Parity-dependent Kondo effect in ultrasmall metallic grains

GIANCARLO FRANZESI$^{1,2}$, ROBERTO RAIMONDI$^3$ and ROSARIO FAZIO$^4$

$^1$ SMC-INFM & Dipartimento di Fisica, Università “La Sapienza” - P.le A. Moro 2, I-00185 Rome, Italy
$^2$ INFM & Dipartimento di Ingegneria dell’Informazione, Seconda Università di Napoli, I-81031, Aversa, Italy
$^3$ NEST-INFM & Dipartimento di Fisica ”E. Amaldi”, Università di Roma Tre – Via della Vasca Navale 84, I-00146 Roma, Italy
$^4$ NEST-INFM & Scuola Normale Superiore, I-56126 Pisa, Italy

PACS. 75.75.+a – Magnetic properties of nanostructures.
PACS. 73.63.-b – Electronic transport in mesoscopic or nanoscale materials and structures.

Abstract. – In this Letter we study the Kondo effect in an ultrasmall metallic grain, i.e. small enough to have a discrete energy-level spectrum, by calculating the susceptibility $\chi$ of the magnetic impurity. Our quantum Monte Carlo simulations, and analytic solution of a simple model, show that the behavior changes dramatically depending on whether the number of electrons in the grain is even or odd. We suggest that the measurements of $\chi$ provide an effective experimental way of probing the grain’s number parity.

Small metallic particles, typically of dimensions of few nanometers, show properties which are intermediate between atomic and bulk condensed matter systems. Because of the finite dimensions, the quasi-continuous spectrum in the bulk splits into discrete energy levels. When the average level spacing $\delta$ is comparable with the other energy scales of the problem interesting new effects appear. For example the physical observables are parity dependent, i.e. differ if the number of electrons in the grain is even or odd. While metallic particles have been investigated in ensembles of grains in the past (see [1] and references therein), only recently spectroscopy of single grains [2] has been achieved experimentally. In the case of superconducting, ferromagnetic and/or antiferromagnetic systems, the effect of a finite level spacing is to enhance quantum fluctuations and consequently suppress the many-body condensation. As a result a superconductor will not possess a fully developed gap [3], the magnetization of a ferromagnet will not be macroscopically large [4], although distinct features reminiscent of the macroscopic order can be detected even in nanosize systems. Recently Thimm et al. [5], in their work on the so-called Kondo box, studied the effect of magnetic impurities in a small metal particle. They found that the Kondo resonance is strongly affected when the mean level spacing in the grain becomes larger than the Kondo temperature [5, 6, 7]. The Kondo box shows the parity effect as well. The Kondo effect [8] is a paradigm in correlated electron systems. It originates from the interaction between the localized spin of a single magnetic impurity and the free electrons of the metal. In bulk systems Kondo correlations manifest in an increase of the resistance for decreasing temperature

© EDP Sciences
$T$, above a characteristic scale $T_K$, the Kondo temperature. If, instead, one looks at the magnetic properties of metals hosting Kondo impurities, one effect is the rapid saturation, for decreasing $T < T_K$, of the impurity magnetic susceptibility $\chi$ (measuring the effect of an external magnetic field on the impurity magnetization $M$) [9]. Mesoscopic physics is another arena in which the Kondo effect is playing a major role. By now, several years since the theoretical prediction [10,11] a series of beautiful experiments have seen it in different devices (see the reviews [12,13]). In these cases the resonant level is realized by suitable fabricated nanostructure and the conduction electrons are provided by the metallic electrodes.

In this Letter we are interested in the Kondo box, and we want to address the parity effect by means of the analysis of the impurity susceptibility $\chi(T)$, since $\chi(T)$ is very sensitive to the number of electrons in the system as demonstrated in superconducting dots [14,15]. Detection of parity effects in various thermodynamical quantities, including the spin susceptibility, were measured for an ensemble of small, normal metallic grains [16]. In similar fashion parity effects can be measured in an ensemble of small grains containing Kondo impurities. As it will be discussed in more details, also in this case, due to parity effects, grains with odd number of electron will give the dominant contribution to $\chi(T)$.

