PHYSICAL REVIEW B **77**, 125121 (2008)

Kondo resonances of transition-metal-atom impurities in a metal host: Dependence on *d*-orbital occupancy

E. C. Goldberg
Instituto de Desarrollo Tecnológico para la Industria Química and Departamento de Materiales, Facultad de Ingeniería Química, Consejo Nacional de Investigaciones Científicas y Técnicas and Universidad Nacional del Litoral, Güemes 3450 CC 91, 3000 Santa Fe, Argentina

F. Flores
Departamento Física Teórica de la Materia Condensada, Universidad Autónoma de Madrid, E-28049 Madrid, Spain

(Received 27 November 2007; revised manuscript received 31 January 2008; published 17 March 2008)

Kondo resonances for transition-metal-atom impurities in a metal host have been analyzed by means of an ionic model as a function of the impurity *d*-orbital occupancy. The ionic Hamiltonian has been obtained by making use of the atomic Hund first rule. This Hamiltonian has been solved using a Green-function equation of motion method up to second order in the transition metal–host interaction. We find Kondo temperatures that decrease with the atomic total spin, the largest one appearing for charge fluctuations $d^0 \leftrightarrow d^1$ and $d^{10} \leftrightarrow d^9$, in good agreement with the experimental evidence.

DOI: 10.1103/PhysRevB.77.125121 PACS number(s): 71.27.+a, 71.10.−w, 72.15.Qm, 71.70.Gm

I. INTRODUCTION

Kondo related problems are still a central issue in many-body condensed matter. In the earliest approaches, an Anderson-like Hamiltonian[1,2] was introduced to model Kondo impurities; in this Hamiltonian, a spin degenerate level with a large intrasite Coulomb interaction U is resonating with a metal band. Kondo-like properties are crucially dependent on the strong electron correlation effects associated with this twofold degenerate level and its large U. This problem has been analyzed using many different techniques and the reader is referred to Ref. 2 for a complete discussion of their different (exact and approximate) solutions. It has been a great success of nanoscience to find the realization of these systems in the quantum wells fabricated using different techniques.[3]

In more conventional condensed matter physics, Kondo resonances have been found in the interplay between the d orbitals (f orbitals) of transition (rare-earth) metal impurities and the surrounding electrons of a metal band. The analysis of these impurities has not yet been fully developed except for the N-fold degenerate case described by the Hamiltonian

$$H = \sum_{k,\mu} \varepsilon_k c^+_{k\mu} c_{k\mu} + E_0 |0,0\rangle\langle 0,0| + \sum_{\mu} E_1 |1,\mu\rangle\langle 1,\mu| + \sum_{k\mu} V_{k\mu} |1,\mu\rangle\langle 0,0| c_{k\mu} + V^+_{k\mu} c^+_{k\mu} |0,0\rangle\langle 1,\mu|, \qquad (1)$$

where $c^+_{k\mu}$ denotes the creation operator of the conduction electron having momentum k and angular momentum μ, $|0,0\rangle$ the nondegenerate ground state of the atomic system, and $|1,\mu\rangle$ its excited N-degenerate levels. Hamiltonian (1) has been used to analyze the Kondo resonances of Ce $4f^1$ ($N=6$) and Yb $4f^{13}$ ($N=8$), systems for which electron fluctuations appear between the atomic states f^0 and f^1, and f^{14} and f^{13}, respectively.[2] In the exact solutions of Hamiltonian (1) for large N, the Kondo temperature T_K has been found to be proportional to $D(N\Delta/\pi D)^{1/N} \exp(-\pi|\varepsilon_0|/N\Delta)$, where $\varepsilon_0 = E_1 - E_0 - E_F$, Δ is the impurity one-electron linewidth, $2D$ the bandwidth of the conduction electrons, and E_F the Fermi energy.[2]

The Kondo problem associated with a transition or a rare-earth metal atom has to be analyzed, however, considering a more general Hamiltonian, similar to Eq. (1) but having a ground state with a given degeneracy larger than 1 and defined by the particular atom under study.[4] This is the ionic model of Hirst[5] that has not yet been studied as much as the Anderson model.

