A "SOLUBLE" CASE OF BOUND STATES OF CONDUCTION ELECTRONS AND MAGNETIC IMPURITY ATOMS

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We consider the problem of bound states when the spin of the impurity atom is unity. In that case, the "parquet" equation for the state amplitude (1) degenerates into a "chain." As a result we get for a number of quantities - the amplitudes themselves, the critical temperature, the specific heat, and magnetic characteristics - solutions without unknown constants. This makes it possible to analyze the temperature dependence of the main properties.

In a previous paper[12] we showed that in the case when there are magnetic impurity atoms in a non-magnetic metal and when the sign of the exchange interaction between the conduction electrons and the impurity spins is antiferromagnetic, bound states of the conduction electrons and the impurity spin may occur. This is a collective effect and the state formed is much closer to the superconductivity case. In fact, in the latter case one can use a calculation technique based upon a Cooper pair in a superconductor than to a normal bound state such as an atom. We obtained in[12] a "parquet" type of equation for the state amplitude and it is difficult to solve this equation completely. The equation was solved with logarithmic accuracy and the amplitude was determined with an unknown constant factor. Since the factor in principle could be equal to zero, the problem could not be considered to be finally solved.

It was already noted in[11] that the amplitude $\Delta(\omega)$ as a function of the energy $\omega$ increases with decreasing $\omega$ when the impurity spin $S=\frac{1}{2}$, and is constant when $S=1$. The case $S=1$ is thus a distinct one and the problem arises whether the "parquet" here would not turn into a simple chain as in the superconductivity case. In fact, in the latter case $\Delta=const$ when $\omega \ll \omega_D$ (Debye frequency). We show in the following that this is indeed the case for $S=1$. As a result the equations simplify and one can solve them completely. One can also find the thermodynamic and magnetic properties of such systems.

The results are partially the same as those obtained by Nagaoka.[13] As we noted already in[11], Nagaoka’s method has no rigorous foundation and is clearly not applicable for $S \neq 1$. In his method the case $S=1$ is not at all a special one. The results obtained by him are therefore also for $S=1$ open to doubt. We shall show below that most of Nagaoka's results are incorrect.

1. CALCULATION METHOD. SINGULARITY OF SCATTERING AMPLITUDE

We showed in the Appendix to[12] that in the case $S=1$ one can use a calculation technique based upon the substitution

$$S = \omega i S_{\rho \sigma} a_\rho$$

without introducing an energy $\lambda \gg T$ for each pseudoparticle corresponding to the operator $a_\rho$. This is a very valuable circumstance. The Green function of a free pseudoparticle has the form

$$G_{\rho \sigma} = - \text{Sp} \left\{ \mathcal{J}(a_\rho (t) a^{\dagger}_\sigma (t')) \right\} = T \sum \frac{g_{\rho \sigma}(\omega_n)}{\omega_n - (t - t')}$$

The trace is here taken over all states including the unphysical states, the critical temperature, the specific heat, and magnetic characteristics - solutions without unknown constants. This makes it possible to analyze the temperature dependence of the main properties.

$$\mathcal{J} = \frac{\text{Sp}_{\text{phys}} \{ e^{\pm iT} \mathcal{A} \} \text{Sp}_{\text{phys}} \{ e^{\mp iT} \}}{\text{Sp} \{ e^{\pm iT} \}}$$

The trace must here be taken only over physical states but by virtue of the property (1) of the operators mentioned above we may assume that in the numerator it is taken over all states. In the denominator it is no longer possible to change to a trace over all states. However, in order to get rid of the unconnected diagrams in the evaluation of $\mathcal{J}$ (see[14]), it is necessary that the trace is taken over a complete set of states. Because of this we can evaluate $\mathcal{A}$ by the usual rules but afterwards divide the average obtained by the ratio

$$Q = \frac{\text{Sp}_{\text{phys}} \{ e^{\pm iT} \mathcal{A} \}}{\text{Sp} \{ e^{\pm iT} \}}$$

