

Many-Body Theory of Localized d States in Metals. I. The Localized Moment*

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The problem of the localization of a magnetic moment around an impurity is formulated in a rotationally invariant way, making possible the calculation of the Curie constant. This calculation is carried out in lowest order, but, in principle, can be extended to arbitrary order.

1. INTRODUCTION

THE Hartree-Fock method has been used to derive conditions for the existence of a localized magnetic moment around a transition element impurity dissolved in a metal by Anderson¹ and from a different standpoint, Wolff.² Anderson¹ demonstrated that in the case in which the impurity is assumed to have only one relevant orbital state whose energy is below the Fermi level of the solvent, when singly occupied, but well above the Fermi level when doubly filled (due to Coulomb energy), the Hartree-Fock equations could yield solutions in which the effective potentials acting on up-spins was different from that acting on down-spins. This, of course, implies a local magnetic moment.

Because a preferred quantization axis is introduced into this theory from the very beginning, one is deprived of the possibility of calculating dynamical quantities such as the spin susceptibility. Figure 1 (dotted curve) shows schematically what the Hartree-Fock calculation will give for the magnetic moment M as a function of field H , at a finite temperature. Even for $H=0$, the calculated moment is finite. Experimentally, however, one finds something like a Curie law until saturating field strengths are reached (solid curve in Fig. 1). (The part of M due to the Pauli susceptibility is not shown in the figure.) Thus, it seems that the Hartree-Fock theory is capable of calculating the saturation moment, but not the effective Curie constant. The same question of principle arises in a ferromagnet in which the magnetic moment is calculated by some self-consistent procedure, e.g., molecular field theory. If no preferred axis is given, the experimental curve must again follow the solid line in Fig. 1; but now it rises extremely steeply because of the large value of the total spin. On the other hand, molecular field theory calculates the dotted curve. In a simple ferromagnet with known total spin, we know of course how to remedy this defect. In the calculation of the partition function we include all the collective states of the form $(S^\pm)^r \Psi$, where Ψ is any eigenstate included in the calculation, S^\pm is the spin lowering or raising operator for the total spin S , and r is an integer ranging from zero to $2S$. Inclusion of these zero wave number spin-wave states will give the required

Curie law, but of course with an enormous Curie constant.

In the context of the alloy problem, it is difficult to see how to derive a correct set of collective states serving the same function as in the ferromagnet, principally because the value of S is not definite (the Hartree-Fock calculation naturally gives no clue to this). For this reason it is necessary to formulate the problem in such a way that rotational invariance is sufficiently well preserved to yield the solid curve in Fig. 1. In this paper we demonstrate that such a calculation is, in fact, possible. We shall use many-body perturbation theory to calculate the partition function. It must be noted at the outset that at a finite temperature this theory, which is, in principle, more rigorous than the Hartree-Fock method, cannot, if carried only to finite order, produce a sharp "yes-no" condition for the existence of a moment. However, even in finite order it yields the correct qualitative behavior for the localized magnetic moment, all the way from small applied fields (Curie range) to the saturation range at large fields.

2. THE RESOLVENT OPERATORS FOR THE MAGNETIC AND NONMAGNETIC MANIFOLDS

We first derive formal expressions for the density of states of the system consisting of the solvent in interaction with a magnetic solute. It is useful for this purpose to introduce the resolvent operator

$$\mathcal{R}(z) = 1/(\mathcal{H} - z), \tag{1}$$

where \mathcal{H} is the Hamiltonian proposed by Anderson¹ for this system:

$$\mathcal{H} = \sum_{k\sigma} \epsilon_{k\sigma} n_{k\sigma} + \sum_{\sigma} \epsilon_{d\sigma} n_{d\sigma} + U n_{d\uparrow} n_{d\downarrow} + V \sum_{k\sigma} (c_{k\sigma}^* c_{d\sigma} + c_{d\sigma}^* c_{k\sigma}). \tag{2}$$

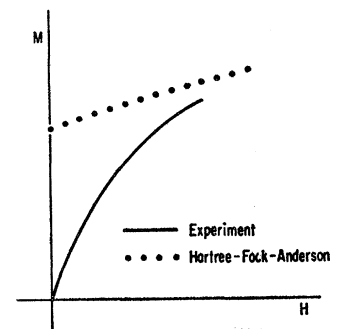


FIG. 1. Comparison of a Hartree-Fock calculation with experiment.

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¹ P. W. Anderson, *Phys. Rev.* **124**, 41 (1961).

² P. A. Wolff, *Phys. Rev.* **124**, 1030 (1961).

Here $\epsilon_{k\sigma}$ and $\epsilon_{d\sigma}$ are the energies, and $n_{k\sigma}$, $n_{d\sigma}$ the occupation numbers, of the band electrons and the d electron, respectively. k is the wave number and σ the spin index. U is the Coulomb repulsion of the electrons in the d state. The last term, involving creation and annihilation operators of the band and the d electrons, describes the scattering of electrons from the d level to the band and vice versa. The spin index on the single electron energies allows for the presence of a magnetic field.

