Real time path integral methods for a system coupled to an anharmonic bath

Gregory Ilk and Nancy Makri
School of Chemical Sciences, University of Illinois, Urbana, Illinois 61801
pp. 6708-6716
Real time path integral methods for a system coupled to an anharmonic bath

Gregory Ilk and Nancy Makri
School of Chemical Sciences, University of Illinois, Urbana, Illinois 61801

(Received 21 January 1994; accepted 28 June 1994)

We propose an efficient path integral scheme for calculating the quantum dynamics of an arbitrary one-dimensional system coupled nonlinearly to many anharmonic noninteracting "bath" degrees of freedom. The starting point is an improved discretization of the path integral in terms of numerically constructed propagators [Chem. Phys. Lett. 193, 435 (1992)]. The resulting influence functional is comprised of one-dimensional correlation functions with step-structured time-dependent potentials and therefore is similar in structure to that employed in the spin-boson calculations of Coakon [J. Chem. Phys. 86, 995 (1987)]. In the present case, though, the influence functional is nonlinear and is computed using numerical iterative wave function propagation methods. Numerical tests on a system coupled to ten anharmonic oscillators demonstrate the efficiency of the proposed scheme, which requires numerical effort that scales only linearly with the number of anharmonic bath degrees of freedom.

I. INTRODUCTION

Significant progress has been made in recent years toward the development of accurate methods for studying the quantum dynamics of chemical systems. Efficient schemes for eigenstate calculations or iterative wave function propagation have proven extremely valuable for systems with only a few atoms but are not practical for studying polyatomic reactions or condensed phase processes where the number of coupled degrees of freedom is large. Substantial attention has been given to Feynman's path integral representation of quantum mechanics,\textsuperscript{1} with the hope that it may lead to algorithms applicable to many-particle problems.

From a numerical point of view, the most appealing feature of the path integral formulation is perhaps that it does not require manipulation of Hamiltonian matrices or storage of multidimensional wave function vectors; for this reason the path integral appears a very attractive candidate among quantum mechanical methods for multidimensional problems. Instead, all dynamical characteristics are included in a discrete path representation of the propagator. For a general time-independent \( n \)-dimensional Cartesian Hamiltonian

\[
\hat{H} = \sum_{i=1}^{n} \frac{\hat{p}_i^2}{2m} + V(\hat{x}_1, \ldots, \hat{x}_n) \tag{1.1}
\]

the discretized path integral expression for the coordinate representation of the propagator is

\[
\langle \mathbf{x}_N | e^{-i\hat{H}t/N} | \mathbf{x}_0 \rangle = \int d^n\mathbf{x}_1 \cdots \int d^n\mathbf{x}_{N-1} \\
\times \prod_{k=1}^{N} \langle \mathbf{x}_k | e^{-i\hat{H}\Delta t/k} | \mathbf{x}_{k-1} \rangle, \tag{1.2}
\]

where \( \mathbf{x}_N \equiv \mathbf{x}_1 \). Each set of coordinate points \( \{\mathbf{x}_0, \mathbf{x}_1, \ldots, \mathbf{x}_N\} \) in Eq. (1.2) defines an \( N \)-point discretization of a path that connects the two endpoints \( \mathbf{x}_0 \) and \( \mathbf{x}_N \) in time \( t \), and \( \Delta t = t/N \) is the time step. The advantage of breaking up the propagator according to Eq. (1.2) is that short time propagators are relatively easy to approximate. Traditionally, short time propagators have been constructed by partitioning the Hamiltonian into kinetic and potential energy terms and approximating the time evolution operator by a (symmetrized) product of exponentials. This procedure introduces numerical error that is kept small by restricting the size of the time increment \( \Delta t \) and requires very fine time slicing if the desired propagation time is long.

As mentioned above, in order to avoid storing large-dimensional matrices the propagation must not be performed in an iterative fashion, and the \( n \times (N-1) \) dimensional integral in Eq. (1.2) must be evaluated by global (multidimensional) integration methods. If the dimensionality of the discretized path integral is large, Monte Carlo techniques\textsuperscript{2} provide the only known option. Monte Carlo path integral methods have proven extremely useful for simulating equilibrium (i.e., imaginary time) properties of many-particle spinless (or boson) systems. In contrast, the case of real time dynamics appears substantially more difficult to deal with and has been a topic of intense research activity. The difficulty lies in the inefficiency of statistical sampling techniques when used to integrate functions of alternating sign, which occur in the case of real time dynamics due to the oscillatory nature of the quantum time evolution operator.

