An iterative scheme for the evaluation of discretized path integrals[a)]

Devarajan Thirumalai, Eric J. Bruskin, and Bruce J. Berne

Department of Chemistry, Columbia University, New York, New York 10027

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A simple iterative scheme which greatly facilitates the evaluation of discretized path integrals is presented. The method is applied to study the motion of a proton in a bistable potential and the resulting configurational distribution function is compared to both the path integral Monte Carlo calculation and to the "exact" result. As a second illustration we present calculations of the radial distribution function for an Ar_2 van der Waals dimer at two temperatures.

INTRODUCTION

The Feynman path integral formulation of the density matrix has been used to calculate various properties of quantum or mixed quantum-classical systems.[1] This is accomplished by writing the canonical density matrix as a Feynman sum over continuous paths with each path obeying well defined boundary conditions. Each continuous path is then made discrete with P segments and the semiclassical approximation for each segment then allows one to identify the canonical density matrix for the N body quantum system as a distribution function of an isomorphic $N\times P$ body classical system. This formulation provides a very powerful technique to calculate equilibrium properties of quantum systems by simulating the corresponding classical system either by Monte Carlo or molecular dynamics. Recently, we have extended the use of path integral techniques to calculate time correlation functions of dynamical properties of quantum or mixed quantum-classical systems.[2] Thus it appears that many interesting quantum systems such as electrons in various solvents, electron or proton transfer reactions in the condensed phase, transport properties of quantum particles interacting with a classical bath, and molecular spectra in the condensed phase can be studied using this general formulation. Indeed, considerable progress has been made towards the calculation of the radial distribution function of an electron in fluid helium as a function of density.[1(c)]

So far, the only numerical method that has been used with success is the classical Metropolis Monte Carlo (MC) algorithm[1(c),2-4] or equivalently molecular dynamics.[5] It is clear that for N body quantum systems, the MC algorithm does indeed seem to be the easiest to implement. Although the MC method is a very powerful numerical technique, it is also beset with problems; the notable one being that if one desires very accurate answers, it may be necessary to perform averages over many configurations and this may become very time consuming. Hence, it is desirable to search for alternate methods of evaluating the multidimensional integrals that arise in these problems. In this article, we describe one such method which not only appears to be time saving but also does not suffer from the usual MC uncertainties. Moreover, the method can be used to determine the Helmholtz free energy. This method uses direct numerical matrix multiplication (NMM) and is particularly suited to systems containing only a few quantum degrees of freedom such as a quantum impurity dissolved in a classical bath. Almost all of the problems described at the end of the last paragraph fall into this category as do very many other problems of interest in chemistry. For simplicity, the method is illustrated for one dimensional systems. The generalization to multidimensional systems will be discussed later.

The basic problem is to solve the Bloch equation

$$\frac{\partial\rho(r,r';\beta)}{\partial\beta}=-H\rho(r,r';\beta) \tag{1}$$

for the density matrix

$$\rho(r,r';\beta)=\langle r|e^{-\beta H}|r'\rangle\ , \tag{2}$$

subject to the initial condition

$$\lim_{\beta\to 0}\rho(r,r';\beta)=\delta(r-r')\ . \tag{3}$$

Because $e^{-2\epsilon H}=e^{-\epsilon H}\cdot e^{-\epsilon H}$, it is easy to show that

$$\rho(r,r';2\epsilon)=\int_{-\infty}^{+\infty}dr''\rho(r,r'',\epsilon)\rho(r'',r';\epsilon)\ . \tag{4}$$

Starting with $\rho(r,r'',\epsilon)$, one can iterate Eq. (4) n times. This gives $\rho(r,r,2^n\epsilon)$ in terms of the $\rho(r,r';\epsilon)$. If ϵ is chosen such that $\epsilon=\beta/2^n$, then n iterations yield the desired density matrix $\rho(r,r';\beta)$. If n is taken to be sufficiently large, $\epsilon=\beta/2^n$ will be small enough to justify using the short time approximation for $\rho(r,r';\epsilon)$:

$$\rho^{(0)}(r,r';\epsilon)=\exp[-(\epsilon/2)V(r)]\rho_0(r,r';\epsilon)\exp[-(\epsilon/2)V(r')]\ , \tag{5}$$

where

$$\rho_0(r,r';\epsilon)\equiv\left[\frac{\mu}{2\pi\hbar^2\epsilon}\right]^{1/2}\exp-\{[(\mu/2\hbar^2\epsilon)(r-r')^2]\}\ . \tag{6}$$

It is important to note that iteration of Eq. (4) using the short time approximation given by Eq. (5) is equivalent to the discretized Feynman path integral formulation (the primitive algorithm) of the density matrix with $P=2^n$ discrete points. Our approach here is to use direct numerical matrix multiplication (NMM) to

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accomplish this iteration rather than to rely on the Monte Carlo algorithm. The evaluation of the integral in Eq. (4) proceeds as follows:

(i) The limits of integration are replaced by $(-S/2, S/2)$, where S is sufficiently large to ensure proper convergence. This point will be elaborated below.

