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PROPERTIES OF MAGNETIC IMPURITY IN A METAL

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The effect of a polarized conduction-electron cloud back on a magnetic impurity dissolved in a metal is studied. It is shown that at a temperature T_c much higher than the Kondo temperature the system becomes unstable against symmetry breaking and that a state with $\langle S_z \rangle \neq 0$ is established. The behaviour of $\langle S_z \rangle$ is derived for all temperatures and magnetic fields except for a very narrow region around T_c and for very low temperatures. The minute role of Kondo-type processes in establishing the symmetry-broken state is pointed out.

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The problem of a magnetic impurity embedded in a sea of conduction electrons is a well studied one [1 - 4]. Despite of this, the effect of the induced conduction electron polarization cloud acting back on the impurity has been treated only incompletely and we want to reconsider this problem here. The model investigated is that of an impurity coupled via an exchange interaction to a system of noninteracting conduction electrons. Both signs of the exchange interaction are considered. It is well known that for an antiferromagnetic coupling (Kondo Hamiltonian) a perturbation expansion leads to diagrams which diverge in the low temperature limit. Despite this as we shall show, the effect of the polarization cloud back on the impurity leads at a relatively high temperature T_c to an instability of the isotropic state against a symmetry broken one with $\langle S_z \rangle \neq 0$. Here S_z is the z-component of the spin of the magnetic impurity. The divergent diagrams are of little importance for the size of T_c.

Starting point is a Hamiltonian of the form

$$H = H_0 - \sum_{\alpha} \int d^3r \Psi_{\alpha}^{+}(\mathbf{r})(V_1(\mathbf{r}) + V_2(\mathbf{r})(\mathbf{S}\sigma))\Psi_{\alpha}(\mathbf{r}) = H_0 + H_{int}. \quad (1)$$

Here H_0 is the Hamiltonian of the conduction electrons and of a free impurity spin in an applied external magnetic field $\mathbf{H}$, i.e., H_0 contains a Zeeman contribution of the form

$$H_{Ze} = -\mu\mathbf{S}\cdot\mathbf{H} - \frac{\mu_e}{2}\sigma\mathbf{H}. \quad (2)$$

Note, that usually $\mu_e = 2\mu_B$.

The quantities $V_1(\mathbf{r})$ and $V_2(\mathbf{r})$ represent short-range potentials of the impurity and as usually $V_2 \ll V_1$. We shall not consider the ordinary scattering potential $V_1(\mathbf{r})$ here, but rather limit ourselves to the magnetic part $V_2(\mathbf{r})$ for which we make the approximation

$$V_2(\mathbf{r}) = g\delta(\mathbf{r}). \quad (3)$$

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As usual, the $\Psi_\alpha(\mathbf{r})$, $\Psi_\alpha^+(\mathbf{r})$ in Eq. (1) are conduction-electron field operators.

Our aim is to calculate $\langle S_z\rangle$. Consider first the case when $g = 0$. The partition function of the impurity is then given by

$$Z_0 = \sum_{S_z} e^{(\mu H S_z/T)} = \frac{\mathrm{sh}[(S+\frac{1}{2})\mu H/T]}{\mathrm{sh}[\mu H/(2T)]}, \tag{4}$$

and

$$\langle S_z\rangle_0 = T\frac{\partial \ln Z_0}{\partial(\mu H)} = (S+\frac{1}{2})\,\mathrm{cth}[(S+\frac{1}{2})\mu H/T] - \frac{1}{2}\,\mathrm{cth}(\mu H/(2T)), \tag{5}$$

which is the well-known Brillouin function.

