Kondo effect of magnetic impurities on nanotubes

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Abstract

The zero-bias anomalies observed in STS conductance spectroscopy through adsorbed magnetic impurities and to some extent in metal break junctions have recently revived interest in the Kondo effect. Addressing these systems theoretically poses several problems. In the first place, and unlike quantum dots, ab initio electronic structure calculations such as density functional theory (DFT) are essential to establish a quantitatively meaningful starting point. Which among the impurity-related levels and resonances drive the spin polarization, what is their multiplicity, their hybridization, etc. are all questions that need an “ab initio” calculation. Next, this information must be translated into a manageable Hamiltonian, possibly without the loss of the brute quantitative information provided by DFT. Finally, the many body Hamiltonian(s) must be solved, to extract Kondo parameters and the predicted conductance features near zero bias, possibly with their behavior with parameters such as nanocontact geometry, temperature and external field, to be eventually compared with experiment. One approach in this direction was recently taken by our group [1]. Given a nanocontact between two leads, one identifies, with the help of symmetry, the impinging and outgoing channels that carry current across the impurity. From the matching symmetry selected local densities of states at the impurity, one identifies the important impurity orbitals with their different magnetic splittings and hybridizations. This leads to formulate multi-orbital Anderson models, which contain a multiplicity of parameters to be adjusted. In our scheme the parameters are adjusted to yield, within the Hartree-Fock approximation, the same channel- and spin-dependent impurity scattering phase shifts as those that we calculate ab initio by DFT – whose input information is therefore put to maximal use. For the last step, solving the Anderson models, we employed a standard numerical renormalization group (NRG) scheme. While other groups have dealt with the overall Kondo problem in different ways [2, 3], we find our “DFT + NRG” route extremely instructive, and worth exploring in more complex situations than the simple Au-Ni-Au contact studied in Ref [1]. In the present application we consider a single wall carbon nanotube (SWNT) as our linear conducting system, and a single externally adsorbed transition metal atom, either Co or Fe, as the magnetic impurity. To begin with, the metallic nanotube has two conducting channels instead of only one as Au. The magnetic atoms in turn have in principle a richer multiplicity of magnetic levels than Ni. We wish to explore what this richness might bring.

1. Introduction

The zero-bias anomalies observed in STS conductance spectroscopy through adsorbed magnetic impurities and to some extent in metal break junctions have recently revived interest in the Kondo effect. Addressing these systems theoretically poses several problems. In the first place, and unlike quantum dots, ab initio electronic structure calculations such as density functional theory (DFT) are essential to establish a quantitatively meaningful starting point. Which among the impurity-related levels and resonances drive the spin polarization, what is their multiplicity, their hybridization, etc. are all questions that need an “ab initio” calculation. Next, this information must be translated into a manageable Hamiltonian, possibly without the loss of the brute quantitative information provided by DFT. Finally, the many body Hamiltonian(s) must be solved, to extract Kondo parameters and the predicted conductance features near zero bias, possibly with their behavior with parameters such as nanocontact geometry, temperature and external field, to be eventually compared with experiment. One approach in this direction was recently taken by our group [1]. Given a nanocontact between two leads, one identifies, with the help of symmetry, the impinging and outgoing channels that carry current across the impurity. From the matching symmetry selected local densities of states at the impurity, one identifies the important impurity orbitals with their different magnetic splittings and hybridizations. This leads to formulate multi-orbital Anderson models, which contain a multiplicity of parameters to be adjusted. In our scheme the parameters are adjusted to yield, within the Hartree-Fock approximation, the same channel- and spin-dependent impurity scattering phase shifts as those that we calculate ab initio by DFT – whose input information is therefore put to maximal use. For the last step, solving the Anderson models, we employed a standard numerical renormalization group (NRG) scheme. While other groups have dealt with the overall Kondo problem in different ways [2, 3], we find our “DFT + NRG” route extremely instructive, and worth exploring in more complex situations than the simple Au-Ni-Au contact studied in Ref [1]. In the present application we consider a single wall carbon nanotube (SWNT) as our linear conducting system, and a single externally adsorbed transition metal atom, either Co or Fe, as the magnetic impurity. To begin with, the metallic nanotube has two conducting channels instead of only one as Au. The magnetic atoms in turn have in principle a richer multiplicity of magnetic levels than Ni. We wish to explore what this richness might bring.

