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Semiclassical approximations for the calculation of thermal rate constants for chemical reactions in complex molecular systems

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Two different semiclassical approaches are presented for extending flux correlation function methodology for computing thermal reaction rate constants, which has been extremely successful for the ''direct'' calculation of rate constants in small molecule ($\sim 3-4$ atoms) reactions, to complex molecular systems, i.e., those with many degrees of freedom. First is the popular mixed quantum-classical approach that has been widely used by many persons, and second is an approximate version of the semiclassical initial value representation that has recently undergone a rebirth of interest as a way for including quantum effects in molecular dynamics simulations. Both of these are applied to the widely studied system-bath model, a one-dimensional double well potential linearly coupled to an infinite bath of harmonic oscillators. The former approximation is found to be rather poor while the latter is quite good. © *1998 American Institute of Physics.* [S0021-9606(98)01323-3]

I. INTRODUCTION

Considerable progress has been made over the last few years in the development of quantum mechanical methods for the calculation of thermal (and also microcanonical) rate constants for chemical reactions.[1] These methods are both ''direct,'' in that they avoid the necessity of having to solve the state-to-state quantum reactive scattering problem, but also ''correct,'' in principle exact and limited only by numerical parameters. Applications to a number of reactions ($O+HCl \rightarrow OH+Cl$,[2] $Cl+H_2 \rightarrow HCl+H$,[3] $F+H_2 \rightarrow HF+H$,[4] and $O+OH \rightarrow O_2+H$[5]) have been carried out successfully using this methodology.

To summarize the approach in brief, the thermal rate constant, $k(T)$, is expressed as the time integral of a flux–flux autocorrelation function[6,7]

$$k(T)=Q_r(T)^{-1}\int_0^\infty dt C_{ff}(t), \tag{1.1a}$$

where

$$C_{ff}(t)=\mathrm{tr}[e^{-\beta\hat{H}/2}\hat{F}e^{-\beta\hat{H}/2}e^{i\hat{H}t/\hbar}\hat{F}e^{-i\hat{H}t/\hbar}], \tag{1.1b}$$

or in the integrated form[6(b)] as the long time limit of the flux-position correlation function,

$$k(T)=Q_r(T)^{-1}\lim_{t\to\infty}C_{fs}(t), \tag{1.2a}$$

where

$$C_{fs}(t)=\mathrm{tr}[e^{-\beta\hat{H}/2}\hat{F}e^{-\beta\hat{H}/2}e^{i\hat{H}t/\hbar}\hat{h}e^{-i\hat{H}t/\hbar}]. \tag{1.2b}$$

Here $\hat{F}$ is the flux operator,

$$\hat{F}=\frac{i}{\hbar}[\hat{H},\hat{h}], \tag{1.3}$$

where h is a function of coordinates that is 0 or 1, respectively, on the reactant or product side of a dividing surface, $Q_r(T)$ is the reactant partition function per unit volume, and $\beta=(k_BT)^{-1}$. Since the Boltzmannized flux operator, $\hat{F}(\beta)$,

$$\hat{F}(\beta)\equiv e^{-\beta\hat{H}/2}\hat{F}e^{-\beta\hat{H}/2}, \tag{1.4}$$

is of low rank, a Lanczos iteration procedure[8,9] provides an extremely efficient way to obtain the small number of its eigenvectors $\{|u_m\rangle\}$ with eigenvalues $\{f_m\}$ significantly different from zero.[2–5] $\hat{F}(\beta)$ is then expressed in terms of its eigenfunction expansion,

$$\hat{F}(\beta)=\sum_m f_m|u_m\rangle\langle u_m|, \tag{1.5}$$

and the trace in Eq. (1.1b) can be evaluated in this much smaller basis. It should also be noted that Light *et al.*,[10] Metiu *et al.*,[11] and Manthe *et al.*[12] have developed approaches similar in spirit to that described here, though differing in various specifics.

Even with this ''considerable progress,'' however, these completely rigorous quantum approaches are only applicable at present to chemical reactions involving a few (3–4) atoms. This is because these finite basis (e.g., discrete variable representation) methods are based on a quadrature discretization for each degree of freedom of the molecular system, and the resulting number of grid points increases exponentially with the number of degrees of freedom. Some kind of approximation is thus necessary in order to deal with complex molecular systems, those with many degrees of freedom. One could, of course, immediately revert to the use of classical mechanics, i.e., molecular dynamics simulations, but there will certainly be many situations where quantum effects are important. We thus wish to retain as much of the above rigorous quantum formulation as possible.

In this paper we consider two approximate approaches. First is the popular mixed quantum-classical model,[13] whereby one integrates the time-dependent Schrödinger

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equation for (a few) degrees of freedom (with coordinates **s**) that are treated quantum mechanically, simultaneously with the classical equations of motion for the (many) degrees of freedom (with coordinates **q**) that are treated by classical mechanics. The two sets of degrees of freedom are coupled in that the quantum degrees of freedom see a time-dependent potential,

$$V_{\mathrm{QM}}(\mathbf{s},t)=V(\mathbf{s},\mathbf{q}(t)), \tag{1.6}$$

where $V(\mathbf{s},\mathbf{q})$ is the total potential energy function and $\mathbf{q}(t)$ the trajectory of the classical degrees of freedom, and the classical degrees of freedom see a time-dependent potential that is the Ehrenfest average over the quantum degrees of freedom,

$$\begin{aligned}V_{\mathrm{CL}}(\mathbf{q},t)&=\langle\Psi(t)|V|\Psi(t)\rangle\\&=\int d\mathbf{s}\Psi(\mathbf{s},t)^{*}V(\mathbf{s},\mathbf{q})\Psi(\mathbf{s},t).\end{aligned} \tag{1.7}$$

This model can be thought of as the (partial) classical limit of the time-dependent self-consistent field (TDSCF) approximation[14] and has been widely used by many persons.[13,15] Section II shows explicitly how it can be adapted to the ''direct'' rate constant methodology summarized above.

The second approximate approach we consider is based on the semiclassical initial value representation[16] (SC-IVR) that has had a rebirth of interest[17–23] as a way for including quantum effects in molecular dynamics simulations. The SC-IVR, which treats all degrees of freedom within the same framework, provides an explicit (approximate) representation for the time evolution operator $e^{-i\hat{H}t/\hbar}$ which can be immediately applied in Eqs. (1.1) and (1.2) above. Section III shows how this is carried out and also introduces some approximations that make the resulting approach quite practical for complex systems.

Both of these approximate approaches are tested by application to the well-studied system-bath model, a one-dimensional double well potential linearly coupled to an infinite bath of harmonic oscillators, for which the Hamiltonian is

$$H=\frac{p_s^2}{2m_s}+V_s+\sum_j\left[\frac{P_j^2}{2m_j}+\frac{1}{2}m_j\omega_j^2\left(Q_j-\frac{c_js}{m_j\omega_j^2}\right)^2\right], \tag{1.8}$$

and which has been widely used to model the effect of a condensed phase environment on a reaction coordinate of interest.[24] The essential property of the harmonic bath is its spectral density[25]

$$J(\omega)=\frac{\pi}{2}\sum_j\frac{c_j^2}{m_j\omega_j}\,\delta(\omega-\omega_j), \tag{1.9}$$

which is chosen in the continuous Ohmic form with an exponential cutoff[25]

$$J(\omega)=\eta\omega e^{-\omega/\omega_c}, \tag{1.10}$$

where the cutoff frequency ω_c is chosen as 500 cm^{-1}. V_s is the 1-d double well potential

$$\begin{aligned}V_s&=-a_1s^2+a_2s^4,\\&=-\frac{1}{2}m_s\omega_b^2s^2+\frac{m_s^2\omega_b^4}{16V_0^{\ddagger}}s^4,\end{aligned} \tag{1.11}$$

where ω_b is the imaginary harmonic frequency at the top of the barrier, and $V_0^{\ddagger}$ the barrier height with respect to the bottom of the well. The specific parameters we have chosen for study correspond to the DW1 model potential used in the previous work of Topaler and Makri,[26] who performed essentially exact quantum path integral calculations which serve as the benchmark for the present approximate treatments. The barrier height and imaginary frequency for the DW1 potential are 2085 and 500 cm^{-1}, respectively, and the mass of the ''system'' is that of a proton. A quadrature discretization scheme is used to cast Eq. (1.10) in the form of Eq. (1.9); we found that 300 bath modes provide an adequate description for the problem. After discretization, the couplings in Eq. (1.8) are directly related to the spectral density.