On the other hand, recent experimental evidence points out to the need to understand what happens for the more general case just mentioned. In particular, using scanning tunneling spectroscopy,[6–11] Jamneala *et al.* have studied systematically the low-energy excitations of different impurity elements across the $3d$ row of the Periodic Table, adsorbed on a Au(111) substrate at 6 K, finding impurity trends while varying parameters such as d-orbital energy and d-orbital filling. In particular, they found 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 (LDOS) at low energy, while atoms near the ends of the row, such as Ti, Co, and Ni, show narrow resonances near the Fermi energy.[11] Their measurements confirm the trends of previous measurements for ensembles of magnetic impurities, where it was found that the Kondo temperature is lower for elements located near the middle of the $3d$ row and higher for elements near the ends of the row.[12] The spectroscopic features of these impurities can be interpreted as a mixture of the bare d resonance and the Kondo resonance, but questions remain concerning the reason why particular d resonances appear and others do not.

Recently, in the conduction of single molecule transistors based on transition metal coordination complexes, resonances with Kondo temperatures in excess of 50 K, comparable to those in pure metallic systems,[13] has been reported. A gate dependence of T_K, which is inconsistent with observations in semiconductor quantum dots and a simple single-dot-level model, has also been reported. An important conclusion is that intramolecular exchange cannot be neglected in these devices, and that a complete understanding will require more sophisticated models (such as the ones mentioned above) and further measurements.[13]

In this work, we present an ionic model for analyzing the behavior of the Kondo resonances as a function of the d filling of transition metal impurities that reproduces the trends observed experimentally. Our main assumption is that the exchange energy is large enough to determine the atomic low-energy electronic configurations (first Hund rule). Based on this assumption, we deduce an ionic model Hamiltonian that generalizes Eq. (1) and then, by means of an approach based on the equation of motion method, we calculate T_K and the associated LDOS.

II. THEORY

The general form of our initial Hamiltonian is as follows:

$$\begin{aligned}\hat{H}=&\sum_{k,\sigma}\varepsilon_k\hat{n}_{k\sigma}+\sum_{m,\sigma}\varepsilon_m\hat{n}_{m\sigma}+\sum_{m}U_d\hat{n}_{m\uparrow}\hat{n}_{m\downarrow}\\&+\frac{1}{2}\sum_{m\neq m',\sigma}J_d\hat{n}_{m\sigma}\hat{n}_{m'-\sigma}+\frac{1}{2}\sum_{m\neq m',\sigma}(J_d-J_d^x)\hat{n}_{m\sigma}\hat{n}_{m'\sigma}\\&-\frac{1}{2}\sum_{m\neq m',\sigma}J_d^x\hat{c}^+_{m\sigma}\hat{c}_{m-\sigma}\hat{c}^+_{m'-\sigma}\hat{c}_{m'\sigma}+\sum_{km\sigma}(V^{\sigma}_{km}\hat{c}^+_{k\sigma}\hat{c}_{m\sigma}+\text{c.c.})\\&+(\text{crystal field terms}),\end{aligned}\tag{2}$$

where $\hat{c}^+_{k\sigma}$ and $\hat{c}^+_{m\sigma}$ denote the creation operators of the conduction electrons and the localized d electrons in the orbital m with spin σ, respectively. The intra-atomic Coulomb interactions U_d and J_d and the intra-atomic exchange interaction J_d^x for the localized d orbitals are assumed to be constants independent of the m-orbital index. The sixth term related with spin-flip processes restores the invariance under rotation in spin space, and the V^{σ}_{km} are the couplings between conduction and localized electrons. The crystal field terms responsible for the crystalline splitting are not given explicitly because they are expected to be small for d electrons (compared with the energies associated with the first Hund rule).

Assuming the exchange interaction J_d^x, to be large enough for the first Hund rule determines the atomic lower energy configuration, we obtain the following atomic states as a function of the d level occupation $n=0,\ldots,5$ electrons (cases $n=6,\ldots,10$ will be discussed below):

$$n=0\rightarrow\text{one state }|\phi\rangle_0^0=|0,0,0,0,0\rangle,$$

$$n=1\rightarrow\text{the five states }|\phi\rangle_1^i=|\uparrow,0,0,0,0\rangle;|0,\uparrow,0,0,0\rangle;\ldots;|0,0,0,0,\uparrow\rangle,$$

as well as all the states with spin down corresponding to a total spin $S=1/2$ (5×2 states);

$$n=2\rightarrow\text{the ten states }|\phi\rangle_2^j=|\uparrow,\uparrow,0,0,0\rangle;|\uparrow,0,\uparrow,0,0\rangle;\ldots;|0,0,0,\uparrow,\uparrow\rangle$$

