Pseudospin in Optical and Transport Properties of Graphene

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(Received 3 May 2011; published 3 October 2011)

We show that the pseudospin, being an additional degree of freedom for carriers in graphene, can be efficiently controlled by means of the electron-electron interactions which, in turn, can be manipulated by changing the substrate. In particular, an out-of-plane pseudospin component can occur leading to a zero-field Hall current as well as to polarization-sensitive interband optical absorption.

DOI: 10.1103/PhysRevLett.107.156801 PACS numbers: 72.80.Vp, 73.61.Wp, 78.67.Wj

Introduction.—The charge carriers in graphene are described at low energies by an effective Hamiltonian being formally equivalent to the massless two-dimensional Dirac Hamiltonian [1–3], $H_0^\nu = \hbar v_0(\nu\sigma_x k_x + \sigma_y k_y)$, where $\nu = \pm$ refers to the two inequivalent corners K, K' of the first Brillouin zone, $v_0 \approx 10^6$ ms^{-1} is the effective ''speed of light,'' $\mathbf{k}$ is the two-component particle momentum operator, and $\sigma_{x,y}$ are Pauli matrices describing the sublattice degree of freedom also referred to as the pseudospin [3]. In the original Dirac Hamiltonian the Pauli vector $\vec{\sigma}$ represents the spin of a spin-1/2 particle which can be detected in Stern-Gerlach–like experiments. The pseudospin in graphene is formally similar to the true electron spin with an important distinction given by the behavior under time and parity [4] inversion. For the above effective model, the time reversal operator T is just the operator C of complex conjugation, $T = C$, fulfilling $TH_0^\nu T^{-1} = H_0^{-\nu}$, and the operators H_0^+ and H_0^- get interchanged. On the other hand, if one would (formally) interpret the Pauli matrices as components of a genuine spin [5] (i.e., an angular momentum), the time reversal operator would read $\tilde{T} = \sigma_y C$ giving $\tilde{T}H_0^\nu\tilde{T}^{-1} = H_0^\nu$. The parity operator P flips the sign of the spatial coordinates interchanging the two sublattices and, similar to T, fulfills $PH_0^\nu P^{-1} = H_0^{-\nu}$. Thus, the initial Hamiltonian $H_0^+ + H_0^-$ is PT invariant but, as we shall see, the exchange interactions can break either invariance. It also is important that the pseudospin is not linked with the internal magnetic moment of an electron and does not directly interact with the external magnetic field prohibiting Stern-Gerlach type experiments. In contrast to that, we predict situations where the pseudospin manifests itself in observable quantities and can be detected in transport as well as optical measurements on graphene.

First of all, we show that the exchange electron-electron interaction can alter the pseudospin orientation in a very broad range. In an eigenstate of H_0^ν the pseudospin is always in the xy plane. As we shall see shortly, the exchange interactions can turn the pseudospin texture to the out-of-plane phase with the out-of-plane angle depending on the absolute value of the particle momentum. This is due to the huge negative contribution to the Hartree-Fock ground state energy from the valence band (i.e., ''antiparticle'' states) which cannot be neglected in graphene because of the zero gap (i e., zero effective mass of carriers) and large effective fine structure constant $\alpha^* = e^2/(\varepsilon\hbar v_0)$ where ε is the dielectric constant depending on the environment [6]. The exchange contribution to the ground state energy has previously been studied in both monolayer and bilayer graphene regarding properties such as the electronic compressibility [7] and ferromagnetism [8–10], but the importance of the interplay between pseudospin and electron-electron interactions has been recognized only in [11] where single layer graphene was mentioned in passing.

