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Variational Calculations for Solid and Liquid ^{4}He with a "Shadow" Wave Function

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A new class of trial wave functions is introduced to compute variationally the ground-state energy of solid ^{4}He. This wave function is symmetric under particle exchange, translationally invariant, and does not require the *a priori* introduction of a crystal lattice. It gives a lower energy than and has properties comparable with those given by previous calculations in which atoms are explicitly localized. The same functional form of the wave function is used to investigate the liquid phase, where a lower energy than those given by a wave function of the Jastrow form is obtained as well.

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Monte Carlo variational computations for quantum many-body systems were first carried out by McMillan.[1] In this work a trial wave function of the well-known Jastrow form gave reasonable results for liquid ^{4}He. For solid ^{4}He, the same wave function gave too high an energy. The parametrization strength of the Jastrow function which produces long-range order gives rise to a crystal that is too tightly localized to be a good description of a quantum solid.

Good variational energies were obtained with Monte Carlo computations by Hansen and Levesque,[2] using one-body Gaussian factors coupling atoms to lattice sites as previously suggested by Nosanow.[3] This destroys both the translational invariance[4] and the symmetry of the trial wave function that are inherent in the system. We have recently observed that these properties can be restored while retaining a good quantitative description of the crystal. Early attempts to do this were made with use of a self-consistent theory.[5] However, the energies obtained were higher than those determined by Hansen and Levesque.

Our new trial wave function $\Psi_T(R)$, $R\equiv\{\mathbf{r}_1,\mathbf{r}_2,\dots,\mathbf{r}_N\}$, can be conveniently written by the introduction of an artificial or "shadow" set of variables $S\equiv\{\mathbf{s}_1,\mathbf{s}_2,\dots,\mathbf{s}_N\}$ through

$$\Psi_T(R)=\int \Xi(R,S)dS. \qquad (1)$$

Ξ is given by

$$\Xi(R,S)=\exp[-\tfrac{1}{2}\textstyle\sum_{i<j}u(r_{ij})-\sum_k\phi(\mathbf{r}_k-\mathbf{s}_k)-\sum_{l<m}v(s_{lm})], \qquad (2)$$

where $r_{ij}=|\mathbf{r}_i-\mathbf{r}_j|$ is the distance between particles i and j and $s_{lm}=|\mathbf{s}_l-\mathbf{s}_m|$. In Eq. (2) the first sum in the exponential is the usual two-body correlation function of the Jastrow form. The last term is a function of the auxiliary variables $\mathbf{s}_j$, for which model potential of the form s^{-n} has been taken. In this work ϕ was chosen to be $C(\mathbf{r}_k-\mathbf{s}_k)^2$, where C is a variational parameter. The function $\Psi_T(R)$ is both translationally invariant and symmetric under particle interchange.

There were several complementary rationales for experimentation with a wave function having this structure. The first is very simply that classical systems exhibit long-range order at low enough temperatures. To use this directly in the Jastrow factor violates the requirement that the latter solve the Schrödinger equation at small pair separation. In Eq. (1), the shadow particles are the analog of the classical system and can be given a low effective "temperature," while the pair correlations among the "real" particles R can approximate a solution of the Schrödinger equation. The long-range crystalline order of the shadow particles is imposed on the real by the one-to-one coupling of Eq. (2).

A different justification arises from the path-integral picture of a quantum solid.[6] Consider the "center of mass" $\mathbf{r}_i$(c.m.) of all the positions of particle i on a Feynman path in imaginary time.[7] If one averages over fluctuations about the centers of mass, then the repulsive core diameter of the resulting "interaction" between the coordinates $\mathbf{r}_i$(c.m.) should be larger than that in the bare pair potential $V(r)$. Thus the correlations among the $\mathbf{r}_i$(c.m.) will have more structure than for the actual coordinates $\mathbf{r}_i$. Therefore the $\mathbf{r}_i$(c.m.) should resemble a classical system more than a quantum one. We are presently attempting to incorporate these ideas into an approximate theory of quantum solids and fluids. In this paper the centers of mass are modeled by shadow particles. The fluctuation of the real particle with respect to the center of mass, or shadow, can be introduced, at least crudely, by a harmonic interaction.

