

Effects of Orbital Degeneracy on a Magnetic Impurity in a Nonmagnetic Metal*

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We study the Green's-function equations for a version of the two-orbital Anderson model of a magnetic impurity, in an approximation scheme that displays the logarithmic anomalies and enables the Kondo temperature T_K to be calculated as a function of the parameters. The nature of the solutions is explicitly studied for large Hund's-rule exchange constant J , in which case we obtain the following results: If the internal exchange is treated in the Hartree-Fock approximation, it has the same effect as an enormous applied magnetic field, and the logarithmic resonances are removed far from the Fermi level, i.e., $T_K \rightarrow \infty$. However, if exchange is properly treated in a rotationally invariant manner, the nondiagonal terms cancel most of the effect of the Hartree-Fock terms, and the Kondo effect is restored. For large J , our model has an analog in the far simpler s - d exchange model, as we show by a transformation of the Schrieffer-Wolff type. For small J , however, the complicated and extremely structured solution of equations involving some 24 coupled Green's functions is required, and no substantial simplification appears possible in general. An exception is the limit where the transfer matrix element $V_{kd}=0$, for which we display explicit and exact solutions.

I. INTRODUCTION

THE theory of magnetic impurities in metals based on the semiphenomenological s - d exchange Hamiltonian indicates that most interesting properties, including the logarithmic anomalies that one has to associate with the "Kondo effect," are relatively insensitive to the magnitude of the impurity spin, which appears only through a factor $S(S+1)$ without any way affecting the results qualitatively.¹

This remark is important to remember when one studies a more detailed microscopic picture of a magnetic impurity, such as we have in the Anderson model.² Any transition-series atom has partly occupied degenerate levels, the successive occupation of which leads to the various member atoms of the transition series. Various interactions considered important for electrons in these orbits in (approximate) order of decreasing energies, include: the two-body Coulomb repulsion U , the exchange (Hund's rule) corrections thereto J , crystal-field effects, and spin-orbit coupling. In the case of a transition atom in a metal, two further parameters, the transfer matrix element V_{kd} connecting the localized states to the host Bloch states, and the position of the Fermi level relative to the localized states, must be added to this list, usually somewhere following J in magnitude. This large number of parameters, and the exponentially increasing number of states (4^D) associated with a D -fold degeneracy, leads to bewildering complications when one attempts to extract the thermodynamic and transport properties of the model so as to compare with experiment. In contrast, the s - d Hamiltonian which ignores the internal degrees of freedom, is

almost child's play; for a half-filled shell (D electrons) there are $D+1$ distinct states, associated with the various eigenvalues of S^z . Yet in the free atom, this simple vector model adequately describes the ground multiplet, with spin-orbit and crystal-field effects as relatively minor modifications. Will this pleasant simplification persist in the metal?

Starting with one-orbital impurities, we recall that for this special case a unitary transformation discussed by Schrieffer and Wolff³ established the equivalence (at low energies, which is what concerns us) of the microscopic model to the s - d exchange model with inclusion of additional nonmagnetic scattering. Later agreement between detailed nonperturbative calculations on both these models, to within the trivial nonmagnetic-scattering factor, confirms the essential identity of the two models and the legitimacy of the simplified model.

For more than one orbital, the essential equivalence of the microscopic model to the s - d model is no longer automatic, but depends mostly on the magnitude of the exchange parameter J . However, the very existence of a degeneracy can already be used fruitfully in the experimental interpretation of quasimagnetic atoms, such as the phase-shift analysis given by Klein and Heeger⁴ for their data on (nonmagnetic) Ni in Be. To go quantitatively beyond this, some kind of solution to the Schrödinger equation or to the equivalent Green's-function equations has to be provided, and starting with Anderson's original paper on the subject,⁵ it has been traditional to use the Hartree-Fock approximation thereto. This approximation has the virtues of being simple, while providing a complete picture of the impurity atom in parameter space. Of numerous recent work published on this subject, the most ambitious of which we are aware has been the detailed study by Coqblin and Blandin.⁵ Depending upon the relative

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¹ See J. Kondo, *J. Appl. Phys.* **38**, 1177 (1966); M. Daybell and W. Steyert, *Rev. Mod. Phys.* **40**, 380 (1968).

² P. W. Anderson, *Phys. Rev.* **124**, 41 (1961).

³ J. R. Schrieffer and P. A. Wolff, *Phys. Rev.* **149**, 491 (1966).

⁴ A. Klein and A. Heeger, *Phys. Rev.* **144**, 458 (1966).

⁵ B. Coqblin and A. Blandin, *Advan. Phys.* (to be published).

magnitudes of the various parameters, these authors find solutions corresponding to nonmagnetic state, spin magnetism with quenched orbital magnetism, and ultimately spin and orbital magnetism. The transitions from one case to the other may be first or second order in the quasithermodynamic parameter-space diagrams. But it should be pointed out that regardless of the correctness of their results, which cannot be underestimated owing to the success of the Hartree-Fock scheme in most atomic-structure calculations, this sort of scheme misses the essential rotational symmetries of the problem (in real and spin spaces) and consequently misses the Kondo anomalies, which are surely primarily the result of rotational degeneracy. Therefore, the work of Coqblin and Blandin does not provide any useful predictions about the "logarithmic fine structure" of the interacting atom in the metal.

The present paper is intended to bridge the gap between the detailed quantum-mechanical studies of the one-orbital problem⁶⁻⁸ and the multiparameter-space studies of the multiorbital atom. We are essentially concerned with the effects of Coulomb and Hund's-rule exchange energies on the very-low-energy electron correlations responsible for the Kondo effect. To achieve this delicate calculation, we must resort to a model which might be criticized as somewhat artificial, as we discuss in the following pages. Our excuse is that we wish to be able to solve the model, as we might not otherwise have been able to do. Our reward has been the following deductions, the validity of which may transcend the limits of the present model and the (necessarily) limited accuracy of our solution.

We find that if, as has been customary, one treats exchange terms by the Hartree-Fock method, the diagonal part of the exchange acts essentially as an applied static magnetic field of enormous magnitude; the Zeeman splitting correspond in magnitude to atomic energies, i.e., is of the order of megagauss in magnetic units. Such fields are more than sufficient to wipe out all logarithmic singularities associated with the magnetic impurity. If, on the other hand, the full exchange interaction is treated in a rotationally invariant manner, the tremendous effects of the diagonal terms are almost precisely cancelled by the nondiagonal terms.

For arbitrary values of the exchange coupling constant, the problem is still inordinately difficult to solve. However, for sufficiently large J ,

$$|J| > \frac{2}{3}\sqrt{3}|E|$$

(where E is the energy of the magnetic orbitals relative to the Fermi level), the results simplify greatly and one recovers resonances in the Green's functions analogous to those which give the Kondo effect for a single or-

bital, excepting for changes in certain factors no more serious than $S(S+1)$. Within the context of our stated model, we thus demonstrate the necessity of treating exchange in a rotationally invariant manner. However, the difficulty of doing this for more general Hamiltonians or in more sophisticated Green's function decoupling schemes may be a bar to ever understanding the multiorbital impurity in the same detail as the one-orbital model. For this reason, in the discussion of Sec. III we try to establish a connection between the two-orbital model and the s - d exchange model with $S=1$, the latter being more readily analyzed in many cases.

The paper is organized in the following manner: In Sec. II the existence of certain poles in the Green functions is related to T_K . In Sec. III our model Hamiltonian is postulated, a proof that it follows from the Anderson model is given and a correspondence with the s - d model established. In Sec. IV the exact solution of the Green's-function equations of motion is given, and the Hartree-Fock approximation is compared thereto, both in the special case of an isolated atom ($V_{kd}=0$). With Hund's rule exchange treated in the Hartree-Fock approximation, the effects of the band-mixing matrix element V_{kd} are calculated and shown in Sec. V to result (improperly) in $T_K \rightarrow \infty$. With Hund's rule treated exactly, the correct T_K is found in Sec. VI.

II. ANOMALOUS RESONANCES AND ANDERSON HAMILTONIAN

Kim⁷ has previously solved the Anderson model in an approximation which leads to the appearance of "anomalous" resonances near the Fermi surface in the neighborhood of a temperature T_K , called the Kondo temperature. He finds that these resonances are responsible for the well-known anomalous behavior in the transport and thermodynamic properties. We will briefly discuss a related treatment of the problem.

The Anderson Hamiltonian takes the form

$$H = H_0 + H_{s-d} + H_{\text{Coul}}, \quad (2.1)$$

where

$$H_0 = \sum_{\mathbf{k},s} \epsilon_{\mathbf{k}} n_{\mathbf{k}s} + \sum_s E n_{d,s},$$

$$H_{\mathbf{k}-d} = \sum_{\mathbf{k},s} V_{\mathbf{k}} (c_{\mathbf{k}s}^\dagger d_s + d_s^\dagger c_{\mathbf{k}s}), \quad (2.2)$$

$$H_{\text{Coul}} = U n_{d\uparrow} n_{d\downarrow}.$$

The first term in H_0 is the unperturbed band energy in which $n_{\mathbf{k}s} = c_{\mathbf{k}s}^\dagger c_{\mathbf{k}s}$ is the number operator for a band electron of wave vector \mathbf{k} , spin s , and energy $\epsilon_{\mathbf{k}}$ measured from the Fermi surface. The second term in H_0 is the unperturbed energy for a single localized d orbital in which $n_{d,s} = d_s^\dagger d_s$ is the number operator for an orbital electron of energy E and spin s . E , which is also mea-

⁶ Going beyond the Hartree-Fock approximation of Ref. 2, e.g., J. R. Schrieffer and D. C. Mattis, Phys. Rev. **140**, 455 (1966).

