Numerical path integral techniques for long time dynamics of quantum dissipative systems

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Recent progress in numerical methods for evaluating the real-time path integral in dissipative harmonic environments is reviewed. Quasi-adiabatic propagators constructed numerically allow convergence of the path integral with large time increments. Integration of the harmonic bath leads to path integral expressions that incorporate the exact dynamics of the quantum particle along the adiabatic path, with an influence functional that describes nonadiabatic corrections. The resulting quasi-adiabatic propagator path integral is evaluated by efficient system-specific quadratures in most regimes of parameter space, although some cases are handled by grid Monte Carlo sampling. Exploiting the finite span of nonlocal influence functional interactions characteristic of broad condensed phase spectra leads to an iterative scheme for calculating the path integral over arbitrary time lengths. No uncontrolled approximations are introduced, and the resulting methodology converges to the exact quantum result with modest amounts of computational power. Applications to tunneling dynamics in the condensed phase are described. © 1995 American Institute of Physics.

I. INTRODUCTION

Since its original formulation in 1948, Feynman's path integral representation of time-dependent quantum mechanics has attracted enormous attention. For many years the path integral has provided a powerful formal tool for deriving quantum mechanical and semiclassical approximations. However, numerical applications have become increasingly important during the last decade and have often led to new physical results not obtainable by other methods.

From a computational point of view, the path integral is attractive for treating many-body quantum mechanics problems without introducing uncontrolled approximations. Unlike wavefunction-based methods, which require numerical effort that grows exponentially with the size of the system, the Feynman paths are one-dimensional lines independent of the number of degrees of freedom involved. However, numerical summation over paths is far from straightforward in general.

Numerical evaluation of the path integral requires discretization of the paths via time slicing, which leads to multidimensional integrals. The conventional trapezoid rule discretization of the action, which is equivalent to splitting each short time evolution operator into kinetic and potential parts, requires very short time increments for accuracy; accordingly, the dimension of the resulting integral can be very high if the desired propagation time is long. In pure imaginary time, i.e., when equilibrium properties of bosons are considered, Monte Carlo sampling is very useful for evaluating the multidimensional discretized path integral; a number of demanding equilibrium many-body calculations have become possible using Monte Carlo path integral methods. However, extension of these methods to extract dynamical information is far from straightforward, due to the oscillatory nature of the real time propagator which leads to dramatic phase cancellation and failure of Monte Carlo schemes, known as the sign problem. In recent years, significant effort has been expended toward developing numerical techniques for evaluating path integrals in real time.

Early approaches to real time path integrals utilized analytic continuation ideas, direct sto-
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stochastic sampling of the complex time propagator,\textsuperscript{10} or coordinate rotation\textsuperscript{11,12} and were met with limited success. A major step forward was the development of stationary-phase-based Monte Carlo methods,\textsuperscript{13-18} which take advantage of the semiclassical limit of the path integral. These methods are very efficient for sampling around a single classical path (and thus for obtaining short time dynamics in most ordinary cases) but converge very slowly if the dynamics is dominated by many interfering classical trajectories. A different approach was the construction of effective system-specific propagators,\textsuperscript{19,20} which are sufficiently accurate for a particular problem but much better behaved than the standard short time propagator. Although this method allows efficient fully quantum sampling for short time, the statistical error grows rapidly with the dimensionality of the integral (and therefore with the total propagation time).\textsuperscript{19(b)} Other Monte Carlo approaches include a stochastic resummation method,\textsuperscript{21,22} coherent state representations,\textsuperscript{23} or recursive summation over classes of paths.\textsuperscript{24} While these methods have improved the statistics of path integral calculations, they have not managed to provide converged results for nontrivial problems for times longer than two or so periods of motion of the quantum particle. A recent approach\textsuperscript{25} to time correlation functions based on analytic continuation of imaginary time quantities via the maximum entropy method appears promising.

This article reviews a different approach\textsuperscript{26-35} which has allowed for the first time converged path integral calculations for quantum particles in dissipative environments over extremely long time lengths. With the exception of a small favorable section of parameter space, this methodology does not employ Monte Carlo procedures and thus yields numerically exact results free of statistical noise. A wide variety of intriguing problems in physics and chemistry can now be treated exactly. These include generic quantum mechanical processes such as hydrogen tunneling and electron transfer, in which the coupling to condensed phase or biological environments often leads to a wealth of behaviors that range from semi-coherent population relaxation to exponential rate kinetics or even complete localization.

The starting point is expression of the path integral in terms of improved propagators which by construction incorporate the exact dynamics of physically motivated reference systems.\textsuperscript{26} Apart from leading to converged results with large time steps, these propagators are relatively smooth, allowing evaluation of the path integral by quadratures.

Specializing to processes in dissipative media described by a system coordinate coupled to a harmonic bath, the one-dimensional Hamiltonian with the potential along the adiabatic path has been shown to provide an excellent reference system for partitioning the propagator. The result is a modified path integral expression\textsuperscript{26} that involves one-dimensional propagators which describe the exact dynamics of the system along the adiabatic path, as well as a (nonlocal) influence functional that incorporates multidimensional nonadiabatic corrections. In many situations this \textit{quasi-adiabatic propagator path integral} (QUAPI) converges with only a few (at most) time steps for each period of motion.

Finite temperature correlation functions\textsuperscript{36} are often expressed in terms of complex time propagators. If the real time is shorter than (or on the order of) the inverse temperature, the oscillations are damped to a large extent and Monte Carlo algorithms can be used successfully to evaluate the QUAPI. Most other situations cannot be treated by Monte Carlo due to the phase oscillation problem and therefore must be dealt with using efficient numerical quadratures. It has been noted recently\textsuperscript{29} that system-specific discrete variable representations\textsuperscript{37-44} (i.e., appropriately discretized versions of coordinate states) and their time-dependent extensions\textsuperscript{45} offer maximal efficiency for this purpose.

The practical applicability of the above schemes for global (multidimensional) evaluation of the discretized path integral depends critically on the dimension of the latter, which (for systems coupled to harmonic environments) is roughly equal to the number of time slices necessary for convergence. For this reason, global evaluation of the discretized path integral requires numerical effort that grows exponentially with the total real time,\textsuperscript{19(b)} and calculations over many periods of motion are not feasible. The ability to evaluate numerically the path integral over long times...
requires departing from global integration methods and devising iterative schemes. In the past, iterative methods for evaluating the real time path integral were ruled out due to the nonlocality of the dissipative influence functional. It has been shown recently, though, that the range of nonlocal interactions in the influence functional is always finite if the bath is characterized by a broad spectrum and proposed an iterative procedure for evaluating the path integral for arbitrary time intervals.\textsuperscript{32,33}

Section II reviews the conventional discretized path integral representation of the quantum propagator and discusses the phase oscillation problem. Section III describes the numerical construction of propagators that are accurate over large time increments based on physically motivated reference systems. This idea is applied to a system in contact with a dissipative bath in Sec. IV, where an adiabatic reference leads to the quasi-adiabatic propagator path integral with an influence functional that describes nonadiabatic corrections. Section V presents quadrature as well as Monte Carlo procedures suitable for evaluating the resulting path integral. The finite length of nonlocal interactions in the influence functional is established in Sec. VI, which introduces the tensor multiplication scheme for iterative calculation of the dynamics. Recent applications to tunneling dynamics are reviewed briefly in Sec. VII, and Sec. VIII summarizes with remarks for further applications and future directions.

II. THE PRIMITIVE DISCRETIZED PATH INTEGRAL AND THE SIGN PROBLEM

In this section we review briefly the conventional discretized path integral representation of the quantum propagator for time-independent Hamiltonians and discuss the numerical problems that arise in real time. Extensive reviews of the discretized path integral, as well as discussions of various ways of dealing with the sign problem, can be found in Refs. 17 and 18.

Because most physical systems are described by Hamiltonians that are quadratic in momentum but may involve rather arbitrary potential terms, the most useful representation of the time evolution operator is in terms of position states. The starting point for the discretized path integral is the observation that the short time propagator of any system can be well approximated by a variety of methods. The discretized path integral expresses the propagator for any (arbitrary) time \( t \) in terms of the known short time propagator.

Throughout this section we consider a general Cartesian Hamiltonian in \( n \) degrees of freedom:

\[
H(x,p) = \sum_{j=1}^{n} \frac{p_j^2}{2m_j} + V(x_1, \ldots, x_n). \tag{2.1}
\]

We define an integer \( N \) which is sufficiently large that \( t/N = \Delta t \) is a “short time” for the system of interest, such that there exist sufficiently accurate approximations to the corresponding propagator. \( N \) is usually referred to as the number of time slices or discretizations. Next, the time evolution operator is factored into a product of \( N \) exponential operators, each one of which propagates the system for time \( t/N \):

\[
e^{-iHt/\hbar} = e^{-iH\Delta t/\hbar} e^{-iH\Delta t/\hbar} \cdots e^{-iH\Delta t/\hbar} = \prod_{k=1}^{N} e^{-ih(t_k-t_{k-1})/\hbar}, \tag{2.2}
\]

where \( t_k = kt/N \). Using the completeness property of position eigenstates

\[
\int dx_k |x_k\rangle \langle x_k| = 1
\]

repeatedly, one arrives at the result
\begin{equation}
\langle x_f | e^{-iHt/\hbar} | x_0 \rangle = \int dx_1 \ldots \int dx_{N-1} \prod_{k=1}^{N} \langle x_k | e^{-iH\Delta t/\hbar} | x_{k-1} \rangle
\end{equation}

\begin{equation}
= \int dx_1 \ldots \int dx_{N-1} \prod_{k=1}^{N} \langle x_k | e^{-iH(t_k-t_{k-1})/\hbar} | x_{k-1} \rangle.
\end{equation}

(2.3)

where $x_N = x_f$. Each point $x_k$ in Eq. (2.3) is associated with a particular time $t_k = k\Delta t$, and thus each set of points $\{x_k\}$ in the integrand defines a path composed of straight line segments (see Fig. 1). Note that Eq. (2.3) is an exact expression, for any value of $N$. It follows that the required number of time discretizations can be reduced if the accuracy of the short time propagators used can be extended to longer time interval $\Delta t$.

