The effect of spin-orbit (SO) coupling in graphene represents an example of a stimulating theoretical study that remains difficult to detect experimentally. The form of intrinsic SO coupling in the graphene band structure, suggested by Kane and Mele [1], has fuelled the theoretical scenarios and find that it lifts the aforementioned saturation of weak localization correction rather than antilocalization, suggested by Kane and Mele [1], has fuelled the theoretical approach to determine how electronic spin may be combined with lattice and valley degrees of freedom. We focus on the region near the Fermi level which lies in the vicinity of two inequivalent corners of the Brillouin zone, known as valleys, with wave vectors $\mathbf{K}_\pm$ consisting of two valleys $\mathbf{K}_+ / \mathbf{K}_-$, two lattice sites $A / B$, and two spin components $\uparrow / \downarrow$. We use three sets of Pauli matrices $\mathbf{1} \mathbf{1} [12]$ to describe spin $\hat{s} = (s_x, s_y, s_z)$, sublattice ‘isospin’ $\Sigma = (\Sigma_x, \Sigma_y, \Sigma_z)$ and valley ‘pseudospin’ $\Lambda = (\Lambda_x, \Lambda_y, \Lambda_z)$ [20]. The matrices $\hat{s} \Sigma \Lambda$ all change sign upon time inversion so that their products are time-inversion symmetric and $\Sigma_a s_j, s_j \Lambda_l$ may be used as a basis for a phenomenological description of static disorder leading to SO scattering.

The results of this symmetry-based approach are summarized in Table I which shows how $\hat{s}, \Sigma, \Lambda$ may be combined to form irreducible representations of the planar group $C_{6v}$ [21] which combines the point group $C_{6v}$ of strictly two-dimensional graphene with primitive translations, as appropriate for the description of two valleys $\mathbf{K}_\pm$. Matrices $\Sigma$ and $\Lambda$ are confined to the two-dimensional plane of graphene and their behavior under symmetry operations is impervious to the third spatial dimension. Thus, they are invariant under mirror reflection in the graphene plane so that, in the absence of spin, they only appear in the representations that are $z \to -z$ symmetric. The presence of spin, however, introduces a

\[ z \to -z \] symmetry of spin-orbit coupling and weak localization in graphene

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We show that the influence of spin-orbit (SO) coupling on the weak localization effect for electrons in graphene depends on the lack or presence of $z \to -z$ symmetry in the system. While for $z \to -z$ symmetric and antisymmetric SO coupling, disordered graphene should display a weak anti-localization behavior at lowest temperature, $z \to -z$ symmetric coupling leads to an effective saturation of decoherence which can be partially lifted by an in-plane magnetic field, thus, tending to restore the weak localization effect.

The effect of spin-orbit (SO) coupling on the weak localization effect for electrons propagating along long diffusive trajectories [6–16]. In contrast to simple metals and semiconductors where the typical behavior of electrons in metals with strong magnetic fields on the interference correction to conductivity is negative. For detection by conventional spectroscopic methods [1–3, 5, 16–19] the intrinsic SO coupling [1–3, 4, 16] in the graphene Hamiltonian:

\[ \hat{H} = v \mathbf{p} + \hat{h}_{KM} + \hat{h}_{BR} + \hat{U} + \hat{V}_{sym} + \hat{V}_{asy} + \mu_B \mathbf{B}_\parallel, \]

\[ \hat{h}_{KM} = \lambda \Sigma z \sigma_z, \quad \hat{h}_{BR} = \mu (\Sigma_x s_y - \Sigma_y s_x). \]
TABLE I: Irreducible representations of the planar group $C_{6v}^\prime$ as provided by matrices $\Sigma_a, \Lambda_l$, and $s_j$. Representations $A_1, A_2, B_1, B_2, E_1, E_2$ are part of the point group of two-dimensional graphene $C_{6v}$, representations $E'_1, E'_2, G'$ incorporate primitive translations.

