

Singlet Ground State of the Localized d -Electrons Coupled with Conduction Electrons in Metals

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The theory of the singlet ground state for the s - d exchange model is extended to the core of d -electrons with orbital degeneracy. The effective s - d Hamiltonian is derived from the extended Anderson Hamiltonian by the Schrieffer-Wolff canonical transformation. On the basis of the effective Hamiltonian, the ground-state wave function and the ground-state energy are calculated. The anomalous part of the ground-state energy is given by $-D \exp[N/(2l+1)\rho J]$, independently of the d -electron number, when the Hund coupling is neglected compared with the effective s - d interaction. This binding energy is much larger than that for a localized s -electron because of an extra factor of $1/(2l+1)$ in the exponent. This large value is caused mainly by the orbital quenching. For a more realistic case in which the Hund coupling is larger than the s - d interaction, it reduces to a smaller value of $-D \exp[(2l+1)N/\rho J]$ for a half-filled shell in which orbital exchange does not exist. This value is due purely to the spin quenching. Qualitative discussion is given about the spin quenching and orbital quenching on the effective Hamiltonian derived for $n=2l$, n being the number of d -electrons.

§ 1. Introduction

This paper deals with a problem concerning the ground state for d -electrons of a magnetic impurity atom in nonmagnetic metals, by extending the theory of the singlet ground state developed for the s - d exchange model.^{1)~8)}

The usual s - d exchange Hamiltonian is expressed by

$$H_{sd} = -\frac{J}{2N} \sum_{\substack{\mathbf{k}\mathbf{k}' \\ s s'}} a_{\mathbf{k}'s'}^\dagger \sigma_{s's} a_{\mathbf{k}s} \cdot \mathbf{S}, \quad (1.1)$$

where σ represents the Pauli spin matrix and \mathbf{S} the localized spin possessed by the impurity atom. $a_{\mathbf{k}s}^\dagger$ and $a_{\mathbf{k}s}$ are the creation and annihilation operators for a conduction electron with wave vector \mathbf{k} and spin s . This form of the s - d exchange Hamiltonian describes s -wave scattering of the conduction electrons by the localized spin. Therefore, this Hamiltonian is a correct expression for the local s -orbital with spin the magnitude of which is $1/2$.

For local d -electrons, d -wave scattering is important and in this case d -part of s - d exchange integral $J(\mathbf{k}', \mathbf{k})$

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$$\begin{aligned}
 J(k', k) &\simeq \sum_l J_l P_l(\cos \theta_{kk'}) \\
 &= \sum_l \frac{4\pi}{2l+1} J_l \sum_{m=-l}^l \bar{Y}_l^m(\Omega_k) Y_l^m(\Omega_{k'}) \quad (1.2)
 \end{aligned}$$

should be taken. In (1.2), P_l and Y_l^m are respectively Legendre polynomials and the spherical harmonics and Ω_k represents the direction of wave vector \mathbf{k} . If l -part of (1.2) is used in place of J in (1.1), the s - d exchange Hamiltonian for d -wave scattering is obtained as

$$\begin{aligned}
 H_{sd} &= -\frac{J_l}{2N} \frac{4\pi}{2l+1} \sum_{\substack{k, k' \\ s, s'}} \sum_m (Y_l^m(\Omega_{k'}) a_{k's'}^\dagger \sigma_{s's} (\bar{Y}_l^m(\Omega_k) a_{ks}) \cdot S \\
 &= -\frac{J_l}{2N} \frac{1}{2l+1} \frac{2R^2}{3} \sum_{k, k'} \sum_{m, s, s'} a_{k'lms}^\dagger \sigma_{s's} a_{klms} \cdot S, \quad (1.3)
 \end{aligned}$$

where a_{klms}^\dagger represents the creation operator of the electron whose wave function is given by the spherical l, m -wave

$$\phi_{klm}(\mathbf{r}) = \sqrt{\frac{2}{R}} j_l(kr) Y_l^m(\Omega_r), \quad (1.4)$$

R being the radius of the spherical crystal, j_l the spherical Bessel function, and it is related to a_{ks}^\dagger

$$a_{klms}^\dagger = (-i)^l \frac{kR}{\sqrt{6\pi}} \int d\Omega_k Y_l^m(\Omega_k) a_{ks}^\dagger. \quad (1.5)$$

This form of H_{sd} expressed by (1.3) may be used for discussing the Kondo effect of the localized d -orbitals of iron-group impurities. Since this Hamiltonian does not express the orbital states of d -electrons explicitly, some ambiguities remain except for a special case of the half-filled shell, for which (1.3) represents the proper s - d Hamiltonian as will be shown in this paper.

In order to derive the s - d effective Hamiltonian which describes the orbital states for d -electrons explicitly, one should start with the Anderson Hamiltonian⁹⁾ extended to the case of local degenerate d -orbitals. This is done in the next section for d -orbitals by the use of the Schrieffer-Wolff transformation.¹⁰⁾ In § 3 the starting ground-state wave function in perturbative approach is investigated for the case in which an impurity atom has one d -electrons. The scattering t -matrix for this effective Hamiltonian is calculated in the approximation that the most divergent terms are retained in § 4. In § 5 the energy and the wave function of the singlet ground state are calculated by the perturbational method developed so far for the usual s - d exchange Hamiltonian (1.1). This calculation is extended to the general case in which an impurity atom has n d -electrons in § 6 without taking into account the Hund coupling and the case in which the Hund coupling is taken account of is discussed in § 7.

§ 2. Effective Hamiltonian for local d -electrons

The usual s - d exchange Hamiltonian for $S=1/2$ is derived from the Anderson Hamiltonian in the limit of a large intra-Coulomb integral U between two localized electrons, by the perturbation method or by the Schrieffer-Wolff transformation.^{10),11)} The Anderson Hamiltonian for degenerate d -orbitals may be written as^{12)~14)}

$$H_A = H_s + H_d + H_{\text{mix}}, \quad (2.1)$$

$$H_s = \sum_{ks} \epsilon_k a_{ks}^\dagger a_{ks}, \quad (2.2)$$

$$H_d = \epsilon_d \sum_{m_s} d_{m_s}^\dagger d_{m_s} + \frac{U}{2} \sum_{\substack{m_1 m_2 \\ s_1 s_2}} d_{m_1 s_1}^\dagger d_{m_2 s_2}^\dagger d_{m_2 s_2} d_{m_1 s_1} \\ + \frac{J_t}{2} \sum_{\substack{m_1 m_2 \\ s_1 s_2}} d_{m_1 s_1}^\dagger d_{m_2 s_2}^\dagger d_{m_1 s_2} d_{m_2 s_1}, \quad (2.3)$$

$$H_{\text{mix}} = \sum_{km_s} [V_{km} a_{ks}^\dagger d_{m_s} + V_{mk} d_{m_s}^\dagger a_{ks}]. \quad (2.4)$$

Here H_s and H_d represent respectively the energy of the conduction electrons and that of the localized d -electrons, and H_{mix} represents the mixing Hamiltonian expressing mutual transfer between conduction and localized d -electrons. a_{ks}^\dagger and $d_{m_s}^\dagger$ are the creation operators for conduction and d -electrons, respectively. The second and the third terms in H_d express the intra-Coulomb and exchange interactions between d -electrons in the impurity atom. This form of interaction which satisfies rotational invariance in the real space and the spin space was adopted by Dworin,¹⁵⁾ and it can also be expressed as

$$\frac{U}{2} (n_d^2 - n_d) - \frac{J_t}{2} (2S_d^2 + \frac{n_d^2}{2} - 2n_d), \quad (2.5)$$

where n_d , S_d are, respectively, the number and spin operators of d -electrons.