The most common procedure of approximating the propagator for short time $\Delta t$ utilizes the Trotter splitting of the time-evolution operator based on partitioning the Hamiltonian into kinetic and potential energy terms:

\begin{equation}
\exp(-iH\Delta t/\hbar) = \exp\left(-\frac{iV\Delta t}{2\hbar}\right) \exp\left(-\frac{iT\Delta t}{\hbar}\right) \exp\left(-\frac{iV\Delta t}{2\hbar}\right).
\end{equation}

(2.4)

Use of this approximation leads to the following "primitive" coordinate propagator, valid for short time:\textsuperscript{3}

\begin{equation}
\langle x_k | e^{-iH\Delta t/\hbar} | x_{k-1} \rangle \approx \langle x_k | e^{-iT\Delta t/\hbar} | x_{k-1} \rangle e^{-i(\Delta t/2\hbar)[V(x_k) + V(x_{k-1})]}.
\end{equation}

(2.5)

If the kinetic energy part is evaluated exactly, one obtains the standard result

\begin{equation}
\langle x_k | e^{-iT\Delta t/\hbar} | x_{k-1} \rangle = \prod_{j=1}^{n} \left( \frac{m_j}{2\pi i \hbar \Delta t} \right)^{1/2} \exp \left[ \frac{i m_j}{\hbar} \frac{(x_{j,k} - x_{j,k-1})^2}{2\Delta t} \right].
\end{equation}

(2.6)

Use of this result in Eq. (2.5) leads to the following discretized path integral expression of the propagator:\textsuperscript{1-3}
\begin{align}
\langle x_f | e^{-iHt/\hbar} | x_0 \rangle \approx \prod_{j=1}^n \left( \frac{m_j N}{2 \pi i \hbar t} \right)^{1/2} \int d^n x_1 \cdots \int d^n x_{N-1} \\
\times \exp \left\{ \frac{i}{\hbar} \sum_{k=1}^N \left[ \sum_{j=1}^n \frac{m_j N}{2t} (x_{j,k} - x_{j,k-1})^2 - \frac{t}{2N} \left[ V(x_k) + V(x_{k-1}) \right] \right] \right\}
\end{align}

(2.7)

which becomes an equality in the limit \( N \to \infty \). One easily recognizes the exponent in the last equation as the trapezoid rule discretization of the action in Feynman's path integral expression,

\begin{align}
\langle x_f | e^{-iHt/\hbar} | x_0 \rangle = \int \mathcal{D} x_t \left( \exp \frac{i}{\hbar} S[x_t] \right),
\end{align}

(2.8)

where \( S[x_t] \) is the classical action functional along the path \( x_t \) connecting the initial and final points. We will refer to Eq. (2.7) as the primitive discretized path integral.

The above discretized path integral expression is a highly oscillatory function of the coordinates. These rapid oscillations, along with the fact that the integrand is delocalized throughout the entire integration volume, prohibit use of Monte Carlo methods in the evaluation of Eq. (2.7).

Numerous approaches have been proposed for alleviating the phase oscillation problem in Monte Carlo path integral calculations.\textsuperscript{11-23} Although efficient filtering may indeed improve the situation substantially, all known Monte Carlo schemes fail in practice to converge at long time. This appears to be due to the intrinsic structure of quantum mechanics, which at long times leads to observables through dramatic phase cancellation, regardless of the particular filtering technique employed in the discretized path integral.

Aside from real-time dynamics, the discretized path integral expression is also applicable to the Boltzmann operator, \( \exp(-\beta \hat{H}) \), characterizing a system at thermal equilibrium.\textsuperscript{46} (Here \( \beta = 1/k_B T \) where \( T \) is the absolute temperature and \( k_B \) is the Boltzmann constant.) Indeed, the discretized path integral representation of the Boltzmann operator can be obtained from Eq. (2.7) by the substitution \( it/\hbar \to \beta \), implying that the formalism of equilibrium quantum statistical mechanics is identical to that of quantum dynamics if the time becomes imaginary. An important difference between the real and the imaginary time path integral is that the integrand is real and positive in the case of the latter, such that no phase cancellation takes place in equilibrium calculations. For this reason, discretized path integral expressions for thermal equilibrium properties of many-body problems are handled very successfully by Monte Carlo algorithms.\textsuperscript{8} Finally, the Boltzmann operator is often combined with the (real) time evolution operator in the calculation of time-dependent observables at finite temperature, resulting in complex time path integral expressions. Depending on the relative magnitude of the real and imaginary parts of the integrand, the phase cancellation problem may be mild or very severe. Thus, finite temperature calculations based on Monte Carlo evaluation of Eq. (2.7) usually converge easily for short time but become extremely demanding if the real time exceeds one or two periods of motion.

III. ACCURATE PROPAGATORS FOR SIMPLE REFERENCE SYSTEMS

From the discussion of the previous section it should be clear that the sign problem encountered in Monte Carlo path integral methods is a fundamental problem originating from the nature of quantum mechanics. Except in certain favorable regimes, then, the prospect of overcoming that problem in Monte Carlo path integral calculations does not appear very promising. This reasoning led us to explore different routes toward the goal of making many-body path integral calculations feasible in real time.

Numerical evaluation of the discretized path integral according to Eq. (2.7) is problematic only because the number of integration variables is large for the time lengths of interest. As can be seen from Fig. 2, the conventional discretization calculates the propagator by making many constant potential (i.e., free particle) steps, with the potential value adjusted at each discrete time. For this reason many (typically on the order of 30–100) time steps per period are necessary for adequate representation of the dynamics in smooth potentials, implying that even a single-particle problem (which should hardly require any numerical work if solved by other techniques) requires demanding multidimensional integration if treated along those lines. It is therefore clear that the path integral discretization of Eq. (2.7) cannot be expected to offer a successful approach to truly demanding many-body quantum mechanics problems. Rather than attempting to evaluate Eq. (2.7), it appears more profitable to reformulate the path integral such that its computation becomes effortless in trivial cases, for example, in the limit of a separable Hamiltonian, devoting the entire numerical work to the treatment of nonseparable interactions. Since summation over paths is problematic, one concludes that the exact dynamics of one-dimensional (or other treatable) subsystems should be calculated by other techniques and built into the path integral.

To implement the above strategy, we partition the many-body Hamiltonian into a reference part $H_{\text{ref}}$ whose solution can be obtained by a combination of analytic and numerical techniques and a term $H_{\text{int}}=H-H_{\text{ref}}$ which contains nonseparable interactions. In typical Cartesian Hamiltonians of the type shown in Eq. (2.1) the kinetic energy operator is diagonal and $H_{\text{int}}$ depends on coordinates only. The time evolution operator for a time increment $\Delta t$ is then split symmetrically in the form

$$
\exp\left(-\frac{i}{\hbar} H \Delta t\right) = \exp\left(-\frac{i}{\hbar} H_{\text{ref}} \Delta t\right) \exp\left(-\frac{i}{\hbar} H_{\text{int}} \Delta t\right) \exp\left(-\frac{i}{\hbar} H_{\text{int}} \Delta t\right). \quad (3.1)
$$

Since $H_{\text{ref}}$ and $H_{\text{int}}$ do not commute, this factorization is not exact. However, the error is of order $[H_{\text{int}},[H_{\text{ref}}, H_{\text{int}}]]\Delta t^3$ and therefore vanishes if $\Delta t \to 0$.

Evaluation of Eq. (3.1) in the coordinate representation gives the following result for the coordinate propagator:
FIG. 3. Solid line: real part of the effective system propagator, Eq. (3.3), constructed numerically in terms of 8 eigenstates for a symmetric double well potential. The time step is approximately equal to a tenth of the vibrational period. The dotted line shows the real part of the primitive propagator, Eq. (2.7) with the same parameters.

\[
\langle x_k | e^{-iH_{\text{eff}} \Delta t / \hbar} | x_{k-1} \rangle \approx \langle x_k | e^{-iH_{\text{ref}} \Delta t / \hbar} | x_{k-1} \rangle \exp \left( -\frac{i}{\hbar} \frac{\Delta t}{2} \left[ H_{\text{inf}}(x_k) + H_{\text{inf}}(x_{k-1}) \right] \right).
\]  (3.2)

If \( H_{\text{ref}} \) is chosen as the bare kinetic energy part of the Hamiltonian, Eq. (3.2) reverts to the primitive coordinate propagator. Here, however, \( H_{\text{ref}} \) is allowed to include important potential terms and thus can be chosen as an improved reference problem whose physics resembles as closely as possible that of the full Hamiltonian.\(^{26}\) Physically meaningful choices of the reference Hamiltonian should lead to accurate propagators with large time steps, and the exact propagator (for any value of \( \Delta t \)) is recovered if the potential coupling terms vanish. Use of such improved propagators in the path integral satisfies the necessary condition detailed above for a successful numerical path integral methodology.

