Many-Body Theory of Localized d States in Metals. II. Pair of Impurities*

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A previous rotationally invariant perturbation treatment of localized d states is extended to the case of neighboring sites interacting via direct d-d exchange and indirect s-d scattering. It is found that the parallel alignment of two localized moments is never the ground state of the pair. For certain values of the unperturbed d-state energy (depending upon the exchange interactions) only one of the sites will be occupied by a d electron so the pair can have a net moment. If the conditions are such that both sites are occupied by d electrons, these electrons must be aligned antiparallel so there is only a small net moment due to scattering to and from the band states.

I. INTRODUCTION

IN a previous paper,[1] a rotationally invariant perturbation calculation of the susceptibility of a localized d state in a metal was made, using a model of this state proposed by Anderson.[2] In this model the "d state" is assumed to have no orbital degeneracy, and to have a wave function distinct from the Wannier functions of electrons on the sites of the host lattice. When this state is singly occupied, its energy is ϵ_d, when doubly occupied by electrons with antiparallel spins, is $2\epsilon_d+U$, where U is positive. The Hamiltonian of the model consists of the band electron energies, the aforementioned "d state" energies, and a scattering term capable of converting electrons on the local "d" site into band electrons and conversely. No other terms (such as Coulomb interaction between conduction electrons and electrons on the "d" site) are included. Physical reasons for restriction of the energies to the ones mentioned above, are given by Anderson.[2] Within the framework of this model, he showed that, provided the scattering to the band was not too strong relative to the correlation energy U, and provided ϵ_d was below the Fermi surface and $2\epsilon_d+U$ above, a localized magnetic moment would result, which could be calculated by the Hartree-Fock method. Since this method violates rotational invariance, it is hard to see how one can use it to compute a Curie constant as distinct from a saturation magnetization.

In SFI it was shown how this calculation may be done by perturbation theory. The method divided the possible states of the system into magnetic and nonmagnetic ones, and calculated two partition functions $\mathfrak{Z}_M$, $\mathfrak{Z}_S$ in these two manifolds. The Curie constant then has the form

$$C_{\text{eff}}=C_{1/2}[\mathfrak{Z}_M/(\mathfrak{Z}_M+\mathfrak{Z}_S)].$$

The actual calculation used the resolvent technique, deriving resolvents $\mathfrak{R}_M$ and $\mathfrak{R}_S$ for the two manifolds with the help of projection operators. These resolvents were then evaluated by perturbation theory, keeping only the lowest order self-energy corrections and, in fact, only their imaginary parts. The crucial point is the following: If these imaginary parts (due, of course, to the band scattering) were neglected, the partition function $\mathfrak{Z}_S$ of the nonmagnetic manifold would be smaller than $\mathfrak{Z}_M$ by a factor $e^{\beta\epsilon_d}$, for the "empty" component of the nonmagnetic manifold, and by a factor $e^{-\beta(2\epsilon_d+U)}$ for the "filled" component of that manifold. (Energies are measured from the Fermi level.) Hence, at very low temperatures, the magnetic moment would be essentially that of the isolated "d" state without scattering to the band. The imaginary parts of the self-energies appropriate to $\mathfrak{Z}_S$, which are in effect the damping rates of the states of S due to the presence of M, cause $\mathfrak{Z}_S$ to assume the *same* exponential dependence on the temperature as that of $\mathfrak{Z}_M$. For this reason there is always a reduction of the moment. Qualitatively, the results agreed with those of Anderson, except no sharp cutoff was found in the moment, which tended to zero smoothly with increasing scattering. This might be a basic feature of perturbation theory, unless prescriptions are found for solving for the self-energies consistently in the way in which this is done in other many body problems. The complicating feature here, which makes the standard recipes hard to apply, is that the "d"-state correlation energy is treated rigorously as part of the unperturbed propagator.

In the case of two d states, we distinguish between two situations: (1) The d sites are nearest neighbors and electrons on them interact directly, and (2) the d sites are far apart and interact only via band electrons.

In case (1), we must include in the Hamiltonian an

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[1] H. Suhl and D. R. Fredkin, Phys. Rev. **131**, 1063 (1963) (hereafter called SFI).
[2] P. W. Anderson, Phys. Rev. **124**, 41 (1961).

essentially single-particle scattering between electrons on the two "d" sites. In addition, we will show that the direct Coulomb interaction between electrons on these sites may become important even if smaller than the former, provided its exchange part has ferromagnetic sign. To these interactions we must, of course, add the same Hamiltonians as in SFI, one for each site. In case (2), all direct d interaction is neglected and only the sum of the two Hamiltonians of SFI remains.

Problem (1) has also been treated in Hartree-Fock approximation by Alexander and Anderson,[3] who conclude that the pair aligns antiparallel with zero net moment unless one of the energies ϵ_d or $2\epsilon_d+U$ is close to the Fermi level. In that event, they can obtain parallel coupling, and therefore a net moment. As we shall see, perturbation theory parallels these conclusions somewhat.

