

Path integrals for dissipative systems by tensor multiplication. Condensed phase quantum dynamics for arbitrarily long time

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Abstract

Feynman's influence functional that arises from many-particle environments is nonlocal in time but the nonlocality has finite range, even at very low temperature. Use of our numerically constructed quasi-adiabatic propagators permits large time steps in the path integral, such that the nonlocality of the influence functional spans only a few time steps. We exploit these observations to propose an iterative scheme for the evaluation of path integrals by stepwise multiplication of a propagator tensor, thereby making exact quantum dynamics calculations in condensed phase systems feasible for arbitrarily long times.

1. Introduction

Significant advances have been made during the last decade in the development of efficient numerical algorithms for studying the dynamics of quantum mechanical systems. Accurate eigenstate and time-dependent methods have become very efficient for systems of only a few degrees of freedom and are used routinely in chemical physics to yield fully quantum results for triatomic or tetratomic processes. In the time domain most commonly used methods are based on iterative schemes, such as multiplication of a propagator matrix by a wavefunction vector, that integrate the Schrödinger equation on a grid with finite time steps. However, wavefunction-based methods are not practical for polyatomic molecules or condensed phase systems because they require computer memory that grows exponentially with the number of degrees of freedom. In the past, most attempts to study the dynamics of polyatomic systems have been based on approximate treatments, such as factorization of the wavefunction, perturbative approaches, or mixed quantum-classical schemes.

Feynman's path integral formulation of time-dependent quantum mechanics [1,2] appears as an attractive alternative. By avoiding explicit computation of multidimensional wavefunctions (which contain much more detailed information than desired in polyatomic cases), the path integral approach seems ideal for allowing many-particle dynamical calculations of observable quantities without the need for simplifying assumptions. However, numerical evaluation of the real-time path integral is far from straightforward because it requires integration of a large-dimensional highly oscillatory function; the resulting phase cancellation, known as the sign problem, prohibits use of statistical sampling methods suitable for well-behaved multidimensional integrals.

The path integral representation of the propagator simplifies enormously in cases where the Hamiltonian is described by a one- or two-dimensional 'system' coupled to a 'bath' of harmonic oscillators. Such Hamiltonians are most commonly encountered in condensed phase problems [3], where the harmonic bath may correspond to lattice phonon vibrations or may arise from a linear response description of a macroscopic environment. In

addition, system–bath models have been utilized in reaction path Hamiltonian descriptions of polyatomic chemical reactions [4–9]. Because the propagator for harmonic degrees of freedom involves the coordinates in Gaussian form, the harmonic bath can be integrated out analytically, leading to a path integral expression for the system coordinates with the effects of the bath contained in an influence functional [2,10]. Due to the non-local character of the latter, the reduced dimension path integral cannot be evaluated by iterative matrix–vector multiplication; instead, global (multidimensional) integration methods must be used. The conventional discretization of the path integral, which is based on factoring the time evolution operator into kinetic and potential energy parts [11], requires fairly small time steps Δt for accuracy. As a consequence, the number N of integration variables is typically large, and calculations are still hampered by the sign problem. Considerable progress has been made in recent years toward developing schemes that partly alleviate the sign problem. For reviews see refs. [12,13]. See also ref. [14] for references to recent numerical path integral methods.

A powerful path integral scheme has been developed recently in our group [14–19], which is based on improved propagators that are accurate for large time steps. These propagators are constructed numerically using basis set methods and allow dramatic reduction of the dimensionality of the discretized path integral. In the case of a system coupled to a harmonic bath, we have defined [15,16] a *quasi-adiabatic propagator* that corresponds to an adiabatic partitioning of the Hamiltonian. Its use leads to an influence functional that includes multidimensional non-adiabatic corrections to the dynamics of the adiabatic reference system, and the required number of time slices in the resulting path integral is typically small enough to allow integration by a combination of Monte Carlo and optimized quadrature methods. Using this approach we have been able to follow the quantum dynamics of polyatomic systems for time sufficiently long to extract interesting kinetic information [14,17–19].

Even though the dimension of the discretized path integral is usually fairly small when the latter is expressed in terms of the quasi-adiabatic propagator, such that the dynamics can be obtained for moderately long times by employing efficient multidimensional integration methods, it would still be highly desirable to have an iterative method for evaluating the path integral with the nonlocal influence functional. There are numerous situations where the dynamics must be known for extremely long time intervals, and these situations cannot be dealt with using global integration methods. Iterative schemes have the advantage of requiring computer time that increases linearly with the number of time steps and could thus be used to extend the dynamics to arbitrarily long times, whereas global evaluation of the path integral requires effort that grows exponentially with the required number of time slices.

