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A Schwinger Variational Method for the Bloch Equation

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A Schwinger variational principle has been derived for use in quantum, many-body systems at finite temperatures. The variational principle is a stationary expression for the density matrix which may be iterated to improve an approximate density matrix. It also can be used to find stationary expressions for observables. If an approximate, parametrized density matrix is used, the parameters are varied to find the regions where the variational principle is stationary. The variational density matrix obtained with the optimal parameters can be regarded as optimal for that observable. The method has been applied to two model problems, a particle in a box and two hard spheres at finite temperatures. The advantages and shortcomings of the method are discussed.

KEY WORDS: Bloch equation; quantum systems; Schwinger variational principle.

1. INTRODUCTION

Variational calculations of the properties of ground-state condensed ^{4}He have been of great importance in studying this significant many-body quantum system.[1] The calculations use the Monte Carlo technique of Metropolis *et al.*[2] to yield a strict upper bound to the energy within a statistical uncertainty which can be made small. The variational method allows the use of parametrized trial wave functions and elucidates the physics embodied in these wave functions. For example, several recent variational calculations[3] showed the importance of three-body correlations in the wave-function for liquid ^{4}He. Variational calculations are also

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useful as a means of finding optimized importance functions used to accelerate convergence in exact GFMC computations[4] of ground-state properties.

Heretofore, however, no variational method has been applied to strongly interacting finite-temperature quantum systems.[5] We propose a method for such systems based upon the Schwinger variational principle.[6] In Section 2 we describe the derivation of the variational principle and a general discussion of its application. Section 3 shows the method applied to two model systems at finite temperatures: a particle in a one-dimensional box and two hard spheres in a three-dimensional box.

2. DERIVATION OF THE VARIATIONAL PRINCIPLE

The equilibrium properties of quantum systems at finite temperatures may be inferred from knowledge of the density matix which, in coordinate space, may be described by

$$\rho_B(R, R_0; \beta) = \sum_k \psi_k^*(R_0)\psi_k(R)e^{-\beta E_k} \tag{1}$$

For an N-body system, R and R_0 are vectors in $3N$-dimensional Euclidean space (configuration space) and β equals $1/k_B T$. The ψ_k, $k = 0, 1, 2 \ldots$ are the complete eigenfunctions of the Hamiltonian H with eigenvalues E_k. Properly symmetrized states for Fermi–Dirac or Bose–Einstein statistics may be constructed from them. The density matrix for Bose–Einstein statistics is

$$\rho_B(R, R_0; \beta) = \sum_P \sum_k \psi_k^*(R_0)\psi_k(PR)e^{-\beta E_k}$$

where P is a permutation. For Fermi–Dirac statistics the density matrix becomes

$$\rho_B(R, R_0; \beta) = \sum_P \sum_k (P)^{-1}\psi_k^*(R_0)\psi_k(PR)e^{-\beta E_k}$$

where $(P)^{-1}$ is $+1$ for even permutations and -1 for odd permutations. The density matrix satisfies a differential equation, the Bloch equation, which is

$$\left(H_R + \frac{\partial}{\partial \beta}\right)\rho_B(R, R_0; \beta) = 0 \tag{2}$$

or

$$\left[-\nabla^2 + V(R) + \frac{\partial}{\partial \beta}\right]\rho_B(R, R_0; \beta) = 0$$

Here $h^2/2\mu = 1$; $-\nabla^2$ is the Laplacian in full coordinate space and $V(R)$ is

the full, many-body potential. At $\beta = 0$, the density matrix satisfies the boundary condition

$$\rho_B(R, R_0; 0) = \sum_k \psi_k^*(R_0)\psi_k(R) = \delta(R - R_0) \tag{3}$$

and so $\rho_B(R, R_0; \beta)$ is Green's function for $H_R + \partial/\partial\beta$.

Suppose we introduce a trial density matrix, $\rho_T(R, R_0; \beta)$, which also satisfies the condition

$$\rho_T(R, R_0; 0) = \delta(R - R_0) \tag{4}$$

We may write an integral equation for $\rho_B(R, R_0; \beta)$ in terms of the trial density matrix as

$$\begin{aligned}\rho_B(R, R_0; \beta) &= \rho_T(R, R_0; \beta) \\ &\quad - \int_0^\beta \int dR'\, d\beta'\, \rho_B(R, R'; \beta - \beta')\left[-\nabla'^2 + V(R') + \frac{\partial}{\partial \beta'} \right] \\ &\quad \times \rho_T(R', R_0; \beta')\end{aligned} \tag{5}$$

Equation (5) may be shown correct by applying the Bloch operator to both sides. Also, when β becomes zero the integral becomes zero and $\rho_T(R, R_0; 0) = \rho_B(R, R_0; 0) = \delta(R - R_0)$. A variational principle may be derived from Eq. (5) by replacing $\rho_B(R, R'; \beta - \beta')$ by $\rho_T(R, R'; \beta - \beta')$ in the integral to yield

$$\begin{aligned}\rho_v(R, R_0; \beta) &= \rho_T(R, R_0; \beta) - \int_0^\beta \int dR'\, d\beta'\, \rho_T(R, R'; \beta - \beta') \\ &\quad \times \left[-\nabla'^2 + V(R') + \frac{\partial}{\partial \beta'} \right] \rho_T(R', R_0; \beta')\end{aligned} \tag{6}$$