The unperturbed states ($V=0$) can be divided into two manifolds M and S , according to whether a single electron occupies the d state with up or down spin (M), or whether it is empty or doubly occupied (S). We now obtain an *exact* expression for a new resolvent operator, R , which has no matrix elements connecting states in M with states in S .

Let H_1 denote the term in \mathcal{H} proportional to V , and H_0 the remainder. Clearly, if P_M and P_S are the projection operators of the M and S manifolds, H_0 commutes with each:

$$(P_M, H_0) = (P_S, H_0) = 0,$$

whereas

$$\begin{aligned} P_M H_1 &= H_1 P_S, \\ P_S H_1 &= H_1 P_M. \end{aligned}$$

We may similarly write

$$\mathcal{R} = R + R_1,$$

where

$$(P_M, R) = (P_N, R) = 0,$$

whereas

$$\begin{aligned} P_M R_1 &= R_1 P_S, \\ P_S R_1 &= R_1 P_M. \end{aligned}$$

The complete \mathcal{R} satisfies the integral equation

$$\mathcal{R} = \frac{1}{H_0 - z} - \frac{1}{H_0 - z} H_1 \mathcal{R}$$

which may be resolved into two equations:

$$\begin{aligned} R &= \frac{1}{H_0 - z} - \frac{1}{H_0 - z} H_1 R_1, \\ R_1 &= -\frac{1}{H_0 - z} H_1 R_0. \end{aligned}$$

Substituting the latter equation in the former, we arrive at the starting point of our theory:

$$R = \frac{1}{H_0 - z} + \frac{1}{H_0 - z} H_1 \frac{1}{H_0 - z} H_1 R$$

or, equivalently,

$$R = \frac{1}{H_0 - z - H_1 [1/(H_0 - z)] H_1}. \quad (3)$$

This equation is exact, and obviously decouples the magnetic manifold M and the nonmagnetic manifold S . Though we shall not make explicit use of this fact,

it is easy to see that

$$H_0 - H_1 [1/(H_0 - z)] H_1 \quad (4)$$

acts as some kind of Hamiltonian, and the projection of $H_1 [1/(H_0 - z)] H_1$ onto M closely resembles an exchange interaction between the localized, singly occupied d state, and the conduction electrons.

3. PARTITION FUNCTIONS

Next we make use of (3) to derive an expression for the partition function of the perturbed system. The density of the perturbed system is

$$\rho(z) = (1/\pi) \text{Im Tr} \mathcal{R}(z + i\delta)$$

in the limit $\delta \rightarrow 0$ (which from here on will always be implied), where z is real. The trace may be evaluated in the unperturbed representation, and in this representation $\text{Tr} R_1 = 0$. The density of states is, therefore,

$$\rho(z) = (1/\pi) \text{Im Tr} R(z + i\delta).$$

We may first take the partial trace over the band states, arriving at

$$\rho_{M\sigma}(z) = (1/\pi) \text{Im Tr}^{(b)} R_{M\sigma}(z + i\delta)$$

for the contribution to the density of states from the part of the M manifold with the one localized electron having spin orientation σ , and at

$$\rho_{S\sigma, f}(z) = (1/\pi) \text{Im Tr}^{(b)} R_{S\sigma, f}(z + i\delta)$$

for the contribution to the density of states from the S manifold completely empty (e), or completely filled (f). Trace^(b) indicates: trace over all the band-electron states. Clearly, if $\rho_b(E)$ is the density of band states (evaluated in the presence of a magnetic field), then

$$\begin{aligned} \rho_{M\sigma}(z) &= \frac{1}{\pi} \int dE \rho_b(E) \\ &\times \frac{\text{Im} \sum_{\alpha} (\Psi_{\alpha}(E), R_{M\sigma}(z + i\delta) \Psi_{\alpha}(E))}{\sum_{\alpha} 1}. \end{aligned} \quad (5)$$

Here α is the set of all quantum numbers consistent with energy E . We write

$$\text{Im} \sum_{\alpha} (\Psi_{\alpha}(E), R_{M\sigma} \Psi_{\alpha}(E)) / \sum_{\alpha} 1 = D_{M\sigma}. \quad (5a)$$

The important point about $D_{M\sigma}$ is that to a good approximation, provided the temperature is not too high, it is a function of $z-E$ alone. This property results from replacing band-state occupation numbers by their average values [cf. Eq. (8) *et seq.*].

One further point must be made here: If the system as a whole has $N+1$ electrons, then $\rho_b(E)$ in the above formula is the density of states of a system of exactly N band electrons, i.e., the density of levels with energy $\sum \epsilon_{k\sigma} n_{k\sigma}$ subject to $\sum_{k\sigma} n_{k\sigma} = N$. We should, therefore, write $\rho_b(E, N)$. In the same way, we may define D_{S_e} and D_{S_f} , and in writing down the corresponding formula, (5), we must use $\rho_b(E, N+1)$ and $\rho_b(E, N-1)$, re-

spectively. Since we expect to find a local moment of the order of a single Bohr magneton, it is safest to work for the time being in a canonical ensemble.

