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# Ionic Hamiltonians for transition metal atoms: effective exchange coupling and Kondo temperature

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## Abstract

An ionic Hamiltonian for describing the interaction between a metal and a  $d$ -shell transition metal atom having an orbital singlet state is introduced and its properties analyzed using the Schrieffer–Wolf transformation (exchange coupling) and the poor man’s scaling method (Kondo temperature). We find that the effective exchange coupling between the metal and the atom has an antiferromagnetic or a ferromagnetic interaction depending on the kind of atomic fluctuations, either  $S \rightarrow S - 1/2$  or  $S \rightarrow S + 1/2$ , associated with the metal-atom coupling. We present a general scheme for all those processes and calculate, for the antiferromagnetic interaction, the corresponding Kondo-temperature.

Keywords: ionic Hamiltonian, Kondo, spin fluctuations, inelastic electron scattering

(Some figures may appear in colour only in the online journal)

## 1. Introduction

Most works on the Kondo effect use very idealistic models [1–3], with a very poor description of the inner structure of the magnetic atom involved in the problem [4]. Although this approach is very convenient to start analyzing the basic properties of the Kondo many-body problem [5], it might be in order to take into account that inner structure of the atom by introducing an appropriate Hamiltonian to better understand the general properties of the system [4, 6, 7]. In our approach, we concentrate our discussion on  $d$ -shell magnetic atoms with an orbital singlet state; this is particularly relevant for cases where the symmetry of the magnetic atom environment is low, as may happen with  $d$ -transition metal atoms adsorbed on surfaces or in the gap of a STM-microscope (see [4] for a discussion of the symmetry of the problem with respect to the orbital singlet state in real metals). To be specific, this is the

case of ‘inelastic tunneling spectroscopy’ of magnetic atoms [8–11] or in single-atom transistors [12].

In the Anderson model [2], the interaction between an atom with a non-degenerate  $d$ -level and a metal is described by the Hamiltonian  $\widehat{H}_A = \widehat{H}_0 + \widehat{H}_{\text{int}}$ , where  $\widehat{H}_0 = \sum \varepsilon_k \widehat{c}_{k\sigma}^+ \widehat{c}_{k\sigma} + \varepsilon_0 (|\uparrow\rangle\langle\uparrow| + |\downarrow\rangle\langle\downarrow|)$ ,  $\sigma$  is the spin projection,  $k$  and  $|\sigma\rangle$  being the metal and the atomic states, respectively (here we assume, for simplicity, the doubly occupied state to be forbidden, implying that  $U \rightarrow \infty$ ); and  $\widehat{H}_{\text{int}} = \sum_{k\sigma} [V_k |\sigma\rangle\langle 0| \widehat{c}_{k\sigma} + V_k^* \widehat{c}_{k\sigma}^+ |0\rangle\langle\sigma|]$ , describing how electrons are transferred between the atom and the metal (the metal Fermi energy,  $E_F$ , is taken as the origin of energies). We stress that, for the convenience of our discussion below, we are using the projector operators  $|\sigma\rangle\langle\sigma|$  and  $|0\rangle\langle 0|$  for the atom instead of the more conventional creation and annihilation operators [13].

Hamiltonian  $\widehat{H}_A$  can be transformed into an effective spin scattering Hamiltonian by means of a Schrieffer–Wolf transformation [14], assuming that the atom is mostly in a spin state with  $S = 1/2$ . This transformation yields the following

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exchange coupling between the atomic spin,  $S$ , and the metal states:

$$H_{\text{eff}} = \sum_{kk'} J_{kk'} \hat{S} \cdot \hat{s}_{kk'} + \frac{1}{2} \sum_{kk'} J_{kk'} \{ \hat{c}_{k\uparrow}^+ \hat{c}_{k'\uparrow} + \hat{c}_{k\downarrow}^+ \hat{c}_{k'\downarrow} \} - \sum_k \frac{|V_k|^2}{|\varepsilon_0|} \quad (1)$$

where  $J_{kk'} = V_k V_{k'}^* / |\varepsilon_0|$  and

$$\hat{s}_{kk'}^+ = \hat{c}_{k\downarrow}^+ \hat{c}_{k'\downarrow}; \quad \hat{s}_{kk'}^- = \hat{c}_{k\uparrow}^+ \hat{c}_{k'\uparrow}; \quad \hat{s}_{z,kk'}^+ = 1/2 \{ \hat{c}_{k\uparrow}^+ \hat{c}_{k'\uparrow} - \hat{c}_{k\downarrow}^+ \hat{c}_{k'\downarrow} \}. \quad (2)$$

If the  $k$ -band and the atom interact through a single channel state  $|\alpha\rangle$ , the atomic spin part of Hamiltonian (1) can be written as follows:

$$\hat{H}_{\text{eff}}^{(\text{spin})} = 2J_0 \hat{S} \cdot \hat{s}_\alpha \quad (3)$$

with  $J_0 = |V_\alpha|^2 / |\varepsilon_0|$ . Equation (3) represents the  $s$ - $d$  model [15] of the Anderson Hamiltonian with an antiferromagnetic interaction; that exchange interaction was used by different authors [1, 16] to calculate, by means of the poor man's scaling method, the corresponding Kondo temperature.

