

Iterative path integral formulation of equilibrium correlation functions for quantum dissipative systems

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We present an iterative path integral algorithm for computing multitime correlation functions of a quantum system coupled to a dissipative bath of harmonic oscillators. By splitting the Boltzmann operator into two parts and reordering the propagators in the expression for canonical correlation functions, we are able to transform the evolution time contour into a symmetric one so that a forward propagation and a backward one are specified. Because the memory induced by the bath through the Feynman–Vernon influence functional decays rapidly in the complex time plane, long-time correlations are negligible. Taking advantage of this fact, we show that the correlation function can be obtained via an iterative procedure. The method is used to calculate three-time correlation functions of a dissipative two-level system. © 2002 American Institute of Physics. [DOI: [10.1063/1.1423936]]

I. INTRODUCTION

Understanding the quantum dynamics of large molecular systems is one of the central problems of modern physical chemistry. Due to advances in laser techniques that employ pulses with varying temporal resolution and intensity, rich spectroscopic results are now available for molecules in the gas phase, on surfaces, or in solution. Studies of the dynamics of simple models often shed light on the main features of the spectra and can offer valuable insight. However, even with simple models of dissipative systems, following the quantum dynamics presents a challenging problem. Extracting dynamical information from spectroscopic data on complex systems is a nontrivial and often impossible task. Thus, developing methods that are capable of following the quantum evolution of systems in condensed phase environments is a long-standing goal, and progress in this direction will impact practically all areas of physical chemistry.

In a complex structure often only a small number of degrees of freedom, usually referred to as the “system,” are of direct physical significance and are probed in experiments. The other degrees of freedom, which form the so-called “bath,” can exchange energy with the system and alter its phase, thus affecting its dynamics. Therefore, so long as the system of study is not isolated, following its quantum dynamics requires an accurate solution of the time-dependent Schrödinger equation, which is a formidable many-body problem. With the most powerful computers available at present one can obtain numerically exact solutions only for systems of a few atoms. Since condensed phase or biological

environments consist of many degrees of freedom, direct solution of the Schrödinger equation is not possible. The easiest strategy for tackling the quantum dynamics of condensed phase systems is to replace the actual environment by a simpler one. The obvious choice is offered by baths composed of harmonic degrees of freedom. If the spectral density of the latter is a continuous function, such baths can successfully capture the common features of dissipative dynamics.^{1–3} However, following the quantum dynamics is not an easy task even in the case of a harmonic bath, and numerically exact methods for evaluating the system’s reduced density matrix have become available only during the last few years. Another strategy is to develop approximate methods for simulating the dynamics of the system plus environment as a whole. A host of approximate techniques have been suggested and applied to the dynamics of large systems, which employ quantum-classical, variational, perturbation theoretic or semiclassical tools.

A generic bath that comprises an infinite number of harmonic oscillators can be integrated out analytically within the path integral formulation of quantum mechanics^{4,5} to yield an influence functional of the Feynman–Vernon type.⁶ If the system and bath are initially uncorrelated the initial density operator factorizes and the Feynman paths run along the real time contour. In this case the decoherence effects of dissipative media restrict the span of two-time interactions, allowing evaluation of the path sum via an iterative procedure.^{7–14} On the other hand, when the whole system+bath density starts out at equilibrium, a segment of the quantum paths lies along the imaginary time axis.¹⁵ The influence functional method can also be used in conjunction with complex time propagators that appear in symmetrized correlation functions. By dividing the evolution in imaginary time into two identical events, we recently found¹⁶ that the correlation in each individual event decays rapidly as the

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time difference gets larger. This observation allowed us to specify the two evolutions as a forward one and a backward one, respectively. As a consequence, one can evaluate correlation functions of this type by an iterative method.¹⁶

In the present paper we focus on the Kubo (unsymmetrized) form of equilibrium correlation functions.¹⁷ By splitting the Boltzmann operator into two imaginary time propagators and rearranging their order, a new “symmetrized” evolution (first along the imaginary axis and then along the real axis) is obtained. After the system loses its memory for the imaginary past, the influence functional in real time exhibits time-translational invariance, which leads to an efficient iterative procedure evaluating the path integral.

Throughout this paper we focus on a system coupled to a harmonic bath via the Hamiltonian

$$H = H_{\text{sys}}(q, p) + H_{\text{bath}}(\mathbf{x}, \mathbf{p}) + H_{\text{int}}(\mathbf{q}, \mathbf{x}), \quad (1.1)$$

where the first term is the Hamiltonian of the probed system with coordinate q and conjugate momentum p , the second is the Hamiltonian describing the bath oscillators whose coordinates and momenta x_i, p_i are denoted collectively by the vectors \mathbf{x}, \mathbf{p} and the third term describes the system–bath coupling. We assume that the bath is harmonic and that the system–bath coupling is linear in the coordinates of the bath, i.e.,

$$H_{\text{env}} \equiv H_{\text{bath}} + H_{\text{int}} = \sum_j \left[\frac{p_j^2}{2m_j} + \frac{1}{2} m_j \omega_j^2 \left(x_j - \frac{c_j f(q)}{m_j \omega_j^2} \right)^2 \right], \quad (1.2)$$

where $f(q)$ is a function of arbitrary form.

