Off-Diagonal Long-Range Order and the Momentum Distribution of Electron Pairs in Superconductors, and Helium Atoms in Liquid ^{4}He†

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The momentum distributions of electron pairs in superconductors and of helium atoms in liquid ^{4}He are defined by summing the pair or atomic state occupation probability over all internal states of the pair or ^{4}He atom corresponding to a given value of total translational momentum. By use of the closure relation for internal wave functions, the momentum distribution of electron pairs is expressed in terms of the two-electron density matrix $\rho_2(x_1 x_2, x_1' x_2')$ of the $2n$-electron system. Similarly, for ^{4}He atoms, the momentum distribution is expressed in terms of the single-atom density matrix $\rho_3(x_1 x_2 \vec{R}, x_1' x_2' \vec{R}')$ of the n-atom system, where x_1, x_2, and $\vec{R}$ are the coordinates of two electrons and an α particle. The equivalence of this definition of the momentum distribution with two other plausible definitions is demonstrated. It is shown that exchange and the exclusion principle produce a strong spreading of the momentum distribution both for a superconductor and for liquid ^{4}He, completely suppressing Bose-Einstein condensation in the strong sense of macroscopic occupation of the zero-momentum state. However, a much weaker singularity at zero momentum, characteristic of the off-diagonal long-range order (ODLRO) of ρ_2 for a superconductor and of ρ_3 for liquid ^{4}He, does occur. By comparison with the hypothetical case of pairs of bosons, it is shown that the exclusion principle (not merely exchange) plays an essential role in broadening the momentum distribution in superconductors and liquid ^{4}He.

I. INTRODUCTION

The superconducting state is characterized[1] by "off-diagonal long-range order" (ODLRO) of the two-electron density matrix $\rho_2(x_1 x_2, x_1' x_2')$ in the sense that

$$\rho_2(x_1 x_2, x_1' x_2') \xrightarrow[\text{infinite separation}]{} \chi(x_1 x_2)\chi^*(x_1' x_2') \neq 0 , \quad (1)$$

where $\chi(x_1 x_2)$ is the effective wave function of a single pair (the part of χ representing the motion of the center of mass of the pair is the order parameter). Here each x_j stands for $(\vec{r}_j, \sigma_j)$ with $\vec{r}_j$ the position and σ_j the spin variable ($= \uparrow$ or $\downarrow$) of an electron. The limit implied in (1) is one in which the pair of variables $(\vec{r}_1 \vec{r}_2)$ is taken infinitely far away from the pair $(\vec{r}_1' \vec{r}_2')$, holding $\sigma_1 = \sigma_1' = \uparrow$ and $\sigma_2 = \sigma_2' = \downarrow$, and keeping the distances $|\vec{r}_1 - \vec{r}_2|$ and $|\vec{r}_1' - \vec{r}_2'|$ *within* each pair finite. In the case that the system contains $2n$ electrons and is in a pure quantum state with normalized wave function $\psi(x_1 \cdots x_{2n})$, the two-particle density matrix, normalized to unit trace, is defined by

$$\mu_2(x_1 x_2, x_1' x_2')$$
$$\equiv \int \psi(x_1 \cdots x_{2n})\psi^*(x_1' x_2' x_3 \cdots x_{2n}) dx_3 \cdots dx_{2n} , \quad (2)$$

where $\int dx$ means $\sum_\sigma \int d^3r$. Thus ρ_2 measures the overlap of two wave functions differing only through

displacement of a single electron pair from $(x_1 x_2)$ to $(x_1' x_2')$, and the case (1) of ODLRO means that the state ψ exhibits infinite-range phase memory with respect to displacement of such a pair. In the case of statistical mechanics, (2) generalizes to

$$\rho_2(x_1 x_2, x_1' x_2')$$
$$= \sum_i w_i \int \psi_i(x_1 \cdots x_{2n})\psi_i^*(x_1' x_2' x_3 \cdots x_{2n}) dx_3 \cdots dx_{2n} , \quad (3)$$

where the ψ_i are the orthonormal states of the statistical ensemble and the w_i are their statistical weights (for thermal equilibrium $w_i = Z^{-1} e^{-\beta E_i}$ and ψ_i are the energy eigenstates). The physical significance of ρ_2 and ODLRO remains the same as in the case of a pure state.

In the analogous case of liquid ^{4}He considered to be made up of real ^{4}He atoms each containing an α particle and two electrons, the λ transition and superfluidity are presumably characterized[1-5] by ODLRO of ρ_3 in the sense that

$$\rho_3(x_1 x_2 \vec{R}, x_1' x_2' \vec{R}')$$
$$\xrightarrow[\text{infinite separation}]{} \chi(x_1 x_2 \vec{R})\chi^*(x_1' x_2' \vec{R}') \neq 0 , \quad (4)$$

where ρ_3 is the single-^{4}He-atom density matrix defined in a pure state by

$$\rho_3(x_1 x_2 \vec{R}, x_1' x_2' \vec{R}') \equiv \int \psi(x_1 \cdots x_{2n} \vec{R} \vec{R}_2 \cdots \vec{R}_n)$$

$$\times \psi^*(x_1' x_2' x_3 \cdots x_{2n} \vec{R}' \vec{R}_2 \cdots \vec{R}_n)$$

$$\times dx_3 \cdots dx_{2n} d^3 R_2 \cdots d^3 R_n \quad (5)$$

and for a statistical ensemble by the corresponding analog of (3).

Let $\varphi_\alpha(x_1 x_2)$ be any normalized state of a single electron pair, e.g., a Cooper pair state of the type important in the theory of superconductivity. Then the mean occupation number of this pair state can be defined by[2,3]

$$n_\alpha \equiv n(\varphi_\alpha, \rho_2 \varphi_\alpha)$$

$$\equiv n \int \varphi_\alpha^*(x_1 x_2) \rho_2(x_1 x_2, x_1' x_2') \varphi_\alpha(x_1' x_2') dx_1 dx_2 dx_1' dx_2'$$

$$(6)$$

in analogy with the standard formula

$$n_k = n(\varphi_k, \rho_1 \varphi_k) = n \int \varphi_k^*(x) \rho_1(x, x') \varphi_k(x') dx\, dx' \quad (7)$$

for any normalized orbital $\varphi_k(x)$, ρ_1 being the single-particle density matrix. Since there are $2n$ electrons in the system, one expects that the number of pairs will be n, i.e., one expects that the sum rule

$$\sum_\alpha n_\alpha = n \quad (8)$$

will hold if $\{\varphi_\alpha\}$ is any complete orthonormal set of pair states. This sum rule is easily verified from the completeness relation[6]

$$\sum_\alpha \varphi_\alpha(x_1 x_2) \varphi_\alpha^*(x_1' x_2')$$

$$= \tfrac{1}{2} [\delta(x_1 - x_1') \delta(x_2 - x_2') - \delta(x_1 - x_2') \delta(x_2 - x_1')]$$

$$(9)$$

and the normalization condition

$$\mathrm{Tr}\,\rho_2 = \int \rho_2(x_1 x_2, x_1 x_2) dx_1 dx_2 = 1 . \quad (10)$$

Similarly, for a system of n ^{4}He atoms one can define the mean occupation number of any single-atom state $\varphi_\alpha(x_1 x_2 \vec{R})$ ($\vec{R}$ refers to the nucleus, and x_1 and x_2 to the electrons) as[2,3]

$$n_\alpha \equiv n(\varphi_\alpha, \rho_3 \varphi_\alpha)$$

$$\equiv n \int \varphi_\alpha^*(x_1 x_2 \vec{R}) \rho_3(x_1 x_2 \vec{R}, x_1' x_2' \vec{R}') \varphi_\alpha(x_1' x_2' \vec{R}')$$

$$\times dx_1 dx_2 d^3 R\, dx_1' dx_2' d^3 R' \quad (11)$$

and the same sum rule (8), which now expresses the fact that there are n ^{4}He atoms in the system, applies.

The maximum kinematically attainable pair occupation number n_α for a system of n electrons is limited by the inequality[3]

$$n_\alpha < n/(2n-1) - \tfrac{1}{2} \quad \text{as } n \to \infty \quad (12)$$

which follows from a rigorous upper bound[4,7,8] on the largest eigenvalue of the two-electron density matrix. The fact that the bound (12) is so much smaller than the value of order n that would characterize Bose-Einstein condensation (macroscopic occupation) is a direct result of the Pauli exclusion principle, as can be seen from the derivations[4,7,8] and from the fact that an exchanged product $\varphi_0(x_3 x_2) \varphi_0(x_1 x_4)$ has a nonzero projection onto unexchanged products $\varphi_\alpha(x_1 x_2) \varphi_\beta(x_3 x_4)$ for practically all values of α and β, not merely $\alpha = \beta = 0$. Similarly, for n ^{4}He atoms the atomic occupation numbers are limited by essentially[9] the same inequality.[3] In fact, for a normal fermion system all the n_α are much smaller (of order n^{-1}), and for a normal (non-superfluid) system of ^{4}He atoms all n_α are of order n^{-2}. On the other hand, for a superconductor with ODLRO (1), the occupation number of the single Cooper pair state φ_0 proportional to χ is of order unity (it approaches $\tfrac{1}{2}$ in the limit of zero range of φ_0), and for liquid ^{4}He with ODLRO (4), the occupation number of the single-atom state φ_0 proportional to χ is of order n^{-1}. Because of the distinction between such behavior and true Bose-Einstein condensation, we have called such behavior, characterized by (1) or (4), "Fermi condensation." It seems that in a superconductor, in which many electron pairs move freely through the system but suffer strong exchange effects, the effects of electron exchange would be qualitatively different from those of boson exchange even for tightly bound Cooper pairs. Similarly, in real superfluid liquid ^{4}He the effects of electron exchange are qualitatively different from boson-exchange effects in an idealized model of structureless bosons. There are, however, close analogies[5] between Fermi and Bose condensation, since both are characterized by ODLRO; for the structureless boson models, superfluidity and Bose-Einstein condensation are characterized by ODLRO of the single-boson density matrix $\rho_1(\vec{R}, \vec{R}')$.