Practical implementation of this approach assumes knowledge of the reference propagator, \( \langle x_k | \exp(-iH_{\text{ref}} \Delta t / \hbar) | x_{k-1} \rangle \). By exploiting features of the reference Hamiltonian, the reference propagator can be expressed in terms of propagators for low- (one- or two-) dimensional subsystems. For example, if \( H_{\text{ref}} \) is separable, the reference propagator becomes a product of onedimensional propagators. If \( H_0 \) is a one- or two-dimensional Hamiltonian whose eigenstates \( \Phi_n \) and eigenvalues \( E_n \) can be obtained from numerical diagonalization, the corresponding propagator can be expressed as\(^{19b,26}\)

\[
\langle x_k | e^{-iH_0 \Delta t / \hbar} | x_{k-1} \rangle = \sum_{m=0}^{m_{\text{max}}} \Phi_m(x_k) \Phi_m(x_{k-1}) e^{-iE_m \Delta t / \hbar}.
\]  (3.3)

Although numerical evaluation of Eq. (3.3) requires summation over a finite number of terms, this equation is formally correct only if all eigenstates are included, i.e., if \( m_{\text{max}} \to \infty \). Indeed, the sum in Eq. (3.3) does not include a convergence factor, implying that the infinite series cannot be truncated. Thus, the feasibility of this numerical approach appears questionable. It is easily seen, though, that if the propagator is to be used for calculating the evolution of a nonsingular wave function or density matrix, then high energy terms in Eq. (3.3) will enter with exponentially small weights. Since large quantum number terms do not contribute to the evolution of quantities of interest, the sum in Eq. (3.3) can be truncated at some \( m_{\text{max}} \). Thus, by including a finite number of states in Eq. (3.3) an effective propagator can be constructed, which will lead to accurate time evolution. Furthermore, large quantum number terms are responsible for the highly oscillatory behavior of the real time propagator, and their omission has the additional advantage of leading to smooth and well-behaved propagators.\(^{19}\) These features are illustrated in Fig. 3, which shows the
effective propagator constructed according to Eq. (3.3) for a model double well potential employed in the applications of Sec. VII. The primitive propagator, Eq. (2.5), is also displayed in the same figure for comparison.

IV. QUASI-ADIABATIC PROPAGATOR PATH INTEGRAL FOR A PARTICLE COUPLED TO A DISSIPATIVE HARMONIC BATH

Throughout the remainder of this article we focus on processes that can be modeled by the generic system–bath Hamiltonian,

$$H = \frac{p_s^2}{2m_0} + V_0(s) + \sum_j \left( \frac{p_j^2}{2m_j} + \frac{1}{2} m_j \omega_j^2 \left( Q_j - \frac{c_j s}{m_j \omega_j} \right)^2 \right).$$  (4.1)

Equation (4.1) gives rise to the simplest model of dynamical processes in the condensed phase, which involves a “reaction coordinate” $s$ (describing the nonlinear system of interest) coupled to a large number of harmonic “bath” degrees of freedom (e.g., phonons) that mimic the effects of the environment. In spite of its simple appearance, the harmonic oscillator bath is known to provide a realistic description of common condensed phase environments on the observable dynamics of the microscopic system of interest. This is true not only for crystalline solids, for which the harmonic bath arises naturally from small amplitude lattice vibrations, but also for some processes in liquids; although no simple microscopic model of harmonic modes exists in the latter case, the harmonic bath picture is often successful due to the validity of linear response theory. Electron transfer in solution offers a well-studied example where accurate calculations have shown the free energy surfaces to be parabolic to a very good approximation.

Within the framework of classical mechanics, the dynamics described by the multidimensional potential of Eq. (4.1) is equivalent to that of a one-dimensional system obeying a generalized Langevin equation (GLE):

$$m_0 \frac{d^2}{dt^2} s(t) + m_0 \int_{-\infty}^{t} dt' \chi(t-t') \dot{s}(t') + V'_0(s(t)) = \xi(t).$$  (4.2)

The picture that emerges is that of the particle of interest experiencing frictional damping along the reaction coordinate as well as fluctuating forces $\xi(t)$ which satisfy the fluctuation–dissipation theorem.

Equation (4.1) includes counterterms quadratic in $s$ which renormalize the potential in order to ensure that important potential features such as the barrier height do not change with the coupling strength. The characteristics of the bath pertaining to the dynamics of the reaction coordinate are captured in the spectral density,

$$J(\omega) = \frac{\pi}{2} \sum_j \frac{c_j^2}{m_j \omega_j} \delta(\omega - \omega_j),$$  (4.3)

which for macroscopic environments is practically a continuous function.

In order to construct an accurate propagator for the system–bath problem, one can take advantage of the fact that the propagator for the forced harmonic oscillator is known analytically. This fact implies that the only propagator that must be generated numerically is that for the system coordinate. Following the ideas outlined in Sec. III, we wish to identify a physically motivated one-dimensional reference system for splitting the time evolution operator leading to propagators accurate for fairly large time steps $\Delta t$. The low-frequency bath oscillators, associated with very long time scales $\omega_j^{-1} \gg \Delta t$, are largely insensitive to the choice of reference. For this reason the reference Hamiltonian must be chosen such that it leads to accurate treatment of the high-

frequency bath modes. This suggests use of the adiabatic potential as the reference, \(26\) i.e., the potential along the one-dimensional path that minimizes the total potential energy at each fixed value of the system coordinate (see Fig. 4). Since the adiabatic path is given by the relations \(Q_j = c_j s/m_j \omega_j^2\), the reference Hamiltonian has the simple form

\[
H_0 = \frac{p_s^2}{2m_0} + V_0(s).
\] (4.4)

[If the counterterms \(\sum c_j s^2/2m_j \omega_j^2\) were not included in Eq. (4.1), the adiabatic reference Hamiltonian would have to be renormalized by those terms.]

Thus, the total Hamiltonian is partitioned into the one-dimensional adiabatic reference \(H_0\) and a bath of harmonic oscillators \(H_{\text{env}} = H - H_0\) whose equilibrium positions are adiabatically displaced along the system coordinate:

\[
H_{\text{env}} = \sum_j \frac{p_j^2}{2m_j} + \frac{1}{2} m_j \omega_j^2 \left( Q_j - \frac{c_j s}{m_j \omega_j^2} \right)^2 = \sum_j H_j(Q_j,P_j,s).
\] (4.5)

Employing a symmetric splitting of the time evolution operator based on the adiabatic partitioning of the system–bath Hamiltonian,

\[
\exp \left( - \frac{iH \Delta t}{\hbar} \right) \approx \exp \left( - \frac{iH_{\text{env}} \Delta t}{2\hbar} \right) \exp \left( - \frac{iH_0 \Delta t}{\hbar} \right) \exp \left( - \frac{iH_{\text{env}} \Delta t}{2\hbar} \right)
\] (4.6)

leads to the following quasi-adiabatic propagator:\(26\)

\[
\langle s_k Q_k | e^{-iH_{\Delta t}/\hbar} | s_{k-1} Q_{k-1} \rangle \approx \langle s_k | e^{-iH_0 \Delta t/\hbar} | s_{k-1} \rangle \prod_{j=1}^{k} \langle Q_{j,k} | e^{-iH_j \Delta t/2\hbar} e^{-iH_j \Delta t/2\hbar} | Q_{j,k-1} \rangle.
\] (4.7)

The one-dimensional reference propagator in the last equation is evaluated numerically according to the scheme of Sec. III. On the other hand, each bath factor in Eq. (4.7) is a propagator for a harmonic oscillator displaced from equilibrium by an amount that depends on the value of the
system coordinate. These propagators can be evaluated analytically, introducing Franck–Condon factors (cf. the $\Delta \lambda_{j,k}$ terms below) that account for nonadiabatic corrections to the dynamics along the one-dimensional adiabatic path:

$$
\langle Q_{j,k} | e^{-iH_{j}(s_k)\Delta t/\hbar} e^{-iH_{j-1}(s_{k-1})\Delta t/\hbar} | Q_{j,k-1} \rangle = \left( \frac{m_j \omega_j}{2 \pi \hbar \sin \omega_j \Delta t} \right)^{1/2} \exp \frac{im_j \omega_j}{2 \hbar \sin \omega_j \Delta t} \times \left[ \left( q_{j,k}^2 + q_{j,k-1}^2 \right) \cos \omega_j \Delta t - 2 q_{j,k} q_{j,k-1} \right.
$$

$$
+ 2 \Delta \lambda_{j,k} \Delta q_{j,k} \cos \left( \frac{\omega_j \Delta t}{2} + \frac{\Delta \lambda_{j,k}^2 \cos^2 \omega_j \Delta t}{2} \right),
$$

where

$$
\Delta \lambda_{j,k} = \lambda_{j,k} - \lambda_{j,k-1}, \quad \lambda_{j,k} = \frac{c_j s_k}{m_j \omega_j^2}, \quad q_{j,k} = Q_{j,k} - \lambda_{j,k}, \quad \text{and} \quad \Delta q_{j,k} = q_{j,k} - q_{j,k-1}.
$$

The numerical construction of the adiabatic system propagator guarantees that Eq. (4.7) is exact for any value of the time step in the absence of system–bath coupling. With nonzero coupling the quasi-adiabatic propagator splitting is still exact in the limit of a high-frequency bath ($\omega_j \to \infty$, finite $c_j$). Upon deviating from this limit the factorization of the single-step time-evolution operator according to Eq. (4.7) introduces errors which are proportional to the nonadiabaticity of the Hamiltonian and which vanish as the time step decreases. Finally, the quasi-adiabatic propagator is also exact with any finite $\Delta t$ in the zero frequency limit if the spectral density drops off sufficiently rapidly.

The advantages offered by the adiabatic approximation are well-known and have been exploited in several different contexts. Adiabatic basis functions have been widely used for solving coupled channel scattering equations. Adiabatically shifted basis functions have also proved very useful for basis set calculations on reaction coordinates coupled to several harmonic bath oscillators. Adiabatic displacement operators constitute the basis of the small polaron transformation and have also been employed in the context of kinetic equations arising from phonon-type expansions of the density matrix.

