

Spectral evolution of the SU(4) Kondo effect from the single impurity to the two-dimensional limit

Alejandro M. Lobos,^{1,*} Marcelo Romero,² and Armando A. Aligia³

¹*Joint Quantum Institute and Condensed Matter Theory Center, Department of Physics, University of Maryland, College Park, Maryland 20742, USA*

²*Instituto de Desarrollo Tecnológico para la Industria Química (INTEC-CONICET-UNL) Güemes 3450, CC91, (S3000GLN) Santa Fé, Argentina*

³*Centro Atómico Bariloche and Instituto Balseiro, Comisión Nacional de Energía Atómica, 8400 Bariloche, Argentina*
(Received 17 May 2013; revised manuscript received 18 February 2014; published 10 March 2014)

We describe the evolution of the SU(4) Kondo effect as the number of magnetic centers increases from one impurity to the two-dimensional (2D) lattice. We derive a Hubbard-Anderson model which describes a 2D array of atoms or molecules with twofold orbital degeneracy, acting as magnetic impurities and interacting with a metallic host. We calculate the differential conductance, observed typically in experiments of scanning tunneling spectroscopy, for different arrangements of impurities on a metallic surface: a single impurity, a periodic square lattice, and several sites of a rectangular cluster. Our results point towards the crucial importance of the orbital degeneracy and agree well with recent experiments in different systems of iron(II) phthalocyanine molecules deposited on top of Au(111) [N. Tsukahara *et al.*, *Phys. Rev. Lett.* **106**, 187201 (2011)], indicating an experimental realization of an artificial 2D SU(4) Kondo-lattice system.

DOI: [10.1103/PhysRevB.89.121406](https://doi.org/10.1103/PhysRevB.89.121406)

PACS number(s): 75.20.Hr, 71.10.-w, 72.15.Qm

The Kondo effect is one of the most paradigmatic phenomena in strongly correlated condensed matter systems [1]. It is characterized by the emergence of a many-body singlet ground state formed by the impurity spin and the conduction electrons in the Fermi sea, which form a screening “cloud” around the impurity. Originally observed in dilute magnetic alloys [1], the Kondo effect has reappeared more recently in the context of semiconductor quantum-dot systems [2,3], and in systems of magnetic adatoms (e.g., Co or Mn) deposited on clean metallic surfaces, where the effect has been clearly observed experimentally as a narrow Fano-Kondo antiresonance (FKA) in the differential conductance in scanning tunneling spectroscopy (STS) [4–6].

While most of the experimental realizations of the Kondo effect correspond to spin 1/2 and SU(2) symmetry, more exotic Kondo effects are possible in nanoscopic systems [7]. In particular, an SU(4) Kondo effect can occur when an additional pseudospin 1/2 orbital degree of freedom appears due to robust orbital degeneracy. In practice, however, the stringent conditions to preserve orbital degeneracy limit the observation of the SU(4) Kondo effect to few cases, such as C nanotubes [8–10], and Si fin-type field effect transistors [11] where there is a valley degeneracy [12]. Recently, Minamitani *et al.* [13] have shown that the Kondo effect observed in isolated iron(II) phthalocyanine (FePc) molecules deposited on top of clean Au(111) (in the most usual on-top configuration) [14] is a new realization of the SU(4) case. In the on-top configuration, the degeneracy between partially filled $3d_{xz}$ and $3d_{yz}$ orbitals of Fe is preserved by the Au(111) substrate, leading to a strong FKA in the STS signal. Interestingly, Tsukahara *et al.* [15] showed that at sufficiently high densities, the FePc molecules on Au(111) self-organize into a two-dimensional (2D) square lattice, paving the way to study artificially engineered Kondo lattices by scanning tunneling microscopy (STM). At present, a large class of organic-Kondo adsorbates are being studied

by STM techniques due to their potential applications as electronic [16,17] and/or molecular spintronics [18–20] devices, and therefore it is important to understand their electronic properties. Recent *ab initio* calculations have demonstrated the crucial role of the interaction between the organometallic molecule and the substrate for designing spintronic devices [21]. In this context, the effect of the orbital degrees of freedom in artificially engineered Kondo lattice systems remains to be explored, and to the best of our knowledge the extension of the SU(4) impurity model to the lattice has not been studied so far.