For the case of a uniform system with periodic boundary conditions,[10] the set α of quantum numbers labeling the state φ_α of an electron pair of a ^{4}He atom can be decomposed into a translational wave vector $\vec{k}$ (related to the total linear momentum $\vec{p}$ of the state φ_α by $\vec{p} = \hbar \vec{k}$) and a set ν of internal quantum numbers labeling the state of excitation of the wave function in the c.m. frame. It is therefore natural to define a momentum distribution function $f_{\vec{k}}$ of electron pairs or ^{4}He atoms by summing over all states of internal excitation for a fixed value of momentum:

$$f_{\vec{k}} \equiv \sum_\nu n_{\vec{k},\nu} . \quad (13)$$

Here $n_{\vec{k},\nu}$ is the occupation number n_α [Eq. (6) or (11)] for the case that the set α of quantum numbers

is decomposed as $\alpha = (\vec{k}, \nu)$. One might expect the momentum distribution function $f_{\vec{k}}$ to bear some relationship to the boson momentum distribution function in an (extremely) idealized model in which Cooper pairs are treated as structureless bosons or the commonly used boson models of liquid ^{4}He. It follows from the sum rule (8) that $f_{\vec{k}}$ satisfies the sum rule

$$\sum_{\vec{k}} f_{\vec{k}} = n \tag{14}$$

as does the boson momentum distribution function in a system of n bosons. It is natural to ask the question,[11] "Are the restrictions of the exclusion principle implicit in (12) still present in $f_{\vec{k}}$, or might $f_{\vec{k}}$ exhibit macroscopic occupation (e.g., f_0 of order n) as in the case of Bose-Einstein condensation?" The remainder of this paper is devoted to answering this question. We shall find that the effects of the exclusion principle are still apparent in $f_{\vec{k}}$ both for the case of a superconductor and for liquid ^{4}He. We shall show that in both of these cases $f_{\vec{k}}$ is of order unity [independent of n and the volume Ω in the thermodynamic limit $(n/\Omega) \to$ finite nonzero constant] for all values of $\vec{k}$ including $\vec{k} = 0$, and that ODLRO (1) or (4) manifests itself in $f_{\vec{k}}$ only through a *finite* (independent of n and Ω in the thermodynamic limit) discontinuity at $\vec{k} = 0$[12] in the case of a superconductor, and a negligible $(\sim n^{-1})$ discontinuity in the case of liquid ^{4}He.

In Sec. II an explicit formula for $f_{\vec{k}}$ in terms of ρ_2 or ρ_3 is derived. In order to allay fears that the definition (13) of $f_{\vec{k}}$ might not be the one which is appropriate on physical grounds, in Sec III we introduce two other plausible definitions of $f_{\vec{k}}$, one in terms of a suitable average of ρ_2 or ρ_3 so as to produce an analog of the ρ_1 of a boson system, and the other in terms of the conventional binary or ternary momentum distribution function. Both of these definitions are shown to be equivalent to (13). The properties of $f_{\vec{k}}$ for generalized BCS states, which, as shown by Yang,[1] lead to ODLRO (1) and play an important role in the proof of (12), are investigated in Sec. IV, and the properties of $f_{\vec{k}}$ for analogous states of a system of ^{4}He atoms are determined in Sec. V. The physical significance of the results is discussed in Sec. VI. The hypothetical case of boson pairs is discussed in an Appendix in order to differentiate between the effects of exchange in general and of the exclusion principle in particular.

II. EXPLICIT FORMULA FOR $f_{\vec{k}}$

The summation over internal quantum numbers ν in (13) can easily be effected by introducing a decomposition of the φ_α into internal wave functions u_ν and wave functions describing the motion of the center of mass. Consider first the case of electrons, with pair wave functions $\varphi_\alpha(x_1 x_2)$. These φ_α can be decomposed as follows:

$$\varphi_\alpha(x_1 x_2) = \Omega^{-1/2} e^{i\vec{k}\cdot\vec{R}} u_\nu(x_1 x_2) , \tag{15}$$

where $\alpha = (\vec{k}, \nu)$, $\vec{R}$ is the c.m. coordinate

$$\vec{R} = \tfrac{1}{2}(\vec{r}_1 + \vec{r}_2) , \tag{16}$$

$x_j = (\vec{r}_j, \sigma_j)$ with σ_j the spin variable $(= \uparrow$ or $\downarrow)$, Ω is the volume of the system, and the u_ν are translationally invariant in the sense that

$$u_\nu(x_1 x_2) = u_\nu(\vec{r}_1 \sigma_1, \vec{r}_2 \sigma_2) = v_\nu(\vec{r}_{12}, \sigma_1 \sigma_2) \tag{17}$$

or equivalently

$$u_\nu(\vec{r}_1 + \vec{a}, \sigma_1 ; \vec{r}_2 + \vec{a}, \sigma_2) = u_\nu(\vec{r}_1, \sigma_1 ; \vec{r}_2, \sigma_2) . \tag{18}$$

Here we have $\vec{r}_{12} = \vec{r}_1 - \vec{r}_2$, the relative position of the two electrons. The orthonormality and completeness relations for the v_ν are

$$\sum_{\sigma_1 \sigma_2} \int v_\nu^*(\vec{r}_{12}, \sigma_1 \sigma_2) v_{\nu'}(\vec{r}_{12}, \sigma_1 \sigma_2) d^3 r_{12} = \delta_{\nu\nu'} , \tag{19}$$

$$\sum_\nu v_\nu(\vec{r}_{12}, \sigma_1 \sigma_2) v_\nu^*(\vec{r}_{12}', \sigma_1' \sigma_2')$$

$$= \tfrac{1}{2} [\delta(\vec{r}_{12} - \vec{r}_{12}')\delta_{\sigma_1 \sigma_1'}\delta_{\sigma_2 \sigma_2'} - \delta(\vec{r}_{12} + \vec{r}_{12}')\delta_{\sigma_1 \sigma_2'}\delta_{\sigma_2 \sigma_1'}] ,$$

as is easily verified by substitution of (17) into (9) and the orthonormality relation for the φ_α, and use of appropriate δ-function identities.

It follows from (13) and (6) that

$$f_{\vec{k}} = n\sum_\nu \int \varphi_{\vec{k},\nu}^*(x_1 x_2)\rho_2(x_1 x_2, x_1' x_2')$$

$$\times \varphi_{\vec{k},\nu}(x_1' x_2') dx_1 dx_2 dx_1' dx_2' . \tag{20}$$

Inserting (15) and (17) and performing the closure sum on ν with the aid of (19), one reduces this to

$$f_{\vec{k}} = \tfrac{1}{2}\rho \sum_{\sigma_1 \sigma_2} \int \rho_2(\vec{r}_1 \sigma_1, \vec{r}_2 \sigma_2 ; \vec{r}_1' \sigma_1, \vec{r}_2' \sigma_2) e^{-[i\vec{k}\cdot(\vec{r}_1 + \vec{r}_2 - \vec{r}_1' - \vec{r}_2')]/2} \delta(\vec{r}_{12} - \vec{r}_{12}') d^3 r_1 dr_2^3 d^3 r_1' d^3 r_2'$$

$$= \tfrac{1}{2}\rho \sum_{\sigma_1 \sigma_2} \int \rho(\vec{r}_1 \sigma_1, \vec{r}_2 \sigma_2 ; \vec{r}_1' \sigma_1, \vec{r}_1' + \vec{r}_2 - \vec{r}_1, \sigma_2) e^{-i\vec{k}\cdot(\vec{r}_1 - \vec{r}_1')} d^3 r_1 d^3 r_2 d^3 r_1' , \tag{21}$$

where $\rho = 2n/\Omega$, the number density of electrons (not pairs).

The case of a system of n ^{4}He atoms is similar. The analog of (15) is

$$\varphi_\alpha(x_1 x_2 \vec{R}) = \Omega^{-1/2} e^{i\vec{K}\cdot\vec{R}_{c.m.}} u_\nu(x_1 x_2 \vec{R}) , \qquad (22)$$

where

$$\vec{R}_{c.m.} = \frac{m_\alpha \vec{R} + m_e(\vec{r}_1 + \vec{r}_2)}{m_\alpha + 2m_e} \qquad (23)$$

and m_α and m_e are the masses of the α particle and the electron. The translational invariance of the u_ν, analogous to (18), implies that

$$u_\nu(\vec{r}_1 \sigma_1 ; \vec{r}_2 \sigma_2 ; \vec{R}) = u_\nu(\vec{r}_1 - \vec{R}, \sigma_1 ; \vec{r}_2 - \vec{R}, \sigma_2 ; 0) \qquad (24)$$

$$f_{\vec{k}} = \rho \sum_{\sigma_1 \sigma_2} \int \rho_3(\vec{r}_1 \sigma_1, \vec{r}_2 \sigma_2, \vec{R}; \vec{r}_1 - \vec{R} + \vec{R}', \sigma_1, \vec{r}_2 - \vec{R} + \vec{R}', \sigma_2, \vec{R}') e^{-i\vec{k}\cdot(\vec{R} - \vec{R}')} d^3 r_1 d^3 r_2 d^3 R \, d^3 R' , \qquad (26)$$

where $\rho = n/\Omega$, the number density of ^{4}He atoms.

