Kondo Effect of an Adsorbed Cobalt Phthalocyanine (CoPc) Molecule: The Role of Quantum Interference

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(Received 12 May 2006; published 18 August 2006)

It has been shown that by distorting a CoPc molecule adsorbed on a Au(111) surface a Kondo effect is induced with a temperature higher than 200 K. We examine a model in which an atom with strong Coulomb repulsion (Co) is surrounded by four atoms on a square (molecule lobes), with two atoms above and below it representing the apex of the STM tip and an atom on the gold surface (all with a single atomic orbital). The Hamiltonian is solved exactly for the isolated cluster, and, after connecting the leads, the conductance is calculated by standard techniques. Quantum interference prevents the existence of the Kondo effect when the orbitals on the square do not interact (undistorted molecule); the Kondo resonance shows up after switching on that interaction. The weight of the Kondo resonance is controlled by the interplay of couplings to the STM tip and the gold surface and between the molecule lobes.

PACS numbers: 73.63.Fg, 71.15.Mb, 75.20.Hr

Coupling of localized spins to conduction electrons may lead to a transport anomaly known as the Kondo effect [1,2]. This effect, which usually shows up at low temperatures, consists of a sharp peak at the Fermi level, whose half-width is known as the Kondo temperature (T_K), and a conductance close to 1 conductance quantum $\mathcal{G}_0 = 2e^2/h$. The Kondo temperature in the case of magnetic impurities in nonmagnetic metals is around 50 K [1], whereas in artificial atoms (quantum dots) it is just a few hundred mK [3,4]. In a recent experiment [5,6], it has been shown that it is possible to control the characteristics, and even the existence, of the Kondo resonance by modifying the chemical surroundings of a magnetic atom. The experiments were carried out on a cobalt phthalocyanine molecule (CoPc) adsorbed on a Au(111) surface. Dehydrogenation of this molecule (*d*-CoPc) by means of voltage pulses from a scanning tunneling microscope (STM) triggered a Kondo effect with a rather high Kondo temperature ($T_K \approx 200$ K). This temperature is even higher than that observed for bare Co adsorbed on a similar surface [6,7]. Besides such a high T_K, one of the most remarkable results of Ref. [5] is the fact that the undistorted molecule does not show a Kondo effect, while it is readily promoted by distorting the molecule upon dehydrogenation. Topographic images taken by means of the STM [5] indicated that the CoPc molecule has four almost nonoverlapping lobes symmetrically placed around the Co atom. Dehydrogenation distorts the molecule and forces those lobes to overlap. In addition, it strongly decreases the distance from the molecule lobes to the gold surface and increases the Co-gold surface distance in approximately 30% [5].

We hereby propose a simple model that accounts for some of the salient features of the experiment described above. We take a model Hamiltonian on a small atomic arrangement which is solved exactly and, subsequently, connected to semi-infinite chains used to describe the STM tip and the gold surface. Figure 1 depicts this atomic arrangement. A central site with a single atomic orbital and a strong Coulomb repulsion accounts for the Co atom, while the four lobes of the molecule are described by four atomic orbitals placed on a square whose center is the Co atom. Two additional orbitals located above and below the Co atom are included to represent the apex of the STM tip and an atom on the gold surface, respectively. All atomic orbitals are assumed to be isotropic (*s*-like). The Hamiltonian takes the form
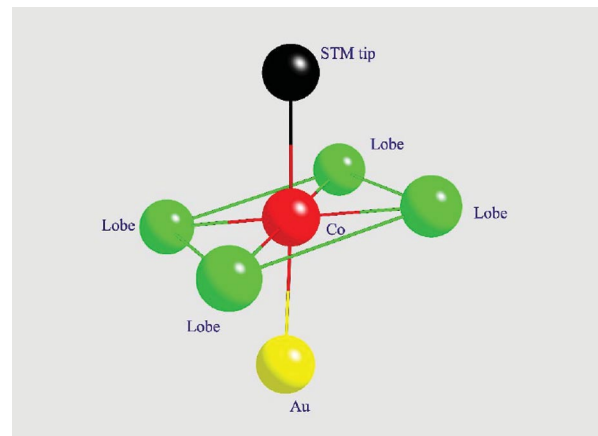

