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

¹Joint Quantum Institute and Condensed Matter Theory Center, Department of Physics, University of Maryland, College Park, Maryland 20742, USA
²Instituto de Desarrollo Tecnológico para la Industria Química (INTEC-CONICET-UNL) Güemes 3450, CC91, (S3000GLN), Santa Fé, Argentina.
³Centro Atómico Bariloche and Instituto Balseiro, Comisión Nacional de Energía Atómica, 8400 Bariloche, Argentina.

(Dated: May 20, 2013)

PACS numbers: 75.20.Hr, 71.10.-w, 72.15.Qm

We have derived a Hubbard-Anderson model which describes a two-dimensional array of atoms or molecules with two-fold orbital degeneracy, acting as magnetic impurities and interacting with a metallic host. We calculate the differential conductance for different arrangements of impurities on a metallic surface: a single impurity, a periodic square lattice, and several sites of a rectangular cluster. The results agree with recent experimental results using scanning tunneling spectroscopy in different systems of of iron(II) phthalocyanine molecules deposited on top of Au(111) [N. Tsukahara et al., Phys. Rev. Lett. 106, 187201 (2011)].

The Kondo effect is one of the most paradigmatic phenomena in strongly correlated condensed matter systems. The phenomenon 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, the Kondo effect has reappeared more recently in the context of semiconductor quantum-dot (QD) systems, 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). Scanning tunneling microscopy (STM) has also enabled to study systems of Kondo adatoms interacting via direct exchange (due to the overlap of d orbitals), or via indirect Ruderman-Kittel-Kasuya-Yosida (RKKY) exchange, opening an exciting field of research and potential applications in electronic devices and molecular spintronics.

Most of the experimental realizations of the Kondo effect correspond to spin 1/2 and SU(2) symmetry. However, when degeneracy between two orbitals is present, a more exotic SU(4) Kondo effect can occur due to the additional pseudospin 1/2 orbital degree of freedom. Until recently, the restriction of robust degeneracy has limited the observation of this effect to C nanotubes, where there is a valley degeneracy as in graphene. Individual iron(II) phthalocyanine (FePc) molecules are known to display a FKA resonance. In a recent work, Tsukahara et al. performed a STM study of FePc molecules deposited on top of clean Au(111). At high enough densities, FePc molecules self-organize into a square lattice. Tsukahara and co-workers analyzed the STS line shapes upon variation of the cluster size and coordination number of the molecules, therefore allowing to observe the spectral evolution of the FKA, from the single-impurity limit to the two-dimensional (2D) lattice. The most prominent feature is the observation of a splitting of the FKA in the case of high coordination number. The authors interpret this phenomenon in terms of the competition between the impurity Kondo effect and the indirect RKKY interaction. However, a problem with this interpretation is that this interaction is too small at the distance R between magnetic Fe ions ($k_F R \approx 16$), where $k_F$ is the Fermi wave vector of Au). As a comparison, for CoCu$_n$Co clusters on Cu(111), with a similar structure of the conduction electrons and about 40 times larger Kondo temperature $T_K$ for the isolated Co impurity, no splitting of the FKA was observed even for $n = 10$. It is therefore important to clarify the origin of this splitting. On the other hand, it has been shown that for isolated FePc molecules (in the most usual on-top configuration), the degeneracy between partially filled 3$d_{xz}$ and 3$d_{yz}$ orbitals of Fe, leads to an SU(4) Kondo effect. To the best of our knowledge, an extension of the SU(4) impurity model to the lattice has not been studied so far.

In this Letter, we theoretically study the evolution of the SU(4) Kondo effect from the single impurity to the 2D limit in system consisting of FePc molecules ontop of a metallic sustrate. We derive the appropriate effective SU(4) Hubbard-Anderson model consistent with the underlying symmetries of the problem, which enables to describe clusters of FePc molecules of different size and connectivity. We focus on the theoretical calculation of 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...
FIG. 1. (Color online) (a) Representation of a iron(II) phthalocyanine (FePc) molecule. The region shaded in green is the FeN₄ substructure which is kept in the theoretical model. (b) System of FeN₄ molecules forming a cluster.

show a good agreement with the experimental results and are important for the correct physical interpretation of the data [18].

