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Valence fluctuations in a lattice of magnetic molecules: Application to iron(II) phthalocyanine molecules on Au(111)

J. FERNÁNDEZ¹, A. A. ALIGIA¹ and A. M. LOBOS²

¹ *Centro Atómico Bariloche and Instituto Balseiro, Comisión Nacional de Energía Atómica - 8400 Bariloche, Argentina*

² *Instituto de Física de Rosario, Universidad Nacional de Rosario - Bv. 27 de Febrero 210 bis, 2000 Rosario, Argentina*

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Abstract – We study theoretically a square lattice of the organometallic Kondo adsorbate iron(II) phthalocyanine (FePc) deposited on top of Au(111), motivated by recent scanning tunneling microscopy experiments. We describe the system by means of an effective Hubbard-Anderson model, where each molecule has degenerate effective d -orbitals with xz and yz symmetry, which we solve for arbitrary occupation and arbitrary on-site repulsion U . To that end, we introduce a generalized slave-boson mean-field approximation (SBMFA) which correctly describes both the non-interacting limit (NIL) $U = 0$ and the strongly interacting limit $U \rightarrow \infty$, where our formalism reproduces the correct value of the Kondo temperature for an isolated FePc molecule. Our results indicate that while the isolated molecule can be described by an $SU(4)$ Anderson model in the Kondo regime, the case of the square lattice corresponds to the intermediate-valence regime, with a total occupation of nearly 1.65 holes in the FePc molecular orbitals. Our results have important implications for the physical interpretation of the experiment.

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The advances in nanotechnology and the degree of control of different parameters in systems with strongly interacting electrons provide a rich and challenging field for the theoretical understanding of strongly correlated materials, and for future applications in spintronics and quantum information [1]. The strong repulsion between $3d$ electrons in the $3d$ series of transition-metal atoms (TMAs) has led to the observation of the Kondo effect in several systems in which these atoms [2–4] or molecules containing them [5–11] are absorbed on noble-metal surfaces. In its simpler form, the Kondo effect arises when a TMA has a (nearly) integer occupation of an odd number of electrons and spin $1/2$, and this spin is “screened” by a cloud of conduction electrons in the metal, building a many-body singlet ground state. As a consequence, a narrow Fano-Kondo antiresonance (FKA) appears in the differential conductance in scanning tunneling spectroscopy (STS) experiments. More exotic Kondo effects involving even occupation and spin 1 [12,13], and orbital degeneracy [10,14,15] were also observed. In particular, it has been shown that STS for a system consisting on a single iron(II) phthalocyanine (FePc) molecule (see the

inset of fig. 1) deposited on top of clean Au(111) (in the most usual “on-top” configuration) can be explained in terms of an effective $SU(4)$ impurity Anderson model [10]. The four degrees of freedom correspond to the intrinsic spin- $(1/2)$ degeneracy times twofold degeneracy between molecular orbitals with the same symmetry as the $3d_{xz}$ and $3d_{yz}$ states of Fe, where z is the direction perpendicular to the surface. The Kondo model is the odd-integer valence limit of the impurity Anderson model, in which localized electrons (like those of the $3d$ shell of a TMA) are hybridized with a conduction band.

Experiments in which an array of effective “impurities” (TMAs or molecules containing TMAs) are deposited on metal surfaces constitute a further challenge to the theory because they should be described by the periodic Anderson model, for which neither exact solutions nor accurate treatments, like the numerical renormalization group, exist. Tsukahara *et al.* studied the STS of a square lattice of FePc molecules on Au(111) [8]. They observed a splitting of the FKA near the Fermi level. A first hint to the correct description of the system came soon when the corresponding experiments for an isolated FePc molecule

could be well described by the effective $SU(4)$ impurity Anderson model [10]. A natural step to construct a lattice model is to introduce an effective hopping between the molecules, which leads to a two-band Hubbard model when the hybridization H_{mix} with the metallic states is neglected. When H_{mix} is included, one obtains an orbitally degenerate Hubbard-Anderson model. Lobos *et al.* [16] derived this model and solved it using a slave-boson mean-field approximation (SBMFA) for infinite on-site repulsion U [17]. These authors were able to reproduce the observed splitting of the FKA, which in simple terms can be interpreted as arising from split van Hove singularities due to the anisotropic hopping terms in the Hubbard part of the model.