Section II describes the theoretical framework for a general two-time correlation function. The latter is expressed in terms of sequential propagation along two symmetrically related time contours and its path integral representation is obtained. In Sec. III we derive the discretized path integral expression of the correlation function and develop an iterative procedure for its evaluation. The methodology is extended to higher order correlation functions relevant to nonlinear spectroscopy in Sec. IV. Section V applies the iterative method to calculate three-time correlation functions for a dissipative two-level system, and Sec. VI concludes with a summary and a brief discussion.

II. PATH INTEGRAL REPRESENTATION OF TWO-TIME CORRELATION FUNCTIONS

We first consider the two-time correlation function defined as

$$C_{AB}(t) = \frac{1}{Z} \text{Tr} \{ e^{-\beta H} A e^{iHt/\hbar} B e^{-iHt/\hbar} \}, \quad (2.1)$$

where $\beta = (k_B T)^{-1}$ is the reciprocal temperature T scaled by the Boltzmann constant k_B , Z is the partition function at the given temperature, and A, B are the operators of the observed system. Using the permutation invariance of the trace, we can rewrite the correlation function as

$$\begin{aligned} C_{AB}(t) &= \frac{1}{Z} \text{Tr} \{ e^{-\beta H/2} A e^{iHt/\hbar} B e^{-iHt/\hbar} e^{-\beta H/2} \} \\ &= \frac{1}{Z} \text{Tr}_{\text{sys}} O_{AB}, \end{aligned} \quad (2.2)$$

where Tr_{sys} denotes the quantum trace with respect to the system only, and

$$\begin{aligned} \langle q_0^- | O_{AB} | q_0^+ \rangle &\equiv O_{AB}(q_0^-, q_0^+) \\ &= \langle q_0^- | \text{Tr}_{\text{bath}} \\ &\quad \times (e^{-\beta H/2} A e^{iHt/\hbar} B e^{-iHt/\hbar} e^{-\beta H/2}) | q_0^+ \rangle. \end{aligned} \quad (2.3)$$

Inserting complete sets of states repeatedly, the last expression becomes

$$\begin{aligned} O_{AB}(q_0^-, q_0^+) &= \int dq_{\text{re}} \int dq_{\text{im}}^+ \int dq_{\text{im}}^- \text{Tr}_{\text{bath}} \\ &\quad \times \langle q_0^- | e^{-\beta H/2} | q_{\text{im}}^- \rangle \langle q_{\text{im}}^- | A e^{iHt/\hbar} | q_{\text{re}} \rangle \\ &\quad \times \langle q_{\text{re}} | B e^{-iHt/\hbar} | q_{\text{im}}^+ \rangle \langle q_{\text{im}}^+ | e^{-\beta H/2} | q_0^+ \rangle \end{aligned} \quad (2.4)$$

which can also be written as

$$\begin{aligned} O_{AB}(q_0^-, q_0^+) &= \int dq_{\text{re}} \int dq_{\text{im}}^+ \int dq_{\text{im}}^- \int dq_A \int dq_B \\ &\quad \times \text{Tr}_{\text{bath}} \langle q_0^- | e^{-\beta H/2} | q_{\text{im}}^- \rangle \langle q_{\text{im}}^- | A | q_A \rangle \\ &\quad \times \langle q_A | e^{iHt/\hbar} | q_{\text{re}} \rangle \langle q_{\text{re}} | B | q_B \rangle \langle q_B | e^{-iHt/\hbar} | q_{\text{im}}^+ \rangle \\ &\quad \times \langle q_{\text{im}}^+ | e^{-\beta H/2} | q_0^+ \rangle. \end{aligned} \quad (2.5)$$

Its path integral representation^{4–6,15,18,19} is

$$\begin{aligned} O_{AB}(q_0^-, q_0^+) &= \int dq_{\text{re}} \int dq_{\text{im}}^+ \int dq_{\text{im}}^- \int dq_A \int dq_B \\ &\quad \times \int \mathcal{D}_{\not\text{re}}^+ \int \mathcal{D}_{\not\text{re}}^- \int \mathcal{D}_{\not\text{re}}^+ \int \mathcal{D}_{\not\text{re}}^- \langle q_{\text{im}}^- | A | q_A \rangle \\ &\quad \times \langle q_{\text{re}} | B | q_B \rangle \text{Tr}_{\text{bath}} \exp \left[\frac{i}{\hbar} (S_{\text{sys}}^{\text{re}}[\not\text{re}^+] \right. \\ &\quad \left. + S_{\text{sys}}^{\text{re}}[\not\text{re}^-] - \frac{1}{\hbar} (S_{\text{sys}}^{\text{im}}[\not\text{im}^+] + S_{\text{sys}}^{\text{im}}[\not\text{im}^-]) \right] \\ &\quad \times \mathfrak{F}[\not\text{re}^+, \not\text{re}^-, \not\text{im}^+, \not\text{im}^-], \end{aligned} \quad (2.6)$$

where $\not\text{re}^+, \not\text{re}^-$ are quantum paths of the system in real time with endpoints $\{q_{\text{im}}^+, q_B\}$ and $\{q_{\text{re}}, q_A\}$, respectively (with $\not\text{re}^-$ running in the negative time direction), $\not\text{im}^+, \not\text{im}^-$ are paths in imaginary time $\hbar\beta/2$ with endpoints $\{q_0^+, q_{\text{im}}^+\}$ and $\{q_{\text{im}}^-, q_0^-\}$, and $S_{\text{sys}}^{\text{re}}, S_{\text{sys}}^{\text{im}}$ are the real and Euclidean time actions that correspond to the system Hamiltonian H_{sys} . Finally, the influence functional is