Section II presents the mixed quantum-classical approach and its application to the system-bath model, and the SC-IVR methodology and its application are presented in Sec. III. Quite surprisingly (to us), the former approximation is found to be rather poor, while the latter (even approximate version of the) SC-IVR approach is quite good, over essentially the entire range from weak to strong coupling between the system and bath. Section IV summarizes and concludes.

II. THERMAL RATE CONSTANTS VIA A MIXED QUANTUM-CLASSICAL APPROACH

A. General methodology

For chemical reactions in a complex molecular system, it is often useful to divide the total Hamiltonian into three parts,

$$\hat{H}=\hat{H}_s+\hat{H}_b+\hat{H}_c, \tag{2.1}$$

where $\hat{H}_s$ is the Hamiltonian for the ''system,'' which consists of a few degrees of freedom most important in the reaction, $\hat{H}_b$ the Hamiltonian for the ''bath,'' which consists of the many degrees of freedom less central to the reaction, and $\hat{H}_c$ the Hamiltonian for the coupling between the two. The specific way the total Hamiltonian is divided up in Eq. (2.1) may, as we will see, be quite critical.

To keep the approach simple enough to be applicable to complex molecular systems, it is necessary to neglect the coupling term $\hat{H}_c$ in the Boltzmann operator [but see Eq. (2.5) below]. Denoting the ''system'' and ''bath'' coordinates by **s** and **q**, respectively, the dividing surface separating reactants and products is chosen to be a function only of the ''system'' coordinates **s**, so that the flux operator involves only the **s** degrees of freedom, i.e., $\hat{F}=\hat{F}_s$. It is then straightforward to show that the time-dependent self-consistent field (TDSCF) approximation[14]—with the classical limit for the bath degrees of freedom—gives the flux correlation function as

$$C_{ff}(t)=\int d\mathbf{p}_0\int d\mathbf{q}_0\rho_b(\mathbf{p}_0,\mathbf{q}_0)\mathrm{tr}[\hat{F}_s(\beta)\hat{U}^{+}(t)\hat{F}_s\hat{U}(t)], \tag{2.2}$$

where $(\mathbf{p}_0,\mathbf{q}_0)$ are the initial conditions for a classical trajectory of the ''bath'' degrees of freedom, $\hat{F}_s(\beta)$ is the Boltzmannized flux operator of the ''system,''

$$\hat{F}_s(\beta)=e^{-\beta\hat{H}_s/2}\hat{F}_s e^{-\beta\hat{H}_s/2}, \tag{2.3}$$

and $\hat{U}(t)$ is the time evolution operator for the quantum ''system'' with the time-dependent Hamiltonian operator,

$$\hat{H}_{\mathrm{QM}}(t)=\hat{H}_s+\hat{V}_c[\hat{\mathbf{s}},\mathbf{q}(t)], \tag{2.4}$$

where it has been assumed that the coupling $\hat{H}_c=\hat{V}_c$ is a potential energy type operator. The trace in Eq. (2.2) involves only operators of the ''system'' degrees of freedom, but since the ''bath'' trajectory $\mathbf{q}(t)$ depends on the initial conditions $(\mathbf{p}_0,\mathbf{q}_0)$, then so do $\hat{H}_c(t)$, $\hat{U}(t)$, and thus the value of the trace in Eq. (2.2). [We also considered the effect of including the coupling $\hat{H}_c$ in the Boltzmannized flux operator, i.e., replacing Eq. (2.3) by

$$\hat{F}_s(\beta,\mathbf{q}_0)=e^{-\beta[\hat{H}_s+\hat{H}_c(\mathbf{s},\mathbf{q}_0)]/2}\hat{F}_s e^{-\beta[\hat{H}_s+\hat{H}_c(\mathbf{s},\mathbf{q}_0)]/2}, \tag{2.5}$$

but this made negligible difference in the results presented in the next section, so we do not consider it further.] $\rho_b(\mathbf{p}_0,\mathbf{q}_0)$, the distribution of initial conditions for the ''bath'' trajectory, is the Wigner distribution function of the ''bath,''

$$\rho_b(\mathbf{p}_0,\mathbf{q}_0)=\frac{1}{(2\pi\hbar)^f}\times\int d\mathbf{\Delta q}e^{-i\mathbf{\Delta q}\cdot\mathbf{p}_0/\hbar}\times\left\langle\mathbf{q}_0+\frac{\mathbf{\Delta q}}{2}\right|e^{-\beta H_b}\left|\mathbf{q}_0-\frac{\mathbf{\Delta q}}{2}\right\rangle, \tag{2.6a}$$

where f is the number of degrees of freedom of the ''bath,'' and we note that the (quantum) partition function of the ''bath'' is given by its integral over all phase space,

$$Q_b(T)=\int d\mathbf{p}_0\int d\mathbf{q}_0\rho_b(\mathbf{p}_0,\mathbf{q}_0)=\mathrm{tr}_b(e^{-\beta\hat{H}_b}). \tag{2.6b}$$

Since the Boltzmannized flux operator of Eq. (2.3) involves only the few degrees of freedom of the ''system,'' it is diagonalized by the same procedure as in the rigorous quantum calculation summarized in the Introduction, yielding the eigenvalues $\{f_m\}$ and eigenvectors $\{|u_m\rangle\}$, and the trace in Eq. (2.2) is evaluated in this basis, so that Eq. (2.2) becomes

$$C_{ff}(t)=\int d\mathbf{p}_0\int d\mathbf{q}_0\rho_b(\mathbf{p}_0,\mathbf{q}_0)\sum_m f_m\langle u_m(t)|\hat{F}_s|u_m(t)\rangle, \tag{2.7a}$$

where

$$|u_m(t)\rangle=\hat{U}(t)|u_m\rangle. \tag{2.7b}$$

The split-operator algorithm[27] can still be used to carry out the time evolution in Eq. (2.7b) even though the Hamiltonian of Eq. (2.4) is time dependent; the specific form we have found to be most stable is

$$\begin{aligned}|u_m(t+\Delta t)\rangle&=e^{-i\hat{H}_c(t+\Delta t)\Delta t/4\hbar}e^{-i\hat{V}_s\Delta t/2\hbar}e^{-i\hat{H}_c(t+\Delta 3t/4)\Delta t/4\hbar}\\&\times e^{-i\hat{T}_s\Delta t/\hbar}e^{-i\hat{H}_c(t+\Delta t/2)\Delta t/4\hbar}\\&\times e^{-i\hat{V}_s\Delta t/2\hbar}e^{-i\hat{H}_c(t+\Delta t/4)\Delta t/4\hbar}|u_m(t)\rangle.\end{aligned} \tag{2.8}$$

Finally, for each value of m in Eq. (2.7b), i.e., each eigenvector $|u_m\rangle$, the classical Hamiltonian which determines the ''bath'' trajectory $\mathbf{q}(t)$ is

$$H_{\mathrm{CL}}(\mathbf{p},\mathbf{q})=H_b(\mathbf{p},\mathbf{q})+\langle u_m(t)|\hat{V}_c|u_m(t)\rangle(\mathbf{q}). \tag{2.9}$$

To summarize the overall procedure, the average over the initial conditions of the ''bath'' trajectory is most conveniently evaluated by Monte Carlo, i.e., by selecting initial conditions from the normalized distribution $\rho_b(\mathbf{p}_0,\mathbf{q}_0)/Q_b(T)$. If $(\mathbf{p}_0^j,\mathbf{q}_0^j)$ is the jth such selection of ''bath'' initial conditions, then Eq. (2.7) for the flux correlation function becomes

$$C_{ff}(t)=Q_b(T)\,\frac{1}{N}\sum_{j=1}^{N}\sum_m f_m\langle u_m^j(t)|\hat{F}_s|u_m^j(t)\rangle, \tag{2.10}$$

where $u_m^j(t)$ is the time-evolved vector for the jth ''bath'' trajectory. The diagonalization of $\hat{F}_s(\beta)$ (to obtain the eigenvalues $\{f_m\}$ and eigenvectors $\{|u_m\rangle\}$) must be carried out only once (for a given temperature T) but the quantum and classical time evolution to produce $\{|u_m^j(t)\rangle\}$ and $\{\mathbf{q}_m^j(t)\}$ must be carried out for each set of initial conditions of the ''bath.''

