Importance of electron-electron interactions in the RKKY coupling in graphene

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We show that the carrier-mediated exchange interaction, the so-called Ruderman-Kittel-Kasuya-Yoshida (RKKY) coupling, between two magnetic impurity moments in graphene is significantly modified in the presence of electron-electron (el-el) interactions. Within the mean-field approximation of the Hubbard-U model we show that for increasing el-el interactions the oscillations disappear and the power-law decay becomes more long ranged. In zigzag graphene nanoribbons the effects are even more striking with any finite U rendering the RKKY coupling distance independent. Since the RKKY coupling is directly proportional to the magnetic susceptibility, these results are important for any physical property of graphene related to magnetism. Comparing our mean-field results with first-principles results we also extract a surprisingly large value of U indicating that graphene is very close to an antiferromagnetic instability.

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Several novel features of graphene, such as two dimensionality, linear energy dispersion, a tunable chemical potential by gate voltage, and a high mobility have helped raising the expectation of graphene being a serious post-silicon era candidate.[1,2] In this context, functionalization of graphene, especially with magnetic atoms or defects, which also opens the door to spintronics,[3] is of large interest. One of the most important properties of magnetic impurities is their effective interaction propagated by the conduction electrons in the host, the so-called Ruderman-Kittel-Kasuya-Yoshida (RKKY) coupling.[4] This coupling is crucial for magnetic ordering of impurities but also offers access to the intrinsic magnetic properties of the host as it is directly proportional to the magnetic susceptibility. Several studies exist for the RKKY coupling in graphene, where the standard perturbative approach applied to a continuum field-theoretic description of graphene[5–7] and exact diagonalization[8] have been shown to give similar results. However, consistently, all detailed treatments have calculated the RKKY coupling using only noninteracting electrons. This is in spite of growing evidence for the importance of electron-electron (el-el) interactions in graphene with theoretical results pointing to intrinsic graphene being close to a Mott insulating state.[9–11] This thus begs the question if properties such as the RKKY coupling, which are intrinsically linked to the magnetic properties of graphene, can accurately be described in a noninteracting electron picture. In this work we will therefore investigate the effect of el-el interactions in the RKKY coupling, both in the bulk and in zigzag graphene nanoribbons (ZGNRs) where the zero-energy edge states[12] can significantly modify the RKKY behavior.[7,8] Since the $1/r$ tail of the Coulomb interaction has been shown to be irrelevant, and that then a transition to a Mott insulating state is necessarily driven by short-range interactions,[11] we will here study the influence of el-el interactions within a mean-field treatment of the Hubbard model. Especially note in this context that the Mott insulating state has been suggested to be an antiferromagnet, just as in the Hubbard model.[11] Moreover, the Hubbard model has been employed several times before in the study of magnetic properties in graphene and ZGNRs, and it has also been shown to yield results consistent with first-principles density-functional theory (DFT) results.[13–15]

We show below that even for small to moderate strengths of the el-el interactions, the RKKY coupling in the bulk is qualitatively modified and gets significantly more long ranged than in the noninteracting electron picture. For ZGNRs the effect is even more striking as any finite interaction causes the long-distance RKKY coupling to become distance independent. We thus conclude that it is imperative to include el-el interactions when studying the RKKY coupling, and, by extension, any other properties closely related to the magnetic properties of graphene.

More specifically, we will use the Hartree-Fock (HF) mean-field approximation of the one-band Hubbard-U model for graphene and include magnetic impurity moments, or spins, $\mathbf{S}=\pm S\hat{\mathbf{z}}$ which couples to a graphene atom with a Kondo coupling term J_k,

$$H=-t\sum_{\langle i,j\rangle,\sigma}(c_{i\sigma}^{\dagger}c_{j\sigma}+\text{H.c.})+U\sum_{i,\sigma}\langle n_{i\sigma}\rangle n_{i-\sigma}+J_k\sum_{i=\text{imp}}\mathbf{S}_i\cdot\mathbf{s}_i. \tag{1}$$