A more formal motivation comes from the ideas of a Green's-function Monte Carlo method,[8] where the integral equation form of the Schrödinger equation is used:

$$\Psi(R)=E\int G(R,S)\Psi(S)dS. \qquad (3)$$

Consider the approximation of $\Psi(S)$ on the right-hand side by a simple Jastrow function

$$\Psi_J(S)=\prod_{i<j}f_0(\mathbf{s}_i-\mathbf{s}_j). \qquad (4)$$

Suppose that $G(R,S)$ is given by the Boltzmann Green's function for free particles at some effective temperature,

$$G_0(R,S) \propto \exp[-C\textstyle\sum_k (\mathbf{r}_k - \mathbf{s}_k)^2], \tag{5}$$

"dressed" by Jastrow factors in R and S to model the correlations in $G(R,S)$ while keeping it symmetric in R and S and so as to satisfy approximately

$$\int H(R)G(R,S)dS \approx 1, \tag{6}$$

where H is the Hamiltonian. With these approximations one is led directly to Eqs. (1) and (2) as a generalization of the Jastrow form.

In the shadow wave function, the correlations among the real particles are enhanced to all orders as compared with a pure Jastrow form for the fluid. One can hope to achieve correlations as strong in the crystal as the Nosanow-Jastrow form while retaining Bose symmetry and translational invariance. In fact, our results show that this is true.

The variational energy is given by

$$E_T = \int dR\,\Psi_T H \Psi_T \Big/ \int dR\,|\Psi_T|^2, \tag{7}$$

or in terms of Ξ, as

$$E_T = \frac{\iiint dR\,dS_1\,dS_2\,\Xi(R,S_1)\Xi(R,S_2)H\Xi(R,S_2)/\Xi(R,S_2)}{\iiint dR\,dS_1\,dS_2\,\Xi(R,S_1)\Xi(R,S_2)}. \tag{8}$$

The evaluation of the energy in Eq. (8) involves $9N$-dimensional integrals. It is evaluated by the standard Metropolis Monte Carlo algorithm.[9] In this method the estimator $H\Xi(R,S_2)/\Xi(R,S_2)$ is averaged with respect to the unnormalized probability density function

$$p(R,S_1,S_2) = \Xi(R,S_1)\Xi(R,S_2)$$

by the expression

$$E_T = \frac{1}{M}\left\langle \sum_{m=1}^{M} (K+V)_m \right\rangle, \tag{9}$$

where M is the number of points in the space $\{R,S_1,S_2\}$ sampled from $p(R,S_1,S_2)$, K is the kinetic energy, and V is the potential energy:

$$V = \textstyle\sum_{i<j} V(r_{ij}). \tag{10}$$

The interparticle potential $V(r_{ij})$ used is the HFDHE2 of Aziz *et al.*[10] For the pseudopotentials the McMillan[1] form has been used:

$$u(r) = (b/r)^5, \quad v(s) = (b_{\mathrm{sh}}/s)^5. \tag{11}$$

Although much better pseudopotentials exist,[11] we wish here to investigate only the improvement that can be gained by adding shadow degrees of freedom. Therefore we choose to keep the form of $u(r)$ fixed and attempt to lower the variational energy by coupling in the shadow particles. Both pseudopotentials are fitted to a third-degree polynomial so that they go smoothly to zero at the sides of the simulation cube. Periodic boundary conditions are applied.

In these computations, the Metropolis random walk involves two types of moves: one for the real particles and another for the shadow particles. Consider first a move of a real particle j. A new coordinate $\mathbf{r}_j'$ is chosen with uniform probability in a cube of side Δ centered at $\mathbf{r}_j$. This move is accepted with probability q given by[12]

$$q = \min\{1, p(R',S_1,S_2)/p(R,S_1,S_2)\}, \tag{12}$$

where R' contains the new coordinate value. The ratio of the density probability functions can be written explicitly as

$$\begin{aligned} p(R',S_1,S_2)/p(R,S_1,S_2) = \exp\{ & -\textstyle\sum_{i\neq j}[u(|\mathbf{r}_j' - \mathbf{r}_i|) - u(|\mathbf{r}_j - \mathbf{r}_i|)] \\ & - C[(\mathbf{r}_j' - \mathbf{s}_{1j})^2 - (\mathbf{r}_j - \mathbf{s}_{1j})^2 + (\mathbf{r}_j' - \mathbf{s}_{2j})^2 - (\mathbf{r}_j - \mathbf{s}_{2j})^2]\}. \end{aligned} \tag{13}$$

An attempt to move the next real particle is then made in the same way. In our program, we cycle through all real particles $\{\mathbf{r}_1, \mathbf{r}_2, \ldots, \mathbf{r}_N\}$ before any shadow moves.