FIG. 1 (color).   Cluster of atoms utilized to describe the CoPc molecule adsorbed on a Au(111) surface. The four atoms on the square account for the four molecule lobes, while the atom at the center represents Co. The upper (lower) atom accounts for the apex of the tip of the STM microscope (the gold surface). To calculate the conductance, semi-infinite chains were attached to the top atom and to either the gold atom or the lobes (see text).

$$\hat{H} = \sum_{i\sigma} \epsilon_i c_{i\sigma}^\dagger c_{i\sigma} + \sum_{\langle ij \rangle;\sigma} t_{i,j} c_{i\sigma}^\dagger c_{j\sigma} + U n_{Co\uparrow} n_{Co\downarrow}, \quad (1)$$

where $c_{i\sigma}^\dagger$ creates an electron at site i with the z component of the spin $\sigma = \uparrow, \downarrow$, while the occupation operator $n_{Co\sigma}$ associated to Co is $n_{Co\sigma} = c_{Co\sigma}^\dagger c_{Co\sigma}$. We just consider the half-filling case, i.e., one electron per atomic orbital.

The parameters of this model Hamiltonian are the following. $t_{i,j}$ is the hopping between atomic orbitals located on sites i and j [the symbol $\langle \rangle$ in Eq. (1) indicates that $i \neq j$], each orbital has an energy ϵ_i, and the local (Hubbard-like) Coulomb repulsion on Co is described by U. In particular, we use the following parameters. We take $\epsilon_{Co} = -U/2$ and the rest of atomic orbitals lying at zero energy. The hoppings incorporated in the model are $t_{Co,t}$ (Co and the STM tip), $t_{Co,Au}$ (Co and the gold surface), $t_{Co,l}$ (Co and the molecule lobes), and $t_{l,l}$ (hopping between lobes). The latter parameter describes the effect of dehydrogenation: null in the undistorted molecule and finite in the dehydrogenized (distorted) molecule. Another important parameter of the model is the hopping between the lobes and the gold surface $t_{l,Au}$. One lead is attached to Co and describes the STM tip. The other lead (the Au surface) is attached to either Co or the lobes.

When the cluster is connected to electrodes, the transmission across the system is given by $T(E) = (2e^2/h)\text{Tr}[t^\dagger t]$ [8], and the conductance is $G = T(E_F)$, where E_F is the Fermi level. In this expression, matrix t is $t = \Gamma_U^{1/2} G^{(+)} \Gamma_L^{1/2} = [\Gamma_L^{1/2} G^{(-)} \Gamma_U^{1/2}]^\dagger$, where $\Gamma_{U(L)} = i(\Sigma_{U(L)}^{(-)} - \Sigma_{U(L)}^{(+)})$, $\Sigma_{U(L)}^{(\pm)}$ being the self-energies of the upper (U) and lower (L) leads, STM tip, and gold surface, respectively. Superscripts $(+)$ and $(-)$ stand for retarded and advanced. The Green function is written as [9] $G^{(\pm)} = ([G_0^{(\pm)}]^{-1} - [\Sigma_U^{(\pm)} + \Sigma_L^{(\pm)}])^{-1}$, where $G_0^{(\pm)}$ is the Green function associated to the isolated cluster, which is obtained by exact diagonalization [10,11]. The electrodes are described by means of semi-infinite chains. This method is *exact* only as far as the calculation of the Green function of the isolated cluster is concerned and does not account for correlation effects that extend beyond its bounds. The method has already been applied to a variety of transport problems [10–14] including transport through hydrogenated Pt nanocontacts [15].

In carrying out calculations, we have taken the hopping within the semi-infinite chains (leads) to be 1 eV, which is slightly larger than the hopping between s orbitals in gold [16]. In addition, we take $U = 8$ eV, not far from the value 6–7 eV recently estimated for the CuPc molecule [17]. The rest of the model parameters have been varied, aiming to identify their role in the behavior of this system. All calculations were done at zero temperature.

