


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

A. A. Aligia *Instituto de Nanociencia y Nanotecnología CNEA-CONICET, Centro Atómico Bariloche and Instituto Balseiro, 8400 Bariloche, Argentina*

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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 two-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 π orbitals of symmetry xz 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 π orbitals caused by spin-orbit coupling (SOC) justifies this approximation. We obtain an abrupt transition from a three-band regime to a two-band one at a value of S , which is about 1/3 of the atomic SOC for Fe, justifying the two-band model for the system.

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I. INTRODUCTION

The Kondo effect, found first in metals containing magnetic impurities [1,2], 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 overscreening are not discussed here [3]).

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 [4–18]. This subject is of interest for its potential use in new electronic devices [19,20]. 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 ~ 20 meV and mounted on it a dip nearly two orders of magnitude narrower [11,14,15]. Application of a magnetic field B transforms the dip into a peak [15]. A similar behavior is observed for MnPc on Au(111) [18]. When the molecule is raised from the surface, weakening the Kondo effect, the dip broadens [14]. All these features have been recently explained in a consistent fashion by a two-channel spin-1 Kondo model with anisotropy [21]. This is an extension to nondegenerate channels of a model for Ni impurities in a Au chain [22,23].

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 nontrivial Friedel sum rule with

nonzero Luttinger integrals. The results of Ref. [21] 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-orbital [24] and two-impurity [25,26] Anderson models. In the latter, the transition was also ascribed as due to a jump in Luttinger integrals [25,26].

LDA+ U calculations [11] indicate that the configuration of Fe in the system is $(d_{xy})^2(d_{z^2})^1(d_{\pi})^3$. Therefore, the partially filled orbitals can be described as one hole with z^2 symmetry and one hole with π (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 three-channel Anderson model, which has been studied by Fernández *et al.* [27] 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 three-channel $S = 1$ Kondo model, which is more involved than the two-channel Kondo model used to describe the system as a *non-Landau* Fermi liquid [21]. The two-channel Kondo model has been chosen because the three-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 two-channel model [21].

However, Fe has a spin-orbit coupling (SOC) ~ 76 meV [28] disregarded before. In first order, the SOC splits the π states by this amount and leaves the z^2 orbitals unchanged. This splitting might justify the two-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 two-channel spin-1 Kondo model with easy plane anisotropy DS_z^2 , the topological 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 three-channel Anderson model including a splitting S between the π 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 noncrossing approximation for this two-channel case (see the Appendix of Ref. [23]) or equations of motion [29], do not reproduce the correct Kondo temperature.

The results indicate that the excited π 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 two-channel model.

This work is organized as follows. In Sec. II we describe the three-band Anderson model used for this study and justify it in detail. In Sec. III we explain the SBMFA used to solve the model in the Kondo or integer valence limit. The results are presented in Sec. IV and Sec. 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 Sec. IV), but in any case they are adjusted from low-energy experimental results.

The ground state corresponds essentially to the $3d^6$ configuration of Fe with one hole in the $3d_{z^2}$ orbital and another hole in a π orbital ($3d_{xz}$ or $3d_{yz}$) 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 [30]. 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 $\exp[i(k_x x + k_y y)]$ [31–34]. 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_1 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 belongs 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 three-channel model studied previously by Fernández *et al.* [27]. However, here we assume that the π orbitals are split by an energy S . We call a (b) the linear combination of π holes with lower (larger) energy. The other configuration, the $3d^7$ one, has a hole in either the $3d_{z^2}$ orbital or in a π orbital. We denote the two spin triplets by $|aM\rangle$ and $|bM\rangle$, depending on which π 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 σ 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.* [27].

