quired. If a vortexlike structure exists in the sheath, the "vortices" should necessarily be aligned nearly parallel to the plane of the foil and not perpendicular as was suggested by Hart and Swartz.[11] If they are pinned nearly normal to the plane of the foil and hence nearly normal to the field, then upon changing the angle by 1° as described in the previous paragraph, large torques are not expected to occur since the effective angle of the vortices is changed to $90° \pm 1°$. On the other hand, if these vortices are parallel to H, a change of 1° is indeed considerable and large torques would occur.

We summarize the results as follows: (1) Equation (6) is consistent with the observed large torques above H_{c2}, the straight-line relation of τ/H vs H along the minor hysteresis paths, and the correct calculation of $(\Delta\tau)_{PQ}$ and M_b. (2) The partially plated sample did exhibit a vanishing $(\Delta\tau)_{PQ}$. Using Eq. (6) we deduce for the first time values for M_s and J and a new model for the current distribution above H_{c2}. In this model the sheath contains either a normal core or a "vortexlike" structure parallel to the plane of the foil.

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[1]D. St. James and P. G. de Gennes, Phys. Letters 7, 306 (1963).
[2]C. F. Hempstead and Y. B. Kim, Phys. Rev. Letters 12, 145 (1964); W. J. Tomasch and A. S. Joseph, ibid. 12, 148 (1964).
[3]References to much of the experimental and theoretical work carried out on the sheath state can be found in R. W. Rollins and J. Silcox, Phys. Rev. 155, 404 (1967).
[4]H. J. Fink and L. J. Barnes, Phys. Rev. Letters 15, 793 (1965).
[5]H. J. Fink and R. D. Kessinger, Phys. Rev. 140, A1937 (1965).
[6]J. G. Park, Phys. Rev. Letters 16, 1196 (1966).
[7]D. J. Sandiford and D. G. Schweitzer, Phys. Letters 13, 98 (1964).
[8]L. J. Barnes and H. J. Fink, Phys. Rev. 149, 186 (1966).
[9]J. Osborn, Phys. Rev. 67, 351 (1945).
[10]G. Bon Mardion, B. B. Goodman, and A. Lacaze, Phys. Letters 2, 321 (1962).
[11]H. R. Hart and P. S. Swartz, Phys. Rev. 156, 402 (1967).

SYMMETRY OF GROUND STATE IN A DILUTE MAGNETIC METAL ALLOY

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It is proved that the spin of the ground state of a magnetic atom having exchange interaction with a nonmagnetic host metal is $s \mp \frac{1}{2}$, where s = spin of noninteracting magnetic atom, the upper sign is appropriate to antiferromagnetic coupling, and the lower, to ferromagnetic coupling. This result is generalized to any number of conduction bands and to nonpointlike impurities, provided that the exchange interactions with the number of conduction bands, or with the various partial waves, are all of the same sign. For p such bands or partial waves, the result is that the ground-state spin $= |s \mp \frac{1}{2}p|$.

The present paper concerns the ground state of a magnetic atom in a nonmagnetic host metal. We use the s-d exchange Hamiltonian to describe this situation, the exchange perturbation having been first shown by Kondo[1] to result in a logarithmic singularity in third and higher orders of perturbation theory. It is not known, in fact, whether the perturbation series converges when carried out to all orders, despite reasonable results of various methods of partial series summations which have been carried out to infinite order[2] in the coupling constant J. Indeed, Silverstein and Duke[3] have demonstrated that even methods which agree to within logarithmic accuracy above the Kondo temperature will disagree below it, and potentially can result in a plethora of predicted ground-state properties. However, recent variational solutions, some of which are based on the assumption that the ground state is a nonmagnetic singlet state,[4] have circumvented the difficulties of perturbation theory, although the problem is far from an exact solution at the present time. For this reason it might be useful to have some exact theorems, and in the present work we shall prove that

for antiferromagnetic coupling and impurity spin $\frac{1}{2}$, the ground state is indeed a singlet.