Having established the possibility of creating an out-of-plane pseudospin orientation by means of the exchange interaction, we apply the Boltzmann approach to derive the electrical conductivity tensor which turns out to have Hall components even though the external magnetic field is absent. The mechanism of this phenomenon is intimately linked to the pseudospin-momentum coupling which can be read out immediately from the Hamiltonian H_0^ν. Similar to the skew scattering of electrons on impurities in spin-orbit coupled systems partly responsible for the anomalous Hall effect [12,13], the carriers in graphene also skew to one side of the Hall bar as long as their pseudospin has a nonzero out-of-plane component. This effect has been intensively studied [14–16] assuming that the out-of-plane component occurs due to the band gap opened by the spin-orbit coupling [14], which, however, seems to be weak in graphene [2]. We emphasize that neither the spin-orbit coupling nor an external magnetic field is necessary to obtain a Hall current in graphene being in the pseudospin out-of-plane phase.

Experimental manifestations of the pseudospin are not limited to the electron skew scattering phenomenon but can also be seen in the interband optical absorption. Performing optical measurements on graphene [17] one can obtain direct information regarding conduction and valence band states without the advanced sample processing that is necessary for transport investigations. Moreover, the peculiar properties discovered so far make graphene a very promising material for optoelectronic applications

[18]. Optical absorption via the direct interband optical transitions in graphene has been investigated in [19] but the mechanism considered there lies essentially in the two-dimensional nature and gapless electronic spectrum and does nor directly involve the pseudospin orientation. Here we show that, due to the out-of-plane pseudospin orientation, the interband absorption can be substantially reduced or enhanced as compared to its universal value $\pi e^2/\hbar c$ just by switching the helicity of the circularly polarized light.

Exchange interactions.—The Coulomb exchange Hamiltonian is given by

$$H^{\nu}_{\mathrm{exch}}(\mathbf{k}) = -\sum_{\kappa'} \int \frac{d^2k'}{4\pi^2} U_{|\mathbf{k}-\mathbf{k}'|} |\chi^{\nu}_{\kappa' k'}\rangle\langle\chi^{\nu}_{\kappa' k'}|, \quad (1)$$

with $U_{|\mathbf{k}-\mathbf{k}'|} = 2\pi e^2/\varepsilon|\mathbf{k}-\mathbf{k}'|$ and $\kappa' = \pm$ being the band index with $\kappa = +$ for the conduction band. The intervalley overlap is assumed to be negligible, and the eigenstates of $H^{\nu} = H^{\nu}_0 + H^{\nu}_{\mathrm{exch}}$ can be formulated as $\Psi^{\nu}_{\mathbf{k}\kappa}(\mathbf{r}) = e^{i\mathbf{k}\mathbf{r}}|\chi^{\nu}_{\pm k}\rangle$ with spinors $|\chi^{\nu}_{+k}\rangle = (\cos\frac{\vartheta_k}{2}, \nu \sin\frac{\vartheta_k}{2} e^{\nu i\varphi})^T$, $|\chi^{\nu}_{-k}\rangle = (\sin\frac{\vartheta_k}{2}, -\nu\cos\frac{\vartheta_k}{2} e^{\nu i\varphi})^T$, and $\tan\varphi = k_y/k_x$. Thus, a nonzero out-of-plane pseudospin component corresponds to $\vartheta_k \neq \pi/2$. To diagonalize H^{ν} the following ν-independent equation for ϑ_k must be satisfied [20]:

$$\hbar v_0 k \cos\vartheta_k + \sum_{\kappa'} \int \frac{d^2k'}{8\pi^2} \kappa' U_{|\mathbf{k}-\mathbf{k}'|} \times [\cos\vartheta_{k'} \sin\vartheta_k - \sin\vartheta_{k'} \cos\vartheta_k \cos(\varphi' - \varphi)] = 0, \quad (2)$$

where the integration goes over the occupied states. Note that the conduction and valence states are entangled, and the latter cannot be disregarded even at positive Fermi energies. Thus, in order to evaluate the integrals in Eq. (2) a momentum cutoff Λ is necessary. Its value $\simeq 0.1$ nm^{-1} is usually chosen to keep the number of states in the Brillouin zone fixed [8], but our outcomes do not depend on any particular choice of Λ. Substituting $x = k/\Lambda$ we arrive at

$$\frac{4\pi x \cos\vartheta_k}{\alpha^*} = \int_0^{2\pi} d\varphi' \int_{k_F/\Lambda}^1 dx' x' \frac{\cos\vartheta_{k'} \sin\vartheta_k - \sin\vartheta_{k'} \cos\vartheta_k \cos\varphi'}{\sqrt{x^2 + x'^2 - 2xx'\cos\varphi'}}. \quad (3)$$