Wahnström *et al.*[28] have earlier employed a semiclassical TDSCF approach very similar to that described above. Besides a different initial distribution function [i.e., these authors utilized the classical distribution $\exp[-\beta H_b(\mathbf{p}_0,\mathbf{q}_0)]$, rather than the Wigner distribution function of Eq. (2.6a)], perhaps the most significant difference is that the above development utilizes the eigenvectors of the Boltzmannized flux operator as the initial states for the time evolution of the ''system,'' while Wahnström *et al.* use a different basis that applies specifically for a one-dimensional ''system.'' We believe that the present treatment is the most systematic way to exploit the low rank character of the quantum trace, especially if the ''system'' has several degrees of freedom. We also note the work by Matzkies and Manthe,[12(b)] where they treat the entire molecular system via a multiconfiguration TDSCF expansion and do not deal explicitly with a ''system''–''bath'' separation. It would, however, be possible to do so within their formulation; e.g., one would use multiconfiguration (i.e., ''correlation'') only within the ''system'' degrees of freedom, and retain a single configuration for each ''bath'' degree of freedom. This approach is certainly a viable one for dealing with ''system''-''bath'' type problems, although in most cases even a single configuration treatment of the ''bath'' is difficult if a fully quantum description is retained.

B. Application to the system-bath model

The above approach can be readily applied to the system-bath model described by Eqs. (1.8)–(1.11) in the Introduction. A Lanczos procedure is first used to find the eigenvectors with largest absolute eigenvalues for the "system" degree of freedom[2–5] (in this one-dimensional case, there are only two eigenvectors with nonzero eigenvalues[10,29]). The initial conditions of the "bath" trajectories are sampled from the Wigner distribution at the saddle points $(s=0)$. For a collection of harmonic oscillators, the normalized Wigner distribution is given by

$$\rho_b(\mathbf{P}_{,0},\mathbf{Q}_0)=\prod_i \frac{\tanh(u_i)}{\pi\hbar} \times \exp\left[-\frac{2\tanh(u_i)}{\hbar\omega_i}\left(\frac{P_{i0}^2}{2}+\frac{\omega_i^2}{2}Q_{i0}^2\right)\right], \tag{2.11}$$

where $u_i=\hbar\beta\omega_i/2$. The real time propagation is then carried out via Eq. (2.8) to generate the flux correlation function $C_{ff}(t)$. Approximately 100 sinc-function discrete variable representation (DVR) functions[30] were used for the "system" degree of freedom and 3000 trajectories for the "bath." The results are reported in terms of the transmission coefficient, defined by

$$\kappa=k/k_{\mathrm{TST,CL}}, \tag{2.12}$$

where $k_{\mathrm{TST,CL}}$ is the classical transition state theory rate constant for the original one-dimensional double well,

$$k_{\mathrm{TST,CL}}=\frac{\omega_{s0}}{2\pi}\,e^{-\beta V_0^{\ddagger}}. \tag{2.13}$$

With the quantum "system" and classical "bath" defined as in Eq. (1.8), however, the rate constants obtained from the methodology of Sec. II A [i.e., Eq. (2.10), etc.] are in quite poor agreement with the accurate quantum results of Topaler and Makri.[26] Figure 1(a) shows the rate constant at 300 K as a function of the dimensionless coupling parameter $\eta/m_s\omega_b$, together with the quantum path integral results; one sees that the mixed quantum-classical approximation gives answers at least twice as large as the accurate quantum mechanical results, which is clearly inadequate.

We attribute the failure of this natural and most commonly used choice of the quantum "system" and classical "bath" to the fact that the s and $\mathbf{Q}$ degrees of freedom are strongly coupled in the transition state region that is most crucial for determining the reaction rate. Matters can thus be somewhat improved by making a different choice for the (quantum) "system" and the (classical) "bath," one that reduces the coupling between them in the transition state region. This is done by transforming to the normal coordinates at the transition state.[31] Written in these new (mass-weighted) coordinates, $(x,\mathbf{q})$, the total Hamiltonian is separated into three parts as follows,

$$H=H_x+H_b(\mathbf{q},\mathbf{p})+V_c(x,\mathbf{q}), \tag{2.14a}$$

where

$$H_x=\frac{1}{2}p_x^2-\frac{1}{2}\lambda^{\ddagger 2}x^2+\frac{1}{16V_0^{\ddagger}}\lambda^{\ddagger 4}x^4, \tag{2.14b}$$

$$H_b(\mathbf{q},\mathbf{p})=\frac{1}{2}\sum_i (p_i^2+\lambda_i^2 q_i^2), \tag{2.14c}$$

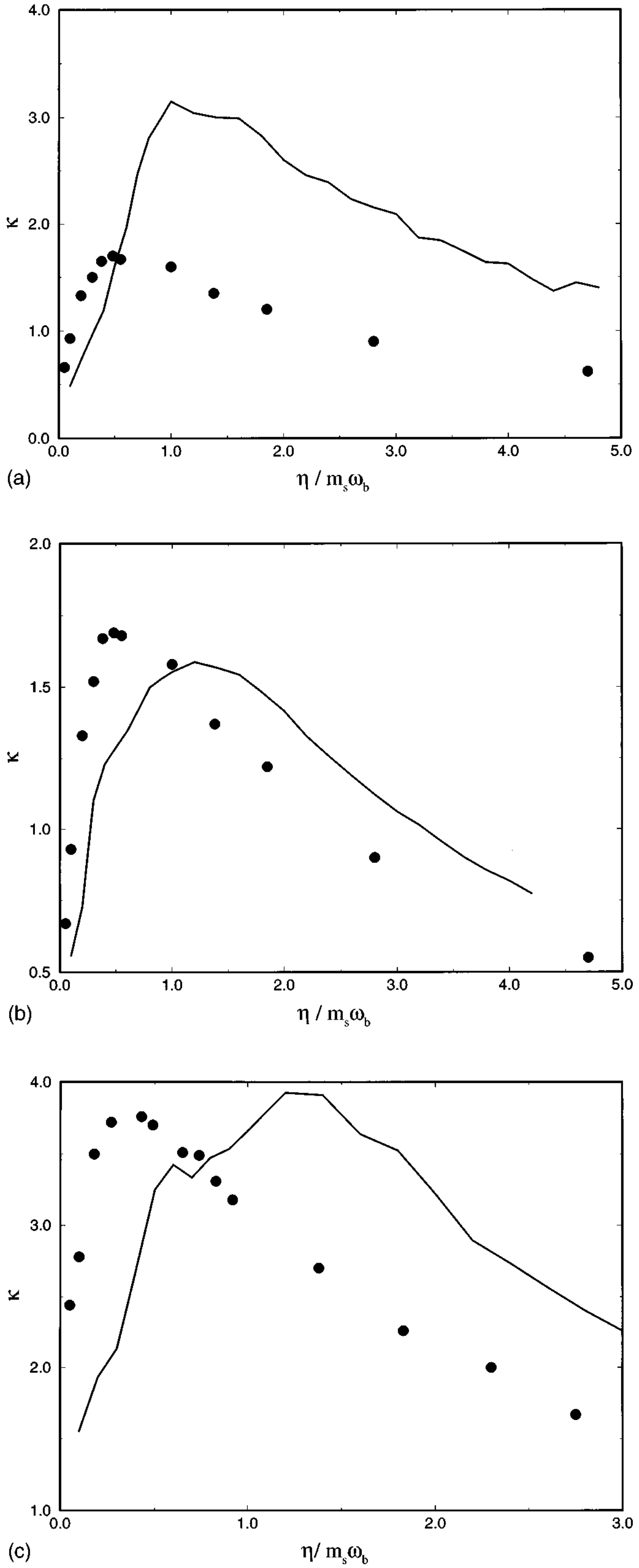

FIG. 1. Transmission coefficient $\kappa=k/k_{\mathrm{TST,CL}}$ as a function of coupling parameter $\eta/m_s\omega_b$ at $T=300$ K; the solid line is the result from the mixed quantum-classical methodology described in Sec. II, and the solid circles are from the accurate quantum path integral calculations of Topaler and Makri, Ref. 26. (a) The "system"-"bath" separation is done via Eq. (1.8); (b) the "system"-"bath" separation is done via Eq. (2.14); (c) same as (b), but for $T=200$ K.