Anderson Hamiltonian was generalized by Hirst [17] who introduced a new Hamiltonian including fluctuations between all the  $d$ -levels of a magnetic atom and the metal. This Hamiltonian was, apparently, rather complicated because of the many parameters required to specify it. However, using Hund's rule and the spin symmetry of the states associated with the  $d$ -shell we have introduced in [18] an ionic Hamiltonian that only depends on one parameter. In this paper, we generalize this Hamiltonian and introduce the Schrieffer–Wolf transformation to calculate the equivalent spin interaction,  $\Gamma \hat{S} \cdot \hat{s}_a + \gamma \hat{I}$  associated with that ionic model; finally, we analyze the Kondo temperature for the resulting antiferromagnetic effective spin Hamiltonian, and present a general picture that embodies all our results.

## 2. The ionic Hamiltonian

We start our discussion of the ionic model by introducing the following Hamiltonian for our transition metal atom/metal system:

$$\hat{H} = \hat{H}_0 + \hat{H}_{\text{int}}. \quad (4)$$

In equation (4)  $\hat{H}_0 = \sum_{k\sigma} \varepsilon_k \hat{n}_{k\sigma} + \hat{H}_{\text{atom}}$  includes the energy terms of both, the solid and the atom. The solid is described by the conduction band energies  $\varepsilon_k$  with an occupation number given by  $\hat{n}_{k\sigma} = \hat{c}_{k\sigma}^+ \hat{c}_{k\sigma}$ . The atomic part,  $\hat{H}_{\text{atom}}$ , in the extended version appropriate for treating any multi-electron atom [19], takes the form:

$$\begin{aligned} \hat{H}_{\text{atom}} = & \sum_{m,\sigma} \varepsilon_m \hat{n}_{m\sigma} + \sum_m U_d \hat{n}_m \hat{n}_{m\downarrow} + \frac{1}{2} \sum_{m \neq m',\sigma} J_d \hat{n}_{m\sigma} \hat{n}_{m'-\sigma} \\ & + \frac{1}{2} \sum_{m \neq m',\sigma} (J_d - J_d^x) \hat{n}_{m\sigma} \hat{n}_{m'\sigma} - \frac{1}{2} \sum_{m \neq m',\sigma} J_d^x \hat{n}_{m\sigma}^+ \hat{n}_{m'-\sigma} \hat{n}_{m'-\sigma}^+ \hat{n}_{m\sigma}. \end{aligned} \quad (5)$$

Here  $\hat{c}_{m\sigma}^+$  ( $\hat{c}_{m\sigma}$ ) are the fermionic operators creating (annihilating) an electron with spin projection  $\sigma$  in the orbital  $m$  and

$\hat{n}_{m\sigma} = \hat{c}_{m\sigma}^+ \hat{c}_{m\sigma}$ ; the intra-atomic coulomb interactions  $U_d$  and  $J_d$ , as well as the intra-atomic exchange interaction  $J_d^x$ , are assumed to be constants independent of the  $m$ -orbital index. The last term, related to spin-flip processes, restores the invariance under rotation in spin space.

The interaction term,  $\hat{H}_{\text{int}}$ , contemplates the charge exchange between the atom and the solid through a one electron tunnelling mechanism described by the following expression:

$$\hat{H}_{\text{int}} = \sum_{k,m,\sigma} [V_{km} \hat{c}_{k\sigma}^+ \hat{c}_{m\sigma} + V_{mk} \hat{c}_{m\sigma}^+ \hat{c}_{k\sigma}]. \quad (6)$$

In our approach we assume that the orbital contribution to the angular momentum is quenched by the crystal field environment, so that the ground state of the atom is an orbital singlet. Then, in agreement with the first Hund rule, the maximum spin associated with a given number of electrons, say  $N$  determines the atomic ground state. Accordingly, we reduce the configurational space spanned by the atomic Hamiltonian (5) to the Hund's states of total spin  $S$  and spin projection  $M$ ,  $|S, M\rangle$ , so that  $\sum_{S,M} |S, M\rangle \langle S, M| = 1$ , in order to project the atomic Hamiltonian and rewrite it as  $\hat{H}_{\text{atom}} = \sum_{S,M} E_S |S, M\rangle \langle S, M|$ , where the total energies  $E_S$  are calculated taking into account equation (5).

