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ON THE SIMULATION OF QUANTUM SYSTEMS: PATH INTEGRAL METHODS

Bruce J. Berne

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

D. Thirumalai

Institute of Physical Science & Technology, and Department of Chemistry and Biochemistry, University of Maryland, College Park, Maryland 20742

INTRODUCTION

Feynman's path integral formulation of quantum statistical mechanics (1) makes possible the computer simulation of quantum many-body systems of chemical and physical interest [(2a,b); for a review of recent progress in this field see (3)]. According to this formulation[1] the canonical partition function is

$$Q(\beta, V) = \int \mathrm{d}x_1 \int_{x_1}^{x_1} Dx(\tau)e^{-S[x(\tau)]} \qquad 1.$$

where

$$S[x(\tau)] = \int_0^{\beta\hbar} \mathrm{d}\tau \mathscr{H}(x(\tau)) \qquad 2.$$

is the Euclidian action corresponding to the path $x(\tau)$ in Euclidean (or

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[1] For simplicity we discuss particle motion in one dimension. These expressions are easily generalized. Because many questions still remain about finite temperature simulation of Fermions, we omit discussion of this here.

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imaginary) time τ; $\mathscr{H}(x(\tau))$ is the path dependence of the Hamiltonian;

$$\int_{x_1}^{x_1} Dx(\tau)\,[\ldots]$$

represents an integration over all paths starting at $x(0) = x_1$ and ending at $x(\beta\hbar) = x_1$. In the discrete path representation, the Euclidean time τ is discretized in units $\varepsilon = \beta\hbar/P$ where P is an integer and the continuous path $x(\tau)$ is approximated by straight-line paths between neighboring Euclidean times. This allows Eq. 1 to be expressed as

$$Q_p = \left(\frac{mP}{2\pi\beta\hbar^2}\right)^{P/2} \int \ldots \int \mathrm{d}x_1 \ldots \mathrm{d}x_p e^{-\beta\Phi_p(x_1 \ldots x_p;\beta)} \qquad 3.$$

where $x_t = x(t\beta\hbar/P)$, $x_{P+1} = x_1$, and

$$\Phi_p(x_1 \ldots x_p;\beta) = \frac{mP}{2\beta^2\hbar^2} \sum_{t=1}^{P} (x_t - x_{t+1})^2 + \frac{1}{P} \sum_{t=1}^{P} V(x_t). \qquad 4.$$

Since Eq. 3 is equivalent to the classical configurational partition function of P classical particles with potential Φ_p, the quantum system is said to be isomorphic (4–6) to a classical P particle cyclic chain polymer in which each particle t interacts with its neighbors $t-1$ and $t+1$ through a harmonic potential with force constant $mP/\hbar^2\beta^2$, and each particle t experiences the potential $V(x_t)/P$. Clearly Q_p is an approximation to the true Q. It is easy to prove (7) that

$$Q_p > Q \quad \text{and} \quad Q = \lim_{P\to\infty} Q_p.$$

The classical isomorphism embodied in Eq. 4 has several features worth noting. For a free chain the rms bond length is proportional to $(\beta\hbar^2/mP)^{1/2}$. The classical isomorphism will be a good approximation only if the potential, $V(x)$, does not vary much over the rms bond length. If σ is a characteristic distance specifying the length scale on which $V(x)$ changes, then

$$\frac{\beta\hbar^2}{m\sigma^2} \ll P,$$

and we see that the lower the temperature (β^{-1}), the larger P must be. In path integral simulations one empirically determines and uses that P beyond which the thermodynamic properties do not effectively change.

The isomorphic classical system can be simulated by Monte Carlo techniques (8).[2] An alternative approach is to use molecular dynamics to

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[2] For an earlier application of path integral Monte Carlo techniques to quantum problems, see (9).

evaluate path integrals (see below) as was done by Parinello & Rahman (10).

To use the classical isomorphism, configurations can be sampled from $\exp[-\beta\Phi_p(x_1\ldots x_p;\beta)]$ by using Monte Carlo techniques, thus generating a trajectory in configuration space. This is called *path integral Monte Carlo* (PIMC). Estimators for various quantum observables can then be averaged over this trajectory. Although this appears to be straightforward, complications can arise, and it is often necessary to devise more accurate estimators. The question of convergence of the properties of the quantum systems as a function of P must be addressed. It is important to realize that different properties converge differently as P is varied. For example, for a harmonic oscillator, the Helmholtz free energy converges much more rapidly with P than does the internal energy.

Eq. 3 can also be cast in the form

$$Q_p = \int \mathrm{d}p_1\ldots\mathrm{d}p_p \int \mathrm{d}x_1\ldots\mathrm{d}x_p \exp[-\beta\mathscr{H}_{\mathrm{eff}}] \tag{5.}$$

where

$$H_{\mathrm{eff}} = \sum_{t=1}^{P}\frac{P_t^2}{2m'} + \Phi_p(x_1\ldots x_p;\beta). \tag{6.}$$

Integration over $(p_1,\ldots,p_p)$ shows that with the proper choice of m' we recover Eq. 3. In fact, m' can be adjusted for convenience. This offers a different method for simulating quantum systems. The effective Hamiltonian, $\mathscr{H}_{\mathrm{eff}}$, gives rise to classical equations of motion

$$\begin{aligned}\dot{x}_t &= \partial\mathscr{H}_{\mathrm{eff}}/\partial p_t \\ \dot{P}_t &= -\partial\mathscr{H}_{\mathrm{eff}}/\partial x_t\end{aligned} \qquad t = 1,\ldots,P. \tag{7.}$$

This suggests that classical MD methods can be used to simulate the equilibrium properties of quantum systems (10). Starting with a given state $(x_1\ldots x_p, p_1\ldots p_p)$, one integrates the equations of motion numerically. If the system is ergodic, averages of estimators over these ergodic trajectories give corresponding thermodynamic properties. The Hamiltonian flow conserves energy. Thus one ages the system as in classical MD by scaling the velocities until the average kinetic energy is $(p/2)kT$. Such molecular dynamics simulations are called *path integral molecular dynamics* (PIMD).