and all the states obtained by rotating the total spin direction $S=1$ (10×3 states);

$$n=3\rightarrow\text{the ten states }|\phi\rangle_3^p=|\uparrow,\uparrow,\uparrow,0,0\rangle;|\uparrow,\uparrow,0,\uparrow,0\rangle;\ldots;|0,0,\uparrow,\uparrow,\uparrow\rangle$$

and the states obtained by rotating $S=3/2$ (10×4 states);

$$n=4\rightarrow\text{the five states }|\phi\rangle_4^q=|\uparrow,\uparrow,\uparrow,\uparrow,0\rangle;|\uparrow,\uparrow,\uparrow,0,\uparrow\rangle;\ldots;|0,\uparrow,\uparrow,\uparrow,\uparrow\rangle$$

and the states obtained by rotating $S=2$; (5×5 states);

$$n=5\rightarrow\text{the one state }|\phi\rangle_5^r=|\uparrow,\uparrow,\uparrow,\uparrow,\uparrow\rangle$$

and the states obtained by rotating $S=5/2$; (1×6 states).

Associated with the degeneracy just discussed, we construct states $|S,M\rangle^{\alpha}$ where $S=0$, $1/2$, 1, $3/2$, 2, and $5/2$ for $n=0$, 1, 2, 3, 4 and 5, respectively. Superindex α denotes the different combinations of atomic states for a given d shell occupation ($\alpha=i,j,p,q,r$; with $i=1,\ldots,5$; $j=1,\ldots,10$; $p=1,\ldots,10$; $q=1,\ldots,5$, and $r=1$ for $S=1/2,\ldots,5/2$, respectively).

By using these states, the atomic part of the Hamiltonian is

$$\hat{H}^{atomic}=\sum_{SM\alpha}\varepsilon_{S\alpha}|S,M\rangle^{\alpha}\langle S,M|^{\alpha}.\tag{3}$$

The $\varepsilon_{S\alpha}$ are calculated according to Hamiltonian (2). For instance,

$$\varepsilon_{5/2,\alpha}=\sum_{m(\alpha)}\varepsilon_m+10J_d-10J_d^x,$$

$$\varepsilon_{2\alpha}=\sum_{m(\alpha)}\varepsilon_m+6J_d-6J_d^x,\quad\text{and so on}.$$

In this atomic basis set $|S,M\rangle^{\alpha}$, the interacting Hamiltonian $\sum_{km\sigma}(V_{km}\hat{c}^+_{k\sigma}\hat{c}_{m\sigma}+\text{c.c.})$ takes the form

$$\begin{aligned}\hat{H}^{\text{int}}=&\sum_{k.SM,\beta\gamma}\{\hat{c}^+_{k\uparrow}|S-1/2,M-1/2\rangle^{\beta}\langle S,M|^{\gamma}V_k(SM,\beta\gamma)+\text{c.c.}\}\\&+\sum_{k.SM,\beta\gamma}\{\hat{c}^+_{k\downarrow}|S-1/2,M-1/2\rangle^{\beta}\langle S,M-1|^{\gamma}\tilde{V}_k(SM\\&-1,\beta\gamma)+\text{c.c.}\}\end{aligned}\tag{4}$$

in such a way that electrons are transferred from the atom to the metal (k state with spin up or down), or the other way around. Notice that the process of transferring (taking) one electron to (from) the metal changes S and M by $1/2$. Equation (4) generalizes the interacting part of Hamiltonian (1) to the problem we are considering. The matrix elements $V_k(SM,\beta\gamma)$ and $\tilde{V}_k(SM-1,\beta\gamma)$ can be written as $V_k(SM,\beta\gamma)=V_k\sqrt{5(S+M)/2S}$ and $\tilde{V}_k(SM-1,\beta\gamma)=V_k(S,-M+1,\beta\gamma)=V_k\sqrt{5(S-M+1)/2S}$ by assuming, for the sake of simplicity, $V_{km}=V_k$ (in a more general case, V_k should be replaced by V_k^{eff} depending on the particular values of V_{km}). All these elements are better described by the diagrams of the Appendix that include all the possible couplings between the SM states normalized to $\sqrt{5}V_k$.