The matrix element V_{km} in H_{sd} is given by

$$V_{km} = \frac{1}{\sqrt{V}} \int e^{-i\mathbf{k}\cdot\mathbf{r}} V_{\text{imp}}(\mathbf{r}) R_d(r) Y_l^m(\Omega_r) r^2 dr d\Omega, \quad (2.6)$$

where the impurity potential is assumed to be spherically symmetric, and $R_d(r)$ represents the radial part of the d -electron wave function. If one introduces the mixing matrix element between the spherical l , m -wave given by (1.4) and the localized d -orbital

$$v_{kl} = \sqrt{\frac{2}{R}} k \int j_l(kr) V_{\text{imp}}(r) R_d(r) r^2 dr, \quad (2.7)$$

V_{km} is given in terms of v_{kl} as

$$V_{km} = \frac{\sqrt{6\pi}}{kR} (-i)^l v_{kl} Y_l^m(\Omega_k). \quad (2.8)$$

With the use of (2.8) in (2.4), H_{mix} can be expressed as

$$H_{\text{mix}} = \sum_{km} v_{ki} a_{kims}^\dagger d_{ms} + \text{h.c.}, \tag{2.9}$$

where the summation over k is the one-dimensional sum.

Now we consider the case in which ϵ_d and U are very large compared with v_{ki} and eliminate H_{mix} from the Anderson Hamiltonian by the Schrieffer-Wolff transformation. In order to do so, we introduce the matrix S which satisfies the following relations;

$$[H_s + H_d, S] = H_{\text{mix}}, \tag{2.10}$$

$$\tilde{H} = e^S H_A e^{-S} = H_s + H_d + \frac{1}{2}[S, H_{\text{mix}}] + \frac{1}{3}[S, [S, H_{\text{mix}}]] + \dots \tag{2.11}$$

For the case of $J_i = 0$, this matrix S can be obtained for general n_d as

$$S = \sum_{kms} [A_k a_{kms}^\dagger d_{ms} - B_k d_{ms}^\dagger a_{kms}], \tag{2.12}$$

$$A_k = v_k \sum_{j=0}^{q-1} \frac{(-1)^{j+1}}{j!(q-j-1)!(\epsilon_k - \Delta E_j)} \prod_{\substack{i=0 \\ (i \neq j)}}^{q-1} (n_d - i), \tag{2.13}$$

$$B_k = \bar{v}_k \sum_{j=0}^{q-1} \frac{(-1)^{j+1}}{j!(q-j-1)!(\epsilon_k - \Delta E_j)} \prod_{\substack{i=1 \\ (i \neq j+1)}}^q (n_d - i), \tag{2.14}$$

$$\Delta E_j = E_d(n_d = j + 1) - E_d(n_d = j) = \epsilon_d + jU. \tag{2.15}$$

Here and also in the following, q denotes the degree of degeneracy of d -electrons, namely, $q = 2(2l + 1) = 10$.

Now, the d -electron number in the most stable unperturbed state is assumed to be $n_d = n$. Then we have

$$\begin{aligned} \Delta E_n &= \epsilon_d + nU > \epsilon_F, \\ \Delta E_{(n-1)} &= \epsilon_d + (n-1)U < \epsilon_F, \end{aligned} \tag{2.16}$$

where ϵ_F is the Fermi energy and is taken as the origin of energy.

With the use of matrix S obtained by (2.12) ~ (2.15), the transformed Hamiltonian is given to second order in v_k by

$$\begin{aligned} H &= H_s + H_d + H_{sd}, \\ H_{sd} &= -\frac{J}{2N} \sum_{\substack{kk' \\ ss'mm'}} [a_{k'm's'}^\dagger a_{kms} d_{ms}^\dagger d_{m's'} - \frac{1}{q} a_{k'm's}^\dagger a_{kms} d_{m's'}^\dagger d_{m's'}], \end{aligned} \tag{2.17}$$

$$\begin{aligned} \frac{J}{2N} &= |v_{kF}|^2 \frac{U}{(\epsilon_d + (n-1)U)(\epsilon_d + nU)} < 0, \\ &= -\frac{4}{U} |v_{kF}|^2. \quad \left(\text{for } \epsilon_d + \left(n - \frac{1}{2}\right)U = 0\right) \end{aligned} \tag{2.18}$$

Here those parts which are constant and which change the number of d -electrons

are omitted, and the ϵ_k -dependence of J is also neglected. The effective s - d interaction of (2.17) is chosen so as to exclude the part due to potential scattering which is diagonal with respect to the d -state by subtracting the second terms.^{10),16)}

When the intra-exchange integral J_i between d -electrons is taken into account, the calculation becomes somewhat complicated, though practicable, because the spin multiplicity should be taken care of. So, here, the effective Hamiltonian for the case in which the impurity atom has one d -electron in the unperturbed state is only written down as

$$H = H_s + H_d + H_{sd},$$

$$H_{sd} = - \sum_{k'km's's'} \left\{ \frac{J_1}{2N} a_{k'm's'}^\dagger a_{kms} d_{m's'}^\dagger d_{m's'} + \frac{J_2}{2N} a_{k'm's'}^\dagger a_{kms} d_{m's'}^\dagger d_{m's'} - \frac{J_2}{2N} a_{k'm's'}^\dagger a_{kms} d_{m's'}^\dagger d_{m's'} - \frac{J_3}{2N} a_{k'm's'}^\dagger a_{kms} d_{m's'}^\dagger d_{m's'} \right\}, \quad (2.19)$$

$$\frac{J_1}{2N} = |v_{kF}|^2 \frac{U(\epsilon_d + U) - J_i^2}{\epsilon_d(\epsilon_d + U - J_i)(\epsilon_d + U + J_i)} < 0, \quad (2.20)$$

$$\frac{J_2}{2N} = |v_{kF}|^2 \frac{-J_i}{(\epsilon_d + U - J_i)(\epsilon_d + U + J_i)} < 0, \quad (2.21)$$

$$\frac{J_3}{2N} = \frac{1}{q} \left(\frac{J_1}{2N} - (2l-1) \frac{J_2}{2N} \right). \quad (2.22)$$

The first term of the effective s - d interaction of (2.19) exchanges both orbital and spin states, the second only orbital states and the third only spin states. The second and third terms seem to be important in distinguishing between orbital and spin states for the case in which the impurity atom has one localized d -electron, but, for simplicity, we shall neglect J_i compared with U in the s - d effective interaction and take account of it only in H_d in this paper.

§ 3. Zero-approximation of the ground-state wave function for the effective Hamiltonian

In this section, we calculate the ground-state wave function of zero-approximation for the effective Hamiltonian for one d -electron given by (2.17), which will be taken as a starting wave function of the ground-state wave function by perturbative approach. The zero-approximate wave function denotes the ground-state eigenfunction for the effective Hamiltonian in the subspace in which only extra one-electron is excited above the Fermi sea or extra one-hole is excited below the Fermi sea. In the present case, these two cases give different results as we shall see later.

First we shall consider the case in which one-hole is added to the Fermi sea. Since the effective Hamiltonian conserves the total angular momentum L_z

and spin S_z , we seek for the solution in the subspace of $L_z=0$ and $S_z=0$. Such a wave function is written as

$$\psi_0^h = \sum_{kms} \Gamma_{kms} a_{kms} a_{ms}^\dagger |F\rangle, \quad (3.1)$$

where $|F\rangle$ represents the wave function of the Fermi sea and amplitudes Γ_{kms} are determined by the Schrödinger equation

$$(H-E)\psi_0^h = 0. \quad (3.2)$$

Inserting (3.1) into (3.2) and cutting the states with electron-hole pair excitations besides one hole excitation, we obtain the following eigenvalue equation with respect to amplitudes Γ_{kms} :

$$(-\varepsilon_k - E)\Gamma_{kms} + \frac{J}{2N} \sum_{k'} \left\{ \sum_{m's'} \Gamma_{k'm's'} - \frac{1}{q} \Gamma_{k'ms} \right\} = 0. \quad (3.3)$$

We assume that the state-density for l -wave conduction electrons is a constant ρ^* between $-D$ and D and zero outside, and introduce G_{ms} and X by

$$\sum_k \Gamma_{kms} = G_{ms}, \quad (3.4)$$

$$-\frac{1}{2N} \sum_k \frac{1}{-\varepsilon_k - E} \approx \frac{\rho}{2N} \log \frac{-E}{D} = \frac{1}{X}. \quad (3.5)$$

Then we have

$$\left(-X - \frac{J}{q}\right) G_{ms} + J \sum_{m's'} G_{m's'} = 0, \quad (3.6)$$

which leads to the following eigenvalue equation:

$$\left\{-X + \left(q - \frac{1}{q}\right)J\right\} \left\{X + \frac{J}{q}\right\}^q = 0. \quad (3.7)$$

Only the first factor of (3.7) gives rise to a negative-value solution for X ,

$$X = \left(q - \frac{1}{q}\right)J. \quad (3.8)$$

This solution expresses the bound state whose binding energy is given by

$$E = -D \exp\left[\frac{2N}{\rho J(q-1/q)}\right]. \quad (3.9)$$

For this solution, amplitudes Γ_{kms} are independent of m and s and so it represents a singlet state with respect to both orbital and spin states, that is, in this state orbital and spin moments are quenched.

