

Free-Energy Shift of Conduction Electrons Due to the s - d Exchange Interaction

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The free-energy shift of the conduction electrons due to the exchange interaction with a localized impurity spin is calculated by perturbation expansion up to the fourth order of the exchange interaction. It is shown that the usual procedure to obtain the free-energy shift at finite temperature by first calculating the energy shift at absolute zero and then replacing the step function by the fermi distribution function involves a serious error. By a careful analysis of this point, we find a logarithmic term in the fourth order. The contribution to the entropy of this term is

$$\Delta S = -16\pi^2 S(S+1)J^4 \rho^4 k_B \log(D/T),$$

which is negative for both signs of J . This term represents a decrease of the entropy of the conduction electrons and may be interpreted in terms of the correlated motion of the spin polarization coupled to the localized spin. This result seems to indicate that the binding energy of the ground state in the case of negative exchange interaction is obtained by calculating the free energy at finite temperature (to infinite order) and then extrapolating the result to zero temperature.

§ 1. Introduction

The low-temperature anomaly¹⁾ associated with the localized spin exchange-coupled to conduction electrons in metals has been studied extensively in recent years. Among the properties studied the specific heat has been a controversial subject. Yosida and Miwa²⁾ calculated the change of the free energy due to the s - d exchange interaction by direct perturbation expansion and found that it involves no $\log T$ term nor $T \log T$ term at least up to the fourth order of the interaction. This means that the free energy is essentially temperature-independent at least up to fourth order. They conjectured that this result might hold in higher orders and gave a physical explanation for this, namely: Although the s - d exchange interaction reduces the magnitude of the localized spin, the $(2S+1)$ -fold degeneracy remains in perturbation calculation and this makes the entropy unchanged and thus the free energy unchanged. On the other hand Bloomfield and Hamann³⁾ calculated the specific heat using their solution to the integral equation obtained from Nagaoka's truncation scheme for the Green's functions. They found a large peak of the specific heat centered around one third of T_K . Since Nagaoka's truncation scheme becomes essentially the same as the perturbation expansion at high temperatures, their result is in contradiction to Yosida

and Miwa's which predicts no contribution to the specific heat. In this paper we recalculate the free-energy shift by perturbation expansion and find a $T \log T$ term in the fourth order of the interaction.

§ 2. Preliminary consideration

Since the point which we are going to make is rather tricky, we first describe in detail the point which the previous perturbation calculations^{2),4)} have missed. We will do this for the third order term as an example, although the $T \log T$ term occurs in the fourth order.

At zero temperature the third order shift of the energy is essentially expressed by

$$\int f_1(1-f_2)(1-f_3)/(\varepsilon_2-\varepsilon_1)(\varepsilon_3-\varepsilon_1)d\varepsilon_1d\varepsilon_2d\varepsilon_3, \quad (1)$$

where $f_1=f(\varepsilon_1)$, etc., and $f(\varepsilon)=1$ for $\varepsilon \leq \varepsilon_F$, $f(\varepsilon)=0$ for $\varepsilon > \varepsilon_F$. It is usually said that (1) gives us the free-energy shift at finite temperature if one takes $f(\varepsilon)$ as the fermi distribution function.^{2),4)} (The divergence due to the vanishing denominator is avoided by taking the principal value of the integral.)

However, this is wrong. By expanding the density matrix in powers of the interaction and taking the traces (see the next section), one obtains in third order the following expression instead of (1):⁵⁾

$$\frac{1}{3} \int \left[\frac{1}{(\varepsilon_2-\varepsilon_1)(\varepsilon_3-\varepsilon_1)} + \frac{\exp(\beta(\varepsilon_1-\varepsilon_2))}{(\varepsilon_3-\varepsilon_2)(\varepsilon_1-\varepsilon_2)} + \frac{\exp(\beta(\varepsilon_1-\varepsilon_3))}{(\varepsilon_3-\varepsilon_2)(\varepsilon_3-\varepsilon_1)} \right] \\ \times f_1(1-f_2)(1-f_3)d\varepsilon_1d\varepsilon_2d\varepsilon_3, \quad (2)$$

where $\beta=1/T$ (we set $k_B=1$). The integrand never diverges when any two or three of ε_i 's become identical, so the integral is well defined. But if one divides the integral into three terms, each one is not defined. A procedure to avoid this difficulty is to take the principal value of each integral, namely to replace (2) by

$$\lim_{\delta \rightarrow 0} \frac{1}{3} \int \left[\frac{1}{(\varepsilon_2-\varepsilon_1)_\delta(\varepsilon_3-\varepsilon_1)_\delta} + \frac{\exp(\beta(\varepsilon_1-\varepsilon_2))}{(\varepsilon_3-\varepsilon_2)_\delta(\varepsilon_1-\varepsilon_2)_\delta} + \frac{\exp(\beta(\varepsilon_1-\varepsilon_3))}{(\varepsilon_3-\varepsilon_2)_\delta(\varepsilon_3-\varepsilon_1)_\delta} \right] \\ \times f_1(1-f_2)(1-f_3)d\varepsilon_1d\varepsilon_2d\varepsilon_3, \quad (3)$$

where

$$\frac{1}{(\varepsilon_2-\varepsilon_1)_\delta} \equiv \frac{\varepsilon_2-\varepsilon_1}{(\varepsilon_2-\varepsilon_1)^2+\delta^2}, \text{ etc.}$$

Then it is easy to show that (3) is equal to

$$\int f_1(1-f_2)(1-f_3)/(\varepsilon_2-\varepsilon_1)_\delta(\varepsilon_3-\varepsilon_1)_\delta d\varepsilon_1d\varepsilon_2d\varepsilon_3. \quad (\delta \rightarrow 0) \quad (4)$$

This is the same as the principal value of (1).

