

## Chapter 2

# Introducing the Inner Structure of the Magnetic Atom in the Interaction Between a Transition Metal Atom Impurity and a Metal Surface

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**Abstract** This paper presents a review of the work performed by the authors to incorporate the inner structure of a d-shell magnetic atom in the description of the many-body interaction between a transition metal atom impurity and a metal host. Two main assumptions are made in this approach: (i) the magnetic atom has an orbital singlet with a total electronic spin  $S$  (as corresponds to a case for which the angular moment is quenched); (ii) the first Hund's rule determines the inner electronic structure of the magnetic atom. Using these two assumptions and the rotational symmetry of the electronic spin, an ionic Hamiltonian is introduced and, in a further step, the effective exchange metal atom coupling and the impurity Kondo temperature are analyzed.

## Introduction

Kondo related problems are still an important issue in many-body condensed matter [1]. In the earliest approaches, very idealistic models [2–5] with a very poor description of the inner structure of the magnetic atom involved in the problem were introduced. This was a very convenient way for understanding the general properties of that basic problem. In particular, in the Anderson-like Hamiltonian a spin

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degenerate level, with an intra-site Coulomb interaction  $U$ , interacting with a metal band is introduced. Kondo-like properties of this Hamiltonian are crucially dependent on the correlation effects associated with its twofold degenerate level and the  $U$ -value. In section “[The Anderson Model Revisited](#)”, we present a summary of the well-known main properties of that Hamiltonian, including the effective exchange coupling between the atom and the metal, and its Kondo temperature.

Although it has been a great success of nanoscience the realization of different many-body systems in the quantum wells fabricated using different techniques, Kondo resonances and their electron correlation properties have been found to play also an important role in the interaction between  $d$  orbitals ( $f$  orbitals) of transition (rare-earth) metal impurities and the electrons of a metal band [6]. However, the analysis of the properties of these impurities has not yet been fully developed except for the so-called  $N$ -fold degenerate case [2].

Recent data in the experiments of inelastic tunneling spectroscopy of transition metal magnetic atoms [7–9] or single atom transistors [10] also points out to the need to understand the properties of those systems including the inner structure of the atom with its Hund’s rule. A first attempt in this direction was taken by Hirst [11] who introduced the following Hamiltonian:

$$\begin{aligned} \hat{H}^{\text{Hirst}} = & \sum_{\mathbf{k}\sigma} \varepsilon_{\mathbf{k}} \hat{c}_{\mathbf{k}\sigma}^{\dagger} \hat{c}_{\mathbf{k}\sigma} + \sum_m [E_{n-1} |n-1, m\rangle \langle n-1, m| + E_n |n, m\rangle \langle n, m|] \\ & + \sum_{\mathbf{k}\sigma m} \left[ V_{\mathbf{k}\sigma}^*(m) \hat{c}_{\mathbf{k}\sigma}^{\dagger} |n-1, m-\sigma\rangle \langle n, m| \right. \\ & \left. + V_{\mathbf{k}\sigma}(m) |n, m\rangle \langle n-1, m-\sigma| \hat{c}_{\mathbf{k}\sigma} \right], \end{aligned} \quad (2.1)$$

where, for simplicity, only fluctuations of one electron in the atom are considered. In the Hamiltonian, Eq. (2.1), one electron from state  $|n, m\rangle$ , with  $n$  electrons and  $S_z = m$ , jumps to a  $\mathbf{k}, \sigma$  state leaving the atom in a  $|n-1, m-\sigma\rangle$  state. Apparently, the Hamiltonian, Eq. (2.1), is rather complicated because it requires many parameters to specify it; however, using Hund’s rule and the spin symmetry of the states associated with the  $d$ -shell we have introduced an ionic Hamiltonian that only depends on one parameter [12].

In section “[The Anderson Model Revisited](#)”, the Anderson Hamiltonian is revisited and used to introduce, in section “[An Ionic Hamiltonian for  \$d\$  Electrons](#)”, the main ideas leading to our generalization of the Hirst Hamiltonian. Then, in section “[Effective Exchange Coupling and Kondo Temperature](#)” we review the main properties of that model, including its effective exchange coupling with the metal and its Kondo temperature [13]. Finally, in section “[Discussion and Conclusions](#)” we present our main conclusions.

## The Anderson Model Revisited

In the Anderson model [3], the interaction between an atom with a nondegenerate  $d$ -level and a metal is described by the following Hamiltonian:

$$\hat{H} = \hat{H}_0 + \hat{H}_{\text{int}}, \quad (2.2)$$

where

$$\hat{H}_0 = \varepsilon_0 [| \uparrow 0 \rangle \langle \uparrow 0 | + | 0 \downarrow \rangle \langle 0 \downarrow |] + (2\varepsilon_0 + U) | \uparrow \downarrow \rangle \langle \uparrow \downarrow | + \sum_{\mathbf{k}\sigma} \varepsilon_{\mathbf{k}} \hat{c}_{\mathbf{k}\sigma}^\dagger \hat{c}_{\mathbf{k}\sigma}, \quad (2.3)$$

$|\mathbf{k}\sigma\rangle$  being the metal states, and  $| \uparrow 0 \rangle, | 0 \downarrow \rangle, | \uparrow \downarrow \rangle$  the single and configurations. The atom-metal interaction is described by