Significant advances have been made during the last few years in the development of stationary phase based Monte Carlo methods for evaluating real time path integrals.\textsuperscript{3-7} Though fairly successful for sufficiently short time, the algorithms developed converge extremely slowly if the time interval exceeds one or two periods of the motion. The convergence problem, known as the "sign problem," is inherent in real time quantum dynamics—even in the strict semiclassical limit.

A dramatic reduction of the required number of integrations is possible if the Hamiltonian can be described by a system coordinate \( s \) coupled to a bath of harmonic oscillators \( Q_j \). The so-called system–harmonic bath Hamiltonian,
\[ \hat{H} = \frac{\hat{p}_s^2}{2m_s} + V_0(\hat{\mathbf{s}}) + \sum_{j=1}^{n} \left[ \frac{\hat{p}_{j}^2}{2m_j} + \frac{1}{2} m_j \omega_j^2 \hat{\mathbf{Q}}_j^2 - f_j(\hat{\mathbf{s}}) \hat{Q}_j \right]. \] (1.3)

is known to offer a successful description of many problems in condensed phase chemistry and physics and has received a great deal of attention. In addition, system–bath models have been utilized in reaction path Hamiltonian descriptions of polyatomic chemical reactions.\(^3\) The propagator for harmonic degrees of freedom involves the coordinates in Gaussian form, and thus all harmonic bath degrees of freedom in Eq. (1.2) can be integrated analytically. This leads to a path integral expression for the system coordinate, with the effects of the bath described by an influence functional \( I \),

\[
\langle s_N | Q_N | e^{-i\hat{H}t/\hbar} | s_0 | Q_0 \rangle = \int_{-\infty}^{s_N} ds_1 \cdots \int_{-\infty}^{s_{N-1}} ds_1 \cdots \int_{-\infty}^{s_N} ds_{N-1} \times \prod_{k=1}^{N} \langle s_k | e^{-i\hat{H}_{\Delta t_k}/\hbar} | s_{k-1} \rangle \times I(s_0, s_1, \ldots, s_N; Q_0, Q_N; \Delta t). \] (1.4)

Equation (1.4) involves only the system coordinate; the multidimensional nature of the problem is incorporated in the influence functional. Due to the nonlocal character of the influence functional, Eq. (1.4) does not correspond to a local Schrödinger equation and therefore must be evaluated by multidimensional integration methods which are bound to suffer from the sign problem if \( N \) is large.

A different numerical methodology has been introduced recently by one of the authors\(^1^0\) and applied to a number of multidimensional system–bath problems.\(^1^1,^1^2\) The key idea is to use a physically motivated reference Hamiltonian to split the time evolution operator, employing \emph{exact} numerical methods to compute the reference propagator. Provided that a reasonable reference system is chosen, this procedure guarantees propagators accurate for large time steps, and therefore leads to path integral expressions that converge with few time slices. In the particular case of a reaction coordinate coupled to a harmonic bath we have found that the Hamiltonian along the adiabatic path often provides a qualitatively correct picture of the dynamics. Using that as the reference Hamiltonian, a \emph{quasi-adiabatic propagator} is constructed\(^1^0\) that describes the exact dynamics along the adiabatic path, while multidimensional nonadiabatic effects due to the bath enter as Franck–Condon factors in an influence functional. A series of recent papers by our group have demonstrated that the number of time slices required for convergence is so small in this scheme that the resulting integrals can be performed by numerical quadrature, thus circumventing the sign problem. Several calculations have already been performed with the quasidiabatic propagator path integral methodology that were not possible by other techniques.\(^1^1,^1^2\) Finally, by extending these ideas, an \emph{iterative} scheme has been proposed\(^1^3\) for condensed phase dynamics, which allows propagation of reduced density matrices for arbitrarily long times.