The system is described by the Anderson model Hamiltonian

$$H = \sum_{n,\sigma} (\epsilon_n - \mu) c_{n,\sigma}^\dagger c_{n,\sigma} + \sum_{\sigma} (\epsilon_d - \mu) d_{\sigma}^\dagger d_{\sigma} + U n_{d,\uparrow} n_{d,\downarrow} + V \sum_{n,\sigma} (c_{n,\sigma}^\dagger d_{\sigma} + c_{n,\sigma} d_{\sigma}^\dagger),$$  \hspace{1cm} (1)

where $c_{n,\sigma}^\dagger$ ($c_{n,\sigma}$) is the rising (lowering) operator in the grain electron state with spin $\sigma = \pm 1/2$ (or $\uparrow, \downarrow$) and energy $\epsilon_n = \epsilon_0 + n\delta$, labeled by the quantum number $n$ starting from the lowest level $\epsilon_0 < 0$ and $d_{\sigma}^\dagger$ ($d_{\sigma}$) is the rising (lowering) operator in the impurity electron state with spin $\sigma$ and energy $\epsilon_d$ with the associated number operator for spin up (down) in the impurity state $n_{d,\uparrow} \equiv d_{\uparrow}^\dagger d_{\uparrow}$ ($n_{d,\downarrow} \equiv d_{\downarrow}^\dagger d_{\downarrow}$). The Fermi level is taken as the zero of the energy. The number of electrons $N$ in the grain is selected by fixing $\epsilon_0$, $\delta$, and the chemical potential to $\mu = 0$ for an odd number and $\mu = \delta/2$ for an even number, with $(\epsilon_0 - \mu) + (N - 1)\delta/2 = 0$. Only the levels up to $-\epsilon_0 > 0$ are relevant to the problem and the density of grain electrons in the bandwidth $2|\epsilon_0|$ is assumed constant. The energy $U > 0$ accounts for the on-site repulsion $\delta$, and remains finite for increasing $\delta$, because, as discussed in Ref. [5], both $\delta$ and $V^2$ scale as the inverse of the grain volume. This is consistent with the increase of the probability ($\sim V^2$) of finding an electron on the impurity site for decreasing grain volume.

In order to put in context our analysis, let us recall some basic concepts concerning the physics associated with the Anderson model. The impurity site may be in one of the four different states: empty, singly occupied with up (down) spin, and doubly occupied. The magnetic properties of the impurity depend on the occupation probability of each state. As discussed in Ref. [17], depending on $T$, one has different regimes. To illustrate how these different regimes develop, it is useful to consider first the case with no hybridization ($V = 0$) and $\epsilon_d < 0$ (Fig. 1). For $k_B T \gg U + \epsilon_d$ (where $k_B$ is the Boltzmann constant), the four impurity states have the same probability to occur. Therefore the probability to have two electrons in the impurity level is $P_2 = 1/4$, the average number of electrons in the impurity level is $N_d = 1$ and the average of the squared value of the total spin in the impurity level is $M^2 = 1/8$. The impurity susceptibility as a function of $T$ is, in this case, $\chi_0(T) = T_K/(2T)$ (hereafter we use the dimensionless susceptibility $\chi_0 \equiv 4\chi k_B T K/(g\mu_B)^2$, where $g$ is the Landé factor and $\mu_B$ is the Bohr magneton), as in the case of a free orbital. For $U + \epsilon_d > k_B T > -\epsilon_d$ the double
occupancy is excluded, resulting in \( P_2 \simeq 0 \), \( N_d \simeq 2/3 \), \( M^2 \simeq 1/6 \) and \( \chi_0(T) \simeq 2T_K/(3T) \). For \( k_B T < -\epsilon_d \) only the single occupied states have a finite probability to occur, with \( P_2 \simeq 0 \), \( N_d \simeq 1 \), \( M^2 \simeq 1/4 \) and \( \chi_0(T) \simeq T_K/T \). The impurity properties in this case are like those of a local (magnetic) moment, i.e. of an isolated electron able to flip its spin \( \sigma \).

If \( V > 0 \), the electrons can tunnel between the impurity level and the grain levels. The virtual transitions to doubly occupied and empty impurity states lead to an effective antiferromagnetic interaction \( J_{\text{eff}} \) between the grain electron spin density and the impurity spin.

For a large grain’s size (\( \delta \to 0 \)), in first approximation (to the lowest-order of the perturbation theory \[8\]), is \( J_{\text{eff}} \sim \Gamma/U \). The higher orders can be taken into account by the renormalization group (RG) approach via an energy-dependent interaction \( J_{\text{eff}}(E) \) \[8,17\]. The RG procedure shows that, at low \( T \), \( J_{\text{eff}}(E) \) increases (strong coupling regime) \[18\]. Below \( T_K \), the impurity spin becomes effectively bound into a singlet (total spin zero) with the grain electrons’ spin. As a consequence in the strong-coupling regime, the impurity susceptibility saturates, for \( T \to 0 \), to \( \chi_0(\delta = 0, T = 0) \simeq 0.4128 \).

