ON THE ENERGY SPECTRUM OF SUPERCONDUCTORS

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A method is proposed, based on the mathematical apparatus of quantum field theory, for the calculation of the properties of a system of Fermi particles with attractive interaction.

T was shown in the work of Cooper¹ that if the interaction of electrons in a metal leads to an effective mutual attraction for two electrons close to the Fermi surface, then the pair of particles which possess mutually opposite momenta and spins can have bound states with negative coupling energies. In the works of Bardeen, Cooper and Schreiffer^{2,3} and of Bogoliubov⁴ a systematic theory of superconductivity has been erected on this principle. It was shown that the ground state of a system of interacting Fermi particles is located below the normal state with a filled Fermi sphere and, in consequence, is separated from the excited states by a gap in order of magnitude equal to the energy of coupling of the individual pair.

In the present work, a method is proposed, based on the physical idea of Cooper, which permits us, with the help of the apparatus of quantum field theory, to obtain all the results by a short and simple method.

We shall start out from a Hamiltonian in the form² which is written in the case of second quantization:

$$\hat{H} = \int \left\{ -\left(\psi^{+} \frac{\Delta}{2m} \psi \right) + \frac{g}{2} \left(\psi^{+} \left(\psi^{+} \psi \right) \psi \right) \right\} d^{3}x, \qquad (1)$$

where

$$\psi_{\mathbf{x}}(\mathbf{x}) = V^{-1/2} \sum_{k\sigma} a_{k\sigma} s_{\sigma\mathbf{x}} e^{i\mathbf{k}\mathbf{x}}; \ \psi_{\mathbf{\beta}}^+(\mathbf{x}') = V^{-1/2} \sum_{k\sigma} a_{k\sigma}^+ s_{\mathbf{\beta}\sigma}^* e^{-i\mathbf{k}\mathbf{x}'}$$

satisfy the usual commutation relations:

$$\{ \psi_{\alpha} (\mathbf{x}), \ \psi_{\beta}^{+} (\mathbf{x}') \} = \delta_{\alpha\beta} \ \delta (\mathbf{x} - \mathbf{x}'),$$

$$\{ \psi_{\alpha} (\mathbf{x}), \ \psi_{\beta} (\mathbf{x}') \} = \{ \psi_{\alpha}^{+} (\mathbf{x}), \ \psi_{\beta}^{+} (\mathbf{x}') \} = 0.$$

$$(2)$$

We shall consider the interaction to be equal to zero everywhere except in a region of energy of the particles 2κ around the Fermi surface, from $\epsilon_{\rm F} - \kappa$ to $\epsilon_{\rm F} + \kappa$.

We transform to the Heisenberg representation, in which the operators ψ and ψ^+ depend on the time and satisfy the following equations:

$$\begin{cases} i\partial/\partial t + \Delta/2m \} \psi(x) - g(\psi^+(x)\psi(x))\psi(x) = 0, \\ \{i\partial/\partial t - \Delta/2m \} \psi^+(x) + g\psi^+(x)(\psi^+(x)\psi(x)) = 0. \end{cases}$$
(3)

We determine the Green's function $G_{\alpha\beta}(x-x')$ as an average over the ground state of the system:

$$G_{\alpha\beta}(x-x') = -i \langle T(\psi_{\alpha}(x), \psi_{\beta}^{+}(x')) \rangle, \qquad (4)$$

where T is time-ordering operator.

For the derivation of the equation for the function G(x - x') we take it into consideration that the ground state of the system differs from the usual state with a filled Fermi sphere by the presence of bound pairs of electrons. In the ground state, all the pairs are at rest as a whole. (This means that the interaction between particles is considered only insofar a's it enters into the formation of the bound pairs. We neglect scattering effects.) A sort of "Bose condensation" of pairs takes place in the case in which the momentum of their motion as a whole is equal to zero, just as in a Bose gas such a condensation takes place by virtue of the statistics for the particles themselves. This circumstance permits us to write down in a definite way the mean form $< T(\psi(x_1) \psi(x_2) \times$ $\psi^+(x_3) \psi^+(x_4) >$, which appears in the equations for G(x-x') by virtue of (3).