The Hamiltonian is

$$\begin{aligned}
 H &= H_{\text{mol}} + H_{\text{band}} + H_{\text{mix}}, \\
 H_{\text{mol}} &= E_z \sum_{\sigma} |z^2\sigma\rangle \langle z^2\sigma| \\
 &\quad + \sum_{\pi\sigma} E_{\pi} |\pi\sigma\rangle \langle \pi\sigma| + \sum_{\pi M} (E_{\pi} + E_d) |\pi M\rangle \langle \pi M|, \\
 H_{\text{band}} &= \sum_{k\nu\sigma} \epsilon_{k\nu\sigma} c_{k\nu\sigma}^{\dagger} c_{k\nu\sigma}, \\
 H_{\text{mix}} &= \sum_{\pi k} \sum_{\sigma\sigma'M} t_{\pi} \left\langle \frac{1}{2} \frac{1}{2} \sigma\sigma' | 1M \right\rangle (c_{k\pi\sigma}^{\dagger} |z^2\sigma'\rangle \langle \pi M| + \text{H.c.}) \\
 &\quad - \sum_{\pi k} \sum_{\sigma\sigma'M} t_z \left\langle \frac{1}{2} \frac{1}{2} \sigma\sigma' | 1M \right\rangle (c_{kz\sigma}^{\dagger} |\pi\sigma'\rangle \langle \pi M| + \text{H.c.}),
 \end{aligned} \tag{1}$$

where H_{mol} 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_{band} represents the three conduction bands, with the same symmetry as the corresponding molecular states ($\nu = z^2, a$, or b). H_{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 π orbitals are (except for an irrelevant phase)

$$\begin{aligned}
 |a\uparrow\rangle &= \frac{|xz\uparrow\rangle + i|yz\uparrow\rangle}{\sqrt{2}}, & |a\downarrow\rangle &= \frac{|xz\downarrow\rangle - i|yz\downarrow\rangle}{\sqrt{2}}, \\
 |b\uparrow\rangle &= \frac{|xz\uparrow\rangle - i|yz\uparrow\rangle}{\sqrt{2}}, & |b\downarrow\rangle &= \frac{|xz\downarrow\rangle + i|yz\downarrow\rangle}{\sqrt{2}},
 \end{aligned} \tag{2}$$

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 $|E_z - E_a|$) the model has been solved exactly by the Bethe ansatz [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) [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[37,38]. 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

$$\begin{aligned} |\pi\sigma\rangle &\leftrightarrow f_{\pi\sigma}^\dagger s_{\pi\sigma}^\dagger |0\rangle, \\ |z^2\sigma\rangle &\leftrightarrow f_{z^2\sigma}^\dagger s_{z^2\sigma}^\dagger |0\rangle, \end{aligned} \quad (3)$$

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

$$\begin{aligned} |\pi 1\rangle &\leftrightarrow d_{\pi 1}^\dagger f_{\pi\uparrow}^\dagger f_{z\uparrow}^\dagger |0\rangle, \\ |\pi 0\rangle &\leftrightarrow \frac{1}{\sqrt{2}} d_{\pi 0}^\dagger (f_{\pi\uparrow}^\dagger f_{z\downarrow}^\dagger + f_{\pi\downarrow}^\dagger f_{z\uparrow}^\dagger) |0\rangle, \\ |\pi - 1\rangle &\leftrightarrow d_{\pi -1}^\dagger f_{\pi\downarrow}^\dagger f_{z\downarrow}^\dagger |0\rangle. \end{aligned} \quad (4)$$