2. Systems and symmetries

We considered alternatively Co or Fe impurities on either (4,4) or (8,8) metallic SWNTs (see fig. 1). If is the SWNT axis, its electronic states of can be classified according to parity with respect to xy plane reflection (\(e\rightarrow o, \text{even-odd}\)) and z plane reflection (\(s\rightarrow a, \text{symmetric and antisymmetric}\)). DFT calculations (see section 3) predict that the externally adsorbed impurities should have minimum energy when at the hollow site (see fig. 2), that is above the center of a carbon hexagon. Assuming that geometry, the impurity electronic states can be classified according to the same parity numbers as those of clean
SWNTs. We are interested in particular in 3d and 4s impurity orbitals, whose parities are shown in tab. [1]

3. Ab initio electronic structure

We carried out standard density-functional theory (DFT) calculations, allowing for full relaxation of all atomic positions in a unit cell, which comprised 80 and 160 carbon atoms for the (4,4) and (8,8) tubes respectively plus one Co or Fe adsorbed impurity. Calculations used the standard plane-wave package Quantum-ESPRESSO [2] within the generalized gradient approximation (GGA) to exchange-correlation functionals in parametrization of Perdew, Burke and Ernzerhof. The plane wave cut-offs were 30 Ry and 300 Ry for the wave functions and for the charge density, respectively. Integration over the one-dimensional Brillouin zone was accomplished using 8 k-points and a smearing parameter of 10 mRy. When necessary to test the sensitivity of DFT results to correlation effects, we extended to “GGA+U” with a reasonably small Hubbard “U” [2]—but generally the straight DFT result was used.

We found that Co behaves as a $S = \frac{1}{2}$ impurity on both (4,4) and (8,8) SWNTs, its $d_{yz}$ orbital driving the spin polarization. The Co atom switches from the $3d^7 4s^2$ configuration of the isolated atom to a slightly surprising low-spin $3d^6 4s^0$ one when adsorbed on the nanotube. Fe behaves as a $S = 1$ impurity on the (8,8) tube, similarly switching from the high-spin $3d^6 4s^2$ of the isolated atom to a low-spin $3d^7 4s^0$ in the adsorbed state. Here the pair of orbitals $d_{xy}$ and $d_{yz}$ is magnetically polarized (see fig. 3 and tab. 2), a result in good agreement with previous calculations [3,5]. Orbitals $d_{xy}$ for Co and $d_{yz}$ for Fe are partly empty, and fall near the Fermi energy in straight DFT: but they promptly move below $E_F$ even when a small $U$ is switched on. We conclude that these orbitals are not going to be involved in Kondo behaviour and can be neglected to a first approximation in order to keep the many-body model simple. The behavior of Fe/(4,4) is complicated. The $s$ orbital is partly filled, and $d_{xy}$ is magnetically polarized besides the $(d_{xy}, d_{yz})$ pair, so here Fe should behave as a $S = \frac{1}{2}$ impurity.

As in previous work [11] we implemented DFT computation of the (spin-polarized) mean-field ballistic conductance and, more importantly, of the impurity-related spin- and channel-selected phase shifts suffered by the SWNT conduction electrons as a function of energy. An example is shown in fig. 4 for Co on the (4,4) SWNT.

