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Double single-channel Kondo coupling in graphene with Fe molecules

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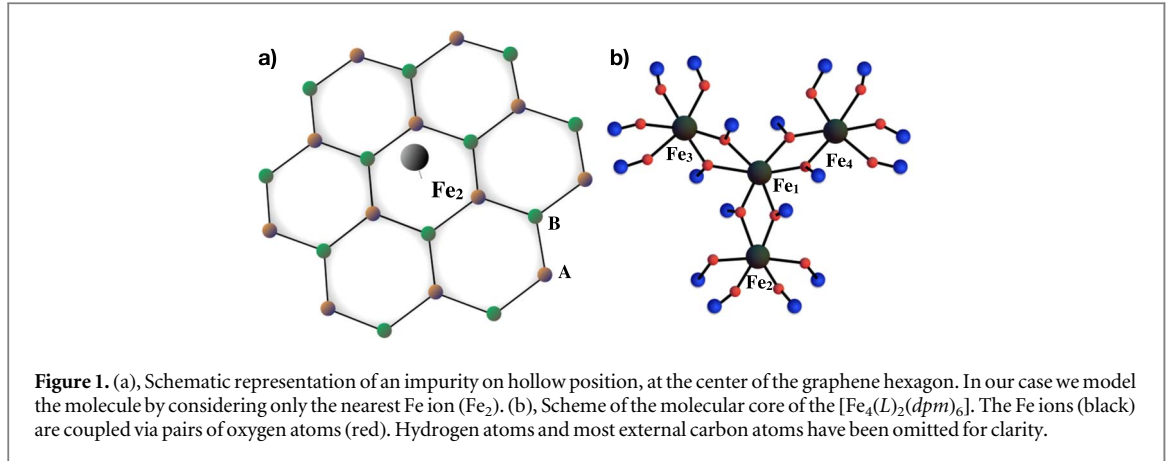
Abstract

We study the interaction between graphene and a single-molecule-magnet, $[Fe_4(L)_2(dpm)_6]$. Focusing on the closest Iron ion in a hollow position with respect to the graphene sheet, we derive a channel selective tunneling Hamiltonian, that couples different d orbitals of the Iron atom to precise independent combinations of sublattice and valley degrees of freedom of the electrons in graphene. When looking at the spin-spin interaction between the molecule and the graphene electrons, close to the Dirac point the channel selectivity results in a channel decoupling of the Kondo interaction, with two almost independent Kondo systems weakly interacting among themselves. The formation of magnetic moments and the development of a full Kondo effect depends on the charge state of the graphene layer.

Introduction

Since the low-temperature magnetic phase transition of metals with magnetic impurities diluted in was explained by Kondo [1] in the middle of the past century, the theoretical framework has been extensively developed [2–6]. Over time, the problem has been extended, particularly with the discovery of the multichannel Kondo effect [7] and the study of the interactions between two magnetic impurities [8, 9]. In carbon 2D materials, a double degeneracy appears in spin and orbital momentum. This double degeneracy allows the emergence of a symmetric $SU(4)$ Kondo effect with a strong coupling between the spin and orbital degrees of freedom [10–13]. The special condition of graphene, positioned halfway between metals and semiconductors, appears as an appealing scenario for Kondo physics. Its linear dispersion relation, and the ease to tune its chemical potential are important elements too [14–17]. Atomic vacancies in the graphene lattices were the first system in which magnetic transitions were founded [18]. The relaxation of the lattice around the vacancy can be solved changing the vacancy by an hydrogen impurity localized on top site [19]. The strong coupling of the impurity and the carbon atom generates a localized magnetic moment by the subtraction of one electron from the Fermi sea [20]. Magnetic molecules [21] offer an easy way to study the magnetic interaction between graphene and localized spin moments due to its clear magnetic properties. Functionalized hybrid of graphene and one of this molecules, $[Fe_4(L)_2(dpm)_6]$, shows interesting properties for the study of the magnetic phase transition [22–25]. We expect other Fe compounds may present similar features.