In order to determine $\langle S_z\rangle$ up to second order in g we also need

$$\langle T_\tau \mathbf{S}(\tau)\mathbf{S}(0)\rangle_0 = \langle S_z^2\rangle_0 + \left(S(S+1) - \langle S_z^2\rangle_0\right)\mathrm{ch}(\mu H\tau) - \mathrm{sh}(\mu H|\tau|)\langle S_z\rangle_0,$$

$$\langle T_\tau S_z(0)\,(\mathbf{S}(\tau)\mathbf{S}(0))\rangle_0 = -\,(\mathrm{ch}(\mu H\tau) - 1)\,\langle S_z^3\rangle_0 + \tag{6}$$

$$+S(S+1)\mathrm{ch}(\mu H\tau)\langle S_z\rangle_0 - \mathrm{sh}(\mu H|\tau|)\langle S_z^2\rangle_0.$$

The averages $\langle S_z^2\rangle_0$ and $\langle S_z^3\rangle_0$ are obtained from

$$\langle S_z^2\rangle_0 = \frac{T^2}{Z_0}\frac{\partial^2 Z_0}{\partial(\mu H)^2} = \langle S_z\rangle_0^2 + T\frac{\partial\langle S_z\rangle_0}{\partial(\mu H)},$$

$$\langle S_z^3\rangle_0 - \langle S_z\rangle_0\langle S_z^2\rangle_0 = T\frac{\partial\langle S_z^2\rangle_0}{\partial(\mu H)}. \tag{7}$$

The following combination will be required below

$$\langle T_\tau S_z(0)(\mathbf{S}(\tau)\mathbf{S}(0))\rangle_0 - \langle S_z\rangle_0\langle T_\tau \mathbf{S}(\tau)\mathbf{S}(0)\rangle_0 =$$

$$(-\mathrm{ch}(\mu H\tau) + 1)(T\frac{\partial\langle S_z^2\rangle_0}{\partial(\mu H)}) - \mathrm{sh}(\mu H|\tau|)(T\frac{\partial\langle S_z\rangle_0}{\partial(\mu H)}). \tag{8}$$

Note that these terms are the ones giving raise to the Kondo effect when a perturbation expansion is made.

We also need the Green's function of the conduction electrons which for $g = 0$ can be written in the form of a (2 x 2) matrix form as

$$G^{(0)}(\tau) = \frac{1}{2}(G_+(\tau) + G_-(\tau))E + \frac{1}{2}(G_+(\tau) - G_-(\tau))\tau_z, \tag{9}$$

where τ_z is the Pauli matrix and

$$G_\pm(\omega_n) = \frac{1}{i\omega_n - (\epsilon_{\mathbf{p}} - \epsilon_F \mp \mu_e H/2)}; \qquad \omega_n = 2\pi T(n+\frac{1}{2}). \tag{10}$$

In the presence of the exchange interaction, i.e., for $g \neq 0$ we must evaluate [5]

$$\langle S_z\rangle = -\frac{T_r\{e^{-(H_0-\epsilon_F N)/T}\,T_\tau S_z(0)\sigma(\frac{1}{T})\}}{T_r\{e^{-(H_0-\epsilon_F N)/T}\sigma(\frac{1}{T})\}} \tag{11}$$

with $\sigma(\frac{1}{T})$ given by

$$\sigma(\frac{1}{T}) = T_\tau e^{-\int_0^{1/T} d\tau_1 H_{int}(\tau_1)} \tag{12}$$

In order to calculate $\langle S_z \rangle$ to second order in g we first determine $G(\tau)$ to first order in g, thereby using

$$G_{\alpha\beta}(\tau) = -\frac{T_\tau\{e^{-(H_0-\epsilon_F N)/T} T_\tau \Psi_\alpha(\tau_1)\Psi_\beta^+(0)\sigma(\frac{1}{T})\}}{T_\tau\{e^{-(H_0-\epsilon_F N)/T}\sigma(\frac{1}{T})\}}. \tag{13}$$

