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Quantum Monte Carlo Dynamics: the Stationary Phase Monte Carlo Path Integral Calculation of Finite Temperature Time Correlation Functions

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Quantum Monte Carlo dynamics: The stationary phase Monte Carlo path integral calculation of finite temperature time correlation functions

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We present a numerically exact procedure for the calculation of an important class of finite temperature quantum mechanical time correlation functions. The present approach is based around the stationary phase Monte Carlo (SPMC) method, a general mathematical tool for the calculation of high dimensional averages of oscillatory integrands. In the present context the method makes possible the direct numerical path integral calculation of real-time quantum dynamical quantities for times appreciably greater than the thermal time ($\beta\hbar$). Illustrative applications involving finite temperature anharmonic motion are presented. Issues of importance with respect to future applications are identified and discussed.

I. INTRODUCTION

In recent years path integral methods¹ have brought about something of a revolution in the study of many-body quantum mechanical systems. Previously considered basically a formal device, path integral methods have been shown to be a convenient numerical tool as well. In particular, Monte Carlo based path integral methods offer a general approach to the study of many-body quantum systems.

Numerical path integral studies have largely focused on equilibrium systems where calculation of thermodynamic averages proves to be a problem quite similar in structure to the corresponding classical Monte Carlo task.² Numerous applications involving diverse phenomenology in physics and chemistry have been reported. Equilibrium methods and applications have been reviewed elsewhere.^{3,4}

More recently, attention has turned to extending path integral Monte Carlo methods to the study of dynamical as well as equilibrium quantities.⁵⁻¹⁴ Although formally similar to the equilibrium problem, the appearance of complex exponentials as opposed to simple, Boltzmann-like factors complicates the mathematics of the dynamics problem. The phase oscillation difficulties associated with the appearance of these complex exponentials have led in the past to a general pessimism concerning the possibility of following real-time dynamics with Monte Carlo based methods for times significantly larger than the thermal time, $\beta\hbar$.

We discuss here details of a quantum Monte Carlo method for the direct calculation of real-time quantities. This method is based on the stationary phase Monte Carlo (SPMC) approach. Preliminary discussions of the basic technique and related methods have appeared previously.^{8,9,12,13} This work unifies previous efforts and develops a methodology for the calculation of dynamical properties. Simply stated, the SPMC method is a general Monte Carlo technique for performing high dimensional averages of (possibly) highly oscillatory integrands. Such tasks arise frequently in physical applications. The calculation of finite temperature time correlation functions is one particular, albeit important, example of such an application.

The essential theme underlying the SPMC approach is to structure the problem at hand in a manner that avoids the necessity of building up local phase interferences with numerical Monte Carlo methods. Instead, an averaging process is developed that synthesizes this local phase interference information, thereby (1) identifying those regions that will ultimately contribute strongly to the final results and (2) accelerating the convergence of the method. It proves possible to formulate this averaging process in a manner that is both formally exact and computationally practical.

The present discussion will be concerned principally with Monte Carlo path integral dynamics. We will not consider further other alternate approaches to quantum dynamics, approaches that include basis set techniques,^{15,16} hybrid basis set/path integral methods,^{17,18} analytic continuation approaches,¹⁹ Fourier transform,²⁰ and semiclassical^{21(a)} and wave packet methods.^{21(b)}

The remainder of this presentation is organized as follows. Section II briefly reviews the basic SPMC approach and illustrates the method with a simple, pedagogical example. Section III formulates the problem of calculating finite temperature time correlation functions within the SPMC framework. We present in Sec. IV applications of the present approach designed to assess issues of feasibility and general utility. Section IV's applications focus on the calculation of simple finite temperature dipole autocorrelation functions for anharmonic systems. We conclude in Sec. V with a discussion of the present results and identify issues of concern for future applications.

II. SPMC THEORY

We present in this section a brief discussion of the general stationary phase Monte Carlo (SPMC) method from the viewpoint of the technique as a mathematical tool. This discussion is made without reference to any particular physical application in order to emphasize the generality of the approach and to simplify the presentation of the essential features of the method. We will demonstrate in Sec. III that the calculation of finite temperature time correlation func-

tions can be reduced to a problem of the type considered below.

We begin by considering the prototype integral

$$I(t) = \int dx \rho(x) e^{itf(x)}, \quad (2.1)$$

where $\rho(x)$ is an arbitrary (normalized) probability distribution function. We will adopt a one-dimensional notation in much of the following, understanding that all results easily generalize to multidimensional form.

The difficulty in evaluating Eq. (2.1) varies with the magnitude of the parameter t . For small values of t , ordinary Monte Carlo (MC) methods are adequate for the evaluation of our prototype integral. In particular, applying ordinary MC methods to Eq. (2.1) produces

$$I(t) = \frac{1}{N} \sum_{n=1}^N e^{itf(x_n)}, \quad (2.2)$$

where the points $\{x_n\}$ are selected at random from the distribution $\rho(x)$. As t becomes large, the phase oscillations arising from the complex exponential become severe making attempts to extend Eq. (2.2) by blindly adding more Monte Carlo points unwise. In order to be successful with ordinary Monte Carlo methods, it would be necessary to include a sufficient number of quadrature points in Eq. (2.2) to capture all of the interference structure arising from the complex exponential, an impractical task for large t . Viewed from a different perspective, we know from conventional stationary phase considerations that for large t the integral in Eq. (2.1) is dominated by contributions from those regions where the phase function $f(x)$ is locally constant. This implies that in a brute force Monte Carlo evaluation of Eq. (2.2) we would be wasting most of our effort in numerically building up local phase interference information to produce a null result. Rather than a brute force approach, the key to progress is to develop a procedure that synthesizes these local phase interferences in some alternate fashion, thereby freeing the Monte Carlo procedure from this difficult task. It is to the description of such a procedure that we now turn.

As has been shown previously,¹³ the integral of interest can be rewritten identically as

$$I(t) = \int dx \rho(x) D(x) e^{itf(x)}, \quad (2.3)$$

where the "damping function" $D(x)$ is given by

$$D(x) = \int dy P(y) \frac{\rho(x-y)}{\rho(x)} e^{it\{f(x-y) - f(x)\}}, \quad (2.4)$$

and where $P(y)$ is an arbitrary (normalized) probability distribution. Equations (2.1) and (2.3) are formally identical, the only restriction being that the x integration must extend over either an infinite interval or over an interval over which the phase function is periodic.

