Local Moment Formation and Kondo Effect in Defective Graphene

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We study the local moment formation and the Kondo effect at single-atom vacancies in graphene. We develop a model accounting for the vacancy reconstruction as well as non-planarity effects induced by strain and/or temperature. Thus, we find that the dangling σ orbital localized at the vacancy is allowed to strongly hybridize with the π-band since the scattering with the vacancy turns the hybridization into singular function of the energy (∼ |ε| ln^2 (ε/D)^{-1}, D ~ the bandwidth). This leads to several new types of impurity phases, which control the magnitude of the vacancy magnetic moment and the possibility of Kondo effect depending on the strength of the local Coulomb interactions, the Hund’s rule coupling, the doping level, and the degree of particle-symmetry breaking.

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Experimental evidence of magnetic local moments (MLM) in irradiated graphene at very low temperatures has been recently reported in [1, 2]. In another experiment using irradiated samples [3], the Kondo effect with surprisingly high Kondo temperatures (T_K ~ 10-100 K), obtained by fitting resistivity data to conventional spin-1/2 Kondo laws [4] was observed. A priori, the latter observation appears to be at odds with the observations of [1, 2]. For instance, at the temperatures of the Manchester group experiment (T = 2K) [1], the measured spin-1/2 MLM of the vacancies created by irradiation should be quenched by the Kondo effect observed in [3]. Furthermore, the authors of [3] reported a T_K with a rather weak dependence on gate voltage. However, theories of the Kondo effect in graphene [6-9] predict a critical coupling below which MLM are stable at the Dirac point (DP) whilst T_K remains small around the DP [7, 8].

The puzzle described above calls for revisiting the magnetic properties of isolated single atom vacancies in graphene. Here we show that earlier theories [6, 7] must be modified to account for the strong scattering potential of the vacancy. Indeed, the latter is responsible for a dramatic change of the energy dependence of the hybridization with the π-band of a level localized at a reconstructed vacancy [12-14]. Thus, the energy dependence of the hybridization is changed to ∼ |ε| ln^2 (ε/D) near the DP (cf. Fig. 1), which is different from the pseudogap behavior ∼ |ε|^r (r > 0) considered earlier [6-9]. Therefore, it becomes possible for vacancy MLM to be quenched at T_K ~ 1 – 100 K (cf. Fig 2).

The possibility of defect-induced magnetism in graphene has been widely discussed in the literature (see e.g. [11, 13, 15], and references therein), mainly using various types of static mean-field theories. However, a recent study [15] using dynamical mean-field theory concluded that vacancies should allow for the formation of MLM that are ferromagnetically coupled to the conduction band of graphene. Within Hartree-Fock, this happens because of the strong local correlations [16] and the large enhancement of the local density of states in the neighborhood of the vacancy [17]. However, the analysis of Refs. [11, 15] focuses only on the contribution to the vacancy magnetic moment from π-band electrons. Ab initio calculations using the generalized gradient approximation (GGA) to density functional theory (DFT) [12, 13], can account for the contribution of the dangling

FIG. 1: Two level Anderson model describing a reconstructed single-atom vacancy in rippled graphene; d is an orbital that is mainly localized at a dangling σ orbital of the apical atom; π_0 is the vacancy-induced localized state. Rippling implies that the d-orbital can hybridize with the π conduction band via sp^2-sp^3 hybridization, V. The hybridization, Δ(ε), is energy (ε) dependent and enhanced by the strong scattering potential at the vacancy. U_{σσ} and J_H describe the Coulomb interaction between the two localized levels. See Eq. [4].
\[ \sigma \text{ orbitals and are also able to describe the possible reconstructions of the vacancy} \text{.} \]

However, such studies predict different values for the vacancy MLM \([12, 14]\).

Indeed, provided the dangling \(\sigma\) orbitals are not passivated, the vacancy reconstructs \([10, 12, 13, 18]\) following a Jahn-Teller distortion. Thus, a carbon pentagon with a strong bond resulting from two of the dangling \(\sigma\) orbitals (cf. Fig. 1) is formed. The remaining dangling \(\sigma\) orbital is mainly localized at the apical atom (opposite to the reconstructed bond), and appears as a level at \(\sim 1\) eV \([12, 13]\) below the DP (cf. Fig. 1). Double occupation of this orbital is strongly suppressed by a rather strong Coulomb repulsion \(U \sim 10\) eV \([16]\), which leads to the formation of a MLM. However, in flat graphene, symmetry forbids the hybridization of \(\sigma\) and \(\pi\) orbitals, meaning that the electron in the dangling \(\sigma\) orbital cannot hybridize with \(\pi\) band and thus exchange with conduction electrons. In absence of other contributions to the MLM \([12]\), this fact is hard to reconcile with the observed vacancy effects on charge \([3]\) and spin transport \([2]\).

The above picture changes if we recall that graphene is a membrane that becomes easily rippled under the effect of strain and temperature \([19]\). Indeed, DFT-GGA calculations \([18]\) indicate that, under rather small (\(\sim 1\%\)) isotropic compression, regions containing reconstructed vacancies do ripple \([20]\). Rippling is achieved by means of \(sp^2-sp^3\) hybridization of the carbon bonds \([21, 22]\), which admixes the \(\sigma\) with \(p_z\) orbitals at a given atom, resulting in new \(\sigma\) orbitals pointing along directions that are no longer perpendicular to the \(p_z\) orbital. Thus, in a typical \(sp^2-sp^3\) hybridized configuration, a carbon atom can stick out of the graphene plane. If the atom contains a dangling \(\sigma\) orbital, as in the case of the apical atom of a reconstructed vacancy, the \(\sigma\) orbital will be able hybridize with the \(\pi\) band. In fact, the hybridization energy, \(V_{\pi\sigma}\), can be substantial already for small deviations from planarity \([21, 22]\): \(\tilde{V}_{\pi\sigma} = A \sqrt{1 - A^2/2} (\epsilon_\sigma - \epsilon_\pi)\), where \(\sin \theta = A/\sqrt{A^2 + 2}\), \(\theta\) being the angle subtended by the dangling \(\sigma\) orbital atom and the graphene plane, and \(\epsilon_\sigma - \epsilon_\pi = -8.31\) eV is the atomic s-p splitting. Thus, in rippled graphene \(\pi\) electrons are allowed to hop on and off the dangling \(\sigma\) orbital, thus leading to an effective (anti-ferromagnetic, AF) exchange with the conduction band. However, this also means that the MLM of the dangling \(\sigma\) orbital may be quenched by the Kondo effect. Indeed, this possibility is not negligible, since the strong scattering potential of the nearby vacancy substantially modifies the local density of states \([17]\).

Following the previous discussion, we introduce a model that contains all the ingredients described above \([23]\) and whose Hamiltonian can be written as

\[
H = H_d + H_{hyb} + H_{V+\pi}, \quad \text{where} \quad [30]
\]

\[
H_d = \epsilon_d n_d + U_n_d n_{d\uparrow} + H_{d\pi},
\]

\[
H_{hyb} = V \left[ d^\dagger_\alpha n_{\sigma 0}^\dagger + b^\dagger_\sigma n_0^\dagger \right]
\]

\[
H_{V+\pi} = \epsilon_0 a^\dagger_\alpha a^\dagger_\beta - \sum_{\alpha \beta} \left( a^\dagger_\alpha b^\dagger_\beta + \text{h.c.} \right)
\]

The term \(H_d\) above describes the dangling \(\sigma\) orbital with \(\epsilon_d \approx -0.75\) eV measured from the DP \([10]\), and \(U \approx 10\) eV \([16]\); \(n_{d\uparrow} = d^\dagger_\alpha d^\dagger_\alpha; H_{d\pi}\) describes the Coulomb interaction between the localized dangling \(\sigma\) orbital (\(d\)-orbital, in what follows) and the \(\pi\) band electrons below. \(H_{hyb}\) is the hybridization with the \(\pi\)-band, where \(V = \varphi_d(0)\tilde{V}_{\pi\sigma} (|\varphi_d(0)|^2 \approx 0.7 \[13, 23]\). In the last term, the limit \(\epsilon_0 \to +\infty\) must be taken in order to describe a single-atom vacancy on the A sublattice at \(R = (0, 0)\). The apical atom corresponds to the B sublattice atom within the same lattice. The fermion operators \(a^\dagger_\alpha, b^\dagger_\sigma\) (\(n^\dagger_\alpha, n^\dagger_\sigma\)) destroy (create) \(\pi\)-band electrons of spin \(\alpha\) on sites belonging to A and B sublattices.