However, there are several indications that the theory needs to be improved in order to reproduce the experimental details. For instance, the energy necessary to add the first hole $E_d \approx -0.1$ eV (see eq. (1)) was estimated from *ab initio* calculations in the local density approximation (LDA), which obtained spectral density of Fe $3d_{xz}$ and $3d_{yz}$ states 0.1 eV above the Fermi energy ϵ_F , which we set as the origin of energies ($\epsilon_F = 0$). However, as described below, more accurate LDA+ U calculations estimate $E_d \approx -1.6$ eV. Since the value $U = 1.8$ eV was estimated [10], $E_d + U$ is small and in principle double occupancy of holes cannot be neglected contradicting the assumptions in ref. [16] (the hole occupancy is between 1 and 2). In addition, that theory does not allow to obtain the position of the split dips in the FKA at the same position as in the experiment, and an *ad hoc* voltage (horizontal) shift in the differential conductance dI/dV was necessary to fit the experiment. While a shift in dI/dV (vertical) might be expected due to uncertainties in the background contribution due to conduction electrons, a voltage shift is more difficult to justify. As a comparison, for a Co atom on Au(111) a SBMFA of the $SU(2)$ impurity Anderson model provides an excellent fit of the observed dI/dV without the need of a voltage shift [18].

The above discussion shows the need of accounting for a finite U and multiple occupancy at the impurity sites. Kotliar and Ruckenstein originally implemented this idea within the SBMFA [19], which was later generalized for orbitally degenerate systems [20–22], and constitutes a very successful tool for describing highly correlated systems [23–25]. However, as we show below, this approach does not lead to the correct Kondo temperature for an isolated molecule in the Kondo regime.

In this work we study the orbitally degenerate Hubbard-Anderson model as an effective model to describe a square lattice of FePc molecules on Au(111), for realistic parameters derived from the LDA+ U . We construct a SBMFA that gives the correct Kondo temperature for one FePc molecule, and also reproduces very accurately the non-interacting limits (NILs) $U = 0$, for both the impurity and the lattice cases. Although physically we expect U to be rather large (*i.e.*, approx. 1.8 eV), reproducing the exactly solvable NIL constitutes an important “san-

ity check” for the entire formalism and is important when multiple occupancies cannot be neglected. To the best of our knowledge, this is a novel theoretical development which improves over previous SBMFAs for orbitally degenerate correlated systems [20–22]. We also stress that the formalism presented here is in principle generic and applicable beyond the case of FePc/Au(111) molecules.

Our method allows for quantitatively accurate fits of the experimental dI/dV , both for the isolated molecule and for the square lattice. The fitting procedure allows to extract the parameters of our model. From here we conclude that while the single FePc molecule is in the Kondo limit, the lattice of FePc molecules is in the intermediate-valence regime.

The Hamiltonian was derived in ref. [16]. We refer the reader to that work for details. It can be split into three parts. H_{mol} is a degenerate Hubbard model that describes the effective molecular states and the hopping between them, H_c contains the conduction states, and H_{mix} is the coupling between molecular and conduction states:

$$\begin{aligned}
 H &= H_{mol} + H_c + H_{mix}, \\
 H_{mol} &= \sum_{ij}^N \left[- \sum_{\sigma\nu} \left(t_2 h_{\mathbf{r}_{ij},\sigma}^{\nu\dagger} h_{\mathbf{r}_{ij}\pm\mathbf{a}_\nu,\sigma}^\nu + t_1 h_{\mathbf{r}_{ij},\sigma}^{\bar{\nu}\dagger} h_{\mathbf{r}_{ij}\pm\mathbf{a}_\nu,\sigma}^{\bar{\nu}} \right) \right. \\
 &\quad \left. + E_d n_{\mathbf{r}_{ij}} + \frac{U}{2} n_{\mathbf{r}_{ij}} (n_{\mathbf{r}_{ij}} - 1) \right], \\
 H_c &= \sum_{ij}^N \sum_{\xi\sigma\nu} \epsilon_\xi c_{\mathbf{r}_{ij},\xi,\sigma}^{\nu\dagger} c_{\mathbf{r}_{ij},\xi,\sigma}^\nu, \\
 H_{mix} &= V \sum_{ij}^N \sum_{\xi\sigma\nu} \left(h_{\mathbf{r}_{ij},\sigma}^{\nu\dagger} c_{\mathbf{r}_{ij},\xi,\sigma}^\nu + \text{H.c.} \right). \tag{1}
 \end{aligned}$$