We can exploit the nature of the damping function in order to simplify the numerical evaluation of Eq. (2.3). In order to appreciate the possible simplifications, it is useful to first examine $D(x)$. If, as is typical in the present applications, we assume $P(y)$ to be a prelimit delta function (e.g., Gaussian) of length scale ϵ , $P_\epsilon(y)$, then the damping func-

tion is given by

$$D_\epsilon(x) = \int dy P_\epsilon(y) \frac{\rho(x-y)}{\rho(x)} e^{it\{f(x-y) - f(x)\}}. \quad (2.5)$$

The exact nature of $D_\epsilon(x)$, its general calculation, and a strategy for choosing the optimal value of ϵ are discussed elsewhere.¹³ The basic structure of $D_\epsilon(x)$ can be seen by considering low-order gradient approximations to the exact result. Assuming that ϵ is small and that $P_\epsilon(y)$ is a Gaussian, $D_\epsilon(x)$ is given approximately by the first order gradient approximation to Eq. (2.5),

$$D(x) \cong D_0(x) \equiv \exp[-(\epsilon t f')^2/2]. \quad (2.6)$$

Higher order gradient approximations as well as cumulant forms for the damping function are discussed elsewhere.^{9,13} We see that $D(x)$ acts as a stationary phase "filter," a filter that is "transparent" only in those regions where the complex exponential is well behaved (i.e., $f' = 0$). The action of $D(x)$ on the complex exponential $\exp[itf(x)]$ is thus to damp out unimportant, nonstationary phase regions, regions that would otherwise be severely oscillatory. With the high frequency oscillations removed, the numerical evaluation of Eq. (2.3) is a simpler task than the corresponding evaluation of the original integral. It is important to emphasize that Eq. (2.3), although simpler than the original integral, remains formally exact.

The Monte Carlo sampling method used to evaluate Eq. (2.3) is an important practical matter in the application of the SPMC technique. In our work we have found two basic approaches to be convenient. The choice of one approach over another depends on the details of the particular problem under consideration. The obvious first approach is to perform a direct MC evaluation of Eq. (2.3), giving

$$I(t) = \frac{1}{N} \sum_{n=1}^N D(x_n) e^{itf(x_n)}. \quad (2.7)$$

This approach, termed "equilibrium importance sampling" for reasons that will become clear in Sec. III, utilizes the same MC quadrature points that would have been used in Eq. (2.2). Here, however, the damping function builds in the local interference structure, meaning that in Eq. (2.7) we no longer require a high density of MC points to capture all of the local interference effects. In practice this means that, for a given number of quadrature points, the statistical errors for the SPMC method, Eq. (2.7), are smaller than for the original MC form, Eq. (2.2). Examples documenting such gains in efficiency have been discussed elsewhere.^{9,12,13}

The equilibrium importance sampling approach makes use of the damping function only retroactively, as a device for killing off contributions from unwisely chosen quadrature points. We can, in fact, use the damping function in a more active manner to improve the choice of the quadrature points themselves. Under certain circumstances it is useful to incorporate a positive approximation [cf. Eq. (2.6)] to the damping function into an importance sampling scheme by writing Eq. (2.3) as

$$I(t) = \int dx \rho(x) D_0(x) \left[\frac{D(x)}{D_0(x)} \right] e^{itf(x)}. \quad (2.8)$$

Equation (2.8) can now be evaluated by MC methods,

where now the quadrature points will be chosen from the modified weight function, $\rho(x)D_0(x)$, rather than simply $\rho(x)$ itself. This "stationary phase importance sampling" scheme will selectively focus attention on the dominant stationary phase regions. In situations where multiple stationary phase regions exist, care must be exercised in order to assure that all regions are properly sampled. We are aided in this matter by the fact that we can analytically characterize these regions as extrema of the phase function. Furthermore, guidance concerning the adequacy of particular MC sampling strategies can be gained by comparing results obtained independently from stationary phase and equilibrium importance sampling approaches. Application of the stationary phase importance sampling method generally requires that we compute by separate means the normalization integral,

$$\langle D_0 \rangle = \frac{\int dx \rho(x) D_0(x)}{\int dx \rho(x)}. \quad (2.9)$$

The calculation of this normalization integral poses no special difficulties. In particular, its evaluation does not involve contending with severe phase oscillations. Care must be exercised, however, to assure ourselves that whatever sampling scheme is utilized to evaluate Eq. (2.9) properly covers the regions where $D_0(x)$ is significant.

In order to apply the SPMC method, we must be able to evaluate the damping function $D(x)$ for arbitrary values of x . One convenient approach¹³ is to write $D(x)$ as

$$D(x) = D_0(x) + \{D(x) - D_0(x)\}_{\text{MC}}. \quad (2.10)$$

In Eq. (2.10) $D_0(x)$ is an approximate damping function, typically the first order gradient form in Eq. (2.6). In practice, if D_0 is greater than a preselected threshold δ , then an unbiased MC estimate of the correction to $D_0(x)$, the term in braces in Eq. (2.10), is added to the result. Such an unbiased MC estimate of the correction to $D_0(x)$ can be based on the expression [cf. Eqs. (2.5) and (2.6)]

$$D(x) - D_0(x) = \int dy P(y) \left[\frac{\rho(x-y)}{\rho(x)} e^{it[f(x-y) - f(x)]} - e^{-itf'(x)y} \right]. \quad (2.11)$$

If, on the other hand, $D_0(x)$ is small (i.e., smaller than our preselected threshold), then we assume in Eq. (2.10) that the x region in question is unimportant and that further corrections are unnecessary. In actual applications the threshold value δ is varied in order to assure that this assumption is appropriate. It is to be emphasized that the procedure is rigorously exact when the threshold δ is taken to be zero.

The following section considers a simple example in order to illustrate the basic SPMC approach and to set the stage for the principal result of the present work, the calculation of quantum mechanical time correlation functions.

A. Illustrative example

In this section we discuss the application of the SPMC method to a simple one-dimensional prototypical integral to

illustrate the utility of the method and the application of the two sampling strategies discussed above. The example we choose is

$$I(t) = \frac{\int_{-\infty}^{\infty} dx e^{-x^2/2} e^{it(x^3/3 - x)}}{\int_{-\infty}^{\infty} dx e^{-x^2/2}}. \quad (2.12)$$

This is of the form of Eq. (2.1) with ρ chosen to be a simple Gaussian of unit width and $f(x) = x^3/3 - x$. The distribution and phase functions are illustrated in Fig. 1. The phase function has two stationary phase points, $x = \pm 1$, and the complex exponential becomes highly oscillatory as t gets large.