We consider now the average

$$\langle \hat{S}^2 \rangle - \text{Sp} \{ e^{\pm iT} \mathcal{A} \}$$

where the trace is taken over all states. It is clear that in the numerator only physical states take part and acting upon them $\hat{S}^2$ gives $S(S+1) = 2$. We have thus

$$Q = \frac{\text{Sp}_{\text{phys}} \{ e^{\pm iT} \mathcal{A} \}}{\text{Sp} \{ e^{\pm iT} \}} = \frac{\langle \hat{S}^2 \rangle}{2}$$

Thus

$$\mathcal{J} = \langle \mathcal{A} \rangle / Q$$

where $\langle \mathcal{A} \rangle$ and $\langle \hat{S}^2 \rangle$ which occur in $Q$ are evaluated by the usual rules of the diagram technique. When

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1) If we substitute (1) we can verify that when $S=1$, the quantity $\hat{S}^2 = N(3 - N)$, where $N = 2p^2 \delta p$. 

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where we get for each link \( N \) the density of atoms in the basic metal. The correction and is sufficient for us, for diagram of Fig. 3e adds to when we make the diagrams of Figs. 3b, c, d. Giving not a simple, but a

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The complete Green function has the form
\[ G = \frac{1}{-i\omega + \mu H, - n - Q^{-1} N_i V(w)} \]
(16)

(allowance for the normalization 1/Q). From this it is clear that, indeed,
\[ a \int G(w) d\omega = -i n \omega \text{ sign } \omega. \]

The Green function which has one end at an impurity starts with the usual G but at its end can interact an arbitrary number of times with the impurity. One sees easily that this gives
\[ G' = G[1 + i\alpha \text{ sign } \omega U(w)]^{-1}. \]

In particular, if both ends of G coincide at one and the same impurity, we have
\[ G'((\omega, 0, 0)) = -i n \omega \text{ sign } \omega \]
(18)

The function \( F^{(\omega)} \) with coordinates in one impurity atom is equal to
\[ F^{(\omega)}(0, 0, \omega) = \left[ -i n \omega \text{ sign } \omega \right] \frac{1}{1 + i n \omega \text{ sign } \omega U(w)} G_{\alpha\beta}, F_{\beta, \sigma}. \]

From Eq. (18) we find for \( \Delta_{\alpha\beta}^{(1)} \)
\[ \Delta_{\alpha\beta}^{(1)} = -\frac{J}{N} \sum_{\omega} F^{(\omega)}(0, 0, \omega) + \frac{J}{N} \gamma \sum_{\omega} F^{(\omega)}(0, 0, \omega), \]
(20)

Substituting here (19), (13), and (12), assuming \( \Delta_{\alpha\beta}^{(1)} \) to be real and introducing the definition
\[ \gamma(t + 2i) = 1. \]

Writing equations similar to (20) for the other components of \( \Delta_{\alpha\beta}^{(2)} \) or for \( \Delta_{\alpha\beta}^{(3)} \) one can verify that the assumed form of solution (13) satisfies the equations. Equation (23) determines \( \delta_0 \) and \( \delta_1 \) apart from the sign. According to (22) only one sign is arbitrary. In the case \( H = 0 \) we shall have \( A = B = \gamma \), \( \delta_0 = -\delta_1 / \gamma \), and for \( J < 0 \) we have
\[ 4\pi \alpha \int \sum_{\omega} \frac{1}{1 + 2n \omega + 3n \omega^2} = 1. \]
(24)

3. BASIC THERMODYNAMIC CHARACTERISTICS

We first of all consider \( \delta_1 \) for \( H = 0 \). We get for \( \delta_1 = 0 \) from Eq. (24) the critical temperature
\[ T_c = \frac{2\pi}{\sqrt{\exp [-N/2a_f^{(1)}]}}. \]

This expression is the same as (7). On the other hand, assuming \( T \rightarrow 0 \), we change from a sum to an integral and find
\[ 3n \delta_1 \delta_1^{(0)} = \frac{\pi}{2} T_c = \frac{T_c}{1.13}. \]
(25)

It follows from (25) that
\[ 3n \delta_1 \delta_1^{(0)} = \frac{\pi}{2} T_c = \frac{T_c}{1.13}. \]
(26)