To see that this is indeed variational, i.e., that ρ_v is correct to second order in the departure in ρ_T from ρ_B, set

$$\rho_T(R, R_0; \beta) = \rho_B(R, R_0; \beta) + \epsilon\rho_1(R, R_0; \beta) \tag{7}$$

where $\rho_1(R, R_0; \beta)$ is some function satisfying $\rho_1(R, R_0; 0) = 0$. Upon substituting Eq. (7) for ρ_T in Eq. (6) we find

$$\begin{aligned}&\rho_v(R, R_0; \beta) \\ &\quad = \rho_B(R, R_0; \beta) + \epsilon\rho_1(R, R_0; \beta) \\ &\qquad - \int_0^\beta \int dR'\, d\beta' \left[\rho_B(R, R'; \beta - \beta') + \epsilon\rho_1(R, R'; \beta - \beta')\right] \\ &\qquad \times \left[-\nabla'^2 + V(R') + \frac{\partial}{\partial \beta'} \right] \left[\rho_B(R', R_0; \beta') + \epsilon\rho_1(R', R_0; \beta')\right]\end{aligned}$$

The term involving the Bloch operator acting on ρ_B in the integral drops out immediately, leaving terms of order ϵ and ϵ^2. Recognizing that the

operator $-\nabla^2 + V(R)$ is Hermitian, and performing an integration by parts on the β' integral, we may eliminate all terms of order ϵ. The resulting equation is

$$\rho_v(R, R_0; \beta) = \rho_B(R, R_0; \beta) + O(\epsilon^2) \tag{8}$$

So Eq. (6) is a stationary expression for the density matrix itself.

The variational principle embodied in Eq. (6) has some interesting characteristics. Applying the principle to a trial density matrix produces a new density matrix which in the sense of Eq. (8) is a better approximation to ρ_B. In addition, the variational principle is stationary with respect to changes in the trial density matrix. If ρ_T is a function with some parameters, we may look for those values of the parameter(s) for which ρ_v has either a saddle point, a maximum, or a minimum. This contrasts with variational methods used in ground-state problems where expectation values are guaranteed to be upper bounds to the exact answer and a minimum in the energy is sought as parameters are varied. Thus the method proposed here requires greater computational efforts than in standard ground-state variational calculations.

Variational estimates of properties of the system can be obtained. Suppose we are interested in the expectation of a function $f(R)$ for a Bose system. An estimate is determined by multiplying Eq. (6) by $f(R)$, integrating over R, and summing over all possible permutations P as follows:

$$\begin{aligned} F_v &= \sum_P \int dR\, f(R)\rho_v(PR, R; \beta) \\ &= \sum_P \int dR\, f(R)\rho_T(PR, R; \beta) \\ &\quad - \sum_P \int_0^\beta \int\int d\beta'\, dR\, dR'\, f(R)\rho_T(PR, R'; \beta - \beta') \\ &\quad \times \left[-\nabla'^2 + V(R') + \frac{\partial}{\partial \beta'} \right] \rho_T(R', R; \beta') \end{aligned} \tag{9}$$

F_v will be stationary with respect to variations in ρ_T, as well. The trial density matrix for which F_v is stationary can be regarded as an optimal ρ_T for the observable. The normalization of ρ_v is unknown and varies with ρ_T, but this shortcoming can be dealt with effectively as follows. Expectations are defined by the quotient

$$F_v = \frac{\sum_P \int dR\, f(R)\rho_v(PR, R; \beta)}{\sum_P \int dR\, \rho_v(PR, R; \beta)} \tag{10}$$

since both the numerator and the denominator are stationary with respect to variations in ρ_T, the quotient will also be stationary. We will therefore use Eq. (10) to calculate variational estimates in our model problems.

To apply Eq. (9) or (10) to a system at finite temperatures modeled explicitly on a many-body level will generally require the use of Monte Carlo techniques. It is not obvious what Monte Carlo procedure will work best for the variational expression since the terms involving $\rho_T(PR, R;\ \beta)$ and $\rho_T(PR, R';\ \beta - \beta') \times (-\nabla'^2 + V + \partial/\partial\beta') \times \rho_T(R', R;\ \beta')$ are on different spaces and are likely to be rather different functions of R and PR. We decided to rewrite Eq. (9) as one multiple integral by multiplying the $\rho_T(PR, R;\ \beta)$ term by arbitrary normalized, probability distribution functions $X(R')$ and $B(\beta')$ and then integrating over R' and β'. That is, we work in the full product space and Eq. (9) becomes

$$\rho_v(PR, R;\ \beta) = \int_0^\beta \int \Big\{ \rho_T(PR, R;\ \beta) X(R') B(\beta') - \rho_T(PR, R';\ \beta - \beta') \Big[-\nabla'^2 + V(R') + \frac{\partial}{\partial \beta'} \Big] \times \rho_T(R', R;\ \beta') \Big\}\, dR'\, d\beta' \tag{11}$$

