GROUND STATE OF AN IMPURITY FLUCTUATING BETWEEN TWO MAGNETIC p CONFIGURATIONS

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We have considered a generalization of the impurity Anderson model to describe valence fluctuations between two realistic ionic configurations. Different simplifications of this model were used previously to describe Tm systems. We solve the model in the atomic limit corresponding to the strong-coupling fixed point of the renormalization group, for several configurations of p ionic shells. We find that the simplifications made earlier, particularly those which led to exactly solvable models, can lead to a wrong ground state. Preliminary results for Tm would suggest a singlet ground state.

In the last years there was much interest in Tm systems. Contrary to the case of other intermediate valence systems, a magnetic ground state is suggested by several properties, like magnetic susceptibility in dilute systems [1] and in compounds [2], specific heat [3], magnetic order of Tm Se [4], neutron scattering [5,6] and its theoretical interpretation in dilute [7] and periodic systems [8]. These properties can be qualitatively understood in terms of a simple model [7], its anisotropic version [9] and the extension of the latter to the lattice [10]. In this model the Tm configurations are replaced by states of total angular momentum 1/2 and 1, and the fluctuations take place exchanging conduction electrons of total angular momentum 1/2. This model has been treated with the renormalization group [11] and solved exactly with the "Bethe ansatz" technique by Proetto, Balseiro and one of us [12,13]. The magnetic character of the ground state was confirmed. The exact solution has been extended by the same group [14], and by P. Schlottmann [15] to two configurations of total angular momenta J_o and $J_o + 1/2$, with J_o arbitrary . For any $J_o \neq 0$, the magnetic susceptibility diverges as $T \to 0$ [16,17].

On the other hand, several other theoretical approaches to Tm impurities [18-20] found a singlet ground state. The difference between both results was ascribed to a different nature of the models used [20]. However, some confusion exists in Ref.19: Yafet et al. argued that the magnetic ground state obtained with variational functions in Ref.7 was wrong because the relevant states were not considered, but it was proved that the ground state for the model of Ref.7 is in fact a doublet [11-13]. Here we show that the different approaches correspond to different

simplifications of the same model. This model is a generalization of the Anderson model [21] to realistic ionic configurations assuming spherical symmetry.

The Hamiltonian can be written as:

$$H = H_{ion} + H_{band} + H_{mix} \tag{1}$$

The first term describes an impurity ionic shell of electrons with given orbital angular momentum (usually an incomplete 4f or 5f shell) with all correlation terms included. In terms of projection operators it can be written as:

$$H_{ion} = \sum E_{nJM_J\gamma} \, |nJM_J\gamma\rangle\langle nJM_J\gamma| \tag{2}$$

where the sum runs over all quantum numbers that characterize an eigenstate of H_{ion}, in particular the number of electrons n, the total angular momentum J and its projection M_J. The energies can be obtained from spectroscopic data. The kets represent a linear combination of products of $f^+_{m\sigma}$ applied to the vacuum, where $f^+_{m\sigma}$ creates a localized electron with orbital angular momentum projection m and spin σ. Usually only the ground state multiplets of two neighbouring configurations given by the Hund rules are important and (2) simplifies to:

$$H_{ion} = E \sum_{M_0} |J_0 \; M_0\rangle\langle J_0 \; M_0| + (E + \Delta) \sum_{M_1} |J_1 \; M_1\rangle\langle J_1 \; M_1| \tag{3}$$

where the first term corresponds to n electrons and the second to n+1. In Refs. 19 and 20, the states $|J_i M_i\rangle$, i=0,1 were chosen using j-j coupling.

