The Kondo Box: A Magnetic Impurity in an Ultrasmall Metallic Grain

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We study the Kondo effect generated by a single magnetic impurity embedded in an ultrasmall metallic grain, to be called a “Kondo box”. We find that the Kondo resonance is strongly affected when the mean level spacing in the grain becomes larger than the Kondo temperature, in a way that depends on the parity of the number of electrons on the grain. We show that the single-electron tunneling conductance through such a grain features Kondo-induced Fano-type resonances of measurable size, with an anomalous dependence on temperature and level spacing.

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What happens to the Kondo effect when a metal sample containing magnetic impurities is made so small that its conduction electron spectrum becomes discrete with a non-zero mean level spacing $\Delta$? More specifically, when will the Kondo resonance at the Fermi energy $\varepsilon_F$ that characterizes bulk Kondo physics begin to be affected? This will occur on a scale $\Delta \simeq T_K$, the bulk Kondo temperature, since a fully-developed resonance requires a finite density of states (DOS) near $\varepsilon_F$, and $\Delta$ will act as low-energy cut-off for the spin scattering amplitude.

To achieve $\Delta \gtrsim T_K$, the sample would have to be an ultrasmall metallic grain containing magnetic impurities, to be called a “Kondo box”: for example, for a metallic grain of volume $(15\text{nm})^3$ with $k_F \simeq 1\text{Å}^{-1}$, the free-electron estimate $\Delta = 1/N_0 \simeq 2\pi^2\hbar^2/(mk_F\text{Vol})$, with $N_0$ the bulk DOS near $\varepsilon_F$, gives $\Delta \simeq 0.5 - 60\text{K}$, which sweeps a range including many typical Kondo temperatures. The discrete DOS of an individual grain of this size can be measured directly using single-electron tunneling (SET) spectroscopy [1], as shown by Ralph, Black and Tinkham [2] in their studies of how a large level spacing affects superconductivity. Analogous experiments on a Kondo box should be able to probe how a large $\Delta \simeq T_K$ affects Kondo physics.

In this Letter we study this question theoretically. We find (1) that the Kondo resonance splits up into a series of sub-peaks corresponding to the discrete box levels; (2) that its signature in the SET conductance through the grain consists of Fano–like line shapes with an anomalous temperature dependence, estimated to be of measurable size; (3) an even/odd effect: if the total number of electrons on the grain (i.e. delocalized conduction electrons plus one localized impurity electron) is odd, the weight of the Kondo resonance decreases more strongly with increasing $\Delta$ and $T$ than if it is even.

The model:— For the impurity concentrations of 0.01% to 0.001% that yield a detectable Kondo effect in bulk alloys, an ultrasmall grain of typically $10^4 - 10^5$ atoms will contain only a single impurity, so that inter-impurity interactions need not be considered. We thus begin by studying the local dynamics of a single impurity in an isolated Kondo box, for which we adopt the (infinite $U$) Anderson model with a discrete conduction spectrum, in the slave-boson representation:

$$H = H_0 + \varepsilon_d \sum_\sigma f_\sigma^\dagger f_\sigma + v \sum_{j,\sigma} \langle c_{j\sigma}^\dagger b^\dagger c_{j\sigma} + h.c. \rangle, \quad (1)$$

where $H_0 = \sum_{j,\sigma} \varepsilon_j c_{j\sigma}^\dagger c_{j\sigma}$. Here $\varepsilon_j$ denotes spin and the $c_{j\sigma}^\dagger$ create conduction electrons in the discrete, delocalized eigenstates $| j\sigma \rangle$ of the “free” system (i.e. without impurity). Their energies, measured relative to the chemical potential $\mu$, are taken uniformly spaced for simplicity: $\varepsilon_j = j\Delta + \bar{\varepsilon}_0 - \mu$. As in [3], we follow the so-called orthodox model and assume that the $\varepsilon_j$’s include all effects of Coulomb interactions involving delocalized electrons, up to an overall constant, the charging energy $E_C$. The localized level of the magnetic impurity has bare energy $\varepsilon_d$ far below $\varepsilon_F$, and is represented in terms of auxiliary fermion and boson operators as $d_\sigma^\dagger = f_\sigma^\dagger b$, supplemented by the constraint $\sum_\sigma f_\sigma^\dagger f_\sigma + b^\dagger b = 1$ [4], which implements the limit $U \to \infty$ for the Coulomb repulsion $U$ between two electrons on the $d$-level. Its hybridization matrix element $v$ with the conduction band is an overlap integral between a localized and a delocalized wave-function, and, due to the normalization of the latter, scales as $(\text{Vol})^{-1/2}$. Thus the effective width of the $d$-level, $\Gamma = \pi v^2/\Delta$, is volume-independent, as is the bulk Kondo temperature, $T_K = \sqrt{2\Gamma D/\pi} \exp(-\pi \varepsilon_d/2\Gamma)$, where $D$ is a high energy band cutoff. To distinguish, within the grand canonical formalism, grains for which the total number of electrons is even or odd, we choose $\mu$ either on $(\mu = \bar{\varepsilon}_0)$ or halfway between two $(\mu = \bar{\varepsilon}_0 + \Delta/2)$ single-particle levels, respectively [5].