Regarding the interaction term, (equation (6)), we assume that the most probable charge fluctuations from the ground state with  $N$  electrons,  $|S, M\rangle$ , are to the states with  $N - 1$  or  $N + 1$  electrons,  $|S - 1/2, M\rangle$  or  $|S + 1/2, M\rangle$ :

$$\begin{aligned} \hat{H}_{\text{int}} = & \sum_{k,M,\sigma} [V_{kM\sigma}^{S*} \hat{c}_{k\sigma}^+ |S - 1/2, M - \sigma\rangle \langle S, M| \\ & + V_{kM\sigma}^S |S, M\rangle \langle S - 1/2, M - \sigma| \hat{c}_{k\sigma}] \\ & + \sum_{k,M,\sigma} [V_{kM\sigma}'^{S+1/2*} \hat{c}_{k\sigma}^+ |S, M - \sigma\rangle \langle S + 1/2, M| \\ & + V_{kM\sigma}'^{S+1/2} |S + 1/2, M\rangle \langle S, M - \sigma| \hat{c}_{k\sigma}]. \end{aligned} \quad (7)$$

The different spin configurations  $|S, M\rangle$  are calculated by ensuring the invariance under spin rotation, which means that all of them are generated from the state  $|S, S\rangle$  by successive applications of the operator  $\hat{S}^-$ . In this way the following expression for the coupling terms,  $V_{kM\sigma}^S$  in equation (7), is obtained for the case of a half-filled or less than half filled shell ( $N \leq 5$  for a  $d$ -shell) [10, 18]:

$$V_{kM\sigma}^S = \sqrt{\frac{S + (-1)^p M}{2S}} V_{kd} \quad (8a)$$

while for an occupation larger than half filled shell ( $N > 5$  for a  $d$ -shell), we arrived to the expression:

$$V_{kM\sigma}^S = (-1)^p \sqrt{\frac{S - (-1)^p M}{2S}} V_{kd}. \quad (8b)$$

In equations (8a) and (8b),  $p$  is equal to 0 if  $\sigma = \uparrow$  and equal to 1 in the opposite case.

In many cases, it is a good approximation to consider only one type of fluctuation, either  $S \rightarrow S - 1/2$  or  $S \rightarrow S + 1/2$ .

In this case, we neglect the terms of Hamiltonian (7) associated with those less probable fluctuations (infinite- $U$  limit).

### 3. The Schrieffer–Wolf transformation

We apply the Schrieffer–Wolf transformation [14] to Hamiltonian (4),  $\widehat{H}_0 + \widehat{H}_{\text{int}}$ , assuming  $\widehat{H}_{\text{int}}$  small and using a second order perturbation theory in  $\widehat{H}_{\text{int}}$  (equation (7)); in this way, we introduce the following effective Hamiltonian,  $\widehat{H}_{\text{eff}}$ :

$$\widehat{H}_{\text{eff}} = - \sum_n \frac{\widehat{H}_{\text{int}}|n\rangle\langle n|\widehat{H}_{\text{int}}}{E_n - E}$$

and assume that the atom is mostly in a state with spin  $S$ ; for simplicity, we also assume that only states  $|n\rangle = |S - 1/2, M\rangle$  contribute. The Schrieffer–Wolf transformation [14] can be achieved by eliminating in that way the atomic excited states  $|n\rangle = |S - 1/2, M\rangle$ :

$$\widehat{H}_{\text{eff}} = \sum_{k, M, \sigma} \frac{V_{kM\sigma}^S \widehat{c}_{k\sigma}^+ |S, M\rangle \langle S, M - \sigma + \sigma' | V_{kM-\sigma+\sigma'}^{S*} \widehat{c}_{k\sigma'}^+}{E^S - E^{S-1/2} - (\varepsilon_{k'} - \varepsilon_k)}.$$

If we consider in the expression above that the energy level ( $E^S - E^{S-1/2}$ ) is very large and negative (the state with spin  $S$  is more stable than the state with spin  $S - 1/2$ ), we can approximate  $E^S - E^{S-1/2} - (\varepsilon_{k'} - \varepsilon_k) \approx E^S - E^{S-1/2} = -\Delta$ . Making use of the expression of  $V_{kM\sigma}^S$  given by equation (8a), we have:

$$\begin{aligned} \widehat{H}_{\text{eff}} = & - \sum_{k, k'} \left( \frac{V_k V_{k'}^*}{2S\Delta} \right) \sum_M \sqrt{(S+M)} c_{k\uparrow} |S, M\rangle \langle S, M | \sqrt{(S+M)} c_{k'\uparrow}^+ \\ & - \sum_{k, k'} \left( \frac{V_k V_{k'}^*}{2S\Delta} \right) \sum_M \sqrt{(S-M)} c_{k\downarrow} |S, M\rangle \langle S, M | \sqrt{(S-M)} c_{k'\downarrow}^+ \\ & - \sum_{k, k'} \left( \frac{V_k V_{k'}^*}{2S\Delta} \right) \sum_M \sqrt{(S+M)} c_{k\uparrow} |S, M\rangle \langle S, M-1 | \sqrt{(S-(M-1))} c_{k'\downarrow}^+ \\ & - \sum_{k, k'} \left( \frac{V_k V_{k'}^*}{2S\Delta} \right) \sum_M \sqrt{(S-M)} c_{k\downarrow} |S, M\rangle \langle S, M+1 | \sqrt{(S+(M+1))} c_{k'\uparrow}^+. \end{aligned} \quad (9)$$

