Kondo Resonance Narrowing in d- and f-Electron Systems

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We develop a simple scaling theory for the effect of Hund's interactions on the Kondo effect, showing how an exponential narrowing of the Kondo resonance develops in magnetic ions with large Hund's interaction. Our theory accounts for the exponential reduction of the Kondo temperature with spin S of the Hund's coupled moment, first observed in d-electron alloys in the 1960s, and more recently encountered in numerical calculations on multiband Hubbard models. We discuss the consequences of Kondo resonance narrowing for the Mott transition in d-band materials, particularly iron pnictides, and the narrow ESR linewidth recently observed in ferromagnetically correlated f-electron materials.

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The theory of the Kondo effect forms a cornerstone in the current understanding of correlated electron systems [1]. Four decades ago, experiments on d-electron materials found that the characteristic scale of spin fluctuations of magnetic impurities, known as the Kondo temperature, narrows exponentially with the spin S of the impurity [2] (Fig. 1). Though a tentative explanation of this effect was proposed [2], based on an observation by Schrieffer [3] that strong Hund's coupling suppresses the Kondo coupling constant, interest in this phenomenon waned and remarkably, no subsequent theoretical treatment was written. Motivated by a resurgence of interest in f- and d-electron systems, especially quantum critical heavy electron systems [4], and pnictide superconductors [5], this Letter revisits this little-known phenomenon, which we refer to as "Kondo resonance narrowing," in a modern context.

The consequences of Kondo resonance narrowing have recently been rediscovered in calculations on multiorbital Hubbard and Anderson models [6,7]. Numerical renormalization group studies found that the introduction of Hund's coupling into the Anderson model causes an exponential reduction in the Kondo temperature [6]. The importance of Hund's effect has also arisen in the context of iron pnictide superconductors [8,9], where it appears to play a key role in the development of a "bad metal" state in which the d moments remain unquenched down to low temperatures.

In this Letter, we show that Kondo resonance narrowing can be simply understood within a scaling theory description of the multichannel Kondo model with Hund's interaction. The main result is an exponential decrease of the Kondo temperature that develops when localized electrons lock together to form a large spin S, given by the formula

$$\ln T_K^*(S) = \ln\Lambda_0 - (2S)\ln\left(\frac{\Lambda_0}{T_K}\right). \tag{1}$$

Here, T_K is the "bare" spin 1/2 Kondo temperature and $\Lambda_0 = \min(J_H S, U + E_d, |E_d|)$ is the scale at which the locked spin S develops under the influence of a Hund's coupling, J_H, while U and E_d are the interaction strength and position of the bare d level. Although the germs of an explanation are implicitly contained in the early works of Schrieffer [3] and Hirst [10], a theoretical treatment of the effect of a finite J_H has not previously been given.

To develop our theory, we consider K Hund's-coupled spin 1/2 moments at a single site, each interacting with a conduction electron channel of bandwidth D via an antiferromagnetic interaction J:

$$H = \sum_{\mathbf{k},\sigma,\mu} \varepsilon_k c^\dagger_{\mathbf{k}\sigma\mu} c_{\mathbf{k}\sigma\mu} - J_H\left(\sum_{\mu=1}^{K} \mathbf{s}_\mu\right)^2 + J\sum_{\mu=1}^{K} \mathbf{s}_\mu \cdot \boldsymbol{\sigma}_\mu, \tag{2}$$

where ε_k is the conduction electron energy, $\mu = 1, K$ is the channel index and $\boldsymbol{\sigma}_\mu = \sum_{\mathbf{k}} c^\dagger_{\mathbf{k}\alpha\mu} \boldsymbol{\sigma}_{\alpha\beta} c_{\mathbf{k}\beta\mu}$ is the conduction electron spin density in channel μ at the origin. We implicitly assume that Hund's scale KJ_H is smaller than D. When derived from an Anderson model of K spin-1/2 impurities, then $D = \min(E_d + U, |E_d|)$ is the crossover scale at which local moments form while $J = |V_{k_F}|^2(1/(E_d + U) + 1/|E_d|)$ is the Schrieffer-Wolff form of the Kondo coupling constant [1], where V_{k_F} is the Fermi surface averaged hybridization.

