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# Graphene with structure-induced spin-orbit coupling: Spin-polarized states, spin zero modes, and quantum Hall effect 

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#### Abstract

Spin splitting of the energy spectrum of single-layer graphene on $\mathrm{Au} / \mathrm{Ni}(111)$ substrate has been recently reported. I show that eigenstates of spin-orbit coupled graphene are polarized in-plane and are perpendicular to electron momentum $\mathbf{k}$; the magnitude of spin polarization $\mathbf{S}$ vanishes when $k \rightarrow 0$. In a perpendicular magnetic field $\mathbf{B}, \mathbf{S}$ is parallel to $\mathbf{B}$, and two zero modes emerge in the Landau level spectrum. Singular $\mathbf{B}$ dependence of their magnetization suggests existence of a new variety of magnetic instability. They also manifest themselves in a new variety of unconventional quantum Hall effect.


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Since the discovery of graphene with its quasirelativistic energy spectrum of zero-gap Dirac fermions ${ }^{1,2}$ and unconventional quantum Hall effect (QHE) in single- and bilayer graphene, ${ }^{3-5}$ this material attracts attention because of its unique electronic properties and prospective applications in nanoelectronics. ${ }^{6,7}$ Applications in spintronics depend strongly on the control of spin-orbit (SO) coupling. This coupling in graphene comprises intrinsic and extrinsic components. ${ }^{8,9}$ First one is known to be very weak in free plane graphene, ${ }^{10,11}$ in carbon nanotubes it is due to their curvature. ${ }^{12-14}$ Extrinsic SO coupling originates from the interface between graphene and substrate. Recently Varykhalov et al. ${ }^{15}$ reported spin angle-resolved photoemission spectroscopy (SARPES) data from single-layer graphene on $\mathrm{Ni}(111)$ intercalated with a Au monolayer. They reveal strong momentum-dependent in-plane spin polarization. The monolayer of Au maintains the symmetry of graphene and strongly reduces the threefold deformation of graphene (originating from its coupling to Ni substrate) and nonequivalence of $A(B)$ lattice sites resulting from it. According to Ref. 15, the technique brings the system closer to ideal freestanding graphene than any other preparation on a solid substrate before. These results call for a systematic theory of spin polarization in freestanding graphene with extrinsic SO coupling, and in this Rapid Communication I provide such a theory for free electrons and electrons in a quantizing magnetic field $\mathbf{B}$. The results are in general agreement with the data of Varykhalov et al. ${ }^{15}$ and predict (i) dependence of spin polarization on the magnitude of the momentum $\mathbf{k}$ at the SO momentum scale, (ii) spin zero modes in a quantizing field indicating a new variety of magnetic instability, and (iii) a new variety of unconventional QHE.

A $4 \times 4$ Hamiltonian of graphene with extrinsic SO coupling can be represented in terms of a Kronecker product of $2 \times 2$ matrices $\boldsymbol{\sigma}=\left(\sigma_{1}, \sigma_{2}\right)$ and $\mathbf{s}$ as ${ }^{9}$

$$
\begin{equation*}
\mathcal{H}_{K}^{0}=\gamma(\boldsymbol{\sigma} \cdot \mathbf{k})+\frac{1}{2} \lambda(\boldsymbol{\sigma} \times \mathbf{s})_{z} . \tag{1}
\end{equation*}
$$

Here $\gamma=\hbar v, v \approx 10^{8} \mathrm{~cm} \mathrm{~s}^{-1}$, and $\lambda$ is a SO coupling constant; for graphene $/ \mathrm{Au} / \mathrm{Ni}(111),|\lambda| \approx 13 \mathrm{meV} .{ }^{15}$ Pauli matrices of pseudospin $\boldsymbol{\sigma}$ operate on $A(B)$ lattice cites, and $\mathbf{s}$ are

Pauli matrices for real spin. It is seen from first term in Eq. (1) that $\boldsymbol{\sigma}$ transforms as momentum $\mathbf{k}$. Therefore, as was pointed out by Kane and Mele, ${ }^{9}$ SO term can be considered as a modified Rashba term with $\mathbf{k} \rightarrow \boldsymbol{\sigma}$; the conventional Rashba term $(\mathbf{k} \times \mathbf{s})_{z}$ is small and will be disregarded. In the same representation, $4 \times 4$ spin matrices are $\sigma_{0} \mathbf{s}$, with $\sigma_{0}$ for a unit matrix in $\boldsymbol{\sigma}$ space. The Hamiltonian $\mathcal{H}_{K}^{0}$ is acting near the $K$ point of the Brillouin zone (Fig. 1); for $K^{\prime}$ point, $\mathcal{H}_{K^{\prime}}^{0}=\sigma_{2} \mathcal{H}_{K}^{0} \sigma_{2}^{-1}$.

