Progress of Theoretical Physics, Vol. 38, No. 3, September 1967

s-d Exchange Interaction in a Superconductor

Toshio SODA, Tamifusa MATSUURA* and Yosuke NAGAOKA*

Department of Physics, Tokyo University of Education, Tokyo
**Department of Physics, Nagoya University, Nagoya*

(Received May 1, 1967)

The scattering of a quasiparticle in a superconductor due to a magnetic impurity is calculated by a perturbation method. It is shown that the ratio of the dominant contribution of the successive order of terms in the perturbation series is given at $T=0$ by the ratio $2J\rho \log(2D/\Delta)$ where ρ is the density of state at the Fermi surface divided by the number of atoms in the superconductor, J is the magnitude of the s-d exchange interaction, $2D$ is the band width, and Δ is the energy gap. If this ratio is greater than one, the perturbation series does not converge. This is connected with the existence of a bound state attached to the impurity atom. Following Yosida's theory on the bound state due to the s-d interaction in a normal metal, we examine the possibility of a bound state in a superconductor. It is shown that, if the s-d interaction is antiferromagnetic and stronger than the pairing interaction, a bound state is formed around the impurity spin, and that, if it is weaker, an excited level appears in the energy gap irrespective of the sign of the interaction. The condition for the existence of the bound state is found to be the same as the condition for the divergence of the perturbation series mentioned above. The effect on the density of states of quasiparticles at finite concentration of magnetic impurities is briefly discussed.

§ 1. Introduction

Investigations of the *s-d* exchange interactions in dilute alloys have produced many new aspects and controversies in regards to new bound states attached to the magnetic impurities of these alloys.[1),2),3)] It is quite interesting to see how these phenomena appear in superconductors and are detected experimentally.

A previous investigation of the Kondo effect in superconductors was given by Liu,[4)] Griffin[5)] and Maki.[6)] Among them Maki used a technique of dispersion theory and showed the existence of a pair of impurity levels inside the gap for the antiferromagnetic exchange interaction. His approach is quite mathematical and hard to see what is inside the black box of dispersion theory. Here we start from perturbation theory and investigate the convergence of the perturbation series. From this we pursue the possibility of the bound state and compute the binding energy.

In § 2 we calculate the scattering of a quasiparticle by the *s-d* exchange interactions due to magnetic impurities in a superconductor in the second Born approximation and see how the famous logarithmic term of the Kondo effect is modified in superconductors near the superconducting transition temperature and near the absolute zero of temperature. In § 3, a general order term of the perturbation and their sum for the scattering matrix at the absolute zero are evaluated and the convergence of the series is investigated. In §§ 4 and 5, from the divergence of the perturbation series, we pursue the possibility of bound states by following Yosida's theory on the bound state in a normal metal, and examine the eigenvalue equation for the binding energy for various cases.

§ 2. Scattering of a quasiparticle due to the *s-d* exchange interaction in the second Born approximation

We investigate how the scattering of a quasiparticle by the *s-d* exchange interaction due to the magnetic impurity in a superconductor behaves in the second Born approximation in comparison with the phenomenon of a resistance minimum of normal dilute alloys.

For simplicity, we assume a single magnetic impurity atom placed in a superconductor. The *s-d* interaction Hamiltonian of the system is given by

$$H_{sd} = -\frac{J}{N}\sum_{kk'}\sum_{ss'}\sum_{i} S_i \sigma_i^{s's} a_{k's'}^{+} a_{ks}, \tag{2·1}$$

where N is the number of atoms in the superconductor, J is the magnitude of an *s-d* exchange interaction, S_i and σ_i are the i-components of the impurity spin operator and the Pauli matrix, respectively. a_{ks}^{+} and a_{ks} are the creation and annihilation operators of an electron with momentum $\boldsymbol{k}$ and spin s. In order to form a superconducting state, we make the Bogoliubov transformation, which is given by

$$a_{k\uparrow} = u_k \alpha_{k0} + v_k \alpha_{k1}^{+}, \tag{2·2}$$

$$a_{-k\downarrow} = u_k \alpha_{k1} - v_k \alpha_{k0}^{+}. \tag{2·3}$$

The electrons are now transformed into quasiparticles in the superconductor. Here u_k and v_k are given by

$$u_k^2 = \frac{1}{2}\left(1+\frac{\epsilon_k}{E_k}\right), \tag{2·4}$$

$$v_k^2 = \frac{1}{2}\left(1-\frac{\epsilon_k}{E_k}\right), \tag{2·5}$$

with $\epsilon_k = \boldsymbol{k}^2/2m - \mu$ and $E_k = (\epsilon_k^2 + \Delta^2)^{1/2}$. μ is the chemical potential measured from the band bottom and the Δ is the energy gap.

After some manipulation, we get the total Hamiltonian in the quasipaticle representation as follows:

$$H_t = \sum_{k,\nu=0,1} E_k \alpha_{k\nu}^{+} \alpha_{k\nu} - \frac{J}{N}\sum_{k,k'}\sum_{\nu,\nu'=0,1}\sum_{i} \{(u_{k'} u_k + v_{k'} v_k) S_i \sigma_i^{\nu'\nu} \alpha_{k'\nu'}^{+} \alpha_{k\nu}$$

$$+\tfrac{1}{2}(u_{k'}v_k - v_{k'}u_k)S_i(\mu_i^{\nu'\nu}\alpha_{k'\nu'}\alpha_{k\nu} + \mu_i^{+\nu\nu'}\alpha_{k\nu}^+\alpha_{k'\nu'}^+)\}, \tag{2·6}$$

where $\sigma_i^{\nu\nu'}$ is the Pauli matrix as before, and $\mu_i^{\nu\nu'}$ is defined by

$$\mu_i^{\nu\nu'} = \sum_{\bar{\nu}=0,1} I^{\nu\bar{\nu}}\sigma_i^{\bar{\nu}\nu'}, \tag{2·7}$$

$$I^{00} = I^{11} = 0,\ I^{01} = -I^{10} = 1. \tag{2·8}$$

In this Hamiltonian, the terms of the scattering between quasiparticles are neglected, because they do not give rise to the anomalous behavior in comparison with the *s-d* exchange term.*)

We now calculate the scattering matrix of a quasiparticle due to the *s-d* interaction for the spin-nonflip process between the states $(\boldsymbol{k}, 0)$ and $(\boldsymbol{k}', 0)$ with $E_k = E_{k'}$, in the second Born approximation. The diagrams are shown in Fig. 1.