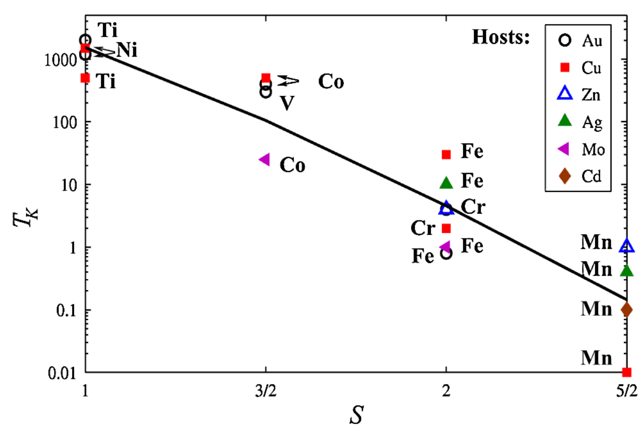

FIG. 1 (color online). Measured values [22] of the Kondo temperature T_K^* in host alloys Au, Cu, Zn, Ag, Mo, and Cd with transition metal impurities, plotted vs the nominal size S of the spin. The solid line is the fit to Eq. (1) with $\Lambda_0 \equiv J_H S$.

The behavior of this model is well understood in the two extreme limits [11]: for $J_H = \infty$, the K spins lock together, forming a K-channel spin $S = K/2$ Kondo model. The opposite limit $J_H = 0$ describes K replicas of the spin-$1/2$ Kondo model. Paradoxically, the leading exponential dependence of the Kondo temperature on the coupling constant $T_K \sim De^{-1/2J\rho}$ in these two limits is independent of the size of the spin. However, as we shall see in the crossover between the two limits, the projection of the Hamiltonian into the space of maximum spin leads to a $(2S)$-fold reduction in the Kondo coupling constant.

We study the properties of this model as a function of energy cutoff Λ. We expect three regions depicted in Fig. 2(a): (I) $\Lambda \gg J_H S$: a spin-$1/2$ disordered paramagnet characterized by a Curie magnetic susceptibility

$$\chi_{\rm I}(T) = K\frac{(3/4)(g\mu_B)^2}{3k_BT}, \tag{3}$$

with effective moment $(\mu_{\rm eff}^{\rm I})^2 = 3K/4$;
(II) $T_K^* \ll \Lambda \ll J_H S$: an unscreened big spin $S = K/2$ is formed above an emergent Kondo energy scale T_K^*;
(III) $\Lambda \ll T_K^*$: the Nozières Fermi liquid ground state of the K-channel $S = K/2$ Kondo problem.

We employ the "poor man's scaling" approach [1,12], in which the renormalization group (RG) flows are followed as conduction electrons are progressively decimated from the Hilbert space. Computing the diagrams shown in Fig. 3, we obtain the following RG equations in region I:

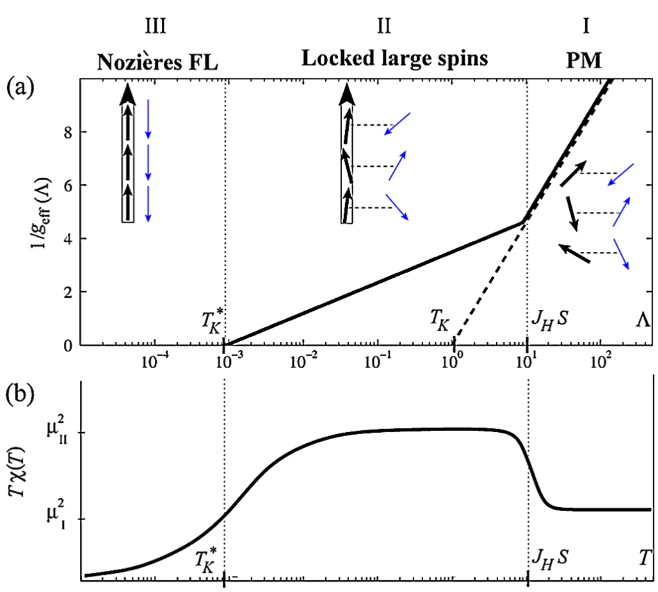

FIG. 2 (color online). (a) Schematic showing the behavior of the running coupling constant $g_{\rm eff}(\Lambda) = J(\Lambda)\rho K_{\rm eff}$ on a logarithmic scale, with $K_{\rm eff}$ the effective number of conduction electron channels per impurity spin ($K_{\rm eff} = 1$ in region I and K in regions II and III). (b) Schematic showing effective moment $\mu_{\rm eff}^2(T) = T\chi(T)$ in terms of the susceptibility $\chi(T)$, showing the enhancement (15) in region II and the loss of localized moments due to Kondo screening in region III.