In this work we describe in detail the interactions between a magnetic molecule and graphene. Initially we simplify the problem considering only the nearest Fe(III) ion to the graphene and subsequently incorporate to the problem the influence of the other ions. The interplay between the different degrees of freedom of the graphene electrons (valley, pseudospin, and spin) with the projection of the angular momentum and the spin of the electrons in the molecule leads to a channel selectivity of the coupling. The type and number of the channels that can couple to the molecule depend on the site that the molecule occupies on the lattice. If the molecule is in the center of the hexagon just two independent combinations of valley, pseudospin and spin are tunnel coupled



to the two relevant orbitals of the Fe(III) ion in the core of the molecule. Due to the orthogonality of the graphene electronic channels involved, we observe the absence of the Ruderman-Kittel-Kasuya-Yoshida (RKKY) interaction between the two orbitals of the molecule, giving rise to a double single-channel Kondo coupling. The analysis presented is not limited to the particular case of the tetra-iron single molecule magnet $[\text{Fe}_4(\text{L})_2(\text{dpm})_6]$, but can be easily extended to other molecules and Fe based compounds based on Fe(III) ions.

The model

We consider a graphene sheet described by a nearest neighbor hopping Hamiltonian

$$H_G = -t \sum_{\langle i,j \rangle, s} a_{s,i}^\dagger b_{s,j} + \text{h. c.}, \quad (1)$$

where a, b are fermionic operators that annihilate an electron with spin $s = \uparrow \downarrow$, on sublattices A and B, respectively, and $t \sim 2.7$ eV is the hopping energy between next nearest neighbors. In momentum space hopping between $a_{\mathbf{k}}$ and $b_{\mathbf{k}}$ is specified by $\gamma_{\mathbf{k}} = -t \sum_i e^{i\mathbf{k} \cdot \mathbf{c}_i}$, with $\mathbf{c}_1 = \hat{x}/\sqrt{3}$, $\mathbf{c}_2 = -(\hat{x} + \sqrt{3}\hat{y})/(2\sqrt{3})$, $\mathbf{c}_3 = (-\hat{x} + \sqrt{3}\hat{y})/(2\sqrt{3})$, nearest-neighbors vectors. Expansion of $\gamma_{\mathbf{k}}$ around the Dirac points $\pm \mathbf{K} = (0, \pm 2\pi/3)$ produces the celebrated graphene Dirac Hamiltonian.

We then consider a single-molecule-magnet (SMM), $[\text{Fe}_4(\text{L})_2(\text{dpm})_6]$ [21, 22] added on top of the graphene sheet. It is a molecule with a $S = 5$ spin moment due to the four Fe(III) ions in its core [26], and it is well described by the Hamiltonian [22]

$$H_{\text{SSM}} = \sum_{i=2}^4 J_{\text{mol}} (\mathbf{S}_1 \cdot \mathbf{S}_i) + \sum_{\langle i,j \rangle (i,j \neq 1)} J_{\text{mol}}' (\mathbf{S}_i \cdot \mathbf{S}_j), \quad (2)$$

