Ferromagnetic Kondo Effect at Nanocontacts

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Magnetic impurities bridging nanocontacts and break junctions of nearly magnetic metals may lead to permanent moments, analogous to the giant moments well known in the bulk case. A numerical renormalization group (NRG) study shows that, contrary to mean field based expectations, a permanent moment never arises within an Anderson model, which invariably leads to strong Kondo screening. By including in the model an additional ferromagnetic exchange coupling between leads and impurity, the NRG may instead stabilize a permanent moment through a ferromagnetic Kondo effect. The resulting state is a rotationally invariant spin, which differs profoundly from mean field.

A sign inversion of the zero-bias anomaly and other spectroscopic signatures of the switch from regular to ferromagnetic Kondo are outlined.

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Zero-bias anomalies that emerge ubiquitously in tunneling spectroscopy across quantum dots [1] and single-molecules [2] are known to be a manifestation – in a context far away from traditional magnetic alloys – of the Kondo effect [3, 4] – the phenomenon that leads magnetic impurities to lose their magnetic moments when diluted in a nonmagnetic metal. Actually, Kondo screening is not an inevitable fate for magnetic impurities in metals. Well known counter-examples are the giant permanent moments that arise when 3d transition metal impurities are diluted in a nearly ferromagnetic metal such as Pd [5]. We consider here the novel possibility that permanent moments may encounter a revival in magnetic contacts and nanoelectronics. A magnetic impurity could act as the bridging atom in a Pd or Pt break junction [6], or close-by STM atomic contact [7]. Alternatively, the short monatomic chains that forms spontaneously in pure Pt or Ir break junctions could spontaneously and locally magnetize, as suggested by calculations [8, 9], giving rise to rather similar physics to that of a magnetic alloy, even though here the host metal (the leads) and the impurity (the nanocontact) are the same material. In either case, the permanent moment will avert Kondo screening by the leads, and the standard zero bias anomaly picture does not apply. On the other hand, one cannot expect like in a ferromagnet two different conductances for spin up and for spin down, because in zero field there is no up and no down, and conductance must be independent of the lead electron spin. Sophisticated many-body techniques have been specifically designed during the years to study the regular Kondo effect [10].

On the contrary, the reverse phenomenon of permanent moment formation has generally been dismissed after a simple treatments such as Hartree Fock (HF) or density functional theory (DFT), whose mean field nature is bound, as we will show, to miss important many-body effects. Actually, for the giant moments generated by magnetic impurities in alloys, the crude static mean field description is in the end justified by finite concentration, giving rise to RKKY-mediated long range ferromagnetic order at low temperature [6]. No such justification is possible for nanocontacts, where quantum fluctuations and many-body effects must play an essential role, since local magnetism cannot induce bulk magnetism in the leads.

In this Letter we examine a magnetic impurity in a nearly ferromagnetic nanocontact (and re-examine that in a bulk host metal too) through an effective Anderson impurity model with parameter values that would suggest ferro coupling and permanent moment formation in mean field. We find that inclusion of many-body effects, accomplished by means of the numerical renormalization group (NRG) [11], alters drastically the mean-field result, and invariably leads to regular Kondo screening, so that no permanent local moment can survive. As NRG shows, only through addition to the bare Anderson model of a direct intersite ferromagnetic exchange coupling between the magnetic impurity and the leads a permanent impurity spin can be stabilized. In this case the regular (antiferromagnetic) Kondo effect and the associated screening with formation of a spin singlet is turned over to a ferromagnetic Kondo effect, with antiscreening and formation of a fully rotationally invariant, integer or half integer spin S. This role of direct impurity-lead ferromagnetic exchange, consistent with the impurity spin dynamics measured by perturbed γ-ray distribution in bulk alloys [12, 13], could be crucial at nanocontacts in nearly ferromagnetic metals, where spectroscopic signatures of the ferromagnetic Kondo effect may be observable in I-V conductance anomalies.