$$\text{(I):}\ \frac{d(J\rho)}{d\ln\Lambda} = -2(J\rho)^2 + 2(J\rho)^3, \tag{4}$$

$$\frac{d(J_H\rho)}{d\ln\Lambda} = 4(J\rho)^2 J_H\rho, \tag{5}$$

where ρ is the density of states of the conduction electrons at the Fermi level. The first equation is the well-known beta function for the Kondo model, which to this order is independent of Hund's coupling. As we decimate the conduction sea, reducing the bandwidth Λ down to the Hund's scale $J_H S$, to leading logarithmic order we obtain

$$\rho J(\Lambda) = \frac{1}{\ln(\frac{\Lambda}{T_K})}\Bigg|_{\Lambda = J_H S} \equiv \rho J_{\rm I}. \tag{6}$$

There is a weak downward-renormalization of the Hund's coupling J_H described by Eq. (5), originating in the two-loop diagrams [Fig. 3(c)]. To leading logarithmic approximation, we may approximate J_H by a constant.

Once Λ is reduced below $J_H S$, the K local moments become locked into a spin $S = K/2$, as discussed in Ref. [13] for the case of two impurities coupled by ferromagnetic RKKY interaction. The low-energy properties of the system in region II are described by a Kondo model of spin $K/2$ with K conduction electron channels:

$$H_{\rm eff}^{\rm II} = \sum_{\mathbf{k},\sigma,\mu} \varepsilon_k c^\dagger_{\mathbf{k}\sigma\mu} c_{\mathbf{k}\sigma\mu} + J^*(\Lambda)\sum_{\mu=1}^{K} \mathbf{S}\cdot\boldsymbol{\sigma}_\mu. \tag{7}$$

To obtain the value of J^*, we must project the original model into the subspace of maximum spin S. By the Wigner-Eckart theorem, any vector operator acting in the basis of states $|S_z\rangle$ of spin $S = K/2$ is related by a constant prefactor to $\mathbf{S}$ itself:

$$\langle SS_z|\mathbf{s}_\mu|SS_z\rangle = g_S\langle S_z|\mathbf{S}|S_z\rangle. \tag{8}$$

Summing both sides of the equation over impurity index $\mu = 1,\ldots,K$, one obtains $\langle SS_z|\sum_\mu \mathbf{s}_\mu|SS_z\rangle = g_S K S_z$. However since $\sum_\mu \mathbf{s}_\mu = K\mathbf{s} \equiv \mathbf{S}$, one arrives at the conclusion that $g_S K = 1$, therefore determining the value of the constant coefficient $g_S = 1/K$ in Eq. (8). Comparing

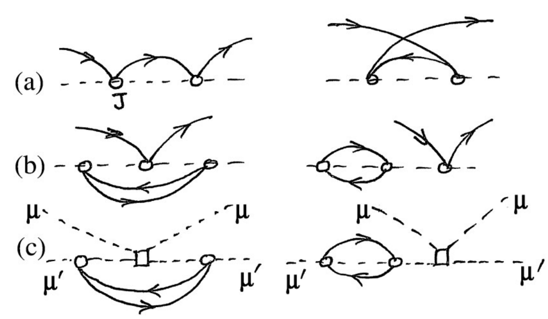

FIG. 3. The diagrams appearing in (a) one-loop and (b) two-loop RG equations for Kondo coupling J (open circles). Solid lines denote the conduction electron propagators and dashed line—the impurity spin. (c) The lowest order diagrams in the RG flow of Hund's coupling (square vertex denotes bare J_H).

Eqs. (2) and (7), we arrive at the effective Kondo coupling:

$$J^* = J/K. \tag{9}$$

This equation captures the key effect of crossover from region I to region II in Fig. 2. This result was first derived in the early work on the multichannel Kondo problem by Schrieffer [3], where the limit of $J_H \rightarrow \infty$ was implicitly assumed, and also appears for the particular case of $K = 2$ in the study of the two-impurity Kondo problem [13].