Model.- We start our theoretical description by deriving 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 by Minamitami et al. on the basis of ab-initio and numerical-renormalization-group calculations [20]. In this case, the low-energy physics is described by two degenerate molecular orbitals of $xz$ 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) [21]. 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 (either direct or mediated through the substrate Au states) will depend on the direction of the hopping. In particular, we assume that the effective hopping between NN 3d Fe orbitals can occur by direct overlap of the organic ligands or via the Au(111) substrate. In the first case, the coupling can be hypothetically thought as occurring via the $p_z$ orbitals of the neighboring N atoms. In that case, defining the $x$ and $y$ directions as those pointing from the Fe atom to its four NN N atoms (see Fig. 1(a)), the Fe $3d_{xz}$ hybridizes only with the $p_z$ orbitals of the N atoms in the $\nu$ direction ($\nu = x$ or $y$), and the hopping with other orbitals $s$ or $p$ vanishes by symmetry. The presence of the remaining atoms of the molecule and the substrate can modify quantitatively these arguments. However, regardless of these microscopic details and of the specific origin of the effective hopping along the $xy$ plane, its directional dependence is a robust feature that remains unchanged, and turns out to be crucial for our description. The effective model then becomes $H = H_{mol} + H_c + H_{mix}$ where $H_{mol}$ describes the molecular states and the hopping between them, $H_c$ the the conduction states, and $H_{mix}$ the mixture between them.

To illustrate the derivation of $H_{mol}$, we consider a simplified system which retains the essential physics. We have calculated the effective hopping between molecular orbitals in a lattice of hypothetical FeN₄ molecules (i.e., the central part of FePc) as shown in Fig. 1(a). For each molecule, the relevant molecular states are:

$$
|x_{r_{ij}, \sigma}⟩ = \left[ \alpha \tilde{d}_{r_{ij}, \sigma}^{\bar{x}} + \beta \left( \tilde{p}_{r_{ij}, \sigma}^{(x)} - \tilde{p}_{r_{ij}, \sigma}^{(t)} \right) \right] ^\dagger |0⟩ \, ,
$$

$$
|\tilde{y}_{r_{ij}, \sigma}⟩ = \left[ \alpha \tilde{p}_{r_{ij}, \sigma}^{(y)} + \beta \left( \tilde{p}_{r_{ij}, \sigma}^{(t)} - \tilde{p}_{r_{ij}, \sigma}^{(b)} \right) \right] ^\dagger |0⟩ \, .
$$

Here, $\tilde{d}_{r_{ij}, \sigma}$ is the destruction operator for electrons with spin $\sigma$ in the $3d_{xz}$ orbital of Fe at center position $r_{ij} = in_a + jn_b$ (with $a_1, a_2$ the Bravais lattice vectors defined in Fig. 1(b)), and $\tilde{p}_{r_{ij}, \sigma}$ is the destruction operator in the $2p_{xy}$ orbital of the N atom located at position $\eta = (r, l, t, b)$ within the molecule (respectively: right, left, top, 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 Fig. 1(b)). The magnitude of this hopping is either $t = |\beta|^2 t_0$ or zero. To simplify the model, one can “rotate” the molecular orbitals defining a new basis set $\{ |x_{r_{ij}, \sigma}, y_{r_{ij}, \sigma}⟩ \}$ such that $\langle x_{r_{ij}, \sigma}| H |y_{r_{ij}, \sigma}⟩ = 0$, for all $r_{ij}, r_{lm}$, therefore conserving the orbital index $\nu = (x, y)$ in the hopping process. It is more convenient for us to work in the hole representation. Calling $h_{r_{ij}, \nu}^{\bar{r}_{ij}, \sigma}$ the operators which destroy a hole (create an electron) in the molecular state $\nu$ in the new basis, we arrive at the effective 2D Hubbard model:

$$
H_{mol} = \sum_{ij}^{N} \left[ - \sum_{\sigma, \nu} \left( t_1 h_{r_{ij}, \nu}^{\bar{r}_{ij}, \sigma} h_{r_{ij}, \pm \eta_{\nu, \sigma}} + t_2 h_{r_{ij}, \sigma}^{\bar{r}_{ij}, \nu} h_{r_{ij}, \pm \eta_{\nu, \sigma}} \right) 
+ E_h n_{r_{ij}} + \frac{U}{2} n_{r_{ij}} (n_{r_{ij}} - 1) \right] ,
$$

where the effective hopping amplitudes $t_1$ and $t_2$ connect NN $h_{\nu}$ orbitals located at $r_{ij}$ and $r_{ij} \pm \eta_{\nu}$, with the compact notation $(a_{c} = a_1, a_{o} = a_2)$, and $(\bar{x} = y, \bar{y} = x)$. $E_h$ and $n_{r_{ij}} = \sum_{\sigma} n_{r_{ij}, \sigma}^{h_{r_{ij}, \sigma}}$, with $n_{r_{ij}, \sigma}^{h_{r_{ij}, \sigma}} = h_{r_{ij}, \sigma}^{\bar{r}_{ij}, \sigma} h_{r_{ij}, \sigma}$ are, respectively, the energy and number of holes. The last term in Eq. (2) accounts for the local Hubbard repulsion between holes at site $r_{ij}$. Note that Hamiltonian Eq. (2) is explicitly SU(4)-invariant. For the simplified system of FeN₄ molecules we obtain $t_1 = 0.618t$ and $t_2 = -1.618t$. This anisotropy of the hopping for a given orbitals should persist by symmetry in the lattice of 2D FePc molecules. One can show that the effective hopping mediated through conduction states in the substrate
shows the same features: it is highly anisotropic and conserves the orbital index.

To consider the coupling to the metallic substrate, we make the simplifying assumption that the distance between the Hubbard sites is $R \gg 1/k_F$, with $k_F$ the Fermi momentum of the metallic substrate. This approximation is not generic, but this limit is well verified in experimental molecular Kondo systems, in particular in ours, where $k_F R \simeq 16$ [19], and allows to neglect indirect correlations among Hubbard sites mediated by the metal (such as RKKY interactions or coherent Kondo correlations arising from the overlap of Kondo screening clouds) [21 27]. 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 $r_{ij}$ [26 27]. Therefore, we describe the metallic substrate as $H_c = \sum_{ij} \xi_{\sigma \tau} c_{r_{ij}}^{\dagger} \epsilon_{\tau_{r_{ij}}, \xi_{\sigma}} c_{r_{ij}, \xi_{\sigma}}$, where $c_{r_{ij}, \xi_{\sigma}}$ is the annihilation operator of a conduction hole with spin $\sigma$ and quantum number $\xi$ at position $r_{ij}$. On the other hand, the coupling to the molecules is described with $H_{mix} = V \sum_{\nu \sigma \nu} (h_{r_{ij}, \sigma}^{\dagger} \epsilon_{r_{ij}, \xi_{\sigma}} + H.c.)$.