Realistic density-functional theory local spin-density
(LSDA) calculations\textsuperscript{14} have long shown that, while earlier transition metal elements impurities like Cr tend to counter-polarize a bulk host metal like Pd, later elements, like Fe and Co, do the reverse, and co-polarize Pd, in accord with the absence/presence of permanent moments experimentally observed in these alloys\textsuperscript{2}. The physical properties that seem to play the essential role in the calculations are: (i) a strong host-impurity $d-d$ hybridization overwhelming $s-d$; (ii) a Pd chemical potential poised at a single-particle density-of-states (DOS) peak close to the upper $d$-band edge; (iii) a $3d$-impurity energy level shifting downwards closer to the host chemical potential by increasing the atomic number from Cr towards Ni. The early finding that a simple Anderson impurity model embodying these three ingredients reproduces correctly at the mean-field level the same behavior obtained in more detailed LSDA calculations\textsuperscript{14,13,10} suggested that no other ingredient was needed to account for permanent (giant) moments of late impurities in Pd – and this might hold in a nanocontact as well. In order to check whether this conclusion is stable against quantum fluctuations we therefore start with the standard Anderson impurity model

\[ \mathcal{H} = \sum_{k\sigma} \epsilon_k c_{k\sigma}^\dagger c_{k\sigma} + \frac{1}{\sqrt{\Omega}} \left( V_k c_{k\sigma}^\dagger d_{\sigma} + \text{H.c.} \right) + \epsilon_d n_d + \frac{U}{2} (n_d - 1)^2, \]  

where $\Omega$ is the volume, $d_{\sigma}^\dagger$ is the creation operator of an impurity electron with spin $\sigma$ and $c_{k\sigma}^\dagger$ of a conduction electron with the same spin and energy $\epsilon_k$. Here $n_d = \sum_{\sigma} d_{\sigma}^\dagger d_{\sigma}$ is the occupation number and $\epsilon_d$ the energy of the impurity level.\textsuperscript{11} describes a single $d$ orbital hybridized with a single conduction band, a deliberately oversimplified situation that nevertheless usually captures the essential physics. We consider two extreme cases: (A) a flat conduction electron DOS $\rho_A(\epsilon) = 1/2 \theta (1 - \epsilon^2)$ (all energies are in units of half the conduction bandwidth); (B) a substitutional impurity in a one-dimensional chain. In the latter case, it is important to note that, while the bulk DOS is $\rho_B(\epsilon) = 1/(\pi \sqrt{1 - \epsilon^2}) \theta (1 - \epsilon^2)$, the DOS of the hybridizing channel is instead $2\sqrt{1 - \epsilon^2}/\pi$. The chemical potential is taken to be $\mu = 0.95$, close to the top of the band, which, in case (B), corresponds to a large DOS mimicking the situation of bulk Pd\textsuperscript{14}.

Fig.\textsuperscript{1} shows the HF mean field phase diagram as a function of $U$ and $\delta \epsilon_d$, the actual impurity level relative to the chemical potential, at constant $V_k = 0.4$, compatible with a situation of large $d-d$ hybridization. We indeed find, confirming earlier results\textsuperscript{14,15,16}, that besides wide antiferromagnetically impurity-host coupled regions there are $(++)$ regions close to $\delta \epsilon_d = 0$ where the impurity is magnetic and ferromagnetically co-polarized with the conduction bath, again in agreement with LSDA results\textsuperscript{14}. We note in particular that a high DOS at the chemical potential, case (B), does favor the tendency towards magnetism, in accord with the Stoner criterion for impurity magnetism\textsuperscript{17} (note also the larger region of co-polarization). The other element which plays a crucial role towards permanent moment formation is the position of the chemical potential close to the top of the band. When $\mu$ is shifted towards the center of the band, the region of co-polarization shrinks and eventually disappears.