It is convenient to change from the $4 \times 4$ to a $2 \times 2$ formalism. First, we perform a unitary transformation of the Hamiltonian, $\mathcal{H}_{K}=U \mathcal{H}_{K}^{0} U^{-1}$ and of spin matrices $\sigma_{0} s$ with a unitary matrix $U=\left[\left(s_{0}+s_{z}\right) \sigma_{0}+\left(s_{0}-s_{z}\right) \sigma_{1}\right] / 2$, with $s_{0}$ being a unit matrix in spin space. Then

$$
\mathcal{H}_{K}=\left(\begin{array}{cc}
0 & C  \tag{2}\\
C^{+} & \lambda s_{y}
\end{array}\right), \quad \hat{\mathbf{S}}=\sigma_{1} \mathbf{s}, \quad \hat{S}_{z}=\sigma_{0} s_{z},
$$

with $C=\gamma\left(s_{0} k_{x}-i s_{z} k_{y}\right)$; here $\left(\hat{\mathbf{S}}, \hat{S}_{z}\right)$ are new spin matrices. Next step is eliminating lower components of eigenbispinors $\Psi=\binom{\varphi}{\phi}$ of the equation $\mathcal{H}_{K} \Psi=\varepsilon \Psi$,

$$
\phi=\left(\varepsilon-\lambda s_{y}\right)^{-1} C^{+} \varphi=\frac{\gamma}{\varepsilon^{2}-\lambda^{2}}\left(\begin{array}{cc}
\varepsilon k_{+} & -i \lambda k_{-}  \tag{3}\\
i \lambda k_{+} & \varepsilon k_{-}
\end{array}\right) \varphi .
$$

Then we arrive at a $2 \times 2$ Hamiltonian,


FIG. 1. (Color online) Spin polarization of the energy spectrum of spin-orbit coupled single-layer graphene with the dispersion law of Eq. (6) and spin-orbit coupling constant $\lambda>0$; energy $|\varepsilon|>\lambda$. Polarization is identical in $K$ and $K^{\prime}$ valleys. External circles: $\mu=+1$; internal circles: $\mu=-1$. For $\lambda<0$, the quantum numbers, $\mu$ and $\nu$, and spin polarizations change their signs for all branches. Brillouin zone of graphene is also shown.

$$
H(\varepsilon)=\frac{\gamma^{2}}{\varepsilon^{2}-\lambda^{2}}\left(\begin{array}{cc}
\varepsilon k_{-} k_{+} & -i \lambda k_{-}^{2}  \tag{4}\\
i \lambda k_{+}^{2} & \varepsilon k_{+} k_{-}
\end{array}\right),
$$

that depends explicitly on its eigenvalues $\varepsilon, H(\varepsilon) \varphi=\varepsilon \varphi$. When $\mathbf{B} \neq 0$, operators $k_{ \pm}=k_{x} \pm i k_{y}$ do not commute; below, $\mathbf{B}=B \hat{\mathbf{z}}$. We note that Eq. (4) is exact, and despite the fact that the problem is nonlinear in $\varepsilon$, calculation of spin polarization in this representation is more concise than in the original $4 \times 4$ representation.

For free carriers, $\mathbf{B}=0$, eigenspinors of $H(\varepsilon)$ are

$$
\begin{equation*}
\varphi_{\nu}(\mathbf{k})=\frac{1}{\sqrt{2}}\binom{i \nu k_{-}^{2} / k^{2}}{1}, \quad \nu= \pm 1 \tag{5}
\end{equation*}
$$

From Eqs. (2) and (4) follows an equation $\varepsilon_{\nu}\left(\varepsilon_{\nu}+\lambda \nu\right)$ $=\gamma^{2} k^{2}$ for the eigenvalues $\varepsilon_{\nu}$. Its solutions are

$$
\begin{equation*}
\varepsilon_{\nu \mu}(k)=\frac{\nu \mu}{2}\left(\sqrt{\lambda^{2}+4 \gamma^{2} k^{2}}-\mu \lambda\right), \quad \mu= \pm 1 . \tag{6}
\end{equation*}
$$

The spectrum includes two zero-gap branches and two gapped branches of the same shape. The gap equals $2|\lambda|$, and the separation between gapped and ungapped branches is $k$ independent and equals $\lambda$. The spectrum is similar to the spectrum of unbiased bilayer graphene without SO coupling, ${ }^{16-18}$ but the nature of eigenstates is quite different.

