

# Localized Magnetic Moments in Dilute Metallic Alloys: Correlation Effects\*

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We discuss qualitatively the importance of the correlation energy in determining the ground state of a metal with an impurity atom. For a single, partly occupied impurity  $d$ -state orbital, the correlation energy acts to prevent the appearance of a nonvanishing ground-state spin, so that this simple nondegenerate model actually has a complicated structure. In *one* dimension, we show that this model of an impurity can never lead to a localized moment. In *three* dimensions, if we take linear combinations of Bloch functions transforming according to the irreducible representations of the point group of the impurity-crystal, we find that most of the new wave functions are entirely decoupled from the impurity, and only a small subset interacts with it. The noninteracting majority of states determine the Fermi level, which we therefore take to be fixed. The ground state of the band states interacting with the impurity states depends on the two-body Coulomb repulsion  $U$ , and we find that for sufficiently small  $U$  the ground state has an even number of electrons with total spin  $S=0$ . As  $U$  is increased above a certain critical value, the ground state of the interacting subsystem changes to an odd number of electrons, having total spin  $S=\frac{1}{2}$ , and a localized moment is said to exist. The introduction of orbital degeneracy for the impurity  $d$  state, and of Hund's rule matrix elements, makes the localized moment much stabler. The results are obtained by a combination of exact energy-level ordering theorems and a Green's-function calculation in the  $t$ -matrix approximation.

## I. INTRODUCTION AND THEOREMS

**T**HE conditions under which a localized magnetic moment is associated with a solute atom in a dilute alloy have been investigated within the frame-

work of the Hartree-Fock (HF) approximation.<sup>1-3</sup> It is well known that in metals the HF approximation overestimates the strength of the effective exchange interaction through the neglect of correlations between electrons of opposite spin orientations (i.e., the "correlation hole"). As a result, the HF theory of ferromagnetism

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<sup>1</sup> J. Friedel, *Nuovo Cimento Suppl.* **7**, 287 (1958).

<sup>2</sup> P. W. Anderson, *Phys. Rev.* **124**, 41 (1961).

<sup>3</sup> P. A. Wolff, *Phys. Rev.* **124**, 1030 (1961).

in the transition metals is qualitatively in error, as discussed most recently by Kanamori.<sup>4</sup> The question arises whether a similar error occurs in the present localized-moment problem. The theory discussed below shows that at least under certain circumstances this is the case. Specifically, we shall see that a well-known simplified model of an impurity, for which a magnetic moment had been calculated to exist for sufficiently strong Coulomb repulsion among the electrons, does not exhibit a moment when a more accurate calculation is performed. One may then well wonder what would be a satisfactory model of a magnetic impurity in a non-magnetic host metal, such as a manganese atom in copper. First, we may discard the effects of the electrostatic potential of the impurity on the conduction electrons, as these are the same for electrons of spin "up" as for spin "down." On the other hand, the *electron-transfer* matrix elements (whereby the conduction electrons of the host metal can hop in and out of the localized, partly occupied orbital states of the impurity) and the *Heisenberg exchange forces* (in particular, the so-called *s-d* exchange interaction) do both provide mechanisms whereby the conduction electrons can have their spins polarized by the spin of the impurity. But for practical purposes these mechanisms will be useless if the impurity does not possess a net spin in the first place, so we must first ask when a net spin is energetically favorable.

A single hydrogen atom has a single electron, hence a magnetic moment of one Bohr magneton. If it is dissolved in a metal one of three things may happen: (a) The electron may ionize, or (b) at the opposite extreme, a second electron may become bound to the proton, depending on the position of the Fermi level, the dielectric constant, etc. Both of these cases,  $H^+$  and  $H^-$ , are nonmagnetic. (c) The third possibility is that the impurity remains in the chemical state  $H^0$  because the Fermi level, dielectric constant, etc., of the host metal permit the proton to retain its electron, but the electron-electron Coulomb repulsion keeps a second electron away. Case (c) is the magnetic prototype stressed by Anderson,<sup>2</sup> except that he found it physically more meaningful to discuss a tightly bound orbital, such as a partly occupied *d* orbital of one of the transition elements, instead of a hydrogen orbital.

Another possible model of magnetic impurities, briefly discussed by Anderson in the Appendix to his paper,<sup>2</sup> has two or more degenerate, localized *d* orbitals on the impurity with a significant probability that these levels will be occupied by two or more electrons (or holes) in the ground state. Then, according to Hund's rules, the state of maximum multiplicity will lie lowest and there will be a net spin of two or more Bohr magnetons. It is possible that nickel and chromium, which normally sustain a magnetic moment not exceeding one Bohr magneton, are examples of the first species, whereas

iron, manganese, and the rare earths are examples of the stabler Hund's-rule-type impurities. Whether there exist two types of magnetic impurities is a question that has not yet been well answered, and which is outside the scope of the present analysis. The question to which we address ourselves, here is more modest, viz.,

*What are the properties of the hypothetical single d-orbital impurity?* Is it always magnetic if the Coulomb repulsion is sufficiently strong? Can we describe paramagnetic impurities, such as manganese in copper, by such a simplified model? These questions have already a definite answer in the Hartree-Fock theories,<sup>2,3</sup> but we shall find that as soon as the correlation energy is included this answer must be considerably modified. The Hartree-Fock theory, as usual, greatly exaggerates the magnetic state and also misses some of the structure of the ground state.