$$\begin{aligned} \mathfrak{F}[\not\text{re}^+, \not\text{re}^-, \not\text{im}^+, \not\text{im}^-] \\ \equiv \text{Tr}_{\text{bath}} (U_{\text{eff}}[\not\text{im}^-] U_{\text{eff}}^{-1}[\not\text{re}^-] U_{\text{eff}}[\not\text{re}^+] U_{\text{eff}}[\not\text{im}^+]), \end{aligned}$$

where U_{eff} is the time evolution operator for the Hamiltonian

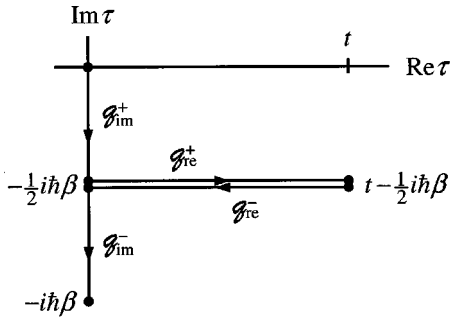


FIG. 1. The time contour employed in the path integral representation of the two-time correlation function.

$$H_{\text{eff}}(\mathbf{x}, \mathbf{p}, \tau) = H_{\text{bath}}(\mathbf{x}, \mathbf{p}) + H_{\text{int}}(\varphi(\tau), \mathbf{x}) \quad (2.7)$$

which is time dependent by virtue of the time parametrization of the system paths. The influence functional can also be written symbolically as

$$\mathfrak{F} = \text{Tr}_{\text{bath}}(U_{\text{eff}}[\varphi]_{\Gamma}), \quad (2.8)$$

where $\varphi(\tau)$ is the coordinate of the quantum system at the time τ along the line Γ in a complex time plane displayed in Fig. 1.

For a harmonic bath linearly coupled to the system of interest the influence functional is given by the expression

$$\mathfrak{F} = Z_{\text{bath}} \exp\left(-\frac{1}{\hbar} \int_{\Gamma} d\tau' \int_{\Gamma} d\tau'' \alpha(\tau_a - \tau_b) \times f(\varphi(\tau')) f(\varphi(\tau''))\right), \quad (2.9)$$

where Z_{bath} is the canonical partition function of the bare bath, τ_a, τ_b are the earlier and later of the times τ', τ'' along the time contour Γ displayed in Fig. 1, and $\alpha(\tau)$ is the bath response to the feedback of the system given by the expression

$$\alpha(\tau) = \sum_j \frac{c_j^2}{2m_j\omega_j} \frac{\cos[\omega_j(\tau + i\hbar\beta/2)]}{\sinh(\hbar\beta\omega_j/2)}. \quad (2.10)$$

It is well known that all characteristics of the bath pertaining to the dynamics of the observable system are captured in the spectral density function

$$J(\omega) = \frac{\pi}{2} \sum_j \frac{c_j^2}{m_j\omega_j} \delta(\omega - \omega_j). \quad (2.11)$$

III. ITERATIVE EVALUATION OF THE PATH INTEGRAL

In numerical calculations, the path integral is recast in a discretized form, in which the total evolution time $\hbar\beta$ along the imaginary time axis is divided into $2M$ slices of length $\Delta\beta = \beta/2M$, while the real time t is split into N slices of length $\Delta t = t/N$. The propagator for any time slice is approximated by the Trotter formula,

$$\exp(H\Delta\tau) = \exp((H - H_{\text{sys}})\Delta\tau/2) \exp(H_{\text{sys}}\Delta\tau) \times \exp((H - H_{\text{sys}})\Delta\tau/2). \quad (3.1)$$

With this time discretization Eq. (2.4) takes the form

$$\begin{aligned} O_{AB}(q_0^-, q_0^+) &= \int dq_1^+ \cdots \int dq_M^+ \cdots \int dq_{M+N}^+ \int dq_1^- \cdots \int dq_M^- \cdots \int dq_{M+N}^- \langle q_0^- | e^{-\Delta\beta H_{\text{sys}}} | q_1^- \rangle \cdots \langle q_{M-1}^- | e^{-\Delta\beta H_{\text{sys}}} | q_M^- \rangle \\ &\times \langle q_M^- | A e^{iH_{\text{sys}}\Delta t/\hbar} | q_{M+1}^- \rangle \langle q_{M+1}^- | e^{iH_{\text{sys}}\Delta t/\hbar} | q_{M+2}^- \rangle \cdots \langle q_{M+N-1}^- | e^{iH_{\text{sys}}\Delta t/\hbar} | q_{M+N}^- \rangle \\ &\times \langle q_{M+N}^- | q_{M+N}^+ \rangle \langle q_{M+N}^+ | B e^{-iH_{\text{sys}}\Delta t/\hbar} | q_{M+N-1}^+ \rangle \langle q_{M+N-1}^+ | e^{-iH_{\text{sys}}\Delta t/\hbar} | q_{M+N-2}^+ \rangle \cdots \langle q_{M+1}^+ | e^{-iH_{\text{sys}}\Delta t/\hbar} | q_M^+ \rangle \\ &\times \langle q_M^+ | e^{-\Delta\beta H_{\text{sys}}} | q_{M-1}^+ \rangle \cdots \langle q_1^+ | e^{-\Delta\beta H_{\text{sys}}} | q_0^+ \rangle \mathfrak{F}(q_0^-, \dots, q_{M+N}^-, q_0^+, \dots, q_{M+N}^+). \end{aligned} \quad (3.2)$$

