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Bound State in Metals due to a Fluctuating Perturbation

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By using a variation function it is shown that there occurs a bound state around a localized spin in a metal when the exchange interaction between the localized spin and the conduction electron is negative This is due to the fluctuation of the spin of the conduction electron, which occurs when the exchange interaction is negative, combined with the restriction imposed on the conduction electrons by the Fermi statistics

§ 1. Introduction

It has been shown that the Pauli principle imposes a restriction upon scattering of the conduction electrons by a localized spin [1] A simple model to account for this restriction is one in which the conduction electron is not permitted to enter the Fermi sea,[2] just as in Cooper's model for superconductivity Sawada[3] noted that there must occur a bound state in this model, in parallel with the case of Cooper's model The only difference is that in our problem a single electron is involved whereas Cooper's model deals with an 'electron-pair Nagaoka[4] examined this point in detail by using a Green's function method similar to that of Zubarev in the case of superconductivity and showed that a quasibound state between the localized spin and the conduction-electron spin occurs at low temperatures for a negative *s-d* exchange interaction Yosida[5] considered the wave function of a single electron outside the Fermi sea and obtained a bound-state wave function He conjectured that the bound state obtained for a positive *s-d* exchange interaction is fictitious Anderson[6] also expected a bound state exchange-coupled to the localized spin to occur at low temperatures

However there has been no argument which explains the physical origin of the occurrence of the bound state and the reason for its connection with the negative exchange interaction We present here an argument in which we ascribe the origin of the bound state to the spin-fluctuation of the conduction electron.

When the *s-d* interaction is negative, the localized spin, which we assume has spin 1/2, couples antiparallel with the spin of the conduction electron Their directions are not fixed in space, however, but are fluctuating rapidly We consider the wave function of the conduction electron in question as constructed from Bloch functions The *s-d* exchange energy is gained if the wave

function is localized at the site of the localized spin. We must also take account of the kinetic energy. If use is made of a Bloch function above the Fermi surface, the energy of this Bloch state is naturally needed. When use is made of a Bloch orbital below the Fermi surface, we encounter a somewhat different situation. Since the spin of the electron which occupies this orbital is fluctuating, there cannot be two electrons in this orbital. But since there were two electrons in it in the unperturbed state, one of them must be raised to the Fermi surface. The energy necessary for this is the energy required to occupy the Bloch orbital below the Fermi surface. Thus we see that the amount of kinetic energy which is needed when occupying a Bloch orbital is increased when we depart from the Fermi surface in *either* direction. Consequently the Bloch orbitals relevant to our problem must be located around the Fermi surface in the $\boldsymbol{k}$ space.

It is instructive here to consider the difference of our problem from that of potential scattering. In the latter case the only relevant effect is the relabelling of the orbitals, and the electrons occupy the lowest relabelled states. The problem is essentially a one-body problem. The kinetic energy competing with the potential energy is just that of the Bloch state and a bound state splits off from the bottom of the band. In this case the shape of the density of states at the bottom is essential, and in the three-dimensional case a bound state is possible only when the strength of the potential is comparable to the band width.[7] Our problem, however, is essentially a many-body problem. The energy of the total system is lost when use is made of the Bloch states far below the Fermi surface in constructing the wave function of the electron with fluctuating spin direction. The wave function must be a linear combination of Bloch orbitals in the vicinity of the Fermi surface. The density of states is nearly constant around the Fermi surface and consequently we have a bound state irrespective of the strength of the interaction.

It would be a difficult problem to substantiate the above argument rigorously. We consider here a simple variation function which takes the fluctuation of spin into account in a simple way.

§ 2. Variation function

The Hamiltonian of the system is the usual one:

$$H=\Sigma_{ks}\varepsilon_k a_{ks}^* a_{ks}-(J/N)\Sigma_{kk'}\{S_z(a_{k\uparrow}^* a_{k'\uparrow}-a_{k\downarrow}^* a_{k'\downarrow}) + S_+ a_{k\downarrow}^* a_{k'\uparrow}+S_- a_{k\uparrow}^* a_{k'\downarrow}\}, \tag{1}$$

where a_{ks} is the destruction operator for the conduction electron with wave vector $\boldsymbol{k}$ and spin direction s, and J is the s-d exchange integral, which we assume to be negative. We take our variation function as follows:

$$\Psi=2^{-1/2}(a_{0\downarrow}^*\alpha-a_{0\uparrow}^*\beta)\Pi_n a_{n\uparrow}^* a_{n\downarrow}^*|0\rangle, \tag{2}$$

where α and β denote the spin functions of the d electron a_0^* and a_n^* are linear combinations of the creation operator a_k^* for the Bloch state:

$$a_0^* = \Sigma_k c_{0k} a_k^* \tag{3}$$

$$a_n^* = \Sigma_k c_{nk} a_k^* . \tag{4}$$

The average of the energy in the state Ψ is obtained in the form

$$E = 2\Sigma_n^{\text{occ}} \Sigma_k |c_{nk}|^2 \varepsilon_k + \Sigma_k |c_{0k}|^2 \varepsilon_k - (3|J|/2N) |\Sigma_k c_{0k}|^2, \tag{5}$$

where ε_k is measured from the Fermi surface. The c's are determined so as to make E a minimum under the ortho-normality conditions

$$\Sigma_k c_{nk}^* c_{n'k} = \delta_{nn'} \qquad (n, n' \text{ including } 0) \tag{6}$$

We first fix c_{0k} and determine the c_{nk} so as to make the first term of E a minimum under the condition that they are orthogonal to c_{0k}. We then vary c_{0k} so as to make the resulting value of E a minimum.

Differentiating E with respect to c_{nk}^*, we obtain

$$c_{nk} = \mu_n c_{0k}/2(\varepsilon_k - \lambda_n), \tag{7}$$

where λ_n and μ_n are Lagrange multipliers, which are determined so that c_{nk} satisfy Eq. (6). From the orthogonality of c_{0k} to c_{nk} we obtain the equation which determines the value of λ_n:

$$\phi(\lambda_n) \equiv \Sigma_k |c_{0k}|^2/(\lambda_n - \varepsilon_k) = 0 \tag{8}$$

λ_n can be regarded as the energy eigenvalue of the conduction electron, because the first term of E, which we denote by $E^{(1)}$, can be expressed as

$$E^{(1)} = 2\Sigma_n^{\text{occ}} \lambda_n , \tag{9}$$

when use is made of Eqs. (7), (8) and the normalization condition for c_{nk}. By using Eq. (8) it can also be shown that c_{nk} satisfy the orthogonality condition, Eq. (6), for $n \neq n'$.

The difference between $E^{(1)}$ and the unperturbed energy E_0 is the sum of the energy shifts of the conduction electrons:

$$E^{(1)} - E_0 = 2\Sigma^{\text{occ}} (\lambda_n - \varepsilon_k) \tag{10}$$

The dependence of $E^{(1)} - E_0$ on c_{0k} is obtained from Eq. (8), because λ_n are determined by Eq. (8) in terms of c_{0k}. We first consider a special case, $c_{0k} = 0$ for $k > k_F$. Then the Bloch states with $k > k_F$ are not influenced by the orthogonality condition with respect to c_{0k} and consequently the energy shift is zero for these states. Then we see that the right-hand side of Eq. (10) is twice the sum of all the zeros of $\phi(\lambda)$ minus the sum of all its poles. This quantity is easily obtained from Eq. (8), by using $\Sigma_k |c_{0k}|^2 = 1$.

$$E^{(1)} - E_0 = -2\Sigma_{k<k_F} |c_{0k}|^2 \varepsilon_k \tag{11}$$

Since the ε_k appearing in Eq (11) are negative, this result indicates that the energy of the conduction electrons is raised by the orthogonality condition to c_{0k} On the other hand, when $c_{0k}=0$ for $k<k_F$, the Bloch states below the Fermi level are not influenced so that the energy shifts of these states and consequently Eq (10), too, are zero Equation (11) is also valid in this case