We now show that (3) is not identical with (2). First we observe that the quantity in the square brackets of (2) becomes $\beta^2/2$ when $|\beta(\epsilon_1 - \epsilon_2)| \ll 1$ and $|\beta(\epsilon_1 - \epsilon_3)| \ll 1$. The corresponding quantity of (3) also becomes $\beta^2/2$ when the same conditions and $\delta \ll |\beta(\epsilon_1 - \epsilon_2)|$, $\delta \ll |\beta(\epsilon_1 - \epsilon_3)|$ are fulfilled. But when $\delta \gg |\beta(\epsilon_1 - \epsilon_2)|$ and $\delta \gg |\beta(\epsilon_1 - \epsilon_3)|$ are satisfied, the quantity in the square brackets of (3) is no longer $\beta^2/2$ but order of δ^{-2} . The interval in which this divergence occurs is given by $(\epsilon_2 - \epsilon_1)$, $(\epsilon_3 - \epsilon_1) \sim \delta/\beta$, so we have a contribution which does not vanish in the limit of $\delta \rightarrow 0$.

To obtain a quantitative result we consider the difference between (3) and (2):

$$\begin{aligned}
 (3) - (2) &= (1/3) \int f_1 d\epsilon_1 \int [(\text{the quantity in the square brackets of (3)}) \\
 &\quad - (\beta^2/2)] (1-f_2) (1-f_3) d\epsilon_2 d\epsilon_3 \\
 &= (1/3) \int f_1 d\epsilon_1 \int \delta^2 [(\epsilon_3 - \epsilon_2)^2 + (\epsilon_2 - \epsilon_1)(\epsilon_3 - \epsilon_1)] (1-f_2) (1-f_3) / \\
 &\quad [(\epsilon_2 - \epsilon_1)^2 + \delta^2] [(\epsilon_3 - \epsilon_1)^2 + \delta^2] [(\epsilon_2 - \epsilon_3)^2 + \delta^2] d\epsilon_2 d\epsilon_3 \\
 &= (\pi^2/3) \int f_1 (1-f_1)^2 d\epsilon_1 = (\pi^2 T/6). \tag{5}
 \end{aligned}$$

This is finite when δ tends to zero. Although this term as well as (3) are not singular as $T \rightarrow 0$,²⁾ we show in the next section that a similar careful consideration leads to the $T \log T$ term in the fourth order.

§ 3. Calculation

We consider a single localized spin of magnitude S exchange-coupled to the conduction electrons. The Hamiltonian of our system is expressed by

$$\begin{aligned}
 H &= H_0 + V, \\
 H_0 &= \sum_{\mathbf{k}\sigma} \epsilon_{\mathbf{k}} a_{\mathbf{k}\sigma}^* a_{\mathbf{k}\sigma}, \\
 V &= -(J/N) \sum_{\mathbf{k}_1 \mathbf{k}_2} [(a_{\mathbf{k}_2 \uparrow}^* a_{\mathbf{k}_1 \uparrow} - a_{\mathbf{k}_2 \downarrow}^* a_{\mathbf{k}_1 \downarrow}) S_z + a_{\mathbf{k}_2 \uparrow}^* a_{\mathbf{k}_1 \downarrow} S_- + a_{\mathbf{k}_2 \downarrow}^* a_{\mathbf{k}_1 \uparrow} S_+], \tag{6}
 \end{aligned}$$

where the notation have the usual meaning.⁶⁾ The free energy F of the system is given by

$$\exp(-\beta F) = \text{Tr} \exp(-\beta(H_0 + V)). \tag{7}$$

By expanding in terms of V , we have

$$\exp(-\beta F) = \exp(-\beta F_0) [1 + \sum_n (-)^n \int_0^\beta \int_0^{s_1} \dots \int_0^{s_{n-1}} \langle V(s_1) V(s_2) \dots V(s_n) \rangle ds_1 ds_2 \dots ds_n], \tag{8}$$

where F_0 is the unperturbed value of the free energy, $\langle \rangle$ denotes a thermal average in the unperturbed system and $V(s) = e^{sH_0} V e^{-sH_0}$. We define an n -th order quantity R_n by

$$\exp(-\beta F) = \exp(-\beta F_0) [1 - \beta \sum_n R_n]. \tag{9}$$

As Bloch and Dominicis have shown,⁵⁾ the integral over s_n of (8) can be carried out. Then R_n is expressed by

$$R_n = [(-)^{n-1}/n] \int_0^\beta \cdots \int_0^{s_{n-2}} \langle V(s_1) \cdots V(s_{n-1}) V \rangle ds_1 \cdots ds_{n-1}. \tag{10}$$