The operators $h_{\mathbf{r}_{ij},\sigma}^{\nu\dagger}$ annihilate a hole (create an electron) in the state $|\nu_{\mathbf{r}_{ij},\sigma}\rangle$, where $\nu = (x, y)$ denotes one of the two degenerate molecular states with spin σ at site with position $\mathbf{r}_{ij} = i\mathbf{a}_1 + j\mathbf{a}_2$ of the square lattice, with \mathbf{a}_i the Bravais lattice vectors in the directions x and y , respectively. For simplicity we denote as x and y the orbitals with symmetry xz and yz . The operator for the total number of holes at the molecule lying at site \mathbf{r}_{ij} is $n_{\mathbf{r}_{ij}} = \sum_{\sigma\nu} n_{\mathbf{r}_{ij},\sigma}^\nu$, with $n_{\mathbf{r}_{ij},\sigma}^\nu = h_{\mathbf{r}_{ij},\sigma}^{\nu\dagger} h_{\mathbf{r}_{ij},\sigma}^\nu$. The meaning of $\bar{\nu}$ is $\bar{x} = y$, and $\bar{y} = x$. The hopping t_2 between x (y) orbitals in the x (y) direction is larger than the hopping t_1 between x (y) orbitals in the y (x) direction.

H_c corresponds to a band of bulk and surface conduction electrons of the substrate. The operator $c_{\mathbf{r}_{ij},\xi,\sigma}$ annihilates a conduction hole with spin σ and quantum number ξ at position \mathbf{r}_{ij} . Note that the form of H_{mix} and H_c assumes that the molecular states of each Hubbard site \mathbf{r}_{ij} is hybridized with a different conduction band. This is an approximation which is valid if the distance between the Hubbard sites is $R \gg 1/k_F$, with k_F the Fermi momentum of the metallic substrate [26–28], as it is the case in our problem. In other words, the molecular states are well

separated and if the hopping between them is neglected, the system behaves as dilute system of impurities.

We use the subscript η to denote any of the four states at each site ($x \uparrow, x \downarrow, y \uparrow, y \downarrow$). The basic idea of the SB approach is to enlarge the Fock space to include bosonic states which correspond to each state in the fermionic description. For example, the vacuum state at site i is now represented as $e_i^\dagger|0\rangle$, where e_i^\dagger is a bosonic operator corresponding to the empty site; similarly $s_{i\eta}^\dagger f_{i\eta}^\dagger|0\rangle$ represents the simply occupied state with one hole with ‘‘color’’ η , $d_{i\eta_1\eta_2}^\dagger f_{i\eta_1}^\dagger f_{i\eta_2}^\dagger|0\rangle$ corresponds to a state with double occupancy and similarly for triple and quadruple hole occupancy (we denote the bosons as $t_{i\eta_1\eta_2\eta_3}^\dagger$ and q , respectively). The fermion operators entering eq. (1) in the new representation are given by

$$h_{\mathbf{r}_{ij},\eta}^\dagger = z_{\mathbf{r}_{ij},\eta} f_{\mathbf{r}_{ij},\eta}^\dagger, \quad (2)$$

$$z_{\mathbf{r}_{ij},\eta}^0 = s_{\mathbf{r}_{ij},\eta}^\dagger e_{\mathbf{r}_{ij}} + \sum_{\eta_1} d_{i\eta_1\eta}^\dagger s_{\mathbf{r}_{ij},\eta_1} + \sum_{\eta_1 < \eta_2} t_{i\eta_1\eta_2\eta}^\dagger d_{\mathbf{r}_{ij},\eta_1\eta_2} + q^\dagger t_{\mathbf{r}_{ij},\eta_1\eta_2\eta_3}, \quad (3)$$

where all $\eta_i \neq \eta$ and where we assume $z_{\mathbf{r}_{ij},\eta} = z_{\mathbf{r}_{ij},\eta}^0$ for the moment. The bosonic operator $z_{\mathbf{r}_{ij},\eta}^0$ corresponds to the creation of the fermion η at site \mathbf{r}_{ij} , in the bosonic sector of the Hilbert space.

