}f\left(\mathcal{R}_i\pm\frac{\mathcal{Z}_i}{2}\right)$$
$$\times\left\{\frac{-i\hbar}{2\mathcal{M}}\frac{\partial}{\partial\mathcal{R}_i}\pm\frac{\mathcal{P}_i}{\mathcal{M}}\right\}g\left(\mathcal{R}_i\mp\frac{\mathcal{Z}_i}{2}\right). \tag{A3}$$

Substituting these relations into the kinetic matrix elements in Eqs. (A1) and (A2), we obtain $(\partial/\partial t)W=(\mathcal{P}_1/\mathcal{M})\times(\partial/\partial\mathcal{R}_1)W$ and $(\partial/\partial t)W=-(\mathcal{P}_2/\mathcal{M})(\partial/\partial\mathcal{R}_2)W$, respectively, which shows that the free-streaming contributions have the desired form. A similar set of manipulations can be carried out to show that the potential-energy parts also have equivalent forms involving $\mathcal{X}_1$ or $\mathcal{X}_2$.

APPENDIX B: ANALYTICAL EXPRESSIONS FOR CORRELATION FUNCTIONS

If the operators $\hat{A}$ and $\hat{B}$ are functions of only $\hat{p}$ or $\hat{q}$, we can further simplify the expression for W. When both $\hat{A}$ and $\hat{B}$ depend only on the position operator, we can integrate $W(x_1,x_2,t)$ over momenta to obtain

$$W(r_1,r_2,t)=\int dp_1'dp_2'W(x_1,x_2,t)$$
$$=\frac{a}{\pi\sqrt{b}}\exp\left[-\frac{a}{b}\{(r_1^2+r_2^2)c_1+r_1r_2c_2(t)\}\right], \tag{B1}$$

where $b\equiv c_1^2-(1/4)c_2^2(t)=1+(1/4)c_3^2(t)$, and the second equality follows because $c_2^2(t)+c_3^2(t)=4c_1^2-4$. Note that the symmetry relation $W(r_1,r_2,t)=W(r_2,r_1,t)$ holds. Similarly, integrating W over position, we find

$$W(p_1',p_2',t)=\int dr_1dr_2W(x_1,x_2,t)$$
$$=\frac{a}{\pi\sqrt{b}}\exp\left[-\frac{a}{b}\{(p_1'^2+p_2'^2)c_1+p_1'p_2'c_2(t)\}\right], \tag{B2}$$

which has the same form as Eq. (B1).

From Eq. (B1) for $W(r_1,r_2,t)$ we can compute the position correlation function as

$$\langle\hat{q}^i\hat{q}(t)^j\rangle=\int dr_1dr_2r_1^ir_2^jW(r_1,r_2,t)$$
$$=\frac{\sqrt{b}}{\pi c_1^2}\left(\frac{b}{ac_1}\right)^{(i+j)/2}F_{mn}(c_1,c_2), \tag{B3}$$

where

$$F_{ij}(x,y)\equiv\begin{cases}\text{(for odd } i \text{ and } j) & -y\Gamma\left(1+\frac{i}{2}\right)\Gamma\left(1+\frac{j}{2}\right){}_2F_1\left(1+\frac{i}{2},1+\frac{j}{2};\frac{3}{2};\frac{y^2}{4x^2}\right)\\ \text{(for even } i \text{ and } j) & x\Gamma\left(\frac{1+i}{2}\right)\Gamma\left(\frac{1+j}{2}\right){}_2F_1\left(\frac{1+i}{2},\frac{1+j}{2};\frac{1}{2};\frac{y^2}{4x^2}\right)\\ \text{(for odd } i+j) & 0.\end{cases} \tag{B4}$$

Here ${}_2F_1$ is the hypergeometric function defined by ${}_2F_1(a,b;c;z) \equiv \Sigma_k((a)_k(b)_k/(c)_k)(z^k/k!)$ and Γ is the gamma function.[29] Since $F_{ij}(x,y) = F_{ji}(x,y)$, one can easily see $\langle \hat{q}^i \hat{q}(t)^j \rangle = \langle \hat{q}^j \hat{q}(t)^i \rangle$. Also, $\langle \hat{p}'^i \hat{p}'(t)^j \rangle = \langle \hat{q}^i \hat{q}(t)^j \rangle$ leads to $\langle \hat{p}^i \hat{p}(t)^j \rangle = (m\omega)^{i+j} \langle \hat{q}^i \hat{q}(t)^j \rangle$.

When $\hat{A}$ is a function of $\hat{p}$ and $\hat{B}$ is a function of $\hat{q}$, the relevant quantity is

$$W(r_1, p_2', t) = \frac{a}{\pi\sqrt{b'}} \exp\left[-\frac{a}{b'} \{ (r_1^2 + p_2'^2) c_1 + r_1 p_2' c_3(t) \} \right], \tag{B5}$$

with $b' \equiv c_1^2 - (1/4)c_3^2(t)$, while when $\hat{A}$ is function of $\hat{q}$ and $\hat{B}$ is function of $\hat{p}$, we need

$$W(p_1', r_2, t) = \frac{a}{\pi\sqrt{b'}} \exp\left[-\frac{a}{b'} \{ (r_2^2 + p_1'^2) c_1 - r_2 p_1' c_3(t) \} \right]. \tag{B6}$$

The analytical solutions for $\langle \hat{p}^i \hat{q}(t)^j \rangle$ or $\langle \hat{q}^i \hat{p}(t)^j \rangle$ have forms similar to that for $\langle \hat{q}^i \hat{q}(t)^j \rangle$

$$\langle \hat{p}^i \hat{q}(t)^j \rangle = \frac{\sqrt{b'}}{\pi c_1^2} \left(\frac{b'}{a c_1} \right)^{(i+j)/2} F_{ij}(c_1, c_3) \tag{B7}$$

and

$$\langle \hat{q}^i \hat{p}(t)^j \rangle = \frac{\sqrt{b'}}{\pi c_1^2} \left(\frac{b'}{a c_1} \right)^{(i+j)/2} F_{ij}(c_1, -c_3). \tag{B8}$$

For general many-body quantum-classical systems similar reduced forms for W enter the correlation functions if the operators depend only either on the bath positions or the momenta. However, equations of motion for $W^{\alpha_1' \alpha_1 \alpha_2' \alpha_2}(R_1, R_2, t)$ or $W^{\alpha_1' \alpha_1 \alpha_2' \alpha_2}(P_1, P_2, t)$ in position or momentum space cannot be obtained in closed form for these quantities and approximations must be employed. In this connection methods based on moments may prove useful since the evaluation of the correlation function involves a low-order moment of W.[30]

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