EQUILIBRIUM AND DYNAMICAL PATH INTEGRAL METHODS

An Introduction

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Abstract. Monte Carlo methods are arguably the single most useful general purpose tool presently available for the study of many-body systems. Being relatively insensitive to dimensionality, these techniques permit one to explore, without untestable approximations, the phenomenology of physically interesting classical and quantum-mechanical systems. The present discussion focuses on the formulation and application of Fourier Path Integral (FPI) methods to both equilibrium and dynamical problems.

1. Introduction

Churchill once noted that it has been said that democracy is the worst form of government except all the others that have been tried. The spirit of this comment captures perfectly the status of Monte Carlo methods. These methods are arguably the "worst" methods for the study of many-body systems, except for all the others that have been devised.

The term "Monte Carlo methods" describes a generic collection of statistically based techniques that emerged from the pioneering work of Fermi, von Neumann, Ulam, Metropolis, and others.[1] On the one hand, they have the less than undesirable characteristic that their accuracy improves only as the square root of the computational effort expended. On the other, they have the ultimate redeeming feature that they are relatively insensitive to the dimensionality of the application. This latter trait makes it possible to utilize these methods to study, without untestable approximations, classical and quantum-mechanical systems that are typically beyond the reach of any other approaches.

The present lectures examine the use of Monte Carlo based path integral methods. While our focus is ultimately on the dynamical application of these methods, we will briefly touch on related, equilibrium applications. We will adopt a Fourier based approach[2-4] to the implementation of the path integral methods. It is with that approach that we personally have the greatest experience. Excellent reviews of related approaches and applications can be found in the literature.[5; 6] For simplicity, we will also phrase the present discussion in terms of Boltzmann statistics. For many problems, the assumption of distinguishable particle statistics is a reasonable one.

Our plan for the overall structure of these lectures is the following: We will first briefly review the Fourier formulation of path integral methods. Using this language, we will then consider their application to problems in quantum dynamics. In keeping with the overall purpose of this NATO Summer School, our discussions of the more highly developed topics related to equilibrium issues organized in a somewhat "tutorial" level. Discussions of the dynamical problem, on the other hand, touch on a number of ongoing research developments.

2. Equilibrium Monte Carlo Methods

In a truly remarkable paper[7] published nearly 50 years ago, Metropolis, et al. produced a numerical tool of unusual generality and power. These authors devised a general procedure for dealing with problems involving high-dimensional, generalized averages. Specifically, they showed that averages of the form

$$< f > \; = \frac{\int dx \, \rho(x) \, f(x)}{\int dx \, \rho(x)} \, , \tag{2.1}$$

where f(x) is a known integrand and ρ(x) is a specified probability distribution function, could be evaluated by a stochastic quadrature in which the quadrature points are generated by a relatively simple random walk procedure. Metropolis, et. al demonstrated that Eq. (1) could be approximated by the discrete average

$$< f > \approx \frac{1}{N} \sum_{n=1}^{N} f(x_n) , \tag{2.2}$$

where the points $\{x_n\}$ are chosen randomly from the distribution function ρ(x). Provided that the quadrature points are selected appropriately, Eq. (2.2) forms an "unbiased" estimate of the true result whose statistical noise decreases as $1/\sqrt{N}$.

As an aside, we will typically utilize a pseudo-one-dimensional notation in the present discussion for convenience. It is important to emphasize that the methods under consideration are in no way limited to such applications. In fact, it is precisely the dimensional tolerance of Monte Carlo methods that gives these techniques their greatest significance.

Consistent with our present objectives, we will not discuss Monte Carlo methods themselves in any great detail. Excellent reviews of these methods are available elsewhere.[8; 9; 1] While recognizing that specific applications can involve important and often difficult technical details, we will hereafter assume that generalized averages of the type in Eq. (2.1) are within our reach.

3. Equilibrium Path Integral Methods

Integral representations of special functions are familiar devices in physical science. These representations provide convenient starting points for establishing formal and/or numerical properties of the associated special functions. For example, from standard sources[10] we know that the Bessel function, $J_0(x)$, is given by

$$J_0(x) = \frac{1}{2\pi} \int_0^{2\pi} e^{ix \sin(\theta)} d\theta . \tag{3.1}$$

Using this equation, we can easily obtain a number of useful expressions for $J_0(x)$.

Expanding the exponential integrand in a power series and integrating term-by-term, for example, produces the usual power series formula for the Bessel function,

$$J_0(x) = 1 - x^2/4 + x^4/64 - \ldots \tag{3.2}$$

Alternatively, the integral representation can be used to derive a cumulant expression[11] for the Bessel function. That is, we can write J_0 as

$$J_0(x) = exp\left\{ \sum_{m=1}^{\infty} \frac{(ix)^m}{m!} << sin^m(\theta) >> \right\}, \tag{3.3}$$

where $<<\sin^m(q)>>$ is the m^{th} order cumulant. Through second order, this becomes

$$J_0(x) \approx exp\left\{ -\frac{x^2}{4} \right\}. \tag{3.4}$$

Finally, a stationary phase evaluation[12] of the the integral expression for J_0 provides a convenient asymptotic approximation to the Bessel function,

$$J_0(x) \approx \left(\frac{2}{\pi x} \right)^{1/2} cos(x - \pi/4). \tag{3.5}$$

Feynman, using a series of steps based on completeness relationships and the group property of the exponential, demonstrated that it was possible to establish infinite-dimensional (functional) integral representations for quantum-mechanical propagators and density matrix elements.[13; 14] As is the case with the one-dimensional example discussed previously, these infinite-dimensional representations provide a convenient starting point for numerical and formal discussions of these important quantum-mechanical objects. In Feynman's approach the quantum-mechanical density matrix element, $\langle x'|\exp(-\beta H)|x\rangle$, is written schematically as

$$< x'|exp(-\beta H)|x > = \sum_{paths} e^{-S[path]}. \tag{3.6}$$

Here the sum denotes a "sum over all paths," $x(\tau)$, that begin at an "initial" point x at a "time" $\tau = 0$ and end at the "final" point x' at a time $\tau = \beta\hbar$. The statistical significance of

each of these paths is governed by the Boltzmann-like factor, exp(-S), where the functional S is given in terms of the path as

$$S[x(\tau)] = \frac{1}{\hbar}\int_0^{\beta\hbar} d\tau \left\{ \frac{m}{2}\left(\frac{dx(\tau)}{d\tau}\right)^2 + V(x(\tau)) \right\}. \tag{3.7}$$

For the present purposes, we will accept these somewhat symbolic results as "given" and focus on turning them into practical numerical tools.

To proceed, we must find a practical way to enumerate the paths that appear in this formal expression and find a practical way of performing the associated summation over these paths that appears in Eq. (3.6). One way to accomplish this task is to introduce a set of "path variables" that characterize the paths, x(τ), in Eq. (3.6). In terms of these variables, the sum over paths then becomes an integral over the relevant path variables. To carry out this procedure, it is convenient to switch to a scaled time variable, u, defined as u = t/(β$\hbar$) and to write the paths, x(u), as[4]

$$x(u) = x + (x' - x)u + \sum_{k=1}^{\infty} a_k \sin(k\pi u). \tag{3.8}$$

In writing the paths in this fashion, we have introduced a "reference path" that builds in the proper u=0 and u=1 boundary conditions. Here the reference path is a simple, linear interpolation between the specified end points. By construction, the remaining "fluctuations" about this reference path must thus vanish at u=0 and u=1. Consequently, these fluctuations can be expanded in a Fourier sine series as indicated in Eq. (3.8).

