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Comments on the Theory of Superconductivity.

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Summary. — Some ideas of the new theory of Bardeen, Cooper and Schrieffer are expressed in a more transparent form. New collective fermion variables are introduced which are linear combinations of creation and annihilation operators of electrons, and describe elementary excitations. They lead to a simple classification of excited states and a great simplification in the calculations. The structure of the excitation spectrum is investigated without equating the matrix element of the interaction potential to a constant at an early stage, and new relationships and equations are derived. The temperature dependent problem is described by means of a statistical operator, and its relationship to that of the grand canonical ensemble is established. Simple new relationships are obtained for the correlation function.

1. - Introduction.

In a recent paper BARDEEN, COOPER and SCHRIEFFER [1] have developed a new approach to the theory of superconductivity. Their model assumes a simple attractive two body interaction between the electrons which expresses the effect of the interactions through the phonon field and of screened Coulomb interactions. It gives a good quantitative account of the thermodynamic and electromagnetic properties of superconductors.

The aim of the present paper is to simplify the conceptual background of the new theory and to obtain a clearer insight into the ideas involved. Improved mathematical tools are introduced which are related to simple physical concepts, and some simple new relationships are brought out.

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[1] J. BARDEEN, L. N. COOPER and J. R. SCHRIEFFER: *Phys. Rev.*, **108**, 1175 (1957).

The important problem of obtaining the two body forces from the phonon interaction will not be touched here, so that the starting point will be a theory with a Hamiltonian containing two body interactions. It will be pointed out that the trial ground state vector introduced by BARDEEN, COOPER and SCHRIEFFER which expresses long range correlations between particles of opposite spin, is related in a natural way to new collective fermion variables which lead to a simple description of the excited states. The calculations are much simplified by the introduction of the new variables, and it can be hoped that they will be of help also in making further progress in the theory.

The structure of the excitation spectrum will then be investigated by expressing the Hamiltonian in terms of the new variables. The error involved by neglecting a non-diagonal part of the Hamiltonian will not be discussed, but the new expressions obtained also make the mathematical formulation of this problem easier. Various relationships will be established without replacing the matrix element of the interaction by an average value at an early stage. This brings out more clearly those features of the theory which are independent of the assumption of a constant matrix element. Equations are obtained for the investigation of more general interactions.

To describe temperature dependent phenomena, BARDEEN, COOPER and SCHRIEFFER formulate a variational problem with two independent functions to be varied. One describes the elementary excitations; the other, a statistically independent distribution of these excitations. This problem will be expressed here in terms of a statistical operator and it will be pointed out that this can be considered as the trial approximation for the statistical operator of the grand ensemble.

Finally, simple expressions will be obtained for the correlation functions which make the interpretation of the relationships of the theory more transparent.

2. – Collective fermion variables.

The Hamiltonian

$$H = T + V \tag{1a}$$

of the theory is the sum of the Bloch energy

$$T = E_0 + \sum_{k,\sigma} \varepsilon_k a_{k\sigma} a^*_{k\sigma} , \tag{1b}$$

$$E_0 = -2 \sum_{k<k_F} \varepsilon_k , \tag{1c}$$

and of a non-local two-body interaction energy

$$V = \tfrac{1}{2} \sum_{\substack{k,k',q \\ \sigma,\sigma'}} V_{k'} a_{k\sigma} a_{q-k,\sigma'} a^*_{q-k',\sigma'} a^*_{k'\sigma} . \tag{1d}$$

The energy ε_k of a Bloch electron with momentum k is counted from the Fermi level. The index σ stands for a definite $\uparrow$ or $\downarrow$ spin direction. The index $\varkappa$ will be used to indicate both momentum k and spin σ, whenever this simplifies the notation. In this case, $-\varkappa$ will stand for opposite momentum and opposite spin. Creation operators are denoted by $a_\varkappa$ and annihilation operators by $a^*_\varkappa$. (This is in accordance with Dirac's notation [2] and with the geometric interpretation [3] of these operators, unstarred quantities representing the unit vectors and the stars being reserved for the basis elements of the dual vectors). It will be found convenient to write $a_{\varkappa_1} \ldots a_{\varkappa_j}$ for the state vector with electrons in the one particle states $\varkappa_1, \ldots, \varkappa_j$, replacing by unity the state $|0\rangle$ in which no particles are present.

