Diluted Graphene Antiferromagnet

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We study RKKY interactions between local magnetic moments for both doped and undoped graphene. In the former case interactions for moments located on definite sublattices fall off as $1/R^2$, whereas for those placed at interstitial sites they decay as $1/R^3$. The interactions are primarily (anti)ferromagnetic for moments on (opposite) equivalent sublattices, suggesting that at low temperature dilute magnetic moments embedded in graphene can order into a state analogous to that of a dilute antiferromagnet. In the undoped case we find no net magnetic moment in the ground state, and demonstrate numerically this effect for ribbons, suggesting the possibility of an unusual spin-transfer device.

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Introduction.—Graphene, a two-dimensional honeycomb network of carbon atoms, has recently become a subject of intense interest. The development of practical fabrication techniques for single graphene sheets [1] has allowed experimental study of this system, confirming its two-dimensional Dirac spectrum in quantum Hall studies and revealing many unique properties [2,3]. In this work we study response functions of graphene in the noninteracting limit, focusing on its consequences for magnetic moments which may be embedded in the system (RKKY interactions). A number of studies of magnetic moments in graphene have identified a tendency toward antiferromagnetic [4–7] or ferromagnetic [8] correlations. These correlations are usually attributed to exchange interactions or other many-body effects. In what follows, we demonstrate that such effects arise even for noninteracting electrons in graphene, and that they are a result of the chirality of the electron states for doped graphene [9], and of the vanishing density of states at the Fermi energy for undoped systems. A noninteracting model of graphene may be justified by its small, density-independent effective r_s parameter, as well as studies suggesting that Fermi liquid theory should work well in physically realizable situations [10–13].

Exchange coupling between local magnetic moments and conduction electrons in metals leads to an effective (RKKY) coupling [14] among the local moments which oscillates with distance with wave vector $2k_F$ (k_F = Fermi wave vector), and an amplitude that decays as $1/R^2$ in two dimensions, with R the separation between impurities. For doped graphene, we shall demonstrate similar behavior, with an important qualitative difference: the sign of the interaction depends on whether the two local moments couple to the honeycomb network on sites of the same sublattice or different ones, and when summed over both sublattices at a fixed distance, the $1/R^2$ contribution to the RKKY coupling is canceled, leaving behind a residue that falls off as $1/R^3$. Interestingly, analogous studies of the linear response to perturbations that do not distinguish between A and B sublattice sites also result in a $1/R^3$ behavior [8,15,16]. We will show that the $1/R^3$ behavior—and the absence of $1/R^2$ behavior in density response functions—is a direct result of the chiral nature of electrons in graphene.

For undoped graphene ($k_F \to 0$) we find the RKKY coupling behaves as $\sim 1/R^3$ at large distances, again with equal magnitudes, that are ferromagnetic when the impurities are on the same sublattice, and antiferromagnetic when on opposite sublattices. This behavior is also connected to that of the full density response, and reflects the vanishing density of states of graphene at the Fermi points. This behavior also dominates in doped graphene for distances $R \lesssim 1/k_F$ where the coupling is greatest in magnitude. Because of this we expect at zero temperature the system will tend to order, with moments oriented in opposite directions for the two sublattices. The state is thus analogous to an ordered state of a dilute antiferromagnet. Analogous behavior has been noted in zigzag graphene ribbons [5] with equal and opposite spin accumulating near the edges, on opposite sublattices. While this effect has been attributed to complicated exchange interactions [5], we present results of simple tight-binding calculations demonstrating that this physics occurs even without interactions, and is a consequence of the unusual nature of the single-particle states in graphene.

Hamiltonian, wave function, and RKKY interaction.—The simplest description of graphene is a tight-binding model representing electrons in π_z orbitals of the carbon atoms, which can hop with matrix element t between nearest neighbor sites, which are always on opposite sublattices for the honeycomb lattice. The energy states of such a model may be straightforwardly computed [9], and one finds that the spectrum possesses particle-hole symmetry, with a zero energy surface consisting of six points at corners of the Brillouin zone, only 2 of which are inequivalent due to symmetry. When undoped the Fermi surface of graphene passes through these points, which are denoted

