Scanning tunneling microscopy of adsorbed molecules on metallic surfaces for nearly localized atomic states

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We consider a Hubbard-Anderson model which describes localized orbitals in five different sites hybridized both among themselves and with a continuum of extended states. A square planar geometry with an atom at the center is used to represent TBrPP-Co molecules. When the renormalized effective hopping between sites is small compared with a Kondo energy scale determined by the site-continuum hybridization, the system can be described as a set of independent Kondo resonances, rather than molecular states. We study the crossover between both regimes and analyze the spectral density of conduction electrons as a function of position. The results are in qualitative agreement with measurements of the differential conductance in a system with TBrPP-Co molecules adsorbed on a Cu(111) surface.

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I. INTRODUCTION

The transport of electrons through molecules is relevant in many branches of science and important for potential applications in electronic devices\textsuperscript{1–3} and molecular spintronics\textsuperscript{4–12}. On the other hand, the study of many-body phenomena in nanoscale systems has attracted much attention in recent years. In particular the Kondo effect, which arises when a magnetic impurity interacts with a continuum of extended states, has been observed in a variety of nanoscopic systems\textsuperscript{4–10}. Scanning tunneling spectroscopy (STS) has made it possible to probe the local density of states and Fano antiresonances have been observed for several magnetic systems on metal surfaces\textsuperscript{11–17}. These antiresonances observed in the differential conductance, reflect a dip in the spectral density of conduction states near the Fermi level caused by the Kondo effect\textsuperscript{11}. The half width of the dip is given by a characteristic energy scale, the Kondo temperature \( T_K \). Furthermore, corrals built on the (111) surface of noble metals or Cu have been used to project the spectral features of the Fano-Kondo antiresonance (FKA) to remote places\textsuperscript{7,11}. The observed Fano line shapes for one magnetic impurity on these surfaces have been reproduced by many-body calculations\textsuperscript{11–17}. For corrals, predictions of the variation of \( T_K \) with the position of the impurity were made\textsuperscript{11,15}.

When several magnetic impurities interacting between them are present, the theoretical analysis is more difficult. For Cr trimers on the Au(111) surface, controversial results were obtained\textsuperscript{12–22} which were in contradiction with at least part of the puzzling observed dependence of \( T_K \) with geometry\textsuperscript{2}. More recently, a qualitative explanation was provided using a Hubbard-Anderson model (HAM) described in Section II\textsuperscript{23}. Recent STS results for TBrPP-Co \textsuperscript{5, 10, 15, 20} molecules adsorbed on a Cu(111) surface are also surprising\textsuperscript{2}. The width of the FKA depends on the position of the microscope tip along the molecule, varying within a factor two among different positions\textsuperscript{24}. Quite generally, for any system in which only one atom is highly correlated (say Co), if the spectral density of the system without this magnetic impurity is featureless around the Fermi energy \( \epsilon_F \), the STS near \( \epsilon_F \) is dominated by the Green’s function of the impurity and the width of the FKA is the same everywhere. Only the intensity varies with position (Eqs. (11) to (14) of Ref\textsuperscript{11}). Experimentally, for a system with one impurity at the focus of an elliptical quantum corral, the observed FKA is similar at both foci and only the amplitude differs\textsuperscript{15}. In systems with several magnetic atoms with a sizable hopping between them, one can define an effective Hamiltonian in terms of molecular extended orbitals and if Kondo physics is present, again the energy dependence of STS near \( \epsilon_F \) is essentially independent of position\textsuperscript{19–23,25}. This results are confirmed by our calculations on the HAM.

In Ref\textsuperscript{5}, the experimental results were interpreted in terms of a single impurity Kondo model, with a position dependent exchange interaction which increases linearly with the local spin density. This is strictly valid only in the limit in which the system can be considered as a continuum of independent magnetic impurities. This situation resembles the Kondo lattice in the limit in which \( T_K \) is larger than the effective intersite exchange \textsuperscript{19}. However, in the molecular system, the competing parameter is the magnitude of the intersite hoppings \( t \) (rather than \( t \)), neglected in the simplified analysis of Ref\textsuperscript{5}. Thus, one expects a crossover between a regime with independent “impurities” for small \( t \) to a collective behavior for large \( t \). In the limit of an infinite molecule disconnected to the metal, one expects that this crossover turns to a Mott localization transition\textsuperscript{27}.

