Topology induced Kondo effect in hydrogenated Pt nanocontacts

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(Dated: November 13, 2018)

It is shown that recent experimental data on electronic transport through Pt nanocontacts in the presence of hydrogen admit an explanation in terms of topological and electron-electron correlation grounds. A model Hamiltonian, which incorporates two orbitals on Pt atoms, a single orbital on hydrogens, and the on-site Coulomb repulsion on the H atoms, is solved exactly, and connected to Pt leads described by a Bethe lattice. When two weakly coupled H atoms are placed between the Pt electrodes transversally to the transport direction (as recently suggested) a Kondo effect related to the symmetry of the Pt-H couplings, stabilizes the conductance around one quantum with a single channel contributing to the current, in agreement with the experiments.

PACS numbers: 73.63.Fg, 71.15.Mb

A recent experimental work reports that electronic transport through Pt nanocontacts is strongly modified in the presence of hydrogen. Specifically, while in Pt nanocontacts the main conductance peak lies close to 1.5 conductance quanta $g_0 = 2e^2/h$, in a hydrogen atmosphere the main peak shows up near one quantum. Although it was suggested that the latter result was due to a H molecule being placed along the nanocontact axis bridging the last two Pt atoms of the left and right electrodes, an alternative explanation has been put forward recently. Extensive quantum chemistry calculations led the authors to conclude that a geometry in which two weakly coupled hydrogen atoms were placed transversally to the nanocontact axis (see Fig. 1), was more probable. Most of the results described in [1] found a reasonable explanation [3], including vibrational frequencies and the isotope effect, but the observed unit conductance to which a single channel apparently contributes. The aim of this work is to study the strong correlation effects that one may expect due to the presence of hydrogen, the role played by topology, recently emphasized in an analysis [1] of transport through two quantum dots in a similar geometry (dots located transversally to the nanostructure axis), and the importance of both in understanding the experimental results [1].

The model Hamiltonian used to describe the Pt-H-H-Pt cluster shown in Fig. 1 is:

\[ \hat{H} = \hat{H}_P + \hat{H}_H + \hat{H}_{P-H} \]

The Pt Hamiltonian includes two isotropic (s-like) orbitals, the first representing the 6s Pt orbital, and the second some average of the five 5d Pt orbitals,

\[ \hat{H}_P = \sum_{i=1,2,\sigma} \left[ \epsilon_a a_i^\dagger a_i + \epsilon_b b_i^\dagger b_i + t a_i^\dagger a_j + t b_i^\dagger b_j \right] \]

As in the geometry of Fig. 1 the H atoms are rather far apart [3] we do not include the interaction between their respective s-orbitals. On the other hand, the Hamiltonian incorporates the on-site Coulomb repulsion through a Hubbard term,

\[ \hat{H}_H = \sum_{i=1,2,\sigma} \epsilon_b h_i^\dagger h_i + U h_i^\dagger h_i^\dagger h_i h_i \]

Finally the Pt-H interactions are written as,

\[ \hat{H}_{P-H} = \sum_{i,j=1,2} (t_{ha} a_i^\dagger a_j + t_{hb} b_i^\dagger b_j) \]
TABLE I: Energies of the Pt and H orbitals and the interactions amongst them (all in eV), as defined in Eqs. (1-4), used to describe the Pt2 and the Pt2H2 clusters. Parameters for bulk Pt were taken equal to those of the Pt2 cluster.

|       | $\epsilon_a$ | $\epsilon_b$ | $t_{sa}$ | $t_{sb}$ | $t_{ba}$ | $t_{bb}$ | $U_b$ |
|-------|---------------|---------------|----------|----------|----------|----------|------|
| bulk Pt | -7.0          | -7.5          | -1       | 0.2      | -        | -        | -    |
| Pt2H2  | -6.75         | -7.75         | 9.5      | -1.2     | 0.2      | -0.5     | (-1)  |

When the cluster is connected to electrodes, the transmission across the system is given by

$$T(E) = \frac{2e^2}{h} \text{Tr}[t^\dagger t],$$

(5)

and the conductance is $G = T(E_F)$, where $E_F$ is the Fermi level that will be hereafter taken as the zero of energy. In this expression, $\text{Tr}$ denotes the trace over all orbitals in the cluster and the matrix $t$ is given by

$$t = \Gamma_R^{1/2} G^{(+)} \Gamma_L^{1/2} = \left[ \Gamma_L^{1/2} G^{(-)} \Gamma_R^{1/2} \right]^{\dagger},$$

(6)

where the matrix $\Gamma_{R(L)}$ is given by $i(\Sigma^{(-)}_{R(L)} - \Sigma^{(+)}_{R(L)})$, $\Sigma_{R(L)}^{(\pm)}$ being the self-energies of the right (R) and left (L) leads. The Green function is written as,

$$G^{(\pm)} = \left( \left[ G_0^{(\pm)} \right]^{-1} - c \left[ \Sigma_R^{(\pm)} + \Sigma_L^{(\pm)} \right] \right)^{-1},$$

