Brief Reports

Estimation of expectation values formed with Jastrow wave functions

Michael A. Day

Department of Physics, Lebanon Valley College, Annville, Pennsylvania 17003

Robert J. Hardy

Behlen Laboratory of Physics, University of Nebraska, Lincoln, Nebraska 68588-0111

A method for estimating expectation values formed with Jastrow wave functions for quantum solids is developed on the basis of the correlated-particles expansion (CPE), which follows from an exact relationship for canonical thermodynamic averages. As a test of the CPE, we obtain estimates for the ground-state energy of fcc solid ^{4}He and Lennard-Jones interatomic potential and a $1/r^5$ effective potential. When the CPE is used through second order, the differences between the kinetic and potential energies obtained and the Monte Carlo values range from 0.2% to 21%. For comparison, the differences between the cluster expansion estimates and the Monte Carlo values range from 18% to 42%.

INTRODUCTION

In the study of quantum solids wave functions of the Jastrow type are often used as trial functions for making estimates of the ground-state energy.[1] Monte Carlo techniques are commonly used to evaluate the formal expressions that result. The problem of evaluating such quantum-mechanical expectation values is mathematically equivalent to the problem of evaluating classical canonical thermodynamic averages.

Recently we have been developing the correlated-particles expansion[2,3] (CPE) as a basis for determining the thermodynamic properties of solids when anharmonic effects are significant. Since solid helium is known to be highly anharmonic and since accurate Monte Carlo values are available, we have tested the accuracy of the CPE by using it to calculate the expectation values for the energy of fcc ^{4}He. Results from three different levels of approximation are compared with the Monte Carlo results for the same model. The comparison indicates that the CPE could be useful as a guide to when and where to carry out Monte Carlo calculations, which although more accurate are much more computationally intensive.

The CPE (and the correlated Einstein model that results when it is applied through second order) is based on the following exact relationship between the harmonic average of a product and the product of the averages:[2]

$$\left\langle \prod_{\substack{k,l \\ (k<l)}} f_{kl}(\mathbf{x}_k,\mathbf{x}_l)\right\rangle_0 = e^{\lambda A(\mathbf{\nabla})} \prod_{\substack{k,l \\ (k<l)}} \langle f_{kl}(\mathbf{x}_k,\mathbf{x}_l)\rangle_0 \Big|_{\lambda=1} . \quad (1)$$

Correlations are accounted for by the exponential of the

differential operator $A(\mathbf{\nabla})$, which acts on the $\mathbf{x}$ dependence of the two-particle functions $f_{ij}(\mathbf{x}_i,\mathbf{x}_j)$ before the canonical averages are performed. $\mathbf{x}_i$ is the displacement of particle i ($i=1,2,\ldots,N$) from its lattice site. The derivation of Eq. (1) and the detailed description of the operator $A(\mathbf{\nabla})$ are given in Ref. 2. Equation (1) is obtained from the result given there by setting all "one-particle functions" equal to unity.

The CPE is obtained by expanding the right-hand side of Eq. (1) in a series of powers of the artificially introduced parameter λ. The power of λ determines the "order of smallness" of the terms in the expansion. A very useful feature of the expansion is that the dimensionality of the integrals that must be evaluated to determine any term in the expansion is independent of the order of the term. All integrals are three dimensional, and in the applications considered to date all but one of these three integrations can be done analytically.

Some years ago Mullin, Nosonow, and co-workers[4] developed a cluster expansion as a basis for estimating expectation values formed with Jastrow wave functions. As discussed in Sec. III, using the cluster expansion in the approximation $E_{01}+E_{02V}$ gives results that are accurate through zeroth order in the CPE. Results that are accurate through first order in the CPE are obtained by including the linear correction terms to the cluster expansion described in an earlier article.[5] New results are presented here that are accurate through second order in the CPE. Approximations that are accurate through successively higher orders in the CPE are successively closer to the Monte Carlo results.

THEORY

The problem being considered is that of estimating the expectation value

$$\langle H \rangle = \langle \Psi | T + U | \Psi \rangle / \langle \Psi | \Psi \rangle , \quad (2)$$

where the Hamiltonian H is a sum of a kinetic part T and a potential part U. Ψ is an unnormalized Jastrow wave function of the form

$$\psi(\mathbf{x}_1, \ldots, \mathbf{x}_N) = \exp\left[-\tfrac{1}{2} A \sum_i |\mathbf{x}_i|^2 \right]$$
$$\times \exp\left[K \sum_{\substack{i,j \\ (i<j)}} \eta(r_{ij}) \right] , \quad (3)$$

where r_{ij} is the distance between particles i and j. It follows from the above that

$$\langle H \rangle = (3NA\hbar^2/4m) + \sum_{\substack{i,j \\ (i<j)}} \langle w(r_{ij}) \rangle , \quad (4)$$

where m is the mass of a particle and

$$w(r) = \frac{\hbar^2 K}{2m} \left[\frac{d^2\eta(r)}{dr^2} + \frac{2}{r} \frac{d\eta(r)}{dr} \right] + v(r) . \quad (5)$$