III. EQUIVALENT DEFINITIONS OF $f_{\vec{k}}$

In the case of ODLRO (1), ρ_2 remains nonzero when $\vec{r}_1'$ and $\vec{r}_2'$ are displaced by an arbitrarily large distance $\vec{a}$ from their original positions $\vec{r}_1$ and $\vec{r}_2$. This suggests defining an average single-particle density matrix $\bar{\rho}_1$ (which by translational invariance depends only on the displacement $\vec{a}$) as follows[14]:

$$\bar{\rho}_1(\vec{a}) \equiv \frac{1}{2}\rho \sum_{\sigma_1 \sigma_2} \int \rho_2(\vec{r}_1 \sigma_1, \vec{r}_2 \sigma_2 ; \vec{r}_1 + \vec{a}, \sigma_1, \vec{r}_2 + \vec{a}, \sigma_2) \times d^3 r_1 d^3 r_2, \qquad (27)$$

with $\rho = 2n/\Omega$, the number density of electrons for the system of $2n$ electrons. If we then define a pair momentum distribution function $f_{\vec{k}}$ by

$$f_{\vec{k}} \equiv \int \bar{\rho}_1(\vec{a}) e^{i\vec{k}\cdot\vec{a}} d^3 a , \qquad (28)$$

then the relationship between $f_{\vec{k}}$ and $\bar{\rho}_1$ is the same as that between the single-particle momentum distribution function $n_{\vec{k}}$ and the single-particle density matrix ρ_1 for a system of structureless bosons.[15] Using the completeness relation for the exponential and the normalization condition (10), one sees that this $f_{\vec{k}}$ satisfies the sum rule (14), as required by the physical interpretation. Combination of (27) and (28) gives

$$f_{\vec{k}} = \frac{1}{2}\rho \sum_{\sigma_1 \sigma_2} \int \rho_2(\vec{r}_1 \sigma_1, \vec{r}_2 \sigma_2 ; \vec{r}_1 + \vec{a}, \sigma_1, \vec{r}_2 + \vec{a}, \sigma_2) \times e^{i\vec{k}\cdot\vec{a}} d^3 r_1 d^3 r_2 d^3 a , \qquad (29)$$

which is easily seen to be equivalent to (21) upon making the substitution $\vec{r}_1' = \vec{a} + \vec{r}_1$. Thus the definitions (13) and (27), (28) are equivalent.

Similarly, for a system of n ^{4}He atoms one can define $\bar{\rho}_1$ by

and their closure relation is[13]

$$\sum_\nu u_\nu(\vec{r}_1 \sigma_1 ; \vec{r}_2 \sigma_2; 0) u_\nu^*(\vec{r}_1' \sigma_1' ; \vec{r}_2' \sigma_2'; 0)$$

$$= \frac{1}{2}[\delta(\vec{r}_1 - \vec{r}_1')\delta_{\sigma_1 \sigma_1'} \delta(\vec{r}_2 - \vec{r}_2')\delta_{\sigma_2 \sigma_2'}$$

$$- \delta(\vec{r}_1 - \vec{r}_2')\delta_{\sigma_1 \sigma_2'} \delta(\vec{r}_2 - \vec{r}_1')\delta_{\sigma_2 \sigma_1'}] . \qquad (25)$$

The analog of (21) is then found to be

$$\bar{\rho}_1(\vec{a}) \equiv \rho \sum_{\sigma_1 \sigma_2} \int \rho_3(\vec{r}_1 \sigma_1, \vec{r}_2 \sigma_2, \vec{R}; \vec{r}_1 + \vec{a}, \sigma_1, \vec{r}_2 + \vec{a}, \sigma_2, \vec{R} + \vec{a})$$

$$\times d^3 r_1 d^3 r_2 d^3 R \qquad (30)$$

and $f_{\vec{k}}$ by (28). Then we have

$$f_{\vec{k}} = \rho \sum_{\sigma_1 \sigma_2} \int \rho_3(\vec{r}_1 \sigma_1, \vec{r}_2 \sigma_2, \vec{R}; \vec{r}_1 + \vec{a}, \sigma_1, \vec{r}_2 + \vec{a}, \sigma_2, \vec{R} + \vec{a})$$

$$\times e^{i\vec{k}\cdot\vec{a}} d^3 r_1 d^3 r_2 d^3 R \, d^3 a , \qquad (31)$$

which reduces to (26) upon defining a new variable of integration $\vec{R}'$ by $\vec{a} = \vec{R}' - \vec{R}$. Thus the definitions (13) and (28), (30) are equivalent.

Still another definition of the pair momentum distribution function in a system of electrons or the atomic momentum distribution function of liquid ^{4}He can be given in terms of suitable averages of the binary or ternary momentum distribution functions. Let $d_2(\vec{k}_1 \vec{k}_2)$ be the binary momentum distribution function of a system of $2n$ electrons, defined in the usual way as

$$d_2(\vec{k}_1 \vec{k}_2) = \sum_{\sigma_1 \cdots \sigma_{2n}} \sum_{\vec{k}_3 \cdots \vec{k}_{2n}} | \varphi(\vec{k}_1 \sigma_1 \cdots \vec{k}_{2n} \sigma_{2n})|^2 , \qquad (32)$$

where φ is the $2n$-electron momentum wave function

$$\varphi(\vec{k}_1 \sigma_1 \cdots \vec{k}_{2n} \sigma_{2n}) = \Omega^{-n} \int \psi(\vec{r}_1 \sigma_1 \cdots \vec{r}_{2n} \sigma_{2n})$$

$$\times e^{-i\vec{k}_1 \cdot \vec{r}_1} \cdots e^{-i\vec{k}_{2n} \cdot \vec{r}_{2n}} d^3 r_1 \cdots d^3 r_{2n} , \qquad (33)$$

and ψ is the $2n$-electron Schrödinger function. Summation of (32) over all values of $\vec{k}_1$ and $\vec{k}_2$ whose sum is $\vec{k}$ gives the probability of finding an electron pair with total momentum $\hbar\vec{k}$, and multiplication by n gives the mean number of such pairs (there are $2n$ electrons in the system). Thus we define the mean number $f_{\vec{k}}$ of electron pairs with momentum $\hbar\vec{k}$ as

$$f_{\vec{k}} \equiv n \sum_{\substack{\vec{k}_1 \vec{k}_2 \\ (\vec{k}_1 + \vec{k}_2 = \vec{k})}} d_2(\vec{k}_1 \vec{k}_2) = n \sum_{\vec{k}_2} d_2(\vec{k} - \vec{k}_2, \vec{k}_2) \ . \quad (34)$$

Then by (32), (33), completeness of the exponential, and (2) one finds

$$f_{\vec{k}} = \tfrac{1}{2}\rho \sum_{\sigma_1 \sigma_2} \int \rho_2(\vec{r}_1 \sigma_1, \vec{r}_2 \sigma_2; \vec{r}_1' \sigma_1, \vec{r}_2 - \vec{r}_1 + \vec{r}_1', \sigma_2)$$

$$\times e^{-i\vec{k}\cdot(\vec{r}_1 - \vec{r}_1')} \, d^3r_1 \, d^3r_2 \, d^3r_1' \ , \quad (35)$$

which agrees with (21). *Thus the three definitions* (13), (28), *and* (34) *are all equivalent.*

Similarly, for a system of n ^{4}He atoms the probability of finding two electrons with momenta $\vec{k}_1$ and $\vec{k}_2$ and an α particle with momentum $\vec{K}$ is

$$d_3(\vec{k}_1 \vec{k}_2 \vec{K})$$

$$= \sum_{\sigma_1 \cdots \sigma_{2n}} \sum_{\vec{k}_3 \cdots \vec{k}_{2n}} \sum_{\vec{K}_2 \cdots \vec{K}_n} |\varphi(\vec{k}_1 \sigma_1 \cdots \vec{k}_{2n} \sigma_{2n}, \vec{K} \vec{K}_2 \cdots \vec{K}_n)|^2 \ , \quad (36)$$

where φ is the $2n$-electron n-α momentum wave function. The mean number of ^{4}He atoms with total momentum $\hbar\vec{k}$ is then

$$f_{\vec{k}} \equiv n \sum_{\substack{\vec{k}_1 \vec{k}_2 \vec{K} \\ (\vec{k}_1 + \vec{k}_2 + \vec{K} = \vec{k})}} d_3(\vec{k}_1 \vec{k}_2 \vec{K}) = n \sum_{\vec{k}_1 \vec{k}_2} d_3(\vec{k}_1 \vec{k}_2, \vec{k} - \vec{k}_1 - \vec{k}_2) \ . \quad (37)$$

A derivation paralleling that of (35) then leads to (26), showing that *the three definitions* (13), (28), · *and* (37) *are all equivalent.*

IV. PAIR MOMENTUM DISTRIBUTION OF GENERALIZED BCS STATES

It has been shown by Yang[1] that ODLRO (1) and hence superconductivity in a system of electrons is exhibited most strongly by states of the general form

$$\psi_{\text{BCS}}(x_1 \cdots x_{2n}) = \mathcal{C} A_{2n} [\, g(x_1 x_2) g(x_3 x_4) \cdots g(x_{2n-1} x_{2n})] \ , \quad (38)$$

where $\mathcal{C}$ is a normalization constant, A_{2n} is the antisymmetrizer with respect to the electron variables $x_1 \cdots x_{2n}$, and g is an antisymmetric and normalized two-electron state or "geminal."[8] Such a state is called an "antisymmetrized geminal power" by Coleman[8,16]; we shall call it a "generalized BCS[17] state." In the limit of zero range of g, or zero electron density for fixed finite range of g, the mean occupation number n_0 of the maximally occupied electron pair state $\varphi_0(x_1 x_2)$ (which turns out to be g in that limit) approaches the largest possible value $\tfrac{1}{2}$ consistent with the kinematical constraint (12) imposed by the exclusion principle.[18] It is therefore of interest to determine the pair momentum distribution function $f_{\vec{k}}$ of generalized

BCS states (38).