We then extend the analysis to a variety of similar problems which have not been so thoroughly investigated as the above. For ferromagnetic coupling, we shall show the ground state to be a triplet. For arbitrary impurity spin $s \geq \frac{1}{2}$, we find the ground state to belong to $s \mp \frac{1}{2}$, with the upper sign for antiferromagnetic and the lower sign for ferromagnetic coupling, a convention to which we shall adhere throughout the present work. Finally, we generalize to the case of a number of conduction bands, or partial waves, all interacting with our magnetic atom with the same sign of the coupling constant. When the number of such bands is p, the result is $|s \mp \frac{1}{2}p|$ for the ground state. The proof is unfortunately rather involved, considering the intuitive character of the results as stated above, but it is the simplest we have been able to concoct. We start with the canonical Hamiltonian

$$H = \sum_{km} \epsilon_k n_{km} + \tfrac{1}{2}(J/N) \sum_{kk'} \vec{S} \cdot \vec{\sigma}_{kk'}, \tag{1}$$

in which

$$\vec{\sigma}_{kk'} = (c_{k\uparrow}^*, c_{k\downarrow}^*) \vec{\sigma} \begin{pmatrix} c_{k'\uparrow} \\ c_{k'\downarrow} \end{pmatrix} \tag{2}$$

and the three components of the vector $\vec{\sigma}$ are the usual Pauli matrices. The d shell of the magnetic atom is presumed embedded in an s-like conduction band, hence the nomenclature "s-d exchange interaction." The conduction-band states are now to be decomposed according to their orbital angular momentum relative to the impurity (or Kubic harmonics[5]) and only $l = 0$ (s-wave) components can interact with a pointlike impurity. We shall see how to relax this condition to take care of several partial waves at the end of the analysis, but at present, according to our assumptions, electrons belonging to $l \neq 0$ do not see the impurity and may therefore be factored out of the problem, being in their usual states in the noninteracting Fermi sea.

The s-wave electrons obey a one-dimensional wave equation in the radial coordinate r, with the exchange interaction at $r = 0$ and the boundary of the crystal at $r = R$. Electrons in this one-dimensional manifold may be ordered, $x_1, x_2, \cdots$, with $x_i < x_{i+1}$ with the x's labeling spin-up electrons, and $y_1, \cdots$, with $y_i < y_{i+1}$ and the y's labeling the radial coordinate of spin-down electrons. The boundary conditions are that the wave functions vanish when any $x_i = x_{i+1}$ or any $y_i = y_{i+1}$, or whenever any coordinate equals R or becomes negative. Each eigenstate of H may be written as follows[6]:

$$\psi = \alpha f_+(x_1, x_2, \cdots | y_0, y_1, y_2, \cdots) + \beta f_-(x_0, x_1, \cdots | y_1, \cdots), \tag{3}$$

where we first study the case of an impurity with spin $s = \frac{1}{2}$, α and β are the eigenstates of spin up and down for the localized spin, and the functions $f_\pm$ vanish whenever any coordinate is negative, or whenever any pair of x's, or of y's, are equal, or whenever any coordinate exceeds R.

The method of proof is the following: We arrange for f_+ and f_- to be both positive in the ground state, and compare them with a model state of known spin. If the two are not orthogonal, then our unknown ground state must belong to the same total spin eigenvalue as the model state.

The model state is the ground state of a system labeled II, which differs from the original one (labeled I henceforth) only by the introduction of a thin impenetrable potential barrier at $r = a$. By this device, we can restrict a single electron to interact with the impurity, all the remaining particles being constrained to the region $r > a$. The minimum kinetic energy of an electron in the region $r < a$ is $\hbar^2\pi^2/2ma^2$, but an electron also benefits from the attractive potential well at the origin, the depth of this well being $\frac{1}{2}|J|s$ (for $J < 0$) and $\frac{1}{2}J(s+1)$ (for $J > 0$). A second electron benefits considerably less from the attractive well because the presence of the first electron according to the exclusion principle forces it either to have a large kinetic energy (one extra spatial node) or else to have unfavorable spin direction with respect to the impurity spin. Either way, we can pick a distance a such that the energy of the first electron near the impurity is below the Fermi level but not that of a second or any successive electron. Assuming the total number of conduction electrons to be odd, the total spin in the ground state of II is $s \mp \frac{1}{2}$, just the spin of impurity plus a single electron; the conduction sea at $r > a$ is in its usual singlet ground state.