There is one major problem with this approach. Hall & Berne (11) have shown that for large P the Hamiltonian system will be in the KAM regime (Kolmogoroff-Arnold-Moser) and the dynamical system will very likely be nonergodic. These authors suggest the following method for circumventing this problem. A classical trajectory is generated for a number of classical time steps, upon which new momenta are sampled from the Maxwell distribution. This ensures the sampling of all important regions of phase space. Variations of this scheme have recently been used by Kogut [for a brief review see (12)] in lattice gauge simulations involving fermionic degrees of freedom.

It is important to recognize that the classical trajectories have nothing to do with the real dynamics of a quantum system. The dynamics in this isomorphic system simply provides a simple algorithm for simulating the equilibrium properties of the system. How then can one simulate the real time dynamics of a quantum system? This is a very difficult problem. Some progress has been made toward the goal of determining two point time-correlation functions using PIMC and PIMD. This is outlined in the section below.

In the foregoing we discussed the problem of evaluating the partition function of quantum systems—the fundamental object in equilibrium statistical mechanics. The canonical density matrix in the position representation is

$$\rho(x,x';\beta) = \langle x|e^{-\beta H}|x'\rangle \qquad 8.$$

and the partition function is

$$Q = Tr\rho = \int \mathrm{d}x\langle x|e^{-\beta H}|x\rangle. \qquad 9.$$

One method for deriving the Feynman path integral is to write ρ as a matrix product,

$$\rho(x_1, x_{p+1};\beta) = \int \mathrm{d}x_2 \ldots \mathrm{d}x_p \prod_{t=1}^{p} \rho(x_t, x_{t+1};\varepsilon) \qquad 10.$$

where $\varepsilon = \beta/p$.

Now in the limit $P \to \infty$, $\varepsilon \to 0$ and one can use the semiclassical approximation (13)

$$\rho(x_t, x_{t+1};\varepsilon) \underset{\varepsilon\text{–}0}{\rightarrow}$$

$$(m/2\pi\hbar^2\varepsilon)^{1/2}\,\exp-\left[\frac{m}{2\hbar^2\varepsilon}(x_t - x_{t+1})^2 + \varepsilon\left(\frac{V(x_t)+V(x_{t+1})}{2}\right)\right]. \qquad 11.$$

Substitution of this into Eqs. 10 and 9 gives Eq. 3. Let $\hat{\rho}(\varepsilon)$ denote the matrix of $e^{-\varepsilon H}$ in the position representation. Matrix products then give

$$\begin{aligned}\hat{\rho}(\varepsilon)\hat{\rho}(\varepsilon) &= \hat{\rho}(2\varepsilon)\\ \hat{\rho}(2\varepsilon)\hat{\rho}(2\varepsilon) &= \hat{\rho}(4\varepsilon) \qquad 12.\\ \hat{\rho}(4\varepsilon)\hat{\rho}(4\varepsilon) &= \hat{\rho}(8\varepsilon), \quad \text{etc.}\end{aligned}$$

Clearly if we start with $\hat{\rho}(\varepsilon)$ (cf Eq. 11), n matrix multiplications (or iterations) give $\rho(2^n\varepsilon)$. If we choose $P = 2^n$, then $2^n\varepsilon = \beta$, and this set of iterations gives the same answer as the full path integral and provides a simple method for determining the density matrix in a small-dimensional problem. For example, consider a one-dimensional system. If the particle moves in a localizing potential, then the space axis can be divided into N equal intervals and by using Eq. 12 $\rho(x, x'; \varepsilon)$ can be calculated at the points of the NXN square lattice. This space latticization yields an NXN matrix for $\hat{\rho}(\varepsilon)$. Then one can perform n matrix multiplications to get $\rho(x, x'; \beta)$ (14a,b). This numerical matrix multiplication scheme (NMM) provides a very rapid and "exact" method for determining the density matrix. It can be used to determine a two-body quantum effective potential. Since $\rho(x, x; \beta) = \rho(x)$ gives the spatial dependence of the density, we define the quantum effective potential $W(x)$,

$$\rho(x) = \rho^{(0)}(x)e^{-\beta W(x;\beta)} \qquad 13.$$

where $\rho^{(0)}(x)$ is the free particle density. NMM can be used to evaluate $W(x; \beta)$, which turns out to be softer and shallower than the potential energy $V(x)$. Following a suggestion of Barker (2a), Pollock & Ceperley (15) proposed that a short time approximation that might converge more rapidly as a function of P than Eq. 12 is one which uses $W(x; \beta)$ in the form

$$\tilde{\rho}(x, x'; \varepsilon) = (m/2\pi\hbar^2\varepsilon)^{1/2} e - \left[\frac{m}{2\hbar^2\varepsilon}(x-x')^2 + \frac{\varepsilon}{2}[W(x;\varepsilon) + W(x';\varepsilon)]\right]. \qquad 14.$$

$\tilde{\rho}$ differs from Eq. 12 in that $V(x) + V(x')$ is replaced by the quantum potential $W(x; \varepsilon) + W(x'; \varepsilon)$. The hope is that with $\tilde{\rho}$ the simulation will converge for much smaller P. This approach has been adopted without any published tests. If $\tilde{\rho}(x, x'; \varepsilon)$ is used in NMM for a harmonic oscillator it turns out that the primitive algorithm converges more rapidly than this effective potential algorithm.

At a given temperature, T, P must be taken large enough such that the results do not change significantly for larger P. If P is very large the force constants in Eq. 4 become so large that only very small particle moves are accepted. One is then dealing with a very stiff polymer chain that relaxes very slowly. Several strategies have been adopted to handle this problem.

1. By transforming the kinetic energy part of the action to normal modes, all modes can be sampled efficiently and, moreover, the zero frequency mode (corresponding to the translation of the whole polymer)

can be sampled such that convergence is much more rapid (15, 16). Even without using normal modes it is advisable to alternate single bead moves with translational moves of the whole polymer. This insures sampling of many more solvent environments.

2. Fourier path integral techniques can be exploited (17). If one truncates the number of Fourier modes, this method is equivalent to the normal mode approach. Recently an algorithm (18) has been discussed that treats the low frequency modes exactly but treats the high frequency modes in a kind of mean field theory. This method looks promising.

3. P can be reduced by using a higher order short time approximation (19, 20) or by using renormalization group techniques to generate an effective potential at the polymer beads (4a,b, 19, 21).