One has to realize that the actual states coupled to each other depend on the starting Hamiltonian. For instance, the

$|2,2\rangle$ state coupled to $|5/2,5/2\rangle$ has to be obtained by applying H^{int} to $|5/2,5/2\rangle$; this procedure has to be repeated at each step to calculate all the different wave functions defining the diagrams shown in the Appendix. Moreover, the different diagrams correspond to different spin fluctuations: in particular, the first one represents a fluctuation between $S=5/2$ and 2, the next one represents fluctuations between $S=2$ and $3/2$, and so on. This means that, in our approximation, we are only considering total spin fluctuations of 1/2 (which is equivalent to taking an infinite-U effective Hamiltonian, with the number of electrons in the atom being allowed to fluctuate only by one).

Hamiltonians (3) and (4) have been solved by using a Green-function equation of motion technique up to second order in the coupling parameter V_k. Although this technique is not as accurate as the renormalization group[14] or quantum Monte Carlo.[15] it provides a very convenient and intuitive way for solving our model Hamiltonian (4). Our Green-function definition in terms of the projector operators is as follows:

$$G^{SM,\gamma}_{S\pm 1/2,M\pm 1/2,\alpha}(t,t') = i\Theta(t'-t)\langle\{|S,M\rangle^{\gamma}\langle S\pm 1/2,M\pm 1/2|^{\alpha}_{t'},|S\pm 1/2,M\pm 1/2\rangle^{\alpha}\langle S,M|^{\gamma}_{t}\}\rangle, \tag{5}$$

where $|S,M\rangle^{\gamma}$ and $|S\pm 1/2,M\pm 1/2\rangle^{\alpha}$ are the states coupled by $V_k(SM,\alpha\gamma)$ or $\widetilde{V}_k(SM-1,\alpha\gamma)$. In Eq. (5), $\{A,B\}$ represents the anticommutator of operators A and B.

We present results for the case $\varepsilon_{S\alpha}=\varepsilon_S$ independent of the m orbitals occupied in the α state; we also present results for $V_{km}=V_k$, also independent of the orbital m. In this case, we have a complete degeneration for each value of SM.

The first step of the equation of motion for the Green function $G^{SM}_{S-1/2,M-1/2}(t,t')$ gives the equation

$$\begin{aligned} i dG^{S,M}_{S-1/2,M-1/2}(t,t')/dt &= \delta(t-t')\langle|S,M\rangle\langle S,M| + |S-1/2,M-1/2\rangle\langle S-1/2,M-1/2|\rangle + (\varepsilon_S-\varepsilon_{S-1/2})G^{S,M}_{S-1/2,M-1/2}(t,t') \\ &+ \sqrt{5}\sum_k V_k G^{S,M}_{S-1/2,M-1/2}(|S-1/2,M-1/2\rangle\langle S-1/2,M-1/2|\hat{c}_{k\uparrow}) + \sqrt{5}\sum_k V_k G^{S,M}_{S-1/2,M-1/2}(|S,M\rangle\langle S,M|\hat{c}_{k\uparrow}) \\ &+ \sqrt{5/(2S)}\sum_k V_k G^{S,M}_{S-1/2,M-1/2}(|S,M-1\rangle\langle S,M|\hat{c}_{k\downarrow}), \end{aligned} \tag{6}$$

where the following notation has been used for the new Green functions that appear in Eq. (6):

$$G^{B}_{A}(|C\rangle\langle D|\hat{c}_k) = i\Theta(t'-t)\langle\{|B\rangle\langle A|_{t'};|C\rangle\langle D|\hat{c}_k(t)\}\rangle,$$

and in all the cases, $\langle\ \rangle$ denotes the mean value in the ground state.

These new Green functions are calculated by closing up to second order in V_k their equations of motion, as explained in Ref. 16. In this way, the following expressions are obtained:

$$\begin{aligned} & i\frac{d}{dt}G^{S,M}_{S-1/2,M-1/2}(|S-1/2,M-1/2\rangle\langle S-1/2,M-1/2|c_{k\uparrow}) \\ &\quad = \delta(t-t')\langle|S,M\rangle\langle S-1/2,M-1/2|c_{k\uparrow}\rangle + \varepsilon_k G^{S,M}_{S-1/2,M-1/2}(|S-1/2,M-1/2\rangle\langle S-1/2,M-1/2|c_{k\uparrow}) \\ &\quad\quad + \sqrt{5}V_k\langle 1-n_{k\uparrow}\rangle G^{S,M}_{S-1/2,M-1/2}(t,t'), \end{aligned} \tag{7}$$

