

Monte Carlo path integration for the real time propagator

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Monte Carlo methods are described for evaluating the Feynman path integral representation of the (real time) propagator (time evolution operator), $\exp(-iHt/\hbar)$. The approach is based on the modified Filinov algorithm presented earlier by Makri and Miller [Chem. Phys. Lett. **139**, 10 (1987)]. Numerical calculations are presented for time evolution in a symmetric double well potential, as well as in a Morse potential.

I. INTRODUCTION

Until recently, the Feynman path integral representation¹ of the propagator (or time evolution operator), $\exp(-iHt/\hbar)$, has found most utility in chemical/molecular dynamics as an elegant tool for deriving semiclassical approximations to quantum dynamical phenomena.^{2,3} Only in the last few years has there begun to be interest in using it as a numerical method for carrying out completely quantum mechanical simulations for the dynamics of complex (i.e., nonanalytically solvable) systems.⁴⁻⁹ The reason for this slow development is that the path integral expression for the propagator (see Sec. III A) is a multidimensional integral whose integrand is a complex exponential function, and thus oscillatory. This appears to obviate the use of the Monte Carlo integration method, which is the only general approach one has for dealing with highly multidimensional integrals. (In contrast, the integrand of the corresponding path integral representation of the Boltzmann operator, $e^{-\beta H}$, is a real exponential and thus directly amenable to Monte Carlo integration methods. A number of impressive calculations for the quantum statistical mechanics of quite complex systems have been carried out this way.¹⁰⁻¹⁴)

We have recently, however, described an approach whereby Monte Carlo methods can in fact be effectively used to evaluate integrals with oscillatory integrands [cf. Eq. (2.1)] of the type that occur in the path integral representation of the propagator.¹⁶ This method, summarized in Sec. II, incorporates the "stationary phase Monte Carlo" idea first suggested by Doll¹⁷ and was obtained with a modified version of an integral transformation employed by Filinov¹⁸ for this type of integral. Test calculations showed that our approach is superior to Filinov's original version; it is also superior to earlier versions of the stationary phase Monte Carlo method¹⁷ in that it properly incorporates the limit of the stationary phase approximation itself.

The purpose of this paper is to report the first actual evaluation of propagator path integrals using this Monte Carlo approach. Section II briefly summarizes the method of Ref. 16, including a method for estimating the error made by the modified Filinov procedure. Specifics of applying the method to real time path integrals are detailed in Sec. III, and the results of test calculations are presented and discussed in Sec. IV.

II. THE METHOD

A. The basic idea

We first summarize the method presented in Ref. 16. To evaluate multidimensional integrals of the type

$$K = \int_{-\infty}^{\infty} d\mathbf{x} e^{iS(\mathbf{x})}, \quad (2.1)$$

we begin, following Filinov,¹⁸ by inserting unity in the form

$$1 = \int_{-\infty}^{\infty} d\mathbf{x}_0 \sqrt{\det(\mathbf{B}/2\pi)} e^{-i(\mathbf{x} - \mathbf{x}_0) \cdot \mathbf{B} (\mathbf{x} - \mathbf{x}_0)} \quad (2.2)$$

(where \mathbf{B} is a positive matrix). Interchanging the order of integration, the integral becomes

$$K = \int_{-\infty}^{\infty} d\mathbf{x}_0 \sqrt{\det(\mathbf{B}/2\pi)} \times \int_{-\infty}^{\infty} d\mathbf{x} e^{iS(\mathbf{x}) - i(\mathbf{x} - \mathbf{x}_0) \cdot \mathbf{B} (\mathbf{x} - \mathbf{x}_0)}. \quad (2.3)$$

Expansion of $S(\mathbf{x})$ in a Taylor series about \mathbf{x}_0 through quadratic terms,

$$S(\mathbf{x}) \approx S(\mathbf{x}_0) + \mathbf{S}_1(\mathbf{x}_0) \cdot (\mathbf{x} - \mathbf{x}_0) + \frac{1}{2} (\mathbf{x} - \mathbf{x}_0) \cdot \mathbf{S}_2(\mathbf{x}_0) \cdot (\mathbf{x} - \mathbf{x}_0) \quad (2.4)$$

[where $\mathbf{S}_1(\mathbf{x}) = \partial S / \partial \mathbf{x}$ and $\mathbf{S}_2(\mathbf{x}) = \partial^2 S / \partial \mathbf{x} \partial \mathbf{x}$] allows the \mathbf{x} integration to be performed analytically, yielding

$$K \approx K(\mathbf{B}) \equiv \int_{-\infty}^{\infty} d\mathbf{x}_0 e^{iS(\mathbf{x}_0)} \{ \det[1 - i\mathbf{S}_2(\mathbf{x}_0) \cdot \mathbf{B}^{-1}] \}^{-1/2} \times e^{-i[\mathbf{S}_1(\mathbf{x}_0) \cdot \mathbf{B}^{-1} \mathbf{S}_1(\mathbf{x}_0)]^{-1/2} \cdot \mathbf{S}_1(\mathbf{x}_0)}. \quad (2.5)$$

At this point we depart from Filinov and allow \mathbf{B} to be a function of \mathbf{x}_0 , namely

$$\mathbf{B} = \mathbf{B}(\mathbf{x}_0) = i\mathbf{S}_2(\mathbf{x}_0) + \mathbf{c}^{-1}, \quad (2.6)$$

so that Eq. (2.5) becomes

$$K \approx K(\mathbf{c}) \equiv \int_{-\infty}^{\infty} d\mathbf{x}_0 e^{iS(\mathbf{x}_0)} \sqrt{\det[\mathbf{1} + i\mathbf{c} \cdot \mathbf{S}_2(\mathbf{x}_0)]} \times e^{-i[\mathbf{S}_1(\mathbf{x}_0) \cdot \mathbf{c} \cdot \mathbf{S}_1(\mathbf{x}_0)]^{-1/2}}. \quad (2.7)$$

The matrix \mathbf{c} is a positive constant matrix; e.g., one may take $\mathbf{c} = c\mathbf{1}$, where $c > 0$. Note that Eq. (2.6) has introduced a second approximation, because Eq. (2.2) is not exact if \mathbf{B} is a function of \mathbf{x}_0 .