In ultrasmall grains, a finite \( \delta \) introduces a further low-energy scale beside \( T_K \). In order to describe the effect of finite level spacing on the Kondo resonance we use a quantum Monte Carlo approach proposed by Hirsh and Fye \[19,20\]. According to this method, after integrating out the grain level degrees of freedom, the resulting impurity problem is mapped into a chain of two-states auxiliary variables (fictitious Ising spins), independent on each other, but interacting with an effective magnetic field, proportional to the impurity magnetization \( M \). The length \( L \) of the chain is proportional to the time-evolution of the system. The method is exact in the limit of an infinite chain of Ising spins and gives results reliable within an approximation \( \sim (TL)^{-2} \). To study the properties of the impurity spin we calculate \( \chi, P_2, N_d \) and \( M^2 \) as a function of \( T \), and \( L \) (verifying, as a check, the exact relation \( 4M^2 = N_d - 2P_2 \) valid at any \( T \)). We consider the symmetric case (i.e. with \( \epsilon_d = -U/2 \). We estimate \( T_K \) for...
\( \delta \to 0 \), by fitting our calculations with the low-\( T \) approximation \[ 8 \]

\[
\frac{4\chi k_B}{(g\mu_B)^2} = \frac{0.68}{T + 1.1427K}
\]

where \( T_K \) is the only free parameter. In this limit our results (Fig. 2) recover, at \( k_BT \approx -\epsilon_d = U/2 \), \( \chi_0 T/T_K \approx 1 \) (local moment regime) and, for \( T \leq T_K \), \( \chi_0 = 0.4128 \) (strong coupling regime). For \( \delta \geq 2k_BT_K \), \( \chi_0 \) (Fig. 2), \( P_2 \) (Fig. 3) and \( M^2 \) (Fig. 4) reveal a clear parity effect. The main features are the following.

For an odd number \( N \) of electrons in the system (dotted lines in Fig. 2-4), i) the local moment regime extends down to the lowest \( T \), with \( \chi_0 \sim 1/T \) (Curie law); ii) \( \chi_0 T/T_K \) saturates to a value that increases with \( \delta \), approaching the value 1 expected for \( \Gamma = 0 \), and iii) for \( T < T^* \) and increasing \( \delta \), \( P_2 \) decreases toward 0 as expected in the local moment regime.

For an even \( N \) (solid lines in Fig. 2-4), iv) the Kondo effect appears to be enhanced and \( \chi \) saturates to a value that decreases with increasing \( \delta \). This can be seen as an increase of the effective Kondo temperature \( T_K(\delta) \) on the base of the Eq. (2). v) For \( T < T^* \) and increasing \( \delta \), \( P_2 \) increases toward 1/4 as in the free orbital regime.

Finally, vi) for \( k_BT < V \), with the hybridization energy \( V \sim \delta^{1/2} \), the non-monotonic behavior of \( P_2 \) is depressed when \( N \) is odd and emphasized when \( N \) is even; vii) for any \( N \), the onset of the parity effect increases with \( \delta \) and, empirically, the onset is at \( k_BT^* \approx \delta/3 \) for all the cases considered. The proportionality of the onset \( T^* \) to \( \delta \), is expected, because, for \( k_BT > \delta \), the approximation of the grain levels with a band is valid.

To understand the odd case, consider the limit \( \delta \to \infty \), equivalent to a system with an impurity level at energy \( \epsilon_d < 0 \) and a doubly occupied grain level at (zero) Fermi energy. The only possible process in this case is a transition of a grain electron to the impurity level, but for \( k_BT < U \) this transition is suppressed, because the double occupancy in the impurity level costs an energy \( U \). Therefore, the impurity electron behaves as an isolated magnetic moment, with \( P_2 \approx 0 \) and following the Curie law \( \chi_0 \sim 1/T \) (Fig. 2), as in i). If \( \delta \) is finite, also the transition of the impurity electron above the Fermi level takes place, but requires an energy \( |\epsilon_d| + \delta \) and occurs with probability \( \sim \exp[-\delta/(k_BT)] \). Therefore, for large \( \delta \) and low \( T \), this transition is suppressed and \( \chi_0 T/T_K \to 1 \) (inset Fig. 2), as in the local moment regime, and \( P_2 \to 0 \) (Fig. 3), as in iii). For decreasing \( \delta \), the system enters the local moment regime only at \( T < T^* \sim \delta \), with \( \chi_0 T/T_K \) saturating at the value reached at \( T^* \). Therefore, the lower \( \delta \), the lower the asymptotic value (inset Fig. 2), as in ii).