$$\begin{aligned} i\frac{d}{dt}G^{S,M}_{S-1/2,M-1/2}(|S,M\rangle\langle S,M|c_{k\uparrow}) &= -\delta(t-t')\langle|S,M\rangle\langle S-1/2,M-1/2|c_{k\uparrow}\rangle + \varepsilon_k G^{S,M}_{S-1/2,M-1/2}(|S,M\rangle\langle S,M|c_{k\uparrow}) \\ &+ \sqrt{5}V_k\langle n_{k\uparrow}\rangle G^{S,M}_{S-1/2,M-1/2}(t,t'), \end{aligned} \tag{8}$$

$$\begin{aligned} i\frac{d}{dt}G^{S,M}_{S-1/2,M-1/2}(|S,M-1\rangle\langle S,M|c_{k\downarrow}) &= -\delta(t-t')\langle|S,M-1\rangle\langle S-1/2,M-1/2|c_{k\downarrow}\rangle + \varepsilon_k G^{S,M}_{S-1/2,M-1/2}(|S,M-1\rangle\langle S,M|c_{k\downarrow}) \\ &+ \sqrt{5/(2S)}V_k\langle n_{k\downarrow}\rangle G^{S,M}_{S-1/2,M-1/2}(t,t'). \end{aligned} \tag{9}$$

[Equations (6)–(9) are Fourier transformed, and we take into account that for a nonmagnetic case (because of spin symmetry), the Green functions are independent of M, $G^{SM}_{S-1/2,M-1/2}(\omega)=G^{S}_{S-1/2}(\omega)$. Then, by using the following equation:

$$\langle|S,M-1\rangle\langle S-1/2,M-1/2|c_{k\downarrow}\rangle = \frac{\sqrt{5/(2S)}}{\pi}V_k\int_{-\infty}^{\infty}d\omega' f_{<}(\omega')\mathrm{Im}\,\frac{G^{S}_{S-1/2}(\omega')}{(\omega'-\varepsilon_k)},$$

we obtain $G^{S}_{S-1/2}(\omega)$ (which is independent of α and γ)

$$\left\{\omega-\varepsilon_0-5\sum_k V_k^2/(\omega-\varepsilon_k)-5/(2S)\sum_k\frac{V_k^2\langle n_{k\sigma}\rangle}{(\omega-\varepsilon_k)}\right\}G^S_{S-1/2}(\omega)$$
$$=\langle|SM\rangle\langle SM|+|S-1/2,M-1/2\rangle\langle S-1/2,M-1/2|\rangle-5/(2\pi S)\sum_k\frac{V_k^2}{(\omega-\varepsilon_k)}\int_{-\infty}^{\infty}d\omega' f_<(\omega')\mathrm{Im}\frac{G^S_{S-1/2}(\omega')}{(\omega'-\varepsilon_k)}, \qquad (10)$$

valid for any S from 1/2 to 5/2. In Eq. (10), $\varepsilon_0=\varepsilon_S-\varepsilon_{S-1/2}$, and $\langle n_{k\sigma}\rangle=f_<(\varepsilon_k)=1/\{1+\exp[(\varepsilon_k-E_F)/k_BT]\}$ is the Fermi–Dirac distribution. On the other hand, the norm constraint necessary to solve Eq. (10) is

$$\sum_M\{|S,M\rangle\langle S,M|+|S-1/2,M-1/2\rangle\langle S-1/2,M-1/2|\}=1.$$

We have also checked that different interacting Hamiltonians (V_{km} dependent on m) also yield similar equations.

In the case of having a crystalline field splitting the d-orbital energies, one has to calculate the Green function of each degenerate resonance and obtain the total electron charge combining the contributions of each case (in this approximation, we neglect the coupling between atomic levels due to the crystalline field splitting, whose effect is assumed to be small with respect to the Hund rule effect; otherwise, all the Green functions of the degenerate resonance should be coupled with each other).

For n=6, 7, 8, 9, and 10, the hole picture is the appropriate one. In this case, we find that the fluctuations $d^{10}\leftrightarrow d^9$, $d^9\leftrightarrow d^8$, $d^8\leftrightarrow d^7$, $d^7\leftrightarrow d^6$, and $d^6\leftrightarrow d^5$ are equivalent to the electron ones, $d^0\leftrightarrow d^1$, $d^1\leftrightarrow d^2$, $d^2\leftrightarrow d^3$, $d^3\leftrightarrow d^4$, and $d^4\leftrightarrow d^5$, respectively, provided the energies ε are changed by, $-\varepsilon$.