| Irr. Rep. | $z \to -z$ symmetric | $z \to -z$ asymmetric |
|-----------|------------------------|------------------------|
| $A_1$     | $\bar{I}, \Sigma_z, s_z$ | $\Sigma_x s_y - \Sigma_y s_x$ | $\Sigma_x s_y + \Sigma_y s_x$ |
| $A_2$     | $\Sigma_x, s_z$         | $\Sigma_x s_y + \Sigma_y s_x$ | $\Sigma_x s_y - \Sigma_y s_x$ |
| $B_1$     | $\Lambda_z$            | $\Sigma_y s_x$          | $\Sigma_y s_x$          |
| $B_2$     | $(\Sigma_z s_z, \Lambda_z s_z)$ | $(\Sigma_x s_y + \Sigma_y s_x, \Lambda_z s_z)$ | $(\Sigma_x s_y - \Sigma_y s_x, \Lambda_z s_z)$ |
| $E_1$     | $(\Sigma_x, \Sigma_y)$ | $(\Sigma_x s_y + \Sigma_y s_x, \Lambda_x s_z)$ | $(\Sigma_x s_y - \Sigma_y s_x, \Lambda_x s_z)$ |
| $E_2$     | $(\Lambda_x, \Sigma_z)$ | $(\Lambda_y s_x)$ | $(\Lambda_y s_x)$ |
| $E'_1$    | $(\Lambda_x, \Sigma_z)$ | $(\Lambda_y s_x)$ | $(\Lambda_y s_x)$ |
| $E'_2$    | $(\Lambda_x, \Sigma_z)$ | $(\Lambda_y s_x)$ | $(\Lambda_y s_x)$ |
| $G'$      | $(\Lambda_x, \Sigma_z)$ | $(\Lambda_y s_x)$ | $(\Lambda_y s_x)$ |

pseudovector that lies in three-dimensional space: $s_z$ is even under $z \to -z$ reflection, but in-plane components $s_x, s_y$ are odd. Thus, SO terms containing $s_z$ appear in $z \to -z$ symmetric representations, terms containing $s_x, s_y$ appear in $z \to -z$ asymmetric representations.

In Table I, $\Sigma_z s_z$ is an invariant of the point group of graphene representing intrinsic Kane-Mele SO coupling $\hbar K_M \bar I \Sigma \Sigma \Sigma \Sigma \Sigma \Sigma$, and $\Sigma_y s_x - \Sigma_x s_y$ describes the Bychkov-Rashba term $\hbar B_R \bar I \Sigma \Sigma \Sigma \Sigma \Sigma \Sigma$, which assumes the existence of a transverse field $\bar I \Sigma$ breaking $z \to -z$ symmetry. The entries in Table II take into account possible SO scattering mechanisms due to defects in graphene: $\tilde{V}_{sym}$ includes terms proportional to $s_z$, and $\tilde{V}_{asy}$ includes $s_x, s_y$.

The term $\tilde{U}$, Eq. (2), describes disorder decoupled from the spin degree of freedom: $u_0(r) \bar I$ describing the influence of remote charges, $u_{z,z}(r) \Sigma_z A_z$ describing different on-site energies of the $A/B$ sublattices, and $u_{x,z}(r) \Sigma_x A_z$ for $u_{y,z}(r) \Sigma_y A_z$ accounting for fluctuations of $A/B$ hopping. The other terms in $\tilde{U}$, $u_{x,z}(r) \Sigma_x A_z$ and $u_{y,z}(r) \Sigma_y A_z$ for $a = x, y, z$, generate intervalley scattering. We assume that different types of disorder in the Hamiltonian are uncorrelated and $x$-$y$ isotropic:

$$\langle u_{a,\ell}(r) u_{a',\ell'}(r') \rangle = u_{a,\ell}^2 \delta_{a,a'} \delta_{\ell,\ell'} \delta(r - r'), \quad \langle \alpha_{a,\ell}(r) \alpha_{a',\ell'}(r') \rangle = \alpha_{a,\ell}^2 \delta_{a,a'} \delta_{\ell,\ell'} \delta(r - r'), \quad \langle \beta_{\ell,\ell'}(r) \beta_{\ell',\ell'}(r') \rangle = \beta_{\ell,\ell'}^2 \delta_{\ell,\ell'} \delta_{\ell',\ell'} \delta(r - r').$$

