Ground State of Solid He³†*

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A ground-state wave function for solid He³ in the body-centered cubic phase is calculated in the form of a product of single-particle orbitals and pair correlations. The correlation part is an eigenfunction of the Pluvinage Hamiltonian with each pair in a state of zero energy in a frame in which their center of mass is at rest. Assuming that exchange effects are small, we obtain an approximate single-particle probability function from this wave function. The many-body energy is obtained from this single-particle probability function from basic principles by a plausibility argument, and leads to a pressure–volume relation that is in good agreement with observation. Exchange effects arise from the original wave function, when suitably antisymmetrized. This predicts an exchange energy of about 0.005°K near the melting curve, in agreement with a recent experiment of Adams, Meyer, and Fairbank; this exchange energy favors antiferromagnetic alignment.

I. INTRODUCTION

THE analytic treatment of the dynamics of the atoms of the isotopes of helium in the liquid or solid phase is a problem which must be attacked from the point of view of quantum mechanics. Other liquid and solid systems can be analyzed using classical considerations to describe the basic dynamics of the interacting particles, with application of quantum theory to describe deviations from classical effects. The calculation of the Debye specific heat is a case in point.

London[1] applied the name "quantum liquid" to helium. Helium likewise forms a quantum solid. We can describe helium quantum mechanically by using the many-body Hamiltonian,

$$H = \sum_i T_i + \tfrac{1}{2} \sum_{ij}{}' V_{ij}(r_{ij}) + \sum_i V_i(\mathbf{r}_i). \qquad (1)$$

Here $T_i \equiv -(\hbar^2/2m)\nabla_i^2$. Primes on the summation sign indicate that all the indices appearing in each member of the sum are different.

We take $V_i(\mathbf{r}_i)$ to be a constant and we use the two-parameter Lennard-Jones potential for the interparticle potential,

$$V_{ij}(r_{ij}) = 4\epsilon[(\sigma/r_{ij})^{12} - (\sigma/r_{ij})^6]. \qquad (2)$$

For He³ and He⁴ we assume $\epsilon = 10.22°K$, $\sigma = 2.556$ Å. Using dimensionless quantities $x_i/\sigma = u_i$ and $r_{ij}/\sigma = \rho_{ij}$, and expressing ∇, V_i, and ψ in these variables, we have the Schrödinger equation

$$-\sum_i \lambda^2 \nabla_{i,u}^2 \psi_u + \tfrac{1}{2}\sum_{ij}{}' 4[\rho_{ij}^{-12} - \rho_{ij}^{-6}]\psi_u = (E/\epsilon)\psi_u, \qquad (3)$$

$$\lambda^2 \equiv \hbar^2/(2m\sigma^2\epsilon). \qquad (4)$$

For He³, $\lambda = 0.347$, and for He⁴, $\lambda = 0.302$.

In the case of normal solids and liquids the term in λ^2 (the zero-point energy) is vanishingly small compared to the term in ρ_{ij}. Equation (3) then reduces to

$$\tfrac{1}{2}\sum_{ij}{}' 4[\rho_{ij}^{-12} - \rho_{ij}^{-6}]\psi_u = (E/\epsilon)\psi_u. \qquad (5)$$

In Eq. (5) the quantum aspects of ψ_u do not affect the result, and we have

$$\tfrac{1}{2}\sum_j{}' 4\epsilon[\rho_{ij}^{-12} - \rho_{ij}^{-6}] = E. \qquad (6)$$

Equation (6) is the basic formula for analysis of most solids. For example, the cohesive energy and lattice spacing can be obtained from (6), and the theory of quantized sound fields is based on Eq. (6) and Newton's second law.

For helium, however, λ^2 does not vanish, a quantum-mechanical treatment of zero-point kinetic energy is called for, and (6) does not hold. In principle, a solution ψ_u of (3) might exist, containing λ as a variable parameter, describing all quantum systems conforming to (3). This general solution has not been found, except as a series expansion good for small λ^2 (expressing quantum-mechanical corrections to classical quantities). Such expansions converge slowly for condensed helium.

In addition to introducing the complication of including zero-point energy in the wave equation on an equal footing with potential energy, the zero-point energy results in an expansion of the system. An important consequence is the fact that at absolute zero, He³ requires over 30 atm of pressure for freezing. Further, the interparticle potential at equilibrium has marked anharmonicity, to such an extent that the usual perturbation methods fail. Hooton[2] has considered nearest neighbor interactions of He⁴ in a consistent way, but has not written a wave function for the ground state.

Still another severe complication lies in the strong interaction described by (2). The expectation value of the potential energy is infinite for a system described by single-particle orbitals, because these simple orbitals

[1] F. London, *Superfluids* (John Wiley & Sons, Inc., New York, 1954), Vol. II.

[2] D. J. Hooton, Phil. Mag. 46, 422 (1955); Phil. Mag. 46, 433 (1955).

are incapable of describing the particle correlations which must exist in strongly interacting systems. Solutions of (3) which overcome the singularity in the potential energy have been obtained by Lee *et al.*[3] and by Jastrow.[4] These theories are valid for dilute gases where $(\rho_n \sigma^3)^{\frac{1}{2}} \ll 1$ ($\rho_n =$ number density). Brueckner[5] has solved (3) in a form suitable for describing dense systems without intrinsic spatial ordering. Since our system is dense and must also show the lattice order of the solid, we cannot use these theories. Other investigators have studied solid helium using an anharmonic oscillator theory, but their calculations do not provide a ground-state wave function useful for considering the statistics of the particles.

Bernardes and Primakoff[6] have presented a theory which provides a ground-state description. Their wave function for solid He^3 is obtained by assuming certain correspondences between solid He^3 and He^4, and assigning values to parameters such that their wave function gives the observed cohesive energy and root-mean-square deviation of atoms from their lattice sites for He^4. They then apply these parameters to He^3. They assume a face-centered cubic lattice, whereas the observed lattice structure is body-centered cubic.[7] They employ a single-parameter correlation function of the form $\exp(\beta r^{-10})$ as a cutoff on the potential to circumvent the problem of the singularity. The function employs a variable parameter, chosen in their method to yield the observed behavior of He^4.

We can write a list of requirements which must all be satisfied simultaneously by our theory. The existing theories, some of which we have just reviewed, all fail in one or more particulars. The theory must:

1. Yield a ground-state wave function which displays the symmetry required by the statistics obeyed by the particles (Fermi-Dirac statistics for He^3, Bose-Einstein statistics for He^4),
2. Include correlations between strongly interacting particles,
3. Be valid in the region of high density where $(\rho_n \sigma^3)^{\frac{1}{2}} \approx 1$,
4. Display the order of the crystal lattice,
5. Include the potential energy and kinetic energy on an equal basis in the Schrödinger equation,
6. Be valid for a nonharmonic potential energy, and
7. Consistently exclude empirically observed inputs, in favor of first principles.

We deviate from this last requirement in that we initially assume a definite lattice structure.

In this work we assume a many-body wave function which includes a functional dependence on the separation of all particle pairs, and which therefore takes account of particle correlations. We obtain a simple single-particle picture of solid He^3 which is based on an approximate solution of the Schrödinger equation. Using the single-particle description we obtain expressions for the cohesive energy, pressure, and exchange energy which agree qualitatively with experiment.

In Sec. II we list our basic assumptions. Most of these appear explicitly in our final result and are thus subject to a self-consistency test. We cannot so test the assumption concerning the particle interaction, which we take to be the Lennard-Jones 6–12 potential, and it remains the fundamental physical assumption of the analysis. In Sec. III we reduce an N-body density matrix to a single-body density matrix $\gamma(\mathbf{r})$ adequate for describing properties of the solid which do not depend on particle exchange. In Sec. IV we obtain a functional form of ψ which approximately conforms to the many-body Schrödinger equation.

In Sec. V we show how this wave function can be used to get a quantitative description of the single-particle probability density of solid He^3 obtained formally in Sec. III. The density is of the form $\gamma(\mathbf{r}_i) = (\text{const}) \sum_j \exp[-\delta^2 (\mathbf{R}_j - \mathbf{r}_i)^2]$, where $\mathbf{R}_j$ is the position of lattice site j, and δ^2 is a function of range and strength of the particle interaction, particle mass, type of lattice, and lattice constant. In Sec. VI we compare theory with experiment studying exchange energy, pressure, and activation energy of diffusion, and find good agreement. Section VII contains a summary of the results.

II. BASIC ASSUMPTIONS

In our description of the ground state of He^3, we use the following assumptions:

1. There exists a single-particle projection of the N-body probability density; that is, a microscopic examination would show a solid with the constituent particles found predominantly near lattice sites.
3. The particles interact with the Lennard-Jones 6–12 (LJ) potential described by Eq. (2).
3. A two-particle separation of the wave function, having correlations given as a function of interparticle separation, contains sufficient information about the state of the system.
4. Solid He^3 exists in the body-centered cubic lattice form, in accordance with experimental observation.
5. (a) Exchange effects involving more than two particles are negligible. (b) Imposing the symmetry requirements of the Pauli principle on the wave functions makes a negligible difference in the single-particle probability density, and gives a small correction to the single-particle energy.