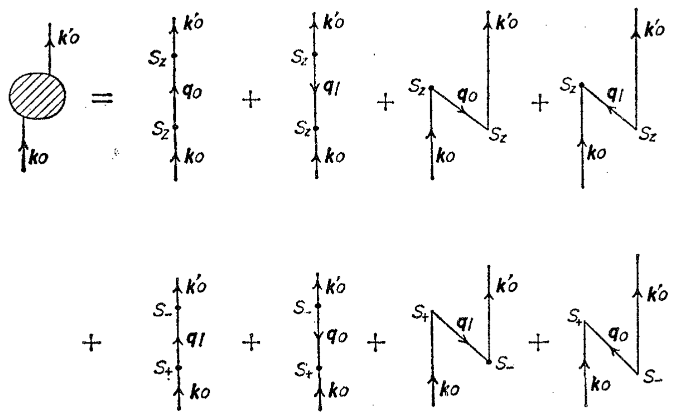

Fig. 1. Quasiparticle scattering diagram by the *s-d* interaction for non spin flip process in the second order Born approximation.

The contractions of quasiparticle operators are given by

$$\langle \alpha_{q\nu}^+ \alpha_{q\nu} \rangle = f_q \tag{2·9}$$

and

$$\langle \alpha_{q\nu} \alpha_{q\nu}^+ \rangle = 1 - f_q, \tag{2·10}$$

where

$$f_q = 1/(\exp(E_q/T) + 1) \tag{2·11}$$

(the Boltzmann constant, k, is taken to be 1).
If we use the following relationship:

*) The indices of the matrix, ↑ and ↓, are replaced here by 0 and 1 respectively. In order to obtain Eq. (2·6) we used the BCS Hamiltonian and the *s-d* interaction Hamiltonian (2·1), and transformed them by the Bogoliubov transformation.

$$S_+S_- = S(S+1) - S_z^2 + S_z \tag{2·12}$$

and

$$S_- S_+ = S(S+1) - S_z^2 - S_z, \tag{2·13}$$

we obtain the following scattering matrix for the whole processes in Fig. 1:

$$\left(-\frac{J}{N}\right)^2 \sum_q \left\{\frac{(u_k u_q + v_k v_q)^2}{E_k - E_q} + \frac{(u_k v_q - v_k u_q)^2}{E_k + E_q}\right\} S(S+1)\, \alpha_{k'0}^{+}\, \alpha_{k0}$$
$$-\left(-\frac{J}{N}\right)^2 \sum_q \left\{\frac{(u_k u_q + v_k v_q)^2}{E_k - E_q} - \frac{(u_k v_q - v_k u_q)^2}{E_k + E_q}\right\} (1-2f_q)\, S_z \alpha_{k'0}^{+}\, \alpha_{k0}. \tag{2·14}$$

From the symmetry properties we obtain the following general scattering matrix by including also the other types of scattering:

$$\left(-\frac{J}{N}\right)^2 S(S+1) \sum_q \left\{\frac{(u_k u_q + v_k v_q)^2}{E_k - E_q} + \frac{(u_k v_q - v_k u_q)^2}{E_k + E_q}\right\} (\alpha_{k'0}^{+}\alpha_{k0} + \alpha_{k'1}^{+}\alpha_{k1})$$
$$-\left(-\frac{J}{N}\right)^2 \sum_q \left\{\frac{(u_k u_q + v_k v_q)^2}{E_k - E_q} - \frac{(u_k v_q - v_k u_q)^2}{E_k + E_q}\right\} (1-2f_q)$$
$$\times \sum_{\nu\nu'} \sum_i S_i \sigma_i^{\nu'\nu}\, \alpha_{k'\nu'}^{+}\, \alpha_{k\nu}. \tag{2·15}$$

The second term gives the logarithmic divergence in the case of normal metals. We put the coefficient of this term as follows:

$$I_k = \frac{1}{N} \sum_q \left\{\frac{(u_k u_q + v_k v_q)^2}{E_k - E_q} - \frac{(u_k v_q - v_k u_q)^2}{E_k + E_q}\right\} (1-2f_q), \tag{2·16}$$

and evaluate it for the three cases, at $T=0°$K and near $0°$K and T_c, assuming the density of states of conduction electrons to be $N\rho = \text{const.}$, and the band width to be $2D$.

1) At $T=0$:

$$I_k = -2\rho \left\{\log \frac{2D}{\Delta} + \frac{E_k^2 + \Delta^2}{E_k |\epsilon_k|} \log \frac{E_k - |\epsilon_k|}{\Delta}\right\}. \tag{2·17}$$

2) At $T \ll T_c$ with $E_k - \Delta \ll T$:

$$I_k \cong -2\rho \left\{\log \frac{2D}{\Delta} - 2\left(1 + \left(\frac{2\pi\Delta}{T}\right)^{1/2} e^{-\Delta/T}\right)\right\}. \tag{2·18}$$

3) At $T \lesssim T_c$ with $E_k - \Delta \ll \Delta$:

$$I_k \cong -2\rho \left\{\log \frac{2\gamma D}{\pi T} - 1\right\}, \tag{2·19}$$

where $\log \gamma = C = 0.577$. The quantity I_k is exact only for the $T=0$ case and is evaluated as a limiting value when E_k goes to Δ for the other cases. We can see that we have $\log T$ dependence as in normal metals for $T \lesssim T_c$. At

$T=0$ the biggest contribution to I_k comes from the term $-2\rho\log(2D/\Delta)$. If we compare this dominant term with the first order scattering matrix element in J, the ratio becomes

$$-2J\rho\log\frac{2D}{\Delta}\cong-\frac{2J}{V_{\text{pair}}}\,. \tag{2·20}$$

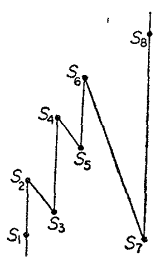

Fig. 2. Diagram of the quasiparticle scattering for the general order of the perturbation.

Here V_{pair} is the magnitude of the pairing interaction. There is a possibility that this ratio becomes the order of one. The famous Kondo term in normal metals now corresponds to $\log(2D/\Delta)$ in our case of $T=0$.