The second term of (1) describes a band of free electrons:

$$H_{band} = \sum_{k l' \mu \sigma} \varepsilon_{k l'} \, c^{+}_{k l' \mu \sigma} \, c_{k l' \mu \sigma} \tag{4}$$

where k is the absolute value of the momentum, l' and μ denote the angular momentum and its projection and σ describes the spin. Due to the assumption of spherical symmetry, only conduction electrons with l'=l can hybridize with the impurity ones and the index l' can be dropped. Therefore H_{mix} can be written as:

$$H_{mix} = V \sum_{k \mu \sigma} \left(f^{+}_{\mu \sigma} \, c_{k \mu \sigma} + h.c. \right) \tag{5}$$

In terms of the total angular momentum $j = l \pm 1/2$ and its projection m, Eqs.(4) and (5) become:

$$H_{band} = \sum_{k j m} \varepsilon_{k} \, c^{+}_{k j m} \, c_{k j m} \tag{6}$$

$$H_{mix} = V \sum_{k j m} \left(f^{+}_{j m} \, c_{k j m} + h.c. \right) \tag{7}$$

Another way of writing the Hamiltonian is obtained if instead of expressing the $|nJM_J\gamma\rangle$ and $\langle nJM_J\gamma|$ in terms of the f operators, the latter are expressed in terms of the former. This is particularly useful in the usual cases in which Eq.(3) holds, because the Hilbert space is restricted. The matrix elements of f_{jm} between states of neighbouring impurity configurations can be expressed in terms of 9-j symbols [22]. Here we use a simpler approach: for given j the relations between these matrix elements can be obtained using the Wigner-Eckart theorem. Thus, in the case where the relevant impurity states are those entering Eq.(3), H_{mix} takes the form:

$$H_{mix} = \sum_{kjmM_0M_1} V_j \langle J_0 j M_0 m | J_1 M_1 \rangle \left(c^{+}_{kjm} | J_0 M_0 \rangle \langle J_1 M_1 | + h.c. \right) \qquad (8)$$

where the $\langle J_0 j M_0 m | J_1 M_1 \rangle$ are Clebsch-Gordan coefficients. In fact, the form of Eq.(8) is the only one allowed by spherical symmetry. In the case of the more realistic Russell-Saunders coupling, the relation between both V_j can be obtained by evaluating the matrix element $\langle (L_1 S_1)\ J_1 M_1 |\ f^{+}_{jm}\ | (L_0 S_0) J_0 M_0 \rangle$ after expressing the states and operators in a basis of states with definite spin and orbital angular momentum projections, using the double-tensor Wigner-Eckart theorem [22]. The result is:

$$V_j = V \langle J_0\ j\ J_0 (J_1 - J_0) |\ J_1\ J_1 \rangle^{-1} \sum \langle L_0\ S_0\ L_0^z\ S_0^z\ |J_0\ M_0 \rangle \cdot$$

$$\cdot \langle L_1\ S_1\ L_1^z\ S_1^z\ |J_1\ M_1 \rangle \cdot \langle 1\ \tfrac{1}{2}\ \mu\sigma\ |\ j\ (J_1 - J_0) \rangle \cdot$$

$$\cdot \langle L_0 1\ L_0^z\ \mu |\ L_1 L_1^z \rangle \cdot \langle S_0\ \tfrac{1}{2}\ S_0^z\ \sigma |\ S_1\ S_1^z \rangle \cdot$$

$$\cdot \langle L_1 S_1 \parallel f^{+}_{1} \parallel L_0 S_0 \rangle \qquad (9)$$

L_0, S_0 (L_1, S_1) are the orbital angular momentum and spin of the ground state multiplet of the impurity configuration with n (n+1) electrons. The sum runs over all possible projections of these operators and the corresponding ones for the f electrons (L_0^z, S_0^z, L_1^z, S_1^z, μ and σ). The last factor is a reduced matrix element. Its value can be absorbed in the parameter V. However, it can also be calculated easily if L_1, S_1 are given by the Hund rules, since in this case the only nonzero matrix element between states of maximum L_1^z and S_1^z is trivial:

$$\langle L_1 S_1 L_1 S_1 | \, f^{+}_{L_1-L_0, S_1-S_0} | L_0 \; S_0 \; L_0 \; S_0 \rangle = 1 \qquad (10)$$

which leads to:

$$\langle L_1 S_1 \parallel f^{+}_{1} \parallel L_0 S_0 \rangle^{-1} =$$

$$= \langle L_0 1 \; L_0 \; (L_1 - L_0) | \; L_1 L_1 \rangle . \; \langle S_0 \; \frac{1}{2} \; S_0 \; (S_1 - S_0) | \; S_1 \; S_1 \rangle \qquad (11)$$