We shall arrive at self-consistency checks on some of these assumptions. The result shows a necessary conformance to assumptions 1 and 5. We shall see that

[3] T. D. Lee, K. Huang, and C. N. Yang, Phys. Rev. **106**, 1135 (1957).
[4] R. Jastrow, Phys. Rev. **98**, 1479 (1955).
[5] H. A. Bethe, Phys. Rev. **103**, 1353 (1956).
[6] N. Bernardes and H. Primakoff, Phys. Rev. **119**, 968 (1960).
[7] A. F. Schuch, E. R. Grilley, and R. L. Mills, Phys. Rev. **110**, 775 (1958).

assumption 3 is reasonably correct, because correction terms, which would indicate an error here, are small. The body-centered cubic lattice is energetically preferred to face-centered cubic, so that assumption 4 is partially substantiated. Assumption 2, the interparticle potential, is then the only unsupported assumption.

Hirschfelder *et al.*[8] give a good description of the interparticle potentials between rare-gas atoms. A phenomenological form of the potential which gives good correspondence with the observed behavior of the gas phase near 1°K is the so-called Buckingham-Hamilton-Massey (BHM) potential.[9] The BHM potential has a form closely following the form of (2) for $\epsilon = 10.22°K$, $\sigma = 2.556$ Å, but has a complicated analytical form. The principal difference between the LJ and BHM forms is in the steepness of the repulsive core in the region of very strong repulsion. We shall see that this repulsive core has the principal effect of excluding states having small separation, and either form is equally effective in this regard.

There is a small three-particle effect, from an induced triple-dipole interaction,[10] which can easily be shown to be negligible up to densities far greater than that studied here.

III. THE SINGLE-PARTICLE DENSITY

In Sec. I we stated the assumption that a two-particle separation of the wave function would serve to describe our system. The Hamiltonian [Eq. (1)] contains the variables r_i and r_{ij}. A wave function ψ expressed in these variables would be capable, in a basic way, of permitting the operations in H to be carried out on ψ. Such a separation of the wave function is

$$\psi = \sum_P P \prod_i \phi_i(\mathbf{r}_i)\eta_i(\zeta_i)\prod_{i>j}\chi_{ij}(r_{ij}), \qquad (7a)$$

$$r_{ij} = [(x_i-x_j)^2 + (y_i-y_j)^2 + (z_i-z_j)^2]^{\frac{1}{2}}. \qquad (7b)$$

Here $\sum_P P$ is the permutation operator for Fermi statistics in the case of He³, and for Bose statistics for He⁴. The spin state $\eta_i(\zeta_i)$ describes particle i with spin ζ_i. The function χ_{ij} is independent of the identity of i and j, is a function of the distance between members of a pair, and is the same function for all pairs. We shall regard the r_{ij} as variables independent of $\mathbf{r}_i$ and $\mathbf{r}_j$, but to prevent difficulties with redundant variables, we must also impose the $N(N-1)/2$ restraints (7b) on the r_{ij}.

Pluvinage[11] and Jastrow[4] have used Eq. (7) for the separation of the wave function. We use it to write the N-body density matrix and then, by integrating over the coordinates of all but one particle, obtain a single-particle density expressed as a function of the position of that single particle. We assume that there exists such

a single-particle description of the solid, in which the particles are most likely to be found near lattice sites, and look for a result consistent with this assumption.

Using the formalism of Löwdin,[12] we write the N-body density matrix,

$$\Gamma^{(N)} = \psi^*\psi,$$

$$\Gamma^{(N)} = (\sum_P P \prod_i \phi_i(\mathbf{x}_i')\prod_{j>k}\chi(r_{jk}')^*)$$
$$\times(\sum_P P \prod_i \phi_i(\mathbf{x}_i)\prod_{j>k}\chi(r_{jk})). \qquad (8)$$

The primes in (8) permit us to use differential and spinor operators in $\Gamma^{(N)}$, which act only on the unprimed coordinates.

Obviously, we can obtain the single-particle density $\gamma(\mathbf{x}_i)$ from $\Gamma^{(N)}$ by the formal expression,

$$\gamma(\mathbf{x}_i) = (\text{const})\int \Gamma^{(N)} \prod_j d\mathbf{x}_j, \quad (j \neq i). \qquad (9)$$

In the usual convention, the normalizing constant is N. Putting (8) into (9), we have

$$\gamma(1) = (\text{const}) \sum_P P_S \phi_1^*(1)\phi_1(1)$$

$$\times \int \left\{ [\sum_P P\phi_2^*(2)\cdots\phi_N^*(N)] \right.$$

$$\times [\sum_P P\phi_2(2)\cdots\phi_N(N)]$$

$$\times [\chi^2(r_{23})\chi^2(r_{24})\cdots\chi^2(r_{N-1N})] \left. \right\}$$

$$\times \chi^2(r_{12})d\mathbf{x}_2 \, \chi^2(r_{13})d\mathbf{x}_3 \cdots \chi^2(r_{1N})d\mathbf{x}_N. \qquad (10)$$

The symbol $\sum_P P_S$ permutes the coordinate indices in the symmetric sense, as follows:

$$P_S\Gamma(1'2'3'\cdots|123\cdots)$$
$$\equiv \Gamma(2'1'3'\cdots|213\cdots) = \Gamma(1'2'3'\cdots|123\cdots),$$

regardless of the symmetry property imposed on ψ. In writing (10) we have neglected overlap terms like

$$\phi_i(1)\phi_j(1)\int \{[\sum_P P\phi_1^*(i)\phi_2^*(2)\cdots\phi_N^*(N)]$$

$$\times[\sum_P P\phi_1(j)\phi_2(2)\cdots\phi_N(N)][\chi^2(r_{23})\cdots\chi^2(r_{N-1N})]\}$$

$$\times\chi^2(r_{12})d\mathbf{x}_2\cdots\chi^2(r_{1N})d\mathbf{x}_N, \quad (i \neq j).$$

In calculating exchange energy in Sec. VI, we shall see that when we include two-particle overlap terms, the change in the single-particle probability density is small in magnitude, and only enters into exchange effects. We expect that three-particle overlap will be much smaller than two-particle overlap because it is essentially the product of two-particle overlaps. Further, for He³, the Pauli principle will work to exclude three-particle encounters.

[8] J. O. Hirschfelder, C. F. Curtiss, and R. B. Bird, *Molecular Theory of Gases and Liquids* (John Wiley & Sons, Inc., New York, 1954).

[9] R. A. Buckingham, J. Hamilton, and H. S. W. Massey, Proc. Roy. Soc. (London) **A179**, 103 (1941).

[10] P. Rosen, J. Chem. Phys. **21**, 1007 (1953).

[11] P. Pluvinage, Ann. phys. **5**, 145 (1950).

[12] P. O. Löwdin, Phys. Rev. **97**, 1474 (1955).

In (10), the term in curly brackets depends on the coordinates of the $(N-1)$ particles which do not include particle 1. This term is the density matrix (in the two-particle approximation) for $(N-1)$ particles, if we permit neglect of overlap of particle i. We are to use this density matrix to locate all the particles $(2, 3, \cdots i, \cdots N)$ in performing the integral in (10). We need only locate all these particles in the single-particle approximation. We can do this by using the expression

$$(\text{const})\pi_k\gamma(\mathbf{x}_k), \quad (k\neq 1) \tag{11}$$

for the density matrix in curly brackets.

We can then write

$$\gamma(1) = (\text{const}) \sum_i |\phi_i(1)|^2 \int \gamma(2)\gamma(3)\cdots\gamma(N)$$
$$\times \chi^2(r_{12})d\mathbf{x}_2\cdots\chi^2(r_{1N})d\mathbf{x}_N$$

still in the single-particle approximation. Then

$$\gamma(1) = (\text{const}) \sum_i |\phi_i(1)|^2 \prod_k \int \gamma(k)\chi^2(r_{1k})d\mathbf{x}_k. \tag{12}$$

Equation (12) is the fundamental equation of this approach to the ground state of He^3.

To get (12) we have taken $\Gamma^{(N)}$ to be

$$|\sum_P P \prod_i \phi_i(\mathbf{x}_i) \prod_{i>j} \chi(r_{ij})|^2$$

on the one hand, and $\prod_i \gamma(\mathbf{x}_i)$ on the other hand. The first form contains superfluous information. However, Eq. (12), in the χ^2 terms, contains just the information needed to give the correlation of particle 1 with all the other particles (neglecting spin). Note that (12) only uses the minimal second description for all the pairs not including particle 1, and it uses the first, more informative description for all pairs including particle 1.

To use (12) in calculations we must use ϕ's and χ's which are descriptive of the physical properties of the system.

IV. THE PLUVINAGE METHOD APPLIED TO HELIUM ATOMS

Pluvinage[11] introduced a method of finding a function in the form of (7) which approximately satisfies the Schrödinger equation for the electrons of He^4. The method has been applied by Walsh and Borowitz[13] to some multi-electron systems. Their zero-order energy results fall within 2 or 3% of experimental values. Many-parameter variational functions give only slightly better results, within about 1% of experiment.

Following Pluvinage, we treat the r_{ij} in (7a), as independent variables, on the same footing as x_i, y_i, or z_i. However, we also apply the constraints (7b) to prevent introducing redundant variables.