The expansion of the free energy up to fourth order is expressed by

$$F - F_0 = R_2 + R_3 + R_4 + (\beta R_2^2/2) + \cdots. \tag{11}$$

The second order term R_2 is easily evaluated. Using (6) together with $a_{k\sigma}^*(s) = \exp(\varepsilon_k s) a_{k\sigma}^*$, $a_{k\sigma}(s) = \exp(-\varepsilon_k s) a_{k\sigma}$, we have

$$\begin{aligned} R_2 &= - (1/2) \int_0^\beta \langle V(s_1) V \rangle ds_1 \\ &= - (J/N)^2 S(S+1) \sum_{k_1 k_2} f_1(1-f_2) \int_0^\beta \exp((\varepsilon_1 - \varepsilon_2) s_1) ds_1, \end{aligned} \tag{12}$$

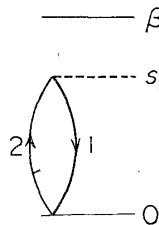


Fig. 1. Diagram for R_2 .

where $\varepsilon_1 = \varepsilon_{k_1}$, etc., and $f_1 = f(\varepsilon_1) = \langle a_{k_1\sigma}^* a_{k_1\sigma} \rangle$. The second order term may be represented by a diagram of Fig. 1, where the line with the arrow pointing up (down) denotes the factor $1 - f_2(f_1)$. The vertex s_1 is integrated from 0 to β .

In order to avoid the indefiniteness associated with the vanishing denominator, we process the integral of (12) as follows:

$$\int_0^\beta \exp((\varepsilon_1 - \varepsilon_2) s_1) ds_1 = \lim_{\delta \rightarrow 0} \text{Re} \int_0^\beta \exp((\varepsilon_1 - \varepsilon_2 + i\delta) s_1) ds_1, \tag{13}$$

where Re denotes "real part of". Then we have

$$\begin{aligned} R_2 &= (J/N)^2 S(S+1) \lim_{\delta \rightarrow 0} \text{Re} \sum_{k_1 k_2} f_1(1-f_2) [(\varepsilon_1 - \varepsilon_2 - i\delta)^{-1} + (\varepsilon_1 - \varepsilon_2 + i\delta)^{-1}] \\ &= 2J^2 \rho^2 S(S+1) \text{P} \int_{-D}^D f_1(1-f_2) / (\varepsilon_1 - \varepsilon_2) d\varepsilon_1 d\varepsilon_2 \end{aligned}$$

$$= -4(\log 2)J^2\rho^2DS(S+1) + O(T^2/D^2), \tag{14}$$

where we have assumed as usual a square band with the density of states ρ between $D \geq \epsilon \geq -D$. P denotes the principal value of the integral. This is the result obtained previously.⁶⁾

We now proceed to the fourth order terms, because the third order term is non-singular. There are nine distinct processes for R_4 which are represented by diagrams in Fig. 2. By a straightforward calculation we find that the contributions of each diagram to R_4 are expressed by

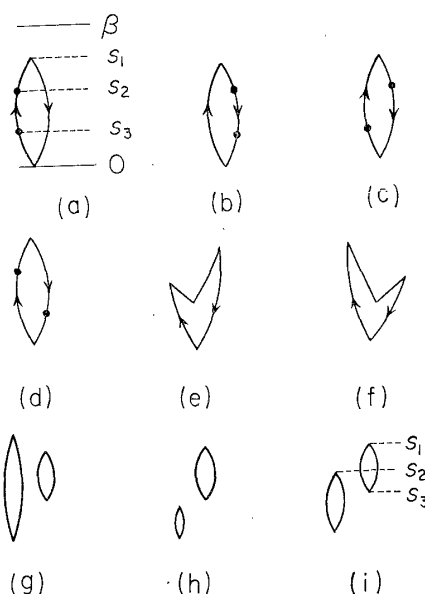


Fig. 2. Diagrams contributing to R_4 .

$$R_4^{(a)} = S^2(S+1)^2(J/N)^4[1 + (S(S+1))^{-1}]Q_a, \tag{15a}$$

$$R_4^{(b)} = S^2(S+1)^2(J/N)^4[1 + (S(S+1))^{-1}]Q_b, \tag{15b}$$

$$R_4^{(c)} = S^2(S+1)^2(J/N)^4[1 - (S(S+1))^{-1}]Q_c, \tag{15c}$$

$$R_4^{(d)} = S^2(S+1)^2(J/N)^4[1 - (S(S+1))^{-1}]Q_d, \tag{15d}$$

$$R_4^{(e)} = S^2(S+1)^2(J/N)^4[1 - (S(S+1))^{-1}]Q_e, \tag{15e}$$

$$R_4^{(f)} = S^2(S+1)^2(J/N)^4[1 - (S(S+1))^{-1}]Q_f, \tag{15f}$$

$$R_4^{(g)} = S^2(S+1)^2(J/N)^4 2Q_g, \tag{15g}$$

$$R_4^{(h)} = S^2(S+1)^2(J/N)^4 2Q_h, \tag{15h}$$

$$R_4^{(i)} = S^2(S+1)^2(J/N)^4 2[1 - (S(S+1))^{-1}]Q_i. \tag{15i}$$

We show only the expressions of Q_a and Q_i , which are the only ones necessary for later calculation:

$$Q_a = - (1/2) \sum_{k_1 \dots k_4} f_1 g_2 g_3 g_4 \int_{\beta > s_1 > s_2 > s_3 > 0} \exp(s_1(\epsilon_1 - \epsilon_4) + s_2(\epsilon_4 - \epsilon_3) + s_3(\epsilon_3 - \epsilon_2)) \times ds_1 ds_2 ds_3, \tag{16}$$

$$Q_i = - (1/2) \sum_{k_1 \dots k_4} f_1 g_2 f_3 g_4 \int_{\beta > s_1 > s_2 > s_3 > 0} \exp(s_1(\epsilon_3 - \epsilon_4) + s_2(\epsilon_1 - \epsilon_2) + s_3(\epsilon_4 - \epsilon_3)) \times ds_1 ds_2 ds_3, \tag{17}$$

where $g_2 = 1 - f_2$, etc. The other contribution to fourth order is easily obtained from (12):

$$\frac{1}{2}\beta R_2^2 = S^2(S+1)^2(J/N)^4 2Q_j, \quad (18)$$

where

$$Q_j = (\beta/4) \left(\sum_{k_1 k_2} f_1 g_2 \int_0^\beta \exp(s_1(\epsilon_1 - \epsilon_2)) ds_1 \right)^2. \quad (19)$$

It is instructive and helps later calculation to consider the case of static potential instead of the exchange interaction. If the conduction electrons interact with a δ -type static impurity potential of magnitude $J[S(S+1)]^{1/2}$, the fourth order shift of the free energy is expressed by

$$\Delta F_4 = S^2(S+1)^2(J/N)^4(Q_a + Q_b + Q_c + Q_d + Q_e + Q_f + Q_g + Q_h + Q_i + Q_j). \quad (20)$$

We now consider the sum of $Q_g + Q_h + Q_i$. Inspection of Figs. 2(g), (h) and (i) shows that the vertex of the left-hand part of the diagrams (s_2 of Fig. 2(i), for example) may be integrated from 0 to β without regards of the positions of the other two vertexes. Thus we find from (17)

$$\begin{aligned} Q_g + Q_h + Q_i = & - (1/2) \sum_{k_1 \dots k_4} f_1 g_2 f_3 g_4 \int_0^\beta \exp(s_2(\epsilon_1 - \epsilon_2)) ds_2 \\ & \times \int_0^\beta ds_1 \int_0^{s_1} ds_3 \exp(s_1(\epsilon_3 - \epsilon_4) + s_3(\epsilon_4 - \epsilon_3)). \end{aligned} \quad (21)$$

A bit manipulation shows that this is minus of Q_j (see (19)), namely

$$Q_g + Q_h + Q_i + Q_j = 0. \quad (22)$$

This is an example of the linked-cluster expansion theorem. From this result and from the fact that the static potential causes no singular term we have

$$Q_a + Q_b + Q_c + Q_d + Q_e + Q_f = \text{non-singular}. \quad (23)$$

Using (22) and (23) in (15) + (18), we see that the only fourth-order term which we now have to look at is

$$2S(S+1)(J/N)^4(Q_a + Q_b - Q_i). \quad (24)$$

For a symmetric band we have $Q_a = Q_b$. We process the integrals in (16) and (17) as we did in (13). For Q_a we have

$$\begin{aligned} Q_a = & - (1/2) \lim_{\delta \rightarrow 0} \text{Re} \sum_{k_1 \dots k_4} f_1 g_2 g_3 g_4 \\ & \times \int_{\beta > s_1 > s_2 > s_3 > 0} \exp(s_1(\epsilon_1 - \epsilon_4 + i\delta) + s_2(\epsilon_4 - \epsilon_3 + i\delta) + s_3(\epsilon_3 - \epsilon_2 + i\delta)) ds_1 ds_2 ds_3 \\ = & - (1/2) \text{Re} \sum_{k_1 \dots k_4} f_1 g_2 g_3 g_4 \left[\frac{1}{(\epsilon_2 - \epsilon_1)_+ + (\epsilon_3 - \epsilon_1)_+ + (\epsilon_4 - \epsilon_1)_+} \right] \end{aligned}$$

$$\begin{aligned}
 & + \frac{1}{(\varepsilon_2 - \varepsilon_1)_- (\varepsilon_3 - \varepsilon_1)_+ (\varepsilon_4 - \varepsilon_1)_+} + \frac{1}{(\varepsilon_2 - \varepsilon_1)_- (\varepsilon_3 - \varepsilon_1)_- (\varepsilon_4 - \varepsilon_1)_+} \\
 & + \frac{1}{(\varepsilon_2 - \varepsilon_1)_- (\varepsilon_3 - \varepsilon_1)_- (\varepsilon_4 - \varepsilon_1)_-} \Big], \tag{25}
 \end{aligned}$$

where

$$\frac{1}{(\varepsilon_2 - \varepsilon_1)_\pm} = P\left(\frac{1}{\varepsilon_2 - \varepsilon_1}\right) \mp \pi i \delta(\varepsilon_2 - \varepsilon_1), \text{ etc.} \tag{26}$$