NCA approach:— We calculated the spectral density $A_{d\sigma}(\omega)$ of the impurity Green’s function $G_{d\sigma}(t) = -i\theta(t)\langle d_{\sigma}(t)d_{\sigma}^\dagger(0)\rangle$ using the noncrossing approximation (NCA) [6]. For a continuous conduction band, the NCA is known to be reliably down to energies of $0.1T_K$ or less, producing spurious singularities only for $T$ below...
this scale. Since these are cut off by the level spacing $\Delta$ in the present case, we expect the NCA to be semi-quantitatively accurate over the entire parameter range studied here ($T$ and $\Delta$ between 0.1 and 5$T_K$). Denoting the retardation auxiliary fermion and boson propagators by $G_{f\sigma}(\omega) = (\omega - \epsilon_f - \Sigma_{f\sigma}(\omega))^{-1}$, $G_{b}(\omega) = (\omega - \Sigma_b(\omega))^{-1}$, respectively, the selfconsistent NCA equations read

$$\Sigma_{f\sigma}(\omega) = \Gamma \int \frac{d\epsilon}{\pi}[1 - f(\epsilon)]A^{(0)}_{f\sigma}(\epsilon)G_{f}(\omega - \epsilon),$$

$$\Sigma_b(\omega) = \Gamma \sum_j \int \frac{d\epsilon}{\pi}f(\epsilon)A^{(0)}_{c\sigma}(\epsilon)G_{f\sigma}(\omega + \epsilon),$$

where $f(\omega) = 1/[\exp(\omega/T) + 1]$. The finite grain size enters through the discreteness of the (dimensionless) single-particle spectral density of the box without impurity, $A^{(0)}_{c\sigma}(\omega) = \Delta \sum_j \delta(\omega - \epsilon_j)$. (We checked that all our results are essentially unchanged if the Dirac $\delta$’s are slightly broadened by a width $\gamma \lesssim 0.1T_K$.) In terms of the auxiliary particle spectral functions $A_{f,b} = \frac{1}{\pi}\text{Im} G_{f,b}$, $A_{d\sigma}(\omega)$ is given by (for details see [3])

$$A_{d\sigma}(\omega) = \int d\epsilon [e^{-\beta\epsilon} + e^{-\beta(\epsilon - \omega)}]A_{f\sigma}(\epsilon)A_b(\epsilon - \omega).$$

**Numerical results:** — The results obtained for $A_{d\sigma}(\omega)$ by numerically solving the NCA equations (2) to (4) for various $T$ and $\Delta$ are summarized in Figs. 1 and 2. (We have checked that the equation-of-motion method [8] yields qualitatively similar results for all quantities discussed below.) For $\Delta \ll T$, the shape of the Kondo resonance is indistinguishable from the bulk case ($\Delta \to 0$): when $\Delta$ is increased well beyond $T$, however, it splits up into a set of individual sub-peaks. With decreasing temperature (at fixed $\Delta$), each sub-peak becomes higher and narrower; its width was found to decrease without saturation down to the lowest temperatures for which our numerics were stable ($T \simeq 0.2\Delta$). This agrees with the expectation following from the Lehmann representation at $T = 0$, $A_{d\sigma}(\omega) = \sum_n \left|\langle n|d_\uparrow|0\rangle\right|^2\delta(\omega - \Delta_n) + \left|\langle n|d_\downarrow|0\rangle\right|^2\delta(\omega + \Delta_n)$, namely that the sub-peaks should reduce to $\delta$-functions with zero width, located at the exact excitation energies $\Delta_n = E_n - E_0$ of the full Hamiltonian (whose spectrum will be discrete too, with mean level spacing of the same order as $\Delta$, as follows from the exact finite-size solutions of the Kondo model [3]).