For example, we shall find that for a chain of 2 or more atoms, with the magnetic impurity at one end, it is possible to prove that the ground state has total spin  $S=0$ . What this signifies is that even if there is one Bohr magneton on the impurity, say of spin "up," the correlation energy favors having a spin "down" near this impurity and to exchange them so as to form a singlet state of total-spin zero. As this state lies below a localized doublet or triplet state by a finite energy, it will be impossible to measure the localized moment on the impurity: an electron which is part of a singlet state has a spin, all components of which average out to zero, and which therefore cannot be measured by a static magnetic field, nuclear hyperfine splitting, or any other method. The hydrogen molecule is a good example.

To be quite specific now, we study the "extra orbital" model of Anderson.<sup>2</sup> In this model one considers band states of momentum *k* which are the Bloch functions of the pure metal and a solitary added localized orbital labeled *d*. The band states and the localized orbital are assumed to be mixed by a one-body potential *V*. All two-body (Coulomb) interactions are neglected except those between opposite-spin electrons occupying the localized orbital. Thus, the Hamiltonian of the model is

$$\mathcal{H} = \sum_{k,s} \epsilon_k n_{k,s} + \sum_s \epsilon_d n_{d,s} + \sum_{k,s} (V_{kd} c_{k,s} + c_{d,s}^\dagger + \text{H.c.}) + U n_{d,+} n_{d,-}. \quad (1.1)$$

Here,  $\epsilon_k$  and  $n_{k,s} = c_{k,s}^\dagger c_{k,s}$  are the energy and number operator for the band state of momentum *k* and spin *s*,  $\epsilon_d$  and  $n_{d,s} = c_{d,s}^\dagger c_{d,s}$  are the energy and number operator for the localized *d* state,  $V_{kd}$  is the matrix element mixing the band and localized-orbital states, and *U* is the Coulomb matrix element between opposite-spin *d* states. The Fermi operators  $c_{k,s}^\dagger$  and  $c_{d,s}^\dagger$  create electrons in the band state *k* and localized orbital *d* state, respectively, with azimuthal spin quantum number  $s = \pm \frac{1}{2}$ . Note that  $\epsilon_k$ ,  $\epsilon_d$ , *U*, and  $NV_{kd}^2$  are all of the order of 1, in a suitable system of units.

<sup>4</sup> J. Kanamori, *Progr. Theoret. Phys. (Kyoto)* **30**, 275 (1963).

In order to make plausible the nonmagnetic character of this Hamiltonian, which is what we want to show, we shall first consider a linear chain in which Anderson's impurity atoms are added at either—or both—ends of the chain. We shall then prove a theorem (1.8) that the ground state of this chain belongs to total spin  $S=0$ , and is nondegenerate with the lowest state of total spin  $S=1$  or higher. Anderson's impurity is thus markedly unlike an atom of manganese; for if we put a manganese atom at the end of a chain of copper atoms we may properly expect it (and the chain) to have a net spin just as when we imbed it in a three-dimensional solid, in contrast to the situation we now analyze.

First consider the case when the impurity is at the farther end of a chain of  $n$  atoms. In terms of localized Wannier operators, the Hamiltonian takes the form (assuming only nearest-neighbor overlap)

$$\mathcal{H}_1 = -\epsilon \sum_{i=1}^{n-1} \sum_{s=+,-} (c_{i,s}^* c_{i+1,s} + \text{H.c.}) + \epsilon_d \sum_s n_{d,s} - V \sum_s (c_{n,s}^* c_{d,s} + \text{H.c.}) + \frac{U}{2} (\sum_s n_{d,s})^2. \quad (1.2)$$

Note that  $\epsilon$ ,  $\epsilon_d$ ,  $U$ , and  $V$  are all of the order of 1. Some discussion may be useful: We have assumed that  $\epsilon$  and  $V$  are real and positive, for if they are otherwise, only a trivial phase change is required to make them so. We have also included such additional one-body terms as  $\frac{1}{2}U(n_{d,s})^2 = \frac{1}{2}Un_{d,s}$ , to complete the square in the interaction terms and make it clear that the interaction is of the electrostatic, spin-independent type (unlike exchange). As for the Bloch energies which appear in (1.1), they are here given by

$$\epsilon_k = -2\epsilon \cos k, \quad (1.3)$$

so that the parameter  $\epsilon$  is one-half the bandwidth. The anticommuting Fermion operators  $c$  and  $c^*$  will now be transformed to Pauli-type operators  $b$  and  $b^*$  by means of the following rules<sup>5,6</sup>:

$$b_{l,-} = \exp\{i\pi \sum_{j<l} n_{j,-}\} c_{l,-}, \\ b_{l,+} = \exp\{i\pi \sum_{j \leq n+1} n_{j,-} + i\pi \sum_{j<l} n_{j,+}\} c_{l,+} \\ l=1, \dots, n+1. \quad (1.4)$$