The quasi-adiabatic propagator offers a way of exploiting these ideas in the path integral context. There is, however, an important advantage associated with incorporating the adiabatic reference in the path integral representation of the propagator; namely, the path integral allows the multidimensional harmonic bath to be integrated out. Indeed, use of Eq. (4.7) in the discretized path integral, Eq. (2.3), and integration over the bath coordinates which appear as Gaussian integrals, leads to quasi-adiabatic propagator path integral (QUAPI) expressions for dynamical observables. Quantum mechanical observables of the system coordinate can be obtained from the reduced density matrix,

$$
\rho_{\text{red}}(s^n, s'; t) = T_{\text{bath}}(s^n|e^{-iHt/\hbar}\rho(0)e^{iHt/\hbar}|s').
$$

(4.9)

If the interaction between system and bath is switched on at $t=0$, i.e., if the initial density matrix is

$$
\rho(0) = \rho_s(0) \rho_{\text{bath}}(0).
$$

(4.10)

then the evolution of the reduced density matrix of the system is given by

$$
\rho_{\text{red}}(s^n, s'; t) = \int ds_0^+ \int ds_0^- \int ds_{N-1}^+ \int ds_{N-1}^- \int ds_1^+ \int ds_1^- \int ds_{N-1}^+ \int ds_{N-1}^-
$$

$$
\times \langle s^n|e^{-iH_0 \Delta t/\hbar}|s_{N-1}^+ \rangle \cdots \langle s_1^n|e^{-iH_0 \Delta t/\hbar}|s_0^+ \rangle \cdots \langle s_1^n|\rho_s(0)|s_0^- \rangle.
$$

\[
\begin{align*}
&\times \langle s_0^- | e^{iH_0 \Delta t/\hbar} | s_1^- \rangle \cdots \langle s_{N-1}^- | e^{iH_0 \Delta t/\hbar} | s' \rangle \\
&\times I(s_0^+, s_1^+, \ldots, s_{N-1}^+, s_{N}^-, s_{N-1}^-, \ldots, s_1^-, s_0^-; \Delta t), \\
&\quad \text{(4.11)}
\end{align*}
\]
where the influence functional is
\[
I(s_0^+, s_1^+, \ldots, s_{N-1}^+, s_{N}^-, s_{N-1}^-, \ldots, s_1^-, s_0^-; \Delta t)
= \text{Tr}_{\text{bath}} e^{-iH_{\text{env}}(s^+)\Delta t/2\hbar} e^{-iH_{\text{env}}(s^-_{N-1})\Delta t/2\hbar} \ldots e^{-iH_{\text{env}}(s^0)\Delta t/2\hbar}
\times \rho_{\text{bath}}(0) e^{iH_{\text{env}}(s^-_0)\Delta t/2\hbar} \ldots e^{iH_{\text{env}}(s^+_{N-1})\Delta t/2\hbar} e^{iH_{\text{env}}(s')\Delta t/2\hbar}. \\
&\quad \text{(4.12)}
\]
Here \(\{s_0^+, s_1^+, \ldots\}\) and \(\{s_0^-, s_1^-, \ldots\}\) denote discretizations of the forward and backward paths with endpoints \((s_0^+, s_N^-)\) and \((s_0^-, s_N^+)\), respectively.

The role of the influence functional in the quasi-adiabatic propagator path integral is to include multidimensional nonadiabatic corrections to the exact dynamics along the adiabatic path; these corrections become more accurate as the time slicing of the path integral becomes finer. Because the quasi-adiabatic propagator is by construction exact for any magnitude of the time increment in the two opposite limits of fast or slow coupled oscillators, the QUAPI converges rapidly (i.e., with fairly large time steps) over wide ranges of bath oscillator frequencies.

Specializing to the case where the bath is initially at temperature \((k_B T)\), the influence functional is given by
\[
I = \exp \left[ -\frac{1}{\hbar} \sum_{k=0}^{N} \sum_{k'=0}^{k} (s_k^+ - s_k^-)(\eta_{kk'} s_{k'}^+ - \eta_{kk'}^* s_{k'}^-) \right], \\
&\quad \text{(4.13)}
\]
where \(s_N^+ = s''_0, s_N^- = s'\), and the coefficients \(\eta_{kk'}\) are equal to
\[
\eta_{kk'} = \frac{2}{\pi} \int_{-\infty}^{\infty} d\omega \frac{J(\omega) \exp(\hbar \omega \beta/2)}{\omega^2 \sinh(\hbar \omega \beta/2)} \sin^2(\omega \Delta t/2)e^{-i\omega \Delta t(k-k')}, \quad 0 < k' < k < N, \\
&\quad \text{(4.14a)}
\]
\[
\eta_{kk'} = \frac{1}{\pi} \int_{-\infty}^{\infty} d\omega \frac{J(\omega) \exp(\hbar \omega \beta/2)}{\omega^2 \sinh(\hbar \omega \beta/2)} (1 - e^{-i\omega \Delta t}), \quad 0 < k < N, \\
&\quad \text{(4.14b)}
\]
\[
\eta_{NN0} = \frac{2}{\pi} \int_{-\infty}^{\infty} d\omega \frac{J(\omega) \exp(\hbar \omega \beta/2)}{\omega^2 \sinh(\hbar \omega \beta/2)} \sin^2\left(\frac{\omega \Delta t}{4}\right)e^{-i\omega (t - \Delta t/2)}, \\
&\quad \text{(4.14c)}
\]
\[
\eta_{00} = \eta_{NN} = \frac{1}{2} \int_{0}^{\infty} d\omega \frac{J(\omega) \exp(\hbar \omega \beta/2)}{\omega^2 \sinh(\hbar \omega \beta/2)} (1 - e^{-i\omega \Delta t/2}), \\
&\quad \text{(4.14d)}
\]
\[
\eta_{0k} = \frac{2}{\pi} \int_{-\infty}^{\infty} d\omega \frac{J(\omega) \exp(\hbar \omega \beta/2)}{\omega^2 \sinh(\hbar \omega \beta/2)} \sin\left(\frac{\omega \Delta t}{4}\right) \sin\left(\frac{\omega \Delta t}{2}\right)e^{-i\omega (k \Delta t - \Delta t/4)}, \quad 0 < k < N, \\
&\quad \text{(4.14e)}
\]
\[
\eta_{Nk} = \frac{2}{\pi} \int_{-\infty}^{\infty} d\omega \frac{J(\omega) \exp(\hbar \omega \beta/2)}{\omega^2 \sinh(\hbar \omega \beta/2)} \sin\left(\frac{\omega \Delta t}{4}\right) \sin\left(\frac{\omega \Delta t}{2}\right)e^{-i\omega (t - k \Delta t - \Delta t/4)}, \quad 0 < k < N, \\
&\quad \text{(4.14f)}
\]

Here the spectral density for negative frequencies is defined as $J(-\omega) = -J(\omega)$.

This QUAPI-discretized influence functional is nothing but the expression obtained by Feynman and Vernon\cite{256} where the forward and backward paths consist of constant $s$ segments, $s^+(t) = s^+_k, (k - \frac{1}{2})\Delta t < t < (k + \frac{1}{2})\Delta t$ (see Fig. 5). This particular stepwise change of the time-dependent force (which is different from that resulting from straightforward trapezoid-rule-type discretization of the action) arises from the exact treatment of the system dynamics. In the limit where the system coordinate is discretized using only two grid points, the influence functional described by Eq. (4.13) is similar to that employed in several previous studies of the spin-boson problem\cite{10,57}.

V. QUADRATURE AND MONTE CARLO PROCEDURES

The QUAPI discretization of the reduced density matrix in a dissipative harmonic bath involves $2N$ integrations. Finite temperature correlation functions are often expressed in terms of complex time propagators, whose oscillations are damped such that the integrand has significant amplitude only in certain localized regions of this $2N$-dimensional space. This feature allows, in some cases, use of Monte Carlo integration methods, but the convergence characteristics of such schemes depend critically on the smoothness of the integrand as well as on the dimensionality of the integral. In general, we have found Monte Carlo procedures to be successful and often the method of choice at strong solvent friction and short time; the details of the sampling procedure are described in part A of this section. All other sections of parameter space including long time, weak friction, and/or zero temperature calculations must be treated by efficient quadrature methods. System-specific quadratures that appear optimal for this purpose are discussed in the second part of this section.

A. Grid Monte Carlo sampling

Here we describe a Monte Carlo procedure for evaluating a finite-temperature symmetrized time correlation function $C(t)$ expressed in terms of the complex time, $t_c = t - i\hbar\beta/2$:

$$C(t) = Tr_{\text{bath}}[Ae^{iHtc\hbar/B}Be^{-iHtc\hbar}],$$

where $A$ and $B$ are quantum mechanical operators in the space of the system coordinate.

A Monte Carlo random walk is performed on a $2N$-dimensional grid (assuming that the total number of integration variables is $2N$). No stationary phase or other filtering is introduced because the reference propagators constructed according to Eq. (3.3) are not rapidly oscillatory functions.
For this purpose, the one-dimensional system propagator is calculated according to Eq. (3.3) and stored as a complex-valued matrix on a one-dimensional grid that spans the system coordinate; the value of the $s$ coordinate is incremented during each step of the random walk by randomly selected multiples of the grid spacing.

