VARIABLE QUADRATIC PROPAGATOR FOR QUANTUM MONTE CARLO SIMULATIONS

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A new propagator for the Monte Carlo evaluation of path integrals is proposed. The propagator has a quadratic form which varies with position. The variable quadratic propagator (VQP) approximation combines features of Taylor series and quasiharmonic expressions; it is constructed to interpolate between the low- and high-temperature limit for the anharmonic propagator. Using two model potentials, the quartic and Morse oscillators, we demonstrate the accuracy that may be achieved with a simple diagonal approximation to the propagator.

1. Introduction

Quadratic potentials occupy a special role in quantum mechanical theory, because exact analytical results are available for most quantities of interest. Many approximate methods utilize these exact solutions as a basis for attacking more complicated problems. Approaches along these lines include path integral calculations with a quadratic reference system [1], Gaussian wavepacket propagation schemes [2], and various projection operator techniques in which the projected degrees of freedom are assumed to have a quadratic form [3]. In this paper, we study the use of quadratic approximations under simple conditions, i.e. the calculation of static equilibrium averages for a one-dimensional Hamiltonian. Because such problems can be solved with arbitrary accuracy via a basis set calculation, they provide a useful way to test new computational methods. The insights gained from such work can then be used to investigate coupled multidimensional potentials, for which a basis set approach rapidly becomes intractable as the number of degrees of freedom increases.

In a previous communication [1] we proposed the use of harmonic propagators for the Monte Carlo evaluation of discretized path integrals. In the quasiharmonic approximation [4] a global fit to the potential (as a function of temperature) was made, and the resulting quadratic form was used as a reference system. While this resulted in a substantial advantage as compared to the use of a free particle propagator, use of a single, fixed expression over the entire potential is clearly not optimal.

An alternative approach involves fitting the propagator to a quadratic form which varies with position. The simplest implementation of this formalism involves a local quadratic approximation to the propagator in which the potential is expanded in a second-order Taylor series about the local position. For time-dependent problems this approach forms the basis of Gaussian wavepacket techniques developed by Heller and co-workers [2]. However, the local Taylor series expansion for the propagator breaks down when the potential is steep and the wavepacket displays substantial uncertainty broadening. Unfortunately these are precisely the cases where quantum effects are strong, i.e. a purely classical approximation is qualitatively inadequate.

In the present work, we attempt to synthesize the insights contained in these two disparate perspectives. We

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develop approximations to the propagator $G(x, x', \beta)$ and diagonal density matrix $\rho(x, x', \beta)$ which employ a different quadratic form for each x, x', but avoid the limitations of a Taylor series expansion. The basic idea is that for a diffuse (i.e. highly quantal) wavepacket, a highly accurate fit at the center which does poorly in other regions, is inappropriate. Rather, a reasonable fit over the range of the wavepacket spread will yield superior results. In the numerical examples, we compute equilibrium statistical averages for the quartic oscillator and Morse potential. We emphasize the accuracy that can be achieved using a diagonal approximation to the propagator. In section 4, we briefly discuss generalizations of our approach to multidimensional and time-dependent problems.

2. The variable quadratic propagator

The unnormalized propagator in equilibrium statistical mechanics satisfies the Bloch equation:

$$\partial G_u(x, x', \beta)/\partial\beta = -H(x)\, G_u(x, x', \beta)\,, \tag{1}$$

where H is the Hamiltonian and $\beta = 1/k_B T$. In the energy representation, G_u has the form

$$G_u = \sum_n \psi_n(x)\, \psi_n(x') \exp(-\beta E_n)\,. \tag{2}$$

Normalization by the partition function is performed after obtaining G_u from the partial differential equation (1). Our basic approach is the following: we propose a functional form for $G(x, x', \beta)$ based on the harmonic oscillator solution and asymptotic low- and high-temperature limits. The propagator is then a functional of a variable harmonic frequency, $\omega(x, x')$. At each β, a WKB-like equation for $\omega(x, x')$ can be derived. For the harmonic oscillator, the substitution $\omega(x, x') = \omega_0$ yields an exact solution. For anharmonic potentials, our procedure discussed below yields an effective quadratic Hamiltonian which varies with (x, x'). We have found that the use of a local quadratic approximation (Taylor series expansion) is much less efficient than the variable quadratic propagator we employ for the computation of equilibrium expectation values. For low temperatures and highly anharmonic potentials, the numerical results presented in section 3 demonstrate that order of magnitude improvements over a purely local quadratic formulation can be achieved.

