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Optimization of ^{4}He wave functions for the liquid and solid phases

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We present a method using a basis set to calculate the optimized Jastrow pair function in trial wave functions for quantum fluids and solids. Using three-body terms in the variational trial wave function, as well, the variational Monte Carlo binding energies obtained are significantly lower than determined previously. The radial distribution functions $g(r)$ with these Jastrow functions are presented and discussed.

I. INTRODUCTION

Optimized Jastrow pair functions have been developed and used with cluster expansion methods for many years.[1-3] Variational Monte Carlo calculations, for the most part, have relied on these Jastrow functions or on simple parametrizations of the Jastrow function and a straightforward energy minimization.[4,5]

In this paper, we generalize Pandharipande's idea of solving a two-body Schrödinger-like equation, by building a Jastrow function using a basis formed by the eigenfunctions of that equation.[6] The resulting Jastrow function can be described by a fairly small number of parameters, which are the coefficients of the basis functions. An efficient way to optimize the values of the parameters is to use a reweighting scheme where the variance of the energy is minimized. We apply the method to liquid and solid ^{4}He.

In the following sections, we discuss the optimization method, give our results for the Jastrow functions, and present typical radial distribution functions obtained with these calculations. We compare our results to values obtained by Green's-function Monte Carlo methods (GFMC's).[7]

II. THE VARIATIONAL MONTE CARLO METHOD

The Hamiltonian we use to describe N ^{4}He atoms is

$$H=-\frac{\hbar^2}{2m}\sum_{i=1}^{N}\nabla_i^2+\sum_{i<j}v(r_{ij}) , \tag{1}$$

where $v(r_{ij})$ is the HFDHE2 potential of Aziz *et al.*[8] The potential v is a function only of the relative distance $r_{ij}=|\mathbf{r}_i-\mathbf{r}_j|$ between particles i and j with coordinates $\mathbf{r}_i$ and $\mathbf{r}_j$, respectively.

The variational energy E_T is computed using the expression

$$E_0\le E_T=\frac{\int dR\, \Psi_T(R)H\Psi_T(R)}{\int dR\, |\Psi_T(R)|^2} , \tag{2}$$

where $R\equiv\{\mathbf{r}_1,\dots,\mathbf{r}_N\}$. We compute the integral using the Metropolis *et al.* algorithm.[9] Our aim is to optimize the trial function Ψ_T to obtain a good variational upper bound to the ground-state energy E_0.

III. THE VARIATIONAL WAVE FUNCTION

As is well known, in the ground state of a system of ^{4}He atoms both long-range and short-range correlations are present. The short-range correlations are directly induced by the hard core in the interatomic potential. Long-range correlations can be thought of as being due to zero-point phonon motion. Structural information about the very long-range correlations can be obtained directly from variational Monte Carlo calculations only by considering large systems with many particles. Typically, these long-range correlations make relatively unimportant contributions to the energy of the system.[10] We will therefore concentrate on the shorter-range correlations.

We use a trial function that is a product of one-, two-, and three-body functions

$$\psi_t(R)=\prod_{i<j}f_{ij}\prod_{i<j<k}h_{ijk}\prod_{i}\phi_i . \tag{3}$$

This general form, which includes up to three-body terms in the general Feenberg form for the trial function, has been used and developed by many authors.[11-13]

For a liquid state, $\phi_i=1$, and for the solid, ϕ is the Nosanow localized form,[14]

$$\phi_i=e^{-\alpha(\mathbf{r}_i-\mathbf{l}_i)^2} . \tag{4}$$

The l_i are the lattice points, and α is a variational parameter. It is convenient to use a face-centered-cubic lattice since, as demonstrated by GFMC calculations,[15] its energy is very close to the hexagonal-close-packed structure.

We impose the condition, on the Jastrow function,

$$f(r>d)=1 , \tag{5}$$

and require continuity of $f(r)$ and its gradient at $r=d$.

