Orbitally controlled Kondo effect of Co ad-atoms on graphene

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Based on ab-initio calculations we identify possible scenarios for the Kondo effect due to Co ad-atoms on graphene. General symmetry arguments show that for magnetic atoms in high-symmetry positions, the Kondo effect in graphene is controlled not only by the spin but also by the orbital degree of freedom. For a Co atom absorbed on top of a carbon atom, the Kondo effect is quenched by spin-orbit coupling below an energy scale of ~15K. For Co with spin S = 1/2 located in the center of a hexagon, an SU(4) Kondo model describes the entanglement of orbital moment and spin at higher energies, while below ~60meV spin-orbit coupling leads to a more conventional SU(2) Kondo effect. The interplay of the orbital Co physics and the peculiar band-structure of graphene is directly accessible in Fourier transform tunneling spectroscopy or in the gate-voltage dependence of the Kondo temperature displaying a very strong, characteristic particle-hole asymmetry.

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I. INTRODUCTION

Graphene differs from usual metals or semiconductors in three important aspects: It is a truly two-dimensional material1 with the charge carriers resembling massless Dirac fermions2-4 and the chemical potential being tunable by gate voltages5. Recently, scanning tunneling spectroscopy experiments of graphene opened the exciting possibility to address its electronic properties locally and to study the interaction of graphene with magnetic ad-atoms. For single Co atoms adsorbed on heavily doped graphene, the observation of Kondo resonances with Kondo temperatures of the order of $T_K \sim 15K$ has been reported6. Theoretically, Kondo physics in “Dirac materials” defined as class of materials with low energy Dirac type excitations has been first addressed in the context of high Tc superconductors5-11. It has been demonstrated that even in the undoped case a Kondo effect can exist above a certain critical coupling between the impurity spin and the Dirac electrons6,7. The dependence of the critical coupling, Kondo temperatures and impurity spectral functions on doping and localized impurity states has been studied in the context of graphene only in terms of theoretical model systems like single orbital Anderson models or SU(2) Kondo models12-17. The importance of orbital physics for the Kondo effect arises because localized spins in magnetic ions occur almost exclusively in partially filled d or f shells. For graphene the same two-dimensional representations of the hexagonal $C_{6v}$ symmetry group, that determines the orbital degeneracies of ad-atoms in high-symmetry locations, is also responsible for the band degeneracies in graphene at the two Dirac points. Accordingly, the spin of an ad-atom in the center of a carbon hexagon can only couple efficiently by superexchange to graphene bands close to the Dirac point, if it is localized in orbitally degenerate levels. Therefore, the orbital degree of freedom and also spin-orbit coupling naturally govern the Kondo physics in graphene. Indeed, recent studies10,16,18,19 showed that the tunneling into s-wave symmetric impurity orbitals can be strongly suppressed by graphene’s particular symmetries, but the decisive role of the orbital degree of freedom has to our knowledge not been studied. In general one can expect that correlation effects will entangle fluctuating orbital16 and spin degrees of freedoms. This can lead to an SU(4) Kondo effect21,22. We show that symmetry and orbital selection rules govern not only the coupling to the graphene bands close to the Dirac points but also to high-energy van-Hove singularities. We find that virtual high-energy fluctuations control the size of the Kondo temperature, and, in turn, can lead to a strongly asymmetric gate-voltage dependence of $T_K$, that would be characteristic for a specific set of orbitals.

The question, which model is appropriate to describe a certain realistic magnetic impurity system, is indispensable for understanding experiments as in Ref. 5 but is in general not easy: For the classical example of Fe in Au studied since the 1930s, an answer could be found only recently23. In this article, we consider the experimentally important case of Co on graphene and develop a first-principles based model describing the Kondo physics in this system. This example shows, that the non-trivial orbital structure of the impurity indeed controls the Kondo physics.

II. DENSITY FUNCTIONAL SIMULATION OF CO ON GRAPHENE

For an ab-initio description of Co on graphene we performed density functional (DFT) calculations on $6 \times 6$ and $4 \times 4$ graphene supercells containing one Co ad-atom using the Vienna Ab Initio Simulation Package (VASP)24.
with the projector augmented wave (PAW) basis sets. To judge the role of on-site Coulomb interaction, we employed a generalized gradient approximation (GGA) as well as GGA+U with $U = 2\,\text{eV}$, $J = 0.9\,\text{eV}$ and $U = 4\,\text{eV}$, $J = 0.9\,\text{eV}$. We obtained fully relaxed structures for all of these functionals.