Equation (2.7) is the basic result of Ref. 16. This multi-dimensional integral is evaluated by Monte Carlo with the function

$$p(\mathbf{x}_0) = e^{-i\mathbf{S}_1(\mathbf{x}_0) \cdot \mathbf{c} \cdot \mathbf{S}_1(\mathbf{x}_0)} \quad (2.8)$$

as the (unnormalized) probability distribution from which points are sampled. This is the original idea of stationary phase Monte Carlo because the distribution p most strongly weights the regions about the stationary phase points [values of \mathbf{x}_0 for which $\mathbf{S}_1(\mathbf{x}_0) = 0$]. Choosing a large value for the constant c causes very narrow sampling about the stationary phase points, and the Monte Carlo statistics are thus excellent. There is the question, though, of how well $K(\mathbf{c})$ approximates the original integral K when c is large; in the limit $c \rightarrow \infty$, in fact, one can show that $K(\mathbf{c})$ becomes the stationary phase approximation to K . In the opposite limit, that c is small, it is easy to see that the exact integral is recovered [$\lim_{c \rightarrow 0} K(\mathbf{c}) = K$], but the Monte Carlo statistics become poor because the distribution p becomes very broad. In practice, therefore, one evaluates $K(\mathbf{c})$ for several values of c , taking it as small as acceptable Monte Carlo error allows, knowing that in the "worst" limit, $c \rightarrow \infty$, $K(\mathbf{c})$ becomes the stationary phase approximation to K . [In Sec. II B we show how one can actually calculate the error introduced by finite c , i.e., a Monte Carlo estimate of the difference between $K(\mathbf{c})$ and K .] Finally, Eq. (2.7) has the useful property that $K(\mathbf{c}) = K$ identically for all values of c if $S(\mathbf{x})$ is a quadratic function of the integration variables.

Since the stationary phase approximation to a path integral gives semiclassical dynamics,^{2,3} one interesting way to view the application of the modified Filinov procedure to path integrals is as a systematic way to correct semiclassical approximations (e.g., the classical S matrix³ in scattering, etc.). This is a major step forward for, although semiclassical approximations are often quite accurate,^{2,3} there has heretofore been no systematic way to improve on semiclassical results when they were not sufficiently accurate. The modified Filinov algorithm for $c < \infty$ may thus be viewed as a way of "turning on" full quantum mechanics, progressively so as c is decreased, and letting the Monte Carlo calculation correct the semiclassical ($c = \infty$) result.

Finally, it is also useful to note the analogy of the present Monte Carlo calculation to those in classical equilibrium statistical mechanics, for which the (unnormalized) probability distribution function is $p(\mathbf{x}) = e^{-\beta U(\mathbf{x})}$. Comparing to Eq. (2.8), the analogy is $\beta \equiv c$, and the effective "potential" that determines the sampling is $U(\mathbf{x}) \equiv (1/2)|\mathbf{S}_1(\mathbf{x})|^2$. Stationary phase points thus correspond to local minima of the potential, with the value $U_{\min} = 0$. There may be other local minima in this potential that are not zero, i.e., where the phase is not stationary but only more slowly varying than in neighboring regions; these are often related to the existence of nearby complex stationary phase regions that characterize tunneling-like contributions to the integral.¹⁶

B. The error estimate

It is not difficult to obtain an estimate of the absolute error that is introduced by using a nonzero matrix \mathbf{c} in Eq.

(2.7) to approximate the integral of interest, K . The validity of the first approximation that was used in deriving $K(\mathbf{c})$ depends on how well Eq. (2.4) describes $S(\mathbf{x})$ in the region of space that is selected by the exponential

$$e^{-i(\mathbf{x} - \mathbf{x}_0) \cdot \mathbf{B} \cdot (\mathbf{x} - \mathbf{x}_0)} \quad (2.9)$$

in Eq. (2.3). If \mathbf{B} is large, for example, then the integration with respect to \mathbf{x} is restricted to points very close to \mathbf{x}_0 , in which case the expansion of S through quadratic terms about \mathbf{x}_0 will be accurate, even though $S(\mathbf{x})$ itself may be a nonquadratic function when viewed in the entire domain of \mathbf{x} between $-\infty$ and ∞ . This can be checked by comparing the integrand of Eq. (2.5),

$$e^{iS(\mathbf{x}_0)} \{ \det[\mathbf{1} - i\mathbf{S}_2(\mathbf{x}_0) \cdot \mathbf{B}^{-1}] \}^{-1/2} \times e^{-i\mathbf{S}_1(\mathbf{x}_0) \cdot \mathbf{B} \cdot i\mathbf{S}_2(\mathbf{x}_0) \cdot \mathbf{B}^{-1} \cdot \mathbf{S}_1(\mathbf{x}_0)} \quad (2.10)$$

which incorporates the approximation of Eq. (2.4), to the true integrand before any approximation was made, that of Eq. (2.3):

$$\sqrt{\det(\mathbf{B}/2\pi)} \int_{-\infty}^{\infty} d\mathbf{x} e^{iS(\mathbf{x}) - i(\mathbf{x} - \mathbf{x}_0) \cdot \mathbf{B} \cdot (\mathbf{x} - \mathbf{x}_0)}. \quad (2.11)$$