In the following study, we employ the standard diagrammatic technique for disordered systems [20] to calculate the weak localization correction $\delta \sigma$ to the conductivity. We assume that the Dirac-like Hamiltonian $v \Sigma \cdot p$ dominates the electronic behavior and that diagonal disorder, $\bar I u_0(r)$ in Eq. (2), determines the elastic scattering rate, $\tau^{-1} \approx \tau_0^{-1} = \pi 2e^2/g/h$, where $\gamma = p_0/(2\pi\hbar^2 v)$ is the density of states per spin, per valley [11,12]. The current operator corresponding to the Dirac-like Hamiltonian is momentum independent so that the current vertex entering the Drude conductivity is renormalized by vertex corrections. Then, the Drude conductivity is equal to $\sigma = 4e^2/\gamma D$ where the diffusion coefficient is $D = v^2\tau_{tr}/2$ and the transport time is twice the scattering time, $\tau_{tr} = 2\tau_0^{-1}$.

The weak localization correction $\delta \sigma$ may be written in terms of disorder-averaged two-particle correlation functions known as Cooperon propagators $C_s^l$ where index $l$ refers to pseudospin (related to $\bar I$ describing valley degrees of freedom), and $s$ refers to spin (related to $\bar I$). All the Cooperons that we consider are singlets with respect to sublattice isospin $\bar I$ because all isospin-triplet modes have relaxation gaps $\sim 1/\tau_0$ [11,12]. Then, $\delta \sigma$ may be written in terms of a summation with respect to sixteen Cooperons consisting of combinations of spin and pseudospin singlet and triplets:

$$\delta \sigma = \frac{c^2 D}{\pi h} \sum_{s,l=0,1,2,3} c_{s,l} C_s^l(r' = r), \quad (5)$$

$$D \left(\nabla + \frac{2eA}{c \hbar} \right)^2 + \Gamma_s^l + \tau_\phi^{-1} - i\omega \right) C_s^l(r, r') = \delta(r - r').$$

Here, the factors $c_0 = 1$, $c_x = c_y = c_z = -1$ take into account the fact that singlet and triplet Cooperons (of both spin and pseudospin) appear with opposite signs, and $A$ is the vector potential of homogeneous external magnetic field, $B = \text{rot} A$ ($B_z = \partial_x A_y - \partial_y A_x$).

Inelastic dephasing is taken into account in Eq. (5) by $\tau_\phi^{-1}$ and, in general, symmetry-breaking perturbations [such as those contained in the Hamiltonian Eq. (1)], contribute relaxation gaps $\Gamma_s^l$ to the otherwise gapless Cooperons $C_s^l$, as quantified in terms of relaxation rates summarized in Table I. Then, the zero-field temperature-dependent correction, $\delta \rho(0)$, to the sheet resistance, where $\delta \rho(0)/\rho \equiv -\delta \sigma$, may be written as

$$\delta \rho(0) = -\frac{e^2 D}{\pi h} \sum_{s,l=0,1,2,3} c_s c_l \int_0^{\Gamma_s^l} \frac{dq}{2\pi} C_s^l(q), \quad (6)$$

$$= \frac{e^2 D^2}{2\pi h} \sum_{s,l=0,1,2,3} c_s c_l \ln \left(\frac{\tau_\phi^{-1} + \Gamma_s^l}{\tau_\phi^{-1}}\right), \quad (7)$$

and the magnetoresistance, $\Delta \rho(B_z) = \delta \rho(B_z) - \delta \rho(0)$,
TABLE II: Scattering rates, due to symmetry-breaking terms in the Hamiltonian Eq. (1), that produce relaxation gaps \( \Gamma_j^o \) in the otherwise gapless Cooperons \( C_j^o \) where \( j \) refers to spin, \( l \) to valley. The relaxation rate of the intervalley Cooperons \( \tau^{-1}_v \) and the intervalley rate \( \tau^{-1}_o \) result from spin-independent disorder, intrinsic \( \tau^{-1}_{KM} \) and Bychkov-Rashba \( \tau^{-1}_{B_R} \) rates arise from coupling of spin and lattice, rates \( \tau^{-1}_{v_e,v_o}, \tau^{-1}_{v_e,o}, \tau^{-1}_{v_o,e}, \tau^{-1}_{v_o,o} \) account for coupling of valley and spin degrees of freedom.