If we accept the assertion that the D 's are functions of z - E only, we may derive the partition function of the system from (5) (and analogous formulas for S), by taking the Laplace transform of Eq. (5). The total partition function is

$$Z = Z_M + Z_S \\ = \sum_{\sigma} Z_{M\sigma} + Z_{S_e} + Z_{S_f},$$

where

$$Z_{M\sigma}(\beta) = Z_b(\beta, N) \partial_{M\sigma}(\beta).$$

Here $\beta = 1/kT$, k is Boltzmann's constant, $Z_b(\beta, N)$ is the partition function of exactly N band electrons, and $\partial_{M\sigma}(\beta)$ is the Laplace transform of $(1/\pi)D_{M\sigma}$. Similarly,

$$Z_{S_e} = Z_b(\beta, N+1) \partial_{S_e}(\beta), \\ Z_{S_f} = Z_b(\beta, N-1) \partial_{S_f}(\beta).$$

We shall also write $\partial_M = \partial_{M\uparrow} + \partial_{M\downarrow}$, and $\partial_S = \partial_{S_e} + \partial_{S_f}$. The D 's and, therefore, the ∂ 's may be evaluated in terms of linked-cluster methods to any desired order in $H_1[1/(H_0 - z)]H_1$. Before doing this, however, we shall first derive a formula for the magnetic moment.

4. THE TOTAL MAGNETIC MOMENT

Since the energy due to a uniform magnetic field commutes with H , we may write, for the total moment

$$\mathfrak{M} = (1/Z)(\partial Z / \partial \beta H).$$

This may be cast into the form

$$\mathfrak{M} = (1/Z)[Z_b(N) \partial_M \mathfrak{M}_c + Z_b(N) \partial_M \mathfrak{M}_p(N) \\ + Z_b(N-1) \partial_{S_f} \mathfrak{M}_p(N-1) \\ + Z_b(N+1) \partial_{S_e} \mathfrak{M}_p(N+1)], \quad (6)$$

where

$$Z = Z_b(N) \partial_M + Z_b(N+1) \partial_{S_e} + Z_b(N-1) \partial_{S_f}.$$

In formula 6, the various \mathfrak{M}_p denote the Pauli magnetic moments of the indicated exact number of band electrons,³ and

$$\mathfrak{M}_c = (1/\partial_M)(\partial \partial_M / \partial \beta H) \quad (7)$$

is the part of the moment that will be shown to follow very nearly a Brillouin curve of the free ion. Derivatives of ∂_S have been neglected in (6), since they are very nearly zero. (See Appendix.) All the Pauli moments are very nearly temperature-independent, and the various different $Z(N)$'s differ very little from each other. Therefore, the effective strongly temperature-dependent part of the moment is, from (6),

$$\mathfrak{M}_c(\text{eff}) = \mathfrak{M}_c / (1 + (\partial_S / \partial_M)). \quad (7a)$$

As we shall see, the factor $(1 + \partial_S / \partial_M)^{-1}$ has a strong

³ Note that if the number of band electrons is odd, the corresponding M_p will also have a Curie contribution, but for a finite concentration of impurities this effect will not be seen. See also the discussion in Sec. 6.

field dependence [$\partial_M \sim \cosh(g\mu_B H / 2kT)$], but for small H it determines the effective Curie constant C . Neglecting a certain small g shift due to the band electrons, we have

$$C_{\text{eff}} = [1 + (\partial_S / \partial_M)_{H=0}]^{-1} C_{\text{free}}.$$

If we wish to ascribe this result to a new effective moment, we have

$$\mu_{\text{effective}}^2 = [1 + (\partial_S / \partial_M)_{H=0}]^{-1} \mu_B^2.$$

However, at large fields, such that

$$\cosh g\mu_B H / 2kT \gg (\partial_S / \partial_M)_{H=0},$$

μ_{eff} reverts to μ_B .

5. CALCULATION OF ∂_S / ∂_M

Equation (7a) shows that the effective moment will be largest when ∂_S / ∂_M is smallest. From the discussion of the previous section we may infer the following qualitative behavior of this ratio:

Suppose that the situation is favorable to the existence of a magnetic state, that is $\epsilon_d < 0$ (all energies are measured from the Fermi level) and $\epsilon_d + U > 0$, as explained by Anderson.¹ In the lowest linked-cluster approximation, the imaginary part of D_M has a numerator of the form

$$\delta + \text{Im} \left\langle M \left| H_1 \frac{1}{H_0 - z - i\delta} H_1 \right| M \right\rangle.$$

The second term in this expression is simply the damping of a particular "magnetic" state calculated by the lowest order "golden rule" formula. This damping, when averaged with the Boltzmann factor as weight (to obtain ∂_M), goes to zero with the temperature, because then no nonmagnetic states are available for the magnetic one to decay into. It follows that δ becomes dominant everywhere in D_M , so that eventually

$$\partial_{M\sigma} \sim \frac{1}{\pi} \int \frac{\delta e^{-\beta x}}{x^2 + \delta^2} dx \\ \rightarrow 1$$

as $\delta \rightarrow 0$.