We now insert D as indicated in Eqs. (2.2) and (2.3) and examine the effects of the damping function on the integrand. The approximate first order gradient expansion, Eq. (2.6), is used here to show pictorially the effect of the damping function. Corrections are applied below in the actual calculation of the integral. The approximate damping function, the complex exponential, and the product of the two at two different values of t are presented in Figs. 2 and 3. Notice first the highly oscillatory nature of the complex exponential

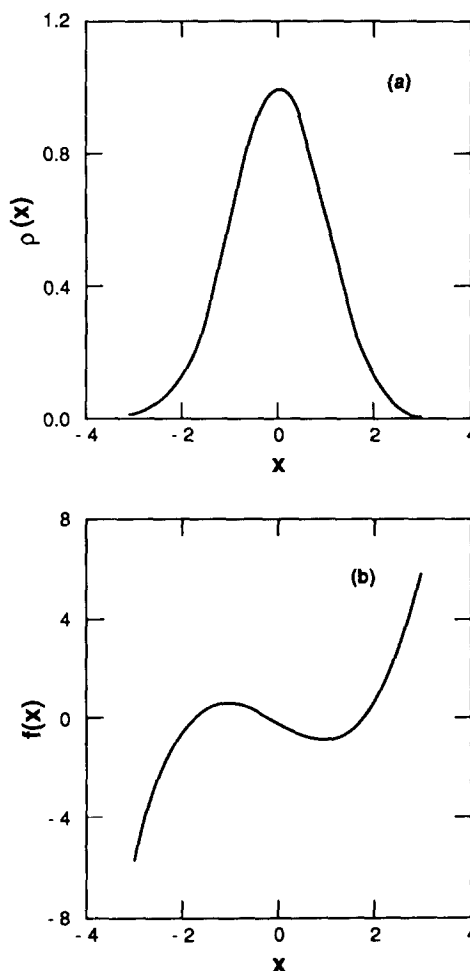


FIG. 1. Shown in (a) is the distribution function $\rho(x)$ for the prototype problem specified by Eq. (2.12). (b) gives the corresponding phase function.

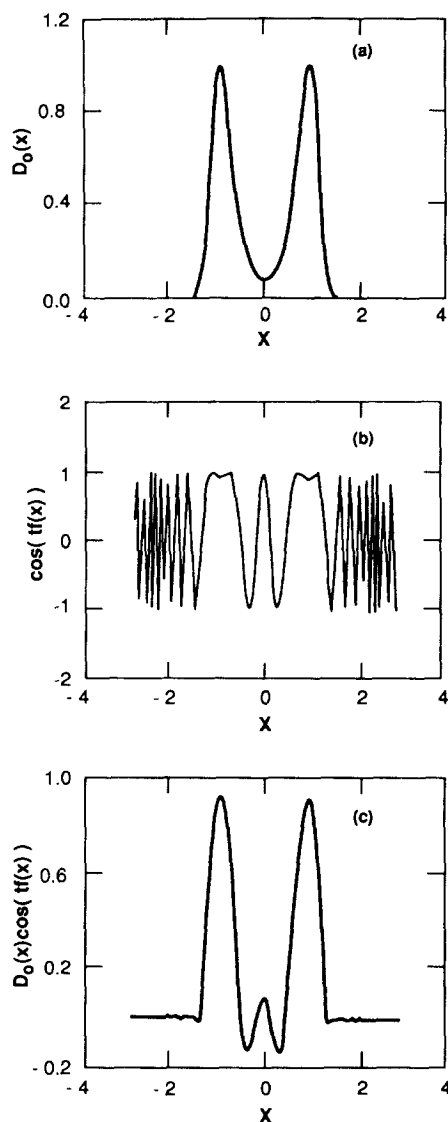


FIG. 2. Plotted for the prototype problem specified by Eq. (2.12) ($t = 10$) is (a) the first-order gradient approximation to the damping function D_0 [Eq. (2.6)], (b) the real part of the undamped complex exponential, and (c) the real part of the product of the complex exponential and D_0 . The value of ϵ in D_0 was chosen as described in Ref. 13 and was 0.2236.

away from the two stationary phase regions. At $t = 10$, the stationary phase regions are noticeable at $x = \pm 1$, with strong oscillations elsewhere. At $t = 100$, the signal is barely recognizable due to the rapid oscillations. When the product of the complex exponential and the damping function is taken, however, the important regions of the integrand become apparent. As described above, D_0 acts as a stationary phase filter to damp out the highly oscillatory regions.

The characteristics of the two sampling strategies can also be seen by comparing Fig. 1 with Figs. 2 and 3. The equilibrium sampling method uses the Gaussian as the importance sampling function and accumulates the product of the damping function and the complex exponential. This distribution has appreciable density covering the two stationary phase regions and there is no problem in passing between the two during the course of a Metropolis random walk. However, the set of points generated by this sampling scheme will

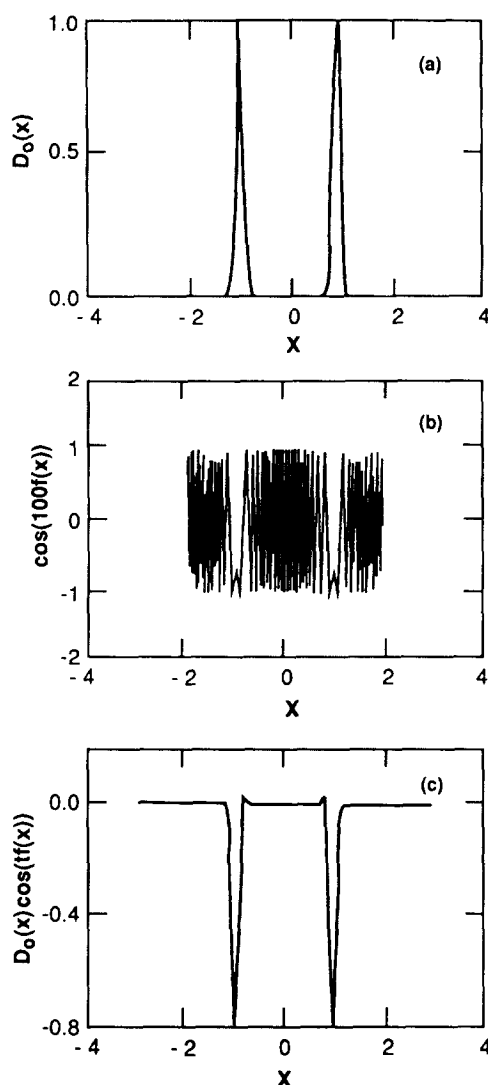


FIG. 3. As in Fig. 2, except that $t = 100$ and $\epsilon = 0.0707$.

contain a majority of zero values since the stationary phase points are not selectively visited. On the other hand, if stationary phase importance sampling is utilized, the sampling distribution will be sharply peaked at $x = \pm 1$ for large t . This sampling function will selectively weight the two stationary phase regions, but special care may be necessary to assure that the associated Metropolis Monte Carlo walk adequately samples both stationary phase regions. Both sampling methods were carried out in the present application, and yielded comparable results.

