

Bound State Due to the *s-d* Exchange Interaction

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The possibility is discussed that the *s-d* exchange interaction gives rise to a bound state between the conduction electrons and a localized spin, and it is shown that a singlet bound state is realized for the case of antiferromagnetic exchange interaction. It is therefore concluded that the logarithmic divergence which appears in the perturbation expansion is connected with the appearance of this bound state.

1. INTRODUCTION

SINCE Kondo¹ has found the logarithmic singularity in the scattering of a conduction electron by an impurity spin in third-order perturbation theory, many investigations have been made in order to clarify the origin of this logarithmic singularity.²⁻⁶ Nagaoka³ has pointed out that the perturbational treatment breaks down below a critical temperature and that a quasi-bound-state would appear near the Fermi surface if the interaction were antiferromagnetic. On the other hand, Yosida and Okiji⁵ have calculated the magnitude of the localized spin and the spin polarization of the conduction electrons by the perturbational approach and have shown that for the case of antiferromagnetic interaction the perturbational treatment leads to unreasonable results for the magnitude of the localized spin below a certain critical temperature, namely that the magnitude of the localized spin decreases and becomes negative through zero as temperature is lowered. Basing themselves on this result, they have confirmed Nagaoka's assertion that the perturbational treatment breaks down and furthermore have inferred that the localized moment would disappear below the critical temperature. The purpose of this paper is to show that a bound state does really appear due to the *s-d* exchange interaction.

2. BOUND STATE DUE TO THE TRUNCATED HAMILTONIAN

The Hamiltonian for the system consisting of the conduction electrons and a localized spin is expressed as

$$H = \sum_{k\sigma} \epsilon_k a_{k\sigma}^\dagger a_{k\sigma} - \frac{J}{2N} \sum_{kk'} \{ (a_{k'\uparrow}^\dagger a_{k\uparrow} - a_{k'\downarrow}^\dagger a_{k\downarrow}) S_z + a_{k'\uparrow}^\dagger a_{k\downarrow} S_- + a_{k'\downarrow}^\dagger a_{k\uparrow} S_+ \}, \quad (1)$$

where $a_{k\sigma}^\dagger$ and $a_{k\sigma}$ are the usual creation and annihilation operators of the conduction electron with wave

vector k and spin σ , ϵ_k is its band energy measured from the Fermi energy, and S_z and S_\pm are the components of the localized spin. In this Hamiltonian, we assume that electrons below the Fermi level are unaffected by the *s-d* exchange interaction, namely, that the summation in the second term of Eq. (1) is taken over the states higher than the Fermi level. Such a simplification for the Hamiltonian has been used with a great success by Cooper⁷ for explaining the formation of Cooper pairs in the theory of superconductivity and it may also be justified for the present case in which a dynamical character of the localized spin is taken into consideration. The same simplification for the present Hamiltonian has been used by Kondo⁸ for another purpose. Then, we can consider the eigenstates of an electron with wave vector k larger than k_F .

The eigenfunction of an electron for the truncated Hamiltonian can be expressed by a linear combination of plane waves as

$$\psi = \sum_{k > k_F} \{ (\Gamma_{k\uparrow}^\alpha a_{k\uparrow}^\dagger + \Gamma_{k\downarrow}^\alpha a_{k\downarrow}^\dagger) \psi_v \alpha + (\Gamma_{k\uparrow}^\beta a_{k\uparrow}^\dagger + \Gamma_{k\downarrow}^\beta a_{k\downarrow}^\dagger) \psi_v \beta \}, \quad (2)$$

where ψ_v denotes the wave function for the Fermi sea and α and β denote, respectively, the eigenfunctions for up and down spin states for the localized spin, whose magnitude is assumed to be $\frac{1}{2}$.