*) ρ is connected with the state density ρ_p for plane waves by $\rho = (3/2k_F^2 R^2) \rho_p$. On the other hand, $|v_{k_F}|^2 = \frac{2}{3} k_F^2 R^2 \langle |v_{k_F m}|^2 \rangle$ by (2.8). Therefore, the relation $\rho J = \rho_p J_p$ holds if one defines J_p by replacing $|v_{k_F}|^2$ in the expression of J with $\langle |v_{k_F m}|^2 \rangle$.

As shown above, we have obtained the singlet bound state by making an extra hole excited below the Fermi sea coupled with a localized d -electron, while the state with an extra electron added to the Fermi sea coupled with the localized d -electron does not give any singlet bound state. For this case, the zero-approximate wave function is given by

$$\psi_0^e = \sum_{kms} \Gamma_{kms} a_{kms}^\dagger d_{-m-s}^\dagger |F\rangle. \quad (3.10)$$

Inserting this wave function into the Schrödinger equation, we obtain the following equation for amplitudes Γ_{kms} :

$$(\epsilon_k - E)\Gamma_{kms} - \frac{J}{2N} \sum_{k'} \left\{ \Gamma_{k'-m-s} - \frac{1}{q} \Gamma_{k'ms} \right\} = 0. \quad (3.11)$$

Corresponding to (3.4) and (3.5) we introduce G_{ms} and X in which the summation is now taken over the states above the Fermi energy. Then (3.11) gives

$$\left(X - \frac{1}{q} J \right) G_{ms} + J G_{-m-s} = 0, \quad (3.12)$$

which leads to the eigenvalue equation

$$\left\{ X - \left(1 + \frac{1}{q} \right) J \right\}^{2l+1} \cdot \left\{ X + \left(1 - \frac{1}{q} \right) J \right\}^{2l+1} = 0. \quad (3.13)$$

The bound-state solution is given by

$$\begin{aligned} X &= \left(1 + \frac{1}{q} \right) J, \\ E &= -D \exp \left[\frac{2N}{\rho (1 + (1/q) J)} \right]. \end{aligned} \quad (3.14)$$

The amplitudes for this solution satisfy

$$\begin{aligned} \Gamma_{k-ms} &= -\Gamma_{kms}, \\ \Gamma_{km-s} &= \Gamma_{kms}. \end{aligned} \quad (3.15)$$

This state has $(2l+1)$ -fold degeneracy. If one introduces the intra-exchange J_t , this level splits into two levels having l -fold and $(l+1)$ -fold degeneracies. These belong to the states of $(S, L) = (1, 1), (1, 3)$ and those of $(S, L) = (0, 0), (0, 2)$ and $(0, 4)$ for $l=2$. Thus, in the zero-approximation, the degeneracy of the ground state is not removed by the s - d interaction in contrast to the case in which a hole is coupled to the d -electron. This is quite natural, because our Hamiltonian has not particle-hole symmetry from the beginning for the present case where one of ten local d -states is occupied.

For the usual s - d exchange model, the fact is recognized that if the bound-state solution in its zero-approximation is degenerate, this bound-state solution disappears in its final stage in which particle-hole excitations are taken into

account by the perturbation calculation starting from the zero-approximate state.^{7),17)} For the present case, also, the bound state solutions having degeneracy in the starting approximation disappear as particle-hole excitations are taken into account and only the non-degenerate solution survives in the final stage. Before we show this fact by taking into account higher-order effects, we shall calculate the scattering t -matrix for the present effective Hamiltonian (2·17) in the approximation in which the most divergent terms are taken into account.

§ 4. Scattering t -matrix

In this section we calculate the scattering t -matrix for one occupied d -electron in the most divergent approximation after the Abrikosov theory¹⁸⁾ for the usual s - d model. This calculation can be done in a way quite parallel to what Abrikosov has done for the s - d model and we have the following integral equation for the scattering matrix $\tau(\omega)$:

$$\begin{aligned} & \langle m_1 s_1, m_3 s_3 | \tau(t) | m_2 s_2, m_4 s_4 \rangle \\ &= -\frac{J}{2N} \delta_{m_1 m_4} \delta_{m_2 m_3} \delta_{s_1 s_4} \delta_{s_2 s_3} + \frac{J}{2N} \frac{1}{q} \delta_{m_1 m_2} \delta_{m_3 m_4} \delta_{s_1 s_2} \delta_{s_3 s_4} \\ & \quad - \int_0^t ds \sum_{\substack{m_1, m_3 \\ s_1, s_3}} \{ \langle m_1 s_1, m_3 s_3 | \tau(s) | m_5 s_5, m_6 s_6 \rangle \langle m_5 s_5, m_6 s_6 | \tau(s) | m_2 s_2, m_4 s_4 \rangle \\ & \quad - \langle m_5 s_5, m_6 s_6 | \tau(s) | m_2 s_2, m_6 s_6 \rangle \langle m_1 s_1, m_6 s_6 | \tau(s) | m_5 s_5, m_4 s_4 \rangle \}. \end{aligned} \quad (4.1)$$

In the matrix element $\langle m_1 s_1, m_3 s_3 | \tau(t) | m_2 s_2, m_4 s_4 \rangle$, $m_1 s_1$ and $m_3 s_3$ denote orbital and spin states of the conduction electron and $m_2 s_2$ and $m_4 s_4$ denote those of the local d -electron. t is defined by $\rho \log(D/|\omega|)$. The first and the second terms are nothing but the matrix element of the effective s - d interaction, and the third term consists of two parts A_1 and A_2 . A_1 represents the contributions from process (a) and A_2 those from process (b) shown in Fig. 1. The matrix element of τ can be put as

$$\begin{aligned} & \langle m_1 s_1, m_3 s_3 | \tau | m_2 s_2, m_4 s_4 \rangle \\ &= \tau_{12} \delta_{m_1 m_4} \delta_{m_2 m_3} \delta_{s_1 s_4} \delta_{s_2 s_3} + \tau_0 \delta_{m_1 m_2} \delta_{m_3 m_4} \delta_{s_1 s_2} \delta_{s_3 s_4}, \end{aligned} \quad (4.2)$$

because it is expected that τ has the same structure as the s - d interaction. If one inserts this form of τ into (4.1), the following integral equations for τ_{12} and

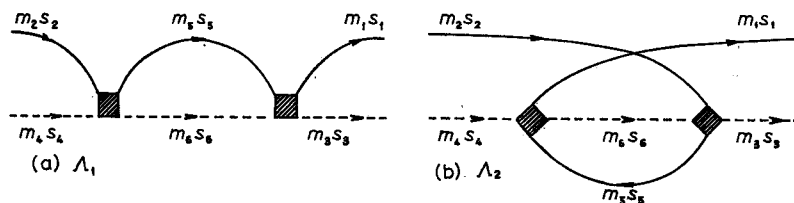


Fig. 1. Two types of vertex function.