We performed SPMC evaluation of Eq. (2.12) at three different large values of t with the two sampling strategies discussed above, both with and without corrections to the first order gradient approximation to the damping function. The t values chosen are large enough so that an analytical stationary phase estimate of the integral is valid and can be used as a check on the absolute accuracy of the Monte Carlo procedure. The results along with the stationary phase values are presented in Table I.

The inclusion of the damping function in the integrand increases the efficiency of the Monte Carlo procedure at all

TABLE I. Listed are the computed values for the model integral in Sec. II A [Eq. (2.2)] for various t values. For comparison, the stationary phase approximation (SP) is also tabulated. Both the stationary phase importance sampling (SPIS) and the equilibrium importance sampling (EIS) results were computed using corrected first-order gradient approximations to the damping function [cf. Eq. (2.10)]. Uncorrected values obtained using equilibrium sampling methods are also shown. Since for each individual t value all methods utilized the same number of Monte Carlo quadrature points (200 000), the relative efficiencies of the various approaches can be judged by comparing the squares of the corresponding statistical errors.

t	SP	SPIS	EIS	EIS- D_0 only	MC
10	0.6257	0.6251 ± 0.0053	0.6174 ± 0.0036	0.5793 ± 0.0035	0.6065 ± 0.0070
100	-0.2141	-0.2135 ± 0.0017	-0.2165 ± 0.0028	-0.1730 ± 0.0017	-0.2126 ± 0.0051
1000	0.0674	0.0676 ± 0.0008	0.0669 ± 0.0011	0.0559 ± 0.0009	0.0619 ± 0.0068

values of t , with the greatest improvement being achieved for the largest value where the integrand is most highly oscillatory. At $t = 1000$, the efficiency increases by over a factor of 60 relative to the standard Monte Carlo integration. At both $t = 100$ and $t = 1000$, a large Metropolis step size was chosen for the stationary phase importance sampling procedure (which resulted in a correspondingly small acceptance probability) to permit infrequent "hops" between the two stationary phase regions. Corrections were applied to the first order gradient results via the Monte Carlo procedure discussed above. These secondary Monte Carlo corrections removed the small, systematic error present in the first order gradient results while increasing the statistical error in the calculation only slightly.

This simple example illustrates the utility of the stationary phase Monte Carlo procedure in the evaluation of integrals of the form of Eq. (2.1). It also gives an indication of steps that are useful in treating the presence of multiple stationary phase points. As illustrated in the following section, the SPMC method is found to work well when extended to the multidimensional, oscillatory integrals occurring in the calculation of finite temperature time correlation functions.

III. FINITE TEMPERATURE TIME CORRELATION FUNCTIONS

The results of Sec. II describe a generic Monte Carlo method for the calculation of averages of (possibly) highly oscillatory integrands. We turn in this section to a more specific problem, the study of finite temperature quantum mechanical time correlation functions. In particular, in the present section we cast the calculation of such correlation functions into a form amenable to SPMC evaluation. We focus first in Sec. III A on the calculation of "thermally symmetrized" correlation functions, functions simply related to the more familiar finite temperature time correlation functions, but functions that are frequently simpler computational objectives than their more familiar counterparts. In Sec. III B we develop similar procedures aimed at the calculation of more customary finite temperature time correlation functions. Illustrative applications of the developments in the present section are presented in Sec. IV.

A. Thermally symmetrized time correlation functions

We begin by considering quantum mechanical time correlation functions of the type defined by

$$G_{AB}(t) = \frac{\text{tr}[Ae^{-\beta_c^* H} B e^{-\beta_c H}]}{\text{tr}[e^{-\beta H}]}, \quad (3.1)$$

where the parameter β_c is given by

$$\beta_c = \beta/2 + it/\hbar, \quad (3.2)$$

and where β is the customary reciprocal temperature, $1/k_B T$. As discussed by Berne and Harp²², $G_{AB}(t)$ is closely related to the time correlation function $C_{AB}(t)$, defined as

$$C_{AB}(t) = \frac{\text{tr}[e^{-\beta H} A e^{iHt/\hbar} B e^{-iHt/\hbar}]}{\text{tr}[e^{-\beta H}]}, \quad (3.3)$$

through the Fourier transform identity

$$\hat{G}_{AB}(\omega) = e^{-\beta\hbar\omega/2} \hat{C}_{AB}(\omega), \quad (3.4a)$$

or, equivalently, through an identity reminiscent of the approximation due to Schofield²³:

$$C_{AB}(t) = G_{AB}(t - i\beta\hbar/2). \quad (3.4b)$$

G_{AB} and C_{AB} thus contain the same physical information, although $G_{AB}(t)$ may sometimes be a simpler computational objective since its propagators always appear in combination with thermal Boltzmann factors. Miller, Schwartz, and Tromp⁶ have utilized these thermally symmetrized correlation functions in their formulation of the calculation of thermal rate coefficients.

In what follows we will consider the particular case where the operators A and B in Eq. (3.1) are diagonal in the coordinate representation. Evaluating the quantum mechanical traces in Eq. (3.1) in the coordinate representation gives

$$G_{AB}(t) = \frac{\int dx dx' |\langle x' | e^{-\beta_c H} | x \rangle|^2 A(x) B(x')}{\int dx dx' |\langle x' | e^{-\beta H} | x \rangle|^2}. \quad (3.5)$$

Equation (3.5) expresses the quantum dynamical object of interest as a simple average over a positive probability distribution function. Equation (3.5) is, in fact, reminiscent of equilibrium thermodynamic averages. Here, however, the variables x and x' are *dynamically* correlated through the appropriate time and the temperature dependent quantum mechanical density matrix element.

Equation (3.5) is a convenient starting point for a variety of approaches to the calculation of time correlation

functions. Since we have, at least in principle, statistical procedures to estimate the complex temperature density matrix elements that appear in Eq. (3.5), one approach is to regard the x and x' integrations in Eq. (3.5) as a Monte Carlo problem with a "noisy" weight function. The mathematics of this generic type of problem have been addressed by Kennedy and Kuti²⁴ and deserves further consideration. We have had practical success following such a line of development. For example, applications similar to those in Sec. IV have been

successfully pursued. For the present, however, we choose to formulate the calculation of time correlation functions as a single Monte Carlo procedure rather than as a "nested" (Monte Carlo within Monte Carlo) approach.

