Chirality and Correlations in Graphene

Yafis Barlas,[1] T. Pereg-Barnea,[1] Marco Polini,[2] Reza Asgari,[3] and A. H. MacDonald[1]
[1]*Department of Physics, University of Texas at Austin, Austin, Texas 78712, USA*
[2]*NEST-CNR-INFM and Scuola Normale Superiore, I-56126 Pisa, Italy*
[3]*Institute for Studies in Theoretical Physics and Mathematics, Tehran 19395-5531, Iran*
(Received 11 January 2007; published 5 June 2007)

Graphene is described at low energy by a massless Dirac equation whose eigenstates have definite chirality. We show that the tendency of Coulomb interactions in lightly doped graphene to favor states with larger net chirality leads to suppressed spin and charge susceptibilities. Our conclusions are based on an evaluation of graphene's exchange and random-phase-approximation correlation energies. The suppression is a consequence of the quasiparticle chirality switch which enhances quasiparticle velocities near the Dirac point.

DOI: 10.1103/PhysRevLett.98.236601 PACS numbers: 72.10.−d, 73.21.−b, 73.50.Fq

Introduction.—Graphene can be described at low energies by a massless Dirac-fermion (MDF) model [1] with chiral quasiparticles that are responsible for a number of unusual properties [2]. The recent experimental realization of single-layer graphene sheets [3] has made it possible to confirm some theoretical expectations, notably an unusual half-quantized quantum Hall effect [4–6]. In this Letter we show that quasiparticle chirality in weakly doped graphene layers also leads to a peculiar suppression of the charge and spin susceptibilities. We predict that both quantities are suppressed by approximately 15% in current samples and that the suppression will be larger if uniform samples with much lower densities can be realized. At a qualitative level, these effects arise from an interaction energy preference for MDF states with larger chiral polarization. Our conclusions are based on an evaluation of the exchange and random-phase-approximation (RPA) correlation energies of uniform spin-polarized MDF systems with Coulomb interactions.

RPA theory of graphene.—We study the following MDF model Hamiltonian (with $\hbar = 1$),

$$\hat{\mathcal{H}} = v \sum_{\mathbf{k},\alpha=\uparrow,\downarrow} \hat{\psi}^{\alpha\dagger}_{\mathbf{k}} [\tau^3 \otimes (\boldsymbol{\sigma}\cdot\mathbf{k})] \hat{\psi}^{\alpha}_{\mathbf{k}} + \frac{1}{2S} \sum_{\substack{\mathbf{q}\neq 0 \\ \alpha,\alpha'=\uparrow,\downarrow}} v_q \hat{n}^{\alpha}_{\mathbf{q}} \hat{n}^{\alpha'}_{-\mathbf{q}}, \tag{1}$$

where τ^3 is a Pauli matrix that acts on the two-degenerate (K, K') valleys, $\mathbf{k}$ is a two-dimensional vector measured from the K and K' points, σ^1 and σ^2 are Pauli matrices that act on graphene's pseudospin (A, B) degrees of freedom, S is the sample area, $\hat{n}^{\alpha}_{\mathbf{q}} = \sum_{\mathbf{k}} \hat{\psi}^{\dagger\alpha}_{\mathbf{k}-\mathbf{q}} \hat{\psi}^{\alpha}_{\mathbf{k}}$ is the single-spin density operator, and $v_q = 2\pi e^2/(\epsilon q)$ is the 2D Fourier transform of the Coulomb interaction potential $e^2/(\epsilon r)$. In Eq. (1) the field operator $\hat{\psi}^{\alpha\dagger}_{\mathbf{k}} = (\hat{\psi}^{\alpha\dagger}_{K+\mathbf{k},A}, \hat{\psi}^{\alpha\dagger}_{K+\mathbf{k},B}, \hat{\psi}^{\alpha\dagger}_{K'+\mathbf{k},B}, \hat{\psi}^{\alpha\dagger}_{K'+\mathbf{k},A})$ is a four-component spinor. In this work chirality refers to the eigenvalues $(s, s' = \pm)$ of $\boldsymbol{\sigma}\cdot\mathbf{k}/|\mathbf{k}|$.