Here $c_{i\sigma}$ ($c_{i\sigma}^{\dagger}$) annihilates (creates) an electron at site i with spin σ, $\langle i,j\rangle$ means nearest neighbors, and $\mathbf{s}=\frac{1}{2}c_{\alpha}^{\dagger}\sigma_{\alpha\beta}c_{\beta}$, with $\sigma_{\alpha\beta}$ being the Pauli matrices, is the electron spin. The constants entering, apart from J_k which depends on the particular impurity moment, are the nearest-neighbor hopping in graphene $t\approx 2.5$ eV and the on-site repulsion U. The value of U is hard to determine exactly but, depending on the choice of exchange-correlation potential, $U/t=1-2$ has been shown to be consistent with DFT results.[13] Below we are able to extract $U/t=2.1$ when comparing the RKKY coupling in a spin chain with DFT results.[16] The expectation value of the spin-resolved electron density $n_{i\sigma}=c_{i\sigma}^{\dagger}c_{i\sigma}$ needs to be calculated self-consistently in Eq. (1) and gives the spin-polarization density as $s_i^z=(n_{i\uparrow}-n_{i\downarrow})/2$. Before proceeding it is worth noting that we have found that any local doping induced by the magnetic impurity does not change the RKKY coupling to any significant degree. Thus our RKKY results are robust toward the specifics of the magnetic impurities and the simplified model in Eq. (1) is indeed appropriate even for experimentally realistic systems.

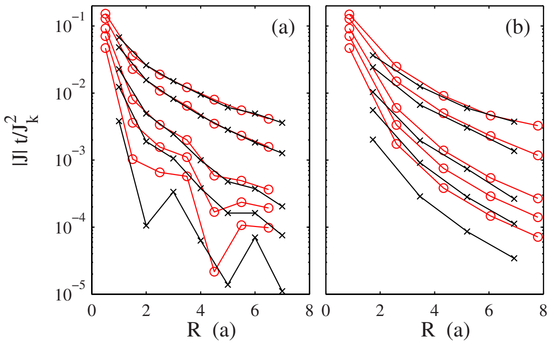

FIG. 1. (Color online) Dimensionless RKKY coupling $|J|t/J_k^2$ as a function of impurity distance R in units of the lattice constant along (a) zigzag and (b) armchair directions for $U/t=0$, 1, 1.5, 2, and 2.15 (increasing $|J|$). A-A sublattice impurities (black, ×) has FM coupling ($J_{AA}<0$) and A-B sublattice impurities (red, ○) has AFM coupling ($J_{AB}>0$). Lines are only guides to the eye.

In standard RKKY perturbation theory[17] the leading interaction between two impurity moments at sites i and j is given by

$$H_{\mathrm{RKKY}} = J(\mathbf{R})\mathbf{S}_i \cdot \mathbf{S}_j, \tag{2}$$

where the effective RKKY coupling constant J is a function of the impurity-impurity distance $\mathbf{R}=\mathbf{R}_i-\mathbf{R}_j$ and directly proportional to the static spin susceptibility of the imbedding bulk. Here we will instead self-consistently solve Eq. (1) for two impurity spins in a ferromagnetic (FM) and an antiferromagnetic (AFM) configuration, respectively, and then explicitly calculate the RKKY coupling as the energy difference between these two configurations: $J=[E(\mathrm{FM})-E(\mathrm{AFM})]/2$. More details on our method applied to noninteracting graphene can be found in Ref. 8. We note in passing that a straightforward application of the random-phase approximation to the noninteracting spin susceptibility results in Ref. 5 does not produce a consistent critical coupling for the AFM Mott insulating state and is therefore not a valid approach.

Bulk impurities. Figure 1 shows the magnitude of the RKKY coupling as a function of impurity distance $R=|\mathbf{R}|$ along both the (a) zigzag and (b) armchair directions of the graphene lattice for several values of U/t. The RKKY coupling in the large R limit for noninteracting graphene is $J \propto [1+\cos(2\mathbf{k}_D\cdot\mathbf{R})]/|\mathbf{R}|^3$ with $J=J_{AA}<0$ for A-A sublattice coupling, i.e., for impurities on the same sublattice (black), and $J=J_{AB}>0$ and three times larger for A-B (or different) sublattice coupling (red).[5,8] Here $\mathbf{k}_D$ is the reciprocal vector for the Dirac points. Apart from minor deviations at small R, these results are displayed in the lowest black and red curves in Fig. 1. The nonoscillatory R dependence for the armchair direction is a consequence of only sampling the cos function at the graphene lattice sites. When including el-el interactions these results are, however, qualitatively modified even for small U. For $U/t=1.5$ (middle curves) essentially all evidence of the (1+cos) oscillations is gone, as is the factor of 3 difference between A-A and A-B sublattice coupling. Also, the power-law decay exponent α decreases notably with increasing U. For noninteracting electrons $\alpha=3$ but α is