The results depicted in Fig. 2 are addressed to identify the origin of the emergence of the Kondo resonance upon distortion of the molecule [18–20]. The figure shows results for either the Co atom [Fig. 2(a)] or the lobes [Fig. 2(b)] connected to the gold surface. In addition, we
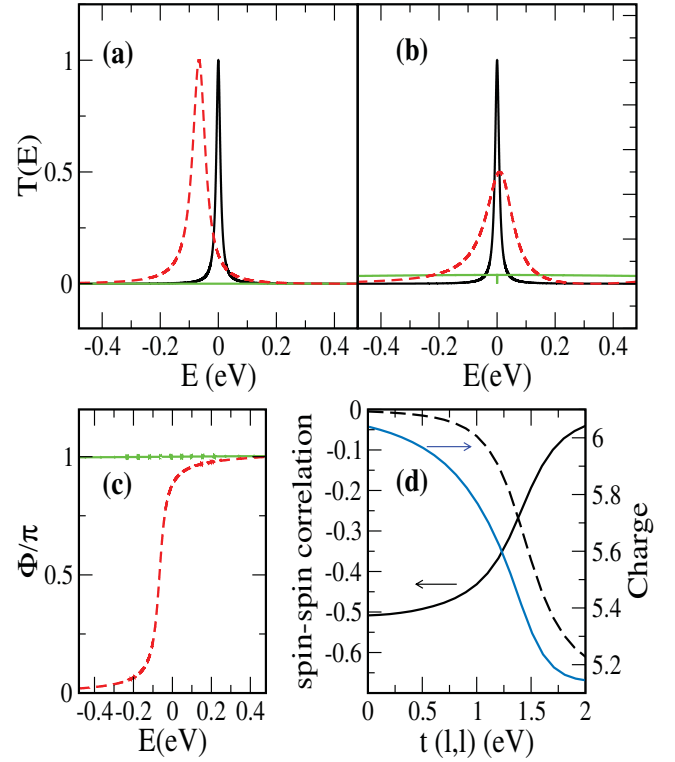

FIG. 2 (color). Transmission T (in units of the conductance quantum) versus the energy E (in eV) referred to the Fermi energy, and phase difference Φ between the direct path from the gold surface to the STM tip going through the Co atom and the path that passes through the molecule lobes (see text). (a) $t_{l,Au} = 0$, $t_{Co,t} = t_{Co,Au} = 0.25$ eV, and $t_{Co,l} = 1.25$ eV; $t_{l,l} = 0$ (green line) and $t_{l,l} = 2$ eV (red line). (b) $t_{Co,Au} = 0$, $t_{Co,t} = 0.25$ eV, $t_{l,Au} = 1$ eV, and $t_{Co,l} = 1.25$ eV; $t_{l,l} = 0$ (green line) and $t_{l,l} = 2$ eV (red line). The standard Kondo resonance, obtained with $t_{Co,l} = 0$ and $t_{Co,t} = t_{Co,Au} = 0.25$ eV (black line), is plotted in both (a) and (b). (c) Phase difference calculated for the parameters used in (a). (d) Spin-spin correlation for Co/lobes (solid line) and Co/STM tip (dashed line) and total charge on the lobes plus Co (solid blue line) versus $t_{l,l}$, for the parameters used in (a).

take either noninteracting lobes (green curves) or a finite hopping between lobes (red curves). For comparison, we also show the results for the standard Kondo effect in which the Co is decoupled from the molecule lobes (black curves). The most appealing result is that when the molecule lobes do not interact no Kondo effect shows up [21]. The origin of this remarkable result is likely related to quantum interference [2,12,15,22–25]. To illustrate this assessment, we have calculated the phase difference between the direct path, from the gold surface to the STM tip going through the Co atom, and the path that passes through the molecule lobes. This phase difference can be derived from the following element of the Green function:

$$G^{(+)}(Au, t) = g^{(+)}(Au, t)$$
$$+ 4g^{(+)}(Au, Co)\Sigma(Co, l)G^{(+)}(l, t), \quad (2)$$

where $\Sigma(Co, l)$ is a many-body self-energy that accounts for the lobes-Co coupling, and lowercase "g" are the Green functions in the case that lobes and Co are decoupled [26]. The results shown in Fig. 2(c) are just the phase difference between the two terms in the right-hand side of Eq. (2). When there is no hopping between lobes, the phase difference is π, indicating that the two terms may totally cancel each other, as actually occurs [27]. An alternative way to look at this issue is to calculate the local density of states (LDOS) on the Co atom that is obtained from the diagonal element of the Green function