II. RESOLVENT METHOD

We will treat the "d" pair Hamiltonian rigorously, and, as in SFI, only the band scattering as a perturbation. (A simultaneous treatment of both these mechanisms will be briefly considered at the end of this paper.) Then we may divide the unperturbed states of the system into three manifolds, broadly describable as singlet, doublet, and triplet, and the effective Curie constant, by a trivial generalization of the formula in SFI as[4]

$$C_{\text{eff}}=\frac{C_1\mathfrak{Z}_T+C_{1/2}\mathfrak{Z}_D}{\mathfrak{Z}_T+\mathfrak{Z}_D+\mathfrak{Z}_S}, \tag{1}$$

where C_1 and $C_{1/2}$ are the "bare" Curie constants appropriate to a free spin one and a free spin $\frac{1}{2}$, respectively, and $\mathfrak{Z}_T$, $\mathfrak{Z}_D$, $\mathfrak{Z}_S$ are the partition functions of the three manifolds. These manifolds, split into submanifolds, which may be classified according to their origin before the single particle scattering between the two sites is turned on. The result is as follows:

(S) One electron on each site, the pair forming a singlet. Two antiparallel electrons on one site, the other site empty. Both sites doubly occupied by antiparallel electrons. Both sites empty.

(D) One electron on either site, the other empty. Two antiparallel electrons on one site, the other singly occupied.

(T) One electron on each site, the pair forming a triplet.

Including the possible S_z states in D and T, this gives a total of 16 *unperturbed basis states*. When the single-particle scattering between the two sites is turned on, some of these form admixtures. The d part of the Hamiltonian (exclusive of the band scattering) is

$$\mathcal{H}_d=\sum_\sigma \epsilon_d(n_{1\sigma},+n_{2\sigma})+U(n_{1\uparrow}n_{1\downarrow}+n_{2\uparrow}n_{2\downarrow}) +V_{12}\sum_\sigma(d_{1\sigma}{}^*d_{2\sigma}+d_{2\sigma}{}^*d_{1\sigma}), \tag{2}$$

where d^*, d are creation and annihilation operators on the sites indicated by the subscripts, σ is the spin index and the n's are occupation numbers on the indicated sites. Coulomb interation is neglected for the present. Under the V_{12} term in Eq. (2), the submanifolds enumerated above (linearly combined where required) combine and regroup as in the following table. In the ket symbols, the first and second places denote occupancies of sites 1 and 2, respectively. The results are given in Table I.

The low-temperature behavior of the partition functions of *all* these manifolds is dictated by that of the partition function of the energetically lowest manifold. (Just as in SFI, the others are "damped" by lowest manifold and so acquire its temperature dependence.) For this reason we need only determine which energy is lowest as the parameters ϵ_d, U and V_{12} are varied.

We assume $\epsilon_d<0$, $2\epsilon_d+U>0$ so that the isolated sites favor single occupancy let $V_{12}>0$. If $V_{12}>\frac{2}{3}U$, the $E(S_{m1})$ is always lowest. If $V_{12}<\frac{1}{3}U$, then $E(S_{m1})$ or $E(D_1{}^+)$ is lowest according to whether

$$-\epsilon_d \gtrless V_{12}\{1-8(V_{12}/U)[1+(1+(16V_{12}{}^2/U^2))]^{-1}\}.$$

If $V_{12}<0$, the same result holds, but with V_{12} replaced by $|V_{12}|$ and $D_1{}^+$ by $D_1{}^-$. Presumably for *reasonably* small V_{12}, the situation with singlet lowest is more common. Only when ϵ_d approaches the Fermi level to within $\sim V_{12}$, can the doublet energy become lowest.

It follows that in the common situation, any moment exhibited by the pair is due to band scattering. For small values of the scattering energy V, such moment as there is comes principally from $\mathfrak{Z}_D$, since the doublet manifold can reach the singlet manifold by lowest order damping involving V^2. The triplet manifold connects to the singlet only in order V^4. Qualitatively, this agrees with the Hartree-Fock procedure of Alexander and Anderson, who find no moment at all unless $|V_{12}|\sim|\epsilon_d|$.

The triplet energy is *always* above $E(S_{m1})$. It is also below $E(D_1{}^+)$, unless

$$V_{12}>-\epsilon_d>V_{12}\{1-8(V_{12}/U) \times[1+(1+(16V_{12}{}^2/U^2))^{1/2}]^{-1}\},$$

in which case $E(D_1{}^+)$ lies between the singlet S_{m1} and the triplet. In that case the triplet partition function acquires the exponential temperature dependence of that of the doublet, but at temperatures such that kT is much less than a quantity of order $V_{12}{}^2/U$, the damping process still favors the singlet.

[3] S. Alexander and P. W. Anderson, Phys. Rev. **133**, A1594 (1964).

[4] It should be emphasized again that formulas like (1) and (7a) of SFI give *only* the thermal expectation value of $n_{d\uparrow}-n_{d\downarrow}$ in the case of (7a) SFI, and of the total moment on the pair of d sites alone in the case of (1) of the present paper. Any polarization effects of the conduction electrons over and above their background Pauli moment are not determined by these formulas.