4. Staging algorithms have proven useful (22). In a staging algorithm one moves a primary polymer chain with relatively small P as though it represents a free quantum particle and accepts or rejects the move by introducing secondary chains between each Euclidean-time adjacent pair of beads.

5. Umbrella sampling techniques can be used to reduce P. If $V^{(0)}(x)$ is a reference potential for which the *exact density matrix* $\rho^{(0)}(x, x', \varepsilon)$ is known, since $V(x) = V^{(0)}(x) + \Delta V(x)$ one can write the short time approximation as

$$\rho(x, x', \varepsilon) = \rho^{(0)}(x, x'; \varepsilon) \exp\{-\varepsilon/2[\Delta V(x) + \Delta V(x')]\} \qquad 15.$$

and configurations are sampled from the distribution

$$\left\{\prod_{t=1}^{P} \rho^{(0)}(x_t, x_{t+1}; \varepsilon)\right\} e^{-\varepsilon} \sum_{t=1}^{P} \Delta V(x_t).$$

Friesner & Levy (23) have used a harmonic reference system with considerable success. Clearly, this general approach can be quite useful.

All of these methods have proven useful in different systems. For example, staging (22) is particularly useful in the study of strong short-range repulsive potentials. Nevertheless, it should not be assumed that because it is particularly effective in treating one kind of system it is naturally superior to other methods when applied to another system, as is sometimes claimed in the literature. For example, tests show that staging (method 4) is no better than method 1 for soft potentials like harmonic oscillators (D. F. Coker, B. J. Berne, work in progress). In fact, if one alternates single particle moves and center of mass (COM) moves, one can achieve convergence times comparable to those found by using staging. It is clear that much remains to be learned about the simulation of equilibrium systems.

TIME CORRELATION FUNCTIONS IN QUANTUM SYSTEMS

Time correlation functions play a central role in the theory of dynamic processes in many-body systems (25–27). Transport properties, chemical reaction rate constants, spectroscopic lineshapes, and neutron and light scattering spectra can all be related to well-defined time correlation functions. In classical many-body systems, Hamiltonian dynamics or stochastic dynamics provide a basis for simulating time correlation functions. Unfortunately, the calculation of these functions in quantum systems is a formidable problem. Here we review a method for calculating time correlation functions in quantum and mixed quantum-classical systems based on path integral techniques.

Equilibrium properties of the quantum system can be obtained by solving the equivalent classical problem by using standard numerical techniques (e.g. Monte Carlo and MD), as reviewed above. This formulation of the density matrix has now been successfully applied to the calculation of the equilibrium properties of several systems. Extending this procedure to calculate time correlation functions necessitates inclusion of paths with weights that are nonpositive in character. This arises because in the expression for time correlation functions, both imaginary (thermal) times and real times are simultaneously present. Direct application of Monte Carlo leads to large phase fluctuations and thereby to very inaccurate results. We have suggested two methods for circumventing this problem (28–30a,b). In addition to these approaches, Hirsch & Schrieffer (31) have proposed a method to evaluate dynamic correlation functions in the ground state of the system. This method has been generalized to finite temperatures as well (32). Behrman et al (33) have attempted to evaluate time correlation functions by direct application of importance sampling techniques. Application of this method to the calculation of spin-spin correlation function for a two-level system coupled linearly to a single oscillator revealed that the method is reliable only at short times. In one of the methods we have suggested, one defines a symmetrized time correlation that lends itself to direct PIMC or PIMD simulation (29, 30a,b). In the second method, we simulate the system by using imaginary time propagators only, and the real time behavior can then be inferred by analytic continuation (28). This is very similar to the analytic continuation used to determine properties of real time Green's functions in N body quantum systems from the knowledge of the corresponding imaginary time (finite temperature) Green's functions (34).

It is well known from linear response theory that the response of a system to a weak external field can be expressed in terms of a time correlation function of a dynamical property of the system (D. F. Coker, B. J. Berne, work in progress). For example, the infrared absorption spectrum is explicable in terms of the dipole-dipole correlation function, and the translational diffusion coefficient is related to the velocity autocorrelation function, etc. In this section we provide a general method to calculate the autocorrelation function $\langle A(t)A(0)\rangle$ where A can, in principle, be any quantum mechanical operator representing the N body system. For simplicity, let us consider the motion of a particle in a potential. The generalization to N body systems is conceptually straightforward. The Hamiltonian for the system is taken to be

$$H = \frac{p^2}{2m} + U(r), \tag{16.}$$

where p is the momentum, $U(r)$ is the potential, and r is the coordinate of the particle.

Consider the two functions,

$$C_{AB}(t) = Q^{-1} Tr[e^{-\beta H} A e^{iHt/\hbar} B e^{-iHt/\hbar}] \tag{17.}$$

and

$$G_{AB}(t) = Q^{-1} Tr A e^{-H\tau} B e^{-H\tau^*}, \tag{18.}$$

where t is the Minkowski (real) time and $\tau = (\beta/2 - it/\hbar)$ is a complex time. It is easily shown (29) that $\bar{G}_{AB}(\omega) = \exp(-\beta\hbar\omega/2)\bar{C}_{AB}(\omega)$ so that $C_{AB}(t)$ can be obtained from $G_{AB}(t)$ by Fourier inversion. If A and B are position dependent operators, then in the coordinate representation

$$G_{AB}(t) = Q^{-1} \int \mathrm{d}x \int \mathrm{d}x' \, A(x)B(x') |\langle x|e^{-H\tau}|x'\rangle|^2 \tag{19.}$$

so that we need only determine the Green's operator $\langle x|e^{-H\tau}|x'\rangle$. Only for autocorrelation functions is $G_{AA}(t)$ an even real function of time. These operators can be evaluated by using numerical matrix multiplication together with the short time approximations (cf Eq. 12). This has been applied to a tunneling oscillator; $G_{\mu\mu}$ converges rapidly whereas a similar evaluation of $C_{\mu\mu}(t)$ (cf Eq. 17) leads to numerical instabilities even at short times. This study shows that it would be inadvisable to use Monte Carlo methods to evaluate $C_{\mu\mu}(t)$. However, such methods should be stable in the direct evaluation of $G_{\mu\mu}(t)$. This can be appreciated by studying the explicit path integral form of $G_{AB}(t)$:

$$G_{AB}(t) = \frac{\int \mathrm{d}x_1 \ldots \mathrm{d}x_{2P} A(x_1) B(x_{P+1}) P(x_1 \ldots x_{2P}) W(x_1 \ldots x_{2P})}{\int \mathrm{d}x_1 \ldots \mathrm{d}x_{2P} P(x_1 \ldots x_{2P}) W(x_1 \ldots x_{2P})} \tag{20.}$$

where $P(x_1 \ldots x_{2P})$ is the Monte Carlo sampling function (and the denominator insures normalization),

$$P(x_1 \ldots x_{2P}) = \left(\frac{m^2P^2}{\pi\hbar^2(\beta^2\hbar^2+4t^2)}\right)^{Pd/2} \exp\left[-\beta\Phi(x_1 \ldots x_{2P})\right] \qquad \text{21a.}$$

$$\Phi(x_1 \ldots x_{2P}) = \sum_{j=1}^{2P}\left\{\frac{mP}{\hbar^2(\beta^2\hbar^2+4t^2)}(x_j-x_{j+1})^2+\frac{1}{2P}V(x_j)\right\} \qquad \text{21b.}$$

and where W is

$$W[x_1 \ldots x_{2P}] = \exp\left(-it\Omega(x_1 \ldots x_{2P})\right) \qquad \text{22a.}$$

$$\Omega = \sum_{j=1}^{P}\left\{\frac{2mP}{(\hbar^2\beta^2+4t^2)}\left[(x_j-x_{j+1})^2-(x_{j+P}-x_{j+P+1})\right]^2 - \frac{1}{P}\left[V(x_j)-V(x_{j+P})\right]\right\}. \qquad \text{22b.}$$

The basic approach is to sample the configurations $(x_1 \ldots x_{2P})$ from Eqs. 21a,b, evaluate $A(x_1)B(x_{P+1})$, and weight its contribution by $W(x_1 \ldots x_{2P})$. Values of W must also be evaluated so that the denominator in Eq. 20 can be calculated. Because W involves a phase factor that depends on the differences between functions of the sampled configurations, it is expected that cancellation will result and that the average will be much more stable than would be the case for a direct attack on $C_{AB}(t)$. This is borne out in an NMM study of the tunneling of a particle in a double well potential (29). Nevertheless, as $t \to \infty$, the harmonic force constant (cf Eq. 21b) decreases, the polymer becomes delocalized, and the cancellation is less, with concomitant large phase fluctuations. When there is rapid damping by a bath or only short time information is required, the phase fluctuations do not cause problems. For nondissipative systems that must be followed for short times, more accurate high temperature approximations for the Green's operator in Eq. 19 must be employed. Recently, it has been found that by using a harmonic oscillator reference system with the exact density matrix it is possible to use this method for nondissipative systems (32). Behrman & Wolynes have successfully used this method to study real time correlation functions in a two-level tunneling system coupled to a harmonic bath with an Ohmic density of states (35). Their calculation indicates that the simulation of the time correlation function from using $G(t)$ enables one to investigate the dynamics of quantum systems over times longer than in their earlier study. This enabled them to test the validity of various approximate theories as well.

This direct method can also be used to determine electronic absorption and emission spectra at finite temperatures (30a,b). It offers a simple and more accurate alternative to wavepacket dynamics (36). Another method for calculating quantum mechanical time correlation functions appears to be promising (28). In this method the time correlation function is calculated by Monte Carlo techniques at several values along the pure imaginary axis of the complex time plane. Using the periodicity of the Euclidean time correlation function, the real time behavior is inferred by analytic continuation. This technique has been used to calculate the dipole-dipole autocorrelation function for a particle moving in a Morse potential (28).

Recently, Miller et al have been applying path integral techniques to calculate canonical rate constants for bimolecular reactions (37–39). The purpose of this study is to explore the possibility of obtaining quantum mechanical rate constants without having to obtain state-to-state rate constants and then perform the usual Boltzman averaging. The necessary formalism, which exploits the time correlation formalism for rate constants for bimolecular reactions, is outlined by Miller et al (37). In a subsequent application, Yamashita & Miller (39) have used the reaction path Hamiltonian formalism to calculate the flux-flux correlation function for the three-dimensional $H+H_2$ reaction at 300 K. They have found that the ratio of the rate constant over the transition state result is in good agreement with the calculation of Schatz & Kuppermann (40). In another example, Jacquet & Miller (38) have calculated the quantum mechanical rate constant for the diffusion of a hydrogen atom on a model W[100] surface. The model assumes that the reaction coordinate is coupled to a single surface phonon mode, and the coupling is assumed to be linear in the phonon coordinate and nonlinear in the reaction coordinate. For this model it was found that the coupling to the phonon coordinate tends to increase the rate constant and thus the diffusion rate. The reason for this is that the coupling to the phonon coordinate induces a shift in the effective potential seen by the reaction coordinate (see also 41).

One of the important achievements in bimolecular reaction dynamics has been the investigation of state-to-state reaction cross sections (42–44). The calculation of microcanonical rate constants as a function of energy for a given Born-Oppenheimer potential energy surface is a well-posed problem in reactive scattering theory, and the solution can be reduced to a set of N coupled channel Schrödinger equations (see e.g. 45). The solution of the N-channel problem yields the S matrix from which the state-to-state reaction cross section can be obtained. This procedure was followed by Schatz & Kuppermann (46, 47) for the reaction $H+H_2$; however, this approach is impractical for more complicated reactions. The microcanonical rate constant, $k(E)$, can also be expressed as the flux-flux autocorrelation function evaluated on the energy shell. Recently, Thirumalai et al (48) have shown how to evaluate $k(E)$ by using path integral techniques. The success of this procedure was demonstrated by calculating the tunneling probability as a function of energy for a particle tunneling through an Eckart barrier. This basic methodology can be combined with the reaction path Hamiltonian in the hope of calculating $k(E)$ for elementary bimolecular reactions (49). These methods provide an alternate approach to the N-coupled channel technique.