We can write Eq. (24) in the form of an integral, using the tanh function to go from imaginary to real \( \omega \). This gives
\[ 2a \int \frac{1}{N} \sum_{\omega} \tanh(\omega/2T) \frac{1}{1 + i\omega \text{ sign } \omega}, R \omega = 1, \]
(27)

where \( R \) denotes \( 3n \delta_1^{(1)} \).
We can write Eq. (24) also in another form. Adding and subtracting from the sum over \( \omega \) its value at \( R = 0 \), we get
\[
\ln T_e = \psi \left( \frac{R}{2nT_e} + \frac{1}{2} \right) - \psi \left( \frac{1}{2} \right),
\]
(28)
where \( \psi(x) \) is the logarithmic derivative of the gamma-function. Near \( T_c \), i.e., for small \( R \), we find from this
\[
R \approx 1.27 (T_e - T) - 0.2 (T_e - T)^2 / T_c.
\]
(29)

It is convenient to use Eq. (27) near \( T = 0 \). From it we find for \( T < T_c \)
\[
R = R(0) - \frac{2\pi^2}{\Omega(0)} + \frac{3\pi T}{4TR(0)},
\]
(30)
where \( R(0) \) is given by Eq. (26).

Nagaoka\(^{[2]}\) found the results (7) and (25) to (30) for arbitrary \( S \). However, as we noted already earlier, his method is open to doubt. The derivation given here validates these results only for \( S = 1 \).

Let us now find the specific field. To do this we use Eqs. (21) and (23). For \( d_1 = d_0 = 0 \) we get from (21)
\[
\lambda = \frac{1}{\Omega} \ln \left[ \frac{1}{\Omega} + \frac{1}{\Omega} \right] - \frac{1}{\Omega} \ln \left[ \frac{1}{\Omega} + \frac{1}{\Omega} \right] - \frac{1}{\Omega} \ln \left[ \frac{1}{\Omega} + \frac{1}{\Omega} \right].
\]
(31)

Substitution into (23) gives the field \( H_c \). As \( T \to 0 \) the sum in (31) can be replaced by an integral and we get
\[
\lambda = \frac{1}{\Omega} \ln \left[ \frac{1}{\Omega} \right].
\]
(32)

From (23) we have
\[
2 \lambda \left[ \frac{1}{\Omega} \right] \ln \left[ \frac{1}{\Omega} \right] = \left[ 2 \theta \frac{1}{\Omega} \right] \ln \left[ \frac{1}{\Omega} \right].
\]
(33)

Then, as \( T \to 0 \), the quantity \( g_H H_c \) \( \sim \lambda \) as follows
\[
g_H H_c \approx \lambda \left[ 1 - \left( \frac{2}{\Omega} \lambda \right) \ln \left[ \frac{1}{\Omega} \right] \right].
\]
(34)

When, on the other hand, \( T \to T_c \), clearly \( H_c \to 0 \). Then
\[
\lambda = \frac{1}{\Omega} \left[ \frac{1}{\Omega} \right] \ln \left[ \frac{1}{\Omega} \right] - \frac{1}{\Omega} \ln \left[ \frac{1}{\Omega} \right].
\]
(35)

Substituting this into (23) we find
\[
g_H H_c \approx n \left( \frac{1}{\Omega} \right) \ln \left[ \frac{1}{\Omega} \right] - \frac{1}{\Omega} \ln \left[ \frac{1}{\Omega} \right].
\]
(36)

Hence, the \( H_c(T) \) curve does not at all resemble the curve of the critical field of a superconductor.

We now find the thermodynamic potential. We put \( H = 0 \). Taking the derivative with respect to the interaction constant, we have
\[
\frac{\partial \Omega}{\partial (J/N)} = - \zeta^{\text{int}}_{\text{vol}} (J/N)(\Omega V).
\]
(37)

The normalisation \( 1/Q \) gives the change from the complete to the physical average. The potential \( \Omega \) is normalized to unit volume.

If (in (10)) we take only \( \zeta^{\text{int}}_{\text{vol}} \) into account, we get from (35)
limitation will first of all be connected with the fact that we took in our calculations only the "pole" part of the interaction Hamiltonian \( H_{\text{int}} \), into account. The problem arises of the role of \( H_{\text{int}} \). This part has the same form as when there is no pairing but, drawing the diagrams, it is necessary to fit in this time not only the functions \( G \) and \( \beta \), but also the functions \( F \) and \( \beta \) and after this it is necessary to subtract the "normal" expression. We shall not go into this estimate in detail.