Our exponential ansatz for the propagator has the form

$$G(x, x', \beta) = \exp[S_0(\beta) + S_1(x, x', \beta)]\,. \tag{3}$$

$S_0(\beta)$ is a coordinate-independent prefactor which will play the role of eigenvalue or Lagrange multiplier in the WKB-type equation derived for S_1. At low temperature, S_0 has the form $-\beta E_0$ (where E_0 is the ground state energy) while in the classical limit ($\beta \to 0$) S_0 becomes $S_0(\beta) = \ln[(2\pi m k_B T)^{1/2}]$.

Substituting eq. (3) into eq. (1) yields

$$\frac{\partial S_0}{\partial\beta} + \frac{\partial S_1(x, x', \beta)}{\partial\beta} = -\frac{\hbar^2}{2m}\frac{\partial^2 S_1(x, x', \beta)}{\partial x^2} - \frac{\hbar^2}{2m}\left(\frac{\partial S_1}{\partial x}\right)^2 + V(x)\,. \tag{4}$$

Our strategy is to fix β and x' and to determine $S_1(x, x', \beta)$ by solving the resultant one-dimensional differential equation. From a comparison with the WKB form of the Schrödinger equation,

$$\partial^2 S(x)/\partial x^2 + [\partial S(x)/\partial x]^2 + V(x) = E\,, \tag{5}$$

it is clear that the term $\partial S_0(\beta)/\partial\beta$ plays the role of the energy E in eq. (4). Once $\partial S_0(\beta)/\partial\beta$ has been determined at each β, $S_0(\beta)$ itself could be determined by integration, although this is not necessary for the quantum Monte Carlo algorithm since $S_0(\beta)$ is independent of coordinates.

A numerical solution to eq. (4) could in principle be obtained by a variational procedure. First, a functional

form for $S_1(x, x', \beta)$ is assumed, in which the dependence on x and x' is parameterized via the set $\{\lambda_1, ..., \lambda_N\}$. The derivatives of $S_1(x, x', \beta)$ can then be evaluated and eq. (4) has the form

$$F(\lambda_1, ..., \lambda_N, x, x', \beta) = \left[\frac{\partial S_1}{\partial \beta} + \frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2} S_1(x, x', \beta) + \frac{\hbar^2}{2m}\left(\frac{\partial S_1}{\partial x}\right)^2 - V(x) + \frac{\partial S_0}{\partial \beta}\right]^2 , \tag{6a}$$

$$F(\lambda_1, ..., \lambda_N, x, x', \beta) = 0 , \tag{6b}$$

the best values of the parameters $\lambda_1, ..., \lambda_N$ and $\partial S_0/\partial\beta$ could then be found by solving a variational equation:

$$\frac{\partial}{\partial \lambda_j}\left(\int\int \mathrm{d}x\, \mathrm{d}x'\; F(\lambda_1, ..., \lambda_N, x, x', \beta)\right) = 0 . \tag{7}$$

In practice, the procedure outlined above would be difficult to extend to multidimensional systems. Therefore, our approach is to use simple functional forms for $S_1(x, x', \beta)$ which interpolate between low- and high-temperature limits.

The harmonic oscillator propagator has the form [4]

$$G_u(x, x', \beta) = \left(\frac{m\omega}{2\pi\hbar \sinh(\beta\hbar\omega)}\right)^{1/2} \exp\left(\frac{-m\omega}{2\hbar \sinh(\beta\hbar\omega)}\left[(x^2 + x'^2)\cosh(\beta\hbar\omega) - 2xx'\right]\right) . \tag{8}$$

We identify $S_0(\beta)$ with the prefactor of eq. (8) and $S_1(x, x', \beta)$ with the exponent:

$$S_1(x, x', \beta) = \frac{-m\omega}{2\hbar \sinh(\beta\hbar\omega)}\left[(x^2 + x'^2)\cosh(\beta\hbar\omega) - 2xx'\right] . \tag{9}$$

We propose to retain the functional form of $S_1(x, x', \beta)$ in eq. (9) but to introduce a space-dependent frequency $\omega(x, x')$. In the context of a variational formulation of the problem (eq. (7)), the optimal $\omega(x, x')$ would be the function which satisfied the functional derivative equation

$$\int\int \frac{\delta F(x, x', \omega(x, x'), \beta)}{\delta \omega(x, x')}\, \mathrm{d}x\, \mathrm{d}x' = 0 . \tag{10}$$

We emphasize that a space-dependent frequency $\omega(x, x')$ should not be incorporated in $S_0(\beta)$, since this would constitute in effect a different ansatz for $S_1(x, x', \beta)$ in the solution of eq. (4). A numerical demonstration of this is presented in section 3.