The discretized influence functional \mathfrak{F} is now a function of all the positions specifying the path of the system. The above expression can be rewritten in the compact form

$$\begin{aligned} O_{AB}(q_0^-, q_0^+) &= \int dq_1^{\pm} \cdots \int dq_{M+N}^{\pm} \prod_{k=1}^M K_{\text{im}}(q_{k-1}^{\pm}, q_k^{\pm}) K_{\text{re}}^A(q_M^{\pm}, q_{M+1}^{\pm}) \\ &\times \prod_{k=M+2}^{M+N-1} K_{\text{re}}(q_{k-1}^{\pm}, q_k^{\pm}) K_{\text{re}}^B(q_{M+N-1}^{\pm}, q_{M+N}^{\pm}) \delta(q_{M+N}^+, q_{M+N}^-) \mathfrak{F}(q_0^{\pm}, \dots, q_{M+N}^{\pm}), \end{aligned} \quad (3.3)$$

where

$$K_{\text{im}}(q_{k-1}^{\pm}, q_k^{\pm}) \equiv \langle q_{k-1}^- | e^{-\Delta\beta H_{\text{sys}}} | q_k^- \rangle \langle q_k^+ | e^{-\Delta\beta H_{\text{sys}}} | q_{k-1}^+ \rangle, \quad (3.4)$$

$$K_{\text{re}}(q_{k-1}^{\pm}, q_k^{\pm}) \equiv \langle q_{k-1}^- | e^{iH_{\text{sys}}\Delta t/\hbar} | q_k^- \rangle \langle q_k^+ | e^{-iH_{\text{sys}}\Delta t/\hbar} | q_{k-1}^+ \rangle, \quad (3.5)$$

$$K_{\text{re}}^A(q_M^{\pm}, q_{M+1}^{\pm}) \equiv \langle q_M^- | A e^{iH_{\text{sys}}\Delta t/\hbar} | q_{M+1}^- \rangle \langle q_{M+1}^+ | e^{-iH_{\text{sys}}\Delta t/\hbar} | q_M^+ \rangle, \quad (3.6)$$

$$K_{\text{re}}^B(q_{M+N-1}^{\pm}, q_{M+N}^{\pm}) \equiv \langle q_{M+N-1}^- | e^{iH_{\text{sys}}\Delta t/\hbar} | q_{M+N}^- \rangle \langle q_{M+N}^+ | B e^{-iH_{\text{sys}}\Delta t/\hbar} | q_{M+N-1}^+ \rangle. \quad (3.7)$$

The time points at which the system imposes a new force on the bath are the series $\tau_0=(0,0)$, $\tau_k=-i(k-\frac{1}{2})\hbar\Delta\beta$ for $1\leq k\leq M$, $\tau_{M+1}=-i\hbar\beta/2$, $\tau_{M+k}=(k-\frac{1}{2})\Delta t-i\hbar\beta/2$ for $1\leq k\leq N-1$, and $\tau_{M+N}=t-i\hbar\beta/2$. The discretized influence functional \mathfrak{F} reads

$$\mathfrak{F} = Z_{\text{bath}} \exp \left[-\frac{1}{\hbar} \sum_{k=0}^{M+N} \sum_{k'=0}^k (\eta_{kk'}^{++} f_k^+ f_{k'}^+ + \eta_{kk'}^{--} f_k^- f_{k'}^- + \eta_{kk'}^{+-} f_k^+ f_{k'}^- + \eta_{kk'}^{-+} f_k^- f_{k'}^+) \right], \quad (3.8)$$

where $f_k^\pm = f(q_k^\pm)$ and the coefficients in the quadratic interaction form are determined by the response function Eq. (2.5) as

$$\begin{aligned} \eta_{kk}^{++} &= (\eta_{kk}^{--})^* \\ &= \frac{1}{\pi} \int_{-\infty}^{\infty} d\omega \frac{J(\omega)}{\omega^2} \frac{\sin(\omega(\tau_{k+1}-\tau_k)/2)}{\sinh(\hbar\beta\omega/2)} \\ &\quad \times \sin(\omega(\tau_{k+1}-\tau_k+i\hbar\beta)/2), \end{aligned} \quad (3.9)$$

$$\begin{aligned} \eta_{kk}^{+-} &= \frac{2}{\pi} \int_{-\infty}^{\infty} d\omega \frac{J(\omega)}{\omega^2} \frac{\sin(\omega(\tau_{k+1}-\tau_k)/2)}{\sinh(\hbar\beta\omega/2)} \\ &\quad \times \sin(\omega(\tau_k^* - \tau_{k+1}^*)/2) \\ &\quad \times \cos(\omega(\tau_{k+1}^* + \tau_k^* - \tau_{k+1} - \tau_k - i\hbar\beta)/2), \end{aligned} \quad (3.10)$$

$$\begin{aligned} \eta_{kk'}^{++} &= (\eta_{kk'}^{--})^* \\ &= \frac{2}{\pi} \int_{-\infty}^{\infty} d\omega \frac{J(\omega)}{\omega^2} \frac{\sin(\omega(\tau_{k+1}-\tau_k)/2)}{\sinh(\hbar\beta\omega/2)} \\ &\quad \times \sin(\omega(\tau_{k'+1}-\tau_k)/2) \\ &\quad \times \cos(\omega(\tau_{k+1} + \tau_k - \tau_{k'+1} - \tau_k + i\hbar\beta)/2), \end{aligned} \quad (3.11)$$

