A Note of the Excited State at $T=0^\circ$K 
in the Superconducting State

Shozo SHINOHARA

(Received Sept. 15, 1959)

A wave function of the excited state in the superconducting state slightly more general than what in BARDEEN-COOPER-SCHRIEFER's theory is adopted, and it is shown that in the case of weak interaction the minimum energy gap at $T=0^\circ$K comes out to be $2\varepsilon_s$.

§ 1. Introduction

The energy gap at $T=0^\circ$K estimated from the experiments on specific heat, microwave transmission, etc., proves to be about $3kT_c$ for some superconductors, while BARDEEN-COOPER-SCHRIEFER's theory shows that it should be $3.5kT_c$. They claim that their result is in the quantitative agreement with experiments. However, the excited state wave function at $0^\circ$K assumed in B.C.S.-theory may not be so general; being appropriate only in the case where the $k'$ and $k''$ states each occupied by a single electron are related with each other by a special condition (expression (11) given below).

We consider a more general excited state in which any arbitrary $k'$ and $k''$ states are each occupied by a single excited electron. For convenience's sake, the method adopted by B.C.S.-theory of calculating the energy gap at $0^\circ$K will be briefly outlined in the following, the notations being the same as in their theory.

The wave function of the superconducting ground state and the reduced Hamiltonian are assumed to be

$$\psi = \prod_k \left[ (1-h_k)^{\frac{1}{2}} + h_k^{\frac{1}{2}} b_k^* \right] \phi_s,$$

$$\phi_s: \text{vacuum state}$$

and

$$H_{\text{red}} = 2 \sum_{k > k'} \varepsilon_k b_k^* b_{k'} + 2 \sum_{k < k'} |\varepsilon_k| b_k b_{k'} - V \sum_{k, k'} b_k^* b_k,$$

respectively.
When \( N \) pairs of electrons are considered in the ground state, \( h_k \) must satisfy the condition:

\[
\sum_k h_k = N .
\]

The expectation value of \( H_{\text{red}} \) of the ground state is

\[
W_0 = 2 \sum_{k > \epsilon_F} \epsilon_k h_k + 2 \sum_{k < \epsilon_F} |\epsilon_k|(1 - h_k) - V \sum_{k, k'} \left[ h_k(1 - h_k) h_{k'}(1 - h_{k'}) \right]^{1/2},
\]

in which \( h_k \) is to be determined from the variational equation

\[
\frac{\partial W_0}{\partial h_k} = 0 ,
\]

the subsidiary condition (3) being taken into account.

The effective contribution to \( W_0 \) is only due to the electrons in the region \(-h_\omega < \epsilon_k < h_\omega\), provided the Fermi-surface is taken as the origin of energy; and \( h_k \) in (4) naturally satisfies the condition (3), so far as the electrons above the Fermi-surface and the holes below it are concerned. From the equations (4) and (5), the following relation is obtained:

\[
h_k = \frac{1}{2} \left[ 1 - \frac{\epsilon_k}{\epsilon_k^2 + \epsilon_{\text{F}}^2} \right] ,
\]

where

\[
\epsilon_k = V \sum_k \left[ h_k(1 - h_k) \right]^{1/2} = N(0) V \epsilon_k \int_{-\epsilon_\omega}^{\epsilon_\omega} \frac{d\epsilon}{(\epsilon^2 + \epsilon_{\text{F}}^2)} .
\]

In the excited state, \(-k'\downarrow\) and \(k''\uparrow\) states are each occupied by one electron, while all the other states in \( k \)-space are occupied by pairs with the same probability as the ground states. Thus, the wave function of the excited state takes the form

\[
\psi_{\text{exc}} = \Pi_{(\sim k', k'')} \left\{ (1 - h_k)^{1/2} + h_k^{1/2} b_k^+ \right\} c_{-k'} c_{-k'}^+ \cdot \Phi_0 .
\]

