Pseudospin in optical and transport properties of graphene

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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.

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 \( H'_0 = \hbar v_0 (\sigma_x k_x + \sigma_y k_y) \), where \( \nu = \pm \) refers to the two inequivalent corners \( K, K' \) of the first Brillouin zone, \( v_0 \approx 10^6 \text{ms}^{-1} \) is the effective “speed of light”, \( k \) is the two-component particle momentum operator, and \( \sigma_x, \sigma_y \) 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 \( T H'_0 T^{-1} = H'_0^\nu \), and the operators \( H'_0^\nu \) 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 \( T = \sigma_y C \) giving \( T H'_0 T^{-1} = H'_0 \). The parity operator \( P \) flips the sign of the spatial coordinates interchanging the two sublattices and, similar to \( T \), fulfills \( P H'_0 P^{-1} = H'_0 \). 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 \( H'_0^\nu \) 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 \( \alpha' = e^2/(\epsilon_0 v_0) \) where \( \epsilon \) 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 to create 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 \( H'_0 \). 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 do also skew to one side of the Hall bar as long as their pseudospin has non-zero out-of-plane component. This effect has been intensively studied [14] assuming that the out-of-plane component occurs due to the band gap opened by spin-orbit coupling [14] which, however, seems to be weak in graphene [2]. We emphasize that neither 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 advanced sample processing necessary for transport investigations. Moreover, the peculiar properties discovered so far make graphene a very promising material for optoelectronic applications [13]. 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 not 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
\[ H_{\text{exch}}^\nu(k) = -\sum_\nu \int \frac{d^2k'}{4\pi^2} U_{|k-k'|}^\nu |\chi_{k'}\rangle \langle \chi_{k'}^\nu| \] (1)
with $U_{|k-k'|}^\nu = 2\pi e^2/\varepsilon |k-k'|$ and $\nu' = \pm$ being the band index with $\nu = +$ for the conduction band. The inter-valley overlap is assumed to be negligible, and the eigenstates of $H^\nu = H_0^\nu + H_{\text{exch}}^\nu$ can be formulated as $\Psi_{k\nu}(r) = e^{ikr}|\chi^\nu_+\rangle = (\cos \frac{\nu}{2}, \nu \sin \frac{\nu}{2} e^{i\varphi'})^T$, $|\chi^\nu_-\rangle = \left(\sin \frac{\nu}{2}, -\nu \cos \frac{\nu}{2} e^{i\varphi'}\right)^T$, and $\tan \varphi = k_y/k_x$. Thus, a non-zero out-of-plane pseudospin component corresponds to $\theta \neq \pi/2$. To diagonalize $H^\nu$ the following $\nu$-independent equation for $\vartheta_k$ must be satisfied
\[ \hbar v_0 k \cos \vartheta_k + \sum_\nu \int \frac{d^2k'}{8\pi^2} U_{|k-k'|}^\nu \left[ \cos \vartheta_k \sin \vartheta_{k'} - \sin \vartheta_k \cos \vartheta_{k'} \cos (\varphi' - \varphi) \right] = 0, \] (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 cut-off $\Lambda$ is necessary. Its value $\approx 0.1\text{nm}^{-1}$ is usually chosen to keep the number of states in the Brillouin zone fixed, but our outcomes do not depend on any particular choice of $\Lambda$. Substituting $x = k/\Lambda$ we arrive at
\[ \frac{4\pi x \cos \vartheta_k}{2\pi} = \alpha^* \int_0^{2\pi} d\varphi' \int_{k_F/\Lambda}^1 dx' \frac{1 - \sin \vartheta_{k'} \sin \vartheta_k \cos (\varphi' - \varphi) - \cos \vartheta_k \cos \vartheta_{k'} \cos \varphi'}{\sqrt{x'^2 + x^2 - 2xx' \cos \varphi'}}. \] (3)
The momentum cut-off 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 non-trivial ones $\vartheta_1 = \vartheta(k)$ and $\vartheta_2 = \pi - \vartheta(k)$ with $\vartheta(k)$ shown in Fig. 1 for different $\alpha^*$. The solutions $\vartheta_0$ and $\vartheta_1, \vartheta_2$ represent to two phases with different total ground state energies $E_{\text{in}}^\text{tot} (E_{\text{out}}^\text{tot})$ for the in-plane (out-of-plane) pseudospin phase. The difference $\Delta E_{\text{tot}} = E_{\text{in}}^\text{tot} - E_{\text{out}}^\text{tot}$ per volume for a given spin and valley reads
\[ \Delta E_{\text{tot}} = \frac{1}{\hbar v_0 \Lambda^3} \int_0^{2\pi} d\varphi \int_0^{2\pi} d\varphi' \int_0^1 dx \int_0^{1-x} dx' \frac{(1 - \sin \vartheta_k \sin \vartheta_{k'}) \cos (\varphi' - \varphi) - \cos \vartheta_k \cos \vartheta_{k'} \cos \varphi'}{2\pi^3 \sqrt{x^2 + x'^2 - 2xx' \cos \varphi'}}. \] (4)