The trial ground state vector of Bardeen, Cooper and Schrieffer can be written as a product of commuting factors in the form

$$\Phi_0 = \prod_\varkappa \frac{1 + g_\varkappa a_\varkappa a_{-\varkappa}}{(1 + |g_\varkappa|^2)^{\frac{1}{2}}} , \tag{2a}$$

with

$$g_{k\uparrow} = g_{-k\uparrow} = g_k = -g_{k\downarrow} = -g_{-k\downarrow} . \tag{2b}$$

This corresponds to an indeterminate number of particles, but with a sharp peak in the probability distribution of the particle number for the actual values of $g_\varkappa$. The choice of such a state vector exploits the advantages of the fact that the Hamiltonian (1*a*, *b*, *d*) is valid for any number of particles and the quantum field equations of the problem are independent of the special value of the number operator $N = \sum_\varkappa a_\varkappa a^*_\varkappa$. The projection operator of the state (2*a*) can be considered as a trial approximation for the statistical operator of the grand ensemble in the limit of temperature $T = 0$.

Separating the state vectors and operators by a stroke, whenever this seems convenient, equations can be written like $a^*_\varkappa | a_\varkappa a_{\varkappa'} = a_{\varkappa'}$, $a^*_\varkappa | 1 = 0$ or $a_\varkappa | 1 = a_\varkappa$. One obtains the simple relations

$$a^*_\varkappa | (1 + g_\varkappa a_\varkappa a_{-\varkappa}) = g_\varkappa a_{-\varkappa} , \tag{2c}$$

$$a_{-\varkappa} | (1 + g_\varkappa a_\varkappa a_{-\varkappa}) = a_{-\varkappa} . \tag{2d}$$

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[2] P. A. M. DIRAC: *The Principles of Quantum Mechanics*, 3rd ed. (Oxford, 1947), p. 249.

[3] J. G. VALATIN: *Journ. Phys.*, **12**, 131 (1951).

Accordingly, it is rather natural to introduce the new variables

$$(3a) \qquad \xi_\varkappa^* = \frac{a_\varkappa^* - g_\varkappa a_{-\varkappa}}{(1+|g_\varkappa|^2)^{\frac{1}{2}}}, \qquad \xi_\varkappa = \frac{a_\varkappa - g_\varkappa^* a_{-\varkappa}^*}{(1+|g_\varkappa|^2)^{\frac{1}{2}}},$$

since from $(2a, c, d)$ one sees immediately that

$$(3b) \qquad \xi_\varkappa^* | \Phi_0 = 0 \qquad \text{for all } \varkappa.$$

The anticommutation relations of $a_\varkappa$, $a_\varkappa^*$ give with $(3a)$

$$(3c) \qquad \xi_{\varkappa'}^* \xi_\varkappa + \xi_\varkappa \xi_{\varkappa'}^* = \delta_{\varkappa\varkappa'}, \quad \xi_\varkappa \xi_{\varkappa'} + \xi_{\varkappa'} \xi_\varkappa = 0, \quad \xi_{\varkappa'}^* \xi_\varkappa^* + \xi_\varkappa^* \xi_{\varkappa'}^* = 0.$$

The equations $(3a)$ represent a canonical transformation, and the products

$$(3d) \qquad \Phi_{\varkappa_1 \dots \varkappa_j} = \xi_{\varkappa_1} \dots \xi_{\varkappa_j} \Phi_0$$

form a complete orthonormal set of state vectors.

From

$$(4a) \qquad \xi_\varkappa | \frac{1 + g_\varkappa a_\varkappa a_{-\varkappa}}{(1+|g_\varkappa|^2)^{\frac{1}{2}}} = a_\varkappa,$$

$$(4b) \qquad \xi_\varkappa \xi_{-\varkappa} | \frac{1 + g_\varkappa a_\varkappa a_{-\varkappa}}{(1+|g_\varkappa|^2)^{\frac{1}{2}}} = \frac{a_\varkappa a_{-\varkappa} - g_\varkappa^*}{(1+|g_\varkappa|^2)^{\frac{1}{2}}},$$

one can see that the states

$$\xi_\varkappa \Phi_0 \qquad \text{and} \qquad \xi_\varkappa \xi_{-\varkappa} \Phi_0$$

are the excited states of Bardeen, Cooper and Schrieffer with a « single particle » and a « real pair » excited. They appear here on the same footing, and the set of products $\xi_{\varkappa_1} \dots \xi_{\varkappa_j} \Phi_0$ gives a natural description of their system of excited states. As seen from $(4a)$, though the state $\xi_\varkappa \Phi_0$ contains an explicit particle creation operator factor $a_\varkappa$, at the same time a « virtual pair » factor $(1+|g_\varkappa|^2)^{-\frac{1}{2}}(1+g_\varkappa a_\varkappa a_{-\varkappa})$ of Φ_0 is missing. The operation of $\xi_\varkappa$ on Φ_0 corresponds to a collective excitation of all the particles; $\xi_\varkappa$ creates an elementary excitation, or a « quasi-particle », with the properties of a fermion (+).

(+) Analogous phonon variables for a boson system were introduced by BOGOLUBOV (4) in 1947. At the time of writing this paper a preprint of a recent work by BOGOLUBOV arrived in which essentially the same fermion variables as given here are used independently in investigating the interacting electron-phonon system.