Since the number of electrons occupying the excited state must be the same as that in the ground state, the number of pairs in the excited state is \((N-1)\):

\[
\sum_{(\sim k', k'')} h_k = N - 1 .
\]
From the equations (3) and (9), it results that $h_{k'}$ and $h_{k''}$ satisfy the relation

$$h_{k'} + h_{k''} = 1.$$  \hspace{1cm} (10)

It is to be noticed that this relation holds, not for arbitrary $k'$ and $k''$ states, but only for those whose energies are of the same magnitude:

$$\epsilon_{k'} = -\epsilon_{k''}. \hspace{1cm} (11)$$

To get the minimum value of the energy difference between the ground and the excited one, $\epsilon_{k'}$ and $\epsilon_{k''}$ must be brought to zero under the state condition (11), and thus comes out to be the value of energy gap at $0^\circ K$

$$dW = W_{\text{exc}} - W_0 = 2\epsilon_0. \hspace{1cm} (12)$$

So far is the result of B.C.S.-theory.

We now assume as the excited state at $0^\circ K$ the state which corresponds to the breaking-up of the pairs in any two arbitrary states, $k'$ and $k''$, and of a portion of the pair in every other state in the ground state, such that the total sum of the broken-up portions amounts to one pair, and each of the $-k'\downarrow$ and $k''\uparrow$ states is occupied by a single electron.

That is to say, the excited state is none other than the state produced from the vacuum state by exciting a single electron into each of the $-k'\downarrow$ and $k''\uparrow$ states and distributing $2(N-1)$ electrons as pairs in the $k$-space except $k'$ and $k''$ states.

\section{2. Energy gap at $T=0^\circ K$}

The wave function of the excited state and its expectation value of the reduced Hamiltonian (2) are respectively

$$\Psi_{\text{exc}} = \Pi_{(s,k',k'')} \left\{ (1-p_s h_k)^{\frac{1}{2}} + (p_s h_k)^{\frac{1}{2}} h_k^a \right\} c_{k',k}^a c_{k',k}^b \Phi_0, \hspace{1cm} (13)$$

and

$$W_{\text{exc}} = 2 \sum_{k>\tilde{k}} \epsilon_k p_s h_k + 2 \sum_{k<\tilde{k}} \left[ \epsilon_k (1-p_s h_k) + \epsilon_{k'} + \epsilon_{k''} \right]$$

$$-V \sum_{i<l} \left[ p_i h_i (1-p_l h_l) p_l h_l (1-p_i h_i) \right]^{\frac{1}{2}}, \hspace{1cm} (14)$$

where $h_k$ has the same value as in the ground state, so that $p_s$ is the
A Note of the Excited State at T=0°K in the Superconducting State

ratio of the probability with which the \( \vec{k} \) state is occupied by pair in the excited state to that in the ground state. By minimizing \( W_{\text{exc}} \) with respect to \( p_{\vec{k}} \), an integral equation for determining \( p_{\vec{k}} \) is obtained for \( k > k_{F'} \):

\[
2\varepsilon_{\vec{k}h_k} - V \sum_{\langle \vec{k}', \vec{k}'' \rangle} p_{\vec{k}''}^{-\frac{1}{2}} [h_k(1-p_{\vec{k}h_k}) p_{\vec{k}''} h_{\vec{k}''} (1-p_{\vec{k}''} h_{\vec{k}''})]^{\frac{1}{2}}
- V \sum_{\langle \vec{k}', \vec{k}'' \rangle} (1-p_{\vec{k}h_k})^{\frac{1}{2}} [p_{\vec{k}''} h_{\vec{k}''}]^{\frac{1}{2}} h_k [p_{\vec{k}''} h_{\vec{k}''} (1-p_{\vec{k}''} h_{\vec{k}''})]^{\frac{1}{2}} = 0. \tag{15}
\]