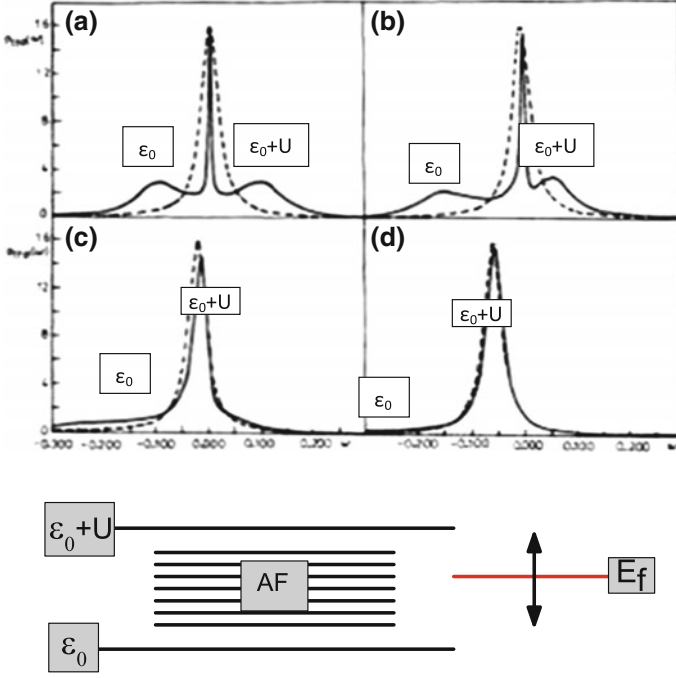
$$\hat{H}_{\text{int}} = \sum_{\mathbf{k}} \{ V_{\mathbf{k}} [| \uparrow 0 \rangle \langle 00 | \hat{c}_{\mathbf{k}\uparrow} + | 0 \downarrow \rangle \langle 00 | \hat{c}_{\mathbf{k}\downarrow} + | \uparrow \downarrow \rangle \langle 0 \downarrow | \hat{c}_{\mathbf{k}\uparrow} - | \uparrow \downarrow \rangle \langle \uparrow 0 | \hat{c}_{\mathbf{k}\downarrow} ] + \text{c.c.} \} \quad (2.4)$$

with electrons being 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 for the atom instead of the more conventional creation and annihilation operators [14].

This Hamiltonian has been analyzed using many different (exact and approximate) solutions [2]; we mention here the solution obtained using a many-body technique that uses a Green function method combined with an appropriate self-energy [15, 16]. Figure 2.1 shows the DOS calculated with that approach taking  $U = 0.2$ ,  $U/\Gamma = 10$  ( $\Gamma$  is the usual linewidth of the one-electron problem:  $\Gamma = \pi |V|^2 \rho_0$ ,  $\rho_0$  being the metal density of states and  $V = V_{\mathbf{k}}$  assuming that  $V_{\mathbf{k}}$  is  $\mathbf{k}$ -independent), and different values of  $\varepsilon$  ( $-0.1$ ,  $-0.15$ ,  $-0.2$ , and  $-0.25$ ). For  $\varepsilon_0 = -0.1$ , the solution has an electron-hole symmetry with a narrow Kondo peak at the Fermi level; for  $\varepsilon_0 = -0.15$  the solution is asymmetric, but still there is a Kondo peak at  $E_F$ ; for  $\varepsilon_0 = -0.20$ ,  $\varepsilon_0 + U = 0$ , the Kondo peak disappears and the second electron level,  $\varepsilon_0 + U$ , is already the only one appearing practically in the DOS; finally for  $\varepsilon_0 = -0.25$  this regime is completely developed and the one-electron solution coincides practically with the many-body one.

The Hamiltonian, Eq. (2.2) can be transformed into an effective spin scattering Hamiltonian by means of a Schrieffer-Wolff transformation [17], assuming that the atom is mostly in a spin state with  $S = 1/2$ . We illustrate here briefly how this transformation can be obtained using the projector operators just discussed; this will also be useful for our discussion below.

The main idea is to eliminate the atomic excited states,  $|00\rangle, | \uparrow \downarrow \rangle$ , using a second-order perturbation theory in  $\hat{H}_{\text{int}}$ :



**Fig. 2.1** Upper panel (from Ref. [14]): DOS for  $U/\Gamma = 10$ ,  $U = 0.2$  and **a**  $\epsilon_0 = -0.1$ ; **b**  $\epsilon_0 = -0.15$ ; **c**  $\epsilon_0 = -0.2$ , and **d**  $\epsilon_0 = -0.25$ . Dashed line one-electron solution without correlation effects. Full line many-body solution following Ref. [15]. Lower panel indicates the energy window,  $\epsilon_0 < E_F < \epsilon_0 + U$ , for which the effective atom-metal exchange coupling is antiferromagnetic

$$\hat{H}_{\text{eff}} = - \sum_n \frac{\hat{H}_{\text{int}} |n\rangle \langle n| \hat{H}_{\text{int}}}{E_n - E}. \quad (2.5)$$

Taking  $|n\rangle = |00\rangle$  and  $|n\rangle = |\uparrow\downarrow\rangle$  in Eq. (2.5), and assuming the energy levels,  $\epsilon_0$  ( $\epsilon_0 + U$ ), much lower (higher) than the Fermi level, so that  $E_0 - E \approx |\epsilon_0|$  and  $E_{\uparrow\downarrow} - E \approx |\epsilon_0 + U|$ , Eq. (2.5) yields:

$$\begin{aligned} \hat{H}_{\text{eff}} &= - \sum_{\mathbf{k}\mathbf{k}'\sigma\sigma'} \left[ \frac{V_{\mathbf{k}} V_{\mathbf{k}'}^*}{|\epsilon_0|} + \frac{V_{\mathbf{k}} V_{\mathbf{k}'}^*}{|\epsilon_0 + U|} \right] |\sigma\rangle \langle \sigma'| \hat{c}_{\mathbf{k}\sigma} \hat{c}_{\mathbf{k}'\sigma'}^\dagger \\ &= - \sum_{\mathbf{k}\mathbf{k}'\sigma\sigma'} J_{\mathbf{k}\mathbf{k}'} |\sigma\rangle \langle \sigma'| \hat{c}_{\mathbf{k}\sigma} \hat{c}_{\mathbf{k}'\sigma'}^\dagger, \end{aligned} \quad (2.6)$$

where  $|\sigma\rangle = |\uparrow 0\rangle$  for  $\sigma = \frac{1}{2}$ , and  $|\sigma\rangle = |0 \downarrow\rangle$  for  $\sigma = -\frac{1}{2}$ , and we have introduced

$$J_{\mathbf{k}\mathbf{k}'} = V_{\mathbf{k}} V_{\mathbf{k}'}^* \left[ \frac{1}{|\epsilon_0|} + \frac{1}{|\epsilon_0 + U|} \right]. \quad (2.7)$$