4. Generalized Anderson model

The Kondo model is usually understood by means of a many-body Anderson Hamiltonian [17]. In our case we need to extend it in principle to the four SWNT conduction bands, each hybridized with some impurity orbital among the 3d and 4s, of same symmetry. These impurity orbitals in turn are mutually coupled by an intra-atomic ferromagnetic Hund exchange term,

$$H_{\text{Hund}} = J \sum_{i < j, \sigma = \uparrow, \downarrow} \vec{\sigma}_i \cdot \vec{\sigma}_j$$  \hspace{1cm} (2)

where $\vec{\sigma}$ creates an electron on the impurity orbital with symmetry $i$, $c_{ik}^\dagger$ creates an electron in a $k$ conduction state with symmetry $i$, $\vec{s}$ are the Pauli matrices, $\delta$ is a potential scattering term due to the charge density of the impurity, $V_i$ is the coupling of the impurity orbital with the conduction electron states, $\epsilon_k$ is the bare energy of the impurity orbital, $U_i$ is the Hubbard repulsion on the orbital, $J < 0$ is a global Hund exchange parameter (favouring high spin for the isolated impurity), and the single particle energies of conduction electrons $\epsilon_{ik}$ are such as to give a constant density of states, with exactly the same value as that of the clean SWNT (per spin direction) as computed by DFT:

$$\sum_k \delta(\epsilon - \epsilon_{ik}) = \rho \equiv \frac{1}{12eV} \quad i = es, eo, as, ao$$  \hspace{1cm} (5)

We are particularly interested in 3d impurities. Of the isolated atom to a low-spin $3d^5$ impurity (once orbital $d_{xy}$ is partly filled, and $d_{yz}$ is magnetically polarized besides the $(d_{xy}, d_{xz})$ pair, so here Fe should behave as a $S = \frac{1}{2}$ impurity.

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In practice, only conduction bands coupled to a magnetic orbital are retained in our NRG procedure (see section 5). This leaves us with a single band coupled to a single impurity level in the case of Co (once orbital $d_{xy}$ is ignored), and with two bands, each coupled to one impurity level, in the case of Fe/(8,8) (once orbital $d_{yz}$ is ignored). The case of Fe/(4,4) is more involved and we will presently not deal with it.

5. Joining up DFT and many body

Hamiltonian eq. [11] is easily solved in the (unrestricted) Hartree-Fock approximation [17], breaking spin rotational symmetry. This leads to a phase shift in conduction electrons of symmetry $i$ ($i = es, eo, as, ao$) at the Fermi energy

$$\delta^\gamma_i = \phi_i + \arctan \frac{\Gamma_i}{\epsilon_i}$$  \hspace{1cm} (6)

where $\phi_i = \arctan \pi \nu_i \approx 0$ is the phase shift caused by the impurity charge scattering. This is numerically found to be negligible, so we shall ignore it from now on. The peak of the impurity DOS is found to be at

$$\epsilon_i^\gamma = \epsilon_i + U_i \langle n_i^\gamma \rangle - \sigma \frac{J}{2} (m_{\text{tot}} - m_i)$$  \hspace{1cm} (7)

where

$$\langle n_i^\gamma \rangle = \frac{1}{\pi} \arctan \frac{\Gamma_i}{\epsilon_i}$$  \hspace{1cm} (8)

is the average occupation of up/down orbital

$$m_i = \langle n_i^\uparrow \rangle - \langle n_i^\downarrow \rangle$$  \hspace{1cm} (9)

is the magnetization of each orbital and

$$m_{\text{tot}} = \sum_{i=1}^n m_i$$  \hspace{1cm} (10)
is the total magnetization of the atom. As in [1], we choose to
reproduce the same phase shifts at the Fermi energy for each
symmetry, and the same peaks in the density of states of the
impurity orbitals as those computed by DFT. This allows to
uniquely fix $\epsilon_i$, $U_i$ and $\Gamma_i$ as long as just one magnetic orbital
is considered in eq. [1]—that is the case of Co ($i = os$). When
more than one orbital is involved, such as in Fe, (or in Co if or-
dital $d_v$ were to be taken into account) we need to fix $J$ as well.
We can extract $J$ from the DFT calculated exchange splitting of
filled orbitals, according to

$$ e^f_j - e^d_j = \frac{J}{2} m_{tot} \tag{11} $$

Since different $d$ orbitals have slightly different splittings, we
just took an average value as deduced from di