⁷ D. J. Kim, Phys. Rev. **146**, 455 (1966).

⁸ L. Dworin, Phys. Rev. **164**, 818 (1967); **164**, 841 (1967); Alba Theumann, *ibid.* (to be published).

sured from the Fermi surface, is negative for the cases of interest. H_{k-d} represents mixture of the band and the localized d electrons, V_k being the electron transfer matrix element. Finally, H_{Coul} represents the Coulomb energy U between electrons situated on the localized d orbital.

We utilize the Green's-function formalism of Zubarev⁹ in which the retarded Green's function for two operators $A(t)$ and $B(t)$ is defined by:

$$\langle\langle A(t); B(t') \rangle\rangle = -i\theta(t-t')\langle[A(t), B(t')]_+\rangle, \quad (2.3)$$

where $\langle \rangle$ denotes the statistical average taken with respect to a grand canonical ensemble. $\langle\langle A(t); B(t') \rangle\rangle$ may be determined from the differential equation

$$i\frac{\partial}{\partial t}\langle\langle A(t); B(t') \rangle\rangle = \langle[A(t), B(t)]_+\rangle\delta(t-t') + \langle\langle[A(t), H(t)]_-; B(t') \rangle\rangle. \quad (2.4)$$

Averages are then calculated from the relation

$$\langle B(t)A(t) \rangle = -2\int_{-\infty}^{\infty} d\omega f(\omega) \text{Im}\langle\langle A; B \rangle\rangle_{\omega+i0^+}, \quad (2.5)$$

in which $f(\omega)$ is the usual Fermi function and $\langle\langle A; B \rangle\rangle_{\omega+i0^+}$ is the Fourier transform of the Green's function with respect to $t-t'$ and with ω replaced by $\omega+i0^+$ in order to properly handle the singularity in the Fourier transform. We will henceforth always display our equations in terms of Fourier transforms and will omit the ω subscript in the remainder of the paper.

The relevant Green's function in the analysis is $\langle\langle d_{\uparrow}; d_{\uparrow}^{\dagger} \rangle\rangle$. As can be seen from (2.4), d_{\uparrow}^{\dagger} will appear to the right of the semicolon in all Green's functions arising from the differential equation. For simplicity we will then make the notational simplification

$$\langle\langle \dots; d_{\uparrow}^{\dagger} \rangle\rangle \rightarrow \langle\langle \dots \rangle\rangle. \quad (2.6)$$

Starting with $\langle\langle d_{\uparrow}^{\dagger} \rangle\rangle$ using (2.4), we find the set of equations

$$\begin{aligned} (\omega - E - \Lambda)\langle\langle d_{\uparrow}^{\dagger} \rangle\rangle &= 1/2\pi + U\langle\langle n_{d\uparrow} d_{\uparrow} \rangle\rangle \\ (\omega - E - U)\langle\langle n_{d\uparrow} d_{\uparrow} \rangle\rangle &= \frac{\langle n_{d\uparrow} \rangle}{2\pi} + \sum_k V_k \\ &\times \{ \langle\langle c_{k\uparrow} n_{d\uparrow} \rangle\rangle + \langle\langle d_{\uparrow} d_{\uparrow}^{\dagger} c_{k\uparrow} \rangle\rangle - \langle\langle d_{\uparrow} c_{k\uparrow}^{\dagger} d_{\uparrow} \rangle\rangle \}. \end{aligned} \quad (2.7)$$

Denoting the three Green's functions in brackets by g_{1k} , g_{2k} , and g_{3k} , we find

⁹ D. N. Zubarev, Usp. Fiz. Nauk **71**, 71 (1960) [English transl.: Soviet Phys.—Usp. **3**, 320 (1960)].

$$\begin{aligned} (\omega - \epsilon_k)g_{1k} &= V_k\langle\langle n_{d\uparrow} d_{\uparrow} \rangle\rangle + \sum_{k'} V_{k'} \{ \langle\langle c_{k\uparrow} d_{\uparrow}^{\dagger} c_{k'\uparrow} \rangle\rangle \\ &\quad - \langle\langle c_{k\uparrow} c_{k'\uparrow}^{\dagger} d_{\uparrow} \rangle\rangle \} \\ (\omega - \epsilon_k)g_{2k} &= \frac{1}{2\pi} \langle d_{\uparrow}^{\dagger} c_{k\uparrow} \rangle + \sum_{k'} V_{k'} \{ \langle\langle c_{k'\uparrow} d_{\uparrow}^{\dagger} c_{k\uparrow} \rangle\rangle \\ &\quad + \delta_{k,k'} \langle\langle n_{d\uparrow} d_{\uparrow} \rangle\rangle - \langle\langle d_{\uparrow} c_{k\uparrow}^{\dagger} c_{k\uparrow} \rangle\rangle \} \\ (\omega + \epsilon_k - 2E - U)g_{3k} &= \frac{1}{2\pi} \langle c_{k\uparrow}^{\dagger} d_{\uparrow} \rangle + \sum_{k'} V_{k'} \{ \langle\langle c_{k'\uparrow} c_{k\uparrow}^{\dagger} d_{\uparrow} \rangle\rangle \\ &\quad - \delta_{k,k'} \langle\langle n_{d\uparrow} d_{\uparrow} \rangle\rangle + \langle\langle d_{\uparrow} c_{k\uparrow}^{\dagger} c_{k\uparrow} \rangle\rangle \}, \end{aligned} \quad (2.8)$$

where

$$\begin{aligned} \Lambda(\omega) &= \sum_k \frac{V_k^2}{\omega - \epsilon_k} \xrightarrow{\omega \rightarrow \omega + i0^+} \text{Re}\Lambda + i\Gamma, \\ \Gamma &\approx \pi N(0) |V_k|^2. \end{aligned} \quad (2.9)$$

The approach used to decouple these equations is a so-called "high-density" approximation whose validity rests on the parameter V_k being sufficiently small. It is the opposit limit to that considered by Schrieffer and Mattis.⁶ The exact decoupling scheme utilized here is the following: a Green's function containing two band operators is replaced by the expectation value of these operators multiplied by the resultant Green's function with the two operators removed. The expectation value is taken with respect to the noninteracting ($V_k=0$) Hamiltonian. As an example,

$$\langle\langle d_{s_1} c_{k s_2}^{\dagger} c_{k' s_3} \rangle\rangle \rightarrow \delta_{k,k'} \delta_{s_2, s_3} f(\epsilon_k) \langle\langle d_{s_1} \rangle\rangle. \quad (2.10)$$

Making this decoupling, and solving the resulting set of equations, one finds

$$\begin{aligned} \langle\langle d_{\uparrow} \rangle\rangle &= \frac{1}{2\pi} \left(\frac{1 - \langle n_{d\uparrow} \rangle + F(\omega) [U/(U + \bar{E} - \omega)]}{\omega - E - \Lambda - K(\omega) [U/(U + \bar{E} - \omega)]} \right) \\ \langle\langle n_{\uparrow} d_{\uparrow} \rangle\rangle &= \frac{1}{2\pi} \left(\frac{\langle n_{d\uparrow} \rangle + F(\omega) - 2\pi K(\omega) \langle\langle d_{\uparrow} \rangle\rangle}{\omega - \bar{E} - U} \right), \end{aligned} \quad (2.11)$$

where

$$\begin{aligned} \bar{E} &= E + 2\Lambda(\omega) - \Lambda(U + 2E - \omega) \\ F(\omega) &= \sum_k V_k \left(\frac{\langle d_{\uparrow}^{\dagger} c_{k\uparrow} \rangle}{\omega - \epsilon_k} + \frac{\langle c_{k\uparrow}^{\dagger} d_{\uparrow} \rangle}{U + 2E - \omega - \epsilon_k} \right) \\ K(\omega) &= \sum_k |V_k|^2 f(\epsilon_k) \left(\frac{1}{\omega - \epsilon_k} - \frac{1}{U + 2E - \omega - \epsilon_k} \right) \\ &\sim -\frac{\Gamma}{\pi} \ln \frac{|U + 2E - \omega|}{[\omega^2 + (kT)^2]^{1/2}} + i\Gamma f(\omega) \end{aligned} \quad (2.12)$$

and we have replaced ω by $\omega+i0^+$ in the last expression for $k(\omega)$. The explicit evaluation of the integral is discussed in Sec. VI.

Rather than review the calculation of the transport and thermodynamic properties, we will limit ourselves

to a discussion of the anomalous resonances. This will be sufficient for our needs since we are interested in the effect of degeneracy on the relevant physical quantities and, as we have already mentioned, this behavior is governed by the anomalous resonances.