Now, introducing the spin operators for the atom and the  $\mathbf{k}$  states, respectively,

$$\hat{S}^+ = |\frac{1}{2}\rangle\langle-\frac{1}{2}|; \quad \hat{S}^- = |-\frac{1}{2}\rangle\langle\frac{1}{2}|; \quad \hat{S}_z = \frac{1}{2} \left[ |\frac{1}{2}\rangle\langle\frac{1}{2}| - |-\frac{1}{2}\rangle\langle-\frac{1}{2}| \right], \quad (2.8a)$$

$$\hat{s}_{\mathbf{k}\mathbf{k}'}^+ = \hat{c}_{\mathbf{k}\uparrow}^\dagger \hat{c}_{\mathbf{k}'\downarrow}; \quad \hat{s}_{\mathbf{k}\mathbf{k}'}^- = \hat{c}_{\mathbf{k}\downarrow}^\dagger \hat{c}_{\mathbf{k}'\uparrow}; \quad \hat{s}_{z,\mathbf{k}\mathbf{k}'} = \frac{1}{2} \left[ \hat{c}_{\mathbf{k}\uparrow}^\dagger \hat{c}_{\mathbf{k}'\uparrow} - \hat{c}_{\mathbf{k}\downarrow}^\dagger \hat{c}_{\mathbf{k}'\downarrow} \right], \quad (2.8b)$$

we can write Eq. (2.6) in the following way:

$$\hat{H}_{\text{eff}} = \sum_{\mathbf{k}\mathbf{k}'} J_{\mathbf{k}\mathbf{k}'} \hat{S} \cdot \hat{s}_{\mathbf{k}\mathbf{k}'} + \frac{1}{2} \sum_{\mathbf{k}\mathbf{k}'} J_{\mathbf{k}\mathbf{k}'} \left[ \hat{c}_{\mathbf{k}\uparrow}^\dagger \hat{c}_{\mathbf{k}'\uparrow} + \hat{c}_{\mathbf{k}\downarrow}^\dagger \hat{c}_{\mathbf{k}'\downarrow} \right] - \sum_{\mathbf{k}} J_{\mathbf{k}\mathbf{k}}. \quad (2.9)$$

This equation can be written in a more transparent way if we assume a localized description of the  $\mathbf{k}$ -band states,  $\phi_{\mathbf{k}} = \sum_{\alpha} a_{\alpha}^{\mathbf{k}} \varphi_{\alpha}$ , with the index  $\alpha$  denoting the different metal local (Wannier) orbitals. If the  $\mathbf{k}$ -band and the atom interact through a single channel state  $\alpha$  [18], the atomic spin part of Hamiltonian, Eq. (2.9), can be written as follows:

$$\hat{H}_{\text{eff}}^{(\text{spin})} = 2J_{\alpha} \hat{S} \cdot \hat{s}_{\alpha}, \quad (2.10)$$

a  $\hat{S}$ - $\hat{s}_{\alpha}$  antiferromagnetic interaction, with  $J_{\alpha} = |V_{\alpha}|^2 [1/|\varepsilon_0| + 1/|\varepsilon_0 + U|]$  (remember that we have assumed  $\varepsilon_0 < E_F < \varepsilon_0 + U$ ). Equation (2.10) represents the  $s$ - $d$  model of the Anderson Hamiltonian [19]. Notice that in the limit of  $U \rightarrow \infty$ ,  $J_{\alpha} \approx |V_{\alpha}|^2/|\varepsilon_0|$ ; however, when  $E_F < \varepsilon_0$ ,  $J_{\alpha} = -|V_{\alpha}|^2/|\varepsilon_0|$ , so that the  $\hat{S}$ - $\hat{s}_{\alpha}$  interaction becomes ferromagnetic. Likewise, if the  $(\varepsilon_0 + U)$  level is much closer to  $E_F$  than  $\varepsilon_0$ ,  $J_{\alpha} \approx |V_{\alpha}|^2/|\varepsilon_0 + U|$ ; but if  $E_F < \varepsilon_0 + U$ ,  $J_{\alpha} \approx -|V_{\alpha}|^2/|\varepsilon_0 + U|$ , showing that there is a  $\hat{S}$ - $\hat{s}_{\alpha}$  ferromagnetic interaction. This is shown schematically in the lower panel of Fig. 2.1, where the window of energy is indicated,  $\varepsilon_0 + U > E_F > \varepsilon_0$ , for which there appears an antiferromagnetic interaction and, consequently, a Kondo resonance, as it can be seen in the upper panel of Fig. 2.1.

This Kondo-temperature,  $T_K$ , can be calculated by applying the poor man's scaling method to the antiferromagnetic interaction given by Hamiltonian, Eq. (2.6) [2, 3, 5], whereby metal  $\mathbf{k}$ -states in the energy intervals  $(D, D - \delta D)$  and  $(-D, -D + \delta D)$  are removed from that Hamiltonian, Eq. (2.6); the metal states are characterized by a constant density of states per spin,  $\rho_0$ , and a bandwidth extending from  $-D$  to  $D$ . This is achieved by using second-order perturbation theory and summing upon the  $\mathbf{K}$ -states in the following equation:

$$\delta H_{\text{eff}} = - \sum_{\mathbf{K}} \frac{\hat{H}_{\text{eff}} |\mathbf{K}\rangle \langle \mathbf{K}| \hat{H}_{\text{eff}}}{E_{\mathbf{K}} - E_0}, \quad (2.11)$$