We shall now show that the ground state of II as described above is not orthogonal to the

ground state of I. We now make use of Frobenius' theorem, which states that the ground state of a Hamiltonian, all of whose nondiagonal elements are nonpositive and real, is a linear sum of configurations all with positive coefficients.[6] Now if J is negative, the off-diagonal matrix elements of the interaction Hamiltonian,

$$\tfrac{1}{2}J(S_+\sigma_- + S_-\sigma_+), \tag{4}$$

are naturally negative; both these negative matrix elements and the kinetic energy are minimized in a nodeless ground state[7]; so it follows that the functions f_+ and f_- must have the same sign in the ground state (chosen for convenience to be positive). Now this holds true for both systems I and II because the details of the potential do not enter into the proof.[6] The ground states of I and II, which can both be expanded in a common complete set of basis functions all with positive coefficients, thus cannot be orthogonal to one another. Finally we prove the nondegeneracy of the ground state: All the eigenstates of H are orthogonal to one another and as two nodeless states cannot be orthogonal to one another, it follows that the (nodeless) ground state is unique and nondegenerate in a subspace of fixed $S_{z\,\text{total}}$.

The proof for antiferromagnetic sign of coupling ($J>0$) is preceded by a rotation of the local spin operators by 180° about the S_z axis. This again renders the off-diagonal elements (4) negative leaving the rest of the Hamiltonian unaffected. Once again the kinetic energy and off-diagonal matrix elements conspire to a nodelesss ground state[7] for both systems I and II. The ground states of these systems are not orthogonal, from which it follows that the ground state of I is an eigenstate of total spin of eigenvalue $s-\frac{1}{2}$ and is nondegenerate in subspace of fixed $S_{z\,\text{total}}$. This terminates the proof for point impurities in a nondegenerate conduction band.

The extensions to $l\neq 0$ for a nonpointlike impurity, or to the case of several conduction bands, are entirely analogous. It is required that all the bands interacting with the impurity do so with the same sign of exchange coupling constant, although the magnitudes of J may be arbitrary. In practice it should never be necessary to consider more than two or three partial waves, or more than half a dozen conduction bands. The model system II is defined as having the following properties: There is an impenetrable thin barrier at a_1 for band No. 1, $\cdots$, at a_p for band No. p, placed exactly such that a single electron from each band lies in the interval near the origin, the remaining electrons being at the far side of their respective barriers. The word "band" also stands for partial wave, and we may, moreover, have any number of partial waves in any number of bands, provided only that all the J's have the same sign. Now the a_i are picked so that any additional electrons could be brought to the neighborhood of the impurity only at the expense of raising their energy above the Fermi level (which is determined by the large number of particles in the Fermi sea); this promotion will not occur in the ground state which we are studying. For a total of p such bands, or partial waves, there is a total of p electrons confined near and interacting with the impurity. The magnetic part of the Hamiltonian may be expressed as follows, once all the electrons have been placed in their spatial ground states:

$$H_{\text{mag}} = \sum_{\alpha=1}^{p} \tfrac{1}{2}g_\alpha \vec{\mathbf{S}}\cdot\vec{\sigma}_\alpha$$

in which the g's are calculable functions of the J's (well depths), a's, band structure parameters, etc. The g's can be assumed to be given parameters (and certainly have the same signs as the original couplings constants, the J's), but as they cannot all be presumed to have equal magnitudes, it turns out that the eigenstates of (5) are difficult to obtain in general. As we are not interested in the details of the solutions of (5) but only in the symmetry of the ground state of this effective Hamiltonian, we proceed as follows[7]: Introduce a new model system III, in which g has the same sign as the g's in (5):

$$H_{\text{III}} = \tfrac{1}{2}g\vec{\mathbf{S}}\cdot\left(\sum_{\alpha=1}^{p}\vec{\sigma}_\alpha\right). \tag{6}$$

The ground state of H_{III} is found trivially to belong to total spin $|s\mp\frac{1}{2}p|$. But the ground state of this Hamiltonian is not orthogonal to the ground state of (5), which in turn has the same quantum numbers as the ground state of system I, which we are studying. This completes the proof of the statements in the introduction.

