REAL TIME PATH INTEGRALS WITH QUASI-ADIABATIC PROPAGATORS:

QUANTUM DYNAMICS OF A SYSTEM COUPLED TO A HARMONIC BATH

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I. INTRODUCTION

The model of a “system” coupled to a harmonic “bath” is useful in many areas of chemistry and physics. Even though modeling the environment as a collection of harmonic oscillators involves in many cases a strong (and sometimes hard to justify) assumption, the model has been found to offer a surprisingly successful—and perhaps the only possible—theoretical description of many complex phenomena. Despite its simplicity, the system-bath model can adequately describe phenomena such as friction and incoherent relaxation encountered in the condensed phase. The idea of expressing a complex problem in terms of a system coupled to a bath has also found considerable utility in the area of gas-phase dynamics, where it leads to reaction path descriptions of reactive processes.

The quantum mechanics of system-bath problems is particularly rich and remains poorly understood. Nearly all known analytic and numerical quantum mechanical methods have been applied to system-bath Hamiltonians, in an attempt to elucidate some intriguing features that these systems possess. Even though the quadratic bath assumption constitutes an enormous simplification, the problem is highly nonlinear due to the coupling with the system degree of freedom. As a result, analytic solutions are possible only in special cases. Nevertheless, simple approximations have been able to provide valuable physical insight in certain regimes (e.g. weak coupling, adiabatic limit, etc.1). However, many realistic problems cannot be described by any of the above limits, as they involve intermediate coupling strengths and time scales of the same order. Understanding the behavior of these systems depends on one’s ability to perform reliable numerical calculations.

The dynamical description of the problem requires knowledge of the (time-dependent) density matrix. Feynman’s path integral approach2,3 offers a unique advantage in the case of a system coupled to a harmonic bath. Because quadratic Lagrangians lead to Gaussian integrals in the path integral formalism, the harmonic bath can be integrated out analytically in this case, reducing the problem to a path integral that involves only the system degree of freedom with the effect of the bath included via an influence functional.4 The latter involves interactions nonlocal in time, and therefore the path integral over the system does not correspond to an ordinary (local) Schrödinger equation; thus, it cannot be evaluated by iterative techniques. Since in the conventional formulation the path integral is a multidimensional integral, Monte Carlo techniques5 offer the only conceivable way of evaluating it. Monte Carlo methods work best if the integrand is positive, which
is the case if one is interested in equilibrium properties (i.e., averages over the Boltzmann operator). Indeed, Monte Carlo path integral methods have managed to provide extremely useful information regarding the equilibrium statistical mechanical properties of many-body quantum systems. Recent work in this area has attempted to extend Monte Carlo path integral techniques to deal with real time, where the integrand is oscillatory; the developed methodology has been fairly successful in calculating short time dynamical properties. The long real time dynamics of multidimensional problems, though, is extremely hard to extract in most interesting cases, because Monte Carlo techniques fail to converge due to the phase interference nature of quantum mechanics. For these reasons the nonlocal path integral that arises in the case of a system coupled to a harmonic bath is extremely hard to evaluate.

In this article we describe a different approach to the dynamics of a system coupled to a harmonic bath. The path integral is formulated in terms of an adiabatic propagator for the system, with an influence functional that incorporates the non-adiabatic corrections. With parameters typical of problems in chemical physics, converged results are achieved with a very small number of time slices in this formulation, such that the nonlocal path integral for the system can be evaluated by quadrature. The idea and the resulting expressions for the influence functional are presented in section II. Section III discusses some preliminary applications of the quasi-adiabatic propagator formulation to the tunneling dynamics of a symmetric double well potential coupled to a bath of ten harmonic oscillators. Finally, some concluding remarks appear in section IV.

II. QUASI-ADIABATIC PROPAGATOR AND INFLUENCE FUNCTIONAL

We consider the standard system-bath Hamiltonian, which has the form

\[ \hat{H} = \hat{H}_s + \hat{H}_Q - \sum_{i=1}^{\nu} f_i(\delta) \hat{Q}_i. \]  

(2.1a)

Here \( \hat{H}_s \) describes the system,

\[ \hat{H}_s = \frac{\hat{p}_s^2}{2m} + V(\delta), \]  

(2.1b)

and

\[ \hat{H}_Q = \sum_{i=1}^{\nu} \hat{H}_i = \sum_{i=1}^{\nu} \frac{\hat{p}_i^2}{2m} + \frac{1}{2} \omega_i^2 \hat{Q}_i^2 \]  

(2.1c)

is the Hamiltonian for the \( \nu \) harmonic oscillators \( \{Q_i\} \) which are linearly coupled to the system and which constitute the bath.