The model (1) requires an ultraviolet cutoff, as we discuss below. To evaluate the interaction energy we follow a familiar strategy [7] by combining a coupling constant integration expression for the interaction energy valid for uniform continuum models,

$$E_{\text{int}} = \frac{N}{2} \int_0^1 d\lambda \int \frac{d^2\mathbf{q}}{(2\pi)^2} v_q [S^{(\lambda)}(q) - 1], \tag{2}$$

with a fluctuation-dissipation-theorem (FDT) expression [7] for the static structure factor,

$$S^{(\lambda)}(q) = -\frac{1}{\pi n} \int_0^{+\infty} d\Omega \chi^{(\lambda)}_{\rho\rho}(\mathbf{q}, i\Omega), \tag{3}$$

where n is the total electron density. This form of the FDT theorem takes advantage of the smooth behavior of the density-density response function along the imaginary axis $\chi^{(\lambda)}_{\rho\rho}(\mathbf{q}, i\Omega)$. The RPA approximation for the interaction energy then follows from the RPA approximation for χ:

$$\chi^{(\lambda)}_{\rho\rho}(\mathbf{q}, i\Omega) = \frac{\chi^{(0)}(\mathbf{q}, i\Omega)}{1 - \lambda v_q \chi^{(0)}(\mathbf{q}, i\Omega)}, \tag{4}$$

where $\chi^{(0)}(\mathbf{q}, i\Omega)$ is the noninteracting density-density response function. We have derived the following compact expression for the $\chi^{(0)}$ contribution for an individual MDF model channel [8]:

$$\chi^{\text{MDF}}(\mathbf{q}, i\Omega) = -\frac{q^2}{16\sqrt{\Omega^2 + v^2 q^2}} - \frac{\varepsilon^c_F}{2\pi v^2} + \frac{q^2}{8\pi\sqrt{\Omega^2 + v^2 q^2}} \Re e\left[\sin^{-1}\left(\frac{2\varepsilon^c_F + i\Omega}{vq}\right) + \left(\frac{2\varepsilon^c_F + i\Omega}{vq}\right)\sqrt{1 - \left(\frac{2\varepsilon^c_F + i\Omega}{vq}\right)^2}\right]. \tag{5}$$

In Eq. (5) $\varepsilon^c_F = v k^c_F$ where k^c_F is the channel Fermi momentum. $\chi^{(0)}$ in Eq. (4) is constructed by summing the channel response function (χ^{MDF}) over valley and spin with appropriate ε^c_F values. For a spin- and valley-unpolarized system $\chi^{(0)} = g\chi^{\text{MDF}}$ [with $k^c_F \to k_F = (4\pi n/g)^{1/2}$] where $g = g_s g_v = 4$ accounts for spin and valley degeneracy.

The energy constructed by combining Eqs. (2)–(5) is clearly divergent since $\chi^{(0)}$ increases with q at large q and falls only like Ω^{-1} at large Ω. The divergence is expected since the energy calculated in this way includes the interaction energy of the model's infinite sea of negative energy particles. The MDF model can be expected to describe only changes in energy with density and spin density at small ε_F^c values. For definiteness we choose the total energy of undoped graphene ($\varepsilon_F^c = 0$ in all channels) as our zero of energy. For pedagogical and numerical reasons it is also helpful to separate the contribution that is first order in e^2, the exchange energy, from the higher order contributions conventionally referred to in electron gas theory as the correlation energy. Using Eqs. (2)–(5) we find that for unpolarized doped graphene the excess exchange energy per excess electron is

$$\delta\varepsilon_x = -\frac{1}{2\pi n}\int\frac{d^2\mathbf{q}}{(2\pi)^2}v_q\int_0^{+\infty}d\Omega[\chi^{(0)}(\mathbf{q},i\Omega) - \chi^{(0)}(\mathbf{q},i\Omega)|_{\varepsilon_F=0}] \equiv -\frac{1}{2\pi n}\int\frac{d^2\mathbf{q}}{(2\pi)^2}v_q\int_0^{+\infty}d\Omega\,\delta\chi^{(0)}(\mathbf{q},i\Omega), \quad (6)$$

and that the corresponding correlation energy is

$$\delta\varepsilon_c^{\mathrm{RPA}} = \frac{1}{2\pi n}\int\frac{d^2\mathbf{q}}{(2\pi)^2}\int_0^{+\infty}d\Omega\left\{v_q\delta\chi^{(0)}(\mathbf{q},i\Omega) + \ln\left[\frac{1-v_q\chi^{(0)}(\mathbf{q},i\Omega)}{1-v_q\chi^{(0)}(\mathbf{q},i\Omega)|_{\varepsilon_F=0}}\right]\right\}. \quad (7)$$

With this regularization the Ω integrals are finite and the q integrals have logarithmic ultraviolet divergences. The remaining divergences are physical and follow from the interaction between electrons near the Fermi energy and electrons very far from the Fermi energy as we discuss at length later. The best we can do in using the MDF model to make predictions relevant to graphene sheets is to introduce an ultraviolet cutoff for the wave vector integrals k_c. k_c should be assigned a value corresponding to the wave vector range over which the MDF model describes graphene. Based on this criterion [9] we estimate that $k_c \sim 1/a$ where $a \sim 0.246$ nm is graphene's lattice constant. The MDF is useful when k_c is much larger than k_F in all channels.