Inserting the wave function (2) in

$$H\psi = E\psi, \quad (3)$$

we obtain the following four equations which determine Γ_k and the energy eigenvalue:

$$\Gamma_{k\uparrow}^\alpha (\epsilon_k - E) - (J/4N) \sum_{k'} \Gamma_{k'\uparrow}^\alpha = 0, \quad (4a)$$

$$\Gamma_{k\downarrow}^\alpha (\epsilon_k - E) + (J/4N) \sum_{k'} \Gamma_{k'\downarrow}^\alpha - (J/2N) \sum_{k'} \Gamma_{k'\uparrow}^\beta = 0, \quad (4b)$$

$$\Gamma_{k\uparrow}^\beta (\epsilon_k - E) + (J/4N) \sum_{k'} \Gamma_{k'\uparrow}^\beta - (J/2N) \sum_{k'} \Gamma_{k'\downarrow}^\alpha = 0, \quad (4c)$$

$$\Gamma_{k\downarrow}^\beta (\epsilon_k - E) - (J/4N) \sum_{k'} \Gamma_{k'\downarrow}^\beta = 0. \quad (4d)$$

¹ J. Kondo, *Progr. Theoret. Phys. (Kyoto)* **32**, 37 (1964).
² H. Suhl, *Phys. Rev.* **138**, A515 (1965); *Physics* **2**, 39 (1965).
³ Y. Nagaoka, *Phys. Rev.* **138**, A1112 (1965).
⁴ A. A. Abrikosov, *Zh. Eksperim. i Teor. Fiz.* **48**, 990 (1965) [English transl.: *Soviet Phys.—JETP* **21**, 660 (1965)]; *Physics* **2**, 5 (1965).
⁵ K. Yosida and A. Okiji, *Progr. Theoret. Phys. (Kyoto)* **34**, 505 (1965).
⁶ H. Miwa, *Progr. Theoret. Phys. (Kyoto)* **34**, 1040 (1965).

⁷ L. N. Cooper, *Phys. Rev.* **104**, 1189 (1956).
⁸ J. Kondo, *Progr. Theoret. Phys. (Kyoto)* **34**, 204 (1965).

From these four equations, we obtain the two secular equations corresponding to triplet and singlet states as

$$1 - \frac{J}{4N} \sum_k \frac{1}{\epsilon_k - E} = 0, \quad (5)$$

$$1 + \frac{3J}{4N} \sum_k \frac{1}{\epsilon_k - E} = 0. \quad (6)$$

It can easily be shown that for $J > 0$, Eq. (5) gives a triplet bound state whose energy is lower than the Fermi level by

$$E = -D / [\exp(4N/\rho J) - 1] \sim -D \exp(-4N/\rho J), \quad (7)$$

and that for $J < 0$, Eq. (6) gives a singlet bound state whose energy is

$$E = -D / [\exp(4N/3\rho|J|) - 1] \sim -D \exp(-4N/3\rho|J|), \quad (8)$$

where ρ and D express the state density and the bandwidth. The eigenfunctions of these bound states can be obtained as

$$\psi_t = \text{const} \sum_{k > k_F} \frac{1}{\epsilon_k - E} a_{k\uparrow}^\dagger \alpha \psi_v, \quad (9)$$

$$\psi_s = \text{const} \sum_{k > k_F} \frac{1}{\epsilon_k - E} (a_{k\downarrow}^\dagger \alpha - a_{k\uparrow}^\dagger \beta) \psi_v, \quad (10)$$

and their spatial extension is given by $\cos k_{\text{eff}} r / r^2$ for large

$$\psi = \left[\sum_k \{ \Gamma_k^\alpha a_{k\downarrow}^\dagger \alpha + \Gamma_k^\beta a_{k\uparrow}^\dagger \beta \} + \sum_{kk'k''} \{ \Gamma_{kk'k''}^{\alpha\downarrow} a_{k\downarrow}^\dagger a_{k'\downarrow}^\dagger a_{k''\downarrow}^\dagger \alpha + \Gamma_{kk'k''}^{\beta\uparrow} a_{k\uparrow}^\dagger a_{k'\uparrow}^\dagger a_{k''\uparrow}^\dagger \beta \right. \\ \left. + \Gamma_{kk'k''}^{\alpha\uparrow} a_{k\downarrow}^\dagger a_{k'\uparrow}^\dagger a_{k''\uparrow}^\dagger \alpha + \Gamma_{kk'k''}^{\beta\downarrow} a_{k\uparrow}^\dagger a_{k'\downarrow}^\dagger a_{k''\downarrow}^\dagger \beta \} + \dots \right] \psi_v, \quad (11)$$

where $\Gamma_{kk'k''}$ are regarded as quantities of higher order in J , compared with Γ_k . Then, we insert this wave function in the Schrödinger equation (3) in which the full Hamiltonian is used, and solve Γ_k , $\Gamma_{kk'k''}$, etc. by the successive approximation.

