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Combining semiclassical time evolution and quantum Boltzmann operator to evaluate reactive flux correlation function for thermal rate constants of complex systems

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The semiclassical (SC) initial value representation (IVR) provides a way for including quantum effects into classical molecular dynamics simulations. Implementation of the SC-IVR to the thermal rate constant calculation, based on the reactive flux correlation function formalism, has two major obstacles: (1) the SC integrand may be highly oscillatory with respect to the initial phase space variables; and (2) matrix elements of the Boltzmannized flux operator, which are crucial in generating the initial (or final) distribution for the SC trajectories, are generally not available in analytic forms. In this paper, we present practical ways of overcoming these two barriers for the SC calculation of thermal rate constants. For the first problem, we show that use of a symmetric flux–flux correlation function, together with the generalized Filinov transformation technique, can significantly smooth the corresponding SC integrand and make the calculation practical for quite large systems. For the second problem, we propose a general method for evaluating matrix elements of the Boltzmannized flux operator “on-the-fly,” based on the combination of the imaginary-time path integral technique with the Metropolis random walk algorithm. Using these approaches, it is shown that thermal rate constants can be obtained for systems with more than 100 degrees of freedom, as well as for reactions in the deep tunneling regimes where quantum effects are significant. © 2002 American Institute of Physics. [DOI: 10.1063/1.1464539]

I. INTRODUCTION

One of the most fundamental and important tasks in chemical reaction dynamics is the accurate evaluation of thermal (or microcanonical) rate constants. Though straightforward (i.e., basis set) quantum mechanical methods are quite successful in this regard for small molecular systems (consisting of 3 or 4 atoms), such approaches are difficult to extend to more complex systems (e.g., chemical reactions in solution, clusters, proteins, etc.) because of the exponential growth of the basis set with system size. To treat complex systems, classical molecular dynamics (CMD) simulations are widely used, but these are of course unable to describe any quantum mechanical aspects of the dynamics. There has thus been a recent revival of interest in using semiclassical (SC) theory, implemented via various initial value representations (IVR),1 to add quantum effects to CMD simulations. A number of applications of SC-IVR approaches to small molecular systems—where the accuracy can be compared to accurate quantum calculations—have shown the SC theory to provide a good description of quantum interference and tunneling phenomena.2–12 so the primary remaining task is to implement SC-IVR approaches for complex systems.

Our purpose in this paper is to describe the further development of SC-IVR approaches applied specifically to the calculation of thermal rate constants for systems with many degrees of freedom. Starting with the rigorous expression for the rate in terms of quantum flux correlation functions,13,14 there are two primary obstacles to be overcome in evaluating these correlation functions via the SC-IVR. First, the SC-IVR integrand may be highly oscillatory (with respect to the initial phase space variables) for some versions of the flux correlation functions. Monte Carlo phase space averages, an essential aspect of the SC-IVR approaches, may thus experience significant difficulties in achieving numerical convergence. Second, to calculate the rate constant at a given temperature, it is necessary to evaluate matrix elements of the Boltzmann operator, and the accuracy of these matrix elements is quite important in describing large quantum effects (tunneling in particular) in a rate constant calculation.

The linearized semiclassical method,15 the LSC-IVR, side-steps the first obstacle by including the effects of nearby trajectories only to the first order, resulting in the classical Wigner model.16 Though successful for some model condensed phase problems,17 the LSC-IVR/classical Wigner model cannot describe quantum coherence in dynamical processes.18 To improve this situation, the “forward–backward” initial value representation (FB-IVR)19–21 was developed based on an idea introduced earlier for the numerical evaluation of influence functionals in path integral

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calculations. The FB-IVR combines the forward and backward time evolution operators into one semiclassical time propagation, with the resulting integrand being less oscillatory and comparatively easy to converge. Several applications have shown that the FB-IVR is reasonably accurate. The drawback of it is the additional stationary phase-type approximations to the double phase space IVR expression, which make it less adequate in some circumstances. This motivated the development of the generalized FB-IVR (GFB-IVR) method that parametrically tunes between the two limits of the FB- and the full blown SC-IVR, at the expense of having as much oscillatory integrals as those in the double phase space IVR for certain types of problems.

For the second obstacle in the SC-IVR calculation of thermal rate constants, i.e., the evaluation of matrix elements of the Boltzmann operator, a local harmonic approximation (normal mode) is often invoked to make the expression analytical, i.e., the same approximation as is often used in “quasi-classical” trajectory simulations. The accuracy of this approximation depends on the property of the potential energy surface, the temperature, and other physical parameters. Usually such harmonic approximations cannot be made at low temperatures and/or with very anharmonic potentials, which are often encountered in simulations of realistic systems. For the special case of thermal rate constant calculations using the flux correlation functions, the accuracy of the matrix elements for the “Boltzmannized” flux operator directly determines the extent of the tunneling contributions to the rate constant that can be described in the spirit of quantum transition state theory (vide infra). Therefore, an efficient as well as accurate scheme for this evaluation is an essential ingredient to make the SC-IVR a truly feasible alternative to quantum mechanical methods for general complex molecular systems.

In this paper, we report recent progress made in overcoming both of these major barriers to the semiclassical calculation of thermal rate constants. In the first part, we summarize various forms of reactive flux correlation functions and demonstrate how a particular choice, the symmetric flux–flux autocorrelation function, can be applied in the full double phase space SC-IVR framework to significantly reduce the oscillatory character of the SC integrand. We also show how the generalized Filinov transformation, a practical filtering procedure introduced recently for dealing with the oscillatory nature of the IVR phase space average, is implemented for the present application. Numerical applications of these approaches are reported for a system–bath problem with more than 100 degrees of freedom. In the second part of the paper, we describe how to use the imaginary-time path integral method to numerically generate matrix elements of the Boltzmannized flux operator. These matrix elements serve as initial conditions/weightings for trajectories in the SC-IVR calculation, and contain important information of quantum mechanical tunneling contributions to the rate constant. We then show how to combine the numerical evaluation of these matrix elements with the Metropolis random walk algorithm to make the SC-IVR applicable to deep tunneling regimes, and thus establish a practical scheme for the semiclassical calculation of thermal rate constants for reactions in a general molecular system.

II. SMOOTHING THE SC-IVR FOR THE THERMAL RATE CONSTANT CALCULATION

A. The flux correlation function formalism

A formally exact expression for the thermal rate constant \( k(T) \) of a chemical reaction is given in terms of a reactive flux correlation function,

\[
 k(T) = \lim_{T \to \infty} \frac{1}{Q_r(T)} \int_0^T dt C_{\text{ff}}(t),
\]

where \( Q_r(T) \) is the reactant partition function (per unit volume) and \( C_{\text{ff}}(t) \) is the “flux-side” correlation function,

\[
 C_{\text{ff}}(t) = \text{tr} \left[ \hat{F}(\beta) e^{i\hat{H}t/\hbar} e^{-i\hat{H}t/\hbar} \right].
\]

Here \( \hat{F}(\beta) \) is the “Boltzmannized” flux operator \( \beta = 1/(k_B T) \)

\[
 \hat{F} = \frac{i}{\hbar} \left[ \hat{H}, \hat{h} \right].
\]

\( \hat{H} \) is the total molecular Hamiltonian, \( \hat{h} = h(\hat{s}) \) the projection operator that projects the wavefunctions to the product side. Usually \( h(s) \) is chosen as the Heaviside step function that depends on a reaction coordinate \( s \), and takes a value of \( 0 \) (1) in the reactant (product) side.

An alternate (but equivalent) expression for the thermal rate constant is the time integral of the flux–flux autocorrelation function,

\[
 k(T) = \lim_{T \to \infty} \frac{1}{Q_r(T)} \int_0^T dt C_{\text{ff}}(t),
\]

where \( C_{\text{ff}}(t) = \text{tr} \left[ \hat{F}(\beta) e^{i\hat{H}t/\hbar} e^{-i\hat{H}t/\hbar} \right] \)

is the time derivative of \( C_{\text{ff}}(t) \). Furthermore, using the fact that the Boltzmann operator \( e^{-\beta \hat{H}} \) and the time evolution operator \( e^{-i\hat{H}t/\hbar} \) commute, and also performing cyclic permutation within the trace expression in Eq. (2.5), one can write \( C_{\text{ff}}(t) \) in the following more symmetrized form:

\[
 C_{\text{ff}}(t) = \text{tr} \left[ \hat{F}(\beta/2) e^{i\hat{H}t/\hbar} \hat{F}(\beta/2) e^{-i\hat{H}t/\hbar} \right],
\]

where the “half-Boltzmannized” flux operator, \( \hat{F}(\beta/2) \), is given as

\[
 \hat{F}(\beta/2) = e^{-\beta \hat{H}/2} \hat{F} e^{-\beta \hat{H}/2}.
\]