Moreover, using the following equations for  $\widehat{S}$ :

$$\begin{aligned} \widehat{S}_+ &= \sum_M \sqrt{S(S+1) - M(M+1)} |SM+1\rangle \langle SM| \\ \widehat{S}_- &= \sum_M \sqrt{S(S+1) - M(M-1)} |SM-1\rangle \langle SM| \\ \widehat{S}_z &= \sum_M M |SM\rangle \langle SM| \end{aligned} \quad (10)$$

and the expressions of  $\widehat{s}_{kk'}^+$ ,  $\widehat{s}_{kk'}^-$  and  $\widehat{s}_{z, kk'}$  given by equation (2), we can write equation (9) as:

$$H_{\text{eff}} = \sum_{k, k'} \left( \frac{J_{kk'}}{S} \right) [\widehat{S} \cdot \widehat{s}_{kk'}] + \sum_{k, k'} \frac{J_{kk'}}{2} (c_{k'\uparrow}^+ c_{k\uparrow} + c_{k'\downarrow}^+ c_{k\downarrow} - 2\delta_{kk'}) \quad (11)$$

which defines a Heisenberg exchange interaction between a local moment and the conduction electrons with a coupling constant  $J_{kk'} = V_k V_{k'}^* / \Delta$ . The last term in equation(11) provides

the scattering potential which has to be added to the  $s$ - $d$  Hamiltonian [1]. This equation can be written in a more transparent way if we assume that the  $k$ -band and the magnetic atom interact through a single channel state  $|\alpha\rangle$ ; then, we replace  $\sum_{kk'} J_{kk'} \widehat{s}_{kk'}$  by  $\sum_{\alpha\alpha'} J_{\alpha\alpha'} \widehat{s}_{\alpha\alpha'} = J_\alpha \widehat{s}_\alpha$ , and equation (11) reads:

$$H_{\text{eff}} = \frac{J_\alpha}{S} [\widehat{S} \cdot \widehat{s}_\alpha] - \frac{J_\alpha}{2} I_\alpha \quad (12)$$

where we have introduced the spin-1/2 operator for the orbital channel  $\alpha$ , and have defined  $J_\alpha = |V_\alpha|^2 / \Delta$  and  $I_\alpha = c_{\alpha\uparrow}^+ c_{\alpha\uparrow} + c_{\alpha\downarrow}^+ c_{\alpha\downarrow}$  (the unit tensor in the  $s_\alpha$ -space). Equation (12) shows the antiferromagnetic character of this interaction.

Up to this point we have assumed the atom to fluctuate from the spin  $S$  (the normal state of the atom) to spin  $S - 1/2$ . If the atom fluctuates to  $S + 1/2$ , our analysis yields that the effective Hamiltonian is (written in the channel-representation):

$$H_{\text{eff}} = - \frac{J_\alpha}{S+1/2} [\widehat{S} \cdot \widehat{s}_\alpha] + \frac{J_\alpha(S+1)}{(S+1/2)} I_\alpha \quad (13)$$

which appears to be a ferromagnetic interaction.

A similar argument can be applied to the case  $N \geq 5$ , with the magnetic atom of spin  $S$  fluctuating to spin  $S - 1/2$ :  $S \rightarrow S - 1/2$ ,  $S$  defining the normal state of the atom. In general, our analysis yields the same result, equation (12), for the corresponding effective Hamiltonian, while for the fluctuations  $S \rightarrow S + 1/2$  we also obtain equation(13).

Notice that in all these cases, there appear renormalization factors,  $S$  or  $S + 1/2$ , changing the  $J$ -coupling, defined in the conventional way  $J_\alpha = |V_\alpha|^2 / \Delta$ , to either  $J/S$  [6] or  $J/(S + 1/2)$ . Obviously, we can redefine this new interaction as  $J'$  in such a way that the effective Hamiltonian has the conventional form  $J' \widehat{S} \cdot \widehat{s}_\alpha$ ; one should remember, however, that a large spin would imply a reduction in the effective ( $\widehat{S} \cdot \widehat{s}_\alpha$ ) interaction [6]. On the other hand, it is worth mentioning that our results for the effective exchange coupling keeps the rotational symmetry of the problem, giving an independent confirmation to the validity of the ionic Hamiltonian introduced above.