6. Results of NRG calculations
We solved the Anderson Hamiltonian by means of NRG
[8, 9], which allows to compute all the needed static and dy-
amic quantities we need in an almost exact, albeit numeri-

cal, way. We extracted the conduction electrons phase shifts
from the single particle energies at the zero energy fixed point,
and the Kondo temperature from the impurity Green function at
imaginary frequency:

$$ G(i\epsilon) = \frac{1}{i\epsilon - \epsilon_i - \Sigma'(i\epsilon) + i\Gamma_i} = \frac{1}{Z_{part}} \sum_n \frac{|GS|dn|^2}{i\epsilon - \epsilon_n} \tag{12} $$

($Z_{part}$ is the partition function and $GS$ the ground state). The
Kondo temperature is given by

$$ T_K = \frac{\pi w Z T}{4 k_b} \tag{13} $$

where $w = 0.4128$ is the Wilson coefficient and $Z$ is the quasi-
particle residue

$$ Z^{-1} = 1 - \frac{\partial \Sigma'(i\epsilon)}{\partial (i\epsilon)} \tag{14} $$

Alternatively, an approximate formula [10], valid for one impu-
ritv coupled to one channel,

$$ T_K \approx 0.4107 \sqrt{\frac{U_i \Gamma_i}{2}} e^{\pi (\epsilon_f + U_i)/2 \Gamma_i} \tag{15} $$

could be used, with similar results.

The zero-bias conductance is given, in terms of the final
phase shifts, by

$$ g = \frac{G}{G_0} = \cos^2(\delta_{sa} - \delta_{oa}) + \cos^2(\delta_{oa} - \delta_{ma}) \equiv g_s + g_a \tag{16} $$

where $G_0 \equiv \frac{2 e^2}{h}$ is the quantum of conductance. Note that in
the clean tube $G = 2 G_0$. Phase shifts are only computed for
Kondo channels, and are found to be always $\approx \pi/2$. For the
non-Kondo channels, they can be directly extracted from DFT.

Since in DFT they are $\approx 0$, they can be safely neglected. Sum-
ming up, both Co/(4,4) and Co/(8,8) should exhibit a (zero tem-
perature and zero bias) conductance $G \sim G_0$, whereas Fe/(8,8)
should have $G \sim 0$. These results remain valid so long as ei-
ther temperature and/or bias remain well below $T_K$. However,
it turns out that Kondo temperatures $T_K$ are quite low (see tab.
[5], which might make this effect hard to observe in a real ex-
periment. Interestingly, a much higher Kondo temperature of
about 15 K has been quoted for Co/graphene[11]. While the
reasons for this difference between graphene and nanotubes are
presently being investigated, it should be noted that several fac-
tors differ, including symmetry, and heavy doping in real, de-
posited graphene.

Finally, we can qualitatively address the predicted bias-
dependent lineshape of the Kondo conductance anomaly. Through
the Keldysh technique for non-equilibrium Green-
functions it is possible to compute the finite-bias conductance
[12], once the impurity Green function $G_\epsilon(\epsilon)$ is calculated from
NRG [13]:

$$ g_{s,a} = 1 - \frac{1}{2} \frac{G_\epsilon(\epsilon)}{G_\epsilon(0)} \tag{17} $$

For simplicity, we have taken

$$ G_\epsilon(\epsilon) = \frac{\Gamma_k(\epsilon)}{\epsilon + i\Gamma_k} \tag{18} $$

where

$$ k_B T_K = \frac{w \pi}{4} \pi K = 0.342 \Gamma_k \tag{19} $$

This gives rise to a Fano lineshape [14]

$$ g_{s,a} = \frac{(q + v)^2}{(q^2 + 1)(v^2 + 1)}, \quad v \equiv \epsilon/\Gamma_k \tag{20} $$

with $q = 0$, so for each band ($s - a$) the lineshape is predicted
to be a symmetric antilorentzian, with a width proportional to
the Kondo temperature. Small sources of asymmetry will arise
from a) the potential scattering $t_i$ which we ignored in Eq. [4]b;
from the interference with orbitals belonging to the same band
$a$ or $s$, but with different symmetry $e/\alpha$; and c) from particle-
hole asymmetries in eq. [18]. However, we estimate that the
asymmetry parameter $q$ should generally remain below 0.1. In
Co/(4,4) and Co/(8,8), only $g_s$ contributes to the lineshape, $g_a$ being
almost one – and moreover independent from energy on
the Kondo energy scale. In Fe/(8,8), both $g_s$ and $g_a$ have an
antilorentzian shape, although with very different widths. The
total lineshape is just their sum (see fig. [5]).