At small separations, the two-body potential $v(r)$ dominates and $f(r)$ should satisfy a two-body Schrödinger equation,

$$-(\hbar^2/m)\nabla^2 f(r)+v(r)f(r)=\lambda f(r) \ . \tag{6}$$

If we enforce the boundary conditions given above, this defines an eigenvalue equation. Pandharipande and Bethe have used the ground state of this equation to define $f(r)$.[6,16]

We improve the Jastrow function $f(r)$ by writing it as a linear combination of $f_n(r)$, the spherically symmetric eigenfunctions of Eq. (6),

$$f(r)=\sum_n c_n f_n(r) \ . \tag{7}$$

The coefficients c_n are variational parameters. In our minimization method the number of eigenfunctions used in Eq. (7) can be chosen big enough to include all the important components of the complete set of functions $\{f_n\}$.

The Jastrow function f of Eq. (7) is automatically correct for small pair separations independent of the coefficients c_n, since it is a solution of the two-body Schrödinger equation. This is especially convenient for Monte Carlo calculations; when a pair separation distance is small, the wave function of the system is small too, and it is difficult to sample and optimize the wave function in these regions.

The parameter d of Eq. (5) may be chosen to be $d \leq l/2$, half the side of the simulation cell, making it easy to construct a Jastrow function $f(r)$ that heals smoothly to 1 inside the simulation cell. Other boundary conditions could be used; $f(r)-1$ could be matched to its correct behavior, proportional to r^{-2}, at large r.

We take the three-body function h_{ijk} to be[12,13]

$$h_{ijk}=\exp\left[-\frac{\lambda}{2}\sum_{\text{cycl}} \xi_{ij}\xi_{ik}\mathbf{r}_{ij}\cdot\mathbf{r}_{ik}\right] , \tag{8}$$

where λ is a variational parameter, cycl denotes a sum over cyclic permutations of $\{i,j,k\}$, $\xi_{ij}=\xi(r_{ij})$ depends on two parameters r_0 and w and on the size of the simulation cell l; the functional form of ξ is

$$\xi(r)=\left[\frac{2r-l}{l}\right]^3 \exp\left[-\left[\frac{\mathbf{r}-\mathbf{r}_0}{w}\right]^2\right] . \tag{9}$$

IV. THE OPTIMIZATION METHOD

The simplest way of optimizing a trial wave function in variational Monte Carlo calculations is to adjust its parameters and minimize the expectation value of the energy. A more robust and efficient method, where a moderate number of variational parameters is used, is to minimize the energy variance using a reweighting scheme, as has been demonstrated recently by Umrigar, Wilson, and Wilkins[17] and previously by other authors.[18]

To minimize the energy variance, we start with our best trial functions $\psi_t(R)$ and generate a set of $\{R_1,R_2,\ldots,R_M\}$ configurations using the Metropolis *et al.* algorithm.[9] Using these configurations, we adjust the parameters of the variational wave function to obtain $\psi_{\text{opt}}(R)$ such that the energy variance,

$$\sigma_E^2=\frac{\displaystyle\sum_{i=1}^{M}\left[\frac{H\psi_{\text{opt}}(R_i)}{\psi_{\text{opt}}(R_i)}-E_b\right]^2\frac{\psi_{\text{opt}}^2(R_i)}{\psi_t^2(R_i)}}{\displaystyle\sum_{i=1}^{M}\frac{\psi_{\text{opt}}^2(R_i)}{\psi_i^2(R_i)}} , \tag{10}$$

is minimized. We can also take the ratio $\psi_{\text{opt}}^2/\psi_t^2$ equal to 1 in Eq. (10), although the resulting expression is no longer equal to the energy variance, it is still minimized by the exact wave function. In our calculations, this second form gives convergence with less computer time. We chose a value for E_g that is our best estimate of the ground-state energy, although its value could be taken as an additional variational parameter. Its value is not critical. After the new values for the variational parameters have been determined by minimizing Eq. (10), we sample a new set of configurations and calculate the energy expectation with these new values of the parameters. The whole process of performing variational computation and optimization is repeated iteratively until the energy has converged.