Taking U large—but not infinite, since it enters logarithmically into $K(\omega)$ —both for simplicity and for the reason that it corresponds to the physically most interesting case, we obtain for the denominator of $\langle\langle d_1 \rangle\rangle$

$$\omega - E - \text{Re}\Lambda - \frac{\Gamma}{\pi} \ln \frac{|U+2E|}{[\omega^2 + (kT)^2]^{1/2}} - i\Gamma(1+f(\omega)). \quad (2.13)$$

The anomalous resonances occur for values of this expression near zero. Since Γ is a small quantity, the expression will be small when the logarithmic term is of order of E . This will occur for small ω . (The denominator is also small for $\omega \sim E$. This, however, corresponds to the unperturbed d orbital and is not important in calculating the anomalous behavior.) In order to approximately locate the resonances, we will set the real part of the expression equal to zero for ω along the real axis. Ignoring ω with respect to E , we are led to the equation

$$\omega^2 + (kT)^2 = |U+2E| e^{-\pi|E|/|\Gamma|} \equiv U e^{-\pi|E|/\Gamma} \equiv (kT_K)^2. \quad (2.14)$$

This equation, which defines the Kondo temperature T_K , has no real solutions for $kT > kT_K$. Below T_K a pair of resonances, situated symmetrically about the Fermi surface and separated by a distance of $\Delta\omega = 2[(kT_K)^2 - (kT)^2]^{1/2}$ occur. A detailed calculation shows the resonance widths can be less than the distance between resonances.

Had we included a magnetic field in the original Hamiltonian ($E \rightarrow E - mh$, $m = \pm 1$), (2.14) would be replaced by

$$(\omega - 2mh)^2 + (kT)^2 = (kT_K)^2. \quad (2.15)$$

The effect of the field is to shift the “center of gravity” of the resonances with respect to the Fermi surface. A field of sufficient strength to drive the resonances out of the region lying within kT_K of the Fermi surface will result in the loss of anomalous behavior by the system.

To complete this section we would like to mention that a paper by Dworin⁸ has recently appeared, in which the analysis is carried out to very high order. Some features, such as the value of T_K [see (2.14)], are qualitatively unaffected by the higher-order corrections, i.e., remain unchanged within a factor of 2, whereas other details (specific heat, magnetic susceptibility, and resistivity) appear to depend on the ultimate order to which the calculation is carried out. A nonperturbative extension of Eqs. (2.7)–(2.12) has been solved exactly by Theumann,⁹ with results that also appear to have a self-consistent validity at all temperatures, and which reduce essentially to the present solution above T_K . But these more complex equations are, in every case, very difficult to extend to the multiorbital model in the manner that we have found it possible to extend the simpler procedure discussed herein.

III. DERIVATION AND CRITIQUE OF MODEL HAMILTONIAN

We demonstrate in this section that the model Hamiltonian discussed in the Introduction follows under certain conditions from a direct generalization of the single-orbital model considered by Anderson.² The generalized Anderson model takes the form

$$H = H_0 + H_{kd} + H_{\text{Coul}} + H_{\text{ex}}, \quad (3.1)$$

where

$$\begin{aligned} H_0 &= \sum_{\mathbf{k}, s} \epsilon_{\mathbf{k}} n_{\mathbf{k}, s} + \sum_{\alpha, s} E n_{\alpha, s} \\ H_{k-d} &= \sum_{\mathbf{k}, \alpha} V_{\mathbf{k}, \alpha} (c_{\mathbf{k}s}^\dagger c_{\alpha, s} + c_{\alpha, s}^\dagger c_{\mathbf{k}, s}) \\ H_{\text{Coul}} &= U \sum_{\substack{\alpha < \alpha' \\ s, s'}} n_{\alpha, s} n_{\alpha', s'} \\ H_{\text{ex}} &= -2J[\mathbf{S}_1 \cdot \mathbf{S}_2 + \frac{1}{4}(n_{1\uparrow} + n_{1\downarrow})(n_{2\uparrow} + n_{2\downarrow})]. \end{aligned} \quad (3.2)$$

The first term in H_0 is the unperturbed band energy in which $n_{\mathbf{k}s} = c_{\mathbf{k}s}^\dagger c_{\mathbf{k}s}$ is the number operator for a band electron of wave vector \mathbf{k} , spin s , and energy $\epsilon_{\mathbf{k}}$ measured from the Fermi level. The second term in H_0 is the unperturbed energy for the degenerate d orbitals in which $n_{\alpha, s} = c_{\alpha, s}^\dagger c_{\alpha, s}$ is the number operator for an orbital electron in orbital α ($\alpha = 1, 2$), spin s , and energy E . The energy, which is also measured from the Fermi level, will be negative for the cases of interest. H_{k-d} represents the mixing of band and localized electrons, $V_{\mathbf{k}\alpha}$ being the electron transfer matrix element. H_{Coul} represents the Coulomb repulsion U between electrons situated on the localized d orbitals. H_{ex} represents the intra-atomic exchange coupling between the localized orbitals. J , which will always be positive, is the exchange constant, while \mathbf{S}_1 and \mathbf{S}_2 are the spin- $\frac{1}{2}$ operators expressed in second quantized form for the two d orbitals.

We now make an approximation, which, although rather restrictive in nature, considerably simplifies the Hamiltonian while retaining many of its important characteristics. We assume that $V_{\mathbf{k}, \alpha}$ is independent of α . What is implied by this approximation may be seen by noting the identity

$$\begin{aligned} \sum_{\mathbf{k}} \frac{V_{\mathbf{k}\alpha} V_{\mathbf{k}\alpha'}}{\omega - \epsilon_{\mathbf{k}}} &= \sum_{\mathbf{k}} \langle \alpha | V(\omega - H_{\text{Bloch}})^{-1} V | \alpha' \rangle \\ &= \delta_{\alpha, \alpha'} \sum_{\mathbf{k}} \frac{|V_{\mathbf{k}, \alpha}|^2}{\omega - \epsilon_{\mathbf{k}}}, \end{aligned} \quad (3.3)$$

which holds if $|\alpha\rangle$ and $|\alpha'\rangle$ are different members of a representation of the symmetry group of the operator $V(\omega - H_{\text{Bloch}})^{-1} V$. For example, if we assume our system is isotropic with the exception of $V = V(r)$, then $|\alpha\rangle$ and $|\alpha'\rangle$ would correspond to the ordinary spherical harmonics and the theorem would obviously hold. Our assumption is then essentially either that our two orbitals have the same symmetry, or that $V_{\mathbf{k}, \alpha}$ is independent of \mathbf{k} , a common approximation.

Writing

$$V_{k1} = V_{k2} = V_k \quad (3.4)$$

and introducing the canonical transformation

$$c_{1s} = \frac{d_{1s} + d_{2s}}{\sqrt{2}}, \quad c_{2s} = (d_{1s} - d_{2s})/\sqrt{2} \quad (3.5)$$

our Hamiltonian becomes

$$H = H_0 + H_{k-d} + H_{ex} + H_{Coul}, \quad (3.6)$$

where

$$\begin{aligned} H_0 &= \sum_{k,s} \epsilon_k n_{ks} + \sum_{\alpha,s} E n_{\alpha,s} \\ H_{Coul} &= U [n_{1\uparrow} n_{1\downarrow} + n_{2\uparrow} n_{2\downarrow} + n_{1\uparrow} (n_{2\uparrow} + n_{2\downarrow}) \\ &\quad + n_{1\downarrow} (n_{2\uparrow} + n_{2\downarrow})] \\ H_{k-d} &= \sum_{k,s} \sqrt{2} V_k (c_{ks}^\dagger d_{1s} + d_{1s}^\dagger c_{ks}) \\ H_{ex} &= -J \left[\frac{1}{2} (s_1^+ s_2^- + s_2^- s_1^+) - \frac{1}{2} (n_{1\uparrow} n_{1\downarrow} + n_{2\uparrow} n_{2\downarrow}) \right. \\ &\quad \left. + n_{1\downarrow} (n_{2\downarrow} + \frac{1}{2} n_{2\uparrow}) + n_{1\uparrow} (n_{2\uparrow} + \frac{1}{2} n_{2\downarrow}) \right. \\ &\quad \left. - \frac{1}{2} (d_{1\uparrow}^\dagger d_{1\downarrow}^\dagger d_{2\uparrow}^\dagger d_{2\downarrow}^\dagger + d_{1\downarrow}^\dagger d_{1\uparrow}^\dagger d_{2\downarrow}^\dagger d_{2\uparrow}^\dagger) \right], \end{aligned} \quad (3.7)$$

where 1 and 2 and n refer to the new orbitals.

Notice that in the new representation the second orbital now has no matrix elements connecting it directly to the band. Furthermore, a state with one particle in the second orbital is not connected by the Hamiltonian to states with zero or two particles in that orbital. The states with even occupancy of the second orbital are not affected by the dynamic exchange terms in the new representation and their study is identical to the one-orbital model. In the remainder of this section we will specialize to the nontrivial case, in which the second orbital is singly occupied, so that $n_{2\uparrow} + n_{2\downarrow} = 1$.