$$V_c(x,\mathbf{q}) = \frac{\omega_b^4}{16V_0^\ddagger}\left(U_{11}x + \sum_i U_{1,i+1}q_i\right)^4 - \frac{1}{16V_0^\ddagger}\lambda^{\ddagger 4}x^4, \tag{2.14d}$$

where $\lambda^\ddagger$ is the imaginary frequency of the unstable normal mode obtained by diagonalizing the full force constant matrix $\mathbf{F}$ at the transition state, λ_i's are the frequencies of the stable normal modes, and $\mathbf{U}$ is the eigenvector matrix of $\mathbf{F}$, all of which change as a function of the coupling parameter η. The new ''system'' is still chosen as a double well[32] in the unstable normal mode direction, with barrier height $V_0^\ddagger$ invariant to the coupling η.

With this improved definition of the ''system'' and ''bath,'' the rate constants given by the mixed quantum-classical model are decidedly better, as seen in Fig. 1(b), though still not particularly good: Figure 1(c) shows the results of the calculations at the lower temperature, $T = 200$ K, where agreement with the correct quantum results becomes decidedly worse, which is perhaps to be expected since quantum effects are more prominent at lower temperature. (With the original choice of ''system'' and ''bath'' the results are even worse.) Overall, the results given by the mixed quantum-classical model are not very good, a sobering observation for such a widely used approach.

Finally, we note that in previous work[33] Stock has performed semiclassical TDSCF calculations for a spin-boson (i.e., two state) system coupled to the harmonic bath in a similar fashion as done in this paper, and observed ''good agreement'' with accurate quantum path integral calculations for the survival probability of an initial state of the ''system.'' The dimensionless parameters used by Stock, however, are so far from the range of our physical model that little comparison with these calculations is possible. For example, using simple semiclassical arguments,[34] one can estimate from our barrier height ($V_0^\ddagger = 2085\ \mathrm{cm}^{-1} \simeq 6$ kcal/mol) and frequency that the exchange matrix element between the two lowest localized vibrational states in the two minima of our double well potential is $\sim 10^{-3}\ \mathrm{cm}^{-1}$, which is at least four orders of magnitude smaller than Stock's comparable parameter for a reasonable choice of the temperature.

III. THERMAL RATE CONSTANTS VIA THE SEMICLASSICAL INITIAL VALUE REPRESENTATION

A. General formulation

To employ the semiclassical initial value representation[16–23] (SC-IVR), we find it most convenient to use the integrated form of the rate expression, Eq. (1.2b):

$$k(T) = Q_r(T)^{-1}\lim_{t\to\infty} C_{fs}(t), \tag{3.1}$$

where t is a large positive value. Specifically,

$$\begin{aligned} C_{fs}(t) &= \mathrm{tr}[\hat{F}(\beta)e^{i\hat{H}t/\hbar}\hat{h}(\hat{s})e^{-i\hat{H}t/\hbar}] \\ &= \int d\mathbf{q}\int d\mathbf{q}'\int d\mathbf{q}_0\int d\mathbf{q}_0'\langle\mathbf{q}|\hat{F}(\beta)|\mathbf{q}'\rangle \\ &\quad\times\langle\mathbf{q}'|e^{i\hat{H}t/\hbar}|\mathbf{q}_0'\rangle\langle\mathbf{q}_0'|\hat{h}(\hat{s})|\mathbf{q}_0\rangle\langle\mathbf{q}_0|e^{-i\hat{H}t/\hbar}|\mathbf{q}\rangle. \end{aligned} \tag{3.2}$$

Here $s(\mathbf{q})$ is some function of the coordinates $\mathbf{q}$ that is positive (negative) on the product (reactant) side of the dividing surface—i.e., $s(\mathbf{q}) = 0$ defines the dividing surface—so that

$$\langle\mathbf{q}_0'|\hat{h}(\hat{s})|\mathbf{q}_0\rangle = h[s(\mathbf{q}_0)]\,\delta_f(\mathbf{q}_0' - \mathbf{q}_0), \tag{3.3}$$

where $h(s)$ is the Heaviside function ($=0$ or 1 for $s<0$ or >0, respectively). We also note the following symmetry relations of the matrix elements of the time evolution operator,

$$\langle\mathbf{q}'|e^{-i\hat{H}t/\hbar}|\mathbf{q}\rangle = \langle\mathbf{q}|e^{-i\hat{H}t/\hbar}|\mathbf{q}'\rangle \tag{3.4a}$$

$$= \langle\mathbf{q}'|e^{i\hat{H}t/\hbar}|\mathbf{q}\rangle^*. \tag{3.4b}$$

The semiclassical initial value representation[16–23] (SC-IVR) is now used for the time evolution operator, i.e.,

$$\langle\mathbf{q}|e^{-i\hat{H}t/\hbar}|\mathbf{q}_0\rangle = \int d\mathbf{p}_0\,\delta_f(\mathbf{q} - \mathbf{q}_t) \times\left[\det\left(\frac{\partial\mathbf{q}_t}{\partial\mathbf{p}_0}\right)\bigg/(2i\pi\hbar)^f\right]^{1/2} e^{iS_t(\mathbf{p}_0,\mathbf{q}_0)/\hbar}, \tag{3.5}$$

where $\mathbf{q}_t(\mathbf{p}_0,\mathbf{q}_0)$ is the trajectory determined by initial conditions $(\mathbf{p}_0,\mathbf{q}_0)$ and $S_t(\mathbf{p}_0,\mathbf{q}_0)$ the classical action integral along it. Utilizing Eqs. (3.3)–(3.5) in Eq. (3.2) gives the basic SC-IVR result for the integrated flux correlation function,

$$\begin{aligned} C_{fs}(t) &= (2\pi\hbar)^{-f}\int d\mathbf{q}_0 h[s(\mathbf{q}_0)] \\ &\quad\times\int d\mathbf{p}_0\int d\mathbf{p}_0'\langle\mathbf{q}_t|\hat{F}(\beta)|\mathbf{q}_t'\rangle\exp\{i[S_t(\mathbf{p}_0,\mathbf{q}_0) \\ &\quad - S_t(\mathbf{p}_0',\mathbf{q}_0)]/\hbar\}\left[\det\left(\frac{\partial\mathbf{q}_t}{\partial\mathbf{p}_0}\right)\right]^{1/2}\left[\det\left(\frac{\partial\mathbf{q}_t'}{\partial\mathbf{p}_0'}\right)\right]^{1/2}, \end{aligned} \tag{3.6}$$

where $\mathbf{q}_t = \mathbf{q}_t(\mathbf{p}_0,\mathbf{q}_0)$ and $\mathbf{q}_t' = \mathbf{q}_t(\mathbf{p}_0',\mathbf{q}_0)$.