It is perhaps useful at this point to clarify a number of points concerning the ansatz in Eq. (3.8). As emphasized by Lanczos and Hamming,[15; 16] the device of introducing a reference path to satisy specified boundary conditions is a standard technique for *accelerating* the convergence of Fourier expansions. To illustrate this, we consider the simple case of the function f(u) = u(1 - u) defined on the interval (0,1). If we utilize the direct sine expansion, we obtain

Sine Expansion:

$$f(u) = \sum_{k=1}^{\infty} a_k \sin(k\pi u),$$

(3.9)

where

$$a_k = 2\int_0^1 du\, f(u) \sin(k\pi u) = \frac{4(1-(-1)^k)}{(k\pi)^3} \tag{3.10}$$

If, on the other hand, we utilize a "full" Fourier expansion, we find

"Full" Fourier Expansion:

$$f(u) = \frac{b_0}{2} + \sum_{k=1}^{\infty} b_k \cos(2k\pi u) + \sum_{k=1}^{\infty} a_k \sin(2k\pi u), \tag{3.11}$$

where

$$\frac{b_0}{2} = \int_0^1 du\, f(u) = \frac{1}{6}, \tag{3.12}$$

$$b_k = 2\int_0^1 du\, f(u) \cos(2k\pi u) = -\frac{1}{(k\pi)^2} \tag{3.13}$$

and

$$a_k = 2\int_0^1 du\, f(u) \sin(2k\pi u) = 0. \tag{3.14}$$

We note that the coefficients of the sine expansion vanish as $1/k^3$ whereas those of the "full" expansion decay as $1/k^2$. Defining an r.m.s error for the series expansions, $f_{series}(u)$, as

$$error = \left\{ \int_0^1 du\, (f(u) - f_{series}(u))^2 \right\}^{1/2}, \tag{3.15}$$

it is easy to verify that the error for the sine-expansion vanishes asymptotically as $1/k_{max}^2$, whereas the corresponding result for the "full" expansion scales as $1/k_{max}$. Although this

example is a specific one, the basic results concerning the convergence of the expansions are general. Interested readers are referred to the work of Lanczos and Hamming[15; 16] for further details.

Substituting the Fourier ansatz for the path into Feynman's "sum over paths" expression, we obtain

$$< x'|exp\,(-\beta H)|x> \approx \int da\, exp\,(-S(x',x,a))\,, \tag{3.16}$$

where the integral is over the Fourier coefficients, $\{a_k\}$, and S(x',x,**a**) is given by

$$S(x',x,a) = \frac{m(x'-x)^2}{2\hbar^2\beta} + \sum_{k=1}^{\infty} a_k^2 / 2\sigma_k^2 + \beta\bar{V}\,. \tag{3.17}$$

In this expression, the quadratic terms are associated with the kinetic energy portions of Eq. (3.7). The "widths" associated with the Fourier path variables are given by

$$\sigma_k^2 = \frac{2\beta\hbar^2}{m\pi^2k^2}\,. \tag{3.18}$$

The path average of the potential along the path, x(u), specified by the Fourier path variables is given by

$$\bar{V} = \int_0^1 du\, V(x(u))\,. \tag{3.20}$$

If desired, it is straightforward to work out the Jacobian factors that accompany the "change of variables" that is associated with rewriting the sum over all paths as an integral over all Fourier coefficients and thereby turn the proportionality in (3.16) into an equality. However, it turns out that we can avoid this normalization factor by a bit of sleight of hand.. Specifically, if we repeat the above analysis with a free particle (i.e. V = 0), then we obtain the same type of expression except that the term involving the potential energy in the "action" term is absent. Therefore, the ratio of the density matrix to its free-particle counterpart is given by

$$< x'|exp\,(-\beta H)|x > \;= \frac{\int d\boldsymbol{a}\; exp\,(-\sum_{k=1}^{\infty} a_k^2 / 2\sigma_k^2 \; - \beta \bar{V})}{\int d\boldsymbol{a}\; exp\,(-\sum_{k=1}^{\infty} a_k^2 / 2\sigma_k^2 \;)}\,,$$

(3.21)

and the Jacobian factor, common to both numerator and denominator, cancels from the resulting expression.

Equation (3.21) is a valuable result. In particular, it provides us with a formal, infinite dimensional integral representation of the density matrix element. Although it may be unnecessary to do so for many applications, one can readily evaluate the multidimensional gaussian averages that appear in Eq. (3.21) by means of established Monte Carlo methods.[1] If we are interested in the construction of general thermodynamic properties, however, it is not generally necessary to construct these elements explicitly. For example, if we are interested in the average of the potential energy, <V>, then it is simpler to write <V> as

$$< V > \;= \frac{\int dx < x|exp\,(-\beta H)|x > \; V(x)}{\int dx < x|exp\,(-\beta H)|x >}\,.$$

(3.22)

Inserting the integral representation of the density matrix elements from Eq. (3.16), we obtain

$$< V > \;= \frac{\int dx\, d\boldsymbol{a}\; e^{-S(x,\boldsymbol{a})} \; V(x)}{\int dx\, d\boldsymbol{a}\; e^{-S(x,\boldsymbol{a})}}\,,$$

(3.23)

where S(x,x,**a**) (written here as S(x,**a**) for simplicity) is given by Eq. (3.17). Since this example involves the calculation of a coordinate-diagonal property, only the x'=x density matrix elements are required. For arbitrary thermodynamic averages, one may ultimately require the more general, off-diagonal density matrix elements.

Equation (3.23) is representative of the structure of general, quantum-mechanical equilibrium path integral results. Properties emerge as generalized averages over position

and path variables whose statistical weights are governed by a known, Boltzmann-like distribution function. Such averages are generally amenable to Monte Carlo techniques. As emphasized by others,[17] what started as a one-dimensional quantum problem has effectively become an infinite-dimensional classical one. That is, viewed from the perspective of the combined (x,**a**) space, the structure of Eq. (3.23) is essentially a classical-like average in which S(x,**a**) plays the role of an effective potential. The dimensional tolerance of Monte Carlo methods make the device of utilizing dimensionality to defeat the quantum-mechanical aspects of the problem an effective one.

In actual practice, two important issues remain. The first of these involves the construction of a suitable procedure for extracting the property in question from the known distribution function. A second involves the way in which one handles the truncation of the formally infinite Fourier expansion of the quantum-mechanical paths. These two topics are each important and rather technical in nature. We have discussed the issue of the choice of estimators, particularly in the context of the construction of the kinetic energy, in the published literature[2-4] and have nothing further to add at this time. We thus turn our attention to the latter topic.