In the specific model considered U is a sum of pair potentials $v(r)$ of the Lennard-Jones type with $\epsilon = 10.22$ K and $\sigma = 2.556$ Å, and the "effective potential" is

$$\eta(r) = (\sigma/r)^5 . \quad (6)$$

The nearest-neighbor distance is $r_{nn} = 3.695$ Å. An estimate for the ground-state energy is obtained by adjusting the variational parameters A and K until the expectation value $\langle H \rangle$ is minimized.

In order to use the CPE to estimate $\langle H \rangle$ we reexpress the second term on the right-hand side of Eq. (4) as

$$\sum_{\substack{i,j \\ (i<j)}} \langle w(r_{ij}) \rangle = \frac{d}{d\alpha} \ln \langle \prod_{\substack{i,j \\ (i<j)}} e^{-\Delta\phi_{ij} + \alpha w(r_{ij})} \rangle_0 |_{\alpha=0} , \quad (7)$$

where the subscript on the angle brackets indicates a "harmonic" average of the form

$$\langle F \rangle_0 = \frac{\int d^{3N}x e^{-\Phi_0} F(\mathbf{x}_1, \ldots, \mathbf{x}_N)}{\int d^{3N}x e^{-\Phi_0}} . \quad (8)$$

We assume that

$$\Delta\phi_{ij} = 2K\eta(r_{ij}) - \tfrac{1}{2}\mathbf{x}_i \cdot \overset{\leftrightarrow}{\mathbf{k}}_{ij} \cdot \mathbf{x}_i$$
$$- \tfrac{1}{2}\mathbf{x}_j \cdot \overset{\leftrightarrow}{\mathbf{k}}_{ji} \cdot \mathbf{x}_j + \boldsymbol{\gamma}_{ij} \cdot \mathbf{x}_i + \boldsymbol{\gamma}_{ji} \cdot \mathbf{x}_j \quad (9)$$

and

$$\Phi_0 = \sum_i (\tfrac{1}{2}\mathbf{x}_i \cdot \overset{\leftrightarrow}{\mathbf{K}}_i \cdot \mathbf{x}_i - \boldsymbol{\Gamma}_i \cdot \mathbf{x}_i) . \quad (10)$$

The terms linear and quadratic in the $\mathbf{x}_i$ that result from substituting this expression for $\Delta\phi_{ij}$ into the right-hand side of Eq. (7) must exactly cancel the linear and quadratic terms that result from using in the "harmonic potential energy" Φ_0. As can be verified by direct substitution, this leads to a requirement that the parameters $\boldsymbol{\gamma}_{ij}$, $\overset{\leftrightarrow}{\mathbf{k}}_{ij}$, $\boldsymbol{\Gamma}_i$, and

$\overset{\leftrightarrow}{\mathbf{K}}_j$ must satisfy

$$\sum_{\substack{j \\ (j\neq i)}} \boldsymbol{\gamma}_{ij} = \boldsymbol{\Gamma}_i = 0 , \quad (11)$$

where one can set $\boldsymbol{\Gamma}_i = 0$ because of the high symmetry of the lattice considered, and

$$2A\overset{\leftrightarrow}{\mathbf{I}} + \sum_{\substack{j \\ (j\neq i)}} \overset{\leftrightarrow}{\mathbf{k}}_{ij} = \overset{\leftrightarrow}{\mathbf{K}}_i . \quad (12)$$

$\overset{\leftrightarrow}{\mathbf{I}}$ is the unit tensor.

The CPE is obtained by using Eq. (1) to reexpress the average on the right-hand side of Eq. (7) as an operator acting on a product of averages and by expanding the logarithm that enters through Eq. (7) in powers of λ before differentiating with respect to α. Our best approximation is obtained by choosing the parameters $\boldsymbol{\gamma}_{ij}$ and $\overset{\leftrightarrow}{\mathbf{k}}_{ij}$ introduced in $\Delta\phi_{ij}$ so that all of the terms in the CPE proportional to λ and to λ^2 are zero. This is done by choosing $\boldsymbol{\gamma}_{ij}$ and $\overset{\leftrightarrow}{\mathbf{k}}_{ij}$ so that