The momentum cufoff is obviously much larger than the Fermi momentum k_F at any reasonable electron doping, and therefore we can set the lower integral limit to zero. Besides a trivial solution with $\vartheta_0 = \pi/2$ independent of k, there are nontrivial ones $\vartheta_1 = \vartheta(k)$ and $\vartheta_2 = \pi - \vartheta(k)$ with $\vartheta(k)$ shown in Fig. 1 for different α^*. The solutions ϑ_0 and $\vartheta_{1,2}$ represent to two phases with different total ground state energies $E^{\mathrm{in}}_{\mathrm{tot}}$ ($E^{\mathrm{out}}_{\mathrm{tot}}$) for the in-plane (out-of-plane) pseudospin phase. The difference $\Delta E_{\mathrm{tot}} = E^{\mathrm{in}}_{\mathrm{tot}} - E^{\mathrm{out}}_{\mathrm{tot}}$ per volume for a given spin and valley reads

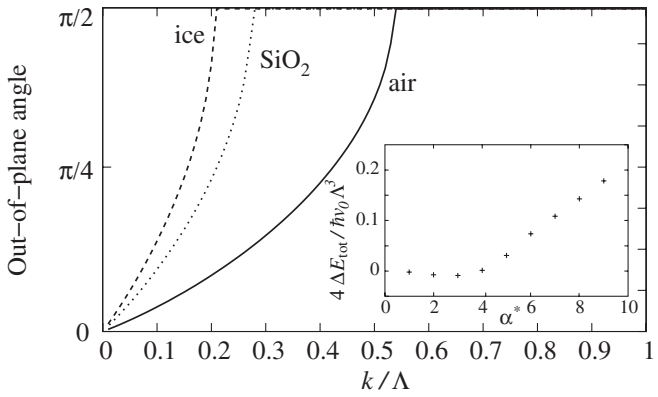

FIG. 1. The pseudospin out-of-plane angle $\vartheta(k)$ for different environments numerically calculated from Eq. (3). The corresponding values of the substrate-dependent effective fine structure constant α^* are taken from Ref. [6]. The inset shows the total ground state energy difference (4) between the in-plane and out-of-plane phases for different effective fine structure constants $\alpha^* = e^2/\varepsilon\hbar v_0$. Increasing α^* makes the out-of-plane phase preferable.

$$\frac{\Delta E_{\mathrm{tot}}}{\hbar v_0 \Lambda^3} = -\int_0^1 \frac{dx'}{2\pi} x'^2 (1 - \sin\vartheta_{k'}) - \alpha^* \int_0^{2\pi} d\varphi \int_0^{2\pi} d\varphi' \int_0^1 dx \times \int_0^1 dx' x' \frac{(1 - \sin\vartheta_{k'} \sin\vartheta_k)\cos(\varphi' - \varphi) - \cos\vartheta_{k'} \cos\vartheta_k}{32\pi^3 \sqrt{x^2 + x'^2 - 2xx'\cos(\varphi - \varphi')}}. \quad (4)$$

The energy difference for $\alpha^* \sim 1$ is small because the integrand in Eq. (4) is always multiplied by x' and therefore vanishes at $x' \to 0$, but at larger x' the $\vartheta_{k'}$ gets close to $\pi/2$ and the integrand vanishes again. The inset in Fig. 1 shows, however, that strong electron-electron interactions make the out-of-plane phase energetically preferable. The estimates of α^* for clean graphene vary from 2 (Ref. [6]) to 2.8 (Ref. [8]) and are on the borderline of the out-of-plane phase. Moreover, the presence of disorder can change this qualitative picture essentially [8]. Most important, Eq. (4) is valid for both valleys and both solutions $\vartheta_{1,2}$. Thus, it is possible to choose either the same or opposite solutions for two valleys. The former choice breaks the parity invariance whereas the latter one does so with the time reversal symmetry. Both cases are worthy of consideration.

