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Ground state of an ion fluctuating between two magnetic valence states

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As a model for mixed-valence thulium which fluctuates between the configurations f^{13}, $S=\frac{1}{2}$, and f^{12}, $S=1$, we consider an ion with orbital degeneracy embedded in a free-electron continuum. We construct variational states of different total-spin multiplicity, namely singlet, doublet, and triplet. We find that the ground state is a singlet, with the triplet and doublet lying higher in energy and in that order. If we confine ourselves to the simplest variational functions, i.e., those that do not include electron-hole excitations of the Fermi sea, then the splitting between singlet and triplet is very small, of the order of a few percent of the mixing width. (Under the same approximation, this splitting for the case where one of the valence states is nonmagnetic, is of the order of the mixing width.) When excited states of the Fermi sea are included, we find that the $1/N$ expansion, which shows that in f^0 to f^1 fluctuating valence the corrections due to these states are small for large N, is not applicable to the present case because the degeneracies of f^1 and f^2 are comparable, and so N is of order unity. We do a perturbation calculation to all orders, keeping only the dominant logarithmic terms. This has the effect of enhancing the energy separation between singlet and magnetic states by a factor of order 3. This separation is still very small however; we conclude that the magnetism of TmSe is probably caused by interactions between ions.

I. INTRODUCTION

Phenomenologically, mixed-valence materials appear to fall in two distinct classes, one in which one of the valence states has no magnetic moment (class I), as in Ce and Yb compounds, and the other in which both valence states have magnetic moments (class II), as in TmSe. It has been recognized[1] that (for significant valence ratios) the former remain a normal Fermi liquid (i.e. show no spontaneous moment or magnetic ordering) at low temperatures, while the latter undergo a transition to a magnetically ordered state.

A significant question raised in this connection is whether this difference arises from the nature of an isolated mixed-valence atom or whether it arises due to a difference in the interaction between mixed-valence atoms in the two different cases. It has been shown[2] in a Hartree-Fock approximation that the interactions differ significantly for the two cases. Using this, a transition from antiferromagnetic to ferromagnetic order was predicted on alloying TmSe with TmTe, which was subsequently observed.[3] One may argue,[4] however, that the ground state of an isolated ion may differ between the two cases. In this paper we show that this is not so, using methods employed earlier.[5]

Several years ago we constructed[5] a variational wave function for the mixed-valence impurity of class I and calculated the energy and the magnetic susceptibility of the ground state, which is a singlet. The variational function used was

$$|\psi(S=0)\rangle=\left[\alpha_0+\sum_{k,\sigma}\alpha_k c_{a\sigma}^{\dagger}c_{k\sigma}\right]|\psi_0\rangle\ , \tag{1a}$$

where $|\psi_0\rangle$ is the filled Fermi sea, σ the spin index, $c_{a\sigma}^{\dagger}$ the creation operator for the local orbital assumed nondegenerate, and $c_{k\sigma}$ the annihilation operator for conduction electrons projected on a spherical basis around the impurity. The binding energy of the singlet, ω (defined to be positive), was found to be given by

$$\omega=\epsilon_f+(2\Gamma/\pi)\ln[(W+\omega)/\omega]\ . \tag{1b}$$

Here ϵ_f is the energy of the f level measured from the Fermi level ($\epsilon_f\leq 0$), Γ is the virtual level width arising from the mixing interaction with the conduction band, and W is the width of the occupied part of the band. In Eq. (1) we have assumed a constant density of states, while in Ref. 2 we had taken a free-electron density of states, resulting in a slightly different expression.

The result Eq. (1b) has been reobtained through a scaling analysis by Haldane,[6] by summing an infinite class of diagrams by Bringer and Lustfeld,[7] by means of Brillouin-Wigner perturbation theory by Ramakrishnan,[8] and by Keiter and Grewe.[9] Bringer and Lustfeld showed that their results for the Green's function are exactly equivalent to having Eq. (1a) as the wave function. Ramakrishnan and Sur considered also the case of orbital degeneracy N and found that the factor 2 in Eq. (1b), which comes from the spin degeneracy, is replaced by the full degeneracy $2N$. Gunnarson and Schönhammer[10] also considered the case of orbital degeneracy and showed that the generalization of Eq. (1a),

$$|\psi\rangle=\left[\alpha_0+\sum_{k,m,\sigma}\alpha_{km}c_{am\sigma}^{\dagger}c_{km\sigma}\right]|\psi_0\rangle\ , \tag{1c}$$

is exact in the limit $N=\infty$. They did this by considering higher-order terms, which, because of angular-momentum conservation, give corrections of $O(1/N)$. The $1/N$ expansion has also been developed, using other techniques, by Coleman,[11] Read and Newns,[12] Lee,[13] and by several others.

The validity of our earlier approach having been established, it is worthwhile to consider mixed-valence impurities of class II by similar methods. Such a calculation was recently presented by Mazzaferro *et al.*;[14] unfortunately they did not examine the different possible spin states of the impurity—Fermi-sea system and concluded erroneously that the ground state is magnetic. More recently, Lustfeld,[15] in a comprehensive paper, investigated in great generality the mixed-valence problem for a rare-earth ion in jellium, using the methods of scaling theory. Lustfeld finds that for a large number of ions, including Tm, the ground state of the system is a singlet.

Here we present a treatment confined to the ion Tm for which the f-shell valence fluctuates between one and two holes (f^{13} and f^{12}). Because the ionic states have only one or two holes (we will be treating them as electrons to simplify the writing), the angular-momentum machinery required to deal with them is considerably simpler than in the general case and we are able to use the simple variational methods of our earlier paper.

To recall the mixed-valence problem, consider an ion having an impurity level f lying within a partly filled band at an energy ϵ_f relative to the Fermi level. If E_0 is the total energy of the Fermi sea in the absence of any mixing interaction, the ground state of the system has one electron in the f level, and the total energy is $E_0+\epsilon_f$. Suppose now a second electron is transferred from the Fermi level to f: If U is the Coulomb repulsion between two electrons localized on f, the total energy becomes $E_0+2\epsilon_f+U$. The system is mixed valent when the energy cost of adding the second electron is small, either positive or negative, i.e. $\epsilon_f+U=\delta$ and $|\delta| \lesssim \Gamma$, the level width.

We show that for such an ion in an isotropic Fermi sea, with an isotropic mixing interaction between the localized and the conduction states, the ground state of the complete system is a singlet. This conclusion is not obvious since both ionic configurations are magnetic. The energy separation between the singlet and the lowest-energy magnetic states is, however, very small, of the order of a few percent of the level width [in contrast to the situation in materials of class I (see Appendix A), where this energy separation is of the order of the level width]. This fact has a bearing on the question of the origin of magnetic order in these materials.

The paper is organized as follows: In Secs. II and III the simplest variational functions are used, namely those containing no electron-hole excitations. This is the same approximation that was made in Ref. 5. Section II deals with a case of minimal orbital degeneracy, corresponding to a fictitious orbital angular momentum $l=\frac{1}{2}$. This is the simplest model with the right physics, and it has the advantage that the calculations can be carried through without the complications of angular-momentum recoupling. Section III deals with the realistic case of orbital degeneracy with l arbitrary. The spin-orbit coupling is included from the start in the description of the one-electron localized state because typical level widths are of the order $\Gamma \approx 0.01$ eV, while spin-orbit splittings range from 0.25 eV in Ce to 1.0 eV in Tm. The cases of singlet and magnetic states of the system are treated, making use of angular-momentum recoupling techniques. The case of LS coupling, with the lowest ionic state given by Hund's rule, is also treated and shown to reduce, for the value $l=\frac{1}{2}$, to the result of Sec. II for minimal degeneracy.