(ii) A grid is constructed of equally spaced points over a square lattice between $-S/2$ and $S/2$. Let Δ be the spacing between successive points and $2M+1$ be the total number of points in the interval $(-S/2, S/2)$ so that $S=M\Delta$, then any set of points r, r'' can be specified as $i\Delta$; $j\Delta$ on this square lattice. The integral in Eq. (4) is evaluated over this grid using a simple trapezoidal-like rule

$$\rho(i\Delta, j\Delta; 2\epsilon) = \Delta \sum_{k=-M}^{M} \rho(i\Delta, k\Delta; \epsilon)\rho(k\Delta, j\Delta; \epsilon) \ . \tag{7}$$

(iii) Starting with the short time approximation for $\rho(i\Delta, j\Delta; \epsilon)$, Eq. (7) gives $\rho(i\Delta, j\Delta, 2\epsilon)$. Substitution of $\rho(i\Delta, j\Delta; 2\epsilon)$ into Eq. (7) then gives $\rho(i\Delta, j\Delta; 4\epsilon)$. Repeating this iteration n times gives $\rho(i\Delta, j\Delta; 2^n\epsilon)$.

Before applying this numerical matrix multiplication (NMM) method to calculate distribution functions, certain comments on the technical aspects of the method are in order.

(a) Replacement of the infinite range of integration over the intermediate points by a finite interval does not pose a problem in practice because the off-diagonal elements of ρ decrease as $\exp(-\mu\rho(r-r')^2/2\hbar^2\beta)$. This implies that for a given r and r', the maximum contribution comes when both r and r' are close to r'', the intermediate integration point.

(b) In evaluating the integral in Eq. (4), a value of $P=2^n$ must be chosen so that the high temperature approximation, namely Eq. (5), is valid. On the other hand, for a given separation Δ, β/P should be large enough so that the exponential term in the high temperature approximation does not decrease too rapidly as k differs from i. This implies that one should choose the quantity $\delta = \mu\Delta^2 P/2\hbar\beta^2$ as small as possible. In all the problems we have studied, a value of $\delta < 0.3$ seems to ensure proper convergence. The arguments presented show that Δ is an implicit function of P and β and should be chosen so that the above criteria are satisfied. For a given short time approximation [cf. Eq. (6)], the NMM yields the density matrix at half the initial temperature after one iteration. Because the range of integration over the intermediate point has been made finite [see Eq. (7)], this results in an inaccurate estimation of $\rho(r, r'; 2\epsilon)$ over a distance of λ from S. The quantity can be inferred to be of the order of the thermal de Broglie wavelength at the temperature $(\epsilon)^{-1}$. This, of course, is not a serious problem because S can be made large enough so that the contribution to $\rho(r, r'; 2\beta)$ for $r \sim (S-\lambda)$ is negligible.

In this paper, we present an application of NMM to several simple systems (see Secs. II and III). First proton tunneling between two geometrical isomeric states of H_2O_2 is studied. Then the case of two particles (argon) interacting through a Lennard-Jones potential in three dimensions is studied. In Sec. IV, it is shown how NMM can be applied to calculate the thermal properties of a mixed quantum classical system. We conclude the paper in Sec. V with a short discussion.

II. PROTON TUNNELING

Proton tunneling in tautomerization reactions and in hydrogen bonded systems is of considerable interest. The evaluation of path integrals using direct numerical matrix multiplication is particularly well suited to the study of the motion of protons in a double well potential, because the size of the configuration space is limited and, consequently, the dimension of the density matrix can be kept small. In this section, we treat the motion of a proton in the bistable potential

$$V(x) = \begin{cases} A\cos 3x + B\cos 2x + C\cos x + D;\, 0 < x < 2\pi \\ \infty \qquad\qquad \text{otherwise} \end{cases} \ . \tag{8}$$

The parameters of this potential were chosen[6] to mimic the proton motion in the isomerization of H_2O_2. The values of the parameters A, B, C, and D are 81.08, 973.63, 1824, and 1320 K, respectively, and the temperature is taken to be 200 K. At this temperature, the proton tunneling should give rise to considerable delocalization of the proton over the two wells with penetration into the barrier region. Because this is a one-dimensional problem, it is a simpler matter to numerically determine the exact (numerically) energy eigenvalues E_n and corresponding energy eigenfunctions $\psi_n(z)$. This is done using the "equation of motion" method. The configurational distribution function is then given by

$$P(x) \equiv \frac{\rho(x,x)}{\mathrm{Tr}\rho(x,x)} = \frac{\sum_n |\psi_n(x)|^2 e^{-\beta E_n}}{\sum_n e^{-\beta E_n}} \ . \tag{9}$$

This provides the result against which both path integral Monte Carlo and direct numerical matrix multiplication can be compared. The "exact" $P(x)$ calculated on the basis of 46 states is shown in Fig. 1.