We begin by returning to Eq. (3.8). In principle, the Fourier path expansion in Eq. (3.8) is formally infinite. Practical considerations, however, dictate that this formally infinite expansion be truncated at some finite number of terms, here designated as k_{max}. The most natural procedure for truncating the partition the path expansion into low and high-order terms,

$$x(u) = x + (x' - x)u + \sum_{k=1}^{k_{max}} a_k \sin(k\pi u) + \sum_{k=k_{max}+1}^{\infty} a_k \sin(k\pi u), \tag{3.24}$$

and to simply discard the high order coefficients (i.e. the last term on the r.h.s of Eq. (3.24)). Rather than dropping the high-order coefficients entirely as in this "primitive" approach, a second, more effective procedure is to include their effects approximately.[18-20; 4] To do this, it is useful to write Eq. (3.21) as

$$< x'|\exp(-\beta H)|x > = \frac{\int d\mathbf{a} \exp(-\sum_{k=1}^{k_{max}} a_k^2 / 2\sigma_k^2) \left\langle \exp(-\beta \bar{V}) \right\rangle}{\int d\mathbf{a} \exp(-\sum_{k=1}^{k_{max}} a_k^2 / 2\sigma_k^2)}, \tag{3.25}$$

where $\left\langle exp(-\beta\bar{V})\right\rangle$ is given by

$$\left\langle exp\,(-\beta\bar{V})\right\rangle = \frac{\int da\; exp\,(-\sum_{k=k_{max}+1}^{\infty} a_k^2/2\sigma_k^2)\; exp\,(-\beta\bar{V})}{\int da\; exp\,(-\sum_{k=k_{max}+1}^{\infty} a_k^2/2\sigma_k^2)} .$$

(3.26)

The average in Eq. (3.26) is over the high-order Fourier coefficients that are discarded in the primitive approach. As can be seen in Eq. (3.18), the length scale of the Fourier coefficients decays as $1/k^2$. Assuming that the potential involved has a natural length scale, it is thus possible to make k_{max} large enough that the high-order Fourier coefficients can be considered "small." If this is the case, cumulant approximations to Eq. (3.26) are a convenient way to include the effects of the high-order path variables.. Through lowest order, we have

$$\left\langle exp\,(-\beta\bar{V})\right\rangle \approx exp\,(-\beta\left\langle\bar{V}\right\rangle) .$$

(3.27)

which amounts to replacing the average of the exponential over the high-order coefficients by the exponential of the corresponding average. From Eq. (3.24), we see that the right hand side of Eq. (3.27) depends on the high order Fourier terms only through the linear combination of variables, y, given by

$$y = \sum_{k=k_{max}+1}^{\infty} a_k\, sin\,(k\pi u) .$$

(3.28)

In the first-order cumulant result, the a_k variables are gaussian in nature. This makes it possible to replace the infinite linear combination of gaussian variables by a single gaussian variable whose variance, $\sigma^2(u)$, is given by

$$\sigma^2(u) = \sum_{k=k_{max}+1}^{\infty} \sigma_k^2\, sin\,(k\pi u) .$$

(3.29)

Using (3.18) and standard summation formulas,[21] it is possible to rewrite (3.29) as

$$\sigma^2(u) = \frac{\beta\hbar^2}{m}\left[u(1-u) - \frac{2}{\pi^2}\sum_{k=1}^{k_{max}} \frac{sin^2\,(k\pi u)}{k^2}\right] .$$

(3.30)

The net effect of these steps has been to transform Eq. (3.27) into

$$\left\langle exp\,(-\beta\bar{V})\right\rangle \;\approx exp\,(-\beta\bar{V}_{PA})\,. \tag{3.31}$$

In Eq. (3.31) the effects of the high-order path fluctuations are included (approximately) through a mass and temperature-dependent effective potential, V_{PA}, given by

$$V_{PA}(x,u) \;= \frac{\int dy\; V(x\;+\;y)\; exp\,(-\dfrac{y^2}{2\sigma^2(u)})}{\int dy\; exp\,(-\dfrac{y^2}{2\sigma^2(u)})}\,. \tag{3.32}$$

In practice, two approximations are often convenient. First, it is typically possible to replace the u-dependent variance (c.f. Eq. (3.30)) by its average value over the (0,1) interval. Second, since it is not always possible to calculate the gaussian transform analytically, it is often convenient to develop Eq. (3.32) in terms of a gradient expansion. Through lowest order, this gives

$$V_{PA}(x,u) \;\approx V(x) \;+\; \frac{1}{2}\,V''(x)\;\sigma^2(u)\,. \tag{3.33}$$

Two comments are in order concerning the partial averaging procedure. First, the use of a gradient expansion in Eq. (3.33) may, at first glance, seem a questionable step. Attempts to use such expansions to account for all quantum effects are generally unsuccessful from a practical point of view.[13] The difference here is that in Eq. (3.33) we have a natural "small" variable in the problem. Unlike the situation where we are attempting to include all quantum-mechanical corrections by means of a gradient expansion, in Eq. (3.33) we are seeking the more modest goal of only including those effects coming from the high-order path variables. By making k_{max} sufficiently large, these effects can be made as small as desired. Second, there is no certainty that the gaussian transform of arbitrary potentials exists. This is the case for empirical Lennard-Jones potentials, for example. In situations where the potential has a natural length scale, Eq. (3.33) remains useful, however, since by selecting k_{max} sufficiently large, one can always make the high-order path fluctuations small on the length scale of the potential. For potentials having no natural length scale (e.g. hard-sphere interactions), one can retain the partial averaging procedure by "undoing"

the cumulant structure of Eq. (3.27). Explicitly, one must return to Eq. (3.26). By replacing the high-order portions of the path by its u-average value, Eq. (3.26) again becomes a gaussian average of a function that depends only on a linear combination of gaussian variables. Repeating steps similar to those discussed above, one can then replace the integral over the high-order Fourier coefficients by a single gaussian average.

Finally, we note that it is possible to establish the asymptotic convergence rates of thermodynamic properties calculated using the Fourier approach. Using steps analogous to those involved in the construction of the partial average approach, on can show that the errors in the the potential and kinetic energies converge as $1/ k_{max}$ for the "primitive" Fourier approach and as $1/ k_{max}^2$ if partial averaging is included. The details of these results are discussed elsewhere.[22]

4. Dynamics

As emphasized by the topics in the present NATO school, there has been significant progress in the study of many body quantum mechanical systems. In particular, numerical path integral methods have been shown to be effective tools for the treatment of a wide range of equilibrium quantum mechanical problems. More recently, numerical path integral methods have been generalized beyond their traditional equilibrium domain to permit "real time" quantum dynamical applications.[23-25; 2; 26; 27; 4; 28-52] In some current developments, real time approaches confront an intrinsic numerical difficulty associated with such problems, the calculation of many dimensional averages of highly oscillatory integrands, by introducing a formally exact, yet computationally practical analog of the stationary phase method.[2; 4] Significant progress has also been reported in the direct calculation of the spectral densities associated with various time correlation functions using maximum entropy and other regularized inverse methods.[53-56]

In the present discussion we wish to step back a bit from the specifics of the formal development and application of these dynamical Monte Carlo methods and explore more generally issues concerning the structure of quantum mechanical time correlation functions. We will find that by emphasizing the separate and distinct roles of equilibrium and dynamical quantum effects, connections between the new and somewhat unfamiliar real-time quantum methods and more traditional approaches are clarified. In particular, it proves possible to develop a common theoretical viewpoint that encompasses a variety of methods ranging from classical molecular dynamics approaches to numerically exact, real time

quantum Monte Carlo techniques. This unified viewpoint should prove particularly convenient for the development and testing of various dynamical approaches.

The present developments focus on the formal structure of finite temperature time correlation functions. The central findings are: (1) there exists a conditional (Bayesian) transition probability that permits both a formal and a computational simplification of the quantum dynamical problem, and (2) the essential dynamical information required in the resulting approach is, for fixed times, typically *spatially local* in character. The introduction of spatial locality suggests that few as well as many-body dynamical methods can be brought to bear on the analysis.