§ 3. Behavior of perturbation series for the scattering matrix

We investigate the behavior of the perturbation series at $T=0$, keeping only the dominant contribution as we did in § 2.

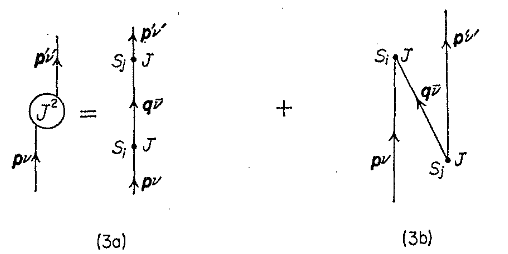

Fig. 3. Quasiparticle scattering containing only J^2 interaction splitted from the first part of the diagram in Fig. 2.

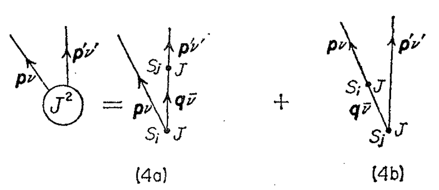

Fig. 4. Quasiparticle pair creation containing only J^2 interaction splitted from the first part of the diagram in Fig. 2.

Now we consider a diagram of a general order in a perturbation as shown in Fig. 2. We analyze this diagram by separating the first part which contains interactions in J^2. It is shown in Figs. 3 and 4. The contributions from Fig. 3 to the scattering matrix are computed as follows:
for the process (3a)

$$\left(-\frac{J}{N}\right)^2\sum_q\sum_{i,j}\frac{(u_{q'}u_q+v_{p'}v_q)\,(u_pu_q+v_pv_q)}{E_k-\{E_{q'}\}-E_q}\,S_jS_i(\sigma_j\sigma_i)^{\nu\nu'}\,\alpha^+_{p'\nu'}\,\alpha_{p\nu}, \tag{3·1}$$

for the process (3b)

$$\left(-\frac{J}{N}\right)^2\sum_q\sum_{i,j}\frac{(u_pv_p-v_qu_p)\,(u_qv_{p'}-v_qu_{p'})}{E_k-\{E_{q'}\}-E_q}\,S_iS_j(\mu_j{}^+\mu_i)^{\nu'\nu}\,\alpha^+_{p'\nu'}\,\alpha_{p\nu}, \tag{3·2}$$

where $\{E_{q'}\}$ is the sum of the energy of the quasiparticles in the intermediate state except for E_q.*) Similarly we have the contributions from Fig. 4: for the process (4a)

$$\left(-\frac{J}{N}\right)^2 \sum_q \sum_{i,j} \frac{(u_p u_q + v_p v_q)(u_{p'} v_q - v_{p'} u_q)}{E_k - \{E_{q'}\} - E_q} S_i S_j (\sigma_i \mu_j^+)^{\nu\nu'} \alpha_{p'\nu'}^+ \alpha_{p\nu}^+, \tag{3·3}$$

for the process (4b)

$$-\left(-\frac{J}{N}\right)^2 \sum_q \sum_{i,j} \frac{(u_p u_q + v_p v_q)(u_{p'} v_q - v_{p'} u_q)}{E_k - \{E_{q'}\} - E_q} S_j S_i (\sigma_i \mu_j^+)^{\nu\nu'} \alpha_{p'\nu'}^+ \alpha_{p\nu}^+. \tag{3·4}$$

The summation over $\boldsymbol{q}$ in Eqs. (3·3) and (3·4) is carried out in a way similar to the calculation of Eqs. (4·9) and (4·10). Near the edge of the excitation spectrum we have

$$\frac{1}{N}\sum_q \frac{u_q^2}{E_k - \{E_{q'}\} - E_q} = \frac{1}{N}\sum_q \frac{v_q^2}{E_k - \{E_{q'}\} - E_q}$$
$$= -2\rho\left[\log\frac{2D}{\varDelta} + 0(1)\right], \tag{3·5}$$

$$\frac{1}{N}\sum_q \frac{u_q v_q}{E_k - \{E_{q'}\} - E_q} = \rho 0(1). \tag{3·6}$$

(See Eq. (4·16).) If we take the most divergent term, $\log(2D/\varDelta)$, we have the following results for the contributions from Fig. 3:

$$\left(-\frac{J}{N}\right)(2J\rho)\log\frac{2D}{\varDelta}(u_p u_{p'} + v_p v_{p'})$$
$$\times \sum_{i,j} [S_j S_i (\sigma_j \sigma_i)^{\nu'\nu} - S_i S_j (\mu_j^+ \mu_i)^{\nu'\nu}] \alpha_{p'\nu'}^+ \alpha_{p\nu}$$
$$= -\left(-\frac{J}{N}\right)\left(-2J\rho\log\frac{2D}{\varDelta}\right)(u_p u_{p'} + v_p v_{p'}) \sum_k S_k \sigma_k^{\nu'\nu} \alpha_{p'\nu'}^+ \alpha_{p\nu}, \tag{3·7}$$

and from Fig. 4

$$\left(-\frac{J}{N}\right)\left(2J\rho\log\frac{2D}{\varDelta}\right)(u_p v_{p'} - v_p u_{p'})$$
$$\times \sum_{i,j} [S_j S_i (\sigma_j \mu_i^+)^{\nu'\nu} + S_i S_j (\sigma_i \mu_j^+)^{\nu'\nu}] \alpha_{p'\nu'}^+ \alpha_{p\nu}^+ \tag{3·8}$$
$$= \left(-\frac{J}{N}\right)\left(-2J\rho\log\frac{2D}{\varDelta}\right)(u_p v_{p'} - v_p u_{p'}) \sum_k S_k \mu_k^{\nu'\nu} \alpha_{p'\nu'}^+ \alpha_{p\nu}^+.$$

*) The sum of the quasiparticle energies, $\{E_{q'}\}$, cannot be defined uniquely. As will be shown in the text, however, this does not affect the most divergent contributions. In the following discussion in the text, the non-commutativity of spin operators is neglected except for those in the successive pair of vertices. In the diagram of Fig. 2, for example, we treat S_6 and S_7 correctly, but S_5 and S_7 as if they were commutative. This approximation is also allowed if we are interested only in the most divergent contributions, as in the case of a normal metal.[7]

Here we used properties such as

$$\mu_j^+\mu_i=\sigma_j\sigma_i,$$
$$\sigma_j\mu_i^+-\sigma_i\mu_j^+=\mu_k,\quad (i, j, k\,;\ \text{cyclic}).$$

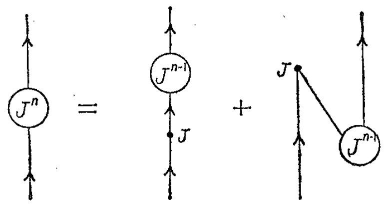

Fig. 5. Quasiparticle scattering diagram of the n-th order in J.