by K and K'. At long wavelengths, the wave functions near each of these points can be described by two component spinor envelope functions $[\phi^{A(I)}(\mathbf{r}), \phi^{B(I)}(\mathbf{r})]$, the entries of which are proportional to the amplitude for the electron to be present at unit cell located at $\mathbf{r}$ on sublattices A or B. The wave functions may be regarded as possessing a quantum number $\tau = K, K'$ denoting which Dirac point they reside near. The Hamiltonian near such a point is approximately

$$H^{(I)} = \pm v_F \begin{pmatrix} 0 & -i\partial_x \mp \partial_y \\ -i\partial_x \pm \partial_y & 0 \end{pmatrix}$$

with the upper (lower) sign denoting the Hamiltonian for states near the K (K') point, and $v_F = \sqrt{3}t/2$. These Hamiltonians have eigenenergies $\epsilon_{\mathbf{k},s} = s v_F |k|$, and associated eigenstates $\psi^{(I)}_{\mathbf{k},s} = (e^{\mp i\theta_{\mathbf{k}}}, \pm s)$, where again the upper (lower) sign denotes the solution for the K (K') valley, $s = \pm 1$, and $\theta_{\mathbf{k}} = \arctan(k_x/k_y)$.

Consider local spin degrees of freedom $\mathbf{S}_\mu(\mathbf{R}_1)$ and $\mathbf{S}_\nu(\mathbf{R}_2)$ weakly coupled to electrons in graphene by an exchange interaction J at positions at or near sites in sublattices μ and ν. In perturbation theory [17,18] the induced interaction between the spins has the form $H_{\mu\nu} = J^{\mu,\nu}_{\mathrm{RKKY}} \mathbf{S}_\mu \cdot \mathbf{S}_\nu$, where $J^{\mu,\nu}_{\mathrm{RKKY}} = -J^2 \chi^0_{\mu,\nu}(\mathbf{R}_1 - \mathbf{R}_2)$, and $\chi^0_{\mu,\nu}$ is the Fourier transform of

$$\chi^0_{\mu,\nu}(q) = -g_v \frac{1}{N} \sum_{s,s',\mathbf{k}} \frac{f(\epsilon_{\mathbf{k},s}) - f(\epsilon_{\mathbf{k}+\mathbf{q},s'})}{\epsilon_{\mathbf{k},s} - \epsilon_{\mathbf{k}+\mathbf{q},s'}} F^{\mu,\nu}_{s,s'}(\mathbf{k},\mathbf{q}). \tag{1}$$

Here $g_v = 2$ is the degeneracy due to the valley index, N is the number of unit cells in the system, f is the Fermi function, and $F^{\mu,\nu}_{s,s'}(\mathbf{k},\mathbf{q})$ is a factor arising from the matrix element of the spinors associated with the single-particle states, which in general depend on the angles $\theta_{\mathbf{k}}$ and $\theta_{\mathbf{k}+\mathbf{q}}$ [19].

Site-symmetric moments.—When the local moments are located at the centers of the hexagons in the honeycomb network, it becomes appropriate to replace $F^{\mu,\nu}_{s,s'}$ Eq. (1) with a sum, $F_{s,s'} = \sum_{\mu,\nu} F^{\mu,\nu}_{s,s'} = \frac{1}{2}(1 + ss' \cos\Delta\theta_{\mathbf{k}+\mathbf{q}})$, where $\Delta\theta_{\mathbf{k}+\mathbf{q}}$ is the angle formed by the vectors $\mathbf{k}$ and $\mathbf{k} + \mathbf{q}$. The resulting χ_0 is then identical to the standard density-density response function, which may be computed straightforwardly [16,20,21], with a result that may be expressed conveniently in the form $\chi^0(q,\mu) = \chi^0(q,\mu = 0) + \Delta\chi^0(q,\mu)$ with $\mu = v_F k_F$ the chemical potential (assumed positive), $\chi^0(q,\mu = 0) = \frac{g_v q}{16 v_F}$, and

$$\Delta\chi^0(q,\mu) = \frac{g_v k_F}{2\pi v_F}\left(1 - \frac{\pi}{4}\frac{q}{2k_F}\right)\Theta(2k_F - q) + \frac{g_v k_F}{2\pi v_F}\left(1 - \frac{1}{2}\sqrt{1 - \left(\frac{2k_F}{q}\right)^2} - \frac{1}{2}\frac{q}{2k_F}\arcsin\frac{2k_F}{q}\right)\Theta(q - 2k_F). \tag{2}$$