where  $|\mathbf{K}\rangle$  represents excited states like  $\hat{c}_{\mathbf{k}\sigma}^\dagger |\sigma'\rangle$  or  $\hat{c}_{\mathbf{k}\sigma} |\sigma'\rangle$ . This analysis yields the following  $T_K$ :

$$k_B T_K \approx D \exp \left( -\frac{1}{2} \rho_0 J_0 \right). \quad (2.12)$$

## An Ionic Hamiltonian for $d$ Electrons

We describe the interaction between a metal and a  $d$ -shell atom by the following Hamiltonian:

$$\hat{H} = \hat{H}_0 + \hat{H}_{\text{int}}. \quad (2.13)$$

In Eq. (2.13)  $\hat{H}_0 = \sum_{\mathbf{k}\sigma} \varepsilon_{\mathbf{k}} \hat{n}_{\mathbf{k}\sigma} + \hat{H}_{\text{atom}}$  includes the energy terms of both, the solid and the atom. The solid is described by the conduction band energies  $\varepsilon_{\mathbf{k}}$  with an occupation number given by  $\hat{n}_{\mathbf{k}\sigma} = \hat{c}_{\mathbf{k}\sigma}^\dagger \hat{c}_{\mathbf{k}\sigma}$ . The atomic part,  $\hat{H}_{\text{atom}}$ , in the extended version appropriate for treating any multi-electron atom [20], takes the form:

$$\begin{aligned} \hat{H}_{\text{atom}} = & \sum_{m\sigma} \varepsilon_m \hat{n}_{m\sigma} + \sum_m U_d \hat{n}_{m\uparrow} \hat{n}_{m\downarrow} + \frac{1}{2} \sum_{m \neq m', \sigma} J_d \hat{n}_{m\sigma} \hat{n}_{m' - \sigma} \\ & + \frac{1}{2} \sum_{m \neq m', \sigma} (J_d - J_d^x) \hat{n}_{m\sigma} \hat{n}_{m'\sigma} - \frac{1}{2} \sum_{m \neq m', \sigma} J_d^x \hat{c}_{m\sigma}^\dagger \hat{c}_{m - \sigma} \hat{c}_{m' - \sigma}^\dagger \hat{c}_{m'\sigma}. \end{aligned} \quad (2.14)$$

Here,  $\hat{c}_{m\sigma}^\dagger$  ( $\hat{c}_{m\sigma}$ ) are the fermionic operators creating (annihilating) an electron with spin projection  $\sigma$  in the orbital  $m$  and  $\hat{n}_{m\sigma} = \hat{c}_{m\sigma}^\dagger \hat{c}_{m\sigma}$ ; 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 orbital index  $m$ . The last term, related to spin-flip processes, restores the invariance under rotation in spin space.

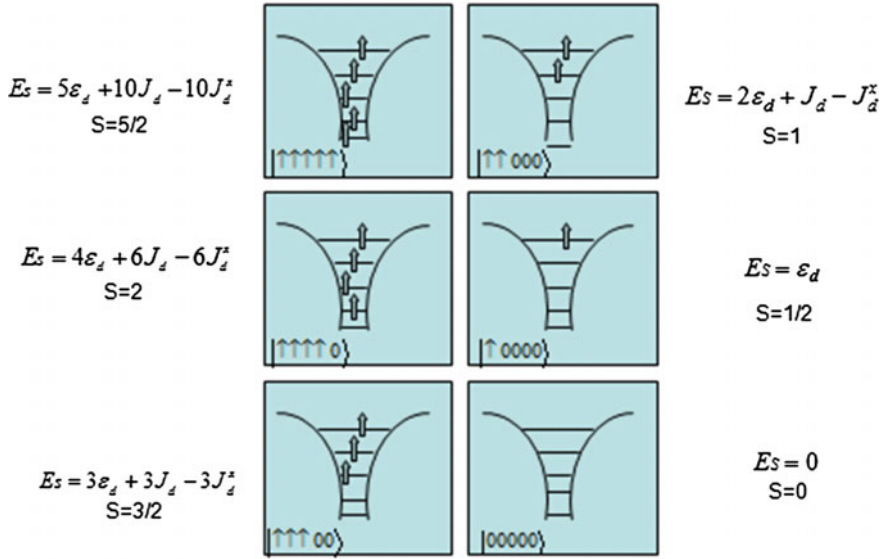
The interaction term,  $\hat{H}_{\text{int}}$ , contemplates the charge exchange between the atom and the solid through a one-electron tunneling mechanism described by the following expression:

$$\hat{H}_{\text{int}} = \sum_{\mathbf{k}m\sigma} \left[ V_{\mathbf{k}m} \hat{c}_{\mathbf{k}\sigma}^\dagger \hat{c}_{m\sigma} + V_{\mathbf{k}m}^* \hat{c}_{m\sigma}^\dagger \hat{c}_{\mathbf{k}\sigma} \right]. \quad (2.15)$$

In transition metal atoms where the orbital contribution to the angular momentum is often quenched due to crystal field effects associated with the low symmetry of the environment (this implies that the ground state of the atom is an angular singlet), the maximum spin associated with a given number of electrons, say  $N$ , determines the atomic ground state (first Hund rule). Figure 2.2 shows the atomic states and their corresponding energies as defined by the atomic Hamiltonian, Eq. (2.14), for  $N \leq 5$ ; for  $N > 5$ , we find a hole–electron symmetry with respect to the previous case (their energies are included in the caption of Fig. 2.2).