For example, we have

$$\langle T (\psi_{\alpha} (x_{1}) \psi_{\beta} (x_{2}) \psi_{\gamma}^{+} (x_{3}) \psi_{\delta}^{+} (x_{4})) \rangle =$$

$$- \langle T (\psi_{\alpha} (x_{1}) \psi_{\gamma}^{+} (x_{3})) \rangle \langle T (\psi_{\beta} (x_{2}) \psi_{\delta}^{+} (x_{4})) \rangle$$

$$+ \langle T (\psi_{\alpha} (x_{1})) \psi_{\delta}^{+} (x_{4})) \rangle \langle T (\psi_{\beta} (x_{2}) \psi_{\gamma}^{+} (x_{3})) \rangle$$

$$+ \langle N | T (\psi_{\alpha} (x_{1}) \psi_{\beta} (x_{2})) | N$$

$$+ 2 \rangle \langle N + 2 | T (\psi_{\gamma}^{+} (x_{3}) \psi_{\delta}^{+} (x_{4})) | N \rangle,$$
(5)

where $|N\rangle$ and $|N+2\rangle$ are the ground states of the system with numbers of particles N and N + 2. The quantity

$$\langle N \mid T (\psi \psi) \mid N + 2 \rangle \langle N + 2 \mid T (\psi^{+} \psi^{+}) \mid N \rangle, \qquad (5a)$$

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evidently has the order of the density of the number of pairs, while $\langle T(\psi\psi^+) \rangle$ is the particle number density.

It is easy to show that the quantities thus introduced can be written in the form

$$\langle N | T (\psi_{\alpha} (x) \psi_{\beta} (x')) | N + 2 \rangle = e^{-2i\mu t} F_{\alpha\beta} (x - x'),$$

$$\langle N + 2 | T (\psi_{\alpha}^{+} (x) \psi_{\beta}^{+} (x')) | N \rangle = e^{2i\mu t} F_{\alpha\beta}^{+} (x - x').$$
(6)

The function G(x-x') depends only on the difference x-x', because of the homogeneity of the problem. So far as the additional dependence on t in Eq. (6) is concerned, its origin is seen from the general quantum mechanical formula for the time derivative of an arbitrary operator $\hat{A}(t)$:

$$\frac{\partial}{\partial t} \langle N | \hat{A}(t) | N + 2 \rangle = i \left(E_N - E_{N+2} \right) \langle N | \hat{A}(t) | N + 2 \rangle.$$

The value of the energy difference $E_{N+2} - E_N$ is obviously equal to $2\mu (\partial E/\partial N = \mu)$.

Making use of Eq. (3), we obtain equations for the functions $\hat{G}(x-x')$ and $\hat{F}(x-x')$:

$$\{i\partial / \partial t + \Delta / 2m\} \hat{G} (x - x')$$

- $ig \hat{F} (0+) \hat{F}^+ (x - x') = \delta (x - x'),$
 $\{i\partial / \partial t - \Delta / 2m - 2\mu\} \hat{F}^+ (x - x')$ (7)

$$+ ig F^{+}(0+) G(x-x') = 0.$$

Here terms are omitted which correspond to the first two terms in Eq. (5), inasmuch as they only change μ , which one can neglect, and the notations

$$F_{\alpha\beta}^{+}(0+) = e^{-2i\mu t} \langle \psi_{\alpha}^{+}(x) \psi_{\beta}^{+}(x) \rangle \equiv \lim_{x \to x'(t > t')} F_{\alpha\beta}^{+}(x - x')$$

and introduced, and correspondingly,

$$F_{\alpha\beta}(0+) = e^{2i\mu t} \langle \psi_{\alpha}(x) \psi_{\beta}(x) \rangle.$$

The complex conjugate yields

$$(F_{\alpha\beta}^{+}(0+)^{*} = -F_{\alpha\beta}(0+).$$
(8)

We transform in Eqs. (7) to the Fourier components of all functions, for example,

$$G_{\alpha\beta}(\mathbf{x}-\mathbf{x}') = (2\pi)^{-4} \int G_{\alpha\beta}(p\omega) \exp \{i\mathbf{p} (\mathbf{x}-\mathbf{x}') - i\omega (t-t')\} d\omega d^3p,$$