We proceed by expressing the density matrix elements in Eq. (3.5) in Fourier path integral form, the details of which are described elsewhere.^{1,25} Within the Fourier path integral language the complex temperature density matrix elements in Eq. (3.5) are given by²⁶

$$\langle x' | e^{-\beta_c H} | x \rangle = \rho_{fp}(x', x, \beta_c) \frac{\int d\mathbf{a} \exp\left(-\sum_{k=1} a_k^2 / 2\sigma_k^2 - \beta_c \langle V \rangle_{\mathbf{a}}\right)}{\int d\mathbf{a} \exp\left(-\sum_{k=1} a_k^2 / 2\sigma_k^2\right)}, \quad (3.6)$$

where ρ_{fp} corresponds to the free-particle density matrix element evaluated at the complex temperature β_c ,

$$\rho_{fp}(x', x, \beta_c) = \left(\frac{m}{2\pi\hbar^2\beta_c}\right)^{1/2} \exp\left[-m(x' - x)^2 / (2\hbar^2\beta_c)\right], \quad (3.7)$$

the Gaussian widths are given by

$$\sigma_k^2 = 2\beta_c \hbar^2 / (m\pi^2 k^2), \quad (3.8)$$

and where the quantum mechanical paths connecting x and x' are parametrized in terms of the Fourier coefficients \mathbf{a} by

$$x_{\mathbf{a}}(u) = x + (x' - x)u + \sum_k a_k \sin(k\pi u). \quad (3.9a)$$

The variable u in Eq. (3.9) sweeps over the range $[0, 1]$. Equation (3.6) is the general starting point for the calculation of complex temperature density matrix elements. The Gaussian terms in Eq. (3.7) are from the quadratic kinetic energy portions of the original path integral "action" integral. While these kinetic energy portions can be evaluated analytically, the corresponding potential energy average,

$$\langle V \rangle_{\mathbf{a}} = \int_0^1 du V[x_{\mathbf{a}}(u)], \quad (3.10)$$

is generally available only through one-dimensional numerical quadrature. Inserting such path integral forms for each of the complex temperature density matrix elements into Eq. (3.5), we ultimately obtain

$$G_{AB}(t) = \frac{\int dx dx' d\mathbf{a} d\mathbf{b} \rho([\mathbf{a}], [\mathbf{b}]) \exp\{i\tau f([\mathbf{a}], [\mathbf{b}])\} A(x) B(x')}{\int dx dx' d\mathbf{a} d\mathbf{b} \rho([\mathbf{a}], [\mathbf{b}]) \exp\{i\tau f([\mathbf{a}], [\mathbf{b}])\}}, \quad (3.11)$$

where τ is the ratio of the physical to thermal times [$\tau = t / (\beta\hbar/2)$]. The paths $x_{\mathbf{a}}(u)$ and $x_{\mathbf{b}}(u)$ are parametrized by the Fourier coefficients \mathbf{a} and \mathbf{b} by Eq. (3.9a) and by (note the reversed transit from x' to x)

$$x_{\mathbf{b}}(u) = x' + (x - x')u + \sum_k b_k \sin(k\pi u). \quad (3.9b)$$

With the parametrizations in Eq. (3.9), the path integral "sum over paths" becomes an ordinary multidimensional integration over the coefficients \mathbf{a} and \mathbf{b} . The weight and phase functions in Eq. (3.11) are functionals of the paths $x_{\mathbf{a}}(u)$ and $x_{\mathbf{b}}(u)$. Explicitly,

$$\rho([\mathbf{a}], [\mathbf{b}]) = |\rho_{fp}(x', x, \beta_c)|^2 e^{-(S_+([\mathbf{a}]) + S_-([\mathbf{b}]))} \quad (3.12)$$

and

$$f([\mathbf{a}], [\mathbf{b}]) = S_-([\mathbf{a}]) - S_-([\mathbf{b}]). \quad (3.13)$$

For notational simplicity we have suppressed indications of the dependence of the weight and phase functions on the particle mass and on the complex temperature β_c . For the $x_{\mathbf{a}}$ paths the S_{\pm} pieces are given in the Fourier path integral method by²⁶

$$S_{\pm}([\mathbf{a}]) = \sum_k a_k^2 / 2s_k^2 \pm \frac{\beta}{2} \langle V \rangle_{\mathbf{a}}, \quad (3.14)$$

where

$$s_k^2 = 2|\beta_c|^2 \hbar^2 / [m\pi^2 k^2 (\beta/2)] \quad (3.15)$$

and where $\langle V \rangle_a$ is given by Eq. (3.10). The corresponding terms for the x_b paths are the obvious extensions of Eqs. (3.14) and (3.10). Additional details concerning the basic Fourier path integral approach can be found in Ref. 25.

The point of the above discussion is that Eq. (3.11) is now of the form considered in the preceding section. In particular, both the numerator and denominator of Eq. (3.11) are averages over a positive weight function of an oscillatory exponential. Here the weight function ρ is (essentially) an equilibrium Boltzmann factor (kinetic *plus* potential energy) familiar from time independent path integral applications. The phase function, on the other hand, is associated with the dynamical (kinetic *minus* potential energy) combination. As the ratio of physical to thermal time increases, the phase oscillations of the complex exponential become more severe, leading to a stationary-phase-like dynamical structure. These increasingly severe oscillations, a central obstacle to the development of a general Monte Carlo theory of quantum dynamics, can be treated by the methods discussed in Sec. II.

We now consider the practical details of the SPMC calculation of $G_{AB}(t)$. Motivated by the developments of Sec. II, we search for a damping function that will simplify the numerical calculation of Eq. (3.11). This can be accomplished by defining $D_\epsilon([a],[b])$ by [cf. Eqs. (2.4) and (3.11)]

$$D_\epsilon([a],[b]) = \int da' db' P_\epsilon(a',b') \frac{\rho([a-a'],[b-b'])}{\rho([a],[b])} \exp(i\tau f([a-a'],[b-b']) - f([a],[b])). \quad (3.16)$$

We then insert this damping function, which involves only convolutions over a and b degrees of freedom, into *both* the numerator and denominator of Eq. (3.11), giving

$$G_{AB}(t) = \frac{\int dx dx' da db \rho([a],[b]) D_\epsilon([a],[b]) \exp\{i\tau f([a],[b])\} A(x) B(x')}{\int dx dx' da db \rho([a],[b]) D_\epsilon([a],[b]) \exp\{i\tau f([a],[b])\}}. \quad (3.17)$$

It is important to recognize that the same damping function appears in both numerator and denominator of Eq. (3.17), a consequence of including only convolutions over a and b degrees of freedom in Eq. (3.16). We have found no difficulties to date caused by not damping the x and x' degrees of freedom. We know on the basis of general arguments presented in Sec. II that the damping function leaves the numerator and denominator individually unchanged while simplifying the troublesome phase oscillations otherwise present. From Sec. II we also know that if the damping function is computed exactly, then the results obtained from Eq. (3.17) are formally independent of the choice of the probability distribution function $P_\epsilon(a',b')$. As a practical matter we have found that it is convenient to choose $P_\epsilon(a',b')$ to be a multidimensional Gaussian whose first moments are all zero and whose second moments are uncorrelated. A procedure for selecting these second moments is described below. Reasons for choosing $P_\epsilon(a',b')$ to be a Gaussian are that for such a choice (1) there exists a convenient approximate analytic approximation to the damping function and (2) it is possible to develop a simple Monte Carlo correction scheme for estimating corrections to the approximate results so obtained.