We seek the true wave function $f_0(x_1,y_1,z_1,x_2,y_2,\cdots z_N)$, a function of the positions of all the particles. Using

[13] P. Walsh and S. Borowitz, Phys. Rev. 115, 1206 (1959); Phys. Rev. 119, 1274 (1960).

a set of intermediate variables $r_{ij}=r_{ij}(x_i,y_i,z_i,x_j,y_j,z_j)$ we can write a function $f_1(x_1,y_1,z_1,x_2,\cdots z_n,r_{12},r_{13}, \cdots r_{23},r_{24}\cdots r_{N-1N})$, and require that $f_1=f_0$ everywhere. Then by the usual rules of differentiation, we have

$$\frac{\partial f_0}{\partial x_i} = \frac{\partial f_1}{\partial x_i} + \sum_j \frac{\partial f_1}{\partial r_{ij}}\frac{\partial r_{ij}}{\partial x_i}. \tag{13}$$

If we can obtain the function f_1, then we also have f_0, the true wave function.

The true wave function is determined by the Schrödinger equation $Hf_0=Hf_0$, where

$$H \equiv \sum_i -(\hbar^2/2m)\nabla_i^2 + \sum_{ij}' \tfrac{1}{2}V_{ij}(r_{ij}). \tag{14}$$

Here

$$\nabla_i^2 \equiv \partial^2/\partial x_i^2 + \partial^2/\partial y_i^2 + \partial^2/\partial z_i^2.$$

Since the operator H includes the variable r_{ij}, we should investigate the possibility of performing our calculations by using the function f_1 and relation (13). We do this by rewriting the Laplacian in (14), applying (13) twice in succession, with the result

$$\sum_i \nabla_i^2 \rightarrow \sum_i \nabla_i^2 + \sum_{ij}' \left[\frac{\partial^2}{\partial r_{ij}^2} + \frac{2}{r_{ij}}\frac{\partial}{\partial r_{ij}}\right]$$
$$+ \sum_{ij}' \left[\frac{\mathbf{s}_{ij}\cdot\mathbf{\nabla}_{s,ij}}{r_i}\frac{\partial}{\partial r_i}\right] + \sum_{ijk}' \left[\frac{\mathbf{s}_{ij}\cdot\mathbf{s}_{ik}}{r_{ij}r_{ik}}\frac{\partial}{\partial r_{ik}}\frac{\partial}{\partial r_{ij}}\right]. \tag{15}$$

Here, primes indicate that no two indices are equal in a sum. The vector $\mathbf{s}_{ij}$ is the displacement between particles i and j, and $\mathbf{\nabla}_{s,ij} \equiv (\partial/\partial s_{x,ij})\mathbf{i} + (\partial/\partial s_{y,ij})\mathbf{j} + (\partial/\partial s_{z,ij})\mathbf{k}$, $s_{x,ij}=x_j-x_i$. Note that $\partial/\partial r_{ij}$ operates only on r_{ij}, and that $\partial/\partial x_i$ and $\mathbf{\nabla}_{s,ij}$ operate only on x_i, y_i, z_i, etc.

We write the Schrödinger equation for the wave function f_1, in the form of (7):

$$Hf_1 = Ef_1. \tag{16}$$

Here, since we have the parameters r_{ij}, in f_1, we use the transformed Laplacian in H.

Let us divide H into two parts, $H=H_0+H'$, where

$$H_0 \equiv \sum_i \left(-\frac{\hbar^2}{2m}\right)\nabla_i^2 + \sum_{ij}' \left(-\frac{\hbar^2}{2m}\right)\left(\frac{\partial^2}{\partial r_{ij}^2} + \frac{2}{r_{ij}}\frac{\partial}{\partial r_{ij}}\right)$$
$$+ \sum_{ij}' V_{ij}(r_{ij}), \tag{17}$$

$$H' \equiv \left(-\frac{\hbar^2}{2m}\right)\left[\sum_{ij}' \frac{\mathbf{s}_{ij}\cdot\mathbf{\nabla}_{s,ij}}{r_{ij}}\frac{\partial}{\partial r_{ij}}\right.$$
$$\left. + \sum_{ijk}' \frac{\mathbf{s}_{ij}\cdot\mathbf{s}_{ik}}{r_{ij}r_{ik}}\frac{\partial}{\partial r_{ik}}\frac{\partial}{\partial r_{ij}}\right]. \tag{18}$$

The function ψ of Eq. (7a) is a simple function of the type f_1. If we use ψ in (16), the resulting simplified

equation is not separable because H' contains mixed derivatives. However, if we can treat H' as a small perturbation, we may approximate ψ closely by solving the separable equation

$$H_0\psi = E_0\psi. \tag{19}$$

In using (19), we must keep in mind the role of the parameters r_{ij}, and follow these rules:

(a) First, solve (19) for ψ.

(b) In applying H_0 and H', let $\partial/\partial x_i$ operate on x_i alone, and let $\partial/\partial r_{ij}$ operate on r_{ij} only.

(c) After differentiating [step (b)], introduce the constraint $r_{ij} = (\mathbf{s}_{ij}\cdot\mathbf{s}_{ij})^{\frac{1}{2}}$.

(d) After performing the derivative and constraint operations, evaluate matrix elements by integration.

In what follows, we use the definition

$$T_{ij} \equiv -\left(\frac{\hbar^2}{2m}\right)\left[\frac{\partial^2}{\partial r_{ij}^2} + \frac{2}{r_{ij}}\frac{\partial}{\partial r_{ij}}\right].$$

In (19), $H_0\psi$ contains terms depending on r_{ij}:

$$\sum_P \sum_{ij}{}' [T_{ij}+\tfrac{1}{2}V_{ij}(r_{ij})]\prod_{i>j}\chi(r_{ij})\prod_k \phi_k(\mathbf{x}_k).$$

These terms contain the singularities of the interparticle potentials. We can easily make each of these terms vanish by requiring that $\chi(r_{ij})$ satisfy the equation

$$[T_{ij}+\tfrac{1}{2}V_{ij}]\chi(r_{ij}) = 0. \tag{20}$$

Equation (20), with the right-hand side taken to be $E_{ij}\chi(r_{ij})$, would be the Schrödinger equation describing a pair of interacting particles in an s state of energy E_{ij}. If we were to take E_{ij} to be a positive quantity, there would be oscillations in χ at large distances, and attendant difficulties with interference of the correlations of different pairs. The choice $E_{ij}=0$ places each pair in the lowest state available to them (there being no bound state), and leads to the lowest energy for a system satisfying (19) (neglecting interactions of three and more particles).

Writing (20) in detail, using the potential in (2), we have

$$\left\{-\frac{\hbar^2}{4m\epsilon}\left[\frac{1}{r^2}\frac{\partial}{\partial r}r^2\frac{\partial}{\partial r}\right]+\left[\left(\frac{\sigma}{r}\right)^{12}-\left(\frac{\sigma}{r}\right)^{6}\right]\right\}\chi(r) = 0. \tag{21}$$

Our particles are most likely to be in regions where $r>\sigma$, so we seek a series solution of χ which converges in that region. Defining $q\equiv\sigma/r$, $B\equiv 4m\sigma^2\epsilon/\hbar^2$, (21) becomes

$$d^2\chi/dq^2 = B[q^8-q^2]\chi. \tag{22}$$

For He^3, $B=16.60$; for He^4, $B=22.2$. There are two independent solutions of (22) which converge in the region $r>\sigma$.

$$\chi = C_0F_0(q)+C_1qF_1(q), \quad (q<1). \tag{23}$$

Here

$$F_0(q) = 1 - B(4\times3)^{-1}q^4 + B^2(8\times7\times4\times3)^{-1}q^8$$
$$+ B(10\times9)^{-1}q^{10} - B^3(12\times11\times8\times7\times4\times3)q^{12}$$
$$+\cdots+C_nq^n+\cdots,$$

$$F_1(q) = 1 - B(5\times4)^{-1}q^4 + B^2(9\times8\times5\times4)^{-1}q^8$$
$$+ B(11\times10)^{-1}q^{10} - B^3(13\times12\times9\times8\times5\times4)q^{12}$$
$$+\cdots+C_nq^n+\cdots,$$

$$C_n = \frac{B}{n(n-1)}(C_{n-10}-C_{n-4}), \quad n=14, 16, 18\cdots.$$

For $r=\infty$, $q=0$, correlation effects have no effect on the wave function and χ is unity; therefore $C_0=1$. The term $C_1qF_1(q)$ gives an outgoing flux at large distances, an unsatisfactory characteristic which cannot be permitted in ψ. We thus choose $C_1=0$.

In Fig. 1, we show $\chi(r)$, $\chi^2(r)$ and $\chi\chi'/r$ for He^3 atoms, obtained from (23). Jastrow[4] and others find that of several used, the variational function $\chi_\gamma = 1-(r_0/r)$ $\times\exp[-\gamma(r-r_0)]$ gives the lowest energy in liquid He^4. If we take $\gamma=0.696$ Å and $r_0=2.52$ Å, our χ and that of Jastrow are indistinguishable out to $r=5$ Å, where his curve rises slightly above ours. The similarity in these functions is not surprising, since χ_γ is the ground state of a Yukawa-type potential, which can be fitted very closely to our Lennard-Jones potential.

For $r<\sigma$, the series of (23) does not converge, but inspection of Fig. 1, together with the observation that relative distances between helium atoms less than 2.5 Å are most unlikely, justifies assigning a vanishingly small value to $\chi(r)$ for values $r<\sigma$.