$$G^{(+)}(Co, Co) = (\omega - \epsilon_l)g^{(+)}(Co, Co) \times [(\omega - \epsilon_l)$$
$$+ \Sigma^2(Co, l)g^{(+)}(Co, Co)]^{-1}, \qquad (3)$$

where ω is the energy referred to the Fermi energy. It is readily seen that, when the lobe orbitals lie at the Fermi energy ($\epsilon_l = 0$), the Green function $G^{(+)}(Co, Co)$ vanishes at that energy and, thus, the LDOS at the Co atom [28,29]. A null density of states at the Fermi energy on the strongly correlated Co atom implies that no Kondo resonance should show up, in accordance with the phase analysis. Full cancellation of the two terms in the right-hand side of Eq. (2) is removed when the lobes orbitals do not lie exactly at E_F, a result that can be derived from Eq. (3). When coupling between lobes is switched on, the phase difference is no longer π [Fig. 2(c)], and the Kondo resonance shows up [Fig. 2(a)]. This results from the fact that switching on that coupling opens new paths for the electrons to go from the lobes to Co that contribute to the phase difference. Besides, the peak width becomes significantly widened with respect to the standard Kondo effect [black curve in Fig. 2(a)] despite the fact that the molecules lobes are not connected to the gold surface. Figure 2(d) shows the spin-spin correlation for Co/lobes and Co/STM tip (a similar result is obtained for Co/Au). Remarkably, switching on the lobe/lobe coupling shifts the antiferromagnetic correlation from the Co/lobes to the Co/STM tip. In addition, six electrons are localized in the undistorted molecule (lobes plus Co), a number that is reduced down to five when the lobe/lobe coupling is switched on (see Fig. 2). These results are consistent with the existence (absence) of a magnetic moment on the distorted (undistorted) molecule, as derived from the *ab initio* calculations reported in Ref. [5]. We believe that the mechanism hereby put forward for switching on and off the Kondo resonance may apply to a variety of situations.

Cutting out the bond between Co and the gold surface, and switching on those from lobes to gold, does not qualitatively change these results. Again, as shown in Fig. 2(b), in the absence of lobe-lobe coupling, no Kondo effect shows up. We note that, even though the lobes/Au surface hopping in Fig. 2(b) is much higher than the Co/Au surface hopping used to obtain the results in Fig. 2(a), the width of the resonance is similar and the peak height considerably smaller (compare the red curves in those two figures). These results suggest that providing more ways to

hybridize the atomic orbitals on the magnetic ion to the continuum sates (as may, in principle, occur due to coupling of lobes to the gold surface) may not inevitably be beneficial as far as the Kondo effect is concerned.

The effects of coupling to the leads on the width of the Kondo resonance are illustrated in Fig. 3. All results correspond to the set of parameters we use to describe the distorted molecule: finite coupling between the molecule lobes and no hopping between the Co atomic orbital and the gold surface. In addition, we note that, in view of the experimental information reported in Ref. [5], it seems reasonable that the lobe/Au hopping be greater than that related to the Co/STM tip coupling. Both Figs. 3(a) and 3(b) show the results for fixed coupling of Co to the STM tip and a variable hopping between the lobes and the gold surface. For the lower value of the Co/STM tip hopping [Fig. 3(a)], it is noted that, while the width of the Kondo resonance follows the expected qualitative trend, it depends only weakly on coupling. The effect of quantum interference is demonstrated by the presence of a nonuni-
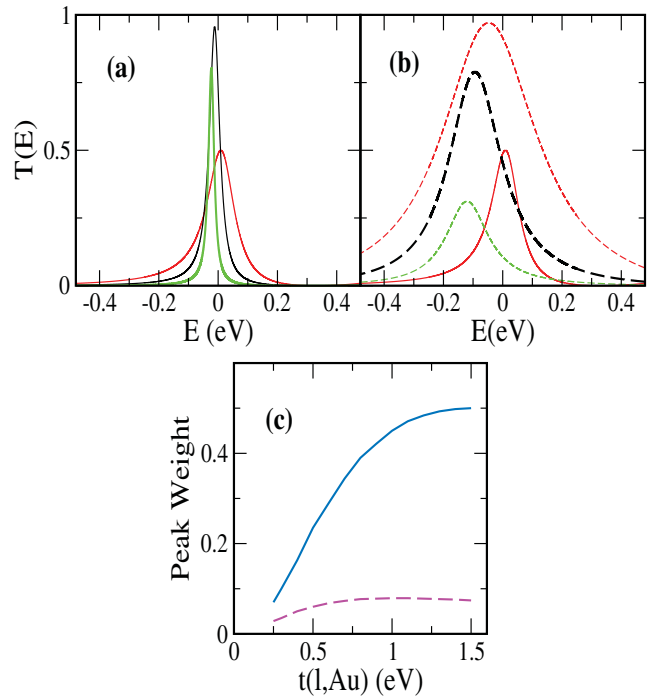