Although all of these flux correlation functions give formally identical thermal rate constants, they may differ in terms of numerical efficiency for an SC-IVR calculation. This fact is discussed below.
\[
e^{-i\hat{H}t/\hbar} = (2\pi\hbar)^{-N} \int dp_0 \int dq_0 \int dp'_0 \int dq'_0 \times C_i(p_0, q_0) \exp\left[-\frac{1}{2}(x-q)^T \cdot \gamma \cdot (x-q) + \frac{i}{\hbar} p^T \cdot (x-q)\right].
\]

where \( N \) is the number of degrees of freedom, \((p_0, q_0)\) are the initial momenta and coordinates for a classical trajectory, \(p_t = p_0, q_t = q_0\) and \(q_t = \dot{q}_t(p_0, q_0)\) are the values at time \(t\) that result from this trajectory, and \(S_i\) is the classical action integral along it.

\[
S_i(p_0, q_0) = \int_0^t dt \mathbf{p}.\mathbf{q} - H(p_0, q_0).
\]

The wavefunction for the coherent states \(^27\) in Eq. (2.8) is

\[
\langle x|pq \rangle = \left(\frac{\pi^N}{\gamma}\right)^{1/4} \exp\left[-\frac{1}{2}(x-q)^T \cdot \gamma^{-1} \cdot (x-q)\right] + \frac{i}{\hbar} p^T \cdot (x-q),
\]

where \(\gamma\) is a constant matrix, and the HK “pre-factor” \(C_i(p_0, q_0)\) in Eq. (2.8) is given by \(^4\)

\[
C_i(p_0, q_0) = \left|\frac{1}{2} \left[ \gamma^{1/2} M_{qq} \gamma^{-1/2} + \gamma^{-1/2} M_{pp} \gamma^{1/2} - i\hbar \gamma^{1/2}\right] \times M_{qq} \right|^{1/2},
\]

where \(M_{qq}\), etc., are elements of the monodromy matrix, \(^28\)

\[
M = \begin{bmatrix} M_{pp} & M_{pq} \\ M_{qp} & M_{qq} \end{bmatrix} = \begin{bmatrix} \partial p / \partial p_0 & \partial p / \partial q_0 \\ \partial q / \partial p_0 & \partial q / \partial q_0 \end{bmatrix}.
\]

Since the Heisenberg time evolution in the flux correlation functions involves two time evolution operators, use of the IVR for the propagators, Eq. (2.8), leads to the double phase space average for Eqs. (2.2), (2.5), and (2.6),

\[
C_{ij}(t) = (2\pi\hbar)^{-2N} \int dp_0 \int dq_0 \int dp'_0 \int dq'_0 \times C_i(p_0, q_0) C_j(p'_0, q'_0) \times e^{iS_j(p'_0, q'_0)} \exp\left[-\frac{1}{2}(x-q)^T \cdot \gamma \cdot (x-q) + \frac{i}{\hbar} p^T \cdot (x-q)\right].
\]

The procedure here is that one samples a pair of initial conditions, \((p_0, q_0)\) and \((p'_0, q'_0)\), from an appropriately chosen (time-independent) weighting function, and propagates the two trajectories forward in time. Their time-evolved phase space variables \((p_t, q_t)\) and \((p'_t, q'_t)\) are then used to evaluate the flux correlation functions semiclassically. One can also use Liouville’s theorem to change the integrations from \(\int dp_0 \int dq_0\) to \(\int dp_0 \int dq'_0\), resulting in the generalized forward–backward IVR.\(^{23}\) The weighting function becomes time-dependent in this case.

Double phase space averages, such as those appearing in Eq. (2.13), are generally believed to have a highly oscillatory integrands. Such expressions have never been evaluated successfully for systems with more than a few degrees of freedom; e.g., our test calculations for the system–bath model (see below) with Eqs. (2.13a) and (2.13b) had trouble achieving convergence even with five degrees of freedom. On the other hand, the symmetric flux–flux autocorrelation function in Eq. (2.13c) is significantly more stable, suggesting quite different numerical properties.

In using Monte Carlo methods to evaluate the double phase space average such as Eq. (2.13)—which is necessary because of the high dimensionality of the integrals—it is extremely convenient to be able to use a Monte Carlo weight function that is directly related to the SC integrand at time zero. The major difference between the expressions in Eq. (2.13) is that the first two have complex-valued integrands at \(t=0\),

\[
C_{ij}(0) = (2\pi\hbar)^{-2N} \int dz_0 \int dz'_0 \exp\left(-\frac{1}{2}(z-z_0)^T \cdot \gamma \cdot (z-z_0) + \frac{i}{\hbar} p^T \cdot (z-z_0)\right),
\]

whereas the integrand for the symmetric version is positive definite:

\[
C_{ij}(0) = (2\pi\hbar)^{-2N} \int dz_0 \int dz'_0 \exp\left(-\frac{1}{2}(z-z_0)^T \cdot \gamma \cdot (z-z_0)\right).\]

[For simplicity, we use the shorthand notation \(z= (p, q)\).] Note that \(C_{ii}(0) = 0\) in Eq. (2.14a), and \(C_{ij}(0) = C_{ji}(0)\) for Eqs. (2.14b) and (2.14c).

At \(t=0\), therefore, the SC version of the symmetric flux–flux correlation function has a much smoother integrand than the other expressions. This property also holds for longer times, as will be seen in the examples below. This enables a faster convergence of the Monte Carlo calculation for the double phase space integration over \(z_0\) and \(z'_0\). Moreover, the positive definite integrand in Eq. (2.14c) serves as a
natural weighting function for evaluating the symmetric flux–flux correlation function; i.e., the weighting function for a pair of initial conditions is chosen as

$$W(z_0, z'_0) = (2\pi\hbar)^{-2N}\langle z_0|\hat{F}^{(2)}|z'_0\rangle^2,$$  \hfill (2.15)

and using this weighting function, $C_{ff}(t)$ in Eq. (2.13c) can be rewritten as

$$C_{ff}(t) = C_{ff}(0) \times R_{ff}(t),$$  \hfill (2.16)

where $R_{ff}(t)$ is a normalized correlation function,

$$R_{ff}(t) = \frac{\langle \hat{z}'_0|\hat{F}(\beta/2)|\hat{z}_0\rangle}{\langle \hat{z}_0|\hat{F}(\beta/2)|\hat{z}_0\rangle} C_i(z_0) C_i(z'_0) \times \frac{e^{i[S(z_0) - S(z'_0)]/\hbar}}{w},$$  \hfill (2.17a)

with $\langle \cdots \rangle_W$ being a Monte Carlo average over $W(z_0, z'_0)$:

$$\langle \cdots \rangle_W = \frac{\int dz_0 \int dz'_0 W(z_0, z'_0) \times \langle \cdots \rangle}{\int dz_0 \int dz'_0 W(z_0, z'_0)}.$$  \hfill (2.17b)

Note that $C_{ff}(0)$ in Eq. (2.16), the normalization constant for the Monte Carlo average over $W(z_0, z'_0)$, is related to the “quantum transition state theory” rate constant (and thus contains the tunneling contributions). It is equivalent to the following quantum mechanical trace:

$$C_{ff}(0) = \int dz_0 \int dz'_0 W(z_0, z'_0) = \text{tr}[e^{-\beta i\hbar/2 \hat{F}} e^{-\beta i\hbar/2 \hat{F}}],$$  \hfill (2.18)

and can thus be evaluated in any other convenient representations (e.g., position states $|q\rangle$), rather than restricting oneself to using the coherent state basis $|z\rangle$ and performing the explicit integration of $W(z_0, z'_0)$ over the double phase space variables. We emphasize that the above trace formula only includes the Boltzmann operator (without real-time propagation), so that it can be obtained via well-established imaginary-time path integral techniques.

Although the SC integrand in $C_{ff}(t)$ is significantly smoother than those in other versions of the flux correlation function, it may still experience undesired oscillations at longer times and/or for certain physical regimes. This problem is solved by combining the SC-IVR with the generalized Filinov transformation method, which is summarized below.

**C. Generalized Filinov transformation of the SC-IVR**

The generalized Filinov transformation was proposed recently as an efficient way for carrying out the phase space average in SC-IVR calculation. This method goes beyond the conventional Filinov method by adding an explicitly oscillatory factor to the filtering function and was seen to have the effect of distorting the integration contour into the complex plane. The basic idea can be explained by considering a general $f$-dimensional integral:

$$I = \int_{-\infty}^{\infty} d\mathbf{z} R(\mathbf{z}) e^{i\Phi(\mathbf{z})},$$  \hfill (2.19)

where $R(\mathbf{z})$ is a slowly varying function of the integration variables $\mathbf{z}$, and $\Phi(\mathbf{z})$ may be complex. One inserts the following expression for unity:

$$1 = \sqrt{\frac{|\alpha|}{\pi}} e^{1/4 \beta^T \cdot \alpha - 1/2} \int_{-\infty}^{\infty} d\mathbf{z}_0 \ e^{-(\mathbf{z} - \mathbf{z}_0)^T \cdot \alpha \cdot (\mathbf{z} - \mathbf{z}_0)} e^{i\beta^T \cdot (\mathbf{z} - \mathbf{z}_0)},$$  \hfill (2.20)

into the integrand of Eq. (2.19), expands $\Phi(\mathbf{z})$ quadratically about $\mathbf{z}_0$, and then performs the Gaussian integral over $\mathbf{z}$ to give the following approximation to the original integral in Eq. (2.19):

$$I = \int_{-\infty}^{\infty} d\mathbf{z}_0 \ R(\mathbf{z}_0) \sqrt{\frac{|2\alpha|}{2\alpha + \theta'(\mathbf{z}_0)^T \cdot \theta(\mathbf{z}_0)}} e^{i\Phi(\mathbf{z}_0)} \times \exp \left\{ \frac{1}{4} \beta^T \cdot \alpha^{-1} \cdot \beta - \frac{1}{2} \left\{ \Phi'(\mathbf{z}_0) + \beta \right\}^T \right\} \cdot \left\{ 2\alpha + \theta'(\mathbf{z}_0) \right\}^{-1} \cdot \left\{ \Phi'(\mathbf{z}_0) + \beta \right\}.$$  \hfill (2.21)

In the expressions above, $\alpha$ is a real $f \times f$ matrix, and $\beta$ is a real vector with length $f$. It can be seen that in Eq. (2.21) there is some explicit oscillatory character to the filtering function, which will be helpful in canceling out some of the oscillatory behavior of the original integrand.