The Monte Carlo calculation is performed in the primitive algorithm using $P=100$ discrete points. From our previous work on the linear harmonic oscillator,[4] it is known that the use of the direct Metropolis MC algorithm involving single particle moves results in slow convergence. To accelerate the convergence, we found it useful to transform to the harmonic normal modes of the chain. These correspond to the kinetic energy contribution to the Hamiltonian. When this is done, each mode has a different force constant and we can choose step sizes appropriate to that force constant; e.g., a small step size is chosen for the high frequency modes and a large step size is chosen for the low frequency modes. We adjusted the step sizes of the normal modes so that the acceptance ratio of all the modes was roughly equal to 0.4. The one particle distribution $P(x)$ was calculated as a function of x in the range $(0, 2\pi)$ and the result of this calculation after 12000 passes is shown in Fig. 1.

The distribution function $P(x)$ is also evaluated using NMM. To this end, the initial density matrix $\rho(x_t, x_{t+1}, \beta/P)$ is evaluated on a square grid with $M=50$,

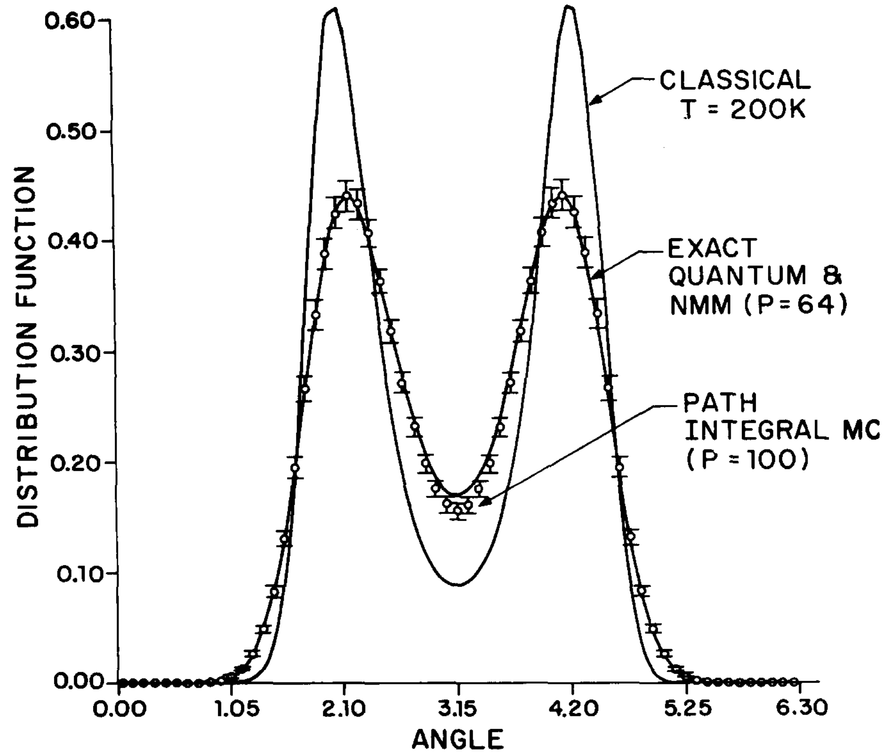

FIG. 1. The distribution function $P(x)$ for proton tunneling in H_2O_2 at $T = 200$ K. The data points 000 correspond to a path integral Monte Carlo run using the primitive algorithm with $P = 100$. Error bars indicate the uncertainty based on one standard deviation. The exact quantum distribution function and the distribution function determined from the path integral using NMM are given by the labeled solid curve. These are in quantitative agreement. The classical distribution function is given by the labeled solid curve for purposes of comparison.

$\Delta = 0.02\pi$, and $P = 2^6$. Thus we require only six iterations of Eq. (7) to reach the inverse temperature β^{-1} of the system. For the set of parameters used, $\delta = m\Delta^2 P/2\hbar^2\beta$ turns out to be 0.145 and this is sufficiently small to guarantee convergence. The result is shown in Fig. 1.