Intuitively, finite temperature time correlation functions involving the coordinate-diagonal quantities A and B are expressed by averages of the type

$$G_{AB}(t) = \frac{\int dx\, \rho(x) \left\{ \int dx'\, P(x \rightarrow x', t) A(x) B(x') \right\}}{\int dx\, \rho(x)} \,. \tag{4.1a}$$

Here the averages are over initial positions, x, weighted by the appropriate equilibrium density, $\rho(x)$, and over final positions, x', that are distributed according to P(x -> x',t), a conditional probability distribution. This latter object is a dynamical quantity that describes the likelihood that a system characterized by a temperature T moves to a particular final position, x', given that it was at a specified initial position, x, a time t earlier.

With the anticipation that statistical methods will prove useful in the numerical evaluation of the averages of the type given in Eq. (4.1a), we write an N-point Monte Carlo estimate of the time correlation function given in Eq. (4.1a) as

$$G_{AB}(t) = \frac{1}{N} \sum_{n=1}^{N} A(x_n) B(x'_n) \,. \tag{4.1b}$$

In Eq. (4.1b) each initial position, x_n, is selected at random from the equilibrium distribution, $\rho(x)$, and is associated with a final position, x'_n, chosen at random from the transition probability, P(x -> x',t). The conditional probability expresses the dynamical correlation between initial and final positions.

It is straightforward both to formulate classical time correlation functions as suggested in Eq. (4.1) and to devise methods for performing the statistical averages involved. Classically, the equilibrium distribution is the usual Boltzmann density. This can be sampled using well established "Metropolis methods" and requires no special discussion. While perhaps less familiar, the required conditional probability, $P_{cm}(x \rightarrow x', t)$, is given classically by

$$P_{cm}(x \rightarrow x',t) = \int dp\, f(p) \delta\,(x'(x,p,t) - x') \quad . \tag{4.2}$$

Here x' (x, p,t) denotes the position of a classical trajectory at time t that starts at position x at time zero with momenta p. The delta function in Eq. (4.2) selects from the equilibrium momentum distribution, f(p), those values that produce the desired final position. The general problem of sampling probability distributions of the form given in Eq. (4.2) is reviewed by Kalos and Whitlock.[1]

The above results are more familiar when combined to produce an "initial value representation" of the time correlation function

$$G_{AB}^{(cm)}(t) = \frac{\int dxdp\ \rho(x)\, f(p)\, A(x) B(x'(x,p,t))}{\int dxdp\ \rho(x)\, f(p)} \, . \tag{4.3}$$

Here the averages are over *initial* positions and momenta of the system rather than over *initial* and *final* positions as in Eq. (4.1). The combined phase space average in Eq. (4.3) is typically performed by combining conventional Metropolis methods and molecular dynamics.

We turn now to an analysis of quantum mechanical time correlation functions. As discussed previously,[4] it is often convenient to define "thermally symmetrized" correlation functions for the operators A and B by

$$G_{AB}^{(qm)}(t) = \frac{Tr\,[A\, e^{-\beta_c^{*} H} B e^{-\beta_c H}]}{Tr\,[\, e^{-\beta H}\,]}\,. \tag{4.4}$$

Here β_c is is a complex "temperature" given in terms of the physical temperature and time by

$$\beta_c = \beta/2 + it/\hbar\,. \tag{4.5}$$

In what follows, we will often drop the "cm" and "qm" designations on the time correlation functions with the understanding that the relevant classification is clear from context. As noted by Berne and Harp,[57] $G_{AB}(t)$ is closely related to the usual quantum time correlation function, $C_{AB}(t)$, defined as

$$C_{AB}(t) = \frac{Tr\,[e^{-\beta H} A e^{\,iHt/\hbar}\, B e^{-iHt/\hbar}]}{Tr\,[\, e^{-\beta H}\,]}\,, \tag{4.6}$$

through the Fourier transform identity

$$\hat{G}_{AB}(\omega) = e^{-\beta\hbar\omega/2}\,\hat{C}_{AB}(\omega)\,. \tag{4.7}$$

In the time domain this relationship is

$$C_{AB}(t) = G_{AB}(t - i\beta\hbar/2)\,, \tag{4.8}$$

an identity that underlies the approximation due to Schofield.[58; 57] G_{AB} and C_{AB} thus contain the same physical information, although $G_{AB}(t)$ may be a simpler computational objective since its propagators are always appear in combination with thermal Boltzmann factors. Miller, Schwartz and Tromp[59] have utilized these symmetrized correlation functions in their formulation of the calculation of thermal rate coefficients and a number of investigators have explored various algorithms for their calculation.

We will consider in what follows the situation where the operators A and B in Eq. (4.4) are diagonal in the coordinate representation. For this case Eq. (4.4) becomes

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

(4.9)

Multiplying and dividing in the numerator of Eq. (4.9) by the density matrix element

$$\rho(x) = \langle x | e^{-\beta H} | x \rangle ,$$

(4.10)

$G_{AB}(t)$ becomes

$$G^{qm}_{AB}(t) = \frac{\int dx \, \rho_{qm}(x) \int dx' \, P_{qm}(x \to x', t) \, A(x) \, B(x')}{\int dx \, \rho_{qm}(x)} ,$$

(4.11)

where P_{qm} is given by

$$P_{qm}(x \to x', t) = \frac{|\langle x' | exp(-\beta_c H) | x \rangle|^2}{\langle x | exp(-\beta H) | x \rangle} .$$

(4.12)

The structure of Eq. (4.12) is that anticipated in Eq. (4.1). In particular, “initial" positions, x, are weighted by the relevant equilibrium probability, the quantum mechanical density, $\rho_{qm}(x)$, while the final positions, x', are distributed according to what appears to be a conditional probability associated with the $x \to x'$ dynamical transition.

The quantity defined by Eq. (4.12) has a number of properties that we expect of a conditional quantum transition probability. In particular, it

- is positive,
- is normalized with respect to integration over final positions,
- satisfies detailed balance, and
- preserves an equilibrium distribution.

Moreover, it is straightforward to show that the semiclassical limit of P_{qm} is given by

$$\lim_{\hbar \to 0} P_{qm}(x \to x',t) = \left| \sum_n \frac{1}{(2\pi m k_B T)^{1/4}} \frac{exp(-\beta_c p_n^2/2m)}{\sqrt{\partial x'/\partial p_n}} \right|^2 ,$$

(4.13)

where the sum is over all roots, p_n, that produce classical trajectories that connect the desired initial and final positions in a time t. Specifically, the roots, p_n, satisfy

$$x'(x,p_n,t) = x'.$$

(4.14)

Equation (13) is to be compared with the corresponding classical result (obtained by performing the momentum integration in Eq. (2) using standard properties of the delta function)

$$P_{cm}(x \to x',t) = \sum_n f(p_n) / \left| \partial x'/\partial p \right|_n .$$

(4.15)

If we drop all interference terms from Eq. (4.13), then we see that P_{qm} reduces to the corresponding classical result, Eq. (4.15). We thus accept P defined by Eq. (4.12) as a quantum generalization of the classical Bayesian transition probability. In passing we note that P_{qm} is built from the absolute square of a quantum mechanical amplitude and not from the sum of probabilities, an indication that interference effects are properly included.

With formal expressions for the required probability distribution functions in hand (Eqs. (4.10) and (4.12)), the quantum dynamical problem is reduced to the problem of evaluating the coordinate averages involved in Eq. (4.11). Generating the required initial positions involves a straightforward application of established equilibrium path integral methods and thus requires no further elaboration. It thus remains to sample the Bayesian transition probability with respect to its final positions.