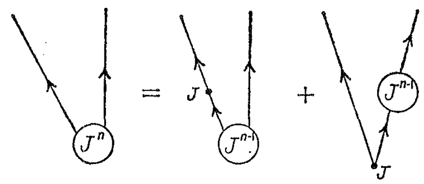

Fig. 6. Quasiparticle pair creation diagram of the n-th order in J.

In general orders, the diagram is decomposed as in Figs. 5 and 6. If we take only the commutator of $(\boldsymbol{\sigma S})$ in the successive vertices, the most divergent contribution for the n-th order matrix in J becomes the following:
for Fig. 5

$$\left(-\frac{J}{N}\right)\left(-2J\rho\log\frac{2D}{\Delta}\right)^{n-1}(u_pu_{p'}+v_pv_{p'})\,S_k\sigma_k^{\nu'\nu}\,\alpha^+_{p'\nu'}\,\alpha_{p\nu},\tag{3·9}$$

and for Fig. 6

$$\left(-\frac{J}{N}\right)\left(-2J\rho\log\frac{2D}{\Delta}\right)^{n-1}(u_pv_{p'}-v_pu_{p'})\,S_k\,\mu_k^{+\nu'\nu}\,\alpha^+_{p'\nu'}\,\alpha^+_{p\nu}.\tag{3·10}$$

Summing up the matrices over n from $n=1$ to infinity, we obtain the perturbation series for the scattering matrix for a quasiparticle scattering as

$$\frac{-J/N}{1+2J\rho\log(2D/\Delta)}(u_pu_{p'}+v_pv_{p'})\sum_k S_k\sigma_k^{\nu'\nu}\,\alpha^+_{p'\nu'}\,\alpha_{p\nu}.\tag{3·11}$$

It is to be noted here that the denominator of Eq. (3·11) is identical with the expression appearing in the cross section obtained by Abrikosov, if Δ is replaced by T. The scattering matrix diverges if

$$2(-J\rho)\log\frac{2D}{\Delta}\simeq-\frac{2J}{V_{\text{pair}}}\gtrsim 1,\tag{3·12}$$

in a similar way as we discussed in § 2. We shall see in § 4 how this condition is connected with the existence of a bound state.

§ 4. Bound states in the lowest order approximation

In this and next sections we examine the possibility of a bound state assuming $S=\frac{1}{2}$ for simplicity. Following Yosida,[2] we first take the wave function as

$$\Psi=\sum_K\{(\Gamma^\alpha_{K_0}\alpha^+_{K_0}+\Gamma^\alpha_{K_1}\alpha^+_{K_1})\alpha+(\Gamma^\beta_{K_0}\alpha^+_{K_0}+\Gamma^\beta_{K_1}\alpha^+_{K_1})\beta\}\Phi_0,\tag{4·1}$$

where Φ_0 is the wave function of the ground state of a pure superconductor, and α and β are respectively the wave functions of the up- and down- spin states of the impurity. Inserting the wave function in

$$H_t \Psi = E\Psi, \tag{4·2}$$

we get the following equations which determine Γ_k and the energy eigenvalue:

$$(E_k - E)\Gamma_k^s + \frac{3}{2}\frac{J}{N}\sum_{k'}(u_k u_{k'} + v_k v_{k'})\Gamma_{k'}^s = 0 \tag{4·3}$$

for

$$\Gamma_k^s = \frac{1}{\sqrt{2}}(\Gamma_{k1}^\alpha - \Gamma_{k0}^\beta), \tag{4·4}$$

and

$$(E_k - E)\Gamma_k^t - \frac{1}{2}\frac{J}{N}\sum_{k'}(u_k u_{k'} + v_k v_{k'})\Gamma_{k'}^t = 0 \tag{4·5}$$

for

$$\Gamma_k^t = \Gamma_{k0}^\alpha,\ \frac{1}{\sqrt{2}}(\Gamma_{k1}^\alpha + \Gamma_{k0}^\beta)\ \text{and}\ \Gamma_{k1}^\beta. \tag{4·6}$$

From these equations, we have the following secular equations:

$$[1 + 3JU(E)][1 + 3JV(E)] - 9J^2 W(E)^2 = 0 \tag{4·7}$$

for the singlet state and

$$[1 - JU(E)][1 - JV(E)] - J^2 W(E)^2 = 0 \tag{4·8}$$

for the triplet state, where

$$U(E) = \frac{1}{2N}\sum_k \frac{u_k^2}{E_k - E}, \tag{4·9}$$

$$V(E) = \frac{1}{2N}\sum_k \frac{v_k^2}{E_k - E} \tag{4·10}$$

and

$$W(E) = \frac{1}{2N}\sum_k \frac{u_k v_k}{E_k - E}. \tag{4·11}$$

If the band is assumed to be symmetrical around the Fermi level, it is easily shown that

$$U(E) = V(E). \tag{4·12}$$

By using this relationship, Eqs. (4·7) and (4·8) reduce respectively to

$$1+3JU_{\pm}(E)=0 \quad \text{(singlet)}, \tag{4·13}$$

$$1-JU_{\pm}(E)=0 \quad \text{(triplet)}, \tag{4·14}$$

where the function $U_{\pm}(E)$ is defined as

$$U_{\pm}(E)=U(E)\pm W(E). \tag{4·15}$$

To calculate the function $U_{\pm}(E)$, we assume the density of states of conduction electrons to be $N\rho=\text{const.}$ for $-D<\epsilon_k<D$, and to vanish otherwise, as before. Then we have

$$U_{\pm}(E)=\begin{cases} \dfrac{\rho}{2}\left[\log\dfrac{2D}{\Delta}-\dfrac{E\pm\Delta}{[E^2-\Delta^2]^{1/2}}\log\dfrac{|-(\Delta^2/2D)+E+[E^2-\Delta^2]^{1/2}|}{\Delta}\right] & \text{for } E<-\Delta, \\ \dfrac{\rho}{2}\left[\log\dfrac{2D}{\Delta}+\dfrac{E\pm\Delta}{[\Delta^2-E^2]^{1/2}}\left(\dfrac{\pi}{2}+\arcsin\dfrac{E}{\Delta}\right)\right] & \text{for } |E|<\Delta. \end{cases} \tag{4·16}$$