The adiabatic approximation is known to provide a reasonable zeroth order description of many problems in chemistry. However, correction terms to the adiabatic approximation are usually very hard to calculate. This is so because the size of the problem to be solved in order to correct the adiabatic approximation to order \( n \) grows typically (e.g., if adiabatic basis functions are used) as \( n^5 \).

Our purpose is to exploit the adiabatic approximation as a good zeroth order representation in the path integral context. The advantage that we shall gain this way is that the harmonic bath can be eliminated, and thus the numerical effort associated with the \( n \)th order correction term will now scale linearly with the number of bath degrees of freedom. On the other hand, if the adiabatic approximation is a reasonable zeroth order approximation to the dynamics, we expect that
the path integral (which will include non-adiabatic correction terms) will converge very rapidly as
the number of time slices is increased, such that we may be able to evaluate it by quadrature, thus
avoiding Monte Carlo procedures (which would have to deal with the "sign problem").

We begin by partitioning the Hamiltonian into a form suggested by the adiabatic approxima-
tion. i.e., Eq. (2.1a) is split into an adiabatically displaced harmonic oscillator Hamiltonian,

$$
\hat{H}_Q = \sum_{i=1}^{p} \hat{H}_i = \sum_{i=1}^{k} \frac{\hat{p}_i^2}{2m_i} + \frac{1}{2} m \omega_i^2 \left( \hat{Q}_i - \frac{f_i(s)}{m_i \omega_i^2} \right)^2.
$$

(2.2)

and a rescaled Hamiltonian for the system, in which \( V(s) \) is replaced by the potential along the
adiabatic path \( Q_i(s) = f_i(s) / m \omega_i^2 \):

$$
\hat{H}_s = \frac{\hat{p}_s^2}{2m_i} + V(s) - \sum_{i=1}^{p} \frac{f_i(s)^2}{2m_i \omega_i^2}.
$$

(2.3)

Using this partitioning, we split the time evolution operator as follows:

$$
\exp(-iH_\Delta t / \hbar) \approx \exp(-i\hat{H}_Q \Delta t / 2\hbar) \exp(-i\hat{H}_s \Delta t / \hbar) \exp(-i\hat{H}_Q \Delta t / 2\hbar).
$$

(2.4)

Since the shifted oscillator Hamiltonians depend only parametrically on the system coordinate, the
coordinate representation of the propagator that results by using Eq. (2.4) is

$$
\langle s_k Q_{k-1}, e^{-iH \Delta t / \hbar} | s_{k-1} Q_{k-1} \rangle \\
\approx \langle s_k, e^{-iH_s \Delta t / \hbar} | \prod_{i=1}^{p} \langle Q_{i,k-1}, e^{-iH_i \Delta t / 2\hbar} e^{-iH_i \Delta t / 2\hbar} | Q_{i,k-1} \rangle.
$$

(2.5)

(We use the indices \( k-1 \) and \( k \) to label the coordinate points because we plan to use Eq. (2.5) as
the short time propagator in a path integral.) The propagator that appears in Eq. (2.5), with \( \hat{H}_s \)
given by Eq. (2.2), is easily shown to be equal to

$$
\langle Q_{i,k}, e^{-iH_s \Delta t / \hbar} \rangle \langle Q_{i,k-1} \rangle \langle Q_{i,k-1} \rangle = \left( \frac{m \omega_i}{2 \hbar \sin \omega_i \Delta t} \right)^{\nu} \exp \left( \frac{im \omega_i}{2 \hbar \sin \omega_i \Delta t} \right) \cos \omega_i \Delta t

- 2q_{i,k} q_{i,k-1} + 2\Delta q_{i,k} \Delta q_{i,k} \cos \omega_i \Delta t / 2 + \Delta \lambda_{i,k}^2 \cos^2 \omega_i \Delta t / 2.
$$