V. APPROXIMATE SOLUTION FOR THE SINGLE-PARTICLE DENSITY

According to assumption 1 of Sec. II, we should seek an approximate form for the single-particle probability density peaked near lattice sites. A simple function of this type is

$$\gamma(\mathbf{r}_i) = (\pi/\delta^2)^{\frac{3}{2}}\sum_{j}^{N} \exp[-\delta^2(\mathbf{R}_j-\mathbf{r}_i)^2]. \tag{24}$$

Note that $\int\gamma(\mathbf{r}_i)d^3(\mathbf{x}_i)=N$, and this function has normalization according to Löwdin's scheme.

Let us define

$$\gamma_j(\mathbf{r}_i) \equiv (\pi/\delta^2)^{\frac{3}{2}} \exp[-\delta^2(\mathbf{R}_j-\mathbf{r}_i)^2]; \tag{25}$$

then $\gamma(\mathbf{r}_i) = \sum_j \gamma_j(\mathbf{r}_i)$.

If $|\mathbf{R}_j-\mathbf{r}_i|>a$, the function $\gamma_j(\mathbf{r}_i)$ is without meaning (here a is the lattice constant or distance between nearest neighbors). When a particle is equally distant from two lattice sites, we must use a two-particle density, if three sites must be included, a three-particle density matrix must be used and so on. Hence, in the

single-particle approximation we can say $\gamma_j(\mathbf{r}_i)$ vanishes for $|\mathbf{R}_j - \mathbf{r}_i| \gtrsim a$.

Our purpose is to use (24) in (12), and obtain $\gamma(\mathbf{r}_i)$ by calculating δ^2. Since we will find that $\delta^2 \gg 1/a^2$, all the terms of $\sum_j \gamma_j(\mathbf{r}_i)$ are negligible except the term with the smallest value of $|\mathbf{R}_j - \mathbf{r}_i|$. (When we consider exchange, we will limit our concern to the two largest such terms, with the smallest and next smallest values of $|\mathbf{R}_j - \mathbf{r}_i|$.) Hence we can get the functional form of $\gamma(1)$ by taking $\gamma(1) = \gamma_1(1)$ in Eq. (12). Since $\chi(r_{ij})$ vanishes for small values of r_{ij}, only one particle may be near each lattice site, and the ground state has all lattice sites occupied. Therefore, in the product $\pi_k \gamma(k)$ of Eq. (12), each atom appears near a particular lattice site, for each number of the product.

We may therefore write (12) in the form

$$\gamma_i(i) = (\text{const}) w(i) \pi_k f_k(u_{ik}). \tag{26}$$

Here

$$w(\mathbf{r}_i) \equiv \sum_j |\phi_j(\mathbf{r}_i)|^2, \tag{27}$$

and,

$$f_k(u_{ik}) \equiv \int \gamma_k(k) \chi^2(r_{ik}) d\mathbf{x}_k, \tag{28}$$

where u_{ik} is the distance from the field point at $\mathbf{r}_i$ to the lattice site at $\mathbf{R}_k$.

Since we will learn that $\chi^2(r_{ik})$ is slowly varying compared to the peaked function $\gamma_k(k)$, where $\gamma_k(k)$ has appreciable value, we take $\gamma_k(k)$ in (28) as a Dirac δ function, as a first approximation. Then

$$f_k(u_{ik}) = \chi^2(u_{ik}) + O\left(\frac{\chi\chi'}{\delta^2 u}, \frac{\chi^2 \exp[-\delta^2(u-\sigma)^2]}{\delta u}\right). \tag{29}$$

Here we have shown the form of the lowest order correction terms to the δ-function approximation, obtained by expanding $\chi^2(r)$ about $r = u$. These correction terms are of higher order, and can be shown to have negligible effect on our results.

We now perform the product indicated in (26), and in that way build up $\gamma(1)$. We expand $f_k(u_{ik})$ in a Taylor series about $u_{ik} = R_\lambda$. R_λ is an arbitrary length; later we will take R_λ to be the distance from lattice point i to a shell of atoms equidistant from i. We then have

$$f_k(u) = f_k(R_\lambda) G_k$$
$$= f_k(R_\lambda) \exp[\ln G_k]. \tag{30}$$

Here,

$$G_k \equiv (1 + \Delta_k f'/f + \tfrac{1}{2}\Delta_k^2(f''/f) + \cdots),$$

$$\Delta_k \equiv (|\mathbf{u}_{ik}| - R_\lambda).$$

The quantity Δ_k is the difference between (a) the distance from particle i to the lattice point at k, and (b) the distance from lattice point i to lattice point k. Writing an expansion for $\ln G_k$ in terms of $(1 - G_k)$, performing the product as a sum of logarithms, and rewriting the terms involving second derivatives, we
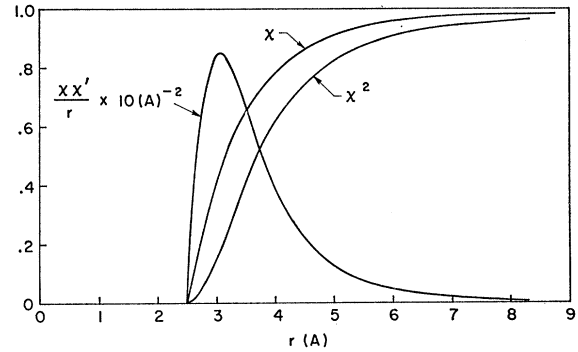

FIG. 1. Correlation function χ, correlation density χ^2, and $(\chi\chi'/r)$, plotted against particle separation r, in Å.

obtain

$$\prod_k f_k(u_{ik}) = \left[\prod_k f_k(R_\lambda)\right]$$

$$\times \exp\left\{\sum_k \left[\Delta_k \frac{f_k'(u)}{f_k(u)} + \frac{\Delta_k^2}{2} \frac{d}{du} \frac{f_k'(u)}{f_k(u)}\right]_{U=R_\lambda} + \cdots\right\}. \tag{31}$$

The redundant variables r_{ik} do not appear in (31) because in performing the product over k in (26) [or the sum over k in (31)], we have fully imposed the constraint $r_{ik} = (\mathbf{s}_{ik} \cdot \mathbf{s}_{ik})^{\frac{1}{2}}$.

We now perform the sum over k. It is convenient to perform the sum over all atoms at a distance R_λ from the lattice site i. In general,

$$\sum_k \Delta_k = \sum_k (|\mathbf{u}_{ik}| - R_{ik})$$
$$= \sum_k [(R_{ik}^2 + q_i^2 - 2q_i R_{ik} \cos\theta_{ik})^{\frac{1}{2}} - R_{ik}]. \tag{32}$$

Here, $R_{ik} \equiv |\mathbf{R}_i - \mathbf{R}_k|$, and we have introduced the quantity q_i, the distance from the particle of interest (particle i) to the lattice site i. The angle θ_{ik} is the angle subtended at lattice site i by the lines to particle i and lattice site k.

We expand the square root in (32), and assume that $\sum_k \cos\theta_{ik} = 0$ (correct for a Bravais lattice, e.g., body-centered cubic; correct in the spherically symmetric approximation for an hexagonal close-packed lattice.) We take $\sum_k \cos^2\theta_{ik} = \tfrac{1}{3}$, and assume that $(q_i^2/R_{ik}) \ll 1$. Then, we have

$$\sum_k \Delta_k = \sum_\lambda [n_\lambda q_i^2/3R_\lambda], \tag{33}$$

where there are n_λ atoms in the shell of atoms at distances R_λ from lattice site i. Similarly, we can obtain

$$\sum_k \Delta_k^2 = \sum_\lambda \tfrac{1}{3} n_\lambda q_i^2. \tag{34}$$

To obtain (34) we need not assume that $\sum_k \cos\theta_{ik} = 0$. Using (33) and (34) in (31), (26) becomes

$$\gamma_i(i) = (\text{const}) \left(\prod_\lambda [f(R_\lambda)]^{n_\lambda}\right) w(i)$$

$$\times \exp\left\{\sum_\lambda \frac{n_\lambda q_i^2}{3}\left[\left(\frac{1}{u} + \frac{1}{2}\frac{d}{du}\right)\frac{f'(u)}{f(u)}\right]_{U=R_\lambda}\right\}. \tag{35}$$

In (35), we have excluded terms of higher order than q^2.

