

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

M. Romero¹ and A. A. Aligia²

¹*Instituto de Desarrollo Tecnológico para la Industria Química (INTEC-CONICET-UNL) Güemes 3450, CC91, (S3000GLN), Santa Fé, Argentina*

²*Centro Atómico Bariloche and Instituto Balseiro, Comisión Nacional de Energía Atómica, 8400 Bariloche, Argentina*

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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 devices¹⁻³ and molecular spintronics^{4,5}. 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 systems⁴⁻¹⁰. 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 surfaces⁴⁻⁹. 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 effect¹¹. 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^{7,11}. The observed Fano line shapes for one magnetic impurity on these surfaces have been reproduced by many-body calculations¹¹⁻¹⁷. For corrals, predictions of the variation of T_K with the position of the impurity were made^{11,18}.

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 obtained¹⁹⁻²² which were in contradiction with at least part of the puzzling observed dependence of T_K with geometry⁹. More recently, a qualitative explanation was provided using a Hubbard-Anderson model (HAM) described in Section II²³.

Recent STS results for TBrPP-Co [5, 10, 15, 20-Tetrakis-(4-bromophenyl)-porphyrin-cobalt] molecules

adsorbed on a Cu(111) surface are also surprising⁵. The width of the FKA depends on the *position* of the microscope tip along the molecule, varying within a factor two among different positions²⁴. 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 ϵ_F , the STS near ϵ_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.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 differs⁷. 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 ϵ_F is essentially independent of position^{19-23,25}. This results are confirmed by our calculations on the HAM.

In Ref.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 I ²⁶. However, in the molecular system, the competing parameter is the magnitude of the intersite hoppings t (rather than I), neglected in the simplified analysis of Ref.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 transition²⁷.

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.⁵ 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 as²³

$$\begin{aligned}
 H &= H_{\text{mol}} + H_{\text{met}} + H_V, \\
 H_{\text{mol}} &= \sum_{i\sigma} E_i d_{i\sigma}^\dagger d_{i\sigma} + U_i d_{i\uparrow}^\dagger d_{i\uparrow} d_{i\downarrow}^\dagger d_{i\downarrow} \\
 &\quad - \sum_{\langle ij \rangle \sigma} t_{ij} (d_{i\sigma}^\dagger d_{j\sigma} + \text{H.c.}), \\
 H_{\text{met}} &= \sum_{\mathbf{k}\sigma} \epsilon_{\mathbf{k}} c_{\mathbf{k}\sigma}^\dagger c_{\mathbf{k}\sigma}, \\
 H_V &= \sum_{\mathbf{k}j\sigma} (V_j e^{i\mathbf{k}\cdot\mathbf{R}_j} d_{j\sigma}^\dagger c_{\mathbf{k}\sigma} + \text{H.c.}). \quad (1)
 \end{aligned}$$

H_{mol} is a Hubbard model that describes the isolated molecule. Here $d_{i\sigma}^\dagger$ creates an electron at site i lying at \mathbf{R}_i with spin σ . H_{met} corresponds to the conduction band of the metallic substrate, and H_V is the hybridization between the atoms of the molecule and the extended states of the metal, assuming that the wave functions of the latter are plane waves¹¹. Following earlier work^{28,29} we represent the molecule with 5 sites, one at the center representing the Co atom and four at the corners of a square representing bromophenyl lobes. The model has C_{4v} symmetry. We assume that the tip of the scanning tunneling microscope (STM) is far enough from the system in such a way that it does not alter its electronic structure.

This model is similar to the one proposed by Chiappe and Verges for similar molecules^{28,29}. The main difference is that we consider that not only Co, but all sites are highly correlated, as suggested by recent *ab initio* calculations⁵. In addition H_V is somewhat more realistic and contains phase factors $\exp(i\mathbf{k}\cdot\mathbf{R}_j)$, which were essential in the description of Cr trimers on Au(111)²³. We also take $U_i \rightarrow +\infty$. Since the U_i are expected to be of several eV, the t_{ij} were proposed of the order of 0.2 eV, and the resonant level widths $\pi\rho V_j^2$ are smaller than 1 eV (see below), this assumption is not a serious one, and on the other hand allows us to use the slave-boson mean-field approximation (SBMFA) introduced by Coleman^{25,30,31}.

In this treatment, the creation operators for localized electrons are represented as a product of a boson and a new fermion as $d_{i\sigma}^\dagger = b_i f_{i\sigma}^\dagger$, 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 are replaced 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 work²³, we have approximated the angular average of $\sum_{\mathbf{k}} \exp[i\mathbf{k}\cdot(\mathbf{R}_i - \mathbf{R}_j)]$, by its value at the Fermi surface β_{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 corners²³. 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 ρ if the hybridizations V_j are scaled keeping ρV_j^2 constant. Following Ref.²⁹, we take $t_0 = 0.15$ eV for the Co-lobe hopping and $t_1 = 0.2$ eV for the lobe-lobe one. From experiment⁴, the first occupied orbital is located 0.7 eV below the Fermi level ϵ_F and is assigned to the $3d_{z^2}$ orbital of the Co atom. Choosing the origin of energies at $\epsilon_F = 0$, then $E_{\text{Co}} = -0.7$ eV and the on-site energy for the lobes should be smaller. We take $E_l = -3$ eV. The hybridizations $V_{\text{Co}} = 0.68$ eV and $V_l = 1.68$ 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 $t_0 \langle b_{\text{Co}} \rangle \langle b_{\text{Co}} \rangle = 3.6$ 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 ($\langle b_l \rangle < \langle b_{\text{Co}} \rangle$) is consistent with results of *ab initio* calculations which find a larger spin density at the bromophenyl units⁵.