We now present the procedure for obtaining $\omega(x, x')$. First we fix the minimum of the effective potential at the true minimum. Our rationale is that the region of the potential minimum is important at low temperatures for all phase points (x, x'). With this requirement the effective potential has the functional form

$$V_{\mathrm{eff}}(x) = \tfrac{1}{2} m\omega^2 (x - x_0)^2 + C , \tag{11}$$

with $V(x_0) = C$.

Next, we require that the propagator on the effective quadratic potential converge to the exact propagator in the high-temperature limit. The expression for $S_1(x, x', \beta)$ on an arbitrary potential in the high-temperature limit is [5]:

$$\lim_{\beta \to 0} S_1(x, x', \beta) = -\frac{m}{2\hbar^2\beta}(x - x')^2 + \frac{\beta}{\hbar^2 (x - x')}\int_x^{x'} V(y)\, \mathrm{d}y . \tag{12}$$

In order to evaluate eq. (12) on an arbitrary potential we introduce a quadrature scheme; here we employ a two-point trapezoidal approximation:

$$\frac{\beta}{\hbar^2(x-x')}\int_x^{x'} V(y)\,\mathrm{d}y \approx \frac{\beta}{2\hbar^2}\left[V(x)+V(x')\right]. \tag{13}$$

Equating the integral along the effective and exact potentials in eq. (12) and using the two-point quadrature leads to the following expression for the position-dependent frequency:

$$\omega^2(x,x') = \frac{2}{m}\frac{V(x)+V(x')+2C\hbar^2}{(x-x_0)^2+(x'-x_0)^2}. \tag{14}$$

This completes the approximation scheme. A different approach to the problem of determining an optimal form for ω has been proposed by Feynman and Kleinert [6]. They consider only the diagonal propagator elements and calculate the partition function for model systems including the anharmonic oscillator studied below. While their approximation scheme is highly accurate for the one-dimensional problems they study, iteration is required at each point to obtain ω and this may present practical problems when applied to multidimensional systems. In any case, our formalism provides a useful initial guess for an iterative procedure used to optimize the effective classical potential. Furthermore, the generalization to off-diagonal form also permits use of discretized path integral procedures with $p>1$. Finally, the results reported below are of quite high accuracy for all values of temperature and anharmonicity. Thus the computational simplicity ($\omega(x, x')$ is available analytically) does not lead to a substantial degradation in accuracy.

3. Results

In this section we present results for quantum Monte Carlo studies of the quartic and Morse oscillators. Quantum Monte Carlo results are compared with converged basis set calculations for positional moments $\langle x^n\rangle$, with $n\leqslant 8$ and for the energy $\langle H\rangle$. Classical results are also included for comparison. The basis set calculations were carried out with matrices dimensioned 200×200. The quantum Monte Carlo simulations were carried out for between 10^5 and 10^6 times P steps (where P is the number of quadrature points, equal to 1 for most simulations). The step size was varied to yield acceptance rates of between 40 and 60%. The variation in the moments obtained in successive simulations was less than 1%; shorter trajectories would have been sufficient for these studies. The quartic oscillator Hamiltonian is