Then, we introduce the electronic states of total spin  $S$  and spin projection  $M$ ,  $|S, M\rangle_e$  and  $|S, M\rangle_h$  for  $N \leq 5$  and  $N > 5$  respectively, to rewrite the atomic Hamiltonian, Eq. (2.14), as follows:

$$\hat{H}_{\text{atom}} = \sum_{SM} [E_{S,e} |S, M\rangle_e \langle S, M|_e + E_{S,h} |S, M\rangle_h \langle S, M|_h], \quad (2.16)$$



**Fig. 2.2** It is shown the atomic  $d^N$  states and their energies for different number of electrons,  $N$ ;  $S = N/2$  and  $M$  is taken equal to  $S$  ( $N \leq 5$ ). For  $N > 5$  we find:  $E_S = 6\varepsilon_d + U_d + 14J_d - 14J_d^x$  for  $N = 6$ ;  $E_S = 7\varepsilon_d + 2U_d + 19J_d - 19J_d^x$  for  $N = 7$ ;  $E_S = 8\varepsilon_d + 3U_d + 25J_d - 25J_d^x$  for  $N = 8$ ;  $E_S = 9\varepsilon_d + 4U_d + 32J_d - 32J_d^x$  for  $N = 9$  and  $E_S = 10\varepsilon_d + 5U_d + 40J_d - 40J_d^x$  for  $N = 10$

where the energies  $E_S$  are given in Fig. 2.2. In this way we reduce the configuration space of Hamiltonian, Eq. (2.14), to the one spanned by those eigenvalues, so that we have  $\sum_{SM} [|S, M\rangle_e \langle S, M|_e + |S, M\rangle_h \langle S, M|_h] = 1$ .

Notice that the one-electron levels,  $E(d^N)$ , associated with the many-body Hamiltonian, Eq. (2.16), are defined by the equation:  $E(d^N) = E_S(N) - E_{S-\frac{1}{2}}(N-1)$ . This yields:

$$E(d^1) = \varepsilon_d, \quad (2.17a)$$

$$E(d^2) = \varepsilon_d + J_d - J_d^x, \quad (2.17b)$$

$$E(d^3) = \varepsilon_d + 2J_d - 2J_d^x, \quad (2.17c)$$

...

$$E(d^5) = \varepsilon_d + 4J_d - 4J_d^x, \quad (2.17d)$$

$$E(d^6) = \varepsilon_d + U_d + 4J_d - 4J_d^x, \quad (2.17e)$$

$$E(d^7) = \varepsilon_d + U_d + 5J_d - 5J_d^x, \quad (2.17f)$$

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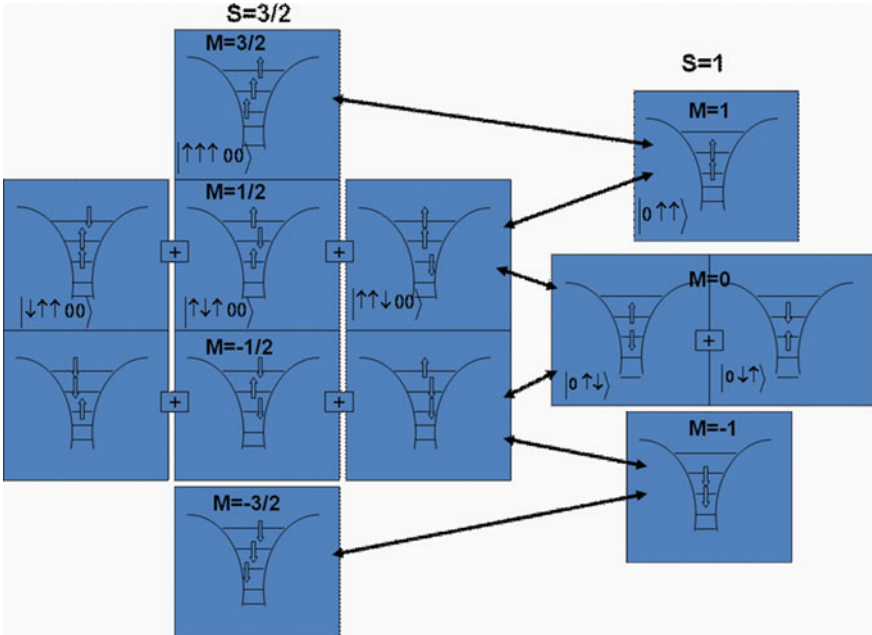
$$E(d^{10}) = \varepsilon_d + U_d + 8J_d - 8J_d^x. \quad (2.17g)$$

For  $E(d^N) < E_F < E(d^{N+1})$  we can expect the atom to have  $N$  electrons. However, when  $E_F$  approaches the levels  $E(d^N)$  or  $E(d^{N+1})$ , the atom should start to have fluctuations to either  $N - 1$  or  $N + 1$  electrons.

We describe those metal atom processes by assuming that an atomic ground state with  $N$  electrons,  $|S, M\rangle$ , has fluctuations to the states with  $N - 1$  or  $N + 1$  electrons, which for  $N < 5$ , correspond to the states  $|S - \frac{1}{2}, M\rangle_e, |S + \frac{1}{2}, M\rangle_e$  respectively. For the sake of simplicity, we restrict our discussion to  $N < 5$ , and neglect the sub-index  $e$  from the atomic states. Then, the corresponding interaction Hamiltonian has the form:

$$\begin{aligned} \hat{H}_{\text{int}} = & \sum_{\mathbf{k}M\sigma} \left[ V_{\mathbf{k}M\sigma}^{S*} \hat{c}_{\mathbf{k}\sigma}^\dagger |S - \frac{1}{2}, M - \sigma\rangle \langle S, M| + V_{\mathbf{k}M\sigma}^S |S, M\rangle \langle S - \frac{1}{2}, M - \sigma| \hat{c}_{\mathbf{k}\sigma} \right] \\ & + \sum_{\mathbf{k}M\sigma} \left[ V_{\mathbf{k}M\sigma}^{S+\frac{1}{2}*} \hat{c}_{\mathbf{k}\sigma}^\dagger |S, M - \sigma\rangle \langle S + \frac{1}{2}, M| + V_{\mathbf{k}M\sigma}^{S+\frac{1}{2}} |S + \frac{1}{2}, M\rangle \langle S, M - \sigma| \hat{c}_{\mathbf{k}\sigma} \right], \end{aligned} \quad (2.18)$$

where the different interaction elements,  $V_{\mathbf{k}M\sigma}^S$  and  $V_{\mathbf{k}M\sigma}^{S+\frac{1}{2}}$ , are calculated by ensuring to have spin rotation invariance. This is illustrated in Fig.2.3, where we