In Sec. IV we generalize our wave functions so as to include electron-hole excitations of the Fermi sea. Since the energy of such excitations is arbitrarily small, it is not clear that perturbation theory can be used and it is necessary to include these excitations to all orders. We show that the N of the $1/N$ expansion is not a large number in class-II fluctuating valence ions, and that N ranges between $\frac{1}{2}$ and 2. We give our conclusions in Sec. V.

II. LOWEST-ORDER VARIATIONAL CALCULATION

Let f^1 and f^2 be the two valence states of the impurity. We assume that any other occupation states are so far removed in energy that they do not need to be considered. Since f^2 has spin 1, there must be at least two distinct localized orbitals, $|a\rangle$ and $|b\rangle$, differing in their orbital magnetic quantum number, say $m_l(a)=1$ and $m_l(b)=0$. We take as the simplest model an f level with only two orbitals. The Hamiltonian is

$$H=H_{\text{band}}+H_f+H_{\text{mix}} \ . \tag{2}$$

The mixing interaction is assumed to be spherically symmetric (and spin independent), so it conserves m_l. We use the radial representation, $|k,l,m_l\rangle$, for the free-electron band, and drop the l index. Because of spherical symmetry, $|a\rangle$ mixes only with $|k,1\rangle$ and $|b\rangle$ mixes only with $|k,0\rangle$, i.e.,

$$\langle a|H_{\text{mix}}|k,1\rangle=\langle b|H_{\text{mix}}|k,0\rangle=V \ . \tag{3}$$

We also assume V and the density of states ρ to be constant, independent of k. These approximations are not essential, but they simplify the calculation while not altering the results in any meaningful way.

The most general wave function for the Hamiltonian (2) is a sum of terms, each having the following form: The f level is occupied by one or two electrons; there is a corresponding number of holes in the Fermi sea so as to conserve the total number of electrons, and there are any number 0,1,2,. . . of electron-hole excitations. In this section we will omit any terms containing electron-hole excitations.

Since the impurity states have, respectively, $S_f=\frac{1}{2}$ and $S_f=1$, the possible ground states of the system are a singlet, a doublet, or a triplet. Wave functions having these spin multiplicities are now constructed and their energies calculated. First, the simplest wave functions, i.e., those having no electron-hole excitations, are considered.

A. Spin doublet

Let $|\psi_0\rangle$ be the ground state of the singlet Fermi sea. We take as a variational wave function

$$|\psi_D\rangle_\uparrow=\alpha c_{a\uparrow}^\dagger|\psi_0\rangle + \sum_k [\beta(k)/\sqrt{6}] \times[(c_{a\uparrow}^\dagger c_{b\downarrow}^\dagger + c_{a\downarrow}^\dagger c_{b\uparrow}^\dagger)c_{k0\downarrow}+2c_{a\uparrow}^\dagger c_{b\uparrow}^\dagger c_{k0\uparrow}]|\psi_0\rangle , \tag{4}$$

where the $c_{i\sigma}^\dagger, c_{i\sigma}$ are creation and destruction operators. [Throughout we will use $k,k',\ldots$ to label states below the Fermi level, and $q,q',\ldots$ to label states above; the similar wave function with $\downarrow$ spin is degenerate with (4).]

Note that of the four singly occupied states $a\sigma, b\sigma$, $\sigma=\pm1$, Eq. (4) contains only one. The reason for this can be seen as follows: Start with the filled Fermi sea and state $a\sigma$ occupied. Under the action of H_{mix} an electron $(k,0)$ is transferred to orbital b. The next effect of H_{mix} can only be to transfer the electron in b back to state $(k,0)$ as there is no hole available in band $(k,1)$ to which the electron in state $a\sigma$ could go. We can represent this by the sequence

$$(a)\leftarrow V\rightarrow(ab;k0)\leftarrow V\rightarrow(a)\leftarrow V\rightarrow(ab;k'0)\leftarrow V\rightarrow(a)\cdots , \tag{5}$$

which results in the wave function (4). Hence, there is no mixing between the states in which a and b are, respectively, singly occupied. As will be seen below, this is the reason why the doublet state is higher in energy than the singlet.

Let the total energy be

$$E=E_0+\epsilon_f-\omega , \tag{6}$$

where ω is positive. If $\epsilon_f+U=\delta$ is ≥ 0, then ω is the binding energy of the impurity to the Fermi sea; if $\delta<0$, the binding energy is $\omega+\delta$.

The variational equations,

$$\delta_V\langle\psi_D|H|\psi_D\rangle-(E_0+\epsilon_f-\omega)\delta_V\langle\psi_D|\psi_D\rangle=0, \tag{7}$$

where α and $\beta(k)$ are varied, give the following equation for ω_D, the value of ω for the doublet state:

$$\omega_D=\frac{3\Gamma}{2\pi}\ln\left[\frac{W+\omega_D+\delta}{\omega_D+\delta}\right] . \tag{8}$$

This is the result obtained in Ref. 14.

B. Spin singlet

Consider a singlet state obtained by transferring an electron from states $(k,1,\sigma)$ to the f states (a,σ). Let now H_{mix} act and transfer electrons. As was done in Eq. (5), this can be represented by

$$(a;k1)\leftarrow V\rightarrow(ab;k1,k'0)\leftarrow V\rightarrow(b;k'0) \leftarrow V\rightarrow(ab;k''1,k'0)\leftarrow V\rightarrow(a;k'1)\leftarrow V\rightarrow\cdots . \tag{9}$$

Note that, in contrast to the doublet case where the singly occupied a state did not mix with the singly occupied b state, here these same states are connected in order V^2. Hence they are both present in the wave function, which we take to be of the form

$$|\psi_S\rangle=\sum_k[\alpha_1(k)/\sqrt{2}](c_{a\uparrow}^\dagger c_{k1\uparrow}+c_{a\downarrow}^\dagger c_{k1\downarrow})|\psi_0\rangle+\sum_{k'}[\alpha_0(k')/\sqrt{2}](c_{b\uparrow}^\dagger c_{k'0\uparrow}+c_{b\downarrow}^\dagger c_{k'0\downarrow})|\psi_0\rangle + \sum_{k,k'}[\beta(k,k')/\sqrt{3}][c_{a\uparrow}^\dagger c_{b\uparrow}^\dagger c_{k'0\uparrow}c_{k1\uparrow}+c_{a\downarrow}^\dagger c_{b\downarrow}^\dagger c_{k'0\downarrow}c_{k1\downarrow}+\tfrac{1}{2}(c_{a\uparrow}^\dagger c_{b\downarrow}^\dagger+c_{a\downarrow}^\dagger c_{a\uparrow}^\dagger)(c_{k'0\uparrow}c_{k1\downarrow}+c_{k'0\downarrow}c_{k1\uparrow})]|\psi_0\rangle . \tag{10}$$

The last term, in $\beta(k,k')$, is formed by coupling the triplet ab state to a triplet two-hole state so as to form a singlet. The variational equations are

$$\alpha_1(k)(\omega+\epsilon_k)=-\sqrt{3/2}\sum_{k'}V\beta(k,k') , \tag{11a}$$

$$\alpha_0(k')(\omega+\epsilon_{k'})=-\sqrt{3/2}\sum_{k}V\beta(k,k') , \tag{11b}$$

$$\beta(k,k')(\omega+\delta+\epsilon_k+\epsilon_{k'})=-\sqrt{3/2}V[\alpha_1(k)+\alpha_0(k')] , \tag{11c}$$

where $\epsilon_k,\epsilon_{k'}$ are the positive, one-hole excitation energies relative to the Fermi level. Substitution of (11c) into (11a) and (11b) gives two coupled integral equations for $\alpha_1(k)$ and $\alpha_0(k')$. These two equations are compatible if α_1 and α_0 are the same function, α. Since the mixing interaction is the same for orbitals a and b, it is to be expected that they will, in fact, occur in a symmetric way in the wave function. We obtain for the eigenvalue equation the homogeneous integral equation

$$\alpha(k)(\omega+\epsilon_k)=\tilde{\Gamma}\int_0^W\frac{\alpha(k)+\alpha(k')}{\omega+\delta+\epsilon_k+\epsilon_{k'}}d\epsilon_{k'} , \tag{12}$$

where we have made use of

$$V^2\sum_k=(\Gamma/\pi)\int d\epsilon_k$$

in doing the summations, and have introduced $\tilde{\Gamma}=(3\Gamma/2\pi)$.