In this work, we describe the system with a HAM in...
which each magnetic site is hybridized with a continuum of extended states and in addition there is a hopping between magnetic sites. We obtain that for reasonable parameters (most of them used before), the essential features of the experiment of Ref.\textsuperscript{22} are reproduced. Moreover we study the above mentioned crossover between localized and extended behavior.

In Section II, we describe the model. The STS spectra, comparison with experiment, and the crossover from the regime of nearly isolated impurities to collective molecular behavior (either with one Kondo peak or with split Kondo peaks) is presented in Section III. Section IV contains a short summary and discussion.

II. MODEL, APPROXIMATIONS AND PARAMETERS

The Hamiltonian can be written as\textsuperscript{23}

\[
H = H_{\text{mol}} + H_{\text{met}} + H_V,
\]

\[
H_{\text{mol}} = \sum_{i\sigma} \epsilon_i d_{i\sigma}^\dagger d_{i\sigma} + U d_{i\uparrow}^\dagger d_{i\uparrow} d_{i\downarrow}^\dagger d_{i\downarrow} - \sum_{\langle ij \rangle \sigma} t_{ij} (d_{i\sigma}^\dagger d_{j\sigma} + \text{H.c.}),
\]

\[
H_{\text{met}} = \sum_{k\sigma} \epsilon_k c_k^\dagger c_k + H.c.,
\]

\[
H_V = \sum_{k\sigma} (V_j e^{ik \cdot R_j} d_{jk\sigma}^\dagger c_k + \text{H.c.}).
\] 

In this treatment, the creation operators for localized electrons are represented as a product of a boson and a new fermion as \( d_{i\sigma} = b_i f_{i\sigma}^\dagger \), with the constraint \( b_i^\dagger b_i + \sum_{\sigma} f_{i\sigma}^\dagger f_{i\sigma} = 1 \). The approximation consists in replacing the boson operators \( b_i^\dagger \), \( b_i \) by their expectation values \( \langle b_i^\dagger \rangle = \langle b_i \rangle^* \) obtained minimizing the free energy. This approximation reproduces correctly the spectral density near the Fermi level, and the exponential dependence of \( T_K \) with the parameters in the Kondo regime.

As in a previous work\textsuperscript{23}, we have approximated the angular average of \( \sum_k \exp[i \mathbf{k} \cdot (\mathbf{R}_i - \mathbf{R}_j)] \), by its value at the Fermi surface \( \beta_{ij} \). For an isotropic three-dimensional (3D) band \( \beta_{ij} = \sin(k_F r_{ij})/(k_F r_{ij}) \), where \( k_F \) is the Fermi wave vector and \( r_{ij} = |\mathbf{R}_i - \mathbf{R}_j| \). We take \( k_F R = 3.8 \), where \( R \) is the distance between the Co site at the center and any lobe at the corners\textsuperscript{23}. We also assume for simplicity a constant density of conduction states \( \rho = 0.1/\text{eV} \). The results practically do not change for other values of \( \rho \) if the hybridizations \( V_j \) are scaled keeping \( \rho V_j^2 \) constant. Following Ref\textsuperscript{29}, we take \( t_0 = 0.15 \text{ eV} \) for the Co-lobe hopping and \( t_1 = 0.2 \text{ eV} \) for the lobe-lobe one. From experiment\textsuperscript{1}, the first occupied orbital is located 0.7 eV below the Fermi level \( \epsilon_F \) and is assigned to the 3d\textit{z} orbital of the Co atom. Choosing the origin of energies at \( \epsilon_F = 0 \), then \( E_{\text{Co}} = -0.7 \text{ eV} \) and the on-site energy for the lobes should be smaller. We take \( E_l = -3 \text{ eV} \). The hybridizations \( V_{\text{Co}} = 0.68 \text{ eV} \) and \( V_l = 1.68 \text{ eV} \) were chosen to reproduce approximately the observed width of the resonances when the tip is on a specific site.