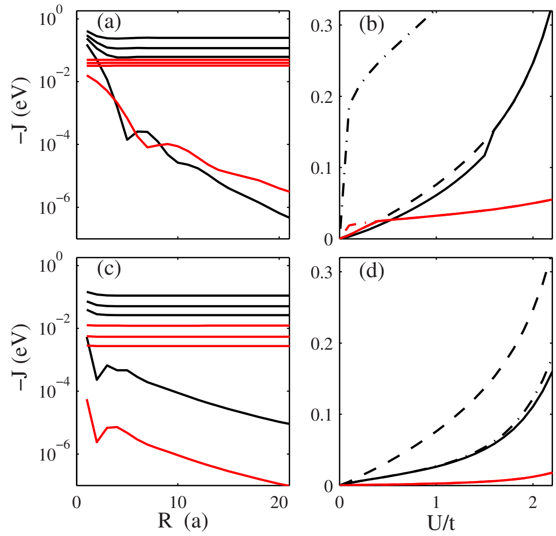

FIG. 2. (Color online) $-J$ for $J_k=t$ (black) and $J_k=t/10$ (red) (a) and (c) as a function of impurity distance R for $U/t=0$, 1, 1.5, and 2 (increasing $-J$) and (b) and (d) as a function of U/t for (a) and (b) A-A edge impurities and (c) and (d) A-A impurities inside a narrow ZGNR of width $W=8/\sqrt{3}a$. Dashed lines shows E_{DW} whereas dashed-dotted lines are equal to $J_k S s_i^z$ with s_i^z being the graphene polarization at the impurity sites but with the impurities absent.

changed to ~2.3 (2.6) for $U/t=1.5$ and 1.9 (2.1) for $U/t=2$ for the zigzag (armchair) direction. Furthermore, for $U/t>2$ (uppermost curves), the armchair and zigzag RKKY couplings are equal and thus all lattice specific details, apart from $J_{AA}<0$ and $J_{AB}>0$, have been washed out for such values of the el-el interactions. With the mean-field quantum critical coupling for the AFM insulating state being $U_c/t=2.23$,[18] it is perhaps not surprising that the RKKY coupling becomes independent of the small length scale details close to this point. However, what is rather unexpected is that this "washing" out of the lattice details is clearly present even at such low values as $U/t=1$, a value which is very likely lower than the physical value of U in graphene. This shows that it is imperative to include el-el interactions when studying the RKKY interaction in graphene. Without them, not only are the magnitude of the RKKY coupling grossly underestimated but, more importantly, the results do not even have a qualitatively correct R dependence.

ZGNR impurities. Within the noninteracting electron picture we recently showed that for impurities along a zigzag graphene edge (A-A impurities) the RKKY interaction decays exponentially for large R, but that, quite counterintuitively, smaller J_k gives a longer decay length.[8] These results are a consequence of the extreme easiness by which an edge impurity can polarize the zero-energy edge state present on the zigzag edge. In contrast, for A-A impurities inside a narrow ZGNR bulk properties of the RKKY coupling are largely regained, notably $J\propto J_k^2/R^3$, in the noninteracting limit. The effect of the edge is thus only limited to edge impurities in the noninteracting limit. These results are shown in the two lowest curves in Fig. 2 for impurities (a) along the edge and (c) inside the ribbon for $J_k=t$ (black) and $J_k=t/10$ (red). When including el-el interactions this picture is dramatically changed. As is well established, any finite U