Despite developing sub-peaks, the Kondo resonance retains its main feature, namely significant spectral weight within a few $T_K$ around the Fermi energy, up to the largest ratios of $\Delta/\max(T, T_K)$ ($\simeq 5$) we considered. This implies that the Kondo correlations induced by the spin-flip transitions between the $d$-level and the lowest-lying unoccupied $j$-levels persist up to remarkably large values of $\Delta/\max(T, T_K)$ [6]. However, they do weaken systematically with increasing $\Delta$, as can be seen in the inset of Fig. 2, which shows the average peak height of the Kondo resonance (which quantifies the “strength” of the Kondo correlations) as function of $\Delta$ at fixed $T$: the peak height drops logarithmically with increasing $\Delta$ once $\Delta$ becomes larger than about $T$. Conversely, at fixed $\Delta$, it drops logarithmically with increasing $T$ once $T$ becomes larger than about 0.5$\Delta$ (main part of Fig. 2), thus reproducing the familiar bulk behavior. Qualitatively, these features are readily understood in perturbation theory, where the logarithmic divergence of the spin flip amplitude, $t(\omega) \propto \sum_{j \neq \omega} \frac{f(\epsilon_j)}{\omega - \epsilon_j}$, is cut off by either $T$ or $\Delta$, whichever is largest.

**Parity Effects:** — For $\Delta \gg T$, the even and odd spectral functions $A_{d\sigma}$ in Fig. 1 differ strikingly: the former has a single central main peak, whereas the latter has two main peaks of roughly equal weight. This can be understood as follows: For an even grain, spin-flip transitions lower the energy by roughly $T_K$ and the conduction electrons into a Kondo singlet, in which the topmost, singly-occupied $j$ level of the free Fermi sea carries the dominant weight, hence the single dominant peak in $A_{d\sigma}$. For an odd grain, in contrast, the
free Fermi sea’s topmost $j$ level is doubly occupied, blocking such energy-lowering spin-flip transitions. To allow the latter to occur, these topmost two electrons are redistributed with roughly equal weights between this and the next-higher-lying level, causing two main peaks in $A_{d\sigma}$ and reducing the net energy gain from $T_K$ by an amount of order $\Delta$. This energy penalty intrinsically weakens Kondo correlations in odd relative to even grains; indeed, the average $A_{d\sigma}$ peak heights in Fig. 2 are systematically lower in odd than in even grains, and more so the larger $\Delta$ and the smaller $T$.

**SET conductance:** The above physics should show up in SET spectroscopy experiments: When an ultrasmall grain is connected via tunnel junctions to left ($L$) and right ($R$) leads [1] and if the tunneling current through the grain is sufficiently small (so that it only probes but does not disturb the physics on the grain), the tunneling conductance $G(V)$ as function of the transport voltage $V$ has been demonstrated [1] to reflect the grain’s discrete, equilibrium conduction electron DOS. Such measurements are parity-sensitive [1] even though a non-zero current requires parity-fluctuations, since these can be minimized by exploiting the huge charging energies ($E_c > 50k$) of the ultrasmall grain. To calculate the SET current, we describe tunneling between grain and leads by $H_T = \sum_{k\sigma\alpha} (w_{k\sigma\alpha} c^\dagger_{k\sigma\alpha} c_{\sigma\alpha} + h.c.)$, where $c^\dagger_{k\sigma\alpha}$ creates a spin $\sigma$ electron in channel $k$ of lead $\alpha \in \{L,R\}$. Neglecting non-equilibrium effects in the grain, the tunneling current has the Landauer–Büttiker form [12]

$$I(V) = \frac{e}{h} \int d\omega F_V(\omega) \sum_{j\sigma} \left[ \frac{\gamma^L \gamma^R}{\gamma^L + \gamma^R} \right] A_{c,j\sigma}(\omega), \quad (5)$$

where $F_V(\omega) = f(\omega - eV/2) - f(\omega + eV/2)$, $A_{c,j\sigma}$ is the spectral density of $G_{\epsilon_{j\sigma}} = -\nu(t)(\{c_{\epsilon_{j\sigma}}(t), c^\dagger_{\epsilon_{j\sigma}}(0))\}$, and $\gamma_{\alpha}^\sigma = 2\pi \sum_k |w_{k\alpha\sigma}|^2$ [3]. Neglecting the $\alpha\sigma$ dependence of $\gamma$, the current thus is governed by the conduction electron DOS, $A_c(\omega) = \sum_{j\sigma} A_{c,j\sigma}(\omega)$. Exploiting a Dyson equation for $G_{c,j\sigma}$, it has the form

$$A_c(\omega) = -\frac{1}{\pi} \sum_{\alpha\sigma} \text{Im} \left[ G_{0,j\sigma}(\omega) + v^2[G_{c,j\sigma}(\omega)]^2 G_{\sigma\sigma}(\omega) \right],$$