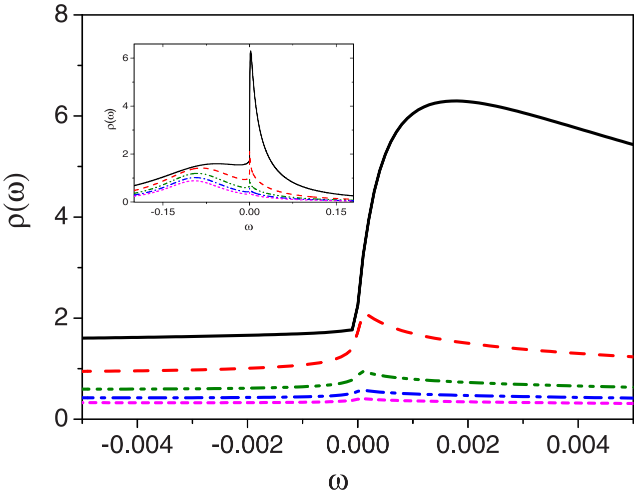


FIG. 1. (Color online) The impurity density of states $\rho(\omega)$ around the Fermi level for the cases $d^0\leftrightarrow d^1$ (solid line), $d^1\leftrightarrow d^2$ (dash line), $d^2\leftrightarrow d^3$ (dash-dot-dot line), $d^3\leftrightarrow d^4$ (dash-dot line), and $d^4\leftrightarrow d^5$ (short dash line). Inset: the same using a more extended range of energy values. Atomic units are used.

III. RESULTS AND DISCUSSION

Equation (10) is the main result of this paper, showing how the Kondo resonance depends on the atomic occupancy n. This is mainly reflected in the term $5/(2S)\Sigma_k V_k^2 n_{k\sigma}/(\omega-\varepsilon_k)$ appearing in Eq. (10). The factor $5/(2S)$ is basically controlling the weight of the Kondo resonance. For large S, the Kondo peak decreases. This is seen in the impurity density of states, $\rho(\omega)=(1/\pi)\mathrm{Im}\, G^S_{S-1/2}(\omega)$, shown in Fig. 1 for atomic charges between 0 and 5 (electron picture) and in Fig. 2 for charges between 5 and 10 (hole picture). It is found that the Kondo resonance appears at positive (negative) energies in the case of d occupancies below (above) the half-filling shell, which is also in good agreement with the trends observed when going from Ti to Ni impurities in Ref. 11. The calculation has been performed for a flatband approximation at T=6 K by considering a level width Δ=0.01D and ε_0'=−0.1D.

The factor $1/(2S)$, reducing the weight of the Kondo resonance as a function of the orbital occupancies, can be understood in terms of the matrix elements $V_k(SM,\alpha\gamma)$ and $\tilde{V}_k(SM-1,\beta\gamma)$ introduced in Hamiltonian (4) and shown in the Appendix. The crucial point to realize is how the spin fluctuations fix the Kondo resonance. For instance, for the case $|5/2,5/2\rangle^{(1)}\Leftrightarrow|2,2\rangle^{(1)}$ and the Green function $G^{5/2,5/2}_{2,2}$, the Kondo resonance is associated with the fluctuations whereby electrons are transferred between states $|2,2\rangle^{(1)}$ and $|5/2,3/2\rangle^{(1)}$ [Eqs. (6) and (9)]. This makes this contribution

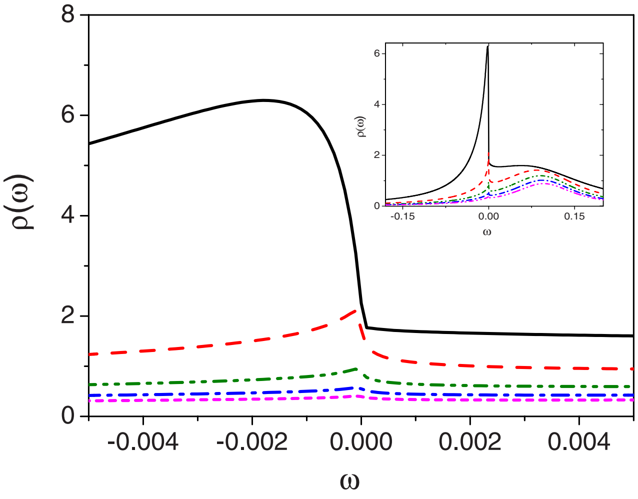


FIG. 2. (Color online) The same as in Fig. 2 for the cases $d^{10}\leftrightarrow d^9$ (solid line), $d^9\leftrightarrow d^8$ (dash line), $d^8\leftrightarrow d^7$ (dash-dot-dot line), $d^7\leftrightarrow d^6$ (dash-dot line), and $d^6\leftrightarrow d^5$ (short dash line).