It is

$$G(\tau) = G^{(0)}(\tau) - g\langle S_z \rangle I(\tau)\tau_z, \tag{14}$$

where $\langle S_z \rangle$ is the *exact* expression for the impurity spin and

$$I(\tau) = \int_0^{1/T} d\tau_1 G(\tau - \tau_1)G(\tau_1). \tag{15}$$

For the local exchange interaction (3) considered here

$$I(0) = -\frac{mp_F}{2\pi^2}A = -N(0)A \tag{16}$$

where A is of order unity and depending on the hitherto neglected potential V_1. As usual, m is the electron mass and p_F the Fermi momentum. The effect of the impurity spin polarization on the electrons as contained in Eq. (14) was studied in Ref. [2]. Here we need only $I(0)$ as given by Eq. (16). If instead of Eq. (3) a potential $V_2(\mathbf{r})$ with a short but finite range is taken into account, the function $I(\tau)$ is replaced by the more general one

$$I(\mathbf{r}, \mathbf{r}', \tau) = \frac{1}{g}\int_0^{1/T} d\tau_1 \int d^3r_1 G(\mathbf{r}, \mathbf{r}_1, \tau - \tau_1)V_2(\mathbf{r}_1 - \mathbf{r_a})G(\mathbf{r}_1, \mathbf{r}', \tau_1),$$

where $\mathbf{r_a}$ is the position of the impurity. The corrections in $\langle S_z \rangle$ to order g^2 follow from Eq. (11), i.e., from the numerator as well as denominator.

The denominator is simply given by the partition function which to order g^2 is

$$\begin{aligned} Z \;=\; & Z_0\{1 + \frac{g}{T}(n_+ - n_-)\langle S_z \rangle - \frac{2g^2}{T}\langle S_z \rangle^2 I(0) - \\ & - g^2 \int_0^{1/T} d\tau_1 \int_0^{1/T} d\tau_2 G(\tau_1 - \tau_2)G(\tau_2 - \tau_1)\langle T_\tau(\mathbf{S}(\tau_1)\mathbf{S}(\tau_2))\rangle\}. \end{aligned} \tag{17}$$

The quantities $n_\pm$ are the densities of spin up and down electrons. They are given by

$$n_\pm = n \pm N(0)\frac{\mu_e H}{2}. \tag{18}$$

The third term on the right hand side of Eq. (17) comes from the correction of the electron Green's function. When the numerator of Eq. (11) is similarly evaluated we find

$$\langle S_z\rangle = \langle S_z\rangle_0 + \frac{\partial\langle S_z\rangle_0}{\partial(\mu H)}(gN(0)\mu_e H - 2g^2 I(0)\langle S_z\rangle) - \tag{19}$$

$$-g^2\int_0^{1/T} d\tau_1\int_0^{1/T} d\tau_2 G(\tau_1-\tau_2)G(\tau_2-\tau_1)(\langle T_\tau S_z(0)(\mathbf{S}(\tau_1)\mathbf{S}(\tau_2))\rangle_0 - \langle T_\tau(\mathbf{S}(\tau_1)\mathbf{S}(\tau_2))\rangle_0).$$

It is important to realize and in fact has been pointed out before, that on the right hand side of Eqs. (17, 19) it is the exact expectation value $\langle S_z\rangle$ rather $\langle S_z\rangle_0$ which is appearing. This is so since these terms should be considered as a Hartree-like contribution to the electron Green's function. Some further justification is given below. Note also that the product $G(\tau)G(-\tau)$ in Eq. (19) consists of a singularity of the form $\delta(\tau)$ plus a smooth function of τ. Therefore multiplying it by integer powers of $|\tau|$ yields integrals of order $max\{T,\mu H\}/\epsilon_F$. By making use of Eq. (4) we obtain the following result

$$\langle S_z\rangle - \langle S_z\rangle_0 = \frac{\partial\langle S_z\rangle_0}{\partial(\mu H)}(gN(0)\mu_e H - 2g^2\langle S_z\rangle I(0)) +$$

$$+2g^2\int_0^{1/T} d\tau_1\int_0^{\tau_1} d\tau G(\tau)G(-\tau)[(\mathrm{ch}(\mu H\tau)-1))(T\frac{\partial\langle S_z^2\rangle_0}{\partial(\mu H)})+$$

$$+\mathrm{sh}(\mu H\tau)(T\frac{\partial\langle S_z\rangle_0}{\partial(\mu H)})]. \tag{20}$$