Note that in the first term of the integral, $\rho_T(PR, R;\ \beta)$ does not depend on R' or β', so the structure of Eq. (9) has not been altered. The integral is now in a form which can now be evaluated in a straightforward manner by using the algorithm of Metropolis *et al.*[2]

In the normal application of the Metropolis algorithm to the evaluation of a many-dimensional integral, the integrand (or part of it) is sampled directly. However, in Eq. (11) the integrand is not manifestly nonnegative, which is a necessary condition for sampling. Therefore we must introduce a sampling function, $p(R, R', P,\ \beta' \mid \beta)$ into the integral for the variational estimate of an expectation value

$$F_v = \sum_P \int_0^\beta \int \int d\beta'\, dR'\, dR\, f(R) p(R, R', P,\ \beta' \mid \beta) \times \Big\{ \rho_T(PR, R;\ \beta) X(R') B(\beta') - \rho_T(PR, R';\ \beta - \beta') \times \Big[-\nabla'^2 + V(R') + \frac{\partial}{\partial \beta'} \Big] \rho_T(R', R;\ \beta') \Big\} \Big/ p(R, R', P,\ \beta' \mid \beta) \times \left[\sum_P \int_0^\beta \int \int d\beta'\, dR'\, dR\, \frac{p(R, R', P,\ \beta' \mid \beta)}{p(R, R', P,\ \beta' \mid \beta)} \rho_v(PR, R;\ \beta) \right]^{-1} \tag{12}$$

The Monte Carlo calculation will involve sampling $p(R, R', P,\ \beta' \mid \beta)$ by

using the Metropolis algorithm and then summing the quantity

$$f(R)\frac{\{\rho_T(PR,R;\beta)X(R')B(\beta') - \rho_T(PR,R';\beta-\beta')\lfloor -\nabla'^2 + V(R') + \partial/\partial\beta'\rfloor\rho_T(R',R;\beta')\}}{p(R,R',P,\beta'\mid\beta)} \tag{13}$$

to obtain the numerator of Eq. (12). The same quantity without $f(R)$ is used to obtain an estimate of the denominator of Eq. (12). The variational estimate of F_v is then the quotient of the sums of the quantities found in Eq. (13). This is an asymptotically unbiased estimate of F_v.

The better $\rho_T(PR,R;\beta)$ approximates to $\rho_B(PR,R;\beta)$, the smaller the contribution the second term of Eq. (11) will make. Thus the two terms of the integrand do behave differently even in the transformed variational expression Eq. (11). In the applications that follow, we do not analyze any further this aspect of the problem. We note in passing, however, that the different behavior of the two terms could be investigated by reweighted sampling.

In summary, a variational principle involving a trial density matrix for use in finite-temperature problems has been developed. The principle does not yield an upper bound, but is stationary when the trial function ρ_T is in the neighborhood of ρ_B. We sketch how a Monte Carlo evaluation of the varitional principle could be accomplished and we will next apply the procedure to two model problems.

3. APPLICATION OF THE VARIATIONAL PRINCIPLE TO MODEL PROBLEMS

The variational principle is first used in a solvable problem: a particle in a one-dimensional box. The Bloch equation for this is

$$\frac{-d^2}{dx^2}\rho_B(x,x';\beta) + \frac{\partial}{\partial\beta}\rho_\beta(x,x';\beta) = 0 \tag{14}$$

with

$$\rho_B(x,x';0) = \delta(x-x')$$

The exact density matrix is given by

$$\rho_B(x,x';\beta) = \frac{1}{L}\sum_{i=1}^{\infty} Q_i(\alpha_i x)Q_i(\alpha_i x')e^{-\alpha_i^2\beta} \tag{15}$$

where L is the box side, $Q_i(x)$ is an eigenfunction $Q_i(x) = (\sqrt{L/2})^{-1}\cos\alpha_i x$, of the corresponding Schrödinger equation, and α_i^2 is the

associated eigenvalue, $\alpha_i^2 = (2k+1)^2\Pi^2/L^2$. An alternative form of the density matrix can be derived from an image expansion. That is, one starts with the free particle density matrix and adds on correction terms (images) which correct for the presence of the hard walls,

$$\rho_{BI}(x,x';\beta) = \frac{1}{(4\Pi\beta)^{1/2}} e^{-(x-x')^2/4\beta} + \frac{1}{(4\Pi\beta)^{1/2}} \sum_{n=1}^{\infty} - e^{-[2(2n-1)a-(x+x')]^2/4\beta} - e^{-[2(2n-1)a+(x+x')]^2/4\beta} + e^{-[4na+(x-x')]^2/4\beta} + e^{-[-4na+(x-x')]^2/4\beta} \quad (16)$$

Either Eq. (15) or (16) can be used to calculate expectation values; Eq. (15) will converge faster at small β (high temperatures) and Eq. (16) will converge faster at large β (low temperatures).