The single-particle spectrum is independent of the valley index and given by

$$\frac{E_{\kappa}(x)}{\hbar v_0 \Lambda} = \kappa x \sin\vartheta_k - \frac{\alpha^*}{4\pi} \int_0^{2\pi} d\varphi' \int_0^1 dx' x' \times \frac{1 - \kappa(\cos\vartheta_{k'} \cos\vartheta_k + \sin\vartheta_{k'} \sin\vartheta_k \cos\varphi')}{\sqrt{x^2 + x'^2 - 2xx'\cos\varphi'}}, \quad (5)$$

and the group velocity can be written as $\mathbf{v}_\kappa = v_\kappa(\cos\varphi, \sin\varphi)^T$ with v_κ being

$$\frac{v_\kappa}{v_0} = \kappa \sin\vartheta_k + \frac{\alpha^*}{4\pi}\int_0^{2\pi} d\varphi' \int_0^1 dx' x' x(1-\cos\varphi') \times \frac{1-\kappa(\cos\vartheta_{k'}\cos\vartheta_k + \sin\vartheta_{k'}\sin\vartheta_k\cos\varphi')}{(x^2+x'^2-2xx'\cos\varphi')^{3/2}}. \quad (6)$$

The dispersion law (5) is depicted in Fig. 2 for graphene placed on the SiO_2 substrate. The interactions shift the bands down to lower energies and change the density of states but, most important, they open a gap [21] between the valence and conduction band as soon as the system changes to the pseudospin out-of-plane one phase. The gap at $k = 0$ equals $\frac{e^2\Lambda}{\varepsilon}\int_0^1 dx' \cos\vartheta_{k'}$. Note that the group velocity (6) vanishes at small momentum $k/\Lambda \ll 1$ as long as the system is in the out-of-plane phase corresponding to the almost flat bands close to $k = 0$, which is shown in the inset of Fig. 2. From now on we assume n-doping so that the Fermi energy is always higher than the bottom of the conduction band.

Zero-field Hall current.—To describe the Hall conductivity due to skew scattering we utilize the semiclassical Boltzmann approach, which allows a physically transparent interpretation of this mechanism [13,15]. In general, the anomalous Hall conductivity contributions can be classified by their mechanism: (i) The intrinsic contribution is due to the anomalous velocity of carriers (being nondiagonal with respect to the band index [22]) which is coupled to the equilibrium part of the distribution function. (ii) The side-jump contribution follows from coordinate shifts during scattering events. It occurs in the nonequilibrium part of the distribution function as well as in the anomalous velocity [13,15]. (iii) The skew scattering contribution is independent of the coordinate shift and of the anomalous velocity. It occurs when the scattering rate is asymmetric