Motivated by these recent developments, in this Rapid Communication, we theoretically study the evolution of the SU(4) Kondo effect, from the single impurity to the 2D Kondo-lattice limit. Guided by general symmetry principles, we derive an effective SU(4) Hubbard-Anderson model describing coupled magnetic impurities with an additional orbital degree of freedom, forming clusters on the metallic substrate. While our results are generic, and in principle applicable to other organometallic Kondo systems, in what follows we specify our results for the case of Ref. [15], as we believe this to be the first realization of an artificial 2D SU(4) Kondo lattice. We calculate the STS differential conductance dI/dV (as observed experimentally), and analyze the line shapes upon variation of the size and connectivity of the cluster. Our results show good agreement with experiment and are important for the correct physical interpretation of the data. In particular, we show that the most prominent feature of the experiment (i.e., the splitting of the FKA in the case of high coordination number [15]) is a consequence of the orbital degeneracy [22]. As explained below, this opens up new and exciting possibilities, such as the existence of new phases with orbitally ordered ground states [23,24].

Model. We derive an effective minimal Hubbard-Anderson model for the 2D lattice of FePc molecules. For the case of an isolated molecule [see Fig. 1(a)], the effective SU(4) Anderson model has been derived previously [13]. The low-energy physics is described by two degenerate molecular orbitals of

*alobos@umd.edu

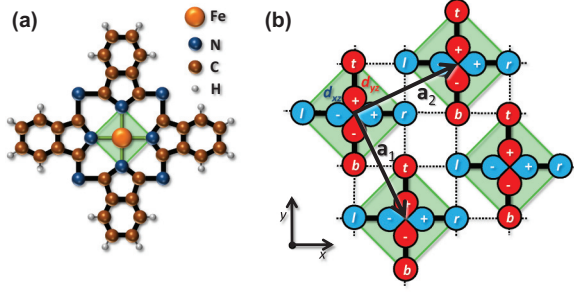


FIG. 1. (Color online) (a) Representation of aFePc molecule. The region shaded in green is the FeN_4 substructure which is kept in the theoretical model. (b) System of FeN_4 molecules forming a cluster.

xz and yz symmetry, which have most of their weight on the corresponding $3d$ orbitals of the Fe atom. To extend this impurity model to the lattice, we add the hopping between nearest-neighbor (NN) molecules, leading to a model similar to the one used to describe a trimer of Co atoms on Au(111) [25]. However, in the present case, the orbital degeneracy and the symmetry of the molecular orbitals introduce peculiar features. On general symmetry grounds, one expects that the effective hopping between any two NN molecular orbitals will depend on the *direction* of the hopping. In particular, we assume that the effective hopping between NN $3d$ Fe orbitals can occur either by direct overlap of the organic ligands, or via the Au substrate. In the first case, the coupling can be thought as occurring via the p_z orbitals of the neighboring N atoms. Defining the x and y directions as those pointing from the Fe atom to the organic ligands in the molecule, as in Fig. 1, the Fe $3d_{vz}$ hybridizes only with the p_z orbitals of the N atoms in the v direction ($v = x$ or y), and the hopping with other orbitals vanishes by symmetry. The presence of the substrate modifies these arguments [26], but the crucial directional dependence of the effective hopping is a robust feature that remains.

The effective model is $H = H_{\text{mol}} + H_c + H_{\text{mix}}$, where H_{mol} describes the molecular states and the hopping between them, H_c the conduction states, and H_{mix} the coupling between them. To illustrate the derivation of H_{mol} , we have calculated the effective hopping between molecular orbitals in a lattice of hypothetical FeN_4 molecules (i.e., the central part of FePc) as shown in Fig. 1. For each molecule, the relevant molecular states are

$$\begin{aligned} |\tilde{x}_{\mathbf{r}_{ij},\sigma}\rangle &= [\alpha \tilde{d}_{\mathbf{r}_{ij},\sigma}^x + \beta (\tilde{p}_{\mathbf{r}_{ij},\sigma}^{(r)} - \tilde{p}_{\mathbf{r}_{ij},\sigma}^{(l)})]^\dagger |0\rangle, \\ |\tilde{y}_{\mathbf{r}_{ij},\sigma}\rangle &= [\alpha \tilde{d}_{\mathbf{r}_{ij},\sigma}^y + \beta (\tilde{p}_{\mathbf{r}_{ij},\sigma}^{(t)} - \tilde{p}_{\mathbf{r}_{ij},\sigma}^{(b)})]^\dagger |0\rangle. \end{aligned} \quad (1)$$