That we should have obtained an integral equation is not surprising in view of the comment following (9), i.e., that the two kinds of terms $c_{a\sigma}^\dagger c_{k1\sigma}$ and $c_{b\sigma}^\dagger c_{k'0\sigma}$ interact in order V^2 (or $\tilde{\Gamma}$). Thus we have a kind of Schrödinger equation in momentum space for the amplitude $\alpha(k)$: The kinetic energy is ϵ_k and the effective potential in $\tilde{\Gamma}$ couples $\alpha(k)$ to all the other amplitudes $\alpha(k')$. The term in $\alpha(k')$ in Eq. (12) is responsible for the difference in binding energy between the doublet and the singlet. This can be seen by letting $\alpha(k')\equiv 0$ (i.e., excluding the $c_{b\sigma}^\dagger c_{k'0\sigma}$

terms) and taking $\epsilon_k=0$ to obtain the ground state. Equation (12) reduces then to Eq. (8).

The interaction responsible for the binding energy of the doublet is of order V (the mixing strength), while that responsible for the doublet-singlet difference is of order V^2. Thus we expect this difference to be small compared to ω_D. We denote by ω_S the solution of Eq. (12), so that the singlet binding energy (relative to the doublet) is $\omega_S-\omega_D$. We have not been able to solve Eq. (12) analytically. Before discussing the numerical solution we shall discuss the triplet state.

C. Spin triplet

We start as we did for the singlet, by transferring an electron from state $k\,1\sigma$ to the f state $a\sigma$. As in the singlet case, H_{mix} connects this state in second order to the state where the orbital b is singly occupied, but now we have two kinds of states in which both a and b are occupied: First, two holes in the singlet state coupled to the triplet (ab), and second, two holes in the triplet state coupled to the triplet (ab) to form a triplet. The wave function of the triplet for $M_S=0$ is taken to be

$$|\psi_T\rangle_0=\sum_k[\alpha_1(k)/\sqrt{2}](c^\dagger_{a\downarrow}c_{k1\downarrow}-c^\dagger_{a\uparrow}c_{k1\uparrow})|\psi_0\rangle+\sum_{k'}[\alpha_0(k')/\sqrt{2}](c^\dagger_{b\downarrow}c_{k'0\downarrow}-c^\dagger_{b\uparrow}c_{k'0\uparrow})|\psi_0\rangle$$
$$+\tfrac{1}{2}\sum_{k,k'}\beta(kk')(c^\dagger_{a\downarrow}c^\dagger_{b\uparrow}+c^\dagger_{a\uparrow}c^\dagger_{b\downarrow})(c_{k'0\uparrow}c_{k1\downarrow}-c_{k'0\downarrow}c_{k1\uparrow})|\psi_0\rangle+\frac{1}{\sqrt{2}}\sum_{k,k'}\gamma(kk')(c^\dagger_{a\downarrow}c^\dagger_{b\downarrow}c_{k'0\downarrow}c_{k1\downarrow}-c^\dagger_{a\uparrow}c^\dagger_{b\uparrow}c_{k'0\uparrow}c_{k1\uparrow})|\psi_0\rangle\ . \qquad (13)$$

The variational equations are

$$\alpha_1(k)(\omega+\epsilon_k)=-\frac{V}{\sqrt{2}}\sum_{k'}\beta(kk')-V\sum_{k'}\gamma(kk')\ , \qquad (14a)$$

$$\alpha_0(k')(\omega+\epsilon_{k'})=\frac{V}{\sqrt{2}}\sum_{k}\beta(kk')-V\sum_{k}\gamma(kk')\ , \qquad (14b)$$

$$\beta(kk')(\omega+\delta+\epsilon_k+\epsilon_{k'})=-\frac{V}{\sqrt{2}}\alpha_1(k)+\frac{V}{\sqrt{2}}\alpha_0(k'), \qquad (14c)$$

$$\gamma(kk')(\omega+\delta+\epsilon_k+\epsilon_{k'})=-V\alpha_1(k)-V\alpha_0(k')\ . \qquad (14d)$$

Taking the functions α_1 and α_0 to be the same as before, we obtain the eigenvalue equation

$$\alpha(k)(\omega+\epsilon_k)=\tilde{\Gamma}\int_0^W\frac{\alpha(k)+\frac{1}{3}\alpha(k')}{\omega+\delta+\epsilon_k+\epsilon_{k'}}d\epsilon_{k'}\ . \qquad (15)$$

This differs from Eq. (12) for the singlet in having the factor $\frac{1}{3}$ in front of $\alpha(k')$. Thus the effective potential that couples $\alpha(k)$ to $\alpha(k')$ is only $\frac{1}{3}$ of what it is for the singlet, and hence we expect the triplet binding energy to be much smaller than that of the singlet.

D. Numerical results

To solve Eq. (12) numerically, the integration is replaced by a discrete summation (i.e., $d\epsilon\to s\sum_{i=1}^{n}$) which converts it to a system of homogeneous linear equations. In order to choose a reasonable value for the mesh, it is necessary to consider the rate of change with energy of the symmetric kernel and of the eigenvector $\alpha(k)$. The kernel is largest at $\epsilon_k=\epsilon_{k'}=0$ and falls off slowly with energy. The eigenvector $\alpha(k)$ is also maximum at $\epsilon_k=0$, but it falls off sharply away from it. To see this, perform the integration of the first term on the right-hand side of Eq. (12), which converts it to

$$\alpha(k)\left[\omega_S+\epsilon_k-\tilde{\Gamma}\ln\left[\frac{W+\omega_S+\epsilon_k}{\omega_S+\epsilon_k}\right]\right]=\tilde{\Gamma}\int_0^W\frac{\alpha(k')}{\omega_S+\epsilon_k+\epsilon_{k'}}d\epsilon_{k'}\ . \qquad (16)$$

The coefficient of $\alpha(k)$, expanded to first order in ϵ_k and neglecting ω_S/W, is given by

$$\omega_S-\tilde{\Gamma}\ln[(W+\omega_S)/\omega_S]+(1+\tilde{\Gamma}/\omega_S)\epsilon_k\ .$$

Now,

$$\omega_D-\tilde{\Gamma}\ln[(W+\omega_D)/\omega_D]=0\ ,$$

and it will be seen below that ω_S is only a little larger than ω_D, so that

$$\omega_S-\tilde{\Gamma}\ln[(W+\omega_S)/\omega_S]\equiv\nu\tilde{\Gamma}\ ,$$

where $\nu<1$ is a small number. The right-hand side of Eq. (16) varies slowly with ϵ_k, and hence $\alpha(k)$ varies as $[\nu\tilde{\Gamma}+(1+\tilde{\Gamma}/\omega_S)\epsilon_k]^{-1}$ for $\epsilon_k\lesssim\tilde{\Gamma}$, which is a rapid rate of variation. On the other hand, for ϵ_k large compared to $\tilde{\Gamma}$, $\alpha(k)$ can be seen to vary slowly, as $(1/\epsilon_k)^2$. Accordingly, we choose a fine mesh, s_1 for $\epsilon_k\lesssim\tilde{\Gamma}$, and a coarse mesh, s_2 for larger ϵ_k; n_1 and n_2 are the corresponding numbers of intervals. From here on we express all energies in units of $\tilde{\Gamma}$. We also take $\delta=0$ in all our calculated values except as noted otherwise.