By taking three principal parts or one principal part and two δ -functions, we have

$$\begin{aligned}
 Q_a = & -2\rho^4 P \int f_1 g_2 g_3 g_4 / (\varepsilon_2 - \varepsilon_1) (\varepsilon_3 - \varepsilon_1) (\varepsilon_4 - \varepsilon_1) d\varepsilon_1 \cdots d\varepsilon_4 \\
 & + 2\pi^2 \rho^4 P \int f_1 g_1^2 g_2 / (\varepsilon_2 - \varepsilon_1) d\varepsilon_1 d\varepsilon_2. \tag{27}
 \end{aligned}$$

The second term (minus a non-singular term) of (27) is processed as

$$\begin{aligned}
 & 2\pi^2 \rho^4 P \int [f_2 - (1/2)] f_1 g_1^2 / (\varepsilon_1 - \varepsilon_2) d\varepsilon_1 d\varepsilon_2 \\
 & = \pi^2 \rho^4 P \int [f_2 - (1/2)] f_1 (1 - f_1) / (\varepsilon_1 - \varepsilon_2) d\varepsilon_1 d\varepsilon_2 \\
 & = \pi^2 \rho^4 T \int [f_2 - (1/2)] (df_1 / d\varepsilon_1) / (\varepsilon_2 - \varepsilon_1) d\varepsilon_1 d\varepsilon_2 \\
 & = \pi^2 \rho^4 T \log(D/T). \tag{28}
 \end{aligned}$$

The first term of (27) is more tedious to handle with. The integral in the first term of (27) is calculated as

$$\begin{aligned}
 & P \int f_1 g_2 g_3 g_4 / (\varepsilon_2 - \varepsilon_1) (\varepsilon_3 - \varepsilon_1) (\varepsilon_4 - \varepsilon_1) d\varepsilon_1 d\varepsilon_2 d\varepsilon_3 d\varepsilon_4 \\
 & = - \int g_2 g_3 g_4 / (\varepsilon_1 - \varepsilon_2)_\delta (\varepsilon_1 - \varepsilon_3)_\delta (\varepsilon_1 - \varepsilon_4)_\delta d\varepsilon_1 \cdots d\varepsilon_4 \\
 & + \int g_1 g_2 g_3 g_4 / (\varepsilon_1 - \varepsilon_2)_\delta (\varepsilon_1 - \varepsilon_3)_\delta (\varepsilon_1 - \varepsilon_4)_\delta d\varepsilon_1 \cdots d\varepsilon_4. \tag{29}
 \end{aligned}$$

To calculate the first term we consider an integral ϕ and ϕ' :

$$\begin{aligned}
 \phi & = \int \frac{1}{(\varepsilon_1 - \varepsilon_2)_\delta (\varepsilon_1 - \varepsilon_3)_\delta (\varepsilon_1 - \varepsilon_4)_\delta} d\varepsilon_1, \\
 \phi' & = \int \left[\left(\frac{1}{(\varepsilon_1 - \varepsilon_2)_\delta} - \frac{1}{(\varepsilon_1 - \varepsilon_4)_\delta} \right) \frac{1}{\varepsilon_2 - \varepsilon_4} - \left(\frac{1}{(\varepsilon_1 - \varepsilon_3)_\delta} - \frac{1}{(\varepsilon_1 - \varepsilon_4)_\delta} \right) \frac{1}{\varepsilon_3 - \varepsilon_4} \right] \\
 & \quad \times \frac{1}{\varepsilon_3 - \varepsilon_2} d\varepsilon_1.
 \end{aligned}$$

Then from direct calculation we observe that ϕ and ϕ' are not identical:

$$\phi - \phi' = \pi^2 \int \left[\frac{\delta(\varepsilon_1 - \varepsilon_2) \delta(\varepsilon_1 - \varepsilon_3)}{(\varepsilon_1 - \varepsilon_4)_\delta} + \frac{\delta(\varepsilon_1 - \varepsilon_2) \delta(\varepsilon_1 - \varepsilon_4)}{(\varepsilon_1 - \varepsilon_3)_\delta} + \frac{\delta(\varepsilon_1 - \varepsilon_3) \delta(\varepsilon_1 - \varepsilon_4)}{(\varepsilon_1 - \varepsilon_2)_\delta} \right] d\varepsilon_1. \quad (30)$$

ϕ' is easily evaluated as

$$\begin{aligned} \phi' = & [\log |(D - \varepsilon_2)/(D + \varepsilon_2)| - \log |(D - \varepsilon_4)/(D + \varepsilon_4)|] / (\varepsilon_2 - \varepsilon_4) (\varepsilon_2 - \varepsilon_3) \\ & - [\log |(D - \varepsilon_3)/(D + \varepsilon_3)| - \log |(D - \varepsilon_4)/(D + \varepsilon_4)|] / (\varepsilon_3 - \varepsilon_4) (\varepsilon_2 - \varepsilon_3). \end{aligned} \quad (31)$$