$$\langle \mathbf{x}_i e^{-\Delta\phi_{ij}} \rangle_0 / \langle e^{-\Delta\phi_{ij}} \rangle_0 = \langle \mathbf{x}_i \rangle_0 = 0 , \quad (13)$$

where $\langle \mathbf{x}_i \rangle_0$ is zero when $\boldsymbol{\Gamma}_i$ is zero, and

$$\langle x_i^\mu x_i^\nu e^{-\Delta\phi_{ij}} \rangle_0 / \langle e^{-\Delta\phi_{ij}} \rangle_0 = \langle x_i^\mu x_i^\nu \rangle_0 = (\overset{\leftrightarrow}{\mathbf{K}}_i^{-1})^{\mu\nu} , \quad (14)$$

where μ and ν label different vector components. When only terms through second order are kept, one obtains

$$\langle H \rangle = \frac{3NA\hbar^2}{4m} + \sum_{\substack{i,j \\ (i<j)}} \frac{\langle w(r_{ij}) e^{-\Delta\phi_{ij}} \rangle_0}{\langle e^{-\Delta\phi_{ij}} \rangle_0} , \quad (15)$$

where only zeroth-order terms remain.

The above equations reduce the problem of evaluating $\langle H \rangle$ to the problem of evaluating a phase-function average with the methods presented in Ref. 2, where Eq. (15) is referred to as the "correlated Einstein model approximation." Φ_0 is the "Einstein potential-energy function." Equations (11) and (12) are the "self-consistency conditions." Equations (13) and (14) are the "zeroing conditions."

RESULTS

The results of our calculations for the expectation values $\langle H \rangle$, $\langle T \rangle$, and $\langle U \rangle$ as functions of the variational parameters A and K are given in Figs. 1 and 2 along with the Monte Carlo estimates of Hansen and Levesque.[6] Three different levels of approximation are given. Equation (15) and the analogous equations for $\langle T \rangle$ and $\langle U \rangle$ were used in all three levels of approximation, and conditions (11) and (12) were satisfied in every case.

Our best CPE values are accurate through second order. They were obtained with the parameters $\boldsymbol{\gamma}_{ij}$ and $\overset{\leftrightarrow}{\mathbf{k}}_{ij}$ determined so that both conditions (13) and (14) are satisfied.

The next best CPE values are accurate through first order. They were obtained with the parameters $\boldsymbol{\gamma}_{ij}$ deter-
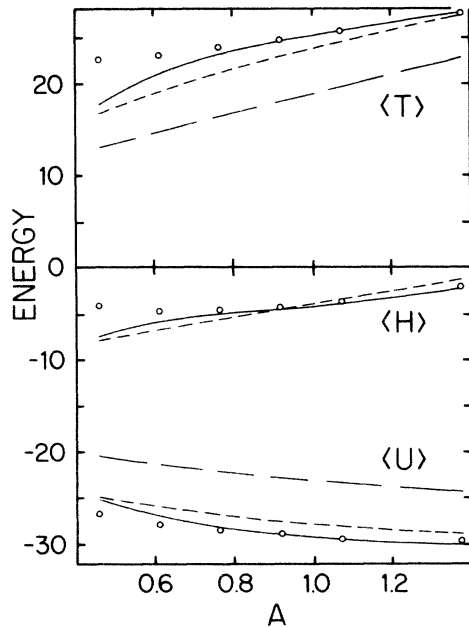
FIG. 1. Kinetic $\langle T \rangle$, potential $\langle U \rangle$, and total $\langle H \rangle$ energy per particle (kelvin) vs variational parameter A (Å^{-2}) for fcc ^{4}He with $K = 1.050$ and $r_{nn} = 3.695$ Å. Circles are for Monte Carlo; solid curve for second-order CPE; dashed curve for first-order CPE; dotted-dashed curve for cluster expansion.
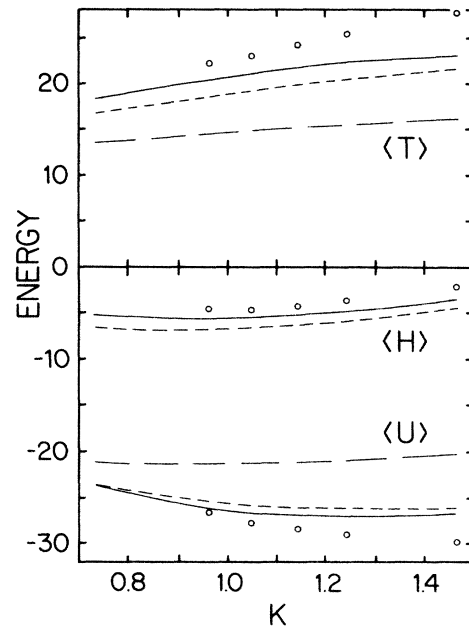
FIG. 2. Kinetic $\langle T \rangle$, potential $\langle U \rangle$, and total $\langle H \rangle$ energy per particle (kelvin) vs variational parameter K for fcc ^{4}He with $A = 0.612$ Å^{-2} and $r_{nn} = 3.695$ Å. Circles are for Monte Carlo; solid curve for second-order CPE; dashed curve for first-order CPE; dotted-dashed curve for cluster expansion.