τ_0 are obtained:

$$\tau_{is}(t) = -\frac{J}{2N} + q \int_0^t ds \tau_{is}^2(s), \quad (4.3)$$

$$\tau_0(t) = \frac{J}{2N} \frac{1}{q} - \int_0^t ds \tau_{is}^2(s). \quad (4.4)$$

Equation (4.3) can easily be solved and leads to

$$\tau_{is}(\omega) = -\frac{J}{2N} \left\{ 1 + q \frac{\rho J}{2N} \log \frac{D}{|\omega|} \right\}^{-1} \quad (4.5)$$

and

$$\tau_0(\omega) = -\frac{1}{q} \tau_{is}(\omega). \quad (4.6)$$

$\tau_{is}(\omega)$ and $\tau_0(\omega)$ have a pole at $|\omega| = \omega_k = D \exp[2N/q\rho J] = T_k$. This value of T_k is very big compared with the value of $D \exp[N/\rho J]$ on account of an extra factor $q=10$ for $l=2$ in the denominator in the exponent. With the use of these results A_1 and A_2 of the third term on the right-hand side of (4.1) are calculated as

$$\begin{aligned} & \langle m_1s_1, m_3s_3 | A_1(\omega) | m_2s_2, m_4s_4 \rangle \\ &= -\left(\frac{J}{2N}\right) \left\{ \frac{\rho J}{2N} \log \frac{D}{|\omega|} \left/ \left(1 + q \frac{\rho J}{2N} \log \frac{D}{|\omega|} \right) \right\} \\ & \quad \times \left\{ \left(1 + \frac{1}{q^2} \right) \delta m_1 m_2 \delta m_3 m_4 \delta s_1 s_2 \delta s_3 s_4 - \frac{2}{q} \delta m_1 m_4 \delta m_2 m_3 \delta s_1 s_4 \delta s_2 s_3 \right\}, \end{aligned} \quad (4.7)$$

$$\begin{aligned} & \langle m_1s_1, m_3s_3 | A_2(\omega) | m_2s_2, m_4s_4 \rangle \\ &= \left(\frac{J}{2N}\right) \left\{ \frac{\rho J}{2N} \log \frac{D}{|\omega|} \left/ \left(1 + q \frac{\rho J}{2N} \log \frac{D}{|\omega|} \right) \right\} \\ & \quad \times \left\{ \frac{1}{q^2} \delta m_1 m_2 \delta m_3 m_4 \delta s_1 s_2 \delta s_3 s_4 + \left(q - \frac{2}{q} \right) \delta m_1 m_4 \delta m_2 m_3 \delta s_1 s_4 \delta s_2 s_3 \right\}. \end{aligned} \quad (4.8)$$

These two A 's play the role of integration kernel of integral equation which the the amplitude for the ground-state wave function satisfies.¹⁹⁾

§ 5. The ground-state wave function and its energy eigenvalue for one local *d*-electron

After the method developed for the *s-d* model, we expand the ground-state wave function in the perturbation series, starting with the zero-approximate wave function (3.1) or (3.10). For the case in which a hole is coupled with the

d -electron, this expansion becomes

$$\begin{aligned}
 \psi^h = & \sum_{kms} \Gamma_{kms} a_{kms} a_{ms}^\dagger |F\rangle \\
 & + \sum_{\{k_1 m_1 s_1\}} \Gamma \begin{bmatrix} k_1 k_2 k_3 \\ m_1 m_2 m_3 \\ s_1 s_2 s_3 \end{bmatrix} a_{k_1 m_1 s_1}^\dagger a_{k_2 m_2 s_2} a_{k_3 m_3 s_3} a_{m_2+m_3-m_1, s_2+s_3-s_1}^\dagger |F\rangle \\
 & + \sum_{\{k_1 m_1 s_1\}} \Gamma \begin{bmatrix} k_1 k_2 k_3 k_4 k_5 \\ m_1 m_2 m_3 m_4 m_5 \\ s_1 s_2 s_3 s_4 s_5 \end{bmatrix} a_{k_1 m_1 s_1}^\dagger a_{k_2 m_2 s_2}^\dagger a_{k_3 m_3 s_3} \\
 & \times a_{k_4 m_4 s_4} a_{k_5 m_5 s_5} a_{m_3+m_4+m_5-m_1-m_2, s_3+s_4+s_5-s_1-s_2}^\dagger |F\rangle \\
 & + \dots
 \end{aligned} \tag{5.1}$$

By inserting (5.1) into the Schrödinger equation, the following relations between the amplitudes Γ are obtained:

$$\begin{aligned}
 (-\epsilon_k - E) \Gamma_{km} + \frac{J}{2N} \left\{ \sum_{k_1 m_1} \Gamma_{k_1 m_1} - \frac{1}{q} \sum_{k_1} \Gamma_{k_1 m} \right. \\
 \left. - \sum_{k_1 k_2 m_1} \Gamma \begin{bmatrix} k_1 & k_2 k \\ m & m_1 m \end{bmatrix} + \frac{1}{q} \sum_{k_1 k_2 m_1} \Gamma \begin{bmatrix} k_1 & k_2 k \\ m_1 & m_1 m \end{bmatrix} \right\} = 0,
 \end{aligned} \tag{5.2a}$$

$$\begin{aligned}
 (\epsilon_6 - \epsilon_7 - \epsilon_8 - E) \Gamma \begin{bmatrix} k_6 & k_7 k_8 \\ m_6 & m_7 m_8 \end{bmatrix} + \frac{J}{2N} \left\{ -\Gamma_{k_6 m_6} \delta_{m_6 m_6} + \Gamma_{k_7 m_7} \delta_{m_7 m_6} + \frac{1}{q} \Gamma_{k_8 m_6} \delta_{m_7 m_6} \right. \\
 - \frac{1}{q} \Gamma_{k_7 m_7} \delta_{m_6 m_6} + \sum_{k_1} \left(-\Gamma \begin{bmatrix} k_1 & k_7 k_8 \\ m_7 + m_8 - m_6 & m_7 m_8 \end{bmatrix} \right. \\
 \left. + \sum_{m_1} \Gamma \begin{bmatrix} k_6 & k_1 k_8 \\ m_6 & m_1 m_6 \end{bmatrix} \delta_{m_6 m_6} - \sum_{m_1} \Gamma \begin{bmatrix} k_6 & k_1 k_7 \\ m_6 & m_1 m_6 \end{bmatrix} \delta_{m_7 m_6} + \frac{1}{q} \Gamma \begin{bmatrix} k_1 & k_7 k_8 \\ m_6 & m_7 m_8 \end{bmatrix} \right. \\
 \left. - \frac{1}{q} \Gamma \begin{bmatrix} k_6 & k_1 k_8 \\ m_6 & m_7 m_8 \end{bmatrix} + \frac{1}{q} \Gamma \begin{bmatrix} k_6 & k_1 k_7 \\ m_6 & m_8 m_7 \end{bmatrix} \right) \\
 \left. + \sum_{k_1 k_2 m_2} \left(\Gamma \begin{bmatrix} k_1 & k_6 & k_2 k_7 k_8 \\ m_7 + m_8 - m_6 & m_6 & m_2 m_7 m_8 \end{bmatrix} \right. \right. \\
 \left. \left. - \frac{1}{q} \Gamma \begin{bmatrix} k_1 k_6 & k_2 k_7 k_8 \\ m_2 m_6 & m_2 m_7 m_8 \end{bmatrix} \right) \right\} = 0.
 \end{aligned} \tag{5.2b}$$

In (5.2a) and (5.2b), a single suffix m is used for m_s and $[\dots]$ in Γ indicates the antisymmetrized form:

$$\Gamma \begin{bmatrix} k_1 & k_2 k_3 \\ m_1 & m_2 m_3 \end{bmatrix} = \Gamma \begin{bmatrix} k_1 k_2 k_3 \\ m_1 m_2 m_3 \end{bmatrix} - \Gamma \begin{bmatrix} k_1 k_3 k_2 \\ m_1 m_3 m_2 \end{bmatrix}. \tag{5.3}$$