Denoting $\omega - \mu = \omega'$, we find

$$(\omega' - \xi_p) \hat{G} (p\omega) - ig\hat{F} (0+) \hat{F}^+ (p\omega) = 1, (\omega' + \xi_p) \hat{F}^+ (p\omega) + ig\hat{F}^+ (0+) \hat{G} (p\omega) = 0,$$
 (9)

where

$$\xi_{p} = p^{2}/2m - \mu \approx v_{\mathrm{F}}(p - p_{\mathrm{F}}),$$

and p_F is the Fermi momentum. In what follows, we shall only have ω' in the formulas, hence we shall omit the prime.

It follows from Eq. (8) that $\hat{F}(0+)$ and $\hat{F}^+(0+)$ have the following matrix form:

$$\hat{F}^{+}(0+) = J\begin{pmatrix} 0 & 1 \\ -1 & 0 \end{pmatrix} \equiv J\hat{I}; \ \hat{F}(0+) = -J\hat{I},$$

$$\hat{I}^{2} = -\hat{E};$$
(10)

equal both to $\hat{F}^+(p\omega)$ and $\hat{F}(p\omega)$, and the Green's function, in accord with (9), is proportional to the unit matrix. Substituting (10) in (9), we obtain

 $(\omega^2 - \xi_p^2 - g^2 J^2) F^+(p\omega) = -igJ,$ $(\omega - \xi_p) G(p\omega) = 1 + igJF^+(p\omega).$

Hence

$$F^{+}(p\omega) = -ig \frac{J}{\omega^{2} - \xi_{p}^{2} - \Delta^{2}};$$

$$G(p\omega) = \frac{\omega + \xi_{p}}{\omega^{2} - \xi_{p}^{2} - \Delta^{2}},$$
(12)

(11)

where

$$\Delta^2 = g^2 J^2.$$

As is evident from the first equation of (11), $F^+(p\omega)$ is determined with accuracy up to a solution of the homogeneous equation of the form $A(p)\delta(\omega^2 - \xi_p^2 - \Delta^2)$. It is not difficult to verify the fact that this term reduces in the expression for $G(p\omega)$ to an arbitrary imaginary part. In other words, Eqs. (11) determine only the real part of the Green's function.

We determine the rule for circling the poles in (12), making use of a theorem given by Landau,⁵ according to which the imaginary part of the Green's function of a Fermi system is positive for $\omega < 0$ and changes sign in the transition from negative to positive frequencies.

As a result, we obtain

$$F^{+}(p\omega) = -igJ/(\omega - \varepsilon_{p} + i\delta)(\omega + \varepsilon_{p} - i\delta), \qquad (13)$$

$$G(p\omega) = u_p^2 (\omega - \varepsilon_p + i\delta)^{-1} + v_p^2 (\omega + \varepsilon_p - i\delta)^{-1}, \quad (14)$$

where $\epsilon_p = \sqrt{\xi_p^2 + \Delta^2}$ and the functions μ_p^2 and v_p^2 are equal to

$$u_{p}^{2} = \frac{1}{2} \left(1 + \frac{\xi_{p}}{\epsilon_{p}} \right); \quad v_{p}^{2} = \frac{1}{2} \left(1 - \frac{\xi_{p}}{\epsilon_{p}} \right)$$
(14')

For the determination of the quantity Δ , we make use of the fact that

$$J = (2\pi)^{-4} \int F^+(p\omega) \, d\omega \, d^3k.$$
 (15)

Substituting (13), we obtain the equation

$$1 = -\frac{g}{2(2\pi)^3} \int \frac{d^3k}{\sqrt{\xi_k^2 + \Delta^2}} (|\xi| < \varkappa).$$
 (16)

For small g < 0 (attraction), this equation has a solution of the form

where

$$\rho = p_{\rm F} |g| m / 2\pi^2.$$

 $\Delta = 2 \varkappa e^{-1/2\rho},$

The positive pole in (14) determines the excitation spectrum which, as is shown, has a gap of magnitude Δ . These results coincide with those obtained in Refs. 2-4.