In this paper we pursue the question of how to perform multidimensional path integral calculations when most degrees of freedom cannot be described properly by harmonic potentials. While the construction of improved numerical propagators can significantly reduce the required number of time slices for \emph{any} (arbitrary) Hamiltonian (assuming a reasonable reference can be found), the dimension of the resulting integral may still be prohibitively large if all degrees of freedom appear explicitly. Rather than attempting to deal with the most general (and demanding) situation, we consider here a generalization of the system–bath Hamiltonian. Specifically, in the present paper we retain the system–bath structure, but allow the bath degrees of freedom to be anharmonic and the system–bath coupling functions to have arbitrary form. For example, the Hamiltonian may be expressible as

\[ \hat{H} = \frac{\hat{p}_s^2}{2m_s} + V_0(\hat{s}) + \sum_{j=1}^{n} \left[ \frac{\hat{p}_{j}^2}{2m_j} + V_j(\hat{s}, \hat{Q}_j) \right], \] (1.5)

where \( V_j \) are arbitrary functions.

It is clear that the above system–anharmonic bath Hamiltonian is not sufficiently flexible to offer a valid description of arbitrary chemical processes. For example, Eq. (1.5) cannot be expected to provide a microscopic picture of a complex system such as a fluid, where each atom interacts with many neighboring atoms via complex nonlinear forces. Condensed phase systems, though, are often (within the regime of validity of linear response theory) described adequately by effective harmonic modes and therefore can be treated by path integral methods specific to harmonic baths. The present paper focuses on certain molecular systems of intermediate size, in which several anharmonic vibrations are strongly coupled to the coordinate of interest. Although Eq. (1.5) excludes interactions off-diagonal in the bath, it is otherwise quite flexible and is expected to offer an improved description of various molecular processes. For example, a Hamiltonian of this type would arise naturally out of a reaction path description of a polyatomic process, where the reaction coordinate would be allowed to couple anharmonically to the orthogonal vibrational modes that can be included beyond second order from known cubic and quartic force fields. Dynamical effects due to diagonal bath anharmonicity may be fairly substantial in many cases and should be examined. Furthermore, Eq. (1.5) allows to include several dissociation channels which may be necessary in order to deal with weakly bound degrees of freedom. Finally, we anticipate that the system–anharmonic bath model will be useful for the study of intramolecular vibrational relaxation (IVR) processes. We will comment more extensively on the utility of system–anharmonic bath models for such processes in the Conclusions.

Compared to an arbitrary multidimensional Hamiltonian, the practical advantage offered by the system–anharmonic bath Hamiltonian of Eq. (1.5) is that it leads to a path integral with the effects of the anharmonic bath incorporated in an influence functional that factorizes into independent mode contributions. However, unlike the harmonic bath case, the influence functional cannot be obtained in closed form for
general anharmonic potentials, and we propose a numerical scheme for evaluating it. The method involves one-dimensional wave function propagation in a time-dependent Hamiltonian for each bath mode and requires numerical effort that scales linearly with the number of anharmonic degrees of freedom coupled to the system coordinate, thus allowing numerical calculations with many bath modes.

The concepts involved in our scheme for calculating the nonlinear influence functional are not new. In the specific case where the bath is harmonic, Feynman and Vernon\textsuperscript{14} have shown that the influence functional from each mode is essentially the correlation function of a forced harmonic oscillator with a time-dependent force. A discrete version of this time-dependent force appeared in the spin-boson calculation of Coielson,\textsuperscript{15} where the time dependence was caused by spin flips along each path of the two-level system. In this sense, the scheme proposed in this paper can be viewed as a generalization of Coielson's spin-boson approach, applicable to an arbitrary system described by a continuous potential coupled to a bath of modes which, though not interacting directly with one another, are anharmonic and therefore must be treated by numerical techniques.

Section II reviews the path integral methodology with numerically constructed propagators and introduces the influence functional for a general (anharmonic) bath. In Sec. III a numerical scheme is proposed for evaluating the anharmonic influence functional. Section IV completes the methodology description by outlining the discrete variable representation that we adopt to evaluate the path integral over the system coordinate. Some numerical examples are presented in Sec. V, and Sec. VI concludes with general remarks and future applications.

