Kondo resonance narrowing in d- and f-electron systems

Andriy H. Nevidomskyy and P. Coleman
Department of Physics and Astronomy, Rutgers University, Piscataway, N.J. 08854, USA
(Dated: June 22, 2009)

By developing a simple scaling theory for the effect of Hund’s interactions on the Kondo effect, we show how an exponential narrowing of the Kondo resonance develops in magnetic ions with large Hund’s interaction. Our theory predicts an exponential reduction of the Kondo temperature with spin S of the Hund’s coupled moment, a little-known effect first observed in d-electron alloys in the 1960’s, and more recently encountered in numerical calculations on multi-band Hubbard models with Hund’s interactions. 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.

PACS numbers: 75.20.Hr, 71.27.+a, 71.20.Be

The theory of the Kondo effect forms a cornerstone in current understanding of correlated electron systems [1]. More than forty years 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 size $S$ of the impurity spin [2] (Fig 1). An explanation of this effect was proposed [2] based on an early theory of the Kondo effect by Schrieffer [3], who found that strong Hund’s coupling leads to a 2S-fold reduction of the Kondo coupling constant. Surprisingly, interest in this phenomenon waned after the 1960’s. Motivated by a recent resurgence of interest in f- and d-electron systems, especially quantum critical heavy electron systems [4], and pnictide superconductors [5], this paper revisits this little-known phenomenon, which we refer to as “Kondo resonance narrowing”, placing it in a modern context.

The consequences of Kondo resonance narrowing have recently been re-discovered in calculations on multi-orbital 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], this paper revisits this little-known effect first observed in d-electron alloys in the 1960’s, and more recently encountered in numerical calculations on multi-band Hubbard models with Hund’s interactions. 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.

The behavior of this model is well understood in the two-channel 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

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

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, while $U$ and $E_d$ are the interaction strength and position of the bare d-level. Although this result is implicitly contained in the early works of Schrieffer [3] and Hirst [10], a detailed treatment has to our knowledge, not previously been given.

To develop our theory, we consider $K$ spin 1/2 impurity spins at a single site, ferromagnetically interacting via Hund’s coupling $J_H$, each coupled to a conduction electron channel of band-width $D$ via an antiferromagnetic interaction $J$:

$$H = \sum_{k,\sigma,\mu} \varepsilon_k c_{k\sigma\mu}^\dagger c_{k\sigma\mu} - J_H \left( \sum_{\mu=1}^K s_\mu \right)^2 + J \sum_{\mu=1}^K s_\mu \cdot \sigma_\mu, \quad (2)$$

where $\varepsilon_k$ is the conduction electron energy, $\mu = 1, K$ is the channel index and $\sigma_\mu = \sum_k c_{k\sigma\mu}^\dagger c_{k\sigma\mu}$ is the conduction electron spin density in channel $\mu$ 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 cross-over scale at which local moments form while $J = |V_{kr}|^2 (1/(E_d + U) + 1/|E_d|)$ is the Schrieffer–Wolff form for the Kondo coupling constant [1], where $V_{kr}$ is the Anderson hybridization averaged over the Fermi surface and $E_d < 0$ is negative.

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in Fig. 3, we obtain the following renormalization group (RG) from the Hilbert space. By computing the diagrams depicted electrons in the conduction band are systematically decimated which the leading renormalization flows are followed as the 

\[ \tilde{\chi}(T) = T \chi(T) \]

terms of the susceptibility \( \chi(T) \) showing the enhancement in region II and the loss of localized moments due to Kondo screening in region III.

The opposite limit \( \mu \sim T \) is the g-factor of the electron), with effective moment \( \mu_{\text{eff}}(T) \) describes the Kondo coupling constant. Paradoxically, the leading exponential dependence of the Kondo temperature on the coupling constant \( T_K \sim D e^{-1/2J} \) in these two limits is independent of the size of the spin. However, as we shall see in the cross-over 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 now study the properties of this model as a function of energy scale or cut-off \( \Lambda \). Qualitatively, we expect three distinct regions depicted in Fig. 2a:

(I) \( \Lambda \gg J_H S \): a spin-1/2 disordered paramagnet characterized by a high temperature Curie magnetic susceptibility

\[ \chi(T) = K \frac{(3/4)(g \mu_B)^2}{2k_B T} \]

(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 \[1,13\], in which the leading renormalization flows are followed as the electrons in the conduction band are systematically decimated from the Hilbert space. By computing the diagrams depicted in Fig. 3 we obtain the following renormalization group (RG)

\[ H_{\text{eff}} = J^*(\Lambda) \sum_{\mu=1}^K \mathbf{S} \cdot \mathbf{\sigma}_\mu, \]