It is not obvious at first glance that iterative evaluation of the path integral is possible when the latter involves a nonlocal influence functional. The reduction in number of degrees of freedom accomplished by integrating out the bath causes the resulting system dynamics to be non-Markovian. Yet, it is well-known that dissipation tends to destroy quantum coherence, resulting in loss of memory of initial conditions – at least if the damping is sufficiently strong. It is therefore conceivable that the temporal non-locality of the influence functional is of finite range, a fact that would allow iterative evaluation of the path integral, though not of the common matrix–vector multiplication type.

In this Letter, we demonstrate that this is indeed the case in ordinary condensed phase problems; i.e. the influence functional contains nonlocal interactions of finite range that extend over just a few time slices when our improved propagators are used. We then exploit this fact to propose an iterative scheme for evaluating path integrals in condensed matter, which is based on stepwise multiplication of a propagator *tensor*^{#1}; the latter does not correspond to a unitary operation and is thus capable of accounting for damping due to dissipative effects and even rate kinetics.

Section 2 reviews the quasi-adiabatic propagator formulation of the discretized path integral for system–bath Hamiltonians and derives the relevant influence functional. In section 3 we analyze the properties of the influ-

^{#1} We use the word *tensor* as synonymous with multidimensional array or matrix and do not refer to the transformation properties of a tensor, which are not necessarily satisfied.

ence functional, in light of which we propose the iterative scheme for evaluating the path integral. Numerical examples presented in section 4 illustrate the efficiency of the method, which is capable of yielding numerically exact values for arbitrarily long times as long as the nonlocal interactions are not truncated too soon. Section 5 concludes with general remarks and possible applications of these ideas.

2. Quasi-adiabatic propagator path integral (QUAPI)

We begin by reviewing the quasi-adiabatic propagator formulation of the path integral [15,16] that allows large time steps. In this Letter, we are concerned with condensed phase processes described by the generic system–bath Hamiltonian,

$$H = \frac{p_s^2}{2m_0} + V(s) + \sum_j \left[\frac{P_j^2}{2m_j} + \frac{1}{2} m_j \omega_j^2 \left(Q_j - \frac{c_j s}{m_j \omega_j^2} \right)^2 \right], \quad (1)$$

where the coordinate s corresponds to the nonlinear system and the harmonic oscillators Q_j describe through linear coupling terms the effects of the environment. This Hamiltonian includes standard counterterms quadratic in s , which ensure that important features (e.g., the barrier height) do not depend on the coupling strength [3]. In addition, we assume that the bath is described by a (continuous) spectral density

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

We construct a propagator for large time steps by partitioning the total Hamiltonian into a one-dimensional reference system Hamiltonian H_0 with the potential along the adiabatic path,

$$H_0(s, p_s) = \frac{p_s^2}{2m_0} + V(s) \quad (3)$$

and a bath $H_{Q,s}$ of oscillators whose equilibrium positions are adiabatically displaced along the system coordinate,

$$H_{Q,s} \equiv \sum_j H_j(Q_j, P_j, s) \equiv \sum_j \left[\frac{P_j^2}{2m_j} + \frac{1}{2} m_j \omega_j^2 \left(Q_j - \frac{c_j s}{m_j \omega_j^2} \right)^2 \right]. \quad (4)$$

Employing a symmetric splitting of the short-time evolution operator

$$\exp(-iH\Delta t/\hbar) \approx \exp(-iH_{Q,s}\Delta t/2\hbar) \exp(-iH_0\Delta t/\hbar) \exp(-iH_{Q,s}\Delta t/2\hbar), \quad (5)$$

leads to the following quasi-adiabatic propagator [15,16]:

$$\begin{aligned} \langle s_k Q_k | \exp(-iH\Delta t/\hbar) | s_{k-1} Q_{k-1} \rangle &\approx \langle s_k | \exp(-iH_0\Delta t/\hbar) | s_{k-1} \rangle \\ &\times \prod_j \langle Q_{j,k} | \exp[-iH_j(s_k)\Delta t/2\hbar] \exp[-iH_j(s_{k-1})\Delta t/2\hbar] | Q_{j,k-1} \rangle, \end{aligned} \quad (6)$$

where the coordinate points have been labeled by the integers $k-1$ and k in anticipation of the discretized path integral expression, Eq. (10) below.