mined so that conditions (13) were satisfied. The parameters $\overleftrightarrow{k}_{ij}$ were set to zero, which caused conditions (12) to simplify to $\overleftrightarrow{K}_i = 2A\overleftrightarrow{I}$. Without the possibility of adjusting the $\overleftrightarrow{k}_{ij}$'s it is impossible to satisfy conditions (14). As a result, not all second-order terms vanish. The resulting approximation is equivalent to that used by the authors in an earlier paper,[5] where the approximation was developed more intuitively by including linear correction terms in the Jastrow wave function.

The cluster expansion values are given in the approximation labeled $E_{01}+E_{02V}$ by Nosonow[4] and are equivalent to CPE results accurate through zeroth order. They were obtained by setting both the parameters γ_{ij} and the parameters $\overleftrightarrow{k}_{ij}$ to zero, which caused conditions (11) to be trivially satisfied and conditions (12) to simplify. Without the possibility of adjusting either the parameters γ_{ij} or $\overleftrightarrow{k}_{ij}$ it is impossible to satisfy either conditions (13) or conditions (14). As a result, neither the second- nor the first-order terms vanish.

The difference between the second-order CPE estimates for the kinetic and potential energies and the Monte Carlo values plotted in the figures range from 0.2% to 21%. For comparison, the differences between the cluster expansion estimates and the Monte Carlo values range from 18% to 42%.

The numerical accuracy of our results was checked by varying the integration mesh, the number of shells of neighboring particles considered, etc. We believe that any differences between the values calculated for $\langle H \rangle$, etc., and the values defined by Eq. (15), etc., are in the fourth or higher significant figure. The values calculated contain an integral approximation for the sum of the contributions

to the energy from all shells of particles beyond those for which the integrals were carried out numerically.

DISCUSSION

As can be seen from the figures, the estimates for the expectation values become more accurate as successively higher-order approximations are considered. This gives one confidence in the CPE as a basis for estimating expectation values. If greater accuracy is desired, third and higher-order terms in the CPE can be added to the second-order result presented here. Since the dimensionality of the integrals that must be evaluated is independent of the order of the term considered, higher-order corrections are relatively simple to determine. For example, all of the integrations in a recent calculation of the third-order corrections to the thermodynamic properties of a hard-sphere solid could be reduced to one-dimensional numerical integrations, which can be easily done on a microcomputer.[3] If needed, three-particle functions (or correlations) could be included in the CPE.[2]

In general, the values obtained for the total energy $\langle H \rangle$ are not as accurate as those for the kinetic and potential energies $\langle T \rangle$ and $\langle U \rangle$. This is a simple consequence of losing a significant figure when the negative potential energy is added to the positive kinetic energy. Unfortunately, for the $1/r^5$ effective potential the improvements to the cluster expansion estimates that result from using the CPE through second order are not sufficient to allow one to determine an optimum value for the variational parameter A in the trial wave function for solid ^{4}He.

[1]For recent references see, e.g., X.-Z. Ni and L. W. Bruch, Phys. Rev. B **33**, 4584 (1986), who consider two-dimensional monolayers, and P. A. Whitlock and G. V. Chester, Phys. Rev. B **35**, 4719 (1987), who consider three-body correlations.

[2]R. J. Hardy and M. A. Day, Phys. Rev. B **29**, 4108 (1984).

[3]R. J. Hardy and M. A. Day, J. Chem. Phys. **86**, 7089 (1987).

[4]L. H. Nosonow, Phys. Rev. **146**, 120 (1966). See also W. J. Mullin, *ibid.* **134**, A1249 (1964); J. H. Hetherington, W. J. Mullin, and L. H. Nosonow, *ibid.* **154**, 175 (1967); and W. J. Mullin, L. H. Nosonow, and P. M. Steinbach, *ibid.* **188**, 410 (1969).

[5]M. A. Day and R. J. Hardy, J. Low Temp. Phys. **52**, 63 (1983).

[6]J.-P. Hansen and D. Lavesque, Phys. Rev. **165**, 293 (1968). Also see J.-P. Hansen, Phys. Lett. **30A**, 214 (1969); and J. Phys. (Paris) Colloq. **31**, C3-67 (1970).