It is easily seen from Eqs. (2) and (5) that $\left\langle\varphi_{\nu}\right| \hat{S}_{z}\left|\varphi_{\nu}\right\rangle=0$; hence, spins are in-plane polarized. Because $\hat{\mathbf{S}}$ includes $\sigma_{1}$, calculation of in-plane polarization involves the lower spinor $\phi$ and is more cumbersome. Nevertheless, it is straightforward, and applying Eqs. (3), (5), and (6) results in in-plane spin polarizations $\mathbf{S}_{\nu \mu}(\mathbf{k})$ for all $(\nu, \mu)$ states,

$$
\begin{equation*}
\mathbf{S}_{\nu \mu}(\mathbf{k})=\frac{\left\langle\Psi_{\nu \mu}\right| \hat{\mathbf{S}}\left|\Psi_{\nu \mu}\right\rangle}{\left\langle\Psi_{\nu \mu} \mid \Psi_{\nu \mu}\right\rangle}=\frac{2 \mu \gamma(\mathbf{k} \times \hat{\mathbf{z}})}{\sqrt{\lambda^{2}+4 \gamma^{2} k^{2}}} \tag{7}
\end{equation*}
$$

proportional to the group velocity $\mathbf{v}_{\nu \mu}(\mathbf{k})=\partial \varepsilon_{\nu \mu} / \hbar \partial \mathbf{k}$. Equation (7) indicates transverse spin polarization (Fig. 1), as concluded by Varykhalov et al. ${ }^{15}$ Its magnitude is $k$ dependent. When $k \gtrdot k_{\lambda}$, with $k_{\lambda}=|\lambda| / 2 \gamma$ being a characteristic SO momentum, it saturates, $\left|\mathbf{S}_{\nu \mu}\right| \rightarrow 1$. In the $k \ll k_{\lambda}$ limit, it vanishes as $k / k_{\lambda}$. Vanishing of all $\mathbf{S}_{\nu \mu}(\mathbf{k} \rightarrow 0)$, with $\hat{\mathbf{S}}^{2}=3$, is a unique property of the Dirac points.

Chirality of the spinor $\varphi_{\nu}(\mathbf{k})$ is defined by $\nu$, spin polarization $\mathbf{S}_{\nu \mu}$ by $\mu$, and the product $\mu \nu$ specifies electron and hole spectrum branches. Experiments of Ref. 15 measured the magnitude of $\lambda,|\lambda| \approx 13 \mathrm{meV}$. Measuring the sign of $\mathbf{S}_{\nu \mu}$ would allow finding the sign of $\lambda .{ }^{19}$ Indeed, it is seen from Eq. (6) that $\mu / \lambda>0$ for external Fermi circles. Due to the requirements of time-inversion symmetry, spin polarization is identical near $K$ and $K^{\prime}$ points. It is not clear currently which of the factors (experimental resolution, temperature, or staggered potential of Ni substrate) was the main obstacle for measuring SARPES spectra for $k \leqq k_{\lambda}$. However, measurement of $\mathbf{S}_{\nu \mu}$ for $k \gtrsim k_{\lambda}$ should shed additional light on the role of these factors.

Application of well-developed techniques for detecting in-plane polarization $\mathbf{S}(\mathbf{k})$, based on Kerr spectroscopy ${ }^{20-22}$ and spin-galvanic effect, ${ }^{23}$ is hampered by the conductivity of metallic substrate. Reducing its thickness to only a few
monolayers or developing insulating substrates can render them proper efficacy.

For $\mathbf{B} \| \hat{\mathbf{z}}$, applying a Peierls substitution $\mathbf{k}=-i \nabla+e \mathbf{A} / \hbar c$, with $\mathbf{A}$ being a vector potential, one expresses $k_{ \pm}$in terms of Bose operators, $k_{+}=(\sqrt{2} / \ell) a^{+}, k_{-}=(\sqrt{2} / \ell) a$, and $\left[a, a^{+}\right]=1$; here, $\ell=\sqrt{c \hbar / e B}$ is a magnetic length. Then, instead of Eq. (4), one arrives at

$$
\hat{H}(\epsilon)=|\lambda| \frac{2 \Gamma^{2}}{\epsilon^{2}-1}\left(\begin{array}{cc}
\epsilon a a^{+} & -i \beta a^{2}  \tag{8}\\
i \beta\left(a^{+}\right)^{2} & \epsilon a^{+} a
\end{array}\right)
$$

where $\beta=\lambda /|\lambda|, \epsilon=\varepsilon /|\lambda|$, and $\Gamma=\gamma / \ell|\lambda|$. The Hamiltonian $\hat{H}(\epsilon)$ depends explicitly on its eigenvalues $\epsilon$. From here on, energy $\epsilon$ is measured in units of $|\lambda|$.