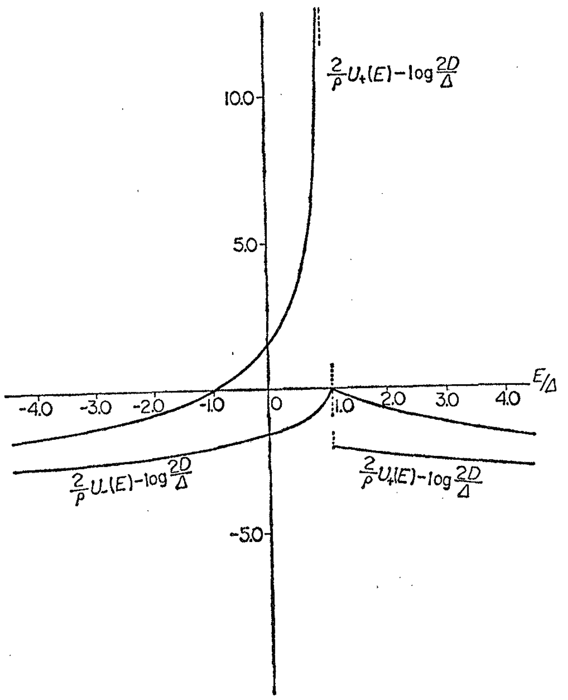

Fig. 7. The function $U_{\pm}(E)$ is plotted as a function of E.

The function $U_{\pm}(E)$ is shown in Fig. 7.

Now we look for the solutions of Eqs. (4·13) and (4·14) for $E<\Delta$. Because $U_{\pm}(E)>0$ for $|E|\ll D$, the existence of the solution for a singlet state requires $J<0$, and the existence for a triplet state requires $J>0$.

We first examine the case

$$|J|\rho\log\frac{2D}{\Delta}\gg 1 \quad \text{or} \quad |J|\gg V_{\text{pair}}.$$

In this case, it is seen from Fig. 7 that the solution satisfies $E<0$ and $|E|\gg\Delta$. For $|E|\gg\Delta$, Eq. (4·16) becomes

$$U_{\pm}(E)=\frac{\rho}{2}\left[\log\frac{D}{|E|}\pm\frac{\Delta}{E}\log\frac{\Delta}{2|E|}\right]. \tag{4·17}$$

Inserting Eq. (4·17) into Eqs. (4·13) and (4·14), we get the solutions

$$E=-D\exp\left(-\frac{2}{3|J|\rho}\right)\pm\frac{2}{3}\frac{\Delta}{|J|\rho} \quad \text{for } J<0 \text{ (singlet)}, \tag{4·18}$$

and

$$E=-D\exp\left(-\frac{2}{J\rho}\right)\pm\frac{2\Delta}{J\rho} \quad \text{for } J>0 \text{ (triplet)}. \qquad (4\cdot19)$$

They reduce to the same solutions as obtained by Yosida in the limit $|J|\gg V_{\text{pair}}$ as expected. It should be noticed here that the both solutions have two-fold degeneracy in this limit besides the spin degeneracy for the triplet state. It corresponds to the degeneracy of the electron-trapped and hole-trapped bound states in a normal metal. The degeneracy is removed in a superconductor, because there is a non-vanishing matrix element between the electron-trapped and the hole-trapped states. There exist, however, some arguments on this degeneracy in a normal metal, and it is not clear whether the exact ground state is really degenerate.[2),3)] If it is a fictitious one which appeared due to the approximation, one of the two levels obtained above, maybe the upper one, will also be fictitious and disappear if the higher order corrections are considered.

For $|J|\ll V_{\text{pair}}$ the situation is quite different. In this case, Eqs. $(4\cdot13)$ and $(4\cdot14)$ with minus subscript have no solution, while those with plus subscript have solutions such that $0<\Delta-E\ll\Delta$. For $0<\Delta-E\ll\Delta$, we have from Eq. $(4\cdot16)$,

$$U_+(E)\cong\frac{\pi\rho}{2}\left[\frac{2\Delta}{\Delta-E}\right]^{1/2}. \qquad (4\cdot20)$$

Inserting Eq. $(4\cdot20)$ into Eqs. $(4\cdot13)$ and $(4\cdot14)$, we obtain the solutions

$$E=\Delta\left[1-\frac{9}{2}\pi^2(J\rho)^2\right] \quad \text{for } J<0 \text{ (singlet)}, \qquad (4\cdot21)$$

$$E=\Delta\left[1-\frac{1}{2}\pi^2(J\rho)^2\right] \quad \text{for } J>0 \text{ (triplet)}, \qquad (4\cdot22)$$

which means that there exist discrete excited levels in the energy gap.

When the magnitude of J increases, the solutions become negative for J larger than some critical values J_c, which are determined by putting $E=0$ in Eqs. $(4\cdot13)$ and $(4\cdot14)$. From

$$1+\frac{3}{2}J_c\rho\left(\log\frac{2D}{\Delta}\pm\frac{\pi}{2}\right)=0 \quad \text{for } J<0 \text{ (singlet)} \qquad (4\cdot23)$$

and

$$1-\frac{1}{2}J_c\rho\left(\log\frac{2D}{\Delta}\pm\frac{\pi}{2}\right)=0 \quad \text{for } J>0 \text{ (triplet)}, \qquad (4\cdot24)$$

we get

$$|J_c|\cong\frac{2}{3}V_{\text{pair}} \quad \text{for } J<0 \text{ (singlet)}, \qquad (4\cdot25)$$

$$J_c\cong2V_{\text{pair}} \quad \text{for } J>0 \text{ (triplet)}. \qquad (4\cdot26)$$

Though these values coincide with Eq. (3·12) in the order of magnitude, numerical factors are different between them. This point will be discussed in the next section.