In agreement with Refs. [18,28,29], our GGA calculations find Co positioned above the middle of a hexagon on graphene (h-site), with Co on top of carbon (t-site) or above a bridge site (b-site) being both more than 0.5 eV higher in energy. GGA predicts the electronic configuration of Co close to spin $S = 1/2$ at all adsorption sites. For $U = 2\,\text{eV}$, $J = 0.9\,\text{eV}$ h-site adsorption is still the global total energy minimum with two different electronic configurations: First, Co can be in a spin $S = 1/2$ at all adsorption sites. The corresponding GGA+U local density of states configuration of Co: First, Co can be in a spin $S = 1/2$ at all adsorption sites. For $U = 2\,\text{eV}$, $J = 0.9\,\text{eV}$ h-site adsorption is still the global total energy minimum with two different electronic configurations of Co: First, Co can be in a spin $S = 1/2$ state. The corresponding GGA+U local density of states at the Co site is depicted in Fig. 1a: the Co 4s-orbital is unoccupied in this configuration and one hole resides in the Co d-orbitals with $E_1$ symmetry ($d_{xz}, d_{yz}$). The other solution at $U = 2\,\text{eV}$, $J = 0.9\,\text{eV}$ (Fig. 1b) yields the Co $d$-electrons can carrying approximately spin $S = 1$ and a state derived from the Co s-orbital directly at the Fermi level. We note that this solution becomes unstable upon decreasing of $U$ and energetically unfavorable upon increasing of $U$. At $U = 2\,\text{eV}$, there exists a metastable configuration for Co at a t-site with $S = 3/2$ (Fig. 1c), which is 0.04 eV higher in energy than the $S = 1/2$ h-site configuration. For $U = 4\,\text{eV}$, $J = 0.9\,\text{eV}$ the global minimum energy is found for Co with $S = 3/2$ on a t-site, which is 0.2 eV and 0.08 eV lower in energy than the h- and b-sites, respectively.

In the following we will consider all relevant cases, first $S = 3/2$ on the t-site, then $S = 1$ on the h-site and, finally, $S = 1/2$ on the h-site as the most interesting case.

### III. SCENARIOS FOR THE KONDO EFFECT

For Co adsorbed on a t-site the crystal fields have $C_{3v}$ symmetry: the 5 d-orbitals split into two orbital doublets corresponding to the two-dimensional representation (E) of $C_{3v}$ and a singlet of the one-dimensional representation (A1). As can be seen from the LDOS (Fig. 1 b), the spin $3/2$ of the Co atom is made up by a spin 1 residing in the Co 3d-orbitals of E symmetry ferromagnetically coupled to a spin $1/2$ mainly from the Co 4s orbital. The four low-energy graphene bands close to the Dirac points can also be decomposed into one two-dimensional and two one-dimensional representation which hybridize efficiently with the E and A1 orbitals, respectively. In the absence of spin-orbit coupling (SOC) one can expect a two-stage Kondo effect: first, the direct coupling of the s-orbital to the C atom beneath quenches $1/2$ of $S = 3/2$ resulting in a spin 1 coupling to the two bands of $E$ symmetry via the next-nearest C atoms which screen the remaining spin in a second stage. To estimate the strength of SOC, we calculate the magnetic anisotropy, $E_{\text{MAE}} = E_{||} - E_{\perp} \approx 1.0\,\text{meV}$, as the energy difference between magnetization parallel and perpendicular to the graphene plane in GGA+U with $U = 4.0\,\text{eV}$ and $J = 0.9\,\text{eV}$. This translates into different energies, $E_{|S_z|=1/2} - E_{|S_z|=3/2} \approx 1.3\,\text{meV}$, depending on the $z$-component, $S_z$, of the Co spin $S = 3/2$ in this configuration. Ignoring Kondo physics, the ground state $|S_z|=3/2$ and exhibits Kramers degeneracy but spin flips $S_z = 3/2 \rightarrow S_z = -3/2$ induced by electron scattering are only possible in higher order processes. Hence, the Kondo effect is efficiently suppressed for Co in this configuration, as soon as $T_K \lesssim 1.3\,\text{meV}\approx 15\,\text{K}$.