Solution of the corresponding eigenspinor problem can be found in terms of oscillator eigenfunctions ${ }^{24} \psi_{n}$,

$$
\begin{align*}
\varphi_{n} & =\binom{c_{1} \psi_{n-2}}{c_{2} \psi_{n}}, \quad \phi_{n}=\binom{c_{3}}{c_{4}} \psi_{n-1}, \\
\binom{c_{3}}{c_{4}} & =\frac{\Gamma \sqrt{2}}{\epsilon^{2}-1}\binom{\epsilon \sqrt{n-1} c_{1}-i \beta \sqrt{n} c_{2}}{i \beta \sqrt{n-1} c_{1}+\epsilon \sqrt{n} c_{2}}, \tag{9}
\end{align*}
$$

for $n \geq 2$. The coefficients $c_{1,2}=c_{1,2}(n)$, normalized as $\left|c_{1}\right|^{2}+\left|c_{2}\right|^{2}=1$, read as

$$
\begin{equation*}
\frac{c_{1}}{c_{2}}=\frac{i \beta \epsilon\left(1+2 n \Gamma^{2}-\epsilon^{2}\right)}{2 \sqrt{n(n-1)} \Gamma^{2}}, \quad c_{2}=\frac{\sqrt{n}}{2 n\left(1+\Gamma^{2}\right)-\epsilon^{2}} . \tag{10}
\end{equation*}
$$

Eigenvalues obey the equation

$$
\begin{equation*}
\epsilon^{4}-\left[1+2 \Gamma^{2}(2 n-1)\right] \epsilon^{2}+4 n(n-1) \Gamma^{4}=0 \tag{11}
\end{equation*}
$$

and are

$$
\begin{equation*}
\left(\epsilon_{n}^{ \pm}\right)^{2}=\frac{1}{2}\left[1+2(2 n-1) \Gamma^{2} \pm \sqrt{1+4(2 n-1) \Gamma^{2}+4 \Gamma^{4}}\right] \tag{12}
\end{equation*}
$$

Equation (12) coincides with the expression for bilayer graphene in absence of SO coupling. ${ }^{18,25,26}$

In addition to the solutions with $n \geq 2$, there are solutions with $n \leq 1$ that are of special interest because of their peculiar spin properties. For $n=0$, there is a single solution $c_{1}(0)=0, c_{2}(0)=1$, and $\phi_{0}=0$, with $\epsilon_{0}=0$. For $n=1$, there are three solutions with $c_{1}(1)=0$ and $c_{2}(1)=1$; they differ by their $\phi_{1}$ spinors. For one of them the eigenvalue vanishes, $\epsilon_{1}^{0}=0$, and components of the spinor $\phi_{1}^{0}$ are $c_{3}=i \beta \Gamma \sqrt{2}$ and $c_{4}=0$. Two nonvanishing eigenvalues are $\epsilon_{1}= \pm \sqrt{1+2 \Gamma^{2}}$; the components of the corresponding spinors $\phi_{1}$ are $c_{3}=-i \beta / \Gamma \sqrt{2}, c_{4}=\epsilon_{1} / \Gamma \sqrt{2}$. These expressions can also be found from Eqs. (9) and (12) [with the upper sign in Eq. (12)] by plugging $n=1$. Hence, there exist two zero modes, $\epsilon_{0}=0$ and $\epsilon_{1}^{0}=0$, and SO coupling of $(\boldsymbol{\sigma} \times \mathbf{s})$ type preserves twofold degeneracy of the $\epsilon=0$ state typical of single-layer graphene ${ }^{3,4,27}$ but changes its nature: degeneracy is dynamical rather than symmetry conditioned (small Zeeman splitting ${ }^{28}$ is disregarded).

It follows from Eq. (9) that the in-plane spin polarization $\mathbf{S}$ vanishes in all eigenstates. Indeed, because of the factor $\sigma_{1}$ in $\hat{\mathbf{S}}=\sigma_{1} \mathbf{S}$, it mixes different components of the bispinor $\Psi, \varphi$
and $\phi$, and the mean value of their product is proportional to scalar products of the oscillator functions $\psi_{m}$ with quantum numbers that never coincide. Therefore, $\mathbf{S}_{n}=0$ for all $n$. This result is expected because $\mathbf{S}_{\nu \mu}(\mathbf{k})$ of Eq. (7) vanishes after averaging over the direction of $\mathbf{k}$ and follows from axial symmetry of the problem.