The second approximation was introduced by Eq. (2.6). The accuracy of this approximation, however, is closely related to that of the approximation described in the previous paragraph; the integrand of Eq. (2.2) is only large for values of \mathbf{x}_0 near \mathbf{x} , within a range determined by the magnitude of \mathbf{B} . If S is well described by a quadratic function in this region, i.e., $\mathbf{S}_2(\mathbf{x}_0)$ is nearly constant there, then $\mathbf{B}(\mathbf{x}_0)$ will also be nearly constant, and Eq. (2.2) will be accurate. Therefore, if one compares

$$e^{iS(\mathbf{x}_0)} \sqrt{\det[\mathbf{1} + i\mathbf{c} \cdot \mathbf{S}_2(\mathbf{x}_0)]} e^{-i\mathbf{S}_1(\mathbf{x}_0) \cdot \mathbf{c} \cdot \mathbf{S}_1(\mathbf{x}_0)} \quad (2.12)$$

to

$$\sqrt{\det[(i\mathbf{S}_2(\mathbf{x}_0) + \mathbf{c}^{-1})/2\pi]} \times \int_{-\infty}^{\infty} d\mathbf{x} e^{iS(\mathbf{x}) - i(\mathbf{x} - \mathbf{x}_0) \cdot [\mathbf{S}_2(\mathbf{x}_0) + \mathbf{c}^{-1}] \cdot (\mathbf{x} - \mathbf{x}_0)} \quad (2.13)$$

which are obtained by substituting Eq. (2.6) in Eqs. (2.10) and (2.11), respectively, one will be testing both approximations. The integration in Eq. (2.13) can be performed using

$$e^{-i(\mathbf{x} - \mathbf{x}_0) \cdot \mathbf{c}^{-1} \cdot (\mathbf{x} - \mathbf{x}_0)} \quad (2.14)$$

as the weighting function. If this comparison is carried out at several different values of \mathbf{x}_0 and the above quantities [Eqs. (2.12) and (2.13)] are in good agreement with one another, then Eq. (2.7) will be a good approximation to the exact integral, Eq. (2.1). This test is easy to perform. The rule will be to take c to be as small as the Monte Carlo statistics permit; in general, this means $c < 1$. Then c^{-1} will be large, and Eq. (2.14) will be a sharp weighting function, so that the integral of Eq. (2.13) can be evaluated using a small number of Monte Carlo points. Another attractive feature of this method is that the sampling function that is used is a normalized distribution, and thus no normalization integral (see Sec. III) need be computed numerically.

This method was originally reported by us at the American Conference on Theoretical Chemistry (July 1987), and essentially the same idea has recently been suggested by Doll, Freeman, and Gillan.¹⁹ Tests of this approach have

been made by us on the Airy integral originally used in Ref. 16, as well as in all the applications considered in the present paper, verifying that this procedure does indeed provide an accurate estimate of the difference between $K(\mathbf{c})$ and K . As stated above, it is easier to implement if c is assigned small values, in which case the Monte Carlo integral of Eq. (2.13) has very good statistics. Estimating the error is thus an excellent way to determine (without too much additional effort) whether the results of Eq. (2.7) for a specific value of c should be trusted. Unlike Doll *et al.*'s results,¹⁹ however, our work indicates that the actual calculation of the correction to Eq. (2.7) by means of integrating the difference between Eqs. (2.12) and (2.13) requires (in multidimensional problems, in particular) a large amount of additional computational effort. Since our method gives very accurate results with small values of c , the correction would be needed only if one wanted to evaluate Eq. (2.7) with relatively large c , a choice that would render the Monte Carlo error bars small. Unfortunately, this is not easily feasible, because the statistics of the correction integral are then poor. Furthermore, as will be explained in detail in Sec. IV, the computational evaluation of Eq. (2.7) with large c presents certain challenges, which necessitate the use of special Monte Carlo techniques. [Problems of this nature do not, however, occur in the evaluation of the integral involved in estimating the error according to Eq. (2.13).] We therefore conclude that one is more likely to gain in computational effort and simplicity by taking c to be small, in which case calculating the correction to Eq. (2.7) in the way described in this paragraph will not be necessary.

III. APPLICATION: TIME EVOLUTION VIA PATH INTEGRATION

In this section, we describe the path integral evaluation of the time evolution operator in the coordinate representation and of the survival probability in two one-dimensional potentials: a symmetric double well potential, and a Morse potential.

A. The path integral expressions

The path integral expression for the coordinate representation of the propagator for a one-dimensional potential $V(x)$ is

$$\langle x_N | e^{-iHt/\hbar} | x_0 \rangle = \left(\frac{mN}{2\pi i \hbar t} \right)^{N/2} \int_{-\infty}^{\infty} dx_1 \cdots \int_{-\infty}^{\infty} dx_{N-1} e^{-\frac{mN}{2i\hbar} \sum_{k=1}^N (x_k - x_{k-1})^2 - \frac{i}{\hbar} \sum_{k=0}^N w_k V(x_k)} \quad (3.1)$$

where $w_k = 1$ for $k = 1, \dots, N-1$, $w_0 = w_N = 1/2$, and $N-1$ is the number of time discretizations. This expression becomes exact in the limit where $N \rightarrow \infty$. To evaluate Eq. (3.1) using the Monte Carlo algorithm, it is useful first to make a transformation of the integration variables to diagonalize the kinetic energy part; this leads to Coalsen's quasi-Fourier representation,²⁰

$$\langle x_N | e^{-iHt/\hbar} | x_0 \rangle = \sqrt{\frac{m}{2\pi i \hbar t}} e^{-i(N-1)\pi/4} e^{-|m/(2\hbar t)|(x_N - x_0)^2} \times \int_{-\infty}^{\infty} da_1 \cdots \int_{-\infty}^{\infty} da_{N-1} e^{i\pi \sum_{k=1}^{N-1} a_k^2 - \frac{i}{\hbar} \sum_{k=0}^N w_k V(x_k)} \quad (3.2)$$

where

$$x_k = x_0 + (x_N - x_0) \frac{k}{N} + \sqrt{\frac{\pi \hbar t}{m}} \frac{1}{N} \sum_{k'=1}^N a_{k'} \frac{\sin(\pi k k' / N)}{\sin(\pi k' / 2N)} \quad (3.3)$$