This is a well-defined function of ε_2 , ε_3 and ε_4 . There is no divergence when two of ε_i 's become identical, or no logarithmic dependence when ε_i 's are near the fermi surface. The first term of (29) is then calculated as

$$\begin{aligned} & - \int \phi g_2 g_3 g_4 d\varepsilon_2 d\varepsilon_3 d\varepsilon_4 \\ & = - \int \phi' g_2 g_3 g_4 d\varepsilon_2 d\varepsilon_3 d\varepsilon_4 - \int (\phi - \phi') g_2 g_3 g_4 d\varepsilon_2 d\varepsilon_3 d\varepsilon_4. \end{aligned}$$

The first term is non-singular. The second term becomes

$$\begin{aligned} & - 3\pi^2 \int \delta(\varepsilon_1 - \varepsilon_2) \delta(\varepsilon_1 - \varepsilon_3) g_2 g_3 g_4 / (\varepsilon_1 - \varepsilon_4)_\delta d\varepsilon_1 \cdots d\varepsilon_4 \\ & = - 3\pi^2 \int g_1^2 g_4 / (\varepsilon_1 - \varepsilon_4)_\delta d\varepsilon_1 \cdots d\varepsilon_4 \\ & = - 3\pi^2 T \log(D/T) + \text{non-singular terms}. \end{aligned} \quad (32)$$

The second term of (29) is calculated as

$$\begin{aligned} & \int \frac{g_1 g_2 g_3 g_4}{(\varepsilon_1 - \varepsilon_2)_\delta (\varepsilon_1 - \varepsilon_3)_\delta (\varepsilon_1 - \varepsilon_4)_\delta} d\varepsilon_1 d\varepsilon_2 d\varepsilon_3 d\varepsilon_4 \\ & = \frac{1}{4} \int \left[\frac{1}{(\varepsilon_1 - \varepsilon_2)_\delta (\varepsilon_1 - \varepsilon_3)_\delta (\varepsilon_1 - \varepsilon_4)_\delta} + \frac{1}{(\varepsilon_2 - \varepsilon_1)_\delta (\varepsilon_2 - \varepsilon_3)_\delta (\varepsilon_2 - \varepsilon_4)_\delta} \right. \\ & \quad \left. + \frac{1}{(\varepsilon_3 - \varepsilon_2)_\delta (\varepsilon_3 - \varepsilon_1)_\delta (\varepsilon_3 - \varepsilon_4)_\delta} + \frac{1}{(\varepsilon_4 - \varepsilon_2)_\delta (\varepsilon_4 - \varepsilon_3)_\delta (\varepsilon_4 - \varepsilon_1)_\delta} \right] \\ & \quad \times g_1 g_2 g_3 g_4 d\varepsilon_1 \cdots d\varepsilon_4. \end{aligned} \quad (33)$$

If we set $\delta=0$, the integrand vanishes when none of two of ε_i 's is identical. Actually this integral remains finite when $\delta \rightarrow 0$, because after reducing the integrand to a common denominator we have

$$\begin{aligned} (33) & = 3\delta^2 \int \frac{g_1 g_2 g_3 g_4}{(\varepsilon_1 - \varepsilon_2)_\delta (\varepsilon_1 - \varepsilon_3)_\delta (\varepsilon_1 - \varepsilon_4)_\delta [(\varepsilon_3 - \varepsilon_4)^2 + \delta^2]} d\varepsilon_1 \cdots d\varepsilon_4 \\ & = 3\delta^2 \int \frac{g_1^2 g_2}{(\varepsilon_1 - \varepsilon_2)_\delta} d\varepsilon_1 d\varepsilon_2 \int \frac{yz}{(y^2 + \delta^2)(z^2 + \delta^2)[(y - z)^2 + \delta^2]} dy dz \end{aligned}$$

$$= \pi^2 \int \frac{g_1^3 g_2}{(\epsilon_1 - \epsilon_2)_\delta} d\epsilon_1 d\epsilon_2 = (3\pi^2/2) T \log(D/T). \tag{34}$$

Adding (32) and (34) we find

$$\begin{aligned} & P \int f_1 g_2 g_3 g_4 / (\epsilon_2 - \epsilon_1) (\epsilon_3 - \epsilon_1) (\epsilon_4 - \epsilon_1) d\epsilon_1 \dots d\epsilon_4 \\ &= (3\pi^2/2) T \log(T/D) + \text{non-singular terms}. \end{aligned} \tag{35}$$

From (28) and (35) we find

$$Q_a = 4\pi^2 \rho^4 T \log(D/T) + \text{non-singular terms}. \tag{36}$$

Adding the contribution from Q_b we have a singular fourth-order contribution to the free-energy shift as

$$\Delta F_4 = 16\pi^2 J^4 \rho^4 S(S+1) T \log(D/T). \tag{37}$$

Q_i is processed in a similar way.