We are going now to consider the case of having more than one channel for the metal [4]. In our approach, new channels can be introduced by considering several  $kr$ -states ( $r = 1 \dots R$ ) which are assumed to interact with the atom through their corresponding channel orbitals,  $|r\rangle$  [20]. Then, we can proceed as done for the case of one channel, apply the Schrieffer–Wolf transformation and obtain the following equation (for  $N \leq 5$ ):

$$H_{\text{eff}} = \sum_{kr, kt} \left( \frac{J_{kr, kt}}{S} \right) [\widehat{S} \cdot \widehat{s}_{kr, kt}] + \sum_{kr, kt} \frac{J_{kr, kt}}{2} (c_{kr\uparrow}^+ c_{kt\uparrow} + c_{kr\downarrow}^+ c_{kt\downarrow} - 2\delta_{kr, kt}) \quad (14)$$

which, in the channel representation, takes the form ( $J_{r, t} = V_r V_t^* / \Delta$ ):

$$H_{\text{eff}} = \widehat{S} \cdot \sum_{r, t} \frac{J_{r, t}}{S} \widehat{s}_{r, t} - \sum_{r, t} \frac{J_{r, t}}{2} (c_{r\uparrow}^+ c_{t\uparrow} + c_{r\downarrow}^+ c_{t\downarrow}) \quad (15)$$

to be compared with equation (12).

On the other hand, we should mention that for fluctuations  $S \rightarrow S + 1/2$ , we obtain the following effective Hamiltonian, as written in the localized channel representation:

$$H_{\text{eff}} = -\hat{S} \cdot \sum_{r,t} \frac{J_{r,t}}{S + 1/2} \hat{s}_{r,t} + (S + 1) \sum_{r,t} \frac{J_{r,t}}{S + 1/2} (c_{r\uparrow}^{\dagger} c_{t\uparrow} + c_{r\downarrow}^{\dagger} c_{t\downarrow}) \quad (16)$$

to be compared with equation (13). Similar equations are obtained for  $N \geq 5$  in both cases.

#### 4. The Kondo temperature

We analyze the Kondo temperature,  $T_K$ , associated with the antiferromagnetic multichannel Hamiltonian (15), by means of the poor man's scaling method [20, 21] used successfully for similar problems. We start with the atomic spin part of Hamiltonian (14):

$$H_{\text{eff}} = \sum_{kr,kt} \left( \frac{J_{kr,kt}}{S} \right) [\hat{S} \cdot \hat{s}_{kr,kt}] \quad (17)$$

and assume to have a metal band between  $-D$  and  $D$ . Then, we remove the  $kr$ -states in the intervals,  $(D, D - \delta D)$  or  $(-D, -D + \delta D)$ , by summing upon the  $K$ -states in the equation:

$$\delta H_{\text{eff}} = - \sum_K \{ \hat{H}_{\text{eff}} | K \rangle \langle K | \hat{H}_{\text{eff}} \} / (E_K - E_0) \quad (18)$$

where  $|K\rangle$  represents excited states like:  $\hat{c}_{qr\sigma}^{\dagger} |S, M\rangle$  (or  $\hat{c}_{qr\sigma}^{\dagger} |S, M\rangle$ ) with the momentum  $q_r$  in the energy interval  $(D, D - \delta D)$  or  $(-D, -D + \delta D)$ ; due to the high energy of the excited  $qr$ -states,  $(E_K - E_0)$  can be approximated by  $D$ . Then, we calculate  $-\sum_K \{ \hat{H}_{\text{eff}} | K \rangle \langle K | \hat{H}_{\text{eff}} \} / D$  and obtain the following renormalization of the effective exchange coupling:

$$\delta \left\{ \sum_{kr,kt} (J_{kr,kt}/S) \hat{S} \cdot \hat{s}_{kr,kt} \right\} = - \sum_{qr} (J_{qr,qr}/S) \rho_{qr} \delta D \left\{ \sum_{kr,kt} (J_{kr,kt}/S) \hat{S} \cdot \hat{s}_{kr,kt} \right\} / D.$$

For the sake of simplicity, it is convenient to analyze this expression using the channel representation; moreover, identifying each  $(kt, kr)$ -term in this equation gives:

$$D \delta (J_{r,t}/S) = - \sum_{r'} \{ (J_{r',r}/S) \rho_{r'} \delta D \} (J_{r,t}/S) \quad (19a)$$

this equation shows that  $\delta(J_{r,t})/J_{r,t}$  is independent from  $r$  or  $t$  along the renormalization process, so that the symmetry of the interaction,  $\sum_{r,s} (J_{r,s}/S) \hat{S} \cdot \hat{s}_a$ , is preserved along the scaling [4]. This implies that along our scaling trajectory the system develops only one fixed point and an equivalent one channel Kondo physics. The corresponding Kondo temperature can be calculated taking  $r = t$  in equation (19a), multiplying it by  $\rho_r$ , the assumed constant density of states associated with the  $r$ -channel, and summing upon  $r$ ; this leads to:

$$D \delta [\sum_r (J_r/S) \rho_r] = - [\sum_r (J_r/S) \rho_r]^2 \delta D \quad (19b)$$

where  $J_r = |V_r|^2/\Delta$ . Integrating equation (19b) in  $\delta D$ , we obtain the following Kondo temperature:

$$k_B T_K \approx D' = D \exp \{ -S / \sum_r \rho_r J_r \}. \quad (20)$$

Notice that for one channel,

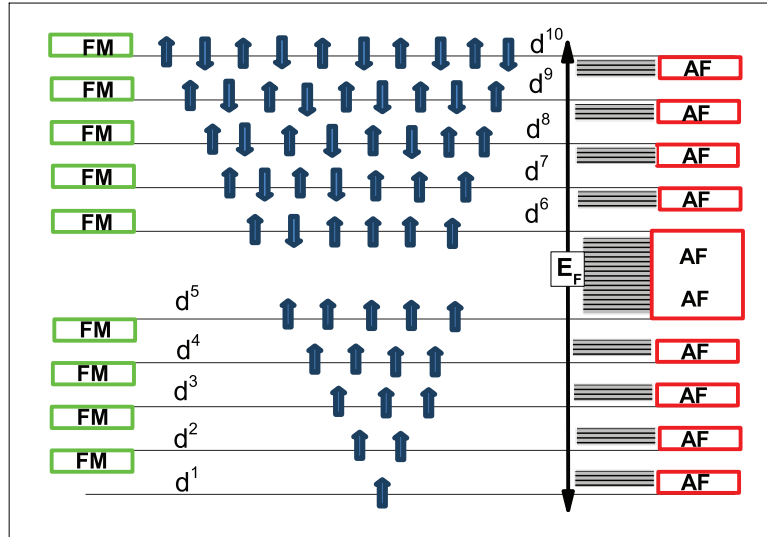
$$k_B T_K \approx D' = D \exp \{ -S / \rho_0 J \}. \quad (21)$$

Equation (21) highlights the importance played by the exponent,  $\exp(-S/\rho_0 J)$ , where a correction associated with the spin  $S$  appears [6], correction that makes  $T_K$  smaller for large  $S$ , as it was found experimentally [22, 23].

#### 5. Results and discussion

Our results for the effective spin interaction are summarized in figure 1. In this figure we show the different levels associated with the atomic wave-functions  $|S, M\rangle$ . The atomic occupancy is determined by the position of the Fermi level; for  $E(d^{N+1}) > E_F > E(d^N)$ , we can expect the atom to be in the  $d^N$ -state (with  $N$  electrons and  $S = N/2$  for  $N \leq 5$  and  $S = (10 - N)/2$  for  $N > 5$ ), and to develop charge fluctuations to states with either  $N + 1$  ( $d^{N+1}$ ) or  $N - 1$  ( $d^{N-1}$ ) electrons. Depending on those fluctuations we find different effective spin interactions with the metal. For example, consider the case  $E(d^2) > E_F > E(d^1)$ : if  $E_F$  is closer to the  $E(d^1)$  level, the system develops an antiferromagnetic (AF) interaction with  $d^1 \rightarrow d^0$  fluctuations; when  $E_F$  approaches the  $E(d^2)$  level, the effective spin interaction is ferromagnetic (FM) and  $d^1 \rightarrow d^2$ . Things evolve in a similar way when  $E_F$  crosses  $E(d^2)$  and  $E(d^3) > E_F > E(d^2)$ ; then, the system is initially AF and develops a Kondo resonance with  $d^2 \rightarrow d^1$  fluctuations, while for  $E_F$  closer to  $E(d^3)$  the system is FM with  $d^2 \rightarrow d^3$  fluctuations. Things continue in this way up to the case  $E(d^6) > E_F > E(d^5)$ , which shows in both cases, for  $E_F$  close to either  $E(d^6)$  or  $E(d^5)$ , an AF interaction; this is due to the electron-hole symmetry of the system between the cases  $N < 5$  and  $N > 5$ . For example, the case  $E(d^3) > E_F > E(d^2)$  is the symmetric of  $E(d^8) < E_F < E(d^9)$ , the system being in both cases AF if  $E_F$  is closer to either  $E(d^9)$  or  $E(d^2)$ ; for that AF interaction, we find the following fluctuations:  $d^2(S = 1) \rightarrow d^1(S = 1/2)$  or  $d^8(S = 1) \rightarrow d^9(S = 1/2)$ , and a similar effective spin interaction:  $(J_a/S) [\hat{S} \cdot \hat{s}_a]$  (equation (12)) with  $S = 1$ .

It is also worth commenting that we can combine into a single equation the AF and FM interactions appearing for a given level,  $d^N$ , due to its fluctuations to either  $d^{N-1}$  or  $d^{N+1}$  (equation (7)). The reason is the second order perturbation theory used to eliminate those states; this approach allows us to combine the effective spin interactions for  $d^N$  ( $N < 5$ ) in the following equation:  $(J_a/S) \hat{S} \cdot \hat{s}_a - [J'_a/(S + 1/2)] \hat{S} \cdot \hat{s}'_A$ . This equation suggests that the AF interaction changes to the FM one, around  $(J_a/S) \approx [J'_a/(S + 1/2)]$ ; as  $J_a = |V_a|^2/\Delta$  ( $\Delta$ , defined as  $E^{S-1/2} - E^S$  or  $E^S - E^{S+1/2}$ , is equal to  $|E_F - E(d^N)|$ ), that condition can be approximated by  $\Delta/\Delta' = S/(S + 1/2)$  assuming  $V_a \approx V'_a$ . Notice that for  $E(d^6) > E_F > E(d^5)$  and combining both fluctuations  $d^5(S = 5/2) \rightarrow d^4(S = 2)$  and