We assume that g is translationally invariant and a spin singlet, i.e., that

$$g(x_1 x_2) = (2\Omega)^{-1/2} g(\vec{r}_{12})(\delta_{\sigma_1 \uparrow} \delta_{\sigma_2 \downarrow} - \delta_{\sigma_1 \downarrow} \delta_{\sigma_2 \uparrow})$$

$$= 2^{-1/2} \Omega^{-3/2} (\delta_{\sigma_1 \uparrow} \delta_{\sigma_2 \downarrow} - \delta_{\sigma_1 \downarrow} \delta_{\sigma_2 \uparrow}) \sum_{\vec{k}} g_{\vec{k}} e^{i\vec{k}\cdot\vec{r}_{12}} \ , \quad (39)$$

where $g(\vec{r}_{12})$ is an even function of $\vec{r}_{12} = \vec{r}_1 - \vec{r}_2$ [the original BCS states[17] are of this form with spherically symmetric $g(\vec{r}_{12})$]. The normalization condition on g then reads, after doing the trivial spin summation,

$$\int |g(x_1 x_2)|^2 dx_1 \, dx_2 = \Omega^{-1} \int |g(\vec{r}_{12})|^2 d^3r_1 \, d^3r_2$$

$$= \int |g(\vec{r}_{12})|^2 d^3r_{12}$$

$$= \Omega^{-1} \sum_{\vec{k}} |g_{\vec{k}}|^2$$

$$= (2\pi)^{-3} \int |g_{\vec{k}}|^2 d^3k = 1 \ . \quad (40)$$

Then ρ_2 will be of the form[18]

$$\rho_2(\vec{r}_1 \sigma_1, \vec{r}_2 \sigma_2; \vec{r}_1' \sigma_1', \vec{r}_2' \sigma_2')$$

$$= \chi(\vec{r}_{12}, \sigma_1 \sigma_2) \chi^*(\vec{r}_{12}', \sigma_1' \sigma_2') + \rho_1(\vec{r}_1 \sigma_1, \vec{r}_1' \sigma_1') \rho_1(\vec{r}_2 \sigma_2, \vec{r}_2' \sigma_2')$$

$$- \rho_1(\vec{r}_1 \sigma_1, \vec{r}_2' \sigma_2') \rho_1(\vec{r}_2 \sigma_2, \vec{r}_1' \sigma_1') \ , \quad (41)$$

where[18]

$$\chi(\vec{r}_{12}, \sigma_1 \sigma_2) = (2n)^{-1}(\delta_{\sigma_1 \uparrow} \delta_{\sigma_2 \downarrow} - \delta_{\sigma_1 \downarrow} \delta_{\sigma_2 \uparrow})(2\pi)^{-3}$$

$$\times \int \frac{q^{1/2} g_{\vec{k}}}{1 + q |g_{\vec{k}}|^2} e^{i\vec{k}\cdot\vec{r}_{12}} d^3k \ , \quad (42)$$

$$\rho_1(\vec{r}_1 \sigma_1, \vec{r}_2 \sigma_2) = (2n)^{-1}(\delta_{\sigma_1 \uparrow} \delta_{\sigma_2 \uparrow} + \delta_{\sigma_1 \downarrow} \delta_{\sigma_2 \downarrow})(2\pi)^{-3}$$

$$\times \int \frac{q |g_{\vec{k}}|^2}{1 + q |g_{\vec{k}}|^2} e^{i\vec{k}\cdot\vec{r}_{12}} d^3k \ ,$$

and the parameter q is determined by the condition that the density of electrons, $2n/\Omega$, has some specified value ρ:

$$2(2\pi)^{-3} \int \frac{q |g_{\vec{k}}|^2}{1 + q |g_{\vec{k}}|^2} d^3k = \rho \ . \quad (43)$$

Upon substitution of (42) and (41) into (21), one can carry out the spin summations and volume integrations trivially, with the result[19]

$$f_{\vec{k}} = n_0 \delta_{\vec{k}0} + f_{\vec{k}}' \ ,$$

$$n_0 = \rho^{-1}(2\pi)^{-3} \int \frac{q |g_{\vec{k}}|^2}{(1 + q |g_{\vec{k}}|^2)^2} d^3k \ ,$$

$$f'_{\vec{k}} = 2\rho^{-1}(2\pi)^{-3} \int \left(\frac{q|g_{\vec{k}-\vec{k}'}|^2}{1+q|g_{\vec{k}-\vec{k}'}|^2}\right)\left(\frac{q|g_{\vec{k}'}|^2}{1+q|g_{\vec{k}'}|^2}\right) d^3k' \quad . \tag{44}$$

As a check on the derivation, we verify the sum rule (14). Making use of the convolution theorem, one has

$$\sum_{\vec{k}} f'_{\vec{k}} = 2\rho^{-1}\Omega(2\pi)^{-6}|\gamma(0)|^2 , \tag{45}$$

where

$$\gamma(\vec{r}) = \int \frac{q|g_{\vec{k}}|^2}{1+q|g_{\vec{k}}|^2} e^{i\vec{k}\cdot\vec{r}} d^3k \quad . \tag{46}$$

Then by (43), we have

$$\sum_{\vec{k}} f'_{\vec{k}} = \tfrac{1}{2}\rho\Omega = n \quad , \tag{47}$$

verifying (14) to order n. The term n_0 is only of order unity, hence negligible,[20] as is the contribution of the term of order n^{-1} which was dropped from $f'_{\vec{k}}$. The fact that n_0 is negligible in the sum rule (14) does not, of course, mean that *all* effects of the ODLRO are negligible. In fact, this ODLRO leads directly to the Meissner effect and superconductivity of the system.[1]

Let us now examine the qualitative behavior of (44). We note first that *the pair momentum distribution function* $f_{\vec{k}}$ *is of order unity* (independent of n and Ω) *for all values of* $\vec{k}$ *including* $\vec{k}=0$. At $\vec{k}=0$ there is a *finite* discontinuity of magnitude n_0, in contrast with the case of true Bose-Einstein condensation, for which the discontinuity would be proportional to n. In spite of the fact that this discontinuity is only of order unity, it is a direct reflection of the ODLRO (1) and hence the superconductivity of the system, since it arises precisely from the separable term $\chi\chi^*$ in (41). In fact, n_0 is just the occupation number[21] of the normalized pair state φ_0 proportional to χ. For $k>0$ there is a weak tail extending up to high momenta, described by the function $f'_{\vec{k}}$ which, being a convolution, has range $\sim 2k_0$ where k_0 is the range of $g_{\vec{k}}$.

In order to make this behavior more explicit it is helpful to consider a simple special case:

$$g_{\vec{k}} = \text{const} \equiv c, \quad k < k_0$$
$$= 0 , \qquad\qquad k > k_0 \quad . \tag{48}$$

Then the normalization condition (43) on q is

$$(k_0^3/3\pi^2)[qc^2/(1+qc^2)] = \rho \quad . \tag{49}$$

Recalling that $3\pi^2\rho = k_F^3$ where $\hbar k_F$ is the Fermi momentum, one finds

$$qc^2 = x/(1-x) , \tag{50}$$

where

$$(k_F/k_0)^3 \equiv x, \quad 0 < x < 1 \quad . \tag{51}$$

The limit $x\to 0$ corresponds to tight binding (zero range of the Cooper-pair relative wave function), whereas $x\to 1$ corresponds to the ideal Fermi gas. The integral (44) for $f'_{\vec{k}}$ is then readily evaluated, being proportional to the overlap volume of two spheres of radius k_0 with separation k. One finds thus

$$f_{\vec{k}} = \tfrac{1}{2}(1-x)\delta_{\vec{k}0} + x[1 - \tfrac{3}{4}(k/k_0) + \tfrac{1}{16}(k/k_0)^3] , \quad k \leq 2k_0$$
$$= 0 , \qquad\qquad\qquad\qquad\qquad\qquad k > 2k_0. \tag{52}$$

An equivalent way of writing (52) is

$$f_{\vec{k}} = \tfrac{1}{2}(1+x)\delta_{\vec{k}0} + x[1 - \tfrac{3}{4}(k/k_0) + \tfrac{1}{16}(k/k_0)^3](1-\delta_{\vec{k}0}) ,$$

$$k \leq 2k_0$$

$$= 0 , \qquad\qquad\qquad k > 2k_0 \quad . \tag{53}$$

This function is plotted in Fig. 1 for the cases $x=\tfrac{1}{2}$ (intermediate between very weak and tight binding of the Cooper pair) and $x=1$ (ideal Fermi gas). As a partial check on (52), one can easily perform the integration, verifying the sum rule (14) to order n.

The qualitative behavior of $f_{\vec{k}}$ for the case of any spherically symmetric $g_{\vec{k}}$ of finite range k_0 [hence any spherically symmetric $g(\vec{r}_{12})$ of finite range k_0^{-1}] will be similar to the special case (52). In the
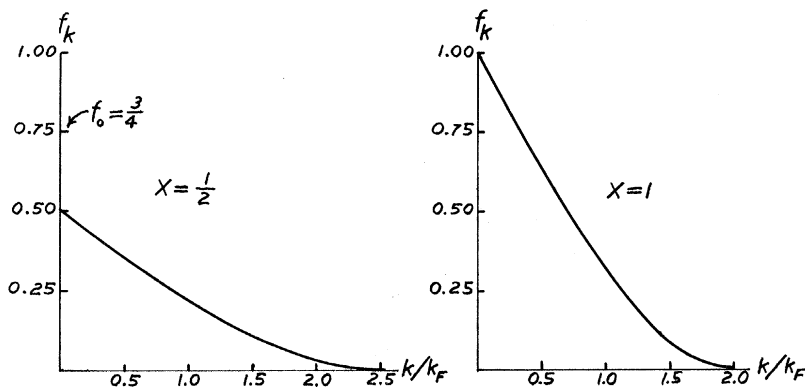

FIG. 1. Pair momentum distribution for a superconducting state with $x=\tfrac{1}{2}$ and for an ideal Fermi gas $(x=1)$.

limit of very tight binding of $g(\vec{r}_{12})$, i.e., $k_0 \gg k_F$, f_0 approaches $\frac{1}{2}$ and $f_{\vec{k}}$ becomes very small for $k > 0$, but its range k_0 becomes very large, since Fourier components of very high momenta are necessary to make a tightly bound Cooper pair. As k_0 drops toward k_F, the discontinuity n_0 in $f_{\vec{k}}$ at the origin decreases, vanishing at $k_0 = k_F$, in which limit the effects of the exclusion principle [antisymmetrization in (38)] become so large that the ODLRO (1) and superconductivity are completely suppressed. The fact that $f_{\vec{k}}$ vanishes for $k > 2k_F$ for the ideal Fermi gas is to be expected, since the maximum momentum of a pair of electrons within the Fermi sea is $2\hbar k_F$, when their momenta nearly coincide just under the Fermi surface.