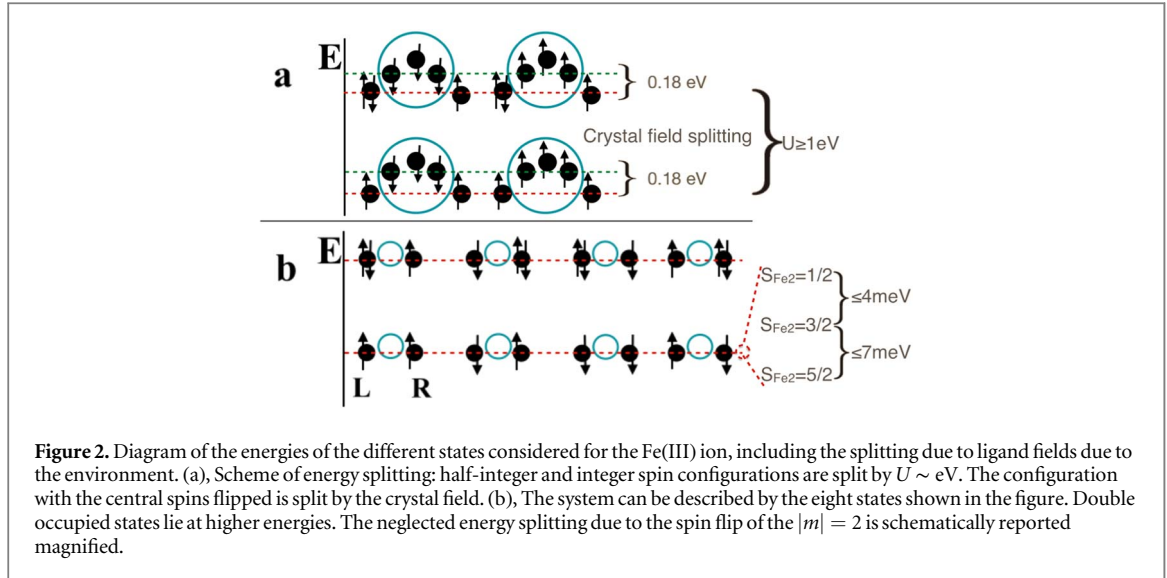
where J_{mol} and J_{mol}' are the exchange couplings between nearest and next nearest Iron atoms, respectively. $\mathbf{S}_i$ are the $S = 5/2$ spin matrices describing the spin of each Iron ion. As shown in figure 1, Fe_1 is one ion surrounded by the other three. The coupling $J_{\text{mol}} > 0$ is antiferromagnetic whereas the coupling $J_{\text{mol}}' < 0$ is ferromagnetic, with $|J_{\text{mol}}'| \ll J_{\text{mol}}$. This way, the three outer ions, $\text{Fe}_{2,3,4}$ anti align with respect to the central ion Fe_1 .

Since the distance of the graphene sheet to the ion Fe_2 is more than twice smaller than the distance to the other ions, the tunneling from graphene to the molecule involves only the ion Fe_2 , see figure 1. We then focus on Fe_2 and consider the effect of other three ions by their contribution in the energy levels of Fe_2 . Fe(III) has five electrons distributed in five spin-degenerate outermost d -orbitals. In the $S = 5/2$ state, all five d -orbitals are singly occupied and the spin of the ion can be described as the sum of five aligned localized spin $1/2$. The Hamiltonian of the ion Fe_2 reads

$$H_{\text{Fe}_2} = \sum_{m,s} \epsilon_{m,s} d_{m,s}^\dagger d_{m,s} + H_U, \quad (3)$$

where $d_{m,s}$ are fermionic operators describing the five d -orbitals, $\epsilon_{m,s}$ their associated energies, m is the angular momentum projection of the different states of angular momentum $l = 2$. The symmetry of the system, (C_{3v}), shifts the energy of the orbitals of the Fe(III) ion creating two pairs of degenerate states with the same $|m| \neq 0$. In the case of the Fe (III) ions the lowest levels are the doublets $d_{\pm} = (d_{x^2-y^2} \pm id_{xy})/\sqrt{2}$.

The electrostatic repulsion between the Fe(III) electrons is measured by $U_{mm'}$, and the exchange energy $J_{mm'}$, between the localized electrons in different orbitals.



$$H_U = \sum_{m,m'} U_{m,m'} \hat{n}_{m,\uparrow} \hat{n}_{m',\downarrow} + \frac{1}{2} \sum_s \sum_{m \neq m'} (U_{m,m'} - J_{m,m'}) \hat{n}_{m,s} \hat{n}_{m',s}, \quad (4)$$

where $\hat{n}_{m,s} = d_{m,s}^\dagger d_{m,s}$. For simplicity we are going to consider $U_{mm} = U_{mm'}$ and $J_{mm} = J_{mm'}$.