For a (first stage) Kondo temperature of the order of $15\,\text{K}$ or above, a definite determination of the relevant low-energy model is very difficult, but a possible scenario is that first the Kondo effect partially screens $1/2$ out of $S = 3/2$, then spin-orbit coupling stabilizes a low energy doublet ($S_z = \pm 1$), which is finally screened at very low temperatures by an anisotropic Kondo effect.

For Co at an h-site, the situation is more interesting and a quantitative analysis easier: crystal fields of the $C_{6v}$ symmetry decompose the d-orbitals into two non-equivalent two-dimensional irreducible representations $E_1$ ($d_{xz}, d_{yz}$) and $E_2$ ($d_{x^2-y^2}, d_{xy}$) plus one one-dimensional representation $A_1$ ($d_{3z^2-r^2}$). For both, the $S = 1/2$ and the $S = 1$ configuration, the spin mainly

![FIG. 1: (Color online) Orbitally resolved spin-polarized local density of states (LDOS) (left) and corresponding energy level diagrams (right) for a Co ad-atom at an h-site (a) and a t-site (c) for $U = 2\,\text{eV}$ and $J = 0.9\,\text{eV}$. At the h-site, Co has either spin 1/2 due to one hole in the 3d orbitals with $E_1$ symmetry $(d_{xz}, d_{yz})$ (a) or spin 1 with two holes in the E orbitals (b). For Co on a t-site we find spin 3/2 due to two holes in the Co 3d orbitals and one electron in the Co 4s orbital.](image-url)
resides in the E1 orbitals, as shown in Fig. 1 a) and b). We calculated the strength of the SOC for Co on graphene using VASP and obtained $\lambda = 60$ meV for the single particle SOC operator $H_{\text{SOC}} \approx \lambda \cdot s$, with $s$ being the orbital and spin angular momentum operators, respectively. Moreover, in the GGA calculations we obtained the crystal field splitting from the d-level energies as $\epsilon_{2g} - \epsilon_{E1} = -0.85$ eV and $\epsilon_{4t2g} - \epsilon_{E1} = -0.56$ eV for Co at the h-site. Diagonalizing a Co atom with $S = 1$ in $d^3$ configuration in this crystal field yields a singlet as the ground state, which is separated by about 0.008 eV $\approx 90$ K from a doublet of first excited states. Hence, for a high-spin Co at an h-position an $S = 1$ Kondo effect is quenched if $T_K \lesssim 90$ K and a much lower $T_K^0$ is only consistent with the low-spin configuration.

For Co at an h-site with $S = 1/2$ in $d^3$ configuration (see Fig. 1 a) one obtains a four-fold degenerate state. SOC lifts this degeneracy, resulting in a twice degenerate atomic ground state, which is separated from a doublet of excited states by an energy of the order of $\lambda$. In this more than half-filled regime, the spin- and orbital moment are aligned in parallel (c.f. Hund’s 3rd rule). The d-hole resides in the highest crystal field orbitals, $E1$, which have $|z| = 1$. Hence, the Zeeman splitting for out-of-plane magnetic fields, $B_z$, is $\Delta E = \mu_B B_z (g_{sz} + g_{il}|z|)/\hbar = \pm \mu_B B_z$ resulting in the effective g-factor of $g_{sz}/\hbar = 2$. The SOC induced lifting from four fold to two fold degeneracy will lead to SU(4) Kondo physics above the scale of $\lambda$ and SU(2) Kondo physics at lower energies.