A preliminary study[19] has shown that a basis using the first ten eigenfunctions of Eq. (6) is large enough to give a good description of the Jastrow function. As a further test that our method with only ten eigenfunctions is able to generate nearly optimal Jastrow functions, we have optimized a wave function with the Jastrow function of Eq. (7), and compared our results with those using a Jastrow function from paired phonon analysis (PPA).[2] In Table I we show these results for the variational Monte Carlo ground-state energy at the equilibrium density of liquid ^{4}He. In this calculation, as in the rest of this work, we have used a periodic system of 108 particles. In Table I we also compare to calculations using other trial functions and to GFMC results. The good agreement between our calculations and those using PPA Jastrow functions indicates that our method determines a nearly optimal Jastrow function.

In our calculations, we start by generating a set of configurations using a trial function with a Jastrow function of the McMillan form,[20] which had been energy optimized previously. We sample a set of configurations from this wave function, and then optimize the coefficients c_n of Eq. (7) by variance minimization. For most of the calculations, the parameters in the other correlations are kept fixed. Using the new values of c_n, new configurations are generated for the next optimization step. Typically we use 1000 configurations in the optimizations. This iterative procedure is continued until convergence in the energy is reached. Usually three iterations are sufficient. In a few calculations, we minimized the energy variance with respect to the other parameters in the trial wave function. However, as shown later, this did not improve the energy within our statistics, and most of our calculations have optimized only the c_n coefficients. The minimizations were performed using the Levenberg-Marquardt method since they are highly

TABLE I. Ground-state energies for liquid ^{4}He at the equilibrium density $\rho=0.0218$ Å^{-3}. In the first five lines we present variational results obtained with the following trial functions: a functional optimization of the two-body Jastrow function using the basis-set approach [$2B$(BS)]; the same optimization made by paired-phonon analysis [$2B$(PPA)]; A two-body Jastrow (M) trial wave function with a pseudopotential of the McMillan form (Ref. 20); a two-body Jastrow function together with explicit three-body correlations ($2B+3B$); a two-body Jastrow function in which the correlation factor is optimized by paired-phonon analysis and explicit triplet correlations [$2B$(PPA)$+3B$]; and our best two-body basis-set Jastrow function with an explicit three-body correlation result [$2B$(BS)$+3B$]. In the last line we give the energy obtained by the Green's-function Monte Carlo method (GFMC). The calculations have been performed for systems of 108 particles, except the ones using $2B$(PPA), where 64 particles were used.

Variational		Energies (K)		
trial function	This work	Ref. 7	Ref. 23	Ref. 24
$2B$(BS)	-5.938 ± 0.028			
$2B$(PPA)		-5.87	-5.93 ± 0.01	
M				-5.717 ± 0.021
$2B+3B$			-6.674 ± 0.007	
$2B$(PPA)$+3B$			-6.741 ± 0.008	
$2B$(BS)$+3B$	-6.862 ± 0.016			
GFMC				
Importance function				
J(PPA)		-7.120 ± 0.024		

nonlinear, although many other minimization methods, for example the simplex method, also will work.

V. Results

We have presented the variational energies and the corresponding variational parameters in Table II at the liquid densities of $\rho=0.0196$ Å^{-3}, at the equilibrium density, $\rho=0.0218$ Å^{-3}, at $\rho=0.0240$ Å^{-3}, and $\rho=0.0262$ Å^{-3}. This last value is the freezing density determined by the GFMC method.[7] At all densities, we get an improvement over values previously calculated using a McMillan form for the Jastrow function along with the same three-body term.

In Fig. 1, we show the radial distribution function $g(r)$ and the Jastrow function $f(r)$ obtained at the equilibrium density using the values in Table II. Our maximum of $g(r)$ is 1.372 ± 0.004 at $r=3.425$ Å, while GFMC (Ref. 7) gives 1.3812 at $r=3.527$ Å. Our variational peak is a little smaller and has been displaced by 3% from the GFMC value.