II. DISCRETIZED PATH INTEGRAL WITH NUMERICALLY CONSTRUCTED PROPAGATORS

As discussed in the Introduction, propagators accurate for long time can be constructed by identifying a suitable reference Hamiltonian whose propagator can be computed exactly using basis set methods.\textsuperscript{10,16} The Hamiltonian is expressed in terms of a one-dimensional reference part $H_0$ involving the system coordinate alone and a set of anharmonic degrees of freedom coupled to the system

$$\hat{H} = H_0(\hat{s}, \hat{p}_s) + \sum_{j=1}^{n} H_j(\hat{s}, \hat{Q}_j, \hat{p}_j).$$ (2.1)

The one-dimensional system part may provide a good reference if the bath is coupled to the system solely via anharmonic terms and/or the time scales for system and bath are similar. In that case

$$\hat{H}_0 = \frac{\hat{p}_s^2}{2m_s} + V_0(\hat{s})$$

and

$$\hat{H}_j = \frac{\hat{p}_j^2}{2m_j} + V_j(\hat{s}, \hat{Q}_j).$$ (2.2)

On the other hand, if the most significant bath degrees of freedom involve frequencies higher than that of the system and are coupled linearly to the $s$ coordinate, then a renormalized system Hamiltonian with the potential along the adiabatic path\textsuperscript{4,10} seems more appropriate as a reference. Specifically, one minimizes the potential for fixed values of the system coordinate, solving (analytically or numerically)

$$\frac{\partial}{\partial Q_j} V_j(s, Q_j) = 0$$ (2.3a)

to obtain an equation for the adiabatic path in the form

$$Q_j = \xi_j(s).$$ (2.3b)

The adiabatic potential is

$$V_{ad}(s) = V_0(s) + \sum_{j=1}^{n} V_j[s, \xi_j(s)].$$ (2.3c)

Therefore, in that case the reference Hamiltonian for the system is

$$\hat{H}_0 = \frac{\hat{p}_s^2}{2m_s} + V_{ad}(\hat{s})$$ (2.4a)

and the bath oscillators have their equilibrium positions shifted along the adiabatic path

$$\hat{H}_j = \frac{\hat{p}_j^2}{2m_j} + V_j(\hat{s}, \hat{Q}_j) - V_j[\hat{s}, \xi_j(\hat{s})].$$ (2.4b)

Using the partitioning of the Hamiltonian described in Eq. (2.1), the time-evolution operator is split symmetrically

$$\exp\left(-i \frac{\hat{H}}{\hbar} \Delta t\right) = \exp\left(-i \frac{\Delta t}{\hbar} \sum_{j=1}^{n} \hat{H}_j\right) \times \exp\left(-i \frac{\Delta t}{\hbar} \hat{H}_0 \Delta t\right) \times \exp\left(-i \frac{\Delta t}{\hbar} \sum_{j=1}^{n} \hat{H}_j\right).$$ (2.5)

In zero-temperature gas-phase dynamics and spectroscopy, one is usually interested in the survival amplitude of a state, i.e., the correlation of a given initial wave function $\Psi_0$ with the wave function $\Psi(t)$ that develops after time $t$. The survival probability is defined as the square of the survival amplitude,

$$P(t) = |\langle \Psi_0 | \Psi(t) \rangle|^2.$$ (2.6)

If the above expression is modified to include a dipole moment operator, it can be related through Fourier transforms to line shapes observed spectroscopically. For simplicity we will focus on the calculation of the survival amplitude throughout this paper. Furthermore, we assume that there is no correlation among different bath modes initially, so that the wave function has the form

$$\Psi_0(s, Q_1, \ldots, Q_n) = \prod_{j=1}^{n} \phi_j(s, Q_j).$$ (2.7)
This assumption is essential for the proposed scheme, yet quite reasonable for many intramolecular processes. (Often the initial state is completely factorizable, i.e., \( \phi_j \) depends only on the corresponding bath coordinate \( Q_j \).)