(2.6)

where

$$
\Delta \lambda_{i,k} = \lambda_{i,k} - \lambda_{i,k-1}, \quad \lambda_{i,k} = \frac{f_i(s_i)}{m \omega_i^2}.
$$

$$
q_{i,k} \equiv Q_{i,k} - \lambda_{i,k-1}, \quad \text{and} \quad \Delta q_{i,k} = q_{i,k} - q_{i,k-1}.
$$
With this particular splitting of the Hamiltonian the error due to the factorization of the time evolution operator, Eq. (2.4), is proportional to
\[ \Delta t^3 \sum_{i=1}^F \left[ \hat{p}_i^2, [\hat{p}_i^2, (\hat{Q}_i - \frac{f_i(\hat{s})}{m \omega_i^2})^2] \right]. \]
The inner commutator in the last equation is a measure of the non-adiabaticity of the problem; i.e., the derived propagator is exact (for any value of \( \Delta t \)) if only points on the adiabatic path, \( Q_i = f_i(s) \) for \( s \approx 1 \), are important.

The above expression for the propagator leads to the following simple picture of the dynamics. The first (bath-independent) factor in Eq. (2.5) is the exact quantum propagator for motion along the adiabatic path, and therefore this part of the system-bath propagator corresponds to adiabatic dynamics; non-adiabatic effects are accounted for in Eq. (2.5) by Franck-Condon factors in the displaced bath propagator [cf. the \( \Delta \lambda_{i,j} \) terms in Eq. (2.6)]. For moderately non-adiabatic problems this correction factor is accurate for fairly large \( \Delta t \).

Our strategy is to use the path integral formulation of time-dependent quantum mechanics in order to improve systematically the accuracy of the non-adiabatic correction factor. We can accomplish this by incorporating the derived quasi-adiabatic propagator in the path integral. Splitting the total time \( t \) into \( N \) time slices \( \Delta t = t/N \) yields the discretized path integral
\[
<s_f | Q_f | e^{-i \hbar \Delta t} | s_0 Q_0> = \int ds_1 \cdots \int ds_{N-1} \int dQ_{1,1} \cdots \int dQ_{1,N-1} \cdots \int dQ_{F,1} \cdots \int dQ_{F,N-1} \times \prod_{t=1}^N <s_t | Q_t | e^{-i \hbar \Delta t} | s_{t-1} Q_{t-1}>,
\]
and use of equations (2.5) and (2.6) leads to the following path integral expression for the system-bath propagator:
\[
<s_f | Q_f | e^{-i \hbar \Delta t} | s_0 Q_0> = \int ds_1 \cdots \int ds_{N-1} \int dQ_{1,1} \cdots \int dQ_{1,N-1} \cdots \int dQ_{F,1} \cdots \int dQ_{F,N-1} \times \prod_{t=1}^N \left\{ \frac{m \omega_i}{2 \pi i \sin \omega_i \Delta t} \right\}^{\frac{m}{2}} \exp \left\{ \frac{i m}{2 \pi i \sin \omega_i \Delta t} \left( q_{i,j}^2 + q_{i,j-1}^2 \right) \cos \omega_i \Delta t \right\} - 2q_{i,j} q_{i,j-1} + 2 \Delta \Lambda_{i,j} \Delta q_{i,j} \cos \omega_i \Delta t/2 + 2 \Lambda_{i,j}^2 \cos^2 \omega_i \Delta t/2 \right\}.
\]
where \( s_N = s_f \) and \( Q_{1,N} = Q_{f,f} \).