In Fig. 2, we compare the optimized pseudopotential $u(r)$, $u(r)=-\ln[f(r)]$, obtained with a wave function that explicitly includes a three-body term and one where only the Jastrow function is used. At $r\approx4.8$ Å, the wave function that contains only two-body terms exhibits a small shoulder that disappears when three-body terms are present. This behavior is in agreement with a specula-

TABLE II. Variational energies for ^{4}He in K per atom in the liquid phase for the given set of parameters at several densities (ρ in units of Å^{-3}). The λ parameter is given in units Å^{-2}, $\mathbf{r}_0$ and w in units of Å.

ρ	0.0196	0.0218	0.0240	0.0262
c_1	0.906 61	0.910 31	0.913 44	0.914 49
c_2	0.105 05	0.101 00	0.101 20	0.088 38
c_3	−0.013 74	−0.017 12	−0.021 85	−0.009 90
c_4	0.004 89	0.008 74	0.008 89	0.008 81
c_5	−0.004 40	−0.004 93	−0.003 82	−0.004 77
c_6	0.002 77	0.004 13	0.003 69	0.003 06
c_7	−0.001 83	−0.002 77	−0.002 10	−0.002 99
c_8	0.001 09	0.000 93	0.000 98	0.001 96
c_9	−0.001 37	−0.001 19	−0.001 43	−0.000 52
c_{10}	0.000 92	0.000 92	0.000 99	0.001 47
λ	−2.143	−2.143	−2.143	−2.143
$\mathbf{r}_0$	2.096	2.096	2.096	2.096
w	1.278	1.278	1.278	1.278
E_0	-6.804 ± 0.015	-6.862 ± 0.016	-6.524 ± 0.020	-5.837 ± 0.023

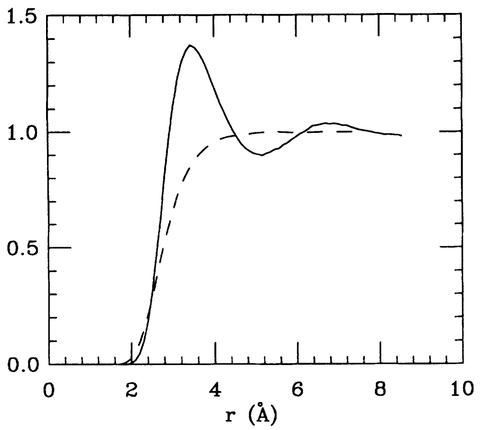

FIG. 1. Radial distribution function g, solid line, and Jastrow function f, dashed line, as a function of the pair separation in angstroms at the equilibrium density. The trial function used in the calculations is given by $f(r)$ times the triplet term.

tion[21] that the effect of a three-body term can be mimicked to some extent by a shoulder in the Jastrow function. A similar result to ours is given by the maximum overlap criterion,[22] a different method of optimizing $f(r)$.

Figure 3 shows our results for the radial distribution function $g(r)$ and Jastrow function $f(r)$ determined at the freezing density $\rho=0.0262$ Å^{-3}. The $g(r)$ has a peak located at the same position as found with GFMC, but the maximum of $g(r)$ is again smaller.

Comparing Figs. 1 and 3, we see somewhat more structure in $f(r)$ as the density increases. The structure of the Jastrow function increases with density, as expected, in all cases that we have studied.