In the even case, when there is only one electron in the Fermi level, transitions between the Fermi level and the impurity level are allowed and this results in a strong hybridization between the two levels. We perform in this case an exact calculation of \( \chi_0(T) \) for \( \delta \to \infty \) (Fig. 3). In this limit, only the grain level at the Fermi energy couples with the impurity, resulting in an interacting two-level system. For very large, but finite \( \delta \), this two-level system is still a good approximation since the grain levels away from the Fermi level can be taken into account in perturbation theory up to second order. Their main effect is to renormalize the impurity parameters. In particular, the energy of the impurity level is renormalized to a higher energy, closer to the Fermi level. This is just what is left of the logarithmic renormalization, familiar in the bulk system. The two-level system has six possible different many-body two-electron states: (1) with one electron with spin \( \uparrow \) in the Fermi level and one with spin \( \downarrow \) in the impurity \(|1\rangle = c_1^\dagger d_1^\dagger |0\rangle \); (2) with inverted spins with respect to the first state \(|2\rangle = c_1^\dagger d_1^\dagger |0\rangle \); (3) with two electrons with opposite spins in the Fermi level \(|3\rangle = c_1^\dagger c_1^\dagger |0\rangle \); (4) with two electrons with opposite spins in the impurity level \(|4\rangle = d_1^\dagger d_1^\dagger |0\rangle \); (5) with one electron with spin \( \uparrow \) in the Fermi level and one with spin \( \uparrow \) in the impurity \(|5\rangle = c_1^\dagger d_1^\dagger |0\rangle \), and (6) with inverted spins with
Fig. 2 – The parity effect on the magnetic susceptibility. The (dimensionless) susceptibility $\chi_0$, as a function of the (dimensionless) temperature $T/T_K$, for a magnetic impurity embedded in a non-magnetic metallic grain, shows a clear parity effect when the level spacing $\delta$ is large: dotted lines correspond to odd number $N$ of electrons in the system, solid lines to even $N$. We show the quantum Monte Carlo calculations for $L = 300$ for the symmetric Anderson model with $\Gamma/(\pi k_B T_K) \simeq 1.62 \ll U/(k_B T_K) \simeq 20.45$ and $|\epsilon_0| = 2556.25 k_B T_K$, for $\delta/(k_B T_K) \simeq 0.01$ (bold line), recovering the $\delta \to 0$ limit, and, starting from the bold line and going outward, for $\delta/(k_B T_K) \simeq 2.04$ (rhombus) $3.37$ (full circles), $5.11$ (up triangles), $10.22$ (open circles), $25.56$ (crosses), and $255.57$ (down triangles). The corresponding values of $N$ range from $2508$ (solid line with rhombus) to $21$ (dotted line with down triangles). Where not shown, errors are smaller than symbols. Inset: the same results times $T/T_K$ are shown to emphasize the local moment regime for $k_B T \simeq U/2$.

Fig. 3 – The parity effect on the probability $P_2$ of finding two electrons localized on the impurity. Symbols and lines are like those in Fig. 2. The calculations for $\delta \simeq 0.01 k_B T_K$ (bold line) show a non-monotonic behavior with a maximum for $T < T_K$. Dotted lines are for odd $N$; solid lines for even $N$. The calculations are for $L = 200$. Comparison with calculations for $L = 300$ do not show any relevant finite-size effect for $\delta > 1.5 k_B T_K$.

Fig. 4 – The parity effect on the squared impurity magnetization $M^2$. Symbols and lines are like those in Fig. 3. Since $N_d = 4M^2 + 2P_2$, all our calculations have $N_d \simeq 1$. 
respect to the fifth state $|6\rangle = c_\uparrow^d c_\downarrow^d |0\rangle$. These six states form three singlet ($M = 0$) and one triplet ($M = 0, \pm 1$) states. The singlet states are given by $(|1\rangle - |2\rangle)/\sqrt{2}$, $|3\rangle$, and $|4\rangle$. The triplet components are instead given by $(|1\rangle + |2\rangle)/\sqrt{2}$, $|5\rangle$, and $|6\rangle$. To probe the impurity susceptibility we couple exclusively the impurity spin with an external magnetic field $h$. The model, in this case, can be described by a diagonal block matrix, with a $4 \times 4$ block $H_a$, for the states from (1) to (4), and a $2 \times 2$ block $H_b$, for the states (5) and (6), with