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

\[ \langle SS_z|s_\mu|SS_z\rangle = g_S \langle S_z|SS_z\rangle \]

Summing both sides of the equation over impurity index \( \mu = 1, \ldots, K \), one obtains \( \langle SS_z|\sum_\mu s_\mu|SS_z\rangle = g_S K S_z \). However since \( \sum_\mu s_\mu = K S = \mathbf{S} \), 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 Eqs. (2) and (7), we arrive at the effective Kondo coupling:

\[
J^* = J/K. 
\]

(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 multi-channel Kondo problem by Schrieffer [3], where the limit of \( J_H \to \infty \) was implicitly assumed, and also appears for the particular case of \( K = 2 \) in the study of the two-impurity Kondo problem by Jayaprakash et al. [14].

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 \( \chi^* \), now acquires a pre-factor, weakly renormalized so that

\[
\tilde{\chi} = g_{\text{eff}} \chi^* \left( J^* \right),
\]

from which formula (1) follows. This exponential suppression of the spin tunneling rate can be understood as a result of a Kondo scale. Comparing this with the bare Kondo scale \( T_K \equiv D e^{-1/2J} \), we deduce

\[
T_K^* \sim J_H S \left( \frac{T_K}{J_H S} \right)^K = T_K \left( \frac{J_H S}{T_K} \right)^{-K-1},
\]

(11)

from which formula (11) follows. This exponential suppression of the spin fluctuation 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 pre-factor, \( T_K^* = D \sqrt{J} e^{-1/2J} \) and \( J_H \) is weakly renormalized so that

\[
T_K^* = (J_H S) \left( \frac{T_K}{\sqrt{J_H S}} \right)^K,
\]

(12)

where \( J_H \) is determined from the quadratic equation

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

(13)

where \( x = \ln(J_H S/T_K) \) and \( x_0 \equiv \ln(J_H S/T_K) \).

The magnetic impurity susceptibility in region II becomes

\[
\chi_{\text{imp}}^* = \frac{(g\mu_B)^2}{3k_B T} S(S + 1) \left( 1 - \frac{1}{\ln(D/T_K)} + \mathcal{O} \left( \frac{1}{\ln^2(D/T_K)} \right) \right),
\]

(14)

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

\[
\left( \frac{\mu_{\text{eff}}^*}{\mu_{\text{eff}}^0} \right)^2 = \frac{K + 2}{3},
\]

(15)

When the temperature is ultimately reduced below the exponentially suppressed Kondo scale \( T_K^* \), the big spins \( S \) become screened to form a Nozieres Fermi liquid [15]. A phase-shift description of the Fermi liquid predicts that the Wilson ratio \( W \equiv \frac{\chi_{\text{imp}}^*}{\chi_{\text{imp}}^0} \) is given by

\[
W_K = \frac{2(K + 2)}{3} = \left( \frac{\mu_{\text{eff}}^*}{\mu_{\text{eff}}^0} \right)^2,
\]

(16)

which, compared with the classic result \( W_1 = 2 \) for the one-channel model [15], 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 inter-channel Hund’s coupling \( J_H^* \) in the Fermi liquid phase-shift analysis, giving rise to

\[
W_K (\eta) = 2 \left( 1 + \frac{K - 1}{2(1 + \eta) + 1} \right).
\]

(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 sixties [2]. Our treatment brings out the important role of Hund’s coupling in this process. 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. Taking together with the early data, Fig. 1, we are able to essentially confirm the early speculation [3] that were Hund’s coupling absent, the Kondo effect would take place at such high temperatures that dilute \( d \)-electron magnetic moments would be unobservable. This is, in essence, the situation for Ti impurities in gold, where the Kondo temperature of \( S = 1 \) moments becomes so high that magnetic behavior is absent below the melting temperature of gold. On the other hand, the Kondo resonance narrowing effects of Hund’s interaction can become so severe, that the re-entry from region II into the quenched Fermi liquid becomes 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 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 multi-band 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 family of high-temperature superconductors [5, 17, 18, 19].
Current wisdom argues that in a multi-band system, the critical interaction $U_c$ necessary for the Mott metal-insulator transition grows linearly with the number of bands $N$ [22,[21], favoring a viewpoint that iron pnictide materials 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 $K/N$ [22], rather than $1/N$. By repeating the large-$N$ argument of Florens et al. [20], we conclude that the critical value of the on-site interaction $U$ for the Mott transition is

$$U_c \propto (N/K) V_{kF} \rho.$$  \hspace{1cm} (18)