Proceeding with the calculation, we have for H_{Coul}

$$H_{Coul} = U n_{1\uparrow} n_{1\downarrow} + U (n_{1\uparrow} + n_{1\downarrow}), \quad (3.8)$$

an easily interpretable result. Secondly, within our permitted subspace

$$H_{orb2} = E (n_{2\uparrow} + n_{2\downarrow}) = E, \quad (3.9)$$

a constant. Finally, after a somewhat longer calculation H_{ex} becomes

$$H_{ex} = -J \left[\frac{3}{4} (n_{1\uparrow} + n_{1\downarrow}) - \frac{1}{2} n_{1\uparrow} n_{1\downarrow} + \mathbf{s}_1 \cdot \mathbf{s}_2 \right]. \quad (3.10)$$

The first group of terms renormalize H_{Coul} and H_{orb} . If we now represent the spin operators on the second orbital by Pauli spin operators, we can write our complete model Hamiltonian in the form

$$\begin{aligned} H &= E + \sum_s \hat{E} n_{1s} + \sum_k \tilde{V}_k (c_{ks}^\dagger d_{1s} + d_{1s}^\dagger c_{ks}) + \bar{U} n_{1\uparrow} n_{1\downarrow} \\ &\quad - \bar{J} s_2^+ d_{1\downarrow}^\dagger d_{1\uparrow} - \bar{J} s_2^- d_{1\uparrow}^\dagger d_{1\downarrow} - \bar{J} s_2^z (n_{1\uparrow} - n_{1\downarrow}), \end{aligned} \quad (3.11)$$

where

$$= E + U - \frac{3}{4} J \hat{E}, \quad \tilde{V}_k = \sqrt{2} V_k, \quad \bar{V} = U + \frac{1}{2} J, \quad \bar{J} = \frac{1}{2} J. \quad (3.12)$$

In the future we will drop the constant and omit the bars, carets, etc., from the renormalized energies and the orbital subscripts from the d orbital. With these changes (3.11) is the model Hamiltonian we will consider in the paper. It is precisely Anderson's single-orbital Hamiltonian *augmented by an intra-atomic exchange term to account for orbital degeneracy*.

A few comments are now required to place this model Hamiltonian into suitable context. The principal approximation is the assumed constancy of V_{kd} , difficult to justify for the usual orbital symmetries and band structures, but essential if one wishes to simplify the equations sufficiently to arrive at a formal solution. Having made this approximation, we find it leads to certain unexpected advantages. For example, the valency of the impurity, Z , has the values $Z=0$ and $Z=\pm 1$ only, so that the *excess* electrostatic energy is small in all accessible configurations; this is compatible with Van Vleck's criterion¹⁰ of "minimum polarity," whereas a nonconstant V_{kd} allowing $Z=\pm 2$ is not. Our assumption also enables a correspondence to be drawn between the microscopic model and the more widely investigated semiphenomenological s - d exchange model, as we now do by extending the method of Schrieffer and Wolff.³

We separate the Hamiltonian of (3.11) into two parts: the Hamiltonian of the isolated atom H_A and the mixing term H_{kd} . The latter connects states of even occupation of the impurity with states of odd occupation, and vice-versa, but never even with even or odd with odd. Thus let Ψ , an eigenfunction of the total H with eigenvalue ω , be written $\Psi = \phi + \chi$, where ϕ is even in impurity occupation number and χ is odd. Thus,

$$(H_A - \omega)\phi + H_{kd}\chi = 0 \quad (3.13)$$

and

$$(H_A - \omega)\chi + H_{kd}\phi = 0.$$

Solving either equation and inserting into the other, we find a new eigenvalue equation

$$\left(H_A - H_{kd} \frac{1}{H_A - \omega} H_{kd} - \omega \right) \xi = 0 \quad (3.14)$$

in which ξ stands for an arbitrary linear combination of ϕ and χ , such as the ground state Ψ^0 itself. For small V_k the true ground-state energy will not differ much from the ground state of H_A , denoted E_A , so we may use the preceding to construct an effective Hamiltonian,

$$H_{\text{eff}} = H_A - H_{kd} \frac{1}{H_A - E_A} H_{kd}.$$

The interactions in this Hamiltonian include a velocity-dependent s - d antiferromagnetic exchange potential and a spin-independent scattering potential. In the single-orbital case, the above coincides exactly with the results of Schrieffer and Wolff,³ which were derived from slightly

¹⁰ J. H. Van Vleck, Rev. Mod. Phys. **25**, 220 (1953).

different considerations. In the case of interest the excitation spectrum which determines the denominator in (3.15) becomes rather complicated, except in the limit of large J and even larger U , compared to the other parameters, where the low-lying excitations are $O(J)$; thus the effective s - d coupling constant should be $O(V^2/J)$, and $T_K \sim U e^{-\pi J/U}$. But, as we shall see, while roughly agreeing with these estimates, the actual calculation includes some numerical factors which it would be difficult to anticipate at this point [cf. Eq. (6.27)].

IV. EXACT SOLUTION FOR ISOLATED ATOM

While our general objective in this paper is to study the effect of the host metal on the isolated atom, it is imperative for us to first understand the behavior of the isolated atom. In particular, in order that we might better understand the modifications brought about by the host, we are concerned with the form and interpretation of the relevant Green's functions for $V_k=0$. We consider two subclasses: (a) $S^z S^z$ exchange terms only, and (b) complete $\mathbf{S} \cdot \mathbf{S}$ exchange. Fortunately, both cases are exactly soluble.

(a) $V_k=0$, $S^z S^z$ terms only. From (2.3) and (3.11) we find for the Green's function $\langle\langle d_\uparrow \rangle\rangle$ and the associated Green's functions the exact set of equations

$$\begin{aligned} \chi \langle\langle d_\uparrow \rangle\rangle &= 1/2\pi + U \langle\langle n_\uparrow d_\uparrow \rangle\rangle - J \langle\langle s^z d_\uparrow \rangle\rangle, \\ (\chi - U) \langle\langle n_\uparrow d_\uparrow \rangle\rangle &= \langle n_\uparrow \rangle / 2\pi - J \langle\langle s^z n_\uparrow d_\uparrow \rangle\rangle, \\ \chi \langle\langle s^z d_\uparrow \rangle\rangle &= \langle s^z \rangle / 2\pi + U \langle\langle s^z n_\uparrow d_\uparrow \rangle\rangle \\ &\quad - \frac{1}{4} J \langle\langle d_\uparrow \rangle\rangle, \\ (\chi - U) \langle\langle s^z n_\uparrow d_\uparrow \rangle\rangle &= \langle s^z n_\uparrow \rangle / 2\pi - \frac{1}{4} J \langle\langle n_\uparrow d_\uparrow \rangle\rangle, \end{aligned} \quad (4.1)$$

where

$$\chi = \omega - E. \quad (4.2)$$

If we solve these equations, we find without approximation

$$\begin{aligned} \langle\langle d_\uparrow \rangle\rangle &= \frac{1}{4\pi} \left(\frac{1 - \langle n_\uparrow \rangle - 2\langle s^z n_\uparrow \rangle + 2\langle s^z \rangle}{\chi + \frac{1}{2}J} \right. \\ &\quad + \frac{1 - \langle n_\uparrow \rangle + 2\langle s^z n_\uparrow \rangle - 2\langle s^z \rangle}{\chi - \frac{1}{2}J} + \frac{\langle n_\uparrow \rangle + 2\langle s^z n_\uparrow \rangle}{\chi - U + \frac{1}{2}J} \\ &\quad \left. + \frac{\langle n_\uparrow \rangle - 2\langle s^z n_\uparrow \rangle}{\chi - U - \frac{1}{2}J} \right), \end{aligned} \quad (4.3)$$

with similar expressions for the other Green's functions.

We can find a similar expression for $\langle\langle d_\downarrow \rangle\rangle$ merely by letting $S^z \rightarrow -S^z$. In order to obtain a complete solution to the equations, we need $\langle s^z n_\uparrow \rangle$, of course, which can be readily obtained from the Green's function $\langle\langle s^z d_\uparrow \rangle\rangle$. From symmetry it is clear that $\langle s^z \rangle = 0$. We therefore have an exact solution to the set of equations. Rather than discussing the explicit form of $\langle\langle d_\uparrow \rangle\rangle$ given above, we note that in the absence of dynamic terms, S^z is a good quantum number, so that we can solve our equations for $S^z = \pm \frac{1}{2}$. Quantities of interest

may then be obtained by taking appropriate averages of the two solutions. Calculation is greatly simplified in this case since the third equation reduced to the first and the fourth to the second. If we solve the $S^z = \frac{1}{2}$ set, we find

$$\begin{aligned} \langle\langle d_\uparrow \rangle\rangle &= \frac{1}{2\pi} \left(\frac{1 - \langle n_\uparrow \rangle}{\chi + \frac{1}{2}J} + \frac{\langle n_\uparrow \rangle}{\chi - U + \frac{1}{2}J} \right), \\ \langle\langle d_\downarrow \rangle\rangle &= \frac{1}{2\pi} \left(\frac{1 - \langle n_\uparrow \rangle}{\chi - \frac{1}{2}J} + \frac{\langle n_\uparrow \rangle}{\chi - U - \frac{1}{2}J} \right). \end{aligned} \quad (4.4)$$

These expressions are easily interpreted. The pole at $\omega = E - \frac{1}{2}J$ corresponds to adding a particle in the first orbital parallel to the fixed particle in the second orbital in the absence of a particle in n_\uparrow . The spectral density $1 - \langle n_\uparrow \rangle$ reflects that if there is a particle in n_\uparrow , then the pole is given by $\omega = E + U - \frac{1}{2}J$. The poles of $\langle\langle d_\downarrow \rangle\rangle$ correspond to a particle antiparallel to that of the second orbital and thus differ in the sign of J from $\langle\langle d_\uparrow \rangle\rangle$.