Table I lists the values of ω_D from Eq. (8) and the values of $\omega_S-\omega_D$ calculated for the range $W=20$, 50, 100 and 200. Equation (16) was approximated by a system of linear equations of order 300, with values of $s_1=0.02, n_1=100$ and $s_2=0.09, n_2=200$. (The energy range covered in the summation is thus 20, which is only part of the actual W, except for $W=20$; this does not introduce any detectable error because at large energies the

TABLE I. Doublet and singlet binding energies, $\omega_D^{(0)}$ and $\omega_S^{(0)}-\omega_D^{(0)}$, for different values of W. Energies expressed in units of $\tilde{\Gamma}$. Calculation done with $s_1=0.02, n_1=100$ and $s_2=0.09, n_2=200$.

W	20	50	100	200
$\omega_D^{(0)}$	2.2797	2.9028	3.4115	3.9453
$\omega_S^{(0)}-\omega_D^{(0)}$	0.0457	0.0270	0.0171	0.0107

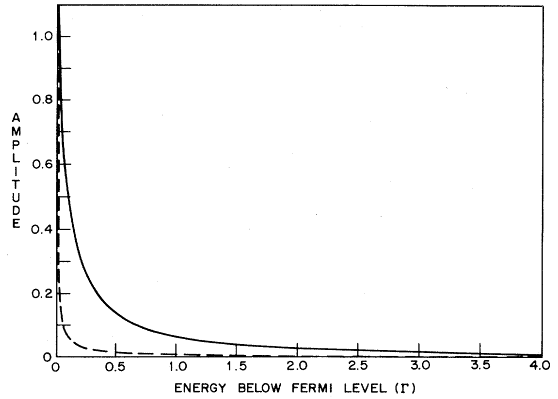

FIG. 1. Wave functions of the singlet and triplet states in k space, normalized to unity at the Fermi energy, for $W=20\Gamma$. The solid line refers to the singlet, the dashed line to the triplet.

eigenfunction $\alpha(k)$ is negligible, $[\alpha(k)/\alpha(0)]\approx 10^{-4}$ for $\epsilon_k>20$).

It is seen that the singlet binding energy $\omega_S-\omega_D$ decreases from 0.0457 to 0.0107 as W changes from 20 to 200. This decrease is to be understood from the fact that ω_D increases logarithmically with W, so that the effective potential

$$V_{\text{eff}}(k,k')=-\frac{3}{2}\frac{V^2}{\omega_S+\epsilon_k+\epsilon_{k'}} \tag{17}$$

decreases as W increases, because $\omega_S\approx\omega_D$.

The binding energy of the triplet, $\omega_T-\omega_D$, has also been examined and found to be, somewhat unexpectedly, exceedingly small, more so than what the factor $\frac{1}{3}$ in the right-hand side of Eq. (15) would have suggested. For $W=20$, taking $s_1=0.0001, n_1=200$ and $s_2=0.02, n_2=100$, we found $\omega_T-\omega_D=0.00005$, i.e., a factor 10^3 smaller than $\omega_S-\omega_T$. (At the energy $\epsilon_k=2.0$, the wave function was down to 2×10^{-5} of its value at the origin so that we can neglect contributions from higher-energy states).

In Fig. 1 we have plotted the eigenfunctions in k space of the singlet and triplet states for $W=20$. The wave function of the triplet is much more localized near the Fermi level (that of the doublet is a δ function!) than that of the singlet state. The physical origin of the large singlet binding energy can be seen to be the fact that with a wave function that is extended in k space, the off-diagonal contributions of H_{mix} are more effective in lowering the energy. The eigenfunctions transformed to real space have characteristic oscillations at the inverse Fermi wave vector.

III. ARBITRARY ORBITAL DEGENERACY

We begin with the case, valid for thulium, that the spin-orbit coupling is large compared to the level width, so that the f^1 configuration (we associate f^1 with Tm^{2+} and f^2 with Tm^{3+}) must be described by f electrons with quantum numbers j_+,m where $j_+=l+s$ is the total angular momentum. If the spin-orbit interaction had been large compared to the Coulomb interaction, then jj coupling would have been valid for the f^2 configuration and one would only have to consider one-electron states having $j_+=l+s$. The lowest f^2 state would then be obtained by coupling two j_+ states to give $J=2j_+-1$. This is what we shall do in detail in the first part of this section, using straightforward angular-momentum recoupling methods. In fact, LS coupling gives a better description of the rare earths, although for Tm one should really use intermediate coupling. Any departure from pure jj coupling makes it necessary to consider also one-electron states with angular momentum $j_-=l-s$. We have included these states in an extension of our recoupling calculation, and will give the results for the pure LS-coupling case, following the jj-coupling treatment.

Just as in Sec. II, we will do the calculation for three different values of the total angular momentum J. The first is the case $J=j$ (we drop the subscript $+$ until we need it again). This case occurs when the total number n_j of electrons of angular momentum j in the system is equal to one plus a multiple of $2j+1$. (Free-electron states with other values of angular momentum do not interact and are irrelevant.) The second and third cases are $J=0$ and $J=1$. Both occur when n_j is equal to a multiple of $2j+1$.

We should make a remark about comparing the ground states of systems with different total number of electrons, and, in fact, about considering systems where the number n_j is a multiple of $(2j+1)$. Superficially, this appears to be an artificial restriction. However, it is not so. The free-electron sea corresponds to the infinite-volume limit of the system, and so the actual number n_j is arbitrarily large. When we prescribe the value of n_j to within a multiple of 2_j+1, we are in fact leaving out of our calculations, no matter what n_j actually is, a number of states which is at most $2j+1$. Since n_j tends to infinity, the fraction $(2j+1)/n_j$ tends to zero, and so the neglected free-electron states do not affect our results.

We shall construct variational wave functions that are of the same form as those of Sec. II. For the $J=j$ case, for instance, we take

$$|\psi\rangle_j=\alpha\,|\psi_1,j\rangle+\sum_k\beta(k)\,|\psi_2(k),j\rangle\ , \tag{18}$$

where the states $|\psi_1,j\rangle$ and $|\psi_2(k),j\rangle$ have, respectively, one and two electrons on the f level. Specific expressions for the families of states $|\psi_1,J\rangle$ and $|\psi_2,J\rangle$ with one or two holes in the Fermi sea and for total angular momentum J of the system will be given below. To find the value of J of the ground state, we need the matrix element of the mixing interaction,

$$H_{\text{mix}}=V\sum_m c_{fjm}^{\dagger}c_{kjm}+c_{kjm}^{\dagger}c_{fjm}\ ,$$

between the families of states $|\psi_1,J\rangle$ and $|\psi_2,J\rangle$.