In conformity to this prescription, the Schrödinger equation can be written down as

$$\left[\sum_k (\epsilon_k - E) \{ \Gamma_k^\alpha a_{k\downarrow}^\dagger \alpha + \Gamma_k^\beta a_{k\uparrow}^\dagger \beta \} + \sum_{kk'k''} (\epsilon_k + \epsilon_{k'} - \epsilon_{k''} - E) \{ \Gamma_{kk'k''}^{\alpha\downarrow} a_{k\downarrow}^\dagger a_{k'\downarrow}^\dagger a_{k''\downarrow}^\dagger \alpha + \Gamma_{kk'k''}^{\beta\uparrow} a_{k\uparrow}^\dagger a_{k'\uparrow}^\dagger a_{k''\uparrow}^\dagger \beta \right. \\ \left. + \Gamma_{kk'k''}^{\alpha\uparrow} a_{k\downarrow}^\dagger a_{k'\uparrow}^\dagger a_{k''\uparrow}^\dagger \alpha + \Gamma_{kk'k''}^{\beta\downarrow} a_{k\uparrow}^\dagger a_{k'\downarrow}^\dagger a_{k''\downarrow}^\dagger \beta \} + \frac{J}{4N} \sum_\mu \Gamma_\mu^\alpha \sum_k a_{k\downarrow}^\dagger \alpha + \frac{J}{4N} \sum_\mu \Gamma_\mu^\beta \sum_k a_{k\uparrow}^\dagger \beta \right. \\ \left. - \frac{J}{2N} \sum_\mu \Gamma_\mu^\alpha \sum_k a_{k\uparrow}^\dagger \beta - \frac{J}{2N} \sum_\mu \Gamma_\mu^\beta \sum_k a_{k\downarrow}^\dagger \alpha - \frac{J}{4N} \sum_k \Gamma_k^\alpha (a_{k\downarrow}^\dagger a_{k'\uparrow}^\dagger a_{k''\uparrow}^\dagger \alpha - a_{k\downarrow}^\dagger a_{k'\downarrow}^\dagger a_{k''\downarrow}^\dagger \alpha) \right. \\ \left. + \frac{J}{4N} \sum_k \Gamma_k^\beta (a_{k\uparrow}^\dagger a_{k'\uparrow}^\dagger a_{k''\uparrow}^\dagger \beta - a_{k\uparrow}^\dagger a_{k'\downarrow}^\dagger a_{k''\downarrow}^\dagger \beta) - \frac{J}{2N} \sum_k \Gamma_k^\alpha a_{k\downarrow}^\dagger a_{k'\uparrow}^\dagger a_{k''\downarrow}^\dagger \beta - \frac{J}{2N} \sum_k \Gamma_k^\beta a_{k\uparrow}^\dagger a_{k'\downarrow}^\dagger a_{k''\uparrow}^\dagger \alpha \right. \\ \left. + \frac{J}{4N} \{ \sum_{kk'k''} \Gamma_{kk'k''}^{\alpha\downarrow} (a_{k\downarrow}^\dagger \alpha - a_{k'\downarrow}^\dagger \alpha) + \sum_{kk'k''} \Gamma_{kk'k''}^{\beta\uparrow} (a_{k\uparrow}^\dagger \beta - a_{k'\uparrow}^\dagger \beta) \} \right. \\ \left. + \frac{J}{2N} \sum_{kk'k''} \{ \Gamma_{kk'k''}^{\alpha\uparrow} a_{k\downarrow}^\dagger \beta + \Gamma_{kk'k''}^{\beta\downarrow} a_{k'\downarrow}^\dagger \alpha \} - \frac{J}{4N} \sum_{kk'k''} \{ \Gamma_{kk'k''}^{\alpha\downarrow} a_{k\downarrow}^\dagger \alpha + \Gamma_{kk'k''}^{\beta\uparrow} a_{k\uparrow}^\dagger \beta \} + \dots \right] \psi_v = 0. \quad (12)$$

distance from the impurity atom. The bound state will disappear at a temperature of an order of $kT_s \sim |E|$.