Adopting the splitting of the time evolution operator given in Eq. (2.5), and inserting repeatedly the identity operator in terms of eigenstates of the system position operator,

\[
1 = \int ds_0 |s_0\rangle \langle s_0|
\]

the discretized path integral representation of the survival amplitude takes the form

\[
\langle \Psi_0 | \Psi(t) \rangle = \int ds_0 \int ds_1 \cdots \int ds_N \chi_0(s_0) \chi_0(s_N) \\
\times \prod_{k=1}^N \langle s_k | e^{-iH_0 \Delta t / \hbar} | s_{k-1} \rangle \\
\times \prod_{j=1}^n \langle \phi_j(s_N) | e^{-iH_j(s_j) \Delta t / 2\hbar} | \phi_j(s_0) \rangle
\]

\[
\times e^{-iH_j(s_1) \Delta t / \hbar} e^{-iH_j(s_0) \Delta t / 2\hbar} | \phi_j(s_0) \rangle
\]

(3.1)

constitutes the influence functional which describes the effects of the bath (with the initial state described by the functions \( \phi_j \)) on the dynamics of the system. The influence functional depends on the discretized system path \( \{s_k, k=0,\ldots,N\} \) through the potential coupling terms and possibly also through the initial wave functions.

In general, the influence functional cannot be obtained in closed form if the bath is characterized by arbitrary potential functions. However, its product structure allows the influence functional to be evaluated by a separate calculation for each bath degree of freedom, rather than requiring a single multidimensional calculation. In this section we describe a numerical scheme suitable for calculating anharmonic influence functionals.

Reading Eq. (3.1) from right to left with a particular realization \( \{s_0, s_1, \ldots, s_N\} \) of a system path, it is seen that each factor \( j \) involves a given initial state \( |\phi_j\rangle \) that is propagated initially for half a time step under the Hamiltonian \( H_j \) for that bath mode; \( H_j \) includes interaction with the system, but the system coordinate is kept constant at the value \( s_0 \) during this time interval and thus appears as a parameter. The state that develops at time \( \Delta t / 2 \) is subsequently propagated for a full time step by the evolution operator for the bath Hamiltonian \( H_j \) but with the value of the system coordinate fixed at \( s_1 \). This process is repeated with the bath Hamiltonian at each step evaluated at the appropriate value of the system coordinate, until the total time \( t \) is reached. Finally, the state that has been generated at the final time \( t \) is projected onto the initial state to yield the survival amplitude.

Therefore, the influence functional is composed of independent mode correlation functions, each one of which involves propagation of the initial state under a time-dependent Hamiltonian that arises from the system–bath interaction evaluated at a value of the system coordinate determined by the instantaneous position of the system on the particular discrete path. As the system position increments by discrete amounts in the present discretization of the path integral, the bath Hamiltonian changes in a stepwise fashion. This particular time dependence of the “force” (which is different from that resulting from straightforward discretization\(^{17}\) of the Feynman–Vernon\(^{16}\) action) arises from the exact treatment of the system dynamics and is very similar to that discussed by Coalsin\(^{15}\) in his study of the spin-boson dynamics. Our scheme is more general, though, as it applies to an arbitrary system described by a general continuous potential; in addition, we allow the bath to be anharmonic (though it must be separable) and thus we must resort to numerical methods to calculate the bath correlation function appearing in the influence functional.
It is clear from the above that one can use standard one-dimensional wave function propagation algorithms (allowing for sudden changes of the potential) to calculate each factor in the influence functional. However, speed is of essential importance for the present purpose, as the propagation scheme will have to be repeated for each distinct realization of the system path \( \{ s_j \} \).