The Hamiltonian $H(J_0 , J_1 , \Delta, \varepsilon_{kj}, V_j)$ given by Eqs. (1), (3), (6) and (8) has an important symmetry property, of which we shall make use later on. Transforming the band operators:

$$c^{+}_{kjm} \longrightarrow (-1)^{J_1 - J_0 + 2j+m} \; c_{k} \; , \qquad (12)$$

and using the following property of Clebsch-Gordan coefficients [23]:

$$\langle J_0 j M_0 m \; | \; J_1 M_1 \rangle = (-1)^{J_1 - J_0 + 2j - m} \left[\frac{2J_1 + 1}{2J_0 + 1} \right]^{1/2} \cdot$$

$$\cdot \langle J_1 j M_1 (-m) \; | \; J_0 M_0 \rangle \; , \qquad (13)$$

it can be easily shown that:

$$H(J_0 , J_1 , \Delta, \varepsilon_{kj}, V_j) = \text{constant} +$$

$$H\left[J_1, \; J_0, \; -\Delta, \; -\varepsilon_{kj}, \; -\left[\frac{2J_1 + 1}{2J_0 + 1} \right]^{1/2} V_j \right] \qquad (14)$$

Thus, if the solution of the problem for given J_0 and J_1 and arbitrary V_j is known, this special electron-hole transformation gives the solution for the case where the total angular momenta of

both configurations J_0 and J_1 are interchanged.

$H(J_0, J_1, \Delta, \varepsilon_{kj}, V_j)$ with one $V_j = 0$, was studied by Lustfeld [24,18] in the Kondo limit [14], by P. Schlottmann [25] (although he stated that "the model is not derivable from a Hamiltonian of the Anderson type" [26]) and in Ref. 14. In the latter work, it is shown that the only solvable cases using the Bethe ansatz are those with one non-magnetic configuration (J_0 or J_1 zero) and those for which both configurations are magnetic ($J_1 J_0 \neq 0$) only if $j = 1/2$. The solution of the latter models was constructed and the ground state was found to be magnetic [14,15]. However, Lustfeld finds a non- magnetic ground state for Tm [18].

Since in the case of j-j coupling, one of the $V_j = 0$ automatically, this model is in fact equivalent to the one studied, using different approximations, in refs. 19 and 20, where also a non-magnetic ground state for Tm is found. In all these works, one of both V_j was neglected, mainly on the basis of its smaller magnitude. Here we show that this criterion is wrong: the smallest V_j could determine the ground state.

In the original Anderson model [21], $l = 0$ was taken. Thus, necessarily either $J_0 = 0$ or $J_1 = 0$ and there is only one possible choice of j ($j = 1/2$). Though localized impurity electrons correspond in general to $l = 3$, the model describes the essential qualitative features of valence fluctuations between one magnetic and one non- magnetic configuration. Similarly, several properties of Tm systems can be qualitatively explained [7-10] in terms of $H(J_0, J_1, \Delta, \varepsilon_{kj}, V_j)$ (Eqs. (1), (3), (6), (8)) with $J_0 = 1/2$, $J_1 = 1$ (or conversely) and only $V_{1/2} \neq 0$. However, this model is not realistic for Tm. It would represent fluctuations between some p configurations ($l = 1$) if $V_{3/2}$ could be neglected. For example one

could choose as $|J_0 M_0>$ the states with 2 p electrons with $L_0 = 1$, $S_0 = 0$, and for $|J_1 M_1>$ one of the two possible doublets ($S_1 = 1/2$) with $L_1 = 0$ constructed with 3 p electrons (in this case $V_{3/2} = \sqrt{2} V_{1/2}$). Less artificial physical representations can be given keeping $J_1 = J_0 \pm 1/2$, if J_0 is allowed to vary. These cases are also exactly solvable if only $V_{1/2} \neq 0$ [14,15] and its properties are similar to those of the previous case [14-17,26]. Fluctuations between two magnetic, realistic p^n and p^{n+1} configurations with $|J_1 - J_0| = 1/2$ take place for n = 3 and n = 4 (see Table I). These problems, with l = 1, are the simplest generalizations of the Anderson model that retain the essential features of valence fluctuations between two magnetic configurations.