Tunneling Hamiltonian

The most stable position for atoms such as Fe on a graphene lattice is at the center of the hexagons, the hollow site [27–31], which is the case that we will consider here. For the hollow position the Hamiltonian describing the tunneling between the localized states of the impurity and the conduction electrons of graphene can be generically written as

$$H_V = \sum_{m,s} \sum_{i=1}^3 [V_{a,i}^m a_s^\dagger(\mathbf{a}_i) + V_{a,i}^m b_s^\dagger(-\mathbf{a}_i)] d_{m,s} + \text{h. c.}, \quad (5)$$

where $V_{c,i}^m$ ($c = a, b$) are tunneling matrix elements between the localized states with angular momentum m with each of the six carbon atoms surrounding the hollow position. These can be specified by a unique Slater-Koster-like matrix element V . States with $m = \pm 2$ on the Fe ion are invariant under C_{∞}^z , and the tunneling process selects combinations of $a_{\mathbf{k}}$ and $b_{\mathbf{k}}$ that are C_3^z invariant. This yields a selectivity between angular momentum m , sublattice and valley⁵. By expanding the expression around the Dirac points the tunneling Hamiltonian takes the form,

$$H_V = \frac{V}{\sqrt{2}} \sum_{\mathbf{k}} d_{\uparrow}^\dagger (a_{\mathbf{k},K} + b_{\mathbf{k},K'}) + d_{\downarrow}^\dagger (a_{\mathbf{k},K'} + b_{\mathbf{k},K}) + \text{H.c.}, \quad (6)$$

where a factor $3/\sqrt{2}$ has been reabsorbed in V and the spin label has been suppressed, as the tunneling conserves the spin. This expression can be considered as a low energy expansion around the Dirac point of graphene, in powers of the electron energy, ϵ/W , where W is the width of the p_z band in graphene. Corrections to the couplings, as the momenta of the graphene states deviates from the Dirac point are neglected.

The tunneling term connects the graphene states only with $|m| = 2$ orbitals of Fe_2 . The ground state configuration of the Fe ions consists in five electrons with the same $S_z = \pm 1/2$, the ground state has $S = 5/2$, and the first excited states with $S = 3/2, 1/2$ are less than 5 and 7 meV above the ground state [21, 22]. The states with integer S_z are much more energetic, as schematically depicted in figure 2. Due to the small difference between the four low-energy states, we can neglect the splitting between them, and consider all of them as degenerate. This assumption implies that the energy required to flip the spin of a given orbital is negligible. We keep, on the other hand, the crystal field splitting between orbitals with different values of $|m|$, of order $1470 \text{ cm}^{-1} \approx 0.18 \text{ eV}$ [21] \cite{Uchoa1}. Hence, the interaction between the graphene electrons and the Fe_2 ion is through the atomic orbitals of energy closest to the Dirac point of graphene, which we assume to have $m = \pm 2$ (the calculations are equivalent for $m = \pm 1$).

⁵ The explicit calculations are in the Supplementary Material available online at stacks.iop.org/JPCO/5/075010/mmedia.

We now diagonalize the graphene Hamiltonian around the Dirac points and introduce eigenoperators $c_{\mathbf{k},\beta,\tau,s} = (a_{\mathbf{k},\tau,s} + \beta\tau e^{i\tau\theta_{\mathbf{k}}} b_{\mathbf{k},\tau,s})/\sqrt{2}$, with $\tan \theta_{\mathbf{k}} = k_y/k_x$, $\beta = \pm$ distinguishing between valence and conduction bands, and $\tau = \pm$ indexing the valley. The Hamiltonian of the Fe_2 ion and the graphene electrons reads

$$H_0 = \sum_{\mathbf{k},s,\tau,\beta} \epsilon_{\beta,\mathbf{k}} c_{\mathbf{k},\beta,\tau,s}^\dagger c_{\mathbf{k},\beta,\tau,s} + \sum_{m=\pm 2,s} \epsilon_0 d_{m,s}^\dagger d_{m,s} + \frac{U}{2} N_d (N_d - 1). \quad (7)$$