The (un-normalized) sampling function is chosen as the absolute value $f$ of the integrand:

$$C(t) = D_f \int_{-\infty}^{\infty} ds_0^+ \int_{-\infty}^{\infty} ds_1^+ \cdots \int_{-\infty}^{\infty} ds_0^- \int_{-\infty}^{\infty} ds_1^- \cdots [D_f^{-1} f(s_0^+, s_1^+, \ldots, s_0^-, s_1^-)] \times R(s_0^+, s_1^+, s_0^-, s_1^-),$$

where $R$ is the phase of the integrand and $D_f$ is the normalization integral, i.e., the integral of the sampling function $f$. The normalization integral is calculated by a separate Monte Carlo procedure using as the sampling function the integrand without the influence functional part:

$$D_f = D_g \int_{-\infty}^{\infty} ds_0^+ \int_{-\infty}^{\infty} ds_1^+ \cdots \int_{-\infty}^{\infty} ds_0^- \int_{-\infty}^{\infty} ds_1^- \cdots [D_g^{-1} g(s_0^+, s_1^+, \ldots, s_0^-, s_1^-)] \times \frac{f(s_0^+, s_1^+, \ldots, s_0^-, s_1^-)}{g(s_0^+, s_1^+, \ldots, s_0^-, s_1^-)},$$

where

$$g(s_0^+, s_1^+, \ldots, s_0^-, s_1^-) = \frac{f(s_0^+, s_1^+, \ldots, s_0^-, s_1^-)}{|I(s_0^+, s_1^+, \ldots, s_0^-, s_1^-)|}.$$  \hspace{1cm} (5.3)

Finally, the second normalization integral, $D_g$, involves only the absolute value of system propagator (as well as initial conditions); since the system propagator employed here is not a rapidly oscillatory function, $D_g$ can be computed iteratively by ordinary matrix multiplication.\(^{60}\)

### B. Discrete variable representation of the reduced dimension path integral

As argued in earlier sections, stochastic sampling methods become extremely inefficient if the integrand is oscillatory and one must resort to quadrature methods. It is essential that the number $M$ of quadrature points required for each integration variable be as small as possible. From our experience, Simpson’s rule and related integration methods require on the order of 30–100 points per dimension and therefore are not practical for evaluating the multidimensional path integral.

Clearly, a more economical discretization of the path integral would be in terms of bound basis functions. In particular, the adiabatic system propagator is diagonal in the basis of eigenstates of $H_0$, implying that no summations would be necessary in the absence of system–bath coupling (except at endpoints, e.g., for the trace operation) if such basis functions were used in place of coordinate states in Eq. (2.7). Furthermore, it is clear from experience with low-dimensional systems (and from the presence of Boltzmann factors that restrict the excitation of the bath) that a small number (typically 2–20) of such basis functions should provide an adequate representation of the coupled problem, including the influence functional. In the case of a double well potential, for example, even inclusion of only the two lowest energy states results in the spin-boson Hamiltonian, a prototype for dissipative tunneling characterized by a rich variety of intriguing effects.\(^{51}\) In spite of these advantages, though, the serious difficulty associated with use of the energy representation in the path integral is that potential coupling terms are not diagonal in the eigenstate basis, and thus use of the latter does not lead to well-behaved influence functionals.

Therefore, the question that arises is whether one can find a discrete basis that requires for completeness the same (small) number of terms as the eigenstate basis, but which also diagonal-
FIG. 6. DVR states obtained from the six lowest eigenstates of a symmetric double well potential. The three states corresponding to grid points located in the left well are shown. The remaining three DVR functions are mirror images of the ones shown in the figure. Adapted from Ref. 35.

izes the potential coupling. Such basis sets, known as discrete variable representations\textsuperscript{37–44} (DVRs), were introduced many years ago as convenient schemes for evaluating potential matrix elements.\textsuperscript{37,38} In the last decade, Light and co-workers extended the DVR ideas to develop powerful methods for treating vibrational eigenvalue problems.\textsuperscript{39,40} Uniform-grid discrete variable representations of the kinetic energy matrix and of the free particle propagator have been utilized recently in reactive scattering calculations.\textsuperscript{41} The DVR grids have also been combined with Fourier grids in iterative wave packet propagation algorithms.\textsuperscript{42,43} Topaler and Makri have recently proposed\textsuperscript{29} a system-specific (non-Gaussian in general) DVR quadrature, similar to the potential optimized DVR of Echave and Clary,\textsuperscript{44} in order to evaluate the multidimensional integral that appears in QUAPI expressions. Specifically, the DVR grid is constructed from the exact eigenstates of the adiabatic system Hamiltonian $H_0$.

The DVR basis is obtained by performing a unitary transformation on the basis \{$\Phi_i$\} of the $M$ lowest energy eigenstates of $H_0$:

$$|u_i\rangle = \sum_{i'=1}^{M} L_{ii'} |\Phi_{i'}\rangle,$$

where $L_{ii'}$ is the orthogonal transformation matrix. The DVR states \{|$u_i$\rangle\} are further specified by the requirement that the system position operator $s$ be diagonal in the new basis:

$$\langle u_i | s | u_{i'} \rangle = \delta_{ii'} \delta_{ii'}.$$

The DVR states |$u_i$\rangle are the discrete analog of the ordinary coordinate eigenstates, and the eigenvalues $\delta_i$, $i = 1, \ldots, M$ form the DVR grid. Their wave functions for a symmetric double well potential are displayed in Fig. 6 with $M=6$. The fact that the |$u_i$\rangle basis is nothing but a rotation of the eigenstate basis implies that the DVR grid will be quite sparse; yet, the potential operator is diagonal, leading to appealing path integral expressions.

Discretization of the path integral in the DVR basis and repeated use of the standard spectral expansion for the displaced bath time-evolution operator,

$$e^{-iH\langle Q_j, P_j; z \rangle} = \sum_{i=1}^{M} |u_i\rangle e^{-iH\langle Q_j, P_j; z \rangle} \langle u_i|,$$

leads\textsuperscript{29} to the following DVR representation of the QUAPI for the reduced density matrix:
\[
\rho_{\text{red}}(s^n, s'; t) = \sum_{k_0 = 1}^{M} \sum_{k_{N-1} = 1}^{M} \cdots \sum_{k_1 = 1}^{M} \sum_{k_0 = 1}^{M} \sum_{k_{N-1} = 1}^{M} \cdots \sum_{k_1 = 1}^{M} 
\times \langle s^n | e^{-iH_0 \Delta t/k} | u_{k_0}^+ \rangle \cdots \langle u_{k_1}^+ | e^{-iH_0 \Delta t/k} | u_{k_{N-1}}^+ \rangle \langle u_{k_{N-1}}^+ | \rho_s(0) | u_{k_0}^- \rangle 
\times \langle u_{k_0}^- | e^{iH_0 \Delta t/k} | u_{k_1}^- \rangle \cdots \langle u_{k_{N-1}}^- | e^{iH_0 \Delta t/k} | s' \rangle 
\times I(s_0^-, s_0^+, \cdots, s_{k_{N-1}}^-, s_{k_{N-1}}^+, \cdots, s_{k_1}^-, s_{k_1}^+; \Delta t). \tag{5.7}
\]

Equation (5.7) is the DVR analog of Eq. (4.11). The expression for the influence functional is unchanged but is now evaluated at the specific DVR points. The DVR representation of the one-dimensional propagator for the adiabatic system Hamiltonian is constructed numerically with the aid of the basis transformation relations, Eqs. (5.4) and (5.5). It is worth noting that the discrete variable representation of the QUAPI offers a simple way of reducing an extended double well potential to a two-level system continuously by decreasing the number of DVR states. More generally, the DVR evaluation of the path integral offers a unified approach to the quantum of extended coordinates and of discrete (lattice) systems in dissipative environments.

In the absence of system–bath coupling, the number \( M \) of terms required in Eq. (5.7) would be exactly equal to the minimum number \( m_{\text{max}} \) of terms required to represent the system propagator, Eq. (3.3). For nonzero coupling, though, the spectral expansion of Eq. (5.6) requires for completeness a certain number \( M \) of terms, which may be larger than \( m_{\text{max}} \). Our experience suggests that the number \( M \) of DVR points required for convergence is typically only slightly larger than the number \( m_{\text{max}} \) of states that are relevant to the dynamics of the one-dimensional system. For low-lying bound states or low-temperature processes, we have found that inclusion of only 4–10 DVR points usually leads to converged results. It is thus apparent that the introduction of system-specific DVR grids to the real time path integral can result in dramatic increase of efficiency compared to primitive quadrature schemes, particularly if the number of QUAPI integration variables is large.

Nevertheless, there are several situations where the basis of system eigenstates does not offer a compact representation of time-dependent quantities. Typical examples include motion in unbound potentials (which can be represented in terms of quasi-discrete states arising from diagonalization of the Hamiltonian in a large “box”), as well as vibrational relaxation of highly excited diatomic molecules in the condensed phase. In both of these situations the reduced density matrix is expected to visit a large number of reference system eigenstates during the course of time, and therefore the required DVR grid may be prohibitively large if constructed in terms of those states. It is therefore of practical interest to seek construction of DVRs for evaluation of the QUAPI that (at any given time) sample only a small subset of the relevant eigenstates. Sim and Makri have recently addressed this issue by proposing a novel time-dependent discrete variable representation (TD-DVR), which is constructed in terms of appropriate moving basis sets. In a scattering problem, for example, a single wave packet following the time-dependent Schrödinger equation for the reference Hamiltonian would provide an exact representation in the absence of system–bath coupling, and addition of a few orthogonal wave functions should lead to an adequate basis for evaluating the path integral with the influence functional. Such a time-dependent basis set samples at any instant in time only part of the available energy spectrum, selecting different parts of the spectrum at different times as required by the evolution of the zeroth-order solution. Within the path integral context, diagonalization of the system coordinate in such time-dependent basis sets has been shown to give rise to very powerful TD-DVR schemes where the DVR states now depend on the index \( \pm k \) labeling the time, \( t_k^\pm = \pm k \Delta t \), on the path integral contour.
VI. TENSOR PROPAGATOR FOR LONG TIME QUANTUM DYNAMICS

The QUAPI discretization of the system–bath path integral described in Sec. IV, combined with the advantages offered by relatively smooth reference propagators, expressed in optimal discrete variable representations, allows with modest numerical effort calculation of the dynamics for short to intermediate times (typically, a few periods of motion of the quantum particle). However, long time calculations are not feasible by multidimensional evaluation of the discretized path integral: both Monte Carlo methods (plagued by the sign problem) and multidimensional quadrature require effort that grows exponentially with the number of path integral variables; in turn, the latter is proportional to the number of time slices and therefore to the total propagation time. Makarov and Makri have recently addressed this problem \cite{32,33} by showing that the full 2N-dimensional integration can indeed be replaced by a series of low-dimensional operations. The starting point is the observation that dissipative environments characterized by broad spectra lead to influence functionals with nonlocal interactions of finite length. This feature allows evaluation of the path integral via iterative schemes which yield numerically exact results over arbitrarily long time intervals.