To restrict the bosonic Hilbert space to the physical subspace, the following constraints must be satisfied at each lattice site (in what follows we drop the site index \mathbf{r}_{ij} for simplicity):

$$\begin{aligned} 1 &= e^\dagger e + \sum_{\eta} s_{\eta}^\dagger s_{\eta} + \sum_{\eta_1 < \eta_2} d_{\eta_1\eta_2}^\dagger d_{\eta_1\eta_2} \\ &+ \sum_{\eta_1 < \eta_2 < \eta_3} t_{\eta_1\eta_2\eta_3}^\dagger t_{\eta_1\eta_2\eta_3} + q^\dagger q, \\ h_{\eta}^\dagger h_{\eta} &= s_{\eta}^\dagger s_{\eta} + \sum_{\eta_1 \neq \eta} d_{\eta\eta_1}^\dagger d_{\eta\eta_1} + \sum_{\eta_1 < \eta_2 \neq \eta} t_{\eta\eta_1\eta_2}^\dagger t_{\eta\eta_1\eta_2} \\ &+ q^\dagger q. \end{aligned} \quad (4)$$

The interaction term in eq. (1) can be written as

$$H_U = U \left(\sum_{\eta_1 < \eta_2} d_{\eta_1\eta_2}^\dagger d_{\eta_1\eta_2} + 3 \sum_{\eta_1 < \eta_2 < \eta_3} t_{\eta_1\eta_2\eta_3}^\dagger t_{\eta_1\eta_2\eta_3} + 6q^\dagger q \right). \quad (5)$$

The advantage of the SB representation is that using eq. (5) in the saddle-point approximation, in which all bosonic variables are replaced by numbers, the problem is reduced to a non-interacting one, in which the values of the bosons are obtained minimizing the free energy. A shortcoming of this procedure is that using eqs. (2), (3), the exactly solvable NIL $U = 0$ is not recovered after performing the mean-field approximation (MFA). In this limit,

all bosonic numbers become independent of position \mathbf{r}_{ij} and color η , they can be chosen real and positive and for a total fermion occupation $n = \langle n_{\mathbf{r}_{ij}} \rangle$, calling $p = n/4$, one has $e^2 = (1-p)^4$ (probability of finding an empty site), $s^2 = p(1-p)^3$, $d^2 = p^2(1-p)^2$, $t^2 = p^3(1-p)$ and $q^2 = p^4$. This leads to $z_{i\eta}^0 = [p(1-p)]^{1/2}$, while the correct result is $z_{i\eta}^0 = 1$ for $U = 0$. To remedy this problem for the $SU(2)$ case, Kotliar and Ruckenstein have replaced the $z_{i\eta}^0$ operator for another one $z_{i\eta}$ which is equivalent to $z_{i\eta}^0$ in the restricted Hilbert space, but when evaluated in the MFA for $U = 0$ gives $z_{\eta} = 1$ [19]. They have shown that with this correction, the SBMFA is equivalent to the Gutzwiller approximation. This procedure was generalized for an arbitrary number M of colors [20–22]. For $M = 4$ we can write (dropping again the site indices for simplicity)

$$z_{\eta} = O_{\eta L}^{-1/2} z_{\eta}^0 O_{\eta R}^{-1/2}, \quad (6)$$

$$\begin{aligned} O_{\eta L} &= 1 - A_4 e^\dagger e - A_3 \sum_{\eta_1 \neq \eta} s_{\eta_1}^\dagger s_{\eta_1} \\ &- A_2 \sum_{\eta_1 < \eta_2 \neq \eta} d_{\eta_1\eta_2}^\dagger d_{\eta_1\eta_2} - A_1 t_{\eta_1\eta_2\eta_3}^\dagger t_{\eta_1\eta_2\eta_3}, \end{aligned} \quad (7)$$

$$\begin{aligned} O_{\eta R} &= 1 - A_1 s_{\eta}^\dagger s_{\eta} - A_2 \sum_{\eta_1 \neq \eta} d_{\eta\eta_1}^\dagger d_{\eta\eta_1} \\ &- A_3 \sum_{\eta_1 < \eta_2 \neq \eta} t_{\eta\eta_1\eta_2}^\dagger t_{\eta\eta_1\eta_2} - A_4 q^\dagger q, \end{aligned} \quad (8)$$