As one can easily see, there are two difficulties in these bound states. One difficulty is that the truncation of the Hamiltonian gives rise to bound states for both ferro- and antiferromagnetic couplings and even for an attractive impurity potential. Since there has been found no difficulty in the perturbation expansion for the ferromagnetic interaction,^{2,3,5} the bound state found for the ferromagnetic interaction may be fictitious. On the other hand, the bound state found for the antiferromagnetic interaction is expected to be real. However, even for this case the other difficulty occurs that the numerical factor of the exponent in the energy expression (8) is $\frac{4}{3}$ instead of unity, contrary to the inference drawn from the perturbation calculation.

These two difficulties are obviously originated from the truncated Hamiltonian which takes into account only the electron-electron or hole-hole interactions but neglects the electron-hole interactions. Thus, the second step which we should take is to investigate how the bound states will be affected by the existence of the electron-hole interactions.

3. EFFECT OF THE ELECTRON-HOLE INTERACTIONS

In order to take into account the electron-hole interactions in the results obtained in the preceding section, we proceed along a similar principle to the perturbation method. First, we expand the ground-state wave function in the following series:

From this expression we obtain the relations which hold among Γ_k and $\Gamma_{kk'k''}$ as follows:

$$\Gamma_k^\alpha(\epsilon_k - E) + (J/4N) \sum_\mu \Gamma_\mu^\alpha - (J/2N) \sum_\mu \Gamma_\mu^\beta + (J/4N) \sum_{\mu\nu} (\Gamma_{k\mu\nu}^{\alpha\downarrow} - \Gamma_{\mu k\nu}^{\alpha\downarrow}) + (J/2N) \sum_{\mu\nu} \Gamma_{\mu k\nu}^{\beta\downarrow} - (J/4N) \sum_{\mu\nu} \Gamma_{k\mu\nu}^{\alpha\uparrow} = 0, \quad (13)$$

$$\Gamma_k^\beta(\epsilon_k - E) + (J/4N) \sum_\mu \Gamma_\mu^\beta - (J/2N) \sum_\mu \Gamma_\mu^\alpha + (J/4N) \sum_{\mu\nu} (\Gamma_{k\mu\nu}^{\beta\uparrow} - \Gamma_{\mu k\nu}^{\beta\uparrow}) + (J/2N) \sum_{\mu\nu} \Gamma_{\mu k\nu}^{\alpha\uparrow} - (J/4N) \sum_{\mu\nu} \Gamma_{k\mu\nu}^{\beta\downarrow} = 0, \quad (14)$$

$$(\Gamma_{kk'k''}^{\alpha\downarrow} - \Gamma_{k'k''k}^{\alpha\downarrow})(\epsilon_k + \epsilon_{k'} - \epsilon_{k''} - E) + (J/4N)(\Gamma_k^\alpha - \Gamma_{k'}^\alpha) = 0, \quad (15)$$

$$(\Gamma_{kk'k''}^{\beta\uparrow} - \Gamma_{k'k''k}^{\beta\uparrow})(\epsilon_k + \epsilon_{k'} - \epsilon_{k''} - E) + (J/4N)(\Gamma_k^\beta - \Gamma_{k'}^\beta) = 0, \quad (16)$$

$$\Gamma_{kk'k''}^{\alpha\uparrow}(\epsilon_k + \epsilon_{k'} - \epsilon_{k''} - E) - (J/4N)\Gamma_k^\alpha + (J/2N)\Gamma_{k'}^\beta = 0, \quad (17)$$

$$\Gamma_{kk'k''}^{\beta\downarrow}(\epsilon_k + \epsilon_{k'} - \epsilon_{k''} - E) - (J/4N)\Gamma_k^\beta + (J/2N)\Gamma_{k'}^\alpha = 0. \quad (18)$$