A. The dissipative influence functional

For concreteness, we focus on the case where the bath is initially at thermal equilibrium at temperature $1/k_B\beta$ so that its density matrix is $\rho_{\text{bath}}(0)=\exp(-\beta H_{\text{bath}})$ where

$$H_{\text{bath}} = \sum_j \frac{p_j^2}{2m_j} + \frac{1}{2} m_j \omega_j^2 Q_j^2.$$

In the continuous limit (i.e., for $\Delta t \to 0$, $N \to \infty$) the influence functional has been calculated by Feynman and Vernon: \cite{56}

$$I = \exp \left[ -\frac{1}{\hbar} \int_0^t \int_0^{t'} dt'' \left[ \frac{c_j^2}{2m_j\omega_j} \left( s^+(t')^2 - s^-(t')^2 \right) \right] \right].$$

(6.1)

where $\alpha(t)$ is the bath response function

$$\alpha(t) = \sum_j \frac{c_j^2}{2m_j\omega_j} \left[ \coth \left( \frac{\hbar\omega_j\beta}{2} \right) \cos(\omega_j t) - i \sin(\omega_j t) \right].$$

(6.2)

which can be expressed in terms of the spectral density as

$$\alpha(t) = \frac{1}{\pi} \int_0^\infty \! d\omega J(\omega) \left[ \coth \left( \frac{\hbar\omega\beta}{2} \right) \cos(\omega t) - i \sin(\omega t) \right].$$

(6.3)

The last term in Eq. (6.1) arises from the counterterms which are grouped with the bath Hamiltonian in the quasi-adiabatic splitting of the propagator.

For ohmic spectral density, $J(\omega) = \gamma \omega$, the dynamics in the classical limit is described by the Langevin equation [cf. Eq. (4.2)] with $\chi(t-t') \approx \delta(t-t')$ which is Markovian. Indeed, Caldeira and Leggett have shown \cite{59} that in the limit $\beta \to 0$ the real part of the kernel $\alpha(t)$ behaves as the delta function $\delta(t)$, while its imaginary part behaves as $\delta'(t)$; this means that the double integral in Eq. (6.1) becomes a single integral and the Markovian behavior is recovered at infinite temperature. In the language of discretized path integrals, this fact implies that Eq. (4.11) [or its DVR...
FIG. 7. Real (solid line) and imaginary (dashed line) parts of the bath response function, Eq. (6.3), for the spectral density $J(\omega) = \gamma \omega^2 \exp(-\omega \omega_c)$: (a) $p = 1$, $\hbar \beta \omega_c = 0.2$; (b) $p = 1$, $\hbar \beta \omega_c = \infty$; (c) $p = 3$, $\hbar \beta \omega_c = \infty$. Adapted from Ref. 33(a).
analog, Eq. (5.7)) can be evaluated in this case using the ordinary matrix multiplication scheme,\(^{60}\) common in low-dimensional problems. In the general case, though, \(a(t)\) is not a delta function and the resulting dynamics are not Markovian.

Motivated by the Markovian nature of the dynamics in the classical limit, Makarov and Makri examined\(^3\) the behavior of the nonlocal kernel for finite temperatures and a more general form of the spectral density, \(J(\omega) = \gamma \omega^p \exp(-\alpha \omega^2), p \geq 1\). For \(p = 1\) and infinitely high temperature \((\beta = 0)\) the real part of the kernel takes a Lorentzian form with width proportional to \(\omega_\gamma^{-1}\) [and thus reduces to \(\delta(t)\) in the limit \(\omega_\gamma \to \infty\)]. For high but finite temperature, Taylor expansion in \(\hbar \omega \beta\) shows that, for any value of \(p \geq 1\), \(a(t)\) is comprised of multiple terms which have the form of powers of Lorentzians; their sum results again in a sharply peaked kernel, though broader than the one in the \(\beta = 0, p = 1\) case. A similar analysis leads to analogous observations for zero or low temperature. Similar behavior is observed by numerical calculation of the bath response function at intermediate temperatures. Therefore it is seen that the nonlocal interactions that arise from the kernel \(a(t' - t'')\) in Eq. (6.1) have finite range independent of the coupling strength \(\gamma\) at all temperatures if the environment has a smooth continuous spectrum, and thus the dynamics is in general non-Markovian though of finite memory. A graphical illustration of the kernel is given in Fig. 7 for different temperatures and spectral densities. One sees that even at zero temperature the width of the memory kernel remains finite.

The finite span of nonlocal couplings in the dissipative influence functional is a consequence of destructive phase interference among a continuum of frequencies in broad spectra characteristic of macroscopic environments. This results largely in disruption of phase coherence and loss of memory, implying that the long-time reduced dimension path integral can be broken into multiple integrals of finite dimension.

**B. Markovian dynamics for a reduced density tensor**

In the discretized form, the observations of the last subsection concerning the short-range nonlocality of the influence functional imply that the magnitude of the coefficients \(\eta_{kk'}\) should drop off rapidly as \(\Delta k\) increases. This fact suggests neglecting in Eq. (4.13) those \(\eta_{kk'}\) for which \(|k - k'|\) is greater than a certain value, \(\Delta k_{\text{max}}\), which is roughly equal to the number of time steps required to span the width of the kernel \(a(t - t')\). If the system coordinate \(s\) can take only two values, the problem described by Eqs. (5.7) and (4.13) resembles an Ising model that includes non-nearest-neighbor interactions (though of finite length) and should therefore be treatable by transfer matrix techniques. The remainder of this subsection describes the basic idea of an iterative procedure for evaluation of the real time path integral.

Since the QUAPI discretization permits use of large time steps, \(\Delta k_{\text{max}}\) is generally small. If \(\Delta k_{\text{max}} \leq 1\), the resulting path integral can be evaluated using the standard matrix multiplication procedure [cf. Eqs. (6.6) and (6.9) below], where we refer to the grid points corresponding to pairs \((s_k^+ , s_k^-)\) collectively as an \(M^2\)-dimensional vector in order to conform with the conventional language used in wave function propagation. In other words, the dynamics in the case of short-range nonlocality is still Markovian, although dissipative effects are taken into account. If the nonlocality extends over longer time, terms with \(\Delta k_{\text{max}} > 1\) will have to be included in order to obtain accurate results. However, inclusion of such terms is not possible within the matrix multiplication scheme. The key idea of Ref. 32 was that after discarding the negligible “long distance interactions” (with \(|k - k'| > \Delta k_{\text{max}}\)), the resulting path integral can be evaluated iteratively by multiplication of a tensor of rank \(2\Delta k_{\text{max}}\). In other words, there exists an (augmented) reduced density tensor of rank \(\Delta k_{\text{max}}\) that obeys Markovian dynamics. To illustrate this, we rewrite the influence functional, Eq. (4.13), as a product of terms corresponding to different \(\Delta k\):

\[
I = \prod_{k=0}^{N} I_0(s_k^+ ) \prod_{k=0}^{N-1} I_{k}(s_k^+, s_{k+1}^+) \cdots \prod_{k=0}^{N-\Delta k} I_{k}(s_k^+, s_{k+\Delta k}^+) \cdots \prod_{k=0}^{N-\Delta k_{\text{max}}} I_{\Delta k_{\text{max}}}(s_k^+, s_{k+\Delta k_{\text{max}}}^+),
\]

where

\[
I_0(s_k) = \exp \left[ -\frac{1}{\hbar} \left( s_k^+ s_k^- - s_k^- s_k^+ \right) \left( \eta_{kk} s_k^+ s_k^- - \eta_{kk} s_k^- s_k^+ \right) \right],
\]

\[
I_{\Delta k}(s_k^+, s_{k+\Delta k}^+) = \exp \left[ -\frac{1}{\hbar} \left( s_{k+\Delta k}^+ s_{k+\Delta k}^- - s_{k+\Delta k}^- s_{k+\Delta k}^+ \right) \left( \eta_{k+\Delta k,k} s_{k+\Delta k}^+ s_{k+\Delta k}^- - \eta_{k+\Delta k,k} s_{k+\Delta k}^- s_{k+\Delta k}^+ \right) \right], \quad \Delta k > 0.
\]

Note that since $\eta_{k,k+\Delta k}$ does not depend on $k$ for $0 < k < N - \Delta k$, in this range of indices the quantities $I_0$ and $I_{\Delta k}$ may be thought of as functions of one and two variables, respectively, independent of $k$.

In the absence of the bath, the system density matrix $\rho_{\text{sys}}(s_k^+, s_k^-; t) = \rho_{\text{sys}}(s_k^+; t)$ can be propagated through time $\Delta t$ by the matrix-vector multiplication

\[
\rho_{\text{sys}}(s_{k+1}^+, s_{k+1}^-; t+\Delta t) = \int ds_k^+ K(s_k^+, s_{k+1}^+) \rho_{\text{sys}}(s_k^+; t),
\]

where

\[
K(s_k^+, s_{k+1}^-) = \langle s_{k+1}^+ | e^{-iH_0 \Delta t/\hbar} | s_k^+ \rangle \langle s_k^- | e^{iH_0 \Delta t/\hbar} | s_{k+1}^- \rangle
\]

is the propagator matrix for the bare system.