Longitudinal polarization $S_{z}$, after eliminating $\phi$ component of $\Psi$, can be expressed in terms of its $\varphi$ component,

$$
\begin{equation*}
S_{z}=\langle\varphi| s_{z}+\frac{\Gamma^{2}}{\epsilon^{2}-1}\left[s_{0}+\left(a a^{+}+a^{+} a\right) s_{z}\right]|\varphi\rangle /\langle\Psi \mid \Psi\rangle \tag{13}
\end{equation*}
$$

$\epsilon$ is the energy of the state $\varphi$, and normalization factor

$$
\begin{align*}
\langle\Psi \mid \Psi\rangle= & 1+\frac{\Gamma^{2}}{\left(\epsilon^{2}-1\right)^{2}}\langle\varphi| 2 i \beta\left[\left(a^{+}\right)^{2} s_{-}-a^{2} s_{+}\right] \\
& +\left(\epsilon^{2}+1\right)\left[\left(a a^{+}+a^{+} a\right) s_{0}+s_{z}\right]|\varphi\rangle \tag{14}
\end{align*}
$$

Explicit expressions for Eqs. (13) and (14) follow from Eqs. (9) and (10). Their original form is cumbersome but greatly simplifies after higher powers of $\epsilon^{2}$ are eliminated by employing Eq. (11), and $\beta^{2}=1$ is applied. The final equation, when expressed in terms of $\epsilon_{n}^{ \pm}$, is rather concise,

$$
\begin{equation*}
\left(S_{z}\right)_{n}^{ \pm}=\frac{2 \Gamma^{2}\left(2 n \Gamma^{2}-\epsilon^{2}\right)}{\epsilon^{2}\left(1-2 \Gamma^{2}\right)+2 n \Gamma^{2}\left(1+2 \Gamma^{2}\right)}, \quad \epsilon=\epsilon_{n}^{ \pm} \tag{15}
\end{equation*}
$$

This equation, together with Eq. (12), provides exact expressions for $B$ dependence of spin polarization for all states with $n \geq 1$ and $\epsilon \neq 0$. Because $\epsilon$ appears in Eq. (15) only as $\epsilon^{2}$, polarization $S_{z}$ is charge symmetrical: it coincides for electron and hole states with the same $n$ and $\left|\epsilon_{n}^{ \pm}\right|$.

In the weak field limit, $n \Gamma^{2} \ll 1, \epsilon^{2}$, eigenvalues are $\epsilon_{n}^{+} \approx 1$ and $\epsilon_{n}^{-} \approx 2 \sqrt{n(n-1)} \Gamma^{2}$, and $S_{z}$ is $n$ independent and proportional to $B,\left(S_{z}\right)_{n}^{ \pm} \approx \mp 2 \Gamma^{2}\left(n>1\right.$ for $\epsilon_{n}^{-}$states $)$. Because of the spectrum degeneracy at the $k=0$ point, the sequence $\epsilon_{n}^{-}$is nonequidistant despite the parabolicity of the spectrum. ${ }^{24}$ In the strong field limit, $\Gamma^{2} \rightarrow \infty$, eigenvalues are $\epsilon_{n}^{-} \approx \Gamma \sqrt{2 n}$ and $\epsilon_{n}^{+} \approx \Gamma \sqrt{2(n-1)}$, and spin magnetization saturates, $\left(S_{z}\right)_{n}^{ \pm} \approx \mp 1$. In this limit, two ladders nearly overlap and are split by $\Delta \epsilon_{n} \approx \sqrt{n / 2} /(2 \Gamma)$; the splitting increases with $n$ but for $\Gamma^{2} \gtrdot n$ is small compared with the level separation $\Gamma / \sqrt{2 n}$ inside each ladder. For $\lambda \approx 13 \mathrm{meV}$, the field separating these two limit cases, found from the condition $\Gamma=1$, equals $B_{\mathrm{cr}}=c \lambda^{2} /\left(e \hbar v^{2}\right) \approx 0.3 \mathrm{~T}$.