$$\begin{aligned} Q_i &= - (1/2) \lim_{\delta \rightarrow 0} \text{Re} \sum_{k_1 \dots k_4} f_1 g_2 f_3 g_4 \\ &\times \int_{s > s_1 > s_2 > s_3 > 0} \exp(s_1(\epsilon_3 - \epsilon_4 + i\delta) + s_2(\epsilon_1 - \epsilon_2 + i\delta) + s_3(\epsilon_4 - \epsilon_3 + i\delta)) ds_1 ds_2 ds_3 \\ &= - (1/2) \rho^4 \text{Re} \int \left[\frac{g_1 f_2 f_3 g_4}{(\epsilon_4 - \epsilon_3)_+ (\epsilon_1 - \epsilon_2)_+ (\epsilon_1 + \epsilon_4 - \epsilon_2 - \epsilon_3)_+} \right. \\ &+ \frac{g_1 f_2 f_3 g_4}{(\epsilon_4 - \epsilon_3)_- (\epsilon_1 - \epsilon_2)_+ (\epsilon_1 + \epsilon_4 - \epsilon_2 - \epsilon_3)_+} - \frac{f_1 g_2 g_3 f_4}{(\epsilon_4 - \epsilon_3)_- (\epsilon_1 - \epsilon_2)_+ (\epsilon_1 + \epsilon_4 - \epsilon_2 - \epsilon_3)_+} \\ &\left. - \frac{f_1 g_2 g_3 f_4}{(\epsilon_4 - \epsilon_3)_+ (\epsilon_1 - \epsilon_2)_+ (\epsilon_1 + \epsilon_4 - \epsilon_2 - \epsilon_3)_+} \right] d\epsilon_1 \dots d\epsilon_4. \end{aligned} \tag{38}$$

There occur three types of the principal-value integrals. The first one is obtained by taking two δ -functions.

$$\begin{aligned} & P \int \delta(\epsilon_4 - \epsilon_3) \delta(\epsilon_1 - \epsilon_2) g_1 f_2 f_3 g_4 / (\epsilon_1 + \epsilon_4 - \epsilon_2 - \epsilon_3) d\epsilon_1 \dots d\epsilon_4 \\ &= \int f_1 g_1 d\epsilon_1 \int \delta(\epsilon_4 - \epsilon_3) f_3 g_4 / (\epsilon_4 - \epsilon_3) d\epsilon_3 d\epsilon_4 \\ &= (T/2) \int [(f_3 - f_4) / (\epsilon_4 - \epsilon_3)] \delta(\epsilon_4 - \epsilon_3) d\epsilon_3 d\epsilon_4 = T/2. \end{aligned} \tag{39}$$

The second one also contains two δ -functions.

$$\begin{aligned} & P \int \delta(\epsilon_1 + \epsilon_4 - \epsilon_2 - \epsilon_3) \delta(\epsilon_1 - \epsilon_2) g_1 f_2 f_3 g_4 / (\epsilon_4 - \epsilon_3) d\epsilon_1 \dots d\epsilon_4 \\ &= \int g_1 f_1 d\epsilon_1 \int \delta(\epsilon_4 - \epsilon_3) f_3 g_4 / (\epsilon_4 - \epsilon_3) d\epsilon_3 d\epsilon_4 = T/2. \end{aligned} \tag{40}$$

The third one contains three energy-differences in the denominator

$$P \int \frac{g_1 f_2 f_3 g_4 - f_1 g_2 g_3 f_4}{(\varepsilon_4 - \varepsilon_3)(\varepsilon_1 - \varepsilon_2)(\varepsilon_1 + \varepsilon_4 - \varepsilon_2 - \varepsilon_3)} d\varepsilon_1 \cdots d\varepsilon_4. \quad (41)$$

The numerator may be regrouped as

$$(41) = P \int \frac{(f_1 - f_2)(1 - f_3)f_4}{(\varepsilon_4 - \varepsilon_3)(\varepsilon_1 - \varepsilon_2)(\varepsilon_1 + \varepsilon_4 - \varepsilon_2 - \varepsilon_3)} d\varepsilon_1 \cdots d\varepsilon_4 \\ - P \int \frac{(1 - f_1)f_2(f_3 - f_4)}{(\varepsilon_4 - \varepsilon_3)(\varepsilon_1 - \varepsilon_2)(\varepsilon_1 + \varepsilon_4 - \varepsilon_2 - \varepsilon_3)} d\varepsilon_1 \cdots d\varepsilon_4. \quad (42)$$

By changing the numbering of ε_i 's one finds that the second term is identical to the first. They are easily found to involve no $T \log T$ term (see the Appendix). Then one sees that Q_i involves no singular term. (37) is the only singular contribution in fourth order.

§ 4. Discussion

From (37) one obtains the entropy change due to the s - d interaction:

$$\Delta S = -16\pi^2 S(S+1) J^4 \rho^4 [\log(D/T) - 1] k_B. \quad (43)$$

This is negative for both signs of J . This result may be interpreted in terms of the correlation between the localized spin and the conduction electron spin. Thus the conduction electrons may be polarized by the exchange interaction. The polarization is either positive or negative, depending on the sign of J . But in any case this polarization will follow the motion of the localized spin. Thus although the entropy arising from the $(2S+1)$ -fold degeneracy may be unchanged, the entropy of the conduction electrons may be decreased for both signs of J . This decrease of the entropy of the conduction electrons may correspond to the specific heat anomaly found by Bloomfield and Hamann. It must be noted that there certainly is a contribution to the specific heat for positive J . Whether it has a large peak as was found for negative J by Bloomfield and Hamann or not must be determined by examining higher order terms, but it seems unlikely that it does. For negative J we may expect that the decrease of the entropy of the conduction electrons becomes quite appreciable ($\sim k_B$) as the temperature becomes of the order of T_K and tends to cancel the entropy arising from the $(2S+1)$ -fold degeneracy of the spin, thus producing a binding energy of the order of $k_B T_K$.