Equation (3.6) is the general result of the SC-IVR for the thermal rate constant, and it is what we would indeed like to evaluate. In this paper, however, we consider an approximation to the full-blown SC-IVR expression, one that leads to a much simpler result. Similar to the analysis used previously by two of us,[23(c)] we make a sum and difference change of integration variables from $\mathbf{p}_0$ and $\mathbf{p}_0'$ to $\overline{\mathbf{p}_0}$ and $\mathbf{\Delta p}_0$,

$$\overline{\mathbf{p}_0} = \frac{1}{2}(\mathbf{p}_0 + \mathbf{p}_0'), \tag{3.7a}$$

$$\mathbf{\Delta p}_0 = \mathbf{p}_0 - \mathbf{p}_0', \tag{3.7b}$$

and then make a linear expansion of all relevant quantities in the difference variable $\mathbf{\Delta p}_0$,

$$\mathbf{q}_t(\mathbf{p}_0) = \mathbf{q}_t(\overline{\mathbf{p}_0} + \mathbf{\Delta p}_0/2) \simeq \mathbf{q}_t(\overline{\mathbf{p}_0}) + \frac{\partial\mathbf{q}_t(\overline{\mathbf{p}_0})}{\partial\overline{\mathbf{p}_0}}\cdot\frac{\mathbf{\Delta p}_0}{2}, \tag{3.8a}$$

$$\mathbf{q}_t'(\mathbf{p}_0') = \mathbf{q}_t(\overline{\mathbf{p}_0} - \mathbf{\Delta p}_0/2) \simeq \mathbf{q}_t(\overline{\mathbf{p}_0}) - \frac{\partial\mathbf{q}_t(\overline{\mathbf{p}_0})}{\partial\overline{\mathbf{p}_0}}\cdot\frac{\mathbf{\Delta p}_0}{2}, \tag{3.8b}$$

$$\frac{\partial\mathbf{q}_t(\mathbf{p}_0)}{\partial\mathbf{p}_0} \simeq \frac{\partial\mathbf{q}_t'(\mathbf{p}_0')}{\partial\mathbf{p}_0'} \simeq \frac{\partial\mathbf{q}_t(\overline{\mathbf{p}_0})}{\partial\overline{\mathbf{p}_0}}, \tag{3.8c}$$

$$S_t\left(\overline{\mathbf{p}_0}+\frac{\Delta\mathbf{p}_0}{2},\mathbf{q}_0\right)-S_t\left(\overline{\mathbf{p}_0}-\frac{\Delta\mathbf{p}_0}{2},\mathbf{q}_0\right)$$
$$\simeq\frac{\partial S_t(\overline{\mathbf{p}_0},\mathbf{q}_0)}{\partial\overline{\mathbf{p}_0}}\cdot\Delta\mathbf{p}_0=\overline{\mathbf{p}_t}\cdot\frac{\partial\mathbf{q}_t}{\partial\overline{\mathbf{p}_0}}\cdot\Delta\mathbf{p}_0.\tag{3.8d}$$

(Our abbreviated notation is, for example, that $\partial\mathbf{q}_t/\partial\overline{\mathbf{p}_0}$ is the matrix $(\partial\mathbf{q}_t/\partial\overline{\mathbf{p}_0})_{i,i'}=\partial q_{i,t}/\partial\overline{p}_{i',0}$.) Equation (3.6) then becomes

$$C_{fs}(t)=(2\pi\hbar)^{-f}\int d\mathbf{q}_0 h[s(\mathbf{q}_0)]$$
$$\times\int d\overline{\mathbf{p}_0}\int d\Delta\mathbf{p}_0\exp\left(i\overline{\mathbf{p}}_t\cdot\frac{\partial\mathbf{q}_t}{\partial\overline{\mathbf{p}_0}}\cdot\Delta\mathbf{p}_0/\hbar\right)$$
$$\times\det\left(\frac{\partial\mathbf{q}_t}{\partial\overline{\mathbf{p}_0}}\right)\left\langle\mathbf{q}_t+\frac{\partial\mathbf{q}_t}{\partial\overline{\mathbf{p}_0}}\cdot\frac{\Delta\mathbf{p}_0}{2}\right.$$
$$\left.\times|\hat{F}(\beta)|\mathbf{q}_t-\frac{\partial\mathbf{q}_t}{\partial\overline{\mathbf{p}_0}}\cdot\frac{\Delta\mathbf{p}_0}{2}\right\rangle.\tag{3.9}$$

If we make the further change of integration variables from $\Delta\mathbf{p}_0$ to $\Delta\mathbf{q}$,

$$\Delta\mathbf{q}=\frac{\partial\mathbf{q}_t}{\partial\overline{\mathbf{p}_0}}\cdot\Delta\mathbf{p}_0,\tag{3.10}$$

then the correlation function simplifies to

$$C_{fs}(t)=\int d\mathbf{q}_0\int d\overline{\mathbf{p}_0}h[s(\mathbf{q}_0)]F_w^\beta(\mathbf{q}_t,-\overline{\mathbf{p}_t}),\tag{3.11}$$

where $F_w^\beta(\mathbf{q}_t,-\overline{\mathbf{p}_t})$ is the Wigner/Weyl transform[35] of the Boltzmannized flux operator $\hat{F}(\beta)$, which is defined as

$$F_w^\beta(\mathbf{q},\mathbf{p})=(2\pi\hbar)^{-f}\int d\Delta\mathbf{q}e^{-i\mathbf{p}\cdot\Delta\mathbf{q}/\hbar}$$
$$\times\left\langle\mathbf{q}+\frac{\Delta\mathbf{q}}{2}|\hat{F}(\beta)|\mathbf{q}-\frac{\Delta\mathbf{q}}{2}\right\rangle.\tag{3.12}$$

Finally, we make some ''housecleaning'' changes to Eq. (3.11): it is easy to show that $F_w^\beta(\mathbf{q},\mathbf{p})$ is an odd function of $\mathbf{p}$, and it is well known[6(b)] that $C_{fs}(t)$ is an odd function of t, so the changes $t\rightarrow-t$ and $\mathbf{p}_t\rightarrow-\mathbf{p}_t$ leave the result unchanged,

$$C_{fs}(t)=\int d\mathbf{q}_0\int d\mathbf{p}_0 h[s(\mathbf{q}_0)]F_w^\beta(\mathbf{q}_{-t},\mathbf{p}_{-t}),\tag{3.13}$$

where we have also dropped the ''bar'' over $\mathbf{p}_0$ and $\mathbf{p}_{-t}$ since they no longer serve any purpose. Liouville's theorem is now used to change the phase space integral from one over $(\mathbf{q}_0,\mathbf{p}_0)$ to one over $(\mathbf{q}_{-t},\mathbf{p}_{-t})$, and the new zero of time is taken to be $-t$, so that $(\mathbf{q}_{-t},\mathbf{p}_{-t})\rightarrow(\mathbf{q}_0,\mathbf{p}_0)$, and $(\mathbf{q}_0,\mathbf{p}_0)\rightarrow(\mathbf{q}_t,\mathbf{p}_t)$, whereby the final and central result of this approximate SC-IVR approach is given by

$$C_{fs}(t)=\int d\mathbf{q}_0\int d\mathbf{p}_0 F_w^\beta(\mathbf{q}_0,\mathbf{p}_0)h[s(\mathbf{q}_t)].\tag{3.14}$$

Equation (3.14), along with Eq. (3.1), provides an extremely practical procedure for computing thermal rate constants: one averages over the phase space of initial conditions, weighted by the distribution function $F_w^\beta(\mathbf{q}_0,\mathbf{p}_0)$, and then integrates the classical trajectory with these initial conditions to determine whether $\lim_{t\rightarrow\infty}h[s(\mathbf{q}_t)]=0$ or 1, i.e., whether the trajectory goes to reactants or products, respectively. The only difference between this and an ordinary classical trajectory calculation is the weighting function for the initial conditions, which classically would be as follows:

$$F_w^\beta(\mathbf{q}_0,\mathbf{p}_0)\rightarrow(2\pi\hbar)^{-f}e^{-\beta H(\mathbf{q}_0,\mathbf{p}_0)}\delta[s(\mathbf{q}_0)]\frac{\partial s(\mathbf{q}_0)}{\partial\mathbf{q}_0}\cdot\mathbf{p}_0/m.\tag{3.15}$$

We note that this ''Wigner overlap'' type result in Eq. (3.14) has appeared in many approximate dynamical theories. For example, it is very similar to one put forth many years ago by one of us;[6(a)] that work had the Wigner distribution function for the Boltzmann operator, $e^{-\beta\hat{H}}$, and the classical factor for $\hat{F}\hat{h}(\hat{s}_t)$. Heller[36] has given a very illuminating discussion of this type of approximation (and its limitations) and used it for photodissociation.[36(b)] Lee and Scully[37] have used it to treat inelastic scattering. More recently, Filinov[38] has presented an approach for evaluating time correlation functions, such as $C_{fs}(t)$ above, that starts with the Wigner transform of the quantum trace expression, the lowest order approximation to which is Eq. (3.14). Also, Pollak *et al.*[39] have presented a ''quantum transition state theory'' that corresponds to Eq. (3.14) with a further approximation to the time-evolved factor (that of a separable one-dimensional reaction coordinate) that allows no recrossing trajectories (which is the basic transition state theory approximation). Finally, it is interesting that unlike this earlier work, the above development leading to Eq. (3.14) did not begin with the Wigner transformation of the trace expression, but rather the Wigner transform of $\hat{F}(\beta)$ falls out ''automatically'' once the linearization approximation is made to the general SC-IVR expression.