Several comments are in order. (i) In spite of the presence of step functions Θ in this expression, its first derivative with respect to q is continuous at $q = 2k_F$, in sharp contrast with the situation for a normal two-dimensional electron gas (2DEG). The discontinuity in the 2DEG arises from a singularity in the integrand in Eq. (1) (with $F = 1$ for a 2DEG) when $\epsilon_{\mathbf{k}} = \epsilon_{\mathbf{k}+\mathbf{q}}$ and $q = 2k_F$—the Kohn anomaly [22]. For graphene, $F_{s,s'}$ vanishes precisely where the singularity would otherwise occur, removing the discontinuity in the slope. This behavior is a direct result of the chirality of electrons in graphene and the resulting absence of backscattering that it entails [9]. (ii) For undoped graphene the response vanishes at $q = 0$. We can understand this as follows. The $q = 0$ response may be understood as arising from a shift in the chemical potential, plus more generally a part coming from changes in the single-particle wave functions. However, the total charge of the system cannot shift due to changes in the single-particle wave functions, in accordance with the Friedel sum rule [23]. Moreover, in undoped graphene the response from a differential chemical potential shift vanishes because the density of states at the Fermi energy is zero. Thus there can be no net $q = 0$ response. (iii) The vanishing of χ_0 at $q = 0$ means that the total population of either spin flavor cannot be changed by a perturbation in undoped graphene, even if the perturbation is different for the two spin directions—as would be the case for a (possibly inhomogeneous) Zeeman coupling. This result is consistent with the observation that graphene ribbons can have an inhomogeneous spin configuration but net spin zero [5].

Site-specific moments.—Local moments can in many circumstances be more strongly coupled to a specific site in the honeycomb network, which lies on a definite sublattice. One can also consider situations in which the moment is a substitutional impurity, or is an induced moment due to a vacancy in the lattice [7,8]. In such cases the coupling among moments has the form $J^{\mu,\nu}_{\mathrm{RKKY}} \propto \chi^0_{\mu,\nu}$, and $\chi^0_{\mu,\nu}$ is given by Eq. (1) with $F^{A,A}_{s,s'}(\mathbf{k},\mathbf{q}) = \frac{1}{4}$ for impurities on the same sublattice, and $F^{A,B}_{s,s'}(\mathbf{k},\mathbf{q}) = \frac{1}{4} ss' e^{i\Delta\theta_{\mathbf{k}+\mathbf{q}}}$ for impurities on opposite sublattices. We first consider the case of impurities on the same sublattice. Decomposing the response function as $\chi^0_{A,A}(q) = \chi^0_{A,A}(q,\mu = 0) + \Delta\chi^0_{A,A}(q,\mu)$, the first term, corresponding to undoped graphene, may be shown to have the form

$$\chi^0_{A,A}(q,\mu = 0) = \frac{1}{2}\frac{g_v}{4\pi v_F}\left(\Lambda - \frac{\pi}{8}q\right) \tag{3}$$

where $\Lambda \sim \pi/a_0$ is the momentum cutoff. The contribution due to doping may also be evaluated, and has the form

$$\Delta\chi^0_{A,A}(q,\mu) = \frac{g_v}{64 v_F} q\Theta(2k_F - q) + \frac{g_v q}{32\pi v_F}\left[\arcsin\left(\frac{2k_F}{q}\right) - \frac{2k_F}{q}\sqrt{1 - \frac{4k_F^2}{q^2}}\right]\Theta(q - 2k_F) \tag{4}$$

In Eq. (4) the derivative is discontinuous at $q = 2k_F$: the chiral overlap factor F^{AA} does not vanish in this case, and one obtains a Kohn anomaly analogous to that of the standard 2DEG. This has important consequences for RKKY coupling in real space, which is proportional to the Fourier transform of Eqs. (3) and (4). For the first of these we find

$$J^{AA}_{\mathrm{RKKY}}(R, \mu = 0) \propto -\chi(R, \mu = 0) = -\frac{\pi}{32}\frac{g_v}{v_F}\frac{1}{R^3} \quad (5)$$

so that in undoped graphene, moments are ferromagnetically coupled when they are on the same sublattice. The correction due to doping, $\Delta J^{AA}_{\mathrm{RKKY}}(R, \mu) \propto -\Delta\chi^0_{A,A}(R, \mu)$ can be computed in the asymptotic limit ($k_F R \gg 1$), with the result

$$\Delta\chi^0_{A,A}(R, \mu) \simeq \frac{g_v k_F}{4v_F R^2}\sin(2k_F R) + g_v\frac{\cos(2k_F R) - 1}{8v_F R^3}. \quad (6)$$