where in eq. (7) all $\eta_i \neq \eta$. We have written the coefficients A_j in eqs. (7), (8) so that the formalism is electron-hole symmetric, giving the same z_{η} for occupation n and $4-n$. Note that z_{η}^0 gives a non-vanishing result on states which do not contain η , while all terms of eq. (8) except the first do contain this particle. Therefore $z_{\eta}^0 O_{\eta R}^{-1/2} = z_{\eta}^0$. Similarly, since z_{η}^0 creates this particle in the bosonic language, and all terms except the first in eq. (8) project over states which do not contain it, $O_{\eta L}^{-1/2} z_{\eta}^0 = z_{\eta}^0$. Then $z_{\eta} = z_{\eta}^0$ in an exact treatment. However this is no more true in the MFA. Choosing $A_j = 1$, the second of eqs. (4) gives $\langle O_{\eta R} \rangle = 1-p$, and by electron-hole symmetry $\langle O_{\eta L} \rangle = p$. This implies $\langle z_{\eta} \rangle = 1$ for $U = 0$ recovering the correct NIL in the SBMFA for any occupation.

Nevertheless, the widely used choice $A_j = 1$ leads to an incorrect Kondo temperature T_K for the impurity case in the limit $U \rightarrow +\infty$. From exact Bethe ansatz results, the Kondo temperature in this limit for the $SU(N)$ Anderson model is (except for a factor of the order of 1 that depends on the way in which it is defined) [29]

$$T_K \simeq D \exp \left(\frac{\pi E_d}{N\Delta} \right), \quad (9)$$

where a constant density of conduction states ρ per color (spin and symmetry) extending from $-D$ to D and the Kondo regime $-E_d \gg \Delta$ are assumed, with $\Delta = \pi\rho V^2$. The problem is reduced to an effective one-fermion model, in which the hybridization term is reduced by the factor

$\langle z_{i\eta} \rangle = z$, the term H_U is added, and the constraints of eqs. (4) should be added. Using the first constraint one can eliminate one of the bosons, and the second one is taken into account by introducing a Lagrange multiplier λ , leading to an effective impurity level at $\tilde{E}_d = E_d + \lambda$. The Green function of the pseudofermions is

$$G_\eta^f(\omega) = (\omega - \tilde{E}_d + i\tilde{\Delta})^{-1}, \quad (10)$$

where $\tilde{\Delta} = z^2\Delta$ is one of the definitions used for T_K . The change in energy due to the impurity becomes [29]

$$E = \frac{1}{\pi} \left[-4\tilde{\Delta} + 2\tilde{\Delta} \ln \left(\frac{\tilde{E}_d^2 + \tilde{\Delta}^2}{D^2} \right) + 4\tilde{E}_d \arctan \left(\frac{\tilde{\Delta}}{\tilde{E}_d} \right) \right] - 4\lambda(s^2 + 3d^2 + 3t^2 + q^2) + 6U(d^2 + 2t^2 + q^2). \quad (11)$$

For $U \rightarrow +\infty$, one has $d = t = q = 0$, and one can use $e^2 = 1 - 4s^2$ (from eq. (4)). The condition $\partial E / \partial \lambda = 0$ gives $\tilde{E}_d = \tilde{\Delta} \cot(\pi s^2)$ and minimizing eq. (11) with respect to s one obtains

$$\frac{2\Delta}{\pi} \frac{\partial z^2}{\partial s} \ln \left(\frac{\tilde{E}_d^2 + \tilde{\Delta}^2}{D^2} \right) + 8sE_d = 0. \quad (12)$$

In the Kondo limit, $-E_d \gg \Delta$, the total occupation $n \rightarrow 1$, and then $s \rightarrow 1/2$ and eq. (12) gives

$$\tilde{\Delta} = \frac{D}{\sqrt{2}} \exp \frac{\pi E_d}{C\Delta}, \quad C = - \left. \frac{\partial z^2}{\partial s} \right|_{s=1/2}. \quad (13)$$