Here we have relabeled  $c_{d,s}$  as  $c_{n+1,s}$  for convenience. The operators  $b^*$  are obtained from the above by Hermitian conjugation. As for the occupation-number operators, they are clearly the same in the  $b$  and  $c$  languages:

$$n_{l,s} = b_{l,s}^* b_{l,s} = c_{l,s}^* c_{l,s}, \quad (1.5)$$

therefore, the transformation (1.4) is easily inverted to give the  $c$ 's as functions of the  $b$ 's. Two  $b$ 's with different

indices commute with one another (regardless of whether one or both are  $*$ ), but for equal subscripts the rules are

$$b_\alpha^2 = (b_\alpha^*)^2 = 0, \quad b_\alpha^* b_\alpha + b_\alpha b_\alpha^* = 1, \quad (1.6)$$

just as for fermions or Pauli spin matrices. Because the  $b$ 's all commute, the various configurations can be specified merely by specifying which states are occupied and which are not. The order in which the  $b$ 's appear is immaterial, and the sign of each configuration making up the Hilbert space can unambiguously be taken to be positive. Substitution for the  $c$ 's in the Hamiltonian now yields

$$\mathcal{H}_1 = -\epsilon \sum_{i=1}^{n-1} \sum_s (b_{i,s}^* b_{i+1,s} + \text{H.c.}) + \epsilon_d \sum_s n_{n+1,s} - V \sum_s (b_{n,s}^* b_{n+1,s} + \text{H.c.}) + \frac{1}{2}U(\sum_s n_{n+1,s})^2, \quad (1.7)$$

an expression involving the commuting operators only. A straightforward application of the method of proof of Ref. 6 leads to the following inequality: Defining  $E_0(S)$  to be the lowest energy eigenvalue belonging to total spin  $S$ , we have

$$E_0(S)E_0(S \not\leq +1). \quad (1.8)$$

The same inequality can also be proved if we add a *second* impurity atom at the other end of the chain, merely by labeling the new  $d$ -state operators  $c_{-1,s}$  and  $c_{-1,s}^*$  and the new band-state operators  $c_{0,s}$  and  $c_{0,s}^*$ , so that the ordering sequence (1.4) can be used without modification. The Hamiltonian for this case then reads

$$\mathcal{H}_2 = -\epsilon \sum_{i=0}^{n-1} \sum_s (b_{i,s}^* b_{i+1,s} + \text{H.c.}) + \epsilon_d \sum_s (n_{-1,s} + n_{n+1,s}) - V \sum_s (b_{-1,s}^* b_{0,s} + \text{H.c.} + b_{n,s}^* b_{n+1,s} + \text{H.c.}) + \frac{1}{2}U[(\sum_s n_{-1,s})^2 + (\sum_s n_{n+1,s})^2], \quad (1.9)$$

and the method of proof leading to the inequality (1.8) can be used also without modification, so that the addition of a second impurity changes nothing. [It might be argued that if we added some electrostatic repulsions among the conduction-band electrons the situation might be changed, but this argument may also be disposed of. For if we add to the above an arbitrary interaction Hamiltonian

$$\mathcal{H}' = \sum_{i,j} V_{i,j} (\sum_s n_{i,s}) (\sum_{s'} n_{j,s'}), \quad (1.10)$$

the inequality above may be proved *again without modification*.] Without repeating the proof in Ref. 6, we may briefly note that the "kinetic-energy" operators involving  $\epsilon$  and  $V$  are the nondiagonal operators in the present representation, and because of their negative signs one may invoke variational arguments to prove that the various configurations must enter into the ground state all with the same sign, regardless of the magnitude of  $U$ . The nonmagnetic character of the inter-

<sup>5</sup> D. Mattis, *Theory of Magnetism* (Harper and Row, New York, 1965), Chaps. 4 and 7.

<sup>6</sup> E. Lieb and D. Mattis, *Phys. Rev.* **125**, 164 (1962), Appendix.

acting system is thus caused by the desire of the electrons to minimize the kinetic energy just as is the case for noninteracting electrons; this they must do by correlations beyond the HF theory. We may also ask *how much* energy it would cost to magnetize the impurity, i.e., to create a doublet or triplet state in the vicinity of the impurity atom. This is different from  $E_0(1) - E_0(0)$  which is an energy of the order of  $1/N$ , and which is the excitation energy for a state in which two Bohr magnetons are more or less uniformly distributed throughout the chain, so that the spin on the impurity is also of the order of  $1/N$ . To achieve a spin of the order of 1 in the vicinity of the impurity, it is easy to see (variationally) that one must in effect break the bond  $n \rightarrow (n-1)$  or  $n \rightarrow (n+1)$ , and so the energy required will be  $\sim \epsilon$  or  $\sim V$ , whichever is smaller. Both these energies are of the order of 1, and therefore the nonmagnetic state of the impurity lies below the localized magnetic states by a *finite amount*.

If the impurity is in the exact center of the chain, half the Bloch waves (those corresponding to the  $\sin kx$  functions) will have a node at the impurity and so will *not* interact with it. Similarly for an impurity in the center of a three-dimensional crystal, only the functions which have the full point symmetry of the impurity + crystal will have a nonvanishing amplitude at the site of the impurity, and there are only  $\sim N^{1/3}$  such functions out of a total of  $N$ . Thus in general, there are two sets of band states: those which interact with the impurity and those which do not, the latter fixing the Fermi level at some value  $\epsilon_F$ . By a simple extension of the method of proof given above, we can prove (1.8) for interacting subsystem in three dimensions as well as in one, as discussed in the Appendix. Thus we find, now *without restriction as to the number of dimensions*,

$$E_0(0) < E_0(1) < E_0(2) < \text{etc.} \quad (1.11a)$$

or

$$E_0(1/2) < E_0(3/2) < E_0(5/2) < \text{etc.} \quad (1.11b)$$

for the interacting subsystem. The actual values of  $\epsilon$ ,  $V$ ,  $U$ ,  $E_F$ , and  $\epsilon_d$  will determine whether the number of electrons in the ground state of the interacting subset is even as in (a) above or odd as in (b) and so whether, associated with the impurity, we find one Bohr magneton or not.