The same procedure is used for the shadow particles except with a cube of side Δ_{sh}. In this case, if an attempt to move particle s_{1j} is made, the probability ratio reads

$$p(R,S_1',S_2)/p(R,S_1,S_2) = \exp\{-\textstyle\sum_{i\neq j}[v(|\mathbf{s}_{1j}' - \mathbf{s}_{1i}|) - v(|\mathbf{s}_{1j} - \mathbf{s}_{1i}|)] - C[(\mathbf{r}_j - \mathbf{s}_{1j}')^2 - (\mathbf{r}_j - \mathbf{s}_{1j})^2]\}. \tag{14}$$

By S_1' we mean the set of shadow variables $\{\mathbf{s}_{11}, \ldots, \mathbf{s}_{1j}', \ldots, \mathbf{s}_{1N}\}$. After we attempt to move all the shadow particles of set S_1, the same is done for those in set S_2. The parameters Δ and Δ_{sh} were adjusted so that the acceptance was near 50%.

We have computed the energy per particle and the Lindemann ratio (rms deviation about a lattice site divided by the nearest-neighbor distance) in the solid phase of ^{4}He for extensive sets of the variational parameters. Starting from an fcc lattice, our best result for the energy together with the Lindemann ratio are shown in Table I. The Lindemann ratios were computed with respect to the starting lattice shifted by the amount that the real particles' center of mass had diffused. Long runs were performed to insure that the crystal remained stable. For sake of comparison, we also made runs using a wave function of the Nosanow-Jastrow form. These

TABLE I. Variational results for the solid phase obtained with the shadow wave function and with a wave function of the Jastrow form localized with a Gaussian at the density $\rho\sigma^3 = 0.55$. The energies are given in kelvins per particle, and the unit of length is $\sigma = 2.556$ Å.

		Lindemann ratio		Parameters		
	E_T	Real	Shadow	b	b_{sh}	C
Shadow	-3.52 ± 0.04	0.23	0.16	1.10	1.68	5.7
JG	-3.36 ± 0.02	0.22	···	1.10	···	4.8

results are displayed in Table I as well.

As can be seen in Table I, the shadow wave function has an energy lower by several standard deviations than the results that one can get from a wave function of the localized Jastrow type. As expected, the Lindemann ratios of the real particles are in good agreement for both wave functions. For the shadow particles, this ratio is comparable with those obtained at melting for a classical Lennard-Jones systems.[13] As with most computational simulations of this kind, the use of periodic boundary conditions in a particular box predisposes the system —here both shadow and real particles—toward a particular lattice. The use of shadow particles does not avoid this difficulty.

The results obtained with the shadow wave function for the ^{4}He liquid phase are shown in Table II, along with those determined from a wave function of the Jastrow form. Once again the shadow wave function gives a lower energy. We want to stress that the same functional form of the wave function was used in both the solid and the fluid phases; the only difference was in the choice of the parameters b, b_{sh}, and C. Although both phases were started from a perfect fcc crystal, when parameters are chosen to give a liquid phase, both the real and shadow particles rapidly reach equilibrium as liquids. The pair distribution functions reflect this fact. One can follow the system from the liquid phase to the solid by simply using the shadow wave function and appropriate parameters as functions of density.

It has been demonstrated that the new class of wave functions used in this work yields lower energies than those that use Jastrow and Nosanow-Jastrow variational wave functions with the same simple forms of the pseudopotential. The translational invariance, symmetry under particle exchange, and the physical picture that can be drawn from the shadow particles will certainty enable one to study a wider range of properties than those previously examined in the solid phase. We are actively pursuing investigations based on this work. Our previous work on quantum crystals using Nosanow-Jastrow importance functions left open whether certain results such as the one-body distribution were influenced to some degree by the Gaussian localization factors. Using these factors, it would, of course, be impossible for us to calculate a possible condensate in the crystal. Finally, in our current work on two-dimensional helium crystals, it has become clear that the effects of symmetry are much stronger than in three dimensions.[14] A quantitative theory of melting in two dimensions can almost surely not be carried out with Nosanow-Jastrow importance functions. We are confident that such calculations will be reliable with shadow wave functions.

TABLE II. Variational results determined for ^{4}He liquid at the density $\rho\sigma^3 = 0.365$. Energies are in kelvins per particle and lengths in σ.

			Parameters	
	E_T	b	b_{sh}	C
Shadow	-6.03 ± 0.04	1.13	1.40	4
Jastrow	-5.72 ± 0.02	1.20	···	···

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