**Fig. 2.3** Illustrates how to calculate the matrix elements between the states  $|S, M\rangle$  and  $|S - \frac{1}{2}, M'\rangle$  due to the interaction:  $\sum_{\mathbf{k}\sigma} \left[ V_{\mathbf{k}} \hat{c}_{\mathbf{k}\sigma}^\dagger \hat{c}_{1\sigma} + V_{\mathbf{k}}^* \hat{c}_{1\sigma}^\dagger \hat{c}_{\mathbf{k}\sigma} \right]$

consider states with  $S = \frac{3}{2}$  and  $S = 1$ , and assume to have the following interaction:  $\sum_{\mathbf{k}\sigma} [V_{\mathbf{k}} \hat{c}_{\mathbf{k}\sigma}^\dagger \hat{c}_{1\sigma} + V_{\mathbf{k}}^* \hat{c}_{1\sigma}^\dagger \hat{c}_{\mathbf{k}\sigma}]$  between them, where 1 refers to the first  $d$  state in the sequence of the 5  $d$ -states shown in that figure. In Fig. 2.3, the different  $|S, M\rangle$  or  $|S - \frac{1}{2}, M'\rangle$  states are generated by successive application of the operator  $\hat{S}^-$ . In this way the following expression for the coupling terms,  $V_{\mathbf{k}M\sigma}^S$  in Eq. (2.18), with  $N \rightarrow N - 1$ , is calculated for the case of a half-filled or less than half-filled shell ( $N \leq 5$ ) [21]:

$$V_{\mathbf{k}M\sigma}^S = \sqrt{\frac{S + (-1)^p M}{2S}} V_{\mathbf{k}d}. \quad (2.19)$$

For the sake of completeness, we also mention that for  $N \geq 5$  and fluctuation from  $N$  to  $N + 1$  ( $S$  to  $S - \frac{1}{2}$  in the hole picture), we obtain:

$$V_{\mathbf{k}M\sigma}^S = (-1)^p \sqrt{\frac{S - (-1)^p M}{2S}} V_{\mathbf{k}d}. \quad (2.20)$$

## Effective Exchange Coupling and Kondo Temperature

Equations (2.16), (2.18), and (2.19) define our ionic Hamiltonian. In this section, we are going to analyze the effective exchange coupling and the Kondo temperature associated with it [13]. We calculate the effective exchange coupling by using the Schrieffer–Wolff transformation as performed above for the case  $S = \frac{1}{2}$ . We also start by considering only the atomic fluctuations,  $|S, M\rangle \rightarrow |S - \frac{1}{2}, M'\rangle$  and  $N \leq 5$ . Then, using Eq. (2.5), and  $|n\rangle = |S - \frac{1}{2}, M\rangle$  we find the following effective Hamiltonian:

$$\hat{H}_{\text{eff}} = \sum_{\substack{\mathbf{k}M\sigma \\ \mathbf{k}'\sigma'}} \frac{V_{\mathbf{k}M\sigma}^S \hat{c}_{\mathbf{k}\sigma} |S, M\rangle \langle S, M - \sigma + \sigma'| V_{\mathbf{k}'M-\sigma+\sigma'\sigma'}^* \hat{c}_{\mathbf{k}'\sigma'}^\dagger}{E^S - E^{S-\frac{1}{2}} - (\varepsilon_{\mathbf{k}'} - \varepsilon_{\mathbf{k}})}. \quad (2.21)$$

Next, approximate  $E^S - E^{S-\frac{1}{2}} - (\varepsilon_{\mathbf{k}'} - \varepsilon_{\mathbf{k}})$  by  $E^S - E^{S-\frac{1}{2}} = E(d^N) \equiv -\Delta$ , use the expression, Eq. (2.19) for  $V_{\mathbf{k}M\sigma}^S$ , the following equations for  $\hat{S}$ ,

$$\hat{S}^+ = \sum_M \sqrt{S(S+1) - M(M+1)} |S, M+1\rangle \langle S, M|, \quad (2.22a)$$

$$\hat{S}^- = \sum_M \sqrt{S(S+1) - M(M-1)} |S, M-1\rangle \langle S, M|, \quad (2.22b)$$

$$\hat{S}_z = \sum_M M |S, M\rangle \langle S, M|, \quad (2.22c)$$

and the expressions of  $\hat{s}_{\mathbf{k}\mathbf{k}'}^+$ ,  $\hat{s}_{\mathbf{k}\mathbf{k}'}^-$ , and  $\hat{s}_{z,\mathbf{k}\mathbf{k}'}$  given by Eq. (2.8b). All this leads to

$$\hat{H}_{\text{eff}} = \sum_{\mathbf{k}\mathbf{k}'} \frac{J_{\mathbf{k}\mathbf{k}'}}{S} \hat{S} \cdot \hat{s}_{\mathbf{k}\mathbf{k}'} + \sum_{\mathbf{k}\mathbf{k}'} \frac{J_{\mathbf{k}\mathbf{k}'}}{2} \left( \hat{c}_{\mathbf{k}'\uparrow}^\dagger \hat{c}_{\mathbf{k}\uparrow} + \hat{c}_{\mathbf{k}'\downarrow}^\dagger \hat{c}_{\mathbf{k}\downarrow} - 2\delta_{\mathbf{k}\mathbf{k}'} \right) \quad (2.23)$$

which defines a Heisenberg exchange interaction between a local moment and the conduction electrons with a coupling constant  $J_{\mathbf{k}\mathbf{k}'} = V_{\mathbf{k}} V_{\mathbf{k}'}^* / \Delta$ .