The behavior of $f_{\vec{k}}$ for a real superconductor is somewhat more complicated, since there is then a quiescent Fermi sea which does not participate in the superconductivity, with all superconducting effects coming from the electrons in a narrow shell of energy width $\hbar\omega$ about the Fermi surface, within which $g_{\vec{k}}$ varies rapidly. For the case of the variational state of the original BCS theory[17] one has[22]

$$q|g_{\vec{k}}|^2 = h_{\vec{k}}(1 - h_{\vec{k}}) , \qquad (54)$$

where

$$h_{\vec{k}} = \frac{1}{2}[1 - \epsilon_{\vec{k}}/(\epsilon_{\vec{k}}^2 + \epsilon_0^2)^{1/2}] ,$$
$$\epsilon_0 = \hbar\omega/\sinh[1/N(0)V] , \qquad (55)$$

$N(0)$ is the density of states at the Fermi surface, V is the strength of the pairing interaction, and $\epsilon_{\vec{k}}$ is the single-electron energy relative to the Fermi surface. Then (44) becomes

$$f_{\vec{k}} = n_0 \delta_{\vec{k}0} + f'_{\vec{k}} ,$$
$$n_0 = \rho^{-1}(2\pi)^{-3} \int h_{\vec{k}}(1 - h_{\vec{k}}) d^3k , \qquad (56)$$
$$f'_{\vec{k}} = 2\rho^{-1}(2\pi)^{-3} \int h_{\vec{k}-\vec{k}'} h_{\vec{k}'} d^3k' .$$

Since $\hbar\omega \ll \epsilon_F$, where ϵ_F is the energy of an electron at the Fermi surface, $h_{\vec{k}}$ is unity inside the Fermi sea, zero outside, and drops rapidly from unity to zero in an energy interval of order $\hbar\omega$ about the Fermi surface. Thus $f'_{\vec{k}}$ differs very little from the pair momentum distribution of an ideal Fermi gas, so that by (52), with $x = 1$ and $k_0 = k_F$,

$$f'_{\vec{k}} \approx 1 - \frac{3}{4}(k/k_F) + \frac{1}{16}(k/k_F)^3 , \quad k \leq 2k_F$$
$$\approx 0 , \quad k > 2k_F . \qquad (57)$$

On the other hand, there will be a small discontinuity $n_0\delta_{\vec{k}0}$ not present in the ideal Fermi gas, and the contribution to the integral (56) for n_0 comes entirely from an energy interval of order $\hbar\omega$ about the Fermi surface. Making the usual approximations of the BCS theory,[17,23] one has

$$n_0 \approx \rho^{-1} N(0) \int_{-\hbar\omega}^{\hbar\omega} \frac{\epsilon_0^2}{4(\epsilon^2 + \epsilon_0^2)} d\epsilon$$
$$= \frac{1}{2}\rho^{-1}N(0)\epsilon_0 \tan^{-1}(\hbar\omega/\epsilon_0) . \qquad (58)$$

Substituting BCS's[17] Eq. (2.40) for ϵ_0, one finds[24]

$$n_0 \approx \frac{1}{2}\rho^{-1}N(0)\hbar\omega \frac{\tan^{-1}\{\sinh[1/N(0)V]\}}{\sinh[1/N(0)V]} . \qquad (59)$$

In the strong- and weak-coupling limits one has

$$n_0 \rightarrow \frac{1}{2}\rho^{-1}N(0)\hbar\omega \quad \text{as } N(0)V \rightarrow \infty$$
$$n_0 \approx \frac{1}{2}\pi\rho^{-1}N(0)\hbar\omega \, e^{-1/N(0)V} , \quad N(0)V \ll 1 . \qquad (60)$$

In the weak-coupling limit $N(0)V \rightarrow 0$, the discontinuity n_0 in $f_{\vec{k}}$ at $\vec{k} = 0$ vanishes exponentially, but it is nonzero for all positive values of $N(0)V$. In the strong-coupling limit $N(0)V \rightarrow \infty$, n_0 is still very small, of the order of the ratio of the volume of the narrow energy shell $\hbar\omega$ to the total volume of the Fermi sea. This is entirely consistent with the fact[17] that superconductivity arises from correlations in the positions of this small fraction of the total number of electrons.

V. ATOMIC MOMENTUM DISTRIBUTION FUNCTION OF LIQUID ^{4}He

The atomic momentum distribution function $f_{\vec{k}}$ of liquid ^{4}He is similar, although more complicated. We shall evaluate it here in an approximation in which the liquid-^{4}He ground state is approximated by the following[4] analog of (38):

$$\psi_0(x_1 \cdots x_{2n} \vec{R}_1 \cdots \vec{R}_n)$$
$$= \mathcal{C} A_{2n}[f_0(x_1 x_2 \vec{R}_1)f_0(x_3 x_4 \vec{R}_2) \cdots f_0(x_{2n-1}x_{2n}\vec{R}_n)] , \qquad (61)$$

where $\mathcal{C}$ is a normalization constant, A_{2n} is the antisymmetrizer with respect to the electron variables $x_1 \cdots x_{2n}$, and f_0 is an orbital approximation to the ground state of a single ^{4}He atom:

$$f_0(x_1 x_2 \vec{R}) = (2\Omega)^{-1/2} u_0(|\vec{r}_1 - \vec{R}|)u_0(|\vec{r}_2 - \vec{R}|)$$
$$\times (\delta_{\sigma_1\dagger}\delta_{\sigma_2\dagger} - \delta_{\sigma_1\dagger}\delta_{\sigma_2\dagger}) . \qquad (62)$$

The density matrix ρ_3 of this state is of the form[4]

$$\rho_3(x_1 x_2 \vec{R}, x'_1 x'_2 \vec{R}')$$
$$= \chi(\vec{r}_1 - \vec{R}, \vec{r}_2 - \vec{R}, \sigma_1\sigma_2)\chi^*(\vec{r}'_1 - \vec{R}', \vec{r}'_2 - \vec{R}', \sigma'_1\sigma'_2)$$
$$+ \rho'_3(x_1 x_2 \vec{R}, x'_1 x'_2 \vec{R}') , \qquad (63)$$

where the term $\chi\chi^*$ leads to ODLRO (4), whereas ρ'_3 approaches zero as the single-atom variables $(\vec{r}_1\vec{r}_2\vec{R})$ are displaced to new positions $(\vec{r}'_1\vec{r}'_2\vec{R}')$ in-

finitely far away from $(\vec{r}_1\vec{r}_2\vec{R})$. Corresponding to this decomposition of ρ_3 there is a decomposition of the atomic momentum distribution function $f_{\vec{k}}$ [Eq. (26)] analogous to (44):

$$f_{\vec{k}} = n_0\delta_{\vec{k}0} + f'_{\vec{k}} ,$$

$$n_0 = n\Omega\delta_{\vec{k}0}\sum_{\sigma_1\sigma_2}\int |\chi(\vec{r}_1, \vec{r}_2, \sigma_1\sigma_2)|^2 d^3r_1 d^3r_2 ,$$
(64)

$$f'_{\vec{k}} = \rho\sum_{\sigma_1\sigma_2}\int \rho'_3(\vec{r}_1\sigma_1, \vec{r}_2\sigma_2, \vec{R}; \vec{r}_1 - \vec{R} + \vec{R}', \sigma_1, \vec{r}_2$$

$$- \vec{R} + \vec{R}', \sigma_2, \vec{R}') e^{-i\vec{k}\cdot(\vec{R} - \vec{R}')}d^3r_1 d^3r_2 d^3R d^3R' .$$

The expression (64) for n_0 approaches the upper limit $\frac{1}{2}n^{-1}$ as the density of the system approaches zero[25]:

$$n_0 \to \tfrac{1}{2}n^{-1} \text{ as } \rho a_0^3 \to 0 .$$
(65)

Here a_0 is the Bohr radius and $\rho = n/\Omega$. Furthermore, n_0 decreases as ρa_0^3 increases.[25] Hence the term $n_0\delta_{\vec{k}0}$ in $f_{\vec{k}}$ is negligible in the thermodynamic limit, i.e., the ODLRO and superfluidity[5] of the system are not directly reflected in the atomic momentum distribution $f_{\vec{k}}$ aside from the infinitesimal term of order n^{-1}.

Next consider the term $f'_{\vec{k}}$ in Eq. (64). In order to evaluate it we need an expression for ρ'_3, the nonseparable term in the full two-atom density matrix[26]

$$\rho_3(\vec{r}_1\sigma_1, \vec{r}_2\sigma_2, \vec{R}; \vec{r}'_1\sigma'_1, \vec{r}'_2\sigma'_2, \vec{R}') = [2n(2n-1)n]^{-1}$$

$$\times\langle\psi_0|\psi^\dagger(\vec{r}'_1\sigma'_1)\psi^\dagger(\vec{r}'_2\sigma'_2)\psi^\dagger(\vec{R}')\psi(\vec{R})\psi(\vec{r}_2\sigma_2)\psi(\vec{r}_1\sigma_1)|\psi_0\rangle .$$
(66)

Here $|\psi_0\rangle$ is the normalized state vector corresponding to (61) and (62), and the ψ and $\psi^\dagger$ operators are the usual quantized-field annihilation and creation operators for electrons and α particles. In order to extract those terms[27] in ρ_3 which have non-negligible contributions to $f'_{\vec{k}}$, it is convenient to make use of the operator identity

$$|\psi_0\rangle\langle\psi_0| + \mathcal{P}_{ex} = 1 ,$$
(67)

where $\mathcal{P}_{ex}$ is the projection operator onto the subspace of n-atom states orthogonal to $|\psi_0\rangle$. Using

the Bose and Fermi commutation and anticommutation relations, one first rewrites the expectation value in (66) in the form

$$\langle\psi_0|\psi^\dagger\psi^\dagger\psi^\dagger\psi\psi\psi|\psi_0\rangle$$

$$= \langle\psi_0|\psi^\dagger(\vec{r}'_1\sigma'_1)\psi(\vec{r}_1\sigma_1)\psi^\dagger(\vec{r}'_2\sigma'_2)\psi(\vec{r}_2\sigma_2)\psi^\dagger(\vec{R}')\psi(\vec{R})|\psi_0\rangle$$

$$- \delta(\vec{r}_1 - \vec{r}'_2)\delta_{\sigma_1\sigma'_2}\langle\psi_0|\psi^\dagger(\vec{r}'_1\sigma'_1)\psi(\vec{r}_2\sigma_2)\psi^\dagger(\vec{R}')\psi(\vec{R})|\psi_0\rangle .$$
(68)