The ϕ_i in $w(i)$ are occupied in order that the Pauli principle may be obeyed by ψ. They are therefore analogous to the Fermi sphere used in considering an electron gas. The ϕ_i must be $N/2$ in number if doubly occupied, must have the symmetry of the lattice, and hence cannot have a node at a lattice point. They must distinguish between any two particles so that their minimum wavelength is double the lattice constant. Such a set of waves for a simple-cubic lattice is

$$\phi_{ijk}(\mathbf{r}_p) = C_{ijk}\cos[(\pi x_p/n_i a) + \beta(n_i)]$$
$$\times\cos[(\pi y_p/n_j a) + \beta(n_j)]$$
$$\times\cos[(\pi z_p/n_k a) + \beta(n_k)]. \quad (36)$$

Here $n_i = 1, 2, 3, \cdots (N/2)^{\frac{1}{3}}$. The phases $\beta(n_m)$ are chosen to place maxima at lattice sites for even n, and maxima midway between lattice sites for odd n. If these states are all equally occupied, it can be shown that all the C_{ikj} are essentially equal if $\delta^2 a^2 \gg 1$. Then, although the ϕ_i are not a complete set, we find that

$$\sum_i |\phi_i(\mathbf{r}_i)|^2 \approx \exp(-\pi^4 q^2/8N^{\frac{2}{3}}a^2) \approx 1.$$

Hence $\sum_i |\phi_i(x_i)|^2$ contributes a term, insignificantly differing from unity, to the coefficient of q^2 in the argument of the exponential on the right side of (35). The term $\prod_\lambda [f_\lambda(R_\lambda)]^{n\lambda}$ is a constant dependent only on the average density. Hence we can take, after comparing Eqs. (35) and (25):

$$\delta^2 = -\sum_\lambda \tfrac{1}{3} n_\lambda g_\lambda, \quad (37)$$

$$g_\lambda \equiv \{[1/u + \tfrac{1}{2}(d/du)]f'/f\}_{R_\lambda}. \quad (38)$$

We obtain g_λ by putting (30) into (38). The result is

$$g_\lambda = -\frac{B\sigma^4}{R_\lambda^6}\left[1 + \frac{B\sigma^4}{9R_\lambda^4} - \frac{\sigma^6}{R_\lambda^6} + \frac{2B^2\sigma^8}{189R_\lambda^8}\right.$$
$$\left. - \frac{2}{27}\frac{B\sigma^{10}}{R_\lambda^{10}} + \frac{13}{14553}\frac{B^3\sigma^{12}}{R_\lambda^{12}} + \cdots\right]$$
$$- \frac{\exp(-\delta^2[R_\lambda - \sigma_0]^2)\delta^3\sigma_0(R_\lambda - \sigma_0)}{\pi^{\frac{1}{2}}\{1 + \phi(\delta[R_\lambda - \sigma_0])\}2R_\lambda}. \quad (39)$$

By $\phi(x)$ we indicate the error integral $\phi(\infty) = 1$. We have provided a correction term containing δ^2 which contributes about 2% to the final sum over λ, and it is relatively insensitive to changes in the lattice constant a. We henceforth drop it from g_λ.

We perform the sum in (37) by making use of the relation

$$\sum_j 1/R_{ij}{}^m = \sum_\lambda n_\lambda/R_\lambda{}^m = C_m/a^m, \quad (40)$$

where C_m is a coefficient depending upon the lattice structure of the $\mathbf{R}_j$. Hirschfelder et al.[9] give tabulations of such constants for many lattice types.

We get

$$\delta^2 = \frac{B\sigma^4}{3a^6}C_6\left[1 + \frac{BC_{10}\sigma^4}{9C_6 a^4} - \frac{C_{12}\sigma^6}{C_6 a^6} + \frac{2B^2 C_{14}\sigma^8}{189 C_6 a^8} + \cdots\right]. \quad (41)$$
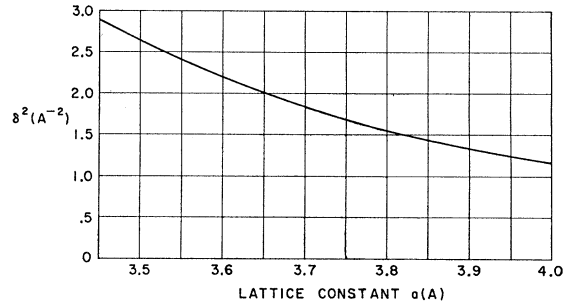

FIG. 2. The single-particle density parameter δ^2 vs lattice constant a in Å. The single-particle density of the solid at $\mathbf{r}_1$ is proportional to $\sum_j \exp[\delta^2(\mathbf{R}_j - \mathbf{r}_i)]$, where $\mathbf{R}_j$ is the position of lattice site j.

For He³, $B = 16.60$ and with the C_n for a body-centered cubic lattice, we have

$$\delta^2 = 10.4(\sigma/a)^6[1 + 1.44(\sigma/a)^4 - 0.745(\sigma/a)^6$$
$$+ 4.44(\sigma/a)^8 + \cdots], \quad (\delta^2 \text{ in Å}^{-2}). \quad (42)$$

Using (42) in (26) we express the probability density of the ground state of solid He³ in the single-particle approximation, where correlations of all pairs of atoms have been taken into account. We have assumed that the particle interaction is given by the Lennard-Jones potential, that the ground state satisfies a Schrödinger equation with a Pluvinage-type Hamiltonian, and that $\langle q^2\rangle/a^2 \ll 1$, or $(2a^2\delta^2/3) \gg 1$. For solid He³ $3.5 \lesssim a \lesssim 3.8$ Å; (42) converges rapidly in this range, and the condition $(2a^2\delta^2/3) \gg 1$ is satisfied.

In Fig. 2 we show Eq. (42), plotting δ^2 vs a.

VI. ENERGY DENSITY

To obtain the single-particle energy density we write the N-particle energy-density matrix, using the wave function of Eq. (7)

$$\langle E\rangle = \frac{1}{A}\int \sum_i \{T_i + \sum_j [T_{ij} + \tfrac{1}{2}V_{ij} + H_{ij}']\}$$
$$\times\sum_P P\sum_{P'} P'[\phi_1^*(1')\cdots\phi_N^*(N')\phi_1(1)\cdots\phi_N(N)]$$
$$\times\pi_{i>j}\chi(r_{ij}')\chi(r_{ij})d\mathbf{x}_i. \quad (43)$$

Here A is a normalization integral, and the operator $(T_{ij} + \tfrac{1}{2}V_{ij})$ makes no contribution because of Eq. (21), Then, neglecting exchange effects, we have for (43), noting that the sum over i contains N identical terms,

$$\langle E\rangle = \langle T_1 + \sum_j H_{1j}'\rangle N$$
$$= N/A \int d\mathbf{x}_1[T_1 + \sum_j H_{1j}'][\sum_i \phi_i^*(1)\phi_i(1)]$$
$$\times\{[\phi_1^*(i')\phi_1(i)]\sum_P P\sum_{P'} P'[\phi_2^*(2')\cdots\phi_N(N')$$
$$\times\phi_2(2)\cdots\phi_N(N)\chi^2(r_{23})\cdots\chi^2(r_{N-1N})]\}$$
$$\times\chi(r_{12}')(r_{12})d\mathbf{x}_2\cdots(r_{1N}')\chi(r_{1N})d\mathbf{x}_N. \quad xx \quad (44)$$

Again, as in Eq. (10), the curly bracket of (44) is the $(N-1)$-body density matrix, neglecting overlap with r_i and the spin of particle 1. Putting (11) into (44) and defining $\mathbf{E}_1 \equiv T_1 + \sum_j \langle H_{1j}' \rangle_{\text{av over } j}$, we have

$$\langle E \rangle = \frac{N}{A} \int d\mathbf{x}_1 \, \mathbf{E}_1 \sum_j \phi_j^*(1') \phi_j(1)$$
$$\times \prod_k \int \gamma(k) \chi(r_{1k}') \chi(r_{1k}) d(\mathbf{x}_k). \quad (45)$$

The terms involving the derivative operator $\mathbf{E}_1$ acting on ϕ_j are very small, because

$$\sum_j |\phi_j(1)|^2 \approx \exp(-\text{const} q_1^2/N^{\frac{4}{3}}) \approx 1.$$

In (45) the operator $\mathbf{E}_1$ is to measure the kinetic energy of particle 1, using the description of the motion of particle 1 relative to all the other particles contained in $\prod_j \chi(r_{ij})$. In obtaining the single-particle probability density, we learned that $\gamma(k)$ is essentially a delta function in each of the integrals of (45). We therefore get

$$\langle E \rangle = \frac{N}{A} \int d\mathbf{x}_1 \prod_j \chi(u_{1j}) \mathbf{E}_1 \prod_k \chi(u_{1k}). \quad (46)$$

Again, u_{1k} is the distance from lattice site k to particle 1. In performing the product over k, we must use the same care as in obtaining the probability density of Eq. (31). For each member of the product over k, $\mathbf{E}_1$ contributes kinetic energy for a single degree of freedom, corresponding to motion along the line connecting lattice point 1 and lattice point k as measured by the distance u_{1k}. The function $\exp(-\delta^2 q^2/2)$ gives a good approximation for $\prod_k \chi(u_{1k})$, but $\nabla_1^2 \exp(-\delta^2 q^2/2)$ contributes kinetic energy of relative motion as though the particle described by $\exp(-\delta^2 q^2/2)$ involved three degrees of freedom instead of just one. The function is spherically symmetric, so that for the one degree of freedom we can simply take, say $\nabla^2 \to 3\partial^2/\partial x^2$, so that

$$\langle E \rangle = -\frac{\hbar^2}{2m} \frac{\int \exp(-\delta^2 q^2/2m)(\nabla_1^2/3) \exp(-\delta^2 q^2/2) dv_1}{\int \exp(-\delta^2 q^2) dv_1}$$
$$= (\hbar^2/4m)\delta^2. \quad (47)$$

The result of Eq. (47) is an approximation. The effect of approximations incidental to the calculation [e.g., assuming γ_k is a δ function in $\int \gamma(k)\chi^2(r_{ik})d\mathbf{x}_i$] are undoubtedly small compared to the physical assumption that H' is a small perturbation. It can be shown, by estimating the matrix elements involved, that $\sum_j \langle H_{1j}'(r_{ij}) \rangle$ is of the order of and is somewhat less than $\langle E \rangle$ for values of lattice constant a of interest to us. This perturbation energy is much less than either $\sum_j \langle T_{ij} \rangle$ or $|\sum_j \langle \frac{1}{2} V_{ij} \rangle|$. We may then say with some confidence that H' has a small modifying effect on the function generated by H_0.