On the other hand, the S manifold, since it is not the ground state of the uncoupled system, can decay into magnetic states even at zero temperature. Therefore,

$$\text{Im} \left\langle S \left| H_1 \frac{1}{H_0 - Z - i\delta} H_1 \right| S \right\rangle$$

dominates the expressions for D_S and for ∂_S . Hence, ∂_S depends on V , ϵ_d , and U . It will, in fact, turn out that in the lowest linked-cluster approximation⁴ ∂_S is least when ϵ_d is as far below the Fermi level as $\epsilon_d + U$ is above, and this agrees with Anderson's Hartree-Fock calculation. On the other hand, in contrast with the Hartree-Fock result, while ∂_S decreases with increasing U and decreasing V , no sharp lower bound on $U/V^2 \rho_s$ is

⁴ Corresponding to ordinary lowest order damping theory.

obtained in the present theory, which is only carried as far as the lowest linked-cluster approximation. It is not inconceivable however that the inclusion of an infinite class of linked cluster terms⁵ might give such a sharp lower bound. (ρ_s denotes the density of states of single band electrons of both spins.)

In the basically nonmagnetic situation (ϵ_d , ϵ_d+U both above or both below the Fermi level) the opposite situation prevails; ∂_S is of order unity, and ∂_M comes from low-order damping processes. However, in that case the moment becomes exponentially small in $1/T$ as the temperature tends to zero.

The linked-cluster theorem⁶ states that

$$\begin{aligned} (\sum_{\alpha} 1)D_{M\sigma}(E) &= \text{Im} \sum_{\alpha} (\Psi_{\alpha}(E), R_{M\sigma} \Psi_{\alpha}(E)) \\ &= \text{Im} \sum_{\alpha} \{1/[E + \epsilon_{d\sigma} - z - i\delta - G_{M\sigma}(z, E, \alpha)]\}, \end{aligned}$$

where

$$G_{M\sigma}(z, E, \alpha) = \left(\Psi_{\alpha}(E), \left[-\mathcal{V} + \mathcal{V} \frac{1}{H_0 - z - i\delta} \mathcal{V} - \dots \right]_{\text{linked}} \Psi_{\alpha}(E) \right)$$

and where the subscript $M\sigma$ always implies that the expectation value over the single-particle d state, with spin orientation σ is to be taken, although it is not explicitly shown. The effective perturbation here is

$$\mathcal{V} = -H_1[1/(H_0 - z - i\delta)]H_1.$$

Thus, we have

$$(\sum_{\alpha} 1)D_{M\sigma} = \sum_{\alpha} \frac{\delta + \text{Im}G_{M\sigma}(z, E, \sigma)}{(E - z + \epsilon_{d\sigma})^2 + \{\delta + \text{Im}G_{M\sigma}(z, E, \alpha)\}^2} \quad (8)$$

and, in lowest approximation, we take

$${}^0G_{M\sigma}(z, E, \alpha) = \left(\Psi_{\alpha}(E) H_1 \frac{1}{H_0 - z - i\delta} H_1 \Psi_{\alpha}(E) \right).$$

Ultimately, we thermally average D . Clearly the α represent the various possible distributions of band-state occupation numbers consistent with E . At low temperatures the overwhelming weight will be attached to those distributions for which the n_k 's are very nearly Fermi factors, $(1 + e^{\beta\epsilon_k})^{-1}$. Therefore, we retain only this one distribution, and then $\sum_{\alpha} 1 = 1$, and the summation over α on the right-hand side of (8) can be omitted. It follows that G , and therefore D is a function of $z-E$ alone.

$$\begin{aligned} \pi \partial_{M\sigma} &= \int_{-\infty}^{+\infty} {}^0D_{M\sigma}(\xi) e^{-\beta\xi} d\xi \\ &= \int_{-\infty}^{+\infty} \frac{\{\frac{1}{2}\pi V^2 \rho_s [1 - n(\xi) + n(-\xi + 2\epsilon_d + U)] + \delta\} e^{-\beta\xi} d\xi}{(\xi - \epsilon_{d\sigma})^2 + \{\frac{1}{2}\pi V^2 \rho_s [1 - n(\xi) + n(-\xi + 2\epsilon_d + U)] + \delta\}^2} \\ &= e^{-\beta\epsilon_{d\sigma}} \int_{-\infty}^{+\infty} \frac{\{\pi V^2 \rho_s [1 - n(\xi + \epsilon_d) + n(-\xi + \epsilon_d + U)] + \delta\} e^{-\beta\xi} d\xi}{\xi^2 + \{\pi V^2 \rho_s [1 - n(\xi + \epsilon_d) + n(-\xi + \epsilon_d + U)] + \delta\}^2}. \end{aligned}$$

⁵ Or of a finite number of *irreducible* linked-cluster terms using modified propagators (that is to say, self-consistent propagators).