Then, making use of the definitions[28]

$$\rho_1(\vec{r}\sigma, \vec{r}'\sigma') = (2n)^{-1}\langle\psi_0|\psi^\dagger(\vec{r}'\sigma')\psi(\vec{r}\sigma)|\psi_0\rangle ,$$

$$\rho_1(\vec{R}, \vec{R}') = n^{-1}\langle\psi_0|\psi^\dagger(\vec{R}')\psi(\vec{R})|\psi_0\rangle ,$$
(69)

and inserting factors of (67) judiciously inside the top matrix element in (68), one finds

$$\rho_3(\vec{r}_1\sigma_1, \vec{r}_2\sigma_2, \vec{R}; \vec{r}'_1\sigma'_1, \vec{r}'_2\sigma'_2, \vec{R}')$$

$$= [2n/2n-1)]\rho_1(\vec{r}_1\sigma_1, \vec{r}'_1\sigma'_1)$$

$$\times \rho_1(\vec{r}_2\sigma_2, \vec{r}'_2\sigma'_2)\rho_1(\vec{R}, \vec{R}') + \cdots ,$$
(70)

where the terms "$\cdots$" arise from the term in (68) with the prefactor $\delta(\vec{r}_1 - \vec{r}'_2)$ and from matrix elements containing the factor $\mathcal{P}_{ex}$. These terms can be shown to make contributions to $f'_{\vec{k}}$ which are only of orders n^{-1} and smaller, and hence negligible.[29] One notes immediately that the normalization condition

$$\text{Tr}\rho_3 \equiv \sum_{\sigma_1\sigma_2}\int \rho_3(\vec{r}_1\sigma_1, \vec{r}_2\sigma_2, \vec{R}; \vec{r}_1\sigma_1, \vec{r}_2\sigma_2, \vec{R})$$

$$\times d^3r_1 d^3r_2 d^3R = 1$$
(71)

is satisfied apart from negligible terms of order n^{-1}, as a result of the corresponding normalization conditions on the single-electron and single-nucleus density matrices (69).

Noting that the terms exhibited in (70) consist precisely of those terms in ρ'_3 which contribute to $f'_{\vec{k}}$ in the thermodynamic limit ($n \to \infty$ for constant ρ), one finds by (64), in this limit,

$$f'_{\vec{k}} = \rho\sum_{\sigma_1\sigma_2}\int \rho_1(\vec{r}_1, \sigma_1; \vec{r}_1 - \vec{R} + \vec{R}', \sigma_1)\rho_1(\vec{r}_2, \sigma_2; \vec{r}_2 - \vec{R} + \vec{R}', \sigma_2)\rho_1(\vec{R}, \vec{R}') e^{-i\vec{k}\cdot(\vec{R} - \vec{R}')}d^3r_1 d^3r_2 d^3R d^3R'$$

$$= n\Omega^2\sum_{\sigma_1\sigma_2}\int \rho_1(\vec{R}, \sigma_1; 0, \sigma_1)\rho_1(\vec{R}, \sigma_2; 0, \sigma_2)\rho_1(\vec{R}, 0)e^{-i\vec{k}\cdot\vec{R}}d^3R$$

$$= 4n\Omega^2\int [\rho_1(\vec{R}, \sigma; 0, \sigma)]^2\rho_1(\vec{R}, 0)e^{-i\vec{k}\cdot\vec{R}}d^3R .$$
(72)

The second and third inequalities follow from the facts that $\rho_1(\vec{r}, \sigma; \vec{r}', \sigma)$ is spin independent and depends on position only through the displacement

$\vec{r} - \vec{r}'$, and similarly that $\rho_1(\vec{R}, \vec{R}')$ depends only on $\vec{R} - \vec{R}'$. Noting that the Fourier transforms of $\rho_1(\vec{R}, 0)$ and $\rho_1(\vec{r}, \sigma; 0, \sigma)$ are, respectively, the α-

particle and single-electron momentum distribution functions $n_\alpha(\vec{k})$ and $n_e(\vec{k})$:

$$n_\alpha(\vec{k}) = n \int \rho_1(\vec{R}, 0)e^{-i\vec{k}\cdot\vec{R}}d^3R ,$$

$$n_e(\vec{k}) = 4n \int \rho_1(\vec{r}, \sigma; 0, \sigma)e^{-i\vec{k}\cdot\vec{r}}d^3r , \qquad (73)$$

one can write (72) as a convolution:

$$f'_{\vec{k}} = \tfrac{1}{4}\rho^{-2}(2\pi)^{-6}\int n_\alpha(\vec{k} - \vec{k}')n_e(\vec{k}' - \vec{k}'')n_e(\vec{k}'')d^3k'd^3k'' . \qquad (74)$$

To the lowest two orders in ρa_0^3 one has[30]

$$n_\alpha(\vec{k}) = \rho a_0^3 x_{\vec{k}}$$

$$+ \tfrac{2}{3}(\rho a_0^3)^2\left[xx_{\vec{k}} + \tfrac{1}{2}x_{\vec{k}}^2 - (2\pi)^{-3}a_0^3\int z_{\vec{k}-\vec{k}'}z_{\vec{k}'}d^3k'\right] , \quad (75)$$

where $x_{\vec{k}}$ and $z_{\vec{k}}$ are defined by

$$\int w^2(R)e^{-i\vec{k}\cdot\vec{R}}d^3R = x_{\vec{k}}a_0^3 ,$$

$$\int w(R)e^{-i\vec{k}\cdot\vec{R}}d^3R = z_{\vec{k}}a_0^3 \qquad (76)$$

and $w(R)$ is the overlap integral between atomic wave functions:

$$w(R) = \int u_0^*(r)u_0(|\vec{r}+\vec{R}|)d^3r . \qquad (77)$$

Similarly, $n_e(\vec{k})$ can be shown[4] to be, in the same approximation,

$$n_e(\vec{k}) = 2\rho a_0^3 z_{\vec{k}} + \tfrac{2}{3}(\rho a_0^3)^2 z_{\vec{k}}(x - y - z_{\vec{k}} + t_{\vec{k}}) , \qquad (78)$$

where

$$\int w^2(R)d^3R = xa_0^3 , \quad \int w^4(R)d^3R = ya_0^3 ,$$

$$\int w^3(R)e^{-i\vec{k}\cdot\vec{R}}d^3R = t_{\vec{k}}a_0^3 . \qquad (79)$$

Upon substituting (75) and (78) into (74) one finds

$$f'_{\vec{k}} = (2\pi)^{-6}\rho a_0^3\int x_{\vec{k}-\vec{k}'}z_{\vec{k}'-\vec{k}''}z_{\vec{k}''}d^3q'd^3q'' + O((\rho a_0^3)^2) , \qquad (80)$$

where $\vec{q}' = \vec{k}'a_0$, $\vec{q}'' = \vec{k}''a_0$; it should be noted that $x_{\vec{k}}$ and $z_{\vec{k}}$ have range of order a_0^{-1} in $\vec{k}$ space, hence range of order unity in $\vec{q}$ space. The function (80) is of order of magnitude ρa_0^3 and range a_0^{-1} for $\rho a_0^3 \ll 1$. The normalization condition can be verified directly from (72) and the fact that $\rho_1(0,\sigma;0,\sigma)$ $= \tfrac{1}{2}\Omega^{-1}$, whereas $\rho_1(0, 0) = \Omega^{-1}$ as a result of translational invariance and the fact that ρ_1 is normalized to unity.

Although (64), (65), and (80) have been derived for the special case of the approximate liquid-^{4}He ground state (61), one expects the situation to be similar for the true ground state, i.e., one expects that $f_{\vec{k}}$ will be a smooth function of order of magnitude ρa_0^3 and range[31] $\sim 3a_0^{-1}$, with no trace (except for the term $n_0\delta_{\vec{k}0}$ or order n^{-1}) of the singular behavior characteristic of Bose-Einstein condensation. This spreading of the atomic momentum distribution is not a result of the internal motion of the electrons and nuclei within the atoms, but

instead results from interatomic electron exchange.[32] In fact, it is easy to show[33] that for a single ^{4}He atom ($n = 1$) in its ground state $f_0(x_1x_2\vec{R})$, the atomic momentum distribution function is just $f_{\vec{k}} = \delta_{\vec{k}0}$. More generally, for an unsymmetrized product

$$f_0(x_1x_2\vec{R}_1)\cdots f_0(x_{2n-1}x_{2n}\vec{R}_n) , \qquad (81)$$

ρ_3 is the same[33] as for the case $n = 1$, and hence (26) gives by the same argument[33]

$$f_{\vec{k}} = n\,\delta_{\vec{k}0} \quad \text{(exclusion principle neglected).}$$

However, the simple product (81) is incompatible with the exclusion principle, which can be satisfied by antisymmetrization as in (61). The profound difference between Eq. (82) and Eqs. (64), (65), and (80) for a macroscopic system ($n \sim 10^{23}$) is thus seen to arise directly from the effects of electron exchange. It seems that the usual approximation of simulating such electron exchange effects by a phenomenological hard-core interatomic potential breaks down in the case of those many-atom wave functions in which exchange plays a major role, as is the case for (61) and presumably also for the true low-lying states of liquid ^{4}He.

VI. DISCUSSION

It has been shown that for a system of electrons, the momentum distribution function $f_{\vec{k}}$ of electron pairs is very different from what it would be if the electron pairs could validly be treated as bosons. The electron exchange effects act in such a way as to prevent f_0 from acquiring a macroscopic (order n) value characteristic of true Bose-Einstein condensation.[34] In a superconducting state with ODLRO of ρ_2, $f_{\vec{k}}$ does have singular behavior at $\vec{k} = 0$, but the singularity consists of only a *finite* (independent of n) discontinuity, and exchange and the exclusion principle also manifest themselves in a spreading of $f_{\vec{k}}$ for $\vec{k} \neq 0$ by an amount not less than $2k_F$, where k_F is the Fermi wave vector of an ideal electron gas of the same density.