From the set of equations (5.2a), (5.2b), \dots , we derive the equation for the lowest amplitudes Γ_{kms} . This equation for the bound-state solution in which $\Gamma_{kms} = \Gamma_k$ holds is calculated as

$$\begin{aligned}
 \Gamma(\epsilon_6) & \left\{ -\epsilon_6 - E + \left(\frac{J}{2N}\right)^2 \sum_{4,5} \left(\frac{1}{q} - q\right) \frac{1}{D_{4,56}} + \dots \right\} \\
 & = -\left(q - \frac{1}{q}\right) \left(\frac{J}{2N}\right) \sum_1 \Gamma_1 + \left(1 - \frac{1}{q^2}\right) \left(\frac{J}{2N}\right)^2 \sum_{1,2} \frac{1}{D_{2,16}} \Gamma_1 \\
 & \quad - \left(1 - \frac{1}{q^2}\right) \left(\frac{J}{2N}\right)^3 \sum_{123} \left[\frac{1}{D_{2,36}} \left\{ \frac{q}{D_{1,36}} \Gamma_3 - \frac{q}{D_{2,18}} \Gamma_3 \right. \right. \\
 & \quad \left. \left. - \frac{1}{D_{2,18}} \Gamma_1 \right\} - \frac{1}{q} \frac{1}{D_{3,26}} \left\{ \frac{1}{D_{3,16}} \Gamma_1 - \frac{1}{D_{1,26}} \Gamma_2 \right. \right. \\
 & \quad \left. \left. - \frac{q^2}{D_{3,12}} \Gamma_2 + \frac{1}{D_{3,21}} \Gamma_3 \right\} \right] - \left(1 - \frac{1}{q^2}\right) \left(\frac{J}{2N}\right)^4 \\
 & \quad \times \sum_{1345} \left[\frac{1}{D_{4,56}} \left\{ \frac{1}{D_{4,16}} \left(\frac{q^2}{D_{4,31}} \Gamma_1 - \frac{q^2}{D_{3,16}} \Gamma_1 \right) + \dots \right\} + \dots \right] \\
 & \quad + \dots, \tag{5.4}
 \end{aligned}$$

where the suffixes k_i are abbreviated simply to i , and $D_{1,23}$ is used for energy denominator $(\epsilon_1 - \epsilon_2 - \epsilon_3 - E)$. Carrying out the summations in (5.4) with logarithmic accuracy or in the most divergent approximation, we obtain

$$\begin{aligned}
 (-\epsilon_k - \tilde{E}) \Gamma_k & = -\left(1 - \frac{1}{q^2}\right) \frac{qJ}{2N} \sum_{k'} \Gamma_{k'} \\
 & \quad - \left(1 - \frac{1}{q^2}\right) \frac{1}{q^2} \left(\frac{qJ}{2N}\right)^2 \rho \sum_{k'} \Gamma_{k'} \log \frac{-\epsilon_k - \epsilon_{k'} - \tilde{E}}{D} \\
 & \quad \times \left[1 + \frac{q\rho J}{2N} \log \frac{-\epsilon_k - \epsilon_{k'} - \tilde{E}}{D} + \left(\frac{q\rho J}{2N} \log \frac{-\epsilon_k - \epsilon_{k'} - \tilde{E}}{D}\right)^2 + \dots \right].
 \end{aligned}$$

If we here identify the series in $\rho J/2N$ in the integration kernel as the geometric series, (5.5) can be written as

$$\begin{aligned}
 (-\epsilon_k - \tilde{E}) \Gamma(\epsilon_k) & = -\left(1 - \frac{1}{q^2}\right) \frac{qJ\rho}{2N} \int_{-D}^0 \Gamma(\epsilon') d\epsilon' - \left(1 - \frac{1}{q^2}\right) \frac{1}{q^2} \left(\frac{qJ\rho}{2N}\right)^2 \\
 & \quad \times \int_{-D}^0 \Gamma(\epsilon') \left\{ \log \frac{-\epsilon_k - \epsilon' - \tilde{E}}{D} \left/ \left(1 - \frac{qJ\rho}{2N} \log \frac{-\epsilon_k - \epsilon' - \tilde{E}}{D} \right) \right. \right\} d\epsilon'. \tag{5.5}
 \end{aligned}$$

\tilde{E} is defined by

$$\tilde{E} = E - \Delta E, \tag{5.6}$$

where ΔE is called the normal part of the energy which is obtained by the usual perturbation calculation.

The integral equation (5.5) can be more generally written as

$$\begin{aligned}
 (-\epsilon_k - \tilde{E}) \Gamma_{km} & = \sum_{k'm'} \Gamma_{k'm'} \{ \langle m', m | H_{sd} | m, m' \rangle \\
 & \quad + \langle m', m | A_1(-\epsilon_k - \epsilon_{k'} - \tilde{E}) | m, m' \rangle \}, \tag{5.7}
 \end{aligned}$$

where $\langle m_1, m_3 | H_{sd} | m_2, m_4 \rangle$ and $\langle m_1, m_3 | A_1(\omega) | m_2, m_4 \rangle$ are given, respectively, by the sum of the first and second terms of (4.1) and by (4.7). The corresponding integral equation for the amplitudes Γ_{km} of ψ^e , (3.10), in which an extra electron excited above the Fermi sea is coupled with the d -electron, is given by

$$(\epsilon_k - \tilde{E}) \Gamma_{km} = - \sum_{k'm'} \Gamma_{k'm'} \{ \langle m, -m | H_{sd} | m', -m' \rangle + \langle m, -m | A_2(\epsilon_k + \epsilon' - \tilde{E}) | m', -m' \rangle \}, \tag{5.8}$$

where $\langle m_1, m_3 | A_2 | m_2, m_4 \rangle$ is given by (4.8). With the use of (4.8) for A_2 and relation (3.15) which says $\Gamma_{k-m\pm s} = -\Gamma_{kms} = -\Gamma_k$, (5.8) can be written as

$$\begin{aligned} (\epsilon_k - \tilde{E}) \Gamma_k &= - \left(\frac{1}{q} + \frac{1}{q^2} \right) \frac{qJ}{2N} \sum_{k'} \Gamma_{k'} \\ &\quad - \left(\frac{1}{q} + \frac{1}{q^2} \right) \left(1 - \frac{1}{q} - \frac{1}{q^2} \right) \left(\frac{qJ}{2N} \right)^2 \rho \sum_{k'} \Gamma_{k'} \\ &\quad \times \log \frac{\epsilon_k + \epsilon_{k'} - \tilde{E}}{D} \left[1 - \frac{q\rho J}{2N} \log \frac{\epsilon_k + \epsilon_{k'} - \tilde{E}}{D} \right]^{-1}. \end{aligned} \tag{5.9}$$

This integral equation can also be derived by direct calculation. The integral equations (5.5) and (5.9) can be solved with logarithmic accuracy by applying Yoshimori's method.⁶⁾ Calculation is straightforward. Putting

$$G(\epsilon) = \int_{\epsilon}^0 \Gamma(\epsilon') d\epsilon', \tag{5.10}$$

$$P(\epsilon) = 1 - \frac{q\rho J}{2N} \log \frac{-\epsilon - \tilde{E}}{D}, \tag{5.11}$$

$$\alpha = 1 - \frac{1}{q^2}, \quad \beta = \frac{1}{q^2}, \tag{5.12}$$

we obtain a bound-state solution for (5.5) as

$$G(\epsilon) = G(-D) \frac{[P(\epsilon)]^\alpha - [P(0)]^{(\alpha-\beta)} [P(\epsilon)]^\beta}{1 - (\beta/\alpha) [P(0)]^{(\alpha-\beta)}}. \tag{5.13}$$

The eigenvalue \tilde{E} is determined by the relation obtained by putting $\epsilon = -D$ in (5.13),

$$1 = \frac{1 - [P(0)]^{(\alpha-\beta)}}{1 - (\beta/\alpha) [P(0)]^{(\alpha-\beta)}}. \tag{5.14}$$

This relation is satisfied by $P(0) = 0$, namely,

$$\tilde{E} = -D \exp \left[\frac{N}{(2l+1)\rho J} \right]. \tag{5.15}$$

It is noted that the binding energy $|\tilde{E}|$ is enlarged by a factor $(2l+1)$ in the denominator of the exponent.

