Low-energy physics for an iron phthalocyanine molecule on Au(111)

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The system of an iron phthalocyanine molecule on the Au(111) surface, has been studied recently due to its peculiar properties. In particular, several surprising results of scanning tunneling spectroscopy changing the position of the molecule and applying magnetic field can be explained by the non-Landau Fermi liquid state of a 2-channel spin-1 Kondo model with anisotropy. The localized orbitals near the Fermi level are three, one of symmetry $z^2$ and two (nearly) degenerate $\pi$ orbitals of symmetry $xy$ and $yz$. Previous studies using the numerical renormalization group neglected one of these orbitals to render the problem tractable. Here we investigate, using a slave-boson mean-field approximation, if the splitting $S$ between $\pi$ orbitals caused by spin-orbit coupling (SOC) justifies this approximation. We obtain an abrupt transition from a 3-band regime to a 2-band one at a value of $S$ which is about 1/3 of the atomic SOC for Fe, justifying the 2-band model for the system.

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I. INTRODUCTION

The Kondo effect, found first in metals containing magnetic impurities, is a paradigmatic example of a strongly correlated system in condensed matter physics. In the simplest form, it arises when the free electrons of a metallic host screen completely the magnetic moment of an impurity (under- and over-screening are not discussed here). The high resolution and atomic control of the scanning tunneling microscope (STM) allow experimentalists to deposit magnetic molecules on metallic surfaces leading to a large class of realizations of Kondo phenomena in which the current can be controlled by different external parameters. This subject is of interest for its potential use in new electronic devices. The differential conductance $G(V) = dI/dV$ as a function of the sample bias $V$, where $I$ is the current flowing through the STM provides information of the low-energy electronic structure of the system. This technique is called scanning tunneling spectroscopy.

This spectroscopy for FePc on Au(111) at low temperature shows several striking features. $G(V)$ around $V = 0$ shows a broad peak of half width $\sim 20$ meV and mounted on it a dip nearly two orders of magnitude narrower. Application of a magnetic field $B$ transforms the dip into a peak. A similar behavior is observed for MnPc on Au(111). When the molecule is raised from the surface, weakening the Kondo effect, the dip broadens. All these features have been recently explained in a consistent fashion by a 2-channel spin-1 Kondo model with anisotropy. This is an extension to non-degenerate channels of a model for Ni impurities in a Au chain.

For $B = 0$, these models display a topological quantum phase transition between an ordinary Fermi liquid with a peak in the spectral density at the Fermi energy and a non-Landau Fermi liquid with a pseudogap at the Fermi level, topologically characterized by a non-trivial Friedel sum rule with non-zero Luttinger integrals. The results of Ref. indicate that FePc on Au(111) is near the topological transition at the non-Landau side of it. Pressing the molecule against the substrate by the STM tip should induce the transition.

An abrupt transition from a peak to a dip in the spectral density has been found previously in other two-orbitals and two-impurities Anderson models. In the latter, the transition was also ascribed as due to a jump in Luttinger integrals.

LDA+U calculations indicate that the configuration of Fe in the system is $(d_{xy})^2(d_{z^2})^3(d_{x^2-y^2})^3$. Therefore the partially filled orbitals can be described as one hole with $z^2$ symmetry and one hole with $\pi$ ($xz$ or $yz$) symmetry. They are coupled forming a spin $S = 1$ by the Hund rules. If this configuration is hybridized with the different excited configurations with one hole, one has a 3-channel Anderson model, which has been studied by Fernández et al. using a slave-boson mean-field approximation (SBMFA). This model is justified in more detail in Sec. II of this work. In the limit of small hybridization compared with the difference between the energies of both configurations, the model is equivalent to a 3-channel $S = 1$ Kondo model, which is more involved than the 2-channel Kondo model used to describe the system as a non-Landau Fermi liquid. The 2-channel Kondo model has been chosen because the 3-channel case is very difficult to treat by the numerical renormalization group due to the huge increase in the Hilbert space at each iteration, while the essence of the physics is expected to be captured by the 2-channel model.