In approaching the task of sampling P_{qm}(x -> x',t), it is important to emphasize that one can often *sample* an unknown probability distribution *without first explicitly constructing* it. Green's function Monte Carlo theory[5] is an important practical example of this general point. It is also important to emphasize that the minimal information

required to sample a distribution by, for example, the Metropolis algorithm is not the probability distribution itself, but rather the ratio of two such distributions. It is thus generally possible that the elemental information required for sampling and the probability distribution being sampled may have *qualitatively different characteristics.*

Based on the above argument, the essential information required to sample P_{qm}(x -> x',t) is thus the ratio of P_{qm}(x -> x", t)/P_{qm}(x -> x',t). In other words, the required transition probability ratio shares a common set of initial positions, and, depending on the details of the sampling procedure, may differ in final positions by as little as a single coordinate of a *single particle.* Over a specified time, t, the dynamics of "distant" portions of the system are essentially uncorrelated with those of the single particle being moved {note: particle statistics render the notion of locality subtle}. Thus, while P_{qm}(x -> x',t) is generally an intrinsically many-body object and depends on the dynamics of the entire system, the information required for sampling tends to be rather more *local* in character. In particular, it involves principally the particle being moved and its dynamically relevant environment.

In order to make the notions of locality discussed above more explicit, it is convenient to examine the required probability ratio in greater detail. From Eq. (4.12), we see that the required probability ratio is the absolute square of the ratio of the underlying complex temperature density matrix elements, R, where

$$R(\beta_c) = \frac{<x''|e^{-\beta_c H}|x>}{<x'|e^{-\beta_c H}|x>} . \tag{4.16}$$

In Eq. (4.16) and in what follows we assume that x' and x" are two sets of final positions in a single particle Metropolis sampling move. Since R is sufficient to provide us with the required sampling information and since R can be expressed in a convenient path integral form, we will focus our attention on this quantity. To proceed, we begin with the Fourier expression for the ratio of a generic, complex temperature matrix element to its free particle counterpart,

$$Q(z) = \frac{<z|e^{-\beta_c H}|x>}{<z|e^{-\beta_c H}|x>_{fp}} = \frac{\int d\mathbf{a}\, exp(-\sum_k a_k^2/2\sigma_k^2 - \beta_c \bar{V}_{x->z})}{\int d\mathbf{a}\, exp(-\sum_k a_k^2/2\sigma_k^2)} . \tag{4.17}$$

In Eq. (4.17) the integrals are over Fourier coefficients, $\{a_k\}$, that label paths, x(u), that begin and end at positions x and z, respectively. Specifically,

$$x(u) = x + (z - x)\, u + \sum_k a_k \sin(k\pi u), \tag{4.18}$$

where the variable u ranges over the interval (0,1). The potential energy terms

$$\bar{V}_{x->z} = \int_0^1 du\, V(x(u)), \tag{4.19}$$

depend on the Fourier coefficients through the path, x(u), specified by Eq. (4.9). Finally, the gaussian width parameters are given by

$$\sigma_k^2 = \frac{2\beta_c \hbar^2}{m\pi^2 k^2}. \tag{4.20}$$

Using the familiar Kirkwood "charging" device,[60] we note that the z-derivative of Q(z) can be written as

$$\frac{\partial log(Q(z))}{\partial z} = -\beta_c \frac{\int d\mathbf{a}\, exp(-\sum_k a_k^2/2\sigma_k^2 - \beta_c \bar{V}_{x->z}) \left(\frac{\partial \bar{V}x->z}{\partial z}\right)}{\int d\mathbf{a}\, exp(-\sum_k a_k^2/2\sigma_k^2 - \beta_c \bar{V}_{x->z})} \equiv -\beta_c \left\langle \frac{\partial \bar{V}}{\partial z} \right\rangle_{S(z)}. \tag{4.21}$$

The subscript on the right hand side of Eq. (4.21) is to remind us that the average is over a complex action that involves paths that begin at point x and end at point z. Integrating Eq. (4.21) from z = x' to z = x" gives

$$log\left(\frac{Q(x'')}{Q(x')}\right) = -\beta_c \int_{x'}^{x''} dz \left\langle \frac{\partial \bar{V}}{\partial z} \right\rangle_{S(z)}, \tag{4.22}$$

which, in turn, implies that R, relative to its free particle counterpart, is given by

$$\frac{R(\beta_c)}{R_{fp}(\beta_c)} = exp\left\{ -\beta_c \int_{x'}^{x''} dz \left\langle \frac{\partial \bar{V}}{\partial z} \right\rangle_{S(z)} \right\}. \tag{4.23}$$

Equation (4.23) provides us with a formal route to the desired matrix element ratio, Eq. (4.16). Assuming for the moment that we have a means of evaluating the complex averages involved, Eq. (4.16) provides us the information necessary to sample the Bayesian probability, P(x -> x', t), with respect to final position, x', and thus to evaluate Eq. (4.1b). The complex action averages in Eq. (4.23) are of the type amenable to real time path integral methods. If invoked, such methods will produce a statistical estimate of the required probability ratio. The practical issues of sampling from a statistically known distribution have been considered previously.

Continuing our theme of analyzing the general structure of the quantum dynamical problem, we wish to point out that Eq. (4.23) enables us to establish a number of properties of the ratio of interest, $R(\beta_c)$. Perhaps the most important one to note is that R is a "local" property. That is, we see from Eq. (4.23) that although the matrix elements involved in the construction of R are many-body objects and depend on the dynamics of the entire system, the matrix element ratio depends on the complex temperature analog of the reversible work necessary to displace the end of the path of the particle being moved from x' -> x". For a specified physical time and for typical molecular interactions, the average that appears in the exponential of Eq. (4.23) is thus a local quantity. Next, from the mean value theorem and Eq. (23), we also note that R is guaranteed to be a simple function of difference, x" - x'. It is valuable to observe that Eq. (23) has isolated a substantial amount of the analytic structure of the desired ratio. Specifically, while the individual matrix elements involved have a square root non-analyticity, the ratio R/R_{fp} appears to be an exponential of an analytic function of β_c. If generally true, such behavior may prove of significance in designing analytic continuation procedures for the calculation of R starting from real temperature data. In this context, we note that from Eqs. (4.16) and (4.23) that both the low and high temperature forms of R are relatively simple. Performing a spectral expansion of Eq. (4.16) in terms of energy eigenstates, $\{\psi_n(x)\}$, we see that the low temperature form of R is given by the ratio of the ground state wavefunctions. Explicitly,

$$lim_{\beta -> \infty} \left\{R(\beta)\right\} = \frac{\psi_0(x'')}{\psi_0(x')} , \tag{4.24}$$

where $\psi_0(x)$ is the ground state wavefunction. From Eq. (4.23), on the other hand, we see that the high temperature limit of R is given by

$$lim_{\beta -> 0} R(\beta)/R_{fp}(\beta) = exp\{-\beta (\bar{V}(x'') - \bar{V}(x'))\} \tag{4.25}$$

where the averages in the potential energy terms are along straight-line paths connecting the initial and final positions.