In order for this equation to be consistent with eq. (9), minus the derivative of z^2 evaluated at $s = 1/2$ should be $C = N = 4$. Using eqs. (3), (6), (7), and (8), and taking $A_4 = 1$ (to have a finite z for $n \rightarrow 0$) one obtains

$$z^2 = \frac{1 - 4s^2}{(4 - 3A_3)(1 - A_1s^2)}, \quad U \rightarrow +\infty, \quad (14)$$

$$C = \frac{16}{(4 - 3A_3)(4 - A_1)}. \quad (15)$$

Thus, using $A_j = 1$ leads to an incorrect exponential dependence of T_K on E_d for $U \rightarrow +\infty$. To remedy this, we modify the coefficients A_j so that the condition $C = 4$ is satisfied, and at the same time we try to recover the NIL $U = 0$ as accurately as possible. To reproduce the NIL for $n = 4p \rightarrow 0$, in which $e^2 \simeq 1 - 4p$, $s^2 \simeq p$, and the rest of the bosons can be neglected, we must choose $A_4 = A_3 = 1$. This gives $O_{\eta R} = p$ (see eq. (8)) and compensates the factor \sqrt{p} of z_0 , while $O_{\eta L} \rightarrow 1$. Then, the condition $C = 4$ implies $A_1 = 0$. To determine the remaining coefficient we impose that the NIL for $n = 1$ is also recovered. This leads to a quadratic equation for A_2 . Its solution nearest to 1 gives $A_2 = 1.3185$. Note that because of electron-hole symmetry, $z = 1$ also for $n = 3$ and $n \rightarrow 4$. We have represented the resulting z as a function of n for $U = 0$. It is a very flat function with a value

near 1, and the maximum deviation is at $n = 2$ for which $z = 0.989$. Therefore, our SBMFA reproduces accurately not only the Kondo limit for one impurity at large U , but also the NIL in the general case. Another possibility to optimize the A_j is to relax the correct NIL for $n \rightarrow 0$ and $n \rightarrow 4$ and to ask that the formalism captures the correct Kondo temperature $T_K \simeq D \exp[-\pi U / (16\Delta)]$ for $E_d = -3U/2$ such that the system is in the electron-hole symmetric case (with $n = 2$) for large but finite U . This condition would imply $A_2 = 2 \pm \sqrt{3/2}$. However, for realistic parameters (as described below) this estimate gives $T_K \simeq 5 \times 10^{-7}$ K which is too small, indicating that these values of E_d are not realistic. Thus, we keep the values of A_j described above.

The differential conductance $G(V_b) = dI/dV_b$ measured in STS experiments, is a non-equilibrium process in which the conduction states of the tip of the scanning-tunneling microscope at a bias voltage V_b hybridizes with a linear combination $l_{\mathbf{r}_{ij}}$ of molecular and conduction states. This amounts to adding a perturbation $V_t \sum_k (t_k^\dagger l_{\mathbf{r}_{ij}} + \text{H.c.})$ to the Hamiltonian, where t_k refers to the tip states and $l_{\mathbf{r}_{ij}} = \alpha [\sum_\eta (c_{\mathbf{r}_{ij},\eta} + qh_{\mathbf{r}_{ij},\eta})]$, where α is a normalization constant. In the limit in which V_t is small, $G(V_b)$ is proportional to the density of states $\rho_l(eV_b)$ of the states $l_{\mathbf{r}_{ij}}$ at the position \mathbf{r}_{ij} of the tip [18,30]. Here q controls the ratio of the hybridization of the tip with the molecular states with respect to the corresponding value for the conduction states (this interference is the physical origin of the Fano effect). Once the Green function of the molecular states $G_{\mathbf{r}_{ij}\eta}^h(\omega) = z_{\mathbf{r}_{ij},\eta}^2 G_{\mathbf{r}_{ij},\eta}^f(\omega)$ (see eq. (10) for the impurity case) is obtained from the SBMFA, $\rho_l(\omega) = -\text{Im}[G_l(\omega)]/\pi$ is given by a simple expression obtained using equations of motion [18]. One has

$$G_{\mathbf{r}_{ij}}^l(\omega) = \sum_\eta [G_{\mathbf{r}_{ij},\eta}^{0c}(\omega) + (VG_{\mathbf{r}_{ij},\eta}^{0c}(\omega) + q)^2 G_{\mathbf{r}_{ij},\eta}^f(\omega)], \quad (16)$$

where $G_{\mathbf{r}_{ij},\eta}^{0c}$ is the Green function of the conduction states before adding the molecules (we take that corresponding to a constant density of states $\rho = 1/(2D)$ extending from $-D$ to D).