7. Conclusions
We implemented our recently devised DFT+NRG scheme
[1] to calculate the Kondo effect caused by Co and Fe adsorbed
impurities on the conductance of (4,4) and (8,8) nanotubes. On
the methodological side, the present calculation represents a
good pedagogical illustration of our technique. For the systems
chosen, the predicted anomalies are symmetric antilorentzian
dips, reducing total zero bias conductance to zero for Fe, and
by a factor 1/2 for Co. While there are no data to compare with,
The symmetries of \( d \) and \( s \) orbitals with respect to the \( xy \) plane are as follows:

| Impurity | Magnetic Orbital | Symmetry | Spin |
|----------|-----------------|----------|------|
| Co       | \( d_{zc} \)    | \( os \)  | \( 1/2 \) |
|          | \( (d_{sy}) \)  | \( ea \)  | \( 0 \)  |
| Fe       | \( d_{zc} \)    | \( os \)  | \( 1/2 \) |
|          | \( d_{sy} \)    | \( ea \)  | \( 0 \)  |

Table 1: Symmetries of \( d \) and \( s \) orbitals with respect to the \( xy \) plane (even - odd) and the \( zc \) plane (symmetric \( s \) - antisymmetric \( a \)).

For \( (4,4) \) and \( (8,8) \) SWNTs, the magnetic orbitals are:

| Impurity | SWNT | Orb. | \( \epsilon_p \) (eV) | \( U \) (eV) | \( \Gamma \) (eV) | \( T_K \) (K) |
|----------|------|------|-----------------------|-------------|-------------|-------------|
| Co       | (4,4)\( d_{zc} \) | \( -1.62 \) | 2.17 | 0.082 | \( \sim 1 \) |
|          | (8,8)\( d_{zc} \) | \( -1.83 \) | 2.11 | 0.054 | \( \sim 1 \) |
| Fe       | (8,8)\( d_{zc} \) | \( -1.24 \) | 2.01 | 0.060 | \( \sim 10^{-4} \) |
|          | \( d_{sy} \)    | \( -1.38 \) | 2.13 | 0.043 | \( \sim 10^{-4} \) |

Table 2: Magnetic orbitals as found from DFT calculations, their symmetry, and spin they carry \((S = 1/2\) for each magnetic orbital\). Orbitals in parentheses are not Kondo orbitals, so do not contribute to the total spin of the impurity and are ignored in the many-body model, but still participate in transport.

This prediction should in principle be amenable to experimental check. However, we note that our calculated Kondo temperatures are very small, which might constitute an experimental challenge.

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Figure 2: A schematic view of (4,4) and (8,8) SWNTs with an impurity adsorbed in the hollow position.

Figure 3: Projected density of states of impurity 3d and 4s orbitals. Above: Co on (4,4) SWNT; below: Fe on (8,8) SWNT.

Figure 2: A schematic view of (4,4) and (8,8) SWNTs with an impurity adsorbed in the hollow position.
Figure 4: Above: conductance as a function of energy of conduction electrons for Co on (4,4) SWNT, for each symmetry $s-a$ and spin direction $u-d$ (up-down); below: phase shift of conduction electrons for different symmetries $s-a$, $e-o$ and spin directions $u-d$.

Figure 5: Predicted zero-bias anomaly for Co impurity on both (4,4) and (8,8) SWNTs (above) and for Fe on (8,8) SWNT (below) ($g \equiv G/G_0$, $G_0 = 2e^2/h$).