(4) N. BOGOLUBOV: *Journ. Phys. U.S.S.R.*, **11**, 23 (1947).

From (3a) one can write

$$a_\varkappa = \frac{\xi_\varkappa + g_\varkappa^* \xi_{-\varkappa}^*}{(1+|g_\varkappa|^2)^{\frac{1}{2}}}, \qquad a_\varkappa^* = \frac{\xi_\varkappa^* + g_\varkappa \xi_{-\varkappa}}{(1+|g_\varkappa|^2)^{\frac{1}{2}}}, \tag{5}$$

and any operator expressed in terms of $a_\varkappa$, $a_\varkappa^*$ can be transformed into an expression in the collective variables $\xi_\varkappa$, $\xi_\varkappa^*$. Ordering the factors in each term in such a way that creation operators $\xi_\varkappa$ stand at the left of the annihilation operators $\xi_\varkappa^*$, the constant term of the expression represents the expectation value of the operator in the ground state Φ_0.

For the number of particles in state $\varkappa$,

$$n_\varkappa = a_\varkappa a_\varkappa^* \tag{6a}$$

one obtains

$$n_\varkappa = \frac{(\xi_\varkappa + g_\varkappa^* \xi_{-\varkappa}^*)(\xi_\varkappa^* + g_\varkappa \xi_{-\varkappa})}{1+|g_\varkappa|^2}. \tag{6b}$$

The ground state expectation value

$$\bar{n}_\varkappa = h_\varkappa \tag{6c}$$

results from ordering the term with $\xi_{-\varkappa}^* \xi_{-\varkappa}$, and one obtains

$$h_\varkappa = \frac{|g_\varkappa|^2}{1+|g_\varkappa|^2}. \tag{6d}$$

From (2b) one concludes that

$$h_{k\uparrow} = h_{k\downarrow} = h_{-k\uparrow} = h_{-k\downarrow} = h_k. \tag{6e}$$

For real g_k, this gives

$$(h_k)^{\frac{1}{2}} = \frac{g_k}{(1+|g_k|^2)^{\frac{1}{2}}}, \quad (1-h_k)^{\frac{1}{2}} = \frac{1}{(1+|g_k|^2)^{\frac{1}{2}}}, \quad (h_k(1-h_k))^{\frac{1}{2}} = \frac{g_k}{1+|g_k|^2}, \tag{6f}$$

which establishes the connection with the expressions of Bardeen, Cooper and Schrieffer.

The expression (6b) of $n_\varkappa$ contains a term with $\xi_\varkappa \xi_{-\varkappa}$ and one with $\xi_{-\varkappa}^* \xi_\varkappa^*$ which have vanishing expectation values for states $\xi_{\varkappa_1} \ldots \xi_{\varkappa_j} \Phi_0$. The remaining

terms can be written in the form

$$(n_\varkappa)_0 = (1 - h_\varkappa)\mathcal{N}_\varkappa + h_\varkappa(1 - \mathcal{N}_{-\varkappa}) , \tag{6g}$$

where

$$\mathcal{N}_\varkappa = \xi_\varkappa \xi_\varkappa^* \tag{6h}$$

represents the number of elementary excitations in state $\varkappa$.

In a similar way, the substitution (5) gives for the « diagonal part » of the pair creation and annihilation operators $a_\varkappa a_{-\varkappa}$ and $a_{-\varkappa'}^* a_{\varkappa'}^*$,

$$(a_\varkappa a_{-\varkappa})_0 = \chi_\varkappa^*(1 - \mathcal{N}_\varkappa - \mathcal{N}_{-\varkappa}) , \tag{7a}$$

$$(a_{-\varkappa'}^* a_{\varkappa'}^*)_0 = \chi_{\varkappa'}(1 - \mathcal{N}_{\varkappa'} - \mathcal{N}_{-\varkappa'}) , \tag{7b}$$

with

$$\chi_\varkappa = \frac{g_\varkappa}{1 + |g_\varkappa|^2} . \tag{7c}$$

One particle operators $B = \sum_{\varkappa\varkappa'} B_{\varkappa\varkappa'} a_\varkappa a_{\varkappa'}^*$ are transformed with (5) into a form, from which the matrix elements between states $\xi_{\varkappa_1} \ldots \xi_{\varkappa_j} \Phi_0$ which are tabulated in a section of the paper by BARDEEN, COOPER and SCHRIEFFER can be immediately obtained.

3. – Structure of the excitation spectrum.