As discussed in Sec. II it is convenient to have available an analytic approximation for the damping function. Several possible such expressions can be obtained from various gradient or cumulant expansions of Eq. (3.16). We have found the first-order gradient result [cf. Eq. (2.6)]

$$D_{0,\epsilon}([a],[b]) = \exp\left(-\frac{1}{2} \sum_{k=1} \tau^2 \epsilon_k^2 \times \left[\left(\frac{\partial f([a],[b])}{\partial a_k} \right)^2 + \left(\frac{\partial f([a],[b])}{\partial b_k} \right)^2 \right] \right) \quad (3.18)$$

to be especially convenient. This expression involves only

first derivatives of the phase function. If required, corrections to Eq. (3.18) can be computed by a Monte Carlo procedure based on the multidimensional generalizations of Eqs. (2.10) and (2.11).

In the present applications we have evaluated Eq. (3.17) using both equilibrium sampling and using stationary phase or "dynamical" importance sampling. In the former procedure Monte Carlo points are drawn from the weight function $\rho([a],[b])$, given by Eq. (3.12). This weight function corresponds (essentially) to the equilibrium Boltzmann factor, hence the name "equilibrium" sampling. In the latter procedure, we include dynamical information in the importance sampling scheme by sampling from ρD_0 rather than ρ itself. These two sampling methods emphasize different regions of the multidimensional (x,x',a,b) space. Comparison of results obtained by these two different approaches is one safeguard against possible sampling difficulties with either approach if used separately.

Stationary phase importance sampling affords a rather natural algorithm for the selection of the SPMC parameters, $\{\epsilon_k\}$. Although in principle the SPMC approach is formally independent of these parameters if the damping functions are computed exactly, in practice it is wise to choose these parameters judiciously. It is obviously inconvenient to have a large number (one for each Fourier path integral degree of freedom) of adjustable parameters in the calculation. In our applications we have written

$$\epsilon_k = \epsilon_0 \Delta_k, \quad (3.19)$$

where ϵ_0 is a single adjustable parameter, and Δ_k is the value of the Metropolis parameter corresponding to the k th Fourier degree of freedom that produces a preselected (typically 50%) acceptance probability for single particle Monte Carlo moves in that variable. The physical idea contained in Eq. (3.19) is that we typically want the SPMC width parameter

to be some small fraction (0.1–0.3) of the natural width of the sampling distribution (see discussion in Ref. 9). Since Δ_k is some measure of the width of the sampling distribution with respect to the k th Fourier degree of freedom, it is convenient to slave the corresponding SPMC parameter to this variable.

B. Direct time correlation functions

In the previous section we have presented the developments necessary to compute an important class of thermally

symmetrized time correlation functions. We sketch below how the same methods can be utilized to calculate the more familiar correlation functions of the type defined by Eq. (3.3). These “direct” time correlation functions are frequently more closely related to experimentally measured properties, and, in certain circumstances (e.g., low temperature), can actually be more readily calculated than their thermally symmetrized counterparts.

Expanding Eq. (3.3) in the coordinate representation, again considering the case where A and B are diagonal, the function $C_{AB}(t)$ becomes

$$C_{AB}(t) = \frac{\int dx dx' dx'' \langle x | e^{-\beta H} | x' \rangle \langle x' | e^{iHt/\hbar} | x'' \rangle \langle x'' | e^{-iHt/\hbar} | x \rangle A(x') B(x'')}{\int dx dx' dx'' \langle x | e^{-\beta H} | x' \rangle \langle x' | e^{iHt/\hbar} | x'' \rangle \langle x'' | e^{-iHt/\hbar} | x \rangle} \quad (3.20)$$

Equivalently, using cyclic invariance of the trace we can write $C_{AB}(t)$ as

$$C_{AB}(t) = \frac{\int dx dx' \langle x | e^{iHt/\hbar} | x' \rangle \langle x' | e^{-(\beta + it/\hbar)H} | x \rangle A(x) B(x')}{\int dx dx' \langle x | e^{iHt/\hbar} | x' \rangle \langle x' | e^{-(\beta + it/\hbar)H} | x \rangle} \quad (3.21)$$

Since these expressions are equivalent, either can be utilized to compute $C_{AB}(t)$. Equation (3.21) is convenient in analyzing the classical limit of $C_{AB}(t)$. Focusing on Eq. (3.20) for the moment, we proceed in much the same way as we did in Sec. III A. Without writing out all of the details, the propagator and complex temperature density matrix elements in Eq. (3.21) are first expressed in a Fourier path integral language. The manipulations with the complex temperature density matrix element in Eq. (3.21) are identical to those in the previous section, with the exception that here the complex temperature is $\beta + it/\hbar$ rather than $\beta/2 + it/\hbar$. The pure propagator term poses no special difficulty, and can be written down by inspection by taking the $\beta \rightarrow 0$ limit of the appropriate results of Sec. III A. Having done this the expression for $C_{AB}(t)$ is again of the form considered in Sec. II, meaning that we can proceed with SPMC evaluation as before. Such applications are currently under study.

IV. APPLICATIONS

We present in this section prototypical applications of the SPMC approach to the calculation of time correlation functions. These applications have been selected to demonstrate the feasibility of the present approach and as a first step in gaining the experience in utilizing the present methods that will be necessary to solve more ambitious problems. For simplicity, the present work emphasizes applications involving the thermally symmetrized time correlation functions discussed in Sec. III A. The construction of the more familiar finite temperature time correlation functions by the present approach is also feasible (Sec. III B) and such studies are currently in progress.