The energy difference for $\alpha^* \approx 1$ 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 $\alpha^*$ for clean graphene vary from 2 (Ref. [1]) 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 importantly, 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
\[ \frac{E_\nu(x)}{\hbar v_0 \Lambda} = \kappa x \sin \vartheta_k - \frac{\alpha^*}{4\pi} \int_0^{2\pi} d\varphi' \int_0^1 dx' \frac{1}{\sqrt{x'^2 + x^2 - 2xx' \cos \varphi'}} \left[ 1 - \kappa (\cos \vartheta_k \cos \vartheta_{k'} + \sin \vartheta_k \sin \vartheta_{k'} \cos \varphi') \right] \] (5)
and the group velocity can be written as $v_k = v_\nu (\cos \varphi, \sin \varphi)^T$ with $v_\nu$ being
\[ \frac{v_\nu}{v_0} = \kappa \sin \vartheta_k + \frac{\alpha^*}{4\pi} \int_0^{2\pi} d\varphi' \int_0^1 dx' x (1 - \cos \varphi') \left[ 1 - \kappa (\cos \vartheta_k \cos \vartheta_{k'} + \sin \vartheta_k \sin \vartheta_{k'} \cos \varphi') \right] \] (6)
The dispersion law [4] is depicted in Fig. 2 for graphene placed on SiO$_2$ substrate. The interactions shift the bands down to lower energies and change the density of states but, most importantly, they open a gap [21].
of the conduction band. That the Fermi energy is always higher than the bottom
of the inset of Fig. 2. From now on we assume n-doping so
the Boltzmann approach which allows a physically transpar-
tivity due to skew scattering we utilize the semiclassical
curves) and out-of-plane (solid curves) phases for different effective fine struc-
ture constant $\alpha^* = e^2\epsilon/\hbar\nu_0$. Increasing $\alpha^*$ makes the out-of-
plane phase more preferable.

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 $\frac{\pi^2}{2m} \int_0^1 dx' \cos \vartheta_{k'}$. 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 corre-
sponding to the almost flat bands close to $k = 0$ 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 conduc-
tivity due to skew scattering we utilize the semiclassical
Boltzmann approach which allows a physically transpar-
ent interpretation of this mechanism[13, 15]. In general
the anomalous Hall conductivity contributions can be
classified by their mechanism: (i) The intrinsic contribu-
tion is due to the anomalous velocity of carriers (be-
ing non-diagonal with respect to the band index [22])
which is coupled to the equilibrium part of the distri-
bution function. (ii) The side-jump contribution follows
from coordinate shifts during scattering events. It occurs
in the non-equilibrium part of the distribution function
as well as in the anomalous velocity[13, 15]. (iii) The
skew scattering contribution is independent of the co-
ordinate shift and of the anomalous velocity. It occurs
when the scattering rate is asymmetric with respect to
the initial and final states and, therefore, must be con-
sidered beyond the first Born approximation. The first
two conductivity contributions do not depend on disor-
der but on the out-of-plane angle $\vartheta_{k'}$ and can be adopted
from[13]. Here, we focus on the skew scattering contribu-
tion which can be described using the interband inco-
herent Boltzmann equation where the anomalous velocity
is neglected but the scattering probability is calculated
up to the third order in the short-range scattering po-
tential with the momentum-independent Fourier trans-
form $V$. In linear order in the homogeneous electric field
$E$ this equation reads $-eV\vartheta_k \left[ -\partial f^0(E_k)/\partial E_k \right] = I[f_k^1]$, where
$f^0(E_k)$ is the Fermi-Dirac function, $f_k^1$ is the non-
equilibrium addition, and $\nu_k, E_k$ are given by Eqs. (3)
with $\kappa = +$. The collision integral can be written as
$I[f_k^1] = \int \frac{d^2k'}{(2\pi)^2} w_{kk'} (f_k^1 - f_k^0)$ with $w_{kk'}$ being the scat-
tering probability. We divide $w_{kk'}$ 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 scat-
tering respectively which can be alternatively expressed
in terms of the momentum relaxation times, cf. Ref.[14]
\begin{equation}
(\tau_{xx}^\nu)^{-1} = n_k V^3 (1 + 3 \cos^2 \vartheta_k') / (4\hbar^2 \nu_k),
(\tau_{yy}^\nu)^{-1} = \nu_k k^2 V^3 \cos \vartheta_k' \sin^2 \vartheta_k' / (8\hbar^3 \nu_k^2). \tag{7}
\end{equation}
Here, $n_k$ is the concentration of such scatterers. Since
$\tau_{xx}^\nu \propto 1/V^3$ whereas $\tau_{yy}^\nu \propto 1/V^2$ it is natural to assume
$\tau_{xx}^\nu \gg \tau_{yy}^\nu$, and the Hall conductivity for a given valley
can be estimated as $\sigma_{yx}^\nu \approx \sigma_{xx}^\nu \tau_{yy}^\nu / \tau_{xx}^\nu |_{k=k_F}$ which
\begin{figure}
\centering
\includegraphics[width=\textwidth]{fig1}
\caption{The pseudospin out-of-plane angle $\vartheta(k)$ for differ-
et environments numerically calculated from Eq. (3). The
-corresponding values of the substrate-dependent effective fine
-structure constant $\alpha^*$ 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 struc-
ture constant $\alpha^* = e^2\epsilon/\hbar\nu_0$. Increasing $\alpha^*$ makes the out-of-
-plane phase more preferable.
\end{figure}