If we separate explicitly the real and imaginary parts of $\Phi(\mathbf{z})$, i.e.,

$$\Phi(\mathbf{z}) = \phi(\mathbf{z}) + i \theta(\mathbf{z}),$$  \hfill (2.22)

and also assume that the Hessian of its real part, $\phi(\mathbf{z})$, is negligible, then Eq. (2.21) becomes

$$I = \int_{-\infty}^{\infty} d\mathbf{z}_0 \ R(\mathbf{z}_0) \sqrt{\frac{|2\alpha|}{2\alpha + \theta'(\mathbf{z}_0)^T \cdot \theta(\mathbf{z}_0)}} \exp \left\{ i \left\{ \phi(\mathbf{z}_0) - \theta'(\mathbf{z}_0)^T \cdot (2\alpha + \theta'(\mathbf{z}_0))^{-1} \cdot \left( \phi'(\mathbf{z}_0) + \beta \right) \right\} \right\} \times \exp \left\{ - \theta(\mathbf{z}_0) + \frac{1}{4} \beta^T \cdot \alpha^{-1} \cdot \beta - \frac{1}{2} \left\{ \phi'(\mathbf{z}_0) + \beta \right\}^T \right\} \cdot \left\{ 2\alpha + \theta'(\mathbf{z}_0) \right\}^{-1} \cdot \left\{ \phi'(\mathbf{z}_0) + \beta \right\} + \frac{1}{2} \theta^T(\mathbf{z}_0) \theta,$$  \hfill (2.24)

The criterion for choosing the “Filinov parameters” $\alpha$ and $\beta$ is to make the integrand of Eq. (2.24) as slowly varying as possible, i.e., to make its phase (approximately) stationary,

$$\frac{\partial}{\partial \mathbf{z}_0} \left[ \phi(\mathbf{z}_0) - \theta'(\mathbf{z}_0)^T \cdot (2\alpha + \theta'(\mathbf{z}_0))^{-1} \cdot (\phi'(\mathbf{z}_0) + \beta) \right] = 0.$$  \hfill (2.25a)

If we assume Eq. (2.23) and neglect third order derivatives of $\theta(\mathbf{z}_0)$, then Eq. (2.25a) becomes
\[ \phi'(z_0) - \theta'(z_0) \cdot [2 \alpha + \theta'(z_0)]^{-1} \cdot [\phi'(z_0) + \beta] = 0, \]

(2.25b)

which is satisfied if
\[ \beta = 2 \alpha \cdot \theta'(z_0)^{-1} \cdot \phi'(z_0) = \beta_0. \]

(2.25c)

In applications one wishes to choose the matrix \( \alpha \) as large as possible and the vector \( \beta \) as small as possible so that the Filinov-transformed integral is as close as possible to the original integral one is attempting to evaluate. A practical procedure\(^{24} \) is to introduce two scalar parameters \( \alpha \) and \( \beta \),
\[ \alpha = \alpha_0, \quad \beta = b \beta_0, \]

(2.26)

where \( \alpha_0 \) can be a constant matrix (with the simplest to be an identity matrix) or the choice given previously\(^{24} \) and with \( \alpha > 1 \) and \( b < 1 \). As discussed in Ref. 24, one can obtain results for many \((\alpha, b)\) pairs from a single batch of IVR trajectory calculations, and pick the pair that has an acceptable standard deviation and at the same time is closest to the correct theoretical limit, i.e., \( \alpha \to \infty \) and \( b \to 0 \).

**D. Numerical example**

To demonstrate the efficiency of the methodology described above, we consider a problem that has been studied extensively, i.e., the calculation of the thermal rate constant for a one-dimensional double well linearly coupled to a harmonic bath. The Hamiltonian, written in the mass-weighted coordinates, is
\[ H = H_s(p_s, s) + \sum_{i=1}^{N_b} \left[ \frac{1}{2} p_i^2 + \frac{1}{2} \omega_i^2 Q_i - \frac{c_i^2}{\omega_i^2} s^2 \right]. \]

(2.27a)

where
\[ H_s(p_s, s) = \frac{1}{2} p_s^2 - \frac{1}{2} \omega_b^2 s^2 + \frac{\omega_b^4}{16V_0^2} s^4. \]

(2.27b)

\( \omega_b \) is the imaginary frequency at the top of the barrier, and \( V_0 \) is the barrier height with respect to the bottom of the well. The essential property of the harmonic bath is its spectral density,
\[ J(\omega) = \frac{\pi}{2} \sum_j \frac{c_j^2}{\omega_j} \delta(\omega - \omega_j), \]

(2.28)

which is chosen in the Ohmic form with an exponential cutoff,
\[ J_\phi(\omega) = \eta \omega e^{-\omega/\omega_c}. \]

(2.29)

The specific parameters we have chosen correspond to the model DW1 studied by Topaler and Makri\(^{32} \) using path integral methods, i.e., \( \omega_b = 500 \text{ cm}^{-1}, \quad V_0 = 2085 \text{ cm}^{-1} \), and \( \omega_c = 500 \text{ cm}^{-1} \). Discretization of the continuous bath to the form of Eq. (2.28) has been discussed previously\(^{15,21} \) and the number of modes is systematically increased to ensure a satisfactory description of the condensed phase media.

For a high enough temperature, matrix elements of the Boltzmannized flux operator can be obtained analytically via a normal mode approximation\(^{15,21} \) and the SC-IVR implementation of the rate constant, Eq. (2.13), is straightforward. As expected from the previous analysis, SC-IVR calculations based on Eqs. (2.13a) and (2.13b) show extremely slow convergence. Even for a bath of only four modes, the statistical error is too large to make the results reliable, and things become progressively worse as the number of bath modes increases. This is presumably due to the fact that the \( t=0 \) integrands in Eqs. (2.13a) and (2.13b) are complex. Thus even for short time dynamics one has to distort the integration contour to obtain the correct IVR integral, a procedure difficult (or less accurate) in numerical practice.

Convergence becomes significantly better if the symmetric flux–flux correlation function expression, Eq. (2.13c), is used. Figure 1 shows the time-dependent transmission probability \( \kappa(t) \) at \( T = 300 \text{ K} \) for two coupling strengths, \( \eta/\omega_b = 1.0 \) and \( \eta/\omega_b = 0.5 \). For a bath of 100 modes, statistical convergence is achieved from a simple Herman–Kluk double phase space average of Eq. (2.13c) with 20 000 pairs of trajectories. Here \( \kappa(t) \) is related to the flux correlation function via
\[ \kappa(t) = \frac{C_{fs}(t)}{Q_r(T)k_{TST}}, \]

(2.30a)

\[ C_{fs}(t) = \int_0^t d\tau C_{fs}(\tau), \]

(2.30b)

where \( k_{TST} \) is the classical transition state theory rate constant for the original one-dimensional double-well,
\[ k_{TST} = \frac{\omega_b}{2\pi} e^{-\beta E_b}. \]

(2.30c)

For a strong system–bath coupling as in Fig. 1(a), \( \kappa(t) \) reaches a plateau within a relatively short time (\( \sim \hbar \beta = 25.5 \text{ fs} \) for \( T = 300 \text{ K} \)), and gives a rate constant in the spirit of a quantum transition state theory. For this regime, the double phase space IVR of Eq. (2.13c) gives excellent convergence without any additional smoothing. In Fig. 1(b) the coupling is weaker, and the flux correlation function displays some recrossing character. Still, statistical convergence (within 10% relative error) is also quite good for this case.

For very weak coupling strength, recrossing dynamics become more profound and a longer time is required for the flux correlation function to reach its plateau. As shown in Fig. 2(a), a straightforward Herman–Kluk IVR cannot give statistical convergence for a sampling size of 50 000 pairs of trajectories. With the help of the generalized Filinov transformation, however, the result is converged to the desired accuracy as shown in Fig. 2(b).