§ 5. Bound states with higher order effects

It was shown by Yosida[2)] that higher order effects are essentially important to examine the possibility of the bound state in a normal metal. In particular, the bound state obtained in the lowest approximation for $J>0$ becomes unstable, if higher order effects are taken into account successively. In order to study the effects in a superconductor, we take the wave function as

$$\Psi=\Psi_1+\sum_{k_1,k_2,k_3,}\sum_{\nu_1,\nu_2,\nu_3=0,1}\{\Gamma^{\alpha}_{k_1\nu_1,k_2\nu_2,k_3\nu_3}\ \alpha^+_{k_1\nu_1}\alpha^+_{k_2\nu_2}\alpha^+_{k_3\nu_3}\alpha$$
$$+\Gamma^{\beta}_{k_1\nu_1,k_2\nu_2,k_3\nu_3}\ \alpha^+_{k_1\nu_1}\alpha^+_{k_2\nu_2}\alpha^+_{k_3\nu_3}\beta\}\Phi_0, \tag{5·1}$$

where Ψ_1 is given by Eq. (4·1). Then, following the same procedure as that of Yosida, we get the following equations:

$$(E_k-E+\Delta E_k)\Gamma^s_k+3\left(\frac{J}{2N}\right)\sum_{k'}(u_ku_{k'}+v_kv_{k'})\Gamma^s_{k'}$$
$$+3\left(\frac{J}{2N}\right)^2\sum_{k',k''}\frac{(u_{k'}v_{k''}-u_{k''}v_{k'})(u_{k''}v_k-u_kv_{k''})}{E_k+E_{k'}+E_{k''}-E}\Gamma^s_{k'}=0, \tag{5·2}$$

$$(E_k-E+\Delta E_k)\Gamma^t_k-\left(\frac{J}{2N}\right)\sum_{k'}(u_ku_{k'}+v_kv_{k'})\Gamma^t_{k'}$$
$$-5\left(\frac{J}{2N}\right)^2\sum_{k',k''}\frac{(u_{k'}v_{k''}-u_{k''}v_{k'})(u_{k''}v_k-u_kv_{k''})}{E_k+E_{k'}+E_{k''}-E}\Gamma^t_{k'}=0, \tag{5·3}$$

where

$$\Delta E_k=-3\left(\frac{J}{2N}\right)^2\sum_{k',k''}\frac{(u_{k'}v_{k''}-u_{k''}v_{k'})^2}{E_k+E_{k'}+E_{k''}-E} \tag{5·4}$$

is the shift of the quasiparticle energy. It is easily shown that this term is not anomalous as a function of E. Omitting ΔE_k,*) we get the secular equations

$$1+3\,JU_\pm(E)-9J^3K_\pm(E)=0\ \ \text{(singlet)} \tag{5·5}$$

and

$$1-JU_\pm(E)-5J^3K_\pm(E)=0\ \ \text{(triplet)} \tag{5·6}$$

instead of Eqs. (4·13) and (4·14), where

*) This means that we redefine E as the bound state energy: If we put $E=E'+\Delta E$, where ΔE is the ground state energy calculated by the usual perturbation, ΔE almost cancels ΔE_k. Denoting E' by E again, we get Eqs. (5·5) and (5·6).

$$K_{\pm}(E) = -\left(\frac{\rho}{2}\right)^2 \int_0^D\int_0^D \frac{1}{([\epsilon^2+\Delta^2]^{1/2}-E)([\epsilon'^2+\Delta^2]^{1/2}-E)}$$

$$\times\left(1\pm\frac{\Delta}{[\epsilon^2+\Delta^2]^{1/2}}\right)\left(1\pm\frac{\Delta}{[\epsilon'^2+\Delta^2]^{1/2}}\right)U_{\mp}(E-[\epsilon^2+\Delta^2]^{1/2}-[\epsilon'^2+\Delta^2]^{1/2})\,d\epsilon d\epsilon'. \tag{5·7}$$

For $|E|\gg\Delta$, Eqs. (5·5) and (5·6) coincide with the equations obtained by Yosida (Eqs. (31) and (34) of the first paper in reference 2). Therefore the higher order effects on the solutions (4·18) and (4·19) are exactly the same as those in a normal metal; i.e. the secular equation has no solution for a triplet state, while the numerical factor of the exponent of the solution (4·18) for a singlet state changes from 2/3 to 1·22/2.

For $0<\Delta-E\ll\Delta$, we have

$$K_{+}(E)\cong-\pi^2\left(\frac{\rho}{2}\right)^3\cdot\log\frac{2D}{\Delta}\cdot\left(\frac{2\Delta}{\Delta-E}\right). \tag{5·8}$$

The solutions (4·21) and (4·22) for $|J|\ll V_{\text{pair}}$ are modified respectively to

$$E\cong\Delta\left[1-\frac{9}{2}\pi^2(J\rho)^2(1-J\rho\log\frac{2D}{\Delta})\right]\qquad\text{for } J<0 \text{ (singlet)}, \tag{5·9}$$

and

$$E\cong\Delta\left[1-\frac{1}{2}\pi^2(J\rho)^2(1-5J\rho\log\frac{2D}{\Delta})\right]\qquad\text{for } J>0 \text{ (triplet)}. \tag{5·10}$$

The correction terms are small compared with the lowest order terms by the factor

$$|J|\rho\log\frac{2D}{\Delta}=\frac{|J|}{V_{\text{pair}}}\ll1.$$

Thus it is seen that the discrete impurity levels in the energy gap obtained in the lowest approximation are essentially unchanged by the higher order effects both for the singlet and for the triplet states. The situation will not change even if we take into account the fourth and higher order terms of J.

The condition for the existence of the bound state, or the solution $E<0$, is modified by the higher order effects in the following way. As

$$K_{+}(0)\simeq-\frac{1}{3}\left(\frac{\rho}{2}\right)^3\left(\log\frac{2D}{\Delta}\right)^3, \tag{5·11}$$

the equations to determine J_c become

$$1+3\left(\frac{J_c\rho}{2}\log\frac{2D}{\Delta}\right)+3\left(\frac{J_c\rho}{2}\log\frac{2D}{\Delta}\right)^3=0 \text{ for } J<0\quad\text{(singlet)} \tag{5·12}$$

and

$$1-\frac{J_c\rho}{2}\log\frac{2D}{\Delta}+\frac{5}{3}\left(\frac{J_c\rho}{2}\log\frac{2D}{\Delta}\right)^3=0 \quad \text{for } J>0\,(\text{triplet}). \tag{5·13}$$

It should be noticed here that Eqs. (5·12) and (5·13) are of the same form as Eqs. (31) and (34) of the first paper in reference 2 for the energy eigenvalue. Then it is easily seen that Eq. (5·13) has no solution, and that the numerical factor of Eq. (4·23) changes from 2/3 to 1·22/2. In § 3, we found that the critical value of J for the convergence of perturbation is just given by $J_c=2^{-1}V_{\text{pair}}$. The situation is parallel between the numerical factor of the exponent of the bound state energy in a normal metal, and that of the critical value J_c in a superconductor. It is expected in both cases that the factor tends to 1/2 from 2/3 in the lowest approximation as we proceed to higher orders.