SIMULATION OF QUANTUM MANY BODY SYSTEMS

Structure of Liquid Neon

Argon, krypton, and xenon all obey the law of corresponding states whereas helium and neon do not (50a,b). The reason is that helium and neon display quantum effects at liquid state temperatures, whereas the other inert gases are essentially classical at their liquid state temperatures. The quantum properties of liquid helium give rise to superfluidity, while neon does not display such dramatic effects, although quantum effects cannot be ignored. Thirumalai, Hall & Berne (51) undertook the path integral Monte Carlo simulation of liquid neon at $T = 40$ K. The potential of interaction between the neon atoms was taken to be the Lennard-Jones potential with $\varepsilon = 35.8$ K and $\sigma = 2.75$ Å. In this calculation the number of quantum particles used was 108 and the number of beads on each neon ring polymer was taken to be 40. It was shown that this was sufficient to achieve convergence. This simulation also neglected exchange of identical particles, because it was argued that the exchange contribution to the partition function was negligible. The calculated radial distribution function indicates that at $T = 40$ K quantum effects are important. The notable feature is the appearance of tunneling into the classically forbidden region. In addition, the height of the first peak was lowered by a few percent. It was noted that for $r > 1.56\,\sigma$, the quantum $g(r)$ is in good agreement with the classical $g(r)$. This indicates that quantum effects are negligible at large distances, a conclusion that was independently reached by Powles & Abascal (52), based on a semiclassical calculation. This represents the first finite temperature simulation of quantum effects in liquids by using path integral techniques. Thirumalai et al determined a quantum effective pair potential by using NMM (cf Eq. 13) for neon and showed that classical MD in this effective potential agrees well with the quantum simulation.

Low Temperature Properties of Liquid ^{4}He

As reported in a recent paper, Ceperley & Pollock (100) have successfully carried out simulations of liquid ^{4}He in the temperature range 1–4 K. Their calculations correctly incorporate the Bose statistics, and they were able to devise numerical techniques to sample both the direct paths and paths due to the permutation of the particles. The details of the simulations, which involve the construction of the trial paths for multiparticle moves, have not yet been provided. The simulations were carried out for a periodic system of 64 atoms. Ceperley & Pollock found that the pair distribution function at 2 K was in excellent agreement with the neutron scattering data (101) and that the exchange paths contribute very little to $g(r)$ at this temperature. The calculated values of the specific heat as a function of T were also in good agreement with the experimental measurements. However, the simulations of the condensate fraction, i.e. the fraction of particles in the zero momentum state, were found to be higher than that seen in experiments. This is probably due to finite size effects and is expected to be quite an issue near the λ transition. This study is nevertheless impressive and marks the first attempt in the proper treatment of exchange effects for Bose particles at finite temperatures.

Simulation of Pure Water

The thermal de Broglie wavelength, $\lambda_T = (\hbar^2/mkT)^{1/2}$, of a proton at room temperature is about 0.4 Å. Consequently, it is of interest to examine the importance of quantum effects on the structure of liquid water. This project was undertaken by Kuharski & Rossky (53) for the ST2 model of water (54) and by Wallqvist & Berne (55) for the central force potential for water with the internal vibrations modeled by a set of Morse potentials (56a,b, 57). In the ST2 model, the water molecule is treated as a rigid body, and consequently the location of the ith water molecule is specified by the coordinates of the center of mass and that of the orientation. Thus, in the short time approximation formula to obtain the primitive algorithm one should include the term due to free rotation. This contribution, $\rho_0(\Omega_i^{(t)}, \Omega_i^{(t+1)}; \varepsilon)$, where $\Omega_i^{(t)}$ denotes the orientation vector of the ith water molecule at time t, is generally difficult to obtain for the asymmetric top molecules. Kuharski & Rossky (53) obtained an approximate value for $\rho_0(\Omega_i^{(t)}, \Omega_i^{(t+1)}; \varepsilon)$ by calculating the action for rotation at constant angular velocity around a fixed axis. With the appropriate short time approximation, they were able to obtain the primitive algorithm and calculate the structural properties by using the standard Metropolis technique. For details of the methodology the reader is encouraged to refer to the original articles.

It is interesting that both these studies indicated that only small changes in the radial distribution functions $[g_{OH}(r), g_{HH}(r), g_{OO}(r)]$ were observed. Rossky has pointed out that to produce such changes in classical ST2 water, one would have to change the temperature by 40 K. There is the usual softening of the structure with diminished peaks and raised valleys due to tunneling effects. The maximum difference between these studies occurs in the oxygen–oxygen radial distribution function. Wallqvist & Berne (55) found that the first peak is slightly lowered and shifted outward, and no effect is seen in the second solvation shell. In contrast, in the simulation of Kuharski & Rossky, quantum effects seem to markedly move the second peak outward, and the peak is much less structured compared to its classical counterpart. This difference is perhaps due to the difference in the model used.

Wallqvist & Berne (55) also simulated the structure of clusters of water molecules, $(H_2O)_n$ with $n = 1, 2, 3$ at $T = 100$ K. This simulation can be used to interpret the expected structure seen in molecular beam experiments. [For a recent experimental study of the IR spectra of water clusters generated in molecular beam experiments see (58).] The clusters were simulated for the central force model of water. Quantum effects have a profound influence on the structure of the moiety as inferred from the radial distribution functions. Examination of the oxygen–hydrogen and hydrogen–hydrogen radial distribution functions for the monomer indicate that quantum widths are much larger than the classical widths. The difference between the classical and the quantum $g_{HH}(r)$ are more dramatic. In the classical dimer there are two distinct structures; one corresponds to the energy minima of the water dimer and the other corresponds to a slightly tilted dimer, in which the hydrogen in the hydrogen bond is displaced from the O–O axis. It has been shown by Wallqvist et al (59) that when the temperature is lowered to 5 K, the classical dimer can actually freeze into these distinct conformers. The quantum PCFS, however, are much more diffuse, and the $g_{HH}(r)$ does not show any nonequivalent configurations. These differences are even more exaggerated at 5 K. Two conformers of the water trimer were simulated. Following Reimers & Watts, they are labeled the single dimer linear (SDL) and single donor cyclic (SDC) conformers. The binding energy for the quantum SDC and SDL trimers is higher than the corresponding classical trimers. The most dramatic quantum effects are seen in the HH radial distribution function. The classically ordered HH peaks are dramatically smoothed out by quantum effects; the hydrogens tunnel into the classically forbidden regions of configuration. A study of these effects at lower temperatures is presented elsewhere (59).