TABLE I. Energies of various states.[a]

States	Energies
Singlets	
both sites empty, $S_e=\|0;0\rangle$	0
both sites filled, $S_f=\|\uparrow\downarrow;\uparrow\downarrow\rangle$	$4\epsilon_d+2U$
"polar" singlet; $S_p=(2)^{-1/2}(\|\uparrow\downarrow;0\rangle-\|0;\uparrow\downarrow\rangle)$	$2\epsilon_d+U$
"mixed" singlets	
$S_{m1}=(2)^{-1/2}[a(\|\uparrow;\downarrow\rangle-\|\downarrow;\uparrow\rangle)+b(\|\uparrow\downarrow,0\rangle+\|0,\uparrow\downarrow\rangle)]$	$2\epsilon_d-U\sinh^2(\theta/2)$
$S_{m2}=(2)^{-1/2}[-b(\|\uparrow;\downarrow\rangle-\|\downarrow;\uparrow\rangle)+a(\|\uparrow\downarrow,0\rangle+\|0,\uparrow\downarrow\rangle)]$	$2\epsilon_d+U\cosh^2(\theta/2)$
Doublets	
one-electron doublets; $D_1^{\pm}=(2)^{-1/2}(\|\uparrow,0\rangle\pm\|0,\uparrow\rangle)$	$\epsilon_d\mp\frac{1}{4}U\sinh\theta$
three-electron doublets: $D_3^{\pm}=(2)^{-1/2}(\|\uparrow\downarrow,\uparrow\rangle\pm\|\uparrow,\uparrow\downarrow\rangle)$	$3\epsilon_d+U\mp\frac{1}{4}U\sinh\theta$
and two similar pairs with the spins reversed.	
Triplets	
$\|\uparrow;\uparrow\rangle$	$2\epsilon_d$
$T=(2)^{-1/2}(\|\uparrow;\downarrow\rangle+\|\downarrow;\uparrow\rangle)$	$2\epsilon_d$
$\|\downarrow;\downarrow\rangle$	$2\epsilon_d$

[a] In this table $\sinh\theta=4V_{12}/U$, $a=-\coth(\theta/2)/[1+\coth^2(\theta/2)]^{1/2}$, and $b=1/[1+\coth^2(\theta/2)]^{1/2}$. For brevity, the energies of these states S_f, S_p, etc. will be denoted by $E(S_f)$, $E(S_p)$, etc.

Finally, when $E(D_1^+)$ is also below $E(S_{m1})$ (see inequality), the susceptibility for small band scattering is dominated by spin $\frac{1}{2}$ with V^2 corrections from spin 1, and spin 0. This is the situation in which Alexander and Anderson find triplet coupling favored. In the present theory no such coupling ever occurs.

However, some caution is indicated by the fact that in the present model the singlet-triplet separation is only of order V_{12}^2/U. If a Coulomb interaction between the electrons on the d sites is added, and its exchange energy W, say, turns out to have ferromagnetic sign, the above conclusions become invalid as soon as W exceeds V_{12}^2/U. The triplet would then tend to be lowest, and the susceptibility would be dominated by spin one.

III. EVALUATION OF THE PARTITION FUNCTIONS

We use the resolvent technique (as in SFI) for evaluation of the partition function. The complete Hamiltonian is taken to be

$$\begin{aligned}\mathcal{H}&=\sum_{k,\sigma}\epsilon_k c_{k,\sigma}^\dagger c_{k,\sigma}\\&\quad+V\sum_{k,\sigma}\sum_{i=1}^{2}(e^{+i\mathbf{kr}}c_{k,\sigma}^*d_{i,\sigma}+e^{-i\mathbf{kr}}d_{i,\sigma}^*c_{k,\sigma})+\mathcal{H}_d\\&\equiv\mathcal{H}_b+\mathcal{H}_d+\mathcal{V}=\mathcal{H}_0+\mathcal{V},\end{aligned}\tag{3}$$

where $\mathcal{H}_d$ is the Hamiltonian of the "d" states alone, $\pm\mathbf{r}$ are the position vectors of the sites, and $\mathcal{V}$ is the band scattering operator. The resolvent operator $\mathfrak{R}=(\mathcal{H}-z)^{-1}$, could be projected onto the unperturbed singlet, doublet, and triplet manifolds as in SFI. The result will involve "nested" propagators and have an extremely complicated appearance, each propagator involving the manifold one more remote than its predecessor. We have calculated one of these nested expressions in the approximation in which, at most, two conduction electrons or holes are excited in the intermediate states.