Each bath factor in the last equation is a propagator for a harmonic oscillator displaced from equilibrium by an amount that depends on the system coordinate. These propagators can be evaluated analytically, introducing Franck–Condon factors that account for non-adiabatic corrections to the exact dynamics along the one-dimensional adiabatic path. Because the one-dimensional potential usually provides a reasonable zeroth-order approximation to the dynamics, the quasi-adiabatic propagator given by Eq. (6) is accurate for fairly large time steps. The one-dimensional system propagators are constructed numerically in terms of a finite number of system eigenstates Φ_n and eigenvalues E_n of H_0 :

$$\langle s_k | \exp(-iH_0 \Delta t / \hbar) | s_{k-1} \rangle = \sum_{n=0}^{n_{\max}} \exp(-iE_n \Delta t / \hbar) \Phi_n(s_{k-1}) \Phi_n(s_k). \quad (7)$$

This propagator matrix is generated at the beginning of the calculation and stored on the chosen grid.

Use of Eq. (6) leads to *quasi-adiabatic propagator path integral* (QUAPI) expressions for the dynamical quantities of interest. For example, if the interaction between the system and the bath is switched on at $t=0$, i.e. if the initial density matrix is

$$\rho(0) = \rho_s(0) \rho_{\text{bath}}(0), \quad (8)$$

then the evolution of the reduced density matrix of the system

$$\tilde{\rho}(s'', s'; t) = \text{Tr}_{\text{bath}} \langle s'' | \exp(-iHt/\hbar) \rho(0) \exp(iHt/\hbar) | s' \rangle \quad (9)$$

is described by

$$\begin{aligned} \tilde{\rho}(s'', s'; t) = & \int ds_0^+ \int ds_1^+ \dots \int ds_{N-1}^+ \int ds_0^- \int ds_1^- \dots \int ds_{N-1}^- \\ & \times \langle s'' | \exp(-iH_0 \Delta t / \hbar) | s_{N-1}^+ \rangle \dots \langle s_1^+ | \exp(-iH_0 \Delta t / \hbar) | s_0^+ \rangle \\ & \times \langle s_0^+ | \rho_s(0) | s_0^- \rangle \langle s_0^- | \exp(iH_0 \Delta t / \hbar) | s_1^- \rangle \dots \langle s_{N-1}^- | \exp(iH_0 \Delta t / \hbar) | s' \rangle \\ & \times I(s_0^+, s_1^+, \dots, s_{N-1}^+, s'', s_0^-, s_1^-, \dots, s_{N-1}^-, s'; \Delta t). \end{aligned} \quad (10)$$

where the influence functional is

$$\begin{aligned} I(s_0^+, s_1^+, \dots, s_{N-1}^+, s'', s_0^-, s_1^-, \dots, s_{N-1}^-, s'; \Delta t) \\ = \text{Tr}_{\text{bath}} \{ \exp[-iH_{Q,s}(s'') \Delta t / 2\hbar] \exp[-iH_{Q,s}(s_{N-1}^+) \Delta t / \hbar] \dots \exp[-iH_{Q,s}(s_0^+) \Delta t / 2\hbar] \\ \times \rho_{\text{bath}}(0) \exp[iH_{Q,s}(s_0^-) \Delta t / 2\hbar] \dots \exp[iH_{Q,s}(s_{N-1}^-) \Delta t / \hbar] \exp[iH_{Q,s}(s') \Delta t / 2\hbar] \}. \end{aligned} \quad (11)$$

The influence functional incorporates multidimensional non-adiabatic corrections to the exact dynamics along the adiabatic path described by the one-dimensional system propagators in Eq. (10). It is given by the expressions obtained by Feynman and Vernon [10] (see section 3), where the forward and backward paths consist of constant s segments, $s^\pm(t) = s_k^\pm$, $(k - \frac{1}{2})\Delta t \leq t < (k + \frac{1}{2})\Delta t$.