However, Fe has a spin-orbit coupling (SOC) $\sim 76$ meV disregarded before. In first order, the SOC splits the $\pi$ states by this amount and leaves the $z^2$ orbitals unchanged. This splitting might justify the 2-channel model, supporting the quantitative validity of previous results. Naively, one would think that comparing the magnitude of the SOC with another energy scale might solve the issue. However, this is not so simple. Note that for degenerate channels in the 2-channel spin-1 Kondo model with easy plane anisotropy $DS^2_z$, the topological

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quantum phase transition takes place for \( D = D_c \sim 2.5T_K \), where \( T_K \) is the Kondo temperature.\(^{22}\) However for inequivalent channels, there is no simple relation between the critical anisotropy \( D_c \) and the Kondo temperatures for both channels.\(^{21}\)

In this work we study the 3-channel Anderson model including a splitting \( S \) between the \( \pi \) orbitals. Due to the complexity of the problem, we treat it in a SBMFA described below. Since the approximation is unable to describe the non-Landau Fermi liquid, we neglect the anisotropy \( D \). We modify previous treatments of the SBMFA in such a way that the correct Kondo temperature is reproduced in known limits. We note that alternative methods, like the non-crossing approximation for this two-channel case (see appendix of Ref. \(^{23}\)) or equations of motion\(^{27}\) do not reproduce the correct Kondo temperature.

The results indicate that the excited \( \pi \) orbital can be neglected for \( S > S_c \), where the critical value \( S_c \) is about a third of the SOC for Fe, supporting the validity of the 2-channel model.

This work is organized as follows. In section \(^{[1]}\) we describe the 3-band Anderson model used for this study and justify it in detail. In section \(^{[III]}\) we explain the SBMFA used to solve the model in the Kondo or integer valence limit. The results are presented in Section \(^{[IV]}\) and Section \(^{[V]}\) contains a summary and a discussion.

II. MODEL

We describe the system by an Anderson model containing two magnetic configurations. This implies that we take the limit of infinite Coulomb repulsion. This approximation does not affect the essential physics at low energies, including the Kondo effect. The neglected configurations might affect slightly the parameters of the model (discussed at the beginning of Section \(^{[IV]}\)), but in any case they are adjusted form low-energy experimental results.

The ground state corresponds essentially to the 3 \( d \) configuration of Fe with one hole in the 3 \( d_{z^2} \) orbital and another hole in a \( \pi \) orbital (3 \( d_{xz} \) or 3 \( d_{yz} \)) forming a triplet. The \( d_{xy} \) orbitals are occupied by both spins and the \( d_{x^2-y^2} \) are empty. It is known that to have a Kondo effect, one needs either spin degeneracy or orbital degeneracy in the ground-state configuration of the magnetic "impurity" (the FePc molecule in our case). Therefore, the completely filled \( d_{xy} \) orbitals and the empty \( d_{x^2-y^2} \) orbitals might affect slightly the parameters of the low-energy effective model, but not the form of it.

The three relevant 3d orbitals of Fe have some admixture with linear combinations of orbitals of neighboring \( N \) atoms, forming molecular states of the same symmetry\(^{23}\). In turn, these states also hybridize with surface and conduction bands of the same symmetry. In particular the surface band can be accurately described by a free electron band with plane waves \( \exp[i(k_x x + k_y y)] \). Neglecting the discrete nature of the substrate, the symmetry of the system is \( C_{4v} \). The molecular orbital with symmetry \( z^2 \) belongs to the irreducible representation \( A_2 \) of \( C_{4v} \) and hybridizes only with surface states (combination of plane waves) of the form \( \cos(k_x x) \cos(k_y y) \) which also belong to \( A_1 \). Similarly the molecular orbital with \( xz \) symmetry (a component of the two-dimensional irreducible representation \( E \)) hybridizes only with surface states of the form \( \sin(k_x x) \cos(k_y y) \), and for the \( xy \) symmetry the corresponding conduction states are \( \cos(k_x x) \sin(k_y y) \). These arguments can be extended to the bulk conduction states.