MIXED QUANTUM CLASSICAL SYSTEMS

In many physical situations a single quantum particle will interact strongly with a classical bath. Several interesting examples of this include electron and proton transfer reactions, electron transport, spectroscopy of molecules, and isomerization reactions. In all of these examples one can usually treat the environment (be it a liquid, solid, glass, or cluster of heavier atoms and molecules) classically and only a few of the degrees of freedom quantum mechanically. To a large extent the path integral method has been used to treat problems that can be viewed as mixed quantum-classical systems. In this section we discuss such applications.

Electron Localization in Molten KCl

The properties of solutions of alkali metals in molten alkali halides vary significantly as a function of the concentration of the dissolved metal (60, 61). The behavior of these solutions at a high concentration of the metal is quite complicated, and the simulations of such systems involve the study of strongly interacting fermions. However, in very dilute solutions it has been noted that the dissolved metal ionizes to yield an electron and a corresponding cation. The generally accepted physical picture is that the electron substitutionally occupies the position of an anion, and these electrons are thus analogous to F centers in crystalline alkali halides (62). Parrinello & Rahman (10) simulated the behavior of a single electron in a molten KCl. Using path integral molecular dynamics (cf Eqs. 15–17), they calculated various equilibrium properties of this system, including the binding energy of the electron, its diamagnetic susceptibility, the structure of the molten KCl around the electron, and the extent of localization of the electron in KCl. The calculations were performed at 1000 K and 10.4 kb pressure with 150 K^+ ions, 149 Cl^- ions, and a single electron. The ions were treated classically and the electron was treated as a cyclic chain polymer with P beads. P was varied until convergence was obtained. One of the advantages of this system is that the intermolecular potentials are well known. The ions K^+ and Cl^- were allowed to interact through a Born-Mayer potential,

$$V_{ij}(r) = A_{ij}e^{-r/\rho_{ij}} + \frac{Z_i Z_j e^2}{r_{ij}}, \tag{23.}$$

where the parameters ρ_{ij} and A_{ij} are documented by Fumi & Tosi (63). The interaction potential between the electron and Cl^- was taken to be purely Coulombic,

$$V_{eCl}(r) = e^2/r, \tag{24.}$$

while the potential between the electron and K^+ was modeled by

$$V_{eK^+}(R) = \begin{matrix} -e^2/R & r \leq R \\ -e^2/r & r > R \end{matrix} \tag{25.}$$

where $R = 1.96$ Å. As is customary, periodic boundary conditions were used. Because the Coulomb potentials involved are long ranged, Ewald summation was used [for a clear exposition see (64)].

The results of this simulation indicated that the binding energy of the electron, which was taken to be the sum of the kinetic energy and the potential energy, lies between -3.74 eV and -4.27 eV as P is varied from 25 to 201. The variation in the binding energy with P for $P > 25$ is within the statistical uncertainty of the simulation. It was also noted that the variance in the kinetic energy is smaller when the virial estimator is used. In order to test the hypothesis that the electron in the molten salt occupies the position of a Cl^- ion with a solvation shell of the K^+ ions surrounding it, Parrinello & Rahman performed a simulation with an electron ring polymer with 201 beads dispersed over the entire system. They constrained the electron ring polymer in this dispersed state for several thousand time steps while the ions were allowed to execute the classical equations of motion. After this they released the constraint on the electron ring polymer; they noticed that in about 1000 time steps the electron ring polymer took a compact localized structure. The electron K^+ pair correlation function clearly indicates that the coordination number of the electron is close to 4. Thus, unlike the F center in a solid, where the electron is surrounded by 6 K^+ ions arranged in an octahedral configuration, it appears that the geometrical configuration of K^+ions around the localized electron in molten KCl is a tetrahedron. Finally, the radius of the electron cloud was estimated to be $\langle r^2 \rangle \simeq 4$ Å^2, a value that is in accord with the size of the hole seen in the F center in solid alkali halides.

Excess Electron in Alkali Halide Clusters

In light of these simulations of an electron in molten KCl, it is quite natural to ask about the nature of electron localization in alkali halide clusters. Landman et al (65) undertook a study of this problem. The parameters in the interaction potentials [the forms of which are precisely the same as those used by Parrinello & Rahman (10)] were adjusted to mimic an electron in sodium chloride clusters. The clusters investigated were e^--$(Na_{14}Cl_{13})^+$, e^--$(Na_{14}Cl_{12})^{2+}$, and $(e^-$-$[Na_5Cl_4])^+$. The electron was found to be localized by both $(Na_{14}Cl_{13})^+$ and $(Na_{14}Cl_{12})^{2+}$ clusters. However, the nature of the localized states in these systems were markedly different. In the case of the doubly charged cluster the electron was internally localized by the cluster and the electron was surrounded by six Na^+ ions arranged in an octahedral configuration. This is exactly like the F center in solids. However, in the case of the singly charged cluster, the electron is essentially localized by a single Na^+ atom and the electron cloud is quite diffuse. Landman et al refer to this as a *cluster-surface localized state*.

Muonium in Water

Muonium (Mu), which contains a positive muon, has one ninth the mass of hydrogen. Since Mu is an easily observable species, the study of the reaction of Mu in solution has become a tool for understanding the dynamics of light atoms in solution (66). Despite the mass difference between H and Mu, for a large class of diffusion controlled reactions the rate is determined by the solvent properties (66). In addition, the diffusion constant of both these solutes are essentially the same in water. Using MD techniques and empirical potentials for the hydrogen-water interaction, Tse & Klein (67) discovered that the classical hydrogen does not occupy the interstitial site of the hydrogen bounded network. They observed that the H atom is clathrated in water, with a coordination number of around 18. In order to estimate quantum effects on the structure of Mu and H in water, De Raedt et al (68) performed a path integral MD simulation. They used 63 water molecules (whose motion was treated classically) and one Mu with $P = 20$ and 40, or one H with $P = 5$ to 10. The SPC model for water was used. The results of their study indicated that there was little difference between the classical H and quantum H and that Mu is also clathrated in water but with a coordination number of 23. The difference in solvation between H and Mu is attributed to quantum effects. Based on this simulation they speculate that diffusion of Mu or H in water may involve the motion of the clathrated species as a whole and hence will involve the breaking and formation of the solvent hydrogen bonds. If this is the mechanism, it may explain the lack of isotope effects seen in both the self-diffusion and in the kinetics of the diffusion controlled reactions.