With this regularization the properties of graphene's MDF model depend on the dimensionless coupling constant (restoring $\hbar$)

$$f \equiv g\frac{e^2}{\epsilon v\hbar} = \frac{g}{\epsilon}\frac{c}{v}\alpha, \quad (8)$$

and on $\Lambda = k_c/k_F$. In Eq. (8), $c \sim 300v$ is the speed of light, $\alpha \approx 1/137$ is the fine structure constant, and ϵ depends on the dielectric environment of the graphene layer. In typical circumstances $f \sim 2$. Λ is ~ 10 in the most heavily doped samples studied experimentally and can in principle be arbitrarily large in lightly doped systems. We expect, however, that many of the electronic properties of graphene layers will be dominated by disorder when the doping is extremely light.

In Figs. 1 and 2 we plot the exchange and correlation energies of the graphene MDF model as a function of f for a range of Λ values. Note that both $\delta\varepsilon_x$ and $\delta\varepsilon_c^{\mathrm{RPA}}$ have the same density dependence as $\varepsilon_F \propto n^{1/2}$ apart from the weak dependence on Λ. The exchange energy is positive because our regularization procedure implicitly selects the chemical potential of undoped graphene as the zero of energy; doping either occupies quasiparticle states with positive energies or empties quasiparticles with negative energies. Note that including the RPA correlation energy weakens the Λ dependence so that the exchange energy per electron scales more accurately with ε_F. It is possible to analytically extract the asymptotic behavior of the exchange and correlation energies at large Λ by Laurent expanding the integrands of Eqs. (6) and (7) in q and retaining only the $1/q$ terms:

$$\delta\varepsilon_x = \frac{1}{6g}f\varepsilon_F\ln(\Lambda) + \text{regular terms}, \quad (9)$$

and

$$\delta\varepsilon_c^{\mathrm{RPA}} = -\frac{1}{6g}f^2\xi(f)\varepsilon_F\ln(\Lambda) + \text{regular terms}, \quad (10)$$

where

$$\xi(f) = 4\int_0^{+\infty}\frac{dx}{(1+x^2)^2(8\sqrt{1+x^2}+f\pi)}. \quad (11)$$

[Note that $\xi(f=0) = 1/3$ so that the exchange and correlation energies are comparable in size for typical f values.]

Charge and spin susceptibilities.—In an electron gas, the physical observables most directly related to the energy

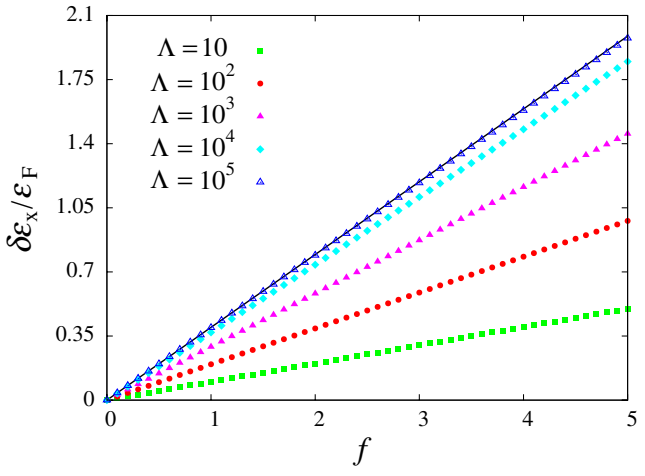

FIG. 1 (color online). Cutoff Λ and coupling constant f dependence of the regularized exchange energy $\delta\varepsilon_x$ in units of the Fermi energy ε_F. The black solid line corresponds to the highest value of the cutoff that we have chosen, $\Lambda = 2.7 \times 10^5$.