The Hamiltonian in this representation takes the form

$$\begin{aligned} H = & E_z \sum_{\sigma} s_{z\sigma}^\dagger s_{z\sigma} + \sum_{\pi\sigma} E_{\pi} s_{\pi\sigma}^\dagger s_{\pi\sigma} \\ & + \sum_{\pi M} (E_{\pi} + E_d) d_{\pi M}^\dagger d_{\pi M} + \sum_{k\nu\sigma} \epsilon_{k\nu\sigma} c_{k\nu\sigma}^\dagger c_{k\nu\sigma} \\ & + \left\{ t_{\pi} \sum_{\pi\sigma} \left[f_{\pi\sigma}^\dagger c_{\pi\sigma} \left(d_{\pi 2\sigma}^\dagger s_{z\sigma} + \frac{1}{\sqrt{2}} d_{\pi 0}^\dagger s_{z\bar{\sigma}} \right) O_{\pi} \right] \right. \\ & \left. + t_z \sum_{\pi\sigma} \left[f_{z\sigma}^\dagger c_{z\sigma} \left(d_{\pi 2\sigma}^\dagger s_{\pi\sigma} + \frac{1}{\sqrt{2}} d_{\pi 0}^\dagger s_{\pi\bar{\sigma}} \right) O_z \right] + \text{H.c.} \right\}, \end{aligned} \quad (5)$$

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:

$$\begin{aligned} 1 = & \sum_{\sigma} \left(\sum_{\pi} s_{\pi\sigma}^\dagger s_{\pi\sigma} + s_{z\sigma}^\dagger s_{z\sigma} \right) + \sum_{\pi M} d_{\pi M}^\dagger d_{\pi M}, \\ f_{\pi\sigma}^\dagger f_{\pi\sigma} = & s_{\pi\sigma}^\dagger s_{\pi\sigma} + d_{\pi 2\sigma}^\dagger d_{\pi 2\sigma} + \frac{1}{2} d_{\pi 0}^\dagger d_{\pi 0}, \end{aligned}$$

$$f_{z\sigma}^\dagger f_{z\sigma} = s_{z\sigma}^\dagger s_{z\sigma} + \sum_{\pi} \left(d_{\pi 2\sigma}^\dagger d_{\pi 2\sigma} + \frac{1}{2} d_{\pi 0}^\dagger d_{\pi 0} \right). \quad (6)$$

The idea of the introduction of the operators O_{ν} 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 noninteracting limit is reproduced. In this case, the approximation becomes equivalent to the Gutzwiller approximation [36]. However, this choice, even in the one-channel case, leads to a too large Kondo temperature for large Coulomb repulsion [39]. In our model, this repulsion is infinite since only two neighboring configurations of the localized states are retained. Therefore, we determine the O_{ν} requiring that, when only one hybridization channel is relevant and in the Kondo limit (small relevant t_{ν} compared to the difference between the smallest energies of both configurations), the correct exponent of the Bethe ansatz result [35] for the corresponding Kondo temperature is reproduced

$$\begin{aligned} T_K^{\pi} &\sim \Delta_{\nu} \exp \left[\frac{\pi(E_d + E_{\pi} - E_z)}{2\Delta_{\pi}} \right], \\ T_K^z &\sim \Delta_z \exp \left[\frac{\pi E_d}{2\Delta_z} \right], \end{aligned} \quad (7)$$

where $\Delta_{\nu} = \pi \rho_{\nu} t_{\nu}^2$, with ρ_{ν} the density of conduction electrons with symmetry ν , is called the resonant-level width for orbitals of symmetry ν and coincides with half of the width at half maximum of the corresponding peak in the spectral density of the molecular orbitals with symmetry ν in the noninteracting 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 π states are degenerate ($S = 0$) and $t_z = 0$ (two-channel degenerate case) the exponent in T_K^{π} is doubled [generalizing the SU(4) case [27]]. These limiting cases can be easily treated as in Ref. [27]. We find that a possible choice is

$$\begin{aligned} O_{\pi} = & \left[1 - A \sum_{\pi M} d_{\pi M}^\dagger d_{\pi M} \right. \\ & \left. - B \left(\sum_M d_{aM}^\dagger d_{aM} \right) \left(\sum_M d_{bM}^\dagger d_{bM} \right) \right]^{-1/2}, \\ O_z = & \left(1 - A \sum_{\pi M} d_{\pi M}^\dagger d_{\pi M} \right)^{-1/2}, \end{aligned} \quad (8)$$