In Fig. 1, these three methods for determining $P(x)$ are compared. This figure shows that NMM *agrees quantitatively* with the exact solution of the Schrödinger equation. Path integral Monte Carlo method gives reasonably good agreement with the exact result, but at a much higher overhead in computer time. Figure 1 clearly shows that at 200 K, the proton is more delocalized than predicted classically. This delocalization is due to tunneling in the quantum system and arises because the thermal de Broglie wavelength is larger than the width of the barrier.

It is now well established that one requires a large number of points in the primitive algorithm to achieve convergence.[7] However, the efficacy of the NMM method enables us to use a large number of particles and, hence, we are assured of obtaining the exact answer. To illustrate this, we have calculated the Helmholtz free energy of a proton in the bistable potential at $T = 10$ K. The convergence of the free energy and the partition function Q are shown in Fig. 2 as a function of P. It is clear that with $P = 2048$ [11 iterations of Eq. (7)], we have obtained quantitative agreement with the exact result. The exact answer was obtained from the energy levels of this potential. It must also be emphasized that the CPU time required to calculate Q with $P = 2048$ was a factor of ten less than the CPU time needed to compute the exact Q. In addition, we have determined $P(x)$ as a function of the number of discrete points used in the primitive algorithm. Figure 3 shows that $P(x)$ converges to the exact result for $P \sim 256$, a number considerably smaller than the $P = 2048$ required for the convergence of the partition function. It is expected that for very low temperatures, convergence will be attained only for such large values of P that path integral Monte Carlo methods may become impractical. Even for P as small as 100 such MC calculations using the primitive algorithm require large amounts of computer time. Thus recent efforts to reduce the number of discrete points using variational[10(b)]

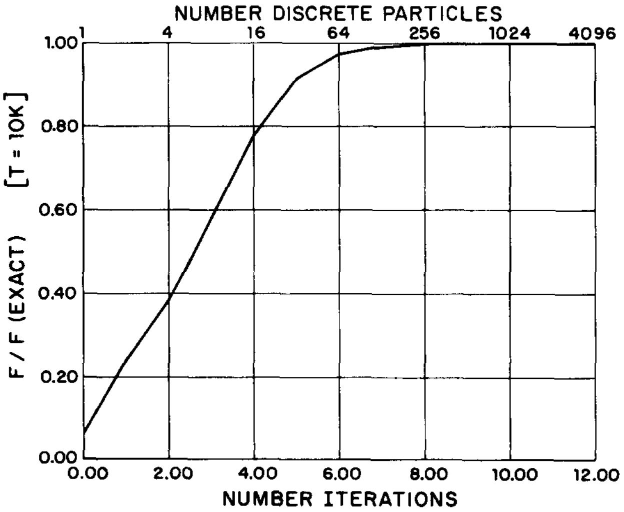

FIG. 2. The Helmholtz free energy F relative to the exact result F_{ex}, F/F_{ex} at $T = 10$ K for the proton motion in H_2O_2 as a function of the number of iterations n using NMM. Also shown are the number of particles P used in the primitive algorithm. Note that $P = 2^n$.

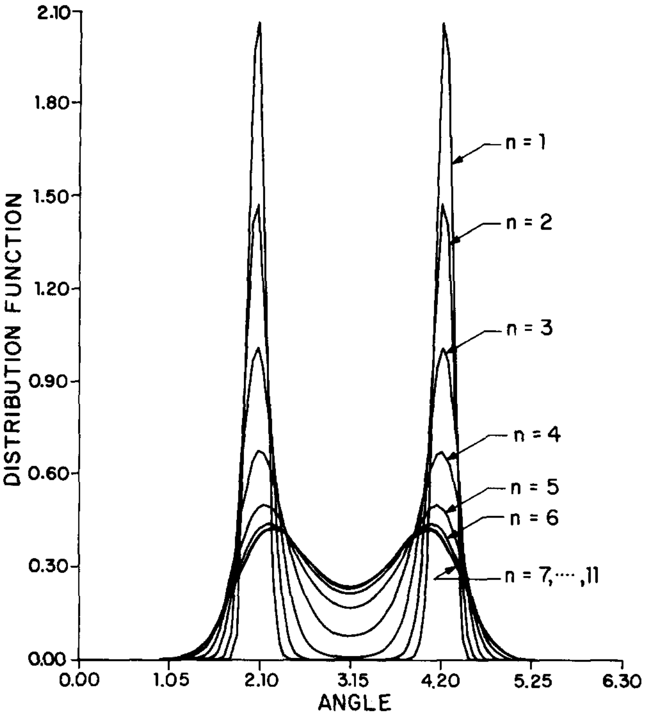

FIG. 3. The distribution function $P(x)$ for proton tunneling in H_2O_2 at 10 K, as a function of the number of iterations n using the NMM method.

and renormalization group techniques [1(f)] should lead to practical methods for simulating quantum systems. Fortunately, the NMM method is so fast that systems with large P present no obstacle. Thus if NMM can be applied to a problem, it will not be necessary to resort to difficult algorithms for reducing P.