On the other hand, for (5.9) we have no bound-state solution except for $l=0$. Defining, as before,

$$P'(\varepsilon) = 1 - \frac{q\rho J}{2N} \log \frac{\varepsilon - \tilde{E}}{D}, \tag{5.16}$$

$$\alpha' = \frac{1}{q} + \frac{1}{q^2}, \quad \beta' = 1 - \frac{1}{q} - \frac{1}{q^2}, \tag{5.17}$$

we have the relation, corresponding to (5.14), which determines the eigenvalue $-\tilde{E}$ as

$$1 = \frac{1 - [P'(0)]^{(\alpha' - \beta')}}{1 - (\beta'/\alpha') [P'(0)]^{(\alpha' - \beta')}}. \tag{5.18}$$

Since $\alpha' - \beta' = \frac{1}{2} > 0$ for $l=0$, the binding energy is obtained as

$$\tilde{E} = -D \exp\left[\frac{N}{\rho J}\right],$$

but for $l \geq 1$, $\alpha' - \beta'$ becomes negative, and therefore, we have $P'(0) = \infty$ which means $\tilde{E} = 0$. Thus, we have no bound-state solution from (5.9).

§ 6. Ground state for n *d*-electrons

In the preceding section we have derived the ground singlet wave function for one localized *d*-electron coupled with the conduction electrons by the *s-d* effective interaction. In this and the next sections we consider the case in which the impurity atom carries n *d*-electrons ($1 < n < 10$). For this case, the intra-exchange interaction between *d*-electrons may be neglected in the effective *s-d* Hamiltonian, but it may not be neglected in H_d . On account of this Hund coupling included in H_d , the situation becomes complicated. Therefore, to avoid this difficulty, we take two extreme cases; in one case the intra-exchange coupling J_i is assumed to be zero, and in the other case J_i is much greater than H_{id} .

We begin with the consideration for the first case. By inferring from the results obtained for one *d*-electron, a starting wave function for the ground singlet state may be put as

$$\psi_0 = \sum_{\substack{\{k_i m_i s_i\} \\ (m_i s_i) \neq (m_j s_j)}} \Gamma \begin{bmatrix} k_1 & k_2 & \dots & k_n \\ m_1 & m_2 & \dots & m_n \\ s_1 & s_2 & \dots & s_n \end{bmatrix} \prod_{i=1}^n a_{k_i m_i s_i} d_{m_i s_i}^\dagger |F\rangle, \tag{6.1}$$

where n is assumed $n \leq 2l + 1$. For $n > 2l + 1$, electrons and holes are exchanged. Inserting (6.1) into the Schrödinger equation and cutting the higher-order states with particle-hole excitations, we obtain the equation for amplitudes Γ as

$$\begin{aligned}
 & \left(-\sum_i \varepsilon_i - E\right) \Gamma \begin{bmatrix} k_1 & k_2 & \cdots & k_n \\ m_1 & m_2 & \cdots & m_n \\ s_1 & s_2 & \cdots & s_n \end{bmatrix} \\
 & + \frac{J}{2N} \sum_{k'} \sum_{i=1}^n \left\{ \sum_{\substack{(m_i' s_i') \neq (m_j s_j) \\ j=1, 2, \dots, i-1, i+1, \dots, n}} \Gamma \begin{bmatrix} k_1 & k_2 & \cdots & k' & \cdots & k_n \\ m_1 & m_2 & \cdots & m_i' & \cdots & m_n \\ s_1 & s_2 & \cdots & s_i' & \cdots & s_n \end{bmatrix} \right. \\
 & \left. - \frac{n}{q} \Gamma \begin{bmatrix} k_1 & k_2 & \cdots & k' & \cdots & k_n \\ m_1 & m_2 & \cdots & m_i & \cdots & m_n \\ s_1 & s_2 & \cdots & s_i & \cdots & s_n \end{bmatrix} \right\} = 0. \tag{6.2}
 \end{aligned}$$

Here we put Γ as $\Gamma = \prod_{i=1}^n \Gamma_{k_i m_i s_i}$ and divide (6.2) by Γ . Then we obtain

$$\sum_i \left(-\varepsilon_{k_i} - \frac{E}{n}\right) + \frac{J}{2N} \sum_{i=1}^n \frac{1}{\Gamma_{k_i m_i s_i}} \sum_{k'} \left\{ \sum_{\substack{(ms) \neq (m_j s_j) \\ (i \neq j)}} \Gamma_{k' m s} - \frac{n}{q} \Gamma_{k' m_i s_i} \right\} = 0, \tag{6.3}$$

where the summation over ms is taken over the unoccupied states and $m_i s_i$. If $\Gamma_{k m s}$ are independent of ms and satisfy the equation

$$\left(-\varepsilon_k - \frac{E}{n}\right) \Gamma_k + \frac{J}{2N} \left\{ q - (n-1) - \frac{n}{q} \right\} \sum_{k'} \Gamma_{k'} = 0, \tag{6.4}$$

Eq. (6.3) is satisfied by such Γ_k . From (6.4) the energy eigenvalue is calculated as

$$E = -nD \exp \left[\frac{2N}{\{q - (n-1) - n/q\} \rho J} \right]. \tag{6.5}$$

In order to take into account the higher-order effects due to particle-hole pair excitations, we expand the ground-state wave function as

$$\begin{aligned}
 \psi = & \sum_{\{k_i m_i s_i\}} \Gamma \begin{bmatrix} k_1 & k_2 & \cdots & k_n \\ m_1 & m_2 & \cdots & m_n \\ s_1 & s_2 & \cdots & s_n \end{bmatrix} a_{k_1 m_1 s_1} a_{k_2 m_2 s_2} \cdots a_{k_n m_n s_n} d_{m_1 s_1}^\dagger d_{m_2 s_2}^\dagger \cdots d_{m_n s_n}^\dagger |F\rangle \\
 & + \sum_{\{k_i m_i s_i\}} \Gamma \begin{bmatrix} k_1 & \cdots & k_n & k_{n+1} & k_{n+2} \\ m_1 & \cdots & m_n & m_{n+1} & m_{n+2} & m_i' & \cdots & m_n' \\ s_1 & \cdots & s_n & s_{n+1} & s_{n+2} & s_i' & \cdots & s_n' \end{bmatrix} \\
 & \times a_{k_1 m_1 s_1} \cdots a_{k_n m_n s_n} a_{k_{n+1} m_{n+1} s_{n+1}} a_{k_{n+2} m_{n+2} s_{n+2}} d_{m_1 s_1}^\dagger \cdots d_{m_n s_n}^\dagger |F\rangle + \cdots \tag{6.6}
 \end{aligned}$$

For the suffixes possessed by the second amplitudes,

$$\sum_{i=1}^{n+1} m_i - m_{n+2} = \sum_{i=1}^n m_i', \quad \sum_{i=1}^{n+1} s_i - s_{n+2} = \sum_{i=1}^n s_i'$$

are satisfied. Also in the present case, we can derive an equation for the first amplitudes $\Gamma[k_1 k_2 \cdots k_n]$ that are independent of $(m_i s_i)$ by the same iterative procedure as has been done in § 5. To do this needs a somewhat lengthy calculation but its principle is so simple that we shall here write down only the

result without describing detailed processes of calculation.

$$\begin{aligned}
 & (-\sum_i \varepsilon_i - \tilde{E}) \Gamma(\varepsilon_1, \varepsilon_2, \dots, \varepsilon_n) \\
 &= -\alpha_n \frac{q\rho J}{2N} \int_{-D}^0 d\varepsilon' \sum_i \Gamma(\varepsilon_1, \dots, \varepsilon_{i-1}, \varepsilon', \varepsilon_{i+1}, \dots, \varepsilon_n) - a_n \beta_n \left(\frac{q\rho J}{2N}\right)^2 \\
 &\times \int_{-D}^0 d\varepsilon' \left\{ \log \frac{-\sum_i \varepsilon_i - \varepsilon' - \tilde{E}}{D} \left/ \left(1 - \frac{q\rho J}{2N} \log \frac{-\sum_i \varepsilon_i - \varepsilon' - \tilde{E}}{D} \right) \right. \right\} \\
 &\times \sum_i \Gamma(\varepsilon_1, \dots, \varepsilon_{i-1}, \varepsilon', \varepsilon_{i+1}, \dots, \varepsilon_n), \tag{6.7}
 \end{aligned}$$

where ε_i is used for ε_{k_i} for simplicity, and α_n and β_n are respectively defined by

$$\alpha_n = 1 - \frac{n-1}{q} - \frac{n}{q^2}, \quad \beta_n = \frac{n-1}{q} + \frac{n}{q^2}. \tag{6.8}$$

This equation (6.7) has been obtained within logarithmic accuracy. In deriving the integration kernel those scattering processes in which more-than-one holes participate have not been taken into account. Their contributions are always less-divergent.