Using Eqs. (15)–(18), we can eliminate $\Gamma_{kk'k''}$ from Eqs. (13) and (14) as

$$\Gamma_k^\alpha \left[\epsilon_k - E - 6 \left(\frac{J}{4N} \right)^2 \sum_{\mu\nu} \frac{1}{\epsilon_\mu + \epsilon_k - \epsilon_\nu - E} \right] + \frac{J}{4N} \sum_\mu \Gamma_\mu^\alpha - \frac{J}{2N} \sum_\mu \Gamma_\mu^\beta + 4 \left(\frac{J}{4N} \right)^2 \sum_{\mu\nu} \frac{\Gamma_\mu^\beta}{\epsilon_\mu + \epsilon_k - \epsilon_\nu - E} + \left(\frac{J}{4N} \right)^2 \sum_\mu \frac{\Gamma_\mu^\alpha}{\epsilon_\mu + \epsilon_k - \epsilon_\nu - E} = 0, \quad (19)$$

$$\Gamma_k^\beta \left[\epsilon_k - E - 6 \left(\frac{J}{4N} \right)^2 \sum_{\mu\nu} \frac{1}{\epsilon_\mu + \epsilon_k - \epsilon_\nu - E} \right] + \frac{J}{4N} \sum_\mu \Gamma_\mu^\beta - \frac{J}{2N} \sum_\mu \Gamma_\mu^\alpha + 4 \left(\frac{J}{4N} \right)^2 \sum_{\mu\nu} \frac{\Gamma_\mu^\alpha}{\epsilon_\mu + \epsilon_k - \epsilon_\nu - E} + \left(\frac{J}{4N} \right)^2 \sum_{\mu\nu} \frac{\Gamma_\mu^\beta}{\epsilon_\mu + \epsilon_k - \epsilon_\nu - E} = 0. \quad (20)$$

If we put, here, $\Gamma_k^\alpha = -\Gamma_k^\beta$ for the singlet state and $\Gamma_k^\alpha = \Gamma_k^\beta$ for the triplet state, Eqs. (19) and (20) become, respectively,

$$\Gamma_k \left[\epsilon_k - E - 6 \left(\frac{J}{4N} \right)^2 \sum_{\mu\nu} \frac{1}{\epsilon_\mu + \epsilon_k - \epsilon_\nu - E} \right] + 3 \frac{J}{4N} \sum_\mu \Gamma_\mu - 3 \left(\frac{J}{4N} \right)^2 \sum_{\mu\nu} \frac{\Gamma_\mu}{\epsilon_\mu + \epsilon_k - \epsilon_\nu - E} = 0, \quad (21)$$

$$\Gamma_k \left[\epsilon_k - E - 6 \left(\frac{J}{4N} \right)^2 \sum_{\mu\nu} \frac{1}{\epsilon_\mu + \epsilon_k - \epsilon_\nu - E} \right] - \frac{J}{4N} \sum_\mu \Gamma_\mu + 5 \left(\frac{J}{4N} \right)^2 \sum_{\mu\nu} \frac{\Gamma_\mu}{\epsilon_\mu + \epsilon_k - \epsilon_\nu - E} = 0. \quad (22)$$

In these two equations which determine the energy eigenvalues, the shift of the kinetic energy ϵ_k , $\Delta\epsilon_k$, can be calculated as

$$\begin{aligned} \Delta\epsilon_k &= -6 \left(\frac{J\rho}{4N} \right)^2 \int_0^D d\epsilon_\mu \int_{-D}^0 d\epsilon_\nu \frac{1}{\epsilon_\mu + \epsilon_k - \epsilon_\nu - E} \\ &= +6 \left(\frac{J\rho}{4N} \right)^2 \left[-(\epsilon_k - E) \ln \left| \frac{\epsilon_k - E}{\epsilon_k + D - E} \right| + (\epsilon_k + 2D - E) \ln \left| \frac{\epsilon_k + D - E}{\epsilon_k + 2D - E} \right| \right] \simeq -6 \left(\frac{J\rho}{4N} \right)^2 (\epsilon_k - E) \ln \left| \frac{\epsilon_k - E}{D - E} \right|. \end{aligned} \quad (23)$$

This is expected to have no essential influence on the energy eigenvalue. Therefore, we neglect this shift in later calculations.