Equation (3.2) is an integral of the type discussed in Sec. II, with S of Eq. (2.1) given by

$$S = S(\mathbf{a}) = \frac{m}{2\hbar t} (x_N - x_0)^2 + \pi \sum_{k=1}^{N-1} a_k^2 - \frac{t}{N\hbar} \sum_{k=0}^N w_k V(x_k) \quad (3.4)$$

The survival probability $P(t)$ for the time evolution of a state initially described by the wave function $\Phi(x)$, is given by

$$P(t) = |\langle \Phi | e^{-iHt/\hbar} | \Phi \rangle|^2 = \left| \int_{-\infty}^{\infty} dx_0 \int_{-\infty}^{\infty} dx_N \langle \Phi | x_N \rangle \times \langle x_N | e^{-iHt/\hbar} | x_0 \rangle \langle x_0 | \Phi \rangle \right|^2 = \frac{m}{2\pi \hbar t} \left| \int_{-\infty}^{\infty} dx_0 \int_{-\infty}^{\infty} dx_N \times \int_{-\infty}^{\infty} da_1 \cdots \int_{-\infty}^{\infty} da_{N-1} \Phi^*(x_N) \Phi(x_0) \times e^{-|m/(2\hbar t)|(x_N - x_0)^2} e^{i\pi \sum_{k=1}^{N-1} a_k^2 - \frac{i}{\hbar} \sum_{k=0}^N w_k V(x_k)} \right|^2 \quad (3.5)$$

In applications below the initial state is taken to be a Gaussian centered about x_{in} :

$$\Phi(x) = \frac{\alpha^{1/4}}{\pi^{1/4}} e^{-\frac{\alpha}{2}(x - x_{in})^2} \quad (3.6)$$

B. Method of computation

1. The normalization integral

After making the transformation described in Sec. II A, one must evaluate a multidimensional integral of the type of Eq. (2.7). The most common way of doing this is via the Metropolis algorithm,²¹ which gives a normalized average over the chosen relative distribution function. Equation (2.7) must thus be multiplied and divided by the normalization integral,

$$I \equiv \int_{-\infty}^{\infty} d\mathbf{x} e^{-i\mathbf{S}_1(\mathbf{x}) + c\mathbf{S}_2(\mathbf{x})} = \int_{-\infty}^{\infty} d\mathbf{x} p(\mathbf{x}), \quad (3.7)$$

so that the Metropolis expression for $K(\mathbf{c})$ of Eq. (2.7) is

$$K(\mathbf{c}) = \frac{I}{M} \sum_{j=1}^M e^{iS(\mathbf{x}_j)} \sqrt{\det[\mathbf{1} + i\mathbf{c}\mathbf{S}_2(\mathbf{x}_j)]} \quad (3.8)$$

where $\{x_j\}$ are the M points selected from the distribution $p(\mathbf{x})$ by the Metropolis procedure.

The normalization integral, Eq. (3.7), is similar to integrals that occur in statistical mechanics, where one wants to compute partition functions. We have used the "charging" algorithm²² to evaluate it. The exponent of the weighting function is thus split into two parts,

$$p(\mathbf{x}) = e^{-|g_0(\mathbf{x}) + g_1(\mathbf{x})|}, \tag{3.9}$$

such that $e^{-g_0(\mathbf{x})}$ is analytically integrable. [In the case of the Monte Carlo evaluation of path integrals, there is always a quadratic (and thus analytically integrable) part in the exponent of the weighting function, and therefore this algorithm is directly applicable.] Defining

$$I_\lambda \equiv \int_{-\infty}^{\infty} d\mathbf{x} e^{-|g_0(\mathbf{x}) + \lambda g_1(\mathbf{x})|}, \tag{3.10}$$

one has

$$\begin{aligned} -\frac{d}{d\lambda} \ln I_\lambda &= -\frac{1}{I_\lambda} \frac{d}{d\lambda} I_\lambda \\ &= \frac{\int_{-\infty}^{\infty} d\mathbf{x} g_1(\mathbf{x}) e^{-|g_0(\mathbf{x}) + \lambda g_1(\mathbf{x})|}}{\int_{-\infty}^{\infty} d\mathbf{x} e^{-|g_0(\mathbf{x}) + \lambda g_1(\mathbf{x})|}} = \langle g_1 \rangle_\lambda \end{aligned} \tag{3.11}$$

and therefore

$$I = I_{\lambda=1} = I_{\lambda=0} e^{-\int_0^1 d\lambda \langle g_1 \rangle_\lambda}. \tag{3.12}$$

One must thus compute the normalized average of g_1 with respect to the distribution

$$p_\lambda(\mathbf{x}) = e^{-|g_0(\mathbf{x}) + \lambda g_1(\mathbf{x})|} \tag{3.13}$$

at selected values of λ between 0 and 1 and numerically integrate over λ to obtain the normalization integral I . The Metropolis procedure is used to compute $\langle g_1 \rangle_\lambda$.

In most of the cases presented in this paper, the integrand of Eq. (3.12), $\langle g_1 \rangle_\lambda$, is a very nonsmooth function of λ ; however, by properly selecting the values of λ (typically, 10–20 points are sufficient) at which $\langle g_1 \rangle_\lambda$ is evaluated, this function can be accurately and efficiently integrated.

2. Computation of the survival probability

The exponent of the integrand in Eq. (3.5) for the survival probability, with $\Phi(x)$ given by Eq. (3.6), has a real as well as an imaginary part. Our first inclination was to deal with this by applying the modified Filinov transformation, Eq. (2.7), only to the $\{a_k\}$ variables since there is already a real exponential factor that can serve as the weighting func-

tion for integrating over the variables x_0 and x_N . This turns out not to be a good idea, however, because the resulting Metropolis sampling function does not sample the regions of x_0 and x_N about the stationary phase points of these variables. This causes the phase factor e^{iS} to oscillate wildly with x_0 and x_N , and thus gives poor Monte Carlo statistics.