(b) $V_k=0$, complete $\mathbf{S} \cdot \mathbf{S}$ exchange. In this case we include the dynamic terms S^+ and S^- . The resulting set of equations have far more structure than in the previous case, but fortunately is still exactly soluble. After some calculation, one finds

$$\begin{aligned} \langle\langle d_\uparrow \rangle\rangle &= \frac{1}{8\pi} \left\{ \frac{3 - 3\langle n_\uparrow \rangle - 6\langle s^z n_\uparrow \rangle}{\chi + \frac{1}{2}J} \right. \\ &\quad + \frac{1 - \langle n_\uparrow \rangle + 6\langle s^z n_\uparrow \rangle}{\chi - \frac{3}{2}J} + \frac{3\langle n_\uparrow \rangle - 6\langle s^z n_\uparrow \rangle}{\chi - U - \frac{1}{2}J} \\ &\quad \left. + \frac{\langle n_\uparrow \rangle + 6\langle s^z n_\uparrow \rangle}{\chi - U + \frac{3}{2}J} \right\} \\ \langle\langle s^z d_\uparrow \rangle\rangle &= \frac{1}{2} \langle\langle s^- d_\downarrow \rangle\rangle = \frac{1}{16\pi} \left(\frac{1 - \langle n_\uparrow \rangle - 2\langle s^z n_\uparrow \rangle}{\chi + \frac{1}{2}J} \right. \\ &\quad + \frac{-1 + \langle n_\uparrow \rangle - 6\langle s^z n_\uparrow \rangle}{\chi - \frac{3}{2}J} - \frac{\langle n_\uparrow \rangle + 2\langle s^z n_\uparrow \rangle}{\chi - U - \frac{1}{2}J} \\ &\quad \left. + \frac{\langle n_\uparrow \rangle + 6\langle s^z n_\uparrow \rangle}{\chi - U + \frac{3}{2}J} \right) \\ \langle\langle n_\uparrow d_\uparrow \rangle\rangle &= \frac{1}{8\pi} \left(\frac{3\langle n_\uparrow \rangle - 6\langle s^z n_\uparrow \rangle}{\chi - U - \frac{1}{2}J} + \frac{\langle n_\uparrow \rangle + 6\langle s^z n_\uparrow \rangle}{\chi - U + \frac{3}{2}J} \right) \\ \langle\langle s^z n_\uparrow d_\uparrow \rangle\rangle &= \frac{1}{2} \langle\langle s^- n_\downarrow d_\downarrow \rangle\rangle = \frac{1}{16\pi} \left\{ \frac{2\langle s^z n_\uparrow \rangle - \langle n_\uparrow \rangle}{\chi - U - \frac{1}{2}J} \right. \\ &\quad \left. + \frac{6\langle s^z n_\uparrow \rangle + \langle n_\uparrow \rangle}{\chi - U + \frac{3}{2}J} \right\} \end{aligned} \quad (4.5)$$

for the relevant Green's function.

It will be fruitful for us to discuss these results in some detail. We will begin by examining the poles of the Green's function. If we let $|0\rangle$, the vacuum state, corre-

spond to the case in which no electrons are present in the first orbital, while the spin of the fixed electron in the second orbital is down, then the triplet-up state, which corresponds to adding an electron to the impurity level parallel to the fixed electron, can be represented by the eigenvector

$$|\psi_1\rangle = d_\uparrow^\dagger s^\dagger |0\rangle, \quad (4.6)$$

which is an eigenstate of the Hamiltonian corresponding to the energy $E - \frac{1}{2}J$ and hence gives rise to a pole at $\omega = E - \frac{1}{2}J$. For this triplet state and also for the triplet state with $S_{\text{tot}}^z = -1$, the dynamic terms do not contribute to the energy and the poles are found at the same locations as in the preceding example (S^z components only). The remaining triplet may be represented by the eigenvector

$$|\psi_2\rangle = \frac{1}{\sqrt{2}}(d_\downarrow^\dagger s^\dagger |0\rangle + d_\uparrow^\dagger |0\rangle). \quad (4.7)$$

Although in this case the dynamic terms do contribute to the calculation of the energy, we find that all triplet states give rise to the same energies, as would be expected.

The singlet state, represented by the eigenvector

$$|\psi_3\rangle = \frac{1}{\sqrt{2}}(d_\downarrow^\dagger s^\dagger |0\rangle - d_\uparrow^\dagger |0\rangle), \quad (4.8)$$

gives us our first new result. The energy is $E + \frac{3}{2}U$, with the corresponding pole $\omega = E + \frac{3}{2}J$. For positive J the triplet state therefore has the lowest energy.

The final state, which is represented by the eigenstate

$$|\psi_4\rangle = d_\downarrow^\dagger d_\uparrow^\dagger s^\dagger |0\rangle, \quad (4.9)$$

is in many ways the most interesting. It represents the situation in which an electron is added to the impurity level given that an electron is already present in the level. Although the energy of the state is $U + 2E$, we remember that a pole of the Green's function represents the change in energy of the system upon the addition of an electron, so that this process will give rise to two poles, one if we are initially in the singlet state and another if we are in the triplet. For the triplet state we find $\omega = U + E + \frac{1}{2}J$ and for the singlet $\omega = U + E - \frac{3}{2}J$.

To gain some understanding of the spectral density we will consider the specific case $T \rightarrow 0$, $U \rightarrow \infty$. In this limit the self-consistency equations are easily solved. For $J > 0$ we find $\langle n_\downarrow \rangle = \frac{1}{2}$ and $\langle s^z n_\downarrow \rangle = -\frac{1}{4}$. The $\langle s^z n_\downarrow \rangle = -\frac{1}{4}$ is exactly the result we would obtain if we averaged the operator $S^z n_\downarrow$ over the three triplet states, omitting the singlet and the state of double occupancy. In addition the spectral density "coefficients" for the $\omega = E - \frac{1}{2}J$ and the $\omega = E + \frac{3}{2}J$ poles each go to 2, while the coefficients for the $\omega = E - \frac{1}{2}J$ and the $\omega = E + U - \frac{3}{2}J$ poles both go to zero. These results are consistent with the ground state's being the triplet state, the last result following since only poles corresponding to adding particles to triplet states can survive.

If, on the other hand, one considers $J < 0$, then one obtains results based on the singlet state's being the ground state, the other pair of spectral density coefficients vanish, and $\langle s^z n_\downarrow \rangle = \frac{1}{4}$ and $\langle n_\downarrow \rangle = \frac{1}{2}$.

V. INTERACTING CASE FOR DIAGONAL INTRA-ATOMIC EXCHANGE

Having considered the noninteracting atom in Sec. IV, we now turn in this section to the problem of the interacting atom for the case in which only the diagonal part of the intra-atomic exchange coupling is retained in the Hamiltonian. In light of our previous comments, we will set $S^z = +\frac{1}{2}$ throughout the discussion. This is the first case of those that we have considered that is not exactly soluble. Using (2.4) and (3.11), we are eventually led to the set of equations

$$\begin{aligned} (\omega - E - \Lambda) \langle\langle d_\uparrow \rangle\rangle &= 1/2\pi + U \langle\langle n_\downarrow d_\uparrow \rangle\rangle - \frac{1}{2}J \langle\langle d_\uparrow \rangle\rangle, \\ (\omega - E - U) \langle\langle n_\downarrow d_\uparrow \rangle\rangle &= \frac{\langle n_\downarrow \rangle}{2\pi} + \sum_{\mathbf{k}} V_{\mathbf{k}} \\ &\times (\langle\langle n_\downarrow c_{\mathbf{k}\uparrow} \rangle\rangle + \langle\langle d_\uparrow d_\downarrow^\dagger c_{\mathbf{k}\downarrow} \rangle\rangle + \langle\langle d_\uparrow d_\downarrow c_{\mathbf{k}\downarrow}^\dagger \rangle\rangle) - \frac{1}{2}J \langle\langle n_\downarrow d_\uparrow \rangle\rangle, \\ (\omega - \epsilon_{\mathbf{k}}) \langle\langle n_\downarrow c_{\mathbf{k}\uparrow} \rangle\rangle &= V_{\mathbf{k}} \langle\langle n_\downarrow d_\uparrow \rangle\rangle, \\ (\omega - \epsilon_{\mathbf{k}}) \langle\langle d_\uparrow d_\downarrow^\dagger c_{\mathbf{k}\downarrow} \rangle\rangle &= \langle d_\downarrow^\dagger c_{\mathbf{k}\downarrow} \rangle / 2\pi - V_{\mathbf{k}} f(\epsilon_{\mathbf{k}}) \langle\langle d_\uparrow \rangle\rangle \\ &\quad + V_{\mathbf{k}} \langle\langle n_\downarrow d_\uparrow \rangle\rangle - J \langle\langle d_\uparrow d_\downarrow^\dagger c_{\mathbf{k}\downarrow} \rangle\rangle \\ (\omega + \epsilon_{\mathbf{k}} - 2E - U) \langle\langle d_\uparrow d_\downarrow c_{\mathbf{k}\downarrow}^\dagger \rangle\rangle &= \langle d_\downarrow c_{\mathbf{k}\downarrow}^\dagger \rangle / 2\pi \\ &\quad - V_{\mathbf{k}} f(\epsilon_{\mathbf{k}}) \langle\langle d_\uparrow \rangle\rangle + V_{\mathbf{k}} \langle\langle n_\downarrow d_\uparrow \rangle\rangle, \end{aligned} \quad (5.1)$$

where we have factored the higher-order Green's functions in accordance with the prescription preceding (2.10). These equations reduce to the set (2.7) and (2.8) for $J = 0$ and to the set (4.1) with $S^z = \frac{1}{2}$ for $V_{\mathbf{k}} = 0$.