Here, $\tilde{d}_{\mathbf{r}_{ij},\sigma}^v$ is the destruction operator for electrons with spin σ in the $3d_{vz}$ orbital of Fe at cluster with position $\mathbf{r}_{ij} = i\mathbf{a}_1 + j\mathbf{a}_2$ [with $\mathbf{a}_1, \mathbf{a}_2$ the Bravais lattice vectors defined in Fig. 1(b)], and $\tilde{p}_{\mathbf{r}_{ij},\sigma}^{(\eta)}$ is the destruction operator in the $2p_z$ orbital of the N atom located at position $\eta = \{r, l, t, b\}$ within the molecule (respectively, right, left, top, and bottom, with respect to the central Fe atom in the molecule).

It is easy to calculate the effective hopping between molecular states, in a tight-binding description, assuming a hopping t' between NN N atoms [see dotted lines in Fig. 1(b)] [26]. The magnitude of this hopping is either $t = |\beta|^2 t'$ or

zero. To simplify the model, one can “rotate” the molecular orbitals defining a new basis set $\{ |x_{\mathbf{r}_{ij},\sigma}\rangle, |y_{\mathbf{r}_{ij},\sigma}\rangle \}$ such that $\langle x_{\mathbf{r}_{ij},\sigma} | H | y_{\mathbf{r}_{lm},\sigma} \rangle = 0$, for all $\mathbf{r}_{ij}, \mathbf{r}_{lm}$, therefore conserving the orbital index $v = (x, y)$ in the hopping process. It is more convenient for us to work in the hole representation. Calling $h_{\mathbf{r}_{ij},\sigma}^v$ the operators which destroy a hole (create an electron) in the molecular state $|v_{\mathbf{r}_{ij},\sigma}\rangle$ in the new basis [26], we arrive at the effective 2D Hubbard model:

$$\begin{aligned} H_{\text{mol}} = \sum_{ij} \left[- \sum_{\sigma,v} (t_2 h_{\mathbf{r}_{ij},\sigma}^{v\dagger} h_{\mathbf{r}_{ij} \pm \mathbf{a}_v, \sigma}^v + t_1 h_{\mathbf{r}_{ij},\sigma}^{v\dagger} h_{\mathbf{r}_{ij} \pm \mathbf{a}_v, \sigma}^{\bar{v}}) \right. \\ \left. + E_h n_{\mathbf{r}_{ij}} + \frac{U}{2} n_{\mathbf{r}_{ij}} (n_{\mathbf{r}_{ij}} - 1) \right], \end{aligned} \quad (2)$$

where the effective hopping amplitudes t_1 and t_2 connect NN h^v orbitals located at \mathbf{r}_{ij} and $\mathbf{r}_{ij} \pm \mathbf{a}_v$, with the compact notation ($\mathbf{a}_x = \mathbf{a}_1$, $\mathbf{a}_y = \mathbf{a}_2$), and ($\bar{x} = y$, $\bar{y} = x$). E_h and $n_{\mathbf{r}_{ij}} = \sum_{\sigma,v} n_{\mathbf{r}_{ij},\sigma}^v$, with $n_{\mathbf{r}_{ij},\sigma}^v = h_{\mathbf{r}_{ij},\sigma}^{v\dagger} h_{\mathbf{r}_{ij},\sigma}^v$ are, respectively, the energy and number of holes. The last term in Eq. (2) accounts for the local Hubbard repulsion between holes at site \mathbf{r}_{ij} . Note that Hamiltonian (2) is explicitly SU(4) invariant. For the simplified system of FeN_4 molecules we obtain $t_1 = 0.618t$ and $t_2 = -1.618t$. In the case of an effective hopping mediated by conduction states in the substrate we obtain the same qualitative features: It is highly anisotropic and conserves the orbital index [26].