The above arguments justify the 3-channel model studied previously by Fernández et al.\(^{27}\). However, here assume that the \( \pi \) orbitals are split by an energy \( S \). We call \( a (b) \) the linear combination of \( \pi \) holes with lower (larger) energy. The other configuration, the 3 \( d^7 \) one, has a hole in either the 3 \( d_{xz} \) orbital or in a \( \pi \) orbital. We denote the two spin triplets by \( |a M \rangle \) and \( |b M \rangle \), depending on which \( \pi \) orbital is occupied by a hole, in addition to the \( z^2 \) one, where \( M \) is the spin-1 projection. Similarly, the three spin doublets are represented by \( |z^2 \sigma \rangle, |a \sigma \rangle, \) and \( |b \sigma \rangle \), where \( \sigma \) is the spin-1/2 projection. Both configurations are mixed via hybridization with the conduction bands. The model is an extension to finite \( S \) of that considered previously by Fernández et al.\(^{24}\).

The Hamiltonian is

\[
H = H_{\text{mol}} + H_{\text{band}} + H_{\text{mix}},
\]

\[
H_{\text{mol}} = \sum_{\sigma} E_z |z^2 \sigma \rangle \langle z^2 \sigma | + \sum_{\pi \sigma} E_{\pi \sigma} |\pi \sigma \rangle \langle \pi \sigma | + \sum_{\pi M} (E_{\pi} + E_d) |\pi M \rangle \langle \pi M |
\]

\[
H_{\text{band}} = \sum_{k \nu \sigma} t_{k \nu \sigma} c_{k \nu \sigma}^\dagger c_{k \nu \sigma}
\]

\[
H_{\text{mix}} = \sum_{\pi k} \sum_{\sigma \sigma' M} t_{\pi} \langle \frac{1}{2} 1 \frac{1}{2} \sigma \sigma' |1 M \rangle \left( c_{k \pi \sigma}^\dagger |z^2 \sigma' \rangle \langle \pi M | + H.c. \right)
\]

\[
- \sum_{\pi k} \sum_{\sigma \sigma' M} t_{\pi} \langle \frac{1}{2} 1 \frac{1}{2} \sigma \sigma' |1 M \rangle \left( c_{k \pi \sigma}^\dagger |\pi \sigma' \rangle \langle \pi M | + H.c. \right),
\]

(1)
where \( H_{\text{band}} \) represent the molecular states, with \( E_\pi = E_a \) for \( \pi = a, E_b = E_a + S, \) and \( E_d < 0 \) is the difference between the energies of the lowest lying states of both configurations. \( H_{\text{band}} \) represents the three conduction bands, with the same symmetry as the corresponding molecular states (\( \nu = \frac{1}{2}, a \) or \( b \)). \( H_{\text{mix}} \) describes the mixing Hamiltonian (also called hybridization) in terms of Clebsch-Gordan coefficients and two hopping amplitudes (we assume \( t_a = t_b \)).

In general, the origin of the splitting \( S \) could be either a symmetry breaking which renders the orbital with symmetries \( xz \) and \( yz \) inequivalent or SOC or both. If the origin is the SOC, the states \( |\pi\sigma\rangle \) with one hole in the \( \pi \) orbitals are (except for an irrelevant phase)

\[
|a \uparrow \rangle = \frac{|x\uparrow \rangle + i|y\uparrow \rangle}{\sqrt{2}} , |a \downarrow \rangle = \frac{|x\downarrow \rangle - i|y\downarrow \rangle}{\sqrt{2}},
\]

and similarly for the triplet states \( |\pi M\rangle \) combining with a \( z^2 \) hole to build a spin triplet.

In the limit in which only one multiplet is relevant for each configuration (very large \( S \) and \( |E_a - E_\nu| \) the model has been solved exactly by the Bethe ansatz\textsuperscript{35}. We use this result to refine the SBMFA.

### III. Slave Bosons in Mean-Field Approximation (SBMFA)

We solve the model using a slave-boson treatment similar to that of Kotliar and Ruckenstein (KR\textsuperscript{36}) in the mean-field approximation. This treatment has severe limitations when a magnetic field in an arbitrary direction is applied or when finite Coulomb interactions in the multiorbital case are considered. In these cases the rotationally invariant slave-boson formalism is more convenient\textsuperscript{37}. The disadvantage of this method is that it introduces more bosonic variables and determining them minimizing the energy becomes more involved. Fortunately in our case in which infinite Coulomb repulsion is implicitly assumed and no magnetic field is applied, the KR formalism can be applied.