In Table I we list all the possible cases for fluctuations between two Hund rules multiplets of n and n+1 p electrons. For n = 3 and n = 4 both configurations are magnetic. In the remaining cases, either $J_0 = 0$ or $J_1 = 0$ and the ground state is known to be non-magnetic [27]. A Bethe ansatz solution for n = 3 or n = 4 is possible only if $V_{3/2} = 0$ is assumed. However if one is interested only in the magnetic or non-magnetic character of the ground state, one can resort to Wilson's renormalization -group arguments [28,11] to show that the answer to this question can be obtained assuming all band energies equal to the Fermi energy: $\varepsilon_{kjm} = \varepsilon_F$. This is because in the renormalization iterations, as $T \to 0$, the hybridization V grows faster than all other relevant energies of the problem [28,11]. Similar conclusions are obtained using the multiplicative renormalization group [18]. In this limit, only the band electrons that occupy the Wannier functions at the impurity site can mix with the localized p electrons. Thus, the subscript k

in H_{mix} (Eq.(8)) can be dropped and the relevant Hilbert space reduces to one of finite dimension. Since the total number of particles is conserved, this space can be subdivided into different subspaces according to the sum N of the occupation at the impurity (n or n+1) and the Wannier band states (0 to 6, since up to four electrons with J = 3/2 and two with j = 1/2 can be added). Thus in general $n < N < M = n + 1+2(2l+1)$, and the total number of states is $D = (J_0 + J_1 + 1)2^{M-n}$. In the case of Tm (l=3, J_0=6, J_1= 7/2), D = 344064, but for the interesting cases of Table I, D = 576. We solved the case n = 3 for arbitrary values of V_j. The solution of the case n = 4 is known using Eq.(14). We also studied the case with J_0= 1/2 and J_1 = 1, although as explained before, it does not correspond to Hund rules multiplets. We have diagonalized exactly the Hamiltonian matrix in the subspaces characterized by given N and J_t^z, where J_t^z is the projection of the total angular momentum of the whole system J_t. The J_t of the ground state was obtained comparing the lowest eigenvalues for different low values of J_t^z. We define the ground state as magnetic if under an infinitesimally small applied magnetic field B_z in the z direction, the mean value of the z-projection of the total impurity angular momentum $\langle J_{imp}^z \rangle$ remains $\neq 0$ for $B_z \to 0$. J_{imp}^z is given by:

$$J_{imp}^z = \sum_{M_0} M_0 |J_0 M_0\rangle\langle J_0 M_0| + \sum_{M_1} M_1 |J_1 M_1\rangle\langle J_1 M_1| \qquad (15)$$

In practice, when one V_j= 0 we have disregarded the states that contain c_{jm} electrons, since these electrons affect neither the impurity dynamics nor J_{imp}^z of the ground state. After doing this, the ground state has a well defined J_t in all cases except for one

exception: the state of minimum energy for a certain odd N has $J_t(N) = 1/2$ and is degenerate with the states of minimum energy in neighouring subspaces with $N' = N \pm 1$ and $J_t(N') = 0$. We have taken the ground state as non-magnetic ($J_t = 0$) in this case. We find $\langle J^z_{imp} \rangle = \alpha J_t$ with $0<\alpha<1$ and sometimes $\alpha \sim 0.1$.