The Hamiltonian (1*a*, *b*, *c*, *d*) is separated through (5) into two parts,

$$H = H_0 + H_1 , \tag{8a}$$

where H_1 has a vanishing expectation value for states of the form $\xi_{\varkappa_1} \ldots \xi_{\varkappa_j} \Phi_0$ which are the eigenstates of H_0. The diagonal operator H_0 can be written as

$$H_0 = E_0 + \sum_{k,\sigma} \varepsilon_k (n_{k\sigma})_0 + \tfrac{1}{2} \sum_{k'\sigma} (n_{k'\sigma'})_0 \sum_{k\sigma} V_{kk} (n_{k\sigma})_0 - \tag{8b}$$

$$- \tfrac{1}{2} \sum_{kk'\sigma} V_{kk'} (n_{k\sigma})_0 (n_{k'\sigma})_0 + \tfrac{1}{2} \sum_{kk'\sigma} V_{kk'} (a_{k,\sigma} a_{-k,-\sigma})_0 (a_{-k',-\sigma}^* a_{k',\sigma}^*)_0 ,$$

where $(n_\varkappa)_0$ and $(a_\varkappa a_{-\varkappa})_0$, $(a_{-\varkappa}^* a_{\varkappa'}^*)_0$ are given by (6*g*) and (7*a*, *b*). Accordingly, H_0 is of the form

$$H_0 = W_0 + \sum_\varkappa \tilde{E}_\varkappa \mathcal{N}_\varkappa + \sum_{\varkappa \neq \varkappa'} \mathcal{V}_{\varkappa\varkappa'} \mathcal{N}_\varkappa \mathcal{N}_{\varkappa'} , \tag{8c}$$

in which the ground state expectation value W_0 is given by

$$(8d) \qquad W_0 = E_0 + 2\sum_k \varepsilon_k h_k + 2\sum_{k'} h_{k'} \sum_k V_{kk} h_k - \sum_{kk'} V_{kk'} h_k h_{k'} + \sum_{kk'} V_{kk'} \chi_k^* \chi_{k'} =$$

$$= E_0 + \sum_k (\varepsilon_k h_k + \nu_k h_k - \mu_k^* \chi_k)$$

and the excitation energy $\tilde{E}_{k\uparrow} = \tilde{E}_{k\downarrow} = \tilde{E}_k$ of states $\xi_\varkappa \Phi_0$ is

$$(8e) \qquad \tilde{E}_k = \nu_k(1 - 2h_k) + (\mu_k^* \chi_k + \chi_k^* \mu_k) .$$

The quantities ν_k, μ_k occurring in (8*d*, *e*) are defined by

$$(8f) \qquad \nu_k = \varepsilon_k - \sum_{k'} \overline{V}_{kk'} h_{k'} ,$$

$$(8g) \qquad \overline{V}_{kk'} = \tfrac{1}{2}(V_{kk'} + V_{k'k}) - (V_{kk} + V_{k'k'}) ,$$

$$(8h) \qquad \mu_k = -\sum_{k'} V_{kk'} \chi_{k'} .$$

Considering W_0 as a function of g_k^*, g_k given by (8*d*), (6*d*), (7*c*) and minimizing it with respect to g_k^*, the equation $\partial W^0/\partial g_k^* = 0$ reads

$$(9a) \qquad \mu_k^* g_k^2 + 2\nu_k g_k - \mu_k = 0 .$$

In referring directly to $\partial W_0/\partial g_k^* = 0$ it is assumed that the density of states is symmetric about the Fermi level and ε_k is given with respect to it. Otherwise one would have to add a Lagrangian multiplier to ν_k in (9*a*), corresponding to the supplementary condition of a constant average number of particles.

The solution of the second order algebraic equation (9*a*) gives

$$(9b) \qquad g_k = \frac{1}{\mu_k^*}\left(-\nu_k + (\nu_k^2 + |\mu_k|^2)^{\frac{1}{2}}\right) ,$$

or with

$$(9c) \qquad E_k = +(\nu_k^2 + |\mu_k|^2)^{\frac{1}{2}} ,$$

$$(9d) \qquad g_k = \frac{1}{\mu_k^*}(E_k - \nu_k) .$$

The root with the plus sign is chosen in (9*b*) in order to minimize the energy W_0.

From (9*c*, *d*), (6*d*), (7*c*) one obtains

$$|g_k|^2 = \frac{(E_k - \nu_k)^2}{|\mu_k|^2}, \tag{10a}$$

$$1 + |g_k|^2 = \frac{2E_k(E_k - \nu_k)}{|\mu_k|^2} = \frac{2E_k}{E_k + \nu_k}, \tag{10b}$$

$$h_k = \frac{1}{2}\left(1 - \frac{\nu_k}{E_k}\right), \tag{10c}$$

$$\chi_k = \frac{\mu_k}{2E_k}. \tag{10d}$$

With these values of h_k, χ_k the expression (8*d*) of W_0 gives

$$W_0 = E_0 + \sum_k \left\{\varepsilon_k h_k + \frac{1}{2}\left(\nu_k - \frac{\nu_k^2}{E_k} - \frac{|\mu_k|^2}{E_k}\right)\right\} = \tag{10e}$$

$$= E_0 + \sum_k \left\{\varepsilon_k h_k + \frac{1}{2}(\nu_k - E_k)\right\},$$

and from (8*e*) one obtains

$$\tilde{E}_k = \frac{\nu_k^2}{E_k} + \frac{|\mu_k|^2}{E_k} = E_k; \tag{10f}$$

that is, (9*c*) gives the energy of an elementary excitation (*).