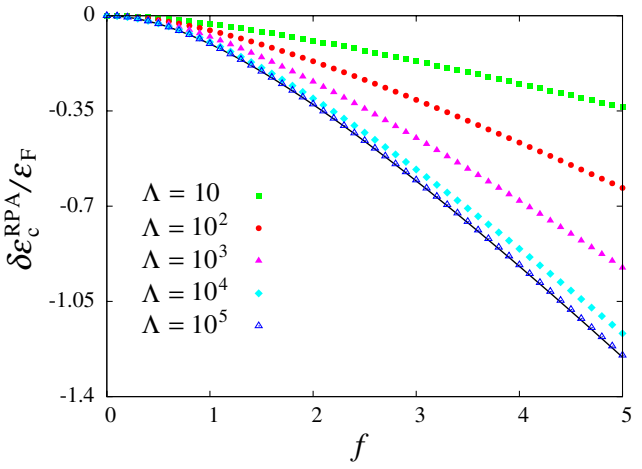

FIG. 2 (color online). Cutoff and coupling constant dependence of the regularized correlation energy $\delta\varepsilon_c^{\mathrm{RPA}}$ in units of the Fermi energy ε_F.

are the $\Omega \to 0$, $q \to 0$ charge and spin susceptibilities, normally discussed in terms of dimensionless ratios between noninteracting and interacting system values. The charge susceptibility is the inverse of the thermodynamic compressibility κ of the system up to a factor of n^2. For the MDF model of doped graphene,

$$\frac{\kappa_0}{\kappa} = \frac{2n}{\varepsilon_F}\frac{\partial^2(n\delta\varepsilon_{\mathrm{tot}})}{\partial n^2} = \frac{2n}{\varepsilon_F}\frac{\partial\mu}{\partial n}, \tag{12}$$

and

$$\frac{\chi_0}{\chi_S} = \frac{2}{\varepsilon_F}\frac{\partial^2[\delta\varepsilon_{\mathrm{tot}}(\zeta)]}{\partial\zeta^2}\bigg|_{\zeta=0}, \tag{13}$$

where $\delta\varepsilon_{\mathrm{tot}}$ includes band, exchange, and correlation contributions. In Eq. (13) $\zeta \equiv (n_\uparrow - n_\downarrow)/(n_\uparrow + n_\downarrow)$, χ_S^{-1} measures the stiffness of the system against changes in the density of electrons with spin $\uparrow$ and spin $\downarrow$. In a 2D electron system the compressibility can be measured [10] capacitively. We note that this type of measurement is less difficult when $\partial\mu/\partial n$ is large, as it is in weakly doped graphene. In bulk electronic systems, the spin susceptibility can usually be extracted successfully from total magnetic susceptibility measurements, but these are likely to be challenging in the case of single-layer graphene. In 2D electron systems, however, information about the spin susceptibility can often [11] be extracted from weak-field magnetotransport experiments using a tilted magnetic field to distinguish spin and orbital response.

Our results for the charge and spin susceptibilities are summarized in Figs. 3 and 4. For experiments performed over the density range over which properties appear to be intrinsic in current samples (Λ between $\sim$10 and $\sim$40), these results predict compressibility and susceptibility suppression (apparent quasiparticle velocity enhancement) by approximately 15%. Both the sign of the interaction effect and the similarity of κ and χ are in remarkable contrast with familiar electron gas behavior. In 3D and 2D nonrelativistic electron gases both are [7,12] strongly enhanced by interactions, with the charge response diverging at intermediate coupling and the spin response diverging at very strong coupling.

Discussion.—The qualitative physics of ferromagnetism in metals is most transparent at the Hartree-Fock (HF) level. Similarly, the mechanism responsible for the unusual interaction physics of weakly doped graphene becomes clear when the exchange energy is expressed in terms of HF theory quasiparticle self-energies. Correlations do, however, play an essential quantitative role. For doped graphene the contribution of an individual channel to the HF theory interaction energy is

$$\delta\varepsilon_x = -\frac{1}{2nS^2}\sum_{s,s'}\sum_{\mathbf{k},\mathbf{k}'} V_{s,s'}(\mathbf{k},\mathbf{k}')\delta n_{\mathbf{k}s}\delta n_{\mathbf{k}'s'} + \frac{1}{nS}\sum_{\mathbf{k},s}\Sigma^{(0)}_{\mathbf{k},s}\delta n_{\mathbf{k}s}, \tag{14}$$

where $s, s' = \pm$ are the chirality indices of the MDF bands (i.e., the eigenvalues of the chirality operator defined above),