$$H = p^2/2m + \tfrac{1}{2}m\omega^2x^2 + bx^4. \tag{15}$$

Expectation values for positional moments calculated with a diagonal approximation to the propagator for several values of the anharmonicity and reduced temperature are shown in table 1. Four sets of results are shown: (a) those corresponding to the variable quadratic propagator with eq. (14) used to calculate $\omega(x, x')$; (b) those for which the positional dependence of ω is also included in the prefactor $S_0(\beta)$, and the corresponding results using a conventional Taylor series expansion for $\omega(x, x')$. It is clear that the $p=1$ diagonal approximation to the propagator produces quantitatively accurate results for the first few moments. The results are particularly striking at the lowest temperature and largest anharmonicity, that is, the set of parameters for which quantum effects are most important. For example, for $\langle x^6\rangle$ at low temperature ($\beta=5$) and large anharmonicity ($b=5$), the classical value is 0.001 while the exact quantum result is 0.048. Although the diagonal ($p=1$) variable quadratic propagator approximation is in error by 15% ($\langle x^6\rangle=0.041$), the Taylor series result is almost ten times smaller than the exact quantum value. For the highest moment $\langle x^8\rangle$, which is difficult to evaluate by Monte Carlo sampling because points far from the minimum with low probability are weighted heavily, the diagonal approximation to the variable quadratic propagator is not quantitatively accurate. We have examined the convergence rate to the exact result with increasing quadrature points for $\langle x^8\rangle$. The results

Table 1
Diagonal propagator approximation anharmonic oscillator

			Classical	Exact quantum	Variable quadratic [a]		Taylor series [a]	
					A	B	A	B
$\beta\hbar\omega=2$	$b=0.05$	$\langle X^2\rangle$	0.403	0.537	0.538	0.525	0.549	0.480
		$\langle X^4\rangle$	0.441	0.823	0.792	0.755	0.840	0.650
		$\langle X^6\rangle$	0.743	2.008	1.820	1.690	1.976	1.361
		$\langle X^8\rangle$	1.646	6.612	5.536	5.010	6.008	3.705
	$b=1.0$	$\langle X^2\rangle$	0.182	0.265	0.272	0.229	0.266	0.138
		$\langle X^4\rangle$	0.079	0.192	0.183	0.135	0.172	0.055
		$\langle X^6\rangle$	0.048	0.217	0.183	0.120	0.159	0.035
		$\langle X^8\rangle$	0.037	0.323	0.235	0.140	0.184	0.029
	$b=5.0$	$\langle X^2\rangle$	0.093	0.161	0.167	0.108	0.143	0.044
		$\langle X^4\rangle$	0.020	0.071	0.068	0.032	0.047	0.006
		$\langle X^6\rangle$	0.006	0.048	0.041	0.015	0.022	0.001
		$\langle X^8\rangle$	0.002	0.044	0.031	0.009	0.012	0.000
$\beta\hbar\omega=5$	$b=0.05$	$\langle X^2\rangle$	0.179	0.448	0.448	0.416	0.360	0.269
		$\langle X^4\rangle$	0.092	0.586	0.565	0.490	0.350	0.203
		$\langle X^6\rangle$	0.076	1.242	1.128	0.916	0.519	0.242
		$\langle X^8\rangle$	0.086	3.601	3.011	2.290	1.004	0.384
	$b=1.0$	$\langle X^2\rangle$	0.099	0.257	0.262	0.154	0.170	0.048
		$\langle X^4\rangle$	0.024	0.182	0.174	0.067	0.070	0.007
		$\langle X^6\rangle$	0.009	0.201	0.172	0.048	0.041	0.002
		$\langle X^8\rangle$	0.004	0.295	0.221	0.045	0.030	0.000
	$b=5.0$	$\langle X^2\rangle$	0.055	0.161	0.166	0.054	0.093	0.012
		$\langle X^4\rangle$	0.007	0.071	0.068	0.009	0.020	0.000
		$\langle X^6\rangle$	0.001	0.048	0.041	0.003	0.006	0.000
		$\langle X^8\rangle$	0.000	0.043	0.032	0.001	0.002	0.000

[a] A: coordinate-dependent prefactor omitted. B: coordinate-dependent prefactor retained.

are compared with those for the free particle propagator in table 2. For the lowest temperature and largest anharmonicity studied the VQP results are converged by $P=15$.

The number of propagator quadrature points required to compute quantum properties accurately depends on both the potential and the particular expectation values under consideration. We have used the Morse os-

Table 2
Convergence of the variable quadratic propagator anharmonic oscillator

	$P=1$	$P=5$	$P=10$	$P=15$
$\beta\hbar\omega=1$, $b=5$, $\langle X^8\rangle=0.052$				
VQP	0.035	0.051	0.052	0.052
free particle	0.010	0.037	0.053	0.054
$\beta\hbar\omega=5$, $b=5$, $\langle X^8\rangle=0.043$				
VQP	0.032	0.036	0.037	0.041
free particle	0.000	0.007	0.016	0.024