The quantities ν_k, μ_k are to be determined from the non-linear equations obtained from (8*f*, *g*, *h*) with (10*c*, *d*) and (9*c*),

$$\nu_k = \bar{\varepsilon}_k + \frac{1}{2}\sum_{k'} \bar{V}_{kk'} \frac{\nu_{k'}}{(\nu_{k'}^2 + |\mu_{k'}|^2)^{\frac{1}{2}}}, \tag{11a}$$

$$\bar{\varepsilon}_k = \varepsilon_k - \frac{1}{2}\sum_{k'} \bar{V}_{kk'}, \tag{11b}$$

$$\mu_k = -\frac{1}{2}\sum_{k'} \bar{V}_{kk'} \frac{\mu_{k'}}{(\nu_{k'}^2 + |\mu_{k'}|^2)^{\frac{1}{2}}}. \tag{11c}$$

(*) Formally very similar expressions to those obtained here, though with a rather different physical content, can be derived for a boson system. They include those of Bogolubov's 1947 method ([4]) as their low density limit. An investigation of this problem in collaboration with D. BUTLER is still in progress.

In the case of a factorisable potential $V_{kk'} = v_k v_{k'}$ these equations can be reduced to integrations and algebraic equations, by introducing quantities of the type

$$\lambda = \tfrac{1}{2} \sum_{k'} \frac{v_{k'} \mu_{k'}}{(\nu_{k'}^2 + |\mu_{k'}|^2)^{\frac{1}{2}}}, \quad \mu_k = -\lambda v_k .$$

The approximations involved in the form of the trial state vector Φ_0 are such that better approximations are obtained by excluding the occupation (or emptiness) of electron states outside a definite energy region $|\varepsilon_k| \leqslant \hbar\omega$ about the Fermi level. This can be done on the ground of physical considerations, where $\hbar\omega$ is a characteristic phonon energy. The trial state vector is chosen accordingly with $h_k = 0$ for $\varepsilon_k > \hbar\omega$ and $h_k = 1$ for $\varepsilon_k < -\hbar\omega$. The equations obtained by minimizing W_0 are unchanged, though the summation extends only over a restricted energy region. Replacing in this region $V_{kk'}$ by an average value $V_{kk'} = -V$, and replacing by their average a part of the terms in H_0 which depend only on the total number N of particles, one obtains $\nu_k \simeq \varepsilon_k$, and $\mu_k = \text{constant} = \varepsilon_0$. The relationships (9*c*), (10*c*), (10*d*) then reduce to those given by BARDEEN, COOPER and SCHRIEFFER, and the equation for the energy gap ε_0 can be solved explicitly.

The equations (11*a*, *b*, *c*) for determining ν_k, μ_k can be put into a simpler linearized form. They can be obtained by minimizing the expression (8*d*) of W_0 which is a quadratic form in h_k, χ_k with respect to the independent variables h_k, χ_k under the supplementary conditions $|\chi_k|^2 + h_k^2 = h_k$, or $|2\chi_k|^2 + (1-2h_k)^2 = 1$.

4. – Statistical operator and grand ensemble.

With the simplified classification of states, the ensemble of states considered by BARDEEN, COOPER and SCHRIEFFER corresponds to a statistical operator of the form

$$U_0 = C_0^{-1} \sum_{j=0}^{\infty} \sum_{\varkappa_1 < \ldots < \varkappa_j} w_{\varkappa_1} \ldots w_{\varkappa_j} P_{\varkappa_1 \ldots \varkappa_j} , \tag{12a}$$

where $P_{\varkappa_1 \ldots \varkappa_j}$ is the projection operator on the state $\xi_{\varkappa_1} \ldots \xi_{\varkappa_j} \Phi_0$ and C_0 is the trace of the operator sum,

$$C_0 = \operatorname{tr} \sum_{j=0}^{\infty} \sum_{\varkappa_1 < \ldots < \varkappa_j} w_{\varkappa_1} \ldots w_{\varkappa_j} P_{\varkappa_1 \ldots \varkappa_j} = \prod_{\varkappa} (1 + w_\varkappa) , \tag{12b}$$

so that $\operatorname{tr} U_0 = 1$. The average number of elementary excitations in the

state $\varkappa$ is

$$\langle \mathcal{N}_\varkappa \rangle = \operatorname{tr} \mathcal{N}_\varkappa U_0 = \frac{w_\varkappa}{1 + w_\varkappa} = f_\varkappa \,, \tag{12c}$$

and it is assumed that

$$f_{k\uparrow} = f_{k\downarrow} = f_{-k\uparrow} = f_{-k\downarrow} = f_k \,. \tag{12d}$$