IV. KONDO EFFECT OF CO AT AN H-SITE

To address the Kondo effect in this configuration, we describe the Co at an h-site in terms of an Anderson impurity model: The conduction electrons residing in graphene’s $\pi$-bands are modeled by a tight-binding Hamiltonian with $t = -2.97$ eV, $t' = -0.073$ eV, and $t'' = -0.33$ eV quantifying the nearest, next-nearest and next-to-next nearest neighbor hopping, respectively. For the Co atom, we consider its 3d orbitals, $H_{\text{imp}} = \sum_{m,\sigma} \epsilon_{E1} n_{m,\sigma} + \frac{U}{2} \sum_{(m,\sigma)\neq (m',\sigma')} n_{m,\sigma} n_{m',\sigma'}$ with $n_{m,\sigma} = d_{m,\sigma}^\dagger d_{m,\sigma}$, where $m$ is the quantum number of the z-component of the orbital momentum, $d_{m,\sigma}$ are Fermi operators, $U$ is the local Coulomb repulsion and $\epsilon_{E1}$ are the bare on-site energies. Here, we include hopping from the localized d-orbital to the nearest-neighbor C-atoms and use the $C_{6v}$ symmetry to write the coupling of Co to graphene in the form

$$\tilde{V} = \sum_{m,\sigma} V_{m|} c_{m,\sigma}^\dagger d_{m,\sigma} + \text{H.c.},$$

where $c_{m,\sigma} = \sum_{\langle j \rangle} e^{i m \phi_j} c_{j,\sigma}/\sqrt{6}$, $c_{j,\sigma}$ is the Fermi operator of electrons at carbon atom at site $j$ and $\phi_j$ is the angle between a fixed crystalline axis and the bond from site $j$ to the Co impurity. All local physics, is contained in the local Hamiltonian, $H_{\text{imp}}$, and the hybridization function $\Delta_{mm'}(\omega)$ defined as $\Delta_{mm'}(\omega) = V_{m|} G_{mm'}^0(\omega) V_{m'|}^\dagger$, where

$$G_{mm'}^0(\omega) = \int dk |m|k)(i\omega - H_k)^{-1} |k|m'|$$

is the bare graphene electron Green function of the states $|m|, |m'|$. $\Delta_{mm'}(\omega) = \Delta_{m}(\omega) \delta_{mm'}$ is diagonal and $\Delta_{m}(\omega)$ by symmetry.

The hybridization functions for different values of $|m| = 0, 1, 2$ are subject to selection rules imposed by the matrix elements $\langle m|k \rangle$: The eigenstates of $H_0$ close to the Dirac points, $K$ and $K' = -K$, transform according to $E1$ and $E2$ under $C_{6v}$, with the $E1$ and $E2$ being degenerate at the Dirac point. Hence, hybridization with $m = 0$ states is cubically suppressed and

$$\Delta_{|m|=1}(\omega)/V_1^2 = \text{Im} \frac{\Delta_{|m|=2}(\omega)/V_2^2}{= -\frac{3\sqrt{3}\omega}{2\pi(1-2\omega^2)^{2}}$$
to leading order in $\omega$.

In contrast to the particle hole symmetry for $\omega \rightarrow 0$, the hybridization functions are largely asymmetric at higher energies. This is caused by the $E1$ and the $E2$ impurity orbitals coupling each to only one of the van-Hove singularities resulting from the graphene bands at the Brillouin zone M point: The $E1$ impurity orbitals as well as the graphene valence electron wave functions at the M point are odd under 180$^\circ$ rotation about the h-site, whereas the $E2$ orbitals and conduction electron wave functions at the M point are even under this transformation. Hence, the $E1$ hybridization exhibits a logarithmic singularity, $\Delta_1(\omega) \sim \ln |\omega - E_{M-}|$, at $E_{M-} = t + t' - 3t'' \approx -2.1$ eV. However, there is no singularity in the $E1$ hybridization at the energy of the conduction band van-Hove singularity, $E_{M+} = -t + t' + 3t'' \approx 1.9$ eV. For the $E2$ orbitals, the situation is reversed: $\Delta_2(\omega) \sim \ln |\omega - E_{M+}|$ for $\omega \rightarrow E_{M+}$.

To obtain realistic hybridization strengths, $V_1$ and $V_2$, we calculate $\Delta_m$ by means of DFT as described in Ref. 18 and fit the tight-binding hybridizations via $V_1$ and $V_2$ (see Fig. 2). The tight-binding (TB) hybridizations are obtained in two ways: (1) by directly evaluating Eq. (2), which models one Co ad-atom on an infinite graphene sheet (TB-inf), and (2) by employing the same 6 x 6 supercell as in the DFT calculations and performing the same supercell Brillouin zone integration (TB-cell).