**Figure 1.** AF and FM indicate the Fermi energy windows for which the magnetic atom has an antiferromagnetic or a ferromagnetic exchange coupling. The one electron energy levels,  $E(d^N)$ , are defined as  $E(N) - E(N - 1)$ , the difference of energies between states with  $N$  and  $N - 1$  electrons, respectively. For the Yoshimori model:  $E(d^2) - E(d^1) = \dots = E(d^5) - E(d^4) = E(d^7) - E(d^6) = \dots = E(d^{10}) - E(d^9) = J_d - J_d^x$ ; while  $E(d^6) - E(d^5) = U_d + 4J_d$ .

$d^5(S = 5/2) \rightarrow d^6(S = 2)$ , the AF effective interaction can be written as  $(J_a/S)\hat{S} \cdot \hat{s}_a + (J'_a/S)\hat{S} \cdot \hat{s}'_a$  with  $S = 5/2$ ; moreover, for the symmetric case with  $E_F = [E(d^6) + E(d^5)]/2$ , that effective interaction becomes  $2(J_a/S)\hat{S} \cdot \hat{s}_a$ .

In a next step, we have used the poor man's scaling method to calculate the Kondo temperature associated with the AF interaction obtained above. Our result for the effective interaction  $(J_a/S)\hat{S} \cdot \hat{s}_a$  is simple: take the well-known  $T_K$ -value [1, 4] for the AF interaction,  $J'\hat{S} \cdot \hat{s}_a$ ,  $k_B T_K \approx D \exp(-1/\rho_0 J')$ , obtained in the scaling method to order  $J'^2$ , and replace  $J'$  by  $(J_a/S)$ ; this yields the following  $T_K$ ,  $k_B T_K \approx D \exp(-S/\rho_0 J_a)$ , for our ionic Hamiltonian [6]. We should also comment that for  $S = 1/2$ , a calculation of the scaling equations up to third order in  $J_a$  [21] yields  $k_B T_K \sim D \sqrt{(2J_a \rho_0)} \exp[-1/(2J_a \rho_0)]$  for the one channel case. This result suggests the following generalization for any value of  $S$ :  $k_B T_K \sim D \sqrt{(J_a \rho_0/S)} \exp[-S/(J_a \rho_0)]$ .

Up to this point we have assumed to have a single channel in the metal; for more channels, the AF interaction reads as:  $\sum_r (J_{r,i}/S)\hat{S} \cdot \hat{s}_{r,i}$  in the channel representation; then, our analysis shows that  $T_K$  is given by:  $k_B T_K \approx D \exp\{-S/\sum_r \rho_r J_r\}$ . If all the channels contribute equally, that equation takes the form:  $k_B T_K \approx D \exp\{-S/R \rho_0 J\}$  where  $R$  is the number of channels; further on, for  $2S = R$  we recover the Kondo temperature of a single channel with  $S = 1/2$ . We also expect that the scaling equations up to third order in  $J_r$  [21] would modify  $T_K$  from  $k_B T_K \approx D \exp\{-S/\sum_r \rho_r J_r\}$  to:

$$k_B T_K \sim D (\sum_r \rho_r J_r / S)^{1/2} \exp[-S/\sum_r \rho_r J_r].$$

The case  $E(d^6) > E_F > E(d^5)$  is different; we only mention that for the symmetric case,  $E_F = [E(d^6) + E(d^5)]/2$ , the spin interaction is  $2(J_a/S)\hat{S} \cdot \hat{s}_a$  and the Kondo temperature

$k_B T_K \approx D \exp\{-S/2 \sum_r \rho_r J_r\}$ , a factor of 1/2 appearing in the exponent due to the contributions from both fluctuations.

In many  $d$ -shell problems associated with transition metal atoms, the ionic Hamiltonian analyzed in this paper is only a first approximation to a more complex case where crystal field effects have to be introduced [8–11]. Typically, those crystal field effects are a small perturbation in front of the more important ionic Hamiltonian; however, they can play an important role in the behavior of the Kondo resonances and/or the structure that can be developed around the Fermi energy. We should stress, however, that our results, as summarized in figure 1, can be of relevance as regards the discussion of the fluctuations that the magnetic atom has. As an example, assume that Co with 7 electrons in the  $d$ -orbitals is adsorbed on a metal and that a Kondo resonance is observed experimentally [9, 10, 12]; an important point that one has to address in this problem is the following: which kind of fluctuations are associated with that Kondo peak,  $d^7 \rightarrow d^8$  or  $d^7 \rightarrow d^6$ ? The answer from figure 1 is clear: when considering crystal field effects, only fluctuations from  $d^7$  to  $d^8$  (or, equivalently, from  $S = 3/2$  to  $S = 1$ ) can develop a Kondo resonance and a small structure around the Fermi energy, because those crystal field effects can introduce only some splitting in the original peak of the ionic Hamiltonian; on the other hand, fluctuations  $d^7 \rightarrow d^6$  ( $S = 3/2$  to  $S = 2$ ) do not develop a Kondo resonance when considering the ionic Hamiltonian, and the small perturbation of the crystal field effects cannot introduce new states at the Fermi level. This has been observed independently by Park *et al* [12] in a single-atom transistor for the ions  $\text{Co}^{2+}$  and  $\text{Co}^{3+}$ .