The $2N$ integrals in Eq. (10) are evaluated on a grid of points that span the s coordinate. A question that arises concerns the optimal choice of grid, that minimizes the number of terms required to evaluate these integrals. We have found [14,19] that for a bound system the optimal grid is given by the discrete variable representation (DVR) that corresponds to the eigenstates of the system Hamiltonian H_0 . The number M of DVR points necessary for the evaluation of the integrals in Eq. (10) is in practice only slightly larger than the number n_{\max} of states required for representing the system propagator, Eq. (7). For short to intermediate times, previous work in our group has shown that the QUAPI representation of Eq. (10) can be evaluated with modest amounts of computer time using a combination of Monte Carlo and multidimensional DVR quadrature schemes [14,17–19].

3. Range of non-local interactions and iterative calculation of the path integral

We now focus on the case where the bath is initially in thermal equilibrium at temperature T so that its density matrix is $\rho_{\text{bath}}(0) = \exp(-\beta H_{\text{bath}})$, $\beta = 1/k_B T$. In the continuous limit (that is, for $\Delta t \rightarrow 0$, $N \rightarrow \infty$) the influence functional has been given by Feynman and Vernon [10],

$$I = \exp \left(-\frac{1}{\hbar} \int_0^t dt' \int_0^{t'} dt'' [s^+(t') - s^-(t')] [\alpha(t' - t'') s^+(t'') - \alpha^*(t' - t'') s^-(t'')] \right. \\ \left. - \frac{i}{\hbar} \int_0^t dt' \sum_j \frac{c_j^2}{2m_j \omega_j^2} [s^+(t')^2 - s^-(t')^2] \right), \quad (12)$$

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

$$\alpha(t) = \sum_j \frac{c_j^2}{2m_j \omega_j} [\coth(\frac{1}{2}\beta\omega_j \hbar) \cos(\omega_j t) - i \sin(\omega_j t)]. \quad (13)$$

For ohmic spectral density, $J(\omega) = \gamma\omega$, and in the limit $\beta \rightarrow 0$ Caldeira and Leggett [20] have shown that 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 (12) becomes a single integral and the dynamics of the reduced density matrix is Markovian. In the language of discretized path integrals this fact implies that Eq. (10) can be evaluated in this case using the ordinary matrix multiplication scheme, common in low-dimensional problems. In the general case, though, the resulting dynamics is not Markovian, and one's ability to evaluate $\tilde{\rho}(s'', s'; t)$ at long times t is limited by the necessity to compute the multidimensional integral Eq. (10).

Motivated by the above Markovian limit, we proceed by examining the behavior of the nonlocal kernel for finite temperatures and more general form of the spectral density, $J(\omega) = \gamma\omega^p \exp(-\omega/\omega_c)$, $p \geq 1$, where ω_c is a cutoff frequency. For $p=1$ and infinitely high temperature ($\beta=0$), the real part of the kernel takes a Lorentzian form with width proportional to ω_c^{-1} (and thus reduces to $\delta(t)$ in the limit $\omega_c \rightarrow \infty$). For high but finite temperature, Taylor expansion in $\hbar\omega\beta$ shows that, for any value of $p \geq 1$, $\alpha(t)$ 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. We therefore conclude that the non-local interactions that arise from the kernel $\alpha(t' - t'')$ in Eq. (12) have finite range independent of the coupling strength γ 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. 1 for two different temperatures.

With the quasi-adiabatic discretization of the path integral, Eq. (10), the influence functional takes the form

$$I = \exp \left[-\frac{1}{\hbar} \left(\sum_{k=1}^N \sum_{k'=0}^{k-1} (s_k^+ - s_{k'}^-) (\eta_{kk'} s_{k'}^+ - \eta_{kk'}^* s_{k'}^-) + \sum_{k=0}^N (\frac{1}{2} \eta_{kk} s_k^+{}^2 + \frac{1}{2} \eta_{kk}^* s_k^-{}^2 - \mu_{kk} s_k^+ s_k^-) \right) \right], \quad (14)$$