The KR approach consists of introducing bosonic operators for each of the states in the fermionic description. In this representation, in our case, we can write the doublets using bosons \( s_{\nu \sigma}^\dagger \) which correspond to the singly occupied states

\[
|\pi \sigma \rangle \leftrightarrow f_{\pi \sigma}^\dagger s_{\pi \sigma}^\dagger |0\rangle
\]

\[
|z^2 \sigma \rangle \leftrightarrow f_{\sigma}^\dagger s_{\sigma}^\dagger |0\rangle,
\]

where \( f_{\pi \sigma}^\dagger (f_{\sigma}^\dagger) \) is a fermionic operator that creates a localized hole with \( \pi \) (\( z^2 \)) symmetry. The triplets are represented using bosons \( d_{\pi M}^\dagger \) for the doubly occupied states as follows

\[
|\pi 1 \rangle \leftrightarrow d_{\pi 1}^\dagger f_{\pi 1}^\dagger |0\rangle
\]

\[
|\pi 0 \rangle \leftrightarrow \frac{1}{\sqrt{2}} d_{\pi 0}^\dagger \left(f_{\pi 1}^\dagger f_{\pi 1}^\dagger + f_{\pi 1}^\dagger f_{\pi 1}^\dagger \right) |0\rangle
\]

\[
|\pi - 1 \rangle \leftrightarrow d_{\pi -1}^\dagger f_{\pi -1}^\dagger f_{\pi -1}^\dagger |0\rangle,
\]

The Hamiltonian in this representation takes the form

\[
H = E_a \sum_{\pi \sigma} s_{\pi \sigma}^\dagger s_{\pi \sigma} + \sum_{\pi \sigma} E_\pi s_{\pi \sigma}^\dagger s_{\pi \sigma} + \sum_{\nu} (E_\pi + E_d) d_{\pi M}^\dagger d_{\pi M} + \sum_{k\nu\sigma} \epsilon_{k\nu\sigma} c_{k\nu\sigma}^\dagger c_{k\nu\sigma}
\]

\[
+ t_\pi \sum_{\pi \sigma} \left[ f_{\pi \sigma}^\dagger c_{\sigma} \left( d_{\pi 2\sigma}^\dagger s_{\pi \sigma} + \frac{1}{\sqrt{2}} d_{\pi 0}^\dagger s_{\pi \sigma} \right) O_\pi \right]
\]

\[
+ t_2 \sum_{\pi \sigma} \left[ f_{\sigma}^\dagger c_{\sigma} \left( d_{\pi 2\sigma}^\dagger s_{\pi \sigma} + \frac{1}{\sqrt{2}} d_{\pi 0}^\dagger s_{\pi \sigma} \right) O_\pi \right]
\]

\[
+ H.c.,
\]

where the operators \( O_\nu = 1 \) in the physical subspace (they are defined below) and the following constraints should be satisfied to restrict the bosonic Hilbert space to the physical subspace

\[
1 = \sum_{\sigma} \left( \sum_{\pi} s_{\pi \sigma}^\dagger s_{\pi \sigma} + s_{\pi \sigma}^\dagger s_{\pi \sigma} \right) + \sum_{\pi M} d_{\pi M}^\dagger d_{\pi M},
\]

\[
f_{\pi \sigma}^\dagger f_{\pi \sigma} = s_{\pi \sigma}^\dagger s_{\pi \sigma} + d_{\pi 2\sigma}^\dagger d_{\pi 2\sigma} + \frac{1}{2} d_{\pi 0}^\dagger d_{\pi 0},
\]

\[
f_{\sigma}^\dagger f_{\sigma} = s_{\sigma}^\dagger s_{\sigma} + \sum_{\pi} \left( d_{\pi 2\sigma}^\dagger d_{\pi 2\sigma} + \frac{1}{2} d_{\pi 0}^\dagger d_{\pi 0} \right).
\]