The high energy particle-hole / E1-E2 asymmetry is striking the DFT as well as in both TB hybridization functions. The DFT hybridization functions display small wiggles and the van-Hove singularities appear to be smeared out. Comparison of the DFT hybridization to the TB supercell hybridization shows that these two effects are supercell artifacts. The tight-binding curves can be well fitted to DFT$^{35}$ with $V_1 = 1.4$ eV and $V_2 = 1.5$ eV. For energies above 3.4 eV and below $-3.1$ eV also further small wiggles and the van-Hove singularities appear to be logarithmic singularity, $A_{1,2}(\omega) \sim \ln(\omega - |E_{1,2}|)$ for $\omega \rightarrow |E_{1,2}|$. The hybridization functions for different values of $|m| = 0, 1, 2$ are subject to selection rules imposed by the matrix elements $\langle m|k \rangle$: The eigenstates of $H_0$ close to the Dirac points, $K$ and $K' = -K$, transform according to $E1$ and $E2$ under $C_{6v}$, with the $E1$ and $E2$ being degenerate at the Dirac point. Hence, hybridization with $m = 0$ states is cubically suppressed and

$$\Delta_{|m|=1}(\omega)/V_1^2 = \text{Im} \frac{\Delta_{|m|=2}(\omega)/V_2^2}{= -\frac{3\sqrt{3}\omega}{2\pi(1-2\omega^2)^{2}}$$
to leading order in $\omega$.
FIG. 2: (color online) Imaginary part, Im $\Delta_{|m|}(E)$, of the hybridization functions of the E1 ($|m| = 1$) and E2 orbitals ($|m| = 2$) of a Co ad-atom adsorbed to a graphene h-site. Hybridization functions obtained from DFT and tight-binding (TB) models of one Co on an infinite graphene sheet (TB-inf) as well as the same supercell (TB-cell) as used in DFT with $V_1 = 1.4$ eV and $V_2 = 1.5$ eV are shown.

To estimate Kondo temperatures and their gate voltage dependence, we solve the scaling equation\textsuperscript{31,32}

$$\frac{dJ(D)}{dD} = -N(D)J^2(D)\frac{\rho(\mu - D) + \rho(\mu + D)}{2D},$$

where $J(D)$ is the renormalized exchange coupling, $D$ the high energy cut-off, $\mu$ the chemical potential in graphene and $\rho(\omega) = -\text{Im} \Delta_1(\omega)/(\pi V^2)$. The degeneracy factor, $N(D) = 4$ for $D > \lambda$ and $N(D) = 2$ else\textsuperscript{32}, accounts for locking the orbital- to the spin-degree of freedom below the energy scale of the spin-orbit coupling.

Like all one-loop renormalization group equations, Eq. (3) is valid as long as the renormalized coupling is small, see Fig. 3, left. It is used to detect the energy scale where the strong coupling regime is approached which we identify with the Kondo temperature. This procedure correctly identifies the exponentially strong sensitivity of the Kondo scale on system parameters. While an exact calculation of the prefactor of $T_K$ in the limit of small $J_0$ and $\mu \neq 0$ requires at least a two-loop calculation\textsuperscript{31}, the one-loop equation (3) captures the main effect of a frequency-dependent density of states. Note, however, that the perturbative renormalization group calculation cannot describe the quantum-critical point\textsuperscript{6-10} obtained for vanishing density of states as the renormalized coupling is not small in this case.

Varying $J_0$ for $\mu = 0.2$ eV (as in the experiment reported in Ref.\textsuperscript{5}), we find the Kondo temperature changing by an order of magnitude for varying $J_0$ within a few percent. (See Fig. 3 left.) While this hinders predictions of the absolute value of the Kondo temperature, realistic values of $V_1$ and $U$. The remarkable asymmetry of the hybridization function leads to a highly asymmetric dependence of the Kondo temperatures on the gate voltages. If the E2 orbitals were carrying the magnetic moment instead of E1 this asymmetry would be reversed.