While these results are exact, they may not be useful if at any finite temperature thermal fluctuations destroy the magnetic moment (or lack thereof in the singlet ground state). Suhl has remarked[8] that the spin of the magnetic atom is a needle in the haystack of thermal fluctuations, and others may also be led to question the meaning one can attach to the ground-state spin quantum number. We therefore propose that one should consider only the n electrons in the vicinity of a magnetic atom, the vicinity of the impurity being a large but finite volume which remains fixed as the total volume and $N \to \infty$. The total spin of the metal may indeed be as large as $kTN^{1/2}/E_F$ at finite temperature, but only a fraction n/N of this is localized in the vicinity of the impurity. Thus we must compare the ground-state spins which are of order unity, with the local thermal fluctuations which are merely of order $kTn/N^{1/2}E_F \to 0$ in the limit $N \to \infty$. This qualitative argument indicates that a knowledge of the ground state and elementary excitations of the magnetic impurity and neighboring electrons, such as one seeks in a variational approach,[4] is indeed sufficient to determine the low-temperature properties. Finally, we remark that model system II provides, in fact, a new variational solution of the problem, albeit an extremely crude one compared with the other more detailed calculations.[4] Therefore it would be interesting if an analogous theorem could be proved using the methods of perturbation theory[2,3] or of Green's functions.

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[1]J. Kondo, Progr. Theoret. Phys. (Kyoto) 32, 37 (1964).

[2]A. A. Abrikosov, Physics 2, 5 (1965); H. Suhl, ibid. 2, 39 (1965), and Phys. Rev. 138, A515 (1965); and numerous recent literature. See review by J. Kondo, J. Appl. Phys. 37, 1177 (1966).

[3]S. Silverstein and C. Duke, Phys. Rev. Letters 18, 695 (1967).

[4]J. Kondo, Progr. Theoret. Phys. (Kyoto) 36, 429 (1966); Phys. Rev. 154, 644 (1967); K. Yosida, Progr. Theoret. Phys. (Kyoto) 36, 875 (1966); Phys. Rev. 147, 223 (1966); A. Okiji, Progr. Theoret. Phys. (Kyoto) 36, 712 (1966); A. J. Heeger and M. A. Jensen, Phys. Rev. Letters 18, 488 (1967); J. Kondo, Phys. Rev. 161, 598 (1967). In addition to the preceding variational theories, there is experimental evidence for a singlet ground state given by M. Jensen, A. Heeger, L. Welsh, and G. Gladstone, Phys. Rev. Letters 18, 997 (1967).

[5]The free-electron theory applies to electrons or holes in the conduction band of a real metal provided the de Broglie wavelength of particles at the Fermi surface greatly exceeds the interatomic spacing; otherwise, instead of spherical harmonics, we must use the Kubic harmonics in the partial wave decomposition of the scattering problem. Only those partial waves which belong to the irreducible representations of the point group of the scatterer can interact with the impurity, and if the potential includes only the central cell, only the s wave (Γ_1) will appear; a discussion of this point will be found in J. Callaway, J. Math. Phys. 5, 783 (1964).

[6]E. Lieb and D. Mattis, Phys. Rev. 125, 164 (1962); the appendix of this paper is relevant if we wish to use the Wannier representation of electrons in a conduction band, in which case the coordinates x and y are discrete coordinates labeling the Wannier functions. The kinetic-energy operator for continuum electrons is replaced by an overlap matrix for Wannier functions, and the conditions for our theorem to hold as in the continuum case are that all the overlap matrix elements connecting different sites be real and nonpositive and restricted to nearest neighbors (Ref. 7), so that we may make use of Frobenius' theorem in the Paulion representation.

[7]E. Lieb and D. Mattis, J. Math. Phys. 3, 749 (1962), and D. Mattis, Phys. Rev. 130, 76 (1963), have proved that interacting spin systems have a nodeless ground state when all off-diagonal matrix elements of the Hamiltonian are negative; the ground-state spin may then be determined by comparison with a known reference state which is also nodeless in the representation which renders the off-diagonal elements of the Hamiltonian negative. The present application is a natural generalization of this result to the case when the kinetic energy of electrons carrying the spins must be taken into account. Because the kinetic-energy operator also favors the nodeless ground state it does not change the conclusions, except that in the cases when the discrete nature of the crystal must be taken into account, as discussed in footnote 6, if the overlap matrix extends to distant neighbors or cannot be made negative for nearest neighbors, our theorem cannot be proved.

[8]H. Suhl, discussion remark at U. S.-Japan Cooperative Seminar on Far Infrared Spectroscopy, Columbus, Ohio, September, 1965 (unpublished).