To consider the coupling to the metallic substrate, we assume that the distance between the Hubbard sites is $R \gg 1/k_F$, with k_F the Fermi momentum of the metallic substrate [26]. This approximation is not generic, but this limit is well verified in experimental molecular Kondo systems, and permits one to neglect indirect correlations among Hubbard sites mediated by the metal [such as Ruderman-Kittel-Kasuya-Yosida (RKKY) interactions or coherent Kondo correlations arising from the overlap of Kondo screening clouds] [25,27–32]. In such a limit, the 2D metal can be effectively described by a collection of uncorrelated “fermionic baths”, each one coupled to each Hubbard site \mathbf{r}_{ij} [31,32]. Therefore, we describe the metallic substrate as $H_c = \sum_{ij\xi\sigma v} \epsilon_\xi c_{\mathbf{r}_{ij},\xi,\sigma}^v c_{\mathbf{r}_{ij},\xi,\sigma}^v$, where $c_{\mathbf{r}_{ij},\xi,\sigma}$ is the annihilation operator of a conduction hole with spin σ and quantum number ξ at position \mathbf{r}_{ij} . The coupling to the molecules is described by $H_{\text{mix}} = V \sum_{ij\xi\sigma v} (h_{\mathbf{r}_{ij},\sigma}^{v\dagger} c_{\mathbf{r}_{ij},\xi,\sigma}^v + \text{H.c.})$ [26].

We note that H is an SU(4) invariant [26] many-body Hamiltonian which cannot be solved exactly. Assuming the limit of strong repulsion $U \rightarrow \infty$, we can neglect configurations with two or more holes in a molecular orbital, and consider only local charge fluctuations between the subspaces with $n = 0, 1$ holes. This limit can be implemented in the slave-boson representation [33] $h_{\mathbf{r}_{ij},\sigma}^v = b_{\mathbf{r}_{ij}}^\dagger f_{\mathbf{r}_{ij},\sigma}^v$, where $b_{\mathbf{r}_{ij}}$ is a bosonic variable describing the $n_h = 0$ state (both molecular levels occupied with both spins) and $f_{\mathbf{r}_{ij},\sigma}^v$ is a renormalized hole operator. These operators must be constrained by the relation $b_{\mathbf{r}_{ij}}^\dagger b_{\mathbf{r}_{ij}} + \sum_{\sigma,v} f_{\mathbf{r}_{ij},\sigma}^{v\dagger} f_{\mathbf{r}_{ij},\sigma}^v = 1$. This representation of SU(\mathcal{N})-invariant Kondo impurities is particularly useful for $\mathcal{N} \rightarrow \infty$, where the saddle-point slave-boson mean field approximation (SBMFA) for the bosonic degrees of freedom $b_{\mathbf{r}_{ij}} = b_{\mathbf{r}_{ij}}^\dagger = \langle b_{\mathbf{r}_{ij}} \rangle = z$ becomes exact [33]. After the SBMFA

(obtained by replacing $h_{\mathbf{r}_{ij},\sigma}^v \rightarrow z_{\mathbf{r}_{ij},\sigma}^v H$ becomes exactly solvable, and we set $\mathcal{N} = 4$ [26]. Physically, the SBMFA describes noninteracting Fermi quasiparticles with renormalized mass $m_e^*/m_e \approx 1/z^2$ and quasiparticle weight z^2 near the Fermi level [33], providing a correct description of the Kondo lattice near the Fermi-liquid fixed point.

In STM experiments, the relevant observable is the differential conductance dI/dV , which in the limit of weak tunneling coupling between the STM tip and the system becomes proportional to the spectral density $dI/dV \sim \rho_t(-eV)$, where the minus sign is needed to pass from hole to electron representation, and t represents a mixed operator $t_{\mathbf{r}_{ij},\sigma}^v = \sum_{\xi} c_{\mathbf{r}_{ij},\xi,\sigma}^v + q h_{\mathbf{r}_{ij},\sigma}^v$ (with q the Fano parameter), reflecting the interference between molecule and substrate states as sensed by the STM tip [27,34,35]. We calculate the density of t states as $\rho_t(\omega) = -\frac{1}{\pi} \sum_{\sigma,v} \text{Im}[G_{\mathbf{r}_{ij},v,\sigma}^t(\omega + i0^+)]$, with $G_{\mathbf{r}_{ij},v,\sigma}^t(\omega + i0^+)$ the retarded local Green's function of the operator $t_{\mathbf{r}_{ij},\sigma}^v$.

Results. We assume a constant density of conduction states $\rho = 0.137/\text{eV}$ per spin, extending from $-W$ to $W = 3.65$ eV. These values are similar to those that provide a good fit of the observed line shape for a Co impurity on Cu(111) [34]. The energy of the molecular states (in the hole representation) E_h was taken near to -0.1 eV, according to *ab initio* calculations which find spectral density of Fe $3d_{xz}$ and $3d_{yz}$ states 0.1 eV above the Fermi energy [13]. We also keep the ratio of hoppings $t_2/t_1 = -3$, similar to the values obtained above for the simplified system (good fits are also obtained for other values). t_1 , V , and q are taken as fitting parameters. We define $\Gamma = \pi\rho V^2$.