⁶ For example, L. Van Hove, *Physica* 21, 901 (1955).

We also note in passing that in writing (8), we have neglected the shift in the $\epsilon_{k\sigma}$ resulting from $\text{Re}G_{M\sigma}$. Since $\text{Re}G_{M\sigma}$ is spin-dependent, this amounts to neglecting any g shift of the d electron arising from coupling with the band electrons. But because of the factor $(1 + \partial_S/\partial_M)^{-1}$ this will almost always be masked by the practical uncertainties concerning ϵ_d , U , and V .

Substituting $H_1 = V \sum (c_{k\sigma}^* c_{d\sigma} + c_{d\sigma}^* c_{k\sigma})$, we find immediately

$$\begin{aligned} {}^0G_{M\sigma}(z-E) &= V^2 \sum_k \frac{n_{k,-\sigma}}{E - z - i\delta + 2\epsilon_d + U - \epsilon_{k,-\sigma}} \\ &\quad + V^2 \sum_k \frac{(1 - n_{k\sigma})}{E - z - i\delta + \epsilon_{k\sigma}}. \quad (9) \end{aligned}$$

In the calculation of $\text{Im}{}^0G_{M\sigma}$, we will, henceforth, neglect the spin dependence, i.e., we will calculate $\text{Im}{}^0G_{M\sigma}$ in the limit of zero field. This is obviously justified so long as the magnetic single-particle energies are much less than the critical energies ϵ_d , U , and V .

In analogy with (8) and (9) we have

$$D_{S_e, f}(z-E) = \frac{\delta + \text{Im}G_{S_e, f}(z-E)}{[E - z + E_{e, f}(d)]^2 + [\delta + \text{Im}G_{S_e, f}(z-E)]^2}, \quad (10)$$

where

$$\begin{aligned} E_e(d) &= 0, \\ E_f(d) &= 2\epsilon_d + U, \end{aligned}$$

and where, in lowest approximation (neglecting spin dependence)

$$\begin{aligned} {}^0G_{S_e} &= V^2 \sum_{k\sigma} \frac{n_{k\sigma}}{E - z - i\delta + \epsilon_d - \epsilon_k}, \\ {}^0G_{S_f} &= V^2 \sum_{k\sigma} \frac{1 - n_{k\sigma}}{E - z - i\delta + \epsilon_d + \epsilon_k}. \end{aligned} \quad (11)$$

As we have already remarked, the n_k 's are Fermi functions of ϵ_k . Thus, we have

$$\text{Im}{}^0G_{M\sigma}(\xi) = \frac{1}{2}\pi V^2 \rho_s [1 - n(\xi) + n(-\xi + 2\epsilon_d + U)] \quad (12a)$$

$$\text{Im}{}^0G_{S_e}(\xi) = \pi V^2 \rho_s n(-\xi + \epsilon_d) \quad (12b)$$

$$\text{Im}{}^0G_{S_f}(\xi) = \pi V^2 \rho_s [1 - n(\xi - \epsilon_d)]. \quad (12c)$$

In these formulas, the variation of the single-particle density ρ_s with energy has been neglected. It follows, then, that

Using the obvious identities

$$e^{-\beta\xi}[1-n(\xi+\epsilon_d)] = e^{\beta\epsilon_d}n(\xi+\epsilon_d)$$

$$e^{-\beta\xi}n(-\xi+\epsilon_d+U) = e^{-\beta(\epsilon_d+U)}n(\xi-\epsilon_d-U),$$

we see that

$$\pi\partial_{M\sigma} = e^{-\beta\epsilon_d\sigma} \left\{ \frac{1}{2}\pi V^2\rho_s e^{\beta\epsilon_d} \int_{-\infty}^{+\infty} \frac{n(\xi+\epsilon_d)d\xi}{\xi^2 + \left\{ \frac{1}{2}\pi V^2\rho_s [1-n(\xi+\epsilon_d) + n(-\xi+\epsilon_d+U)] + \delta \right\}^2} \right.$$

$$+ \frac{1}{2}\pi V^2\rho_s e^{-\beta(\epsilon_d+U)} \int_{-\infty}^{+\infty} \frac{n(\xi-\epsilon_d-U)d\xi}{\xi^2 + \left\{ \frac{1}{2}\pi V^2\rho_s [1-n(\xi+\epsilon_d) + n(-\xi+\epsilon_d+U)] + \delta \right\}^2}$$

$$\left. + \int_{-\infty}^{+\infty} \frac{e^{-\beta\xi}\delta d\xi}{\xi^2 + \left\{ \frac{1}{2}\pi V^2\rho_s [1-n(\xi+\epsilon_d) + n(-\xi+\epsilon_d+U)] + \delta \right\}^2} \right\}. \quad (12d)$$

We are now in a position to proceed to the low-temperature limit inside the integral signs.

A. The First Integral

The first integral extends from $-\infty$ (or more accurately from the bottom of the band) to $-\epsilon_d$. It is thus equal to

$$\int_{-\infty}^{-\epsilon_d} \frac{d\xi}{\xi^2 + \frac{1}{4}\pi^2 V^4 \rho_s^2 n(-\xi + \epsilon_d + U)}$$

and, henceforth, δ may be neglected.