§ 6. Discussion

The conclusions obtained in the preceding sections are summarized as follows. When the exchange interaction is antiferromagnetic and stronger than the pairing interaction in a superconductor, the perturbation series for the scattering matrix of quasiparticles diverges. In this case the Cooper pairs in the vicinity of the impurity are destroyed by the strong exchange interaction, and a bound state is formed around the impurity. If the exchange interaction is weaker, a discrete impurity level is found in the energy gap both for the ferromagnetic and antiferromagnetic exchange interaction.

Although there still remain some ambiguities about the bound state solution even for a normal metal, the solution of the discrete level in the energy gap may be said to be well established in so far as the concentration of impurities is sufficiently low, because it is little affected by higher order corrections. Therefore, it is of some interest to examine whether it is experimentally detectable at finite concentrations. For this purpose, let us consider how the levels are modified as the concentration increases.

The wave function of a singlet state, for example, is given by

$$\Psi=\sum_k \Gamma_k^s(\alpha_{k_1}^+\alpha-\alpha_{k_0}^+\beta)\Phi_0, \tag{6·1}$$

where

$$\Gamma_k^s=\frac{u_k+v_k}{E_k-E}\,\Gamma \tag{6·2}$$

and Γ is the normalization constant. Its spatial behavior can be seen by taking the Fourier transform of the coefficient Γ_k^s, i.e.

$$\Gamma(R)=\sum_k \Gamma_k^s \exp(i\boldsymbol{k}\cdot\boldsymbol{R}). \tag{6·3}$$

Inserting Eqs. (6·2) and (4·21) in Eq. (6·3), we get for sufficiently large R

$$\Gamma(R) \simeq \frac{1}{(k_F\eta)^{1/2}} \frac{\sin k_F R}{k_F R} e^{-R/\eta}, \tag{6·4}$$

where

$$\eta = \frac{\hbar v_F}{\Delta(|J|\rho)} = \frac{\xi}{|J|\rho} \tag{6·5}$$

is the approximate dimension of the impurity level and $\xi = \hbar v_F/\Delta$ is the coherence length of the superconductor. Although Eq. (6·7) is correct only for large R, it gives the correct order of magnitude for small R also. If the mean distance between impurities is larger than η, impurities may be considered as independent. Therefore, denoting the concentration of impurities by c, we get the condition for impurity levels not to overlap with one another:

$$(cN)^{-1/3} > \eta$$

or

$$c < \left(\frac{a}{\xi}\right)^3 (|J|\rho)^3, \tag{6·6}$$

where $a \equiv N^{-1/3}$ is the atomic distance of the crystal.

A different condition is found by the following consideration. It can be seen from Eq. (6·2) that quasiparticle states with $E_k - E \gg \Delta - E$ do not contribute to the formation of the impurity level. Therefore, the number of effective states is approximately given by

$$\int_{|E_k - \Delta| \leq |\Delta - E|} \frac{d^3\boldsymbol{k}}{(2\pi)^3} \simeq N\rho\Delta(|J|\rho).$$

In order that each impurity may have its own impurity level, it is necessary that the number of impurities cN is smaller than the above number of effective states, i.e.

$$cN < N\rho\Delta \cdot (|J|\rho)$$

or

$$c < \left(\frac{a}{\xi}\right) |J|\rho. \tag{6·7}$$

We can find the same condition by a different consideration. As the concentration of impurities increases, the overlapping of the wave functions at different impurity sites becomes important, and at sufficiently large concentrations we have a kind of an impurity band instead of discrete impurity levels. If there are two impurities at $\boldsymbol{R}_i$ and $\boldsymbol{R}_j$, the transfer matrix element between the two states is calculated from Eq. (6·4) as

$$J_{R_iR_j} \simeq \int \Gamma(\boldsymbol{R}-\boldsymbol{R}_i)\, J\delta(\boldsymbol{R}-\boldsymbol{R}_j)\, \Gamma(\boldsymbol{R}-\boldsymbol{R}_j)\, d^3\boldsymbol{R}$$

$$\simeq \frac{J}{k_F\eta} \frac{\sin(k_F|\boldsymbol{R}_i-\boldsymbol{R}_j|)}{k_F|\boldsymbol{R}_i-\boldsymbol{R}_j|} \exp(-|\boldsymbol{R}_i-\boldsymbol{R}_j|/\eta).$$

The width of the impurity band is estimated as the broadening of one impurity level due to its finite lifetime. The transition probability from one impurity level, say at the origin, to another, say at $\boldsymbol{R}$, is given by

$$\frac{1}{\hbar W}|J_{0R}|^2 \simeq \frac{1}{\hbar W} \frac{J^2}{(k_F\eta)^2}\left(\frac{\sin k_F R}{k_F R}\right)^2 \exp(-2R/\eta),$$

where W is the width of the impurity level. W itself is calculated from this as

$$W \simeq \frac{cN}{W}\int_0^\infty |J_{0R}|^2 4\pi R^2 dR \simeq \frac{c}{W} \frac{J^2}{k_F\eta}.$$

Therefore, we obtain

$$W \simeq |J|\left(\frac{ca}{\eta}\right)^{1/2}. \tag{6·8}$$

The condition that the width W is smaller than the energy separation between impurity levels and the continuum, $\Delta(|J|\rho)^2$, is again given by Eq. (6·7).

It is well known that the energy gap of superconductor is reduced by paramagnetic impurities.[8] The reduction of the gap is given approximately by $c|J|^2\rho$. If this exceeds $\Delta(|J|\rho)^2$, impurity levels are completely masked by the continuum. The condition for it is

$$c > \rho\Delta \sim \left(\frac{a}{\xi}\right). \tag{6·9}$$

The density of states for quasiparticle excitations is shown schematically in Fig. 8 for various concentrations of impurities. For $(a/\xi) > c > (a/\xi)^3(|J|\rho)^3$, we get an impurity band in the energy gap or a tail of the continuum whose length is given by Eq. (6·8).