In Fig. 2 we display our fits of the observed dI/dV . From the *ab initio* calculations [13] one can estimate $U = 1.6$ eV, which turns out to be much larger than the value $\Gamma \approx 0.01$ eV that results from the fit of the isolated molecule. It is also much larger than t_i . Therefore, the limit $U \rightarrow \infty$ is well justified. Figure 2 shows good agreement between our theoretical results

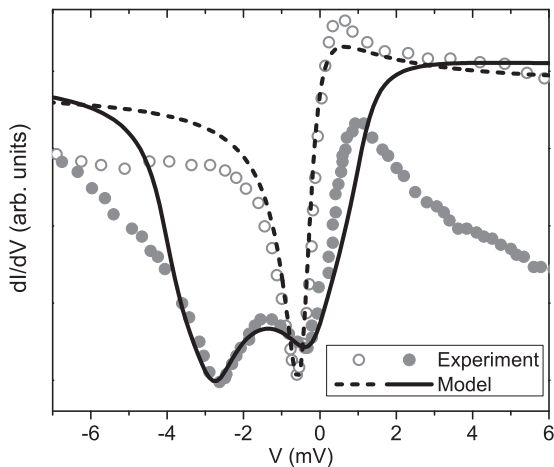


FIG. 2. Differential conductance as a function of voltage for an isolated molecule (open circles and dashed line) and the 2D lattice (solid circles and full line). Circles correspond to experiment [15] and lines to theory with $\Gamma = 10.12$ meV. For one molecule $E_h = -112$ meV, and $q = -0.025$. For the lattice $E_h = -128$ meV, $t_1 = 7$ meV, $t_2 = 3t_1$, and $q = -0.006$.

and the experiment, in accordance with previous results on single Co impurities on Cu(111) [34]. However, in contrast to that case, here the experimental curves had to be slightly shifted 0.55 mV to the left to make both curves coincide. This might be related to experimental uncertainties [36].

The situation is more difficult for the case of the lattice, because of the double-dip structure of the observed FKA. We have kept the same Γ obtained from the fit of the single molecule, but we had to slightly increase the magnitude of E_h to $|E_h| = 0.128$ eV in order to obtain better fits. This is well justified by the fact that the molecular states, and in particular the Fe $3d$ orbitals, increase their occupancy when the molecule is adsorbed on the Au surface [13], and the single-electron levels are expected to increase their energy due to interatomic Coulomb repulsion. In addition, we had to slightly modify the value of q to $q = -0.006$, a fact that might be related to the different experimental conditions in which the single molecule and lattice dI/dV spectra were obtained in Ref. [15]. As shown in Fig. 2, our theory is able to provide semiquantitative agreement with the experiment. In particular, note that the shape of the experimental curve near $V = 0$ is well reproduced. As before, we have shifted the experimental curve to the left by 1.1 mV.

The double-dip structure is a consequence of correlation effects combined with the van Hove singularities (VHS) in the spectral density of H_{mol} , directly related to the different $|t_1| \neq |t_2|$ in Eq. (2) (see Ref. [37]). In the SBMFA, the splitting of the VHS is given by $\Delta = 4z^2||t_1| - |t_2||$, where the quasiparticle weight z^2 introduces a band-narrowing effect due to correlations. In the case of Fig. 2 (solid lines), the minimum of the ground state energy is obtained for $z^2 \approx 0.045$, which results in a splitting of $\Delta \approx 2.5$ meV, consistent with the experimentally observed one. This value of z^2 points to a strong renormalization effect near the Fermi surface, with a mass enhancement $m_e^*/m_e \approx 20$. Correlations are therefore essential to explain the magnitude and the position of the observed feature. The anisotropy of an individual molecular orbital [in spite of the orbital-spin SU(4) and space C_{4v} symmetries [38]] is the key for this splitting. The hybridization with the conduction states broadens the VHS but the splitting persists.