In no case can the ground state of the interacting subset belong to spin  $S \geq 1$ , i.e., have *two* or more Bohr magnetons, so we see that this sort of impurity has a very tenuous sort of magnetism indeed.

In calculating the ground-state energy of the impurity + metal we shall now adopt an approach based on the many-body methods of quantum field theory, the Green's function formalism, which is well adapted to the study of the impurity problem, and which was also used in the HF analyses. We shall calculate the zero-temperature susceptibility  $\chi(0)$  of the system as a function of the system parameters. If, as we change these

parameters, a localized moment begins to appear, i.e., ground state goes from (a) to (b) above),  $\chi(0)$  will become singular. [This follows since if a localized  $d$ -moment exists,  $\chi(T)$  for the impurity + interacting band states will exhibit a Curie law varying as  $T^{-1}$  so that  $\chi(0) = \infty$ .] To calculate this we add to  $\mathcal{H}$  the Zeeman term

$$\mathcal{H}_Z = B \sum_s s (n_{d_s} + \sum_k n_{k_s}), \quad (1.12)$$

where  $B = \mu_B h$  is the Zeeman energy of an up-spin electron in the externally applied magnetic field  $h$  and  $\mu_B$  is the Bohr magneton. The susceptibility is given by

$$\chi = 2\mu_B^2 (\partial/\partial B) \langle n_{d_+} + \sum_k n_{k_+} \rangle |_{B=0} \quad (1.13)$$

with the expectation value taken with respect to the ground state of  $\mathcal{H} + \mathcal{H}_Z$ . Clearly it is sufficient to study  $\chi_d = 2\mu_B^2 (\partial \langle n_{d_+} \rangle / \partial B)$  to determine the existence of a localized moment. If this quantity is finite, the ground state can only belong to  $S=0$ . If it is infinite, the ground state of the impurity system has captured one Bohr magneton, two or more Bohr magnetons being excluded by (1.11). Indeed,  $\chi_d$ , the susceptibility of the  $d$  orbital, is more suitable for study than  $\chi$ , the total susceptibility, because in this way we avoid mixing in questions of the Pauli-spin susceptibility of the whole material, and of whether the total number of electrons is even or odd.  $\chi_d$  is a reasonable fraction of  $\chi$ , and when either is finite or infinite, so is the other.

## II. ONE-PARTICLE GREEN'S FUNCTION

To treat correlation effects it is convenient to study the one-particle Green's function for the localized orbital:

$$G_s(t) = -i \langle T \{ c_{d_s}(t) c_{d_s}^+(0) \} \rangle, \quad (2.1a)$$

defined in the presence of the externally applied magnetic field, where

$$c_{d_s}(t) = e^{i(\mathcal{H} + \mathcal{H}_Z)t} c_{d_s}(0) e^{-i(\mathcal{H} + \mathcal{H}_Z)t}. \quad (2.1b)$$

To simplify the dynamics of the problem we eliminate the band states from the problem by defining the zero-order Green's function

$$G_{0s}(t) = -i \langle T \{ c_{d_s}^{(0)}(t) c_{d_s}^{(0)+}(0) \} \rangle_0, \quad (2.2a)$$

where the time development of the operators is determined by

$$c_{d_s}^{(0)}(t) = e^{i\mathcal{H}_0 t} c_{d_s}^{(0)}(0) e^{-i\mathcal{H}_0 t} \quad (2.2b)$$

with  $\mathcal{H}_0$  the Hamiltonian for noninteracting particles:

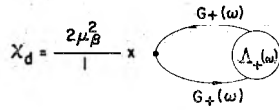
$$\mathcal{H}_0 = \mathcal{H} + \mathcal{H}_Z - U n_{d_+} n_{d_-} \quad (2.2c)$$

and  $\langle \rangle_0$  represents the expectation value in the ground state of  $\mathcal{H}_0$ . It is readily seen that the Fourier transform  $G_{0s}(t)$  is given by

$$G_{0s}(\omega) = [\omega - \epsilon_{d_s} - S_s(\omega)]^{-1}, \quad (2.3a)$$

where

$$\epsilon_{d_s} = \epsilon_d + sB, \quad \epsilon_{k_s} = \epsilon_k + sB \quad (2.3b)$$

FIG. 1. Diagrammatic representation of  $\chi_d$ .

and

$$S_s(\omega) = \sum_k \frac{|V_{kd}|^2}{\omega - \epsilon_{ks} + i\delta \operatorname{sgn}\omega}, \quad \left( \delta = 0^+, \operatorname{sgn}\omega = \frac{\omega}{|\omega|} \right), \quad (2.3c)$$

all energies being measured relative to the Fermi energy. As in Anderson's analysis<sup>2</sup> we neglect the real part of the one-body self-energy  $S(\omega)$  since this is expected primarily to lead to a level shift which can be absorbed into the definition of  $\epsilon_d$ . Thus,  $G_{0s}$  reduces to

$$G_{0s}(\omega) = [\omega - \epsilon_{ds} + i\Gamma \operatorname{sgn}\omega]^{-1}, \quad (2.4a)$$

where

$$\Gamma = \pi N(0) |V_{kd}|_{Av}^2. \quad (2.4b)$$

We have assumed that the density of band states  $N(\omega)$  varies slowly over a level width  $\Gamma$  about the Fermi surface and we have replaced  $N(\omega)$  by  $N(0)$ .