We now proceed to consider exchange energy. The $\phi_i(\mathbf{r})$ given by (36) are introduced to ensure that ψ conforms to the Pauli principle. In our treatment of exchange, we shall limit our attention to two-particle exchange. Such a description is the next refinement to the single-particle scheme of Sec. IV. Further, we shall consider exchange with nearest neighbors only. To consider next nearest neighbors requires a description of the wave function more detailed than that provided by the single parameter δ (corresponding to spherical symmetry). Otherwise the overlap integrals cannot account for the lack of spherical symmetry in the effects of nearest and next nearest neighbors.

The single-particle density $\gamma(1)$ was obtained by requiring that each particle and its neighbors stand in a correlated state of low energy. We shall consider these correlated states where the spins of particle 1 and its neighbors are antiparallel, and second where these spins are parallel, and compare the energies of these two states. We shall require each nearest neighbor pair to obey the Pauli principle.

Let us say that the energy of the pair for spins antiparallel is E_{+1}, and the energy for spins parallel is E_{-1}. We define the exchange integral J by

$$J = E_{+1} - E_{-1}. \quad (48)$$

Our calculations will yield an expectation value for the energy of a pair $\langle E \rangle_{\text{pair}}$ where spin is averaged over, plus a correction term ϵ resulting from including spin. The correction term will be of opposite sign for each of the two cases of spin orientation. There is also a spinless normalization integral $\langle I \rangle$, with a correction term Δ which shows the (small) effect of spin and symmetry on normalization. We can write

$$\langle E \rangle_\eta = \langle E \rangle_{\text{pair}} + \eta\epsilon \quad \text{and} \quad \langle I \rangle_\eta = \langle I \rangle_{\text{pair}} + \eta\Delta.$$

Then the spin-sensitive energy is $E_\eta = \langle E \rangle_\eta / \langle I \rangle_\eta$, where η assumes the values $+1$ or -1 as in the definition of J given by Eq. (48).

We therefore have

$$E_\eta = (\langle E \rangle + \eta\epsilon)/(\langle I \rangle + \eta\Delta). \quad (49)$$

Then we have

$$J = \frac{2[\epsilon - (\Delta\langle E \rangle)/\langle I \rangle]}{\langle I \rangle - \Delta^2/\langle I \rangle}. \quad (50)$$

Exchange in the many-body case is somewhat different from the two-particle case, for which we have just defined J. We consider exchange as exchange with respect to a class of neighbors, for example, exchange energy with next-nearest neighbors.

We will compare the energy of the solid in two cases: one, when the spins of 1 and the class of neighbors are parallel; and two, when these spins are antiparallel. If the exchange energy with respect to a given set of neighbors is positive, that exchange integral is termed ferromagnetic.

We proceed by writing down the Hamiltonian. We delete the term $[T_{ij}+\tfrac{1}{2}V_{ij}]$, because such a term yields zero in the product with χ_{ij}. We take $V_i(\mathbf{r}_i)$ to be a constant. The Hamiltonian (for lowest order exchange energy) is then

$$H=\sum_i \mathbf{E}_i.$$

We arrange these operators as:

$$H=\mathbf{E}_1+\sum_\lambda{}^M \sum_i{}^{n\lambda} \mathbf{E}_{i,\lambda}. \tag{51}$$

Here λ includes all of a class of neighbors like, say, next nearest neighbors of the same spin, which cannot be distinguished within our symmetry of space and spin. We have

$$\sum_\lambda{}^M \sum_i{}^{n\lambda} 1 = N-1.$$

We have learned in obtaining the energy without exchange that we could get $\langle E\rangle$ by putting $\gamma(1'|1)=[\gamma(1')\gamma(1)]^{\frac{1}{2}}$. We shall use this idea to deduce a valid two-particle density matrix from the single-particle form. We want to build up a nondiagonal two-particle density matrix and have a result which shows the necessary conditions

$$\Gamma(1'2'|12)=\Gamma(2'1'|21)=-\Gamma(1'2'|21), \tag{52a}$$

$$\Gamma(12|12)=\gamma(1)\gamma(2)+\text{overlap terms}. \tag{52b}$$

We recall that $\gamma(1)=\sum_j\gamma_j(1)$. The antisymmetric form of the density matrix which we seek is

$$\Gamma^{(2)}(1'2'|12)$$
$$=\{[\gamma_a(1')\gamma_b(2')]^{\frac{1}{2}}+\eta[\gamma_a(1')\gamma_b(1')]^{\frac{1}{2}}\}$$
$$\times(\text{same, prime}\rightarrow\text{unprime})$$
$$=(\text{const})\{\exp[-\tfrac{1}{2}\delta^2((R_a-r_1')^2+(R_b-r_2')^2)]$$
$$+\eta\exp[-\tfrac{1}{2}\delta^2((R_b-r_1')^2+(R_a-r_2')^2)]\}$$
$$\times\{\text{same, prime}\rightarrow\text{unprime}\}. \tag{53}$$

Formula (53) yields the conditions (52), and gives the correct single-particle effects within the approximations used to obtain the Gaussian representation for $\gamma(1)$. Although spin does not appear explicitly, Eq. (53) includes spin through the parameter η.

We shall use the form in (53) as a first approximation valid only so long as the spherically symmetric approximation has little effect on overlap of adjacent γ's.

We can rewrite (53) as $\Gamma^{(2)}=|\psi|^2$, where

$$\psi_\eta=(\text{const})\{\exp[-\tfrac{1}{2}\delta^2((z_1-b)^2+(z_2+b)^2)]$$
$$+\eta\exp[-\tfrac{1}{2}\delta^2((z_1+b)^2+(z_2-b)^2)]\}$$
$$\times\exp[-\tfrac{1}{2}\delta^2(x_1^2+x_2^2+y_1^2+y_2^2)]. \tag{54}$$

Here $b=a/2$. The z axis joins the two lattice sites 1 and 2, and z_1 and z_2 are measured from the midpoint of the line joining the lattice sites (that is, there are lattice sites at $z=\pm b=\pm a/2$). The energy for the pair is

$$\langle E\rangle_\eta=\frac{\int [\mathbf{E}_1+\mathbf{E}_2]\Gamma(1'2'|12)d\mathbf{x}_1d\mathbf{x}_2}{\int \Gamma(1'2'|12)d\mathbf{x}_1d\mathbf{x}_2}, \tag{55}$$

where the subscript η specifies the spin state for which the space integrals on the right side are evaluated.

We can use the function ψ to form the density matrix, but in going from the operator $\mathbf{E}_1$ to $(-\hbar^2/2m)\nabla_1^2$, we must remember to introduce the factor $\tfrac{1}{3}$ as before. Hence the energy of the pair is

$$E_\eta=\int \psi_\eta{}^*(-\hbar^2/2m)(\tfrac{1}{3})(\nabla_1^2+\nabla_2^2)\psi_\eta dv_1 dv_2,$$

$$\tag{56}$$

$$I_\eta=\int \psi_\eta{}^*\psi_\eta dv_1 dv_2,$$

using the notation of Eq. (49). We get, performing the operations,

$$E_\eta=(\text{const})\hbar^2/6m$$
$$\times[3\delta^2-\eta(2\delta^4b^2-3\delta^2)\exp(-2\delta^2b^2)], \tag{57a}$$

$$I_\eta=(\text{const})2[1+\eta\exp(-2\delta^2b^2)]. \tag{57b}$$

The unspecified constant is the same in both instances.

We can identify the following quantities in Eq. (50):

$$\epsilon=-\hbar^2(6m)^{-1}(2\delta^4b^2-3\delta^2)\exp(-2\delta^2b^2),$$
$$\Delta=2\exp(-2\delta^2b^2),$$
$$\langle E\rangle=\hbar^2(2m)^{-1}\delta^2,$$
$$\langle I\rangle=2.$$
$$\tag{58}$$

Neglecting $\Delta^2/\langle I\rangle$ compared to $\langle I\rangle$, we have for $J=E_{+1}-E_{-1}$

$$J=-(\hbar^2/3m)\delta^2(\delta^2a^2/2)\exp(-\delta^2a^2/2). \tag{59}$$

Equation (59) cannot be expected to be valid in the high-density case, since the overlap of the functions $\gamma(k)$ enters strongly in (59) and we have assumed spherical symmetry near lattice site k.

A better approximation would consist of using less than spherical symmetry in (1), for example,

$$\gamma_1(1)=\exp[-\delta_1^2(x^2+y^2+z^2)-\delta_2^2(x^2y^2+y^2z^2+z^2x^2)].$$

VII. COMPARISON WITH EXPERIMENT

Experimental values of the cohesive energy are not available. However, we can apply some data on the temperature dependence of the spin-lattice relaxation time T_1 and the spin-spin relaxation time T_2 reported by Goodkind and Fairbank[14] and by Reich.[15]

With the creation of a vacancy in our body-centered cubic lattice, nearest neighbors will relax toward the vacant site. The vacancy will reduce the kinetic energy of neighbors, but will dispose the nearest neighbors further from their nearest neighbors, making the potential energy less attractive. To lowest order, we can assume that these effects cancel so that the energy to

[14] J. M. Goodkind and W. M. Fairbank, Phys. Rev. Letters 4, 458 (1960).
[15] H. A. Reich, in *Helium Three*, edited by John G. Daunt (Ohio State University Press, Columbus, Ohio, 1960), p. 63.

create a vacancy is the cohesive energy E_C, which must be exerted to install the vacating atom in a lattice site. At constant volume, $PdV=0$. We further assume that there is an energy barrier to diffusion of this vacancy E_B. (We can guess E_B by imagining an ex-nearest neighbor moving across to the vacant site with an energy saddle of a few degrees Kelvin.) The vacancy diffusion coefficient D_V is then $D_{0,V}e^{-E_B/KT}$. Assuming that Goodkind and Fairbank and Reich are correct in attributing their relaxation times T_1 and T_2 to diffusion, the rate of energy transfer from the aligned spins to the lattice will be proportional to $N_V D_V$, where N_V is the number of vacancies and D_V is the vacancy diffusion rate. For a dilute system of vacancies $N_V=Ne^{-E_C/KT}$, hence $N_V D_V = D_{0,V}e^{-(E_C+E_B)/KT}$. If we define E_A as the activation energy for diffusion and for spin relaxation, we have $E_A=E_C+E_B$.