and

$$\begin{aligned} \eta_{kk'}^{+-} &= (\eta_{kk'}^{-+})^* \\ &= \frac{2}{\pi} \int_{-\infty}^{\infty} d\omega \frac{J(\omega)}{\omega^2} \frac{\sin(\omega(\tau_{k+1}-\tau_k)/2)}{\sinh(\hbar\beta\omega/2)} \\ &\quad \times \sin(\omega(\tau_{k'}^* - \tau_{k'+1}^*)/2) \\ &\quad \times \cos(\omega(\tau_{k'+1}^* + \tau_{k'}^* - \tau_{k+1} - \tau_k - i\hbar\beta)/2) \end{aligned} \quad (3.12)$$

for $k' \leq k$. In these expressions the spectral density for negative frequencies is defined as $J(-\omega) = -J(\omega)$.

Full summation of the path integral typically involves an astronomical number of terms, equal to the number of grid points required to discretize the system coordinate raised to the power $2(M+N)$. At the same time, Monte Carlo methods fail to converge except at short times due to the oscillatory nature of the multidimensional integrand. Even though the presence of the influence functional has introduced nonlocal interactions prohibiting a step-by-step evaluation, earlier work in our group has shown that the extent of nonlo-

cality is finite and usually much shorter than the desirable propagation time.⁷ This fact, which is a consequence of decoherence induced by the bath, implies that the path integral can be decomposed into a series of low-dimensional operations. Specifically, rather than attempting simultaneous summation of all paths spanning the propagation time, one needs to carry each summation over only those path segments that span the memory time.^{8,9} Since the number of terms grows exponentially with the number of time steps over which paths must be taken into account, such a decomposition results in a dramatic reduction of effort and enables evaluation of the path integral for long times. Further reduction of effort is possible if one employs a Monte Carlo procedure to filter out path segments with exponentially small contribution.^{11,14,20}

In our recent work we demonstrated that the bath-induced decoherence, initially exploited only in real time, also characterizes the Boltzmann operator, provided the integration is performed inward from both ends of the imaginary time contour.¹⁶ In this case, the loss of memory is a consequence of thermal fluctuations in addition to the standard dephasing arising from multidimensional baths. Thus, coupling of the system to a large number of oscillators is not a necessary condition for finite memory, although the presence of dissipation helps shorten even further the memory length. These features imply that even the partition function, which involves propagation only in imaginary time, is amenable to an iterative procedure, as shown in our recent work.

To implement these ideas, we assume that the response function decays to zero within at most Δk_{max} time steps both in real and imaginary time. This means that the coefficients of the nonlocal terms become practically zero when $|k-k'|$ in Eq. (3.8) exceeds a certain threshold Δk_{max} , and thus the second summation in the exponent of Eq. (3.8) can be truncated without loss of accuracy. To establish the algorithm, we expand the influence functional into a product of functions corresponding to one-point and two-point interactions, namely,

$$\begin{aligned} \mathfrak{F} &= Z_{\text{bath}} \prod_{k=0}^{M+N} F_0(q_k^\pm) \prod_{k=0}^{M+N-1} F_1(q_k^\pm, q_{k+1}^\pm) \cdots \\ &\quad \times \prod_{k=0}^{M+N-\Delta k_{\text{max}}} F_{\Delta k_{\text{max}}}(q_k^\pm, q_{k+\Delta k_{\text{max}}}^\pm), \end{aligned} \quad (3.13)$$

where the one- and two-point functions are

$$\begin{aligned} F_{\Delta k}(q_k^\pm, q_{k+\Delta k}^\pm) &= \exp \left[-\frac{1}{\hbar} (\eta_{k+\Delta k, k}^{++} f_{k+\Delta k}^+ f_k^+ + \eta_{k+\Delta k, k}^{--} f_{k+\Delta k}^- f_k^- \right. \\ &\quad \left. + \eta_{k+\Delta k, k}^{+-} f_{k+\Delta k}^+ f_k^- + \eta_{k+\Delta k, k}^{-+} f_{k+\Delta k}^- f_k^+) \right] \end{aligned} \quad (3.14)$$

for $\Delta k=0, \dots, \Delta k_{\text{max}}$ and $k=0, \dots, M+N-\Delta k_{\text{max}}$. In close analogy with its earlier versions, the iterative procedure con-

sists of the following steps. First, a $2\Delta k_{\max}$ -dimensional array $R^{(k)}(q_k^\pm, \dots, q_{k+\Delta k_{\max}}^\pm)$ (where the superscript k specifies the time index of the first variable) is set up with the initial condition

$$R^{(0)}(q_k^\pm, \dots, q_{k+\Delta k_{\max}}^\pm) = 1. \quad (3.15)$$

The elements of this array are system path segments that span Δk_{\max} time points. We also construct a $2(\Delta k_{\max} + 1)$ -dimensional array Λ , which is defined as

$$\Lambda_{\text{im}}(q_k^\pm, \dots, q_{k+\Delta k_{\max}}^\pm) = K_{\text{im}}(q_k^\pm, q_{k+1}^\pm) \times \prod_{m=0}^{\min\{\Delta k_{\max}, M+N-k\}} F_m(q_k^\pm, q_{k+m}^\pm) \quad (3.16)$$