where $G_{c,j\sigma}(\omega) = f(\omega - \epsilon_{j\sigma}) + 0^+$ is the free conduction electron Green’s function [14], and the corresponding Kondo contribution to the conductance $G(V) = dI(V)/dV = G_0(V) + \delta G(V)$ is

$$\delta G(V) = -\frac{e^2}{h} \frac{\Gamma}{\pi} \sum_{j\sigma} \int d\omega A_{d\sigma}(\omega) \times \left[ \frac{\tilde{F}_V(\omega) - \tilde{F}_V(\epsilon_j)}{(\omega - \epsilon_j)^2} - \frac{d \tilde{F}_V(\omega)/d\omega}{\omega - \epsilon_j} \right], \quad (6)$$

with $\tilde{F}_V(\omega) = -\nu(t)(f(\omega - eV/2) + f(\omega + eV/2))/2$. Even though Kondo physics appears only in the subleading contributions to $A_c(\omega)$ and $G(V)$, these are proportional to $\nu^2 = \Gamma \Delta/\pi$ and thus grow with decreasing grain size.

$\delta G(V)$ is shown in Fig. 3 and have rather irregular structures and line-shapes. The reason for this lies in the interference between $G_{d\sigma}$ and $[G^{(0)}_{c,j\sigma}]^2$ in $A_c$, and correspondingly between $A_{d\sigma}$ and the bracketed factor in (6) for $\delta G(V)$. This interference is reminiscent of a Fano resonance [13], which likewise arises from the interference between a resonance and the conduction electron DOS. Incidentally, Fano-like interference has been observed in STM spectroscopy of a single Kondo ion on a metal surface [13], for which the conduction electron DOS is flat. In contrast, for an ultrasmall grain it consists of discrete peaks, reflected in the last factor in Eq. (6). This leads to a much more complex interference pattern, which does not directly mirror the specific peak structure of $A_{d\sigma}(\omega)$ discussed above.

Nevertheless, $G(V)$ does bear observable traces of the Kondo effect, in that the interference pattern shows a distinct, anomalous $T$-dependence, due to that of the Kondo resonance. In particular, the weights $W_j$ under the individual peaks of $G(V)$ become $T$-dependent. (In contrast, the weight $W_0$ under an individual peak of the bare conductance $G_0(V)$ is $T$ independent, since the $T$ dependence of the peak shapes of $G_0$ are determined solely by $d f(\omega)/d\omega$.) This is illustrated in Fig. 3, which shows the $T$ dependence of the weights $W_1$ and $W_2$ of the first and second conductance peaks (counted relative to $V = 0$ and labelled 1,2 in Fig. 3). When $T$ decreases at fixed $\Delta = T_K$, both $W_1$ and $W_2$ decrease, while at fixed $\Delta = 3T_K$, $W_1$ decreases whereas $W_2$ increases. The fact that the weights can either increase or decrease with decreasing $T$ results from the constructive or destructive Fano-like interference effects discussed above. Moreover, at the larger value for $\Delta$, both $W_1$ and $W_2$ develop a
parity effect in the strength of their T dependence. Since the peak weights in Fig. 3 change by up to \(10\%\) as the grain is cooled below \(T_K\), it should be possible to experimentally \[1\] detect their Kondo-induced anomalous \(T\)-dependence.

Coherence length:— The condition \(\Delta > T_K\) implies a relation between sample volume and the much-discussed spin coherence length \(\xi_K = 2\pi\alpha V/T_K\), namely (in 3D) \(\text{Vol} \ll \xi_K^2/\alpha^2\). Note that this relation involves both the small length scale \(1/\alpha\) and the sample’s volume, and not the smallest of its linear dimensions, say \(L\). This implies that the length scale below which purely finite-size induced modifications of Kondo physics can be expected is not set by \(\xi_K\) alone \[7\], and indeed may be considerably smaller than \(\xi_K\). This is why such modifications were not found in the numerous recent experiments having \(L \lesssim \xi_K\) for one or two sample dimensions \[8\, 11\].

In conclusion, we have analysed the Kondo effect in an ultrasmall metallic grain containing a single magnetic ion. The presence of a new energy scale in the system, the mean level spacing \(\Delta\), leads to rich physical behavior when \(\Delta \sim T_K\), including a distinct even/odd effect. Our NCA calculations, which give a semi-quantitatively reliable estimate of the size of the effects to be expected in future experiments, predict that the SET conductance of the grain acquire a width \(\gamma \approx 0.05\). We assume this to be negligible relative to \(T_K\), and \(T\), since realistic values \[7\] yield \(\gamma \lesssim 0.05\).

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