To begin with, we retain only the nearest neighbor hopping \(t \approx 2.8\) eV \([5]\) and consider the chemical potential to be at the DP (i.e. \(\mu = 0\)). The effect of a nonzero \(\mu\) and the next-nearest neighbor hopping \(-t' \sum_{\langle i, j \rangle} \left( a^\dagger_{\alpha i} a^\dagger_{\beta j} + b^\dagger_{\alpha i} b^\dagger_{\beta j} \right)\) will be discussed at the end. Thus, the spectrum of \(H_{V+\pi}\) contains a localized level (a zero-mode, ZM) pinned at the DP, which is orthogonal to a continuum of waves scattering off the vacancy \([17]\). The ZM wavefunction is not square normalizable \(\left| \varphi_0(R) \right|^2 \sim \frac{1}{16\pi^2}\), but its overlap with the \(d\)-orbital is the largest, which means that the dominant contribution to \(H_{d\pi}\) is from the Coulomb interaction between the electrons in the ZM and the \(d\)-orbital \([23]\), i.e. \(H_{d\pi} = U_{\sigma\pi} n_d n_0 - J_{\pi} S_\sigma \cdot S_\pi\), where \(n_d = n_{d\uparrow} + n_{d\downarrow}\), \(n_0 = n_{\sigma 0}^\dagger n_0^\dagger\), where \(n_{\sigma 0}^\dagger (\pi_{00})\) destroys (creates) electrons in the ZM, and \(S_\sigma = d^\dagger_\sigma \frac{1}{2} \sigma^\dagger \sigma^\dagger_\beta, S_\pi = \pi_{00}^\dagger \frac{1}{2} \pi_{00}^\dagger\), where \(\sigma = (\sigma^\dagger, \sigma^\dagger, \sigma^\dagger)\) are the Pauli matrices. \(J_H > 0\) is the Hund’s coupling and \(U_{\sigma\pi} > 0\) is the Coulomb repulsion between electrons in the ZM and the \(d\) orbitals. The relative value of these parameters determines whether the vacancy spin is a doublet or a triplet. However, the extended nature of the ZM makes it difficult to obtain accurate estimates for \(J_H\) and \(U_{\sigma\pi}\) (some estimates, obtained on dimensional grounds, are provided in \([23]\)). Thus, in absence of accurate input, below we explore the possible magnetic phases for both the doublet and the triplet.

Treating electrons in scattering states as non-interacting, allows us to integrate them out exactly. Their influence on the \(d\)-level can be encapsulated in a self-energy function \([4]\), whose imaginary part is \(\pi |V|^2 \tilde{\rho}_B(\epsilon)\), where \(\rho_B(\epsilon) = \rho_B(\epsilon \neq 0)\), being \(\rho_B(\epsilon)\) the local density of states at the apical atom \([23]\). The latter exhibits a singular behavior \(\rho_B(\epsilon) \sim |\epsilon|^{\frac{1}{2}} |\ln \sqrt{|\epsilon|/D}| (D \sim t)\) around the DP \([17]\). We can mimic the effect of the self-
energy by representing the π band as a electron reservoir with energy-dependent tunneling into the d-level \[\text{III}\], leading to

$$H = H_V + H_{hyb} + \int_{-D}^{+D} d\epsilon \, \epsilon \, \psi_\alpha^\dagger (\epsilon) \psi_\alpha (\epsilon),$$

$$H_V = \epsilon_d n_d + U_n d_d n_d + \epsilon_D n_0 + U_{\pi_\alpha} n_d n_0 - J_H s_d \cdot s_0,$$

$$H_{hyb} = V \int_{-D}^{+D} d\epsilon \, [t(\epsilon) \psi_\alpha^\dagger (\epsilon) + t^*(\epsilon) \psi_\alpha^\dagger (\epsilon) \psi_\alpha (\epsilon)],$$

where \(\epsilon_D = 0\), \(\Delta (\epsilon) = |t(\epsilon)|^2 = \tilde{\rho}_D (\epsilon)\), and \(D = D_0 \sim t\) is a high-energy cut-off of order of the width of the π band. Since (for small angle \(\theta\)) \(\Delta (\epsilon_d)/|\epsilon_d| < 1\), charge fluctuations in the dangling σ orbital are small at low temperatures. However, the charge state of the ZM is determined by the magnitude of the parameter \(G = \frac{J_H}{4U_{\pi \alpha}}\).

The solution of (6) yields \(\bar{H}_K = \bar{H}_c + J_K s_0 \cdot s_V + V_0 f_{0}^0 f_{0}^0\),

where \(s_0 = f_{0}^1 (\frac{\alpha}{2}) f_{0}^0\) and \(s_V = s_d + s_0\), for the triplet \((G \gg 1)\). The expressions for \(J_K\) and the potential \(V_0\) depend on the total spin of the vacancy [23].

However, for \(G \approx 1\), the charge fluctuations in the ZM level are not negligible and the description in terms of Eq. [5] breaks down. In such a case, we must deal with the full Anderson model, Eq. [I]. Having \(G \approx 1\) requires fine tuning as it corresponds to a quantum phase transition between the doublet and the triplet, which will be analyzed elsewhere [21]. Here, we assume that \(U_{\pi \alpha} > [1 - G]\) is large enough so that using Eq. [I] with a cut-off \(D_0 < \min \{\epsilon_d, U_{\pi \alpha} [1 - G]\}\) is sufficient.

Next, we carry out a scaling analysis of [5] [11] [15] [25].

The perturbative scaling equations for \(J_K = J_K / D_0\) and \(v = V_0 / D_0\) read:

$$\frac{dJ_K}{d\ln D} = r(D) j_K - j_K^2 + O(j_K^3), \quad \frac{dv}{d\ln D} = r(D) v,$$

where \(r(D) = (d \ln \Delta (\epsilon) / d \ln \epsilon)_{\epsilon = D}\) is assumed to be a slowly varying function of \(D\), which is the case since near the DP \(\Delta (\epsilon) \sim |\epsilon|^{2/|\epsilon|} (\epsilon / D)^{-1}\) and \(r(D) \sim -1\) with logarithmic accuracy. Thus, as \(D\) is reduced, \(j_K (D)\) and \(v (D)\) grow and the vacancy enters the strong coupling regime. For \(J_K (D)\), a similar conclusion was reached in [26] based on an analysis of the orthogonality catastrophe in defective graphene. In the strong coupling regime where \(j_K (D^*) \sim 1\) (or \(v (D^*) \sim 1\)), [6] break down. However, the Kondo temperature can be related to the crossover scale \(D^*\) where \(j_K (D^*) \sim 1\) (provided \(j_K \sim 1\) before \(v\)). The solution of [6] yields \(T_K \ln^2 (T_K / D_0) \sim J_K\) for \(J_K \ll D_0\) [23]. Note that, this means a dramatic enhancement of \(T_K\) compared to the vanishing (exponentially small) \(T_K\) of the pseudo-gap [6] [7] [23] (flat-band \(\text{III}\)) Kondo models.

In the strong coupling regime, we have to rely on other methods different from Eqs. [6]. In this regard, there are remarkable similarities of the present Kondo model with one studied by Bulla and Vojta [27] using the numerical renormalization group (NRG). These authors considered a spin-1/2 Kondo model where \(\Delta (\epsilon) \sim |\epsilon|\), with \(-1 < r < 0\). With logarithmic accuracy, we can borrow their results for \(r \sim -1\) and \(J_K > 0\). Thus, two stable strong coupling fixed-points (FPs) are known to exist: a particle-hole asymmetric local moment (ALM) FP, at which the vacancy magnetic moment is decoupled from the band, and a singlet-strong-coupling fixed point (SSC) FP, at which the single electron in dangling σ orbital forms a singlet with the conduction band electrons, and vacancy magnetic moment is thus quenched. The flow between ALM and SSC FPs is controlled by a critical point [27].