For \( k < k_{F'} \), in place of the first term in (15) we may use \(-2|\varepsilon_{\vec{k}}|/h_{\vec{k}}\), which equals \( 2\varepsilon_{\vec{k}h_k} \). Therefore, (15) is realized for all \( \vec{k} \)'s. Putting

\[
\eta = V \sum_{\langle \vec{k}', \vec{k}'' \rangle} p_{\vec{k}''} h_{\vec{k}''} (1-p_{\vec{k}''} h_{\vec{k}''}) \tag{16}
\]

we obtain from (15)

\[
\eta = 2\varepsilon_{\vec{k}} (1-2p_{\vec{k}h_k})^{-1} [p_{\vec{k}''} h_{\vec{k}''} (1-p_{\vec{k}''} h_{\vec{k}''})]^{\frac{1}{2}} \tag{17}
\]

and

\[
p_{\vec{k}h_k} = \frac{1}{2} \left\{ 1 - \frac{\varepsilon_{\vec{k}h_k}}{(\varepsilon_{\vec{k}h_k} + \eta)^{\frac{1}{2}}} \right\} \tag{18}
\]

By combining (17) and (18), we get

\[
\eta = V \sum_{\langle \vec{k}', \vec{k}'' \rangle} \eta \frac{\eta}{2(\varepsilon_{\vec{k}h_k} + \eta)^{\frac{1}{2}}} \tag{19}
\]

or, replacing the summation by an integral,

\[
\frac{1}{V} = N(0) \int_{0}^{\hbar_{\text{so}}} \frac{d\varepsilon}{(\varepsilon^2 + \eta)\eta} \frac{1}{2(\varepsilon_{\vec{k}h_k} + \eta)^{\frac{1}{2}}} - \frac{1}{2(\varepsilon_{\vec{k}h_k} + \eta)^{\frac{1}{2}}}. \tag{20}
\]

Substitution of \( \eta \) satisfying equation (20) in (14) gives the minimum value of \( W_{\text{exc}} \):

\[
W_{\text{exc}} = 2 \sum_{\vec{k} > \vec{k}_{F'}} \varepsilon_{\vec{k}h_k} + 2 \sum_{\vec{k} < \vec{k}_{F'}} |\varepsilon| (1-p_{\vec{k}h_k}) + |\varepsilon_{\vec{k}'}| + |\varepsilon_{\vec{k}''}| - \frac{\eta^2}{V}
= 2N(0) \int_{0}^{\hbar_{\text{so}}} \left\{ 1 - \frac{\varepsilon}{(\varepsilon^2 + \eta)\frac{1}{2}} \right\} d\varepsilon + \frac{\varepsilon_{\vec{k}h_k}}{(\varepsilon_{\vec{k}h_k} + \eta)^{\frac{1}{2}}} + \frac{\varepsilon_{\vec{k}''}}{(\varepsilon_{\vec{k}''} + \eta)^{\frac{1}{2}}} - \frac{\eta^2}{V}. \tag{21}
\]

In case the difference of distribution function between the excited state
and the ground state is small,

\[ p_k = 1 - \Delta_k , \]  \hspace{1cm} (22)

where \( |\Delta_k| \ll 1 \).

From equation (16), we obtain in the first order approximation of \( \Delta_k \)

\[ \eta = \varepsilon_0 - V \sum_{x} \frac{\Delta_x h_x (1 - 2h_x)}{2[h_x (1 - h_x)]^{\frac{3}{2}}} - V \left\{ \left[ h_x (1 - h_x) \right] + \left[ h_{x'} (1 - h_{x'}) \right] \right\}^{\frac{1}{2}} + \frac{V}{2} \left\{ \Delta_x h_x (1 - 2h_x) + \Delta_{x'} h_{x'} (1 - 2h_{x'}) \right\}^{\frac{3}{2}} \]

\[ = \varepsilon_0 - \Delta_{\eta_1} - \Delta_{\eta_2} (k', k'') , \]  \hspace{1cm} (23)

where

\[ \Delta_{\eta_1} = V \sum_{(x, x', x'')} \frac{\Delta_x h_x (1 - 2h_x)}{2[h_x (1 - h_x)]^{\frac{3}{2}}} \]  \hspace{1cm} (24)