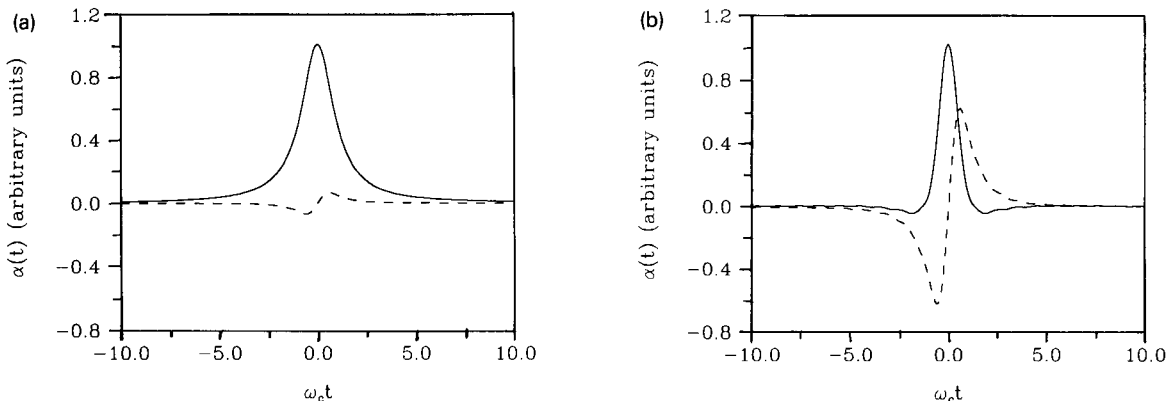


Fig. 1. (—) Real and (---) imaginary parts of the bath response function, Eq. (13), for the spectral density of Eq. (28). (a) $\beta\hbar\omega_c=0.2$ and (b) $\beta\hbar\omega_c=5.0$.

where $s_{\bar{N}}^{\pm} = s''$ and $s_{\bar{N}}^{\pm} = s'$. The coefficients $\eta_{kk'}$ and $\mu_{kk'}$ can be obtained by substituting the discretized path into the Feynman-Vernon expression Eq. (12) and have been given in ref. [14] for $T=0$. They depend only on the difference $\Delta k = k - k'$ if $k, k' \neq 0, N$.

In the discretized form, the above observations concerning the short range nonlocality of the influence functional imply that the magnitude of the coefficients $\eta_{kk'}$ should drop off rapidly as Δk increases. This circumstance invites neglecting in (14) those $\eta_{kk'}$ for which $|k - k'|$ is greater than a certain value, Δk_{\max} , which is roughly equal to the number of time steps needed to span the halfwidth of the kernel $\alpha(t - t')$. Since the QUAPI discretization permits using large time steps, Δk_{\max} should be small. If $\Delta k_{\max} \ll 1$, then the resulting path integral can be evaluated using the standard matrix multiplication procedure, where we refer to the grid points corresponding to pairs $\{s_{\bar{k}}^{\pm}, s_{\bar{k}'}^{\pm}\} \equiv \{s_{\bar{k}}^{\pm}\}$ collectively as an M^2 -dimensional vector (M being the number of DVR points) in order to conform with the conventional language used in wavefunction propagation. In other words, the dynamics in this approximation is Markovian. If the nonlocality extends over longer time, terms with $\Delta k > 1$ will have to be included to obtain accurate results; however, inclusion of such terms is not possible in the matrix multiplication scheme. The key idea of this paper then is that after discarding the negligible 'long-distance interactions' (with $|k - k'| > \Delta k_{\max}$), the resulting path integral can be evaluated iteratively by multiplication of a tensor of rank $2\Delta k_{\max}$. To illustrate this, we rewrite the influence functional (14) as a product of terms corresponding to different Δk ,

$$I = \prod_{k=0}^N I_0(s_{\bar{k}}^{\pm}) \prod_{k=0}^{N-1} I_1(s_{\bar{k}}^{\pm}, s_{\bar{k}+1}^{\pm}) \dots \prod_{k=0}^{N-\Delta k} I_{\Delta k}(s_{\bar{k}}^{\pm}, s_{\bar{k}+\Delta k}^{\pm}) \dots \prod_{k=0}^{N-\Delta k_{\max}} I_{\Delta k_{\max}}(s_{\bar{k}}^{\pm}, s_{\bar{k}+\Delta k_{\max}}^{\pm}), \quad (15)$$

where

$$I_0(s_{\bar{k}}^{\pm}) = \exp\left(-\frac{1}{2\hbar} (\eta_{kk} s_{\bar{k}}^{\pm 2} + \eta_{kk}^* s_{\bar{k}}^{\mp 2})\right) \exp\left(\frac{1}{\hbar} \mu_{kk} s_{\bar{k}}^{\pm} s_{\bar{k}}^{\mp}\right), \quad (16)$$

$$I_{\Delta k}(s_{\bar{k}}^{\pm}, s_{\bar{k}+\Delta k}^{\pm}) = \exp\left(-\frac{1}{\hbar} (s_{\bar{k}+\Delta k}^{\pm} - s_{\bar{k}+\Delta k}^{\mp}) (\eta_{k+\Delta k, k} s_{\bar{k}}^{\pm} - \eta_{k+\Delta k, k}^* s_{\bar{k}}^{\mp})\right), \quad \Delta k \geq 1. \quad (17)$$