Solving for $\langle\langle d_\uparrow \rangle\rangle$ we find

$$\langle\langle d_\uparrow \rangle\rangle = \frac{1}{2\pi} \left(1 - \frac{[\langle n_\downarrow \rangle + F(\omega)]U}{U + \epsilon - \omega - \frac{1}{2}J} \right) / \left(\omega - E - \Lambda + \frac{1}{2}J - \frac{K(\omega)U}{U + \epsilon - \omega - \frac{1}{2}J} \right), \quad (5.2)$$

where

$$\begin{aligned} \Lambda &= \sum_{\mathbf{k}} \frac{|V_{\mathbf{k}}|^2}{\omega - \epsilon_{\mathbf{k}}}, \quad \gamma = \sum_{\mathbf{k}} \frac{|V_{\mathbf{k}}|^2}{\omega + \epsilon_{\mathbf{k}} - 2E - U}, \\ F(\omega) &= \sum_{\mathbf{k}} \left(\frac{V_{\mathbf{k}} \langle d_\downarrow^\dagger c_{\mathbf{k}\downarrow} \rangle}{\omega - \epsilon_{\mathbf{k}} + J} + \frac{V_{\mathbf{k}} \langle d_\downarrow c_{\mathbf{k}\downarrow}^\dagger \rangle}{\omega + \epsilon_{\mathbf{k}} - 2E - U} \right) \\ \bar{\Lambda} &= \sum_{\mathbf{k}} \frac{|V_{\mathbf{k}}|^2}{\omega - \epsilon_{\mathbf{k}} + J}, \quad \epsilon = E + \Lambda + \bar{\Lambda} + \gamma \\ K(\omega) &= \sum_{\mathbf{k}} \left(\frac{|V_{\mathbf{k}}|^2 f(\epsilon_{\mathbf{k}})}{\omega - \epsilon_{\mathbf{k}} + J} + \frac{|V_{\mathbf{k}}|^2 f(\epsilon_{\mathbf{k}})}{\omega + \epsilon_{\mathbf{k}} - 2E - U} \right). \end{aligned} \quad (5.3)$$

For $J = 0$ these results are identical to those of Sec. II.

From an examination of $\langle\langle d_\uparrow \rangle\rangle$ we see that there exists a pole in the neighborhood of $\omega = E - \frac{1}{2}J$. This pole was present in the $V_{\mathbf{k}} = 0$ case and gives rise to no new results. The more interesting questions relate to the effect

of the exchange terms on the so-called anomalous resonances discussed in Sec. II. Using the approximation

$$K(\omega) \cong -\frac{\Gamma}{\pi} \ln \left(\frac{(U+2E-\omega)^2}{(\omega+J)^2+(kT)^2} \right)^{1/2}, \quad (5.4)$$

we are led to the equation

$$(\omega+J)^2+(kT)^2=(U+2E) \times \exp \left(-\frac{2\pi}{\Gamma U} (-E+\frac{1}{2}J)(U+E-\frac{1}{2}J) \right) = (kT_K)^2, \quad (5.5)$$

giving the location of the anomalous resonances. When we compare this equation, written in the form

$$\omega = -J \pm [(kT_K)^2 - (kT)^2]^{1/2}, \quad (5.6)$$

with the equation $\omega = 2mh \pm [(kT_K)^2 - (kT)^2]^{1/2}$ of Sec. II, we see that the exchange term behaves as an effective magnetic field. In general, however, J will be a large energy of the order of electron volts, which will derive the resonances out of the region lying with kT of the Fermi surface. For a J of this magnitude, therefore, the diagonal exchange terms effectively remove the anomalous resonances from the problem and the effects attributed to them are no longer present.

In Sec. VI we will find that the inclusion of the off-diagonal terms in the Hamiltonian return the resonances to the region of the Fermi surface, so that the qualitative results of the one-orbital model are regained.

VI. INTERACTING ATOM WITH OFF-DIAGONAL EXCHANGE

Having studied the behavior of the anomalous resonances under the influence of the diagonal exchange terms, we turn to the more general case in which the off-diagonal exchange terms are retained in the Hamiltonian. The presence of these "dynamic" terms considerably complicates the analysis.

Making use of our model Hamiltonian (3.11) we obtain the relations

$$\begin{aligned} [c_{ks}, H] &= \epsilon_k c_{ks} + V_k d_s, \\ [d_s, H] &= \sum_k V_k c_{ks} + E d_s + U n_{-s} d_s - J s^z d_{\uparrow} \delta_{s,\uparrow} \\ &\quad + J s^z d_{\downarrow} \delta_{s,\downarrow} - J s^+ d_{\uparrow} \delta_{s,\downarrow} - J s^- d_{\downarrow} \delta_{s,\uparrow}, \end{aligned} \quad (6.1)$$

$$[s^z, H] = -J d_{\downarrow}^{\dagger} d_{\uparrow} s^+ + J d_{\uparrow}^{\dagger} d_{\downarrow} s^-,$$

$$[s^{\pm}, H] = J(n_{\uparrow} - n_{\downarrow}) s^{\pm} - 2J d_{\uparrow}^{\dagger} d_{\downarrow} s^z.$$

From spherical invariance we have

$$\begin{aligned} \langle d_{\uparrow}^{\dagger} c_{k\uparrow} \rangle &= \langle d_{\downarrow}^{\dagger} c_{k\downarrow} \rangle, \\ \langle s^+ d_{\downarrow}^{\dagger} c_{k\uparrow} \rangle &= \langle s^- d_{\uparrow}^{\dagger} c_{k\downarrow} \rangle = -2 \langle s^z d_{\downarrow}^{\dagger} c_{k\uparrow} \rangle \\ &= 2 \langle s^z d_{\uparrow}^{\dagger} c_{k\downarrow} \rangle, \\ \langle s^- n_{\downarrow} d_{\uparrow}^{\dagger} c_{k\uparrow} \rangle &= 2 \langle s^z n_{\downarrow} d_{\uparrow}^{\dagger} c_{k\uparrow} \rangle. \end{aligned} \quad (6.2)$$

These relationships permit us to express our results in terms of only three self-consistent averages.

A straightforward calculation leads to a set of 24 Green's functions, six of which we regard as fundamental:

$$\begin{aligned} \langle \langle d_{\uparrow} \rangle \rangle, \quad \langle \langle n_{\downarrow} d_{\uparrow} \rangle \rangle, \quad \langle \langle s^- d_{\downarrow} \rangle \rangle, \\ \langle \langle s^z d_{\uparrow} \rangle \rangle, \quad \langle \langle s^- n_{\uparrow} d_{\downarrow} \rangle \rangle, \quad \langle \langle s^z n_{\downarrow} d_{\uparrow} \rangle \rangle. \end{aligned} \quad (6.3)$$

The remaining Green's functions are similar in structure but contain one band operator c_{ks} or c_{ks}^{\dagger} (a Green's function containing two band operators would be factored). Fortunately, these "band" Green's functions divide into sets, each member of a set being directly connected only to other members of the same set. As an example, consider the Green's function $\langle \langle s^- n_{\uparrow} c_{k\downarrow} \rangle \rangle$. In deriving the differential equation for this Green's function we encounter the commutator $[c_{k\downarrow}, H]$. As we have previously seen, this commutator leads us back to the band operator $c_{k\downarrow}$ plus an orbital operator. The commutator $[s^-, H]$ leads only to orbital operators while the commutator $[n_{\uparrow}, H]$, although it leads to operators of the form $c_{k\uparrow}$, will always lead to a factorizable Green's function since this new operator must always be combined with the already present $c_{k\downarrow}$ operator. Therefore band Green's functions with spin-down band operators never connect to spin-up band Green's functions. This, together with the fact that several band Green's functions connect only to orbital Green's functions, considerably simplifies the analysis.

From the form of the equations one can also show that

$$\langle \langle s^- d_{\uparrow} \rangle \rangle = 2 \langle \langle s^z d_{\uparrow} \rangle \rangle, \quad \langle \langle s^- n_{\downarrow} d_{\uparrow} \rangle \rangle = 2 \langle \langle s^z n_{\downarrow} d_{\uparrow} \rangle \rangle. \quad (6.4)$$

We have seen that these relationships for the corresponding averages follow directly from the spherical symmetry of the Hamiltonian.