The resolvent for the D_1 state (which exhibits the behavior of resolvents of other states as well), with the denominator evaluated to first order in Δ ($\Delta=\pi\rho V^2$, $\rho=$ density of states), may be written as

$$\mathfrak{R}_{D_1(z)}=[E(D_1)-z+\sum_k \mathcal{T}_k+i\delta]^{-1},\tag{4}$$

where δ is an infinitesimal,

$$\mathcal{T}_k=\frac{|\langle D_1|\mathcal{V}|T\rangle|^2 n_k}{E(T)-z-\epsilon_k}+\sum_{S'}\frac{|\langle D_1|\mathcal{V}|S'\rangle|^2 n_k}{E(S')-z-\epsilon_k}+\frac{|\langle D_1|\mathcal{V}|S_e\rangle|^2(1-n_k)}{-z+\epsilon_k},$$

and $\sum_{S'}$ means the sum over the three singlet states with two d electrons, S_p, S_{m1}, S_{m2}. The matrix elements may be evaluated with the aid of the wave functions derived above. For example, $N|\langle D_1^+|\mathcal{V}|S_{m1}\rangle|^2=\gamma_+V^2\times\cos^2\mathbf{k}\cdot\mathbf{r}$, $N|\langle D_1^+|\mathcal{V}|T\rangle|^2=3V^2\sin^2\mathbf{k}\cdot\mathbf{r}$, where $\gamma_\pm=1\pm[4V_{12}/(U^2+16V_{12}^2)^{1/2}]$. The summation over k is somewhat complicated by the presence of $\sin^2\mathbf{k}\cdot\mathbf{r}$ (etc.). Since ϵ_k is isotropic, the angular integration will give

$$\int d\Omega\begin{Bmatrix}\sin^2\mathbf{k}\cdot\mathbf{r}\\ \cos^2\mathbf{k}\cdot\mathbf{r}\end{Bmatrix}=2\pi\begin{Bmatrix}1-\dfrac{\sin 2kr}{2kr}\\ 1+\dfrac{\sin 2kr}{2kr}\end{Bmatrix}=2\pi\begin{Bmatrix}\mu_-\\ \mu_+\end{Bmatrix}.$$

If we assume

$$|\epsilon_k(dk/dE)_F|\ll\max(k_F,1/r),$$

then

$$\frac{\sin 2kr}{2kr}=\frac{\cos 2k_Fr\sin 2[\epsilon_k(dk/dE)_Fr]+\cos 2[\epsilon_k(dk/dE)_Fr]\sin 2k_Fr}{2[k_F+\epsilon_k(dk/dE)_F]r}\approx\frac{\sin 2k_Fr}{2k_Fr}.$$

Then $\mu_\pm$ becomes

$$\alpha_\pm=1\pm(\sin 2k_Fr/2k_Fr).$$

Now we will neglect the real part of $\sum_k \mathcal{T}_k$, and calculate

$$\begin{aligned}(2/\Delta)\mathrm{Im}\sum_k \mathcal{T}_k=&3n[E(T)-z]\alpha_-\\&+n[E(S_p)-z]\alpha_-+n[E(S_{m1})-z]\alpha_+\gamma_-\\&+n[E(S_{m2})-z]\alpha_+\gamma_++2n[-z]\alpha_+,\end{aligned}\quad(5)$$

where $n[z]$ is the Fermi distribution. Following the procedure of SFI, the partition function may be written as

$$\begin{aligned}\mathfrak{Z}_{D1}{}^+=&\int_{-\infty}^{+\infty}\mathrm{Im}\mathfrak{R}(z)e^{-\beta z}dz\\&=e^{-\beta E(D_1{}^+)}\int_{-\infty}^{+\infty}\frac{[\delta+\Delta I(\zeta)]e^{-\beta\zeta}d\zeta}{\zeta^2+[\Delta I(\zeta)+\delta]^2},\end{aligned}\quad(6)$$

where

$$I(\zeta)=\frac{1}{\Delta}\mathrm{Im}\sum_k \mathcal{T}_k$$

and we have substituted $\zeta+E(D_1{}^+)=z$.

$I(\zeta)$ will be infinitesimally small unless $\zeta>E(S_{m1})-E(D_1{}^+)$, and the integrand of Eq. (6) will be infinitesimally small unless $\zeta<0$. The problem then requires consideration of two separate cases depending on the sign of $E(S_{m1})-E(D_1{}^+)$.

A. *Magnetic:* $E_0=E(S_{m1})-E(D_1{}^+)>0$

In this case the integrand behaves like a delta function near $\zeta=0$, in the limit $\delta\to 0$. The $I(\zeta)$ term in the numerator can only contribute for $\zeta>E_0$, and, since $e^{-\beta E_0}\ll 1$, this contribution is negligible. (For large negative values of ζ the integrand could become large because of the exponential factor, even compensating for the small factor δ. However, either the band bottom or the finite spatial extent of the impurity potential V will introduce a cutoff before this happens.) The partition function for the magnetic case is now simply

$$\mathfrak{Z}_{D_1}{}^+=e^{-\beta E(D_1{}^+)}.\quad(7)$$

B. *Nonmagnetic:* $E_0=E(S_{m1})-E(D_1{}^+)<0$

$I(\zeta)$ is now finite at $\zeta=0$ so there is no contribution from the δ in the numerator in the limit $\delta\to 0$. If we make the transformation

$$e^{-\beta\zeta}n(\alpha-\zeta)=e^{-\beta\alpha}n(\zeta-\alpha),$$

then we immediately see that the largest term in $e^{-\beta\zeta}I(\zeta)$ is

$$\tfrac{1}{2}e^{-\beta E_0}\alpha_+n(\zeta-E_0)\gamma_-.$$

Hence, the partition function may be written

$$\mathfrak{Z}_{D_1}{}^+=\gamma_-e^{-\beta E(S_{m1})}\frac{\Delta}{2}\int_{-\infty}^{E_0}\frac{\alpha_+d\zeta}{\zeta^2}.$$