The full Hamiltonian of the system $H$ is a many-body Hamiltonian which cannot be solved exactly, and we need to make further approximations to proceed. Assuming the limit of strong repulsion $U \to \infty$, 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. A representation that implements this limit is the slave-boson representation [28] $b_{r_{ij}, \sigma} = b_{r_{ij}}^{\dagger} f_{r_{ij}, \sigma}$, where $b_{r_{ij}}$ is a bosonic variable describing the $n_h = 0$ state (both molecular levels occupied with both spins) and $f_{r_{ij}, \sigma}$ is a renormalized hole operator. These operators must be constrained by the relation $b_{r_{ij}}^{\dagger} b_{r_{ij}} + \sum_{\nu \sigma} f_{r_{ij}, \sigma}^{\dagger} f_{r_{ij}, \sigma} = 1$. This representation allows to describe SU($N$)-invariant Kondo impurities, and is particularly useful in the limit $N \to \infty$, where the saddle-point (mean-field) approximation for the bosonic degrees of freedom $b_{r_{ij}} = b_{r_{ij}}^{\dagger} = \langle b_{r_{ij}} \rangle = \delta_{r_{ij}}$ becomes exact [28]. After the slave-boson mean field approximation (SBMFA), the mean-field Hamiltonian of the system (obtained by replacing $h_{r_{ij}, \sigma}^{\dagger} \rightarrow z_{r_{ij}} f_{r_{ij}, \sigma}^{\dagger}$) becomes exactly solvable, and we set $N = 4$.

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 $dI/dV \sim \rho_l (-eV)$, where the minus sign is needed to pass from hole to electron representation, and where $t$ represents a mixed operator $t_{r_{ij}, \sigma}^{\dagger} = \sum_{r_{ij}} \epsilon_{r_{ij}, \xi_{\sigma}} + qh_{r_{ij}, \sigma}^{\dagger}$ (with $q$ the Fano parameter), reflecting the interference between molecule and substrate states as sensed by the STM tip. We calculate the density of $t$-states as $\rho_l (\omega) = -\frac{1}{\pi} \sum_{\sigma, \nu} \text{Im} \left[ C_{r_{ij}, \nu, \sigma}^{t} (\omega + i0^+) \right]$, with $C_{r_{ij}, \nu, \sigma}^{t} (\omega + i0^+)$ the retarded local Green’s function of the operator $t_{r_{ij}, \sigma}^{\dagger}$ [22 29 30].

Results.- For the results of $dI/dV$ shown below, we assume a constant density of conduction states $\rho = 0.125/eV$ per spin, extending from $-W$ to $W = 4$ eV. These values are similar to those that provide a good fit of the observed line shape for a Co impurity on Cu(111) [29]. 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 $3dxz$ and $3dyz$ states $0.1$ eV above the Fermi energy [29]. 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). The hopping $t_1$, the hybridization $V$ and $q$ are taken as fitting parameters. We define $\Gamma = \pi \rho V^2$. In Fig. 2 we display our fit of the observed $dI/dV$ for the single molecule. From the ab-initio calculations [20] one can estimate $U = 1.6$ eV, which turns out to be much larger than the value $\Gamma = 0.01$ eV that results from the fit. It is also much larger than $t_1$ (see below). Therefore, the limit $U \to \infty$, that we have taken in our approach is well justified. Fig. 2 shows a good agreement between our theoretical results and the experiment, in accordance with previous results on single Co impurities on Cu(111) [29]. 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 with experimental uncertainties [compare Figs. 3 (a) and 3 (b) in Ref. 20 for zero applied magnetic field]. The situation is however mode difficult for the case of the lattice, because of the double dip structure of the observed FKA (see Fig. 3). We have kept the same $\Gamma$ obtained from the fit of the single molecule, but we had to increase slightly 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 \cite{20}, and the single-electron levels are expected to increase their energy due to interatomic Coulomb repulsion. In addition, we had to modify slightly 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. \cite{18}. As shown in Fig. 3 our theory is able to provide semi-quantitative 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 meV. The double dip structure is essentially a consequence of the van Hove singularities in the spectral density of the molecular states, described by the Hubbard part of the model. The splitting between van Hove singularities is given by $2|\Delta t_1| - |\Delta t_2|z^2$, where $z^2$ (the square of the magnitude of the condensed boson) plays the role of the quasiparticle weight and introduces a band-narrowing effect due to correlations. The anisotropy of the hopping for an individual molecular orbital (in spite of the orbital-spin symmetries\cite{31}) is the key for this splitting. The hybridization with the conduction states broaden the van Hove singularities.