To one-loop order, the scaling equation for $J^*(\Lambda)$ in region II is identical to that of region I (4), namely $d(J^*\rho)/d\ln\Lambda \approx -2(J^*\rho)^2$, though its size is K times smaller. To avoid the discontinuous jump in coupling constant at the crossover, it is more convenient to consider $g_{\rm eff} \equiv J(\Lambda)\rho K_{\rm eff}$, where the effective number of channels $K_{\rm eff} = 1$ and K in regions I and II, respectively. This continuous variable satisfies

$$\text{(II)}: \ \frac{dg_{\rm eff}}{d\ln\Lambda} = -\frac{2}{K}g_{\rm eff}^2 + \frac{2}{K}g_{\rm eff}^3, \tag{10}$$

so the speed at which it scales to strong coupling becomes K times smaller in region II [see Fig. 2(a)]. Solving this RG equation to leading order, and setting $g_{\rm eff}(\Lambda = T_K^*) \sim 1$, we obtain $T_K^* \sim (J_H S)(D/J_H S)^K e^{-(K/2J\rho)}$ for the renormalized Kondo scale. Comparing this with the bare Kondo scale $T_K \sim De^{-1/2J\rho}$, we deduce

$$T_K^* \sim J_H S\left(\frac{T_K}{J_H S}\right)^K \equiv T_K\left(\frac{T_K}{J_H S}\right)^{K-1}, \tag{11}$$

from which formula (1) follows. This exponential suppression of the spin tunneling rate can be understood as a result of a $2S$-fold increase in the classical action associated with a spin flip.

These results are slightly modified when the two-loop terms in the scaling are taken into account. The expression for T_K now acquires a prefactor, $T_K = D\sqrt{J\rho}e^{-1/2J\rho}$ and J_H is weakly renormalized so that

$$T_K^* = (\tilde{J}_H S)\left(\frac{T_K}{\sqrt{K}\tilde{J}_H S}\right)^K, \tag{12}$$

where $\tilde{J}_H$ is determined from the quadratic equation

$$x^2 - x\left(x_0 + \frac{4}{\ln(D/T_K)}\right) + 4 = 0, \tag{13}$$

where $x = \ln(\tilde{J}_H S/T_K)$ and $x_0 \equiv \ln(J_H S/T_K)$.

The magnetic impurity susceptibility in region II is

$$\chi^*_{\rm imp} = \frac{(g\mu_B)^2}{3k_B T}S(S+1)\left[1 - \frac{1}{\ln(\frac{T}{T_K^*})} + \mathcal{O}\left(\frac{1}{\ln^2(\frac{T}{T_K^*})}\right)\right], \tag{14}$$

from which we see that the enhancement of the magnetic moment at the crossover is given by [see Fig. 2(b)]

$$(\mu_{\rm eff}^{\rm II}/\mu_{\rm eff}^{\rm I})^2 = (K+2)/3. \tag{15}$$

When the temperature is ultimately reduced below the exponentially suppressed Kondo scale T_K^*, the big spins S become screened to form a Nozières Fermi liquid [14]. A phase-shift description of the Fermi liquid predicts that [11,15] the Wilson ratio $W \equiv \frac{\chi_{\rm imp}}{\chi_0} / \frac{\gamma_{\rm imp}}{\gamma_0}$ is given by

$$W_K = \frac{2(K+2)}{3} \equiv 2\left(\frac{\mu_{\rm eff}^{\rm II}}{\mu_{\rm eff}^{\rm I}}\right)^2, \tag{16}$$

which, compared with the classic result $W_1 = 2$ for the one-channel model [14], contains a factor of the moment enhancement. This result holds in the extreme limit $J_H \gg T_K$. More generally, W depends on the ratio $\eta = U^*/J_H^*$ of a channel-conserving interaction U^* to an interchannel Hund's coupling J_H^* in the Fermi liquid phase-shift analysis, giving rise to

$$W_K(\eta) = 2\left(1 + \frac{K-1}{2(1+\eta)+1}\right). \tag{17}$$

On general grounds we expect $\eta \sim T_K/J_H$.

We end with a discussion of the broader implications of Kondo resonance narrowing for d- and f-electron materials. This phenomenon provides a simple explanation of the drastic reductions in spin fluctuation scale observed in the classic experiments of the 1960s [2], confirming the important role of Hund's coupling. One of the untested predictions of this theory is a linear rise of the Wilson ratio W with spin $S = K/2$ (16), from a value $W[1] = 2.7$ in Ti and Ni, to $W[5/2] = 4.7$ in Mn impurities. Together with the early data (Fig. 1), we are able to essentially confirm the early speculation [3] that without Hund's coupling, the Kondo effect would take place at such high temperatures that dilute d-electron magnetic moments would be unobservable. This is the situation for $S = 1$ Ti impurities in gold, where the Kondo temperature is so high that magnetic behavior is absent. On the other hand, Kondo resonance narrowing due to Hund's interaction can become so severe, that the reentry from region II into the quenched Fermi liquid is too low to observe. This is the case for $S = 5/2$ Mn in gold, where T_K^* is so low that it has never been observed; the recent observation of a "spin frozen phase" in dynamical mean-field theory (DMFT) studies [7] may be a numerical counterpart.