When the concentration of impurity atoms is finite but small, one may consider that the reduction of the entropy is additive. For N_i impurities it will be $\sim N_i k_B$ at $T \lesssim T_K$. But at $T = T_K$ the entropy of the conduction electrons itself is $\sim N k_B^2 T_K / \varepsilon_F$. Thus we see the impurities are no longer independent when $N_i k_B \gtrsim N k_B^2 T_K / \varepsilon_F$. This condition is rewritten as $R \lesssim (a^2 \xi)^{1/3}$, where R is the average distance between impurities, a is the lattice constant and $\xi = \hbar v_F / k_B T_K$.⁶⁾ This condition is less stringent than the condition, $R \lesssim \xi$, which is obtained in

order that the "wave functions" of the impurity do not overlap.

The above result has a profound effect on the interpretation of the bound-state theories which treat the ground state for negative J .^{7)~9)} It is now well established that the ground state in the case of negative J has a binding energy. It has been a controversial point whether this ground state with the binding energy is reached by perturbation expansion (analytically continued across T_K as Suhl and Wong did¹⁰⁾) or there realizes a bound state which is not obtainable from perturbation theory. If the total entropy were to remain unchanged by perturbation theory as Yosida and Miwa conjectured, it would be said that the true ground state cannot be obtained by perturbation theory. However, now that the entropy turned out to decrease by perturbation theory, there is nothing which prevents from considering that the ground state can be obtained by perturbation theory.

Appendix

The first term of (42) may be calculated as

$$\begin{aligned} \frac{1}{2} \text{P} \int \frac{f_1 - f_2}{\varepsilon_1 - \varepsilon_2} d\varepsilon_1 d\varepsilon_2 \left\{ (1 - f_3) f_4 \left[\frac{1}{\varepsilon_4 - \varepsilon_3 + \varepsilon_1 - \varepsilon_2} + \frac{1}{\varepsilon_4 - \varepsilon_3 - (\varepsilon_1 - \varepsilon_2)} \right] \right\} d\varepsilon_3 d\varepsilon_4 \\ \equiv \frac{1}{2} \text{P} \int \frac{f_1 - f_2}{\varepsilon_1 - \varepsilon_2} I(\varepsilon_1 - \varepsilon_2) d\varepsilon_1 d\varepsilon_2, \end{aligned} \quad (\text{A} \cdot 1)$$

where the last line defines $I(\varepsilon)$ in an obvious way. Since $I(\varepsilon)$ is an even function of ε , we have

$$\begin{aligned} (\text{A} \cdot 1) &= \int f_1 d\varepsilon_1 \text{P} \int \frac{I(\varepsilon_1 - \varepsilon_2)}{\varepsilon_1 - \varepsilon_2} d\varepsilon_2 = - \int f_1 d\varepsilon_1 \text{P} \int_{-D - \varepsilon_1}^{D - \varepsilon_1} \frac{I(\varepsilon)}{\varepsilon} d\varepsilon \\ &= - \int f_1 d\varepsilon_1 \text{P} \int_{-D - \varepsilon_1}^{-D + \varepsilon_1} \frac{I(\varepsilon)}{\varepsilon} d\varepsilon. \end{aligned} \quad (\text{A} \cdot 2)$$

The value of $I(\varepsilon)$ for $\varepsilon \sim 0$ occurs only when ε_1 is near the band edge ($\varepsilon_1 \sim -D$). Singularity arising from sharp cutoff of the density of states, if such exists, can be avoided by changing trivially the shape of the density of states near the band edge. When $|\varepsilon|$ is large compared with kT , $I(\varepsilon)$ is essentially $\log|\varepsilon/D|$. Thus we see (A·2) involves no $T \log T$ term.

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Note added in proof:

Using the procedure described in the text we obtained the third order shift of the free energy, R_3 , as

$$R_3 = O(J^3 \rho^3 D) - (8\pi^2/3) S(S+1) J^3 \rho^3 k_B T.$$

Combining this with the fourth order term, we have

$$\Delta F = \Delta E - (8\pi^2/3) S(S+1) J^3 \rho^3 k_B T [1 + 6J\rho \log(T/D) + \dots],$$

where ΔE is practically independent of T . We may expect that the series in the parenthesis is the expansion of $[1 - 2J\rho \log(T/D)]^{-3}$. Then the entropy change in the leading logarithmic accuracy is given by

$$\Delta S(T) = (8\pi^2/3) S(S+1) J^3 \rho^3 k_B / [1 - 2J\rho \log(T/D)]^3.$$

This is positive for $J > 0$. Thus the interpretation given in Discussion of the result (43) which is negative for both signs of J is not correct for positive J .