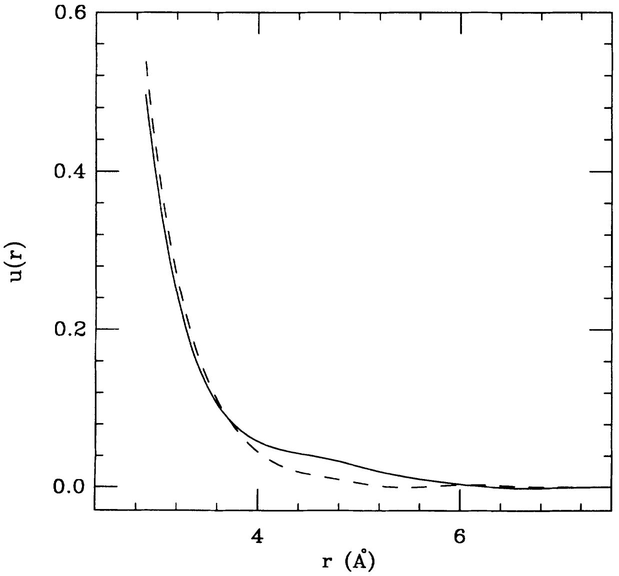

FIG. 2. Optimized pseudopotentials for a trial wave function of the Jastrow form, solid line, and of the Jastrow form plus triplet, dashed line, at $\rho=0.0218$ Å^{-3}.

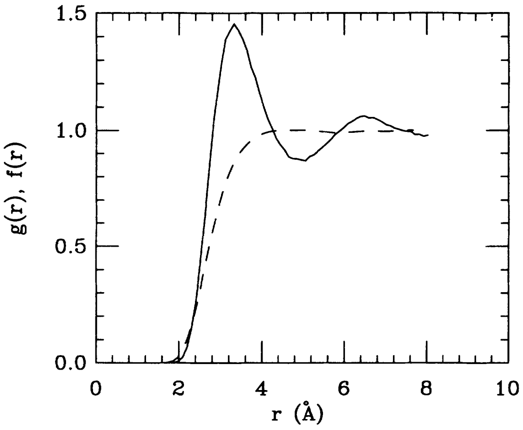

FIG. 3. Radial distribution function $g(r)$, solid line, for a wave function given by the Jastrow function $f(r)$, dashed line, times explicit three-body term. This calculation gives the result at the freezing density.

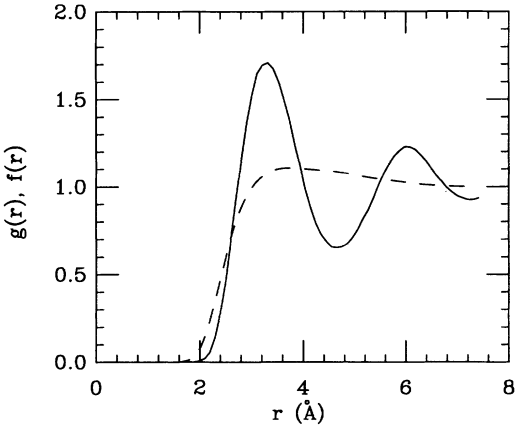

FIG. 4. Radial distribution function $g(r)$, solid line, determined with the Jastrow function $f(r)$, dashed line, times a triplet and one-body term. Results at the solid density $\rho=0.0335$ Å^{-3}.

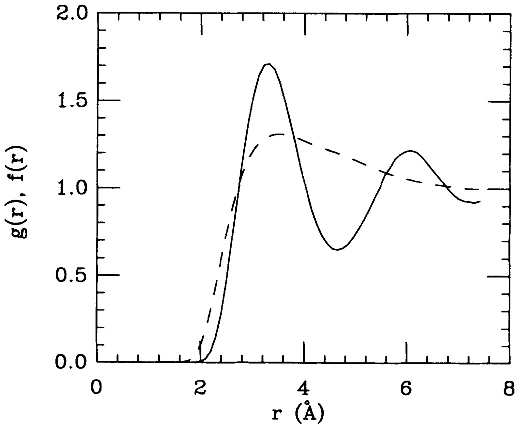

FIG. 5. Jastrow function $f(r)$, dashed line, determined with a different set of coefficients c_n than those employed in Fig. 4. The radial distribution function $g(r)$, solid line, was obtained using the f shown along with triplet and one-body terms.

TABLE III. Variational energies in the crystalline phase for ^{4}He in K per atom for the given set of parameters at several densities (ρ in units of Å^{-3}). The α and λ parameters are given in units of Å^{-2}, $\mathbf{r}_0$ and w in units of Å.