The dI/dV has been measured at different sites of a finite cluster, to study the effects of coordination on the observed spectra [15]. In order to compare with experiment, we have applied our theory to a finite cluster of 5×4 molecules, as shown in Fig. 3 (see Ref. [39]). Some of the curves display an oscillatory behavior, which are likely to disappear for a more realistic calculation [39] or in the presence of disorder or inhomogeneities (not considered here). In any case, the results provide definite conclusions: The differential conductance at the corners (sites of coordination number $Z = 2$) do not show a splitting, while those with $Z = 4$ do show two dips in the FKA. The sites with $Z = 3$ display an intermediate and variable behavior which depends on the specific site. These results also agree with the experimental trends [15].

Summary and discussion. Motivated by recent experiments [13–15], we have derived a Hubbard-Anderson model describing a square lattice of magnetic atoms or molecules with orbital degeneracy on top of a metallic surface. Extension to other lattices is straightforward. While the model has the C_{4v} symmetry of the square lattice, the individual molecular

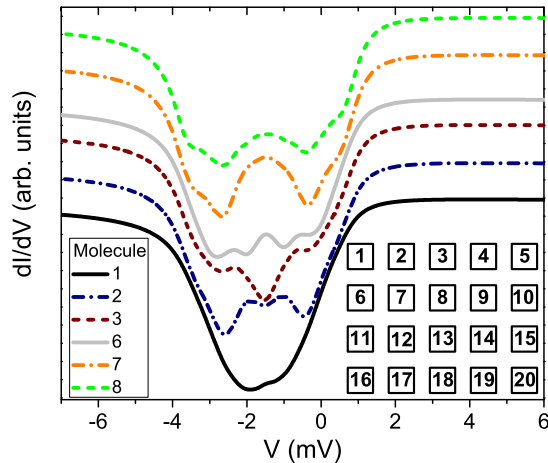


FIG. 3. (Color online) Differential conductance as a function of voltage for several sites of a 5×4 cluster. The figures have been displaced vertically for clarity.

orbitals are coupled via an anisotropic hopping which leads to two strongly renormalized VHS in the density of states of $3d$ electrons. The hybridization to the substrate broadens these VHS, but these features persist and dominate the density of states observed by the STM tip, therefore displaying two dips in the dI/dV around $V = 0$. We conclude that these VHS are the main explanation of the experimentally observed splitting in the FKA. Our results explain the observed behavior in systems of FePc molecules on Au(111), for an isolated molecule, the lattice, and the evolution between them in a consistent way.

Our work has its own interest beyond FePc molecules. A study of a similar 2D model without coupling to the substrate,

suggests a ferromagnetic (FM) orbital ordering and antiferromagnetic (AFM) spin ordering at $T = 0$ for small Hund's rule exchange [24]. The nearest-neighbor AFM interactions are of the order of $4t_2^2/U \approx 10$ K or $4t_1^2/U \approx 1$ K, depending on direction [see Eq. (10) of Ref. [24]], which are of the order of the Kondo temperature $T_K \approx 4.7$ K estimated from the half width at half maximum of the FKA. In addition, while the RKKY interaction I is unlikely to explain the splitting of the FKA, it might also introduce interesting competing effects [22,26]. For our specific system, a preliminary calculation based on the Stoner criterion shows that magnetic order would occur for $|I| > 16.1$ K. While fluctuations in 2D destroy long-range magnetic order at finite temperature, this opens up the intriguing possibility of observing quantum critical behavior at low enough temperatures in 2D molecular Kondo systems. Indeed, the existence of orbitally ordered phases [24] and dissipative quantum phase transitions [31,32] have been suggested in related systems. Recently, long-range FM order was observed for a 2D layer of organic molecules absorbed on graphene [20]. In transition-metal phthalocyanines the coupling to the substrate is very sensitive to the particular transition-metal atom [21]. We also expect a strong dependence on the substrate, as, for example, replacing Au by Ag or Cu. Therefore new physics is likely to appear in the near future, and our theory (or some modification of it) is expected to bring valuable insight.

Acknowledgments. The authors are grateful to N. Takagi and E. Minamitani for useful comments. A.M.L. acknowledges support from JQI-NSF-PFC. M.R. and A.A.A. thank CONICET from Argentina for financial support. This work was partially supported by PIP 11220080101821 and PIP 11200621 of CONICET and PICT R1776 of the ANPCyT, Argentina.