The results for both situations: a) $J_0 = 3/2$, $J_1 = 2$; b) $J_0 = 1/2$, $J_1 = 1$ are summarized in Table II. In both cases, for $V_{3/2} = 0$, the ground state is magnetic and $J_t = \min (J_0, J_1)$ in agreement with the exact results [12-15]. However, in case a) when even an infinitesimally small $V_{3/2}$ is turned on, the ground state becomes non-magnetic. In case b) the ground state remains magnetic for all values of the parameters. The following conclusions can be drawn from these results:

1) The character of the ground state for valence fluctuations between two magnetic configurations depends on the particular configurations. Replacing realistic configurations by simpler ones can lead to results that are not only quantitatively but also qualitatively different.

2) Neglecting one of the hybridization energies $V_{l+1/2}$ or $V_{l-1/2}$, even if it is much smaller than the other, can also change the magnetic or non-magnetic character of the ground state.

From 1) one sees that models solvable with the Bethe ansatz [14] or those based on j-j coupling [19,20], could be inappropriate to describe even qualitatively the physics of Tm systems. Instead, the work of Lustfeld [18] is based on realistic configurations. However all these works took $V_{5/2} = 0$, and the results should be taken with caution, taking into account the conclusion 2) and the approximations made. Thus, the ground state of intermediate valent Tm deserves further study. We have begun

with the task of solving the appropriate narrow band Hamiltonian (as we did for p electrons). Similarly to case a) above, when $V_{l-1/2} = 0$, the ground state is non-magnetic, while for $V_{l+1/2} = 0$ it is magnetic. When both $V_j \neq 0$ we have searched for the ground state only in the subspaces with $N \leq n + 3$. For $N = n + 2$ and $N = n + 3$ the states of minimum energy are degenerate and of lower energy than those of the other subspaces. The first one has $J_t = 0$ and the second one $J_t = 5/2 = 1 - 1/2$. This result is suggestive, since in case a) above we found that the minimum energy as a function of N decreases first, then remains constant for $n + 2 \leq N \leq n + 4$ and then increases again. We do not understand yet the reason for this plateau in the N dependence, which shows the existence of a hidden symmetry in the model. If a similar behaviour occurs in the case of Tm as suggested by our preliminary results, the ground state is non-magnetic. In this case the results of Lustfeld [18] would be correct due to the fact that by chance, the relevant V_j for the ground state is also the largest one. It would seem also that j-j coupling and the approximations made in refs. 19 and 20 do not change the singlet character of the ground state.

In summary, we have studied the generalization of the impurity Anderson model to realistic atomic configurations, in the narrow band limit that corresponds to the strong-coupling limit of the renormalization group. For valence fluctuations between any two Hund rules p^n and p^{n+1} configurations the resulting ground state is non-magnetic . However, for some cases in which both configurations are magnetic and are not given by the Hund rules, the ground state is magnetic, which shows the importance of taking realistic configurations when both are magnetic. In this case it

is also important to take into account both hybridization channels V_j for total angular momentum $j = l \pm 1/2$. Our preliminary results seem to suggest a non-magnetic ground state for Tm impurities in absence of crystal fields.

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Table captions

I - Parameters that characterize the valence fluctuations between two Hund rules p^n and p^{n+1} configurations as a function of n. J_0, J_1 are the respective total angular momentum for n and n+1 p electrons. V_j ($j = 1 \pm 1/2$) are the parameters of H_{mix} (see Eq.(8)), calculated using Eqs. (9) and (11).

II- Results for the total angular momentum of the ground state in cases a) $J_0 = 3/2$, $J_1 = 2$, b) $J_0 = 1/2$, $J_1 = 1$ for different choices of both V_j.

Table I

n	J_0	J_1	$V_{1/2}/V$	$V_{3/2}/V$
0	0	1/2	1	0
1	1/2	0	1.1547	0
2	0	3/2	0	0.5773
3	3/2	2	0.8165	0.8165
4	2	3/2	0.6455	1.2910
5	3/2	0	0	2

Table II

J_0	J_1	$V_{1/2}$	$V_{3/2}$	J_t
3/2	2	≠0	0	3/2
3/2	2	0	≠0	0
3/2	2	≠0	≠0	0
1/2	1	≠0	0	1/2
1/2	1	0	≠0	1
1/2	1	≠0	≠0	3/2