Behavior of an Electron in Helium Gas

The transport properties of an electron in dense gas have been the subject of a great deal of experimental and theoretical investigation. In helium, as the gas density increases beyond a certain point, the electron mobility is observed to drop, faster than the classical rate. Although a pure localization phase transition does not occur, a change in the dominant character of the system seems clear.

R. P. Feynman (unpublished, reported in Ref. 25), Ferrell (70), and Kuper (71) have suggested that at high He density the electron is trapped inside a bubble. Hiroike et al (72a,b) have calculated the radius and energy of this bubble by using a soft electron-He pseudopotential. The radius of the bubble is determined by a compromise between the kinetic energy, which delocalizes the electron, the repulsive electron-He potential, which localizes the electron, and the free energy required to form the He-bubble interface.

Recently, Bartholomew et al (73) reported the results of a path-integral Monte Carlo simulation of an electron in dense He gas as a function of He density that used a realistic, "soft" electron-He interaction (74). The study was done at 77.6 K to make contact with the electric-mobility data of Bartels (77). The results seem to be consistent with bubble formation.

In the simulation, $V_{\text{He-He}}(r)$ is taken to be a Lennard-Jones 12–6 potential with $\sigma = 2.576$ Å and $\varepsilon = 10.22$ K. $V_{\text{e-He}}(|\mathbf{r}_j - \mathbf{x}_t|)$ is given by the pseudopotential of Kestner et al (74). The potential is maximum (0.32 a.u.) at a distance $r = 0.61$ Å and drops by one half at $r = 1.1$ Å.

The radial distribution function of He atoms around the electron barycenter is determined; this quantity is chosen because it can reflect whether or not an electron bubble exists. The nonbarycentric, true distribution function, less suited to signaling bubble formation (where there is no translational invariance) was found not to be as sensitive to changes in density.

The bubble radius, $\approx 4 \pm 1$ Å at high density, is in excellent agreement with the value $R \approx 4.2$ Å given by Jahnke & Silver (78) for He gas at a temperature $T = 77.3$ K, nearly the temperature used in the simulation.

It is interesting to compare these results to the hard sphere models (75, 76) simulated by Sprik et al (79). Their simulations were done for an excess electron in a hard sphere solvent. The electron-solvent interaction was also taken to be a hard sphere with the distance of closest approach being $d = \sigma/2$ where σ is the hard sphere diameter. The simulations were done using the staging algorithm for a temperature corresponding to $\lambda = 65$. They performed their simulations at five densities ranging from $\rho\sigma^3 = 0.05$ to $\rho\sigma^3 = 0.37$. The transition from an extended state of the electron to a relatively compact state was found to occur in the density range 0.1–0.2. Even in the density regime where the states are predominantly delocalized, evidence for localized states induced by infrequent fluctuations in the solvent was found. This, of course, is reminiscent of the Lifshitz traps observed in quenched disordered systems. The results of this simulation are in qualitative accord with the simulations of Bartholomew et al (73).

Electron in a Quenched Disordered System

Sprik et al (79) have attempted to characterize geometrically the localized states of an electron in a topologically disordered system. These states are similar to the Lifshitz tails (80a,b) seen in the density of states in electronically disordered systems at sufficiently low energies. The localized states do exist in a system where the electron interacts with random scatterers through a short-range repulsive potential. According to Lifshitz, the electron would like to reside in a region largely free of scatterers. Thus the probability of observing localized states is proportional to the probability of observing a region of an appropriate size that is free of scatterers. These regions exist due to fluctuations. A simulation to find evidence of the Lifshitz traps is extremely difficult. Using the staging algorithm introduced earlier, Sprik et al (79) were able to simulate the structure of a quantum particle in a quenched disordered system. They used a disordered array of 2197 hard spheres and effectively generated around 10^{37} configurations. For $\rho\sigma^3 = 0.2$ they were able to identify the paths of the electron in regions independent of the scatterer—the so-called Lifshitz trap. The geometry of the trap is like a cavity surrounded by hard spheres.

Electron in Water Clusters

In a series of molecular beam experiments, Haberland et al (81) have examined the stability of e^--$(H_2O)_n$ clusters as a function of n. These experiments are performed by injecting low energy electrons into a beam of water molecules. The species formed, e^--$(H_2O)_n$, is then detected by using standard mass spectrometric methods. In the initial experiment they established that e^--$(H_2O)_n$ is stable when $n \geq 11$. It was subsequently shown that when the beam is seeded with Ar atoms to effectively lower the beam temperature, two water molecules can localize an electron (82). The major numbers for which e^--$(H_2O)_n$ may be stable thus turn out to be $n = 2, 6, 7, 11$. Motivated by these experiments, Wallqvist et al (59, 83) have undertaken the simulation of electron binding in finite sized systems by using path integral techniques. These simulations are based on pseudopotentials to characterize the interaction potential between the electron and the water molecules. The central force model was used for the water molecules. For details of the calculations, the reader is advised to consult the original articles.

The simulations were performed at 5 K, with the number of beads in the electron ring polymer equal to 1000 and the number of pseudoparticles in the ring polymers representing each H atom and each O atom set to 100. The major conclusions of this study were as follows:

1. A single water molecule in its equilibrium geometry does not bind an excess electron.
2. Two water molecules can bind an electron with the electron trapped in a spatially diffuse state. The binding energy of the electron is between 3–6 meV. The attached electron does not induce any major structural changes in the water dimer.
3. A trimer molecule in the single donor cyclic conformer does not localize an excess electron. However, the single donor linear conformer localizes the excess electron, and the binding energy is estimated to between 4–

9 meV. As in the case of the electron-dimer system, the electron is in a diffuse surface state. These results are consistent with a simple dipolar model of the water oligomers.