As a trial density matrix for use in the variational calculation, the first three terms of the image expansion, Eq. (16), were used, modified to ensure that the density matrix is zero at the end points, $\pm a$.

$$\rho_T(x,x';\beta) = \frac{e^{(x-x')^2/4\beta}}{(4\Pi\beta)^{1/2}}(1 - e^{(x^2-2ax+a^2)/b\beta}) \times (1 - e^{(x'^2-2ax'+a^2)/b\beta}) \quad (17)$$

Here b is a parameter which may be varied to obtain stationary expectation values.

Since we are dealing with only one particle, no sum over permutations occurs. The variational principle is simply

$$\rho_v(x,x_0;\beta) = \int_0^\beta \int_{-a}^{a} d\beta'\,dx'\,\rho_T(x,x_0;\beta)X(x')B(\beta') - \rho_T(x,x';\beta-\beta')\left(-\nabla'^2 + \frac{\partial}{\partial\beta'}\right)\rho_T(x',x_0;\beta') \quad (18a)$$

and

$$F_v = \int_0^\beta \int_{-a}^{a}\int_{-a}^{a} d\beta'\,dx'\,dx\,f(x) \times \left\{\rho_T(x,x_0;\beta)X(x')B(\beta') - \rho_T(x,x';\beta-\beta')\left[-\nabla'^2 + \frac{\partial}{\partial\beta'}\right] \times \rho_T(x',x_0;\beta)\right\} \Big/ \int_{-a}^{a} dx\,\rho_v(x,x_0;\beta) \quad (18b)$$

For the normalized probability density functions $X(x')$ and $B(\beta')$ we used

$$X(x') = \frac{1}{2a}, \qquad \int_{-a}^{a} \frac{1}{2a}\, dx' = 1$$

$$B(\beta') = 1/\beta, \qquad \int_{0}^{\beta} \frac{1}{\beta}\, d\beta' = 1$$

Equations (18) were evaluated using the algorithm of Metropolis *et al.* As described in Section 2, values of x, x', and β' were chosen by using a sampling function $p(x, x', \beta' \mid \beta)$, chosen here to be

$$p(x, x', \beta' \mid \beta) = \left\{ \left[\rho_T(x, x_0;\, \beta) X(x') B(\beta') - \rho_T(x, x';\, \beta - \beta') \right. \right.$$
$$\left. \left. \times \left(-\nabla'^2 + \frac{\partial}{\partial \beta'} \right) \rho_T(x', x_0;\, \beta') \right]^2 \right\}^{1/2} \tag{19}$$

Variational estimates are then calculated

$$F_v \sim \frac{\sum_{i=1}^{N} \left[f(x) I(x, x', \beta') / p(x, x', \beta' \mid \beta) \right]}{\sum_{i=1}^{N} \left[I(x, x', \beta') / p(x, x' \beta' \mid \beta) \right]} \tag{20}$$

where I is the integrand of Eq. (18b). This choice of sampling function was motivated by the behavior of the integrand of Eq. (18b). When $\beta - \beta'$ or β' is small and x' is close to x or x_0, the integrand is a delta function and is very large in absolute magnitude. The sampling function should have similar behavior to avoid large fluctuations in the value of the summand in

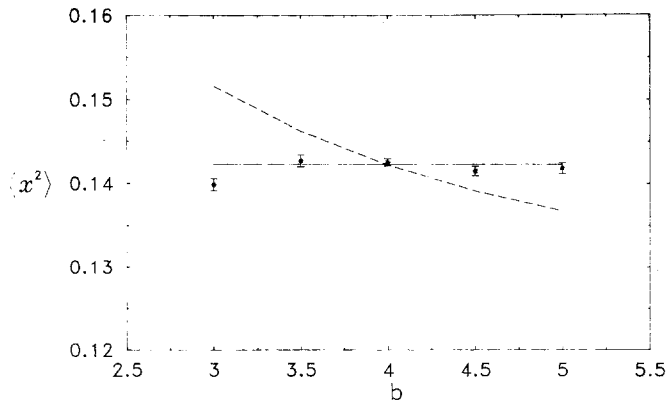

Fig. 1. Values of $\langle x^2 \rangle$ for the particle in a box as a function of the variational parameter b. The points with errors bars are from the Monte Carlo evaluation of the variational principle; the solid line is the exact results and the dotted line is values of $\langle x^2 \rangle$ calculated with ρ_T. All results are at $T = 17.857$ K.

Eq. (20). Sampling the absolute value of I is a good choice when I can become negative. The ratio $I/p = \pm 1$.

In the application of the variational principle to the particle in a box, variational estimates were made of $\langle x^2 \rangle$, the kinetic energy operator, $\langle -\nabla^2 \rangle$, and ρ_v. The calculations were performed at a variety of temperatures. The lowest-energy state of the system is at an energy of 14.952 K, the first excited state is at 134.57 K. Figure 1 shows values of $\langle x^2 \rangle$ as a function of the variational parameter b at $T = 17.857$ K, where only one state is populated. The dotted line represents $\langle x^2 \rangle$ calculated with the trial density matrix, ρ_T, as a function of b; the solid line is the exact value and the points with error bars are the Monte Carlo estimate. As can be seen from the figure, the Monte Carlo results are stationary with respect to b, the variational parameter, and are close to the correct answer. Figure 2 shows the Monte Carlo estimates of $\langle x^2 \rangle$ for a range of temperatures, and stationary behavior is observed in all cases.