As has been shown before, the solution for the equation of zero approximation obtained by omitting the term with the integration kernel can be solved in a form of the products of one-particle amplitudes. For the complete equation of (6.7), a solution cannot be obtained in such a simple product form, but it can be obtained with logarithmic accuracy in the following form:

$$\begin{aligned}
 \Gamma_n(\varepsilon_1, \varepsilon_2, \dots, \varepsilon_n; \tilde{E}_n) &= \Gamma_1\left(\sum_{i=1}^n \varepsilon_i; \tilde{E}_n\right) \\
 &\times \sum_{i=1}^n \Gamma_{n-1}\left(\varepsilon_1, \dots, \varepsilon_{i-1}, \varepsilon_{i+1}, \dots, \varepsilon_n; \frac{n-1}{n} \tilde{E}_n\right), \\
 \Gamma_{n-1}(\varepsilon_1, \varepsilon_2, \dots, \varepsilon_{n-1}; \tilde{E}_{n-1}) &= \Gamma_1\left(\sum_{i=1}^{n-1} \varepsilon_i; \tilde{E}_{n-1}\right) \\
 &\times \sum_{i=1}^{n-1} \Gamma_{n-2}\left(\varepsilon_1, \dots, \varepsilon_{i-1}, \varepsilon_{i+1}, \dots, \varepsilon_{n-1}; \frac{n-2}{n-1} \tilde{E}_{n-1}\right), \\
 &\dots \\
 \Gamma_2(\varepsilon_1, \varepsilon_2; \tilde{E}_2) &= \Gamma_1(\varepsilon_1 + \varepsilon_2; \tilde{E}_2) \left\{ \Gamma_1\left(\varepsilon_1; \frac{1}{2} \tilde{E}_2\right) + \Gamma_1\left(\varepsilon_2; \frac{1}{2} \tilde{E}_2\right) \right\}, \tag{6.9}
 \end{aligned}$$

where suffix n is attached to amplitude Γ to signify explicitly the number of d -electrons. If we introduce Γ_n of this form in (6.7), assume $f(\log((-\varepsilon - \tilde{E})/D)) / (-\varepsilon - \tilde{E})$ for $\Gamma_1(\varepsilon; \tilde{E})$, which will be confirmed later and neglect less-divergent quantities, then (6.7) is reduced to the following one-particle equation:

$$(-\varepsilon - \tilde{E}_n) \Gamma_1(\varepsilon; \tilde{E}_n) = -\alpha_n \frac{q\rho J}{2N} \int_{-D}^0 \Gamma_1(\varepsilon'; \tilde{E}_n) d\varepsilon' - \alpha_n \beta_n \left(\frac{q\rho J}{2N}\right)^2$$

$$\times \int_{-D}^0 \left\{ \log \frac{-\varepsilon - \varepsilon' - \tilde{E}_n}{D} \left/ \left(1 - \frac{q\rho J}{2N} \log \frac{-\varepsilon - \varepsilon' - \tilde{E}_n}{D} \right) \right\} \Gamma_1(\varepsilon'; \tilde{E}_n) d\varepsilon'. \quad (6.10)$$

A bound-state solution for this equation is given by (5.13) modified by replacing α and β by α_n and β_n , and \tilde{E}_n is given by

$$\tilde{E}_n = -nD \exp \frac{N}{(2l+1)\rho J}. \quad (6.11)$$

We can see from this result that the singlet ground state for the n - d -electron system has a binding energy whose exponent is the same as that for one- d -electron system.

§ 7. Effect of a strong Hund coupling

In the actual case, a strong Hund coupling will change the results obtained above. In the limit of a strong Hund coupling, the d -electrons are mutually coupled and they are in the state of the lowest multiplet specified by the total angular momentum L and the total spin S .

For the half-filled shell with d -electron number n equal to $2l+1$, the effective s - d Hamiltonian can easily be written down by taking only the terms of $m=m'$ in (2.17), because in this special case d -electrons cannot change their orbital states, and by projecting them into the subspace of $S=5/2$, that is, by replacing $d_{ms}^\dagger d_{m's'}$ by $(2/q) \sum_m d_{ms}^\dagger d_{m's'}$. The result is

$$H_{sd} = -\frac{J}{2N} \frac{2}{q} \left\{ \sum_{kk'm's'} a_{k'm's}^\dagger a_{kms} \sum_{m'} d_{m's}^\dagger d_{m's'} - \frac{1}{2} \sum_{kk'm's} a_{k'm's}^\dagger a_{kms} \sum_{m's'} d_{m's}^\dagger d_{m's'} \right\}. \quad (7.1)$$

This can be written in the following form:

$$H_{sd} = -\frac{J}{2(2l+1)N} \sum_{kk'm's'} a_{k'm's}^\dagger \sigma_{s's} \cdot S a_{kms}. \quad (7.2)$$

This is nothing but the form given by (1.3) and has first been used for discussing the Kondo effect of degenerate d -orbitals by Schrieffer.¹⁴⁾ However, this form is allowable only for the half-filled shell.

For the s - d exchange Hamiltonian given by (7.2), $2l+1$ conduction electrons or holes can be coupled with the localized spin S , forming a singlet state on account of $2l+1$ d -wave components. The situation is quite similar to the case for the s - d model with $S=1/2$, and the energy lowering is given by

$$\tilde{E} = -(2l+1)D \exp \left[\frac{(2l+1)N}{\rho J} \right]. \quad (7.3)$$

This has a factor $2l+1$ in the numerator of the exponent, and is therefore very small compared with the value given by (6.11). This is due to the absence of

orbital exchange in this case.

For the case in which d -electron number is less than the half-filled value of $2l+1$, the lowest multiplet has an orbital angular momentum L as well as a spin momentum S . Therefore, for such cases, the s - d Hamiltonian should be projected onto the subspace made by L and S . This process can most easily be done for the case in which one electron is removed from the half-filled shell. For this case of $n=2l$, there exists one multiplet with the maximum value of S .

For this case of $n=2l$, the effective Hamiltonian obtained by the projection process mentioned above can be written down as

$$\begin{aligned}
 H_{sd} = & -\frac{J}{2N} \frac{1}{q} \sum_{kk'ms} a_{kms}^\dagger a_{k'ms} - \frac{J}{2N} \frac{1}{S} \sum_{kk'mss'} a_{kms}^\dagger a_{k'ms'} (\mathbf{s} \cdot \mathbf{S})_{ss'} \\
 & + \frac{J}{2N} \frac{(-1)^{2l}}{2} \sum_{\substack{kk'MM' \\ ss'}} (-1)^{-M'-M} a_{k-M's}^\dagger a_{k'-Ms'} T(M' \leftarrow M) \\
 & \times \left[\delta_{ss'} + \frac{2}{S} (\mathbf{s} \cdot \mathbf{S})_{ss'} \right]. \tag{7.4}
 \end{aligned}$$

In this expression the state of the localized d -electrons is specified by z -components M and M_s of the orbital and spin moments L and S whose magnitudes are both equal to l . $T(M' \leftarrow M)$ denotes the operator of changing the orbital state of d -electrons from M to M' . The second term of (7.4) exchanges spins between conduction electrons and the localized d -electrons, and the third term consists of the part which exchanges only orbital states and that which exchanges both orbitals and spins.