Carrying through the analysis just described, we will exhibit our equations in terms of the resultant 3×3 set (by substitution we have removed the $\langle \langle n_{\downarrow} d_{\uparrow} \rangle \rangle$ Green's function since it does not enter into the calculation of any self-consistent averages).

$$c_{i1} \langle \langle d_{\uparrow} \rangle \rangle + c_{i2} \langle \langle s^z d_{\uparrow} \rangle \rangle + c_{i3} \langle \langle s^z n_{\downarrow} d_{\uparrow} \rangle \rangle = b_i, \quad (6.5)$$

where

$$\begin{aligned} c_{11} &= \psi_1 + \left[\frac{\chi - \Lambda_1}{U} \right] \bar{\chi}, \quad c_{12} = -\frac{1}{4} \psi_2 + \frac{3J}{U} \bar{\chi}, \\ c_{13} &= 3(J + \psi_3), \quad b_1 = I_2 + \bar{\chi} / 2\pi U, \\ c_{21} &= \frac{1}{4} J + \frac{1}{4} \psi_3, \quad c_{22} = \chi - \Lambda_1 - J - \frac{1}{2} \psi_2, \\ c_{23} &= -U + 2J + \psi_3, \quad b_2 = I_4, \\ c_{31} &= -\frac{1}{4} \psi_4 + \frac{J(\chi - \Lambda_1)}{2U}, \quad c_{32} = \psi_1 + \frac{3J^2}{2U}, \\ c_{33} &= 2\bar{\chi} + 2J - \psi_4, \quad b_3 = I_7 + J/4\pi U; \end{aligned} \quad (6.6)$$

and

$$\begin{aligned} \psi_1 &= \frac{3}{8}K_2^- + \frac{3}{8}K_2^+ + \frac{1}{4}\Lambda_2 + L_2, \\ \psi_2 &= \frac{3}{2}K_2^- - \frac{1}{2}K_2^+ - \Lambda_2, \\ \psi_3 &= \frac{1}{2}K_2^- + \frac{1}{2}K_2^+ - \Lambda_2, \\ \psi_4 &= \frac{1}{2}K_2^- - \frac{3}{2}K_2^+ + \Lambda_2, \\ \bar{\chi} &= \chi - U - 2\Lambda_1 - L_1, \end{aligned} \tag{6.7}$$

with

$$\begin{aligned} \Lambda_1 &= \sum_k \frac{|V_k|^2}{\omega - \epsilon_k}, & \Lambda_2 &= \sum_k \frac{|V_k|^2 f(\epsilon_k)}{\omega - \epsilon_k}, \\ K_1^- &= \sum_k \frac{|V_k|^2}{\omega - \epsilon_k - 2J}, & K_1^+ &= \sum_k \frac{|V_k|^2}{\omega - \epsilon_k + 2J}, \\ K_2^- &= \sum_k \frac{|V_k|^2 f(\epsilon_k)}{\omega - \epsilon_k - 2J}, & K_2^+ &= \sum_k \frac{|V_k|^2 f(\epsilon_k)}{\omega - \epsilon_k + 2J}, \\ L_1 &= \sum_k \frac{|V_k|^2}{\omega + \epsilon_k - 2E - U}, & L_2 &= \sum_k \frac{|V_k|^2 f(\epsilon_k)}{\omega + \epsilon_k - 2E - U}. \end{aligned} \tag{6.8}$$

$I_2, I_4,$ and I_7 are quantities involving self-consistent averages. They are given by

$$\begin{aligned} I_2 &= \frac{\langle n_4 \rangle}{2\pi} - \frac{1}{2\pi} \left[\sum_k \frac{V_k}{\omega + \epsilon_k - 2E - U} - \sum_k \frac{V_k(\omega^2 - J^2)}{\omega(\omega^2 - 4J^2)} \right] \\ &\quad \times \langle d_{\uparrow}^{\dagger} c_{k\uparrow} \rangle + \sum_k \frac{6V_k J^2 \langle s^z d_{\uparrow}^{\dagger} n_{\downarrow} c_{k\uparrow} \rangle}{\pi\omega(\omega^2 - 4J^2)} \\ &\quad + \sum_k \frac{3V_k J(\omega - J)}{\pi\omega(\omega^2 - 4J^2)} \langle s^z d_{\uparrow}^{\dagger} c_{k\uparrow} \rangle, \\ I_4 &= \sum_k \frac{V_k J^2 \langle d_{\uparrow}^{\dagger} c_{k\uparrow} \rangle}{2\pi\omega(\omega^2 - 4J^2)} + \sum_k \frac{2J^2 V_k \langle s^z d_{\uparrow}^{\dagger} n_{\downarrow} c_{k\uparrow} \rangle}{\pi\omega(\omega^2 - 4J^2)} \\ &\quad + \sum_k \frac{J V_k(\omega - J) \langle s^z d_{\uparrow}^{\dagger} c_{k\uparrow} \rangle}{\pi\omega(\omega^2 - 4J^2)}, \\ I_7 &= \frac{\langle s^z n_4 \rangle}{2\pi} - \sum_k \frac{J V_k(\omega - J) \langle d_{\uparrow}^{\dagger} c_{k\uparrow} \rangle}{2\pi\omega(\omega^2 - 4J^2)} \\ &\quad - \sum_k \frac{2V_k J(\omega - J) \langle s^z d_{\uparrow}^{\dagger} n_{\downarrow} c_{k\uparrow} \rangle}{\pi\omega(\omega^2 - 4J^2)} \\ &\quad + \left[\sum_k \frac{V_k}{\pi(\omega + \epsilon_k - 2E - U)} - \sum_k \frac{V_k(\omega - J)^2}{\pi\omega(\omega^2 - 4J^2)} \right] \\ &\quad \times \langle s^z d_{\uparrow}^{\dagger} c_{k\uparrow} \rangle. \end{aligned} \tag{6.9}$$

Equation (7.5) may be seen to reduce to the results previously obtained for the special cases $V_k=0$ and $J=0$ if we note that for $V_k=0, J \neq 0$.

$$I_2 = \langle n_4 \rangle / 2\pi, \quad I_4 = 0, \quad I_7 = \langle s^z n_4 \rangle / \pi, \tag{6.10}$$

and for $J=0, V_k \neq 0$

$$I_2 = \frac{\langle n_4 \rangle + F(\omega)}{2\pi}, \quad I_4 = I_7 = 0. \tag{6.11}$$

Although we will not make use of the specific forms in this paper, the ψ_i 's may be expressed in terms of digamma functions:

$$\begin{aligned} \psi_1 &= (\Gamma/\pi) \left\{ -\frac{3}{8}\psi^- - \frac{3}{8}\psi^+ - \frac{1}{4}\psi^0 + \psi^U \right. \\ &\quad \left. + i\Gamma \left\{ \frac{3}{8}f^- + \frac{3}{8}f^+ + \frac{1}{4}f^0 + f^U \right\} \right\}, \\ \psi_2 &= (\Gamma/\pi) \left\{ -\frac{3}{2}\psi^- + \frac{1}{2}\psi^+ + \psi^0 \right. \\ &\quad \left. + i\Gamma \left\{ \frac{3}{2}f^- - \frac{1}{2}f^+ - f^0 \right\} \right\}, \\ \psi_3 &= (\Gamma/\pi) \left\{ -\frac{1}{2}\psi^- - \frac{1}{2}\psi^+ + \psi^0 \right. \\ &\quad \left. + i\Gamma \left\{ \frac{1}{2}f^- + \frac{1}{2}f^+ - f^0 \right\} \right\}, \\ \psi_4 &= (\Gamma/\pi) \left\{ -\frac{1}{2}\psi^- + \frac{3}{2}\psi^+ - \psi^0 \right. \\ &\quad \left. + i\Gamma \left\{ \frac{1}{2}f^- - \frac{3}{2}f^+ + f^0 \right\} \right\}. \end{aligned} \tag{6.12}$$

In these expressions a ψ with a superscript is the real part of the digamma function of the appropriate argument. Explicitly,

$$\begin{aligned} \psi^0 &= \text{Re digamma}(\frac{1}{2} + i\beta\omega/2\pi), \\ \psi^- &= \text{Re digamma}[\frac{1}{2} + i\beta(\omega - 2J)/2\pi], \\ \psi^+ &= \text{Re digamma}[\frac{1}{2} + i\beta(\omega + 2J)/2\pi], \\ \psi^U &= \text{Re digamma}[\frac{1}{2} + i\beta(\omega - 2E - U)/2\pi]. \end{aligned} \tag{6.13}$$

In a similar manner f with a superscript denotes a Fermi function of appropriate argument:

$$\begin{aligned} f^0 &= f(\omega), \quad f^- = f(\omega - 2J), \\ f^+ &= f(\omega + 2J), \quad f^U = f(U + 2E - \omega). \end{aligned} \tag{6.14}$$

Since we will be interested in locating the zeros of expressions containing the ψ_i 's, we will next obtain a more manageable, although approximate form, for them. Consider as an example

$$\begin{aligned} \Lambda_2 &= \sum_k \frac{|V_k|^2 f(\epsilon_k)}{\omega - \epsilon_k} \rightarrow N(0) \int_{-D}^D \frac{d\epsilon |V_k|^2 f(\epsilon)}{\omega - \epsilon - i\delta} \\ &= N(0) \int_{-D}^D \frac{d\epsilon |V_k|^2 [f(\epsilon) - \frac{1}{2}]}{\omega - \epsilon - i\delta} \\ &\quad + \frac{N(0)}{2} \int_{-D}^D \frac{d\epsilon |V_k|^2}{\omega - \epsilon - i\delta}. \end{aligned} \tag{6.15}$$

A simple method for calculating the integral is to replace δ by T while replacing the Fermi function by its value at $T=0$. One can convince oneself of the approximate correctness of the procedure by constructing a simple graph of the integrand and by a comparison of the results obtained for the explicitly calculable limiting case.