For the triplet case \((G \gg 1)\), to the best of our knowledge, there are no NRG results available. However, in this case we can tentatively assume that, as \(J_K\) flows to strong coupling, half of the vacancy spin-1 will be quenched. Applying an argument due to Nozières and Blaudin [23], the residual spin-1/2 couples ferromagnetically (FM) to the conduction band, that is, for \(T < T_K\), it is described by \(H_{SC} = H_c + J's_1 s_V'\) where \(s_V'\) is the residual vacancy spin, and \(J' < 0\). In this strong-coupling coupling picture, one electron is captured at the first site (site 0 in our notation above) of the Wilson chain \(\text{III}\) representation of \(H_c\) (cf. Eq. [4]), thus projecting out this site. The residual spin-1/2 couples to the next site of the Wilson chain, whose spin is described by the operator \(s_1\). The hybridization function for this site can be obtained by tridiagonalization, which allows to relate the local Green’s functions at sites 0 and 1 with 0 site projected out (see [4], chap. 4): \(g_1 (\epsilon) = \frac{\epsilon}{|\epsilon|^2} - \frac{1}{|\epsilon|^2 g_0 (\epsilon)}\), with \(V \propto \epsilon\). Hence, with logarithmic accuracy, \(r (D) \approx 1\) in Eq. [6], which, together with \(J_K (0) \sim J' < 0\), implies that \(J'\) renormalizes to zero. Thus, \(H_{SC}\) describes a stable underscreened Kondo FP. Moreover, as in the double case,
for large particle-hole asymmetry, \( V_0 \), it is also reasonable
to expect the existence of a strong-coupling fixed similar
to the ALM FP, and a critical point in the \( V-J_K \) plane
that controls the flow between the two FPs. The possible
phases of (5) are summarized in Table I.

Finally, let us consider the effect and the next neighbor hopping, \( t' \), and a small doping \( \mu \neq 0 \). At first sight,
both perturbations introduce particle-hole asymmetry [17],
which, for \( \mu, t' \ll t \), can be regarded as additional contributions to the bare value of \( V_0 \) in Eq. (5).
Thus, the initial conditions for the scaling equations (6)
are modified from their Schrieffer-Wolff values [23], which
favor the flow towards the ALM FP. For \( \mu \neq 0 \), the flow
towards the ALM FP can be seen as the first stage of a two-stage flow [8], whose final stage occurs at much lower temperatures and may be a crossover from the ALM to a more conventional Kondo-singlet FP (see below). The RG flow for the triplet case will be analyzed elsewhere [24].

To test the above ideas and obtain some quantitative estimates for \( T_K \), we have used a slave-boson mean-field
approach to Anderson model in Eq. (4) in the \( U \to +\infty \)
limit [11, 29]. In the mean-field theory [11, 29], \( T_K \) is
determined from the equation:

\[
T_K \sum_{\omega_n} \frac{g(i\omega_n)}{i\omega_n} e^{i\omega_n 0^+} = \frac{1}{J_K},
\]

where \( \omega_n = 2\pi (n + \frac{1}{2}) T_K \), \( J_K = 2|V|^2/|\epsilon_d| \) is the Kondo coupling for \( U \to +\infty \) [23], and \( g(i\omega_n) = \int d\epsilon \Delta(\epsilon)/(i\omega_n - \epsilon + \mu) \) is the local Green’s function at the apical atom. The results of a numerical solution of this equation are displayed in Fig. 2. From Fig. 2(a), it can be seen that turning on a finite \( \mu \) or \( t' \) strongly suppresses \( T_K \). For finite \( t' \), \( T_K \) appears to vanish at small \( J_K \ll T_K(\mu, \mu = 0, t' \neq 0) \), which we interpret as the ALM FP being favored over the SSC FP. However, the effect of \( \mu \neq 0 \) seems to be slightly different because the curve for \( T_K \) changes its concavity, suggesting a finite but small \( T_K \) at small \( J_K \) (finite-size effects prevent us from obtaining accurate results for \( T_K \) below \( \sim 1 \) K). Fig. 2(b) displays the values of \( T_K \) for \( t'/t = 0.02 \) (i.e. \( t' = 59 \) meV) and several values of \( \mu \). We find that when \( t \) has opposite sign to \( \mu \), their particle-hole symmetry-breaking contributions appear to partially cancel each other, leading to a less pronounced suppression of \( T_K \) (relative to the results in Fig. 2(a)). We believe this is because a reduction of the bare value of \( V_0 \) in Eq. (5) favors the ALM over the SSC FP for large enough \( J_K \).

In conclusion, we have studied a model for a reconstructed single-atom vacancy in graphene, finding that the strong vacancy scattering potential can dramatically affect its magnetic properties. We find that the, if particle-hole symmetry breaking is not too strong, Kondo effect can occur for small doping levels provided the dangling \( \sigma \) orbital is not passivated. However, for sufficiently large particle-hole symmetry breaking, a local moment that becomes increasingly decoupled from the \( \pi \) band as temperatures decreases appears. Further consequences of our theory for existing and future experiments will be presented elsewhere [23].

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large Supplementary Material

DETAILS OF THE MODEL OF THE VACANCY

We next describe the derivation of the model that is analyzed in the main text. In establishing a minimal model for a reconstructed single-atom vacancy in graphene, we shall rely on existing first-principle calculations (e.g., Refs. 1–4). The results of those calculations can be summarized as follows:

1. Removing one carbon atom (i.e., creating a vacancy) leaves three dangling $\sigma$-bonds behind. The latter manifest themselves as three impurity levels splitting off the $\sigma$ band.

2. From a tight-binding perspective, the vacancy $\sigma$-levels can be regarded as essentially the dangling $\sigma$ bonds of the atoms around the vacancy plus some admixture of $\sigma$ states away from the vacancy [2].

3. In an unrelaxed lattice, where all carbon atoms around the vacancy site remain at the same distance as the perfect graphene lattice, the crystal field effects, which correspond to the nearest neighbor hopping between $\sigma$-orbitals in the original lattice) split the three dangling-bond levels into one lower energy level (the symmetric combination) and two degenerate excited levels (cf. Fig. 4).

4. The situation described in the previous point is energetically unstable against a Jahn-Teller distortion, which breaks the $D_{3h}$ symmetry of the unrelaxed lattice and draws two of the three carbon atoms surrounding the vacancy closer to each other (cf. Fig. 1 in the main text and Fig. 3).

5. Further $ab\ initio$ calculations [3] suggest that, in the presence of isotropic compression, the three atoms around the impurity are no longer coplanar. This is possible if e.g. the apical atom (which contains a dangling $\sigma$–bond [2]) is lifted slightly above (or below) the plane of the two atoms opposite to it (i.e., those that form a reconstructed $\sigma$ bond as a result of the Jahn-Teller distortion), see Fig. 1 in the main text. This non-coplanarity is made it possible by sp$_2$-sp$_3$ hybridization of the atoms around the vacancy. In the model below, we assume that such hybridization is particularly important in the case of the apical atom (cf. Fig. 1 in the main text). This allows the electrons to hop in and out of the dangling $\sigma$ orbital at the apical site. This effect can be also achieved by rippling that occurs at any finite temperature.
where $R$ is a site at $\epsilon$.

If we diagonalize the subspace spanned by the vacancy orbitals, diagonalization are given by the first term in

$$\epsilon_0 \sum_{\alpha} a_{\alpha}^\dagger a_{\alpha},$$

where $\sqrt{\sin \theta}$ is the hopping between the vacancy orbitals and $\hat{V}_{\sigma \pi}$ describes the $sp^2$-$sp^3$ hybridization of the apical atom (see Fig. 3 for details about the labeling of the different orbitals):

$$\hat{V}_{\sigma \pi} = A \sqrt{\frac{1 - A^2}{3}} (\epsilon_s - \epsilon_p),$$

where $\sin \theta = A/\sqrt{A^2 + 2}$, $\theta$ being the angle between the $\sigma$ orbitals at the apical atom site (cf. Fig. 3) and the Graphene plane, and $\epsilon_s - \epsilon_p = -8.31 eV$ is the atomic s-p splitting. The above model neglects the local modifications of the hopping parameters around the vacancy site, both resulting from the Jahn-Teller distortion and from the $sp^2$-$sp^3$ hybridization caused by an isotropic compression. In Eq. (4), $H_{\text{hyb}}$ describes the Coulomb interaction between the $\sigma$ and the $\pi$ orbitals, which is particularly strong for the $\pi$ and $\sigma$ orbitals localized around the vacancy (see Sec. 1).