Subcase 1. $\epsilon_d < 0, \epsilon_d + U < 0, 2\epsilon_d + U < 0$

The integral is

$$\int_{-\infty}^{\epsilon_d+U} \frac{d\xi}{\xi^2} + \int_{\epsilon_d+U}^{-\epsilon_d} \frac{d\xi}{\xi^2 + \frac{1}{4}\pi^2 V^4 \rho_s^2} = -\frac{1}{\epsilon_d+U} + \frac{1}{\frac{1}{2}\Delta} \left[\tan^{-1}\left(\frac{-\epsilon_d}{\frac{1}{2}\Delta}\right) - \tan^{-1}\left(\frac{\epsilon_d+U}{\frac{1}{2}\Delta}\right) \right],$$

where

$$\Delta = \pi V^2 \rho_s.$$

Subcase 2. $\epsilon_d > 0, 2\epsilon_d + U > 0$. The integral is simply $1/\epsilon_d$.⁷

B. The Second Integral

This is more conveniently written

$$\int_{-\infty}^{\epsilon_d+U} \frac{[1-n(\epsilon_d+U-\xi)]d\xi}{\xi^2 + \frac{1}{4}\Delta^2 [1-n(\xi+\epsilon_d) + n(-\xi+\epsilon_d+U)]^2}.$$

Subcase 1. $\epsilon_d + U < 0, \epsilon_d < 0, 2\epsilon_d + U < 0$. The integral becomes

$$\int_{-\infty}^{\epsilon_d+U} \frac{d\xi}{\xi^2 + \frac{1}{4}\Delta^2} = \frac{1}{\frac{1}{2}\Delta} \left[\tan^{-1}\left(\frac{\epsilon_d+U}{\frac{1}{2}\Delta}\right) + \frac{\pi}{2} \right].$$

Subcase 2. $2\epsilon_d + U > 0$. Then the integral is⁷

$$\int_{-\infty}^{-\epsilon_d} \frac{d\xi}{\xi^2} + \int_{-\epsilon_d}^{\epsilon_d+U} \frac{d\xi}{\xi^2 + \Delta^2}$$

$$= -\frac{1}{\epsilon_d} + \frac{1}{\frac{1}{2}\Delta} \left[\tan^{-1}\frac{\epsilon_d+U}{\frac{1}{2}\Delta} + \tan^{-1}\frac{\epsilon_d}{\frac{1}{2}\Delta} \right].$$

⁷ If $\epsilon_d < 0$, and $\epsilon_d + U > 0$, the integrands of A and B contain a double pole. The rule is then to omit the divergent parts of the integrals. This is evident, if one disregards δ throughout, but retains the exponentially small n values near $\xi = 0$ in the denominators. The offending portions of the integrals A and B , in the limit $T \rightarrow 0$, then precisely add up to the third integral in the limit $\delta \rightarrow 0$.

The formulas for subcases A2 and B2 are correct only so long as $|\epsilon_d + U|$ and $|\epsilon_d|$ are each larger than kT , otherwise the n factors cannot be replaced by step functions.

C. The Third Integral

This can be neglected, except in the range in which $\xi + \epsilon_d < 0$ and simultaneously $-\xi + \epsilon_d + U > 0$, i.e., in the range

$$\xi < \min(-\epsilon_d, \epsilon_d + U).$$

But in this range, it gives π in the limit $\delta \rightarrow 0$ if $\min(-\epsilon_d, \epsilon_d + U) > 0$, and zero otherwise. Thus, in a nonmagnetic situation, with ϵ_d negative and $\epsilon_d + U$ less than zero, it gives zero. Similarly, for ϵ_d positive it gives zero. For a nonmagnetic case, therefore, only A and B survive.

In the magnetic case, on the other hand, the third integral is π , while A and B become small at low

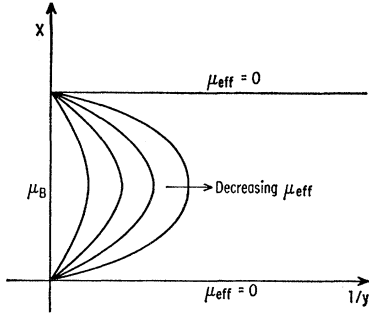


FIG. 2. Contours of constant effective moment in the lowest approximation.