The kinetic energy operator was also estimated. When $-\nabla^2$ operates on the variational expression, a delta function is introduced for small $\beta - \beta'$ or β' and x near x'. The effect of this on the Monte Carlo evaluation of Eq. (18b) is to lead to large fluctuations in the terms of Eq.

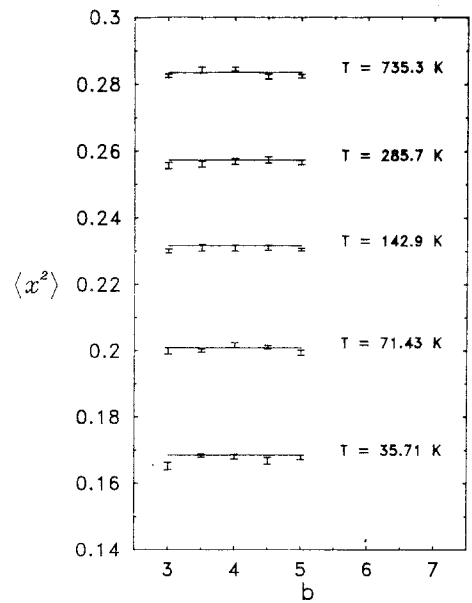

Fig. 2. Values of $\langle x^2 \rangle$ for the particle in a box as a function of the variational parameter at several temperatures. The points with error bars are from the Monte Carlo evaluation of the variational principle and the solid lines are the exact results.

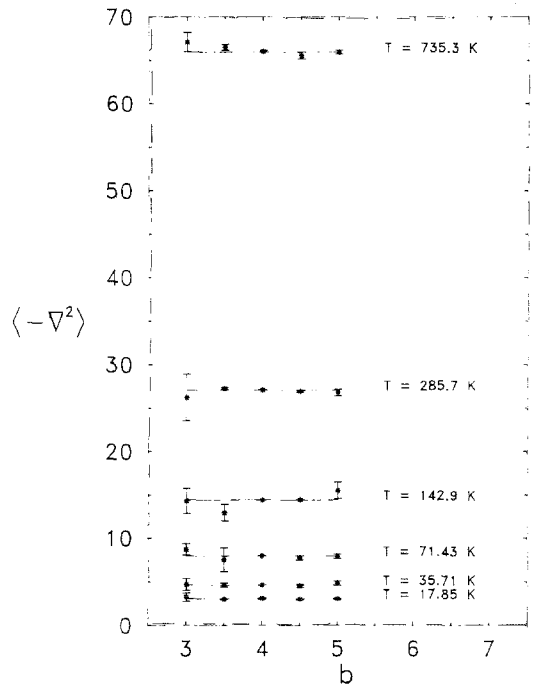

Fig. 3. The expectation value of the kinetic energy as a function of the variational parameter at several temperatures. The points with error bars are from the Monte Carlo calculation and the solid line is the exact results.

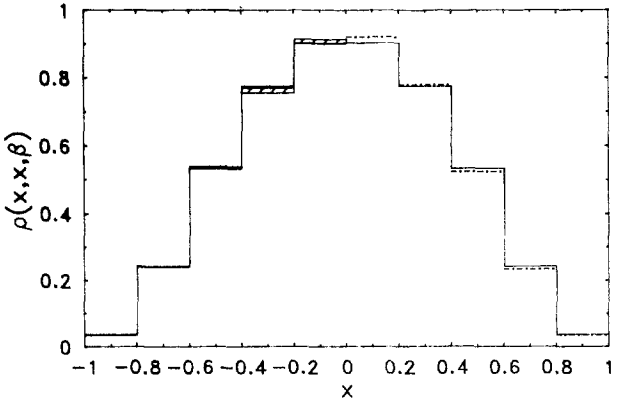

Fig. 4. Histogram representation of $\rho(x, x; \beta)$ at a temperature of $T = 17.857$ K. The solid line is $\rho_B(x, x, \beta)$; the dotted line is $\rho_T(x, x; \beta)$ and the shaded areas are $\rho_v(x, x; \beta)$ showing $\pm$ one standard deviation. A value of $b = 4.5$ was used in the calculation of ρ_T and ρ_v.

(20) and corresponding large statistical errors. Estimates of $\langle -\nabla^2 \rangle$ were computed by performing several Monte Carlo calculations of $\langle -\nabla^2 \rangle$ and computing an average weighted by their statistical errors. Figure 3 shows the Monte Carlo estimates of $\langle -\nabla^2 \rangle$ as a function of b at several temperatures. Though the values are noisier than for $\langle x^2 \rangle$, the behavior is still stationary and close to the exact value. As was mentioned earlier, the trial density matrix for which an observable is stationary can be considered the optimal ρ_T. Thus, when $b = 4.0$, ρ_T, ρ_v, and ρ_B are indistinguishable. The variational density matrix is stationary for all b's in the range $3.4 < b < 5.0$. In Fig. 4, $\rho_v(x, x; \beta)$ for $T = 17.857$ K is compared with the exact density matrix and the trial density matrix for $b = 4.5$. The trial density matrix is a good representation of ρ_B, and within statistics, ρ_v is seen to be a slight improvement on ρ_T.