The vicinity of \( T_c \) occupies a special position. An estimate of the region in which we can expect trouble to occur in the chain corresponds to a relative change in the interaction constant \( a/N \) by the amount

\[
\delta \left( \frac{a}{N} \right) \left| \left( \frac{a}{N} \right) \right| \sim \left( \frac{1}{\varepsilon_F} \right).
\]

This correction may compete with \( |\Delta T - T| \) in the form (6). On this ground, the criterion for the applicability of the theory is thus of the form

\[
\left| \frac{T_c - T}{T_c} \right| \gg \left( \frac{1}{\varepsilon_F} \right).
\]

4. MAGNETIC PROPERTIES

The results obtained make it possible to determine the magnetic moment of the system in any field. Expressed in terms of Green functions, the moment has the form

\[
\langle M_M \rangle = M_e = \frac{\mu \chi}{Q} \sum_{\omega, \lambda} G(\omega, \lambda) \sigma, \frac{\nu_c}{Q} \sum_{\phi, \lambda, \beta} G(\nu, \phi) M_M(\omega). \quad (45)
\]

One checks easily, using Eq. (16), that the first term gives simply the Pauli paramagnetism. To see this we subtract the analogous expression with \( G(0) \). The remainder can immediately be integrated over \( \xi \); this gives zero. We are interested in the second term and we shall consider it now.

Taking \( H_{\text{int}} \) into account, we get

\[
\mathcal{G}_{\text{eff}} = \mathcal{G}_{\text{eff}}^{(0)} + \mathcal{G}_{\text{eff}}^{(1)} \left[ \lambda N_{\text{eff}}(\omega, \phi) - \lambda N_{\text{eff}}(\omega, \phi) \right].
\]

Substituting (19) and a similar expression for \( \mathcal{G}_{\text{eff}}^{(1)} \) and using (13) we get

\[
\mathcal{G}_{\text{eff}} = \frac{1}{\mu_c + \mu \chi} \left[ 1 + 2a \sigma \sigma, \omega \frac{b}{1 + a} \right]^{-1} \times \left[ 1 + 2a \sigma \sigma, \omega \left( \frac{b}{1 + a} + \frac{b}{1 - a} \right) \right]^{-1},
\]

\[
\mathcal{G}_{\text{eff}}^{(1)} = \mathcal{G}_{\text{eff}}^{(0)} \left( -H \right).
\]

Substituting (45) we get

\[
M_e = \frac{2 \mu_c \chi}{Q} \sum_{\omega, \lambda} \left( \omega + \mu \chi H \right) G(\omega, \phi) G(\nu, \phi) M_M(\omega),
\]

\[
+ 2a \sigma \sigma, \omega \left( \gamma \xi \chi H + 2 \sigma \sigma, \xi \chi H \right) \left( \gamma \xi \chi H + 2 \sigma \sigma, \xi \chi H \right).
\]

Bearing in mind that \( \Omega \) also depends on \( H \) it is clear that this is a very complicated expression. We consider limiting cases.

In the case \( T = 0 \) we can in Eq. (18) replace the sum by an integral

\[
\sum_{\omega} \to \frac{1}{2\pi} \int d\omega.
\]

If \( \mu H \ll \pi a \alpha \beta \), the corrections to \( \delta \) are of order \( \left( \mu \gamma \right./2a \alpha \beta \)^2 \) and can be neglected, i.e., the values of \( \delta_0 \) and \( \delta_0 \) are taken for \( H = 0 \). It is not possible to expand immediately in terms of \( H \) in (48) as the expressions inside the square brackets have a pole at the points \( \omega \sim 2a \alpha \beta \), and the path around these poles gives the main contribution to the moment. Integrating and limiting ourselves all the time to zeroth and first order and also taking into account that for this case \( Q = \gamma \beta \) (see the Appendix), we get

\[
M_e = \frac{2}{3} \gamma \beta \left( \chi \mu \right)^2 H + \frac{2}{3} \gamma \beta \left( \chi \mu \right)^2 \left( \chi \mu \right)^2 + \frac{2}{3} \gamma \beta \left( \chi \mu \right)^2 + \frac{2}{3} \gamma \beta \left( \chi \mu \right)^2 + \frac{2}{3} \gamma \beta \left( \chi \mu \right)^2.
\]