A useful first step in applying the SPMC methods is to consider their application to the calculation of the dipole autocorrelation function $G_{xx}(t)$ for the harmonic oscillator

$V(x) = 0.5m\omega^2x^2$. The oscillator is convenient since we can compare our numerical results with analytically available values. We first examine an important practical issue for the present method, the number of Fourier coefficients that might be required in the representations of the quantum-mechanical paths in order to produce numerical convergence of $G_{xx}(t)$. This convergence issue is examined in Fig. 4 for the particular choice of system parameters $m = m_H$, $\hbar\omega/k_B = 1000$ K, and $T = 500$ K. For these particular system parameters, we see that convergence is accomplished with a modest number of coefficients. We also see that the number of coefficients required increases linearly with the physical time. In general, it will be necessary to verify the

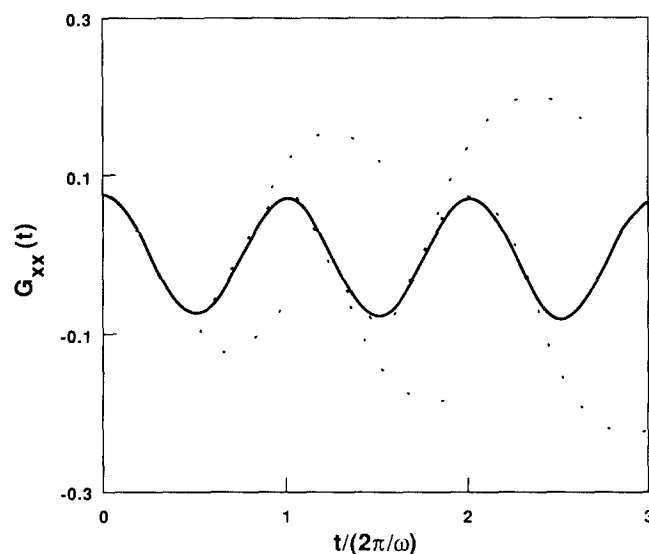


FIG. 4. Shown is the dipole autocorrelation function $G_{xx}(t)$ for the harmonic oscillator [cf. Eq. (3.1)]. The particular system parameters chosen were $m = m_H$, $\hbar\omega/k_B = 1000$ K, and $T = 500$ K. This figure compares the exact result (solid line), $G_{xx}(t) = \{\hbar/[2m\omega \sinh(\beta\hbar\omega/2)]\} \cos \omega t$, with analogous analytic Fourier path integral values obtained using various numbers of Fourier coefficients in the path expansions (dotted lines). The number of path integral Fourier coefficients utilized ranges from one (first curve to deviate from exact results) to five (the last curve to deviate from exact results).

TABLE II. Shown are the results of SPMC calculations of $G_{xx}(t)$ for the harmonic oscillator ($m = m_H, \hbar\omega/k_B = 1000$ K, $T = 500$ K). Listed are Monte Carlo values (MC), stationary phase Monte Carlo results (SPMC), with and without corrections, and the exact analytic results for five Fourier coefficients ($k_{\max} = 5$). These results at one period were all obtained using 10^6 Monte Carlo passes. At two vibrational periods the corresponding MC and SPMC- D_0 results utilized 4×10^6 passes while the corrected results used 16×10^6 passes to verify convergence.

$t/(2\pi/\omega)$	MC	SPMC- D_0	SPMC-corr	Exact- k_{\max}
1	0.0304 ± 0.0324	0.0811 ± 0.0017	0.0746 ± 0.0062	0.0744
2	0.0856 ± 0.0459	0.0830 ± 0.0021	0.0780 ± 0.0023	0.0783

convergence of computed results with respect to the number of path integral degrees of freedom included in the calculation.

Selected results from Fig. 4 are reproduced using numerical SPMC methods in Table II. Results in Table II were generated from Eq. (3.17) using the first order gradient form of the damping function, Eq. (3.18), with and without MC corrections. All results shown in Table II were obtained using stationary phase importance sampling methods. Similar results were also obtained using the equilibrium sampling methods of Sec. II. For comparison, Table II also presents the results of ordinary MC calculations. Several things are evident from Table II. We see first that SPMC results (with corrections) converge to the proper values obtained in Fig. (4) by analytic means. We also see that the quality of the uncorrected first order gradient results (D_0 only) is surprisingly good, suggesting that some cancellation of errors between the numerator and denominator of Eq. (3.17) has occurred. Also from Table II we see the SPMC method of-

fers a substantial gain in efficiency relative to ordinary MC methods. As demonstrated in Table II we can use this increased efficiency to compute finite temperature time correlation functions for times appreciably longer than the thermal times involved (two vibrational periods for the present system corresponds to 12.6 times the relevant thermal time $\beta\hbar/2$, at $T = 500$ K). The results of Table II could be extended to larger physical times at the expense of including additional Fourier coefficients.

We now consider the application of SPMC methods to problems in anharmonic motion. The present examples may be thought of as prototypes of anharmonic molecular or lattice dynamics. Shown in Fig. 5 are results for the dipole autocorrelation function, for the perturbed oscillator,

$$V(x) = \frac{1}{2}m\omega^2x^2(1 + \frac{1}{2}x^2). \quad (4.1)$$

The results in Fig. 5 were obtained using the same mass and frequency factors as in the above harmonic example and using the uncorrected first-order gradient form of the damping function, Eq. (3.18). As with the case of the pure oscillator, we see good agreement with exact results. We note in particular that the SPMC results accurately reproduce the frequency shifts seen for the anharmonic system relative to the

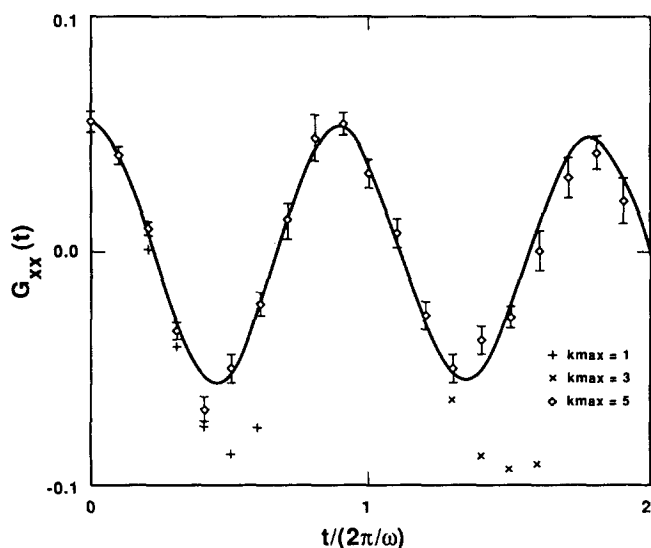


FIG. 5. Shown is the dipole autocorrelation function $G_{xx}(t)$ for the perturbed harmonic oscillator [Eq. (4.1)]. The mass, frequency, and temperature are as in Fig. 4. The exact results (solid line) were obtained via NMM methods (Ref. 30, $P = 64$). The SPMC results utilized from one to five Fourier coefficients and were obtained using stationary phase importance sampling methods and using an uncorrected, first-order gradient form for the damping function. The SPMC parameters were chosen according to Eq. (3.19) with $\epsilon_0 = 0.3$. The SPMC results utilized from 2.5 – 10×10^3 Monte Carlo passes.