The part involving the bath variables appears in the last equation as a Gaussian integral and therefore can be performed analytically to give \(^{14}\)
\[
<s_f | Q_f | e^{-i \hbar \Delta t} | s_0 Q_0> = \int ds_1 \cdots \int ds_{N-1} \prod_{t=1}^N <s_t | Q_t | e^{-i \hbar \Delta t} | s_{t-1}>,
\]
In the last equation \( f \) is an influence functional that describes the effect of the bath on the dynamics of the system and is given by the following expression:
\begin{align}
I(s_0,s_1,\ldots,s_N) &= \prod_{i=1}^T \left( \frac{m \omega_i}{2 \pi i \hbar \sin \omega_i \Delta t} \right)^{\frac{1}{2N}} \prod_{k=1}^{N-1} (2\cos \omega_i \Delta t - 2\cos k \pi / N)^{-\frac{1}{2}} \\
&\times \exp \left( \frac{im \omega_i}{2 \hbar \sin \omega_i \Delta t} \left[ \left( q_{i,0}^2 + q_{i,1}^2 + 2 \sum_{k=1}^{N-1} \lambda_{i,k}^2 \right) \cos \omega_i \Delta t + 2(\lambda_{i,N} Q_{i,N} + \lambda_{i,1} Q_{i,1}) - 2 \sum_{k=1}^{N} \lambda_{i,k} \lambda_{i,k-1} \right] \right) \\
&+ (\cos^2 \omega_i \Delta t / 2 - 2 \cos \omega_i \Delta t / 2) \sum_{k=1}^{N} \Delta \lambda_{i,k}^2 + 2 \cos \omega_i \Delta t / 2 (\Delta \lambda_{i,N} Q_{i,N} - \Delta \lambda_{i,1} Q_{i,1}) \\
&- \frac{1}{N} \sum_{k=1}^{N-1} \sin \frac{k \pi}{N} \sum_{j=1}^{(N-1)} \sin \frac{(N-1)k \pi}{N} (Q_{j,N} - \cos \frac{k \pi}{N})^{-1} \right). \tag{2.9b}
\end{align}

where
\begin{equation}
\alpha_{i,k} = \sum_{j=1}^{N-1} \sin \frac{jk \pi}{N} [-2 \lambda_{i,j} (\cos \omega_i \Delta t - \cos \omega_i \Delta t / 2) + (\lambda_{i,j-1} + \lambda_{i,j+1}) (1 - \cos \omega_i \Delta t / 2)]. \tag{2.9c}
\end{equation}

Since the influence functional involves a simple product over the bath degrees of freedom, the numerical effort associated with the evaluation of Eq. (2.9) grows linearly with the size of the bath.

Equation (2.9) is the main result of this section. The path integral is expressed in terms of a system propagator which corresponds to motion on the potential energy surface along the adiabatic path, times an influence functional which accounts for non-adiabatic effects. Thus, the present idea provides a natural way to calculate non-adiabatic corrections to the adiabatic approximation within the path integral framework.

As we emphasized in the introduction, the presence of the non-local influence functional in Eq. (2.9a) prohibits use of iterative procedures (e.g., matrix multiplication) for the evaluation of the path integral. The practical advantage offered by our formulation is that accurate results are obtained with very small values of \(N\) even for fairly long time \(t\). Specifically, if the dynamics is mostly adiabatic, no time discretization of the path integral is required. For problems relevant in chemistry, though, low frequency vibrations give rise to significant deviations from the adiabatic approximation; in such cases the path integral accounts for the non-adiabatic effects, approaching rapidly the exact dynamical result as \(N\) is increased. The numerical calculations presented in the next section indicate that (with parameters relevant to rate processes in chemistry) virtually exact results are achieved with \(N \leq 6\). This number is perhaps small enough to permit use of Monte Carlo methods for the evaluation of the \(N-1\) dimensional path integral in complex or purely real time. A much more accurate procedure, though, would be to evaluate the path integral of Eq. (2.9) on a grid by numerical quadrature; this is possible with the present formulation because the number of integrations required to produce accurate results is small. Finally, in strongly non-adiabatic problems, where the proposed scheme may not converge to satisfactory accuracy even with the maximum realistic value of \(N\) (which is probably equal to 6 with modest values of \(F\) on present day computers), Richardson extrapolation \(^{15}\) can be employed to extrapolate the noise-free path integral results obtained for \(1/N = 1, 1/2, 1/3, \ldots\) to the desired \(1/N = 0\) limit.

Finally, we show how the derived path integral expression with the quasi-adiabatic propagator can be used to propagate a wavefunction. Let \(\Psi(s,Q_1,Q_2,\ldots,Q_p)\) be the wavefunction that describes the initial state. Clearly, one is interested in time correlation functions, or in probability densities averaged over the bath, and not in the propagated wavefunction in multidimensional space. Therefore we define a time-dependent survival amplitude function by integrating the product of the propagated and initial wavefunctions over the bath coordinates:
\[ \chi(s,t) = \int ds_0 \int ds_1 \cdots \int ds_{N-1} \int dQ_{1,0} \cdots \int dQ_{F,0} \int dQ_{1,N} \cdots \int dQ_{F,N} \Psi(s, Q_{1,0}, \ldots, Q_{F,0}, t) \Psi_0^*(s, Q_{1,N}, \ldots, Q_{F,N}). \]  