- [1] A. C. Hewson, *The Kondo Problem to Heavy Fermions* (Cambridge University Press, Cambridge, 1993).
- [2] S. M. Cronenwet, T. H. Oosterkamp, and L. P. Kouwenhoven, *Science* **281**, 540 (1998).
- [3] D. Goldhaber-Gordon, H. Shtrikman, D. Mahalu, D. Abusch-Magder, U. Meirav, and M. A. Kastner, *Nature (London)* **391**, 156 (1998).
- [4] J. Li, W. D. Schneider, R. Berndt, and B. Delley, *Phys. Rev. Lett.* **80**, 2893 (1998).
- [5] V. Madhavan, W. Chen, T. Jamneala, M. F. Crommie, and N. S. Wingreen, *Science* **280**, 567 (1998).
- [6] N. Knorr, M. A. Schneider, L. Diekhoner, P. Wahl, and K. Kern, *Phys. Rev. Lett.* **88**, 096804 (2002).
- [7] M. R. Galpin, D. E. Logan, and H. R. Krishnamurthy, *Phys. Rev. Lett.* **94**, 186406 (2005); A. K. Mitchell and D. E. Logan, *Phys. Rev. B* **81**, 075126 (2010); S. Di Napoli, A. Weichselbaum, P. Roura-Bas, A. A. Aligia, Y. Mokrousov, and S. Blügel, *Phys. Rev. Lett.* **110**, 196402 (2013); T. Kuzmenko, K. Kikoin, and Y. Avishai, *Phys. Rev. B* **88**, 125102 (2013).
- [8] P. Jarillo-Herrero, J. Kong, H. van der Zant, C. Dekker, L. Kouwenhoven, and S. De Franceschi, *Nature (London)* **434**, 484 (2005).
- [9] C. A. Büsser and G. B. Martins, *Phys. Rev. B* **75**, 045406 (2007).
- [10] F. B. Anders, D. E. Logan, M. R. Galpin, and G. Finkelstein, *Phys. Rev. Lett.* **100**, 086809 (2008).
- [11] G. C. Tettamanzi, J. Verduijn, G. P. Lansbergen, M. Blaauboer, M. J. Calderón, R. Aguado, and S. Rogge, *Phys. Rev. Lett.* **108**, 046803 (2012).
- [12] P. Roura-Bas, L. Tosi, A. A. Aligia, and P. S. Cornaglia, *Phys. Rev. B* **86**, 165106 (2012).
- [13] E. Minamitani, N. Tsukahara, D. Matsunaka, Y. Kim, N. Takagi, and M. Kawai, *Phys. Rev. Lett.* **109**, 086602 (2012).
- [14] L. Gao, W. Ji, Y. B. Hu, Z. H. Cheng, Z. T. Deng, Q. Liu, N. Jiang, X. Lin, W. Guo, S. X. Du *et al.*, *Phys. Rev. Lett.* **99**, 106402 (2007).
- [15] N. Tsukahara, S. Shiraki, S. Itou, N. Ohta, N. Takagi, and M. Kawai, *Phys. Rev. Lett.* **106**, 187201 (2011).
- [16] L. Venkataraman, J. E. Klare, C. Nuckolls, M. S. Hybertsen, and M. L. Steigerwald, *Nature (London)* **442**, 904 (2006).
- [17] Y. F. Wang, J. Kröger, R. Berndt, H. Vázquez, M. Brandbyge, and M. Paulsson, *Phys. Rev. Lett.* **104**, 176802 (2010).
- [18] V. Iancu, A. Deshpande, and S.-W. Hla, *Nano Lett.* **6**, 820 (2006).
- [19] U. G. E. Perera, H. J. Kulik, V. Iancu, L. G. G. V. Dias da Silva, S. E. Ulloa, N. Marzari, and S.-W. Hla, *Phys. Rev. Lett.* **105**, 106601 (2010).