The $I(\zeta)$ does not contribute to the denominator because we are integrating over that portion of the ζ axis where $I(\zeta)=0$. The straightforward evaluation of the integral then gives

$$\mathfrak{Z}_{D_1}{}^+=-(\Delta/2E_0)\gamma_-\alpha_+e^{-\beta E(S_{m1})}.\quad(8)$$

Calculation of Curie constant. We could proceed to evaluate all the other partition functions in the same manner. However, examination of Eqs. (7) and (8) and the analogous results in SFI will enable us to write the following set of simplifying rules for the calculation of the partition functions:

(1) All partition functions have the form $n_iA_ie^{-\beta E_l}$, where A_i is independent of temperature, $E_l=\min\times[E(S_{m1}),E(D_1{}^+)]$, and n_i is an integer indicating the multiplicity of the state.

(2) The partition function for the state of lowest energy has $A=1$.

(3) For any state coupled to the lowest state to first order in $\mathcal{V}$ (states coupled in higher order are neglected in the present paper),

$$A_i=(\Delta\gamma_\pm\alpha_\pm)/(E_i-E_l).$$

The α and γ factors are determined from the square of the appropriate coupling matrix element.

Applying these rules, we can calculate the effective Curie constant from Eq. (1) for the two cases.

Nonmagnetic: $E_0=E(S_{m1})-E(D_1{}^+)<0$

$$C_{\mathrm{eff}}=C_{1/2}F/(1+F),\quad(9)$$

where

$$F=\frac{\Delta}{2}\left[\frac{\alpha_+\gamma_-}{E(D_1{}^+)-E(S_{m1})}+\frac{\gamma_+\alpha_-}{E(D_1{}^-)-E(S_{m1})}+\frac{\gamma_+\alpha_+}{E(D_3{}^+)-E(S_{m1})}+\frac{\gamma_-\alpha_-}{E(D_3{}^-)-E(S_{m1})}\right].$$

The labelings of the energies in the denominators of F indicate the four levels to which S_{m1} is coupled in first order.

Magnetic: $E_0=E(S_{m1})-E(D_1^+)>0$

$$C_{\text{eff}}=\left\{C_{1/2}+\frac{3C_1\Delta\alpha_+}{2[E(T)-E(D_1^+)]}\right\}\times\left\{1+\frac{\Delta}{2}\left[\frac{\gamma_+\alpha_+}{E(S_{m2})-E(D_1^+)}+\frac{\gamma_-\alpha_+}{E(S_{m1})-E(D_1^+)}+\frac{\alpha_+}{E(S_p)-E(D_1^+)}+\frac{3\alpha_+}{E(T)-E(D_1^+)}\right]\right\}^{-1}. \quad (10)$$

Each doublet state is actually counted twice, but since all the terms represent doublets, the factors of two cancel out. The accuracy of these expressions requires $\Delta\ll|E(S_{m1})-E(D_1^+)|$. In the region of transition from magnetic to nonmagnetic, the two levels cross and this inequality cannot hold. We must therefore do a more detailed calculation involving only the S_{m1} and D_1^+ levels.

IV. ZERO TEMPERATURE LEVEL SPLITTING

When the S_{m1} and D_1^+ levels are close together, we are permitted to rediagonalize them with respect to $\mathcal{V}$ and ignore the other levels. In this section we will therefore assume $|E(D_1^+)-E(S_{m1})|\ll|E(T)-E(D_1^+)|$, $|E(S_{m2})-E(D_1^+)|$, etc. For $E(S_{m1})<E(D_1^+)$ it is appropriate to consider a two-electron manifold. We take the wave function for this restricted manifold to be of the form

$$\psi=\sum_{k,\sigma}a_{k,\sigma}|D_1^+\rangle c_{k,-\sigma}+b|S_{m1}\rangle, \quad (11)$$

with the coefficients normalized so that

$$\sum_{k,\sigma}|a_{k,\sigma}|^2(1-n_k)+|b|^2=1.$$

The renormalized eigenvalues are found by minimizing the energy [calculated with Eq. (11) as wave function], minus the normalization condition multiplied by λ, with respect to a_k and b. This procedure gives the equations

$$\begin{aligned}&[E(D_1^+)+\epsilon_k-\lambda]a_k+V(\gamma_-\alpha_+/2)^{1/2}b=0,\\&V(\gamma_-\alpha_+/2)^{1/2}\sum_k a_k(1-n_k)+[E(S_{m1})-\lambda]b=0,\end{aligned} \quad (12)$$

determining the new energies as solutions of

$$-\lambda+E(S_{m1})=\tfrac{1}{2}V^2\gamma_-\alpha_+\sum_k\frac{1-n_k}{E(D_1^+)+\epsilon_k-\lambda}. \quad (13)$$

It should be noted that we have actually renormalized only the states S_{m1} and D_1^+ accompanied by an electron. If $E(S_{m1})>E(D_1^+)$, the appropriate manifold contains only one-electron states. The wave function is then of the form

$$\psi=a|D_1^+\rangle+\sum b_k|S_{m1}\rangle c_k. \quad (14)$$

This leads to the characteristic equation

$$-\lambda'+E(D_1^+)=\tfrac{1}{2}V^2\gamma_-\alpha_+\sum_k\frac{n_k}{E(S_{m1})=\epsilon_k-\lambda'}, \quad (15)$$

which renormalizes the states D_1^+ and S_{m1} accompanied by a hole.