(2.10)

Expressing the evolved wavefunction in terms of the path integral representation of the propagator given by Eq. (2.9) allows the reduced wavefunction to be written in the following form:

\[ \chi(s,t) = \int ds_0 \int ds_1 \cdots \int ds_{N-1} \int dQ_{1,0} \cdots \int dQ_{F,0} \int dQ_{1,N} \cdots \int dQ_{F,N} \times \Psi_0^*(s_N, Q_{1,N}, \ldots, Q_{F,N}) \Psi_0(s_0, Q_{1,0}, \ldots, Q_{F,0}) \times \prod_{k=1}^{N} <s_k | e^{-i\phi_{f,s}/\hbar} | s_{k-1}> I(s_0, s_1, \ldots, s_N). \]  

(2.11)

where \( s \equiv \mathbf{s} \). If the initial state is a product of an arbitrary function of \( s \) times a Gaussian (or, more generally, a harmonic oscillator eigenfunction) in the bath coordinates the integrals over the endpoints \( Q_{1,0}, \ldots, Q_{F,0} \) and \( Q_{1,N}, \ldots, Q_{F,N} \) can be performed analytically, resulting in an \( N \)-dimensional integral to be performed by quadrature.

III. NUMERICAL APPLICATIONS: TUNNELING DYNAMICS OF A SYSTEM COUPLED TO A HARMONIC BATH

In this section we apply the idea described in section II to study the tunneling dynamics of a symmetric double well potential linearly coupled to a harmonic bath. The Hamiltonian is that of Eq. (2.1) with \( f(s) \equiv c_s \); the system potential \( V(s) \) is given by a quartic minus a quadratic term, and the parameters (mass, barrier height, etc.) are typical of proton transfer processes.

In order to assess the accuracy and the convergence characteristics of the proposed scheme, we originally performed calculations with a bath of a single harmonic oscillator \((F=1)\) for which we can generate exact results for comparison. We computed the off-diagonal element of the density matrix,

\[ \rho = <s_0-Q_0|e^{-\phi/\hbar}|s_0-Q_0> \]  

(3.1)

where \( \pm(s_0 Q_0) \) are the coordinates of the two potential minima. This quantity is closely related to the tunneling rate \( \text{e}^{\phi} \) and is therefore very sensitive to the coupling terms in the Hamiltonian. Table 1 shows the results of calculating the off-diagonal density matrix element at 300 K from the path integral expression given in Eq. (2.9) with \( \alpha = 300 \text{cm}^{-1} \) (typical of low frequency molecular vibrations). The path integral (which includes the non-local influence functional) was evaluated by quadrature (i.e., trapezoidal rule); the calculation required storage of just one \( 80 \times 80 \) matrix and (depending on the value of \( N \)) CPU time ranging from a few seconds to a few hours on a SPARCstation 2.

The convergence rate of the path integral is seen to be very fast in this formulation. Even though the single step quasi-adiabatic propagator is off by a factor of 3 for the largest value of the coupling, use of the former in a path integral with \( N = 5 \) reduces the error to 5% or smaller for all values of the coupling constant considered. Also shown in Table 1 are the results of applying Richardson extrapolation \( ^{20} \) (a rational polynomial fit) to the data obtained for various values of \( N \) in order to extrapolate to the \( N \rightarrow \infty \) limit. This procedure is applicable here and indeed very successful, because the extrapolation is based on data free of statistical error; Richardson extrapolation would not have been very reliable if the path integral had been evaluated by Monte Carlo. It is seen that the extrapolated results are accurate to better than 1% for all values of the coupling constant considered, even when the coupling of the bath to the system is strong enough to decrease the value of the density matrix (i.e., diminish tunneling) by four orders of magnitude.
Table 1. Off-diagonal density matrix, Eq. (3.1), for the double well at $T \approx 300$K

<table>
<thead>
<tr>
<th>$\epsilon$ (a.u.)</th>
<th>$N=1^a$</th>
<th>$N=2^a$</th>
<th>$N=3^a$</th>
<th>$N=4^a$</th>
<th>$N=5^a$</th>
<th>$N \to \infty^b$</th>
<th>Exact$^c$</th>
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<td>0.000</td>
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<td>8.18</td>
<td>8.18</td>
<td>8.18</td>
<td>8.18</td>
<td>8.18</td>
<td>8.18</td>
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<tr>
<td>0.001</td>
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<td>2.78</td>
<td>2.79</td>
<td>2.81</td>
<td>2.81</td>
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<td>6.77E-1</td>
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<tr>
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<td>6.03E-4</td>
<td>6.13E-4</td>
</tr>
</tbody>
</table>