We now make a brief comparison of MC and NMM methods: The CPU time on the VAX 11/780 computer needed to obtain $P(x)$ by the MC method was considerably larger (more than two orders of magnitude) than the time needed by the NMM method. In fact, the NMM required considerably less time to calculate $P(x)$ than direct numerical integration of the wave equation and subsequent use of Eq. (9). More importantly there are no fluctuations associated with the NMM method whereas the path integral MC method suffers from this. Although the error bars for the MC method were uniformly small (say 5%–10%), the computational effort required to obtain this good agreement was enormous.

III. THE Ar_2 VAN DER WAALS DIMER

It is of interest to investigate whether the discretized Feynmann path integral is capable of giving accurate bound states for simple van der Waals molecules like Ar_2. To be specific, consider two identical particles interacting via a central potential in a very large box. The Hamiltonian of the system can be written as

$$H=-\frac{\hbar^2}{2M}\nabla_R^2-\frac{\hbar^2}{2\mu}\nabla_r^2+V(r)=T_{\mathrm{c.m.}}+H_{\mathrm{rel}}\ , \tag{10}$$

where $\mathbf{R}$ is the center-of-mass position, $\mathbf{r}$ is the relative coordinate, $T_{\mathrm{c.m.}}$ is the center-of-mass kinetic energy, and H_{rel} is the Hamiltonian for the relative motion. The density matrix $\hat{\rho}$ in the position representation can be written as

$$\begin{aligned}\rho(\mathbf{rR},\mathbf{r}'\mathbf{R}';\beta)&=\langle\mathbf{r},\mathbf{R}|e^{-\beta H}|\mathbf{r}',\mathbf{R}'\rangle \\ &=\langle\mathbf{R}|\exp(-\beta T_{\mathrm{c.m.}}|\mathbf{R}'\rangle\langle\mathbf{r}'|\exp(-\beta H_{\mathrm{rel}}|\mathbf{r}'\rangle\ .\end{aligned} \tag{11}$$

It is possible to write Eq. (11) in the factorized form because the Hamiltonian for the center-of-mass $T_{\mathrm{c.m.}}$ commutes with the Hamiltonian for the relative motion. Strictly speaking, this is not true because the system is enclosed in a box, but the "edge" effects can be made arbitrarily small by making the size of the box very large. Thus for all practical purposes, we treat the system as essentially unbound. The expression for $\langle\mathbf{R}|e^{-\beta T}\mathrm{c.m.}|\mathbf{R}'\rangle\equiv\rho_{\mathrm{c.m.}}(\mathbf{R},\mathbf{R}';\beta)$ is given by

$$\rho_{\mathrm{c.m.}}(\mathbf{R},\mathbf{R}';\beta)\equiv\left[\frac{M}{2\pi\hbar^2\beta}\right]^{3/2}\exp\left\{-\frac{M}{2\hbar^2\beta}(\mathbf{R}-\mathbf{R}')^2\right\}\ . \tag{12}$$

The nontrivial problem is to evaluate $\rho(\mathbf{r},\mathbf{r}';;\beta)\equiv\langle r|e^{-\beta H_{\mathrm{rel}}}|r'\rangle$ which satisfies the Bloch equation [cf. Eq. (1)].

It is well known that for any central potential $\rho(\mathbf{r},\mathbf{r}';\beta)$ for the two bosons can be expanded in partial waves, i.e.,

$$\rho(\mathbf{r},\mathbf{r}';\beta)=\sum_{l=\mathrm{even}}^{\infty}\frac{(2l+1)\rho_l(r,r';\beta)}{2\pi rr'}P_l(\cos\theta)\ . \tag{13}$$

The quantity $\rho_l(r,r',\beta)$ is the lth partial wave contribution to $\rho(\mathbf{r},\mathbf{r}';\beta)$. It satisfies the Bloch equation

$$\frac{\partial\rho_l}{\partial\beta}(r,r';\beta)=-H_l\rho_l(r,r';\rho)\ , \tag{14}$$

where

$$H_l=-\frac{\hbar^2}{2\mu}\frac{d^2}{dr^2}+\frac{\hbar^2l(l+1)}{2\mu r^2}+V(r)\ . \tag{15}$$