A comparison with numerical integration shows that this asymptotic expression works quite well for $k_F R > 0.35$. The oscillating term proportional to $1/R^2$ is present because the Kohn anomaly is not suppressed in the relevant response function. A similar behavior was found recently for Friedel oscillations, where the way in which the perturbation breaks the lattice symmetry determines whether they fall off as $1/R^2$ or $1/R^3$ [15]. While this $1/R^2$ behavior is similar to that of the standard 2DEG, it nevertheless differs from the 2DEG in having a density dependent amplitude [18].

For moments on opposite sublattices, we can easily compute the coupling by noting that $F^{A,A}_{s,s'} + F^{A,B}_{s,s'} = F_{s,s'}/2$. It immediately follows that

$$\chi^0_{A,B}(q, \mu) = -\chi^0_{A,A}(q, \mu) + \tfrac{1}{2}\Delta\chi^0(q, \mu). \quad (7)$$

We thus see that the tendency towards ferromagnetic coupling for moments within a distance $R \lesssim 1/k_F$ for impurities on the same sublattice translates into an antiferromagnetic coupling for impurities on opposite sublattices [24]. Qualitatively this may be understood as a result of a cancellation of Kohn anomalies in $\chi^0_{A,A}$ and $\chi^0_{A,B}$, which must occur since no such anomaly is present in $\Delta\chi^0$ as discussed above. Moreover because the coupling is strongest for short distances, we expect this to result in a tendency towards antiferromagnetic order at low temperatures when the moment density n_i satisfies $k_F/\sqrt{\pi n_i} \lesssim 1$. The low temperature state is analogous to that of a dilute antiferromagnet since the moment locations are random in such models. A special feature of the graphene system, however, is that the coupling among the moments can be manipulated via the electron density, which in turn may be controlled by a gate [1]. In particular, added electrons shorten the distance over which the RKKY coupling has a well-defined (i.e., nonoscillating) sign, so that the antiferromagnetic order may be suppressed via doping. It is interesting to note that analogous, albeit simpler, behavior (e.g., ferromagnetic rather than antiferromagnetic ordering) is believed to occur in dilute magnetic semiconductors [25,26]. The physics associated with the chirality of the single-particle states, as well as the vanishing density of states at the Fermi energy when undoped, give graphene a richer phenomenology.

Numerical investigations.—To test these results we have performed numerical tight-binding calculations on graphene ribbons. We first consider an infinite ribbon with zigzag edges, $N = 80$ atoms wide along an armchair chain, with a Zeeman coupling ($E_z = t/10$) along an (infinite) line of sites all on one sublattice (A) near the center of the ribbon. This type of perturbation models a line of frozen spins. Figure 1 shows the results for the induced spin density, with A sites shown in red and B sites in black. The main panel is essentially identical for both the doped and undoped cases. In the doped case one can see oscillations of wave vector $2k_F$ falling off slowly with distance, which are out-of-phase for the two sublattices. Moreover, the total induced spin *vanishes* for the undoped case. These properties are in precise agreement with our expectation that summing over sublattices leads to a cancellation of the RKKY oscillations due to the absence of backscattering in graphene, and a vanishing net response as $q \to 0$ due to the vanishing density of states for undoped graphene.