$$\Sigma^{(0)}_{\mathbf{k},s} = -\frac{1}{S}\sum_{\mathbf{k}',s'} V_{ss'}(\mathbf{k},\mathbf{k}')n^{(0)}_{s'}(\mathbf{k}') \tag{15}$$

is the HF self-energy of the *undoped* MDF model,

$$V_{s,s'}(\mathbf{k},\mathbf{k}') = \frac{2\pi e^2}{|\mathbf{k}-\mathbf{k}'|}\left(\frac{1+ss'\cos(\theta_{\mathbf{k},\mathbf{k}'})}{2}\right) \tag{16}$$

is the exchange matrix elements between band states s', $\mathbf{k}'$ and s, $\mathbf{k}$, and $\theta_{\mathbf{k},\mathbf{k}'}$ is the angle between $\mathbf{k}$ and $\mathbf{k}'$. For Coulomb interactions, the factor in large parentheses on the right-hand side of Eq. (16) tends to be larger between states in the same band, i.e., states with the same chirality.

The first term on the right-hand side of Eq. (14) is similar to the exchange energy of an ordinary 2D electron system. Because it is negative and increases with density, its con-

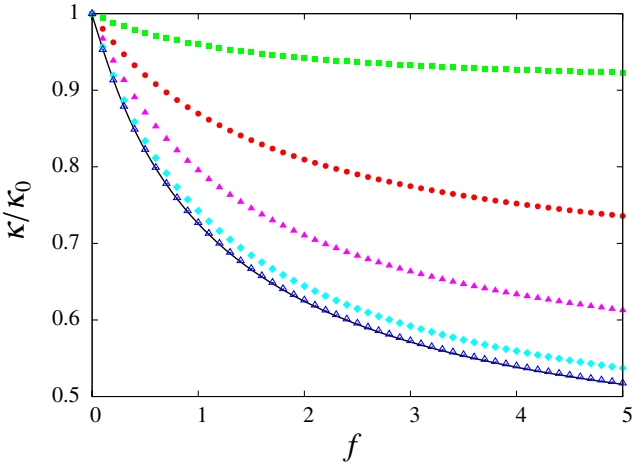

FIG. 3 (color online). Cutoff and coupling constant dependence of κ/κ_0. The color coding is as in Figs. 1 and 2.

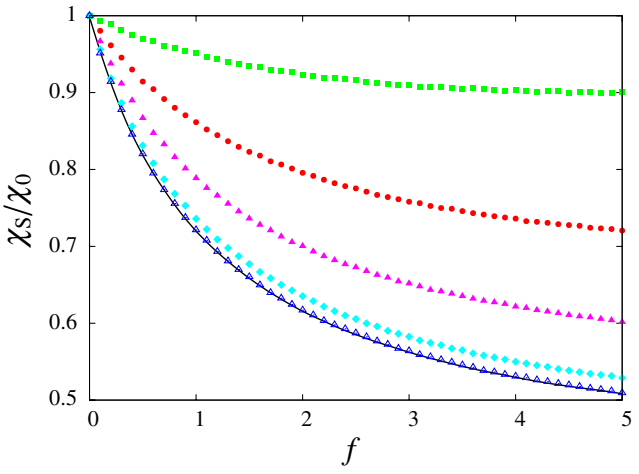

FIG. 4 (color online). Cutoff and coupling constant dependence of the spin susceptibility χ_S. The color coding is as in Figs. 1 and 2.

tribution to the exchange energy is lowered when spins are unequally populated. If this was the only exchange energy contribution, the spin susceptibility and inverse compressibility would be enhanced by interactions as usual. The unusual behavior comes from the second term. For weakly doped graphene it is sufficient to expand $\Sigma^{(0)}_{\mathbf{k},s}$ to first order in k; $\Sigma^{(0)}_{\mathbf{k}=0,s}$ is a physically irrelevant constant that is included in the chemical potential chosen as the zero of energy by our renormalization procedure. Expanding to first order in k gives the leading interaction contribution to the velocity renormalization [13] of undoped graphene. In agreement with previous work we find that for large Λ and small f

$$v \to v\left[1 + \frac{f}{4g}\ln(\Lambda)\right]. \tag{17}$$

The physical origin of the velocity increase is the loss in exchange energy on crossing the Dirac point from states that have the same chirality as the occupied negative energy sea to states that have the opposite chirality. It is easy to verify that this velocity renormalization is responsible for the leading $\ln(\Lambda)$ terms in the exchange energy and in the exchange contributions to κ^{-1} and χ_S^{-1}. The conventional exchange energy contributes negatively to κ^{-1} and χ_S^{-1} and competes with the Dirac point velocity renormalization.