temperatures (which is also the reason why the spin may be neglected in the calculation of 0G_M). In that case, we find

$$\partial_{M\sigma} = e^{-\beta\epsilon_d\sigma}. \quad (13)$$

The calculation of ∂_S proceeds similarly. We have

$$\pi \partial_S = \int_{-\infty}^{+\infty} {}^0D_S(\xi) e^{-\beta\xi} d\xi$$

and so, using (10), (12b), and (12c), we get

$$\begin{aligned} \pi \partial_{S\sigma} &= \int_{-\infty}^{+\infty} \frac{[\Delta n(-\xi + \epsilon_d) + \delta] e^{-\beta\xi} d\xi}{\xi^2 + [\Delta n(-\xi + \epsilon_d) + \delta]^2} \\ &= \int_{-\infty}^{+\infty} \frac{\Delta n(\xi - \epsilon_d) d\xi}{\xi^2 + [\Delta n(-\xi + \epsilon_d) + \delta]^2} e^{-\beta\epsilon_d} \\ &\quad + \int_{-\infty}^{+\infty} \frac{\delta e^{-\beta\xi} d\xi}{\xi^2 + [\Delta n(-\xi + \epsilon_d) + \delta]^2}. \end{aligned}$$

The last term is significant only in the range $-\xi + \epsilon_d > 0$ or $\xi < \epsilon_d$. But ϵ_d is negative in the magnetic case, so that this term goes to zero as $\delta \rightarrow 0$. On the other hand in the nonmagnetic case, it goes to π , if $\epsilon_d > 0$, and to zero if $\epsilon_d < 0$ (see Sec. 6). The first term⁸ is

$$\Delta e^{-\beta\epsilon_d} \int_{-\infty}^{\epsilon_d} \frac{d\xi}{\xi^2} = -\frac{\Delta}{\epsilon_d} e^{-\beta\epsilon_d}, \quad \epsilon_d < 0.$$

Similarly,

$$\begin{aligned} \partial_{Sf} &= \int_{-\infty}^{+\infty} \frac{\{\Delta[1 - n(\xi - \epsilon_d)] + \delta\} e^{-\beta\xi} d\xi}{(\xi - 2\epsilon_d - U)^2 + \{\Delta[1 - n(\xi - \epsilon_d)] + \delta\}^2} \\ &= e^{-\beta(2\epsilon_d + U)} \int_{-\infty}^{+\infty} \frac{\{\Delta[1 - n(\xi + \epsilon_d + U)] + \delta\} e^{-\beta\xi} d\xi}{\xi^2 + \{\Delta[1 - n(\xi + \epsilon_d + U)] + \delta\}^2} \\ &= \int_{-\infty}^{+\infty} \frac{\Delta n(\xi + \epsilon_d + U) d\xi}{\xi^2 + \Delta^2[1 - n(\xi + \epsilon_d + U)]^2} e^{-\beta\epsilon_d} + \text{a } \delta \text{ term.} \end{aligned}$$

Again, the δ term survives only in the range $\xi < -(\epsilon_d + U)$, and as $\delta \rightarrow 0$, goes to zero for the

⁸ For $\epsilon_d > 0$, see remarks at end of subcase A1, in the calculation of ∂_M .

magnetic case. In the nonmagnetic case it is $\pi\eta(-(\epsilon_d + U))e^{-\beta(2\epsilon_d + U)}$.⁹ The other term is

$$\Delta e^{-\beta\epsilon_d} \int_{-\infty}^{-(\epsilon_d + U)} \frac{d\xi}{\xi^2} = \frac{\Delta}{\epsilon_d + U} e^{-\beta\epsilon_d}$$

(for $\epsilon_d + U < 0$, see end of subcase A1 in calculation of ∂_M). Thus, in the magnetic range, we have

$$\begin{aligned} \partial_S &= \partial_{S\sigma} + \partial_{Sf} \\ &= \Delta e^{-\beta\epsilon_d} \left(\frac{1}{\epsilon_d + U} - \frac{1}{\epsilon_d} \right). \end{aligned}$$

And

$$\partial_M = \partial_{M\uparrow} + \partial_{M\downarrow} = 2e^{-\beta\epsilon_d} \cosh(\mu_B g H \beta / 2).$$

Hence,

$$\frac{\partial_S}{\partial_M} = \Delta \left(\frac{1}{\epsilon_d + U} - \frac{1}{\epsilon_d} \right) / 2 \cosh\left(\frac{\mu_B g H \beta}{2}\right).$$

In Anderson's notation,¹ we write $|\epsilon_d|/U = x$ and $y = U/\Delta$. Then

$$\frac{\partial_S}{\partial_M} = \frac{1}{y} \left(\frac{1}{1-x} - \frac{1}{x} \right) / 2 \cosh(\mu_B g H \beta / 2).$$

This is infinite at $x=0$ and $x=1$, and has a minimum, equal to $2/y$, at $x = \frac{1}{2}$. The effective moment as measured via the Curie constant is thus

$$\mu_{\text{eff}} = \left[\frac{2yx(1-x)}{2yx(1-x)+1} \right]^{1/2} \mu_B.$$

[In actual fact for $x=0$ or 1 , the above estimates of the integrals are not reliable. They break down when ϵ_d or $\epsilon_d + U \sim kT$, but this case is not generally important.]

The curves of constant μ_{eff} in the $(x, 1/y)$ plane are shown schematically in Fig. 2, which represents as close as this calculation can come to Fig. 4 of Anderson's paper.