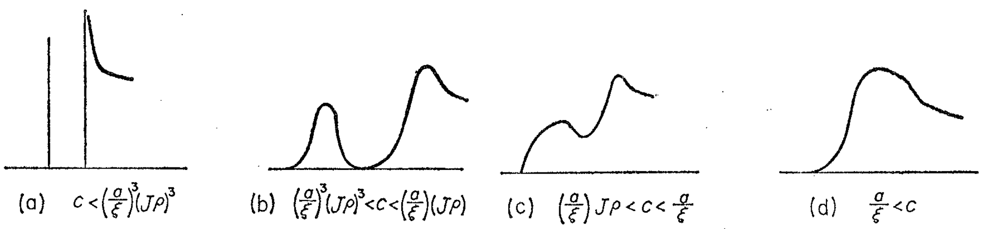

Fig. 8. The density of states for quasiparticle excitations is shown schematically for various concentrations of impurities.

For ordinary superconductors, a/ξ is of order 10^{-4}. The condition (6·7) is extremely severe, and the problem of discrete impurity levels seems to be rather academic. However, the tail of the density of states mentioned above may be detectable experimetally.

For a non-magnetic impurity in a normal metal, Yosida showed that, if a treatment similar to the case of a magnetic impurity is applied to this case, a bound state solution is obtained in the lowest approximation, but that it becomes unstable by higher order effects. This is consistent with the fact that a bound state is not formed by a non-magnetic impurity if the impurity potential is weak enough. We have to examine how it is for the case of a non-magnetic impurity in a superconductor when the same treatment as in §§ 4 and 5 is applied to this case.

The calculation is straightforward. Suppose the interaction Hamiltonian is given by

$$H' = \frac{V}{N}\sum_{k,k'}\sum_{\sigma} a^{+}_{k\sigma}\, a_{k'\sigma}, \tag{6·10}$$

where the impurity potential V is assumed to be independent of the wave vectors. Then, if the wave function is taken as

$$\Psi_{\nu} = \{\sum_{k} \Gamma_{k\nu}\, \alpha^{+}_{k\nu} + \sum_{k,k',k''} \Gamma_{k\nu,k'\nu,k''\bar{\nu}}\, \alpha^{+}_{k\nu}\, \alpha^{+}_{k'\nu}\, \alpha^{+}_{k''\bar{\nu}}\}\Phi_0, \tag{6·11}$$

with $\nu=0,\,1$ and $\bar{\nu}=1,\,0$, the secular equation is obtained as

$$\{2VU_{+}(E)-(2V)^3K_{-}'(E)\}\{2VU_{-}(E)-(2V)^3K_{+}'(E)\}=1, \tag{6·12}$$

where $U_{\pm}(E)$ is given by Eq. (4·16) and $K'_{\pm}(E)$ by

$$K_{\pm}'(E) = \left(\frac{\rho}{2}\right)^2 \int_0^D\!\!\int_0^D \frac{1}{([\Delta^2+\epsilon^2]^{1/2}-E)([\Delta^2+\epsilon'^2]^{1/2}-E)}$$

$$\times\left(1\pm\frac{\Delta}{[\Delta^2+\epsilon^2]^{1/2}}\right)\left(1\pm\frac{\Delta}{[\Delta^2+\epsilon'^2]^{1/2}}\right)U_{\pm}(E-[\Delta^2+\epsilon^2]^{1/2}-[\Delta^2+\epsilon'^2]^{1/2})\,d\epsilon\, d\epsilon'.$$

For the case $|V|\gg V_{\text{pair}}$, Eq. (6·12) should be examined for $|E|\gg\Delta$. In this limit, Eq. (6·12) tends to the corresponding equation for a normal metal. Therefore the conclusion is evidently the same as obtained by Yosida for a normal metal. For the case $|V|\ll V_{\text{pair}}$, Eq. (6·12) should be examined for $0<\Delta-E\ll\Delta$. If the second term of Eq. (6·11) is neglected, the terms $(2V)^3K'_{\pm}(E)$ disappear from Eq. (6·12). Since $U_{+}(E)U_{-}(E)$ tends to infinity as E tends to Δ from the side $E<\Delta$, the equation thus obtained has a solution such that $0<\Delta-E\ll\Delta$, which means a discrete impurity level in the energy gap. If the terms $(2V)^3K'_{\pm}(E)$ are included, however, the left-hand side of Eq. (6·12) is negative as $U_{+}(E)$ and $K'_{+}(E)$ tend to infinity for $E\rightarrow\Delta(E<\Delta)$, and it has no solution at all. Thus we can conclude that a discrete impurity level is not formed in the energy gap by a non-magnetic impurity. This is consistent with the well-known fact that a superconducting state is little affected by non-magnetic impurities.

Acknowledgements

One of the authors (T.S.) acknowledges his gratitude to Professor K. Sawada for very helpful discussions and to Professor F. Takano for good criticism. The others (T.M. and Y.N.) express their thanks to Professor T. Usui and Dr. S. Kashiwamura for valuable discussions. The authors acknowledge the financial aid of the Institute for Fundamental Physics, Kyoto University.

References

1) J. Kondo, Prog. Theor. Phys. **32** (1964), 37.
A. A. Abrikosov, Physics **2** (1965), 5.
J. Suhl, Phys. Rev. **138** (1965), A515; **141** (1964), 483.
Y. Nagaoka, Phys. Rev. **138** (1965), 1112.
S. Doniach, Phys. Rev. **144** (1966), 382.
2) K. Yosida, Phys. Rev. **147** (1966), 223; Prog. Theor. Phys. **36** (1966), 875.
A. Okiji, Prog. Theor. Phys. **36** (1966), 875.
3) J. Kondo, Phys. Rev. **154** (1967), 644; private communication.
4) S. H. Liu, Phys. Rev. **137** (1965), A1209.
5) A. Griffin, Phys. Rev. Letters **15** (1965), 703.
6) K. Maki, Phys. Rev. **153** (1967), 428.
7) H. Shiba and K. Kawamura, private communication.
S. Doniach, Bull. Am. Phys. Soc. Ser. II **11** (1966), 387.