In the case $\Delta k_{\text{max}} = 1$, the influence functional amounts to a modification of this expression; specifically,

\[
\rho_{\text{sys}}(s_N^+, N\Delta t) = A^{(1)}(s_N^+, N\Delta t) I_0(s_N^-),
\]

where the vector $A^{(1)}$ is propagated iteratively according to

\[
A^{(1)}(s_{k+1}^+, (k+1)\Delta t) = \int ds_k^- T^{(2)}(s_k^+, s_{k+1}^-) A^{(1)}(s_k^+, k\Delta t).
\]

Here $T^{(2)}$ is a propagator matrix,

\[
T^{(2)}(s_k^+, s_{k+1}^-) = K(s_k^+, s_{k+1}^-) I_0(s_k^-) I_1(s_k^+, s_{k+1}^-),
\]

and the initial condition is

\[
A^{(1)}(s_0^+, 0) = \langle s_0^+ | \rho_s(0) | s_0^- \rangle.
\]

If $N$ iterations are performed this way, the resulting density matrix is exactly the result obtained from Eq. (4.13) where all $\eta_{k,k'}$ other than $\eta_{kk}$ and $\eta_{k,k \pm 1}$ are neglected. Equation (6.9) is again in the form of matrix multiplication, but the propagator matrix is renormalized by the diagonal and nearest-neighbor couplings of the influence functional. These result in loss of unitarity and introduce damping to the dynamics of the system due to its interaction with the bath.

The iterative scheme described above is easily generalized to arbitrary values of $\Delta k_{\text{max}}$ at which long-distance interactions are cut off. We define a tensor $T$ of rank $2\Delta k_{\text{max}}$ as
\[ T^{(2\Delta k_{\text{max}})}(s_k^+, s_{k+1}^+, \ldots, s_{k+2\Delta k_{\text{max}}-1}^+) = \prod_{n=k}^{k+\Delta k_{\text{max}}-1} I_0(s_n^+) I_1(s_n^+, s_{n+1}^+) I_2(s_n^+, s_{n+2}^+) \cdots I_{\Delta k_{\text{max}}}(s_n^+, s_{n+\Delta k_{\text{max}}}^+) K(s_n^+, s_{n+1}^+). \]  

(6.12)

We also define the augmented reduced density tensor \( A^{(\Delta k_{\text{max}})} \) with the following initial condition.\(^{33(a)}\)

\[ A^{(\Delta k_{\text{max}})}(s_0^+, s_1^+, \ldots, s_{\Delta k_{\text{max}}-1}^+; 0) = \langle s_0^+ | \rho_i(0) | s_0^- \rangle. \]  

(6.13)

In analogy with the common matrix–vector multiplication, Eq. (6.9), the evolution of the reduced density matrix can be obtained via multiplication of the rank-2\(\Delta k_{\text{max}}\) tensor propagator \( T \) times the rank-\(\Delta k_{\text{max}}\) tensor \( A \). Specifically, \( A^{(\Delta k_{\text{max}})} \) is propagated through a time increment \( \Delta k_{\text{max}} \Delta t \) according to the tensor multiplication

\[ A^{(\Delta k_{\text{max}})}(s_k^+, s_{k+\Delta k_{\text{max}}}^+, \ldots, s_{k+2\Delta k_{\text{max}}-1}^+; (k+\Delta k_{\text{max}}) \Delta t) \]

\[ = \int ds_k^+ \cdots \int ds_{k+\Delta k_{\text{max}}-1}^+ T^{(2\Delta k_{\text{max}})}(s_k^+, s_{k+1}^+, \ldots, s_{k+2\Delta k_{\text{max}}-1}^+) \times A^{(\Delta k_{\text{max}})}(s_k^+, \ldots, s_{k+\Delta k_{\text{max}}-1}^+; k \Delta t). \]  

(6.14)

The influence functional interactions included in the propagator tensor \( T \) are shown in Fig. 8 for \( \Delta k_{\text{max}} = 3 \). Finally, the reduced density matrix at time \( t = N\Delta t \) is given by a projection of the tensor \( A \):

\[ \rho_{\text{red}}(s_N^+; N\Delta t) = A^{(\Delta k_{\text{max}})}(s_N^+, s_{N+1}^+, \ldots, s_{N+\Delta k_{\text{max}}-1}^+ = 0; N\Delta t) I_0(s_N^+). \]  

(6.15)

It should be noted that the tensors entering into this equation can be "unfolded," such that \( A^{(\Delta k_{\text{max}})} \) becomes a vector of dimension \((M^2)^{\Delta k_{\text{max}}}\) and \( T^{(2\Delta k_{\text{max}})} \) becomes a matrix of dimension \((M^2)^{2\Delta k_{\text{max}}}\). Thus, Eq. (6.14) can be viewed as an ordinary linear mapping of the matrix–vector type:

\[ A^{(\Delta k_{\text{max}})}(t + \Delta k_{\text{max}} \Delta t) = T^{(2\Delta k_{\text{max}})} \cdot A^{(\Delta k_{\text{max}})}(t). \]  

(6.16)
It is well known that the eigenvalues and (right) eigenvectors of a linear map contain useful information about the dynamical system it describes. After sufficient time, a system in contact with an ordinary heat bath is expected to reach thermal equilibrium. This situation corresponds to a fixed point of the map:

$$A^{(\Delta k_{\text{max}})}(\infty) = T^{(2\Delta k_{\text{max}})} \cdot A^{(\Delta k_{\text{max}})}(\infty).$$  \hspace{1cm} (6.17)

If the eigenvalues of the propagator tensor are written as

$$\lambda_i = \exp(-\Gamma_i \Delta k_{\text{max}} \Delta t),$$  \hspace{1cm} (6.18)

the eigenvalue with the smallest nonzero $\Gamma_i$ will yield the rate of approach to thermal equilibrium.\(^{33(a)}\) Other real eigenvalues are associated with faster relaxation processes, while complex eigenvalues correspond to coherences characterized by oscillation frequencies $\text{Im} \Gamma_i$ and damping rates $\text{Re} \Gamma_i$.

Although the mapping form or Eq. (6.16) is useful for the above eigenvalue analysis, it is desirable from a numerical point of view to express the tensor multiplication scheme in terms of objects of the lowest possible rank. Makri and Makarov have pointed out\(^{33(b)}\) that the rank-2 $\Delta k_{\text{max}}$ propagator tensor $T$ factorizes further into $\Delta k_{\text{max}}$ tensors of rank $\Delta k_{\text{max}} + 1$:

$$T^{(2\Delta k_{\text{max}})}(s_{k}^{\pm}, s_{k+1}^{\pm}, \ldots, s_{k+2\Delta k_{\text{max}}-1}^{\pm}) = \prod_{n=k}^{k+\Delta k_{\text{max}}-1} A^{(\Delta k_{\text{max}}+1)}(s_{n}^{\pm}, s_{n+\Delta k_{\text{max}}}^{\pm}),$$  \hspace{1cm} (6.19)

where

$$A^{(\Delta k_{\text{max}}+1)}(s_{n}^{\pm}, \ldots, s_{n+\Delta k_{\text{max}}}^{\pm}) = K(s_{k}^{\pm}, s_{k+1}^{\pm}) I_0(s_{n}^{\pm}) I_1(s_{n}^{\pm}, s_{n+1}^{\pm}) I_2(s_{n}^{\pm}, s_{n+2}^{\pm}) \cdots I_{\Delta k_{\text{max}}}(s_{n}^{\pm}, s_{n+\Delta k_{\text{max}}}^{\pm}).$$  \hspace{1cm} (6.20)

As illustrated by the diagram of Fig. 9, this tensor includes all interactions between the point $s_{k}^{\pm}$ and later points $s_{k+\Delta k_{\text{max}}}$, $\Delta k \leq \Delta k_{\text{max}}$. Using this lower-dimensional propagator tensor, one can propagate the reduced density tensor $A^{(\Delta k_{\text{max}})}$ through $\Delta t$ via a much more efficient procedure:

$$A^{(\Delta k_{\text{max}})}(s_{k+1}^{\pm}, \ldots, s_{k+\Delta k_{\text{max}}}^{\pm}; (k+1)\Delta t) = \int d s_{k}^{\pm} A^{(\Delta k_{\text{max}}+1)}(s_{k}^{\pm}, \ldots, s_{k+\Delta k_{\text{max}}}^{\pm}) \times A^{(\Delta k_{\text{max}})}(s_{k}^{\pm}, \ldots, s_{k+\Delta k_{\text{max}}-1}^{\pm}; k\Delta t).$$  \hspace{1cm} (6.21)

This scheme requires only $M^2$ operations per propagation step. Since the dimension of the reduced density tensor which is iterated is $(M^2)^{\Delta k_{\text{max}}} = L$, the numerical effort (storage as well as number of operations) scales as $L^{1+1/\Delta k_{\text{max}}}$. Therefore for $\Delta k_{\text{max}} \gg 1$ this scaling is almost linear with $L$.
FIG. 10. Time evolution of $\langle \sigma_z (t) \rangle$ for a symmetric TLS coupled to an ohmic bath at zero temperature for $\omega_c=8\Omega$, $\xi=0.25$. Solid line: exact numerical path integral results. Dashed line: noninteracting blip approximation. Adapted from Ref. 34.