One bonus of using the symmetric flux–flux correlation function, Eq. (2.13c), is that the normal mode approximation can be made at lower temperatures than in the previous work\(^{15,21} \). This is because the effective \( \beta \) in the \( \tilde{F}(\beta) \) of Eq. (2.13c) is half that of the \( \tilde{F}(\beta) \) of Eqs. (2.13a) and (2.13b), resulting in a higher effective temperature. Figure 3 shows \( \kappa(t) \) for two coupling strengths at \( T = 200 \text{ K} \). Again, 20000 pair of trajectories give statistically converged results for a bath of 100 modes. For all the results displayed in Figs. 1–3, the statistical convergence is within 10–15% absolute error.
It is thus quite encouraging to be able to apply the double phase space SC-IVR to the evaluation of the symmetric flux–flux correlation function, Eq. (2.13c), for reactions with many degrees of freedom. In the current example, a bath of 10–20 modes actually provides quite a good representation for the condensed phase media and the use of 100 modes is just for demonstration purposes. On the other hand, this demonstration indicates the feasibility of the current methodology for treating a realistic complex system containing many degrees of freedom. The remaining challenge is the evaluation of coherent state matrix elements for the Boltzmannized flux operator, which in many situations cannot be obtained from a normal mode approximation in accurate or even divergent. To make the SC-IVR truly applicable to a general problem, a more general and reliable method is needed for obtaining these matrix elements. This is presented in the following section.

III. PATH INTEGRAL FOR THE BOLTZMANNIZED FLUX OPERATOR

The calculation of the thermal rate constant via Eqs. (2.16) and (2.17) requires evaluation of the coherent state matrix elements of the “half” Boltzmannized flux operator, \( \langle \mathbf{p}_f \mathbf{q}_f | \mathbf{\hat{F}}(\beta/2) | \mathbf{p}_i \mathbf{q}_i \rangle \), as well as the normalization constant, i.e., the flux–flux correlation function at \( t=0 \), \( \mathcal{C}_f(0) = \text{tr} [ e^{-(\beta/2) \mathbf{\hat{F}}} e^{-(\beta/2) \mathbf{\hat{F}}} ] \). An accurate evaluation of these is an integral part of obtaining accurate rate constants within the SC-IVR. As shown in previous examples, a normal mode approximation can be made in certain cases to obtain analytic expressions. However, this approximation is too restrictive and may not be satisfactory in many situations. In order for the SC methodology to be applicable to general reactive systems, one needs to be able to evaluate the matrix elements of the Boltzmannized flux operator for situations where analytic approximations are not available. In this section we propose to use the imaginary-time path integral technique \(^{33-35}\) specifically tailored to the flux correlation function formalism, to achieve this task.

A. General methodology

Consider a general coherent state matrix element of the original Boltzmannized flux operator \( \mathbf{\hat{F}}(\beta) \) [the discussion for \( \mathbf{\hat{F}}(\beta/2) \) is a trivial modification of the following steps by dividing \( \beta \) by 2]:

FIG. 1. The time dependence of \( k(t) \) (see the text) for two system–bath coupling strengths at \( T=300 \) K. The results are obtained for a bath of 100 modes using the Herman–Kluk IVR, Eq. (2.13c), with 20 000 pairs of trajectories. (a) \( \eta/\omega_s = 1.0; \) (b) \( \eta/\omega_s = 0.5. \)

FIG. 2. The time dependence of \( k(t) \) for the system–bath coupling strength \( \eta/\omega_s = 0.2 \) at \( T=300 \) K. The results are obtained for a bath of 100 modes, using 50 000 pairs of trajectories in (a) Herman–Kluk IVR; (b) HK–IVR with the generalized Filinov transformation.
For a sufficiently large $P$, the resolution of identity, $I = \int dx_k |x_k\rangle\langle x_k|$, in each $e^{-\Delta \beta \tilde{H}}$ leads to the following expression:

$$K_{fi} = \int dx_1 dx_2 \cdots dx_P \langle p_f q_f | e^{-\Delta \beta \tilde{H}/2} | x_P \rangle$$

$$\times \langle x_P | e^{-\Delta \beta \tilde{H}/2} \cdots e^{-\Delta \beta \tilde{H}/2} | x_{P/2} \rangle$$

$$\times \langle x_{P/2} | e^{-\Delta \beta \tilde{H}/2} \cdots e^{-\Delta \beta \tilde{H}/2} | x_{P/4} \rangle$$

$$\times \langle x_{P/4} | e^{-\Delta \beta \tilde{H}/2} \cdots e^{-\Delta \beta \tilde{H}/2} | x_{1} \rangle$$

$$\times \langle x_{1} | e^{-\Delta \beta \tilde{H}/2} | p_f, q_f \rangle \exp \left[ -\Delta \beta \sum_{k=1}^{P} V(x_k) \right].$$

(3.4)

In the above expression, matrix elements involving the exponentiated kinetic energy operator and the flux operator are analytic, i.e.,

$$\langle x | e^{-\Delta \beta \tilde{H}/2} | p q \rangle$$

$$= \left[ \frac{\gamma_I}{\gamma_I + \gamma} \right]^{1/4} \exp \left[ -\frac{\gamma_I}{2(\gamma_I + \gamma)} (x-q)^2 \right]$$

$$- \frac{\gamma_I}{2(\gamma_I + \gamma)} \frac{\gamma_I}{\hbar} \frac{\gamma_I}{\gamma_I + \gamma} p (x-q) \right].$$

(3.5)

$$\langle y | e^{-\Delta \beta \tilde{H}/2} \tilde{F} e^{-\Delta \beta \tilde{H}/2} | x \rangle$$

$$= \langle y | e^{-\Delta \beta \tilde{H}/2} \tilde{F} e^{-\Delta \beta \tilde{H}/2} | x \rangle$$

$$\times \exp \left[ -\gamma_I \left( \frac{y-x}{2} \right)^2 \right].$$

(3.6)

where $\gamma_I = 2m/\hbar^2 \Delta \beta$. Thus, Eq. (3.4) can be written more explicitly as

$$K_{fi} = D_{fi} \int dx_1 dx_2 \cdots dx_P \ (x_{P/2+1} - x_{P/2})$$

$$\times \exp \left[ -\frac{\gamma_I}{2(\gamma_I + \gamma)} [(x_f - x_p)^2 + (x_1 - q_i)^2] \right]$$

$$- \frac{\gamma_I}{4} \sum_{k=2}^{P} (x_k - x_{k-1})^2$$

$$- \frac{\gamma_I}{4} \sum_{k=2}^{P} (x_{P/2+1} + x_{P/2})^2$$

$$+ \frac{i}{\hbar} \frac{\gamma_I}{\gamma_I + \gamma} [p_f (x_f - x_p) + p_i (x_1 - q_i)]$$

$$- \Delta \beta \sum_{k=1}^{P} V(x_k).$$

(3.7)

where $D_{fi}$ is a constant that only depends on the initial and final phase space variables.

It is useful to consider the physical structure of the above path integral formula. The so-called “beads” (i.e., the imaginary-time slices $\{x_k\}$) are connected between $q_f$ and $q_i$ through the following harmonic “spring” terms:

$$\exp \left[ -\frac{\gamma_I}{2(\gamma_I + \gamma)} [(x_f - x_p)^2 + (x_1 - q_i)^2] \right]$$

$$- \frac{\gamma_I}{4} \sum_{k=2}^{P} (x_k - x_{k-1})^2. \right.$$

(3.8)
where the “force constants” of the terminal springs are different from those of the intermediate ones due to the presence of the coherent states. Note that the central beads, namely \( x_{p2} \) and \( x_{p2+1} \), have an additional term arising from the flux operator, i.e., \( \exp\{-\gamma p(x_{p2+1} + x_{p2})/2\} \). This “attracts” them to the dividing surface. (More explicitly, the contribution of a sampled path becomes negligibly small when the mean position of the central beads is far from the dividing surface.) Such localization of the central beads around the dividing surface causes other beads also to reside in the neighborhood of this region, which makes \( K_{fi} \) small for the position parameters \((q_f,q_i)\) far away from the dividing surface. In contrast to the positions, however, there is no obvious term to restrict the momentum parameters \((p_f,p_i)\), though numerically the distribution of \( K_{fi} \) is localized around \( p_f = p_i = 0 \). This comes from the cancellation of the oscillatory term\(^{36}\) in Eq. (3.7), i.e.,

\[
\exp\left\{ \frac{i}{\hbar} \frac{\gamma}{\gamma + \gamma} \left[ p_f(q_f - x_p) + p_i(x_1 - q_i) \right] \right\}.
\]

This fact indicates that the Monte Carlo convergence of the above path integral should be slower for a large momentum than for a large position, i.e., the convergence rate is not uniform as a function of the coherent state parameters.