A. Magnetic state, $J=j$

The states ψ_1 and ψ_2 are given by

$$|\psi_1,j\rangle=(f,j)\ , \tag{19}$$

$$|\psi_2(k),j\rangle=((f,f)2j-1,(k)j;j)\ . \tag{20}$$

The notation used in (19) and (20) is standard; thus, in

(20), there are two electrons on the f orbitals with their orbital momenta coupled to give $2j-1$, and one hole k in the Fermi sea, whose angular momentum j is coupled to $2j-1$ to give a resultant j. A convenient way to find $\langle\psi_2(k),j\,|\,H_{\rm mix}\,|\,\psi_1,j\rangle$ is to act with $H_{\rm mix}$ on $|\,\psi_1,j\rangle$ and to project the resulting normalized state onto $|\,\psi_2(k),j\rangle$. To be able to use angular-momentum recoupling procedures, we formally treat the two-f-electron states as unequivalent (different shells), distinguishing them by a prime, and after the calculation restore the equivalence by multiplying by a factor $\sqrt{2}$. We have

$$H_{\rm mix}\,|\,\psi_1,j\rangle = V\sqrt{(2j+1)}\,|\,\tilde\psi_2(k),j\rangle\ , \tag{21}$$

where the normalized state $|\,\tilde\psi_2(k),j\rangle$ is

$$|\,\tilde\psi_2(k),j\rangle = ((f'k)0,(f)j;j)\ . \tag{22}$$

The projection of $\tilde\psi_2$ onto ψ_2 is given by a 6-j symbol;[16]

$$((f'k)0,(f)j;j\,|\,(f'f)2j-1,(k)j;j) = (-1)^{4j-1}\sqrt{4j-1}\begin{Bmatrix} j & j & 0\\ j & j & 2j-1\end{Bmatrix} = \frac{\sqrt{4j-1}}{2j+1} \tag{23}$$

Substituting in (21) and multiplying by $\sqrt{2}$ to restore the equivalence of the f electrons, we obtain

$$\langle\psi_2(k),j\,|\,H_{\rm mix}\,|\,\psi_1,j\rangle = V\left[\frac{2(4j-1)}{(2j+1)}\right]^{1/2}\ . \tag{24}$$

This quantity replaces, for arbitrary j, the matrix element $V\sqrt{3/2}$ which gave the value $\tilde\Gamma=(3\Gamma/2\pi)$ for the doublet in the minimal degeneracy case.

B. Singlet state, $J=0$

The states ψ_1 and ψ_2 are now

$$|\,\psi_1(k),0\rangle = ((fk)0)\ , \tag{25}$$

$$|\,\psi_2(k',k),0\rangle = ((ff)2j-1,(k'k)2j-1;0)\ . \tag{26}$$

The matrix element of $H_{\rm mix}$ between ψ_1 and ψ_2 is again found by acting with $H_{\rm mix}$ on $|\,\psi_1(k),0\rangle$ and projecting the resulting normalized state $\tilde\psi_2$ onto ψ_2

$$H_{\rm mix}\,|\,\psi_1(k),0\rangle = V\sqrt{(2j+1)}\,|\,\tilde\psi_2(k',k),0\rangle\ , \tag{27}$$

where

$$|\,\tilde\psi_2(k',k),0\rangle = ((f'k')0,(fk)0;0)\ . \tag{28}$$

The projection of $\tilde\psi_2$ onto ψ_2 is given by a 9-j symbol[17] (since there are four angular momenta to recouple), but because all three resultant angular momenta in (28) are zero, this quantity reduces to a 6-j symbol, the same that occurs in (23). It follows that

$$\langle\psi_2(k',k)0\,|\,H_{\rm mix}\,|\,\psi_1(k)0\rangle$$

is equal to

$$\langle\psi_2(k')j\,|\,H_{\rm mix}\,|\,\psi_1j\rangle$$

of the previous (magnetic) case. This result generalizes to an arbitrary value of j the equality between the matrix elements of the singlet and the doublet in the minimal degeneracy case [compare Eqs. (8) and (12)]. To show that one obtains an integral equation of the same form as (12), it is necessary to show that the matrix elements

$$\langle\psi_2(k',k),0\,|\,H_{\rm mix}\,|\,\psi_1(k),0\rangle$$

and

$$\langle\psi_2(k',k),0\,|\,H_{\rm mix}\,|\,\psi_1(k'),0\rangle$$

are equal. It is shown in Appendix B that the state $|\,\psi_2(k',k)0\rangle$ is even under interchange of k' and k because the resultant angular momentum J of k' and k is even, $J=2j-1$. Hence the equality of the matrix elements follows,

$$V_j \equiv \langle\psi_2(k',k),0\,|\,H_{\rm mix}\,|\,\psi_1(\underset{(k)}{k'}),0\rangle = V\left[\frac{2(4j-1)}{2j+1}\right]^{1/2}\ , \tag{29}$$

and one obtains the same integral equation as in the minimal degeneracy case, the only difference being that the effective width $\tilde\Gamma$ is now dependent on j and given by

$$\tilde\Gamma_j = \frac{2(4j-1)}{2j+1}\frac{\Gamma}{\pi} \equiv A(j)\frac{\Gamma}{\pi}\ . \tag{30}$$

The coefficient $A(j)$ increases from a value of 1 for $j=\frac{1}{2}$ to 4 in the limit of large j. It is plotted in Fig. 2. We will see in the next section that the decay width of configuration f^2 to f^1 is 2Γ, so that the effective width Γ_j which determines the scale of the binding is at most twice this decay width. To finish the proof that the singlet has the lowest energy, it remains to be shown that other magnetic states with integral angular momentum have a higher energy.

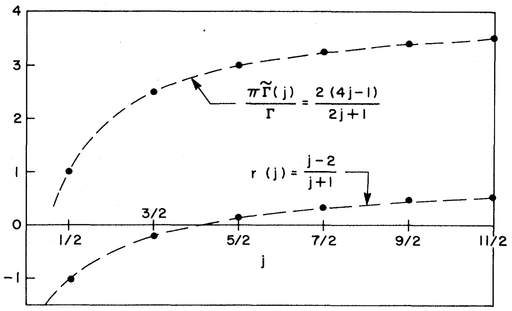

FIG. 2. Coefficients $A(j)$ and $r(j)$ occurring in the integral equation of the singlet and the triplet for $J=1$.

C. Magnetic state with integral J

In this case we have

$$|\,\psi_1(k),J\rangle = ((fk)J)\ , \tag{31}$$

$$|\,\psi_{2c}(k',k),J\rangle = ((ff)2j-1,(k'k)J_c;J)\ , \tag{32}$$

where J can be any integer ($J=1$ for the triplet) up to $2j$, and J_c, the angular momentum of the coupled holes, can range from $2j$ to $|\,2j-1-J\,|$, so as to satisfy the triangular inequality. Note that, unlike cases A and B, there are now several independent two-hole states, depending on J_c. In Appendix B it is shown that for J_c an odd integer, $|\psi_{2c}(k',k)J\rangle$ changes sign when k and k' are interchanged, while for J_c even it remains the same. To find the linear combination of the ψ_{2c} that occurs in the ground-state wave function, we take the latter to be of the form

$$|\psi\rangle=|f^1\rangle+|f^2\rangle$$

where

$$\begin{aligned}|f^1\rangle&=\sum_k\alpha(k)\,|\psi_1(k),J\rangle\ ,\\|f^2\rangle&=\sum_{J_c}\sum_{k}\sum_{\substack{k'\\(k<k')}}\beta_c(k,k')\,|\psi_{2c}(k',k),J\rangle\ .\end{aligned}\tag{33}$$