The other interesting limiting case is that of a weak field \( g_\gamma H \ll T \). We can then expand in (48) and take again for \( \delta \) its value for zero field. The normalization is in that case always equal to \( \gamma \beta \). Hence we get

\[
M_e = \frac{2}{3} \gamma \beta \left( \chi \mu \right)^2 H.
\]

As \( T \to T_c \) the quantity \( \chi \to 0 \) and we get

\[
M_e = \frac{2}{3} \gamma \beta \left( \chi \mu \right)^2 H.
\]

It is interesting that when bound complexes are formed the Curie law is retained although the coefficient turns out to be nine times less. Such a conclusion was qualitatively obtained in [6].

Nagaoka [3] also obtained a Curie law at low temperature but with an incorrect coefficient \( \gamma \beta \) instead of \( \gamma \beta \) for \( S = 1 \). We must also note that at \( T = T_c \) the moment smoothly reaches its normal value without any correction whatever to the Kondo effect. Using the technique discussed here one can check that above the critical temperature the moment is expressed by Eq. (51) with small corrections of order \( \gamma \beta \).

It is very complicated to find the complete temperature dependence of the magnetic susceptibility in explicit form. However, one can obtain an interpolation formula. Using the fact that the main role in (50) is in all cases played by \( \omega \approx 2 \pi T \) we replace in the brackets in the sum \( \omega \approx 2 \pi T \).

As a result we get

\[
\chi = \frac{H}{M_e} = \frac{2N \gamma \beta \left( \chi \mu \right)^2}{\pi T + R}.
\]

Knowing the function \( R(T) \), we can find \( \chi(T) \).

We must, however, bear in mind that we have here considered only the case \( S = 1 \) and that for other cases the situation may be different. We must bear this in mind when we speak about comparing the results with experimental data.
5. THE PROBLEM OF THE ELECTRICAL RESISTIVITY

Nagaoka \cite{2} found an expression for the electrical resistivity at low temperatures. A similar expression can also be obtained using the Green function (16). However, all the same, the expression obtained in \cite{2} gives, apparently, only qualitatively the behavior of the resistivity. The point is that it is obtained without taking into account the "non-pole" part \( j_{\text{int},2} \) of the interaction which in this case plays an essential role. This is clear from the fact that the "pole" part of the scattering probability is \( \Im \! N_j V_R(\omega) \) where \( V_R \) is the retarded analogue of (15), vanishes at \( T = T_c \) while the part connected with \( j_{\text{int},2} \) has clearly the same order of magnitude as \( \Im \! N_j V_R(\omega) \) for \( T = 0 \).

The complete temperature dependence of the resistivity can be described as follows. Above \( T_c \) the resistivity \( \rho \) increases because of the Kondo effect when the temperature decreases and is expressed by the formula obtained in \cite{7}. In the vicinity of \( T_c \) this formula no longer applies as the difference 1 - \( 2\! J/N \mid \ln (\Lambda / T_c) \) which occurs in the denominator is of order \( J/N \mid \alpha \) and the next orders of magnitude must be taken into account.

As to order of magnitude \( \rho(T_c) \) must be the same as for resonance scattering, i.e., \( \rho \sim cm / a e^2 \sim c / e^2 p_o \), where \( c \) is the atomic concentration of the impurity. When the temperature is lowered the lower limit of the logarithmic integrals must remain of order \( T_c \) as the temperature cut-off is replaced by a cut-off because of the appearance of \( \delta \). On the other hand, in this region the pole part appears which too close to \( T_c \) is of the same order of magnitude. The temperature dependence of the non-pole part of the resistivity will for \( T \ll T_c \) be connected primarily with the change in \( \delta \), i.e., it will have the relative order \( (T / \pi a^2)^2 \). The temperature correction from the pole part has the same form. Hence it follows that for \( T \ll T_c \)
\[
\rho = \rho(0) [1 - \eta(T/T_c)]^2, \tag{54}
\]
where \( \rho(0) \sim cm / a e^2 \), \( \eta \sim 1 \). This formula is very similar to the one obtained when there is only one, "pole," part but, of course, the numerical values of the coefficients must be different. This fact must be borne in mind when comparison is made with experiments.\footnote{Preliminary estimates show that the non-pole part for \( T \ll T_c \) is at most of order of magnitude \( (T / T_c)^2 \). Because of this \( \rho(0) \) is for \( T = 0 \) given by only the pole part. From (15), (16), and (14) we get \( \rho(0) \sim 16 c / 312 e^2 p_o \), where \( c \) is the number of electrons per atom of the basic metal. (Added is proof, November 14, 1967).}