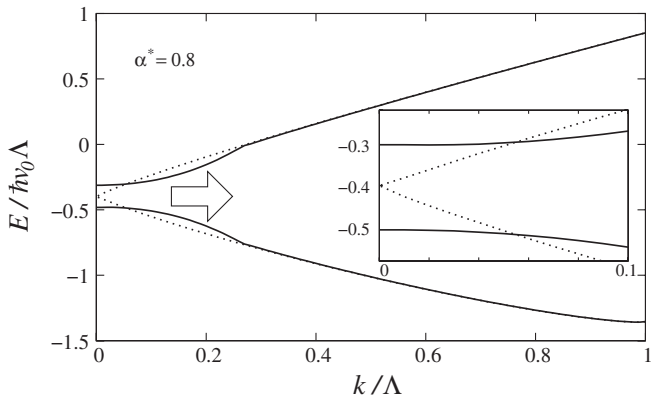

FIG. 2. The dispersion law $E_\kappa(k)$ in the in-plane (dashed curves) and out-of-plane (solid curves) phases for $\alpha^* = 0.8$ corresponding to the SiO_2 substrate [6]. The curves for both phases coincide for momenta larger than a certain critical value where $\vartheta_k = \pi/2$ becomes independent of k; see Fig. 1. The inset shows the gap region in detail.

with respect to the initial and final states and, therefore, must be considered beyond the first Born approximation The first two conductivity contributions do not depend on disorder but on the out-of-plane angle ϑ_k and can be adopted from [15]. Here, we focus on the skew scattering contribution which can be described using the interband incoherent Boltzmann equation where the anomalous velocity is neglected but the scattering probability is calculated up to the third order in the short-range scattering potential with the momentum-independent Fourier transform V. In linear order in the homogeneous electric field $\mathbf{E}$ this equation reads $-e\mathbf{E}\cdot\mathbf{v}_k[-\partial f^0(E_k)/\partial E_k] = I[f^1_k]$, where $f^0(E_k)$ is the Fermi-Dirac function, $f^1_{\mathbf{k}}$ is the nonequilibrium addition, and $\mathbf{v}_k$, E_k are given by Eqs. (5) and (6), with $\kappa = +$. The collision integral can be written as $I[f^1_{\mathbf{k}}] = \int \frac{d^2k'}{(2\pi)^2} w_{\mathbf{k}\mathbf{k}'}(f^1_{\mathbf{k}'} - f^1_{\mathbf{k}})$ with $w_{\mathbf{k}\mathbf{k}'}$ being the scattering probability. We divide $w_{\mathbf{k}\mathbf{k}'}$ into two parts. The first one is proportional to the cosine of the scattering angle and calculated up to the second order in V. The second one is proportional to the sine of the scattering angle and calculated up to the third order in V. These two parts correspond to the conventional and skew scattering, respectively, which can be alternatively expressed in terms of the momentum relaxation times, cf. Ref. [14]

$$(\tau^\nu_\parallel)^{-1} = n_i k V^2(1+3\cos^2\vartheta^\nu_k)/(4\hbar^2 v_k),$$
$$(\tau^\nu_\perp)^{-1} = \nu n_i k^2 V^3 \cos\vartheta^\nu_k \sin^2\vartheta^\nu_k/(8\hbar^3 v_k^2). \quad (7)$$

Here, n_i is the concentration of such scatterers. Since $\tau^\nu_\perp \propto 1/V^3$ whereas $\tau^\nu_\parallel \propto 1/V^2$ it is natural to assume $\tau^\nu_\perp \gg \tau^\nu_\parallel$, and the Hall conductivity for a given valley can be estimated as $\sigma^\nu_{yx} \approx \sigma_{xx}\tau^\nu_\parallel/\tau^\nu_\perp|_{k=k_F}$, which can vary in a quite broad but finite range because neither τ's diverge at low doping thanks to the k-dependent group velocity (6). Note that K and K' contribute identically to the total Hall conductivity $\sigma_{yx} = \sum_\nu \sigma^\nu_{yx}$ if the out-of-plane pseudospin polarization is opposite in the two valleys, i.e., ϑ_1 and ϑ_2 are assigned to ϑ^+_k and ϑ^-_k, respectively, and the time reversal invariance is broken by the exchange interactions. On the other hand, if the out-of-plane pseudospin polarization is the same in both valleys (i.e., either of $\vartheta_{1,2}$ is assigned to both $\vartheta^\pm_k$, breaking the parity invariance) the Hall currents in the two valleys have opposite directions resulting in the valley Hall effect [23]—another analog of the well-known spin Hall effect [14].