ρ	0.0293	0.0315	0.0329	0.0335	0.0353
c_1	0.974 11	0.970 81	0.975 73	0.975 64	0.974 13
c_2	0.020 62	0.023 60	0.018 99	0.019 16	0.020 40
c_3	0.013 46	0.013 51	0.013 74	0.013 58	0.013 83
c_4	−0.015 99	−0.015 73	−0.016 21	−0.016 15	−0.016 20
c_5	0.011 88	0.011 79	0.011 93	0.011 93	0.011 96
c_6	−0.007 19	−0.007 12	−0.007 28	−0.007 26	−0.007 22
c_7	0.004 17	0.004 12	0.004 20	0.004 20	0.004 17
c_8	−0.002 09	−0.002 03	−0.002 12	−0.002 12	−0.002 11
c_9	0.002 01	0.002 01	0.002 02	0.002 03	0.002 03
c_{10}	−0.000 98	−0.000 96	−0.001 02	−0.001 02	−0.000 99
α	0.459 2	0.535 7	0.612 2	0.613 2	0.688 8
λ	−1.225	−1.225	−1.224	−1.227	−1.225
$\mathbf{r}_0$	2.096	2.096	2.093	2.094	2.096
w	1.278	1.278	1.280	1.280	1.278
E_0	-5.409 ± 0.051	-4.662 ± 0.032	-4.011 ± 0.036	-3.584 ± 0.038	-2.368 ± 0.042

The energies and variational parameters for the solid phase calculations are given in Table III. At the two lower densities, $\rho=0.293$ and 0.0315 Å^{-3}, the variational energy is decreased by 0.14 K and 0.2 K, respectively, from values using the McMillan form for the Jastrow function. For the densities of $\rho=0.0329$, 0.0335, and 0.0353 Å^{-3}, the energy decreases by about 0.2 K.

The Jastrow function $f(r)$ and the radial distribution function $g(r)$ at $\rho=0.0335$ Å^{-3} are shown in Fig. 4. Again, we have agreement with GFMC with the position of the first peak at $r=3.233$ Å. Our value for $g(r)$ at the peak is 1.710 ± 0.007 compared to the GFMC result of 1.7411.

We also show in Table III, for the densities $\rho=0.0329$ and 0.0335 Å^{-3}, the parameters where we have reoptimized the one-body and three-body terms from their initial values of $\alpha=0.6123$ Å^{-2}, $\lambda=-1.225$ Å^{-2}, $r_0=2.096$ Å, and $w=1.278$ Å. As can be seen, the reoptimization does not change these parameters significantly.

The coefficients c_n are not always well determined by our procedure due to the insensitivity of the Monte Carlo results to the long-wavelength behavior of the Jastrow function. We have found different sets of the coefficients c_n that give equally good results at a given density. In some cases, these sets produce quite similar looking Jastrow functions. However, it is possible to find sets that give different Jastrow functions $f(r)$. In Fig. 5, we show a plot of the Jastrow function $f(r)$ and its corresponding radial distribution function $g(r)$ at a density $\rho=0.0335$ Å^{-3}. The values of coefficients α, λ, r_0, and w are those quoted in the last paragraph, and the c_n are different from those of Table III and Fig. 4. The variational energy is -3.576 ± 0.036 K in good agreement with the result in Table III. The value and position of the first peak of $g(r)$ are also in good agreement. It is also apparent by examining Figs. 4 and 5 that the two Jastrow functions differ primarily by a multiplicative constant in the region $r<4$ Å. By Fourier transforming the corresponding pseudopotentials, we verified that the two Jastrow functions only differ substantially at long wavelength. The energy and short-range structure of $g(r)$ are rather insensitive to these differences.

VI. CONCLUSIONS

We have shown that a simple basis-set approach using energy-variance minimization gives a straightforward method of optimizing the Jastrow function for quantum fluids and solids. The main difficulty with the method is the necessity of performing a highly nonlinear optimization where some care has to be taken to avoid undesirable local minima. The method is a general technique and should be applicable to other situations and to the Jastrow functions encountered in nonuniform systems.

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