In the one-dimensional example, the results of the application of the variational principle were encouraging. The method worked well at low temperatures where only one state was populated and continued to work at higher temperatures where 3 or 4 states were populated. Estimates of expectation values were stationary as a function of a variational parameter in the vicinity of the "best" choice of ρ_T, and ρ_v itself appeared to be an improvement on the best ρ_T. The variational principle was next applied to a somewhat more interesting and realistic system, two particles in a three-dimensional box.

The Bloch equation for the two-hard-sphere system is

$$\left(-\nabla_1^2 - \nabla_2^2 + \frac{\partial}{\partial \beta}\right)\rho_B(r_1, r_2, r_{01}, r_{02}; \beta) = \delta(r_1 - r_{01})\delta(r_2 - r_{02})\delta(\beta) \tag{21}$$

where

$$\rho_B(r_1, r_2, r_{01}, r_{02}; 0) = \delta(r_1 - r_{01})\delta(r_2 - r_{02})$$

The constraint on the system is that the hard spheres never overlap

$$\rho_B(r_1, r_2, r_{01}, r_{02}; \beta) = 0, \qquad |r_1 - r_2|, |r_{01} - r_{02}| < a$$

where a is the hard-sphere diameter. Periodic boundary conditions were enforced on the box walls. Exact results are available for the radial distribution function of two hard spheres in an infinite medium calculated by an eigenfunction expansion[7] and Green's function Monte Carlo.[8] If the size of the box in our model problem is much larger than the hard-sphere diameter, results from the variational calculation should be comparable with the exact results.

There are two possible permutations in the two-body system, the unit or "direct" and pair or "exchange" permutation. The radial distribution

function may be written as a sum of two terms

$$g(r, \beta) = g_{\text{dir}}(r, \beta) = g_{\text{exch}}(r, \beta)$$

In the high-temperature limit $g_{\text{dir}}(r, \beta)$ goes to the classical pair correlation function and $g_{\text{exch}}(r, \beta)$ approaches zero. The quantity $g_{\text{dir}}(r, \beta)$ refers to the case when $r = |r_{01} - r_{02}| = |r_1 - r_2|$,

$$g_{\text{dir}}(r, \beta) = V \frac{\int dr_1\, dr_2\, \rho_B(r_1, r_2, r_1, r_1; \beta)\delta(r_1 - r_2 - r)}{\sum_P \int dr_1\, dr_2\, \rho_B(r_1, r_2, Pr_1, Pr_2; \beta)} \tag{22}$$

In our application of the Schwinger variational principle to the two-body system, we will investigate the radial distribution function obtained from the variational method.

The trial density matrix used in the variational calculation is the same function that was used as an importance function in the Green's function Monte Carlo[8] study of the two-hard-sphere system. That density matrix

$$\begin{aligned}\rho_T(r_1, r_2, r_{01}, r_{02}; \beta) &= e^{-(|r_1 - r_2| - |r_{01} - r_{02}|)^2/4\beta} \\ &\quad \times \left(1 - \exp\left\{-\left[(r_1 - r_2)^2 - a^2\right]\left[(r_{01} - r_{02})^2 - a^2\right]/ba^2\beta\right\}\right)\end{aligned} \tag{23}$$

where b is again a variational parameter, is expected to reproduce the high-temperature behavior of the system reasonably well but contains no information about the physics at low temperatures. In particular, ρ_T is not expected to be accurate in r neighborhoods important to the exchange permutation.

In the two-particle system, the variational estimate for any quantity of interest is given by Eq. (12), where R and R' are six-dimensional vectors. The probability distribution functions $X(R')$ and $B(\beta')$ are functions analogous to those used in the one-dimensional example. That is, $B(\beta') = 1/\beta$ and $X(R') = 1/(2L)^3$, where L is now one half the box side. The sampling function is again the absolute value of the integrand of Eq. (11). The Metropolis algorithm is used to carry out the sampling of $p(R, R', \beta' \mid \beta)$. The tendency in the calculation of the two-hard-sphere system is for the spheres to stay as far apart as is allowed by the periodic boundary conditions. The most interesting region for studying the radial distribution function is where the spheres are nearly touching, not the asymptotic region. Thus directed sampling was introduced into the Metropolis algorithm to improve the efficiency of the calculation of $g_{\text{dir}}(r)$. In the Metropolis sampling algorithm, a transition matrix $T(R' \mid R)$ is sampled to move from position R to R'. The usual choice for $T(R' \mid R)$ is a constant interval about R in which the next R' is selected uniformly. But there is no requirement that R' be chosen uniformly and at random; any probability

distribution function can in principle be used.[9] We chose a transition matrix that encourages the two spheres to be near each other. That is, r_1', the new position of sphere, 1, is chosen randomly in the box. Then, $r = |r_1 - r_2|$ is sampled from the distribution function

$$T_r(r) = \frac{1}{4\Pi} \frac{1/s - 1}{(L^{-1/3} - 1)} r^{1/s-3}$$

where L is half the box side and s is some real number. The larger s is, the smaller r will be on the average. With this choice of the transition matrix, microscopic reversibility is ensured and the Metropolis algorithm samples $p(R, R', \beta' \mid \beta)$ asymptotically.