Treating again the two f electrons as unequivalent, we find for the mixing matrix element

$$\begin{aligned}\langle f^2|H_{\text{mix}}|f^1\rangle=\sum_{J_c}\sum_{k}\sum_{\substack{k'\\(k<k')}}[\,&\alpha(k)\beta_c(k,k')p_c\\&+\alpha(k')\beta_c(k,k')p_c(-1)]^{J_c}\\&\times V\sqrt{2j+1}\ .\end{aligned}$$

The projection coefficients p_c are found just as in Eq. (27), i.e., by operating with H_{mix} on $|\psi_1(k),J\rangle$, normalizing the two-hole state thus obtained, and projecting it onto $|\psi_{2c}(k',k),J\rangle$. We find

$$\begin{aligned}p_c\equiv\langle\psi_{2c}\,|\,\widetilde{\psi}_2\rangle&=((f'f)2j-1,(k'k)J_c;J\,|\,(f'k')0,(fk)J;J)\\&=[(4j-1)(2J_c+1)(2J+1)]^{1/2}\begin{Bmatrix}j&j&2j-1\\j&j&J_c\\0&J&J\end{Bmatrix}\\&=(-1)^{4j-1+J}\left[\frac{(4j-1)(2J_{c+1})}{2j+1}\right]^{1/2}\begin{Bmatrix}j&J&j\\2j-1&j&J_c\end{Bmatrix}.\end{aligned}$$

The variational equations are found just as in Sec. II, and the result is

$$\alpha(k)(\omega+\epsilon_k)=V^2(2j+1)\sum_{k'}\sum_{J_c}\frac{(p_c)^2\alpha(k)+(-1)^{J_c}(p_c^2)\alpha(k')}{\omega+\delta+\epsilon_k+\epsilon_{k'}}\ .\tag{34}$$

The sums over J_c are obtained by using the sum rules for 6-j symbols,[18] and the result, after multiplying by the factor of 2 to restore the equivalence of the f electrons, is

$$\alpha(k)(\omega+\epsilon_k)=\widetilde{\Gamma}_j\int_0^W\frac{\alpha(k)-(2j+1)\begin{Bmatrix}J&j&j\\2j-1&j&j\end{Bmatrix}\alpha(k')}{\omega+\delta+\epsilon_k+\epsilon_{k'}}d\epsilon_{k'}\ .\tag{35}$$

with $\widetilde{\Gamma}_j$ given by Eq. (30). Equation (35) is a general result, valid for all j and J [including $J=0$ for which it reduces to Eq. (12)]. It shows that the singlet has always the lowest energy because, as seen from Eq. (34), for $J\neq0$, the coefficient of $\alpha(k')$ is the sum of terms of alternating signs and hence is smaller than that of $\alpha(k)$. For $J=1$, the coefficient of $\alpha(k')$ in Eq. (35) is given by the simple expression

$$r(j)=\frac{j-2}{j+1}\ ,$$

where $r(j)$ is plotted in Fig. 2. Curiously, $A(j)$ and $r(j)$ can be made to coincide by two translations, thus $A(j+\frac{1}{2})=r(j)+3$. We do not know whether this has any significance.

D. *LS* coupling in the f^2 configuration

Russell-Saunders coupling is a better approximation for the rare earths and so we will obtain here the modification of Eq. (35) for this case. For the maximum value of the ionic angular momentum, $J_i=2j-1$, the (LSJ_i) state $\phi(L,S,J_i)$ is given in terms of the jj-coupled states by

$$\begin{aligned}\phi(L,S,J_i)=&\left[\frac{2l}{2l+1}\right]^{1/2}\phi(j_+,j_+;J_i)\\&+\left[\frac{1}{2l+1}\right]^{1/2}\phi(j_+,j_-;J_i)\ ,\end{aligned}\tag{36}$$

where $j_\pm=l\pm s$. Only the singlet state $J=0$ will be considered.

Since f states with $j_-=l-s$ are present in the LS wave function, the terms in $c^\dagger_{fj\_m}c_{kj\_m}$ of the mixing Hamiltonian must now be included. As a result, the two-hole wave function will have three kinds of terms, which, in the standard notation for multiple couplings, can be written as

$$\begin{gathered}(f^2LS,\ ((k')j_+,(k)j_+)J_i;0)\ ,\\(f^2LS,((k')j_-,(k)j_+)J_i;0)\ ,\\(f^2LS,\ ((k')j_+,(k)j_-)J_i;0)\ .\end{gathered}\tag{37}$$

To find the matrix element of H_{mix} we take a two-hole state $|f^2\rangle$ which is a sum over k and k' of the three states (37) with coefficients $\beta_i(k,k')$. Making use of the recoupling machinery as in subsection C, we finally obtain the following simple form for the integral equation, valid for LS coupling:

$$\alpha(k)(\omega+\epsilon_k)=\widetilde{\Gamma}_j\int_0^W\left[\frac{4l+1}{4l+2}\alpha(k)+\frac{4l}{4l+2}\alpha(k')\right]\times\frac{d\epsilon_{k'}}{\omega+\delta+\epsilon_k+\epsilon_{k'}}\ .\tag{38}$$

Compared to Eq. (35) (with $J=0$) for jj coupling, this differs in having l-dependent factors multiplying $\alpha(k)$ and $\alpha(k')$. These are both close to unity, but the factor of $\alpha(k')$ is smaller than that of $\alpha(k)$. This break in the symmetry between k and k' is a direct result of breaking the jj coupling in the f^2 state, as the following argument shows: Let k_+,k_- refer to the conduction orbitals k having angular momentum j_+,j_-, respectively, and let $H_{\text{mix}}(j_+)$ and $H_{\text{mix}}(j_-)$ refer to the corresponding parts of the mixing Hamiltonian. Then $H_{\text{mix}}(j_-)$ acting on $|\psi_1(k_+),0\rangle$ gives $|\psi_2(k'_-,k_+),0\rangle$. Now $H_{\text{mix}}(j_-)$ acting on $|\psi_2(k'_-,k_+),0\rangle$ connects it back to $|\psi_1(k_+),0\rangle$, but *not* to $|\psi_1(k'_+),0\rangle$ because the state k'_+ does not occur in $|\psi_2(k'_-,k_+),0\rangle$. By contrast, when jj coupling is valid, only $H_{\text{mix}}(j_+)$ is involved, and $H_{\text{mix}}(j_+)$ connects $|\psi_2(k'_+,k_+),0\rangle$ both to $|\psi_1(k_+),0\rangle$ and $|\psi_1(k'_+),0\rangle$. The break in symmetry is small ($4l$ versus $4l+1$) because the weight of the $\phi(j_+,j_-;j_i)$ state in $\phi(LS,J_i)$ is small [see Eq. (37)].

For $l=3$, the ratio of the coefficients of $\alpha(k')$ and $\alpha(k)$ in Eq. (38) is 0.9231. Numerical calculations including this factor give a reduction of about 25% in the singlet binding energy.

E. Case of no spin-orbit coupling

This is a purely academic case since the spin-orbit interaction is large compared to Γ. The treatment is the same as in the case of jj coupling, except that there are two independent sets of angular momenta, orbital and spin, and they are recoupled separately. The effective width $\widetilde{\Gamma}$ is found to be

$$\widetilde{\Gamma}=[3(4l-1)/(2l+1)](\Gamma/\pi)\ ,$$

where l is the one-electron angular momentum in the valence shell. For the fictitious value $l=\frac{1}{2}$, this reduces to the value $\widetilde{\Gamma}=\frac{3}{2}(\Gamma/\pi)$ of the minimal degeneracy case.