6. THE NONMAGNETIC CASE

It is of interest to examine what happens when conditions for the development of a magnetic moment are unfavorable. In that case, the C integral in ∂_M is zero, while the A and B integrals dominate. ∂_S , on the other hand, is¹⁰

$$\eta(\epsilon_d) + \eta(-(\epsilon_d + U)) e^{-\beta(2\epsilon_d + U)} + O\left(\frac{\Delta}{\epsilon_d}\right).$$

In the calculation of the $\partial_{M\sigma}$, it is now no longer possible to neglect the spin dependence of the intermediate

⁹ If $(\epsilon_d + U) < 0$. If $\epsilon_d + U > 0$, then we certainly have $\epsilon_d > 0$, and the δ term in the calculation of $\partial_{S\sigma}$ then gives π .

¹⁰ For $\epsilon_d < 0$, the empty level can decay by scattering from the band, so that the δ contribution to the $\partial_{S\sigma}$ expression is zero. Not so for $\epsilon_d > 0$. Hence, the η term. [$\eta(x) = 1$ for $x > 0$, $= 0$ otherwise.]

state, because this spin dependence eventually enters the exponentials multiplying the integrals A and B .

The A term arose from an intermediate state in which the d electron with spin σ , was destroyed, and replaced by a band electron with spin σ . The B term involved an intermediate state in which d electron with spin $-\sigma$ was created, and a band electron with spin $-\sigma$ was destroyed. Suppose now that the levels are such that both ϵ_d and ϵ_d+U are negative. Then the B term dominates at low temperatures. If, in the analysis leading to the expression for ∂_M careful count is kept of the spin indices, it is found that the exponential coefficient of the B integral inside the parenthesis of Eq. (12d) is

$$\exp(-\beta(\epsilon_{d,-\sigma}+U+\eta_{-\sigma}))$$

where, for short, $\eta_{-\sigma}$ is the magnetic energy of a band electron in spin state $-\sigma$. Together with the coefficient outside the parenthesis of (12d) we get, since $\epsilon_{d,\sigma}+\epsilon_{d,-\sigma}=2\epsilon_d$, a factor

$$e^{-\beta\eta_{-\sigma}}e^{-\beta(2\epsilon_d+U)}$$

outside the B integral. This would give the appearance of having yielded a Curie-law-type band electron but with negative intrinsic moment. This should indeed occur, since one of the band electrons has become a d electron in a *real* transition. Had we started with an even number of band electrons, we must end up with an odd number, and hence, with a Curie moment, after the transition. Had we started with N odd, this Curie moment should go away in the transition, and indeed it does. Referring to Eq. (6), we see that the Curie part of the band electron moment is very nearly equal to

$$[1/(1+\partial_S/\partial_M)][\partial_N(N)]_{\text{Curie}}.$$

This is cancelled by the newly acquired term just discussed, since that term corresponded to an electron with negative moment.

Of course, as the number of impurities is increased to a finite concentration, the question of even or odd numbers of band electrons becomes immaterial, since these will always arrange themselves in such a way that at $T=0$, at *most one* has a Curie moment, thus contributing negligibly to the total moment.

7. EXTENSION TO PARTIALLY FILLED d SHELLS

Quite obviously the above method can be extended to magnetic states in which the d shell of the impurity has more than one hole. It is necessary only to introduce additional magnetic manifolds corresponding to two, three, or more, holes. This will be done in a later paper.

APPENDIX. THE WEAK FIELD DEPENDENCE OF ∂_S IN THE MAGNETIC CASE

Here we examine the very small field dependence of ∂_S , insofar as such dependence enters the exponential factors outside the various integrals. In the process leading to ∂_{S_e} , a d electron of spin σ is created, and a band electron of spin σ destroyed. The zero of the real part of the denominator in $H^1[1/(H_0-z-i\delta)]H^1$ is thus at

$$\epsilon_k = -\xi + \epsilon_d + \eta_{\sigma^d} - \eta_{\sigma^b},$$

where η^d and η^b are the magnetic energies of the d and band electrons, respectively.

Eventually, in the calculation of ∂_{S_e} , the difference of these quantities appears in the exponential. It follows that ∂_{S_e} is given by

$$\partial_{S_e} = (\partial_{S_e})_{H=0} \cosh[(g^d - g^b)\mu_B H\beta/2].$$

In the calculation of ∂_{S_f} , we note that a d electron of spin σ , say, is destroyed and a band electron of spin σ created. The relevant denominator now vanishes at

$$\begin{aligned} \epsilon_k &= \xi - \epsilon_d - \eta_{\sigma^d} - \eta_{-\sigma^b} \\ &= \xi - \epsilon_d - (\eta_{\sigma^d} - \eta_{\sigma^b}) \end{aligned}$$

and so, once again,

$$\partial_{S_f} = (\partial_{S_f})_{H=0} \cosh[(g^d - g^b)\mu_B H\beta/2].$$

Thus, to the extent that d and b electrons differ in g value, there is an additional magnetic moment, approximately equal to

$$[1/(1+\partial_M/\partial_S)]M,$$

where M is the magnetic moment of a free electron with g value $g^d - g^b$.