Furthermore, in Eq. (1), the term $H_{\text{V-int}}$ describes the interactions between the electrons localized at the vacancy-$\sigma$ orbitals, which we will specify below. In the above equation, the limit $\epsilon_0 \rightarrow +\infty$ is implicitly assumed in order to remove the site at $\mathbf{R} = (0, 0)$ of the $A$ sublattice.

As discussed in point 4 above, two of the dangling bonds bind when the lattice undergoes a Jahn-Teller distortion. If we diagonalize the subspace spanned by the vacancy $\sigma$ orbitals by means of the transformation:

$$\left( \begin{array}{c} d_1^\dagger \\ d_2^\dagger \\ d_3^\dagger \end{array} \right) = \left( \begin{array}{ccc} u_{11} & u_{12} & u_{13} \\ u_{21} & u_{22} & u_{23} \\ u_{31} & u_{32} & u_{33} \end{array} \right) \left( \begin{array}{c} \tilde{d}_1^\dagger \\ \tilde{d}_2^\dagger \\ \tilde{d}_3^\dagger \end{array} \right),$$

where $u_1 = (u_{11}, u_{12}, u_{13}) = N_1(-\frac{1+\sqrt{1+8r^2}}{2r^2}, 1, 1)$, $u_2 = (u_{21}, u_{22}, u_{23}) = N_2(\frac{1-\sqrt{1+8r^2}}{2r^2}, 1, 1)$, $u_3 = (u_{31}, u_{32}, u_{33}) = \frac{1}{\sqrt{2}} (0, 1, -1)$, with $r = T'/T$ and $N_i$ the normalization constants. The energies of the levels resulting from the previous diagonalization are given by the first term in

$$H_V = \sum_{\alpha,i=1}^3 \epsilon_i d_{\alpha i}^\dagger d_{\alpha i} + H_{\text{V-int}},$$

where $\epsilon_i$ are the energies of the levels resulting from the previous diagonalization.

FIG. 3: Labeling of the relevant orbitals around the vacancy. We make the approximation that the vacancy $\sigma$-orbitals correspond essentially to the dangling bonds around the vacancy site (empty circle). See Eq. (1) for details.
where \( \epsilon_1 = \epsilon_\sigma + \frac{1}{2} T \left( \sqrt{1 + 8\sigma^2} - 1 \right) \), \( \epsilon_2 = \epsilon_\sigma - \frac{1}{2} T \left( \sqrt{1 + 8\sigma^2} + 1 \right) \), \( \epsilon_3 = \epsilon_\sigma + T \) (According to the fitting to DFT-LDA calculations carried out by Nanda et al. in Ref. [2] \( T = 1.85 \) eV and \( T' = 1.30 \) eV). Thus, the level number 3 corresponds to an excited state, which lies above the Dirac point, [2] and the level 2 corresponds to a deep level describing the reconstructed bond at the basis of the pentagon opposite to the apical atom (cf. Fig. 1 in the main text and [3]).

The remaining electron from the vacancy \( \sigma \) orbitals occupies the orbital with energy \( \epsilon_1 \), and in flat graphene it cannot not hybridize with the \( \pi \)-band although it has a very large amplitude at the apical atom (see expression for \( \mathbf{u}_1 \) above). However, in rippled graphene (in the presence of isotropic compression) there is hybridization, through the term \( H_{\text{hyb}} \) in Eq. (1). In the following, we shall investigate whether such hybridization could lead to a Kondo effect. Thus, we shall focus on the orbital 1 and, to lighten the notation, henceforth we shall drop the orbital index (the other two orbitals, 2 and 3, will be treated as inert). Furthermore, we shall neglect the last term in Eq. (4), that is, the \( \text{sp}^3 - \text{sp}^3 \) hybridization with the \( s_1 \) and \( s_2 \) \( \sigma \)-orbitals of the apical atom (cf. Fig. 3). Such terms are expected to lead to a renormalization of the hybridization of the vacancy level 1 with the \( \pi \) bands. These considerations lead to the following Anderson model:

\[
H_{\text{AM}} = \epsilon_d \sum_\alpha d_\alpha \dagger d_\alpha + V \sum_\alpha \left[ b_\alpha \dagger b_\alpha + d_\alpha \dagger d_\alpha \right] + Ud_\uparrow d_\downarrow + H_{\pi + V} + H_{d\pi}
\]

where \( H_{\pi + V} \) is given by Eq. (2) with \( \epsilon_0 + + \infty; \epsilon_d = \epsilon_1 = \epsilon_\sigma + \frac{1}{2} T \left( \sqrt{1 + 8\sigma^2} - 1 \right) \simeq -0.75 \) eV, [2] [4] and \( V = |\varphi_\alpha(0)|^2 V_{\pi \sigma}(\theta) \), where \( |\varphi_\alpha(0)|^2 \approx 0.7 \), according to the above tight-binding model, and \( U \approx 10 \) eV [7].

The novelty of (9) lies in the fact that it is a single-impurity Anderson model in the presence of a strong scattering potential that induces a resonance at the Dirac point. Note that in the above model we have neglected any interactions between the electrons in the \( \pi \)-band.

**FIG. 4:** Vacancy \( \sigma \)-levels and evolution when different perturbations are taken into account. For left to right: i) Crystal field splitting (i.e. nearest neighbor hopping \( T = T' \) and ii) Jahn-Teller distortion with \( T > T' \). The lowest level, which has equal weight in the three atoms surrounding the vacancy has lowest energy and it is assumed to be doubly occupied, thus forming a (stretched) \( \sigma \) bond at the basis of a pentagon (cf. figure 1 in the main text). The intermediate level is below the Fermi energy \( \epsilon_F \) (assumed to be at the Dirac point) and we shall assume it to be singly occupied as \( U \approx 10 \) eV [7].

**TWO LEVEL ANDERSON MODEL**

Let us return to the above Hamiltonian and consider first the scattering problem of the \( \pi \) band electrons with the vacancy. Let us assume that we have diagonalized the Hamiltonian [2] and therefore we can write:

\[
H_{\pi + V} = \epsilon_0 \pi_\alpha \pi_\alpha + \sum_{\alpha, p, n} \epsilon_{p\alpha} \pi_\alpha \pi_{p\alpha} \pi_{p\alpha},
\]

where the index \( p = c, v \) describes the valence and conduction band scattering channels and \( \alpha = \uparrow, \downarrow \). The other quantum numbers have been collectively denoted by \( \mathbf{n} \). We have explicitly separated the zero mode, whose energy
coincides with the Dirac point energy ($\varepsilon_0 = 0$ for a particle-hole symmetric case where we neglect next nearest neighbor hopping), and it described by $\pi^\alpha_\alpha$, $\pi^\alpha_\alpha$. The original lattice operators can be expressed in terms of the eigenmodes of $H_{\pi+V}$ as follows:

$$a^\alpha_i = \sum_{p,n} \varphi_{Apn}(R_i) \pi^\alpha_{pn},$$

$$b^\alpha_i = \varphi_0(R_i) \pi^\alpha_0 + \sum_{p,n} \varphi_{Bpn}(R_i) \pi^\alpha_{pn}.$$

In the last expression above, we have used the fact that the zero-mode wavefunction is (within the tight-binding nearest-neighbor hopping approximation) is fully contained within the majority $B$ sublattice (see e.g. Ref. 13 and references therein).