Note that since $\eta_{k, k+\Delta k}$ does not depend on k for $0 < k < N - \Delta k$, then 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 can be propagated through time Δt by the matrix-vector multiplication,

$$\rho_s(s_{\bar{k}+1}^{\pm}; t + \Delta t) = \int ds_{\bar{k}}^{\pm} K(s_{\bar{k}}^{\pm}, s_{\bar{k}+1}^{\pm}) \rho_s(s_{\bar{k}}^{\pm}; t), \quad (18)$$

where

$$K(s_{\bar{k}}^{\pm}, s_{\bar{k}+1}^{\pm}) = \langle s_{\bar{k}+1}^{\pm} | \exp(-iH_0 \Delta t / \hbar) | s_{\bar{k}}^{\pm} \rangle \langle s_{\bar{k}}^{\mp} | \exp(iH_0 \Delta t / \hbar) | s_{\bar{k}+1}^{\mp} \rangle \quad (19)$$

is the propagator matrix for the bare system. In the case $\Delta k_{\max} = 1$ the influence functional amounts to a modification of this expression; specifically, $\tilde{\rho}(s_{\bar{N}}^{\pm}; N\Delta t) = A_1(s_{\bar{N}}^{\pm}; N\Delta t)$, where the vector A_1 is propagated iteratively according to

$$A_1(s_{\bar{k}+1}^{\pm}; (k+1)\Delta t) = \int ds_{\bar{k}}^{\pm} T_2(s_{\bar{k}}^{\pm}, s_{\bar{k}+1}^{\pm}) A_1(s_{\bar{k}}^{\pm}; k\Delta t). \quad (20)$$

Here T_2 is a propagator matrix,

$$T_2(s_{\bar{k}}^{\pm}, s_{\bar{k}+1}^{\pm}) = K(s_{\bar{k}}^{\pm}, s_{\bar{k}+1}^{\pm}) I_0(s_{\bar{k}+1}^{\pm}) I_1(s_{\bar{k}}^{\pm}, s_{\bar{k}+1}^{\pm}) \quad (21)$$

and the initial condition is

$$A_1(s_{\bar{0}}^{\pm}; 0) = \langle s_{\bar{0}}^{\pm} | \rho_s(0) | s_{\bar{0}}^{\mp} \rangle I_0(s_{\bar{0}}^{\pm}). \quad (22)$$

If N iterations are performed in this way, the resulting density matrix is exactly the result obtained from (10) where all η_{kk} , other than η_{kk} and $\eta_{k,k\pm 1}$ are neglected. Eq. (20) is again in the form of a matrix multiplication, but the propagator matrix is renormalized by the diagonal and nearest neighbor couplings of the influence functional. This results in loss of unitarity and introduces damping to the dynamics of the system due to its interaction with the bath.

Next we consider the case $\Delta k_{\max} = 2$, i.e. next nearest neighbor interactions are also included. Iterative evaluation of the path integral is again possible, but the matrix–vector multiplication must be replaced here by the multiplication of a tensor of rank 4 times a matrix (i.e. second rank tensor). For this purpose we define the matrix $A_2(s_k^\pm, s_{k+1}^\pm; k\Delta t)$ (k even) with the initial condition

$$A_2(s_0^\pm, s_1^\pm; 0) = \langle s_0^+ | \rho_s(0) | s_0^- \rangle I_0(s_0^\pm), \quad (23)$$

and the propagator tensor of rank 4,

$$T_4(s_k^\pm, s_{k+1}^\pm, s_{k+2}^\pm, s_{k+3}^\pm) = T_2(s_k^\pm, s_{k+1}^\pm) T_2(s_{k+1}^\pm, s_{k+2}^\pm) I_2(s_k^\pm, s_{k+2}^\pm) I_2(s_{k+1}^\pm, s_{k+3}^\pm). \quad (24)$$

The matrix A_2 is propagated through a time increment $2\Delta t$ according to the tensor multiplication

$$A_2(s_{k+2}^\pm, s_{k+3}^\pm; (k+2)\Delta t) = \int ds_k^\pm \int ds_{k+1}^\pm T_4(s_k^\pm, s_{k+1}^\pm, s_{k+2}^\pm, s_{k+3}^\pm) A_2(s_k^\pm, s_{k+1}^\pm; k\Delta t). \quad (25)$$

The interactions taken into account at each iteration step are shown in the diagram of Fig. 2. Finally, the reduced density matrix at time $t = N\Delta t$ (N even) is given by

$$\tilde{\rho}(s_N^\pm; N\Delta t) = A_2(s_N^\pm, 0; N\Delta t). \quad (26)$$

The tensor multiplication scheme for arbitrary Δk_{\max} can be constructed in a similar fashion.