For each l, Eq. (14) can be solved by direct numerical matrix multiplication (NMM). To proceed, we choose the short time approximation

$$\rho_l^{(0)}(r,r';\epsilon)=\epsilon^{-(\epsilon/2)V_{\mathrm{eff}}(r)}\rho_0(r,r';\epsilon)^{-(\epsilon/2)V_{\mathrm{eff}}(r)}\ , \tag{16a}$$

where

$$V_{\mathrm{eff}}(r)=\frac{l(l+1)\hbar^2}{2\mu r^2}+V(r) \tag{16b}$$

$$\begin{aligned}\rho_0(r,r';\epsilon)=\left[\frac{\mu}{2\pi\hbar^2\epsilon}\right]^{1/2}&\left\{\exp\left[-\frac{\mu}{2\hbar^2\epsilon}(r-r')^2\right]\right.\\ &\left.-\exp\left[-\frac{\mu}{2\hbar^2\epsilon}(r+r')^2\right]\right\}\ .\end{aligned} \tag{16c}$$

Equation (16c) is the 0th partial wave contribution to Eq. (13) at temperature $(\epsilon)^{-1}$. Of course, other choices for the decomposition of H are possible.

N-fold iteration of the equation

$$\rho_l(r,r';2\epsilon)=\int_0^{\infty}dr''\rho_l(r,r'',\epsilon)\rho_l(r'',r';\epsilon)\ , \tag{17}$$

using the short time expansion [Eq. (16a)] for $\rho_l(r,r';\epsilon)$ with $\epsilon=\beta/2^n$, then gives the desired $\rho_l(r,r';\beta)$.

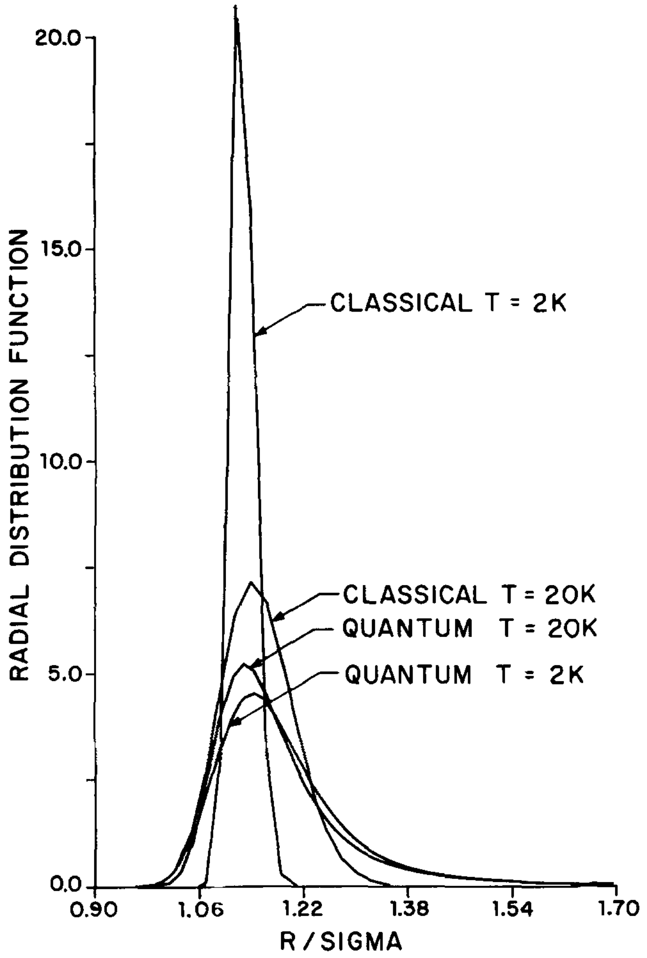

FIG. 4. Normalized radial distribution function $P(r)$ as a function of r/σ for Ar_2 van der Waals dimer at $T = 2$ K and $T = 20$ K. The quantum mechanical results were obtained using NMM. For comparison purposes, we show the classical radial distribution function at these temperatures.

The two Ar atoms are assumed to interact through a LJ 12–6 potential

$$V(r) = 4\epsilon[(\sigma/r)^{12} - (\sigma/r)^6] , \tag{18}$$

with $\epsilon = 119.8$ K and $\sigma = 3.405$ Å. For purposes of calculation, we chose two values of the temperature of the system, namely, $T = 2$ K and $T = 20$ K. The quantity of interest is the normalized radial distribution function

$$P(r) = \frac{4\pi r^2 \rho(r, r; \beta)}{Q} = \frac{\sum_{l=0}^{\infty} (2l+1)\rho_l(r, r; \beta)}{\sum_{l=0}^{\infty} (2l+1)\int_0^{\infty} dr\, \rho_l(r, r; \beta)} , \tag{19}$$

where Bose–Einstein statistics restrict the summation to even values of l. For the LJ potential, it is convenient to use the following set of reduced variables:

$$x = \frac{r}{\sigma}; \quad \epsilon^* = \frac{4\epsilon\mu\sigma^2}{\hbar^2}; \quad \text{and } \beta^* = \frac{\hbar^2\beta}{\mu\sigma^2} . \tag{20}$$