If we formally carry out a perturbation expansion of  $G_s(\omega)$  in powers of the perturbations  $V$  and  $U$ , it is seen that by using propagators  $G_{0s}$  we automatically include to all orders the one-body mixing potential  $V$ . Furthermore, since the Coulomb interaction  $Un_{d+}n_{d-}$  does not involve band states, the band states are thereby eliminated from the problem of determining  $G_s(\omega)$ . Thus, the perturbation series for  $G_s$  involves frequency but not momentum integrations, a major simplification over the corresponding problem in the many-body band theory of ferromagnetism. It is clear that the diagrammatics for determining  $G_s$  with the propagators  $G_{0s}$  are the familiar rules of many-body theory with a 2-body interaction  $U$  except for the absence of momentum indices and momentum sums.

By introducing the proper self-energy  $\Sigma_s(\omega)$  through Dyson's equation

$$G_s(\omega) = [\omega - \epsilon_{ds} - \Sigma_s(\omega) + i\Gamma \operatorname{sgn}\omega]^{-1}, \quad (2.5)$$

we find

$$\begin{aligned} \chi_d &= 2\mu_\beta^2 \frac{\partial}{\partial B} \langle n_{d+} \rangle = 2\mu_\beta^2 \frac{\partial}{\partial B} \int_{\leftarrow} \frac{d\omega}{2\pi i} G_+(\omega) \\ &= 2\mu_\beta^2 \int_{-\infty}^{\infty} G_+^2(\omega) \left( 1 + \frac{\partial \Sigma_+}{\partial B} \frac{d\omega}{2\pi i} \right), \end{aligned} \quad (2.6)$$

where  $\leftarrow$  signifies that the contour along the real axis  $(-\infty, \infty)$  is to be closed in the upper half-plane and the limit  $B \rightarrow 0$  is understood.

It is convenient to define the vertex function  $\Lambda_s(\omega)$  by the Ward-like relation

$$\Lambda_s(\omega) = 1 + s \frac{\partial \Sigma_s(\omega)}{\partial B} \Big|_{B=0}, \quad (2.7)$$

so that

$$\chi_d = 2\mu_\beta^2 \int_{-\infty}^{\infty} \frac{d\omega}{2\pi i} G_+^2(\omega) \Lambda_+(\omega). \quad (2.8)$$

The diagrammatic representation of (2.8) is shown in Fig. 1.

### III. THE VERTEX FUNCTION

To determine the vertex function  $\Lambda_s(\omega)$ , we construct an integral equation for  $\Sigma_s(\omega)$ . Before proceeding to the correlation effects we wish to discuss, we will retrieve Anderson's result by noting that within the HF approximation  $\Sigma_s^{\text{HF}}(\omega)$  is given by

$$\Sigma_s^{\text{HF}}(\omega) = U \int_{\leftarrow} \frac{d\omega'}{2\pi i} G_{-s}^{\text{HF}}(\omega') \quad (3.1)$$

as shown in Fig. 2. Since the right-hand side of (3.1) is independent of  $\omega$ ,  $\Sigma^{\text{HF}}$  is a real constant. From Dyson's equation (2.5) and from (3.1) one immediately finds

$$\Sigma_s^{\text{HF}} = (U/\pi) \cot^{-1} [(\epsilon_{d-s} + \Sigma_s^{\text{HF}})/\Gamma]. \quad (3.2a)$$

This is identical to Anderson's result if one uses the fact that

$$\Sigma_s^{\text{HF}} = U \langle n_{d-s} \rangle_{\text{HF}}. \quad (3.2b)$$

To find the conditions under which a localized moment begins to appear in the HF approximation, suppose we are in a range of parameters  $\epsilon_d$ ,  $\Gamma$ , and  $U$  (for  $B=0$ ) such that there exists no localized moment, i.e.,  $\Sigma_+|_{B=0} = \Sigma_-|_{B=0}$ . To determine  $\Lambda_s^{\text{HF}}(\omega)$ , we differentiate (3.2a) with respect to  $B$  and find

$$\begin{aligned} \Lambda_s^{\text{HF}} &= 1 + s \frac{\partial \Sigma_s^{\text{HF}}}{\partial B} = 1 + U \frac{\Gamma/\pi}{(\epsilon_{d-s} + \Sigma_s^{\text{HF}})^2 + \Gamma^2} \\ &\quad \times \left( 1 - s \frac{\partial \Sigma_s^{\text{HF}}}{\partial B} \right). \end{aligned} \quad (3.3)$$

Here, as before, the limit  $B \rightarrow 0$  is understood. Using the fact that when there is no localized moment in the absence of  $B$

$$\frac{\partial \Sigma_s}{\partial B} \Big|_{B=0} = - \frac{\partial \Sigma_{-s}}{\partial B} \Big|_{B=0}, \quad (3.4)$$

it follows from (3.3) that

$$\Lambda_s^{\text{HF}} = [1 - UA(0)]^{-1}. \quad (3.5a)$$

Here  $A(0)$  is the spectral weight function of  $G_s$  with  $B=0$  evaluated at the Fermi level

$$\begin{aligned} A(0) &= \pi^{-1} |\operatorname{Im} G^{\text{HF}}(0)| \\ &= (\Gamma/\pi) [(\epsilon_d + \Sigma^{\text{HF}})^2 + \Gamma^2]^{-1}. \end{aligned} \quad (3.5b)$$

One can interpret  $A(\epsilon)$  as the density of states in energy of the virtual  $d$  level. Notice that  $\Lambda_s$  (and hence  $\chi$ ) is singular as  $UA(0)$  approaches unity. Thus, the Hartree-

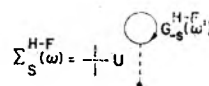


FIG. 2. Hartree-Fock self-energy.