- [20] M. Garnica, D. Stradi, S. Barja, F. Calleja, C. Díaz, M. Alcamí, N. Martín, A. L. Vázquez de Parga, F. Martín, and R. Miranda, *Nat. Phys.* **9**, 368 (2013).
- [21] A. Mugarza, R. Robles, C. Krull, R. Korytár, N. Lorente, and P. Gambardella, *Phys. Rev. B* **85**, 155437 (2012); P. Gargiani, G. Rossi, R. Biagi, V. Corradini, M. Pedio, S. Fortuna, A. Calzolari, S. Fabris, J. C. Cezar, N. B. Brookes *et al.*, *ibid.* **87**, 165407 (2013).
- [22] In Ref. [15] it is suggested that the RKKY interaction I might explain the observed splitting Δ , but our estimations show that it is too small. Assuming that bulk Au electrons dominate the hybridization with the impurity [6,25], from the observed $T_K = W \exp[-1/(\rho J)] \approx 5$ K and the reported $\rho = 0.137/\text{eV}$ one estimates a Kondo coupling $J = 0.8$ eV. Using the RKKY expression for free electrons and known data we obtain for the reported intermolecular distance $R = 14.7$ Å, $|I_{3D}| \leq 0.21$ K. Similarly, using known data for the 2D Shockley states and the expression for I in 2D [40], assuming that half of the Kondo temperature T_K is due to surface states, we obtain $|I_{2D}| \leq 2.17$ K. In any case $I < T_K \ll \Delta$ (see Ref. [26] for more details).
- [23] D. I. Khomskii and K. I. Kugel, *Solid State Commun.* **13**, 763 (1973).
- [24] A. A. Aligia and M. A. Gusmão, *Phys. Rev. B* **70**, 054403 (2004).
- [25] A. A. Aligia, *Phys. Rev. Lett.* **96**, 096804 (2006).
- [26] See Supplemental Material at <http://link.aps.org/supplemental/10.1103/PhysRevB.89.121406> for details of the derivation of the Hamiltonian (2), the generators of its SU(4) symmetry group, the derivation of the SBMFA equations and an estimation of the upper bounds of the RKKY interaction.
- [27] M. Romero and A. A. Aligia, *Phys. Rev. B* **83**, 155423 (2011).
- [28] V. Barzykin and I. Affleck, *Phys. Rev. B* **61**, 6170 (2000).
- [29] J. Simonin, [arXiv:0708.3604](https://arxiv.org/abs/0708.3604) [cond-mat.mes-hall].
- [30] I. Affleck, in *Perspectives of Mesoscopic Physics: Dedicated to Yoseph Imry's 70th Birthday*, edited by A. Aharony and O. Entin-Wohlman (World Scientific, Singapore, 2010); [arXiv:0911.2209](https://arxiv.org/abs/0911.2209) [cond-mat.mes-hall].
- [31] A. M. Lobos, M. A. Cazalilla, and P. Chudzinski, *Phys. Rev. B* **86**, 035455 (2012).
- [32] A. M. Lobos and M. A. Cazalilla, *J. Phys.: Condens. Matter* **25**, 094008 (2013).
- [33] P. Coleman, *Phys. Rev. B* **29**, 3035 (1984); **35**, 5072 (1987); D. M. Newns and N. Read, *Adv. Phys.* **36**, 799 (1987).
- [34] A. A. Aligia and A. M. Lobos, *J. Phys.: Condens. Matter* **17**, S1095 (2005).
- [35] J. Figgins and D. K. Morr, *Phys. Rev. Lett.* **104**, 187202 (2010).
- [36] Compare Figs. 3(a) and 3(b) in Ref. [13] for zero applied magnetic field.
- [37] A tight-binding model in a rectangular lattice with hoppings t_x, t_y in the x, y directions has a dispersion relation $E(k_x, k_y) = -2(t_x \cos k_x + t_y \cos k_y)$. The sign of t_x (t_y) can be changed by a gauge transformation $d_{i,j} \rightarrow (-1)^i d_{i,j}$ [$d_{i,j} \rightarrow (-1)^j d_{i,j}$]. For $t_x, t_y > 0$, the van Hove singularities are at the saddle points of $E(k_x, k_y)$ with wave vectors $(0, \pi)$ and $(\pi, 0)$ and energies $E = 2(t_y - t_x)$ and $E = 2(t_x - t_y)$, respectively.
- [38] The actual point group in the experimental array of molecules [15] is C_4 because the lines of molecules are not parallel to the main directions of the substrate. However, since we are modeling the substrate states with a continuum, the symmetry of our model is higher.
- [39] Since the minimization of the free energy in the SBMFA with respect to all $z_{r_{ij}}$ and Lagrange multipliers $\lambda_{r_{ij}}$ enforcing the constraints for all nonequivalent sites r_{ij} is a formidable task, we have made the additional assumption that $z_{r_{ij}} = z$ and $\lambda_{r_{ij}} = \lambda$, where z and λ are the corresponding values for the lattice. The dependence of these quantities on site would likely act in a similar way as disorder, blurring the oscillations observed in Fig. 3.
- [40] M. T. Béal-Monod, *Phys. Rev. B* **36**, 8835 (1987).