The form of the tunneling suggests the introduction of two new fermionic operators representing the two independent combinations of sublattice and valley appearing in equation (6), $C_{\mathbf{k},\alpha,s} = \sum_{\beta,\tau} A_{\beta,\tau}^\alpha c_{\mathbf{k},\beta,\tau,s}$, so that the tunneling term reads $H_V = V \sum_{\mathbf{k},\alpha,s} C_{\mathbf{k},\alpha,s}^\dagger d_{\alpha,s} + \text{H.c.}$, where the two m orbitals have been relabelled as $\alpha = L, R = \pm 1$ (See footnote 6), in analogy with a double-dot configuration.

Effective low-energy model

In order to see the conditions for which the hopping to graphene can quench this localized moment, we derive an effective spin-spin coupling between the graphene electrons and the Fe_2 ion via eliminating the tunneling at first order through the well known Schrieffer–Wolff transformation [32]. The latter consists in defining a new Hamiltonian $\tilde{H}$ that is obtained via a unitary transformation $\tilde{H} = e^S H e^{-S} = H + [S, H] + \frac{1}{2}[S, [S, H]] + \dots$, with S an anti Hermitian operator on order of the tunneling H_V . By requiring

$$[H_0, S] = H_V, \quad (8)$$

the tunneling Hamiltonian H_V is eliminated at first order. By further truncating the expansion at second order the effective Hamiltonian reads

$$\tilde{H} = H_0 + \frac{1}{2}[S, H_V]. \quad (9)$$

In this problem the existence of different interacting electrons in the ion adds a non-trivial difficulty. Given the form of H_V , the operator S is given by the following expression

$$S = \sum_{ij,\alpha,\mu,\tau,\mathbf{k},s} \frac{V_{\mu\tau}^\alpha P_i d_{\alpha,s}^\dagger c_{\mu,\tau,\mathbf{k},s} P_j}{\epsilon_0 + (i+j-1)U - \epsilon_{\mu,\mathbf{k}}} - \text{H.c.}.. \quad (10)$$

where $V_{\mu\tau}^\alpha = V A_{\mu\tau}^\alpha$ and P_i are the projector operators for the double dot system that satisfy $\sum_{i=0,4} P_i = 1$, with i labelling the number of electrons in the double dot. The correction to the unperturbed Hamiltonian H_0 is composed by several terms and takes the form

$$H' = \frac{1}{2}[S, H_V] = H_K + H_{ch} + H_{mix} + H_C. \quad (11)$$

The result consists in a Kondo term and a charge term, plus a mixing term and a Cooper term. The latter is composed by terms like $c^\dagger c^\dagger d d$, that we discard. The Hamiltonian H' needs to be projected onto the desired subspace, that for the present problem is the double occupancy subspace. Therefore, a further step is carried on as $H' \rightarrow P_2 H' P_2$.

Effective Kondo Model

The double occupancy subspace is in turn composed by states with one electron per dot and states with two electrons in one dot and zero in the other. However if we consider instead of the equal repulsion interaction for the intra-orbital and inter-orbital case that one in which, $U_{m,m} \gg U_{m,m'}$ with $m' \neq m$, we can neglect the double occupancy cases. We then carry on a second projection as $H' \rightarrow P_{1L} P_{1R} H' P_{1L} P_{1R} = H_K + H_{ch}$. Since we are concerned only in the Kondo term we leave the full expression of H_{ch} to the Sup. Mat.⁶. Introducing a cumulative index $\mu \equiv \{\mu, \tau, \mathbf{k}\}$, the full effective Kondo Hamiltonian reads

⁶ Supplementary Material containing details of the Schrieffer–Wolff transformation.