\begin{figure}
\centering
\includegraphics[width=\textwidth]{fig2}
\caption{The dispersion law $E_k(\vartheta)$ in the in-plane (dashed
curves) and out-of-plane (solid curves) phases for $\alpha^* = 0.8$
corresponding to $\text{SiO}_2$ 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.
\end{figure}

\[
(\tau_{xx}^\nu)^{-1} = n_k V^3 (1 + 3 \cos^2 \vartheta_k') / (4\hbar^2 \nu_k),
(\tau_{yy}^\nu)^{-1} = \nu_k k^2 V^3 \cos \vartheta_k' \sin^2 \vartheta_k' / (8\hbar^3 \nu_k^2). \tag{7}
\]
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 $H_0^\nu$ one can deduce the following interaction Hamiltonian between the electromagnetic wave and carriers in graphene $H_{\text{int}}^\nu = \frac{e^2}{c} (\nu \sigma_z A_x + \sigma_y A_y)$ which couples the vector potential $A$ and pseudospin $\vec{\sigma}$. As consequence, the inter-band 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 monochromatic light of frequency $\omega$, 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 $P^\nu$ can be calculated as a ratio between the total electromagnetic power $W_{\text{int}}$ absorbed by graphene per unit square and the incident energy flux $W_i = \omega^2 A^2 / 4 c \epsilon$. Then, the optical absorption for $K$ valley ($\nu = +$) reads

$$P^+ = \frac{\pi e^2}{h c} 4 \Lambda_0 \omega \int_{0}^{\infty} dx \delta \left( \frac{E_+ - E_- - h\omega}{\hbar \nu_0 \Lambda} \right),$$

where the multipliers $\sin^2(\theta^+ / 2) \cos^4(\vartheta^+ / 2)$ 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 $k/\Lambda$ 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 $h\omega$ we can investigate the dependence $\theta(k)$ 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 non-interacting limit it equals to the universal value $\frac{\pi e^2}{\hbar c}$, as expected [14].

*Conclusions.* We have demonstrated that the pseudospin being until now rather uncontrollable and almost unmeasurable quantity can be “unfrozen” by the exchange electron-electron interactions [11] 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 $| \nu^\pm_{x,k} \rangle$ derived above are much more robust because their special pseudospin-momentum entangled structure stems from the free Hamiltonian $H_0^\nu$, and the electron-electron interactions do only modify it making 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. Having 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 [5], and, probably, pseudospin filtering and switching. In a more distant future one can imagine some useful effects based on the pseudospin polarization like an all-electrical counterpart for GMR which is obviously very promising for application. This Letter should be seen as a first step in this direction.

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