To study the effect on the permanent moment of quantum fluctuations, we choose a value of $U = 1.5$ and $\delta \epsilon_d = 0.1$ well inside the Hartree-Fock ferromagnetically co-polarized $(++)$ region, and we study the model by NRG. Surprisingly, we find that NRG reverses the HF result, the co-polarization disappears and at the fixed point the impurity is fully Kondo screened in both cases (A) and (B). Fig.\textsuperscript{2} shows the flow of the many-body low-energy spectrum for case (B) only (the other case is similar) versus NRG iteration $N$. $N$ corresponds to a finite temperature of order $\Lambda^{-N/2}$ in units of half the conduction bandwidth, where $\Lambda$ is the logarithmic discretization parameter\textsuperscript{11} that we take equal to three. The asymptotic spectrum is indeed that of a Kondo screened impurity below a crossover temperature that can be identified with the Kondo temperature $T_K$. This behavior persists on increasing $U$, even though $T_K$ rapidly diminishes. For $U \gtrsim 3$, $T_K$ is found to recover the conventional expression $T_K \sim \exp (-\pi^2 U \rho_0/8)$\textsuperscript{10}, where $\rho_0$ is the impurity density of states per spin at the chemical potential and in the absence of interaction. For realistic parameters, extracted e.g. by LSDA calculations\textsuperscript{14,18}, the pre-

\[ \delta \epsilon_d = \mu - \epsilon_d = \mu - \sum_{k\sigma} \epsilon_k c_{k\sigma}^\dagger c_{k\sigma} + \frac{1}{\sqrt{\Omega}} \left( V_k c_{k\sigma}^\dagger d_{\sigma} + \text{H.c.} \right) + \epsilon_d n_d + \frac{U}{2} (n_d - 1)^2, \]  

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vicous expression would imply a substantial $T_K$ of a few hundred K. Besides contradicting HF, this large result also excludes the other possible explanation for the giant moments in bulk Pd, namely that, because of specific features of Pd, the actual coupling is Kondo-like, but with $T_K$ so small that, at practical dilutions, the RKKY interaction among the impurities always prevails and leads to the ferromagnetism observed in the magnetic alloys.

It must be concluded that the Anderson model is actually insufficient to explain the existence of permanent moments in Pd. Now it is known, in the wide zoo of Kondo models, that the only case where a magnetic impurity retains its moment is that of a ferromagnetic Kondo model \(11\). A way to stabilize a permanent moment and to overwhelm the effective antiferromagnetic electron-impurity coupling just found by NRG is to add an explicit ferromagnetic coupling between the impurity and the conduction electrons. Experimental evidence of the important role of such a direct ferromagnetic exchange has repeatedly been claimed \(12, 13\). Physically, the electron-impurity ferromagnetic exchange must be substantial since the host metal is nearly ferromagnetic and the impurity wavefunction, much like that of a host-metal atom, extends well over neighboring sites. Therefore, we modify the model \(11\) by including a ferromagnetic exchange, of strength $J$, between the impurity and the first hybridization shell, namely

\[
\mathcal{H} \rightarrow \mathcal{H} - J \mathbf{S}_c \cdot \mathbf{S}_d, \quad (2)
\]

where $\mathbf{S}_d$ is the impurity spin-operator and

\[
\mathbf{S}_c = \frac{1}{2} \sum_k |V_k|^2 \sum_{\alpha\beta} V_{k'k} c_{\alpha k}^\dagger \sigma_{\alpha\beta} c_{\beta k'},
\]

with $\sigma$ the Pauli matrices. Upon repeating the NRG calculation for \(2\) we find that increasing $J$ causes a Berezinskii-Kosterlitz-Thouless phase transition at $J = J_*$ from a Kondo screened phase to an antiscreened ferromagnetic Kondo phase. In the ferromagnetic Kondo state the conduction electrons can be seen as scattering off the magnetic impurity and dressing it up with a spin-cloud whose net result is to restore a fully rotationally-invariant state of well defined total spin $S$ and zero-point entropy $K_B \ln(2S + 1)$. The two phases, Kondo screened and antiscreened, also possess different and opposite spectroscopic features, as shown by the impurity DOS, $\rho(\epsilon)$ of Fig. 3. On the screened side, $J < J_*$, a Kondo resonance at the chemical potential is clearly visible within the Mott-Hubbard gap. On the opposite, antiscreened side, $J > J_*$, the impurity DOS develops a cusp-like pseudogap at the chemical potential, $\rho(\epsilon) \sim 1/\ln^2 \epsilon$ \(19\). Unlike the HF approximation, the transition to a permanent moment regime is not accompanied by the full disappearance of spectral weight within the Mott-Hubbard gap; the pseudogap opens continuously inside a broader low-energy feature and is controlled by the scale $J - J_K$, where $J_K$ is the effective antiferromagnetic coupling mediated by the hybridization, rather than by $U$. From this point of view, the antiferro-ferro Kondo transition just described resembles the orbital selective Mott transition recently proposed \(20\) to explain the paramagnetic-to-antiferromagnetic transition in heavy fermions.