In a more general case we first observe that

$$\phi(\lambda)=\Pi_n(\lambda-\lambda_n)/\Pi_k(\lambda-\varepsilon_k).$$

Then we see

$$E^{(1)}-E_0=(\pi\imath)^{-1}\int_C \lambda(d/d\lambda)\ln\phi(\lambda)\,d\lambda, \tag{12}$$

where C is a path from $-\infty$ to zero running just below the real axis and then from zero to $-\infty$ running just above the real axis Integrating by parts we obtain

$$\begin{aligned} E^{(1)}-E_0 &= -(\pi\imath)^{-1}\int_C \ln\phi(\lambda)\,d\lambda \\ &= -(\pi\imath)^{-1}\int_{-\infty}^{0}\{\ln\phi(\lambda-is)-\ln\phi(\lambda+is)\}\,d\lambda \\ &= (2/\pi)\int_{-\infty}^{0}\delta(\lambda)\,d\lambda, \end{aligned} \tag{13}$$

where

$$\delta(\lambda)=\tan^{-1}\{\pi|c_{0k_\lambda}|^2\rho(\lambda)/\int|c_{0k}|^2\rho(\varepsilon_k)(\varepsilon_k-\lambda)^{-1}\,d\varepsilon_k\} \tag{14}$$

k_λ is the wave number defined by $\varepsilon_{k_\lambda}=\lambda$ We have assumed spherical symmetry of c_{0k} ρ is the density of states per unit cell Equations (13) and (14) determine $E^{(1)}-E_0$ as a function of c_{0k} When the c_{0k} are concentrated around k_0 and are zero elsewhere, $\delta(\lambda)$ changes from zero to π when λ passes through k_0 Then we have

$$E^{(1)}-E_0=\begin{cases} 0 & k_0>k_F \\ -2\varepsilon_{k0} & k_0<k_F \end{cases}$$

in agreement with Eq (11)

We may be allowed to use Eq (11) in general cases for the purposes of our qualitative argument Then we have from Eq. (5)

$$E-E_0=\Sigma_k|\varepsilon_k|\cdot|c_{0k}|^2-(3|J|/2N)\,|\Sigma_k c_{0k}|^2 \tag{15}$$

The fact that $|\varepsilon_k|$ rather than ε_k is involved here corresponds to our earlier

statement that the kinetic energy of the system increases when we depart from the Fermi surface in either direction. The eigenvalue is determined by

$$1=(3|J|/2N)\,\Sigma_{k}(|\varepsilon_{k}|-\varepsilon)^{-1} \tag{16}$$

as

$$\varepsilon\simeq -D\exp(-1/3|J|\rho), \tag{17}$$

where $2D$ is the band width, in the range of which ρ is assumed to be constant. This approximation is permitted, because we are mainly interested in the vicinity of the Fermi surface. Because of this fact a bound state appears just below the Fermi surface irrespective of the strength of the interaction, in contrast with the case of potential scattering.

Equation (17) shows that there is a finite separation between the singlet and triplet states at absolute zero, so that the susceptibility due to the localized spin should vanish there. This is in agreement with the conjecture of Yosida and Okiji.

§ 3. Discussion

In Eq. (17) the quantity $3|J|\rho$ is involved in the exponential, whereas $2|J|\rho$ is involved in the expression for the temperature which gives a measure of the breakdown of the perturbation expansion.[2] This discrepancy may be ascribed to the inadequacy of our variation function, Eq. (2) and the approximation involved in Eq. (11). From physical intuition we may expect that only the true quantum mechanical fluctuation gives rise to the effect we have considered here, whereas Eq. (2) over-estimates it in this respect. A revised wave function should be used.

In the case of a positive exchange interaction the d spin couples parallel with the spin of the conduction electron. In Eq. (2) we change the sign of the second term which corresponds to the down-spin state of the localized spin. In this case we still obtain a bound state with a slight change of the factor before J. However, when the two spins couple parallel we may expect that the fluctuation of the spin is not so important as to give rise to the bound state discussed above. We may thus expect that the wave function for positive J is different in nature from that for negative J. In fact if we choose a variation function

$$\Psi=a_{0\uparrow}^{*}\,\alpha\Pi_{n}\,a_{n\uparrow}^{*}\Pi_{m}\,a_{m\downarrow}^{*}|0\rangle,$$

which has an energy lower than the version mentioned above (Eq. (2)), there occurs only a relabelling of the orbitals.

We have shown previously[1] that the anomalous resistivity due to the *s-d* interaction arises from its dynamical nature and is connected with the Fermi statistics of the conduction electrons. These two factors play an important role

in the present case, too, that is, the fluctuation of the spin comes from the dynamical nature of the *s-d* interaction, and the Fermi statistics, which permits only a single electron in an orbit when its spin is fluctuating, brought about the factor $|\varepsilon_k|$ rather than ε_k in Eq (16)

References

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