The idea of the introduction of the operators \( O_\nu \) is to correct the mean-field solution so that certain limits are reproduced. For the Hubbard model, Kotliar and Ruckenstein have chosen the corresponding operators in such a way that the non-interacting limit is reproduced. In this case, the approximation becomes equivalent to the Gutzwiller approximation\textsuperscript{35}. However, this choice, even in the one-channel case, leads to a too large Kondo temperature for large Coulomb temperature\textsuperscript{39}. In our model, this repulsion is infinite since only two neighboring configurations of the localized states are retained. Therefore, we determine the \( O_\nu \) requiring that when only one hybridization channel is relevant and in the Kondo limit (small relevant \( t_\nu \) compared to the difference between the smallest energies of both configurations), the correct exponent of the Bethe ansatz result\textsuperscript{35} for the corresponding Kondo temperature is reproduced

\[
T_K \sim \Delta_\nu \exp \left[ \frac{\pi (E_d + E_\pi - E_a)}{2 \Delta_\pi} \right],
\]

\[
T_K \sim \Delta_a \exp \left[ \frac{\pi E_d}{2 \Delta_\pi} \right],
\]
where $\Delta_\nu = \pi \rho_\nu \delta_{\nu\nu}^2$, with $\rho_\nu$ the density of conduction electrons with symmetry $\nu$, is called the resonant-level width for orbitals of symmetry $\nu$ and concides with half of the width at half maximum of the corresponding peak in the spectral density of the molecular orbitals with symmetry $\nu$ in the non-interacting case. In the SBMFA results the prefactor is replaced by the half band width $D$, but this is not essential and the important point is to recover the correct exponent.

In addition we ask that when the $\pi$ states are degenerate ($S = 0$) and $t_z = 0$ (2-channel degenerate case) the exponent in $T_K^\nu$ is doubled (generalizing the SU(4) case). These limiting cases can be easily treated as in Ref. [27]. We find that a possible choice is

$$O_\pi = [1 - A \sum_{\pi M} d^{\dagger}_{\pi M} d_{\pi M} - B \left( \sum_{M} d^{\dagger}_{a M} d_{a M} \right) \left( \sum_{M} d^{\dagger}_{b M} d_{b M} \right)]^{-1/2},$$

$$O_z = \left[ 1 - A \sum_{\pi M} d^{\dagger}_{\pi M} d_{\pi M} \right]^{-1/2},$$

with $B = 2(1 + 1/\sqrt{2})^2/3 \approx 1.9428$, $A = 1 - B/2 \approx 0.0286$. For simplicity and without affecting the semi-quantitative validity of our results, we take $B = 2, A = 0$, implying $O_z = 1$.

In the mean-field approximation, the bosonic operators are replaced by numbers. Since we consider magnetic field $B = 0$, these numbers do not depend on spin projection. Then, there are five independent bosonic variables ($s_z, s_a, s_b, d_a, d_b$). Using the first constraint Eq. [6] we eliminate $s_z$ [see last Eq. [10]] keeping the formalism symmetric in the $\pi$ ($a$ or $b$) variables. The remaining constraints are treated introducing three Lagrange multipliers $\lambda_\nu$ and adding to the Hamiltonian the term

$$H_{cont} = \lambda_z \sum_{\sigma} \left( f_{z \sigma}^\dagger f_{z \sigma} - \frac{1}{2} + \sum_{\pi} s_\pi^2 \right) + \sum_{\pi \sigma} \lambda_\pi \left( f_{\pi \sigma}^\dagger f_{\pi \sigma} - s_\pi^2 - \frac{3}{2} d_\pi^2 \right).$$

The problem is reduced to a non-interacting fermionic Hamiltonian, where the seven variables $s_\pi, d_\pi$ and $\lambda_\nu$ are obtained minimizing the energy (we take zero temperature). Assuming constant density of conduction states $\rho_\nu$ extending from $-D$ to $D$, where the Fermi energy lies at zero, the Green functions of the pseudofermions take a simple form

$$G_{f_{\nu \sigma}}(\omega) = \langle \langle f_{\nu \sigma}, f_{\nu \sigma}^\dagger \rangle \rangle = \frac{1}{\omega - \nu \lambda + i\Delta_\nu},$$