$$H_K = - \sum_{\alpha\mu\mu'} \frac{J_{\mu,\mu'}^\alpha}{2} [c_{\mu'\downarrow}^\dagger c_{\mu\uparrow} d_{\alpha\uparrow}^\dagger d_{\alpha\downarrow} + c_{\mu'\uparrow}^\dagger c_{\mu\downarrow} d_{\alpha\downarrow}^\dagger d_{\alpha\uparrow} + \frac{1}{2}(c_{\mu'\uparrow}^\dagger c_{\mu\uparrow} - c_{\mu'\downarrow}^\dagger c_{\mu\downarrow})(d_{\alpha\uparrow}^\dagger d_{\alpha\uparrow} - d_{\alpha\downarrow}^\dagger d_{\alpha\downarrow})], \quad (12)$$

with the coupling constant given by

$$J_{\mu,\mu'}^\alpha = V_\mu^\alpha (V_{\mu'}^\alpha)^* \left[\frac{1}{\epsilon_0 + 2U - \epsilon_\mu} + \frac{1}{\epsilon_0 + 2U - \epsilon_{\mu'}} \right] - V_\mu^\alpha (V_{\mu'}^\alpha)^* \left[\frac{1}{\epsilon_0 + 4U - \epsilon_\mu} + \frac{1}{\epsilon_0 + 4U - \epsilon_{\mu'}} \right]. \quad (13)$$

The Kondo Hamiltonian is still quite involved at this stage, as it mixes different bands and couples different channels. However, close to the Dirac point we have that $\epsilon_{\beta,k} \ll \epsilon_0, U$ and we can safely neglect the energy dependence in the coupling. This procedure highly simplifies the expression and highlights the channel selectivity contained in the tunneling Hamiltonian H_V . Due to destructive interference the two orbitals L and R separately couple to two independent channels in the valley and sublattice space.

At the Dirac points at K and K' we define the graphene eight-component spinor $\Psi_{\mathbf{k}}$ and the iron 2-component spinor $\Psi_\alpha^\dagger = (d_{\alpha,\uparrow}^\dagger, d_{\alpha,\downarrow}^\dagger)$. The expression for the Kondo Hamiltonian reads

$$H_K = -J \sum_{\mathbf{k}, \mathbf{k}', \alpha} \Psi_{\mathbf{k}}^\dagger \Sigma_\alpha \mathbf{s} \Psi_{\mathbf{k}'} \cdot \Psi_\alpha^\dagger \mathbf{S}_\alpha \Psi_\alpha, \quad (14)$$

where $\mathbf{s}$ and $\mathbf{S}_\alpha$ are the spin 1/2 Pauli matrix vectors of graphene and of the different orbitals ($\alpha = L, R$) of the iron (See footnote 6) The operators $\Sigma_{\alpha=L,R}$ are given by

$$\Sigma_R = 1 - \sigma_z \tau_z + \sigma_x \tau_x + \sigma_y \tau_y, \quad (15)$$

$$\Sigma_L = 1 + \sigma_z \tau_z + \sigma_x \tau_x - \sigma_y \tau_y, \quad (16)$$

with σ_i, τ_i sublattice and valley Pauli matrices, and define two independent channels in sublattice and valley space, $\Sigma_L \Sigma_R = 0$. We then see that close to the Dirac point a channel decoupling takes place and the two iron orbitals couple to different subspaces of the graphene Hamiltonian, yielding a double single-channel Kondo Hamiltonian. The coupling constant J reads

$$J = \frac{4V^2U}{(\epsilon_0 + 2U)(\epsilon_0 + 4U)}, \quad (17)$$

in complete analogy with the original Kondo Hamiltonian derived by Schrieffer and Wolff from the single impurity Anderson model [32]. The sign of the coupling is negative for $2U < -\epsilon_0 < 4U$, that is assumed to be the ground state energy of the doubly occupied double dot problem, so that the overall Kondo spin-spin interaction is antiferromagnetic.