B. Normal mode approximation for the Boltzmannized flux operator

The major task in applying Eq. (3.14) is the construction of the Wigner distribution function for the Boltzmannized flux operator, $F_w^\beta(\mathbf{q}_0,\mathbf{p}_0)$, defined by Eq. (3.12). For small molecular systems one can use the approach summarized in the Introduction, i.e., exploit the low rank of $\hat{F}(\beta)$ and use Eq. (1.5) to give

$$F_w^\beta(\mathbf{q}_0,\mathbf{p}_0)=\sum_m f_m(2\pi\hbar)^{-f}\int d\Delta\mathbf{q}e^{-i\mathbf{p}_0\cdot\Delta\mathbf{q}/\hbar}$$
$$\times\left\langle\mathbf{q}_0+\frac{\Delta\mathbf{q}}{2}\middle|u_m\right\rangle\left\langle u_m\middle|\mathbf{q}_0-\frac{\Delta\mathbf{q}}{2}\right\rangle.\tag{3.16}$$

We note that the above formula contains no real time dynamics. It requires essentially the same calculational effort as in quantum (nonseparable) transition state theory and is thus much less expensive than a rigorous quantum dynamics calculation. It would be quite interesting to use Eq. (3.16), together with a classical trajectory calculation, to evaluate Eq. (3.14) for the rate constants of some small molecule reactions.

For systems with many degrees of freedom, however, it will not be possible even to evaluate $F_w^\beta(\mathbf{q_0},\mathbf{p_0})$ without further approximations. Note, though, that this does not entail any further approximation to the real time dynamics, but rather to the weighting of the initial conditions for the real time trajectories. A common approximation,[40,41] often used for sampling initial conditions in classical trajectory calculations, is a harmonic approximation in normal mode coordinates at the transition state, which we now employ for the purpose of constructing $F_w^\beta(\mathbf{q_0},\mathbf{p_0})$. Thus the Hamiltonian is approximated by

$$H \simeq H_f + H_b, \tag{3.17a}$$

where H_f involves the one mode with imaginary frequency (the reaction coordinate) and H_b the $f-1$ modes with real frequencies,

$$H_f = \frac{1}{2m_f} p_f^2 - \frac{1}{2} m_f \omega^{\ddagger^2} q_f^2 + V_0^\ddagger, \tag{3.17b}$$

$$H_b = \sum_{j=1}^{f-1} H_{bj} = \sum_{j=1}^{f-1} \left(\frac{1}{2m_j} p_j^2 + \frac{1}{2} m_j \omega_j^2 q_j^2 \right), \tag{3.17c}$$

$\omega^\ddagger$ and ω_j are the imaginary and real frequencies at the saddle point, and q_f, p_f and q_j, p_j are the corresponding coordinates and momenta, respectively. Since the flux operator involves only the reaction coordinate q_f, the Wigner distribution $F_w^\beta(\mathbf{q_0},\mathbf{p_0})$ can be written as

$$F_w^\beta(\mathbf{q_0},\mathbf{p_0}) = F_w^{\beta,f}(q_{f0},p_{f0})\,\rho_w^b(\mathbf{q_0}^b,\mathbf{p_0}^b), \tag{3.18a}$$

where

$$F_w^{\beta,f}(q_{f0},p_{f0}) = (2\pi\hbar)^{-1} \int d\Delta q_f e^{-ip_{f0}\Delta q_f/\hbar} \times \left\langle q_{f0} + \frac{\Delta q_f}{2} \right| \hat{F}_f(\beta) \left| q_{f0} - \frac{\Delta q_f}{2} \right\rangle, \tag{3.18b}$$

$$\hat{F}_f(\beta) = e^{-\beta \hat{H}_f/2} \frac{i}{\hbar} [\hat{H}_f, \hat{h}(\hat{q}_f)] e^{-\beta \hat{H}_f/2}, \tag{3.18c}$$

and

$$\begin{aligned} \rho_w^b(\mathbf{q_0}^b,\mathbf{p_0}^b) &= (2\pi\hbar)^{-(f-1)} \int d\mathbf{\Delta q}^b e^{-i\mathbf{p_0}^b\cdot\mathbf{\Delta q}^b/\hbar} \times \left\langle \mathbf{q_0}^b + \frac{\mathbf{\Delta q}^b}{2} \right| e^{-\beta \hat{H}_b} \left| \mathbf{q_0}^b - \frac{\mathbf{\Delta q}^b}{2} \right\rangle \\ &= \prod_{j=1}^{f-1} (2\pi\hbar)^{-1} \int d\Delta q_j e^{-ip_{j0}\Delta q_j/\hbar} \times \left\langle q_{j0} + \frac{\Delta q_j}{2} \right| e^{-\beta \hat{H}_{bj}} \left| q_{j0} - \frac{\Delta q_j}{2} \right\rangle, \end{aligned} \tag{3.18d}$$

where $\{\mathbf{q}^b,\mathbf{p}^b\}$ denote the $f-1$ coordinates and momenta perpendicular to the reaction coordinate. Making use of the following matrix elements:

$$\langle q_f | \hat{F}_f | q_f' \rangle = \frac{\hbar}{2im_f} [\delta'(q_f)\delta(q_f') - \delta(q_f)\delta'(q_f')], \tag{3.19a}$$

$$\langle q_f | e^{-\beta \hat{H}_f/2} | q_f' \rangle = e^{-\beta V_0^\ddagger} \left[\frac{m_f \omega^\ddagger}{2\pi\hbar \sin(u^\ddagger)} \right]^{1/2} \times \exp\left\{ -\frac{m_f \omega^\ddagger}{2\hbar \sin(u^\ddagger)} [(q_f^2 + q_f'^2) \times \cos(u^\ddagger) - 2q_f q_f'] \right\}, \tag{3.19b}$$

$$\langle q_j | e^{-\beta \hat{H}_{bj}} | q_j' \rangle = \left[\frac{m_j \omega_j}{2\pi\hbar \sinh(2u_j)} \right]^{1/2} \times \exp\left\{ -\frac{m_j \omega_j}{2\hbar \sinh(2u_j)} [(q_j^2 + q_j'^2) \times \cosh(2u_j) - 2q_j q_j'] \right\}, \tag{3.19c}$$

where we denote $u^\ddagger = \hbar\beta\omega^\ddagger/2$ and $u_j = \hbar\beta\omega_j/2$, it is not hard to show that Eqs. (3.18) give

$$F_w^{\beta,f}(q_{f0},p_{f0}) = \frac{m_f \omega^\ddagger e^{-\beta V_0^\ddagger}}{2\pi \sin(2u^\ddagger)} \left\{ \left[\frac{m_f \omega^\ddagger \cot(u^\ddagger)}{\pi\hbar} \right]^{1/2} \times \exp[-m_f \omega^\ddagger \cot(u^\ddagger) q_{f0}^2/\hbar] \right\} \times \left\{ \frac{2p_{f0}}{\hbar m_f \omega^\ddagger \cot(u^\ddagger)} \times \exp\left[-\frac{p_{f0}^2}{\hbar m_f \omega^\ddagger \cot(u^\ddagger)} \right] \right\}, \tag{3.20a}$$

$$\rho_w^b(\mathbf{q_0}^b,\mathbf{p_0}^b) = \prod_{j=1}^{f-1} \frac{1}{2\sinh(u_j)} \left\{ \frac{\tanh(u_j)}{\pi\hbar} \times \exp\left[-\frac{2\tanh(u_j)}{\hbar\omega_j} \left(\frac{p_{j0}^2}{2m_j} + \frac{1}{2} m_j \omega_j^2 q_{j0}^2 \right) \right] \right\}. \tag{3.20b}$$

Equation (3.20), with Eq. (3.18a), thus provides a simple analytic result for the Wigner function of the Boltzmannized flux operator within the normal mode approximation. It can readily be used in Eq. (3.14) to provide the distribution of initial conditions for classical trajectories to obtain $C_{fs}(t \to \infty)$ and thus the rate constant. The procedure is really no more difficult than a standard classical trajectory calculation.