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_σ which depends on the position \mathbf{R} of the tip. For a voltage difference V between the metal and the tip one has^{11,17}

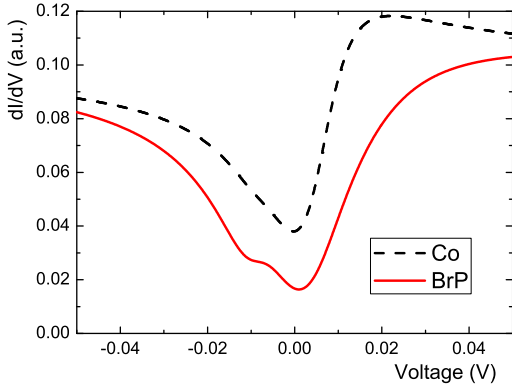


FIG. 1. (Color online) Differential conductance as a function of voltage when the tip is on Co (dashed line) or on a lobe (full line) for $q_{Co} = 0.136$, $q_l = 0.114$.

$$\begin{aligned}
 dI/dV &\sim \rho_h(eV), \\
 \rho_h(\omega) &= \frac{i}{2\pi} (\langle \langle h_\sigma; h_\sigma^\dagger \rangle \rangle_{\omega+i\epsilon} - \langle \langle h_\sigma; h_\sigma^\dagger \rangle \rangle_{\omega-i\epsilon}), \\
 h_\sigma(\mathbf{R}) &= \sum_{\mathbf{k}} e^{i\mathbf{k}\cdot\mathbf{R}_j} c_{\mathbf{k}\sigma} + \sum_j q_j(\mathbf{R}) d_{j\sigma}, \quad (2)
 \end{aligned}$$

where $q_j(\mathbf{R})$ is proportional to the hopping between the tip and the site j and controls the line shape and its asymmetry^{11,17}. It is only significant when the tip is right above the site j . Then, here we assume $q_j(\mathbf{R}) = q_j \delta(\mathbf{R}^{\parallel} - \mathbf{R}_j^{\parallel})$, 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 experiment⁵. 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 surfaces¹¹. A fit of the Kondo temperature using the simple expression given in Ref.⁸ leads to $T_K = 112$ K on Co and $T_K = 208$ K on the lobes. The main features of the experiment are reproduced. 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)³², 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 $\mathbf{R} = \alpha \mathbf{R}_l + (1 - \alpha) \mathbf{R}_{Co}$. Starting at the Co site ($\alpha = 0$),

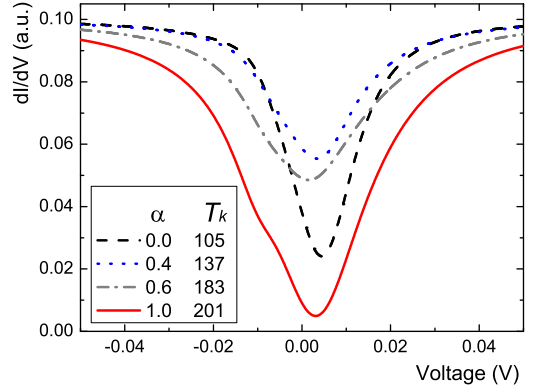


FIG. 2. (Color online) Differential conductance as a function of voltage for $q_j = 0$ and different positions of the tip along the Co-lobe path.

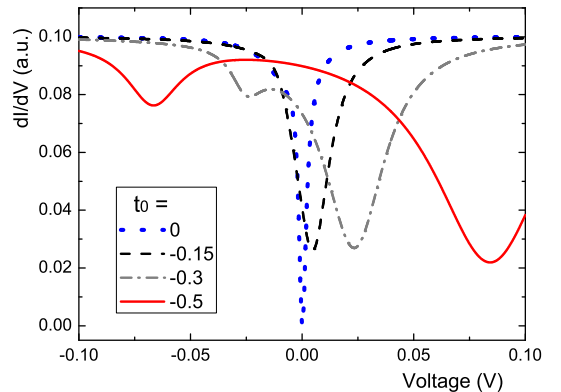


FIG. 3. (Color online) Differential conductance as a function of voltage for $q_j = 0$ and different Co-lobe hopping t_0 with the tip on top of the Co atom.

the dip broadens and loses intensity. The intensity is recovered at the position of the lobe while the peak continues 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 $1/d^2$ ($1/d$) with the distance to the impurity d for a 3D (2D) conduction band⁸. 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 ϵ_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,

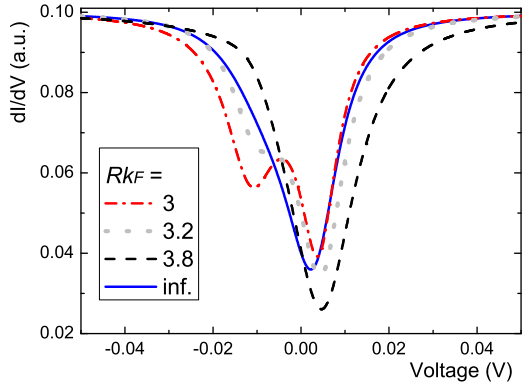


FIG. 4. (Color online) Differential conductance as a function of voltage for $q_j = 0$ and different Fermi wave vectors with the tip on top of the Co atom.

the observed T_K (Ref.⁸) 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 $k_F \rightarrow \infty$). 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^{33,34} and theoretical^{31,35–38} 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 ϵ_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 modified⁴.

For large t_0 and positive E_l , 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)^{9,19–23}.

The value of k_F affects the interference effects mediated by the conduction band, between different sites of the molecule. For $k_F \rightarrow 0$, all conduction states near the Fermi energy mix with the same molecular orbital regardless of its direction resulting in a maximum interference. For $k_F \rightarrow \infty$ 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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