and

\[ \Delta_{\eta_2} = V \left\{ \left[ h_x (1 - h_x) \right]^{\frac{1}{2}} + \left[ h_{x'} (1 - h_{x'}) \right]^{\frac{1}{2}} \right\} \]

\[ = \frac{V}{2} \left\{ \frac{1}{(\varepsilon_0 + \varepsilon_0^{'})^{\frac{1}{2}}} + \frac{1}{(\varepsilon_0 + \varepsilon_0^{'})^{\frac{1}{2}}} \right\} . \]  \hspace{1cm} (25)

In equation (25), the values of \( h_{x'} \) and \( h_{x''} \) for the ground state (6) are used.

Combining (19), (23) and (25) with (9), we can get the equation for \( \Delta_{\eta_2} \), in the first order approximation of \( \Delta_{\eta_1} \) and \( \Delta_{\eta_2} \);

\[ \Delta_{\eta_1} \int \frac{2N(0) k\omega}{\varepsilon_0} \left\{ 1 + \left( \frac{k\omega}{\varepsilon_0} \right) \right\}^{\frac{1}{2}} - \frac{\varepsilon_0}{(\varepsilon_0 + \varepsilon_0^{'})^{\frac{1}{2}}} \frac{\varepsilon_0}{(\varepsilon_0 + \varepsilon_0^{'})^{\frac{1}{2}}} + \frac{\varepsilon_0}{(\varepsilon_0 + \varepsilon_0^{'})^{\frac{1}{2}}} \]

\[ = \left\{ \frac{1}{(\varepsilon_0^2 + \varepsilon_0^2)^{\frac{1}{2}}} + \frac{1}{(\varepsilon_0^2 + \varepsilon_0^2)^{\frac{1}{2}}} \right\} \left[ - \frac{N(0) V k\omega}{\varepsilon_0} \left\{ 1 + \left( \frac{k\omega}{\varepsilon_0} \right) \right\}^{\frac{1}{2}} \right. \]

\[ + 1 + \frac{V \varepsilon_0^2}{2(\varepsilon_0^2 + \varepsilon_0^2)^{\frac{1}{2}}} + \frac{V \varepsilon_0^2}{2(\varepsilon_0^2 + \varepsilon_0^2)^{\frac{1}{2}}} \]. \hspace{1cm} (26)

Thus, \( \Delta_{\eta_1} \) which minimizes \( W_{\text{exc}} \) for the given \( k' \) and \( k'' \) has been obtained on the condition that \( h_k \) has the same value as in the ground state.

From (21) and (23), the energy of the excited state becomes
A Note of the Excited State at \( T=0^\circ K \) in the Superconducting State

\[
W_{\text{exc}} = 2N(0) \int_0^{\infty} \varepsilon \left\{ 1 - \frac{\varepsilon}{(\varepsilon^2 + \varepsilon_\xi^2)} \right\} d\varepsilon - 2N(0) \int_0^{\infty} \varepsilon_\xi^2 \left( \begin{array}{c} \varepsilon \varepsilon + (\Delta \xi_1 + \Delta \xi_2) \\ (\varepsilon^2 + \varepsilon_\xi^2) \end{array} \right) d\varepsilon \\
+ \varepsilon_\xi^2 \left( \begin{array}{c} (\varepsilon^2 + \varepsilon_\xi^2)^{\frac{3}{2}} + (\varepsilon_\xi^2 + \varepsilon_\xi^2)^{\frac{3}{2}} + \varepsilon_\xi (\Delta \xi_1 + \Delta \xi_2) \left( \begin{array}{c} \varepsilon \varepsilon_\xi^2 + \varepsilon_\xi^2 \\ (\varepsilon^2 + \varepsilon_\xi^2) \end{array} \right) \right) \\
+ \varepsilon_\xi^2 \left( \begin{array}{c} (\varepsilon^2 + \varepsilon_\xi^2)^{\frac{3}{2}} \\ \varepsilon \varepsilon_\xi^2 + \varepsilon_\xi^2 \end{array} \right) + \frac{2\varepsilon_\xi^2}{V} (\Delta \xi_1 + \Delta \xi_2) \right). 
\]