The Bloch equation was solved in terms of these reduced variables. The quantity $\rho_l(x, x'; \beta^*)$ was evaluated on a grid with $M = 77$, $\Delta = 0.016$, and $P = 2^4 = 16$ for $T = 20$ K and $M = 65$, $\Delta = 0.023$, and $P = 2^6 = 64$ for $T = 2$ K. The sum given in Eq. (19) was approximated by truncation at $l = 100$. In both cases, the parameters were adjusted to achieve convergence. Furthermore, it was verified that the calculations were independent of the box size. It is worth remarking that we require a smaller number of partial waves at lower temperatures ($l = 30$ at 2 K).

The radial distribution function determined from the path integral by NMM is compared with the classical radial distribution function in Fig. 4. There are significant quantum effects. The distribution function in the quantum system is considerably broader than in the classical system, and, as expected, there is a finite probability of finding the particles in the classically forbidden regions. Of course, the effects are more dramatic at $T = 2$ K.

Another property of considerable interest is the potential of mean force

$$W(r) = -\frac{1}{\beta} \ln g(r) , \tag{21}$$

where $g(r)$ is the pair correlation function

$$g(r) = \frac{QP(r)}{4\pi r^2} . \tag{22}$$

In the classical system $W(r) \equiv V(r)$; but in the quantum system $W(r) \neq V(r)$. These two functions are compared in Fig. 5 for both temperatures. This figure shows that for $T = 2$ K, there is considerable difference in $W(r)$

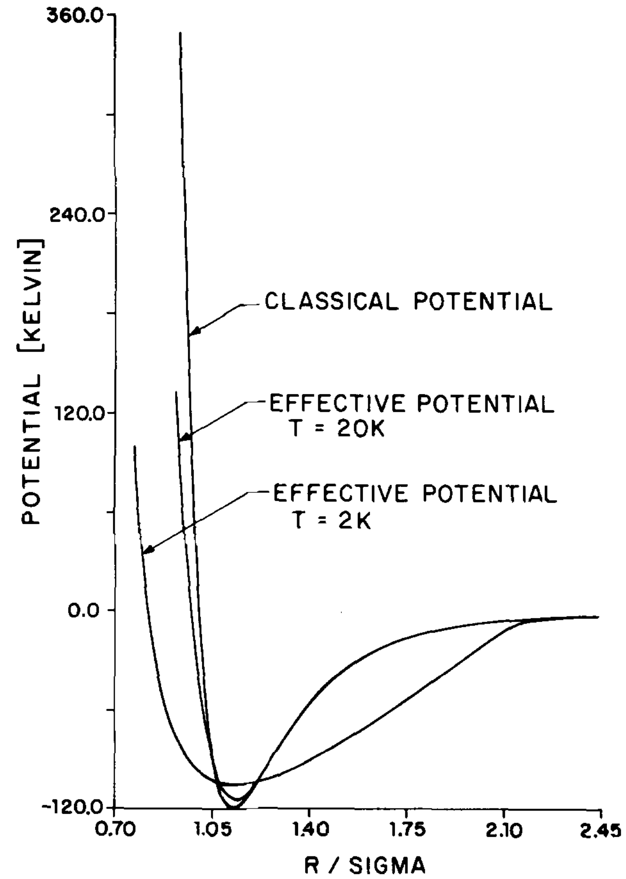

FIG. 5. The effective potential as a function of r/σ at $T = 2$ K and $T = 20$ K. The 6-12 LJ potential is drawn for comparison.

for the quantum and classical system in the range $0.72 < X < 2.1$ whereas, for $T = 20$ K, we observe a noticeable difference in the range $0.92 < X < 1.20$. This is another indication that delocalization due to quantum dispersion is important at this temperature. The quantum effective potential $W(r)$ may be used in either classical integral equations or classical computer simulations to provide a picture of quantum effects in liquids. This approximation can be evaluated by comparing it to the exact asymptotic expansion of the exact quantum distribution functions in powers of $\hbar$.