Among several widely used propagation schemes, we found propagator matrix multiplication in a basis set most efficient for this task. Specifically, for each bath degree of freedom \( j \) we construct a basis set of functions \( \psi_{jm} \), \( m = 1, \ldots, M_j \); these are one-dimensional functions that are chosen as eigenstates of a reasonable zeroth order Hamiltonian for the bath, e.g., as the eigenstates of \( H_j \) with the system-bath coupling turned off. Next, the \( n M_j \) \( M_j \)-dimensional vectors
\[
\langle \psi_{jm} | e^{-i H_j(s) \Delta t / \hbar} | \psi_{jm} \rangle
\]
and the \( n M_j \)-dimensional vectors
\[
\langle \psi_{jm} | e^{-i H_j(s) \Delta t / 2 \hbar} | \phi_j(s) \rangle
\]
are constructed for all values of \( s \) on the chosen grid. These propagators are easily obtained from diagonalization of the coupled bath Hamiltonians \( H_j(s) \) at each grid value of the system coordinate. The influence functional for each bath mode (for a given realization of the system path) is obtained by sequential multiplication of the instantaneous propagator matrix times the corresponding wave function vector, e.g.,
\[
\langle \psi_{jm} | e^{-i H_j(s_j) \Delta t / \hbar} e^{-i H_j(s_0) \Delta t / 2 \hbar} | \phi_j(s_0) \rangle
\]
\[
= \sum_{m' = 1}^{M_j} \langle \psi_{jm} | e^{-i H_j(s_1) \Delta t / \hbar} | \psi_{jm'} \rangle
\]
\[
\times \langle \psi_{jm'} | e^{-i H_j(s_0) \Delta t / 2 \hbar} | \phi_j(s_0) \rangle,
\]
etc. For typical bound bath potentials a basis of a few zeroth order eigenstates is usually adequate for convergence, so that the dimension of these matrices is generally small and the multiplication process very efficient.

**IV. DISCRETE VARIABLE REPRESENTATION OF THE PATH INTEGRAL**

Since the \((N+1)\)-dimensional integral over system coordinates in Eq. (2.8) is not well-suited for Monte Carlo integration, quadrature methods provide the only alternative. Clearly, for quadrature schemes to be practically feasible for multidimensional integration, the number of grid points must be kept as small as possible. A very efficient quadrature method suitable for the evaluation of path integrals with influence functionals has been proposed recently. This method employs a discrete variable representation (DVR) grid chosen to diagonalize the system position operator in the basis of eigenstates of the reference Hamiltonian \( \bar{H}_0 \); i.e., a potential-optimized DVR (Ref. 21) is used for the system coordinate.

![Figure 1](image)

**FIG. 1.** The real and imaginary parts of the effective system propagator, Eq. (2.9), constructed numerically in terms of 10 eigenstates of the system Hamiltonian for the Morse oscillator model used in Sec. V. The time step is 10 fs.

The DVR basis is constructed by performing a unitary transformation on the basis \( \{ \Phi_i \} \) of the \( K \) lowest energy eigenstates of \( \bar{H}_0 \) that are used in the effective system propagator
\[
| u_i \rangle = \sum_{i' = 1}^{K} L_{ii'} | \Phi_i \rangle.
\]
(4.1a)

The orthogonal transformation matrix \( L_{ii'} \) is chosen to diagonalize the system position operator \( \hat{s} \),
\[
(u_i | \hat{s} | u_{i'}) = s^{DVR}_{i} \delta_{ii'} .
\]
(4.1b)

The DVR states \( | u_i \rangle \) correspond to the discrete analog of ordinary coordinate eigenstates, and the eigenvalues \( s^{DVR}_{i} \), \( i = 1, \ldots, K \) form the DVR grid. The construction of the \( | u_i \rangle \) basis via a rotation of the eigenstate basis implies that the required number of DVR states will be small, and the DVR grid may be quite sparse; yet, the potential coupling operator is diagonal in the DVR basis, leaving the influence functional unaltered.

Discretization of the path integral in the DVR basis and repeated use of the spectral expansion for the bath time-evolution operator,
\[
e^{-i \bar{H}_j(t)} \langle t' | \hat{\phi}_j \hat{\rho}_j \rangle = \sum_{i = 1}^{K} | u_i \rangle e^{-i \bar{H}_j(t')} | \hat{\phi}_j \hat{\rho}_j \rangle \langle u_i |,
\]
leads to the following DVR representation of Eq. (2.8) for the survival amplitude.
\[
\langle \Psi_0 | \Psi(t) \rangle = \sum_{i_0=1}^{K} \cdots \sum_{i_N=1}^{K} \langle \chi_0 | u_{i_N} \rangle \\
\times \left( \prod_{k=1}^{N} \langle u_{i_k} | e^{-i\hat{H}_0\Delta t/k} | u_{i_{k-1}} \rangle \right) \langle u_{i_0} | \chi_0 \rangle \\
\times I(s_0^{DVR}, \cdots, s_N^{DVR}; \Delta t).
\]

(4.3)