proportional to $V_k^2/5$, while for the case, say, $|1/2,1/2\rangle^{(5)} \Leftrightarrow |0,0\rangle^{(1)}$, that resonance is proportional to $V_k^2/1$. By considering all the cases shown in the Appendix, we find the factor $1/(2S)$ mentioned above. We conclude that the reduction of the Kondo resonance weight as a function of the orbital occupancy is due to the smaller overlap found between fluctuating states for larger spin.

Finally, it is convenient to compare the Kondo temperatures calculated in our model and in other different approximations. In our approach, an analysis of the poles associated with the Green function of Eq. (10) yields $T_K = D\exp(-4S\pi|\varepsilon_0|/N\Delta)$, where we should take $N=10$ since this is the degeneracy of the states with $S=1/2$ for the fluctuation $d^0 \leftrightarrow d^1$ (this is the N-fold degenerate limit of our model). In the V^2 approximation, one gets $T_K = D\exp(-2\pi|\varepsilon_0|/N\Delta)$ for the N-fold degenerate model, which is equivalent to the one found in this work by changing Δ with $\Delta/(2S)$. If we assume that the same factor is going to modify in a similar way the exact solution calculated for the N-fold degenerate model [where $T_K \approx D(N\Delta/\pi D)^{1/N}\exp(-\pi|\varepsilon_0|/N\Delta)$], we conclude that, for the ionic model presented in this paper, T_K is proportional to

$$D(N\Delta/2SD)^{1/N}\exp(-2\pi S|\varepsilon_0|/N\Delta). \qquad (11)$$

This equation embodies all the properties of the d-Kondo resonances discussed in this paper. In particular, it shows how T_K decreases with S in such a way that the Kondo temperature is the largest for charge fluctuations $d^0 \leftrightarrow d^1$ and $d^{10} \leftrightarrow d^9$, as already illustrated in Figs. 1 and 2.

IV. CONCLUSIONS

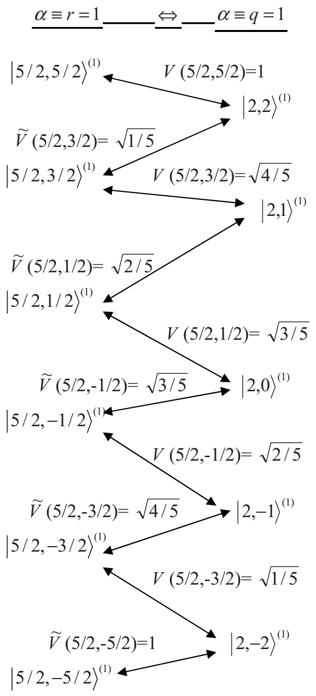
In conclusion, we have shown how to deduce, in the Kondo problem, an ionic Hamiltonian using the first Hund rule for transition metal impurities in a metal host in the limit of an infinite-U value. This Hamiltonian has been analyzed by means of an equation of motion method up to second order in the metal-impurity interaction; comparison with the N-degenerate model has allowed us to deduce its Kondo temperature as a function of the d-orbital occupancy. We found that this Kondo temperature has the largest value for n fluctuating between 0 and 1 or between 10 and 9 electrons, and the smallest one for fluctuations between 4 and 5 or 6 and 5 electrons.

ACKNOWLEDGMENTS

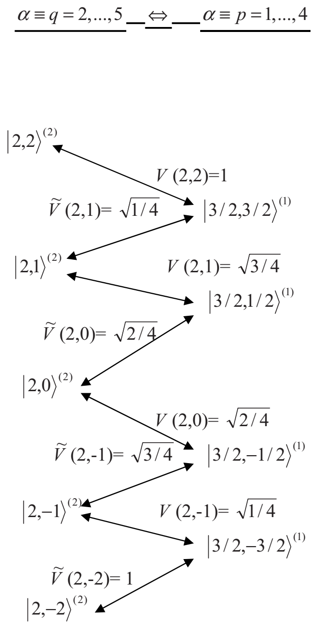
One of the authors (E.C.G.) acknowledges financial support by ANPCyT through PICT14724, CONICET through PIP 5277, and U.N.L. through a CAI+D grant. F.F. has been supported by the Spanish CICYT under Projects No. MAT 2004-09183, No. MAT2004-01271, and No. NAN-2004-09183-C10-07 and the CAM under Project No. 0505-MAT-0303. The authors thank M. C. G. Passeggi for the careful reading of this paper.