What then, are the possible implications for dense d-electron systems? In those materials, the ratio of Kondo temperature to the Hund's coupling will be strongly dependent on structure, screening, and chemistry. In cases where $J_H \ll T_K$, the physics of localized magnetic moments will be lost and the d electrons will be itinerant. On the other hand, the situation where $J_H \gg T_K$ will almost certainly lead to long range magnetic order with localized d electrons. Thus in multiband systems, the criterion $J_H \sim T_K$ determines the boundary between localized and itinerant behavior, playing the same role as the condition $U/D \sim 1$ in one-band Mott insulators.

These issues may be of particular importance to the ongoing debate about the strength of electron correlations in the FeAs superconductors [5,16–18]. Current wisdom argues that in a multiband system, the critical interaction U_c necessary for the Mott metal-insulator transition grows linearly with the number of bands N [19,20], favoring a viewpoint that iron pnictides are itinerant metals lying far from the Mott regime.

In essence, Hund's coupling converts a one-channel Kondo model to a K-channel model (7). Large-N treatments of these models show that the relevant control parameter is the ratio K/N [21], rather than $1/N$. By repeating the large-N argument of Florens *et al.* [19], we conclude that the critical value of the on-site interaction U for the Mott transition is

$$U_c \propto (N/K) V_{k_F}^2 \rho. \tag{18}$$

Thus Hund's coupling restores U_c to a value comparable with one-band models. Recent DMFT calculations on the two-orbital Hubbard model [6] support this view, finding that U_c is reduced by a factor of 3 when $J_H/U = 1/4$.

LDA + DMFT studies of iron pnictide materials [9] conclude that in order to reproduce the incoherent bad metal features of the normal state, a value of $J_H \sim 0.4$ eV is required, resulting in $T_K^* \sim 200$ K. Fitting to Eq. (11) results in a nominal $T_K \sim 3000$ K and a ratio $T_K/J_H S \sim 0.4$. By contrast, for dilute Fe impurities in Cu [22] $T_K^* \approx 20$ K, from which we obtain $T_K/J_H S \sim 0.2$ and $T_K \sim 3500$ K. The bare Kondo temperature is essentially the same in both cases, but $T_K/J_H S$ is significantly increased due to screening of J_H in the iron pnictides, placing them more or less at the crossover $J_H \sim T_K$. A further sign of strong correlations in iron pnictides derives from the Wilson ratio, known to be ~ 1.8 in SmFeAsO [23] and about 4–5 in FeCrAs [24], whereas Eq. (16) would predict $W = 4$.

Finally, we discuss heavy f-electron materials, which lie at the crossover between localized and itinerant behavior [25]. In these materials, spin orbit and crystal field interactions dominate over Hund's interaction. In fact, crystal fields are also known to suppress the Kondo temperature in f-electron systems [26], but the suppression mechanism differs, involving a reduction in the spin symmetry rather than a projective renormalization of the coupling constant. But the main reason that Hund's coupling is unimportant at the single-ion level in heavy f-electron materials, is because most of them involve one f electron (e.g., Ce) or one f hole in a filled f shell (Yb, Pu), for which Hund's interactions are absent.

Perhaps the most interesting application of Kondo resonance narrowing to f-electron systems is in the context of intersite interactions. Indeed, (2) may serve as a useful model for a subset of ferromagnetically correlated f-electron materials, such as CeRuPO [27], where J_H would characterize the scale of ferromagnetic RKKY interactions between moments, as in Ref. [13]. In these systems, our model predicts the formation of microscopic clusters of spins which remain unscreened in region II down to an exponentially small scale $\sim T_K^*$. This exponential narrowing of the Kondo scale may provide a clue to the observation [28,29] of very narrow ESR absorption lines in a number of Yb and Ce heavy fermion compounds with enhanced Wilson ratios. In particular, our theory would predict that the Knight shift of the electron g factor in region II is proportional to the running coupling constant $K(T) \propto g_{\rm eff}(T) \sim 1/\ln(T/T_K^*)$, where T_K^* is the resonance-narrowed Kondo temperature. A detailed study of the ESR line shape in this context will be a subject of future work.

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