In both limits, spin magnetization has opposite sign for $\epsilon^{+}$ and $\epsilon^{-}$ladders; hence, magnetization oscillates when Landau levels cross the Fermi level. These de-Haas-van-Alphen-type oscillations can be detected by Kerr spectroscopy ${ }^{29,30}$ even for ferromagnetic substrates, and by torque magnetometer techniques. ${ }^{31}$

Semiclassical regime is achieved for $\Gamma \ll 1$ and $n \gg 1$ with $n \Gamma^{2}=\kappa^{2} / 2=$ const; for $\kappa=\gamma k /|\lambda|$, one recovers Eq. (6) from Eq. (12). Keeping $\kappa=$ const, one finds for electron branches, $\epsilon_{n}^{ \pm}>0$, in the first order in $1 / n$,

$$
\epsilon_{n}^{ \pm} \approx \frac{1}{2}\left(\sqrt{1+4 \kappa^{2}} \pm 1\right)-\frac{\kappa^{2}}{2 n \sqrt{1+4 \kappa^{2}}},
$$

$$
\begin{equation*}
\left(S_{z}\right)_{n}^{ \pm} \approx \mp \frac{\kappa^{2}}{n \sqrt{1+4 \kappa^{2}}}=\mp \frac{2 \Gamma^{2}}{\sqrt{1+4(\gamma k / \lambda)^{2}}} \tag{16}
\end{equation*}
$$

Therefore, in the leading order of the expansion, level splitting $\Delta \epsilon_{n} \approx 1$ remains $n$ independent, while spin polarization $S_{z}$ has opposite sign for two spectrum branches and decreases with $n$ (or, for $\Gamma=$ const, with the electron momentum $k$ ). The oscillatory dependence of the total spin magnetization on $B$ can be detected as discussed in the previous paragraph.

Therefore, all quantum states with $\epsilon_{n}^{ \pm} \neq 0$ are nondegenerate, and only two states $\epsilon_{0}=\epsilon_{1}^{0}=0$ are degenerate. These two states differ strongly in their spin magnetization. For the $n=0$ state, polarization $\left(S_{z}\right)_{0}=-1$. It does not depend on $B$ but changes abruptly when $\mathbf{B}$ changes sign. For the $n=1$ state with $\epsilon_{1}^{0}=0$, polarization equals $\left(S_{z}\right)_{1}=-\left(1-2 \Gamma^{2}\right) /\left(1+2 \Gamma^{2}\right)$; it tends to -1 for $B \rightarrow 0$, changes sign at $\Gamma^{2}=1 / 2$, and saturates to +1 for $B \rightarrow \infty$. In this limit, contributions of two $\epsilon=0$ states cancel. Such a behavior is unique because it suggests that SO coupled graphene with filled $\epsilon=0$ states is unstable to ferromagnetic ordering in $\hat{\mathbf{z}}$ direction in weak fields $\mathbf{B} \| \hat{\mathbf{z}}$, while with increasing $B$ the magnetization gradually vanishes. This magnetization differs drastically from the edge-state magnetization of graphene zigzag nanoribbons proposed by Fujita et al. ${ }^{32}$ because it originates from SO coupling rather than from the exchange interaction. It also bears no similarity with the Dzyaloshinskii-Moriya weak ferromagnetism ${ }^{33,34}$ because it is dynamical rather than symmetry conditioned and develops in a paramagnet without any magnetic structure. The effect of electron-electron interaction on this peculiar state needs a special investigation. ${ }^{35}$

For comparison with experimental data, one needs to add magnetization $S_{z}$ of the electrons in $K$ and $K^{\prime}$ valleys. Because $\mathcal{H}_{K^{\prime}}^{0}$, is related to $\mathcal{H}_{K}^{0}$ by a $\sigma_{2}$ canonical transformation leaving the operator $\hat{S}_{z}$ of Eq. (2) unchanged, magnetization has the same magnitude and sign in both valleys. This can be also inferred from the time-inversion symmetry requirements. Therefore, total $S_{z}$ equals the magnetization of the $K$ valley multiplied by the factor of 2 .

Novoselov et al. ${ }^{5}$ compared the conventional QHE (Ref. 36) and two types of unconventional QHEs typical of single-layer ${ }^{3,4}$ and bilayer graphene, the material notorious for its exotic QHE properties. ${ }^{37}$ SO coupled single-layer graphene introduces one more type of unconventional QHE. Due to the fourfold degeneracy of zero modes $\left[\epsilon_{0}=\epsilon_{1}^{0}=0\right.$ degeneracy times the factor of 2 from isospin, $K\left(K^{\prime}\right)$ valleys] the step in $\sigma_{x y}$ at $B=0$ equals $4 e^{2} / h$, as in single-layer graphene without SO coupling. However, because spin degeneracy is lifted in each valley by SO interaction, and only isospin degeneracy persists, all $B \neq 0$ steps are of $2 e^{2} / h$. Therefore, the ratio of the magnitudes of the $B=0$ and $B \neq 0$ steps equals 2 , as in bilayer graphene without SO coupling. Depending on the magnitude of $\lambda$, these $2 e^{2} / h$ steps can appear in pairs, as resolved $4 e^{2} / h$ steps, similar to the resolution of two spin components of the traditional QHE. Spin-orbit coupled graphene on an isolating substrate would become the optimal object for observing this new variety of QHE and for spin manipulation, a challenging task for semiconductor spintronics.