Electron in Bulk Water

The study of the structural and spectral characteristics of the solvated electron continues to be considerable interest (84–86). Because the structure of the solvated electron is totally determined by the solvent, it is necessary to model the electron-solvent interaction accurately. The difficulty in obtaining such pseudopotentials has forced many to adopt purely phenomenological models. Recently, several groups (79) have attempted to shed light on the structural aspects of the hydrated electron by using path integral simulations. All of these simulations employ a model potential for the electron-water interaction. They differ considerably in detail, and thus the results of these simulations may collectively provide a detailed microscopic picture of the solvated electron. For the interaction between the solvent molecules, both Jonah et al and Schnitker & Rossky use the SPC model (90)[3] whereas Wallqvist et al employ the central force model (56a,b, 57). Jonah et al (87) used a purely Coulombic interaction between the excess electron and the partial charges on the water molecule (90). In order to avoid the capture of the electron by the hydrogen atom, they used a switching function based on the distance from the electron and the hydrogen atom. For this model they performed path integral molecular dynamics by treating the solvent classically. The number of beads for the electron ring polymer was taken to be 600. They found no significant difference between $P = 200$ and $P = 600$. The results of this simulation indicated the following:

1. The electron is localized in a spherical cavity; the radius of the cavity was estimated to be 2.18 Å.
2. The electron tends to align the O–H bond of the water molecule and not the permanent dipole moment of the water molecule. This is in accord with the experimental observation and is in contrast to what is seen in alcohols (85).
3. Oxygen atoms and consequently water molecules were not arranged evenly around the electron. There was no discernable solvent shell around the excess electron.
4. The calculations done at 50 K, however, showed a well-defined shell structure with four water molecules equidistant from the electron. The

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[3] Jonah et al used a modified version of the SPC model. The intramolecular molecular harmonic potentials were modeled following (91).

> O–H bonds were perfectly aligned with the line connecting the center of mass of the ring polymer and the oxygen atom. This contradicts the expectation that six water molecules are arranged in an octahedral fashion around the electron (85).

The model for the electron-water interaction proposed by Rossky et al (88) consists of the purely electrostatic interaction between the electron and the partial charge distribution of the SPC model and a polarization potential term referred to the oxygen nucleus. Finally, a purely repulsive potential, accounting for the orthogonality of the excess electron state to the water molecular wavefunction, was constructed. The path integral molecular dynamics studies were done using 300 water molecules enclosed in an octahedral box. Rossky et al chose $P = 1000$. The results of their study differ from that of Jonah et al in the following ways: (*a*) the pair correlation functions show a well-defined solvent shell structure; (*b*) six water molecules appear to be arranged at distances in accord with the geometry of the hydrated electron inferred from electron spin echo measurements done at 50 K.

The path integral Monte Carlo study of Wallqvist et al (89), which used a potential similar in construction to that of Schnitker & Rossky, suggests that the electron is localized in a spherical cavity of 3.1 Å radius. The coordination number seems to be between five and six. The solvent shell around the electron is not distinct, as that seen by Schnitker & Rossky, but it is not as diffuse as that obtained by Jonah et al. The details of these simulations are presented elsewhere (89).

Excess Electron in NH_3

Sprik et al (92) have recently reported a PIMC simulation of an excess electron in liquid NH_3. They used a simple model for the solvent–solvent interaction, the details of which are given by Impey & Klein (93). The interaction between the electron and the ammonia molecule was taken to be purely Coulombic. The Monte Carlo calculations were done with the staging algorithm. One additional feature of their calculation was that they used a quantum effective potential for the short time approximation involving the Coulomb potential (94). In this simulation the solvent molecules were moved more often than the electron. The results of this simulation, done at 269 K and at $V = 26.5$ cm^3/mole, indicate that the electron is in a spherical cavity and that the cavity radius is around 4 Å. This is in accord with the experimental observation (95). The electron, center-of-mass, Nitrogen pair correlation function shows some structure, thus indicating the possibility of the formation of weak solvent shell around the electron. The coordination number was estimated to be about eight.

SOLVENT EFFECTS ON THE ELECTRONIC STRUCTURE OF MOLECULES

One of the outstanding problems in theoretical chemistry is the study of the effects of condensed phase systems on the electronic structure of atoms and molecules. In the last two years Wolynes & co-workers (96, 97) have attempted to devise techniques based on path integral methods to address this question. As has been pointed out by Chiles et al (96), the solvent can have a variety of effects on the electronic structure, depending on the kind of bonding and the nature of the solvent. These authors considered the interaction of the hydrogen molecules with a bath. The bath was modeled as a Drude oscillator to mimic the internal excitation of the solvent molecules. The interaction between the H_2 molecule and the solvent was taken to be attributable to the fluctuating dipole of the molecule interacting with the electric field caused by the solvent molecules. In evaluating the partition function for this model, the trace over the bath modes can be evaluated analytically. This results in an effective action for the molecular system that contains the response (influence functional) of the bath. The trace over the molecular system was evaluated in the representation of the wavefunction of the H_2 molecule, which was constructed in terms of the single particle states. In particular, these were built out of Slater determinants involving both single and double excitations. Wolynes et al (96, 97) used the standard double zeta set for constructing the single particle states. With this algorithm they were mainly concerned with the effects of this specialized heat bath on the singlet state of the H_2 molecule. The major conclusion of the study was that when the coupling to the heat bath is strong enough, the H_2 molecule essentially dissociates to ionic species at relatively short distances. This of course is a direct consequence of the dipolar model. At a smaller value of the coupling, the potential energy curve is slightly shifted outward. The purpose of this initial study was to demonstrate the utility of the path integral method in dealing with the important problem of the changes in the electronic structure of molecules due to interactions with the solvent.

CONCLUSIONS

Enormous strides have been achieved in the last several years in the simulation of quantum systems. The examples that we have discussed indicate the versatile way in which path integral methods can be used to study interesting and difficult problems. One major advantage of path integral simulations of quantum systems is the insight gained by examining the details of the quantum paths. It is hoped that examination of the details will provide a sound basis for analytical treatment of some of these problems. Despite the explosion in activity, much remains to be accomplished, even in the simulations of the equilibrium properties of quantum systems. For example, efficient ways to reduce systematically the number of beads for highly quantum mechanical systems are needed. More importantly, reliable and practical methods are needed to treat systems in which the exchange contribution to the partition function is significant. The needed tools include methods for treating systems with fermionic degrees of freedom, thereby providing a natural framework to treat chemical bonding (98). Finally, a practical way to obtain real time dynamics for interacting quantum systems is still lacking. Despite some signs of hope, this is still an open problem, and progress in this area is sorely needed. Some of the problems outlined here and the review of applications should give the reader a perspective on how path integral methods can be used to address problems in fields ranging from particle physics (see 99 for a review) to biological sciences (A. Kuki, P. G. Wolynes, work in progress).

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