It can be seen at once that for $|E(D_1^+)-E(S_{m1})|\gg\Delta$, we have $\lambda=E(S_{m1})$, $\lambda'=E(D_1^+)$. Using this value of λ, and the normalization condition we find

$$a_k=\frac{V(\gamma_-\alpha_+/2)^{1/2}}{(1+F')^{1/2}[E(S_{m1})-E(D_1^+)-\epsilon_k]},$$

where

$$F'=\tfrac{1}{2}V^2\gamma_-\alpha_+\sum_k\frac{1-n_k}{[E(S_{m1})-E(D_1^+)-\epsilon_k]^2}.$$

If the summation is performed, it is readily seen that F' is the same as the first term of the F used in Eq. (9). With this value of a_k, we can obtain the result

$$C_{\text{eff}}=C_{1/2}\sum_k a_k^2(1-n_k), \quad (16)$$

which is the same as Eq. (9), except that the terms involving levels other than S_{m1} and D_1^+ are missing. Hence, the choice of the wave function given by Eq. (11) corresponds to choosing $E(S_{m1})<E(D_1^+)$, as would be expected.

By the same reasoning, we can use $\lambda'=E(D_1^+)$ to find the coefficient a for the wave function given by Eq. (14). In this case

$$C_{\text{eff}}=C_{1/2}a^2, \quad (17)$$

which is easily seen to correspond to Eq. (10), with the terms involving states other than S_{m1} and D_1^+ removed. In order to determine the energy eigenvalues λ' when the states are close together, we rewrite Eq. (15) as

$$+y'=\tfrac{1}{2}V^2\gamma_-\alpha_+\sum_k\frac{n_k}{y'-\epsilon_k+E_0}, \quad (18)$$

where

$$y'=E(D_1^+)-\lambda'.$$

For positive E_0, Eq. (17) will always have one positive root, which gives the shift in energy of the D_1^+ state when it is lowest. If we approximate the density of states by a parabolic band starting at $k=0$, then the sum can be converted to an integral from $k=0$ to $k=k_F$ which can be easily evaluated. If $|y+E_0|\ll E_F$, then the resulting equation simplifies to

$$y'=3V^2\left[\frac{1}{2E_F}\ln\frac{4E_F}{y'+E_0}-\frac{1}{E_F}\right]. \quad (18a)$$

For a convenient numerical example, the parameters $3V^2/E_F^2=10^{-4}$, $E_0=0$ give the solution

$$y'=3.6\times10^{-4}\,E_F.$$

The solution of Eq. (13) is quite similar, provided certain approximations are made. The k summation is over all electron states above the Fermi surface, so a simple parabolic density would cause the integral to diverge. This divergence is always stopped by the actual high-momentum cutoff of the interaction potential V (which has here been assumed independent of k). For purposes of simplicity we will assume the density of conduction electron states to be symmetric with respect to the Fermi surface, although this is actually inconsistent with the assumption of a parabolic band. If we change variable to $y=E(S_{m1})-\lambda$, then Eq. (13) becomes

$$y=\tfrac{1}{2}V^2\gamma_-\alpha_+\sum_k\frac{1-n_k}{y+\epsilon_k-E_0}=\tfrac{1}{2}V^2\gamma_-\alpha_+\sum_k\frac{n_k}{y-\epsilon_k-E_0}.$$

For $E_0<0$ (singlet lowest) this always has a positive root, and the result of the summation is the same as Eq. (18a) with the substitutions $y'\Rightarrow y$, $E_0\Rightarrow -E_0$. Hence, in this approximation, the unperturbed crossing point remains unshifted. Using the value of y' calculated from Eqs. (18a), (16) gives

$$C_{\text{eff}}=\frac{C_{1/2}}{1+[\Delta\gamma_-\alpha_+/2(y'+E_0)]},\quad E_0>0 \tag{19a}$$

and

$$C_{\text{eff}}=\frac{C_{1/2}\Delta\gamma_-\alpha_+/2(y-E_0)}{1+[\Delta\gamma_-\alpha_+/2(y-E_0)]},\quad E_0<0. \tag{19b}$$

The only restriction on the size of Δ is that Δ be very much smaller than the "distance" between $E(S_{m1})$ or $E(D_1^+)$ and any of the neglected states. There is, however, a limitation on the size of the correction term since $\ln 4E_F/y>1$, Eq. (18a) shows that y, $y'>V^2/E_F\approx\Delta$ (for anything resembling a parabolic band), so the Δ terms never become larger than one. This implies that the effective moment is always larger for $E_0>0$ than for $E_0<0$, in agreement with the previous distinction between magnetic and nonmagnetic cases. In general in this order there will be a sharp discontinuity (but no longer an infinity) in the moment at the boundary between the two regimes.