Table 3
Diagonal propagator approximation Morse oscillator energy

$1/k_BT$	Exact	Classical	VQP
2	0.6589	0.4982	0.6601
5	0.5021	0.1005	0.5048

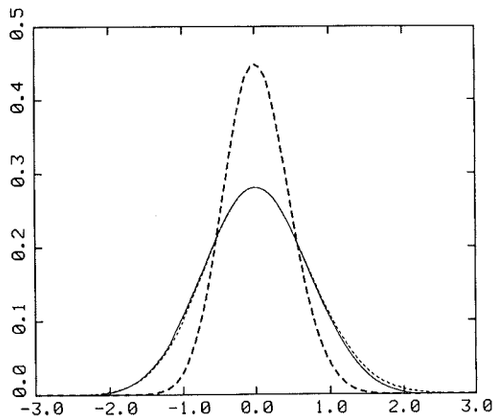

Fig. 1. Diagonal propagator matrix elements $\rho(x, x)$ versus x for a Morse potential having $D=100.25$, $a=0.071$ at inverse temperature $\beta=5$. The solid line depicts the exact values, the short-dashed line is the diagonal ($p=1$) variable quadratic propagator result and the long-dashed line the classical partition function.

cillator potential to study additional features of the variable quadratic propagator. The potential was of the form

$$V(x)=D[1-\exp(-ax)]^2 , \tag{16}$$

with $D=100.25$ and $a=0.071$. The virial theorem was used to calculate the average energy:

$$\langle H\rangle=\langle \tfrac{1}{2}q\,\mathrm{d}V/\mathrm{d}q+V\rangle . \tag{17}$$

The right-hand side of eq. (16) was evaluated by Monte Carlo simulation. The exact classical and quantum average energies are compared in table 3 with the diagonal ($p=1$) VQP results at two temperatures, $\beta=2$ and $\beta=5$. The accuracy of the diagonal approximation to the propagator for these potential parameters is remarkable. At the lower temperature, $\beta=5$, the probability of being in the ground state is $p_0=0.95$; the average energy $\langle H\rangle$ is 0.50 while the classical value is much smaller ($\langle H\rangle=0.10$). Under these highly quantum conditions the diagonal VQP Monte Carlo simulation is within 1% of the exact answer. In fig. 1 $\rho(x, x)$ is plotted versus x for the Morse potential with $\beta=5$. The diagonal VQP approximation is compared with the exact quantum and classical curves. The exact and VQP ($p=1$) curves are nearly identical. It is of interest to note that the low-temperature diagonal propagator is in fact the ground state wavefunction (see eq. (1)). Therefore, the $p=1$ variable quadratic propagator which we construct analytically, is a simple and accurate approximation to the ground state wavefunction for the Morse potential parameters studied here. This construction has applications which will be explored in future communications. Extensive path integral Monte Carlo studies of the Morse potential with the set of parameters used here have been reported previously [7–9]. The accuracy and convergence of several discretization schemes were compared with Fourier and partial averaging Fourier Monte Carlo methods. It was observed that at the temperature $\beta=2$ Monte Carlo integration over at least six variables (discretization points or Fourier coefficients) were required to compute $\rho(x, x)$ accurately. Improved accuracy with less computational effort was obtained with a partial averaging Fourier path integral "PA FPI" procedure proposed in ref. [9]. A comparison of VQP and PA FPI methods would be of interest.

4. Conclusions

In this paper we have developed an approximation for the propagator based on a quadratic form designed to interpolate between the low- and high-temperature limits. As shown in section 3, quite good results were

obtained for two model systems. The level of agreement with exact results is encouraging and is sufficient for making many types of experimental comparisons.

The generalization of the VQP method to anharmonic multidimensional systems will be straightforward for an important class of potentials, i.e. those which have only a few well defined and relevant minima. A simple approach is to determine a set of normal coordinates for each potential well via a quasiharmonic approximation [4] and then to scale the frequencies using the VQP prescription. For complex multidimensional systems it will be necessary to determine the minima numerically. The extension to time-dependent wavepacket propagation mentioned in section 1 is the most challenging application of the method, as real time problems are quite difficult to handle with conventional discretized path integral techniques. Here, one could imagine using a least-squares approximation to define the local quadratic potential, with the region of the fit delineated by the initial wavepacket. The accuracy of such an approach remains to be investigated.

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