Interestingly, for $J_0 > J_c \approx 1.1$ eV we find that the Kondo effect persists even for vanishing doping. This implies that by relative small changes (e.g. using different substrates) it may be possible to realize the quantum critical point of the pseudogap Kondo problem\textsuperscript{6-11}.

V. FOURIER TRANSFORMED STM

The symmetry of Co orbital carrying the magnetic moment can be probed by FT-STS. In the simplest model (see e.g. Ref. 33), FT-STS measures the Fourier transform of the local density of states, $|\rho_k(E)|$, in the vicinity of an impurity with the constant background of a clean sample being subtracted:

$$\rho_k(E) = -\frac{1}{\pi} \int d^2r e^{iE\tau} \text{Im} \left(G(r, r, E) - G_0(r, r, E)\right).$$

Here, $G(r, r, E)$ denotes the full Green function of the graphene-impurity system in position space representation and $G_0(r, r, E)$ is the Green function of clean graphene. Using a resonant level model for the Kondo peak, we employ the T-matrix formalism (see e.g. Refs. 11,33,34) in the discrete position space representation. Then, Eq. (4) leads to
\[
\rho_k(E) = -\frac{1}{\pi} \sum_j \int d^2k' e^{ik'x_j} \frac{1}{4} \left[ \delta G_{k',k+k}(E) - \delta G^*_k + k + k'(E) \right]_{jj},
\]
(5)

where the index \(j\) labels the two atoms per graphene unit cell, \(r_j\) their position w.r.t. the unit cell origin and the \(k'\) integral extends over the first Brillouin zone. The Green functions occurring in Eq. (5) are \(2 \times 2\) matrices in sublattice space and obtained from the unperturbed graphene Green functions \(G^0_k(E)\) by using the \(T\)-matrix:

\[
\delta G_{k',k+k}(E) = G^0_k(E)T_{k',k+k}(E)G^0_{k+k}(E).
\]

In a resonant level model for the Kondo peak, we consider orbitals of \(E_1\) and \(E_2\) symmetry to derive the FT-STS patterns from Eq. (5) using a corresponding \(T\)-matrix with phase \(\pi/2\).

The resulting Fourier transformed LDOS images are shown in Fig. 4. As the Kondo impurity on the \(h\)-site couples equally strong to both \(K\) and \(K'\) points, the inter-valley scattering is very strong. Due to the two sublattices, it depends however strongly on the energy \(E\) and the phase shift \(\delta\) to which extent this \(K-K'\) scattering leads to FT-STS intensity at the \(K\) and \(K'\) points. As Fig. 4 shows, there is a double arc structure of intensity around \(K / K'\) for \(E = 0.4\) eV with the radius given by twice the Fermi wave vector. These structures disappear for \(E \to 0\). The orbital symmetries manifest in distinct FT-STS maps with characteristic gate voltage and tunneling bias dependence: Upon energy, \(E \to -E\), and phase shift reversal, \(\pi/2 + \eta \to \pi/2 - \eta\), the FT-STS patterns of resonances with \(E_2\) and \(E_1\) symmetry interchange.

**VI. CONCLUSIONS**

We showed that the Kondo effect of Co ad-atoms on graphene is controlled by the particular symmetries of the Co 3d orbitals originating from graphene crystal field splitting. Based on first-principles calculations we found different possible scenarios with \(t-\) or \(p\)-site adsorption of Co and consequences for the Kondo physics. For Co at an \(h\)-site we found a surprising asymmetry of Kondo temperatures w.r.t. the chemical potential and predicted characteristic FT-STS patterns. Both of these effects can be probed by STM.

The importance of the orbital degree of freedom for the Kondo effect in graphene can be traced back to the symmetries underlying the peculiar band degeneracies of graphene at the Dirac point. Therefore the orbital degree of freedom is expected to control the Kondo physics in graphene also for other magnetic impurities occupying high-symmetry positions.

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5. L. S. Mattos et al. (2009), To be published.
35 Note that only one fitting parameter is employed per curve. Including an on-site potential at the adjacent C-atoms allows bringing the energy positions of the wiggles in the TB supercell and the DFT hybridization functions into agreement. Here, we focus on qualitative consequences of the particle hole asymmetry in the hybridization function and do not include a second fitting parameter.