Specific realizations of the general properties of R discussed above are illustrated by the results for the simple harmonic oscillator. For an oscillator of mass m and frequency ω, the analytic form for $R_{osc}(\beta)$ can be shown to be

$$R_{osc}(\beta) = \exp\left\{ - \frac{m\omega}{2\hbar \sinh(\beta\hbar\omega)}(x'' - x')((x''+ x') \cosh(\beta\hbar\omega) - 2x) \right\} . \tag{4.26}$$

As expected from the previous discussion, $R_{osc}(\beta)$ is an exponential of (x'' - x') times a relatively simple function of the temperature. The low temperature limit of Eq. (26) is given by

$$R_{osc}(\beta -> \infty) = \exp\left\{ - \frac{m\omega}{2\hbar}\left((x'')^2 - (x')^2\right) \right\} , \tag{4.27}$$

which is the ratio of the ground state wavefunctions predicted by Eq. (24). Furthermore, the high temperature limit of Eq. (4.26) relative to its free particle ($\omega = 0$) counterpart can be shown to be given by Eq. (4.25). Finally, from Eq. (4.26) it is not difficult to show that the conditional transition probability for the oscillator, $P_{osc}(x' -> x'', t)$, is given by

$$P_{osc}(x -> x'', t) = \left(\frac{1}{2\pi\sigma^2}\right)^{1/2} \exp\left(- \frac{1}{2}\frac{(x'' - \mu)^2}{\sigma^2} \right) , \tag{4.28}$$

where

$$\mu = x \frac{\cos(\omega t)}{\cosh(\beta\hbar\omega / 2)} \tag{4.29}$$

and

$$\sigma^2 = \frac{\hbar}{m\omega} \left\{ \frac{\sinh^2(\beta\hbar\omega / 2) + \sin^2(\omega t)}{\sinh(\beta\hbar\omega)} \right\} \tag{4.30}$$

The correct classical and the free particle counterparts of the corresponding quantum mechanical oscillator results emerge from Eq. (28) in the limit that Planck's constant and $\omega \to 0$, respectively.

The spatial locality of R introduces the possibility of utilizing more conventional approaches as opposed to numerical path integral methods to evaluate the necessary sampling information. In particular, for some applications it may prove useful to view the general dynamical question as an "embedded cluster" problem. That is, we can regard the particle being moved and its surroundings as a few-body "cluster" that is "embedded" in various randomly chosen environments corresponding to the various initial positions of the surrounding lattice. The essential information required for final position sampling, Eq. (4.16), can be obtained as a spectral expansion in terms of the wavefunctions and energies of few-body "embedded clusters." The size of the cluster required depends on the physical time involved and on details of the problem. In the extreme situation where the motion involves a single quantum particle in a nearly classical environment, the embedded cluster effectively reduces to a single particle. That is, over short times it is reasonable to view the quantum motion as taking place in the static field of the remaining lattice. At longer times, or in systems that lack a natural separation of time scales, "larger" embedded clusters are required. In general, the proper length scale can be established by examining the convergence of the correlation function in question with increasing cluster size.

The practical significance of the embedded cluster developments is that they offers a bridge between few and many-body dynamical approaches. Specifically, using this approach techniques principally designed for the treatment of few degree of freedom dynamical problems, moment methods, and correlation function Monte Carlo approaches can be extended to more general, many-body contexts. By establishing a convenient point of contact between a number of independent approaches, the embedded cluster formulation

provides a valuable means for cross-checking the predictions of the various methods and for assisting in the development of general purpose, quantum Monte Carlo dynamical techniques.

Finally, we close this discussion by noting that one of the most important features of the quantum transition probability, P(x -> x', t), is that it does not in general approach δ(x'' - x') as t -> 0. Classically, vanishingly small times imply correspondingly small dynamical displacements. Quantum mechanically, however, this is not the case. As t -> 0, the transition probability approaches

$$P(x \; -> x', 0) \; = \; \frac{| < x' | \exp\left(- \beta H / 2 \right) | x > |^2}{< x \, | \exp\left(- \beta H \right) | x >} \, .$$

(4.31)

From path integral developments, we recognize the zero time dispersion of the particle as being the probability distribution of x', the $\beta\hbar/2$ positions of closed path integral loops that begin and end at point x. Only in the classical limit does the physical scale of these loops shrink to zero. The implications on this point for the construction of approximate dynamical theories are discussed elsewhere.[61]

It is useful to note a number of connections between current work and established results. We begin by recalling that the van Hove correlation function, F(k, t), for a single degree of freedom is defined by[60]

$$F(k, t) \; = \; < e^{- ikx(0)} \, e^{ikx(t)} \; > .$$

(4.32)

The many degree of freedom counterpart of this quantity plays a central role in the theory of condensed matter systems. The thermally symmetrized analog of F is given by (c.f. Eqs. (4.32) and (4.11))

$$\hat{G}(k, t) \; = \; \frac{\int \rho(x) \, P(x \; -> x', t) e^{\; - ik(x' \, - \, x)} \, dx \, dx'}{\int \rho(x) \, dx}$$

(4.33)

Fourier transforming Eq. (4.33),

$$G(y,\,t) \;=\; \int \frac{dk}{2\pi}\, e^{-iky}\hat{G}(k,\,t) \tag{4.34}$$

and utilizing the properties of the resulting delta function, we find

$$G(y,\,t) \;=\; \frac{\int dx\;\rho(x)\;P(x\;->\;x\;+\;y,\,t)}{\int dx\;\rho(x)}\,. \tag{4.35}$$

Examination of Eq. (4.35) thus reveals that the (thermally symmetrized) van Hove space time correlation function, G(y, t), has a rather intuitive structure. In particular, it is the probability that a system suffers a displacement y in a time t starting from a particular position x averaged over an equilibrium distribution of all possible initial positions. Many degree of freedom analogs of the above results are easily derived.

As suggested by the previous example, a valuable feature of the current formulation is that it provides a highly intuitive framework for discussing quantum dynamics. As a second illustration of this point, we consider the problem of computing the thermal rate constant for the transformation of reactants A into products B. Without loss of generality we assume that the reaction coordinate, x, carries us between reactants and products. The probability that a system begins in region A at time zero and ends up in region B a time t later, $P_{A\;->\;B}(t)$, is given intuitively as the integral of the Bayesian transition probability as

$$P_{A\;->\;B}(t) \;=\; \frac{\int_A dx\;\rho(x)\int_B dx'\;P(x\;->\;x',\,t)}{\int_A dx\;\rho(x)} \tag{4.36}$$

The rate constant for the A -> B process, $k_{A\;->\;B}$ is thus the time derivative of Eq. (4.36), or

$$k_{A\;->\;B} \;=\; \frac{d}{dt}\left(\frac{\int_A dx\;\rho(x)\int_B dx'\;P(x\;->\;x',\,t)}{\int_A dx\;\rho(x)}\right).$$

(4.37)

Inserting Eqs. (4.9) and (4.12) into Eq. (4.37), we find that our argument has produced, in a very transparent fashion, the reactive flux rate expression derived previously by Miller, Schwartz, and Tromp.[59]

We consider a specific numerical example to examine the issue of spatial locality of the density matrix element ratio defined by Eq. (4.16). Even disregarding issues related to particle statistics, spatial locality is much more subtle in quantum systems than in classical systems. For example, in classical mechanics temporal locality implies spatial locality. This means that in classical systems short time intervals produce small spatial displacements. In quantum mechanics, however, it is possible for particles to delocalize over significantly large spatial dimensions, so that short times do not necessarily imply small displacements. This point has been explored previously in the context of short time quantum dynamics and quantum instantaneous normal modes.[61] A corollary of this result is that the spatial locality of R is a non-trivial matter for a many-body quantum system even in the limit t -> 0.