III. RESULTS FOR THE TUNNELING SPECTRA

The resulting values of the expectation values of the boson operators \( \langle b_{\text{Co}} \rangle = 0.18 \) and \( \langle b_l \rangle = 0.13 \) indicate a strong renormalization of the quasiparticles at the Fermi energy. In particular, the effective \( t_0 \) is renormalized to \( t_0 \langle b_{\text{Co}} \rangle \langle b_{\text{Co}} \rangle = 3.6 \text{ meV} \). This is smaller than the reported \( T_K \). This means that the system is in fact in a regime of rather independent “impurities” with two different \( T_K \). While this picture is useful to gain physical insight, the intersite hopping and the interactions between sites through the conduction band are still important and affect the width and shape of the STS features, as explained below.

The fact that the renormalization is stronger for the lobes \( \langle b_l \rangle \) is consistent with results of \textit{ab initio} calculations which find a larger spin density at the bromophenyl units\textsuperscript{22}.

For weak coupling of the STM tip to the system, the measured differential conductance \( dI/dV \) is proportional to the density of states of a mixed operator \( h_\sigma \) which depends on the position \( \mathbf{R} \) of the tip. For a voltage difference \( V \) between the metal and the tip one has\textsuperscript{11,17}. 

\[
\rho(E) \approx \frac{1}{2\pi} \frac{|\langle h_\uparrow | \mathbf{R} \rangle \langle h_\uparrow | - \langle h_\downarrow | \mathbf{R} \rangle \langle h_\downarrow | \rangle^2}{E^2 - \epsilon_0^2}.
\]
To result in a line shape that agrees with experiment

\[ R \]

function of position along a path between Co and a lobe
ties on Cu or noble metal surfaces

is dominated by the conduction density of states, which
dI/dV

any case, these values are small indicating that
SBMFA)

particles at finite energies (not taken into account in the
this structure disappears if a broadening of the quasi-
185 K, 212 K in Fig. 3 (b) of Ref. 5). In any case,
leads to

\[ T \]

the lobes is shown in Fig. 1. The values of

\[ q \]

of voltage when the tip is on Co (dashed line) or on a lobe
(full line) for \( q_{Co} = 0.136 \), \( q_l = 0.114 \).

where \( q_j(R) \) is proportional to the hopping between the
tip and the site \( j \) and controls the line shape and its asymmetry. It is only significant when the tip is
right above the site \( j \). Then, here we assume \( q_j(R) = q_j \delta(R|R_j|) \), where the superscript on the position
vectors denote the component parallel to the Cu(111)
surface.

The resulting \( dI/dV \) when the tip is either on Co or on
the lobes is shown in Fig. 1. The values of \( q_j \) were chosen
to result in a line shape that agrees with experiment. In
any case, these values are small indicating that \( dI/dV \)
is dominated by the conduction density of states, which
presents a Fano-Kondo antiresonance, as for Co impurities
on Cu or noble metal surfaces. A fit of the Kondo
temperature using the simple expression given in Ref. 6
leads to \( T_K \) = 112 K on Co and \( T_K \) = 208 K on the
lobes. The main features of the experiment are repro-
duced. When the tip is on the lobes, we obtain a structure
near -10 meV. While the experimental results seem rather
noisy, a similar structure seems to be present only
in some of the observed spectra (for example \( T = 109 \) K,
185 K, 212 K in Fig. 3 (b) of Ref. 5). In any case,
this structure disappears if a broadening of the quasi-
particles at finite energies (not taken into account in the
SBMFA) or slightly smaller \( t_{ij} \) or larger \( V_i \) are used.