The chemical potential μ is connected with the particle number density by the relation

$$N/V = \langle \psi^+(x)\psi(x)\rangle = -i(2\pi)^{-4}\int G_{\alpha\alpha}(p\omega)e^{i\omega\delta}d\omega d^3p,$$
 (17)

with accuracy up to small exponential terms: $\mu = \epsilon_{\rm F}$.

The method laid out also permits us to make use of it for temperatures differing from absolute zero. In this case we consider the mean Green's function (thermodynamically averaged)

$$G_{\alpha\beta}(x-x') = -i\sum_{n} \exp\left\{\frac{\Omega+\mu N-E_{n}}{T}\right\} \langle n \mid T \left(\psi_{\alpha}(x)\psi_{\beta}^{+}(x') \mid n\right),$$

where Ω is the thermodynamic potential in the variables T, V, μ . As is well known, the result of averaging does not depend on whether it is carried out with the use of a Gibbs distribution or over the stationary state with a given energy. This corresponds to the choice of the quantity \overline{E} as a thermodynamic variable, in place of the temperature T. Taking the averaging in such a fashion we get the earlier equations (11) for the quantities G, F^+ and F, with this difference, that the corresponding averaging of T products are taken not over the ground state of the system but over a state with total energy E equal to the energy of the system at a given temperature. Equations (11), as we have already noted above, determine uniquely only the real part of the Green's function $G(p\omega)$, which is evidently equal to the real part of Eq. (14). We write down the general solution for the function $F^+(p\omega)$:

$$F^{+}(p\omega) = -igJ/(\omega - \varepsilon_{p} + i\delta)(\omega + \varepsilon_{p} - i\delta) + A_{1}(p, T)\delta(\omega - \varepsilon_{p}) + A_{2}(p, T)\delta(\omega + \varepsilon_{p}).$$
(18)

We have made use of the fact that $1/(x \pm i\delta) = 1/x \pm \pi i\delta(x)$. The value of the quantities $A_1(p,T)$ and $A_2(p,T)$ can be obtained from the relations between the real and imaginary parts of the Green's function,⁵ which has the following form at temperatures different from zero:

$$\operatorname{Re} G(\omega) = -\frac{1}{\pi} \int_{-\infty}^{+\infty} \operatorname{coth} \frac{x}{2T} \frac{\operatorname{Im} G(x)}{\omega - x} dx.$$

We obtain

$$A_1(p, T) = A_2(p, T) = -(\pi \Delta / \dot{\epsilon}_p) n(\epsilon_p)$$

and for the Green's function,

$$G(p\omega) = u_p^2(\omega - \varepsilon_p + i\delta)^{-1} + v_p^2(\omega + \varepsilon_p - i\delta)^{-1} + 2\pi i n(\varepsilon_p) [u_p^2 \delta(\omega - \varepsilon_p) - v_p^2 \delta(\omega + \varepsilon_p)],$$
(19)

where $n(\epsilon_p)$ has the form of the Fermi distribution of excitations at the given temperature:

$$n(\varepsilon_p) = [\exp(\varepsilon_p / T) + 1]^{-1}.$$

The excitation spectrum is then

$$\varepsilon_p = \sqrt{\xi_p^2 + \Delta^2},\tag{20}$$

where Δ is a function of the temperature. Condition (15), upon substitution of $F^+(p\omega)$ in the form (18) in it, gives a relation which determines the magnitude of the gap in its temperature dependence:

$$1 = \frac{|g|}{2(2\pi)^3} \int \frac{d^3 k (1 - 2n(\varepsilon_k))}{\sqrt{\xi_k^2 + \Delta^2(T)}}, \quad (|\xi| < \varkappa).$$
 (21)

Equation (21) was obtained by Bardeen, Cooper and Schrieffer³; it was found that the magnitude of the gap $\Delta(T)$ vanishes at $T = T_c \sim \Delta(0)$. We shall show briefly how calculation of thermodynamical quantities is carried out by our method.