According to the estimations of LDA+ U (see supplemental material of ref. [10]), for an isolated FePc molecule on Au(111), $U = 1.84$ eV and the energy of the localized molecular orbital is $E_0 = -3.91$ eV. Therefore, the energy necessary to add the first hole on a molecular orbital is $E_d = -(E_0 + 3U) = -1.61$ eV. In the rest of this work we take $U = 1.8$ eV and for this system we take $E_d = -1.6$ eV (for the square lattice of FePc molecules we modify E_d as described below). We have chosen $D = 3.65$ eV and $\rho = 1/(2D)$. However, the relevant parameter which controls the hybridization is the product $\Delta = \pi\rho V^2$, while the spectral density of the molecular states, as well as $\rho_l(\omega)/\rho_0$ depend very weakly on D .

To describe the case of a single FePc molecule, we take Δ and q as fitting parameters. The resulting $\rho_l(\omega)$, except for an additive constant, is proportional to the observed

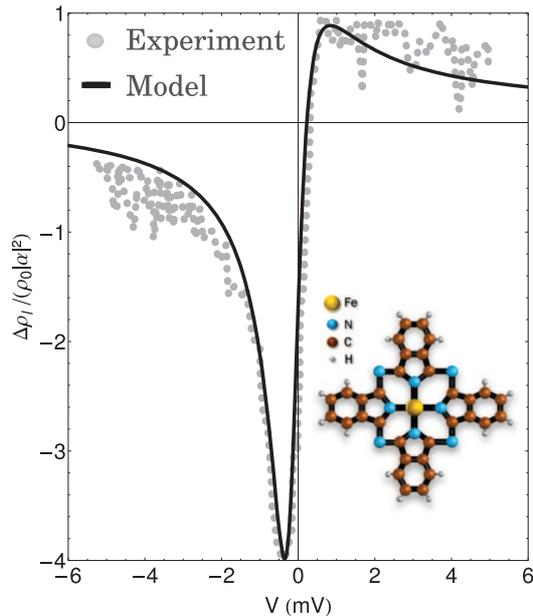


Fig. 1: (Color online) Change of the spectral density of the operator sensed by the STM tip l (see text) as a function of frequency for an isolated FePc molecule. The circles correspond to $3.1G(\omega/eV) - 2.5$, where G in arbitrary units was taken from fig. 3(a) of ref. [10]. Parameters are $U = 1.8$ eV, $E_d = -1.6$ eV, $\Delta = 11$ meV and $q = -0.03$. The inset shows a scheme of the FePc molecule.

G . In fig. 1 we represent the change $\Delta\rho_l(\omega)$ in $\rho_l(\omega)$ after addition of the impurity (last term in eq. (16)) which should be proportional to the change in G , and is less sensitive to the details of the conduction band. From the fit we obtain $\Delta = 11$ meV and $q = -0.03$. Note that the agreement with experiment near the Fermi energy is very good. It is certainly better than the comparison between two different experimental realizations (figs. 3(a) and (b) of ref. [10] for zero magnetic field). For the parameters of our fit, we obtain a total occupation of 1.01 holes (2.99 electrons) in the molecular states. The total probability of double hole occupancy is 1.3% and that of having no holes (4 electrons) is 0.14%. Therefore, we conclude that the single FePc molecule is in the Kondo regime. These results agree with those of Minamitani *et al.* [10] who used the numerical-renormalization group to interpret the experiments. However, those authors did not attempt to fit the experiment.

To model the square lattice of FePc molecules on Au(111), we need to introduce the intermolecular hopping elements t_i . We assume $t_2/t_1 = 3$ as estimated previously [16]. The SBMFA again reduces the problem to an effective non-interacting one. The latter has the same form as that explained in the supplemental material of ref. [16], but in our case a finite U is used and therefore the quasiparticle weight $z_{\mathbf{r}_{ij},\eta}^2$ is different and given by eqs. (3), (6), (7), and (8) with $A_1 = 0$, $A_2 = 1.3185$, and $A_3 = A_4 = 1$ as described above. Although for the lattice, the model is not $SU(4)$ symmetric, the effective