We have found that it is much better simply to generalize Eqs. (2.1)–(2.7) to the case that the phase $S(\mathbf{x})$ is complex. With the replacement

$$S(\mathbf{x}) \rightarrow S(\mathbf{x}) + iW(\mathbf{x}), \tag{3.14}$$

all of the manipulations leading to Eq. (2.7) are the same (at least if W is a quadratic function of \mathbf{x}), so that one obtains

$$\begin{aligned} K(\mathbf{c}) &= \int_{-\infty}^{\infty} d\mathbf{x} e^{iS(\mathbf{x})} e^{-\mathbf{c} \cdot W(\mathbf{x})} \\ &\times \sqrt{\det[\mathbf{1} + i\mathbf{c} \cdot \mathbf{S}_2(\mathbf{x}) - \mathbf{c} \cdot \mathbf{W}_2(\mathbf{x})]} \\ &\times e^{-i(S_1 + \partial \mathbf{W}_1) \cdot \mathbf{c} (S_1 + \partial \mathbf{W}_1)}, \end{aligned} \tag{3.15}$$

where

$$\mathbf{W}_1(\mathbf{x}) = \frac{\partial W(\mathbf{x})}{\partial \mathbf{x}}, \quad \mathbf{W}_2 = \frac{\partial^2 W(\mathbf{x})}{\partial \mathbf{x} \partial \mathbf{x}}.$$

Choosing the Metropolis sampling function as

$$p(\mathbf{x}) = e^{-|S_1(\mathbf{x}) \cdot \mathbf{c} S_1(\mathbf{x}) + W(\mathbf{x}) - i[W_1(\mathbf{x}) \cdot \mathbf{c} W_1(\mathbf{x})]|}, \tag{3.16}$$

Eq. (3.15) becomes

$$\begin{aligned} K(\mathbf{c}) &= \int_{-\infty}^{\infty} d\mathbf{x} p(\mathbf{x}) e^{i[S(\mathbf{x}) - \mathbf{W}_1(\mathbf{x}) \cdot \mathbf{c} S_1(\mathbf{x})]} \\ &\times \sqrt{\det[\mathbf{1} + i\mathbf{c} \cdot \mathbf{S}_2(\mathbf{x}) - \mathbf{c} \cdot \mathbf{W}_2(\mathbf{x})]}. \end{aligned} \tag{3.17}$$

Equations (3.16) and (3.17) are thus the generalization of Eqs. (2.7) and (2.8). For the present application, the integration variables are x_0, x_N , and $\{a_k\}$, S is the real part of the phase given by Eq. (3.4), and W the imaginary part, given by

$$W = \frac{\alpha}{2} [(x_0 - x_m)^2 + (x_N - x_m)^2]. \tag{3.18}$$

Our choice for the matrix \mathbf{c} is an $N + 1$ -dimensional diagonal matrix whose $N - 1$ elements (the ones corresponding to the a_k variables) are equal to a constant c and the two elements that correspond to the integration of the endpoints x_0 and x_N are equal to another constant c' . Equation (3.16) thus gives the Metropolis sampling function as

$$\begin{aligned} p(x_0, x_N, \mathbf{a}) &= e^{-\frac{c'}{2} \sum_k^1 (\partial S / \partial a_k)^2} \\ &\times e^{-\frac{\alpha}{2} (1 - ic') [(x_0 - x_m)^2 + (x_N - x_m)^2]} \\ &\times e^{-c/2 [(\partial S / \partial x_0)^2 + (\partial S / \partial x_N)^2]}, \end{aligned} \tag{3.19}$$

and the expression for the survival amplitude is

$$\begin{aligned} \langle \Phi | e^{-iHt/\hbar} | \Phi \rangle &= \sqrt{\frac{m}{2\pi i \hbar t}} e^{-i(N-1)\pi/4} \sqrt{\frac{\alpha}{\pi}} \int_{-\infty}^{\infty} dx_0 \int_{-\infty}^{\infty} dx_N \int_{-\infty}^{\infty} da_1 \cdots \int_{-\infty}^{\infty} da_N \\ &\times e^{iS(x_0, x_N, a_1, \dots, a_N)} e^{-ic' \alpha [(x_0 - x_m) \partial S / \partial x_0 + (x_N - x_m) \partial S / \partial x_N]} \\ &\times \sqrt{\det[\mathbf{1} + i\mathbf{c} \cdot \mathbf{S}_2(\mathbf{x}_0) - \mathbf{c} \cdot \mathbf{W}_2(\mathbf{x}_0)]} p(x_0, x_N, \mathbf{a}). \end{aligned} \tag{3.20}$$

Since the term $(x_N - x_0)^2$ [which arises from Eq. (3.4)] in Eq. (3.17) becomes dominant at short times, one must be careful to "move" both x_0 and x_N at each step in the Monte Carlo random walk, so that $|x_0 - x_N|$ remains small. (Failure to do so will result in the rejection of most of the steps or—if the step size is small enough so that only half of the steps are rejected—the integration space will be sampled very poorly.) To guarantee this, we carried out the Metropolis sampling using the variables

$$z_+ = \frac{1}{\sqrt{2}}(x_0 + x_N) \text{ and } z_- = \frac{1}{\sqrt{2}}(x_0 - x_N) \quad (3.21)$$

with the step sizes adjusted to give 50% rejection rate.

IV. RESULTS AND DISCUSSION

The methodology described in Secs. II and III was first tested for a harmonic potential, $V(x) = \frac{1}{2}m\omega^2x^2$. In this case the integrand of the path integral, Eq. (3.1) or (3.2), is the exponential of a quadratic function of the integration variables, and as discussed in Sec. II, the modified Filinov transformation gives the integral exactly, for all values of the parameter c . This was verified directly by using the Monte Carlo procedure described in Sec. III.