Equation (18a) will permit positive solutions for y' for slightly negative E_0. These solutions are slightly larger than for small positive values of E_0. However, this does not mean that the corrected energies do not cross. The increase in y' is only logarithmic in E_0 while the unperturbed separation of energies is linear in E_0, and therefore the latter is dominant.

V. LONG-RANGE EFFECT

If the two impurities are separated by many lattice spacings, the d-d exchange interaction V_{12} is negligible. In this case, the s-d scattering will dominate, and the resolvent can be calculated with respect to a simpler set of wave functions than those used above. For the magnetic case ($\epsilon_d<0$; $\epsilon_d+U>0$) the unperturbed ground state consists of single occupancy of the d level of each site. The two electrons can form a spin singlet or triplet, and these two levels will be degenerate in energy (to zero order in V). In order to determine whether the pair is magnetic or nonmagnetic, we must examine the manner in which the s-d interaction removes the degeneracy.

In the unperturbed representation, the triplet and completely empty and filled states are the same as were used previously. The other states are:

State	Energy
$S_1=\lvert\uparrow\downarrow;0\rangle$	$2\epsilon_d+U$
$S_2=\lvert 0;\uparrow\downarrow\rangle$	$2\epsilon_d+U$
$S_m=(2)^{-1/2}(\lvert\uparrow;\downarrow\rangle-\lvert\downarrow;\uparrow\rangle)$	$2\epsilon_d$
$D_1^{1,2}=\lvert\uparrow;0\rangle,\lvert 0;\uparrow\rangle$	ϵ_d
$D_3^{1,2}=\lvert\uparrow;\uparrow\downarrow\rangle,\lvert\uparrow\downarrow;\uparrow\rangle$	$3\epsilon_d+U$

S_m and T are the degenerate unperturbed ground states. As far as s-d scattering is concerned, the only difference between the S_m and T states is that the T state (because of the exclusion principle) will not allow a scattering from the d to the conduction band and back to the d of the opposite site.

The lowest order terms to show this effect will involve coupling the S_m or T to the S_1 or S_2 via D_1 or D_3 intermediate states. For example, the interaction term for the sequence $S_m\rightarrow D_1^1\rightarrow S_1\rightarrow D_1^1\rightarrow S_m$ and $T\rightarrow D_1^1\rightarrow S_1\rightarrow D_1^1\rightarrow T$ is

$$\frac{\tfrac{1}{2}V^4\sqrt{2}\,\mathrm{Tr}(c_{\mathbf{k}'''\uparrow}c_{\mathbf{k}''\uparrow}^*\pm c_{\mathbf{k}'''\downarrow}c_{\mathbf{k}''\downarrow}^*)(c_{\mathbf{k}'\uparrow}c_{\mathbf{k}\uparrow}^*\pm c_{\mathbf{k}'\downarrow}c_{\mathbf{k}\downarrow}^*)\cos(\mathbf{k}+\mathbf{k}'-\mathbf{k}''-\mathbf{k}'')\cdot\mathbf{r}}{(+\epsilon_d-z+\epsilon_{\mathbf{k}}-\epsilon_{\mathbf{k}'}+\epsilon_{\mathbf{k}''})(2\epsilon_d+U-z+\epsilon_{\mathbf{k}}-\epsilon_{\mathbf{k}'})(\epsilon_d-z+\epsilon_{\mathbf{k}})}, \tag{20}$$

where the upper (+) signs refer to the S_m sequence and the lower (−) signs refer to the T sequence. Taking the trace of the c_k operator product gives

$$[n_{\mathbf{k}'\uparrow}(1-n_{\mathbf{k}\uparrow})+n_{\mathbf{k}'\downarrow}(1-n_{\mathbf{k}\downarrow})]\delta_{\mathbf{k}'\mathbf{k}''}\delta_{\mathbf{k}\mathbf{k}''}+[(1-n_{\mathbf{k}''\uparrow})\pm(1-n_{\mathbf{k}''\downarrow})][(1-n_{\mathbf{k}\uparrow})\pm(1-n_{\mathbf{k}\downarrow})]\times\delta_{\mathbf{k}\mathbf{k}'}\delta_{\mathbf{k}''\mathbf{k}'''}. \tag{21}$$