For $n=1$, the effective Hamiltonian (2.17) can be written in the representation in which the d -electron state is specified by M and M_s as

$$\begin{aligned}
 H_{sd} = & \frac{J}{2N} \frac{1}{q} \sum_{kkms} a_{kms}^\dagger a_{kms} \\
 & - \frac{J}{2N} \frac{1}{2} \sum_{kk'mm'ss'} a_{k'm's'}^\dagger a_{kms} T(m \leftarrow m') [\delta_{ss'} + 4(\mathbf{s} \cdot \mathbf{S})_{ss'}]. \tag{7.5}
 \end{aligned}$$

As shown in the previous sections, this Hamiltonian has an effect of quenching spin and orbital moments of the localized d -electron simultaneously. In contrast to this special case, the effective Hamiltonian given by (7.4) has different effects on spin quenching and on orbital quenching through the process of projection to the L - S subspace. This can be seen from the fact that the Abrikosov-type integral equations which are satisfied by three parts of the scattering t -matrix, corresponding to spin exchange, orbital exchange and orbital and spin exchange terms of (7.4) give rise to different ω -dependence for these three parts. Therefore, in the following we shall give qualitative discussion on the quenching of spin and orbital moments on the basis of the effective Hamiltonian (7.4) for $n=2l$.

Hamiltonian (7.4) can also be written as

$$(7.4) = -\frac{J}{2N} \frac{1}{S} \sum_{\substack{kk'm's', M \\ m \neq -M}} a_{kms}^\dagger a_{k'm's'} (s \cdot S)_{ss'} T(M \leftarrow M) \quad (7.6a)$$

$$+ \frac{J}{2N} \frac{(-1)^{2l}}{2} \sum_{kk'M'M's} (-1)^{-M'-M} a_{k-M's}^\dagger a_{k'-M's} T(M' \leftarrow M) \quad (7.6b)$$

$$- \frac{J}{2N} \frac{1}{q} \sum_{kk'm'sM} a_{kms}^\dagger a_{k'm's} T(M \leftarrow M) \\ + \frac{J}{2N} \frac{(-1)^{2l}}{S} \sum_{\substack{kk'M'M'ss' \\ M \neq M'}} (-1)^{-M'-M} a_{k-M's}^\dagger a_{k'-M's'} \\ \times T(M' \leftarrow M) (s \cdot S)_{ss'}. \quad (7.6c)$$

In this expression, three parts mentioned before, namely, spin exchange, orbital exchange and spin and orbital exchange parts are more clearly separated. The first spin exchange term (7.6a) has been adopted by Schrieffer for non- S -state ions. Under this term alone, the ground-state wave function will be described by a bilinear form of the product of d -electron wave function $\phi(M, M_s)$ and the conduction-electron wave function in which $1/2$ m -state hole with up-spin and $1/2$ m -state electron with down-spin are bound around the impurity ion. Here, for simplicity, M_s is taken as its maximum value of S . Thus, in this ground state the localized spin will be quenched, but the orbital moment will be unaffected. The characteristic energy for this spin quenching mechanism will be given by $D \exp[(2S)(N/J\rho)]$.

The second term (7.6b) quenches only the orbital moment of the impurity ion. If one expresses the ground-state wave function stabilized by this term in a form of

$$\sum_M \psi_{\text{cond}}(M) \phi(M, M_s), \quad (7.7)$$

the bound electrons and holes in $\psi_{\text{cond}}(M)$ will be described by the following:

$$\begin{aligned} \text{bound electron number} & 1-a(-M, s), \\ \text{bound hole number} & a(m_1 s)(m_2 s)(m_3 s) \cdots (m_{2l} s) |_{m_l \neq -M}, \end{aligned} \quad (7.8)$$

where the number of bound holes a is given by the neutrality condition $(1-a) = 2la$, namely, $a = 1/(2l+1)$. These numbers of bound holes and electrons are determined by the Anderson condition²⁰⁾ for the matrix elements of (7.6) between two different M -components not to vanish. The characteristic energy for this process is given by $D \exp[(4/2l+1)(N/\rho J)]$.

The third term represents simultaneous exchange of spin and orbital states between conduction electrons and the localized d -electrons and will link mutually independent spin exchange and orbital exchange given by (7.6a) and (7.6b).

In the ground state for the whole s - d effective Hamiltonian (7.6), the local spin and orbital moments are both quenched. The ground-state wave function would be given by

$$\psi_{\text{ground}} = \sum_{M, M_s} \psi_{\text{cond}}(M, M_s) \phi(M, M_s), \quad (7.9)$$

in which the wave function of conduction electrons in each (M, M_s) -component is characterized by the following numbers of bound electrons and holes:

$$\begin{aligned} \psi_{\text{cond}}(M=l, M_s=S) \rightarrow & \begin{array}{l} \text{electron } (1-a) \quad (-l\downarrow) \quad (-l-1\downarrow) \cdots (l\downarrow), \quad (-l\uparrow) \\ \text{hole } a \quad (-l-1\uparrow) \quad (-l-2\uparrow) \cdots (l-1\uparrow) \quad (l\uparrow), \end{array} \\ \psi_{\text{cond}}(M=l-1, M_s=S) \rightarrow & \begin{array}{l} \text{electron } (1-a) \quad (-l\downarrow) \cdots (l\downarrow), \quad (-l-1\uparrow) \\ \text{hole } a \quad (-l\uparrow) \quad (-l-2\uparrow) \cdots (l-1\uparrow) \quad (l\uparrow), \\ \text{etc.} \end{array} \end{aligned} \quad (7.10)$$

a is given by $(1-a)2(l+1) = 2al$, namely, $a = (l+1)/(2l+1)$.

Although in this paper we cannot derive the two characteristic energy values T_{KS} and T_{KO} , corresponding respectively to spin quenching and orbital quenching, the former value being much smaller than the latter, we can derive the phase shifts of the conduction electrons at the Fermi surface from the number of bound electrons and holes in each (M, M_s) -component of the ground-state wave function by the use of the Friedel relation. The phase-shift values thus obtained immediately lead us to the following residual resistivity for $l=2$:

$$\rho = 5\rho_0 \sin^2\left(\frac{n}{10}\pi\right), \quad (n=4) \quad (7.11)$$

where ρ_0 denotes the resistivity value of s - d model ($S=1/2$). This result coincides with the result obtained by the Hartree-Fock approximation for the case in which local spin and orbital moment are quenched. It is expected that this coincidence is generally valid. It is easy to see that the same result as Hartree and Fock's is obtained for general values of n when the Hund coupling is neglected. At high temperatures at which only orbital moment is quenched, the resistivity value can be evaluated by (7.8) as

$$\rho = \frac{5}{2}\rho_0 \sin^2\left(\frac{n}{5}\pi\right). \quad (7.12)$$

§ 8. Summary

Starting from the Anderson Hamiltonian generalized to the case in which the orbital degree of freedom of the localized d -electron is taken into account, we have derived the effective s - d Hamiltonian for any number of localized d -electrons in the limit of strong correlation, $U \gg \Delta$. On the basis of this effective Hamiltonian, the nature of the singlet ground state of the localized d -electrons has been studied in two limiting cases, one unrealistic in which the Hund coupling is completely neglected and the other realistic in which the Hund coupling is so strong that the state of the local d -electrons is restricted into the subspace of the lowest multiplet of the isolated ion.

In the former case, the spin and the orbital moment are simultaneously quenched and the energy gain due to the formation of the singlet bound state is given by $D \exp[(N/\rho J)(1/(2l+1))]$. This large value of the binding energy indicates that the orbital moments of the localized d -electrons are quenched at high-enough temperatures. The residual resistivity is equal to the value obtained by the Hartree-Fock approximation.

For a strong Hund coupling, the effective Hamiltonian for $n=2l+1$ and $n=2l$ has been derived. For the half-filled shell, the situation is so simple that the groundstate wave function and its energy are easily obtained by using the results for s - d exchange model. The binding energy or the Kondo temperature is given by $D \exp[(N/\rho J)2S]$. For general cases, further investigations are needed, but here a qualitative discussion has been given for the ground singlet state for $n=2l$ and it has been concluded with the aid of the Anderson theorem that the residual resistivity again coincides with the Hartree-Fock value.

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