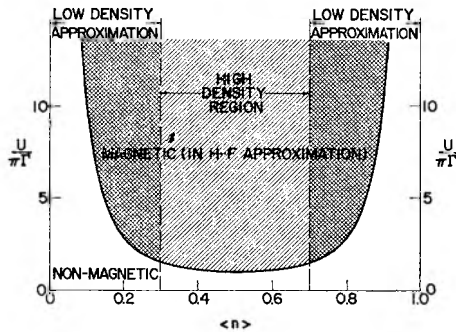


FIG. 3. Regions of validity of low-density theory. HF theory predicts magnetism in shaded and cross-hatched areas.

Fock approximation predicts that a localized moment occurs when

$$UA(0) \geq 1, \quad (\text{HF criterion}). \quad (3.6)$$

It is interesting to note that this result is identical in form to the HF band theory of ferromagnetism in metals with a short range potential  $U$ , namely, the HF theory predicts that a metal will become ferromagnetic when

$$UN(0) \geq 1, \quad (3.7)$$

where  $U$  is the matrix element of the two-body Coulomb repulsion potential between Bloch states near the Fermi surface and  $N(0)$  is the density of states at the Fermi surface. Since (3.7) overestimates the role of exchange in the band problem it is not surprising that (3.6) overestimates the polarization tendency of the impurity.

In order to make progress in including correlation effects, in the integral equation for  $\Sigma_s(\omega)$  we restrict the discussion to those regions of  $\epsilon_d, \Gamma, U$  space in which the average number of electrons (or holes) in the  $d$  orbital is small compared to unity. This simplification corresponds in a Fermi-gas problem to working with a low-density gas with short-range forces. This is a definite limitation, but one which allows us to verify the Hartree-Fock theory in a region where the latter definitely predicts the occurrence of a localized moment. This is illustrated in Fig. 3. The low-density approximation may be presumed valid in the range  $\langle n_d \rangle \lesssim 0.3$  or  $1 - \langle n_d \rangle \lesssim 0.3$ , in which range we know that the particle-particle (hole-hole)  $t$ -matrix graphs dominate the summation<sup>7</sup> to each order in  $U$ . Within this approximation,  $\Sigma_s(\omega)$  is given by

$$\Sigma_s(\omega) = \int \frac{d\omega'}{2\pi i} t(\omega + \omega') G_{-s}(\omega'), \quad (3.8)$$

where the  $t$  matrix satisfies

$$t(\nu) = U + iU \int \frac{dx}{2\pi} G_+(x + \nu) G_-(-x) t(\nu). \quad (3.9)$$

<sup>7</sup> V. M. Galitskii, Zh. Eksperim. i Teor. Fiz. 34, 151 (1958) [English transl.: Soviet Phys.—JETP 7, 104 (1958)].

This approximation for  $\Sigma_s$  is shown in Fig. 4. From (3.9) we find

$$t(\nu) = U/[1 + U\phi(\nu)], \quad (3.10)$$

where

$$\phi(\nu) = \int \frac{dx}{2\pi i} G_+(x + \nu) G_-(-x). \quad (3.11)$$

By differentiating (3.8) with respect to  $B$ , we find

$$\frac{\partial \Sigma_s(\omega)}{\partial B} = - \int t(\omega + \omega') G^2(\omega') \left( s + \frac{\partial \Sigma_s(\omega')}{\partial B} \right) \frac{d\omega'}{2\pi i}, \quad (3.12)$$

where we have used Eq. (3.4) and the relations

$$\left. \frac{\partial t(\nu)}{\partial B} \right|_{B=0} = 0, \quad (3.13a)$$

$$G_{-s}(\omega) = G_s(\omega) = G(\omega), \quad (3.13b)$$

which hold for  $B \rightarrow 0$  in the case considered here, i.e., with no actual localized moment being present in the absence of  $B$ .

We now determine under what conditions  $\chi \rightarrow \infty$  as we vary the system parameters. The singular behavior of  $\chi$  arises from a singular solution to (3.12) as in the corresponding Hartree-Fock case, (3.3) and (3.5). Equivalently,  $\chi$  will be singular if the homogeneous integral equation

$$f(\omega) = - \int t(\omega + \omega') G^2(\omega') f(\omega') \frac{d\omega'}{2\pi i} \quad (3.14)$$

has a solution. In principle, both  $G$  and  $t$  should be determined self-consistently by solving (3.8) and (3.9). In the absence of the detailed solutions of these equations we can make a reasonable estimate of the correlation effects as follows. The main effect of  $\Sigma$  in determining  $G$  and  $t$  is to shift the virtual level relative to the Fermi surface. The level width  $\Gamma$  due to the one-particle potential should primarily determine the form of the spectral weight function  $A(\omega)$ . Thus, we assume that the spectral weight is adequately represented by the Lorentzian function  $A(\omega)$ :

$$A(\omega) = \pi^{-1} |\text{Im}G(\omega)| = (\Gamma/\pi)[(\omega - \epsilon)^2 + \Gamma^2]^{-1}, \quad (3.15)$$

where  $\epsilon$ , rather than  $\epsilon_d$ , is now considered to be a parameter of the theory, i.e., the parameters are  $\epsilon, \Gamma$ , and  $U$ . With this approximation in (3.11), the real and imagi-