where the renormalized half width of the resonances $\Delta_\nu$ (which determine the three Kondo scales) are

$$\Delta_z = \Delta_z \left( 1 + \frac{1}{\sqrt{2}} \right) \left( \sum_{\pi} s_\pi d_\pi \right)^2,$$

$$\Delta_\pi = \Delta_\pi \left( 1 + \frac{1}{\sqrt{2}} \right)^2 \frac{d_\pi^2 s_\pi^2}{1 - 18 d_\pi^2 d_\pi^2},$$

with $s_\pi^2 = 1 - \sum_{\nu} (2 s_{\pi \nu}^2 + 3 d_{\pi \nu}^2)$. Using these Green functions, the change in energy after adding the impurity can be evaluated easily as in similar problems using the SBMFA. The result is

$$\Delta E = E_z - \lambda_z + 2 \sum_{\pi} \left( E_z - E_z + \lambda_z - \lambda_\pi \right) s_\pi^2 + 3 \sum_{\pi} \left( E_\pi + E_d - \lambda_\pi \right) d_\pi^2$$

$$+ \frac{1}{\pi} \sum_{\nu} \left[ -2 \Delta_\nu + \Delta_\nu \ln \left( \frac{\lambda_\nu^2 + \Delta_\nu^2}{D^2} \right) + 2 \lambda_\nu \arctan \left( \frac{\Delta_\nu}{\lambda_\nu} \right) \right].$$

Minimizing Eq. [11] with respect to the Lagrange multipliers one obtains

$$\lambda_z = \frac{\Delta_z}{\tan \left( \frac{\pi}{2} \left( 1 - \sum_{\pi} s_\pi^2 \right) \right)};$$

$$\lambda_\pi = \frac{\Delta_\pi}{\tan \left( \frac{\pi}{2} (2 s_\pi^2 + 3 d_\pi^2) \right)}.$$

The derivatives with respect to $s_\pi$ and $d_\pi$ are lengthy and we do not reproduce them here. Some simplification
In order for the configuration with two holes should have orbital the result gives Kondo temperature for the $z$ result in the same Kondo temperatures. In order that effect in particular) if the hoppings are also changed to $D$ and $z$ weight of the singly occupied states for both $S$ is not the global minimum for small $S$. As expected, this local minimum is restricted in the previous Section. We take the hole Fermi interaction (see for example Ref. 40) restricted of the ground-state localized configuration with realistic Coulomb interaction. We find that for positive splitting $S$, there is always a local minimum of the energy for $s_b = d_b = 0$, indicating a 2-channel situation. As expected, this local minimum is not the global minimum for small $S$. In this case the weight of the singly occupied states for both $\pi$ channels are similar ($s_b^2 \sim s_d^2$) and the same happens for the doubly occupied sites ($d_b^2 \sim d_d^2$). We expected that for large $S$ there would be a global minimum for small non-zero $s_b, d_b$, but this is not the case. There is an abrupt jump in the position of the global minimum between two local minima, one with $s_b = d_b = 0$ and the other one with $s_b^2 \sim s_d^2$ and $d_b^2 \sim d_d^2$.

In Fig. 1 we represent the energy and the difference $P = d_b^2 - d_d^2$ for the 3-channel solution as a function of the splitting $S$. For the 2-channel solution, the energy is constant at the value $\Delta E = -21.5745$ eV. Similarly in this solution $d_b^2 = 0.317$ (slightly below 1/3 as expected, since the weight is shared by all three spin projections of the triplet) and $d_d^2 = 0$. For both solutions in general $d_b^2 + d_d^2 \sim 1/3$, and $s_b^2$ and $s_d^2$ are very small. Therefore $3P$, which is the total orbital polarization of the ground state, is the more relevant bosonic variable.

As observed in the figure, the orbital polarization of the 3-channel solution increases almost linearly (the curvature is small and positive) with $S$, but its magnitude is very small (less than 5% of the maximum value in the range studied) and as a consequence the energy increases fast with $S$ (almost linearly with a negative second derivative). For the parameters chosen, the ground state of the isolated molecule $H_{\text{mol}}$ is $E_a + E_d = 0$. Therefore, a positive $\Delta E$ (as we obtain for the 3-channel solution for large $S$) would indicate that including the mixing terms $H_{\text{mix}}$ of the molecule with the conduction electron increases the energy of the system. This is nonphysical and points out the instability of the 3-channel solution for large $S$. Actually, at the critical splitting $S_c = 27.07$ meV there is a transition to the 2-channel solution which becomes that of lower energy for $S > S_c$.