with $B = 2(1 + 1/\sqrt{2})^2/3 \simeq 1.9428$ and $A = 1 - B/2 \simeq 0.0286$. For simplicity and without affecting the semiquantitative 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 π (a or b) variables. The remaining constraints are treated introducing

three Lagrange multipliers λ_ν and adding to the Hamiltonian the term

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

The problem is reduced to a noninteracting fermionic Hamiltonian, where the seven variables s_{π} , d_{π} , and λ_{ν} are obtained minimizing the energy (we take zero temperature). Assuming constant density of conduction states ρ_{ν} extending from $-D$ to D , where the Fermi energy lies at zero, the Green's functions of the pseudofermions take a simple

form

$$G_{f_{\nu\sigma}}(\omega) = \langle \langle f_{\nu\sigma}; f_{\nu\sigma}^\dagger \rangle \rangle = \frac{1}{\omega - \lambda_{\nu} + i\tilde{\Delta}_{\nu}}, \quad (9)$$

where the renormalized half width of the resonances $\tilde{\Delta}_{\nu}$ (which determine the three Kondo scales) are

$$\begin{aligned} \tilde{\Delta}_z &= \Delta_z \left(1 + \frac{1}{\sqrt{2}} \right)^2 \left(\sum_{\pi} s_{\pi} d_{\pi} \right)^2, \\ \tilde{\Delta}_{\pi} &= \Delta_{\pi} \left(1 + \frac{1}{\sqrt{2}} \right)^2 \frac{d_{\pi}^2 s_{\pi}^2}{1 - 18d_a^2 d_b^2}, \\ \text{with } s_z^2 &= \frac{1 - \sum_{\pi} (2s_{\pi}^2 + 3d_{\pi}^2)}{2}. \end{aligned} \quad (10)$$

Using these Green's functions, the change in energy after adding the impurity can be evaluated easily as in similar problems using the SBMFA [1,27]. The result is

$$\begin{aligned} \Delta E &= E_z - \lambda_z + 2 \sum_{\pi} (E_{\pi} - E_z + \lambda_z - \lambda_{\pi}) s_{\pi}^2 + 3 \sum_{\pi} (E_{\pi} + E_d - \lambda_{\pi}) d_{\pi}^2 \\ &+ \frac{1}{\pi} \sum_{\nu} \left[-2\tilde{\Delta}_{\nu} + \tilde{\Delta}_{\nu} \ln \left(\frac{\lambda_{\nu}^2 + \tilde{\Delta}_{\nu}^2}{D^2} \right) + 2\lambda_{\nu} \arctan \left(\frac{\tilde{\Delta}_{\nu}}{\lambda_{\nu}} \right) \right]. \end{aligned} \quad (11)$$

Minimizing Eq. (11) with respect to the Lagrange multipliers one obtains

$$\begin{aligned} \lambda_z &= \frac{\tilde{\Delta}_z}{\tan \left[\frac{\pi}{2} (1 - \sum_{\pi} s_{\pi}^2) \right]}, \\ \lambda_{\pi} &= \frac{\tilde{\Delta}_{\pi}}{\tan \left[\frac{\pi}{2} (2s_{\pi}^2 + 3d_{\pi}^2) \right]}. \end{aligned} \quad (12)$$

The derivatives with respect to s_{π} and d_{π} are lengthy and we do not reproduce them here. Some simplification is achieved noting that

$$\frac{\partial \Delta E}{\partial \tilde{\Delta}_{\nu}} = \frac{1}{\pi} \ln \left(\frac{\lambda_{\nu}^2 + \tilde{\Delta}_{\nu}^2}{D^2} \right). \quad (13)$$

Equating these derivatives to zero and using Eqs. (12) one obtains a system of four equations with four unknowns s_{π} and d_{π} . For positive splitting S , the results for s_d and particularly d_b indicate if the band of symmetry b is important or not. Furthermore, according to Eqs. (3), (4), (8), (9), and (10), the low energy part of the spectral density of the molecular states becomes

$$\rho_{\text{mol}}^{\nu}(\omega) = \frac{\tilde{\Delta}_{\nu}^2}{\Delta_{\nu} [(\omega - \lambda_{\nu})^2 + \tilde{\Delta}_{\nu}^2]}, \quad (14)$$

which is a Lorentzian centered at λ_{ν} of half width $\tilde{\Delta}_{\nu}$ and weight $\tilde{\Delta}_{\nu}/\Delta_{\nu}$ (the rest of the spectral weight is at high energies and is not captured by the SBMFA).