In Fig. 3, we show the experimental data for E_A, and our theoretical curve for E_C.

The value of the cohesive energy of the solid is not a good check of the theory, because any theory which would confine a He[3] atom to a volume of the order of that external to the hard-core radii of the interactions would get about the same value. However, the pressure vs density is easily observed and can be readily calculated from our theory

$$P = -\partial E/\partial V$$
$$= -(1.30/3a^2)(\partial E/\partial a), \quad (a \text{ in } \text{Å}).$$

In Fig. 4, we have plotted pressure results, and we show the few experimental values reported by Sydoriak, Mills, and Grilly,[16] and by Edwards, Baum, Brewer, Daunt, and McWilliams.[17] The agreement with experiment is good.

We have also compared the cohesive energy for the face-centered cubic lattice with that for the body-
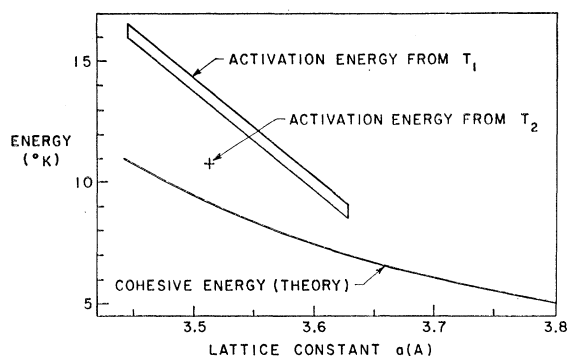

FIG. 3. Cohesive energy and activation energy of spin relaxation. The T_1 activation energy is taken from the data of Goodkind and Fairbank[14] and of Reich.[15] The T_2 activation energy point was reported by Goodkind and Fairbank.
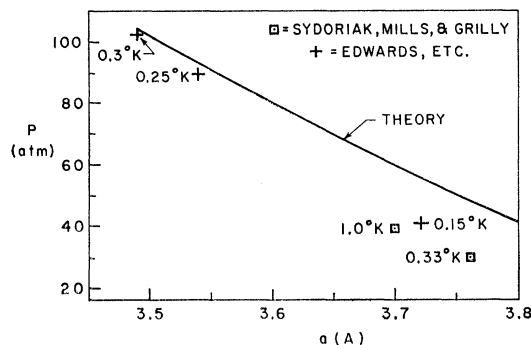
FIG. 4. Pressure (atm) vs lattice constant a (Å). The experimental points were reported by Sydoriak, Mills, and Grilly,[16] and by Edwards et al.[17]

centered cubic, and find that the latter is energetically preferred. This is done by inserting the C_n for the face-centered cubic lattice in Eq. (36).

Additionally, making assumptions covering the ratio of transverse to longitudinal sound velocity, we have calculated the Debye temperature from the second derivative of the cohesive energy (bulk compressibility), and get a value of approximately $57/\sqrt{a}$ °K (a in Å), valid for the range $3.45<a<3.85$. Near the melting curve the Debye temperature is approximately 30°K. Specific heat data are not available, hence no comparison with experiment can be made.

This theory can be compared with the experimental susceptibility data of Adams et al.[18] Figure 5 shows their data. In Fig. 6, we summarize certain aspects of their data, showing the value of the Néel temperature T_N or the Curie temperature T_C given by their data. To obtain the plotted experimental points, we have applied the conclusions of other investigators,[19] which are valid for antiferromagnetic materials in general.

The Néel temperature T_N is the temperature below which spontaneous antiparallel alignment of spins takes place. The susceptibility curves of Fig. 5 at 68.0, 81.6, 95.3, and 112.2 atm are seen to pass through a maximum, or achieve a constant value, at T_N, without developing a range of values which fall off from the straight line $\chi=1/T$ of the Curie law. The other curves, on the other hand, fall off from the Curie law accordingly to the relationship for the experimentally observed susceptibility, χ_0,

$$\chi_0=C_P/(T+T_C), \quad (T_B>T>T_N). \quad (60)$$

We use (60) to define the quantity T_C, and T_B is the temperature below which the breakaway from the Curie law has been passed (about 0.3°K for $P=57.8$ atm, for example). Values of T_C are plotted in Fig. 6 for $P=35.7$,

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[18] E. D. Adams, H. Meyer, and W. M. Fairbank, in Helium Three, edited by John G. Daunt (Ohio State University Press, Columbus, Ohio, 1960), p. 57.

[19] J. H. Van Vleck, J. phys. radium 12, 262 (1951), and T. Nagamiya, K. Yosida, and R. Kubo, Advances in Physics, edited by N. F. Mott (Taylor and Francis, Ltd., London, 1955), Vol. 4, p. 1, give comprehensive reviews of antiferromagnetism.

47.6, 57.8, and 64.6 atm, obtained from Fig. 5 by plotting $1/\chi$ vs T, and observing the zero intercept of the extrapolated curve on the T axis. C_P is 1.1 for the first two pressures, and 1.2 for the other two.

Formula (60) is of the form of the Curie-Weiss law for antiferromagnets.

$$\chi = C/(T+\theta), \quad T < T_N. \tag{61}$$

Here C is the Curie constant, and

$$\theta = -\sum_\lambda J_\lambda/2, \tag{62}$$

where J_λ denotes the exchange integral with neighbor λ. For the data taken at 35.7 atm and 47.6 atm, $C_P = 1.1C \approx C$, and we assume the Curie-Weiss law to be valid here, so we expect that $T_C = \theta$. In our case $\theta = -4J$.

In Fig. 6, we have plotted $4J$ from theory and see excellent agreement with the data at low pressures.

At high pressures we must plot T_N, estimated from the shape of the susceptibility curve, rather than T_C, because in these cases T_N is so high that no dependence such as (60) can develop over an appreciable part of the T vs $1/\chi$ curve. For these points, T_N—and therefore J—varies rapidly with density. This may reflect itself in a temperature dependence of the apparent exchange

integral, since the average value of J during the period of a sound wave density fluctuation will depend on $\partial^2 J/\partial a^2$. This is so because

$$J(a) = J(a_0) + (a-a_0)(\partial J/\partial a)_{a_0}$$
$$+ ((a-a_0)^2/2)(\partial^2 J/\partial a^2)_{a_3} + \cdots$$

and

$$\langle J(a) \rangle_{av} = J(a_0) + \langle (a-a_0)^2 \rangle_{av} \tfrac{1}{2} (\partial^2 J/\partial a^2)_{a_0} + \cdots.$$