The spin part of this effective Hamiltonian in the case where the  $\mathbf{k}$ -band and the atom interact through a single channel is given by:

$$\hat{H}_{\text{eff}}^{(\text{spin})} = \frac{J_\alpha}{S} \hat{S} \cdot \hat{s}_\alpha, \quad (2.24)$$

with  $J_\alpha = |V_\alpha|^2 / \Delta$ . This is an antiferromagnetic exchange interaction between  $\hat{S}$  and  $\hat{s}_\alpha$  with a coupling constant  $J_\alpha / S$  when  $\Delta > 0$ , or equivalently when  $E(S) - E(S - \frac{1}{2}) = E(d^N) < 0$ .

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

$$\hat{H}_{\text{eff}}^{(\text{spin})} = -\frac{J_\alpha}{S + \frac{1}{2}} \hat{S} \cdot \hat{s}_\alpha, \quad \text{for } S \rightarrow S + \frac{1}{2}, \quad (2.25)$$

where  $J_\alpha = |V_\alpha|^2 / \Delta'$ , with  $\Delta' = E(d^{N+1})$ . This is a ferromagnetic exchange interaction if  $E(d^{N+1}) > 0$ .

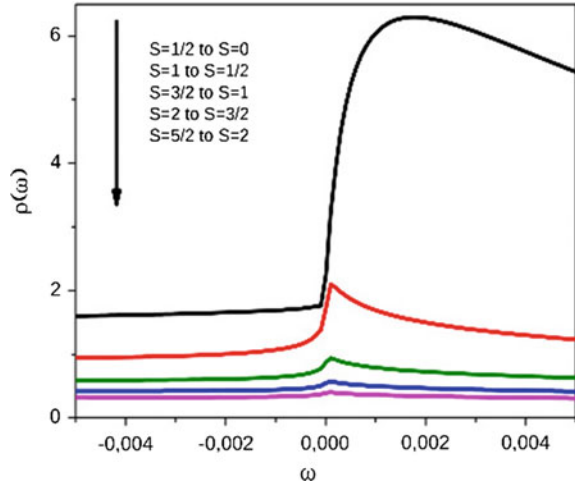
Notice that in all these cases, there appear renormalization factors,  $S$  or  $S + \frac{1}{2}$ , changing the  $J$ -coupling, defined in the conventional way  $J_\alpha = |V_\alpha|^2 / \Delta$ , to either  $J/S$  or  $J/(S + \frac{1}{2})$ . Then, we have that a large spin would imply a reduction in the effective  $\hat{S} \cdot \hat{s}_\alpha$  interaction and in the corresponding Kondo resonance for the antiferromagnetic case. This is illustrated in the results shown in Fig. 2.4. In this figure, we show the impurity atom spectral densities for  $0 \leq N \leq 5$  electrons in the  $d$ -shell and  $S \rightarrow S - \frac{1}{2}$  fluctuations. These ones have been obtained from the imaginary part of the Green function defined in the projection operator language,

$$G_{S-\frac{1}{2} M-\frac{1}{2}}^{SM}(t, t') = i\theta(t - t') \left\{ \left| S, M \right\rangle \left\langle S - \frac{1}{2}, M - \frac{1}{2} \right|_{t'}, \left| S - \frac{1}{2}, M - \frac{1}{2} \right\rangle \left\langle S, M \right|_t \right\} \quad (2.26)$$

and solved by using the equation of motion technique up to second order in the coupling term  $V_{\mathbf{k}}$  [12].

From this figure a decreasing antiferromagnetic exchange interaction between  $\hat{S}$  and  $\hat{s}_\alpha$  accordingly with an effective coupling constant  $J/S$  results evident. Consistently, the corresponding Kondo temperature should decrease with  $S$  (see below). Experimental evidences of these results exist from long time ago [22] being recently confirmed by using scanning tunneling spectroscopy [23]. Jamneala et al. have found

**Fig. 2.4** The impurity density of states  $\rho(\omega)$  around the Fermi level for the antiferromagnetic case with  $\Delta = 0.1D$  and  $\Gamma = 0.01D$ . From up to down:  $d^1 \leftrightarrow d^0$ ,  $d^2 \leftrightarrow d^1$ ,  $d^3 \leftrightarrow d^2$ ,  $d^4 \leftrightarrow d^3$ ,  $d^5 \leftrightarrow d^4$ . The energies  $\omega$  are measured in units of  $D$ . From Ref. [21]



that atoms near the middle of the  $3d$  row, such as V, Cr, Mn and Fe, show no discernible features of the local density of states at low energy, while atoms near the ends of the row, such as Ti, Co, and Ni, show narrow resonances near the Fermi energy [23].

Although the cases  $S \rightarrow S - \frac{1}{2}$  and  $S \rightarrow S + \frac{1}{2}$  have been presented independently, they can be combined simultaneously in one equation because, in the second-order perturbation theory used to calculate the exchange interaction, both terms appear as contributions that add to each other in the effective Hamiltonian. This means that we can combine Eqs. (2.24) and (2.25) into the equation

$$\hat{H}_{\text{eff}}^{(\text{spin})} = \frac{J_\alpha}{S} \hat{S} \cdot \hat{s}_\alpha - \frac{J'_\alpha}{S + \frac{1}{2}} \hat{S} \cdot \hat{s}_\alpha, \quad \text{for } S \rightarrow S - \frac{1}{2} \text{ and } S \rightarrow S + \frac{1}{2} (N < 5). \quad (2.27)$$