IV. NUMERICAL RESULTS

In this section we present our results for the solution of the system of four equations with four unknowns described in

the previous section. We take the hole Fermi energy $\epsilon_F = 0$ as the origin of energies. Following a previous study for degenerate π orbitals [27], we take in eV $D = 10$, $E_z = 1$, $E_a = 2$, and $E_d = -2$. The parameters are justified as follows. From the diagonalization of the ground-state localized configuration with realistic Coulomb interaction (see, for example, Ref. [40]) restricted to the three relevant orbitals, it has been established that $E_a - E_z \sim 1 \pm 0.3$ eV in order for the ground state to be a triplet with one hole in the z^2 orbital and one in the π orbital [27]. A shift in all energies by the same amount is irrelevant. In order for the configuration with two holes to be the ground state of H_{mol} (isolated molecule) one should have $E_a + E_d < E_z + \epsilon_F$. E_d was chosen arbitrarily to result in a difference of 1 eV. However, a change in E_d and D does not affect the low-energy physics (the Kondo effect in particular) if the hoppings are also changed to result in the same Kondo temperatures. In order that the result gives the Kondo temperature for the z^2 channel of the order of the reported one $\tilde{\Delta}_z \sim 20$ meV, we have taken $\Delta_z = 1.2$ eV. Similarly in order to obtain $\tilde{\Delta}_a$ two orders of magnitude smaller than $\tilde{\Delta}_z$, we take $\Delta_{\pi} = 0.35$ eV as a basis for our study.

We find that, for positive splitting S , there is always a local minimum of the energy for $s_b = d_b = 0$, indicating a two-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 π channels are similar ($s_b^2 \sim s_a^2$) and the same happens for the doubly occupied sites ($d_b^2 \sim d_a^2$). We expected that for large S there would be a global minimum for small nonzero 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 $s_b^2 \sim s_a^2$ and $d_b^2 \sim d_a^2$.