We also find an interesting result when the perturbation is applied at one of the edges (Fig. 2). Applying a Zeeman field at a single zigzag edge in undoped graphene induces spin in *both* edges, but in such a way that there is no induced total spin for undoped graphene. This is interesting because the spin state is communicated across the width of the sample even though there is no spin polarization in the bulk. Thus the tendency for undoped graphene to compen-

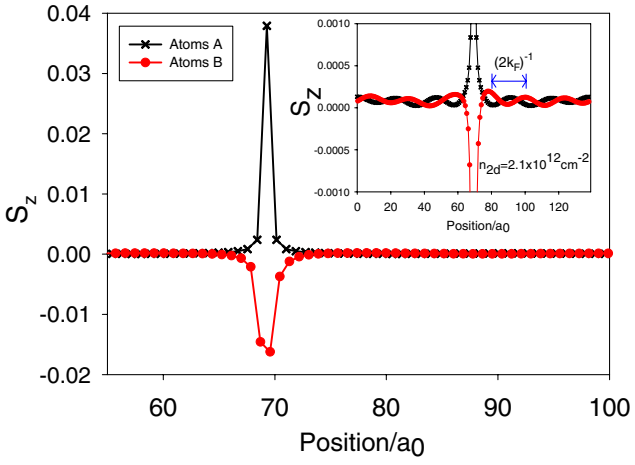

FIG. 1 (color online). Spin density as a function of position (in units of a_0 = distance between nearest atoms of same sublattice) for a Zeeman field $E_z = t/10$ along line of sites in sublattice A for a ribbon geometry. The main panel is essentially identical for doped and undoped graphene. Inset: Blowup for undoped graphene illustrating RKKY oscillations.

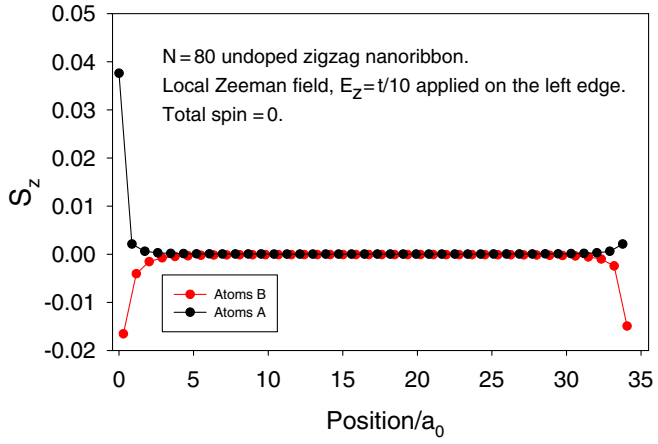

FIG. 2 (color online). Spin density as a function of position for a Zeeman field $E_z = t/10$ along the left edge of an undoped zigzag graphene ribbon, of width $N = 80$ atoms along an armchair chain. Spins induced at both edges, with a profile such the S_z summed over all sites vanishes. Note that the perturbation applied to the left edge induces a strong response at the right edge, of net spin opposite that induced by the Zeeman field.

sate an induced local spin due to a local Zeeman field survives the inclusion of edge effects, which in the zigzag case induces a nonvanishing density of states at zero energy [4] for sufficiently wide ribbons [27]. We find results similar to those of Fig. 2 for doped graphene zigzag ribbons with edge Zeeman fields, with two differences: there are $2k_F$ oscillations in the spin density of small magnitude as one moves in from the edge, and a small net spin is induced. We note that analogous spin configurations have been predicted to *spontaneously* form in ribbons when exchange interactions are important [5]; our calculations demonstrate that such interactions are not needed to induce the tendency towards spin compensation. It is interesting to speculate that this effect might be utilized as a spin-transfer device.

In summary, we have studied RKKY interactions among magnetic moments in graphene using a linear response approach. Our calculations show a strong qualitative difference between moments that couple symmetrically to the sublattices of the graphene honeycomb network and ones that couple to specific sublattices, with the latter showing more pronounced effects. Doped graphene, in particular, supports oscillations due to the Kohn anomaly only in the latter case. The sum of intra- and intersublattice responses was shown to vanish in the long wavelength limit in undoped graphene, leading to RKKY interactions of opposite sign for the two sublattices. Within mean-field theory, impurities coupled via these interactions should form a low temperature state analogous to that of a dilute antiferromagnet. Tight-binding calculations confirm the presence of the $2k_F$ oscillations for doped graphene, and the tendency of opposite sublattices to have compensating spins.

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Note added.—After this work was completed, we became aware of related work [28] by Saremi on undoped graphene, which also concludes that the sign of RKKY interactions depends on whether moments are located on the same or opposite sublattices.

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