A similar argument can be applied to the case  $N \geq 5$ , with the magnetic atom of spin  $S$  fluctuating to spin  $S - \frac{1}{2}$  or  $S + \frac{1}{2}$ ,  $S$  defining the normal state of the atom. In general, our analysis yields the same result, Eq. (2.27), for the corresponding spin effective Hamiltonian. It should be stressed, however, that there is an exception to Eq. (2.27), when the normal state of the atom corresponds to the half-filled shell ( $N = 5$ ). In such a case the  $N$  to  $N - 1$  fluctuation is related to the spin fluctuation  $S \rightarrow S - \frac{1}{2}$  within the electron picture, and the  $N$  to  $N + 1$ , in the hole picture, is related to the same spin fluctuation  $S \rightarrow S - \frac{1}{2}$ . Therefore, due to the hole–electron symmetry of the problem we find that both fluctuations have an antiferromagnetic character if  $E(d^N) < E_F < E(d^{N+1})$ . Then, the effective spin Hamiltonian reads as:

$$\hat{H}_{\text{eff}}^{(\text{spin})} = \frac{J_\alpha}{S} \hat{S} \cdot \hat{s}_\alpha + \frac{J'_\alpha}{S} \hat{S} \cdot \hat{s}_\alpha \quad (S \text{ corresponds to the half-filled shell}). \quad (2.28)$$

On the other hand, it is worth mentioning that our results for the effective Hamiltonian keep the rotational symmetry of the problem in all the cases, giving an independent confirmation to the validity of the ionic Hamiltonian introduced for  $d$ -transition metal atoms.

Regarding the Kondo temperature associated with our ionic Hamiltonian, we can start our analysis with the spin effective Hamiltonians, Eqs. (2.27) and (2.28), and write

$$\hat{H}_{\text{eff}}^{(\text{spin})} = J' \hat{S} \cdot \hat{s}_\alpha, \quad (2.29)$$

where  $J' = (J_\alpha/S) - (J'_\alpha + \frac{1}{2})$  for  $S \neq \frac{5}{2}$ , or  $J' = (J_\alpha/S) + (J'_\alpha/S)$  for  $S = \frac{5}{2}$ . Equation (2.29) allows us to calculate the Kondo temperature for the antiferromagnetic case by using results obtained by other researchers for the same Hamiltonian, Eq. (2.29) [1, 4]. In this way, we can write:

$$k_B T_K \approx D \exp(-1/\rho_0 J'). \quad (2.30)$$

Assuming that the term  $J_\alpha/S$  dominates the  $J$ -value for the case  $S \neq \frac{5}{2}$ , we obtain the following Kondo temperature

$$k_B T_K \approx D \exp(-S/\rho_0 J_\alpha) \quad (S \neq \frac{5}{2}). \quad (2.31a)$$

This equation indicates how the Kondo temperature decreases with increasing values of  $S$ . On the other hand, for  $S = \frac{5}{2}$ , if we assume that  $E_F = [E(d^6) + E(d^5)]/2$  and  $J_\alpha = J'_\alpha$ , we can write

$$k_B T_K \approx D \exp(-S/2\rho_0 J_\alpha) \quad (S = \frac{5}{2}). \quad (2.31b)$$

## Discussion and Conclusions

In this paper, we have discussed the properties of an ionic Hamiltonian introduced to describe the interaction between a metal band and a  $d$ -shell magnetic atom with an orbital singlet. As an introduction to that general problem, we have reviewed in section “[The Anderson Model Revisited](#)” the properties of the Anderson Hamiltonian, where only one-electron  $d$ -level is introduced; in particular we have discussed for this Hamiltonian the exchange coupling between the metal and the atomic spin as well as the corresponding Kondo temperature.

In section “[An Ionic Hamiltonian for  \$d\$  Electrons](#)”, we have presented our ionic Hamiltonian [12] and have shown how the different hopping parameters between the metal and the atomic wave functions,  $|S, M\rangle$ , defined by the first Hund’s rule can be calculated, up to a factor, using the spin rotational symmetry.

In section “[Effective Exchange Coupling and Kondo Temperature](#)”, we have discussed [13] how to apply the Schrieffer–Wolff transformation to our ionic

Hamiltonian to obtain the effective exchange coupling interaction between the metal and the atom. Our results show that this effective interaction has the form:  $\Gamma \hat{S} \cdot \hat{s} + \gamma \hat{I}$ , confirming that our Hamiltonian has the appropriate rotational spin symmetry. Consider the case  $N < 5$ ;  $S$  is related to the number of electrons in the  $d$ -shell by the equation  $2S = N$ . 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  $S = N/2$ ), 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. If  $E_F$  is closer to the  $E(d^N)$  level, the system develops an antiferromagnetic (AF) interaction, with  $N \rightarrow N - 1$  fluctuations; when  $E_F$  approaches the  $E(d^{N+1})$  level, the effective spin interaction is ferromagnetic (FM) and  $N \rightarrow N + 1$ . Things are different when  $E(d^6) > E_F > E(d^5)$ , 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  $E(d^2) > E_F > E(d^1)$  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  $E(d^8)$  or  $E(d^2)$ ; for that AF interaction, we find the following fluctuations  $d^2(S = 1) \rightarrow d^1(S = \frac{1}{2})$  or  $d^8(S = 1) \rightarrow d^9(S = \frac{1}{2})$ , and a similar effective spin interaction,  $(J_\alpha/S) \hat{S} \cdot \hat{s}_\alpha$ , Eq. (2.24), with  $S = 1$ .

Notice an interesting similarity between the conventional  $d$ -shell atom, with a fivefold orbital degeneracy, and the Anderson model. For the Anderson model we have two levels,  $E(d^1)$  and  $E(d^2)$ , and the system shows an AF behavior for  $E(d^1) < E_F < E(d^2)$  (see Fig. 2.1), while for the conventional  $d$ -shell atom we find the same AF behavior for  $E(d^6) > E_F > E(d^5)$ . In this last model we find, however, that for any other Fermi energy interval  $E(d^{N+1}) > E_F > E(d^N)$ ,  $N \neq 5$ , the system shows either an AF or a ferromagnetic behavior depending on the position of  $E_F$  with respect to  $E(d^N)$  or  $E(d^{N+1})$ .

Finally, for an AF exchange interaction we expect to have a Kondo resonance in the electronic density of states as shown in Fig. 2.4 [12]; we have also analyzed the Kondo temperature associated with that resonance and have found that it decreases exponentially with the total spin of the normal atomic state [13, 24].

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