APPENDIX

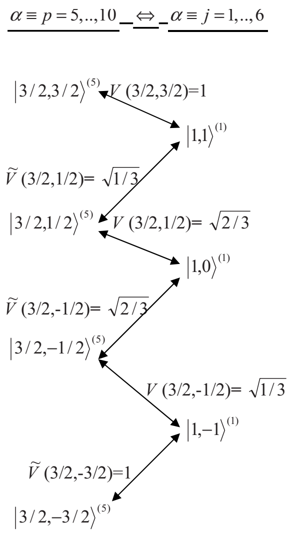
The matrix elements of Hamiltonian (4) normalized to $\sqrt{5}V_k$ are shown in a diagrammatic way. Notice the degeneracy as a function of S: for a multiple degenerate case, only one case is shown, as indicated by the particular superindex introduced in the diagrams.



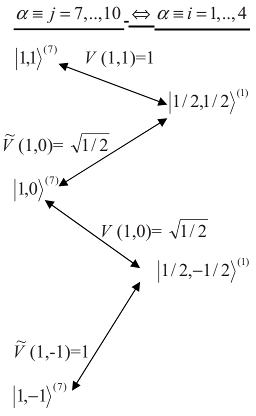
Single degeneracy



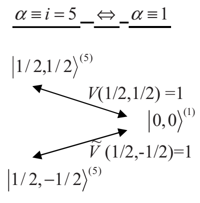
Fourfold degeneracy



Sixfold degeneracy



Fourfold degeneracy



Single degeneracy

[1] P. W. Anderson, Phys. Rev. **124**, 41 (1961).

[2] A. C. Hewson, *The Kondo Problem to Heavy Fermions* (Cambridge University Press, Cambridge, 1993).

[3] D. Goldhaber-Gordon, J. Gores, M. A. Kastner, H. Shtrikman, D. Mahalu, and U. Meirav, Phys. Rev. Lett. **81**, 5225 (1998).

[4] P. Nozières and A. Blandin, J. Phys. (Paris) **41**, 193 (1980).

[5] L. L. Hirst, Adv. Phys. **27**, 231 (1978).

[6] M. F. Crommie, C. P. Lutz, and D. M. Eigler, Phys. Rev. B **48**, 2851 (1993).

[7] A. Davies, J. A. Stroscio, D. T. Pierce, and R. J. Celotta, Phys. Rev. Lett. **76**, 4175 (1996).

[8] A. Yazdani, B. A. Jones, C. P. Lutz, M. F. Crommie, and D. M. Eigler, Science **275**, 1767 (1997).

[9] V. Madhavan, W. Chen, T. Jamneala, M. F. Crommie, and N. S. Wingreen, Science **280**, 567 (1998).

[10] J. Li, W. D. Schneider, R. Berndt, and B. Delley, Phys. Rev. Lett. **80**, 2893 (1998).

[11] T. Jamneala, V. Madhavan, W. Chen, and M. F. Crommie, Phys. Rev. B **61**, 9990 (2000).

[12] G. Gruener and A. Zawadowski, Rep. Prog. Phys. **37**, 1497 (1974).

[13] L. H. Yu, Z. K. Keane, J. W. Ciszek, L. Cheng, J. M. Tour, T. Baruah, M. R. Pederson, and D. Natelson, Phys. Rev. Lett. **95**, 256803 (2005).

[14] H. R. Krishna-murthy, J. W. Wilkins, and K. G. Wilson, Phys. Rev. B **21**, 1003 (1980).

[15] R. N. Silver, J. E. Gubernatis, D. S. Sivia, and M. Jarrell, Phys. Rev. Lett. **65**, 496 (1990); P. Werner, A. Comanac, L. de Medici, M. Troyer, and A. J. Millis, *ibid.* **97**, 076405 (2006).

[16] E. C. Goldberg, F. Flores, and R. C. Monreal, Phys. Rev. B **71**, 035112 (2005).