Similarly, for liquid ^{4}He it has been shown that electron exchange effects prevent Bose-Einstein condensation of ^{4}He atoms in momentum space, in the sense that $f_{\vec{k}}$ has no macroscopic singular term at $\vec{k} = 0$. These exchange effects also cause a spreading in $f_{\vec{k}}$ for $\vec{k} \neq 0$ by an amount of order $3a_0^{-1}$; where a_0 is the Bohr radius ($\approx$ the radius of the ^{4}He atom).

In order to answer the question of to what extent these effects arise merely from exchange and to what extent they arise more specifically from the exclusion principle (*anti*symmetry rather than symmetry under exchange) it is desirable to compare these results with a fictitious model of pairs of bosons rather than pairs of electrons. This is

done in the Appendix. It is found that in that case exchange still has profound effects on $f_{\vec{k}}$, but that, in contradistinction to the case of electron pairs, the boson pair occupation numbers increase to very large values (being limited only by the inequality $f_{\vec{k}} \leq n$) in the neighborhood of $\vec{k} = 0$ as the range of the pair wave function becomes infinite. It therefore follows that the large degree of broadening of $f_{\vec{k}}$ in systems of electrons and in liquid ^{4}He is a direct result of the exclusion principle acting in many-body states with strong spatial overlap.

Our results on the qualitative behavior of $f_{\vec{k}}$ for liquid ^{4}He have important implications for the interpretation of experiments on scattering of high-energy neutrons by liquid ^{4}He. As shall be shown elsewhere, the *atomic* impulse approximation (in which the whole atom, rather than merely its nucleus, recoils freely) leads to the prediction of strong peaking of the scattering cross section analogous to that occurring in boson models. However, the magnitude of the peak has no simple relation to the atomic momentum distribution function $f_{\vec{k}}$, so that such peaking cannot be taken as evidence for Bose-Einstein condensation in real liquid ^{4}He. Nevertheless, it is related to the ODLRO of ρ_3 responsible for the superfluidity of the system.

APPENDIX: MOMENTUM DISTRIBUTION OF PAIRS OF BOSONS

One way of distinguishing the effects of exchange from those of the exclusion principle (*anti*symmetry under electron exchange) is to study the boson pair occupation numbers of a Bose analog of the BCS states studied in Sec. IV. Thus we consider a system of $2n$ identical spinless bosons in a many-body state analogous to (38):

$$\psi_0(\vec{r}_1 \cdots \vec{r}_{2n}) = \mathcal{C} S_{2n}[g(\vec{r}_{12}) g(\vec{r}_{34}) \cdots g(\vec{r}_{2n-1,2n})], \quad (A1)$$

where $\vec{r}_{ij} = \vec{r}_i - \vec{r}_j$ and S_{2n} is the symmetrizer with respect to the boson positions $\vec{r}_1 \cdots \vec{r}_{2n}$. The quantized-field representation for (A1) is

$$|\psi_0(2n)\rangle = [2^n/(2n)!]^{1/2} \mathcal{C} A_0^\dagger |0\rangle , \quad (A2)$$

where $A_0^\dagger$ is the boson pair creation operator

$$A_0^\dagger = 2^{-1/2} \int d^3 r_1 d^3 r_2 g(\vec{r}_{12}) \psi^\dagger(\vec{r}_1) \psi^\dagger(\vec{r}_2) . \quad (A3)$$

As in the case of (38), the properties of the state (A2) are most easily derived asymptotically for $n \to \infty$ by realizing that (A2) is the $2n$-boson projection of the state

$$|\psi_0\rangle = U|0\rangle, \quad U = \exp[c(A_0^\dagger - A_0)], \quad (A4)$$

where c is a nonzero real c number. In fact, the pair occupation numbers of the state (A2) are

asymptotically equal to those of (A4) provided that c is chosen so that

$$\langle \psi_0 | N | \psi_0 \rangle = \langle 0 | U^{-1} N U | 0 \rangle = 2n , \quad (A5)$$

where N is the boson number operator

$$N = \int d^3 r \, \psi^\dagger(\vec{r}) \psi(\vec{r}) . \quad (A6)$$

Introducing the Fourier transform $g_{\vec{k}}$ of $g(\vec{r}_{12})$ and the plane-wave boson annihilation and creation operators $a_{\vec{k}}$ and $a_{\vec{k}}^\dagger$ through

$$g(\vec{r}_{12}) = \Omega^{-1} \sum_{\vec{k}} g_{\vec{k}} \, e^{i\vec{k}\cdot\vec{r}_{12}} , \quad (A7)$$

$$\psi(\vec{r}) = \Omega^{-1/2} \sum_{\vec{k}} e^{i\vec{k}\cdot\vec{r}} a_{\vec{k}} ,$$

one can write (A4) as[35]

$$U = \exp[2^{-1/2} c \sum_{\vec{k}} g_{\vec{k}} (a_{\vec{k}}^\dagger a_{-\vec{k}}^\dagger - a_{-\vec{k}} a_{\vec{k}})] . \quad (A8)$$

The unitary transformation effected by (A8) is a Bogoliubov transformation

$$U^{-1} a_{\vec{k}} U = (a_{\vec{k}} + \varphi_{\vec{k}} a_{-\vec{k}}^\dagger)/(1 - \varphi_{\vec{k}}^2)^{1/2} , \quad (A9)$$

with[36]

$$\varphi_{\vec{k}} = \tanh(2^{1/2} c \, g_{\vec{k}}) . \quad (A10)$$

In terms of $\varphi_{\vec{k}}$, the constraint (A5) is

$$\sum_{\vec{k}} \varphi_{\vec{k}}^2 / (1 - \varphi_{\vec{k}}^2) = 2n . \quad (A11)$$

The two-particle density matrix of the state (A4) is, with (A8)–(A10),

$$\rho_2(\vec{r}_1 \vec{r}_2, \vec{r}_1' \vec{r}_2')$$
$$= [2n(2n-1)]^{-1} \langle \psi_0 | \psi^\dagger(\vec{r}_1') \psi^\dagger(\vec{r}_2') \psi(\vec{r}_2) \psi(\vec{r}_1) | \psi_0 \rangle$$
$$= \chi(\vec{r}_{12}) \chi^*(\vec{r}_{12}') + [2n/(2n-1)][\rho_1(\vec{r}_1, \vec{r}_1') \rho_1(\vec{r}_2, \vec{r}_2')$$
$$+ \rho_1(\vec{r}_1, \vec{r}_2') \rho_1(\vec{r}_2, \vec{r}_1')] , \quad (A12)$$

in analogy with (41), where

$$\chi(\vec{r}_{12}) = [2n(2n-1)]^{-1/2} \Omega^{-1} \sum_{\vec{k}} [\varphi_{\vec{k}}/(1 - \varphi_{\vec{k}}^2)] e^{i\vec{k}\cdot\vec{r}_{12}}$$
$$(A13)$$

and ρ_1 is the single-particle density matrix

$$\rho_1(\vec{r}, \vec{r}') = (2n)^{-1} \langle \psi_0 | \psi^\dagger(\vec{r}') \psi(\vec{r}) | \psi_0 \rangle$$
$$= (2n)^{-1} \Omega^{-1} \sum_{\vec{k}} [\varphi_{\vec{k}}^2/(1 - \varphi_{\vec{k}}^2)] e^{i\vec{k}\cdot(\vec{r}-\vec{r}')} . \quad (A14)$$

It is not difficult to show that the formula (21) for the electron pair momentum distribution also holds for the momentum distribution of boson pairs, provided that the spin arguments and spin summations are omitted. Then in analogy with (44) one has, dropping negligible terms of order n^{-1},

$$f_{\vec{k}} = n_0 \delta_{\vec{k}0} + f_{\vec{k}}' ,$$

$$n_0 = \tfrac{1}{2} \rho^{-1} (2\pi)^{-3} \int [\varphi_{\vec{k}}/(1 - \varphi_{\vec{k}}^2)]^2 d^3 k , \quad (A15)$$

$$f_{\vec{k}}' = \tfrac{1}{2} \rho^{-1} (2\pi)^{-3} \int \left(\frac{\varphi_{\vec{k}-\vec{k}'}^2}{1 - \varphi_{\vec{k}-\vec{k}'}^2} \right) \left(\frac{\varphi_{\vec{k}'}^2}{1 - \varphi_{\vec{k}'}^2} \right) d^3 k' .$$

In order to make the behavior of $f_{\vec{k}}$ more explicit

it is helpful to consider a special case analogous to (48):

$$\varphi_{\vec{k}} = \text{const} \equiv \varphi_0, \quad k < k_0$$
$$= 0, \qquad\qquad k > k_0 . \tag{A16}$$

Then it is not difficult to show that

$$n_0 = \tfrac{1}{2}(1+x)\,\delta_{\vec{k}0} ,$$

$$f'_{\vec{k}} = \tfrac{1}{2}x[1 - \tfrac{3}{4}(k/k_0) + \tfrac{1}{16}(k/k_0)^3], \quad k \le 2k_0$$

$$= 0, \qquad\qquad\qquad k > 2k_0 \tag{A17}$$

in analogy with (52), where the parameter x, which enters via (A11), is defined as

$$x = 6\pi^2 \rho/k_0^3 . \tag{A18}$$

It is clear from (A7) and (A10) that the magnitude of x is a measure of the range of the relative pair wave function $g(\vec{r}_{12})$, i.e., $x \to 0$ as the range of $g(\vec{r}_{12})$ goes to zero and $x \to \infty$ as the range of $g(\vec{r}_{12})$ becomes infinite. In contrast with the electron

case (52), for which $f_{\vec{k}}$ is everywhere $\le 1/2$, the boson pair momentum distribution function (A17) becomes very large at very low momenta ($< k_0$) as $x \to \infty$ ($k_0 \to 0$). Thus the effects of exchange are less extreme in the boson case, the limitation $f_{\vec{k}} \le \tfrac{1}{2}$ in the electron case being a result of the exclusion principle. Nevertheless, the exchange effects in the boson case are sufficient to prevent true Bose condensation of boson pairs ($f_{\vec{k}}$ of order n) so long as the range of g is finite (more precisely, volume independent). Macroscopic values of $f_{\vec{k}}$ only occur if $g(\vec{r}_{12})$ is a continuum state (e.g., $g = \text{const}$, in which case $f_{\vec{k}} = n\delta_{\vec{k}0}$) in which case not only ρ_2 but also ρ_1 has ODLRO,[1] and Bose condensation is exhibited already by the *single*-boson momentum distribution. Although these conclusions have been reached here through study of the special case (A16), it is clear from (A15) that they remain qualitatively valid for any reasonable pair relative wave function $g(\vec{r}_{12})$.