When correlations are included, the leading $\ln(\Lambda)$ contributions to the interaction energy and to κ^{-1} and χ_S^{-1} still follow from the (now altered) undoped system quasiparticle velocity renormalization. The enhanced quasiparticle velocity is tied to the Dirac point, i.e., to the switch in chirality, and results in an interaction energy that tends to be lower when the chemical potential is close to the Dirac point in all channels. Figures 3 and 4 illustrate RPA theory predictions for experimentally observable consequences of the competition between this interband effect and conventional intraband correlations.

This work has been supported by the Welch Foundation, the Natural Sciences and Engineering Research Council of Canada, the Department of Energy under Grant No. DE-FG03-02ER45958, and the National Science Foundation under Grant No. DMR-0606489. M. P. acknowledges useful discussions with F. Poloni.

[1] J. C. Slonczewski and P. R. Weiss, Phys. Rev. **109**, 272 (1958).
[2] G. W. Semenoff, Phys. Rev. Lett. **53**, 2449 (1984); E. Fradkin, Phys. Rev. B **33**, 3263 (1986); F. D. M. Haldane, Phys. Rev. Lett. **61**, 2015 (1988).
[3] K. S. Novoselov *et al.*, Science **306**, 666 (2004).
[4] A. H. MacDonald, Phys. Rev. B **28**, 2235 (1983); A. M. J. Schakel, Phys. Rev. D **43**, 1428 (1991); Y. Zheng and T. Ando, Phys. Rev. B **65**, 245420 (2002); V. P. Gusynin and S. G. Sharapov, Phys. Rev. Lett. **95**, 146801 (2005).
[5] K. S. Novoselov *et al.*, Nature (London) **438**, 197 (2005).
[6] Y. B. Zhang *et al.*, Nature (London) **438**, 201 (2005).
[7] G. F. Giuliani and G. Vignale, *Quantum Theory of the Electron Liquid* (Cambridge University Press, Cambridge, 2005).
[8] The density-density response function $\chi^{(0)}$ of the doped 2D MDF model was first considered by K. W.-K. Shung, Phys. Rev. B **34**, 979 (1986) as a step towards a theory of collective excitations in graphite. The MDF $\chi^{(0)}$ expression has been reconsidered recently by us and by others for applications to single-layer graphene. See X. F. Wang and T. Chakraborty, Phys. Rev. B **75**, 033408 (2007); B. Wunsch, T. Stauber, F. Sols, and F. Guinea, New J. Phys. **8**, 318 (2006); E. H. Hwang and S. Das Sarma, Phys. Rev. B **75**, 205418 (2007).
[9] See, for example, Fig. 1 in Hongki Min *et al.*, Phys. Rev. B **74**, 165310 (2006).
[10] See, for example, J. P. Eisenstein, L. N. Pfeiffer, and K. W. West, Phys. Rev. B **50**, 1760 (1994); S. I. Dorozhkin *et al.*, *ibid.* **63**, 121301 (2001); S. Ilani *et al.*, Phys. Rev. Lett. **84**, 3133 (2000); Similar measurements have recently been performed on carbon nanotubes. See S. Ilani *et al.*, Nature Phys. **2**, 687 (2006).
[11] V. M. Pudalov *et al.*, Phys. Rev. Lett. **88**, 196404 (2002); K. Vakili *et al.*, *ibid.* **92**, 226401 (2004); A. A. Shashkin *et al.*, *ibid.* **96**, 036403 (2006); Y.-W. Tan *et al.*, Phys. Rev. B **73**, 045334 (2006).
[12] The tendency of exchange interactions to suppress ferromagnetism at small doping was noted previously in a Hartree-Fock approximation by N. M. R. Peres, F. Guinea, and A. H. Castro-Neto, Phys. Rev. B **72**, 174406 (2005).
[13] J. Gonzalez, F. Guinea, and M. A. H. Vozmediano, Phys. Rev. B **59**, R2474 (1999); M. I. Katsnelson, Eur. Phys. J. B **52**, 151 (2006); E. G. Mishchenko, Phys. Rev. Lett. **98**, 216801 (2007); O. Vafek, Phys. Rev. Lett. **98**, 216401 (2007).