(7)

where $G_0^{(\pm)}$ is the Green function associated to the isolated Pt2H2 cluster, which is obtained by means of exact diagonalization using the Lanczos method. The bulk of the electrodes is described by means of a Bethe lattice with coordination twelve, while the two Pt in the cluster are connected to $c$ bulk atoms. As discussed below, this effective coordination $c$ is taken as a fitting parameter. In order to single out the contribution of individual channels we diagonalize the matrix $t^\dagger t$. This method, hereafter denoted as the Embedded Cluster Method (ECM), is exact only as far as the calculation of the Green function of the isolated cluster is concerned, and does not account for electron-electron interaction effects that may extend beyond its bounds. In the Kondo regime, many-body effects extend over a length given by the Kondo cloud that is proportional to the inverse of the atomic Kondo temperature $T_k$. In this case, as hydrogen and Pt interact strongly, we expect this temperature to be large enough to guarantee a rather localized cloud. Aiming to highlight the role played by the Kondo effect we also solve this system using Unrestricted Hartree Fock (UHF) that gives an appropriate description for temperatures greater than the Kondo temperature.

The choice of the model parameters (given in Table I) was guided by ab-initio calculations of the Pt2 and Pt2H2 clusters. As that calculation indicates that the $d_{xy}$ orbital is the one that more strongly interacts with the H orbital, orbital $b$ in Eq. (2) was assumed to have that symmetry in the Pt2H2 cluster. The parameters of Table I give a bulk Bethe-lattice Density of States (DOS) with a $d$ band more than half-filled and a $s$ band less than half-filled. All Bethe-lattice and nanocontact calculations were carried out by fixing the charge to one (two) electron per H (Pt) atom. Parameter $c$ in Eq. (7) was chosen to give the experimental conductance in Pt nanocontacts with no hydrogen.

Fig. 2 shows our results for the transmission and the DOS in this nanocontact (with $c=5.5$), which are in line with those reported in. Both channels equally contribute to give a conductance around $1.6 G_0$. Due to the symmetry of the $d_{xy}$ orbital there is no indirect (hydrogen mediated) $s - d$ coupling between Pt atoms. In addition, direct coupling between $s$ and $d$ orbitals on different atoms is small enough to be ignored in our simplified model. As a result, $s$ and $d$ orbitals act independently even in the presence of hydrogen. Our results for the transmission in the hydrogenated Pt nanocontact are depicted in Fig. 3. Comparing these results with those without H (see Fig. 2) we note that the new transmission reaches a maximum (minimum) of around $G_0(0)$ for the $d$ ($s$) eigenchannel. This result is not reproduced by the UHF approximation, as shown in the lower panel of Fig. 3. The latter resembles the transmission for the Pt nanocontact (see Fig. 2), but reduced by the effect of scattering with $H$ orbitals. The local DOS at the H atoms
is shown in the upper panel of Fig. 3. The ECM result shows the Kondo signature at the Fermi level, which is absent in the UHF calculation, that describes the solution for $T > T_k$. The comparison of UHF and ECM results clearly suggest the presence of strong many-body effects. As there is no direct or indirect hybridization between $s$ and $d$ bands, the pair of $H$ can be in the Kondo regime with each $Pt$ band simultaneously and independently, as described in [10] for a one band model. In this regime, both hydrogens become strongly correlated (in a state with each Pt band simultaneously and independently, as described in [10] for a one band model. Then, the conductance in each channel has two contributions coming from: i) direct coupling between $d$ or $s$ orbitals, and, ii) coupling mediated by the CIS1. Charge in the the CIS1 induce a phase shift of $\pi$ respect to the direct contribution, as can be argued from the Friedel sum rule [10], and was also verified numerically by us. Contributions from both ways are similar and therefore a destructive interference take place in the $s$ channel. In the case of the $d$ channel there is an additional $\pi/3$ phase shift, because the $H$ are connected with different sign to each $Pt$. This prevents destructive interference in this channel. Moreover, in this case the dominant contribution to the conductance comes from the impurity channel (see Table I) that is in the Kondo regime given conductance very close to 1. Results for the transmission and local DOS for the model with two $s$-like orbitals ($s_1$ and $s_2$) in place of $s$ and $d$ orbitals are also shown in Figs. 3 and 4. In this case there is no Kondo resonance at the Fermi level, as $s_1$ and $s_2$ orbitals on different Pt atoms are now coupled through the hydrogens. As shown in Fig. 4 this coupling splits the Kondo resonance into two peaks above and below the Fermi level. As a consequence, only the direct coupling between $Pt$ atoms contribute to the conductance and, as interference effects do not show up, the two channels give similar contributions to the conductance (see Fig. 3). This is also the case of a $H_2$ molecule placed longitudinally to the nanocontact axis, as, in this case, each $H$ atom is connected only either to the left or right electrodes, giving an indirect coupling between $s$ and $d$ bands.