Unfortunately, the advantages enjoyed by the case \( S = 1 \) does not at all manifest itself in calculating the resistivity as in the non-pole part states with total spin \( S = 1 / 2 \) take part and for those the "parquet" equation remains.

The most important result of the present paper is the fact that in any case for \( S = 1 \) bound states indeed and are energetically advantageous. For other values of the spin this has, of course, not been shown rigorously, but it is very probable.

On the other hand, in the work of Suhl and Wong \cite{7} and Maleev \cite{8}, who start from the absence of a bound state, the case \( S = 1 \) is not at all a special one. One can conclude from this that the scattering amplitude without singularities corresponding to the absence of a bound state can be obtained even in the case where it surely can exist. From energetic considerations one must prefer a bound state.

The experimental data on the temperature dependence of the resistivity also favor this. Although both theories predict at \( T = 0 \) an approach to a finite value of the same order of magnitude, in the case of bound states this approach follows Eq. (54) while if they are absent the temperature correction is of order \( 1 / \ln^2 (\Lambda / T) \). Daybell and Steyert’s experiments \cite{4} agree well with Eq. (54).

APPENDIX

We evaluate the magnitude of the normalization \( Q \) when there are bound states. From Eq. (3), the footnote referring to it and the definition \( \delta \) we have
\[
Q = \eta(T_c) = 1/\sqrt{\eta(\delta - \Lambda)}.
\]
As a result (see (47)) we get (when \( \mu_H \ll \pi a^2 \))
\[
T \sum_{\omega} \sum_{\omega'} \frac{\rho_{MM}(\omega) e^{i\omega t} - \frac{1}{T} \sum_{\omega'} \sum_{\omega''} \rho_{MM}(\omega') e^{i\omega'' t}}{\omega + \omega' + \delta} - \frac{1}{T} \sum_{\omega''} \sum_{\omega'} \rho_{MM}(\omega') e^{i\omega'' t}.
\]

As a result (see (47)) we get (when \( \mu_H \ll \pi a^2 \))
\[
T \sum_{\omega} \sum_{\omega'} \frac{\rho_{MM}(\omega) e^{i\omega t} - \frac{1}{T} \sum_{\omega'} \sum_{\omega''} \rho_{MM}(\omega') e^{i\omega'' t}}{\omega + \omega' + \delta} - \frac{1}{T} \sum_{\omega''} \sum_{\omega'} \rho_{MM}(\omega') e^{i\omega'' t}.
\]
since only \( \omega \sim \mu_H \) or \( \omega \sim T \) are important.

Substituting these results into (A1) we get
\[
Q = \frac{3}{4} + \frac{1}{36} \text{th} \frac{\mu_H}{T} \tag{A2}
\]
When \( \mu_H \ll T \), we have \( Q = \frac{7}{4} \) and also for \( \delta = 0 \), while when \( \mu_H \gg T \) we shall have \( Q = \frac{7}{4} \). It thus turns out that for \( H = 0 \) the quantity \( Q = \frac{7}{4} \) for all temperatures. In the vicinity of the critical temperature \( (\pi a^2 \ll T) \) we can use Eq. (3).

There remains the limiting case \( \mu_H \gg T \), \( \pi a^2 \). It is clear that then \( \delta = 0 \) is not at all possible to the absence of a bound state. The expression for \( Q \) is more complicated in the intermediate regions, in particular when \( \mu_H \sim \pi a^2 \). However, in that case most interest centers around the critical field and this is evaluated without normalization (see Sec. 3).
5 A. A. Abrikosov, Physics, 2, 5 (1965).
7 H. Suhl and D. Wong, Physics 3, 17 (1967).

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