IV. INCLUSION OF ELECTRON-HOLE EXCITATIONS

States with electron-hole pairs get admixed into the wave functions of Sec. III by repeated applications of the mixing Hamiltonian. Thus, to the component $((ff)2j-1,(k'k)2j-1;0)$ of the singlet wave function, H_{mix} will admix $((fq)2j-1,(k'k)2j-1;0)$, in which an f electron has been promoted to an electron state q. Compared to the $((f)j,(k)j;0)$ component of the same wave function, this term has an electron-hole pair. Further, H_{mix} acting on $((fq)2j-1,(k'k)2j-1;0)$ will give $((ff)2j-1,(qk''k'k)2j-1;0)$, which has two electrons in the f level and an electron-hole pair, and so on. The two processes just described have a qualitative difference, in that the first one does *not* change the total numbers of electrons and holes, simply transferring an electron from an f level to an empty level above the Fermi surface, while the second process increases the numbers of electrons and holes by one each. The matrix elements of H_{mix} for these two processes are different: For the first one, since no recoupling is involved and the label on an electron is simply changed from f to q, the matrix element is $V\sqrt{2}$, the omnipresent $\sqrt{2}$ arising from the equivalence of f electrons. (More simply, since there are two electrons on the f level, the decay width is 2Γ.) For the second process it is necessary to recouple $((fk'')0,(fq)2j-1;2j-1)$ to $((ff)2j-1,(k''q)j_r;\ 2j-1)$ and to sum over j_r. This is done exactly as in Sec. III and the same result is obtained for the matrix element, namely $V\sqrt{2(4j-1)/(2j-1)}$. It is clear that the matrix elements have these values in any order of the interaction since no matter how many other electrons and holes are present, they are simply spectators to the recoupling.

The ratio of the squares of these matrix elements is $(4j-1)/(2j+1)=(2J_i+1)/(2j+1)$, which is just the ratio of the degeneracies of the f^2 and f^1 ionic states. This is a generalization to class-II mixed valence of a similar situation in class-I mixed valence, namely that the ratio of the matrix-element square for (a) transferring an electron to the f-level by creating a hole, and (b) for transferring an f electron to an empty electron level, is equal to the ratio of the degeneracies, $2N$ to 1 of the ionic configurations f^1 and f^0 respectively. Note, however, that this ratio can be a large number in this case, while for the class-II case, the ratio of the degeneracies is always smaller than 2. For Tm, with $J=6$, $j=\frac{7}{2}$, the ratio is 13/8. It follows that while the successive admixtures of electron-hole pairs could be treated by perturbation theory in class I, here it is not possible to do so, and electron-hole terms must be included in all orders. This is simply done by adding terms with electron-hole excitations to the variational wave functions. Thus, instead of Eq. (18), we now take

$$|\psi\rangle_j=\alpha(f,j)+\sum_k\beta(k)((ff)2j-1,(k)j;j)+\sum_k\sum_q\gamma(k,q)((fq)2j-1,(k)j;j)+\sum_{\substack{k\\(k<k')}}\sum_{k'}\sum_q\delta(k,k',q)((ff)2j-1,(kk'q);j)\ ,\tag{39}$$

and attempt to eliminate the higher-order coefficients in terms of the lower ones. Inclusion of the term in $\gamma(k,q)$ poses no problem, but already in sixth order, the term in $\delta(k,k',q)$ makes the algebraic elimination of the $\gamma(k,q)$ coefficients impossible: $\delta(k,k',q)$ introduces a coupling between $\gamma(k,q)$ and $\gamma(k',q)$ [which is not surprising as this is similar to the coupling between $\alpha(k)$ and $\alpha(k')$ introduced by $\beta(k,k')$] and the equations become very complicated.

The situation is illustrated in Fig. 3. The contribution to the energy of the terms in $\delta(k,k',q)$ gives rise to two kinds of diagrams, those in which the electron lines k,k' do not cross (nested), and those in which they do. These contributions have been discussed by Inagaki[19] for class-I mixed valence: The nested diagrams give the dominant, logarithmic contributions to the self-energies of the two valence states f^0 and f^1. If the other diagrams are neglected, these self-energies are expressible as the solutions to two coupled integral equations. Inagaki converted these to coupled differential equations by truncating the high-energy end. He defined two functions, $f(\epsilon)=\epsilon+\Sigma_0(\epsilon)$, and $g(\epsilon)=\epsilon+\delta+\Sigma_1(\epsilon)$ and was able to parametrize f and g in terms of a parameter s related to the energy in a complicated way. We too shall keep only the nested diagrams. This is probably a good approximation, but we have no rigorous proof. The advantage of retaining only these is that we can then eliminate successively the higher-order terms of Eq. (39), using only algebra, and we obtain the following equation for the binding energy ω_j of the magnetic, $J=j$ state (corresponding to the doublet of Sec. II):

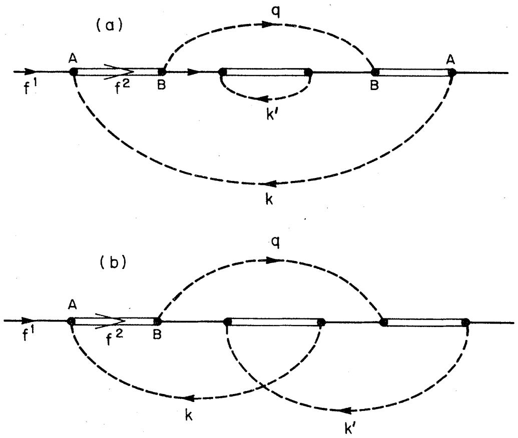

FIG. 3. Diagrams of the sixth order in V occurring in the expansion of the self-energy of the f^1 configuration. The matrix elements at vertices A and B are, respectively, $V\sqrt{2(4j-1)/(2j+1)}$ and $V\sqrt{2}$. Only the nested diagrams of type a, which give the leading logarithmic contributions to the self-energy, are kept in the calculation, to all orders.

$$\omega_j=\widetilde{\Gamma}_j\int_0^W\frac{d\epsilon'}{\omega_j+\delta+\epsilon'-c\widetilde{\Gamma}_j\int\frac{d\epsilon''}{\omega_j+\epsilon'+\epsilon''-\widetilde{\Gamma}\int\frac{d\epsilon'''}{\omega_j+\cdots}}}\ . \tag{40}$$

This can be written

$$\omega_j=F(\omega_j)\ , \tag{41}$$

$$F(\omega)=\widetilde{\Gamma}_j\int_0^W\frac{d\epsilon'}{\omega+\delta+\epsilon'-G(\omega+\epsilon')}\ , \tag{42a}$$

$$G(\omega)=c\widetilde{\Gamma}_j\int_0^W\frac{d\epsilon'}{\omega+\epsilon'-F(\omega+\epsilon')}\ , \tag{42b}$$

where $c=(2j+1)/(4j-1)$ is the ratio of the degeneracies of f^1 and f^2. In Inagaki's case, $c=\frac{1}{2}$, as he had no orbital degeneracy. The functions $F(\omega)$ and $G(\omega)$ are just the negatives of the self-energies $\Sigma_0(\omega)$ and $\Sigma_1(\omega)$ of Inagaki.