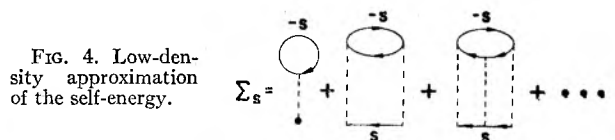


FIG. 4. Low-density approximation of the self-energy.

nary parts of  $\phi(\nu)$  are given by

$$\phi_1 = \frac{-1}{\pi} \frac{\Gamma}{(\omega-2\epsilon)^2 + (2\Gamma)^2} \left[ \ln \left( \frac{(\epsilon-\omega)^2 + \Gamma^2}{\epsilon^2 + \Gamma^2} \right) + \frac{2(\omega-2\epsilon)^2 + (2\Gamma)^2}{\Gamma(\omega-2\epsilon)} \tan^{-1} \frac{\epsilon}{\Gamma} + \frac{4\Gamma}{(\omega-2\epsilon)} \tan^{-1} \frac{\epsilon-\omega}{\Gamma} \right], \quad (3.16a)$$

$$\phi_2 = \frac{1}{\pi} \frac{2\Gamma}{(\omega-2\epsilon)^2 + (2\Gamma)^2} \left( \tan^{-1} \frac{\epsilon}{\Gamma} - \tan^{-1} \frac{\epsilon-\omega}{\Gamma} + \frac{\Gamma}{\omega-2\epsilon} \ln \left[ \frac{(\epsilon-\omega)^2 + \Gamma^2}{\epsilon^2 + \Gamma^2} \right] \right). \quad (3.16b)$$

Here  $\omega > 0$  and  $\phi(\omega < 0) = \phi^*(\omega > 0)$ .

As in Kanamori's treatment of correlation effects in 3- $d$  band metals, we expected the dominant contribution to the magnetization criterion to come from states near the Fermi surface, i.e.,  $\omega \simeq \omega' \simeq 0$ .

If  $t(\omega + \omega')$  were the difference between the Landau Fermi liquid functions  $f_{+-}(\omega, \omega') - f_{++}(\omega, \omega')$  for anti-parallel and parallel spin electrons in the virtual  $d$  state, it would be clear that only states  $\omega$  and  $\omega'$  in the immediate vicinity of the Fermi energy could enter the instability criterion. This is, in fact, the case within the Hartree-Fock approximation, where

$$t \rightarrow U = f_{+-} - f_{++}.$$

When correlations are included,  $t$  plays the role of the "irreducible particle-hole interaction"  $\Gamma^{(1)}$  in the notation of Abrikosov, Gorkov, and Dzyaloshinski,<sup>8</sup> rather than  $\Gamma^{(\omega)}$ , the limit of the full particle-hole vertex function which determines the Landau parameters  $f_{ss'}$ . It appears that  $\Gamma^{(1)}$  is a good approximation for  $\Gamma^{(\omega)}$  in the low-density limit, a question which we are currently investigating. Thus as a rough approximation we have the criterion for the existence of a localized moment,

$$U_{\text{eff}} A(0) \geq 1, \quad (3.17)$$

where the effective potential  $U_{\text{eff}}$  is given by

$$U_{\text{eff}} = t(0) = \frac{U}{1 + (U/\pi\epsilon) \tan^{-1}(\epsilon/\Gamma)}. \quad (3.18)$$

Now  $U_{\text{eff}}$  increases monotonically as  $U$  varies from  $0 \rightarrow \infty$ , so that

$$U_{\text{eff}} < U_{\text{eff}}^\infty = \pi\epsilon / \tan^{-1}(\epsilon/\Gamma). \quad (3.19)$$

Therefore we have the inequalities

$$U_{\text{eff}} A(0) < x / (1 + x^2) \tan^{-1} x < 1, \quad (x = \epsilon/\Gamma). \quad (3.20)$$

When (3.20) is combined with the magnetization condi-

tion (3.17) we see that a localized moment does not occur even as  $U \rightarrow \infty$  in the limit where the number of electrons (or holes) occupying the virtual level is small compared to unity, in contrast to the Hartree-Fock result. This shows that the energy of the system is a local minimum at zero magnetic moment. The question naturally arises whether there might not be a secondary minimum with increasing moment, a minimum which might even lie lower than the energy at  $M=0$ . Kjollerstrom, Scalapino, and Schrieffer<sup>9</sup> have recently shown that the low-density theory does not allow any such subsidiary minimum and that within the limitations of this theory, the ground state definitely belongs to zero moment.

#### IV. DEGENERATE ORBITALS

One can carry out a similar analysis for  $\mathfrak{N}$  degenerate  $d$  orbitals,  $\mathfrak{N}$  being of order 2 or 3 for real  $d$  orbitals with crystal field splitting, but as large as 7 for rare earths. Again we take Anderson's model with the two-body interaction

$$\mathfrak{H}' = \sum_{i \leq j} \sum_{s, s'} U_{ij} n_{is} n_{js'} - \sum_{i \leq j} \sum_s J_{ij} n_{is} n_{js}, \quad (4.1)$$

where

$$U_{ij} \equiv U, \\ J_{ij} \equiv \begin{cases} J & i \neq j \\ U & i = j \end{cases} \quad (i, j = 1, 2, \dots, \mathfrak{N}). \quad (4.2)$$