[1]C. N. Yang, Rev. Mod. Phys. **34**, 694 (1962).

[2]M. D. Girardeau, Phys. Letters **29A**, 64 (1969).

[3]M. D. Girardeau, J. Math. Phys. **11**, 684 (1970).

[4]M. D. Girardeau, J. Math. Phys. **11**, 1845 (1970).

[5]W. Kohn and D. Sherrington, Rev. Mod. Phys. **42**, 1 (1970), in particular, Sec. 6.

[6]The antisymmetrization on the right-hand side of (9) follows from the fact that the φ_α are antisymmetric in x_1 and x_2, and hence only complete in the subspace of antisymmetric functions.

[7]F. Sasaki, Upsala University Quantum Chemistry Group Report No. 77, 1962 (unpublished); Phys. Rev. **138**, B1338 (1965).

[8]A. J. Coleman, Rev. Mod. Phys. **35**, 668 (1963), Sec. 7.

[9]That is, for $n \to \infty$, $n_\alpha \le \tfrac{1}{2}$ for all α.

[10]This restriction is more a matter of convenience than necessity. Even for box-enclosure boundary conditions, the single-particle densities are constant except within a microscopic distance (the "healing length") of the walls. Such a more realistic case could be discussed in analogy with the case of periodic boundary conditions, at the expense of introducing irrelevant complications.

[11]This work was motivated by Peter E. Parks's asking me this question with some insistence.

[12]At this point we are assuming that the state χ has momentum zero; if it has momentum $\hbar\vec{q}$, the discontinuity of $f_{\vec{k}}$ is at $\vec{k} = \vec{q}$.

[13]Substitution of (24) into (25) gives a closure relation for the $u_\nu(\vec{r}_1 \sigma_1; \vec{r}_2\sigma_2; \vec{R})$ which involves *both* electron and nuclear variables.

[14]The reason for this choice of normalization is that the relation between $\bar{\rho}_1$ and the momentum distribution function will then be found to be the same as for the case of structureless bosons.

[15]This is easily seen by making the substitutions $x \to \vec{R}$, $x' \to \vec{R}'$, $\varphi_{\vec{k}}(x) \to \Omega^{-1/2}e^{i\vec{k}\cdot\vec{R}}$ in (7) and noting that $\rho_1(\vec{R}, \vec{R}')$ depends only on $\vec{R}' - \vec{R} \equiv \vec{a}$.

[16]A. J. Coleman, J. Math. Phys. **6**, 1425 (1965).

[17]J. Bardeen, L. N. Cooper, and J. R. Schrieffer, Phys. Rev. **108**, 1175 (1957). The fact that the $2n$-electron projection of a BCS state is of the general form (38) was first pointed out by K. Nakamura, Progr. Theoret. Phys. (Kyoto) **21**, 713 (1959).

[18]See Secs. 5 and 6 of Ref. 3.

[19]A negligible term of order n^{-1} has been dropped in the expression for $f'_{\vec{k}}$.

[20]The expressions (41) and (42) are only valid asymptotically as $n \to \infty$.

[21]See Eq. (80) of Ref. 3. Excited pair states make no contribution to the term in $f_{\vec{k}}$ which arises from $\chi\chi^*$, since these excited states are orthogonal to χ.

[22]See Eq. (105) of Ref. 3.

[23]In addition to the approximation $(2\pi)^{-3}\int \cdots d^3k \approx N(0)\int \cdots d\epsilon$, BCS cut off the energy integrations at $\epsilon = \pm\hbar\omega$. We shall follow the same procedure here.

[24]This differs from Eq. (111) of Ref. 3, since there we only took the electrons within the energy shell $\hbar\omega$ into account in determining the electron density according to (43). Here we take all the electrons into account; then (43) is satisfied by observing that $h_{\vec{k}}$ is unity for $k < k_F$ and zero for $k > k_F$.

[25]See Sec. 6 of Ref. 4.

[26]See Eq. (41) of Ref. 4, in which ρ_3 is called D_3.

[27]The approximate expressions in Appendix B of Ref. 4 are not sufficiently accurate for this purpose; in fact, they do not contain the terms which are important in verifying the normalization condition $\text{Tr}\rho_3 = 1$.

[28]The prefactors in (69) arise from the normalization conditions $\text{Tr}\rho_1 = 1$.

[29]The separable term $\chi\chi^*$ in ρ_3, which leads to ODLRO (4) and superfluidity of the system (Ref. 5), is contained in the terms "$\cdots$" in (70), as are the terms involving ρ_1 but differing from the terms exhibited by electron exchange. However, these terms make no contribution to $f_{\vec{k}}$ in the limit $n \to \infty$.

[30]See Eqs. (28) and (29) of Ref. 4.

[31]The range $\sim 3a_0^{-1}$ arises from the convolution structure of (74) and the fact that n_α and n_e have range $\sim a_0^{-1}$.

[32]In the true ground state there is further spreading due to interatomic Coulomb interactions (e.g., the van der Waals interaction).

[33]In this case (5) reduces to $\rho_3(x_1 x_2 \vec{R}, \; x_1' x_2' \; \vec{R}') = f_0(x_1 x_2 \vec{R})$ $\times f_{\vec{\xi}} (x_1' x_2' \; \vec{R}')$, and the desired result follows immediately from (26) upon noting that f_0 is translationally invariant and normalized.

[34]In fact it is easy to show, in analogy with the derivation of (82), that if one replaces (38) by an unsymmetrized product $g(x_1 x_2)g(x_3 x_4) \cdots g(x_{2n-1} x_{2n})$, then (21) implies

$f_{\vec{\xi}} = n \delta_{\vec{k}0}$ if g is any normalized and translationally invariant two-electron state. However, this result is incompatible with the exclusion principle.

[35]We assume, without essential loss of generality, that $g_{\vec{k}}$ is real and an even function of $\vec{k}$.

[36]See, e. g., M. Girardeau and R. Arnowitt, Phys. Rev. 113, 755 (1959).

Influence of a Magnetic Field on the Transport Coefficients of Oxygen Gas: Anomalies Associated with the $\sigma = 0$ Multiplets*

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The transport coefficients of $^3\Sigma$ molecular oxygen in magnetic fields show large deviations from an H/p law, even at moderate pressures and fields. This complex behavior is explained by the effect of a quadratic Zeeman splitting of the $\sigma = 0$ multiplets, superimposed on the normal linear splitting. Because the normal linear splitting is very small for $\sigma = 0$, the anomalous effects occur at fields far below the true Paschen-Back region. Collisionally uncoupled model calculations give the transverse viscosity coefficients in quite detailed agreement with experiment. The distinct behavior of the single- and double-frequency viscosity coefficients reflects distinct selections from the internal-state frequency spectrum, determined by weight factors $|Y^{2\mu}(\theta, \phi)|^2$ in the orientation of $\vec{J}$. The anomalous behavior of the even coefficients is predicted to be quite complex. In particular the H/p curves of η_1^* at about 4 Torr should show three steps, instead of the usual two, and the behavior of $\lambda_\parallel$ should be similar.

I. INTRODUCTION

The effect of a magnetic field on the thermal conductivity and viscosity of dilute gases is commonly a function of the ratio H/p of the field strength to the pressure. According to the picture of Gorter,[1] the explanation of this H/p dependence is that the effects are functions of the product $\omega\tau$ of a precession frequency, proportional to the field, and a relaxation time, of the order of the time between collisions and proportional to $1/p$. Kikoin et al.,[2] however, found very large deviations from H/p behavior for one of the transverse viscosity coefficients of $^3\Sigma$ oxygen. Recent very precise measurements of Hulsman et al.[3] not only confirm Kikoin's result, but show that the other transverse coefficient is also anomalous, and furthermore that the behavior of the two coefficients is quite distinct. In both H/p plots the shoulder which occurs at lower H/p behaves normally at constant pressures up to one atmosphere. This feature is associated[4,5] with molecules in states belonging to multiplets having total angular momentum $J = N \pm 1$, where N is the [Hund's case (b)] rotational quantum number. Alternatively, these multiplets may be labeled by $\sigma = \pm 1$, where $\sigma = J - N$ is the spin projection on $\vec{J}$ in the classical (large N) limit. The peak occurring

at higher H/p however, and which is associated with multiplets having $\sigma = 0$ $(J = N)$, disappears with increasing pressure. Significant cutting off on the high-field side of this peak occurs at pressures of only a few Torr, and one of the viscosity coefficients, but not the other, changes sign.

Deviations from H/p behavior can likewise be seen in the even thermal-conductivity and viscosity coefficients measured by Kikoin et al.,[2] Korving et al.,[6] and Hermans et al.[7] at room temperature, and indeed—though for higher pressures—in the early measurements of Senftleben and Piezner[8] (see Hermans[7] for a comparison). The very pronounced scatter of the points near saturation is shown clearly in Korving's[6] H/p plots on "probability" paper.

It is the object of this paper to give an explanation of this behavior. The quantitative theory is given for the viscosity only, but the qualitative picture applies, with minor modifications, to the thermal conductivity also.

II. VISCOSITY THEORY FOR SMALL DEVIATIONS FROM LOW-FIELD STATES

Deviations from H/p behavior in the paramagnetic Senftleben effects usually reflect the mixing by the field of states belonging to different zero-field multiplets (the Paschen-Back effect), and in par-