$^a$ Quadrature evaluation of the path integral with the influence functional, Eq. (2.9)

$^b$ Richardson extrapolation

$^c$ Exact results, computed by using the split propagator algorithm$^7$

Next, we present some preliminary results that involve the real time zero-temperature dynamics of the double well system, in the case where the bath consists of ten harmonic oscillators and is described by the spectral density

$$J(\omega) = \frac{\pi}{2} \sum_{i=1}^{F} \frac{c_i^2}{m_i \omega_i} \delta(\omega - \omega_i) = \eta \omega$$  \quad (3.2)

($F=10$).

![Fig. 1. The absolute square of the survival amplitude function [cf. Eq. (2.10)] at $s=s_0$, the coordinate of the left minimum of the double well potential, as a function of time, as obtained by using the single-step quasi-adiabatic propagator in the case where the bath consists of ten harmonic oscillators.](image)
We have calculated the survival amplitude function $\chi(s;t)$ defined by Eq. (2.10) at various times for an initial state that is a Gaussian-centered at the left potential minimum. The survival amplitude function looks roughly like a Gaussian in $s$, whose height oscillates on the time scale of the tunneling period. The single-peak shape of $\chi$ is due to Franck-Condon factors that arise when we integrate over the bath. I.e., at time equal to half the tunneling period, $\chi(s;t)$ is equal to zero at all points, whereas the full system-bath wavefunction has equal amplitudes in both potential wells.

In addition to the tunneling time scale, the wavefunction (and thus $\chi$) evolves on a much shorter time scale, which corresponds to the vibrational frequencies in the individual potential wells. This short time scale gives rise to high frequency fluctuations in the height and width of $\chi(s;t)$ of about 10%. Fig. 1 shows the value of $|\chi(s;t)|^2$ as a function of time at $s=-s_0$, the coordinate of the left minimum, as obtained by using the single-step quasi-adiabatic propagator [$N=1, 2, \text{and } 3$]. The high frequency fluctuations of $|\chi(s;t)|^2$ are not seen in this picture because fewer points are shown. Triangles, $N=1$. Circles, $N=2$. Squares, $N=3$.

Fig. 2 shows the same quantity as obtained from the path integral representation of the propagator [cf. Eq. (2.11)] for $N=1, 2, \text{and } 3$. The results have not fully converged with these values of $N$, but the convergence rate (as well as the calculations in the case of a one-oscillator bath shown in Table 1) indicates that they are converged to within a few percent. Calculations with $N=4$ and 5 and extrapolation to the $N \to \infty$ limit are certainly realistic as they should require just ten times more computer time than in the case of the one-oscillator bath; such results will be reported in a future publication.
It is worth noting that the time steps $\Delta t$ employed in these calculations are larger than the shortest time scale in the problem (i.e., the vibrational period in the potential wells) by three orders of magnitude, and yet the method is numerically stable and accurate. Path integral calculations based on conventional short time propagators, on the other hand, would be completely meaningless if the time step exceeded the vibrational period; i.e., thousands of time steps would have been necessary to study the long time dynamics with conventional methods, and thus such calculations would not have been possible in practice.

IV. CONCLUDING REMARKS

Perhaps the most appealing feature in path integral calculations is that the result is exact once the procedure has converged. The feature that distinguishes the present formulation from more conventional path integral approaches is that converged path integral results can now be obtained (with parameters typical of rate processes in chemistry) for long time, much longer than the shortest time scale present. This is possible with the present approach because the path integral is now constructed to utilize a good zeroth order representation, which permits use of large time steps. The fact that the resulting path integral can often be evaluated by quadrature means that Monte Carlo techniques (which lead to sizable statistical errors when used in real time) can be avoided, yielding accurate results which can be extrapolated to the desirable zero time step limit.

The preliminary results presented here are very encouraging. We believe that the quasi-adiabatic propagator formulation of the path integral will find considerable utility in quantitative studies of tunneling dynamics in the condensed phase and in fully quantum calculations for intramolecular dynamics. Such calculations are in progress.

REFERENCES