The last term yields the Kondo-type corrections. As shown below they are smaller by a factor of order $(max\{T,\mu H\}/\epsilon_F)\ln(\epsilon_F/max\{T,\mu H\})$ than the second term on the right hand side on that equation. To see this we use Eq. (9) to obtain

$$\int_0^{1/T} d\tau_1\int_0^{\tau_1} d\tau G(\tau)G(-\tau)\mathrm{sh}(\mu H\tau) =$$

$$= \int\frac{d^3p d^3p'}{(2\pi)^6}\{\frac{1}{2}(\frac{1}{T}+\mathrm{sh}(\frac{\mu H}{T})\frac{\partial}{\partial(\mu H)})\mathrm{cth}(\frac{\epsilon_{\mathbf{p}}-\epsilon_{\mathbf{p}'}}{2T}) -$$

$$-\mathrm{ch}^2(\frac{\mu H}{2T})\frac{\partial}{\partial(\mu H)}\}\frac{f_{\mathbf{p}}-f_{\mathbf{p}'}}{\epsilon_{\mathbf{p}}-\epsilon_{\mathbf{p}'}-\mu H},$$

$$\int_0^{1/T} d\tau_1\int_0^{\tau_1} d\tau G(\tau)G(-\tau)(\mathrm{ch}(\mu H\tau)-1) =$$

$$= \int\frac{d^3p d^3p'}{(2\pi)^6}\{\frac{f_{\mathbf{p}}-f_{\mathbf{p}'}}{2T}(\frac{1}{\epsilon_{\mathbf{p}}-\epsilon_{\mathbf{p}'}-\mu H}-\frac{1}{\epsilon_{\mathbf{p}}-\epsilon_{\mathbf{p}'}})+$$

$$+(\mathrm{sh}^2(\frac{\mu H}{2T})\,\mathrm{cth}(\frac{\epsilon_{\mathbf{p}}-\epsilon_{\mathbf{p}'}}{2T})-\frac{1}{2}\mathrm{sh}(\frac{\mu H}{T}))\frac{\partial}{\partial(\mu H)}(\frac{f_{\mathbf{p}}-f_{\mathbf{p}'}}{\epsilon_{\mathbf{p}}-\epsilon_{\mathbf{p}'}-\mu H})\}. \tag{21}$$

Here $f_{\mathbf{p}}$ denotes the Fermi function. Within logarithmic accuracy we can write

$$\int_0^{1/T} d\tau_1 \int_0^{\tau_1} d\tau G(\tau)G(-\tau)\mathrm{sh}(\mu H\tau) = -[N(0)]^2(\frac{\mu H}{T}+\mathrm{sh}\frac{\mu H}{T})\cdot\ln(\frac{\epsilon_F}{max(T,\mu H)})\times$$

$$\times\int_0^{1/T} d\tau_1 \int_0^{\tau_1} d\tau G(\tau)G(-\tau)(\mathrm{ch}(\mu H\tau)-1) = -2[N(0)]^2\mathrm{sh}^2(\frac{\mu H}{2T})\cdot\ln(\frac{\epsilon_F}{max(T,\mu H)}). \tag{22}$$

When these results are inserted into Eq. (20) we obtain finally

$$\begin{aligned}\langle S_z\rangle-\langle S_z\rangle_0 &= (gN(0)\mu_e H-2g^2I(0)\langle S_z\rangle)\frac{\partial\langle S_z\rangle_0}{\partial(\mu H)}- \\ &-2g^2[N(0)]^2\ln(\frac{\epsilon_F}{max(T,\mu H)})\{2\mathrm{sh}^2(\frac{\mu H}{2T})(T\frac{\partial\langle S_z^2\rangle_0}{\partial(\mu H)})+ \\ &+(\frac{\mu H}{T}+\mathrm{sh}(\frac{\mu H}{T}))(T\frac{\partial\langle S_z\rangle_0}{\partial(\mu H)})\}.\end{aligned} \tag{23}$$