The model we consider is a two-dimensional Lennard-Jones ^{4}He fluid at various reduced temperatures. A two-dimensional model is used for graphical convenience, and the conclusions regarding the locality of R drawn from the results extend trivially to three dimensions. In the previous subsection it was argued that the complex temperature analog of the work necessary to displace the end of the path of the single particle being moved from x´ to x'' is a local quantity, and from inspection of Eq. (4.23) it was therefore concluded that R/R_{fp} must be a local quantity. To test this assertion, we examine the generalized force,

$$-F \equiv \left\langle \frac{\partial \langle V \rangle_a}{\partial z} \right\rangle_{S(z)} , \tag{4.38}$$

and the associated work

$$W = \int_{x'}^{x''} dz \left\langle \frac{\partial \langle V \rangle_a}{\partial z} \right\rangle \tag{4.39}$$

in the limit of *zero-time* for our model system. The angular brackets in Eqs. (4.38) and (4.39) correspond to an average over a path integral action of the form (c.f. Eq. (4.21))

$$S(\boldsymbol{a},z) = -\sum_{k=1}^{\infty} \frac{a_k^2}{2\sigma_k^2} - \beta\langle V\rangle_{\boldsymbol{a}}. \tag{4.40}$$

Here the parameter z corresponds to the final position of our test particle. Establishing the spatial locality of the generalized force given by Eq. (4.38) is sufficient to demonstrate the locality of R.

In the present calculation, 120 helium atoms were initially arranged on a closed packed hexagonal grid. The nearest neighbor distance was chosen to be 4.91 Å corresponding to $\rho\sigma^2 = 0.36$. Because of this geometrical arrangement of the atoms the generalized force on any one of the atoms is identically zero. To alleviate this problem one of the atoms in the study, the "test" atom, was moved a distance 0.25 σ in a straight line closer to one of its neighbors. The test atom along with several of its nearest neighbors were designated the dynamically "active" particles. N represents the number of dynamically active particles. These active particles were allowed to have quantum mechanical paths that connected their initial and final positions, and the rest of the "inactive" particles in the system were considered to be point particles. For simplicity the initial and final positions of the active particles were identical and equal to their respective lattice position. Shown in Table I are the generalized forces (in dimensionless units) calculated from Eq. (4.38) for three different reduced temperatures and for three different numbers of active particles; N = 1, just the test particle; N = 7 the test particle and its "first solvation shell;" and N = 19 the test particle and its "first and second solvation shells." The calculation was performed using 16 Fourier coefficients to parameterize each path, 10^6 Monte Carlo moves, and 32 quadrature points for calculating the average potential energy of each path. The error bars shown represent one standard deviation estimates of the resulting averages. Boltzmann statistics were used throughout.

The results shown in Table I support our assertion of the spatial locality of R. The result for the force is essentially converged after the test particle and its first "solvation shell" are included in the calculation. This result implies that, for short times and for problems with similar interactions and relative physical temperatures, the minimum cluster in the proposed quantum embedded cluster dynamics technique must contain the particle of interest and its first solvation shell. The expectation is that at very low temperatures more and more active particles must be included in the calculation of R, just as the expectation is that at long times more and more active particles will be required.

Table I

Shown are the generalized forces (in dimensionless units) on the end of the quantum mechanical path of a test particle in a two dimensional Lennard-Jones neon system as a function of N, the number of active particles in the simulation. Discussed in detail in Section IV, N = 1 corresponds to only the test particle being active, N = 7 is the test particle and its first solvation shell, and N = 19 is the test particle and its first two solvation shells. Calculations were performed using 16 Fourier coefficients to parameterize each path, 10^6 Monte Carlo moves, and 32 quadrature points for calculating the average potential energy of each path. The error bars represent one standard deviation estimates of the corresponding averages.

N_{active}	$-\sigma\beta \left\langle \frac{\partial}{\partial z}\left(< V >_a\right) \right\rangle_{S(z)}$
T* = 0.88	
1	0.262 ± 0.002
7	0.204 ± 0.008
19	0.212 ± 0.012
T* = 0.58	
1	0.384 ± 0.006
7	0.176 ± 0.014
19	0.174 ± 0.018
T* = 0.29	
1	0.436 ± 0.018
7	0.078 ± 0.024
19	0.122 ± 0.032

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References

1. Kalos, M. and Whitlock, P. (1986) *Monte Carlo Methods* Wiley-Interscience, New York.

2. Doll, J. D. and Freeman, D. L. (1988) Stationary Phase Monte Carlo Methods, *Adv. Chem. Phys.*, **73**, 289.

3. Freeman, D. L. and Doll, J. D. (1988) The Quantum Mechanics of Clusters, *Adv. Chem. Phys.*, **70B**, 139-179.

4. Doll, J. D., Freeman, D. L. and Beck, T. L. (1990) Equilibrium and Dynamical Fourier Path Integral Methods, *Adv. Chem. Phys.*, **78**, 61.

5. Ceperley, D. and Alder, B. (1986) Quantum Monte Carlo, *Science*, **231**, 555-560.

6. Ceperley, D. M. (1995) Path integrals in the theory of condensed helium, *Rev. Mod. Phys.*, **67**, 279.

7. Metropolis, N., Rosenbluth, A. W., Rosenbluth, M. N., Teller, A. M. and Teller, E. (1953) Equation of State Calculation by Fast Computing Machines, *J. Chem. Phys.*, **21**, 1087.

8. Valleau, J. P. and Torrie, G. M. (1977). Monte Carlo Methods-Byways. Modern Theoretical Chemistry. B. J. Berne. New York, Plenum.

9. Valleau, J. P. and Whittington, S. G. (1977). Monte Carlo Methods-Highways. Modern Theoretical Chemistry. B. J. Berne. New York, Plenum.

10. Abramowitz, M. and Stegun, I. A., Eds. (1964). *Handbook of Mathematical Functions*. Applied Mathematics Series. Washington DC, U. S. Department of Commerce.

11. Risken, H. (1984) *The Fokker-Planck Equation* Springer-Verlag, Berlin.

12. Carrier, G. F., Krook, M. and Pearson, C. E. (1966) *Functions of a Complex Variable: Theory and Technique* McGraw-Hill, New York.

13. Feynman, R. P. and Hibbs, A. R. (1965) *Quantum Mechanics and Path Integrals* McGraw-Hill, New York.

14. Feynman, R. P. (1972) *Statistical Mechanics* Academic Press, New York.

15. Hamming, R. W. (1986) *Numerical Methods for Scientists and Engineers* Dover, New York.

16. Lanczos, C. (1988) *Applied Analysis* Dover, New York.

17. Chandler, D. and Wolynes, P. G. (1981) Exploiting the isomorphism between quantum theory and classical statistical mechanics of polyatomic fluids, *J. Chem. Phys.*, **74**, 4078-4095.

18. Doll, J. D., Coalson, R. D. and Freeman, D. L. (1985) Fourier Path-Integral Monte-Carlo Methods: Partial Averaging, *Phys. Rev. Letts.*, **55**, 1.

19. Coalson, R. D., Freeman, D. L. and Doll, J. D. (1986) Fourier Path Integral Monte Carlo Methods: The Partial Averaging Method, *J. Chem. Phys.*, **85**, 4567.

20. Coalson, R. D., Freeman, D. L. and Doll, J. D. (1989) Cumulant Methods and Short Time Propagators, *J. Chem. Phys.*, **91**, 4242.

21. Gradshteyn, I. S. and Ryzhik, I. M. (1965) *Table of Integrals, Series, and Products* Academic Press, New York.

22. Eleftheriou, M., Doll, J. D., Curotto, E. and Freeman, D. L. (1998) The Asymptotic Convergence Rates of Fourier Path Integral Methods, *J. Chem. Phys.*, (to be submitted).