For the numerical implementation of Eq. (3.7) via the Monte Carlo algorithm, a simple way of computing the necessary matrix elements is to perform a “free-chain” sampling,\(^{35}\) i.e., with the following weighting function for the path:

\[
W_{fi}(X) = \exp\left\{ \frac{-\gamma}{2(\gamma + \gamma)} [(q_f - x_p)^2 + (x_1 - q_i)^2] \right\}
\]

\[
- \frac{\gamma}{4} \sum_{k=2}^{2} (x_k - x_{k-1})^2 + \frac{\gamma}{4} \left[ (x_{p2+1} + x_{p2})^2 \right].
\]

(3.9)

where \( X \) denotes \((x_1, \ldots, x_p)\). Furthermore, when the reaction coordinate is chosen as a component of the whole coordinate set, it is more advantageous to incorporate the “attraction” term arising from the flux operator into the weighting function,

\[
W_{fi}(X) = \exp\left\{ -\frac{\gamma}{2(\gamma + \gamma)} [(q_f - x_p)^2 + (x_1 - q_i)^2] \right\}
\]

\[
\times \exp\left\{ -\frac{\gamma}{4} \sum_{k=2}^{2} (x_k - x_{k-1})^2 \right\}
\]

\[
- \frac{\gamma}{4} \left[ (x_{p2+1} + x_{p2})^2 \right].
\]

(3.10)

(We note in passing that it would be more efficient also to incorporate the potential energy terms into the weighting function, which would be a natural choice in a path integral calculation for the expectation value of a physical quantity. However, in the present case this is not straightforward since the matrix element \( K_{fi} \) is neither an expectation value nor a ratio of similar integrals.)

With the weighting function in Eq. (3.10), it is convenient to use the so-called normal mode sampling algorithm\(^{35}\) to evaluate the path integral in Eq. (3.7). In this method, the weighting function is rewritten in terms of the “normal mode amplitude” of paths,

\[
W_{fi}(X) = W_{fi}(X^*) \exp\left\{ -\frac{1}{2} \frac{\gamma}{\gamma + \gamma} [(q_f - x_p)^2 + (x_1^* - q_i^*)^2] \right\}
\]

\[
= W_{fi}(X^*) \exp\left\{ -\frac{1}{2} \sum_{m=1}^{p} \lambda_m a_m \right\},
\]

(3.11)

where \( X^* \) is the value corresponding to the maximum of \( W_{fi}(X) \), and \( A \) is the related coefficient matrix. \( \{\lambda_m\} \) are the eigenvalues of \( A \), i.e., \( A = U \Lambda U^T \) with \( \Lambda = \text{diag}\{\lambda_m\} \), whereas the path variables \( X \) and the normal mode amplitudes \( a \) are related by \( X - X^* = U a \). Then Eq. (3.7) can be rewritten in the form suitable for a Monte Carlo average,

\[
K_{fi} = D_{fi} \left\{ (x_{p2+1} - x_{p2}) \exp\left\{ \frac{i}{\hbar} \frac{\gamma}{\gamma + \gamma} [(q_f - x_p) + p_i(x_1 - q_i)] - \Delta \beta \sum_{k=1}^{p} V(x_k) \right\} \right\}_{\scriptscriptstyle W_{fi}},
\]

(3.12)

where

\[
\langle \cdots \rangle_{\scriptscriptstyle W_{fi}} = \frac{\int da \exp\left\{ -\frac{1}{2} \sum_{m=1}^{p} \lambda_m a_m^2 \right\} \times (\cdots) \int da \exp\left\{ -\frac{1}{2} \sum_{m=1}^{p} \lambda_m a_m^2 \right\}}{\int da \exp\left\{ -\frac{1}{2} \sum_{m=1}^{p} \lambda_m a_m^2 \right\}},
\]

(3.13)

and \( D_{fi} \) is another constant. This expression will be used in subsequent numerical calculations.

The evaluation of the normalization constant, \( C_{\scriptscriptstyle fi}(0) \), is \( \text{tr}[e^{-\beta \hbar^2 \hat{F}} e^{-\beta \hbar^2 \hat{F}}] \), also proceeds in a similar manner. Inserting the Trotter splitting of Eq. (3.3) into the trace gives

\[
C_{\scriptscriptstyle fi}(0) = \text{tr}[e^{-\Delta \beta \hat{F}} P_{p2} \hat{F} e^{-\Delta \beta \hat{F}} P_{p2}],
\]

which can be written more explicitly, using Eqs. (3.5) and (3.6), as

\[
C_{\scriptscriptstyle fi}(0) = \text{const} \times \int dx_1 \cdots dx_P \exp\left\{ -\Delta \beta \sum_{k=1}^{P} V(x_k) \right\}
\]

\[
\times \langle x_P | e^{-\Delta \beta \hat{F}} P_{p2+1} e^{-\Delta \beta \hat{F}} P_{p2+1} \rangle \cdots \langle x_{p2+1} | e^{-\Delta \beta \hat{F}} P_{p2} e^{-\Delta \beta \hat{F}} P_{p2} \rangle
\]

\[
\times \langle x_{p2} | e^{-\Delta \beta \hat{F}} P_{p2-1} e^{-\Delta \beta \hat{F}} P_{p2-1} \rangle \cdots \langle x_1 | e^{-\Delta \beta \hat{F}} P_{p2} e^{-\Delta \beta \hat{F}} P_{p2} \rangle,
\]

(3.14)

which can be written more explicitly, using Eqs. (3.5) and (3.6), as

\[
C_{\scriptscriptstyle fi}(0) = \text{const} \times \int dx_1 \cdots dx_P \langle x_P - x_1 \rangle (x_{p2+1} - x_{p2+1})
\]

\[
\times \exp\left[ -\frac{\gamma}{4} \sum_{k=1}^{p} (x_k - x_{k-1})^2 \right]
\]

\[
- \frac{\gamma}{4} (x_{p2+1} + x_{p2})^2 - \frac{\gamma}{4} (x_1 + x_P)^2
\]

\[
\times \exp\left[ -\Delta \beta \sum_{k=1}^{P} V(x_k) \right],
\]

(3.15)
where \( x_0 = x_p \). This expression can be evaluated using a similar normal mode sampling technique, where the weighting function is defined as

\[
W(X) = \exp \left\{ -\frac{\gamma}{4} \sum_{k=1}^{p} (x_k - x_{k-1})^2 - \frac{\gamma}{4} (x_{p+2} + x_p)^2 - \frac{\gamma}{4} (x_1 + x_p)^2 \right\}.
\]

The difference here is that all the beads are connected to form a "loop," and the intermediate four beads \((x_1, x_{p+2}, x_{p+2} + 1, \text{and } x_p)\) are attracted to the dividing surface through the term \( \exp\{-\gamma \beta (x_{p+2} + x_p)^2/(4 - \gamma \beta (x_1 + x_p)^2/4)\} \). As a result, all the closed paths that contribute significantly to the above integral reside around the dividing surface.

Thus, the numerical procedure for obtaining the rate constant \( k(T) \) can be summarized, in a two-step form, as follows.

1. Generate a Metropolis random walk of the initial double phase space variables \((p_0, q_0, p_0', q_0')\) according to the weighting function,

\[
W(p_0, q_0, p_0', q_0') \sim |\langle p_0, q_0 | \hat{F}(\beta/2) | p_0', q_0' \rangle|^2.
\]

As usual several components of the whole variable set are given a trial move, and the standard Metropolis criterion is used to determine whether a new "configuration" is accepted. The matrix element of \( \hat{F}(\beta/2) \) in the weighting function is calculated using the path integral expression in Eq. (3.7).

2. Propagate a pair of trajectories in real time for the selected \((p_0, q_0, p_0', q_0')\). In order to obtain \( k(T) \) from the time integral of the flux–flux correlation function, Eq. (2.4), one usually performs a simple trapezoid integration over an equally spaced time grid. At each time grid point, a new matrix element is evaluated using the same path integral technique for this pair of trajectories, i.e. \( \langle p_0', q_0' | \hat{F}(\beta/2) | p_0, q_0 \rangle \). Then all the information is gathered to give the normalized correlation function \( R_{ff}(t) \) in Eq. (2.17). Combining the normalization constant \( C_{ff}(0) \) obtained from a separate path integral calculation finally gives the thermal rate constant \( k(T) \).

Therefore, the procedure is similar in spirit to the "direct" \textit{ab initio} molecular dynamics, where the nuclear potential is evaluated on the fly via electronic structure theory calculations. In the present case the necessary matrix element of \( \hat{F}(\beta/2) \) is computed in the same fashion using the path integral method, and the computer program to generate these matrix elements can be coded independently from the SC-IVR routine. The matrix element of \( \hat{F}(\beta/2) \) plays twofold roles in determining the rate constant, i.e., generating the initial condition for a pair of trajectories [step (1) above] and evaluating the integrand of the flux–flux correlation function [step (2)]. By using the Metropolis algorithm we avoid imposing a "guess" weighting function for \((p_0, q_0, p_0', q_0')\), e.g., some pre-determined weighting function that is obtained from the parabolic barrier/high-temperature approximation.

### B. Numerical examples

#### 1. One-dimensional Eckart barrier

In this subsection we first apply the aforementioned method to a simple one-dimensional problem, i.e., the Eckart barrier that corresponds to the H + H₂ reaction,

\[
H = \frac{p^2}{2m} + \frac{V_0}{\cosh^2(x/a)},
\]

where \( m, V_0, \) and \( a \) are set to 1061.0 a.u., 0.425 eV, and 0.734 a.u., respectively.