The same elimination of the higher-order states goes through for the singlet case, and we obtain the integral equation [compare with Eq. (12)]

$$\alpha(k)(\omega+\epsilon_k)=\widetilde{\Gamma}_j\int_0^W\frac{\alpha(k)+\alpha(k')}{\omega+\delta+\epsilon_k+\epsilon_{k'}-G(\omega+\epsilon_k+\epsilon_{k'})}\ . \tag{43}$$

On transferring the first term to the left, and noting that $f(\epsilon)=\epsilon-F(\epsilon)$ and $g(\epsilon)=\epsilon+\delta-G(\epsilon)$, we obtain the equation

$$\alpha(k)f(\omega+\epsilon_k)=\widetilde{\Gamma}_j\int_0^W\frac{\alpha(k')d\epsilon_{k'}}{g(\omega+\epsilon_k+\epsilon_{k'})}\ , \tag{44}$$

the solution of which determines the eigenvalue ω_S of the singlet. The energy of the magnetic state is simply given by Eq. (41), i.e., $f(\omega_j)=0$. The functions f and g are monotonically increasing functions of their argument. It follows that the eigenvalue ω_S of Eq. (44) is larger than ω_j, which means that the singlet has the largest binding energy.

We have solved Eq. (44) numerically, making use of Inagaki's parametrization of f and g in terms of s. The discretization of the integral equation was more complicated than in the simple case of Sec. II because of the computational necessity to increment $g(\omega+\epsilon_k+\epsilon_{k'})$ by equal energy intervals, while the explicit form of g is known in terms of the variable s but not in terms of the energy. To keep the computation within bounds we took $c=\frac{1}{2}$ instead of $c=\frac{8}{13}$. To estimate the change this made in the calculated energies we also did the calculation with $c=1$, in which case $F(\omega)=G(\omega)$. The binding energy of the singlet was found to be slightly smaller in this case.

The numerical calculation was done for the case $\delta=0$ and a value of $(W/\widetilde{\Gamma})=200$, taking $c=\frac{1}{2}$. Both the cases of jj coupling and of LS coupling in the f^2 configuration were done, the latter by multiplying the right-hand side of Eq. (44) by the factor $(4l/4l+1)=0.9231$. We find $\omega_S-\omega_j=0.035\tilde{\Gamma}$ for the former, and $\omega_S-\omega_j=0.027\tilde{\Gamma}$ for the latter. With the simple wave functions of Sec. II, we had found $\omega_S-\omega_D=0.01\tilde{\Gamma}$, taking the same value for $W/\tilde{\Gamma}$. The inclusion of the self-energy terms raises this energy separation, $\omega_S-\omega_j$, to a value 0.03 $\tilde{\Gamma}$, thus increasing the tendency to singlet formation. However, $\tilde{\Gamma}$ is small in the rare earths: An estimate[20] is $\tilde{\Gamma}\approx 70$ meV, which gives $\omega_S-\omega_j\approx 2$ K, a very small energy.

V. CONCLUSIONS

We have shown that for an isolated mixed-valence impurity in a sea of conduction electrons, the ground state of the complete system is a singlet. The energy separation between this state and a magnetic state is, however, very small, of the order of a few degrees kelvin. The concentrated salt TmSe is magnetic. It seems likely that the origin of the magnetism resides in the interactions between the rare-earth ions. As pointed out in Ref. 2, in concentrated mixed-valence Tm salts, the hopping of electrons between ions (double exchange) and the Ruderman-Kittel-Kasuya-Yosida (RKKY) interaction provide two mechanisms for the occurrence of ordered magnetism. Since the energy difference of ~ 2 K favoring the singlet state of a single impurity is small, it is quite possible that the interactions are responsible for the existence of magnetism in TmSe.

Another tendency toward magnetism may be provided by the crystal field. We have investigated the effect of the crystal-field splitting of the ground state of a single impurity, and find that in any case, it will decrease the energy advantage of the singlet. However, the magnitude of this decrease depends on which crystal-field states represent the ground states of the f^1 and f^2 configurations. We find that, if Γ_a and Γ_b are the representations of the f^1 and f^2 ground states, then if the direct product $\Gamma_a\times\Gamma_a$ contains Γ_b, the energy difference $\omega_S-\omega_j$ is reduced by a factor of the order of 0.5. If $\Gamma_a\times\Gamma_a$ does not contain Γ_b, then $\omega_S-\omega_j$ becomes vanishingly small. Unfortunately, the crystal-field ground states of the f^1 and f^2 configurations are not known in mixed-valence TmSe. Further theoretical work on the interactions and experimental work on the crystal-field states appears necessary for a full understanding of the magnetic properties of TmSe.

ACKNOWLEDGMENT

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APPENDIX A

The binding energy of the singlet for the mixed-valence impurity of class I, given by Eq. (1), was derived in Ref. 5. It was argued there that the binding energy of the triplet will be much smaller. The triplet binding energy for the f^0,f^1 case can be derived with the variational function

$$\psi_t=\left[\sum_{k,\sigma}\alpha(k)c^\dagger_{f,\sigma}c_{k,-\sigma}+\sum_{k,q,\sigma}\beta(q,k)c^\dagger_{q,\sigma}c_{k,-\sigma}\right]|\psi_0\rangle\ . \tag{A1}$$

The binding energy can be seen to be given by (for $\epsilon_f=0$)

$$|\omega_t|=\frac{\Gamma}{\pi}\ln\left|\frac{W+\omega_t}{\omega_t}\right|\ . \tag{A2}$$

Similarly, the binding energy for the doublet can be derived with the variational function

$$\psi_{d,\sigma}=\left[a_0c^\dagger_{f\sigma}+\sum_n a_k c^\dagger_{k\sigma}\right]|\psi_0\rangle\ . \tag{A3}$$

This also gives the binding-energy expression (for $\epsilon_f=0$)

$$|\omega_d|=\frac{\Gamma}{\pi}\ln\left|\frac{W+\omega_d}{\omega_d}\right|\ . \tag{A4}$$

Neither of these states nor the singlet energy, Eq. (1b), contain corrections due to the self-energy terms.

APPENDIX B

It is shown here that the state $((k',k)J)$, obtained by coupling equal angular momenta j of two distinct orbitals k' and k, and antisymmetrizing with respect to the electron coordinates, is even under the interchange of k and k' when J is an even integer, and odd when J is odd. The proof rests on the following symmetry property of the vector-coupling coefficients:[21]

$$(j_1m,j_2(M-m)\,|\,j_1j_2,JM)$$
$$=(-1)^{j_1+j_2-J}(j_2(M-m),j_1m\,|\,j_1j_2,JM)\ . \tag{B1}$$

Associating orbital 1 with k' and orbital 2 with k, (B1) gives

$$(k'm,k(M-m)\,|\,jj,JM)$$
$$=(-1)^{2j-J}(k'(M-m),km\,|\,jj,JM)\ . \tag{B2}$$

Before antisymmetrizing the state $((k'k)J)$, associate electron 1 with orbital k' and electron 2 with orbital k. Then, for each term $k'_m(1)k_{M-m}(2)$ in this state, there will be another in which m and $M-m$ have been interchanged, with the sign given by (B2), namely the term $(-1)^{2j-J}k'_{M-m}(1)k_m(2)$. When the state is antisymmetrized there will be two more terms like these, but with electrons 1 and 2 interchanged and with opposite sign. In all, for each pair $(m,M-m)$, there will be four terms in the antisymmetric state. With the proper relative signs, they are

$$\begin{aligned}&k'_m(1)k_{M-m}(2),\ \ (-1)^{2j-J}k'_{M-m}(1)k_m(2)\ ,\\&-k'_m(2)k_{M-m}(1),\ \ (-1)^{2j+1-J}k'_{M-m}(2)k_m(1)\ .\end{aligned} \tag{B3}$$

Interchanging k and k' in (B3), it is seen that, for J even, the set of terms remains unchanged, while for J odd, the terms of the set have changed sign. This proves our assertion. If the orbitals k and k' are identical, interchanging them must have no effect, and so only even J is allowed, the well-known restriction imposed by the Pauli principle.

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