The DVR representation of the one-dimensional propagator for the system Hamiltonian \( \hat{H}_0 \) is constructed numerically with the aid of the basis transformation relations, Eq. (4.1),

\[
\langle u_{i} | e^{-i\hat{H}_0\Delta t/k} | u_{i'} \rangle = \sum_{m=1}^{K} L_{i,m} e^{-i\epsilon_{m}\Delta t/k}.
\]

(4.4)

Equation (4.3) gives the survival amplitude in the form best suited for numerical calculations. The discretized path integral over the system coordinate has been converted into a multiple sum over a grid that is rather sparse because it corresponds to the optimal DVR basis. [In practice, the number \( K \) of DVR points required for convergence of Eq. (4.3) in the case of the coupled Hamiltonian is only slightly larger than the minimum number of states necessary to represent the one-dimensional system propagator.] The system propagators in the DVR representation are generated from Eq. (4.4) at the beginning of the calculation and stored. The influence functional is calculated according to the matrix multiplication scheme described in the previous section, with the discretized system paths taking values from the DVR grid.

V. NUMERICAL EXAMPLES

To illustrate the methodology presented in Secs. II–IV, we present in this section numerical examples for the relaxation dynamics of a system coupled to an anharmonic bath, Eq. (1.5). The system is described by a Morse potential,

\[
V_0(s) = D_0(e^{-2\alpha_0 s} - 2e^{-\alpha_0 s}),
\]

(5.1)

with well depth \( D_0 = 0.01 \) a.u. and harmonic frequency at the minimum \( \omega_0 = 0.003 \) a.u. The bath oscillators are also described by Morse potentials coupled nonlinearly to the system coordinate

\[
V_f(s_i, Q_i) = D_f(e^{-2\alpha_f Q_i} - 2e^{-\alpha_f Q_i}) - c_f e^{-\lambda^2 s_i^2} e^{-\lambda^2 Q_i^2} Q_i,
\]

(5.2)

where \( \lambda = 10^{-5} \) a.u. Mass-weighted coordinates are used for all degrees of freedom.

In the numerical calculations shown in the figures the bath consists of either \( n = 1 \) or \( n = 10 \) degrees of freedom. The harmonic frequencies are chosen from a Debye distribution and range from 0.0002 to 0.00139 a.u. The coupling constants are proportional to the harmonic frequencies, \( c_f = \gamma \omega_f n^{1/2} \), with \( \gamma = 10^{-3} \) a.u. The well depth is equal to 0.1 a.u. for all bath oscillators. With these parameters, both the system and the bath are very anharmonic; the number of bound states in these Morse potentials is 6 for the system and ranges from 10 to 22 for the bath degrees of freedom. The initial state is chosen as the \( \nu = 3 \) eigenstate of the system Hamiltonian, with all bath oscillators in the ground state; at this excitation, the classical frequency of the system is equal to 0.47 of the frequency at the potential minimum and therefore the system is initially nearly resonant with the highest frequency bath modes. The reference Hamiltonian for the path integral calculation includes the system potential alone [see Eq. (2.2)].

Figure 2 shows the evolution of the survival probability, Eq. (2.6), in the case where the bath consists of a single degree of freedom. The reason for presenting this calculation is to demonstrate that the methodology described in Secs. II–IV converges rapidly to the exact result, which can be obtained for a two-dimensional Hamiltonian using standard techniques. The complex nature of the dynamics is best visualized in Fig. 3, which shows a contour plot of the probability density (i.e., the absolute square of the wave function) at 0, 40, and 70 fs. The peaks following the fast initial decay of the survival probability are small, reflecting the strong anharmonicity of the Hamiltonian. Path integral results are shown for \( N = 1, 5 \) time slices and compared to those obtained with the split propagator algorithm. The influence functional was calculated as described in Sec. III using a basis of 10 states for the bath oscillator. It is seen that the path integral calculation converges rapidly to the exact quantum results; this is so because the zeroth order propagators are obtained in the present scheme from a reasonable reference, which incorporates the entire separable part of the potential. However, the initial state is chosen such that it would not evolve at all under the action of the (separable) reference Hamiltonian alone; dynamical effects result from system–bath coupling, which is described entirely by the influence functional. Thus, the results shown in this and in subsequent figures constitute nontrivial tests of our path integral methodology.