Now we consider the bound state for the antiferromagnetic interaction, namely, for the singlet state. For this

case, Eq. (21) can be written in the following form:

$$\Gamma_k = -3 \frac{J}{4N} \frac{1}{(\epsilon_k - E)} [G + f(\epsilon_k)], \quad (24)$$

$$G = \sum_{\mu} \Gamma_{\mu}, \quad (25)$$

$$f(\epsilon) = \frac{J}{4N} \rho^2 \int_0^D \Gamma(\epsilon_1) \ln \left| \frac{\epsilon_1 + \epsilon - E}{\epsilon_1 + \epsilon + D - E} \right| d\epsilon_1. \quad (26)$$

By the method of successive approximation the integral equation (26) with respect to $f(\epsilon)$ can be solved as

$$f(\epsilon) = G \left\{ -3 \left(\frac{J\rho}{4N} \right)^2 \int_0^D \frac{d\epsilon_1}{\epsilon_1 - E} \ln \left| \frac{\epsilon_1 + \epsilon - E}{\epsilon_1 + \epsilon + D - E} \right| \right. \\ \left. + 9 \left(\frac{J\rho}{4N} \right)^4 \int_0^D \frac{d\epsilon_1}{\epsilon_1 - E} \ln \left| \frac{\epsilon_1 + \epsilon - E}{\epsilon_1 + \epsilon + D - E} \right| \int_0^D \frac{d\epsilon_2}{\epsilon_2 - E} \ln \left| \frac{\epsilon_2 + \epsilon_1 - E}{\epsilon_2 + \epsilon_1 + D - E} \right| - \dots \right\}. \quad (27)$$

Inserting Eq. (27) into Eq. (24), and summing up with respect to ϵ_k we obtain, up to the fifth order in J , the following secular equation:

$$1 = -3 \frac{J\rho}{4N} \int_0^D \frac{d\epsilon}{\epsilon - E} \left[1 - 3 \left(\frac{J\rho}{4N} \right)^2 \int_0^D \frac{d\epsilon_1}{\epsilon_1 - E} \ln \left| \frac{\epsilon_1 + \epsilon - E}{\epsilon_1 + \epsilon + D - E} \right| + 9 \left(\frac{J\rho}{4N} \right)^4 \left\{ \int_0^D \frac{d\epsilon_1}{\epsilon_1 - E} \ln \left| \frac{\epsilon_1 + \epsilon - E}{\epsilon_1 + \epsilon + D - E} \right| \right\}^2 \right]. \quad (28)$$

The integration with respect to ϵ_1 included in this equation can be carried out as follows:

$$I(\epsilon) = \int_0^D \frac{d\epsilon_1}{\epsilon_1 - E} \ln \left| \frac{\epsilon_1 + \epsilon - E}{\epsilon_1 + \epsilon + D - E} \right| \\ = - \sum_{n=1}^{\infty} \frac{1}{n^2} \left\{ \epsilon^n \left[\frac{1}{(\epsilon + D - E)^n} - \frac{1}{(\epsilon - E)^n} \right] - (\epsilon + D)^n \left[\frac{1}{(\epsilon + 2D - E)^n} - \frac{1}{(\epsilon + D - E)^n} \right] \right\} \\ - \frac{1}{2} \ln^2 \left| \frac{\epsilon + D - E}{D - E} \right| + \frac{1}{2} \ln^2 \left| \frac{\epsilon + 2D - E}{D - E} \right| + \frac{1}{2} \ln^2 \left| \frac{\epsilon - E}{E} \right| - \frac{1}{2} \ln^2 \left| \frac{\epsilon + D - E}{E} \right|. \quad (29)$$

[Here $\ln^2 x \equiv (\ln x)^2$.] Neglecting regular parts in this expression, we can put the above integral as

$$I(\epsilon) = \frac{1}{2} \left\{ \ln^2 \left| \frac{\epsilon - E}{E} \right| - \ln^2 \left| \frac{D - E}{E} \right| \right\} \quad (30)$$

With the use of Eq. (30) in Eq. (28), the secular equation for the singlet state becomes

$$1 - 3x - 3x^3 - (18/5)x^5 = 0, \quad (31)$$

$$x = \left(\frac{J\rho}{4N} \right) \ln \left| \frac{E}{D - E} \right|. \quad (32)$$

Since Eqs. (21) and (22) have been obtained by retaining only the first term of $\Gamma_{kk'k''}$ in its expansion, Eq. (31) is correct up to x^3 . Therefore, we neglect x^5 . Then, the

solution of Eq. (31) is obtained as

$$x_0 = 0.305, \quad \text{or} \quad \frac{J\rho}{N} \ln \left| \frac{E}{D} \right| = 1.22. \quad (33)$$

Thus, it is found that for the antiferromagnetic interaction the bound state which has appeared in the starting approximation still survives the effect of the electron-hole interactions. Here, it should be noted that the value of 1.22 is nearer to the expected value of unity than $\frac{4}{3} = 1.33$. The term of x^5 has no essential effect because of a small value of x_0 . The spatial extension of the bound state in this stage of approximation is not essentially different from that of the zero approximation.