23. Doll, J. D. (1984) Monte Carlo Fourier Path Integral Methods in Chemical Dynamics, *J. Chem. Phys.*, **81**, 3536.

24. Doll, J. D., Coalson, R. D. and Freeman, D. L. (1987) Towards a Monte Carlo Theory of Quantum Dynamics, *J. Chem. Phys.*, **87**, 1641.

25. Ceperley, D. M. and Bernu, B. (1988) The Calculation of Excited State Properties with Quantum Monte Carlo, *J. Chem. Phys.*, **89**, 6316.

26. Makri, N. (1989) Effective Non-oscillatory propagator for Feynman path integration in real time, *Chem. Phys. Lett.*, **159**, 489-498.

27. Bernu, B., Ceperley, D. M. and Lester, W. A., Jr. (1990) The calculation of excited states with quantum Monte Carlo. II. Vibrational excited states, *J. Chem. Phys.*, **93**, 552-561.

28. Mak, C. H. and Chandler, D. (1991) Coherent-incoherent transition and relaxation in condensed-phase tunneling systems, *Phys. Rev. A*, **44**, 2352.

29. Makri, N. (1991) Feynman path integration in quantum dynamics, *Computer physics communications*, **63**, 389.

30. Amini, A. M. and Herman, M. F. (1992) Real-time path-integral simulation of vibrational transition probabilities of small molecules in clusters: Theory and application to Br2 in Ar., *J. Chem. Phys.*, **96**, 5999.

31. Kouri, D. J. and Hoffman, D. K. (1992) Toward a New Time-Dependent Path Integral Formalism Based on Restricted Quantum Propagators for Physically Realizable Systems, *J. Phys. Chem.*, **96**, 9631.

32. Kouri, D. J. and Zhu, W. (1992) Monte Carlo Evaluation of Real-Time Feynman Path Integrals for Quantal Many-Body Dynamics: Distributed Approximating Functions and Gaussian Sampling, *J. Phys. Chem.*, **96**, 9622.

33. Mak, C. H. (1992) Stochastic method for real-time path integrations, *Phys. Rev. Lett.*, **68**, 899.

34. Topaler, M. and Makri, N. (1992) Multidimensional path integral calculations with quasiadiabatic propagators: Quantum dynamics of vibrational relaxation in linear hydrocarbon chains, *J. Chem. Phys.*, **97**, 9001.

35. Amini, A. M. and Herman, M. F. (1993) An approximate discretized real time path integral simulation method for nearly classical systems., *J. Chem. Phys.*, **98**, 6975.

36. Egger, R. and Mak, C. H. (1993) Dynamical effects in the calculation of quantum rates for electron transfer reactions, *J. Chem. Phys.*, **99**, 2541.

37. Ma, X., Kouri, D. J. and Hoffman, D. K. (1993) Monte Carlo evaluation of real time Feynman path integrals using distributed approximating functions. Modified-Cayley versus symmetric split-operator formalism, *Chem. Phys. Lett.*, **208**, 207.

38. Mak, C. H. and Gehlen, J. N. (1993) A dynamical test of the centroid formulation of quantum transition state theory for electron transfer reactions, *Chem. Phys. Lett.*, **206**, 130.

39. Makri, N. (1993) On Smooth Feynman Propagators for Real Time Path Integrals, *J. Phys. Chem.*, **97**, 2417.

40. Egger, R. and Mak, C. H. (1994) Low-temperature dynamical simulation of spin-boson systems, *Phys. Rev. B*, **50**, 15210.

41. Egger, R., Mak, C. H. and Weiss, U. (1994) Quantum rates for nonadiabatic electron transfer, *J. Chem. Phys.*, **100**, 2651.

42. Ilk, G. and Makri, N. (1994) Real time path integral methods for a system coupled to an anharmonic bath, *J. Chem. Phys.*, **101**, 6708.

43. Makarov, D. E. and Makri, N. (1994) Path integrals for dissipative systems by tensor multiplication. Condensed phase quantum dynamics for arbitrarily long time, *Chem. Phys. Lett.*, **221**, 482.

44. Kouri, D. J., Huang, Y. and Hoffman, D. K. (1995) Integrated Real-Time Path Integral Evaluation Using a Distributed Approximating Functional Propagator and Average-Case Complexity Integration, *Phys. Rev. Lett.*, **75**, 49.

45. Leung, K., Egger, R. and Mak, C. H. (1995) Dynamical Simulation of Transport in One-Dimensional Quantum Wires, *Phys. Rev. Lett.*, **75**, 3344.

46. Mak, C. H. and Egger, R. (1995) On the mechanism of the primary charge separation in bacterial photosynthesis, *Chem. Phys. Lett.*, **238**, 149.

47. Makri, N. (1995) Numerical path integral techniques for long time dynamics of quantum dissipative systems, *J. Math. Phys.*, **36**, 2430.

48. Makri, N. and Makarov, D. E. (1995) Tensor propagator for iterative quantum time

evolution of reduced density matrices. I. Theory, *J. Chem. Phys.*, **102**, 4600.

49. Makri, N. and Makarov, D. E. (1995) Tensor propagator for iterative quantum time evolution of reduced density matrices. II. Numerical methodology, *J. Chem. Phys.*, **102**, 4611.

50. Sim, E. and Makri, N. (1996) Tensor propagator with weight-selected paths for quantum dissipative dynamics with long-memory kernels, *Chem. Phys. Lett.*, **249**, 224.

51. Stockburger, J. T. and Mak, C. H. (1996) A dynamical theory of electron transfer: Crossover from weak to strong electronic coupling, *J. Chem. Phys.*, **105**, 8126.

52. Sim, E. and Makri, N. (1997) Filtered propagator functional for interative dynamics of quantum dissipative systems, *Computer physics communications*, **99**(335).

53. Gallicchio, E. and Berne, B. J. (1994) The absorption spectrum of the solvated electron in fluid helium by maximum entropy inversion of imaginary time correlation functions from path integral Monte Carlo simulations, *J. Chem. Phys.*, **101**, 9909.

54. Gallicchio, E. and Berne, B. J. (1996) On the calculation of dynamical properties of solvated electrons by maximum entropy analytic continuation of path integral Monte Carlo data, *J. Chem. Phys.*, **105**, 7064.

55. Jarrell, M. and Gubernatis, J. E. (1996) Bayesian Inference and the Analytic Continuation of Imaginary-Time Quantum Monte Carlo Data, *Physics Reports*, **269**, 133-196.

56. Kim, D., Doll, J. D. and Gubernatis, J. E. (1997) The Quantum Dynamics of Interfacial Hydrogen: Path Integral Maximum Entropy Calculation of Adsorbate Vibrational Lineshapes for the H/Ni(111) System, *J. Chem. Phys.*, **106**, 1641.

57. Berne, B. J. and Harp, G. D. (1970) On the Calculation of Time Correlation Functions, *Adv. Chem. Phys.*, **17**, 63-227.

58. Schofield, P. (1960) *Phys. Rev. Lett.*, **4**, 39.

59. Miller, W. H., Schwartz, S. D. and Tromp, J. W. (1983) Quantum mechanical rate constants for bimolecular reactions, *J. Chem. Phys.*, **79**, 4889-4898.

60. McQuarrie, D. A. (1976) *Statistical Mechanics* Harper & Row, New York.

61. Corcelli, S. A. and Doll, J. D. (1996) A Bayesian Approach to Short-Time Quantum Dynamics: Quantum Instantaneous Normal Modes, *Chem. Phys. Lett.*, **264**, 671.