is going to spontaneously polarize the edge state[14,19] and, by extension, the whole ribbon,[8] thus making it harder for an impurity moment to influence the polarization of the graphene. The three upper curves in (a) and (c) are for $U/t=1$, 1.5, and 2, respectively. As seen, the R dependence completely disappears for R larger than a few unit cells for any physically relevant value of U and for all sites in a narrow ZGNR. The R-independent value of the RKKY coupling is analyzed as a function of U/t in Figs. 2(b) and 2(d). As in the bulk, the FM impurity configuration is energetically favored for A-A impurities in ZGNRs. The AFM configuration on the other hand will require modification of the spontaneous graphene polarization to accommodate the impurity moment with the "wrong" orientation. There are two R-independent limiting solutions for the AFM configuration of which the one with lowest energy will give an upper energy bound for the true AFM solution. The first limiting solution has a magnetic domain wall formed between the two AFM-oriented impurity spins. The magnetic domain-wall formation energy per edge, E_{DW}, is equal to the RKKY coupling for this limiting solution and its value, calculated within Eq. (1), is displayed with a dashed line in Figs. 2(b) and 2(d). This limiting solution is not only independent of R but also of J_k, making it especially favorable at high J_k values which is also seen in Fig. 2(b). For smaller J_k it is, however, more likely that the impurity spins do not noticeably change the polarization of the underlying graphene, not even directly at the impurity site. The limiting solution in this case is the unperturbed graphene plus the two impurities and has an energy $2J_kSs_i^z$ above that of the FM solution. Here s_i^z is the graphene polarization at the site of the wrongly oriented impurity but in the absence of the impurities. This unperturbed limiting solution is also naturally R independent and its RKKY coupling is displayed with dashed-dotted lines in Figs. 2(b) and 2(d). Note that since s_i^z is significantly lower inside a narrow ZGNR than on the edge, this solution yields a smaller RKKY coupling for impurities away from the edge. Also note that s_i^z depends rather strongly on U, which causes both limiting solutions to increase sharply with increasing U. The true RKKY coupling follow the lower of these two limiting solutions remarkably well for all four cases studied in Fig. 2, including jumping form one to the other around $U=0.3t$ for edge impurities when $J_k=t/10$. The small deviations from the unperturbed limiting solution are due to limited impact of the impurity spins on the graphene polarization which locally produces small changes in s_i^z in favor of a lower total energy. The only real notable discrepancy is for edge impurities when J_k is large and U moderately small. Here the domain-wall limiting solution is not followed too closely but the system lowers its energy slightly by instead creating a local, half-circle shaped, domain wall around the wrongly oriented impurity spin. This solution naturally creates a spin imbalance in the system as its domain wall does not propagate to the opposite edge. Note that both of the limiting solutions described here are always present, and thus the qualitative RKKY behavior is the same, in any graphene system which has a spontaneous polarization in the absence of impurities. For edge impurities we do not expect the width of the ribbon to change the RKKY behavior as both the spontaneous edge polarization and E_{DW} are weak functions of the ribbon width.

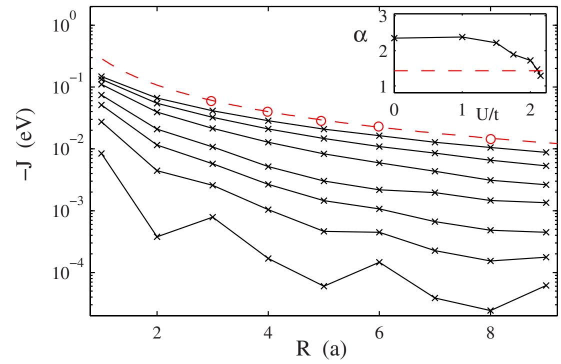

FIG. 3. (Color online) $-J$ (black, ×) for A-A sublattice impurities chains as a function of impurity distance R along the chains for $U/t=0$, 1, 1.5, 1.75, 2.1, and 2.15 (increasing magnitude). DFT results from Ref. 16 (dashed red, ○) are scaled with a factor 0.5. Inset shows the power-law decay exponent α as a function of U/t (black, ×) with the exponent 1.43 from Ref. 16 indicated with a dashed red line.