IV. SIMULATION OF MIXED QUANTUM-CLASSICAL SYSTEMS

In this section, we sketch the use of the NMM method in the simulation of mixed quantum-classical systems. To be specific, let us consider a quantum particle of mass m embedded in a classical bath consisting of N particles of mass m. In addition, we assume that the motion associated with the quantum particle is much faster than the motion associated with the classical particle. This enables us to make the usual Born–Oppenheimer approximation and, therefore, the density matrix for the system can be written as

$$\rho(\mathbf{r}, \mathrm{R}, \mathbf{r}', \mathbf{R}'; \beta) = \left(\frac{M}{2\pi\hbar^2\beta}\right)^{3N/2} \rho(\mathbf{r}, \mathbf{r}'; \beta | R) e^{-\beta U(\mathbf{R})} \delta(\mathbf{R} - \mathbf{R}') , \tag{23}$$

where $U(R)$ is the sum of the solvent–solvent potentials. $\rho(\mathbf{r}, \mathbf{r}'; \beta | R)$ is the density matrix of the quantum particle for a given configuration $\mathbf{R}$ of the bath, and where $\mathbf{r}'$ is the coordinate of the quantum particle and $\mathbf{R}$ denotes collectively the coordinates of the N classical particles. Equilibrium properties like the various distribution functions may be calculated as before. In the usual approach to such a calculation, $\rho(r, r'; \beta | R)$ is written as a path integral and if the paths are discretized into P segments, then the partition function $Q(\beta)$ can be identified as the partition function for a $P + N$ particle classical system, i.e.,

$$Q(\beta) = \left(\frac{M}{2\Pi\hbar^2\beta}\right)^{3N/2} \left(\frac{m}{2\Pi\hbar^2\beta}\right)^{3P/2} \times \int d\mathbf{r}_P \mathbf{R} \exp[-\beta V_{\mathrm{eff}}(\mathbf{r}_P, \mathbf{R})] . \tag{24}$$

With this, the equilibrium properties of the system can be computed by sampling the distribution proportional to $\exp[-\beta V_{\mathrm{eff}}(\mathbf{r}_P, \mathbf{R})]$ by standard Metropolis MC. The details of such a calculation for electrons in fluid He are given in Ref. 1(c).

As described in Sec. I, the right-hand side of Eq. (12) can also be calculated by using NMM. This can be accomplished as follows. (1) Sample the solvent configuration by using the distribution proportional to $\exp[-\beta U(\mathrm{R})]$. (2) For each solvent configuration, $\rho(r, r'; \beta | R)$ can be determined by NMM using a square grid of points as described in Sec. III. In order to do this, we have assumed that the quantum particle interacts with the classical system through a central potential. (3) The equilibrium distribution functions, the energy of the system, and other thermodynamic functions can be calculated by averaging over many solvent configurations in the usual way.

It is anticipated that the use of NMM may eliminate fluctuations in systems which are strongly interacting and highly quantum mechanical, and furthermore, it appears that NMM can be executed in a much shorter time thereby making possible simulations of these mixed quantum-classical mechanical systems.

V. CONCLUSIONS

It is becoming increasingly evident that discretized path integrals provide a practical tool for solving quantum mechanical problems. In this article, we have used a simple numerical method to evaluate the path integrals. In addition to the results presented here we have evaluated partition functions for a simple linear oscillator as well as a Morse oscillator over a wide temperature range. There are several advantages to this simple method that have become transparent from these calculations. First, it has been asserted that the convergence of the primitive algorithm for highly quantum mechanical systems can be very slow and the examples treated by Barker do indeed illustrate this. We have encountered no problems in implementing NMM and the simplicity of the method enables us to treat thousands of particles. Second, NMM appears to be much faster to execute than the MC algorithm. Third, there are no fluctuations associated with NMM. Fourth, NMM allows a direct determination of the partition function and the free energy. Finally, we note that with the use of NMM, we can obtain accurate estimates of the off-diagonal elements of the density matrix and this may sometimes be necessary. Knowledge of the off-diagonal elements are essential to calculate time correlation functions of dynamical operators[2] and it is expected that NMM can be profitably utilized in that context.

Before we conclude, let us list some of the possible limitations of NMM. It is ideally suited to treat systems consisting of only a few quantum degrees of freedom coupled to a classical solvent (bath). The second, and perhaps more serious, problem is that the method is limited by the size of the matrix that can be handled on existing computer systems. Thus it will be difficult to treat problems in which the quantum system is delocalized over very large distances. Finally it would appear that the number of arithmetic operations involved per iteration is given approximately by $(M^2/2)^d$, where d is the dimensionality of the system. This clearly restricts both d and the size of the matrix that can be used. However, due to the fact that the matrix $\rho(i\Delta; j\Delta; \epsilon)$ is sparse, it should be possible to devise a much more efficient algorithm. Despite this potential limitation, it seems that many interesting problems involving quantum degrees of freedom can be attacked. In particular, we have successfully studied the effects of the solvent on tunneling systems over a wide temperature range and the results will be presented in a future communication.[8]

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