Due to the thermodynamic properties of the parabolic barrier, Eq. (3.20a) is only valid for $u^\ddagger = \hbar\beta\omega^\ddagger/2 < \pi/2$ or $T > T_c = \hbar\omega^\ddagger/\pi k_B$. Furthermore, for temperatures only slightly above T_c, the coordinate distribution in Eq. (3.20a) is so broad that the quadratic approximation to the potential may fail. Higher order expansions of the potential are then needed to account for these and other anharmonic effects.

It is quite simple to include diagonal anharmonicity for any (or all) of the modes at the transition state. Though it is unlikely that the Wigner function can be obtained in analytic form, the necessary integrals,

$$F_w^{\beta,f}(q_{f0},p_{f0})=(2\pi\hbar)^{-1}\int d\Delta q_f e^{-ip_{f0}\Delta q_f/\hbar} \times\left\langle q_{f0}+\frac{\Delta q_f}{2}\right|\hat{F}_f(\beta)\left|q_{f0}-\frac{\Delta q_f}{2}\right\rangle \tag{3.21a}$$

and

$$\rho_{w,j}^{b}(q_{0j},p_{0j})=(2\pi\hbar)^{-1}\int d\Delta q_j e^{-ip_{j0}\Delta q_j/\hbar} \times\left\langle q_{j0}+\frac{\Delta q_j}{2}\right|e^{-\beta\hat{H}_{bj}}\left|q_{j0}-\frac{\Delta q_j}{2}\right\rangle \tag{3.21b}$$

are all one-dimensional Fourier transforms and thus readily obtained numerically.

To account for off-diagonal anharmonicity, i.e., nonseparability, is of course more difficult. The evaluation of Eq. (3.12) to obtain $F_w^{\beta}(\mathbf{q_0},\mathbf{p_0})$ without approximation involves an f-dimensional Fourier transform, and with efficiency provided by the fast Fourier transform (FFT) algorithm can thus be evaluated for moderately large systems. One can also resort to approximations in the spirit of Sec. II, i.e., assume that the complete set of degrees of freedom can be divided into a small set that is most important to the reaction, that is treated fully anharmonically, and the remainder that are less important and approximated more primitively (e.g., harmonically). Thus the ability to construct the Wigner function $F_w^{\beta}(\mathbf{q_0},\mathbf{p_0})$ should not prohibit one from being able to apply Eq. (3.16) to a wide range of interesting molecular problems. Also, it should be emphasized that the Wigner distribution function of the Boltzmannized flux operator is only used for weighting initial conditions of classical trajectories; the real time dynamics is still solved with the full Hamiltonian as in any molecular dynamics simulation, thus including the full anharmonicity and nonseparability of the potential energy surface.

C. Applications

Before considering application to the system-bath problem of Eqs. (1.8)–(1.11), it is of pedagogical interest to show how it applies to the one-dimensional parabolic barrier. Equations (3.1) and (3.14) give

$$k(T)Q_r(T)=\int_{-\infty}^{\infty}dq_0\int_{-\infty}^{\infty}dp_0 h(q_{t\to\infty})F_w^{\beta}(q_0,p_0), \tag{3.22}$$

which we break up into four terms as follows,

$$k(T)Q_r(T)=\int_{0}^{\infty}dq_0\int_{0}^{\infty}dp_0 h(q_{t\to\infty})_1F_w^{\beta}(q_0,p_0) \tag{3.23a}$$

$$+\int_{-\infty}^{0}dq_0\int_{0}^{\infty}dp_0 h(q_{t\to\infty})_2F_w^{\beta}(q_0,p_0) \tag{3.23b}$$

$$+\int_{0}^{\infty}dq_0\int_{-\infty}^{0}dp_0 h(q_{t\to\infty})_3F_w^{\beta}(q_0,p_0) \tag{3.23c}$$

$$+\int_{-\infty}^{0}dq_0\int_{-\infty}^{0}dp_0 h(q_{t\to\infty})_4F_w^{\beta}(q_0,p_0), \tag{3.23d}$$

where the initial Wigner distribution function is given in Eq. (3.20a). Since this is a one-dimensional problem, the reaction probability $h(q_{t\to\infty})$ is determined for the above integrals simply by the energy,

$$h(q_{t\to\infty})_1=1, \tag{3.24a}$$

$$h(q_{t\to\infty})_2=h(E_0-V_0^{\ddagger}), \tag{3.24b}$$

$$h(q_{t\to\infty})_3=h(V_0^{\ddagger}-E_0), \tag{3.24c}$$

$$h(q_{t\to\infty})_4=0, \tag{3.24d}$$

where

$$E_0=\frac{1}{2m}p_0^2-\frac{1}{2}m\omega^{\ddagger 2}q_0^2+V_0^{\ddagger}. \tag{3.25}$$

Changing variables and merging the integrals in Eq. (3.23a), one obtains

$$\begin{aligned}k(T)Q_r(T)&=2\int_0^{\infty}dq_0\int_0^{\infty}dp_0 h(E_0-V_0^{\ddagger})F_w^{\beta}(q_0,p_0)\\&=2\int_0^{\infty}dq_0\int_0^{\infty}dp_0 h(p_0-m\omega^{\ddagger}q_0)F_w^{\beta}(q_0,p_0)\\&=\frac{\omega^{\ddagger}e^{-\beta V_0^{\ddagger}}}{4\pi\,\sin(\hbar\beta\omega^{\ddagger}/2)} &(3.26a)\\&=\kappa\,\frac{k_BT}{h}\,e^{-\beta V_0^{\ddagger}}, &(3.26b)\end{aligned}$$

with

$$\kappa=\frac{\hbar\beta\omega^{\ddagger}/2}{\sin(\hbar\beta\omega^{\ddagger}/2)}, \tag{3.27}$$

which is recognized to be the exact result for the parabolic barrier.

Application of Eq. (3.14) to obtain the thermal rate constant of the system-bath model of Eqs. (1.8)–(1.11) is straightforward. Calculations were performed as a function of the coupling parameter η at two temperatures, 200 and 300 K. At $T=300$ K, the temperature is sufficiently far above $T_c=\hbar\omega^{\ddagger}/\pi k_B$ for all η's of interest that the harmonic approximation of Eqs. (3.18) and (3.20) gives accurate results for the Wigner distribution function. We found 3000 trajectories to be sufficient to obtain converged rate constants. At $T=200$ K, however, the temperature is below or near T_c in the small η regime, and Eq. (3.20a) no longer valid. At this temperature we therefore included diagonal anharmonicity in the reaction coordinate, i.e., still applying