In order to investigate how the conductance changes from a situation with no hydrogen up to that where the two $H$ atoms are located as in Fig. 3 we have carried out calculations varying the $H$-$Pt$ parameters as $t_{hi} = x_H t_{hi}$, where $i = a, b$ and $x_H$ varying from 0 (H free nanocontacts) up to 1.5. The most appealing feature of the results shown in the lower panel of Fig. 4 is the wide range of $x_H$ over which the ECM gives a conductance close to one [12]. This is due to the electron-electron interactions that are playing an essential role in this system. The latter statement is corroborated by the spin-spin correlations also shown in Fig. 4. When the hydrogen atoms are not coupled (or just weakly coupled) to Pt, H-H correlations are antiferromagnetic and the total spin of the molecule is zero, as occurs in the free hydrogen molecule. In this limit Pt-$H$ spin-spin correlation is zero, as it should. However,
fluctuations. The ECM results depicted in Fig. 5 clearly show a peak in the conductance histogram near $G_0$, with a minimum in fluctuations. This means that only one channel is contributing to the unit conductance, being this value the most probable. The UHF results, however, show finite fluctuations over the whole range.

Summarizing, the effects of electron-electron interaction on transport through hydrogenated Pt nanocontacts have been investigated. Our results indicate that when two H are located transversally to the nanocontact axis, a Kondo effect stabilizes the conductance around one quantum. Spin-spin correlations are much like those which occur in the standard Kondo effect observed on two dots in a similar geometry. The effect occurs due to the decoupling of $d$ and $s$ bands produced by the combination of the transversal location of the molecule and to the $d_{xy}$ symmetry of the Pt d orbital. The result is robust and largely independent of the model parameters. Besides, a single channel contributes to the conductance, leading to a minimum in the conductance fluctuations, in agreement with experiments. This analysis permits to conclude that the unit conductance observed in this system is the result of a combination of highly Kondo correlated spins and topology.

Financial support by the spanish MCYT (grant MAT2002-04429-C03 and a sabatical grant), the Universidad de Alicante, the Universidad de Buenos Aires (grant UBACYT x210) and Conicet, is gratefully acknowledged. Useful discussions with J. Fernández-Rossier, Y. García, J.J. Palacios, A. Pérez-Jiménez, and E. San Fabián are gratefully acknowledged.

\[ \sigma_{GV} \propto \sqrt{\sum_{n=1}^{N} T_n^2 (1 - T_n)} \]  

where $T_n$ is the transmission probability of channel $n$ and $N$ is the total number of channels. We have calculated the conductance fluctuations by randomly varying $x_H$ over the range $[0,1.5]$. Couplings between Pt atoms in the nanocontact were also multiplied by a random factor in the range $0-1.5$. Averages were done over at least 1000 realizations. To calculate the standard deviation, instead of directly working on the distribution $\partial G/\partial V$ that gives very noisy results, we introduced the results for the transmission of each channel into Eq. (8). As shown in [8], both calculations agree in identifying the minima in fluctuations. The ECM results depicted in Fig. 4 clearly

FIG. 5: Normalized conductance histogram and normalized conductance fluctuations for the hydrogenated nanocontact versus the conductance through it. The results were obtained by using either ECM (upper panel) or UHF (lower panel).

[1] R.H.M. Smit, Y. Noat, C. Untiedt, N.D. Lang, M.C. van Hemert, and J.M. van Ruitenbeek, Nature 419, 906 (2002).
[2] R.H.M. Smit, PhD Thesis, Leiden 2003.
[3] Y. García, J.J. Palacios, E. SanFabián, J.A. Vergés, A.J. Pérez-Jiménez, and E. Louis, Phys. Rev. B 69, 041402 (2004).
[4] V. Apel, M.A. Davidovich, G. Chiappe and E.V. Anda, cond-mat/0404685 and submitted to Phys. Rev. Lett. (2004).
[5] B. Ludoph, M.H. Devoret, D. Esteve, C. Urbina, and J.M. van Ruitenbeek, Phys. Rev. Lett., 82, 1530 (1999).
[6] E. Louis, A.J. Pérez-Jiménez, J.J. Palacios, J.A. Vergés, Y. García, and E. SanFabián, Phys. Rev. B, in press.
[7] R. Landauer, IBM J. Res. Dev. 1, 223 (1957).
[8] V. Ferrari, G. Chiappe, E.V. Anda, and M.A. Davidovich, Phys. Rev. Lett. 82, 5088 (1999).
[9] G. Chiappe and J.A. Vergés, J. Phys. C 15, 8805 (2003).
[10] The Friedel sum rule can be used to calculate the phase shift in each spin channel accross an interacting system. It gives $\pi n_\sigma$, where $n_\sigma$ is the charge per spin at the impurity. In our case $n_\sigma = 1/2$ on each hydrogen, which gives $\pi$ for the phase shift (see [11]).
[11] A.C. Hewson, in The Kondo Problem to Heavy Fermions, Cambridge Studies in Magnetism, edited by D. Edwards.
The Kondo-like peak that shows up in quantum dots only gives unit conductance at half-filling and in the presence of electron-hole symmetry (see, for instance, [4]). This is not the case in the present system.