A non-trivial application, however, and one that is related to some of the chemical applications that we have in mind for future work, is a symmetric double well potential,

$$V(x) = -\frac{1}{2}a_0x^2 + \frac{1}{4}c_0x^4 \quad (4.1)$$

with $a_0 = 0.02$ and $c_0 = 0.04$ atomic units. For a particle with the mass of a hydrogen atom, the harmonic frequency in each well is 1020 cm^{-1} . The barrier that separates the two wells is small and the local potential about each minimum very anharmonic. For this potential, Eq. (2.7) is not exact, except for $c = 0$. Furthermore, this is a case for which semiclassical approximations are not expected to work very well.

Consider first the diagonal element of the propagator, $\langle 0 | \exp(-iHt/\hbar) | 0 \rangle$. This quantity is closely related to the reactive flux correlation function⁴ for the transition state ($x = 0$) on this one-dimensional potential energy surface. It is useful first to examine the case with only one time discretization because it provides useful insight into important aspects of the calculation. Equation (3.4) then reads

$$S(a_1) = \pi a_1^2 - \frac{t}{2\hbar} V(x_1) \quad (4.2a)$$

with

$$x_1 = \sqrt{\frac{\pi\hbar t}{2m}} a_1 \quad (4.2b)$$

and one can readily show that the integral over a_1 in Eq. (3.2) has three points of stationary phase,

$$a_1^{\text{sp}} = 0, \pm \left\{ \frac{2\pi + [(\pi t^2)/(4m)]a_0}{[(\pi^2\hbar t^3)/(8m^2)]c_0} \right\}^{1/2}. \quad (4.3)$$

For short times, i.e., $t \rightarrow 0$, these are all well separated, and the stationary phase approximation to the integral

$$\begin{aligned} & \langle 0 | e^{-iHt/\hbar} | 0 \rangle^{\text{SPA}} \\ & \approx e^{-i\pi/4} \frac{\sqrt{m/(2\pi\hbar t)}}{\sqrt{2 + [t^2/4m]a_0}} \\ & \times \left\{ \sqrt{2}e^{i\pi/4} + 2e^{-i\pi/4} e^{i[2 + (t^2a_0/4m)^2/(4\hbar^2c_0/2m)]} \right\} \quad (4.4) \end{aligned}$$

is accurate. As t increases, however, the three stationary phase points approach each other (coalescing as $t \rightarrow \infty$), and Eq. (4.4) becomes incorrect. (Of course one would not attempt to do the calculation for long times with only one time discretization; our purpose here is merely to examine the behavior of the specific integral.)

Now consider Monte Carlo evaluation of the integral over a_1 with the modified Filinov transformation, Eq. (2.7). It is useful to refer to the analogy with classical statistical mechanics noted at the end of Sec. II A. Thus the Monte Carlo distribution function

$$p(a_1) = e^{-(c/2)S'(a_1)^2}, \quad (4.5a)$$

here with S of Eq. (4.2), is identified with

$$p(a_1) \equiv e^{-\beta U(a_1)}, \quad (4.5b)$$

so that

$$\beta \equiv c, \quad (4.5c)$$

$$U(a_1) \equiv \frac{1}{2}S'(a_1)^2. \quad (4.5d)$$

The three stationary phase points of Eq. (4.3) are thus local minima of the potential $U(a_1)$, $U(a_1^{\text{sp}}) = 0$, and when applying the Metropolis algorithm in such cases one must be careful to sample the various local minima appropriately. When c ($\equiv \beta$) is small enough (high "temperature"), this is easily accomplished, because the optimum step size for the random walk is large enough to provide multiple jumps from one minimum to the other. For larger c ($= \beta$, i.e., low temperature), however, the Metropolis calculation often gets trapped in one minimum, without "seeing" the others within realistic time scales. This problem is often encountered in statistical mechanics, and sophisticated Monte Carlo procedures have been developed for successfully populating the various local minima. The most commonly used procedure, the simulated annealing algorithm,²³ starts the random walk with very small c (high temperature), so that all the local minima can be populated, and successively increases c (i.e., lowers the temperature) to the desired value.

The annealing procedure works well for the above case that the three local minima in $U(a_1)$ all have the same value, $U_{\text{min}} = 0$. It is less efficient, though, for computing the normalization integral, Eq. (3.6), because for $0 < \lambda < 1$ the relative minima in $U_\lambda(a_1) [p_\lambda \text{ of Eq. (3.13)} \equiv \exp(-U_\lambda)]$ do not all have the same value. In this case, we used a technique similar to the staging algorithm²⁴; we first carried out a preliminary Metropolis random walk with a large step size in order to provide the correct relative population of all important regions of space, and then used these configurations to initiate Metropolis sampling with the optimum step size.

We demonstrate the success of this latter method by presenting the Metropolis computation of the real part of $\langle 0 | \exp(-iHt/\hbar) | 0 \rangle$ for the double well potential with $N = 2$. The reason for restricting the calculation to just one

time discretization is to be able to compare with exact results, which can then be computed by simple numerical integration. Basis set calculations (which would normally provide the exact answer) converge extremely slowly in the case of the purely real time propagator. Figure 1 shows the results of this calculation for three different values of c , and compares with the exact results. The results for $c = 0.05$ were obtained using straightforward Metropolis sampling with 500 000 points. The $c = 0.5$ and $c = 1$ results were obtained by carrying out the Metropolis calculation with large step size to create 5000 configurations in the important regions of space, and then sampling about each of these configurations using 100 Monte Carlo points with the optimum step size. All three calculations were performed with the same total number of Monte Carlo points ($5000 \times 100 = 500\,000$); although the quality of the results is the same, the small c calculation is obviously preferable as being the simplest computationally.

Next, we present the calculation of the survival probability $P(t)$ for the double well potential. The initial state was taken to be a Gaussian centered at one minimum. We used two different values for α , one with which the initial state is an eigenstate of the harmonic approximation to the potential about this minimum ($\alpha = 8.57$), and a smaller value ($\alpha = 2$), which corresponds to a broader initial state. In the first case (see Fig. 2) the decay of $P(t)$ is primarily from tunneling of the initial state through the barrier to the other potential well, while in the latter case (see Fig. 3) it is via relaxation of the initial state in its own potential well.