In this eigenmode basis, the minimal Anderson Hamiltonian, Eq. (8), introduced in previous section reads:

$$H_{AM} = \epsilon_\sigma d^\dagger d + U d^\dagger \pi_\alpha d^\alpha + \sum_{\alpha} \left[ \varphi_0(0) d^\dagger_\alpha \pi^\alpha_0 + \varphi^*_0(0) \pi^\alpha_0 d^\alpha \right] + V \sum_{p,n} \left[ \varphi_{Bpn}(0) d^\dagger_\alpha \pi^\alpha_{pn} + \varphi^*_B(0) \pi^\alpha_{pn} d^\alpha \right] + H_d \sigma$$

Note that the zero-mode wavefunction is not normalizable since (neglecting oscillatory terms) $|\varphi_0(R)|^2 \sim N^2_0 / |R|^2$, which implies that

$$\sum_R |\varphi_0(R)|^2 \sim N^2_0 / |R|^2 \sim 2\pi N^2_0 \ln L,$$

diverges as the linear size of the system $L \rightarrow +\infty$. If we insist in normalizing the zero-mode wavefunction to unity, the normalization constant $N_0 \approx (2\pi \ln L)^{-1/2} \rightarrow 0$ as $L \rightarrow +\infty$. This implies that the hybridization of the zero-mode with the localized $\sigma$ level scales as $\sim (\ln L)^{-1/2}$. Though this vanishes in the thermodynamic limit, it does so very slowly. For instance, for a typical experimental device $a_0 \times L 1000$ nm. Since $a_0 \approx 0.25$ nm, $L \approx 4000$, which implies that $N^2_0 \approx 1/50 = 0.02$ (i.e. $N_0 \approx 0.1$).

![FIG. 5: sp²-sp³ hybridization of the dangling σ orbital in the apical atom (cf. Fig. 1 in the main text) with the π orbitals on the same atom vs. angle between the dangling orbital and the Graphene plane.](image-url)
At this point, it is worth considering also the interaction terms between the electrons in the dangling $\sigma$ level and the electrons in the $\pi$ band. Those terms result from the Coulomb interaction,

$$H_C = \frac{e^2}{2\epsilon} \int d\mathbf{r} d\mathbf{r'} \frac{\rho(\mathbf{r})\rho(\mathbf{r'})}{|\mathbf{r} - \mathbf{r'}|},$$

(15)

where $\rho(\mathbf{r}) = \Psi^\dagger_\alpha(\mathbf{r}) \Psi^\alpha(\mathbf{r})$. If we restrict ourselves to the subspace spanned by the $\sigma$ level and the $\pi$ and zero mode, then we can approximate:

$$\Psi^\alpha(\mathbf{r}) \approx \varphi_d(\mathbf{r}) d^\alpha + \varphi_0(\mathbf{r}) \pi^\alpha_0.$$

(16)

Hence,

$$\rho(\mathbf{r}) = |\varphi_d(\mathbf{r})|^2 d^\alpha d^\alpha + |\varphi_0(\mathbf{r})|^2 \pi^\alpha_0 \pi^\alpha_0 + \varphi_d^\dagger(\mathbf{r})\varphi_0(\mathbf{r}) d^\dagger_\alpha \pi^\alpha_0 + \varphi_0^\dagger(\mathbf{r})\varphi_d(\mathbf{r}) \pi^\dagger_\alpha d_\alpha^0.$$

(17)

Upon substitution of the above in Eq. (15), and upon neglecting terms that involve inter-level transitions, we obtain:

$$H_{\text{int}} = \bar{U}_{\sigma\pi} n_d n_0 + U_{\pi\pi} n_0^2 - J_H d^\dagger_\alpha \pi^\alpha_0 \pi^\dagger_\alpha d_0^\beta,$$

(18)

where we have subtracted the self-interaction (i.e. Hubbard-$U$) term for the $\sigma$ level ($\sim U n_d^2$).

$$\bar{U}_{\sigma\pi} = \frac{e^2}{\epsilon} \int d\mathbf{r} \frac{\varphi_d(\mathbf{r})^2 |\varphi_0(\mathbf{r})|^2}{|\mathbf{r} - \mathbf{r'}|},$$

(19)

$$U_{\pi\pi} = \frac{e^2}{\epsilon} \int d\mathbf{r} \frac{\varphi_0(\mathbf{r})^2 |\varphi_0(\mathbf{r})|^2}{|\mathbf{r} - \mathbf{r'}|},$$

(20)

$$J_H = \frac{e^2}{\epsilon} \int d\mathbf{r} \frac{\varphi_d^\dagger(\mathbf{r})\varphi_d(\mathbf{r})}{|\mathbf{r} - \mathbf{r'}|}.$$  

(21)

We also recall that, on dimensional grounds,

$$U \sim \frac{e^2}{\epsilon a_0}.$$  

(22)

Before trying to estimate the above Coulomb integrals, we note that, by using the following identity for the Pauli matrices

$$\sum_{a=x,y,z} (\sigma^a)^\mu_\alpha \delta^\mu_\beta = 2\delta^\nu_\alpha \delta^\beta_\nu - \delta^\nu_\beta \delta^\alpha_\nu,$$

(23)

we can recast

$$d^\dagger_\alpha \pi^\dagger_\beta \pi^\dagger_\alpha d_\beta^\beta = 2S_d \cdot S_0 + \frac{1}{2} n_d n_0,$$

(24)

where $S_0^\alpha = \pi^\dagger_\alpha (\frac{\sigma^a}{2})_\beta \pi^\beta_\alpha$ and $S_\nu^\alpha = d^\dagger_\alpha (\frac{\sigma^a}{2})_\beta d_\beta^\beta$. Thus,

$$H_{d\pi} = U_{d\pi} n_d n_0 + U_{\pi\pi} n_0^2 - J_H S_d \cdot S_0,$$

(25)

where

$$U_{d\pi} = \bar{U}_{d\pi} - \frac{J_H}{2}.$$  

(26)

Let us next find the scaling of the different couplings $U_{\pi\pi}, \bar{U}_{\sigma\pi}$, and $J_H$ with the system size. To this end, we recall that (see e.g. Ref. [13]):

$$\varphi_0(\mathbf{r}) = N_0 \frac{1}{|\mathbf{r}|} \cos((\mathbf{K} + \mathbf{K}') \cdot \mathbf{r}) \sin((\mathbf{K} - \mathbf{K}') \cdot \mathbf{r} + \theta),$$

(27)

$$\varphi_d(\mathbf{r}) = N_d \frac{e^{-\lambda_0|\mathbf{r}|}}{|\mathbf{r}|},$$

(28)
where \( \lambda_d \simeq \alpha_d^{-1} \). We shall not perform the integrals in Eqs. (19,20,21) explicitly but merely note that, from the dependence on \( \varphi_0(\mathbf{r}) \) (i.e. on \( N_0 \)) and, on dimensional grounds,

\[
U_{\pi\pi} \sim \frac{e^2}{\epsilon_0} \left( \frac{1}{2\pi \ln L} \right)^2, \tag{29}
\]

\[
J_H \sim \frac{e^2}{\epsilon_0} \frac{1}{2\pi \ln L}, \tag{30}
\]

\[
U_{\sigma\pi} \sim \hat{U}_{d\pi} \sim \frac{e^2}{\epsilon_0} \frac{1}{2\pi \ln L}, \tag{31}
\]

Note that \( U_{\pi\pi} \) scales faster to zero as \( L \to +\infty \) than the other couplings because the zero-mode self-interaction is strongly suppressed by the fact that its wave-function is only marginally localized. Taking \( U_{\pi\pi} \simeq 10 \text{ eV} \), and \( L^1 \sim 10^7 \), we obtain:

\[
U_{\pi\pi} \sim 1 \text{ meV}, \tag{32}
\]

\[
U_{\sigma\pi} \sim 100 \text{ meV}, \tag{33}
\]

\[
J_H \sim 100 \text{ meV}, \tag{34}
\]

\[
U \sim 10 \text{ eV}. \tag{35}
\]

However, the hybridization energy of the dangling \( \sigma \) orbital with the zero mode is given by \( VN_0 \). For an angle \( \theta \simeq 2 \) degrees, \( |V| \simeq 200 \text{ meV} \), and \( N_0 = 0.1 \) for \( L \simeq 4000 \), \( |V|N_0 \simeq 20 \text{ meV} \). Indeed, whereas the Hund interaction \(-J_H \mathbf{S}_d \cdot \mathbf{S}_0\) tends to align the spins of the \( \sigma \) level and the \( \pi \) zero mode ferromagnetically, the hybridization \( VN_0 \) favors an anti-ferromagnetic alignment, but since \( J_H \gg V^2/|\epsilon_d + U_{\sigma\pi}| \simeq 1 \text{ meV} \), we can safely assume that the triplet (i.e. the ferromagnetism) is favored provided the each level is singly occupied, i.e. \( n_d + n_0 = 2 \). On the other hand, the interaction term \( \propto U_{\pi\sigma} \) tends to favor the emptiness of one of the levels, i.e. \( n_d + n_0 = 1 \), which implies that a spin doublet is favored. In the following section, we analyze the different possibilities for the total spin of the vacancy.