VII. APPLICATIONS TO MODEL PROBLEMS IN CONDENSED MATTER PHYSICS

A. Spin-boson dynamics

The simplest model of tunneling in dissipative media is that of a two-level system (TLS) coupled linearly to a bath of harmonic oscillators described by the Hamiltonian

$$H = \hbar \Omega \sigma_x + \hbar \epsilon \sigma_z + \sum_j \left[ \frac{p_j^2}{2m_j} + \frac{1}{2} m_j\omega_j^2 \left( Q_j - \frac{c_j \sigma_z}{m_j\omega_j^2} \right)^2 \right],$$  

(7.1)

where $\sigma_x$ and $\sigma_z$ are Pauli matrices, $2\hbar \Omega$ is the tunneling splitting, and $\epsilon$ is the asymmetry parameter. This so-called spin-boson Hamiltonian provides a model of relevance to diverse condensed phase processes such as nonadiabatic electron transfer, proton transfer (at very low temperatures), and macroscopic quantum coherence in SQUIDS. Numerous studies of the spin-boson problem have revealed a very rich dynamical behavior. Among various theoretical treatments, the noninteracting blip approximation ($\text{NIBA}$) has demonstrated that, depending on the damping strength and the temperature, the system shows a plethora of evolution patterns ranging from coherent oscillations to incoherent relaxation and even complete localization.

Makarov and Makri have applied the iterative tensor multiplication procedure to study the time evolution of symmetric and asymmetric spin-boson systems over a variety of conditions. These results provide for the first time exact numerical results over many tunneling periods in regions of parameter space where Monte Carlo methods fail to converge, while the NIBA is incorrect.

The zero-temperature time evolution of the average position, $\langle \sigma_z (t) \rangle$, is shown in Figs. 10, 11 and 12 for symmetric and asymmetric two-level systems coupled to a bath of ohmic spectral density,

$$J(\omega) = \gamma \omega \exp(-\omega/\omega_c)$$  

(7.2)

at various values of the Kondo parameter, $\xi=2\gamma/\pi\hbar$. In the symmetric case, the NIBA is generally found to provide a very good approximation to the spin-boson dynamics; representative results are displayed in Fig. 10 for $\xi=0.25$ and $\omega_c=8\Omega$, while the agreement is even better for very small or for large values of the Kondo parameter.
FIG. 11. Time evolution of $\langle \sigma_z(t) \rangle$ for an asymmetric TLS with $\varepsilon=2\Omega$ coupled to an ohmic bath with $\omega_c=7.5\Omega$ for $\xi=0.04, 0.16, 0.25, 0.36,$ and $0.49$ (solid, dashed, dotted and chain-dotted lines and filled circles, respectively). The temperature is $k_B T=0.2\Delta\Omega$. The equilibrium values predicted by the noninteracting blip approximations as well as one-dimensional theory are shown by arrows on the right. Adapted from Ref. 34.

In the asymmetric case, the NIBA provides a good approximation to the spin-boson dynamics for $\varepsilon \gg \Omega$ but fails to predict the correct long time behavior if the bias is on the order of the tunneling splitting, $\varepsilon \approx \Omega$. In fact, the NIBA predicts complete localization of the particle at zero temperature in the lower energy state. The true state of thermodynamic equilibrium, though, is for small $\varepsilon$ a linear combination of left- and right-localized states. The numerical path integral results shown in Figs. 11 and 12 demonstrate that the thermodynamic limit is indeed approached at long time, and $\langle \sigma_z(\infty) \rangle$ varies as the Kondo parameter is increased between the value corresponding to the isolated TLS and that predicted by NIBA.

The rate constant for the spin-boson problem in the parameter regime where relaxation is incoherent has been calculated by Topaler and Makri.\textsuperscript{35} Results are displayed in Fig. 13 as a

FIG. 12. Time evolution of $\langle \sigma_z(t) \rangle$ for an asymmetric TLS with $\varepsilon=0.5\Omega$ coupled to an ohmic bath with $\omega_c=7.5\Omega$ for $\xi=0.04, 0.16, 0.25, 0.36,$ and $0.49$ (solid, dashed, dotted and chain-dotted lines and filled circles, respectively). The temperature is $k_B T=0.2\Delta\Omega$. The thermodynamic equilibrium values obtained from imaginary time path integral calculations are shown by arrows on the right. Adapted from Ref. 34.
FIG. 13. Rate constant for a spin-boson Hamiltonian as a function of inverse temperature for several values of the Kondo parameter $\xi$. Numerical path integral results are shown by markers. The low-temperature NIBA results are indicated by thick lines, while the thin lines show golden rule estimates. Solid line and circles: $\xi=0.1$. Dashed line and squares: $\xi=0.5$. Dash-dotted line and triangles: $\xi=1.5$. Adapted from Ref. 35.

Function of inverse temperature for various values of the Kondo parameter. The low-temperature NIBA results are in very good agreement with the path integral results, while at high temperature the rate agrees well with the golden rule prediction.

**B. Rate constant for a symmetric double well coupled to a dissipative bath**

Chemical reactions in the condensed phase can often be described as barrier crossing events between two locally stable configurations. The simplest model involves a double minimum potential coupled to a dissipative heat bath. The double well problem, which reduces practically to a TLS at low temperature, combines the dissipative tunneling features of the latter with phenomena associated with bound motion in the reactant (or product) well. Such effects result generally in a nonmonotonic dependence of the reaction rate on friction, known as Kramers turnover.\(^{61}\) Extensive theoretical work has been devoted to the quantum rate problem, in recent years, aiming at an improved understanding of barrier crossing dynamics.\(^{62}\)

Using the QUAPI methodology, Topaler and Makri have recently reported\(^{35}\) the first exact quantum calculations for the canonical rate constant in a symmetric double well potential coupled to an ohmic bath. The parameters were chosen to mimic hydrogen transfer reactions in solution or

FIG. 14. Quantum transmission coefficient for a symmetric double well potential as a function of damping strength at a temperature above crossover. $\omega_0$ is the frequency at the top of the potential barrier. Numerical path integral results are shown by filled circles. The Wolynes transmission factor (Ref. 63) (quantum Grote–Hynes theory) is shown by the dotted line. The solid and dashed lines correspond to the quantum turnover theories due to Hänggi, Pollak, and Grabert (Ref. 65), and to Rips and Pollak (Ref. 66), respectively. The triangles correspond to results obtained with the centroid-based quantum transition state theory (Ref. 64). Adapted from Ref. 35.
FIG. 15. Logarithm of the quantum transmission coefficient for a symmetric double well as a function of damping strength at a temperature around crossover. $\omega_0$ is the barrier frequency. Values of $\gamma/m\omega_0$ greater than approximately 0.6 correspond to activated dynamics, while tunneling effects become dominant at smaller values of the friction. Numerical path integral results are shown by filled circles. The triangles correspond to results obtained with the centroid-based quantum transition state theory (Ref. 64). The solid and dashed lines correspond to approximate evaluation of instanton expressions (Refs. 68–70), while the dotted line indicates the results of quantum Grote–Hynes theory (Ref. 63). Adapted from Ref. 35.

in solids. These results provided an accurate picture of the dynamics in most parameter regimes of chemical interest, including low-temperature deep tunneling kinetics that are not described successfully by current analytical theories. Some of these results are outlined below.

The rate exhibits the standard Arrhenius (exponential) temperature dependence at high temperature, crossing over to the (nearly temperature-independent) tunneling regime as $T$ is lowered below a characteristic value $T_0$. Figures 14 and 15 show the quantum transmission factor, i.e., the ratio of the quantum rate constant divided by the classical transition state theory result, as a function of the friction parameter $\gamma$ at two different temperatures. Above the crossover temperature, where thermal activation prevails, the quantum rate constant exhibits a Kramers turnover analogous to the classical behavior with significant quantum corrections (see Fig. 14). This situation is described very well by approximate theories: the large friction (spatial diffusion) path integral results are in excellent agreement with the predictions of quantum transition state approaches, while quantum turnover theories successfully reproduce the turnover. By contrast, the low-temperature numerical results are not predicted accurately by analytic or numerical approximations, as can be seen from Fig. 15. An intriguing feature displayed in this figure is the positive enhancement of the quantum rate constant compared to the prediction of the centroid-based quantum mechanical transition state theory in the deep tunneling regime. This dynamical

FIG. 16. The integrated quantum reactive flux crossing the barrier of the symmetric double well potential whose rate constant is shown in Figs. 14 and 15 as a function of time for the case of low temperature (below crossover) and weak friction. The long-time plateau of this curve yields the quantum transmission coefficient. $\omega_0$ is the vibrational frequency at the potential minimum. Adapted from Ref. 35.
effect, which has no classical analog, has been attributed\textsuperscript{25,67} to quantum vibrational coherences in the potential wells. This coherence effect is illustrated in Fig. 16, which shows the time dependence of the quantum reactive flux that crosses the potential barrier. An upward step structure is observed at time increments equal to the vibrational period in the potential well. The increase of the reactive flux beyond the first step is responsible for the significant enhancement of the rate above the quantum transition state theory value.

VIII. CONCLUDING REMARKS

The numerical path integral methodology reviewed in this article provides the first feasible numerical approach to the dynamics of quantum particles in dissipative environments. Unlike previous treatments, this methodology involves no uncontrolled approximation, and yet converges with modest amounts of numerical effort up to extremely long time. There are three key features responsible for the feasibility of this approach. First, the construction of accurate and smooth propagators based on improved reference systems allows large time steps in the path integral. Second, the various integrals are treated in the bulk of parameter space by efficient quadratures, obviating the need for Monte Carlo sampling which is plagued by the phase oscillation problem. And third, the iterative evaluation of the path integral, which is possible because of the finite memory of the influence functional, allows calculation of the dynamics over arbitrary time lengths.

Straightforward application of these techniques allows simulation of numerous quantum effects in condensed matter physics and chemistry. Apart from such applications, an important goal involves extension of these ideas to treat anharmonic interactions encountered in the liquid phase when the linear response approximation is not accurate. Although some progress has been made in this direction,\textsuperscript{25,30} long-time path integral calculations in anharmonic fluids remain out of reach. Such problems will undoubtedly require significant attention in the future.

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