The results for the different quantities at the transition are indicated in Table 1. In the 2-channel solution, the half width of the resonance for the molecular states of $z^2$ symmetry (identified with the respective Kondo temperature) is $\Delta_2 = 25.7$ meV, somewhat larger than reported previously $\Delta_2 \sim 20$ meV. However, comparison with theory suggest that $\Delta_2 \sim 20$ meV. The position of this peak ($\lambda_2 = 1.88$ meV) is practically at the Fermi energy. The half width of the peak for the molecular $\alpha$ state is $\Delta_\alpha = 0.222$ meV and it lies at the Fermi energy. The
molecular b state is absent at low energies in this solution. Note that the weight of the singly occupied a states is related to the valence fluctuations of the z^2 states and vice versa. Therefore \( \Delta_a > \Delta_z \) implies \( s_a^z > s_z^x \) (\( s_a^z = 0.023 \), \( s_z^x \approx 7 \times 10^{-4} \) in this case).

The 3-channel solution is markedly different. The \( \pi \) (a and b) channels behave as quasi degenerate. The weight of these channels in the ground state configuration of doubly occupied states is very similar (\( d_a^z = 0.156 \), \( d_b^z = 0.152 \)). This fact has an effect of increasing markedly the Kondo temperature of these channels, as expected for example when the symmetry of the SU(2) Kondo model is increased to SU(4). We obtain \( \Delta_a = 6.53 \text{ meV}, \Delta_z = 6.36 \text{ meV} \). The corresponding peaks are shifted from the Fermi energy (below it in the electron representation as opposed to the hole one used here) by \( \lambda_a = 6.89 \text{ meV}, \lambda_b = 6.98 \text{ meV} \). The fact that the position and the half width of the peaks are of the same order is also expected, for example from the SU(4) Anderson model. The increase of the Kondo energy scale for the \( \pi \) channels has the effect of decreasing the corresponding scale for the \( z^2 \) channel. This competition has been studied before for degenerate \( \pi \) channel. As a consequence the half width of the molecular state with \( z^2 \) symmetry is reduced to \( \Delta_z = 15.3 \text{ meV} \).

### Table II. Same as Table I for \( \Delta_z = 0.4 \text{ eV} \).  

| \( z \) | \( a \) | \( b \) |
|-------|-------|-------|
| \( s_a^z \) | \( 2.21 \times 10^{-3} \) | 0.0228 | 0 |
| \( d_a^z \) | - | 0.317 | 0 |
| \( \Delta_a \) (meV) | 25.2 | 0.815 | 0 |
| \( \lambda_a \) (meV) | 1.81 | 5.66 \times 10^{-3} | 0 |

### Table III. Same as Table II for \( \Delta_z = 0.3 \text{ eV} \).  

| \( z \) | \( a \) | \( b \) |
|-------|-------|-------|
| \( s_a^z \) | \( 1.37 \times 10^{-4} \) | 0.0233 | 0 |
| \( d_a^z \) | - | 0.318 | 0 |
| \( \Delta_a \) (meV) | 25.9 | 0.038 | 0 |
| \( \lambda_a \) (meV) | 1.90 | 1.63 \times 10^{-5} | 0 |
| \( s_a^z \) | 0.0145 | 0.00882 | 0.00861 |
| \( d_a^z \) | - | 0.157 | 0.155 |
| \( \Delta_a \) (meV) | 19.0 | 3.54 | 3.50 |
| \( \lambda_a \) (meV) | 1.04 | 3.67 | 3.70 |