The above estimates account for the contribution from the direct Coulomb interaction between the levels localized at the vacancy. However, other contributions may also exist. For example, the hybridization with the conduction band of both levels resulting from a next-nearest neighbor hopping \( t' \) may also lead to an additional (RKKY-type) contribution to the Hund’s rule coupling \( J_H \) [9]. Furthermore, a large enough \( t' \) also shifts energy and broadens the zero-mode, which lead to its disappearance into the continuum of scattering states. For the above reasons, in the main text we have explored the possible magnetic phases treating \( J_H \) and \( U_{\pi\pi} \) as unknown parameters.

**THE ‘ATOMIC’ LIMIT OF THE VACANCY**

Let us momentarily set the hybridization with the rest of the \( \pi \) band to zero and consider the spectrum of the coupled \( \sigma \) and \( \pi \) (zero-mode) levels. The latter are described by the following Hamiltonian:

\[
H_{\pi\sigma} = \epsilon_0 n_d + \epsilon_d n_d + U n_d \tau n_d \downarrow + U_{\sigma\pi} n_d n_0 - J_H \mathbf{S}_d \cdot \mathbf{S}_0 + V_{\sigma\pi} n_0^\alpha + V_{\pi\sigma} n_0^\beta, \tag{36}
\]

where we have introduced

\[
V_{\sigma\pi} = V \varphi_0(0) \simeq VN_0 \simeq V \left( \frac{1}{2\pi \ln L} \right)^{1/2}. \tag{37}
\]

In what follows, we are going to determine the ground state of the two level ‘atom’ described by the Hamiltonian in Eq. (36). To this end, we shall rely on the fact that both \( n_T = n_0 + n_d \) and \( S_T^2 = (\mathbf{S}_0 + \mathbf{S}_d)^2 = S_T(S_T + 1) \) and \( S_T^z = S_0^z + S_d^z \) are good quantum numbers.

1. **Doublet**: For \( n_T = n_0 + n_d = 1 \), \( S_T = 1/2 \), \( S_T^z = \pm 1/2 \), the Hilbert (sub)space of the system is spanned by:

\[
|1, S_z = \pm \frac{1}{2} \rangle = d_{\alpha}^\dagger |0\rangle, \tag{38}
\]

\[
|2, S_z = \pm \frac{1}{2} \rangle = \pi_{\alpha}^\dagger |0\rangle, \tag{39}
\]

(40)
with \( \alpha = \uparrow \) (\( \alpha = \downarrow \)) for \( S_T^z = \frac{1}{2} \) (\( S_T^z = -\frac{1}{2} \)). The eigen energies are \( \epsilon_\pm = \epsilon_d + \epsilon_0 \pm \sqrt{(\epsilon_d - \epsilon_0)^2 - 4|V_{\sigma\pi}|^2} \). Since \( |\epsilon_d - \epsilon_0| \gg 2|V_{\sigma\pi}| \), we find that the lowest energy state in th sector has an energy

\[
E_0(n_T = 1, S_T = \frac{1}{2}) \simeq \epsilon_d - \frac{|V_{\sigma\pi}|^2}{|\epsilon_d - \epsilon_0|} \tag{41}
\]

2. **Singlet**: For \( n_T = n_d + n_0 = 2 \), with \( S_T = S_T^z = 0 \). In this case, the Hilbert space of the system is spanned by the following three states:

\[
|1\rangle = \frac{1}{\sqrt{2}} \left[ d_1^\dagger \pi_0^\dagger - d_1^\dagger \pi_0^\dagger \right]|0\rangle, \tag{42}
\]

\[
|2\rangle = d_1^\dagger \pi_0^\dagger |0\rangle, \tag{43}
\]

\[
|3\rangle = \pi_0^\dagger \pi_0^\dagger |0\rangle. \tag{44}
\]

In this subspace the Hamiltonian \( H_V \) becomes a \( 3 \times 3 \) matrix:

\[
H_{\sigma\pi}(n_T = 2, S_T = 0) = \begin{pmatrix}
\epsilon_d + \epsilon_0 + U_{\sigma\pi} + \frac{3J}{4} & \frac{\sqrt{2}V_{\sigma\pi}}{\sqrt{2}V_{\sigma\pi}} & \frac{\sqrt{2}V_{\sigma\pi}^*}{\sqrt{2}V_{\sigma\pi}} \\
\frac{\sqrt{2}V_{\sigma\pi}^*}{\sqrt{2}V_{\sigma\pi}} & 2\epsilon_d + U + \frac{3J}{4} & 0 \\
\frac{\sqrt{2}V_{\sigma\pi}}{\sqrt{2}V_{\sigma\pi}} & 0 & 2\epsilon_0 + \frac{3J}{4}
\end{pmatrix} \tag{45}
\]

where we have used that \( S_d \cdot S_0 = \frac{1}{4} \left[ S_T^z - S_d^2 - S_0^2 \right] = \frac{1}{4} S_T^z - \frac{3}{4} \). The diagonalization of the above Hamiltonian is not possible explicitly, but under the assumptions that \( \epsilon_0 > \epsilon_d \) and \( U \gg |\epsilon_d|, |\epsilon_0| \), the energy of the lowest state in this sector is:

\[
E_0(n_T = 2, S_T = 0, S_T^z = 0) \simeq \epsilon_d + \epsilon_0 - 2|V_{\sigma\pi}|^2 \left( \frac{1}{|\epsilon_d + U - \epsilon_0 - 2|U_{\sigma\pi}|} + \frac{1}{|\epsilon_d + U_{\sigma\pi} - \epsilon_0|} \right) \tag{46}
\]

3. **Triplet**: For \( n_T = 2, S = 1 \), this space is spanned by (note that the states in this case have different values of \( S_z \), since \( H_V \) commutes with \( S_z \), it automatically becomes diagonal in this subspace):

\[
|S_T = 1, S_T^z = +1\rangle = d_1^\dagger \pi_0^\dagger |0\rangle, \tag{47}
\]

\[
|S_T = 1, S_T^z = 0\rangle = \frac{1}{\sqrt{2}} \left[ d_1^\dagger \pi_0^\dagger + d_1^\dagger \pi_0^\dagger \right]|0\rangle, \tag{48}
\]

\[
|S_T = 1, S_T^z = -1\rangle = d_1^\dagger \pi_0^\dagger |0\rangle. \tag{49}
\]

\[
(S_T = 1, m |H_{\sigma\pi}\rangle |S_T = 1, m'\rangle = \delta_{m, m'} \left( \epsilon_d + \epsilon_0 + U_{\sigma\pi} - \frac{J}{4} \right) \tag{50}
\]

Thus, the triplet consists of three degenerates states with energy:

\[
E_0(n_T = 2, S_T = 1) = \epsilon_d + \epsilon_0 + U_{\sigma\pi} - \frac{J}{4}. \tag{51}
\]

4. **Triply occupied doublet**: For \( n_T = 3, S = \frac{1}{2} \), and \( S^z = \pm \frac{1}{2} \) the Hilbert (subspace) is spanned by:

\[
|1, \alpha\rangle = d_0^\dagger \pi_0^\dagger \pi_0^\dagger |0\rangle, \tag{52}
\]

\[
|2, \alpha\rangle = d_1^\dagger \pi_0^\dagger |0\rangle \tag{53}
\]

To leading order, the energy of these states is given by:

\[
E_1 = \langle 1, \alpha |H_{\sigma\pi}| 1, \alpha \rangle = 2\epsilon_0 + \epsilon_d + 2U_{\sigma\pi}, \tag{55}
\]

\[
E_2 = \langle 2, \alpha |H_{\sigma\pi}| 2, \alpha \rangle = \epsilon_0 + 2\epsilon_d + 2U_{\sigma\pi} + U. \tag{56}
\]

As in the double case, these energies are corrected by terms of order \( |V_{\sigma\pi}|^2/|E_1 - E_2| \) in the next leading order.
5. Full vacancy singlet: For \( n_T = 4 \), \( S_T = S_T^z = 0 \), it is described by the state:

\[
|\text{Full}\rangle = d_1^\dagger d_2^\dagger \pi_0^\dagger \pi_0^\dagger |0\rangle,
\]

with energy \( E_{\text{full}} = 2\epsilon_d + 2\epsilon_0 + 4U_{\sigma\pi} + U \).