![Figure 2](image-url) 

**FIG. 2:** (Color online) NRG flow of the low-energy spectrum for Eq. \(1\), case (B), with $U = 1.5$, $\delta_{c,d} = 0.1$ and odd iterations $N$, i.e. a Wilson chain with even number of sites. Each energy level is identified by the charge $Q$ with respect to half-filling and the spin $S$. Note the three lowest energy states at large $N$ that correspond to the degenerate ground state of a chain with odd number of sites, the impurity site being absorbed by the Kondo effect, split by the deviation from particle-hole symmetry.

![Figure 3](image-url) 

**FIG. 3:** (Color online) Impurity DOS for $U = 4$ and different values of the ferromagnetic exchange $J$ across the transition, $J = 0, 0.025, 0.07, 0.1, 0.2, 0.3$ from top to bottom. The large $U$ is used to well separate the low-energy part, shown in the main panel, from the high-energy Hubbard bands, shown in the inset for $J = 0.025$ and 0.3.
This scenario should describe the spontaneous moment of a magnetic impurity embedded in nearly ferromagnetic metal, and equally well the magnetism of a bridging impurity in a nanointact between nearly ferromagnetic leads. We note that, while the screened phases is Fermi-liquid like in the strict Nozières’ sense [21], the antiscreeened phase is more properly a singular Fermi-liquid [22]. At zero temperature and assuming inversion symmetry across the contact, giving rise to well defined even and odd channels, the zero-bias conductance must recover the Fermi-liquid expression $G = 2e^2/h \sum_a \sin^2 \delta_a$, were $\delta_a$ is the spin-independent difference between the scattering phase shifts of the even- and odd-parity scattering channel $a$ at the chemical potential.

Since the Kondo screened-antiscreeened transition is accompanied by a jump $\pi/2$ of $\delta_a$ in the channels hybridizing with the magnetic orbitals, we should expect a sudden jump of the zero-bias conductance at the transition, upward or downward depending on the specific symmetry of the impurity and lead orbitals that are involved. We also note that, while in the screened regime a magnetic field will, as usual, split the Kondo resonance, in the antiscreeened phase the magnetic field will instead fill the pseudogap. Thus, the contact magnetococonductance should behave in an opposite way on the two sides of the transition. In addition, in the antiscreeened phase a non-analytic dependence on the magnetic field and on temperature should appear [19, 22].

Experimental observations of a ferromagnetic Kondo effect at nanocontacts – even if probably already present – are not obvious to pinpoint in existing data. Transition metal impurities such as Fe or Co, bare or embedded in molecules such as porphyrins or phtalocyanines, contacted by a nearly ferromagnetic metal such as Pd, could represent a starting point. Bare Pd break junctions could develop a local moment at the contact [8], which might lead to a ferro Kondo zero-bias anomaly. Interestingly, Kondo-like anomalies are apparently being found in pure Fe, Co and Ni break junctions [23]. Their relatively small width supports their Kondo origin. However, in view of the many orbital channels that are involved, these anomalies could equally well indicate regular antiferro Kondo or, as previously discussed, a ferro Kondo. Pt or Ir break junctions would also be very interesting systems to look for zero-bias anomalies, owing to the local moment which is expected to form in the chain-like nanointact [24]. Even though the susceptibility of Pt and Ir is not as Stoner-enhanced as that of Pd, it is plausible that there should be enough intersite ferromagnetic exchange in these metals to lead to a ferromagnetic coupling of the leads to the bridging chain. It should be noted however that strong spin-orbit coupling should also give rise here to a colossal [25] or giant magnetic anisotropy [26, 27], an interesting complication not yet described by the present treatment.

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