The thermal rate constant \( k(T) \) is computed using the double phase space average of the symmetric flux–flux correlation function, Eq. (2.13c). The initial conditions for the pair of trajectories, \((z_0, z_0')\), are sampled from the weighting function \( W(z_0, z_0') \) in Eq. (2.15) via the Metropolis algorithm. A cutoff is imposed for the weighting function, i.e., \( W(z_0, z_0') \) is set to zero if it is smaller than a given tolerance \( (10^{-5} \sim 10^{-6} \times \max\{W(z_0, z_0')\}) \). This discards the small tail of the weighting function, and is found to reduce the required number of trajectories by a factor of 3–4 without losing accuracy. The number of trajectories used here is 30 000–50 000 (60 000–80 000) at high (low) temperatures, which is sufficient to converge \( C_{ff}(t) \) with 1–2% statistical accuracy. In this example the generalized Filinov transformation is not used because the statistical convergence can readily be achieved.

Matrix elements of the "half" Boltzmannized flux operator \( \hat{F}(\beta/2) \) are calculated on the fly, using the imaginary-time path integral method presented in Sec. III A. The Box–Muller algorithm is used to sample the Gaussian distribution of the imaginary-time paths, \( W'_f(X) \). The Sobol quasi-random number sequence is also used to accelerate the convergence of the Monte Carlo calculation. The number of imaginary-time slices and paths, \((P, N_{\text{path}})\), are chosen to be \((4,5000)\) for \( T = 1000 \) K, and \((20,20000)\) for \( T = 200 \) K, respectively, which gives very accurate matrix elements (in practice, however, much smaller \( P \) will suffice for obtaining a moderately accurate thermal rate constant).

Figure 4 shows the flux–side correlation functions at several temperatures obtained via the above methodology (labeled as double HK + PI), the exact quantum mechanical results, and the results from the linearized SC-IVR (labeled as LSC-IVR) calculation. Arrhenius plots of thermal rate constants are shown in Fig. 5, where the classical rate constant is given by

\[
k_{\text{CL}}(T) = \frac{1}{2\pi h Q(T)} \int_0^\infty dE \ e^{-\beta E} \ h(E-V_0)
\]

\[
= k_B T \frac{1}{h} \frac{1}{Q(T)} \exp(-\beta V_0),
\]

with \( Q(T) = [m/2\pi \hbar^2 \beta]^{1/2} \). It is seen that the present semiclassical method provides results in excellent agreement with the exact quantum mechanical calculation, including the "almost classical" regime (\( T = 2000 \) K) as well as the deep tunneling regime (\( T = 200 \) K). The differences between the semiclassical and quantum rates are within 5% for the temperature of 300–2000 K, and 5–10% at the lowest tempera-
ture examined ($T = 200$ K). This good agreement is quite encouraging because the tunneling correction is more than 2000 at $T = 200$ K. We emphasize that the majority of the tunneling correction is obtained from the imaginary-time path integral calculation of $C_{ff}(0)$, thus in the spirit of the quantum transition state theory. [If $R_{ff}(t)$ is approximated by the parabolic barrier expression, Eq. (2.16) reduces to the quantum transition state theory given previously.]

In the above comparisons, we have included an approximate version of the SC-IVR, i.e., the LSC-IVR/classical Wigner model, where one replaces the quantum mechanical trace of the time correlation function, $C_{AB}(t)$, by $C_{AB}^{LSC}(t) = \frac{1}{2} \int dp_d dq_0 A_w(p_0, q_0) B_w(p_1, q_1)$. $A_w$ and $B_w$ are the Wigner transforms of the operator $\hat{A}$ and $\hat{B}$ given by

$$A_w(p, q) = \int d\Delta q \ e^{-i\Delta q/\hbar} \left[ q + \Delta q \right] / 2 \right).$$

As shown in the previous work, the LSC-IVR is capable of describing the short-time quantum dynamics accurately, but misses the long-time quantum coherence effect.

In the present case there are two possibilities of implementing the LSC-IVR: the first one [labeled as LSC-IVR (1) in Figs. 4 and 5] is obtained from the linearized approximation to the flux–side correlation function,

$$C_{fs}^{LSC}(t) = \frac{1}{2 \pi \hbar} \int dp_0 dq_0 F_{\beta}(p_0, q_0) h(q_f),$$

and the second one [LSC-IVR (2)] corresponds to the linearized approximation to the symmetric flux–flux correlation function,

$$C_{ff}^{LSC}(t) = \frac{1}{2 \pi \hbar} \int dp_0 dq_0 F_{w}(p_0, q_0) F_{\beta}(p_1, q_1).$$
In Appendix B we present details of the numerical evaluation of the Wigner transform.

The reason to consider version (2) is due to its positive-definite integrand at \( t=0 \), which should facilitate the convergence of the Monte Carlo calculation. The resulting rate constants are shown in Fig. 5, from which we can see that both versions are rather accurate, i.e., they can incorporate the tunneling effect quite well. The agreement between version (1) and the exact result is better, which is shown in Fig. 4 to give the error of less than 20\% for \( T=300 \) K and approximately 40\% at \( T=200 \) K. Version (2) is less accurate; its deviation from the exact result is 2–3 times larger than that of version (1). These results indicate that the LSC-IVR misses some quantum effects in the real-time propagation. Also, as expected the Monte Carlo convergence of version (2) is significantly faster than that of version (1); in fact, 40 000 trajectories is adequate to converge \( C^{\text{LSC}}(t) \) for all the temperatures examined, whereas converged results cannot be obtained for \( C^{\text{LSC}}_{\text{bb}}(t) \) at \( T=300 \) K even with \( 10^7 \) trajectories.

2. Double-well/Harmonic bath problem at low temperature

For the application of the present method to a multidimensional system, we consider the system–bath problem discussed in the previous section. This time we focus on the low-temperature regime, where the previous normal mode approximation is invalid. The bath is discretized to 10 modes, which is satisfactory for our purpose.

The calculation of thermal rate constants proceeds similarly to that in the previous subsection. The only difference is that here we use a harmonic splitting in the path integral expressions for the bath modes (see Appendix A for more details). This allows us to use a relatively small number of imaginary-time slices \( P \), which is determined from the variation of the overall potential along the reaction coordinate rather than along the bath modes with higher frequencies. It should be noted, however, that this harmonic splitting is not mandatory in the current approach, but rather a convenient way to enhance the computational efficiency.

Figure 6 shows the time-dependent transmission coefficient, \( \kappa(t) \), as defined previously. One can see that in the strong coupling regime (\( \eta/\omega_b > 0.5 \)) the transmission coefficient reaches its plateau monotonically, displaying the character of a “direct” reaction. On the other hand, in the weak to moderate coupling regime (\( \eta/\omega_b = 0.05 \) and 0.1) \( \kappa(t) \) shows a step-wise increase before reaching the final plateau. This feature has been attributed to the quantum vibrational coherences in the previous work, and it is encouraging that the SC-IVR results are in quite good agreement with the accurate path integral simulations. Also, it is interesting to note that the coherent feature of \( \kappa(t) \) at this low-temperature regime is significantly different from the recrossing dynamics at higher temperatures, where the transmission coefficient decreases to the second plateau as shown in Fig. 2.

Figure 7 shows the logarithm of the transmission coefficient as a function of the coupling strength, \( \eta/\omega_b \). Here the transmission coefficient is defined as the value of the final plateau in Fig. 6. [For the weakest coupling case, \( \eta/\omega_b \approx 0.05 \), the transmission coefficient does not reach the final plateau value within \( t<140 \) fs, and thus we take the value of \( \kappa(t) \) at \( t=140 \) fs.] It can be seen that the transmission coefficient obtained from the SC-IVR calculation reproduces the dependence of \( \kappa \) on the coupling strength \( \eta \) quite well. In particular, the present SC-IVR calculations reproduce the qualitative feature that the turnover behavior of \( \kappa \) disappears in the low-temperature regime.

It is worthwhile to discuss some technical details in the current Monte Carlo sampling of initial conditions. The Metropolis random walk is carried out according to the weighting function \( W(z_0,z'_0) \) in Eq. (2.15), which is determined numerically from the imaginary-time path integral calculation. Sometimes this numerical weighting function exhibits sizable statistical noise, which is problematic for accuracy purpose. (Things become worse if the Metropolis walk gets
“trapped” in this “bad region.”) In practice, it is found that such behavior tends to occur in the small tail part of the weighting function with large momentum parameters \((p_0, p_f)\) in the same spirit as a typical oscillatory integrand. This is clearly related to the nonuniform convergence behavior of the path integral formula of Eq. (3.7) mentioned in Sec. III A. In the present work, we find that this small tail in the weighting function makes negligible contributions to the final rate constant, and thus we circumvent this problem by simply discarding this tail as described in the previous subsection.

Regarding the computational effort, the number of time slices \(P\) and the number of paths \(N_{\text{path}}\) for evaluating the matrix element of \(\hat{F}(\beta/2)\) are chosen to be 10 and 200 000, respectively. These parameters are checked by comparing the results to those obtained with \(P = 6 - 10\) and \(N_{\text{path}} = 60 000 - 200 000\). The typical number of trajectories used is 20 000–50 000 (50 000–90 000) for a strong (weak) coupling regime, which is enough to converge the flux correlation function with <10\% statistical accuracy. The generalized Filinov transformation is not employed here since the present calculation involves only 10 bath modes and the convergence can be achieved without invoking the smoothing technique. The algorithm is well-suited for a parallel computing environment, and the calculations are performed using the IBM SP2 cluster at the National Energy Research Scientific Computing Center (NERSC). The CPU time for obtaining a single flux correlation function takes a few hours wall clock time.