The error estimate of Sec. II B has also been applied. In each calculation, the average absolute difference between Eqs. (2.12) and (2.13) was of the same order of magnitude or smaller than the Monte Carlo error bars for the values of c that were used.

It is worth pointing out that the computation could also be performed with larger values of the parameter c , as was

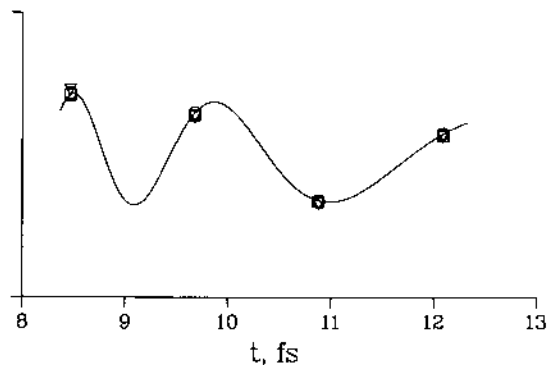


FIG. 1. Calculation of Eq. (3.1) with $N = 2$ for the double well potential. The solid line shows exact results, generated by means of numerical integration. The points show the Monte Carlo evaluation of the same quantity using three different values (in atomic units) for the parameter c : circles, $c = 0.05$; squares, $c = 0.5$; and triangles, $c = 1$. The $c = 0.05$ results were obtained by straightforward Metropolis sampling, while the $c = 0.5$ and $c = 1$ results were obtained by sampling about 5000 configurations that were created using a larger step size for the random walk (see the discussion in Sec. IV).

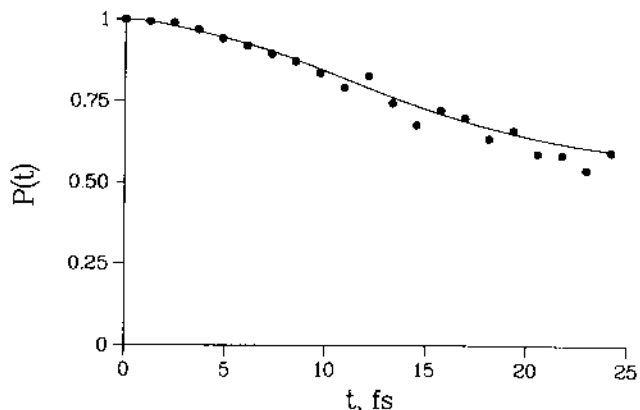


FIG. 2. The survival probability $P(t)$ for a Gaussian which starts out as an eigenstate of the local harmonic approximation to the double well potential, Eq. (4.1), about one minimum. The points show the results of evaluating Eq. (2.7) by Monte Carlo, with the parameter c ranging between 0.02 and 0.1; 100 000–1 000 000 Monte Carlo points were used per dimension of the integral. The solid line shows exact results, generated by basis set methods.

mentioned when discussing the case of the diagonal element of the propagator. However, small values of c have yet another advantage: in order to calculate the square root of the determinant that appears in Eq. (2.7), one must, in general, diagonalize the matrix $\mathbf{1} + ic \cdot \mathbf{S}_2 (-c \cdot \mathbf{W}_2)$, in order to be able to determine the correct phase factors of the product by taking the complex square root of each of the eigenvalues separately. If c is small though, the determinant has a positive real part; therefore the correct phase of the square root can be found without diagonalizing the matrix, and thus the calculation can be considerably accelerated.

Finally, we present a similar calculation for a Morse potential,

$$V(x) = D_e(e^{-2\beta x} - 2e^{-\beta x}). \quad (4.6)$$

We chose the parameters to correspond roughly to those for the vibrational motion of H_2 , i.e., the well depth $D_e = 4.476$

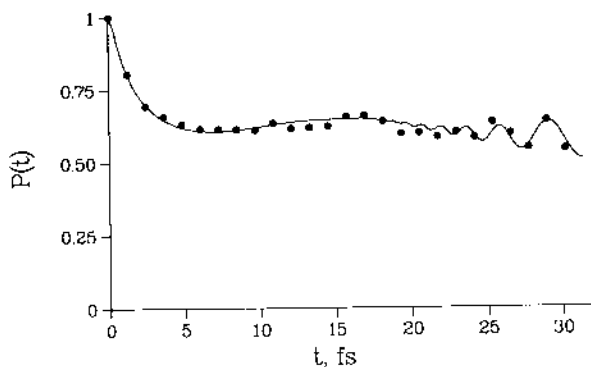


FIG. 3. Same as Fig. 2, except that the initial state was broader ($\alpha = 2$). The Metropolis computation was performed with c ranging between 0.1 and 0.2, with 100 000–200 000 Monte Carlo points per dimension.

eV and the harmonic frequency at the bottom of the well $\omega_e = 4395 \text{ cm}^{-1}$. The initial state was a Gaussian with the width of the ground state wave function and centered at $x_{\text{in}} = -0.21 \text{ \AA}$ (see Fig. 4); the energy of this state corresponds approximately to that of the fourth eigenstate, where the potential is very anharmonic. Figure 5 shows the evolution of the square of the wave function, $|\Phi(x;t)|^2$, with time. The shape of the wave packet is distorted as it moves to the right, especially as it approaches the outer turning point of the Morse potential; although the wave function is very broad there, it is too far away from its original location to have any significant overlap with the initial state, and the survival probability (see Fig. 6) approaches zero. The wave function partially regains its initial localization as it starts moving back toward the left, while the survival probability rises from zero and develops a maximum. However, the localization of the wave packet is totally destroyed as it bounces off the hard wall of the Morse potential. The wave function breaks apart as it starts moving to the right after the reflection, while the survival probability decays to zero again. Other local maxima appear in the survival probability at subsequent times, when the original Gaussian overlaps with smaller peaks of the reflected wave.