RKKY interaction

We now look at the possibility that the graphene electrons mediate an effective interaction between the L and R spins through the RKKY interaction. Considering that the two spins sit at the same spatial position, the RKKY interaction at second order in the coupling J reads

$$H_{\text{RKKY}} = \sum_{\mu,\nu} \chi_{\mu,\nu} \hat{S}_\mu^L \hat{S}_\nu^R, \quad (18)$$

with $\mu, \nu = x, y, z$ labelling the spin components and with the effective spin-spin susceptibility $\chi_{\mu,\nu}$ defined as

$$\chi_{\mu,\nu} = \sum_{k,k'} J^2 \frac{1}{\beta} \sum_{i\omega_n} \text{Tr} [\Sigma_L s_\nu G_{\omega_n k}^0 \Sigma_R s_\mu G_{\omega_n k'}^0]. \quad (19)$$

Having neglected the dependence of J on the momentum, integration of the graphene Green's function over momentum rules out its matrix structure and we are left with

$$\chi_{\mu,\nu} \propto \text{Tr} [s_\mu \Sigma_L s_\nu \Sigma_R] = 0, \quad (20)$$

where the last equality follows from the orthogonality of the two channels defined by $\Sigma_{L,R}$. We then conclude that the model equation (14) effectively described two independent single-channel Kondo Hamiltonians.

Role of other ions

We now finally discuss the role played by the other ions in the description of the spin-spin interaction between the molecule and the graphene sheet. The antiferromagnetic coupling between nearest neighbor ions in the molecule can be seen as the result of onsite Hubbard repulsion on each ion, at second order in the hopping between ions. Going a step back, we modify the Hamiltonian as $H = H_M + H_t + H_V + H_G$, where H_t describes hopping between the ions in the molecule and H_M the onsite Hubbard repulsion on each ion. Treating H_t and H_V on equal footing, we can perform a joint Schrieffer–Wolff transformation through $S = S_V + S_t$ and eliminate both tunneling terms at first order. The full second order correction reads $H' = \frac{1}{2}[S_V + S_t, H_t + H_V]$, where S_V given in equation (10) S_t accounts for intramolecular transitions (see Sup. Mat. (See footnote 6)). Out of the resulting four different terms, $[S_V, H_V]$ results in the Kondo Hamiltonian so far discussed and $[S_t, H_t] = \sum_{i=1,3,4} J S_2 S_i$ [21, 22, 26]. The additional correction produces a well know term in the $t - J$ model [33] that reads

$$H'_{t,V} = V' \left(\sum_{s,\mu} d_{s,2}^\dagger c_{\mu,s} n_1 - d_2^\dagger S c_\mu d_1^\dagger S d_1 \right) + \text{H.C.}, \quad (21)$$

and describes a spin mediated hopping that represents a perturbation of the Kondo Hamiltonian.

Discussion

To summarize, we have studied the interaction between graphene and a molecular magnet. We have focused in the most stable and symmetric case, with the core of the molecule being at the center of a graphene hexagon. The leading coupling, equation (14), shows two Kondo couplings involving the $m = \pm 2$ orbitals in the Iron ion nearest to the graphene layer. The interaction with the other ions involves exchange interaction only at fourth order in perturbation theory. This coupling could be seen as a source of instability at low temperatures. These two Kondo systems involve different combinations of valley and sublattice indices in the graphene layer. Exactly at the Dirac point, the vanishing density of states of graphene makes the Kondo coupling irrelevant, although two Kondo singlets will be formed for sufficiently large values of the coupling J . Away from the Dirac point, the Kondo coupling becomes marginally relevant, and, at the same time, an effective coupling between the two Kondo systems will develop through the graphene electrons. These two effects are of comparable strength, and they can lead to a rich phase diagram. The nature of the most stable phases depends on details at the atomic scale outside the scope of this work.

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Data availability statement

All data that support the findings of this study are included within the article (and any supplementary files).

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