This form of the statistical operator implies that the elementary excitations are statistically independent because, for $\varkappa \neq \varkappa'$ one has

$$\langle \mathcal{N}_\varkappa \mathcal{N}_{\varkappa'} \rangle = \langle \mathcal{N}_\varkappa \rangle \langle \mathcal{N}_{\varkappa'} \rangle = f_\varkappa f_{\varkappa'} \,.$$

U_0 is determined by the two independent functions $g_\varkappa$ and $f_\varkappa$ both of which will be obtained as temperature dependent. From (6g) and (7b) one has the average values

$$\langle n_\varkappa \rangle = (1 - h_\varkappa) f_\varkappa + h_\varkappa (1 - f_\varkappa) = h_\varkappa^{(T)} \,, \tag{13a}$$

$$\langle a^*_{-\varkappa} a^*_\varkappa \rangle = \chi_\varkappa (1 - 2 f_\varkappa) = \chi_\varkappa^{(T)} \,. \tag{13b}$$

The average value of the energy $\langle H \rangle = \langle H_0 \rangle = W_0^{(T)}$ results from (8b) as

$$W_0^{(T)} = E_0 + 2 \sum_k \varepsilon_k h_k^{(T)} + 2 \sum_{k'} h_{k'}^{(T)} \sum_k V_{kk} h_k^{(T)} - \\ - \sum_{kk'} V_{kk'} h_k^{(T)} h_{k'}^{(T)} + \sum_{kk'} V_{kk'} \chi_k^{*(T)} \chi_{k'}^{(T)} \,, \tag{13c}$$

which is of the same form as (8d) with h_k, χ_k replaced by $h_k^{(T)}$, $\chi_k^{(T)}$. In connection with the quantities (13a, b) the relationship

$$|\chi_\varkappa^{(T)}|^2 = h_\varkappa^{(T)} (1 - h_\varkappa^{(T)}) - f_\varkappa (1 - f_\varkappa) \,, \tag{13d}$$

might be mentioned.

With the standard entropy expression for a system of independent fermions given by

$$TS_0 = -2\beta \sum_k \{ f_k \log f_k + (1 - f_k) \log (1 - f_k) \} \,, \tag{14a}$$

one can form an approximate free energy expression

$$W_0^{(T)} - TS_0 \tag{14b}$$

and minimize it independently with respect to the functions g_k and f_k.

The minimization with respect to f_k for a given g_k leads to the fermion distribution

$$f_k = \frac{1}{\exp[\beta \tilde{E}_k^{(T)}]+1}, \tag{15a}$$

$$w_k = \exp[-\beta \tilde{E}_k^{(T)}], \tag{15b}$$

with

$$\tilde{E}_k^{(T)} = \frac{1}{2}\frac{\partial W_0^{(T)}}{\partial f_k} = \nu_k^{(T)}(1-2h_k) + \mu_k^{(T)*}\chi_k + \chi_k^* \mu_k^{(T)}, \tag{15c}$$

where in analogy to (8f, h)

$$\nu_k^{(T)} = \varepsilon_k - \sum_{k'} \overline{V}_{kk'} h_{k'}^{(T)}, \tag{15d}$$

$$\mu_k^{(T)} = -\sum_{k'} V_{kk'} \chi_{k'}^{(T)}. \tag{15e}$$

With (15b), the statistical operator (12a) can be, therefore, written in the form

$$U_0 = \exp[\beta \Lambda_0] \exp[-\beta \mathcal{H}_0], \tag{16a}$$

$$\exp[-\beta \Lambda_0] = \operatorname{tr} \exp[-\beta \mathcal{H}_0]. \tag{16b}$$

with

$$\mathcal{H}_0 = \overline{W}^{(T)} + \sum_{\varkappa} \tilde{E}_\varkappa^{(T)} \mathcal{A}_\varkappa, \tag{16c}$$

where $\tilde{E}_{k\uparrow}^{(T)} = \tilde{E}_{k\downarrow}^{(T)} = \tilde{E}_k^{(T)}$, and $\overline{W}^{(T)}$ is defined by

$$W_0^{(T)} = \overline{W}^{(T)} + \sum_{\varkappa} \tilde{E}_\varkappa^{(T)} f_\varkappa, \tag{16d}$$

so that the additive Hamiltonian $\mathcal{H}_0$ has the same average value in U_0 as H_0 or H.