In the STM experiments, the $dI/dV$ has been measured at different sites of a finite cluster, to study the effects of coordination on the observed spectra. In order to compare with experiment, we have applied our theory to a finite cluster of $5 \times 4$ molecules, as shown in Fig. 4 (cf. Ref. \cite{32}). Some of the results, shown in Fig. 4 display an oscillatory behavior, which are likely to disappear for a more realistic calculation \cite{32} 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 2) do not show a splitting, while those of coordination 4 do show two dips in the FKA. The sites with coordination number 3 display an intermediate and variable behavior which depends on the specific site. These results agree with the experimental trends \cite{18}.

**Summary and discussion.**- Motivated by recent experiments on FePc molecules \cite{18}, we have derived a Hubbard-Anderson model which describes a square lattice of 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 orbitals are coupled via an anisotropic hopping which leads to two van Hove singularities in the density of states of 3d electrons. These van Hove singularities are the main explanation of the observed splitting in the experimental FKA in the $dI/dV$. In the presence of strong interactions (which induce a band-narrowing effect) and hybridization to the substrate (which blurs these van Hove singularities), this feature persists and dominates the density of states observed by the STM tip, therefore displaying two dips in the $dI/dV$ around $V = 0$. 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 conduction band, suggest a ferromagnetic orbital ordering and antiferromagnetic spin ordering at $T = 0$ for small Hund-rules exchange \cite{33}. The nearest-neighbor anisotropic antiferromagnetic interaction is of the order of $4t_1^2/U \approx 10$ K in the main direction and $4t_1^2/U \approx 1$ K, in the other [see Eq. (10) of Ref. \cite{33}], 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. While fluctuations in 2D destroy long-range magnetic order at finite temperature, this opens the intriguing possibility of
observing quantum critical behavior at low enough temperatures in 2D molecular Kondo systems. Indeed, the existence of orbitally-ordered phases \cite{33} and dissipative quantum phase transitions \cite{25,27} has been suggested in related systems. Moreover, recently long-range ferromagnetic order was observed for a 2D layer of organic molecules absorbed on graphene \cite{34}.

The authors are grateful to N. Takagi and E. Minamitani for useful comments. AML acknowledges support from JQI-NSF-PFC, MR and AAA 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.