One notices that for small fields H the second term $\sim g^2I(0)\langle S_z\rangle$ is the largest one. Neglecting for a moment the ln-term which is small, we obtain for $H=0$ an instability of the impurity system towards a fixed moment $\langle S_z\rangle \neq 0$. With $\partial\langle S_z\rangle_0/\partial(\mu H)=\frac{1}{3}S(S+1)/T$ the transition temperature T_c is given by

$$T_c = -2g^2I(0)\frac{S(S+1)}{3}. \tag{24}$$

Below that temperature a spontaneous symmetry reduction takes place. The impurity spin is polarized in a direction which will be determined by the ubiquitous anisotropies.

It is interesting to determine the associated thermodynamical potential Ω. First of all, it is possible to show that all diagrams with intersecting (or crossing) lines obtained from Eqs. (11, 13) are of order T/ϵ_F and therefore small. This holds true for any order in the interaction constant g. Therefore one may neglect them and Eq. (14) holds formally for all orders in g. ¿From that equation one may also conclude that the effect of the exchange interaction on the spin energy is threefold: it produces a large shift in the level positions, secondly an additional $\langle S_z\rangle$ dependent shift and finally also a small shift due to processes of the Kondo type. If the latter are neglected the self-consistency equation for the average value $\langle S_z\rangle$ is of the form

$$\langle S_z\rangle = B(\frac{\mu H-2g^2I(0)\langle S_z\rangle}{T}), \tag{25}$$

where B(x) is the Brillouin function. This equation holds for all values of H and T, except in a narrow temperature regime $|T_c-T|\leq T_c^2/\epsilon_F$ near the transition temperature, where corrections of the Kondo type become important. Note that Eq.(24) follows from (25) when $H=0$.

The correction of the thermodynamics potential due to H_{int} is calculated from

$$\frac{\delta\Omega}{\delta g} = \frac{1}{g}\langle H_{int}\rangle. \tag{26}$$

By making use of Eq. (14) we obtain

$$\frac{\delta\Omega}{\delta g} = 2gI(0)\langle S_z\rangle^2 \tag{27}$$

with $\langle S_z\rangle^2$ given by Eq. (25).

In the regime $\mu H \to 0$ we find for the static magnetic moment near the transition temperature

$$\langle S_z\rangle^2 = \frac{5}{3}(1 - \frac{T}{T_c})\frac{(S(S+1))^2}{(S^2+S+\frac{1}{2})}. \tag{28}$$

Hereby we used an expansion of $\langle S_z\rangle_0$ in powers of $(\mu H/T)$. When inserted into Eq. (27) we obtain for the thermodynamic potential change

$$\Omega - \Omega_0 = -\frac{5}{2T_c}\frac{S(S+1)}{S^2+S+\frac{1}{2}}(T_c - T)^2. \tag{29}$$

This proves that the symmetry broken solution $\langle S_z\rangle \neq 0$ leads to a lowering of the energy as compared with the symmetry conserving one.

In conclusion, we have shown that at a temperature much higher than the Kondo temperature the system of a magnetic impurity coupled to conduction electrons becomes instable against the formation of a polarized impurity-spin state $\langle S_z\rangle \neq 0$. Kondo-type corrections to $\langle S_z\rangle$ are generally small but may become important in the immediate vicinity of the transition temperature. In an isotropic medium the ground state is infinitely degenerate over the direction of the spontaneous magnetization. However, in a real crystal there exists always an anisotropy and the ground state will be only finite degenerate. An exponentially small transition probability between these different states will lead to the appearance of a new scale, that can be considered as the Kondo temperature.

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