The computations with the variational principle were done in detail at two temperatures, $T = 38.85$ K and $T = 0.898$ K. These temperatures correspond to the exact calculations in Refs. 7 and 8 at $\lambda_T/a = 1.4$ and $\lambda_T/a = 10$, respectively, where λ_T is the thermal wavelength, $[4\pi\beta/a^2]^{1/2}$. We would expect the variational calculation to give a better ρ_v at higher temperatures than at lower temperatures, and this is indeed borne out by experience. In Fig. 5, $g_{\text{dir}}(r)$ at dimensionless distance $r/a = 1.55$ is shown as a function of the variational parameter, b. Plotted as well in the figure is the behavior of the direct radial distribution function from the trial density matrix. A region in which the variational $g_{\text{dir}}(r)$ is stationary is apparent and lies within statistics of the exact numerical result in that region. The variational $g_{\text{dir}}(r)$ is compared with the exact $g_{\text{dir}}(r)$ in Fig. 6 for $b = 9.0$.

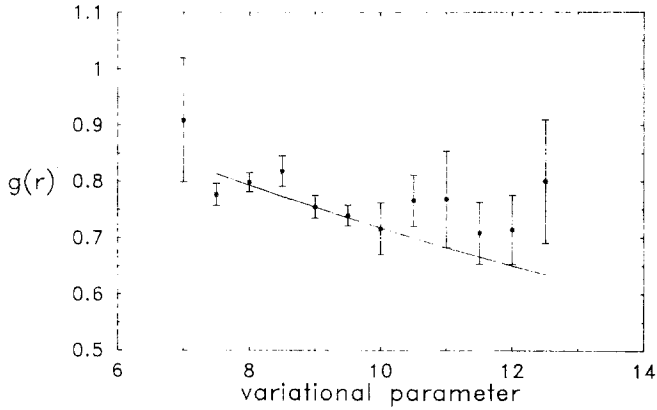

Fig. 5. The value of $g_{\text{dir}}(r)$ for two hard spheres at $r/a = 1.55$ (a = size of hard sphere) as a function of the variational parameter for $\lambda_T/\beta = 1.4$. The points with error bars are from the Monte Carlo evaluation of the variational principle and the solid line represents the behavior of ρ_T.

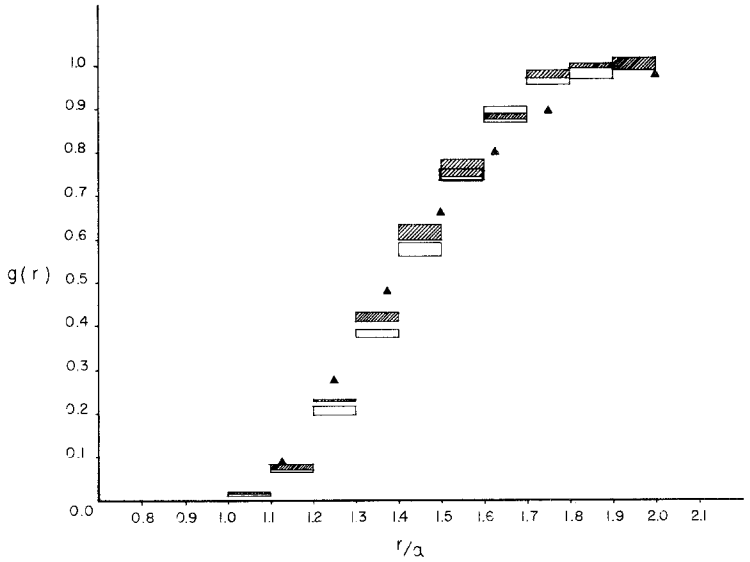

Fig. 6. The direct radial distribution function for the two hard spheres at $\lambda_T/\beta = 1.4$. The triangles are the GFMC results of Ref. 8. The hatched boxes are from the Monte Carlo evaluation of the variational principle; the open boxes are from a Monte Carlo calculation of $g(r)$ using ρ_T.