$$H_a = \begin{pmatrix}
\epsilon_d + h & 0 & V & V \\
0 & \epsilon_d - h & -V & -V \\
V & -V & 0 & 0 \\
V & -V & 0 & 2\epsilon_d + U
\end{pmatrix} \quad \text{and} \quad H_b = \begin{pmatrix}
\epsilon_d - h & 0 \\
0 & \epsilon_d + h
\end{pmatrix}, \tag{3}
$$

where the diagonal elements are the energies in each of the six states, and the square of an off-diagonal element is the transition probability between the corresponding states. By computing the energies $E_i$ corresponding to the eigenstate of these two matrices, we calculate the impurity magnetization $m(T, h) = \sum_i M_i \exp[E_i/(k_B T)]$, where $M_i$ is the impurity magnetization of the eigenstate $i$, and $\chi(T) \equiv (\partial m/\partial h)_{h=0}$.

We find that $\chi \sim 1/T$ for $k_B T > V$ (Fig. 5a). Indeed, for $k_B T > V$ the states $|1\rangle$, $|2\rangle$, $|5\rangle$ and $|6\rangle$ have the same energy (for $h = 0$), while states $|3\rangle$ and $|4\rangle$ have higher energy, therefore the impurity level is singly occupied (local moment regime). For $k_B T < V$, we find $\chi$ saturating to a constant value, decreasing with increasing $V$ (Fig. 5b). Indeed, as a consequence of the hybridization $V$, the ground state is given by the lowest-energy singlet, that has an energy difference with the triplet states larger than $V$. Therefore, $\chi$ is constant and the asymptotic value is approximately given by the Curie law at $k_B T \approx V$. Therefore, the larger $V$ (or $\delta$), the smaller the saturation value of $\chi$ for $T \to 0$, as in iv). All these results are indeed consistent with our quantum Monte Carlo simulations (Fig. 4), by keeping in mind that $V$ scales as $\delta^{1/2}$ for fixed transition rate $\Gamma$. 

Fig. 5 – The exact susceptibility $\chi_0$ for even $N$ and $\delta \to \infty$, as a function of $T/T_K$. The calculations for the symmetric Anderson model with $U = 20.44 k_B T_K$ and $V/(k_B T_K) = 1.0$ (solid line), 2.3 (dashed line) and 3.6 (long-dashed line), are shown in linear scale, in a) to emphasize the maxima of $\chi_0$, and in double logarithmic scale, in b), to emphasize the high-$T$ behavior $\chi_0 \sim 1/T$ (the linear part in b).
Moreover, the actual diagonalization shows that the transition from the local moment to the saturation regime occurs via a non-monotonic behavior (with a maximum depending on the hybridization $V$). This result is not clearly detectable in our quantum Monte Carlo calculations for $\chi$ (Fig. 2), but is consistent with the non-monotonic behavior of $P_2$ (Fig. 3), more evident in the even case, that shows that the local moment regime extends to lower $T$, as in vi). In particular, to understand in the even case the behavior of $P_2$ for finite decreasing $\delta$, we should consider more grain levels in our exact solution. For example, by including one grain level below the Fermi energy and one above, the many-body states are four-electron states, due to three grain levels and one impurity level. As noted before, the hybridization favors a singlet ground state. In this case the weight of the singlet state with doubly-occupied impurity level is decreased, because the singlet state manifold has a larger number of components. As a consequence, the probability $P_2$ decreases with decreasing $\delta$ (Fig. 3, as in vi).

In summary, we have shown that, a magnetic impurity embedded in a small metallic grain, has a striking different behavior depending on the parity of the electron number in the grain. In particular, the Kondo effect is strongly enhanced if the number of electrons is even, while it is strongly depressed if the number is odd. Therefore, the measurement of $\chi$ of a magnetic impurity embedded in an ultrasmall metallic grain is an effective way of probing the number parity of the electrons in the grain.

∗ ∗ ∗

We acknowledge fruitful discussions with G. Falci, A. Mastellone, and A. Tagliacozzo. This work was supported by INFM under the PRA-project ”Quantum Transport in Mesoscopic Devices” and EU by Grant RTN 1-1999-00406, RTN2-2001-00440, and HPRN-CT-2002-00144.