4. Numerical examples

In this section, a number of examples are presented to illustrate the tensor multiplication method. The system is represented by a two-level system (TLS) with the Hamiltonian

$$H_0 = \hbar\Delta_0\sigma_x. \quad (27)$$

This is equivalent to the Hamiltonian for a symmetric double-well potential where only two DVR points are used to discretize the system coordinate. The system–bath interaction is given by Eq. (4) where the continuous coordinate s should be replaced by the Pauli spin operator σ_z . This model is convenient for testing the accuracy of the method because the coordinate in this model takes only two discrete values, ± 1 , and the dynamics of the reduced density matrix can be easily calculated for sufficiently long times (greater than the oscillation period of a free TLS) using Eq. (10), which amounts to multiple summation over two eigenvalues of pseudo-spin. We choose a spectral density of the form

$$J(\omega) = \gamma\omega \exp(-\omega/\omega_c). \quad (28)$$

The system–bath coupling strength is characterized by the Kondo parameter, $\xi = 2\gamma/\pi\hbar$. Fig. 3 presents plots of the average position, $\langle \sigma_z(t) \rangle = \text{Tr}(\tilde{\rho}(t)\sigma_z)$, as a function of $t\Delta_0$. The results were obtained by direct quadrature

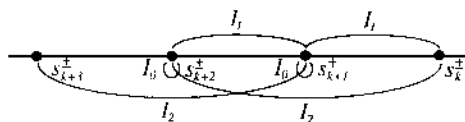


Fig. 2. A diagrammatic representation of Eqs. (24), (25).

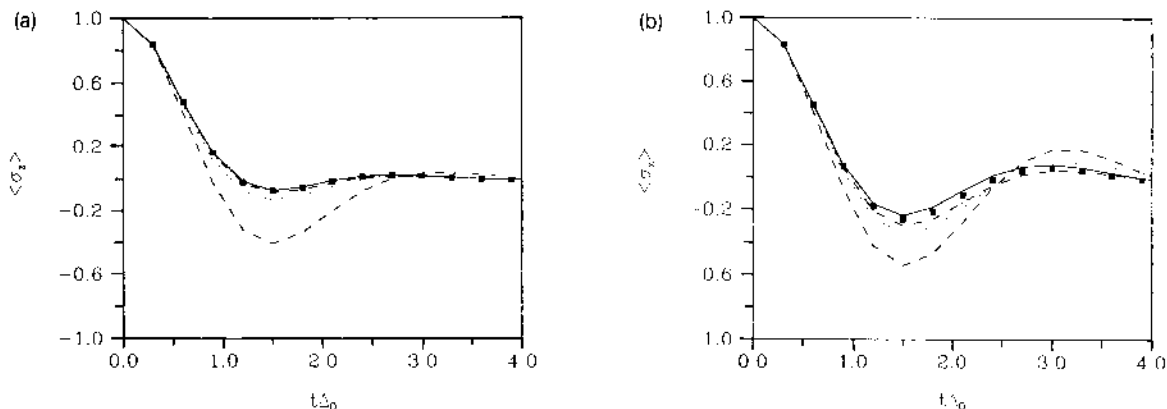


Fig. 3. The expectation value $\langle \sigma_z(t) \rangle$ for the model of a TLS, Eq. (27), coupled to a bath with ohmic spectral density, Eq. (28), plotted as a function of time using direct spin summation (exact QUAPI with two DVR points (—)) and the tensor multiplication method with $\Delta k_{\max} =$ (---) 0, (···) 1, (-·-·) 2 and (■) 3. The number of time slices used is $N=6$. The Kondo parameter ξ and value of $\beta \hbar \Delta_0$ are (a) $\xi=0.09, \beta \hbar \Delta_0=0.1$, and (b) $\xi=0.5625, \beta \hbar \Delta_0=10.0$; the cutoff frequency is $\omega_c=2.5 \Delta_0$.