Figure 6 shows the survival probability, as calculated by Monte Carlo path integration, and compares with exact results, generated by basis set methods. The agreement is very good at all times; the path integral results have been obtained using as many as 20 time discretizations for the points of the

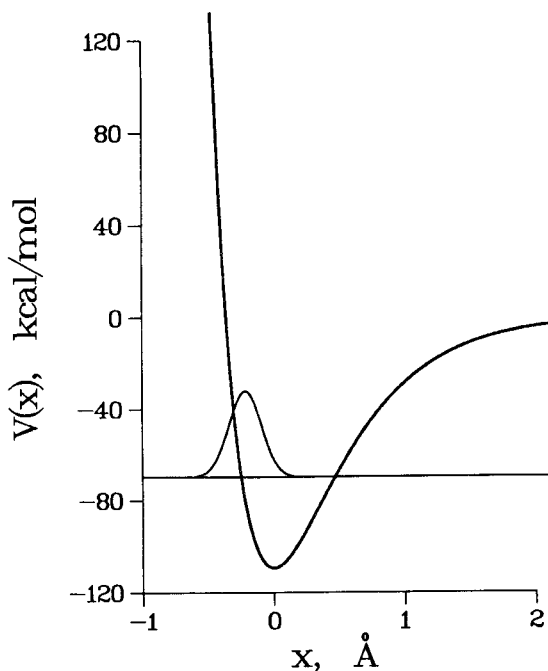


FIG. 4. The Morse potential with parameters that correspond roughly to the vibrational motion of H_2 ($D_e = 4.476 \text{ eV}$, $\omega_e = 4395 \text{ cm}^{-1}$). Also shown is the initial Gaussian wave packet, which has the width of the ground vibrational state and is displaced by -0.21 \AA from the equilibrium position; the energy of this state corresponds approximately to the fourth eigenstate of the potential.

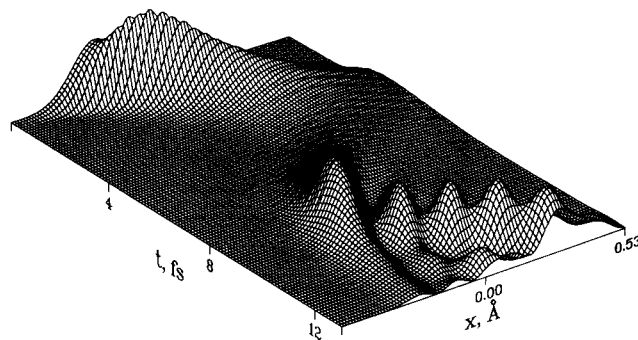


FIG. 5. Time evolution of the wave function shown in Fig. 4. Plotted is the probability density, $|\Phi(x;t)|^2$, as a function of the coordinate x and the time t . The time evolution was computed by basis set expansion.

second peak. More sophisticated methods, such as Doll *et al.*'s partial averaging¹⁵ technique, would allow the time evolution to be followed for much longer times with the same number of time discretizations. We therefore conclude that the modified Filinov method is accurate and efficient for describing the dynamics, even when the processes that are taking place are sufficiently complicated.

V. CONCLUDING REMARKS

The purpose of this paper has been to show that real time propagator path integrals can indeed be evaluated by Monte Carlo methods via the modified Filinov algorithm. The fact that Monte Carlo methods are used means that the integrand of the path integral can be augmented by a nonlocal influence functional that arises, e.g., by integrating out other degrees of freedom to which the remaining one is cou-

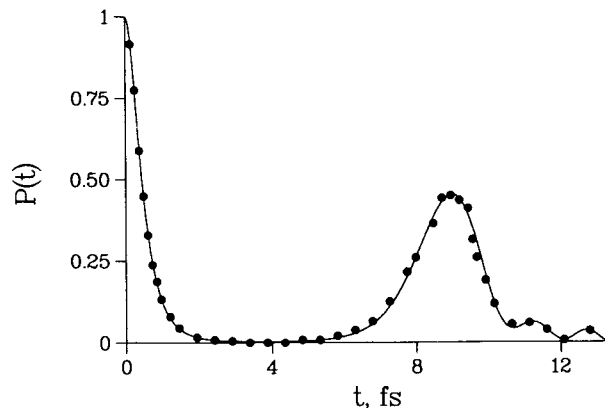


FIG. 6. The survival probability $P(t)$ [see Eq. (3.5)] for the wave packet in the Morse potential of Fig. 4. The calculation was performed with 100 000 points, with $c = 0.2$ and $c' = 0.03$; the Monte Carlo error bars are smaller than the size of the points; even when the dimensionality of the integral is ≥ 20 . The solid line shows exact results.

pled. Such possibilities show the potential power of this approach.

The applications discussed in Sec. IV also show some of the challenges presented to this approach. Namely, when there is more than one stationary phase region in the integrand, the Metropolis procedure must be "smart" enough to insure that it samples them all and in the correct relative amounts. (This is identical to the problem in classical statistical mechanics of evaluating a partition function for a potential with several local minima.) Semiclassical theory, which is the stationary phase approximation to the path integral, explicitly searches out these stationary phase points (i.e., the classical paths) and then adds their contributions appropriately. Presently, though, we do not wish to make the stationary phase approximation but rather let the Monte Carlo procedure sample these regions (in principle, exactly). There exist a variety of sophisticated Monte Carlo techniques for dealing with these multiple minima situations, and they will undoubtedly be useful for application to these modified Filinov-type calculations. For the applications in this paper, however, we have taken the simpler alternative of choosing the constant matrix c small enough that the Monte Carlo weighting function [Eq. (2.7)] samples broadly enough to encompass all the various stationary phase regions. More experience with further applications will be necessary to see which combinations of these various Monte Carlo techniques will be most generally useful for these path integral calculations.

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