and its endpoint versions

$$\Lambda_{\text{re}}^A(q_M^\pm, \dots, q_{M+\Delta k_{\max}}^\pm) = K_{\text{im}}^A(q_M^\pm, q_{M+1}^\pm) \times \prod_{m=0}^{\min\{\Delta k_{\max}, M+N-k\}} F_m(q_M^\pm, q_{M+m}^\pm), \quad (3.17)$$

$$\Lambda_{\text{re}}^B(q_M^\pm, \dots, q_{M+\Delta k_{\max}}^\pm) = K_{\text{im}}^B(q_M^\pm, q_{M+1}^\pm) \times \prod_{m=0}^{\min\{\Delta k_{\max}, M+N-k\}} F_m(q_M^\pm, q_{M+m}^\pm). \quad (3.18)$$

With these definitions, the first propagation step involves the following operation:

$$R^{(1)}(q_1^\pm, \dots, q_{\Delta k_{\max}}^\pm) = \int dq_0^\pm \Lambda_{\text{im}}(q_0^\pm, q_1^\pm, \dots, q_{\Delta k_{\max}}^\pm) \times R^{(0)}(q_0^\pm, \dots, q_{\Delta k_{\max}}^\pm) \delta(q_0^+ - q_0^-). \quad (3.19)$$

Subsequent steps along the imaginary time branches are performed as follows:

$$R^{(k+1)}(q_{k+1}^\pm, \dots, q_{k+\Delta k_{\max}}^\pm) = \int dq_k^\pm \Lambda_{\text{im}}(q_k^\pm, \dots, q_{k+\Delta k_{\max}}^\pm) \times R^{(k)}(q_k^\pm, \dots, q_{k-1+\Delta k_{\max}}^\pm) \quad (3.20)$$

for $k=1, \dots, M-1$.

Propagation along the real time contour starts with the multiplication

$$R^{(M+1)}(q_{M+1}^\pm, \dots, q_{M+\Delta k_{\max}}^\pm) = \int dq_M^\pm \Lambda_{\text{re}}^A(q_M^\pm, \dots, q_{M+\Delta k_{\max}}^\pm) \times R^{(M)}(q_M^\pm, \dots, q_{M-1+\Delta k_{\max}}^\pm), \quad (3.21)$$

followed by $N-2$ steps of the type

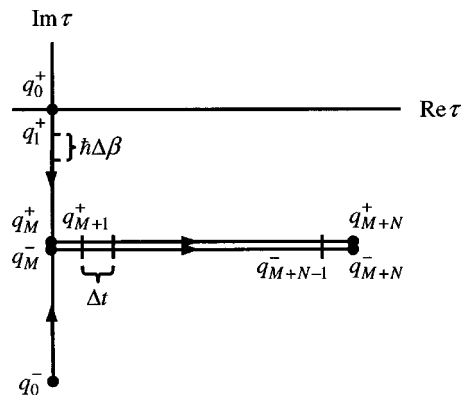


FIG. 2. Path integral coordinates and the direction of the iterative procedure.

$$R^{(k+1)}(q_{k+1}^\pm, \dots, q_{k+\Delta k_{\max}}^\pm) = \int dq_k^\pm \Lambda_{\text{re}}(q_k^\pm, \dots, q_{k+\Delta k_{\max}}^\pm) \times R^{(k)}(q_k^\pm, \dots, q_{k-1+\Delta k_{\max}}^\pm). \quad (3.22)$$

For $k=M+1, \dots, M+N-2$. The last step consists in the operation

$$R^{(M+N)}(q_{M+N}^\pm, \dots, q_{M+N-1+\Delta k_{\max}}^\pm) = \int dq_{M+N-1}^\pm \Lambda_{\text{re}}^B(q_{M+N-1}^\pm, \dots, q_{M+N-1+\Delta k_{\max}}^\pm) \times R^{(M+N-1)}(q_{M+N-1}^\pm, \dots, q_{M+N-2+\Delta k_{\max}}^\pm). \quad (3.23)$$

This sequence of events is illustrated in Fig. 2.

Finally, the correlation function at time t is given by

$$C_{AB}(t) = Z^{-1} R^{(N+M)}(q_{N+M}^\pm, 0, \dots, 0). \quad (3.24)$$

Although the arrays \mathbf{R} and Λ involved in the iterative evaluation of the correlation function depend simultaneously on the variables corresponding to all time points within the memory length, each of the operations presented above involves only the coordinate of a single time point of \mathbf{R} and those of two adjacent time points of Λ . Thus, each propagation step can be considered a matrix-vector multiplication where the dimension of the “vector” \mathbf{R} is equal to the square of the number of grid points required to discretize the system coordinate.

A similar algorithm has recently been developed for evolution along the complex time line.¹⁶ That scheme provides the natural way to proceed in order to calculate a symmetrized time correlation function, as in the case of Miller’s flux correlation function formulation of reaction rate theory.²¹ As is well known, a time correlation function and its symmetrized complex time variant are related by Kubo transforms.¹⁷ Thus, knowledge of one form allows, in principle, calculation of the other, although numerical considerations may become important when evaluating the necessary transformation integral. The present formulation yields the conventional unsymmetrized correlation function *directly*. A practical advantage of the present formulation, where the time contour proceeds along the imaginary and real time

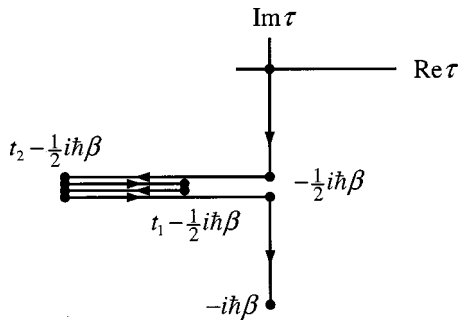


FIG. 3. The evolution contour for the three-time correlation function.

directions via two sequential events (rather than following the diagonal line through the complex time plane) is that during the evolution in the real time direction with fixed imaginary time (except for the first and last propagation step) the propagator Λ is independent of time. This fact is important if one seeks the long-time behavior of the correlation function.