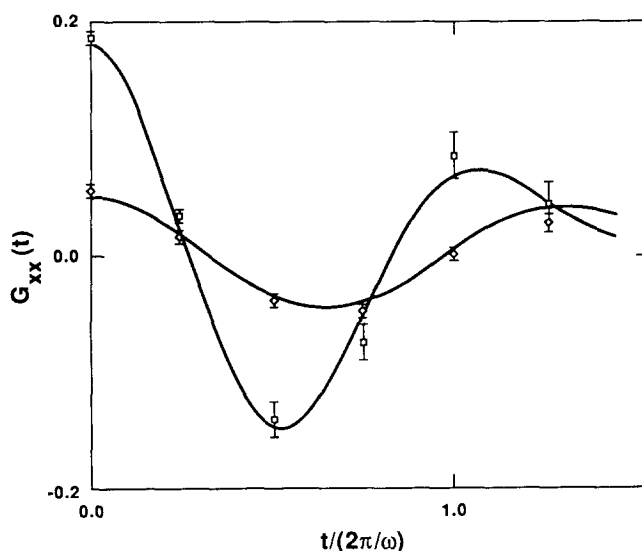


FIG. 6. As in Fig. 5 for the quartic oscillator, Eq. (4.2). The exact results were obtained via NMM methods ($P = 128$) and the corresponding SPMC results were obtained with dynamical importance sampling results (D_0 -only, $\epsilon_0 = 0.2$) and with five Fourier coefficients. The two sets of results correspond to $T = 250$ and 1000 K, respectively.

TABLE III. Shown are the first four energy levels for the quartic oscillator [Eq. (4.2)]. The system parameters were $m = m_H$ and $\hbar\omega/k_B = 1000$ K. The results were obtained by diagonalizing the Hamiltonian within a basis of corresponding harmonic oscillator wave functions. Results below were obtained using 16 oscillator basis functions.

n	E_n (a.u.)
0	$0.093\ 600 \times 10^{-2}$
1	$0.335\ 403 \times 10^{-2}$
2	$0.658\ 125 \times 10^{-2}$
3	$1.027\ 901 \times 10^{-2}$

harmonic oscillator result. We conclude from these results that the SPMC methods can yield useful information for the quantum dynamics for anharmonic systems for times appreciably larger than the thermal time. Figure 5 also indicates that the convergence of the computed results with respect to the number of Fourier coefficients included is similar to the corresponding harmonic oscillator results.

As a last application, we present in Fig. 6 dipole autocorrelation functions computed for the quartic oscillator

$$V(x) = \frac{1}{2}m\omega^2x^4. \quad (4.2)$$

We have again utilized the mass and frequency factors discussed above. We present results for this system to emphasize that the present method in no way utilizes an underlying harmonic structure to obtain a solution. The quartic oscillator is intrinsically anharmonic, as can be seen from the quantum mechanical energy levels listed in Table III. At low temperatures, the behavior of $G_{xx}(t)$ will be harmonic in character since only transitions from the ground to the first excited state will be significant. From the energy levels listed in Table III we thus predict that at low temperatures the period of $G_{xx}(t)$ will be approximately 2600 a.u. Since the energy level spacings are not uniform, there will be a temperature dependence in the frequency of the dipole autocorrelation function, the effective period of $G_{xx}(t)$ decreasing with increasing temperature. It is gratifying to see that the SPMC method accurately reproduces these results for the quartic oscillator. In particular, the SPMC results capture the temperature dependence of the anharmonic frequency and accurately predict the observed dephasing at elevated temperatures.

V. SUMMARY AND DISCUSSION

The present work has been directed at what has been historically perceived as a principal stumbling block to the development of quantum Monte Carlo dynamics, the mathematical difficulties associated with performing high dimensional averages of highly oscillatory integrands. We have summarized an approach, the stationary phase Monte Carlo method, that addresses this principal issue and provides a general framework for the discussion of such problems. This technique appears to expand appreciably the scope of numerical path integral techniques with regard to the general study of quantum dynamics.

The basic result of the work presented here is that we have cast the calculation of an important class of finite temperature time correlation functions in a form amenable to

Monte Carlo evaluation. Since such Monte Carlo based methods are relatively insensitive to issues of dimensionality, the present results suggest a feasible route to the more general study of many-body quantum dynamics. Using the present methods, we have been able to evaluate quantum mechanical time correlation functions for prototype problems designed to model molecular or lattice dynamical motion for times appreciably greater than the thermal time $\beta\hbar$. We are gratified by the level of success achieved, especially in view of the often expressed pessimism concerning the feasibility of such developments.

As a cautionary counterpoint to our enthusiasm concerning the present results, we wish to emphasize that the methods discussed here are relatively new and their capabilities and limitations are, as yet, incompletely characterized. Although the results discussed here provide a new and hopefully significant tool for the discussion of such problems, important practical matters remain. One obvious issue is related to the number of path integral degrees of freedom that will be required for general dynamical studies. As indicated in Sec. III, the number of such degrees of freedom will be larger than required for analogous equilibrium applications, and will increase linearly with increasing physical time. This increase in the number of path integral degrees of freedom will likely necessitate new developments in Monte Carlo sampling methods, at least in more ambitious applications. We know from previous work that the number of explicit degrees of freedom can be reduced using partial averaging^{26,27} and influence functional methods.¹ Nonetheless, we anticipate that sampling methods, appreciably more intelligent than the brute force sweeps over individual degrees of freedom that were utilized in the present study, will ultimately be required. Staging methods²⁸ are a first step in this direction. Ideally, these new methods would have the intelligence to identify relevant length scales and important collective degrees of freedom. Multigrid methods²⁹ are one possible approach to this problem. A second concern relates to possible sampling difficulties associated with the stationary phase importance sampling method. The tedious, if familiar, concern involves assuring that the stochastic walk underlying the Monte Carlo procedure adequately samples all relevant configuration space. It is appropriate to note that this problem is a generic Monte Carlo issue, not unique to the present application. As such, there exists a backlog of experience in related matters on which we can build. In the present application we anticipate that our ability to characterize analytically the underlying stationary phase regions will prove of assistance. Furthermore, we expect that the combination of equilibrium and stationary phase sampling methods discussed in Sec. III will provide at least a partial safeguard against shortcomings of either approach used individually. These cautionary remarks notwithstanding, we feel that the methods described here represent an important step toward the ultimate development of a general Monte Carlo theory of quantum dynamics.

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