Under the assumption that \( U \simeq 10 \text{ eV} \gg \epsilon_d, |\epsilon_d| \gg V_{\sigma\pi} \), we must compare the spin doublet energy with the triplet energy in order to determine the spin state of the vacancy:

\[
\Delta E_{\text{triplet-doublet}} = E_0(n_T = 2, S_T = 1) - E_0(n_T = 1, S_T = \frac{1}{2}) = \epsilon_0 + U_{\sigma\pi} - \frac{J_H}{4} + \frac{|V_{\sigma\pi}|^2}{|\epsilon_d - \epsilon_0|} \geq 0.
\]

For example, if we choose the position of the chemical potential at the Dirac point and measure the energies with respect to it, \( \mu = \epsilon_0 = 0 \),

\[
\Delta E_{\text{triplet-doublet}} = U_{\sigma\pi} - \frac{J_H}{4} + \frac{|V_{\sigma\pi}|^2}{|\epsilon_d + U_{\sigma\pi}|} \simeq U_{\sigma\pi} - \frac{J_H}{4},
\]

since \( \frac{|V_{\sigma\pi}|^2}{|\epsilon_d|} \gg 1 \text{ meV} \) is much smaller than \( U_{\sigma\pi} \sim J_H \sim 100 \text{ meV} \), according to the estimates made in Sect. However, since \( U_{\sigma\pi} \sim J_H \) we cannot decide whether the triplet or the doublet are favored as the ground state of the dangling \( \sigma-\pi \) zero-mode system. Thus, in the following we shall analyze both possibilities.

SCHRIEFFER-WOLF-LIKE PROJECTION

In order to integrate out the charge fluctuations, we shall project the Anderson model introduced above onto the subspace where the vacancy dangling \( \sigma \)-level and the \( \pi \) zero-mode are either in the triplet or doublet state. This requires that \( \langle n_d \rangle \simeq 1 \) and that \( \langle n_0 \rangle \simeq 1 \) for the triplet case and \( \langle n_0 \rangle = 0 \) for the doublet case (see Sec. for a discussion of the validity of these approximations). To this end, we introduce a projection operator, \( P \), onto the subspace where \( n_d = 1 \) and either \( n_0 = 1 \) (triplet) or \( n_0 = 0 \) (doublet); \( Q = 1 - P \) projects states onto the orthogonal subspace where either \( n_d = 0 \) or \( n_d = 2 \). The effective Hamiltonian projected onto the \( P \)-invariant subspace can be obtained from the expression:

\[
H_{\text{eff}}(E) = PHP + PHQ \frac{1}{E - QHQ} QHP,
\]

which we can use to perturbatively powers of \( V \) integrate out the fluctuations in the occupancy of the dangling \( \sigma \) level. However, the results, depend on whether the ground state of the dangling \( \sigma \) level \( \pi \) zero-mode complex is a doublet or a triplet.

Doublet case

Let us assume that the ground state of the the dangling \( \sigma \) level \( \pi \) zero-mode complex is a doublet (i.e. \( U_{\sigma\pi} > J_H/2 \)). In that case \( P \) is the projection operator onto the doublet state of the vacancy level system. To carry out the calculation, we first note that

\[
\begin{align*}
PHP &= H_c + PHP_{\sigma\pi}P + PHP_{\text{hyb}}P, \\
QHQ &= H_c + QH_{\sigma\pi}Q + QH_{\text{hyb}}Q, \\
PHQ &= PH_{\text{hyb}}Q + PH_{\sigma\pi}Q.
\end{align*}
\]

Upon neglecting retardation effects (i.e. setting \( E = \mathcal{E}_0 + E_0(n_T = 1, S_T = \frac{1}{2}) \simeq \mathcal{E}_0 + \epsilon_d \), where \( \mathcal{E}_0 \) is the ground state of the chain) as well constant terms and using the identity [23], we arrive at

\[
\begin{align*}
H_K &= H_c + \frac{|V_0|^2}{\epsilon_d} Pd_\alpha c_\alpha^\dagger c_0^\dagger d^\dagger P - \frac{|V_0|^2}{U + \epsilon_d} P c_{0\alpha}^\dagger d^\alpha d_\beta c_\beta^\dagger P \\
&= H_c + J_K \mathbf{s}_d \cdot \mathbf{s}_0 + V_0 c_{0\alpha}^\dagger c_\alpha^\dagger, \quad \epsilon_d
\end{align*}
\]

where \( \mathbf{s}_d \) and \( \mathbf{s}_0 \) are the spin operators of the dangling \( \sigma \) level and the vacancy, respectively.
where, to leading order in $V_0$,

$$J_K = 2|V_0|^2 \left[ \frac{1}{\epsilon_d} + \frac{1}{U + \epsilon_d} \right] = 2|V_0|^2 \left[ \frac{1}{|\epsilon_d|} + \frac{1}{U + |\epsilon_d|} \right] > 0, \quad (66)$$

$$V_K = -\frac{1}{2}|V_0|^2 \left[ \frac{1}{\epsilon_d} + \frac{1}{U + \epsilon_d} \right] = \frac{1}{2}|V_0|^2 \left[ \frac{1}{|\epsilon_d|} - \frac{1}{U + |\epsilon_d|} \right] > 0 \quad (67)$$

and

$$S_d = Pd^\dagger \frac{\sigma}{2} \beta d^\beta P,$$

$$s_0 = c^\dagger_{\alpha 0} \left( \frac{\sigma}{2} \right)_\beta c^\beta_{0} \quad (68)$$

$$\quad (69)$$

**Triplet case**

We can repeat the same calculation as above by assuming that the ground state of the vacancy is a triplet state. In this case, $P$ projects onto the triplet state of the vacancy dangling $\sigma$ and $\pi$ zero-mode levels. Thus, neglecting retardation $E = \epsilon_0 + E_0(n_T = 2, S_T = 1) = \epsilon_0 + \epsilon_d + \epsilon_0 + U_{\sigma \pi} - \frac{j_\mu}{4}$. Acting upon with the operator $H_{\text{hyb}}$, then produces two kinds of excited states where either $n_d = 0$ (having energy $\approx E_0 + \epsilon_0$ to leading order in $V$) or $n_d = 2$ (having energy $\approx E_0 + 2\epsilon_d + U + \epsilon_0 + 2U_{\sigma \pi}$ to leading order in $V$). Thus,

$$H_K = H_c - J_H P_t S_d \cdot S_0 P_t + 2J_K P_t S_d \cdot s_0 P_t + V_0 c^\dagger_{\alpha 0} c^\alpha_0 \quad (70)$$

In the above expression, $P_t$ is the projection operator onto the triplet state. This results holds for temperatures below the double-triplet energy splitting $\approx \frac{j_\mu}{4} - U_{\sigma \pi}$. As a consequence of rotational invariance,

$$P_t S_d P_t = \frac{1}{2} S_T, \quad (71)$$

where $S_T = S_d + S_0$ and $S^2_T = S_T(S_T + 1)$ being $S_T = 1$. Thus, we can write Eq. (70) as a $S = 1$ impurity Kondo Hamiltonian:

$$H_K = H_c + J_K S_T \cdot s_0 + V_K c^\dagger_{\alpha 0} c^\alpha_0, \quad (72)$$

where (recall that $U_{\sigma \pi} - \frac{j_\mu}{4} < 0$ for the triplet to be the ground state):

$$J_K = |V_0|^2 \left[ \frac{1}{\epsilon_d + U_{\sigma \pi} - \frac{j_\mu}{4}} + \frac{1}{U + \epsilon_d + U_{\sigma \pi} - \frac{j_\mu}{4}} \right] > 0, \quad (73)$$

$$V_0 = \frac{1}{2}|V_0|^2 \left[ \frac{1}{\epsilon_d + U_{\sigma \pi} - \frac{j_\mu}{4}} - \frac{1}{U + \epsilon_d + U_{\sigma \pi} - \frac{j_\mu}{4}} \right] > 0. \quad (74)$$

In the above derivation, we have used that $P_t S_d \cdot S_0 P_t = \frac{1}{2} P_t [S^2_T - S^2_0 - S^2_d] P_t = \frac{1}{4}$ and dropped the resulting constant term.