### V. SUMMARY AND DISCUSSION

We have studied a generalized Anderson model in which two triplets are hybridized with three higher energy doublets, with a variable splitting \( S \) between both triplets assumed to be the same as that between two doublets. The model contains three hybridizing channels and has been proposed to describe the low-energy physics of an isolated iron phthalocyanine molecule deposited on the Au(111) surface. The triplets contain one hole in the Fe 3d orbital with \( z^2 \) symmetry and another one in one of the 3d \( \pi \) orbitals. The split \( \pi \) orbitals are orthogonal linear combinations of \( xx \) and \( yz \) orbitals. If the origin of the splitting is spin-orbit coupling, these combinations to see the sensitivity of the results with \( \tilde{\Delta}_a \) (which has some uncertainty) and in particular if \( S_c \) can be increased substantially, we have increased the resonant-level width of the \( \pi \) states to \( \Delta_z = 0.4 \text{ eV} \). The new critical splitting becomes \( S_c = 46.77 \text{ meV} \).

The corresponding results for the different quantities at this value of the splitting are listed in Table III. The main change in the 2-channel region is that the Kondo temperature of the a channel is increased by a factor near 4 to \( \Delta_a = 0.815 \text{ meV} \), which seems too large for an agreement with experiment. The corresponding result for the \( z^2 \) channel is only moderately decreased to \( \Delta_z = 25.2 \text{ meV} \).

The changes in the 3-channel region are moderate and expected. \( \Delta_a \) and \( \Delta_z \) increase to ~10 meV, \( \Delta_z \) decreases to 12 meV, and correspondingly \( s_a^z \) decreases and \( s_z^x \) decrease.

We have also studied the case \( \Delta_z = 0.3 \text{ eV} \). The critical splitting decreases to \( S_c = 12.94 \text{ meV} \). The values of the different observables at the transition are displayed in Table III. In the 2-channel solution, \( \Delta_a \) decreases by a factor near 5 with respect to the case shown in Table II (for which \( \Delta_z = 0.35 \text{ eV} \)). \( \Delta_z \) increases in 1%. In the 3-channel solution, \( \Delta_z \) = 19 meV is more similar to the value of the 2-channel solution and \( \Delta_z \sim 3.5 \text{ meV} \) with near 1% difference between \( \Delta_a \) and \( \Delta_b \) (they tend to be equal due to the decrease of the splitting).
are given by Eqs. (2). The doublets have one hole in any of the three molecular orbitals. The different channels correspond to the three different symmetries.

Clearly, for large $S$ one of the $\pi$ channels can be neglected at low energies and the model can be reduced to a 2-channel type, justifying previous calculations in which several experiments were explained on the basis of a 2-channel spin-1 Kondo model with easy plane anisotropy.[23] These calculations are particularly interesting because they imply that the system is a topologically non-trivial non-Landau Fermi liquid. We have not included the anisotropy here to avoid entering the topologically non-trivial phase which cannot be described by the approach.

The question we have addressed is how large should $S$ be to justify this further low-energy reduction to a 2-channel model. Our results using a slave-boson mean-field approximation predict an abrupt transition from a 2-channel to a 2-channel regime with increasing splitting. While the first-order nature of the transition is probably an artifact of the mean-field approximation, we believe that the resulting critical splitting $S_c$ has semiquantitative validity. For the parameters which best correspond to experimental observations we obtain $S_c \sim 27$ meV. This is substantially smaller than the spin-orbit coupling of $\sim 76$ meV[23]. Therefore we expect that in fact the 2-channel model is justified, and the relevant $\pi$ channel corresponds to the $a$ states described in Eq. (2). The effective SOC might be reduced by a few percent due to admixture of some amount of $N \rho$ orbitals in the molecular state[39], but this does not affect our conclusions.

The reduction of the model from 3-channel to 2-channel due to spin-orbit coupling has other consequences in the comparison to experiment. The states of the ground state configuration with spin projection $S_z = \pm 1$ have also angular momentum projection $L_z = \pm 1$ [see Eqs. (2) and below them]. Therefore, the effect of a magnetic field $B_2$ in the $z$ direction (perpendicular to the Au(111) surface as applied experimentally[13]), with a correction term $(2S_z + L_z)B_2$, is $3/2$ larger than the case in which only the spin is considered. In addition the effect of magnetic field perpendicular to $z$, involving spin flips induces mixing with excited $b$ states and is smaller than for the case without splitting.

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