Finally, we should comment that the most favorable case for observing the Kondo peak in transition metal atoms corresponds to the case where  $2S = R$  with all the channels contributing equally; then:

$$k_B T_K \approx D \sqrt{(2\rho_0 J)} \exp[-1/2\rho_0 J]$$

$$= D \sqrt{(2\Delta/\pi|\varepsilon_0|)} \exp[-\pi|\varepsilon_0|/2\Delta].$$

Typically,  $D \approx 5$  eV, and  $|\varepsilon_0|/\Delta \approx 3$  corresponds to a well-defined Kondo peak and still a high Kondo temperature; with these values we find  $k_B T_K \approx 20$  meV ( $T_K \approx 200$  K), which we can be taken as the maximum possible limit for that temperature (this high value can be attributed to having a small value of  $|\varepsilon_0|/\Delta$ , which implies a rather large value of the hybridized  $d$ -level half-width,  $\Delta$ ). Transition metal  $ad$ -atoms on simple metals, like Au, have probably very few channels defining the interaction between  $ad$ -atom and metal [20]; for a single channel we find that:

$$k_B T_K \approx D \sqrt{(\Delta/\pi S|\varepsilon_0|)} \exp[-\pi S|\varepsilon_0|/\Delta],$$

the new factor  $S$  reducing  $T_K$  a lot. For example, for  $S = 4$ ,  $D \approx 5$  eV and  $|\varepsilon_0|/\Delta \approx 3$  we find  $k_B T_K \approx 10^{-14}$  meV; even for  $S = 1$ ,  $k_B T_K \approx 0.26$  meV. These numbers indicate the difficulty of detecting Kondo peaks in magnetic atoms with  $S > 1$ , as already noticed in [22, 23].

## 6. Conclusions

In conclusion, we have analyzed the interaction between a metal and a  $d$ -shell transition metal atom by means of an ionic Hamiltonian, and have calculated the exchange metal/atom coupling and the corresponding atom Kondo temperature. Figure 1 summarizes our main results, indicating how the exchange coupling is either ferromagnetic or anti-ferromagnetic depending on the kind of atomic fluctuations associated with the coupling between the atom and the metal surface, and selecting in that way the possible existence of a Kondo resonance.

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## References

- [1] Hewson A C 1993 *The Kondo Problem to Heavy Fermions* (Cambridge: Cambridge University Press)
- [2] Anderson P W 1961 *Phys. Rev.* **124** 41
- [3] Kondo J 1964 *Prog. Theor. Phys.* **32** 37
- [4] Nozières P and Blandin A 1980 *J. Phys.* **41** 193
- [5] Wilson K G 1975 *Rev. Mod. Phys.* **47** 773
- [6] Schrieffer J R 1967 *J. Appl. Phys.* **38** 1143
- [7] Blandin A 1968 *J. Appl. Phys.* **39** 1285
- [8] Hirjibehedin C F *et al* 2007 *Science* **317** 1199
- [9] Otte A F *et al* 2009 *Phys. Rev. Lett.* **103** 107203
- [10] Goldberg E C and Flores F 2013 *J. Phys.: Condens. Matter* **25** 225001
- [11] Spinelli A, Rebergen M P and Otte A F 2015 *J. Phys.: Condens. Matter* **27** 243203
- [12] Park J *et al* 2002 *Science* **417** 722
- [13] Hubbard J 1965 *Proc. R. Soc. A* **285** 542
- [14] Schrieffer J R and Wolf P A 1966 *Phys. Rev.* **149** 491
- [15] Zener C 1951 *Phys. Rev.* **81** 440
- [16] Anderson P W 1970 *J. Phys. C* **3** 2439
- [17] Hirst L L 1978 *Adv. Phys.* **27** 231
- [18] Goldberg E C and Flores F 2008 *Phys. Rev. B* **77** 125121
- [19] Yoshimori A 1976 *Prog. Theor. Phys.* **55** 67
- [20] Cuevas J C and Scheer E 2010 *Molecular Electronics* (Singapore: World Scientific)
- [21] Read N and Hewson A C 1984 (in reference [1])
- [22] Jamneala T *et al* 2000 *Phys. Rev. B* **61** 9990
- [23] Daybell M D and Steyert W A 1968 *Rev. Mod. Phys.* **40** 380