Finally, we note that if the two operators A and B are set equal to the identity operator, we obtain an algorithm for calculating the system-bath partition function Z . This procedure has also been discussed in Ref. 16.

IV. HIGHER ORDER CORRELATION FUNCTIONS

The interest in multitime correlation functions lies in nonlinear spectroscopy which can distinguish homogeneous and inhomogeneous dephasing of a vibrational mode in a liquid.²² For example, the fifth-order polarization is determined by the following response function:

$$R^{(5)}(t_1, t_2) = -\frac{1}{\hbar^2 Z} \text{Tr}([\mathcal{P}(t_1 + t_2), \mathcal{P}(t_1)], \mathcal{P}] e^{-\beta H}), \quad (4.1)$$

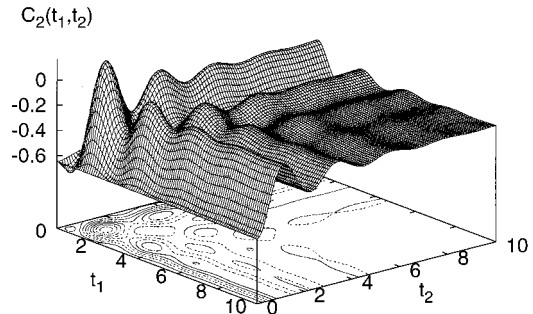
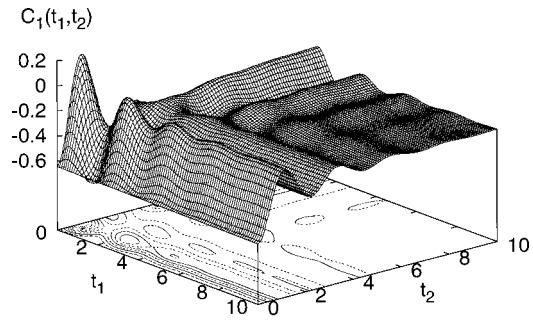
where \mathcal{P} is the polarizability. Although the two commutators on the right-hand side of Eq. (4.1) result in four terms, only two of them need to be calculated because of the permutation invariance of the trace. The signal recorded in the experiments is the square of the response function, namely, $I^{(5)}(t_1, t_2) = (R^{(5)}(t_1, t_2))^2$.

Extending the procedure developed in the previous two sections for the calculation of multitime correlation functions is straightforward. Again, one needs to split the Boltzmann operator into two identical parts and to reorder the evolution propagators for a symmetric expression of the correlation function. For example, a three-time correlation function can be expressed in the form

$$\begin{aligned} C_{ABD}(t_1, t_2) &= \text{Tr}\{e^{-\beta H} A B(t_1) D(t_2)\} \\ &= \text{Tr}(e^{-\beta H/2} e^{-iHt_2/\hbar} A e^{iHt_1/\hbar} \\ &\quad \times B e^{-iHt_1/\hbar} e^{iHt_2/\hbar} D e^{-\beta H/2}). \end{aligned} \quad (4.2)$$

The evolution time contour of the drive path is displayed in Fig. 3.

In this case there are two pairs of forward-backward real time branches. Partitioning the time intervals t_1 and t_2 into N_1 and N_2 time slices, respectively, one can obtain a

FIG. 4. The two third-order correlation functions defined in Eq. (5.5) and (5.6) for an asymmetric two-level system coupled to an Ohmic bath for $\beta^{-1} = \hbar \omega$.

discretized path integral expression similar to Eq. (3.3) but with separate paths discretizing each of the forward/backward real time contours, with a total of $M + N_1 + N_2$ time points. Developing an iterative algorithm along the lines of the preceding section is straightforward.

V. MODEL STUDIES: DISSIPATIVE TWO-LEVEL SYSTEMS

As simple applications, we use the iterative procedure developed in Secs. II–IV to calculate two- and three-time position correlation functions in symmetric and asymmetric two-level systems coupled to a harmonic oscillator bath. This bath is fully specified by the spectral density which is chosen Ohmic, i.e.,

$$J(\omega) = \pi \xi \omega e^{-\omega/\omega_c}, \quad (5.1)$$

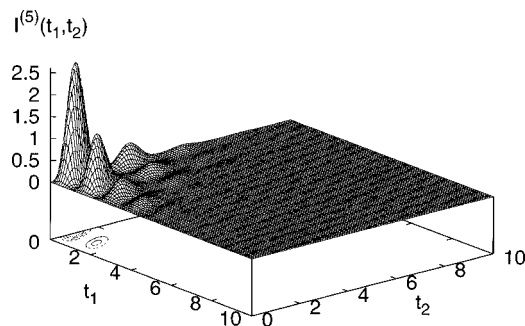
where the Kondo parameter ξ is a measure of the overall system-bath coupling strength.