**IV. CONCLUDING REMARKS**

In this paper, we have presented efficient ways of applying the SC-IVR to the calculation of reactive flux correlation functions. Our aim in this work is to accurately evaluate thermal rate constants for reactions in general complex molecular systems. Two major problems in such implementations have been addressed, i.e., the oscillatory SC integrand in an IVR calculation, and the necessity of evaluating the matrix elements for the Boltzmannized flux operator. Practical solutions have been given to both these problems, thus making the methodology applicable to quite large systems (>100 degrees of freedom) and to physical regimes where quantum tunneling effect is significant.

We have shown that a particular form of the reactive flux correlation function, the symmetric flux–flux autocorrelation function, is significantly advantageous over other forms in terms of an IVR implementation. The full SC double phase space average of this form converges quite easily, in certain physical regimes, for a reactive system with more than 100 degrees of freedom. Combining with the recently proposed generalized Filinov transformation technique, the methodology becomes feasible for even broader physical regimes and/or larger molecular systems. It should be mentioned that this (double phase space) IVR calculation does not include the additional stationary phase approximation used in the FB-IVR, and is thus presumably more reliable.

More importantly, we have proposed a practical method of evaluating the matrix element for the Boltzmannized flux operator based on the imaginary-time path integral technique. Combining with the Metropolis random walk algorithm, “on-the-fly” IVR calculations can now be carried out for reactions where analytic matrix elements for the Boltzmannized flux operator are not available. This makes it possible for the SC treatment of reactions in a general molecular system, as well as for the accurate description of the quantum tunneling effect. Examples have shown that the method is capable of obtaining rate constants for reactions in the “deep tunneling” regime, where corrections to the classical rate become several orders of magnitude.

The methodologies presented in this paper are not restricted to the rate constant calculation. Since essentially all dynamical quantities in a complex system can be expressed in terms of certain time correlation functions, most of the discussions in the paper are equally applicable to the calculation of such quantities. An extension of the current methodology to treating a broader class of phenomena is currently in progress.

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**APPENDIX A: HARMONIC SPLITTING IN MULTIDIMENSIONAL PROBLEM**

In this appendix we describe the path integral formula that is used in Sec. III B 2 for a system–bath problem. The basic steps are the same with those described for a one-dimensional system in Sec. III A, and the only difference is that a harmonic splitting is applied to the bath degrees of freedom in order to facilitate the convergence of a path integral.

First, we express the system–bath Hamiltonian in Eq. (2.27) in terms of the normal-mode coordinates \(\mathbf{q}\) at the transition state (TS) as

\[
H = \frac{1}{2} \mathbf{p}^2 + V(\mathbf{q}).
\]  

(A1)

Here we assume that the first component of \(\mathbf{q}\) (i.e., \(q_1\)) denotes the unstable normal-mode coordinate at TS, which is taken here as the reaction coordinate. The other components \((q_2 \cdots q_N)\) correspond to the stable normal modes (hereafter referred to as the bath modes). The coherent state basis in the HK propagator is written in terms of this normal coordinates as

\[
\langle \mathbf{x}|\mathbf{p}\rangle = \prod_{j=1}^{N} \langle x_j|p_jq_j\gamma_j \rangle,
\]  

(A2)
with \( \gamma_i = 2(h^2 \beta) \) and \( \gamma_j = \omega_j / h \) \((j \geq 2)\), where \( \{\omega_j\} \) represent the normal-mode frequencies at TS, not the original bath frequencies appearing in Eq. (2.27).

In calculating the coherent state matrix element of the Boltzmannized flux operator,

\[
K_{ba} = \langle p_b q_a | \hat{F}(\beta) | p_a q_a \rangle
\]

\[
= \langle p_b q_a | e^{-\Delta \hat{H}^{(p)2} \beta} \hat{F}(\beta) e^{-\Delta \hat{H}^{(p)2} \beta} | p_a q_a \rangle, \quad (A3)
\]

we approximate the high-temperature Boltzmann operator as

\[
e^{-\Delta \hat{H}^{(p)2} \beta} \approx e^{-\Delta \hat{H}_{\text{ref}}^{(p)2} \beta} e^{-\Delta \hat{D} \beta} e^{-\Delta \hat{H}_{\text{ref}}^{(p)2} \beta}, \quad (A4)
\]

where \( \hat{H}_{\text{ref}} \) is a reference Hamiltonian consisting of a free particle Hamiltonian for the reaction coordinate plus a set of harmonic oscillator Hamiltonians for the bath modes,

\[
\hat{H}_{\text{ref}} = \sum_{j=1}^{N} \hat{H}_j, \quad (A5)
\]

\[
\hat{H}_j = \frac{\hat{p}_j^2}{2} + \frac{1}{2} \omega_j^2 \hat{q}_j^2 \quad (j \geq 2), \quad (A6)
\]

\[
\hat{D} = \hat{\Delta} \hat{V} \quad \text{is the difference potential given by} \quad \hat{H} - \hat{H}_{\text{ref}}. \quad \text{Inserting this splitting and the resolution of unity} \quad I = \int d\mathbf{x}^0 |^{(0)} \langle \mathbf{x}^0 | \text{into Eq. (A3) gives the following form:}
\]

\[
K_{ba} = \int d\mathbf{x}^0 \cdots d\mathbf{x}^p | \langle p_b q_a | e^{-\Delta \hat{H}_{\text{ref}}^{(p)2} \beta} | \mathbf{x}^p \rangle \times (\mathbf{x}^p | e^{-\Delta \hat{H}_{\text{ref}}^{(p)2} \beta} | \mathbf{x}^{p-1} \rangle \cdots (\mathbf{x}^{p+2} | e^{-\Delta \hat{H}_{\text{ref}}^{(p)2} \beta} | \mathbf{x}^1 \rangle \times (\mathbf{x}^1 | e^{-\Delta \hat{H}_{\text{ref}}^{(p)2} \beta} | p_a q_a \rangle \times e^{-\Delta \beta \hat{D}} \sum_{k=1}^{p} \Delta \hat{V}(\mathbf{x}^k) \bigg]. \quad (A8)
\]

Note that the indices for the imaginary-time slices and position coordinates are distinguished by superscripts and subscripts, respectively. In the above equation \( \mathbf{X} \) denotes a vector \((x_1^1, x_2^2, \ldots, x_j^j)\), and \( I_j(\mathbf{X}_j) \) is defined by

\[
I_1(\mathbf{X}_1) = \langle p_b q_a | e^{-\Delta \hat{H}_{\text{ref}}^{(p)2} \beta} | x_1^p \rangle \times \langle x_1^p | e^{-\Delta \hat{H}_{\text{ref}}^{(p)2} \beta} | x_1^{p-1} \rangle \cdots \langle x_1^{p+1} | e^{-\Delta \hat{H}_{\text{ref}}^{(p)2} \beta} | x_1^1 \rangle \times \langle x_1^1 | e^{-\Delta \hat{H}_{\text{ref}}^{(p)2} \beta} | p_a q_a \rangle, \quad (A9)
\]

\[
I_j(\mathbf{X}_j) = \langle p_b q_a | e^{-\Delta \hat{H}_{\text{ref}}^{(p)2} \beta} | x_j^p \rangle \times \langle x_j^p | e^{-\Delta \hat{H}_{\text{ref}}^{(p)2} \beta} | x_j^{p-1} \rangle \cdots \langle x_j^{p+1} | e^{-\Delta \hat{H}_{\text{ref}}^{(p)2} \beta} | x_j^1 \rangle \times \langle x_j^1 | e^{-\Delta \hat{H}_{\text{ref}}^{(p)2} \beta} | p_a q_a \rangle \quad (j \geq 2). \quad (A10)
\]