At elevated temperatures $\langle (a-a_0)^2 \rangle_{av}$ has a finite value. Hence, the value of T_N in the range 3.5 Å to 3.65 Å cannot be readily used to calculate a value of J to be expected from experiment because $\partial^2 J/\partial a^2$ appears to be large there. However, it is undoubtedly of the order of 0.1°K where our theoretical curve is of the order of 0.001°K. Our theory assumes that the probability density near a lattice site is spherical and it therefore cannot treat exchange with nearest neighbors (NN) and next nearest neighbors (NNN) simultaneously. Correlations between NN at high densities reduce overlap (and exchange), as our theoretical curve shows. However, at these high densities the probability density near lattice sites must assume a nonspherical shape, permitting overlap with NNN in a configuration favor-
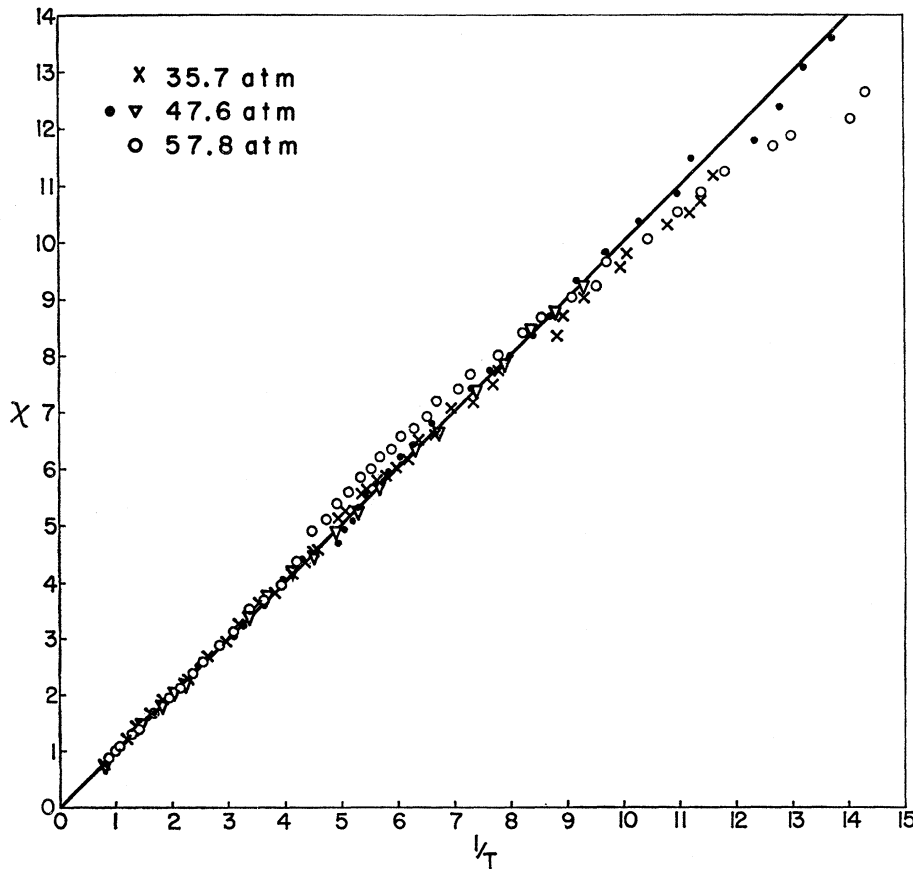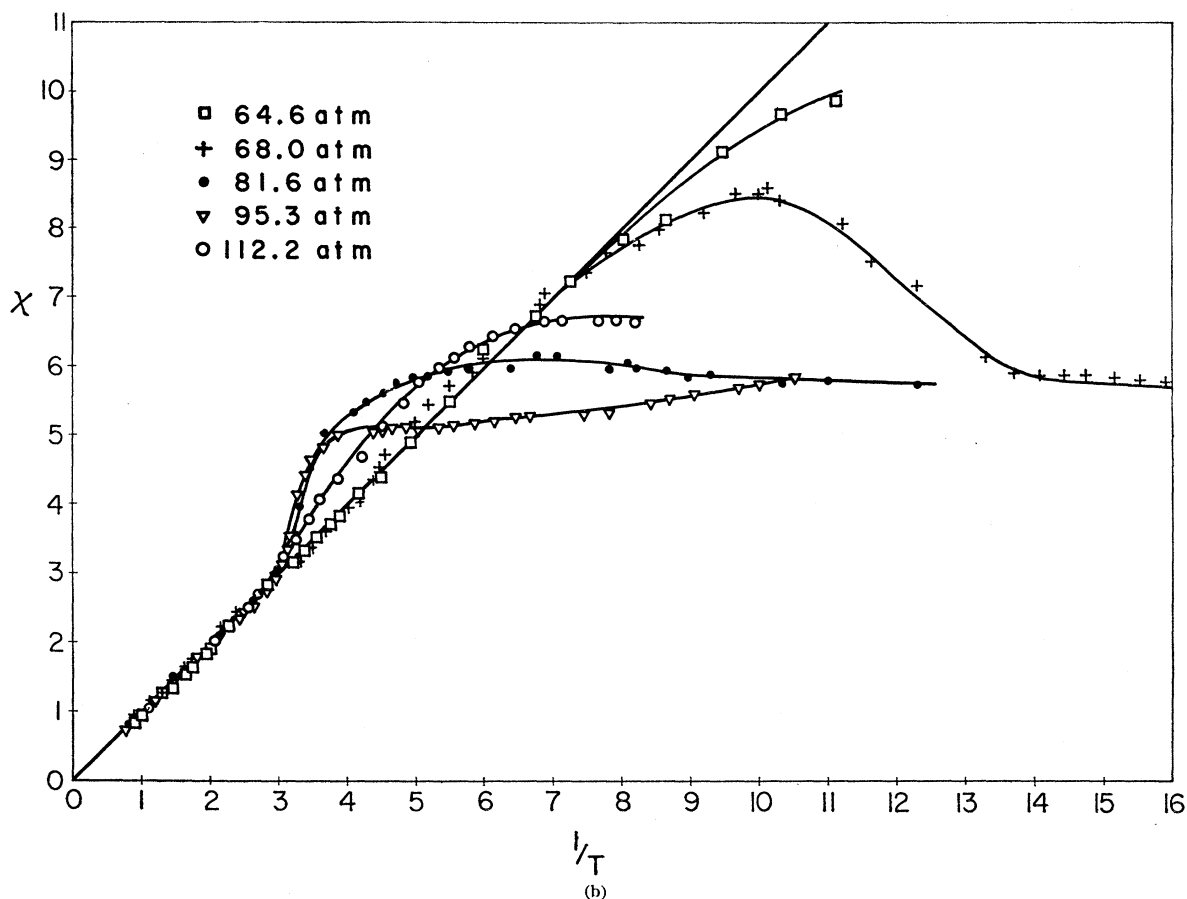

Fig. 5. Bulk susceptibility of He³ vs $1/T$, reported by Adams, Meyer, and Fairbank (reference 18).

(a)

(b)

ing an attractive potential. Hence, an antiferromagnetic exchange integral is again expected, as in the nearest neighbor (NN) case.

It is known that when the interaction between NN and NNN are both important, $\chi(T=T_N)=\frac{3}{2}\chi(T=0)$. The curve at 68.0 atm possesses this quality, and it may thus be evidence for a NNN exchange integral at $a=3.60$ Å of the same order as that for NN. In Fig. 5 the curves at 81.6 and 95.3 atm pressure might represent an antiferromagnet with the NNN interaction strongly predominant.

The 112.2-atm curve shows a T_N somewhat lower than those at 81.6 and 95.3 atm. Carrying the picture of the last paragraph further, this curve could indicate that the NNN correlations have become sufficiently severe to reduce the exchange integral.

It is also interesting to note that if one assumes a lattice constant a in the liquid at a pressure of 27.6 atm, corresponding to a body-centered cubic lattice, and one fits the susceptibility data χ vs T to a low of the form of Eq. (60), one gets $T_C\approx0.07°$K at $a\approx3.87$ Å, in fair agreement with the theoretical prediction for a (non-existent) solid at that density. Hence, the model of the present theory constitutes support for the idea that the exchange interaction in the liquid is stronger than in the solid, and favors antiparallel alignment.

Finally, we have plotted the theoretical prediction of exchange energy due to Bernardes and Primakoff[6] on Fig. 6 for purposes of comparison.
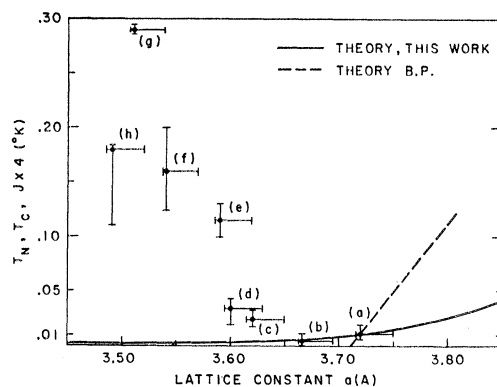

FIG. 6. Characteristic energies, T_N, T_C, and $4J$ vs lattice constant a (Å). The points are obtained from the data of Fig. 5. Points (a), (b), (c), and (d) are taken from the curves for 35.7 atm, 47.6 atm, 57.8 atm, and 64.6 atm, respectively, by fitting the Curie-Weiss law, Eq. (60). The points (e), (f), (g), and (h) correspond to 68.0 atm, 81.6 atm, 95.3 atm, and 112.2 atm, respectively. They are obtained by estimating T_N from Fig. 5. T_N is taken to be the location of the maximum susceptibility. The dashed line is T_C (theory) obtained from the work of Bernardes and Primakoff.[6] The solid line is given by the theory of this paper, and is the quantity $4J$, corresponding to θ in the Curie-Weiss law, formula (61).

VIII. CONCLUSIONS

We have obtained a single-particle description of the ground state of solid He^3 in the body-centered cubic configuration at zero temperature. We find that the strongly repulsive interaction results in strong correlation effects. By considering the correlations of pairs, each in a zero-energy state, we have built up the quantum-mechanical probability density of the solid.

Our solution employs an approximate solution of the wave equation. We find that the neglected part of the Hamiltonian can be treated as a reasonably small perturbation in the density range of solid He^3 in the body-centered cubic phase. We find that the physical parameters of He^3 are such that our formal solution for the probability density has an approximate solution in a simple analytic form, expressed in a single parameter δ^2. We obtain a single-particle energy from the density, using a plausibility argument and basic principles. The effect of exchange on the energy, though small, is appreciable compared to the single-particle energy, and results in a magnetic transition temperature of approximately 0.02°K for densities near the melting curve.

We employ the symmetry of the cubic lattice to the fullest extent possible and thereby simplify the calculation. We find that for a less dense system than ours, the approximations used in calculating δ^2 breakdown.

As the next improvement, cubic symmetry should be included in the single-particle density, with an attempt to calculate exchange with next-nearest neighbors. A workable way of distinguishing between hexagonal close-packed and face-centered cubic lattices has not been developed.

We find that particle correlations result in a probability density for He^3 which is strongly peaked at lattice sites, but with sufficient overlap to give an exchange-dependent part of the energy, favoring antiparallel alignment of nearest neighbors. We obtain good agreement with experimental pressure-density data, and we obtain an exchange energy consistent with experimental susceptibility data taken at low density.