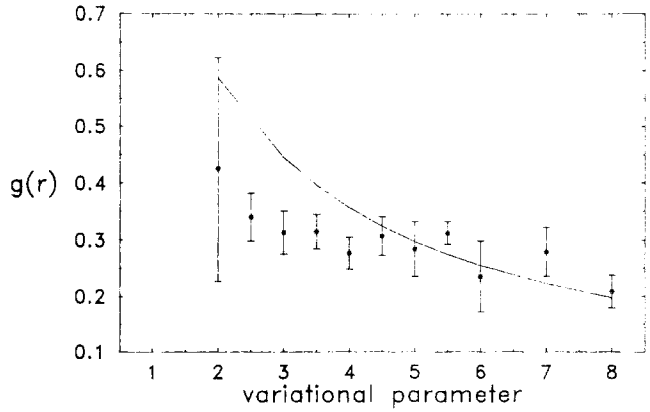

Fig. 7. The value of $g_{\text{dir}}(r)$ for two hard spheres at $r/a = 1.55$ as a function of a variational parameter. The temperature of the system corresponds to $\lambda_T/\beta = 10$. The points with error bars are from the Monte Carlo evaluation of the variational principle; the solid line represents the behavior of ρ_T.

At the lowest temperature, ρ_T is not as good a representation of the exact density matrix. In Fig. 7, the variational $g_{\text{dir}}(r)$ at $r/a = 1.55$ is plotted versus the variational parameter. Again, there is a saddlepoint region where the radial distribution function is stationary in b. However, when we compare the full variational $g_{\text{dir}}(r)$ with the exact values as in Fig. 8, the agreement is not as good as at the higher temperature shown in Fig. 6. The variational $g_{\text{dir}}(r)$ is only a slight improvement over that derived from the trial density matrix but the variational principle cannot compensate for a poor choice of ρ_T.

Furthermore, the exchange contribution to the radial distribution function determined by the variational method exhibits the wrong behavior with large statistical errors. For example, at $\lambda_T/\beta = 10$, the variational $g_{\text{exch}}(r)$ peaks at $r/a = 1.75$ with a value near 1. The exact $g_{\text{exch}}(r)$ peaks at $r/a \sim 3.0$ with a value near 0.2. This emphasizes the power of the GFMC method since it was possible to calculate g_{exch} rather accurately in Ref. 8 with the density matrix given in Eq. (23) as the importance function. An improved trial density matrix[8] was tried where the term $\exp[-(|r_1 - r_2| - |r_{01} - r_{02}|)^2/4\beta]$ in Eq. (23) was replaced by $\exp[-S^2(|r_1 - r_2|, |r_{01} - r_{02}|)]$. The function $S(|r_1 - r_2|, |r_{01} - r_{02}|)$ is the shortest distance between $|r_1 - r_2|$ and $|r_{01} - r_{02}|$ such that $|r_1, r_2|, |r_{01} - r_{02}| > a$. This trial density matrix

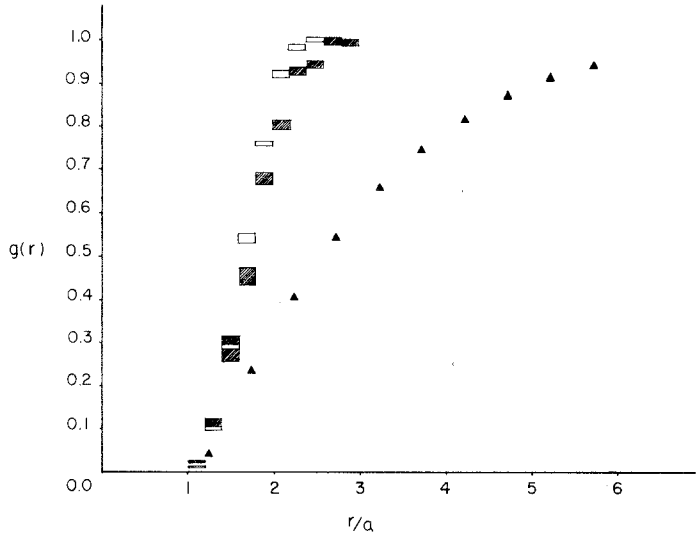

Fig. 8. The radial distribution function for two hard spheres at $\lambda_T/\beta = 10$. The triangles are the GFMC results of Ref. 8. The hatched boxes are from the Monte Carlo evaluation of the variational principle; the open boxes are from a Monte Carlo calculation of $g(r)$ using ρ_T.

should allow more accurate determination of g_{exch}; however, technical problems with the Metropolis sampling have precluded any results at this time. Work is in progress on a more robust version of the Monte Carlo method.

In summary, a Schwinger variational method was developed for use in a finite-temperature system. The distinctive feature is that the variational principle is a stationary expression for the density matrix. Stationary expressions for observables in terms of a parametrized trial density matrix can be derived. The trial density matrix with the best values of the parameters is the optimal density matrix for that observable. The major shortcoming of the method is that variational estimates may be saddle points where $\rho_v \sim \rho_B$, not upper or lower bounds.

The variational principle was applied to two model systems, a particle in a one-dimensional box and two spheres in three-dimensional box. Very good results were obtained in the one-dimensional case due to the good choice for the trial density matrix. In the three-dimensional example, the direct radial distribution function was determined. Agreement with exact calculations was acceptable at high temperatures but poor at lower temperatures. The exchange radial distribution function was poor at all temperatures. The behavior is a reflection of the poor choice for a trial density matrix.

Possible future uses for the variational method could be as a screen for indicating the "best" of a class of parametrized trial density matrices.

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