The heat capacity per unit volume is equal to

$$Vc_{v} = (\partial \overline{E} / \partial T)_{v}.$$

The quantity

$$\overline{E} / V = \left\langle \left\{ -\left(\psi^{+} \frac{\Delta}{2m} \psi \right) + \frac{g}{2} \left(\psi^{+} \left(\psi^{+} \psi \right) \psi \right) \right\} \right\rangle$$

is expressed by the function of G, F^+ and F with accuracy up to inconsequential (constant in temperature) terms in the following fashion:

$$\overline{E} = 2V \left(2\pi\right)^{-3} \int \xi_p \left[v_p^2 \left(1 - n\left(\varepsilon_p\right)\right) + u_p^2 n\left(\varepsilon_p\right)\right] d^3p + gVJ^2.$$

The total contribution to the heat capacity at such temperatures gives the interval $|\xi_p| \ll \kappa$. Substituting here for the functions u_p^2 and v_p^2 their expressions (14'), and making use of Eq. (21), we get for the heat capacity

$$c_V = 2 (2\pi)^{-3} \int \varepsilon_p \frac{\partial n (\varepsilon_p)}{\partial T} d^3 p,$$

i.e., the ordinary formula for heat capacity of a gas of Fermi excitations with a spectrum (20). Computation of the heat capacity and the value of the gap in its temperature dependence was given in Ref. 3.

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³Bardeen, Cooper and Schrieffer, Phys. Rev. 108, 5 (1957). ⁴N. N. Bogoliubov, J. Exptl. Theoret. Phys. (U.S.S.R.) **34**, 58 (1958); Soviet Phys. JETP **7**, 41 (1958).

⁵L. D. Landau, J. Exptl. Theoret. Phys. (U.S.S.R.) **34**, 262 (1958); Soviet Phys. JETP **7**, 182 (1958).

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THE THERMODYNAMICAL THEORY OF RESONANCE AND RELAXATION PHENOMENA IN FERROMAGNETICS

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The methods of irreversible thermodynamics are applied to derive the time variation of magnetization of ferromagnetics. The role of spin-lattice relaxation in the phanomenon of ferromagnetic resonance is discussed. The resultant equations are compared with those of Landau-Lifshitz and Bloch.

1. In the observation of ferromagnetic resonance, the ferromagnetic specimen is placed in a constant magnetic field $H_0 = H_z$. This magnetizes the sample to saturation. A radiofrequency field **h** is then applied perpendicular to H_0 . The amplitude of the field **h** is usually taken to be small ($h \ll H_0$); therefore, the magnetization vector **M** differs only slightly in direction from H_0 . In experiments on the study of relaxation in perpendicular fields, a strong radiofrequency field of high amplitude was applied. This produced a significant deviation of **M** away from H_0 .

For the determination of the frequency dependence of the components of the magnetization M_X , M_y , M_z of the ferromagnetic, there are used the equations of Landau-Lifshitz¹, Bloch,² or various modifications of these equations,³ which are frequently put together without sufficient basis.

In the present paper, it is shown that as a result of the application of irreversible thermodynamics, one can obtain (under very simple and general assumptions) equations for the change in the magnetization with time, with consideration both of spinspin and spin-lattice relaxations, and the role of the latter in the phenomenon of ferromagnetic resonance can also be judged.

From the viewpoint of thermodynamics, we can divide the system of spin moments, which correspond to the magnetic properties of the ferromagnetics, into a separate subsystem with temperature T (the spin system). We shall consider the remaining degrees of freedom of the entire system [analogously to what was done in the thermodynamic theory of paramagnetic relaxation⁴] to be thermostatted, the temperature of which (T_0) we shall consider fixed in the current research. We can show that the latter assumption is related to the conclusions made below and it is easily based on them.

If the subset is found in thermal equilibrium with the thermostat or is isolated completely from it, and the magnetization M has a non-equilibrium value, which does not correspond to the field H, then we shall call the process of the approximation

¹L. Cooper, Phys. Rev. 104, 1189 (1956).

²Bardeen, Cooper and Schrieffer, Phys. Rev. **106**, 162 (1957).