FIG. 3 (color). Transmission T (in units of the conductance quantum) versus energy E (in eV) for the Co uncoupled from the gold surface, i.e., $t_{Co,Au} = 0$, $t_{Co,l} = 1.25$ eV, and $t_{l,l} = 2$ eV. (a) $t_{Co,t} = 0.25$ eV (solid lines); $t_{l,Au} = 0.25$ eV (green line), $t_{l,Au} = 0.5$ eV (red line), and $t_{l,Au} = 1$ eV (black line). (b) $t_{Co,t} = 0.5$ eV (dashed lines); $t_{l,Au} = 0.25$ eV (green line), $t_{l,Au} = 0.5$ eV (red line), and $t_{l,Au} = 1$ eV (black line). One of the curves in (a) has also been plotted in (b) for the sake of comparison. All energies referred to the Fermi energy. (c) Peak weight of the Kondo resonance (in $\mathcal{G}_0$ eV, $\mathcal{G}_0$ being the quantum of conductance) versus the molecule lobes/gold surface hopping, for the two values of $t_{Co,t}$ of (a) and (b) (solid line 0.25 eV and dashed line 0.5 eV).

tary Kondo effect characterized by a conductance smaller than 1 (see also Fig. 2). A far more important effect on the width of the Kondo peak is obtained when the coupling between the Co atomic orbital and the orbital at the apex of the STM tip is increased [see Fig. 3(b)]. Now the same increase in the hopping parameter produces a dramatic broadening of the Kondo resonance. Figure 3(c) illustrates how the weight of the Kondo resonance evolves with the lobe/Au coupling, for the two values of the Co/STM tip hopping $t(Co, t)$ in Figs. 3(a) and 3(b). For the smaller value of $t(Co, t)$ $(= 0.25$ eV), the weight increases only slightly with the lobe/Au coupling, saturating around $0.07 \mathcal{G}_0$ eV for $t(l, Au) \approx 0.7$ eV. Instead, for $t(Co, t) = 0.5$ eV, the peak weight increases steeply, saturating for $t(l, Au) > 1$ eV at around $0.5 \mathcal{G}_0$ eV. These results indicate that both couplings are equally important and that, in order to increase the weight of the Kondo resonance, the STM tip has to get as close as possible to the Co atom. We note that the results in Fig. 3 that more closely resemble the experimental data [5], as far as the peak width is concerned, are those corresponding to the lower value of the $t(Co, t)$ hopping [compare Fig. 3(a) of this work and Fig. 2A of Ref. [5]].

An interesting feature of our results is that, upon switching on the hopping between the molecule lobes, the electron-hole symmetry is broken and the Kondo resonance is no longer peaked at the Fermi level. The peak is displaced either upwards or downwards, depending on the sign of that hopping. As we have assumed that all orbitals are s-like, all hoppings are positive. Interestingly enough, this shifts the Kondo peak below the Fermi energy, in agreement with the experiments [5]. We finally note that, if the calculations of Fig. 3(a) are done for one lobe decoupled from the other three (a situation that may represent the case of Fig. 1E of Ref. [5]), a transmission smaller than $0.1 \mathcal{G}_0$ is obtained. It would be interesting to check experimentally this prediction.

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