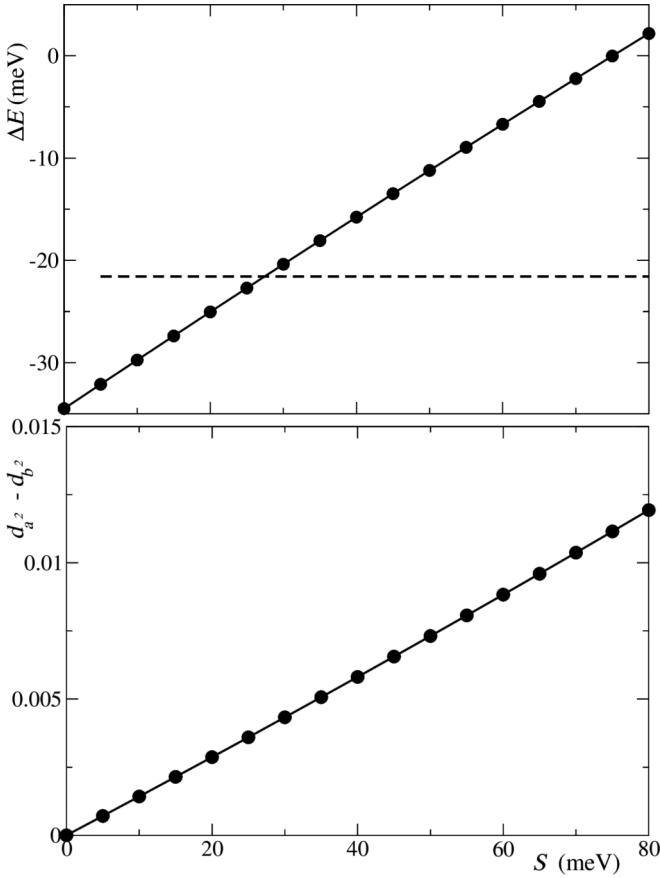


FIG. 1. Energy (top) and orbital polarization (bottom) for the three-channel solution as a function of the splitting S . The dashed line indicates the energy of the two-channel solution.

In Fig. 1 we represent the energy and the difference $P = d_a^2 - d_b^2$ for the three-channel solution as a function of the splitting S . For the two-channel solution, the energy is constant at the value $\Delta E = -21.5745$ eV. Similarly in this solution $d_a^2 = 0.317$ (slightly below $1/3$ as expected, since the weight is shared by all three spin projections of the triplet) and $d_b^2 = 0$. For both solutions in general $d_a^2 + d_b^2 \sim 1/3$ and s_z^2 and s_π^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 three-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_{mol} is $E_a + E_d = 0$. Therefore, a positive ΔE (as we obtain for the three-channel solution for large S) would indicate that including the mixing terms H_{mix} of the molecule with the conduction electron *increases* the energy of the system. This is nonphysical and points out the instability of the three-channel solution for large S . Actually, at the critical splitting $S_c = 27.07$ meV there is a transition to the two-channel solution which becomes that of lower energy for $S > S_c$.

TABLE I. Results for different observables at the transition between both phases for $\Delta_\pi = 0.35$ eV. The two- (three-) channel results are above (below) the horizontal line in the middle.

	z	a	b
s_v^2	6.87×10^{-4}	0.0232	0
d_π^2		0.317	0
$\tilde{\Delta}_v$ (meV)	25.7	0.222	0
λ_v (meV)	1.88	4.80×10^{-4}	0
s_v^2	0.0235	0.00727	0.00691
d_π^2		0.156	0.152
$\tilde{\Delta}_v$ (meV)	15.3	6.53	6.36
λ_v (meV)	0.681	6.89	6.98

The results for the different quantities at the transition are indicated in Table I. In the two-channel solution, the half width of the resonance for the molecular states of z^2 symmetry (identified with the respective Kondo temperature) is $\tilde{\Delta}_z = 25.7$ meV, somewhat larger than reported previously: $\tilde{\Delta}_z \sim 20$ meV [11]. However, comparison with theory suggests that $\tilde{\Delta}_z > 20$ meV [21]. The position of this peak ($\lambda_z = 1.88$ meV) is practically at the Fermi energy. The half width of the peak for the molecular a state is $\tilde{\Delta}_a = 0.222$ 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, $\tilde{\Delta}_z > \tilde{\Delta}_a$ implies $s_a^2 > s_z^2$ ($s_a^2 = 0.023$ and $s_z^2 \sim 7 \times 10^{-4}$ in this case).

The three-channel solution is markedly different. The π (a and b) channels behave as quasidegenerate. The weight of these channels in the ground state configuration of doubly occupied states is very similar ($d_a^2 = 0.156$ and $d_b^2 = 0.152$). 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) [41–43]. We obtain $\tilde{\Delta}_a = 6.53$ meV and $\tilde{\Delta}_a = 6.36$ 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 $\lambda_a = 6.89$ meV and $\lambda_b = 6.98$ 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 [41–43]. The increase of the Kondo energy scale for the π channels has the effect of decreasing the corresponding scale for the z^2 channel. This competition has been studied before for degenerate π channels [27]. As a consequence the half width of the molecular state with z^2 symmetry is reduced to $\tilde{\Delta}_z = 15.3$ meV.