The criterion for magnetism corresponding to (3.17) becomes

$$\left[ \frac{\mathfrak{N}U}{1+U\phi} - \frac{(\mathfrak{N}-1)(U-J)}{1+(U-J)\phi} \right] A(0) \geq 1, \quad (4.3)$$

where

$$\phi = (1/\pi E) \tan^{-1}(E/\Gamma). \quad (4.4)$$

For  $\mathfrak{N}=1$ , we retrieve (3.17), while for  $J \ll U$  one finds

$$\left[ \frac{U}{1+U\phi} + \frac{(\mathfrak{N}-1)J}{(1+U\phi)^2} \right] A(0) \geq 1, \quad (4.5)$$

where the Hartree-Fock theory gives

$$[U + (\mathfrak{N}-1)J] A(0) \geq 1. \quad (4.6)$$

The magnetism of degenerate impurities arises from the fact that if two or more electrons are constrained to remain on the impurity atom, the exchange splitting  $J$  will favor their parallel alignment over some other spin arrangement. Even if the low-density theory is inapplicable and the formulas above become quantitatively wrong, this physical reason for the magnetization (of such impurities as manganese in copper) must be correct. [This is of course quite distinct from the magnetization of the nondegenerate orbital discussed in the

<sup>8</sup> A. A. Abrikosov, L. P. Gorkov, and I. E. Dzyaloshinski, *Methods of Quantum Field Theory in Statistical Physics* (Prentice-Hall, Inc., Englewood Cliffs, New Jersey, 1963).

<sup>9</sup> B. Kjollerstrom, D. J. Scalapino, and J. R. Schrieffer (private communication).

preceding sections, which owes its magnetism—which surely occurs only in the high-density limit  $\langle n_{ds} \rangle > 0.3$ —to the almost accidental fact that a single electron has a magnetic moment.] Anyhow, it is noteworthy that in the case of degenerate orbitals, we find that magnetism is possible even in the low-density limit.

## V. CONCLUSION

Physically, it is suggestive that nickel, which has a fraction of a hole to be shared among its  $d$  orbitals, rarely exhibits a paramagnetic moment in a nonmagnetic host metal, whereas iron, manganese and the rare earths, with a considerable fraction of the localized orbitals occupied, manage to maintain their moments quite constant in a wide range of materials. This is surely no accident, but is indicative of what the properties of a correct solution of Schrödinger's equation should reveal.

Mathematically, we found that the nondegenerate orbital is never magnetic if it is on the last atom of a chain molecule, and most likely it is also nonmagnetic on any other site of the chain molecule. The reason is that in one dimension an attractive potential is always capable of binding, and we visualize the one-dimensional situation as the impurities' electron, say of spin up, binding to its immediate vicinity a conduction-band polarization of spin down, which exchange and combine to give a nonmagnetic singlet ground state. To produce a net localized moment, we have argued that an energy  $0(1)$  is required, and this lack of magnetism is therefore a stable feature. In three dimensions an attractive potential does *not* always have a bound state. As a consequence, the spin up is not necessarily able to "capture" a spin down in its vicinity, and may give up this electron to the vast majority of band states which do not connect to the impurity. This occurs in what we have called the "high-density limit," i.e., the number of electrons on the spin-up  $d$  orbital is  $\sim 1$ , and is correctly predicted by the HF theory. In the low-density limit the HF theory still predicts a net moment over a range of parameters, but we have given arguments that this is incorrect. The "binding," and the correlations which we have found, are outside the framework of the earlier theories, and it is therefore not surprising to find a result which is different.

In addition, we have found that magnetism is possible even in the low-density limit, *provided there are degenerate*

*orbitals to be occupied.* This serves to explain qualitatively why magnetism is almost never observed except in situations where orbital degeneracy plays an important role, and it points out that crystal field effects—which tend to lower the orbital degeneracies—will be important even in metals.

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## APPENDIX

By choosing linear combinations of band functions adapted to the point group symmetry of the impurity + crystal, we can in many cases decouple the vast majority of band states which have vanishing amplitude at the site of the impurity, and which do not interact with it except as a "reservoir" of electrons which maintain the Fermi level fixed. It is possible to illustrate this simply, by making a few plausible approximations, e.g., by appropriate special choices of  $\epsilon_k$  and  $V_{kd}$ .

We replace the Brillouin zone by an equivalent sphere, i.e., we will assume that the Bloch energies  $\epsilon_k$  are given by

$$\epsilon_k = -2\epsilon \cos |k|a \quad (\text{A1})$$

and that likewise  $V_{kd}$  depends only on the magnitude of the wavevector  $|k|$ . This quantity can assume  $N^{1/3}$  closely spaced values ranging from 0 to  $\pi/a$ . By Fourier transforming all the operators in (1.1), the Wannier operators now referring to spherical shells at distances  $R$  from the origin, we may obtain precisely (1.2) in the Wannier representation. The  $n$ th Wannier operator refers to the  $s$ -wave component of a spherical shell at  $R_n = na$ , and the impurity is at the origin. The inequality (1.8) is then provable as before, except that the number of electrons in the one-dimensional manifold is not fixed *a priori* although the Fermi level is. We therefore do not know if there are an even number of electrons and the ground state belongs to  $S=0$ , or if the number is odd and  $S=\frac{1}{2}$ ; however, when  $U \rightarrow 0$  the number is clearly even and at  $U \rightarrow \infty$  it is clearly odd, therefore we know there occurs this level crossing at some intermediate "critical" value. These arguments serve also to establish Eqs. (1.11).