**SOLUTION OF THE SCALING EQUATIONS FOR THE KONDO COUPLING**

Let us next consider the solution of the scaling equations for Kondo coupling:

$$\frac{dj_K}{d\ln D} = \frac{d\ln \Delta(\epsilon)}{d\ln \epsilon} \bigg|_{\epsilon = D} j_K - (j_K - j^2_K). \quad (75)$$

To find the solution to this equation, let us use the ansatz:

$$j_K(D) = f(D)g(D), \quad \frac{dj(D)}{d\ln D} = \frac{df(D)}{d\ln D}g(D) + f(D)\frac{dg(D)}{d\ln D}. \quad (76)$$
and require that our choice of \( f(D) \) cancels the first term on the right hand-side of (75), which leads to

\[
\frac{d}{d \ln D} \left( \frac{f(D)}{\Delta(\epsilon = D)} \right) = 0,
\]

(77)

and therefore \( f(D) = C \Delta(\epsilon = D) \), where \( C \) is a constant. Upon choosing \( C = 1 \), without loss of generality, we find that \( g(D) \) obeys the following equation:

\[
\frac{dg(D)}{d \ln D} = -\Delta(\epsilon = D)g^2(D),
\]

(78)

which can be integrated from \( D = D_0 \) to \( D = T \) to yield \( (g(0) = g(D_0)) \):

\[
\frac{1}{g(T)} - \frac{1}{g(0)} = \int_{D_0}^{T} \frac{\Delta(\epsilon)}{\epsilon} d\epsilon.
\]

(79)

Next we recall that \( j(T) = \Delta(\epsilon = T)g(T) \) and therefore,

\[
g(T) = \frac{j(T)}{\Delta(T)}.
\]

(80)

Hence,

\[
\frac{\Delta(T)}{j(T)} - \frac{\Delta(D_0)}{j(0)} = \int_{D_0}^{T} \frac{\Delta(\epsilon)}{\epsilon} d\epsilon,
\]

(81)

which, when solved for \( j(T) \) yields:

\[
j(T) = \frac{\Delta(T)j(0)/\Delta(D_0)}{1 - \frac{j(0)}{\Delta(D_0)} \int_{D_0}^{T} \frac{\Delta(\epsilon)}{\epsilon} d\epsilon}.
\]

(82)

Again, we can define the Kondo temperature as the value of \( T \) where \( j(T) = C^{-1} \sim 1 \), which form the previous expression leads to:

\[
\int_{D_0}^{T_K} \frac{\Delta(\epsilon)}{\epsilon} - C\Delta(T_K) = \frac{\Delta(D_0)}{j(0)} \propto \frac{1}{J_K}.
\]

(83)

Introducing \( \Delta(\epsilon) \sim [|\epsilon| \ln^2(\epsilon/D_0)] \) in the above equation leads to the condition that \( T_K \ln^2(T_K/D_0) \sim J_K \) quoted in the main text.

**SLAVE-BOSON MEAN-FIELD SOLUTION**

In the present study we employ the slave bosons technique combined with the large -\( N \) mean field treatment of the resulting action. The slave bosons technique aims at enlarging the Hilbert space of the impurity by introducing a slave boson creation operator \( b^\dagger \) and a new fermion \( f^\dagger_\sigma \) that act on a new vacuum state \( \mid \text{vac} \rangle \) such that the physical empty and singly occupied physical states of the impurity orbital are represented as

\[
\mid 0 \rangle = b^\dagger \mid \text{vac} \rangle,
\]

\[
\mid \sigma \rangle = f^\dagger_\sigma \mid \text{vac} \rangle.
\]

(84)

(85)

In terms of the slave boson and the new fermion the original impurity creation operator reads \( d^\dagger_\sigma = f^\dagger_\sigma b \), which satisfies canonical anti-commutation relations provided the Hilbert space is restricted to the physical space. The spin degeneracy is generalized from SU(2) to SU(\( N \)), with \( \sigma = 1, \ldots N \), and we shall consider the \( U = \infty \) limit with a constraint of no double occupancy (for \( N = 2 \)) generalized to

\[
b^\dagger b + \sum_\sigma f^\dagger_\sigma f_\sigma = \frac{N}{2}.
\]

(86)
for arbitrary $N$. The resulting effective action is:

$$S_{\text{eff}} = \int_0^\beta d\tau \left\{ \sum_\sigma f_\sigma^d(\partial_\tau + \varepsilon_d) f_\sigma + b^\dagger \partial_\tau b + i\lambda(\tau) \left[ b^\dagger b + \sum_\sigma f_\sigma^d f_\sigma - \frac{N}{2} \right] \right\}$$

$$- \frac{2|V|^2}{N} \int_0^\beta d\tau \int_0^\beta d\tau' \sum_\sigma f_\sigma^d(\tau)b(\tau)g(\tau - \tau')b^\dagger(\tau')f_\sigma(\tau')$$  (87)

where the Lagrange multiplier $\lambda$ is a dynamical variable introduced to impose the constraint.

In the large $N$ limit, the partition function can be approximated by means of a saddle point evaluation of its defining functional integral. At the saddle point, the Lagrange multiplier becomes static $i\lambda(\tau) \rightarrow \langle i\lambda \rangle = \lambda_0$ and the boson field is replace by its average $b \rightarrow \langle b \rangle = \sqrt{N/2r_0}$ and $b^\dagger \rightarrow \langle b^\dagger \rangle = \sqrt{N/2r_0}$. The values of $r_0$ and $\lambda_0$ at the saddle point are determined by minimizing of the free energy, which leads to the following mean field equations

$$\frac{r_0^2}{2} + \frac{1}{\beta} \sum_{i\omega_n} G_f(i\omega_n) e^{i\omega_n 0^+} = \frac{1}{2}$$  (88)

$$\lambda_0 + \frac{2|V|^2}{\beta} \sum_{i\omega_n} G_f(i\omega_n) g(i\omega_n) e^{i\omega_n 0^+} = 0,$$  (89)

where $G_f$ is the fermion propagator, which reads:

$$G_f(i\omega_n) = \langle f_\sigma^\dagger(i\omega_n) f_\tau(i\omega_n) \rangle = \frac{1}{i\omega_n - \varepsilon_d - \lambda_0 - r_0^2|V|^2 g(i\omega_n)}.$$  (90)

We fix the Kondo temperature $T_K$ at the onset of condensation of the slave boson, $r_0 = 0$. $G_f$ reduces to the standard Green’s function for a free fermion, and therefore Eq. (88) leads to

$$f_F \left( \frac{\varepsilon_d + \lambda}{T} \right) = \frac{1}{2}$$  (91)

where $f_F(u) = 1/(e^u + 1)$ is the Fermi factor. Its solution is given by $\lambda_0 = -\varepsilon_d$. Thus, Eq. (89) becomes:

$$\frac{2}{\beta} \sum_{i\omega_n} \frac{1}{i\omega_n} g(i\omega_n) e^{i\omega_n 0^+} = \frac{\varepsilon_d}{|V|^2},$$  (92)

which we have solved numerically by first computing the local Green’s function a the tight-binding model of the graphene including nearest neighbor $t$ and next-nearest neighbor hopping $t'$.

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