Apparently, among the perturbations that lower the symmetry of the Hamiltonian the largest is the staggering sublattice potential of the substrate violating the equivalence of $A(B)$ lattice cites; manifestation of the broken sixfold symmetry was reported in Ref. 15. A staggered potential can be described by a term $\mathcal{H}_{\mathrm{st}}=u \sigma_{z} \tau_{z}$, where $\tau_{z}$ is a Pauli matrix in the isospin space. ${ }^{9}$ This term creates a gap in the spectrum and lifts the symmetry of $K\left(K^{\prime}\right)$ valleys. Adding $\mathcal{H}_{\text {st }}$ to $\mathcal{H}_{K\left(K^{\prime}\right)}^{0}$ does not change wave functions of $n=0$ modes but changes their energies to $\varepsilon= \pm u$ (in dimensional units). For the $n=1$ soft mode, eigenvectors also change; now $c_{1}=0$ but $c_{2}, c_{3}, c_{4} \neq 0$. Energy spectrum can be found from a cubic equation that for $|u / \lambda| \ll 1$ defines soft modes $\varepsilon_{1} \approx \pm u\left(1-2 \Gamma^{2}\right) /\left(1+2 \Gamma^{2}\right)$. As a result, the $4 e^{2} / h$ step in $\sigma_{x y}$ splits into a plateau near $B=0$ and two $e^{2} / h$ steps on both sides of it. Lifting the $K\left(K^{\prime}\right)$ degeneracy also splits all $2 e^{2} / h$ steps, making the QHE of SO coupled graphene similar to the traditional QHE with a resolved Zeeman splitting. We
notice that $\lambda=13 \mathrm{meV}$ corresponds to a field $B=120 \mathrm{~T}$ for a Landé factor $g=2$.

In conclusion, a theory of the energy spectrum and spin polarization in single-layer graphene, a subject to a substrateinduced spin-orbit coupling, is presented. Energy spectrum consists of two zero-gap bands and two gapped bands, and all states are in-plane spin-polarized perpendicular to the momentum $\mathbf{k}$. This polarization saturates at large $k$ and vanishes at the scale of spin-orbit energy when $k \rightarrow 0$. In a perpendicular magnetic field, two zero modes develop in each of $K\left(K^{\prime}\right)$ valleys. These modes show a peculiar magnetic behavior suggesting a possibility of a perpendicular-to-plane spinorbit conditioned magnetism and produce a new variety of unconventional quantum Hall effect.