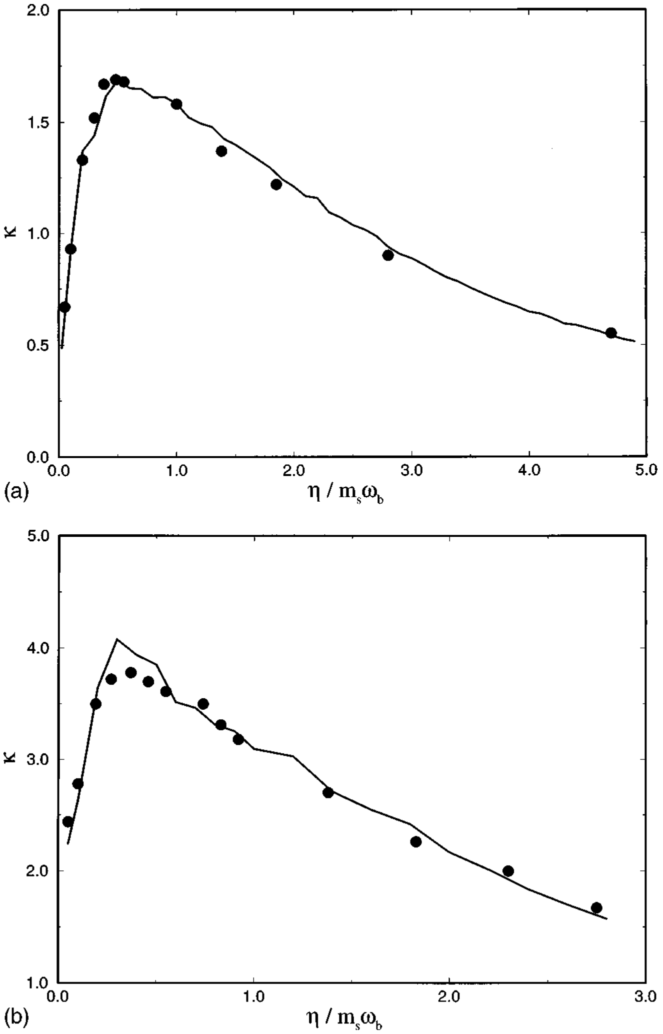

FIG. 2. Transmission coefficient $\kappa = k/k_{\mathrm{TST,CL}}$ as a function of coupling parameter $\eta/m_s\omega_b$ at $T = 300$ K; the solid line is the result from the SC-IVR methodology described in Sec. III, and the solid circles are from the accurate quantum path integral calculations of Topaler and Makri, Ref. 26. (a) $T = 300$ K; (b) $T = 200$ K.

Eq. (3.20b) for the stable normal modes, but performing a numerical evaluation of $F_w^{\beta,f}(q_{f0},p_{f0})$ via Eq. (3.21a). In this case, it is difficult to employ importance sampling, but we nevertheless found that 10 000 trajectories is sufficient to converge the rate constant via simple Monte Carlo sampling.

The results are plotted in Fig. 2 as the transmission coefficient, κ, defined by

$$\kappa = k/k_{\mathrm{TST,CL}}, \tag{3.28}$$

where $k_{\mathrm{TST,CL}}$ is the classical transition state theory rate constant of Eq. (2.13), versus the dimensionless coupling parameter $\eta/m_s\omega_b$. Figure 2(a) shows results for $T = 300$ K, for which there is almost quantitative agreement with the accurate quantum path integral results of Topaler and Makri.[26] The $T = 200$ K results are shown in Fig. 2(b), and though there is some disagreement with the accurate quantum results near the maximum of the curve, the agreement is still very good. Overall, the agreement is excellent, which is very encouraging for this quite practical approach.

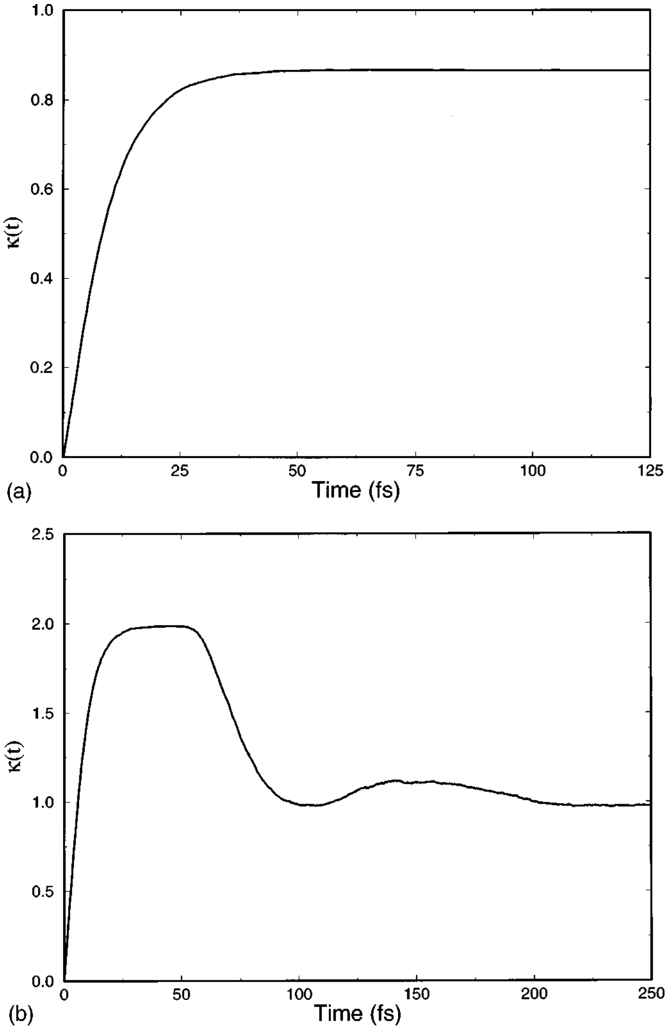

FIG. 3. The time dependence of $\kappa(t)$ [see Eq. (3.29)] for two cases at $T = 300$ K, (a) strong coupling; (b) weak coupling.

To gain some insight into the nature of the dynamics, Fig. 3 shows the time dependence of $\kappa(t)$ which is related to the correlation function $C_{fs}(t)$ by

$$\kappa(t) = (Q_r k_{\mathrm{TST,CL}})^{-1}\ C_{fs}(t), \tag{3.29}$$

at $T = 300$ K for a case of strong coupling [Fig. 3(a)] and also one of weak coupling [Fig. 3(b)]. The long time limit of $\kappa(t)$ would be the quantum transmission coefficient κ defined in Eq. (3.28). Figure 3(a) is a classic example of ''direct'' barrier crossing dynamics for which transition state theory is a good approximation. As seen in many of our previous applications,[1–5] it takes a time of $\sim\hbar\beta$ (27 fs at 300 K) for $\kappa(t)$ to reach its transition state theory (TST) ''plateau'' value, and there is no hint of any recrossing dynamics in this case. Figure 3(b), on the other hand, shows strong characteristic of recrossing: by $\hbar\beta = 27$ fs $\kappa(t)$ has reached its TST plateau value, but here coupling to the bath is not strong enough to prevent trajectories from recrossing the dividing surface. One can recognize at least three recrossings before the $t \to \infty$ limit of the correlation function is reached. It is impressive that the approximate semiclassical theory, Eq. (3.14), is able to describe both of these situations accurately.

IV. CONCLUDING REMARKS

We have tested two semiclassical approaches in this paper for extending the flux autocorrelation function methodology[6,7] to treat chemical reactions in complex molecular systems, i.e., those with many degrees of freedom. The problem treated is that of a double well potential (i.e., a model of unimolecular isomerization) linearly coupled to an infinite bath of harmonic oscillators. The first approach investigated, the popular mixed quantum-classical approximation described in Sec. II, does not give very satisfactory results. An important lesson learned from this study is that the rate constant obtained from the mixed quantum-classical method is, due to its approximate nature, quite sensitive to the specific definition of the quantum ''system'' and the classical ''bath.'' The guideline should be to choose the definition of the ''system'' and the ''bath'' in order to minimize the coupling between them, and this will of course depend on the specific problem under study. The results in Sec. II showed that defining the (quantum) ''system'' and the (classical) ''bath'' in terms of normal modes at the transition state worked better than another obvious choice, yet even with this choice the results of the mixed quantum-classical approach were not so good. This suggests that caution must be taken in using the mixed quantum-classical approximation for the study of chemical reactions in complex molecular systems.

The second approach, presented in Sec. III, is based on semiclassical initial value representation[16–23] (SC-IVR) plus some further approximations that make it easier to apply, and was found to give excellent results over the whole range of coupling strengths and also at low temperature. This approach treats all degrees of freedom equivalently and entails little more effort than a classical molecular dynamics simulation (the primary difference being the weighting of the initial condition for the trajectories). This is thus a very promising result, and it would clearly be of interest to test this approach on other problems, as well as to pursue the full-blown SC-IVR approach [i.e., Eq. (3.6)] without the simplifying approximations we have utilized in this paper. Preliminary results from work of ours in progress suggest that the approximate SC-IVR approach, Eq. (3.14), provides the correct quantum description of the short time (direct barrier-crossing) dynamics, with the longer time (recrossing) dynamics described at the level of classical mechanics. The good agreement seen in Fig. 2 thus suggests that the harmonic bath quenches quantum coherence effects in the recrossing dynamics for these cases.

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