The first term of this expression is the same for both S_m and T; hence, it does not help remove the degeneracy. It is also independent of position because the δ function conditions make the argument of the cos in Eq. (20) equal to zero. The second term will give zero in the T state unless the conduction electrons are polarized. We will therefore consider only that part of Eq. (20) which is due to the second term of Eq. (21). If we assume the density of conduction electrons to be isotropic and sum over k', k''', average the directions of k and k'', and replace k'' by k' for simplicity, then we

have

$$\frac{V^4}{8r^2}\sqrt{2}\frac{f^2}{2\epsilon_d+U-z},$$

where

$$f=\sum_k \frac{(1-n_k)\sin 2kr}{k(\epsilon_d-z+\epsilon_k)}.$$

(It should be noted that this sum is really no longer discrete because the angle has been averaged out.) There are three other sequences of this class, and they are obtained by substituting D_3 and D_1 in one or both places. The result of adding all four terms together is

$$\tau=\frac{V^4\sqrt{2}}{8r^2}\frac{(f+g)^2}{2\epsilon_d+U-z},$$

where

$$g=\sum_k \frac{n_k \sin 2kr}{k(3\epsilon_d+U-z-\epsilon_k)}.$$

The main contribution to the partition function integral will come from z close to $2\epsilon_d$. Both f and g are real in this region. If we make the approximations

$$k_F r\gg 1, \quad -(r\epsilon_d m/hk_F)\gg 1,$$

and neglect terms which are exponentially small in these quantities, then an asymptotic approximation gives

$$f=\frac{\rho_s \cos 2k_F r}{rm(\epsilon_d-z)}, \quad g=\frac{\rho_s \cos 2k_F r}{rm(3\epsilon_d+U-z)}.$$

Now τ only occurs for S_{m1}, and for $z\approx 2\epsilon_d$ we find $\tau>0$. Hence, the S_{m1} is lowered with respect to the T state.

VI. SIMULTANEOUS CONSIDERATION OF *d-d* EXCHANGE AND BAND SCATTERING

The above calculations seem to indicate that the singlet (S_{m1}) is always lower than the triplet (T). In order to show that this is not due to our perturbation treatment for the band scattering, we have performed the diagonalization procedure of Sec. II, with the additional inclusion of all those states coupled by V. (This will be exact in the two-electron manifold.) The trial function consists of the four possible states with two d electrons with opposite spins ($d_{1\uparrow}^*d_{2\downarrow}^*$, $d_{1\downarrow}^*d_{2\uparrow}^*$, $d_{1\uparrow}^*d_{1\downarrow}^*$, $d_{2\uparrow}^*d_{2\downarrow}^*$), the four possible states with one electron and one conduction electron ($d_{1\uparrow}^*c_{k\downarrow}$, $d_{2\uparrow}^*c_{k\downarrow}^*$, $d_{1\downarrow}^*c_{k\uparrow}^*$, $d_{2\downarrow}^*c_{k\uparrow}^*$, with the conduction electron averaged over k states as in Sec. IV), and finally the four possible states with three d electrons and one conduction hole ($d_{1\uparrow}^*d_{2\uparrow}^*d_{2\downarrow}^*c_{k\downarrow}$, $d_{2\uparrow}^*d_{1\uparrow}^*d_{1\downarrow}^*c_{k\downarrow}$, $d_{1\downarrow}^*d_{2\uparrow}^*d_{2\downarrow}^*c_{k\uparrow}$, $d_{2\downarrow}^*d_{1\uparrow}^*d_{1\downarrow}^*c_{k\uparrow}$, with the conduction holes averaged over k). Using the method of Sec. IV we can diagonalize the energy by means of the equations obtained from the energy by differentiating with respect to each of the twelve coefficients of the trial states (remembering that eight of these coefficients depend upon k). The solutions are rather cumbersome, but if we assume $k_F r\gg 1$, then the four states with two d electrons combine in a manner similar to that found in Sec. II. The wave functions and energy eigenvalues have the same form as S_p, S_{m1}, S_{m2}, T ($S_z=0$) with the modifications

$$V_{12}\Rightarrow V_{12}'=V_{12}\left[1+V^2\sum_k \frac{1-n_k}{(\epsilon_d+\epsilon_k-\lambda)^2-W^2} + V^2\sum_k \frac{n_k}{(3\epsilon_d+U-\epsilon_k-\lambda)-W^2}\right]$$

and

$$\epsilon_d\Rightarrow \epsilon_d'=\epsilon_d-V^2\sum_k \frac{(\epsilon_d+\epsilon_k-\lambda)(1-n_k)}{(\epsilon_k+\epsilon_k-\lambda)^2-W^2} - V^2\sum_k \frac{(3\epsilon_d+U-\lambda)n_k}{(3\epsilon_d+U-\epsilon_k-\lambda)^2-W^2}.$$

As in Sec. IV, λ is simply the corrected energy of the state under consideration. Since these corrections have the same form for both S_{m1} and T, it is apparent that they have no effect on the previous conclusion that $E(S_{m1})<E(T)$.

VII. CONCLUSION

The calculations of this paper indicate that in perturbation theory neither the *d-d* exchange, the *s-d* scattering, nor any combination of the two will produce a parallel alignment of a pair of localized moments. The analysis does, however, show that the pair can show a sizable magnetic moment provided that the *d-d* exchange is such that $E(D_1^{\pm})<E(S_{m1})$. The conditions required for this relation are similar to those required by Alexander and Anderson[3] for parallel alignment. This suggests that the two methods may be equivalent, even though the representation of Alexander and Anderson[3] does not characterize the parallel alignment as either doublet or triplet.