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${ }^{1}$ K. S. Novoselov, A. K. Geim, S. V. Morozov, D. Jiang, Y. Zhang, S. V. Dubonos, I. V. Grigorieva, and A. A. Firsov, Science 306, 666 (2004).
${ }^{2}$ P. R. Wallace, Phys. Rev. 71, 622 (1947).
${ }^{3}$ K. S. Novoselov, A. K. Geim, S. V. Morozov, D. Jiang, M. I. Katsnelson, I. V. Grigorieva, S. V. Dubonos, and A. A. Firsov, Nature (London) 438, 197 (2005).
${ }^{4}$ Y. Zhang, Y.-W. Tan, H. L. Stormer, and P. Kim, Nature (London) 438, 201 (2005).
${ }^{5}$ K. S. Novoselov, E. McCann, S. V. Morozov, V. I. Fal'ko, M. I. Katsnelson, U. Zeitler, D. Jiang, F. Schedin, and A. K. Geim, Nat. Phys. 2, 177 (2006).
${ }^{6}$ C. W. J. Beenakker, Rev. Mod. Phys. 80, 1337 (2008).
${ }^{7}$ A. H. Castro Neto, F. Guinea, N. M. R. Peres, K. S. Novoselov, and A. K. Geim, Rev. Mod. Phys. 81, 109 (2009).
${ }^{8}$ G. Dresselhaus and M. S. Dressehaus, Phys. Rev. 140, A401 (1965).
${ }^{9}$ C. L. Kane and E. J. Mele, Phys. Rev. Lett. 95, 226801 (2005).
${ }^{10}$ H. Min, J. E. Hill, N. A. Sinitsyn, B. R. Sahu, L. Kleinman, and A. H. MacDonald, Phys. Rev. B 74, 165310 (2006).
${ }^{11}$ Y. Yao, F. Ye, X. L. Qi, S. C. Zhang, and Z. Fang, Phys. Rev. B 75, 041401(R) (2007).
${ }^{12}$ T. Ando, J. Phys. Soc. Jpn. 69, 1757 (2000).
${ }^{13}$ D. Huertas-Hernando, F. Guinea, and A. Brataas, Phys. Rev. B 74, 155426 (2006).
${ }^{14}$ F. Kuemmeth, S. Ilani, D. C. Ralph, and P. L. McEuen, Nature (London) 452, 448 (2008).
${ }^{15}$ A. Varykhalov, J. Sanchez-Barriga, A. M. Shikin, C. Biswas, E. Vescovo, A. Rybkin, D. Marchenko, and O. Rader, Phys. Rev. Lett. 101, 157601 (2008).
${ }^{16}$ E. McCann and V. I. Fal'ko, Phys. Rev. Lett. 96, 086805 (2006).
${ }^{17}$ J. Nilsson, A. H. Castro Neto, F. Guinea, and N. M. R. Peres, Phys. Rev. Lett. 97, 266801 (2006).
${ }^{18}$ J. M. Pereira, Jr., F. M. Peeters, and P. Vasilopoulos, Phys. Rev. B 76, 115419 (2007).
${ }^{19}$ J. Henk, M. Hoesch, J. Osterwalder, A. Ernst, and P. Bruno, J. Phys.: Condens. Matter 16, 7581 (2004).
${ }^{20}$ Y. Kato, R. C. Myers, A. C. Gossard, and D. D. Awschalom, Nature (London) 427, 50 (2004).
${ }^{21}$ S. A. Crooker and D. L. Smith, Phys. Rev. Lett. 94, 236601 (2005).
${ }^{22}$ L. Meier, G. Salis, I. Shorubalko, E. Gini, S. Schön, and K. Ensslin, Nat. Phys. 4, 77 (2008).
${ }^{23}$ E. L. Ivchenko and S. Ganichev, Spin Physics in Semiconductors (Springer, New York, 2008), p. 245.
${ }^{24}$ J. M. Luttinger, Phys. Rev. 102, 1030 (1956).
${ }^{25}$ M. Nakamura, L. Hirasawa, and K.-I. Imura, Phys. Rev. B 78, 033403 (2008).
${ }^{26}$ E. A. Henriksen, Z. Jiang, L. C. Tung, M. E. Schwartz, M. Takita, Y. J. Wang, P. Kim, and H. L. Stormer, Phys. Rev. Lett. 100, 087403 (2008).
${ }^{27}$ V. P. Gusynin and S. G. Sharapov, Phys. Rev. Lett. 95, 146801 (2005).
${ }^{28}$ Y. Zhang, Z. Jiang, J. P. Small, M. S. Purewal, Y. W. Tan, M. Fazlollahi, J. D. Chudow, J. A. Jaszczak, H. L. Stormer, and P. Kim, Phys. Rev. Lett. 96, 136806 (2006).
${ }^{29}$ D. D. Awschalom and J. M. Kikkawa, Phys. Today 52 (6), 33 (1999).
${ }^{30}$ J. Xia, E. Schemm, G. Deutscher, S. A. Kivelson, D. A. Bonn, W. N. Hardy, R. Liang, W. Siemons, G. Koster, M. M. Fejer, and A. Kapitulnik, Phys. Rev. Lett. 100, 127002 (2008).
${ }^{31}$ M. A. Wilde, D. Reuter, Ch. Heyn, A. D. Wieck, and D. Grundler, Phys. Rev. B 79, 125330 (2009), and references therein.
${ }^{32}$ M. Fujita, K. Wakabayashi, K. Nakada, and K. Kusakabe, J. Phys. Soc. Jpn. 65, 1920 (1996).
${ }^{33}$ I. E. Dzialoshinskii, Sov. Phys. JETP 5, 1259 (1957).
${ }^{34}$ T. Moriya, Phys. Rev. 120, 91 (1960).
${ }^{35}$ K. Nomura and A. H. MacDonald, Phys. Rev. Lett. 96, 256602 (2006).
${ }^{36}$ K. v. Klitzing, G. Dorda, and M. Pepper, Phys. Rev. Lett. 45, 494 (1980).
${ }^{37}$ F. D. M. Haldane, Phys. Rev. Lett. 93, 206602 (2004).