---

\*alobos@umd.edu

[1] A. C. Hewson, *The Kondo Problem to Heavy Fermions* (Cambridge University Press, Cambridge, 1993).
[2] S. M. Cronenwett, 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 **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, Phys. Rev. B **58**, 567 (1998).
[6] N. Knorr, M. A. Schneider, L. Diekhoner, P. Wahl, and K. Kern, Phys. Rev. Lett. **88**, 096804 (2002).
[7] T. Jamneala, V. Madhavan, and M. F. Crommie, Phys. Rev. Lett. **87**, 256804 (2001).
[8] P. Wahl, P. Simon, L. Diekhöner, V. S. Stepanyuk, P. Bruno, M. A. Schneider, and K. Kern, Phys. Rev. Lett. **98**, 056601 (2007).
[9] N. Néel, R. Berndt, J. Kröger, T. O. Wehling, A. I. Lichtenstein, and M. I. Katsnelson, Phys. Rev. Lett. **107**, 106804 (2011).
[10] R. Wiesendanger, Rev. Mod. Phys. **81**, 1495 (2009).
[11] C. N. M. S. H. L. Venkataraman, J. E. Klare and M. L. Steigerwald, Nature (London) **442**, 904 (2006).
[12] Y. F. Wang, J. Kröger, R. Berndt, H. Vázquez, M. Brandbyge, and M. Paulsson, Phys. Rev. Lett. **104**, 176802 (2010), .
[13] A. D. V. Iancu and S.-W. Hla, Nano Lett. **8**, 820 (2006).
[14] 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**, 106801 (2010), .
[15] P. Jarillo-Herrero, J. Hong, K. van der Zant, C. Dekker, L. Kouwenhoven, and S. De Franceschi, Nature (London) **434**, 484 (2005).
[16] F. B. Anders, D. E. Logan, M. R. Galpin, and G. Finkelstein, Phys. Rev. Lett. **100**, 086809 (2008), .
[17] 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).
[18] N. Tsukahara, S. Shiraki, S. Itou, N. Ohta, N. Takagi, and M. Kawai, Phys. Rev. Lett. **106**, 187201 (2011), .
[19] Assuming that bulk electrons are those with stronger hybridization with the impurity \cite{6,21}, a spectral density of states per spin at the Fermi level $\rho = 0.125/eV$ and a band width $2W = 8$ eV, from the observed Kondo temperature $T_K = W \exp[-1/(\rho J)] \approx 5$ K one estimates a Kondo coupling $J = 13.7$ meV. Using the wave vector for Au $k_F = 1.2/\Ang$, the effective RKKY interaction at a distance $R \approx 13\Ang$ is $I \approx J^2\rho(2k_FR)^{-3} \approx 7 \times 10^{-5}$ K. In the less likely case that the impurity couples with the two-dimensional Schokley states one has $k_F = 0.21/\Ang$ \cite{29} and $I \approx J^2\rho(2k_F R)^{-2} \approx 3.6 \times 10^{-2}$ K. In any case $I \ll T_K$.
[20] E. Minamitani, N. Tsukahara, D. Matsumaka, Y. Kim, N. Takagi, and M. Kawai, Phys. Rev. Lett. **109**, 086602 (2012), .
[21] A. A. Aligia, Phys. Rev. Lett. **96**, 096804 (2006), .
[22] M. Romero and A. A. Aligia, Phys. Rev. B **83**, 155423 (2011), .
[23] V. Barzykin and I. Affleck, Phys. Rev. B **61**, 6170 (2000).
[24] J. Simonin, cond-mat/0708.3604 (2007).
[25] A. A. Aligia, cond-mat/0708.3604 (2007).
[26] A. M. Lobos, M. A. Cazalilla, and P. Chudzinski, Phys. Rev. B **86**, 035455 (2012).
[27] A. M. Lobos and M. A. Cazalilla, J. Phys.: Condens. Matter **25**, 094008 (2013).
[28] P. Coleman, Phys. Rev. B **29**, 3035 (1983).
[29] P. Coleman, Phys. Rev. B **35**, 5072 (1987).
[30] D. M. Newns and N. Read, Adv. Phys. **36**, 799 (1987).
[31] A. A. Aligia and A. M. Lobos, J. Phys. Condens. Matter **17**, S1095 (2005).
[32] J. Figgins and D. K. Morr, Phys. Rev. Lett. **104**, 187202 (2010).
[33] The actual point group in the experimental array of molecules \cite{15} is $C_4v$ because the lines of molecules are not parallel to the main directions of the substrate. However, since we are modelling the substrate states with a continuum, the symmetry of our model is higher.
[34] Since the minimization of the free energy in the SBMFA with respect to all $z_{ij}$ and Lagrange multipliers $\lambda_{ij}$ enforcing the constraints for all non-equivalent sites $r_{ij}$ is a formidable task, we have made the additional assumption that $z_{ij} = z$ and $\lambda_{ij} = \lambda$, where $z$ and $\lambda$ are the corresponding values for the lattice. The dependence of these quantities on site would likely act in a similar way as disorder, bluring the oscillations observed in Fig. 4.
[35] A. A. Aligia and M. A. Gusmão, Phys. Rev. B **70**, 054403 (2004).
[36] M. Garnica, D. Stradí, S. Barja, F. Calleja, C. Díaz, M. Alcami, N. Martín, A. L. Vázquez de Parga, F. Martín, and R. Miranda, Nature Physics in press, doi:10.1038/nphys2610 (2013).
[37] M. T. Béal-Monod, Phys. Rev. B **36**, 8835 (1987), .