In Fig. 2 we show the local conduction density of
states \( \rho_h(eV) \) for \( q_j = 0 \) (proportional to \( dI/dV \)) as a
function of position along a path between Co and a lobe
\( R = \alpha R_l + (1 - \alpha) R_{Co} \). Starting at the Co site (\( \alpha = 0 \)),
the dip broadens and loses intensity. The intensity is
recovered at the position of the lobe while the peak con-
tinues to broaden. The space dependence of the depth
of the structure might be expected from what we know
from the one-impurity case, where the amplitude of the
dip decays as \( 1/d^2 \) with the distance to the impurity
\( d \) for a 3D (2D) conduction band. Therefore, the amplitude of the dip has a smaller variation if a 2D band
or smaller \( k_F \) is assumed. In particular, for \( k_F = 0 \),
the dependence of the conduction density of states near \( \epsilon_F \)
with position disappears.

To study the crossover to the regime in which molecular
states dominate the physics, we have increased the
Co-lobe hopping \( t_0 \). The result for \( dI/dV \) when the tip
is on top of the Co atom is shown in Fig. 3. For \( t_0 = 0 \) a
fit of the curve leads to \( T_K = 33 \) K. This agrees with the
fact that for an isolated Co atom on a Cu(111) surface,
FIG. 4. (Color online) Differential conductance as a function of voltage for \( q_j = 0 \) and different Fermi wave vectors with the tip on top of the Co atom.

The observed \( T_K \) (Ref.2) is about a factor 1/2 of that in the molecule (in our case however, there is a remaining interaction with the lobes through the bulk states unless \( k_F \to \infty \)). As \( t_0 \) increases, the peak near the Fermi energy splits in two for large enough \( t_0 \sim 0.2 \) eV, and the splitting increases with \( t_0 \). The physics of this splitting is also present in previous experimental and theoretical\(^{33,34} \) studies of two quantum dots, and for impurities with hopping to discrete extended states (as surface states inside a corral with hard walls\(^{13,14} \)). This structure is also apparent when the tip is on the lobes (not shown), but an additional structure at \( \epsilon_F \) remains due to states that do not mix with the Co ones for symmetry reasons. This structure tends to split when the molecule is distorted to a rectangular shape. However, the effect of this distortion is not dramatic if the other parameters are kept constant. Nevertheless, it is known that this distortion alters the Co-surface distance and as a consequence \( V_{Co} \) should be modified\(^2\).

For large \( t_0 \) and positive \( E_i \), we have verified that there is a Kondo effect with a molecular state, and \( dI/dV \) has a similar shape near the Fermi level for any position of the tip, with the same \( T_K \) within less than 1%. This situation is analogous to the physics of quantum corrals\(^{7,11,13,14} \) and Cr trimers on Au(111)\(^{19-22} \).

The value of \( k_F \) affects the interference effects mediated by the conduction band, between different sites of the molecule. For \( k_F \to 0 \), all conduction states near the Fermi energy mix with the same molecular orbital regardless of its direction resulting in a maximum interference, For \( k_F \to \infty \) the interference occurs only through the hoppings \( t_j \). In Fig. 4 we show how the conduction electron density of states at the Co site changes with \( k_F \). For the smaller values investigated, there is a splitting of the Fano-Kondo antiresonance due to an effective mixing of the molecular states mediated by the band.

IV. SUMMARY AND DISCUSSION

For a molecule with strongly correlated states near the Fermi energy on top of a metallic surface, we have studied the competition between interatomic hopping and the hopping of these atoms with the continuum of extended metallic states. We show that strong correlations can lead to the rather unexpected situation in which the hopping to the metallic substrate dominates, leading to a physics characterized by different Kondo impurities as a first approximation. The resulting \( dI/dV \) and its dependence with position agrees with recent measurements on TBrPP-Co molecules adsorbed on a Cu(111) surface. We have also analyzed the crossover to the most usual regime in which molecular extended states dominate the physics. Our approximation (slave bosons in the mean-field approximation) is known to describe qualitatively the physics near the Fermi level in both limits\(^{11,25,31,38} \).

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