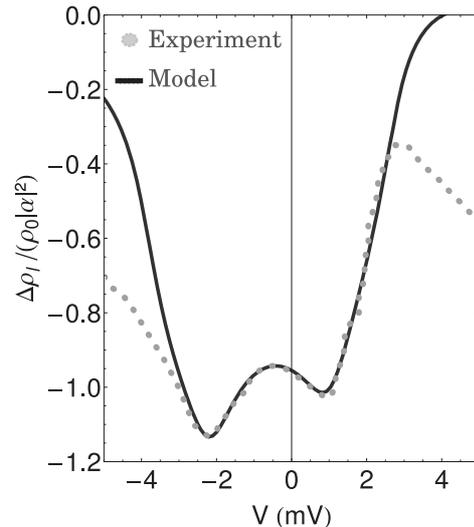


Fig. 2: Same as fig. 1 for a square lattice of FePc molecules. The circles correspond to $0.28G(\omega/eV) - 0.7$, where G in arbitrary units was taken from ref. [8]. Parameters are $U = 1.8$ eV, $E_d = -1.828$ eV, $\Delta = 11$ meV $t_1 = 7.5$ meV, and $q = -0.006$.

non-interacting problem retains this symmetry [31] and in the homogeneous $SU(4)$ symmetric solution $z_{\mathbf{r}_{ij},\eta} = z$ independent of site, spin and orbital. In order to compare with the experimental results for the square lattice [8], we retain the same values of U and Δ as for the impurity case, and use t_1 , q and E_d as fitting parameters. q depends on the distance from the STM tip to molecules and the surface and therefore one expects that it is different from the one-molecule case. Concerning E_d since the molecules are negatively charged as they are placed on the surface [10,32], one expects that E_d lowers for the lattice due to interatomic repulsion, since holes are stabilized. This agrees qualitatively with our findings. The quantitative aspects will be discussed below.

The resulting change in the spectral density sensed by the STM tip is shown in fig. 2. From the fit we obtain $t_1 = 7.5$ meV, $q = -0.006$ and $E_d = -1.828$ eV. The latter is a surprising result since $E_d + U = -28$ meV has become slightly negative, favoring double occupancy but the system is in the intermediate-valence regime, because this energy is of the order of $\Delta = 11$ meV. This value of E_d is imposed by the position in voltage of the observed differential conductance. Higher values of E_d increase the electron occupation and shift the structure to the left. For the parameters of fig. 2 we obtain a total occupation of 1.65 holes (2.35 electrons). The total single hole occupancy is 0.34, the total probability of double hole occupancy is 0.65, and other states can be neglected.

The drastic change in the charge of the molecular xz and yz orbitals is surprising. We should note that first-principle studies of the charges for isolated FePc [10,32] and CoPc [33] on Au(111) indicate that in addition to these orbitals, also the $3d$ orbitals of the TMAs with symmetry $3z^2 - r^2$ are partially occupied. Nevertheless, Minamitani *et al.* showed that the spin of these orbitals

is screened in a first-stage Kondo effect at higher energy and that an effective model containing only xz and yz orbitals as the localized ones describes the low-energy physics [10]. When an isolated FePc molecule is placed on the metal surface, a partial transfer of electrons takes place from the metallic states and also from the xz and yz orbitals to the $3z^2 - r^2$ [32]. Our results suggest that the latter charge transfer is enhanced for a lattice of FePc molecules on Au(111). The intra-atomic inter-orbital repulsion should favor this procedure, since a larger charge in the $3z^2 - r^2$ orbital increases the energy for occupying xz and yz orbitals. These arguments suggest that a more general model that includes $3z^2 - r^2$ localized states might explain the change in the occupancy of xz and yz orbitals.

In summary, we have studied an array of FePc molecules deposited on top of Au(111), described by an effective Hubbard-Anderson model with degenerate effective orbitals with xz and yz symmetry. To that end, we have introduced a generalized slave-boson mean-field approximation (SBMFA), which correctly describes both the non-interacting ($U = 0$) and the strongly interacting ($U \rightarrow \infty$) limits. This is an important improvement over previous formulations of the SBMFA for strongly correlated orbitally degenerate systems, which fail to describe the Kondo limit. We stress that our method is generic and has applications beyond the present case of FePc/Au(111). Our results indicate that while the isolated FePc molecule can be described by an $SU(4)$ Anderson model in the Kondo regime, the case of the square lattice corresponds to the intermediate-valence regime, with a total occupation of nearly 1.65 holes in the FePc molecular orbitals. This conclusion is imposed by the position in voltage of the double-dip structure observed in dI/dV and is independent of the details of the parameters. We believe that the shift in E_d is partly due to intermolecular repulsion, but it might also indicate a redistribution of charge among the Fe $3d$ electrons that is beyond our effective model.

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