For the triplet state, the same procedure applied to Eq. (22) leads to the following secular equation:

$$1 + x - (5/3)x^3 = 0. \quad (34)$$

This equation has no solution in the minus side of x .

Therefore, the solution $x_0 = -1$ which has been obtained in the zero approximation for the ferromagnetic exchange interaction disappears in the present approximation. This seems to be a reasonable result.

4. DISCUSSION AND CONCLUSIONS

We have started, as a zero approximation, with those states of a free-electron gas in which one electron is excited above the Fermi sea and have treated the effect of the $s-d$ exchange interaction of the conduction electrons with a localized spin whose magnitude is one-half by the generalized perturbation method. In the zero-approximation of this approach, bound states have appeared for both ferro- and antiferromagnetic exchange interactions and further it has been found that the bound state for the antiferromagnetic interaction remains with no essential change in its binding energy in the first approximation, although the bound state for the ferromagnetic interaction disappears in this approximation. Whether these results obtained in the first approximation remain unchanged even when the approximation is proceeded up to higher order should be confirmed by the actual calculations. However, it may be concluded from the present calculations that at least the singlet bound state will ultimately be realized for the antiferromagnetic exchange interaction.

In the singlet bound state for the antiferromagnetic exchange interaction each component of the localized spin vanishes in its average and the spin polarization of the conduction electrons also vanishes. Therefore, it is expected that the magnitude of the localized spin moment will begin to vanish with the appearance of the singlet bound state below T_c . This result agrees with the inference drawn out of the perturbation calculations.⁵ Thus, it can be said that the breakdown of the perturbational approach below T_c for the antiferromagnetic exchange is related to the fact that the conservation of the spin moment is broken.

The present calculation can be extended to the case of localized spins greater than $\frac{1}{2}$; for example, for $S=1$ two electrons are expected to form a singlet bound state combined with the localized spin for the antiferromagnetic interaction. The extension of the present calculation to this case and also to higher approximation will be published in another paper.

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Microwave Absorption in Normal-Conducting Films on Superconducting Substrates*†

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The microwave absorption at 9.2 kMc/sec in films of gold and copper plated onto bulk tin has been measured as a function of the temperature in the range $1.4 \leq T \leq 4.2^\circ\text{K}$. The results are extrapolated to zero temperature, where they indicate the presence of an energy gap of 0.61×10^{-23} J at the surface of a 190-Å film of gold and at the surface of a 500-Å film of copper on tin. The normal bulk resistivity of the gold was estimated from dc measurements as well as from the microwave data. The theory of the proximity effect, that is, the influence of adjoining normal and superconducting metals, as given by de Gennes and Werthamer, was applied to the measurements, and yielded an estimate for $N(0)V$ for gold of 9×10^{-3} . Assuming that the sign of $N(0)V$ is positive, this leads to a very low transition temperature.

I. INTRODUCTION

IN recent years several investigators have studied proximity effects between superconductors and normal metals. This interest began after it had been shown¹ that supercurrents can be passed through thin

films of normal conducting metal sandwiched between bulk superconductors. Studies of multiple films consisting of a layer of a superconductor and a layer of a normal metal²⁻⁷ showed that the composite samples

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¹ H. Meissner, *Phys. Rev.* **117**, 672 (1960).

² P. H. Smith, S. Shapiro, J. L. Miles, and J. Nicol, *Phys. Rev. Letters* **6**, 686 (1961).

³ W. A. Simmons and D. H. Douglass, Jr., *Phys. Rev. Letters* **9**, 153 (1962).

⁴ P. Hilsch, *Z. Physik* **167**, 511 (1962).

⁵ P. Hilsch and R. Hilsch, *Z. Physik* **180**, 10 (1964).

⁶ J. J. Hauser, H. C. Theurer, and N. R. Werthamer, *Phys. Rev.* **136**, 637 (1964).

⁷ J. J. Hauser and H. C. Theurer, *Phys. Letters* **14**, 270 (1965).