Thus Hund’s coupling compensates for multi-band behavior, restoring $U_c$ 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 from $U_c \approx 3D$ to $U_c^* \approx 1.1D$ 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 $T_K$ of the order of 200 K. Fitting this with Eq. (11) results in a nominal $T_K \sim 3000$ K and a ratio $T_K/J_HS \sim 0.4$. By contrast, for dilute Fe impurities in Cu [11] $T_K \approx 20$ K, from which we extract a bare ratio $T_K/J_HS \sim 0.2$ and $T_K \sim 3500$ K. The bare Kondo temperature is essentially the same in both cases, but $T_K/J_HS$ 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 $\sim 1.8$ 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 [24]. 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 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. [14]. 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 $K(T) \propto g_{\text{eff}}(T) \sim 1/\ln(T/T_K^*)$, where $T_K^*$ is the resonance-narrowed Kondo temperature. A detailed study of the ESR lineshape in this context will be a subject of future work.

We would like to acknowledge discussions with Elihu Abrahams, Natan Andrei, Kristjan Haule, Gabriel Kotliar and AndrewMillis in connection with this work. This research was supported by NSF grant no. DMR 0605935.

* Electronic address: nevidomskyy@cantab.net

[1] A. C. Hewson, *The Kondo Problem to Heavy Fermions* (Cambridge Univ. Press, 1993).
[2] M. D. Daybell and W. A. Steyert, Rev. Mod. Phys. 40, 380 (1968).
[3] J. R. Schrieffer, J. Appl. Phys. 38, 1143 (1967).
[4] Ph. Gegenwart, F. Steglich, and Q. Si, Nature Physics 4, 186 (2008).
[5] M. R. Norman, Physics 1, 21 (2008).
[6] T. Pruschke and R. Bulla, Eur. Phys. J. B 44, 217 (2005).
[7] P. Werner, E. Gull, M. Troyer, and A. J. Millis, Phys. Rev. Lett. 101, 166405 (2008).
[8] K. Haule, J. H. Shim, and G. Kotliar, Phys. Rev. Lett. 100, 226402 (2008).
[9] K. Haule and G. Kotliar, New J. Phys. 11, 025021 (2009).
[10] L. L. Hirst, Z. Physik 244, 230 (1971).
[11] M. Daybell, in *Magnetism*, Eds. G. Rado and H. Suhl (Academic Press, New York, 1973), vol. 5, pp. 122–147.
[12] P. Nozières and A. Blandin, J. Physique 41, 193 (1980).
[13] P. W. Anderson, J. Phys. C 3, 2439 (1970).
[14] C. Jayaprakash, H. R. Krishnamurthy, and J. W. Wilkins, Phys. Rev. Lett. 47, 737 (1981).
[15] P. Nozières, J. Low Temp. Phys. 17, 31 (1974).
[16] A. Yoshimori, J. Phys. C 15, 5241 (1976).
[17] Y. Kamihara, T. Watanabe, H. Hirano, and H. Hosono, J. Am. Chem. Soc. 130, 3296 (2008).
[18] X. H. Chen et al., Nature (London) 453, 761 (2008).
[19] C. de la Cruz et al., Nature (London) 453, 899 (2008).
[20] S. Florens, A. Georges, G. Kotliar, and O. Parcollet, Phys. Rev. B 66, 205102 (2002).
[21] Y. Ono, M. Potthoff, and R. Bulla, Phys. Rev. B 67, 035119 (2003).
[22] E. Lebanon and P. Coleman, Phys. Rev. B 76, 085117 (2007).
[23] M. R. Cimberle et al., J. Mag. Mag. Materials (in press, 2009).
[24] W. Wu et al., Eur. Phys. Lett. 85, 17009 (2009). 17009 (2009)
[25] P. Coleman, in *Handbook of Magnetism and Advanced Magnetic Materials*, Eds. H. Kronmuller and S. Parkin, vol. 1, pp. 95-148 (John Wiley and Sons, 2007).
[26] K. Hanzawa, K. Yamada, and K. Yosida, J. Mag. Mag. Materials (in press, 2009).
[27] C. Krellner et al., Phys. Rev. B 76, 104418 (2007).
[28] C. Krellner, T. Farster, H. Jeevan, C. Geibel, and J. Sichelschmidt, Phys. Rev. Lett 100, 066401 (2008).
[29] J. Sichelschmidt, V. A. Ivanishin, J. Ferstl, C. Geibel, and F. Steglich, Phys. Rev. Lett. 91, 156401 (2003).