However, for impurities inside a very wide ZGNR the spontaneous polarization inside the ribbon is going to be vanishingly small and bulk properties should eventually be restored for wide ribbons and small J_k. We thus conclude that any finite el-el interaction renders the long-distance RKKY coupling in a narrow ZGNR R independent and linearly dependent on J_k for small J_k, but independent on J_k in the limit of large J_k. In addition, el-el interactions make impurities inside a ZGNR behave similarly to edge impurities, which is completely opposite to the situation for noninteracting electrons.

Determining U. There exist some DFT results for the RKKY coupling in graphene[16,20] but such studies are always limited to very small R unless chains (or lattices) of impurities are studied. Figure 3 shows the RKKY coupling for A-A sublattice impurity chains along the zigzag direction separated by a distance of 25 Å as a function of the impurity distance R along the chains. We see that for $U=0$ (lowest curve) characteristic noninteracting $(1+\cos)$-type oscillations are present but the chain configuration makes the RKKY coupling somewhat longer ranged than R^{-3}. The oscillations however quickly disappear and the decay exponent α decreases (see inset) with increasing U. DFT results using a hybrid density functional on the same chain structure is available in Ref. 16 and these results, scaled with an overall, unimportant prefactor, are displayed with a dashed red line in Fig. 3. There are no oscillations in the DFT results and the exponent α coincides with the results for $U/t=2.1$, which also yields very well-matched results, as indicative in the main plot. At a first glance, this might seem as a large value for the Coulomb repulsion in graphene since the mean-field AFM instability is at $U_c/t=2.23$. However, one should keep in mind that multiple recent theoretical work have classified graphene as being very close to, if not even being, an insulator in vacuum due to strong Coulomb interactions.[9–11] Our results point to the fact that this state might be an AFM insulator which would also be consistent with earlier results.[11] Our extracted value of U also agrees quantitatively with earlier estimations based on the same functional.[13] DFT calculations instead using the local-density approximation

(LDA) or general gradient approximation (GGA) have yielded a somewhat smaller $U/t \sim 0.9-1.3$.[13,21] It is well known that LDA suffers from electron self-interaction and therefore often underestimates U. Hybrid density functionals on the other hand explicitly contains an element of Fock exchange and thus tends to handle this deficiency better. This becomes especially important in strongly correlated systems but hybrid density functionals can still reproduce the LDA results for weakly correlated materials. It is here also important to keep in mind that the DFT and HF methods are both mean-field approximations and thus a direct comparison between them is fully consistent. Results using quantum Monte Carlo to study the Hubbard model yields a higher U_c,[22] as fluctuations are relatively important in two dimensions. However, while the value of U_c increases when going beyond mean-field theory, the change in the RKKY coupling is primarily determined by the closeness to U_c, and, thus, we expect the general features of Figs. 1 and 2 to still be present in a more accurate treatment.

With such high value of U it is also natural to ask about other possible electronically driven ordered states. U_c(AFM) increases with doping[18] and thus undoped graphene is the strongest candidate for an AFM state. However, with increasing doping electronically driven d-wave superconductivity caused by spin-singlet nearest-neighbor correlations appears for any Coulomb interaction.[23] Such correlations were already proposed by Pauling and others[24] for the $p\pi$-bonded planar organic molecules of which graphene is the infinite extension. With the Coulomb interaction extracted from the results in Fig. 3, one would need a chemical doping of $\mu = 1$ eV to reach $T_c(\mathrm{SC}) \sim 5$ K, a value which might be achieved with, for example, chemical doping.

Conclusions. In summary we have shown that it is of vital importance to include el-el interactions when studying the RKKY coupling in graphene and by extension any property of graphene related to the magnetic susceptibility. Even relatively weak el-el interactions qualitatively change the RKKY coupling to be significantly longer ranged and monotonically decaying in the bulk. In a ZGNR the change is even more pronounced and the R dependence disappears entirely. By comparing our mean-field results we have also been able to extract a surprisingly high value for the el-el interactions, demonstrating that graphene might be very close to an AFM insulating instability. With such closeness to an AFM state it is rather natural that magnetic properties, such as the RKKY coupling, are going to be heavily influenced by el-el interactions.

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