Figure 4 shows the convergence of the path integral as a function of the number \( N \) of time slices for a ten-degree-of-freedom bath. Because of the particular scaling of the cou-
pling constants that was used, the time scale of the initial decay is similar to that in the case of a single bath oscillator. However, recurrences are now quenched due to the relatively large number of degrees of freedom available, and the decay of the survival probability is exponential for the most part. The convergence of the path integral with $N$ is seen to be just as good as in the case of Fig. 1, allowing efficient and reliable calculation of the dynamics. We note that for a given value of $N$, the numerical effort required for the calculation with ten bath oscillators was just ten times that needed for the single oscillator model of Fig. 1.

In Fig. 5 we illustrate the efficiency of the system-optimized discrete variable representation of the path integral. Shown is the survival probability in the case of the ten-oscillator bath for different values of $K$, the number of DVR grid points used to discretize the system coordinate integrations. All curves were obtained with three time slices of the path integral, since Fig. 2 indicates that the time discretization is almost exact at that value of $N$. It is seen that convergence is achieved with about 10 DVR points. The adequacy of such a small grid reflects the advantages of DVR methods, which have been exploited as much as possible in the present scheme by constructing DVR states in terms of the true eigenstates of the reference Hamiltonian.

Finally, Fig. 6 demonstrates the convergence of the iterative evaluation of the influence functional proposed in Sec. III. The survival probability (for the ten-degree-of-freedom bath) is plotted vs time using $M=3$, 5, and 10 basis functions for each anharmonic bath oscillator. About 5 to 10 basis functions are sufficient to yield exact results, and therefore iterative evaluation of the influence functional via matrix-vector multiplication is very efficient.

FIG. 3. Contour plots of the potential and the absolute value of the wave function in the case of the single-bath oscillator model of Sec. V at (a) 0, (b) 40, and (c) 70 fs.

FIG. 4. Same as Fig. 2, but with the system coupled to ten Morse oscillators (see Sec. V).

VI. CONCLUDING REMARKS

The numerical examples presented in Sec. V demonstrate the practical usefulness of the methodology proposed in this paper. The factorization and iterative evaluation of the influence functional results in an efficient scheme for calculating the time evolution of quantum system—anharmonic bath Hamiltonians without introducing any ad hoc assumptions. Unlike other exact methods, the numerical effort of the present scheme scales linearly with the number of bath degrees of freedom and thus the method is applicable to multidimensional Hamiltonians of arbitrary (diagonal in the bath) anharmonicity.

We plan to use this methodology to gain insight into a number of questions. An important problem in intramolecular dynamics concerns the rate and specific patterns of internal energy flow during vibrational relaxation. Anharmonicity plays a very important role in this problem, and the model of an anharmonic bath coupled nonlinearly to a local mode may provide a realistic, yet manageable multidimensional Hamiltonian for which the exact quantum dynamics can be calculated. For this purpose one can choose the system coordinate as the initially excited local mode, with the "bath" degrees of freedom described by anharmonic (e.g., Morse-type) potentials in the normal mode coordinate system of the remaining molecular bonds. In this case the strong local mode coupling between system and bath (which is taken into account exactly by our scheme) should dominate the dynamics at short to intermediate times, while the anharmonic character of the bath should allow observation of interesting relaxation mechanisms. Another question of interest is related to the role of anharmonicity on tunneling rates; this is an unexplored question with relevance to gas-phase spectroscopy, since observed tunneling splittings in polyatomic molecules are strongly modulated by coupled intramolecular vibrations which, if excited, may become considerably anharmonic. Exploring some of these questions will be a topic of future research by our group.

ACKNOWLEDGMENTS

Acknowledgment is made to the Donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial support of this research. We are grateful to the referee for bringing Ref. 15 to our attention. N.M. is a recipient of a Beckman Young Investigator Award, a NSF Young Investigator Award and a Packard Fellowship for Science and Engineering.

9 For reviews, see (a) W. H. Miller, J. Phys. Chem. 87, 3811 (1983); (b) in The Theory of Chemical Reaction Dynamics, edited by D. C. Clark (Reidel, Boston, 1986), pp. 27—45.