The two-level system can be regarded as a truncated one-dimensional double-well system and its position coordinate is the 2×2 Pauli spin matrix σ_z . Thus the Hamiltonian for the dissipative two-level system is

$$H = \hbar \Omega \sigma_x + \hbar \varepsilon \sigma_z + \sum_j \left(\frac{p_j^2}{2m_j} + \frac{1}{2} m_j \omega_j^2 x_j^2 - \sigma_z c_j x_j \right), \quad (5.2)$$

where $2\hbar\Omega$ is the energy difference between the excited and ground states, which is closed related the tunneling frequency between the two localized states, $\hbar\varepsilon$ is the bias and the bath spectral density is given by Eq. (5.2) with $\omega_c/\Omega = 7.5$. The correlation functions to be evaluated are

$$C(t) = Z^{-1} \text{Tr}(e^{-\beta H} \sigma_z e^{iHt/\hbar} \sigma_z e^{-iHt/\hbar}) \quad (5.3)$$

FIG. 5. The calculated signal for $\beta^{-1} = \hbar\Omega$.

and

$$C(t_1, t_2) = Z^{-1} \text{Tr} [e^{-\beta H} \sigma_z e^{iHt_1/\hbar} \times \sigma_z e^{-iHt_1/\hbar} e^{iHt_2/\hbar} \sigma_z e^{-iHt_2/\hbar}].$$

To obtain the fifth-order response function we bring Eq. (4.1) in the form

$$R^{(5)}(t_1, t_2) = \frac{2}{\hbar^2 Z} \text{Re} \{ \text{Tr} [e^{-\beta H/2} e^{iHt_1/\hbar} (\mathcal{P} e^{iHt_2/\hbar} \mathcal{P} e^{-iHt_2/\hbar} - e^{iHt_2/\hbar} \mathcal{P} e^{-iHt_2/\hbar} \mathcal{P}) e^{-iHt_1/\hbar} \mathcal{P} e^{-\beta H/2}] \}. \quad (5.4)$$

In the present study we assume that \mathcal{P} is linearly proportional to the position, i.e., $\mathcal{P} \propto \sigma_z$. The two third-order correlation functions to be calculated are thus defined by

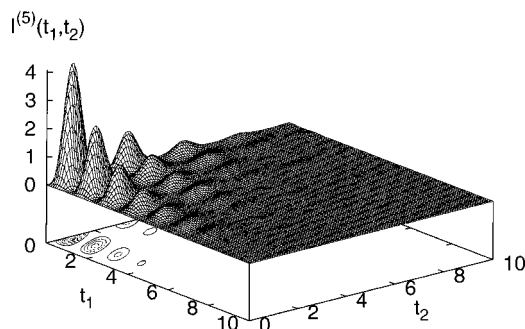
$$C_1(t_1, t_2) = \text{Re} \{ \text{Tr} [e^{-\beta H} \sigma_z(t_1 + t_2) \sigma_z(t_1) \sigma_z(t_2)] \} \quad (5.5)$$

and

$$C_2(t_1, t_2) = \text{Re} \{ \text{Tr} [e^{-\beta H} \sigma_z(t_1) \sigma_z(t_1 + t_2) \sigma_z(t_2)] \}. \quad (5.6)$$

Note that when the two-level system is symmetric ($\varepsilon = 0$), the fifth-order response function is zero since in this case all three-time autocorrelation functions are vanishing. In the calculations presented below we set $\varepsilon = \Omega$ and choose the Kondo parameter as $\xi = 0.1$.

Figure 4 displays the two correlation functions at an intermediate temperature $\beta^{-1} = \hbar\Omega$ and Fig. 5 shows the corresponding signal. Figure 6 shows the signal at a lower temperature, $\beta^{-1} = 0.2\hbar\Omega$. In both cases, the partition function is calculated using full memory, i.e., the evolution in imaginary time is divided into precisely Δk_{max} slices. The real

FIG. 6. The calculated signal for $\beta^{-1} = 0.2\hbar\Omega$.

time step is chosen as $\Delta t = 0.1 \Omega^{-1}$. With the parameters employed in these calculations excellent convergence is achieved with $\Delta k_{\text{max}} = 6$, and the results obtained with $\Delta k_{\text{max}} = 9$ are practically indistinguishable from those presented in the figures.

VI. DISCUSSION

Equilibrium correlation functions encode very rich information. Depending on the type and the operators involved, correlation functions can yield information on linear or nonlinear spectroscopy, reaction kinetics or relaxation phenomena in a variety of systems. Numerical evaluation of correlation functions requires one's ability to solve the quantum mechanical equations of motion in real time and has in the past been possible only in small molecules and simplified models or larger systems.

The methodology described in this paper allows accurate numerical evaluation of time correlation functions in systems interacting with harmonic dissipative media. The common "sign problem" associated with numerical evaluation of the path integral is circumvented through the development of an iterative procedure. In this, the path integral is broken up into a series of matrix-vector multiplications and summed sequentially. Because the number of steps grows linearly with the total propagation interval, very long time behavior becomes accessible. Once converged with respect to the path integral time steps and memory time the method is exact. Further, the matrix operations involved yield definitive results free of statistical error common to Monte Carlo based schemes. For these reasons the present method provides an excellent way to investigate multitime correlation functions and sensitive nonlinear signals in dissipative models of condensed phase experiments.

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