Since \( I_1(\mathbf{X}_1) \) takes precisely the same form as an integrand in Eq. (3.4), we can use the same procedure (namely, a normal-mode sampling) to generate \( \mathbf{X}_1 \) in the Monte Carlo calculation. The path for the \( j \)-th bath mode \( \mathbf{X}_j \) can also be sampled in a similar fashion. Using the following expressions:

\[
\langle x_j | e^{-\Delta \beta \hat{H}_{\text{ref}}^{(p)2} \beta} | p_j q_j \rangle = \frac{\gamma_j^{1/4}}{\gamma_j} \exp \left[ \frac{\gamma_j}{2} (x_j - q_j E_j)^2 + \frac{i}{\hbar} p_j (x_j - q_j E_j) + \frac{p_j^2}{4 \gamma_j} + \frac{\gamma_j}{2 \gamma_j} \right], \quad (A11)
\]

\[
\theta_j = -\frac{1}{4} \omega_j \Delta \beta - (1 - E_j^2) \left( \frac{\gamma_j}{4 \gamma_j} + \frac{p_j^2}{4 \gamma_j} + \frac{i}{\hbar} \frac{p_j q_j}{2 \gamma_j} \right), \quad (A12)
\]

\[
\langle x_j | e^{-\Delta \beta \hat{H}_{\text{ref}}^{(p)2} \beta} | x_j \rangle = \frac{\gamma_j}{2 \pi S_j} \left[ (x_j^2 + x_j^k)^{1/2} \right] \left[ \left( \frac{x_j^2 + x_j^k}{2 S_j} \right) \left( x_j^2 + x_j^k \right)^{1/2} \right] \quad (A13)
\]

\[
\text{with} \quad S_j = \text{sinh}(\omega_j \Delta \beta), \quad C_j = \text{cosh}(\omega_j \Delta \beta) \quad \text{and} \quad E_j = \exp(-\omega_j \Delta \beta / 2), \quad \text{we can rewrite} \quad I_j(\mathbf{X}_j) \quad \text{more explicitly as}
\]

\[
I_j(\mathbf{X}_j) = \text{const} \times \text{exp} \left[ -\frac{\gamma_j}{2} ((x_j^p - q_j E_j)^2 + (x_j^{p-1} - q_j E_j)^2 + (x_j^{p+1} - q_j E_j)^2) \right] + \left( x_j^p - x_j^{p-1} \right) \left( x_j^{p+1} - x_j^{p-1} \right) \left( x_j^2 + x_j^k \right)^{1/2} C_j \quad (A14)
\]

Here the modulus of \( I_j(\mathbf{X}_j) \) can be utilized as the weighting function \( W_j(\mathbf{X}_j) \) for generating the path \( \mathbf{X}_j \), i.e.,

\[
W_j(\mathbf{X}_j) = \text{exp} \left[ -\gamma_j \left( (x_j^p - q_j E_j)^2 + (x_j^{p-1} - q_j E_j)^2 \right) \right] - \frac{\gamma_j}{2 \pi S_j} \sum_{k=2}^{p} \left[ (x_j^2 + x_j^k)^{1/2} C_j - 2 x_j^k \right] \quad (A15)
\]

Since the argument in the last equation is a quadratic, negative definite function of \( \mathbf{X}_j \), we can diagonalize it and perform a normal-mode sampling in the amplitude space.

Finally, the matrix element \( K_{ba} \) is obtained as a Monte Carlo average as

\[
K_{ba} = \text{const} \times \left[ (x_j^{p+1} - x_j^{p-1}) \exp \left[ \frac{i}{\hbar} \frac{\gamma_j}{\gamma_j + \gamma_j} \left[ -p_{ba}(x_j^p - q_{ba}) + q_{ba} E_j \right] + \sum_{j=2}^{N} \frac{i}{\hbar} E_j \left[ -p_{ba}(x_j^p - q_{ba} E_j) \right] - q_{ba} E_j \right] + p_{ba}(x_j^p - q_{ba} E_j) \right] \right] \quad (A16)
\]
where \( W(X_1, X_2, \ldots, X_N) = \prod_j W_j(X_j) \). The important point here is that the potential term in the argument above,
\[
\Delta V(q) = V(q) - \sum_{j=1}^{N} \frac{1}{2} \omega_j^2 q_j^2 ,
\]
is very flat along the direction of the bath modes, and thus we can use a rather small number of time slices \( P \), which can be determined from the variation of the total potential along the reaction coordinate. (Otherwise, \( P \) should be determined from the highest frequency of the bath modes.)

**APPENDIX B: NUMERICAL EVALUATION OF THE WIGNER TRANSFORM**

In Sec. III B 1 we calculated a thermal rate constant using the LSC-IVR/classical Wigner model, where it was necessary to evaluate the Wigner transform of the Boltzmann-nized flux operator numerically. In this appendix we describe a means to accurately evaluate the Wigner transform with a grid basis set, i.e., the discrete variable representations (DVR).\(^{39–41}\)

First, we briefly summarize the useful formulas of the Wigner transform. The Wigner transform of an operator \( \hat{A} \) can be defined as
\[
\hbar A_w(p,q) = \text{tr}[\hat{A}(p,q)\hat{A}],
\]
where \( \hat{A}(p,q) \) represents the (quasi-) density operator given by
\[
\hat{A}(p,q) = \int \frac{dp dq}{2\pi \hbar} e^{i[\hat{p}(\hat{q} - q) + \hat{q}(\hat{p} - p)]/\hbar}.
\]
(Note that in the classical limit (namely, when the coordinate and momentum operators commute), this operator reduces to \( 2\pi \hbar \delta(\hat{q} - q) \delta(\hat{p} - p) \), and thus \( \hbar A(p,q) \) represents a natural generalization to the quantum case where \( \hat{p} \) and \( \hat{q} \) do not commute. The inverse Wigner transform can be written as
\[
\hat{A} = \int \frac{dp dq}{2\pi \hbar} \Delta(p,q)A_w(p,q),
\]
and using the above equation as well as Eq. (B1) leads to the following relation:
\[
\text{tr}[\hat{A}\hat{B}] = \int \frac{dp dq}{2\pi \hbar} A_w(p,q)B_w(p,q).
\]

Hence, we can see that the LSC-IVR [i.e., the approximation of Eq. (3.20) with Eq. (3.21)] is exact at \( t = 0 \). The coordinate representation of \( \Delta(p,q) \) is obtained by rewriting
\[
e^{i(\Delta p(\hat{q} - q) + \Delta q(\hat{p} - p))/\hbar} = e^{i\Delta q(\hat{p} - p)/2\hbar} e^{i\Delta p(\hat{q} - q)/\hbar} e^{i\Delta q(\hat{p} - p)/2\hbar},
\]
and using the relation \( e^{i\Delta q(\hat{p} - p)/2\hbar}|q\rangle = |q - \Delta q/2\rangle \) as follows:
\[
\Delta(p,q) = \int dq \Delta(q) e^{-i p \Delta q/\hbar}\left| q - \Delta q/2 \right\rangle \left\langle q + \Delta q/2 \right|.
\]

Similarly, the momentum representation of \( \Delta(p,q) \) becomes
\[
\Delta(p,q) = \int dq \Delta(q) e^{-i q \Delta p/\hbar}\left| q - \Delta q/2 \right\rangle \left\langle q + \Delta q/2 \right|.
\]

Next, we consider the evaluation of the Wigner transform of Eq. (B1) using the sinc-DVR basis.\(^{31}\) The coordinate representation of the orthonormal sinc-DVR basis is
\[
\langle x | \phi_j \rangle = \frac{1}{\sqrt{\Delta x}} \sin[\pi(x - x_j) / \Delta x],
\]
where sinc(x) = sin(x)/x and the grid points are defined as \( x_j = x_1 + (j - 1)\Delta x \) with a fixed grid spacing of \( \Delta x \). This function appears in the so-called *sampling theorem* which states that any band-limited function can be reproduced exactly by taking a sum of these sinc functions.\(^37\) Using the integral form of the sinc function,
\[
\langle x | \phi_j \rangle = \frac{\sqrt{\Delta x}}{2\pi \hbar} \int_{-\hat{p}}^{\hat{p}} dp e^{i p(x - x_j)\hbar} \left( p = \frac{\pi \hbar}{\Delta x} \right),
\]

It is seen that the momentum representation of the sinc-DVR basis takes a very simple form as
\[
\langle p | \phi_j \rangle = \sqrt{\Delta x} D(p) \langle | x_j \rangle,
\]
where \( D(p) \) is 1 for \( |p| < P \) and 0 otherwise. Thus the sinc-DVR basis is nothing but the Dirac delta function which is truncated in the momentum space.

Now assume that the operator \( \hat{A} \) in Eq. (B1) is expressed in terms of the sinc-DVR basis as
\[
\hat{A} = \sum_i \sum_j A_{ij} | \phi_i \rangle | \phi_j \rangle.
\]

Insertion of this expression into the trace in Eq. (B1) leads to a simple trace of two matrices:
\[
A_w(p,q) = \text{tr}[A\Delta(p,q)],
\]
with the matrix element of \( \Delta(p,q) \) defined by
\[
\Delta_{ij}(p,q) = \langle \phi_j | \Delta(p,q) | \phi_i \rangle.
\]

If we further substitute the momentum representation of \( \Delta(p,q) \) in Eq. (B7) into the above equation, we obtain
\[
\Delta_{ij}(p,q) = \Delta x \int d\Delta p e^{-iq \Delta p/\hbar} D(p + \Delta p/2) \times D(p - \Delta p/2) \left| x_i + p + \Delta p \right\rangle \left\langle x_j - p - \Delta p \right|,
\]
which can be explicitly integrated to give
\[
\Delta_{ij}(p,q) = \frac{\Delta x}{\pi} \sin[2(2P - |p|)(x - q)/\hbar] \times \exp\left[ ip(x_i - x_j + q)/\hbar \right] \left| |p| > P \right|,
\]
where \( x = (x_i + x_j)/2 \) and \( P = \pi \hbar / \Delta x \). Therefore, once the sinc-DVR matrix of the operator \( \hat{A} \) is constructed, its Wigner transform can be obtained simply by using Eqs. (B12) and
(B14). These two equations are the main result of this appendix and were utilized in Sec. III B 1 in the LSC-IVR calculation.