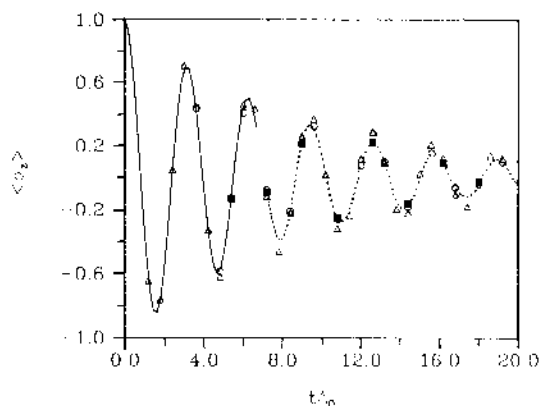


Fig. 4. The expectation value $\langle \sigma_z(t) \rangle$ for the model of a TLS, Eq. (27), coupled to a bath with ohmic spectral density, Eq. (28), plotted as a function of time using direct spin summation (solid line) and the tensor multiplication method with $\Delta k_{\max} =$ (Δ) 1, (\circ) 2 and (\blacksquare) 3. The dotted line is a guide to the eye. The time step used in the matrix multiplication method is $0.6/\Delta_0$. The results of the direct spin summation are given only for those times for which convergence with respect to the number N of time slices can be obtained with $N \leq 10$. The cutoff frequency is $\omega_c=2.5 \Delta_0$, the Kondo parameter $\xi=0.09$, and $\beta \hbar \Delta_0=5.0$.

using the full influence functional, Eq. (14), and by the tensor multiplication method with $\Delta k_{\max}=0, 1, 2$ and 3. For both temperatures considered, the results of the tensor multiplication method rapidly converge to the exact ones as Δk_{\max} is increased, even though the cutoff frequency has not been chosen very large and the memory effects are significant. Specifically, the tensor multiplication scheme is practically exact at $\Delta k_{\max}=2$ in the case of a high temperature bath, and inclusion of the $\Delta k_{\max}=3$ term yields almost exact results in the low temperature case.

For the TLS model one can evaluate Eq. (10) by full summation with N practically up to 10, and the maximum allowed time step Δt imposes a limitation on the maximum time for which accurate dynamics can be obtained. With the present method, however, one can evaluate the path integral for arbitrary N (with the same time slice Δt), as demonstrated in Fig. 4. In Fig. 4, the time dependence of $\langle \sigma_z(t) \rangle$ is plotted using Eq. (10) for times up to the maximum time for which the full path integral calculation converges (solid line), and con-

tinued for longer times using the present method (discrete points). For those times where the full QUAPI result is available, the result given by the tensor multiplication method with $\Delta k_{\max} = 3$ is seen to be practically exact, and one can also see from this Figure that the accuracy of the tensor multiplication method (the convergence with respect to Δk_{\max}) does not deteriorate as time increases. This fact implies that one is able to calculate the dynamics for arbitrarily long times.

5. Concluding remarks

Recently a good deal of effort has been spent on attempts to prove or disprove the so-called ‘quantum regression hypothesis’ that the relaxation of an open quantum system to equilibrium is described by a Markovian process without memory. Studies of system–bath models have shown that this hypothesis is valid only in the weak coupling limit and at high enough temperatures (see, e.g., refs. [20–22], and references therein). In this Letter we have demonstrated that if the evolution of the reduced density matrix is non-Markovian but the memory effects have a finite range – which is indeed the case for the spectral densities conventionally used to describe system–bath interactions in condensed phase – then a tensor can be constructed, which obeys the Markovian dynamics with the desired accuracy.

A crucial ingredient of our method is the use of the QUAPI discretization, which permits the time increment to be large enough such that the range of nonlocal interactions in the influence functional extends over only a few time steps, resulting in a propagator tensor of small rank. This appears to be true for a wide range of parameters, because while the memory range of the influence functional increases with decreasing cutoff frequency of the bath, and the dynamics becomes less Markovian, the time step allowed by the QUAPI representation also increases, preventing Δk_{\max} from becoming very large. Use of the iterative scheme proposed in this paper allows exact quantum calculation of the dynamics in a condensed phase system for arbitrarily long times, which has not been possible in the past. We thus expect this methodology to prove extremely useful for exploring intriguing quantum effects associated with long time coherences in condensed matter environments.

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