Temporarily looking only at the real part of Λ_2 we have

$$\begin{aligned} \text{Re}\Lambda_2 &= \text{Re}N(0) |V_{\mathbf{k}}|^2 \int_{-D}^D \frac{d\epsilon [f(\epsilon) - \frac{1}{2}]_{T=0}}{\omega - \epsilon - iT} \\ &= |V_{\mathbf{k}}|^2 N(0) \ln D - \frac{N(0) |V_{\mathbf{k}}|^2}{2} \ln[\omega^2 + T^2]. \end{aligned} \quad (6.16)$$

In combining the Λ 's, k 's, and L 's to form the ψ_i 's the $\ln D$ terms will cancel. *Omitting these terms*, we have

$$\begin{aligned} \text{Re}\Lambda_2 &= -\frac{1}{2}N(0) |V_{\mathbf{k}}|^2 \ln[\omega^2 + T^2] \\ \text{Re}K_2^- &= -\frac{1}{2}N(0) |V_{\mathbf{k}}|^2 \ln[(\omega - 2J)^2 + T^2], \\ \text{Re}K_2^+ &= -\frac{1}{2}N(0) |V_{\mathbf{k}}|^2 \ln[(\omega + 2J)^2 + T^2] \\ \text{Re}L_2 &= \frac{1}{2}N(0) |V_{\mathbf{k}}|^2 \ln[(U + 2E - \omega)^2 + T^2]. \end{aligned} \quad (6.17)$$

Combining the Λ 's, k 's, and L 's to form the ψ_i 's, we obtain

$$\begin{aligned} \text{Re}\psi_1 &= \frac{\Gamma}{8\pi} \frac{[(U + 2E - \omega)^2 + T^2]^4}{[(\omega - 2J)^2 + T^2]^{3/2} [(\omega + 2J)^2 + T^2]^{3/2} [\omega^2 + T^2]}, \\ \text{Re}\psi_2 &= \frac{\Gamma}{4\pi} \ln \frac{[\omega^2 + T^2]^2}{[(\omega - 2J)^2 + T^2]^3}, \\ \text{Re}\psi_3 &= \frac{\Gamma}{4\pi} \ln \frac{[\omega^2 + T^2]^2}{[(\omega - 2J)^2 + T^2][(\omega + 2J)^2 + T^2]}, \\ \text{Re}\psi_4 &= \frac{\Gamma}{4\pi} \ln \frac{[(\omega + 2J)^2 + T^2]^3}{[(\omega - 2J)^2 + T^2][\omega^2 + T^2]^4}. \end{aligned} \quad (6.18)$$

For convenience we will at this stage permit U to become very large. We must, however, not allow it to become infinite since in addition to its explicit appearance in our equations, we have just seen it enter logarithmically through ψ_1 . Physically, the approximation precludes the simultaneous occupation of the two levels of the band-connected orbital. In the exactly soluble $V_{\mathbf{k}}=0$, $J \neq 0$ problem we considered earlier the large U approximation results in the "removal" of the poles at $\omega = E + U + \frac{1}{2}J$ and $\omega = E + U - \frac{3}{2}J$ from the physically allowed subspace. The sum rule for the spectral density is also violated.

If we let U become large, our c_{ij} coefficients become

$$\begin{aligned} c_{11} &= -(\chi - \Lambda_1 - \psi_1), & c_{12} &= -(\frac{1}{4}\psi_2 + 3J), \\ c_{13} &= 3(J + \psi_3), & c_{21} &= \frac{1}{4}(J + \psi_3), \\ c_{22} &= \chi - \Lambda_1 - J - \frac{1}{2}\psi_2, & c_{23} &= -U, \\ c_{31} &= -\frac{1}{4}\psi_4, & c_{32} &= \psi_1, \\ c_{33} &= -2U. \end{aligned} \quad (6.19)$$

Next we calculate the determinant of the c_{ij} 's. As discussed in Sec. II, for regions in which the numerator

is well behaved, resonances occur for values of ω for which the determinant is small. Calculating the determinant, we find

$$\begin{aligned} 2U \{ \hat{\chi}^2 - [J + \frac{3}{2}\psi_1 + \frac{1}{2}\psi_2] \hat{\chi} - \frac{3}{4}J^2 \\ + \frac{1}{16}J [16\psi_1 - \psi_2 - 12\psi_3 - 6\psi_4] \\ + \frac{1}{2}[\psi_1^2 + \psi_1\psi_2 - \frac{1}{8}\psi_2\psi_3 - \frac{1}{16}\psi_2\psi_4] \}, \end{aligned} \quad (6.20)$$

where

$$\hat{\chi} \equiv \omega - E - \Lambda_1. \quad (6.21)$$

It is useful to reconsider the special cases. For $V_{\mathbf{k}}=0$, $J \neq 0$, all the ψ_i 's go to zero and (6.20) reduces to

$$\begin{aligned} (\omega - E)^2 - J(\omega - E) - \frac{3}{4}J^2 \\ = (\omega - E + \frac{1}{2}J)(\omega - E - \frac{3}{2}J), \end{aligned} \quad (6.22)$$

whose zeros are responsible for just those poles corresponding to a single particle's being present in the band-connected orbital. As stated above, we see that the poles corresponding to two particles being present in the band-connected orbital, $\omega = E + U + \frac{1}{2}J$ and $\omega = E + U - \frac{3}{2}J$ have been eliminated from the problem.

For $J=0$, $V_{\mathbf{k}} \neq 0$ we have

$$\psi_1 = -\ln \frac{U}{\pi(\omega^2 + T^2)^{1/2}} + i\Gamma f(\omega), \quad (6.23)$$

so that

$$\begin{aligned} \hat{\chi}^2 - \frac{3}{2}\psi_1 \hat{\chi} + \frac{1}{2}\psi_1^2 &= (\hat{\chi} - \frac{1}{2}\psi_1)(\hat{\chi} - \psi_1) \\ &= \left(\omega - E - \text{Re}\Lambda_1 - \frac{\Gamma}{2\pi} \ln \frac{U}{(\omega^2 + T^2)^{1/2}} - \frac{1}{2}i\Gamma(1 + f(\omega)) \right) \\ &\quad \times \left(\omega - E - \text{Re}\Lambda_1 - \frac{\Gamma}{\pi} \ln \frac{U}{(\omega^2 + T^2)^{1/2}} - i\Gamma(1 + f(\omega)) \right). \end{aligned} \quad (6.24)$$

This is a case for which the denominator must be carefully considered. From (6.6)–(6.9) the first factor in (6.24) may be seen to be cancelled by an identical factor appearing in the numerator. The second factor is just the result obtained in the single-orbital case, (2.13).

This concludes our check that the zeros of (6.20) yield the previously known limiting cases. We now obtain the new results, for J and $V_{\mathbf{k}}$ both $\neq 0$.

We are most interested in the effect of the exchange coupling on the anomalous resonances. Restricting ourselves to the strong-coupling case ($\Gamma/J \ll 1$), we may omit the $\psi_i \psi_j$ terms in (6.20). In addition to values of ω corresponding to zeros of (6.22), there exist values of ω for which (6.20) is small. In order to approximately locate these values, we proceed as in Sec. II, and set the real part of (6.20) equal to zero. Ignoring ω with respect to E and J , we are led to the equation

$$\omega^2 + (kT)^2 = (kT_{K'})^2, \quad (6.25)$$

where

$$kT_{k'} = \exp \left[-\frac{8\pi \left(\bar{E}^2 - \frac{3}{4}J^2 \right)}{\Gamma \left(\bar{E} - \frac{1}{2}J \right)} - 8 \left(\frac{J + \frac{3}{2}\bar{E}}{\bar{E} - \frac{1}{2}J} \right) \ln U \right. \\ \left. + \left(\frac{13\bar{E} + \frac{5}{2}J}{\bar{E} - \frac{1}{2}J} \right) \ln 2J \right], \quad (6.26)$$

$$\bar{E} = E + \text{Re}\Lambda_1.$$

Values of ω satisfying (6.25) give the approximate location of the anomalous resonances. We find that in terms of the new Kondo temperature, $T_{K'}$, (6.25) is identical to (2.14). Hence, in contrast to the results found in Sec. V for the diagonal exchange coupling where the anomalous resonances are driven away from the

Fermi surface, here we find that for $J > \frac{2}{3}\sqrt{3}|E|$ the anomalous resonances are returned to the region of the Fermi surface. In the large J limit, (6.26) may be written approximately as

$$kT_{K'} \cong U \left(\frac{U}{2J} \right)^{5/11} \exp \left(-\frac{12}{11} \right) \left(\frac{\pi J}{\Gamma} \right), \\ (\text{large } U, J \text{ limit}). \quad (6.27)$$

The exponents 5/11 and 12/11 have no ready explanation, but otherwise this result is not qualitatively different from the one-orbital model. We have thus shown that despite the vast complications which degeneracy introduces into the mathematics, the physical results did not change drastically in the appropriate limit.