Interband optical absorption.—From H^ν_0 one can deduce the following interaction Hamiltonian between the electromagnetic wave and carriers in graphene $H^\nu_{\text{int}} = \frac{ev_0}{c}(\nu\sigma_x A_x + \sigma_y A_y)$, which couples the vector potential $\mathbf{A}$ and pseudospin $\vec{\sigma}$. As consequence, the interband transition matrix elements turn out to be sensitive to the light polarization and pseudospin orientations in the initial and final states. To be specific we assume a monochromatic light of frequency ω, normal incidence (i.e., zero momentum transfer from photons to electrons), and circular

polarization (fulfilling $A_x = \pm iA/\sqrt{2}$, $A_y = A/\sqrt{2}$). The probability to excite an electron from the valence band to an unoccupied state in the conduction band can be calculated using the golden rule. Finally, the absorption P^ν can be calculated as a ratio between the total electromagnetic power W_a absorbed by graphene per unit square and the incident energy flux $W_i = \omega^2 A^2/4\pi c$. Then, the optical absorption for K valley ($\nu = +$) reads

$$P^+ = \frac{\pi e^2}{\hbar c}\frac{4\Lambda v_0}{\omega}\int_0^\infty dx x \times \left\{\begin{matrix}\sin^4\frac{\vartheta_k^+}{2}\\ \cos^4\frac{\vartheta_k^+}{2}\end{matrix}\right\} \times \delta\left(\frac{E_+ - E_- - \hbar\omega}{\hbar v_0 \Lambda}\right), \quad (8)$$

where the multipliers $\sin^4(\vartheta_k^+/2)$ and $\cos^4(\vartheta_k^+/2)$ are for two opposite helicities of light, and for K′ valley they are interchanged. If the out-of-plane pseudospin polarization is chosen to be opposite in the two valleys, then the total absorption $P = \sum_\nu P^\nu$ at small k/Λ turns out to be sensitive to the helicity of light: It is substantially reduced for one and facilitated for another. Moreover, changing the excitation energies $\hbar\omega$ we can investigate the dependence $\vartheta(k)$ shown in Fig. 1. If the out-of-plane pseudospin polarization is chosen to be the same in both valleys, then the total absorption does not depend on the radiation helicity but the two valleys turn out to be differently occupied by the photoexcited carriers which is interesting effect on its own [23]. In the in-plane phase with $\vartheta = \pi/2$ the total absorption does not depend on light polarization, and in the noninteracting limit it equals to the universal value $\frac{\pi e^2}{\hbar c}$, as expected [19].

Conclusions.—We have demonstrated that the pseudospin quantity, being until now rather uncontrollable and almost unmeasurable, can be "unfrozen" by the exchange electron-electron interactions (1) and play an essential role in optical and transport properties of graphene. We hasten to say that the Hartree-Fock approximation employed here has generically a tendency to overestimate ordering such as the pseudospin out-of-plane polarization. We believe, however, that the pseudospin eigenstates $|\chi^\nu_{\kappa k}\rangle$ derived above are much more robust because their special pseudospin-momentum entangled structure stems from the free Hamiltonian H_0^ν, and the electron-electron interactions only modify it, which makes our predictions reliable at the qualitative level. From this point of view, the pseudospin can be seen as an additional degree of freedom similar to the true spin but unaffected by the magnetic field directly. With this similarity in mind, one can think about pseudospin ferromagnetism [11], pseudospin accumulation at the sample's edge by means of the zero-field Hall current, pseudospin selectivity in the optical absorption (8), and, probably, pseudospin filtering and switching. In the more distant future, one can imagine some useful effects based on the pseudospin polarization such as an all-electrical counterpart for giant magnetic resistivity, which is obviously very promising for application. This Letter should be seen as a first step in this direction.

This work was supported by DFG via project GRK 1570.

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