(27)

With the aid of (6), \( W_0 \) can be expressed as

\[
W_0 = 2N(0) \int_0^{\infty} \varepsilon \left\{ 1 - \frac{\varepsilon}{(\varepsilon^2 + \varepsilon_\xi^2)} \right\} d\varepsilon - \frac{\varepsilon_\xi^2}{V}. 
\]

(28)

Therefore, the energy gap at \( T=0^\circ K \) comes out

\[
\Delta W = W_{\text{exc}} - W_0 = \varepsilon_\xi^2 \left( \begin{array}{c} \varepsilon \varepsilon_\xi^2 + \varepsilon_\xi^2 \\ (\varepsilon^2 + \varepsilon_\xi^2) \end{array} \right) \\
+ \varepsilon_\xi^2 \left( \begin{array}{c} (\varepsilon^2 + \varepsilon_\xi^2)^{\frac{3}{2}} + (\varepsilon_\xi^2 + \varepsilon_\xi^2)^{\frac{3}{2}} + \varepsilon_\xi (\Delta \xi_1 + \Delta \xi_2) \left( \begin{array}{c} \varepsilon \varepsilon_\xi^2 + \varepsilon_\xi^2 \\ (\varepsilon^2 + \varepsilon_\xi^2) \end{array} \right) \right) \\
+ \varepsilon_\xi^2 \left( \begin{array}{c} (\varepsilon^2 + \varepsilon_\xi^2)^{\frac{3}{2}} \\ \varepsilon \varepsilon_\xi^2 + \varepsilon_\xi^2 \end{array} \right) \right) \\
\times \left[ \frac{V\varepsilon_\xi^2}{2} \left( \begin{array}{c} 1 \\ (\varepsilon^2 + \varepsilon_\xi^2)^{\frac{3}{2}} \end{array} \right) + \frac{1}{(\varepsilon^2 + \varepsilon_\xi^2)^{\frac{3}{2}}} \right] \left( \frac{1}{V} \right) \varepsilon_\xi \left( \begin{array}{c} \varepsilon \varepsilon_\xi^2 + \varepsilon_\xi^2 \\ (\varepsilon^2 + \varepsilon_\xi^2) \end{array} \right) \right] + \Delta \xi_1. 
\]

(29)

Equation (29) shows that the minimum excitation energy is obtained, when \( \varepsilon_\xi \) and \( \varepsilon_\xi \) tend to zero.

Therefore \( \Delta \xi_1 \) and the minimum excitation energy become

\[
\Delta \xi_1 = \left[ - \frac{N(0) V}{1 + (\hbar \omega / \varepsilon_o)^2} + \varepsilon_o \right] \left[ \frac{N(0) \hbar \omega}{1 + \left( \frac{\hbar \omega}{\varepsilon_o} \right)^2} \right] \frac{1}{2} - 1, 
\]

(30)

and

\[
\Delta W = \left[ \frac{2\varepsilon_\xi^2}{V} - 2N(0) \varepsilon_o \left( \begin{array}{c} 1 \\ N(0) V \end{array} \right) \hbar \omega \right] \\
\left( \frac{1}{1 + (\hbar \omega / \varepsilon_o)^2} \right) \left[ V + \Delta \xi_1 \right]. 
\]

(31)

In the case of weak interaction, we find that, by using a relation \( \hbar \omega > \varepsilon_o \),

\[
\Delta \xi_1 \equiv (1 - N(0) V)/N(0) \]

(32)

and

\[
\Delta W \equiv 2\varepsilon, 
\]

(33)

which is the same result as the B.C.S.-theory.

References

1) BIONDI, FORRESTER, GARFUNDEL and SATTERTHWAITE: Rev. Mod. Phys. 30 (1958) 1109.