In the limit of $T=0$, that is $\beta \to \infty$, (15b) gives $w_k = 0$, and the statistical operator (12a) reduces to the projection operator P_0 of the state Φ_0 given by (2a). The consideration of the mixture of states (12a) includes, therefore, this special case.

The operator (12a) can be considered as the trial approximation of the theory for the statistical operator of the grand ensemble

$$U = \exp[\beta \Lambda] \exp[-\beta(H-\mu N)], \tag{17a}$$

$$\exp[-\beta \Lambda] = \operatorname{tr} \exp[-\beta(H-\mu N)]. \tag{17b}$$

A theorem due to PEIERLS [5], which as shown by SCHULTZ can be extended to include the case of the grand ensemble, shows that, with the diagonal operators H_0 and $N_0 = \sum_\varkappa (n_\varkappa)_0$, the grand potential $\bar{\Lambda}_0$ defined by

$$\exp[-\beta\bar{\Lambda}_0] = \mathrm{tr}\exp[-\beta(H_0 - \mu N_0)], \tag{17c}$$

is an upper bound for the grand potential Λ,

$$\exp[-\beta\Lambda] \geqslant \exp[-\beta\bar{\Lambda}_0]. \tag{17d}$$

The effect of the chemical potential μ in (17a) is to replace ε_k by $\varepsilon_k - \mu$ in the Hamiltonian, as can be seen from the expressions $T \simeq \sum_\varkappa \varepsilon_\varkappa n_\varkappa$ and $\mu N = \sum_\varkappa \mu n_\varkappa$. Assuming a density of states for the electrons which is an even function of ε_k about the Fermi level, and a constant average number of electrons, one obtains that μ is equal to the Fermi energy. The counting of ε_k from the Fermi level means, therefore, $\mu = 0$. In this case, the grand potential Λ reduces to the free energy. For any other choice of the zero of the energy scale, however, the role of the chemical potential μ becomes essential.

The grand potential $\bar{\Lambda}_0$ defined by (17c) still differs from the expression Λ_0 given by (16b) which with (15a) and (14a) is equal to (14b). By an argument due to SCHULTZ, one can, however, show that Λ_0 is an upper bound for $\bar{\Lambda}_0$ and consequently for Λ,

$$\Lambda_0 \geqslant \Lambda. \tag{17e}$$

As the expression of the entropy given by (14a) does not depend explicitly on g_k, the minimization of the free energy (14b) with respect to g_k, for fixed f_k, is equivalent to the minimization of $W_0^{(T)}$. This leads to an equation analogous to (9a) and to the relationships

$$h_k = \frac{1}{2}\left(1 - \frac{\nu_k^{(T)}}{E_k^{(T)}}\right), \tag{18a}$$

$$\chi_k = \frac{\mu_k^{(T)}}{2E_k^{(T)}}, \tag{18b}$$

with

$$E_k^{(T)} = (\nu_k^{(T)2} + |\mu_k^{(T)}|^2)^{\frac{1}{2}}. \tag{18c}$$

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With (18*a*, *b*) one obtains from (15*c*)

$$\tilde{E}_k^{(T)} = E_k^{(T)} . \tag{18d}$$

From (18*a*, *b*, *c*) and (15*d*, *e*) one can deduce equations analogous to (11*a*,*c*). For constant $V_{kk'}$, with $|\varepsilon_k| \leqslant \hbar\omega$, these equations are still of the factorizable type and can be solved exactly. One obtains the temperature dependent energy gap $|\mu_k^{(T)}| \sim \varepsilon_0$ which vanishes at the critical temperature T_c. The free energy calculated as a function of temperature gives the specific heat curve of BARDEEN, COOPER and SCHRIEFFER which explains correctly a great number of experimental facts.

For a system with a large number of particles, the statistical operator U_0 corresponds to a probability distribution for the number N of particles with a sharp peak. This can be seen by comparing the average values $\langle N^2 \rangle$ and $\langle N \rangle^2$ in U_0. A simple calculation gives

$$\langle N^2 \rangle - \langle N \rangle^2 = 2 \sum_\varkappa h_\varkappa^{(T)}(1 - h_\varkappa^{(T)}) - \sum_\varkappa f_\varkappa(1 - f_\varkappa) . \tag{19a}$$

Since one has $0 \leqslant h_\varkappa^{(T)}(1 - h_\varkappa^{(T)}) \leqslant \frac{1}{4}$ and $0 \leqslant f_\varkappa(1 - f_\varkappa) \leqslant \frac{1}{4}$, and both expressions vanish outside an energy region $|\varepsilon_k| \leqslant \hbar\omega$, (19*a*) gives

$$\langle N^2 \rangle - \langle N \rangle^2 < \sum_\varkappa \tfrac{1}{2} \simeq 2N(0)\hbar\omega, \tag{19b}$$

where $N(0)$ is the density of states near the Fermi level. With $2N(0)\hbar\omega \sim$ $\sim 10^{-3}\langle N \rangle$, this leads to an estimate

$$\frac{\langle N^2 \rangle - \langle N \rangle^2}{\langle N \rangle^2} < 10^{-3} \frac{1}{\langle N \rangle} . \tag{19c}$$

5. – Long range correlations.