The critical splitting for the transition $S_c = 27.07$ meV is markedly smaller to the SOC of Fe ~ 76 meV [28]. In order 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 π states to $\Delta_\pi = 0.4$ eV. The new critical splitting becomes $S_c = 46.77$ meV.

The corresponding results for the different quantities at this value of the splitting are listed in Table II. The main change in the two-channel region is that the Kondo temperature of the a channel is increased by a factor near 4 to $\tilde{\Delta}_a = 0.815$ meV,

TABLE II. Same as Table I for $\Delta_\pi = 0.4$ eV.

	z	a	b
s_v^2	2.21×10^{-3}	0.0228	0
d_π^2		0.317	0
$\tilde{\Delta}_v$ (meV)	25.2	0.815	0
λ_v (meV)	1.81	5.66×10^{-3}	0
s_v^2	0.0322	0.00591	0.00544
d_π^2		0.155	0.149
$\tilde{\Delta}_v$ (meV)	12.1	10.0	9.58
λ_v (meV)	0.431	10.7	10.9

which seems too large for an agreement with experiment [21]. The corresponding result for the z^2 channel is only moderately decreased to $\tilde{\Delta}_z = 25.2$ meV.

The changes in the three-channel region are moderate and expected. $\tilde{\Delta}_a$ and $\tilde{\Delta}_b$ increase to ~ 10 meV, $\tilde{\Delta}_z$ decreases to 12 meV, and correspondingly s_z^2 decreases and s_π^2 decrease.

We have also studied the case $\Delta_\pi = 0.3$ eV. The critical splitting decreases to $S_c = 12.94$ meV. The values of the different observables at the transition are displayed in Table III. In the two-channel solution, $\tilde{\Delta}_a$ decreases by a factor near 5 with respect to the case shown in Table I (for which $\Delta_\pi = 0.35$ eV). $\tilde{\Delta}_z$ increases in 1%. In the three-channel solution, $\tilde{\Delta}_z = 19$ meV is more similar to the value of the two-channel solution and $\tilde{\Delta}_\pi \sim 3.5$ meV with near 1% difference between $\tilde{\Delta}_a$ and $\tilde{\Delta}_b$ (they tend to be equal due to the decrease of the splitting).

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 $3d$ π orbitals. The split π orbitals are orthogonal linear combinations of xz and yz orbitals. If the origin of the splitting is spin-orbit coupling, these combinations are given by Eq. (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 π channels can be neglected at low energies and the model can be reduced to a two-channel type, justifying previous calculations in which several experiments were explained on the basis of a two-channel spin-1 Kondo model with easy plane anisotropy [21]. These calcula-

TABLE III. Same as Table I for $\Delta_\pi = 0.3$ eV.

	z	a	b
s_v^2	1.37×10^{-4}	0.0233	0
d_π^2		0.318	0
$\tilde{\Delta}_v$ (meV)	25.9	0.038	0
λ_v (meV)	1.90	1.63×10^{-5}	0
s_v^2	0.0145	0.00882	0.00861
d_π^2		0.157	0.155
$\tilde{\Delta}_v$ (meV)	19.0	3.54	3.50
λ_v (meV)	1.04	3.67	3.70

tions are particularly interesting because they imply that the system is a topologically nontrivial *non-Landau* Fermi liquid. We have not included the anisotropy here to avoid entering the topologically nontrivial phase which cannot be described by the approach.

The question we have addressed is how large S should be to justify this further low-energy reduction to a two-channel model. Our results using a slave-boson mean-field approximation predict an abrupt transition from a three-channel to a two-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 Fe ~ 76 meV [28]. Therefore, we expect that in fact the two-channel model is justified and the relevant π channel corresponds to the a states described in Eq. (2). The effective SOC might be reduced by a few percent due to the admixture of some amount of N p orbitals in the molecular states [30], but this does not affect our conclusions.

The reduction of the model from three channel to two 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_z in the z direction [perpendicular to the Au(111) surface as applied experimentally [15]], with a correction term $(2S_z + L_z)B_z$, 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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