Some of the previous expressions obtain a simple physical interpretation by considering the correlation function of the particles, which is the most important quantity from the point of view of collective behaviour. The two-particle correlations are given by the expectation values of the operator

$$\varrho_{\sigma\sigma'}(x, x') = \Psi_\sigma^+(x)\Psi_\sigma^*(x')\Psi_{\sigma'}(x')\Psi_\sigma(x) . \tag{20a}$$

Expressing the quantized field operators $\Psi_\sigma^*(x)$, $\Psi_{\sigma'}(x')$ by means of creation an annihilation operators of plane wave states $\psi_k(x) = \Omega^{-\frac{1}{2}} \exp[-ikx]$ in the form

$$\Psi_\sigma^*(x) = \sum_k \psi_k^*(x) a_{k\sigma} , \qquad \Psi_{\sigma'}(x') = \sum_{k'} \psi_{k'}(x') a_{k'\sigma'}^* , \tag{20b}$$

the expectation value of $\varrho_{\sigma\sigma'}(x, x')$ in the ground state Φ_0 can be obtained with the help of the relations (6*a*, *c*), (7*a*, *b*, *c*). For the correlation functions of particles with parallel and anti-parallel spin

$$\varrho_p = \varrho_{\uparrow\uparrow} + \varrho_{\downarrow\downarrow}, \qquad \varrho_a = \varrho_{\uparrow\downarrow} + \varrho_{\downarrow\uparrow}, \tag{20c}$$

a simple calculation gives

$$\bar{\varrho}_p(r) = \tfrac{1}{2}\varrho_0^2 - 2h^*(r)h(r), \tag{21a}$$

$$\bar{\varrho}_a(r) = \tfrac{1}{2}\varrho_0^2 + 2\chi^*(r)\chi(r), \tag{21b}$$

where $r = x - x'$, $\varrho_0 = \overline{N}/\Omega$ is the average density, $h(r)$ is the Fourier transform of the number distribution h_k given by (6*c*, *d*, *e*) and $\chi(r)$ is the Fourier transform of the quantity χ_k defined by (7*c*). This throws new light on the role of the quantities h_k, χ_k in the equations. The last two interaction terms in the expression (8*d*) of W_0 for instance correspond to the contributions from parallel and anti-parallel spin correlations.

At temperature T, the average values of ϱ_p and ϱ_a in the mixture of states (12*a*), (16*a*) are in an analogous way

$$\langle\varrho_p(r)\rangle = \tfrac{1}{2}\varrho_0^2 - 2h^{(T)*}(r)h^{(T)}(r), \tag{22a}$$

$$\langle\varrho_a(r)\rangle = \tfrac{1}{2}\varrho_0^2 + 2\chi^{(T)*}(r)\chi^{(T)}(r), \tag{22b}$$

where $h^{(T)}(r)$ and $\chi^{(T)}(r)$ are the Fourier transforms of the quantities $h_k^{(T)}$, $\chi_k^{(T)}$ defined by (13*a*), (13*b*).

The long range correlations are between particles with antiparallel spin and are related to the function χ_k. For $V_{kk'} = \text{constant}$, with $|\varepsilon_k| < \hbar\omega$, they have been calculated by BARDEEN, COOPER and SCHRIEFFER. In the same model, (22*b*) gives the temperature dependence of the long range correlations, the amplitude of which tends to zero with the square of the energy gap near the critical temperature. The integrations carried out explicitly for small values of $\varepsilon_0 \sim \mu_k^{(T)}$, that is near the critical temperature, show that the form of the correlation function is practically the same as at $T = 0$, with a correlation length of the order of 10^{-4} cm.

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RIASSUNTO (*)

Si esprimono in forma più accessibile alcuni significati della nuova teoria di Bardeen, Cooper e Schrieffer. Si introducono nuove variabili fermioniche collettive che sono combinazioni lineari di operatori di creazione e di distruzione di elettroni e descrivono eccitazioni elementari. Essi conducono a una semplice classificazione degli stati eccitati e a grande semplificazione dei calcoli. Si esamina la struttura dello spettro di eccitazione senza eguagliare dapprincipio a una costante l'elemento di matrice del potenziale d'interazione e si derivano nuove relazioni ed equazioni. Il problema dipendente dalla temperatura si descrive per mezzo di un operatore statistico e si stabilisce la sua relazione con quella del grande insieme canonico. Si ottengono nuove semplici relazioni per la funzione di correlazione.

(*) *Traduzione a cura della Redazione.*