| relaxation rates | relaxation rates |
|------------------|------------------|
| \( \Gamma_0^v = 0 \) | \( \tau^{-1}_v = \tau^{-1}_o + \tau^{-1}_e \) |
| \( \Gamma_0^o = \Gamma_0^v + 2\tau^{-1}_{v_e,v_o} + 4\tau^{-1}_{v_e,o} + 2\tau^{-1}_{v_o,e} + 4\tau^{-1}_{v_o,o} \) | \( \tau^{-1}_v = \pi \gamma (u^2_{x,z} + u^2_{y,z} + u^2_{x,y} + u^2_{x,z} + u^2_{y,z}) / \hbar \) |
| \( \Gamma_v^v = 2\tau^{-1}_{v_e,v_o} + 4\tau^{-1}_{v_e,o} + 8\tau^{-1}_{v_o,o} \) | \( \tau^{-1}_v = 2\pi \gamma (u^2_{x,z} + u^2_{y,z} + u^2_{x,y}) / \hbar \) |
| \( \Gamma_o^o = \Gamma_K^v + \Gamma_K^o + 2\tau^{-1}_{v_e,v_o} + 4\tau^{-1}_{v_e,o} + 4\tau^{-1}_{v_o,e} + 4\tau^{-1}_{v_o,o} \) | \( \tau^{-1}_v = 2\pi \gamma (u^2_{x,z} + u^2_{y,z}) / \hbar \) |
| \( \Gamma_o^v = \Gamma_o^v = \Gamma_o^o = \tau^{-1}_e + \tau^{-1}_R + \tau^{-1}_K + 2\tau^{-1}_{v_e,v_o} + 2\tau^{-1}_{v_e,o} + 4\tau^{-1}_{v_o,e} + 4\tau^{-1}_{v_o,o} \) | \( \tau^{-1}_v = 2\pi \gamma (a^2_{x,z} + a^2_{y,z} + a^2_{x,y}) / \hbar \) |
| \( \Gamma_v^v = 2\tau^{-1}_{v_e,v_o} + \tau^{-1}_R + \tau^{-1}_K + 2\tau^{-1}_{v_e,v_o} + 2\tau^{-1}_{v_e,o} + 4\tau^{-1}_{v_o,e} + 4\tau^{-1}_{v_o,o} \) | \( \tau^{-1}_v = 2\gamma \beta^2_{x,z} / \hbar \) |
| \( \Gamma_o^o = 2\tau^{-1}_{v_e,v_o} + \tau^{-1}_R + \tau^{-1}_K + 2\tau^{-1}_{v_e,v_o} + 2\tau^{-1}_{v_e,o} + 4\tau^{-1}_{v_o,e} + 4\tau^{-1}_{v_o,o} \) | \( \tau^{-1}_v = \pi \gamma \beta^2_{x,z} / \hbar \) |
| \( \Gamma_v^v = 2\tau^{-1}_{v_e,v_o} + \tau^{-1}_R + \tau^{-1}_K + 2\tau^{-1}_{v_e,v_o} + 2\tau^{-1}_{v_e,o} + 4\tau^{-1}_{v_o,e} + 4\tau^{-1}_{v_o,o} \) | \( \tau^{-1}_v = \pi \gamma \beta^2_{x,z} / \hbar \) |

The application of an in-plane magnetic field produces an interplay between SO coupling and Zeeman splitting, as in semiconductor quantum dots [24, 25]. In-plane magnetic field \( \vec{B}_{||} \) introduces an additional term in the Hamiltonian \( \delta \hat{H} = (\hbar \omega / 2) \vec{\ell} \hat{S} \) where \( \omega = 2\mu_B B_{||} / \hbar \), \( \epsilon_z = \hbar \omega_c \) is the Zeeman energy and \( \ell = (\ell_x, \ell_y, 0) \), \( |\ell| = 1 \). This couples the spin-singlet \( C^0_0 \) to the triplets \( C^0_1 \) and \( C^0_2 \). The spin part of the matrix equation for the valley singlet Cooperons \( C^0_0, C^0_2, C^0_0, C^0_2 \) \( \equiv C^0 \) has the form

\[
C^0 = \begin{pmatrix}
-\omega_{\ell_x} & -\omega_{\ell_y} & 0 & 0 \\
-\omega_{\ell_x} & \pi + \tau^{-1}_{so} & 0 & 0 \\
-\omega_{\ell_y} & 0 & \pi + \tau^{-1}_{so} & 0 \\
0 & 0 & 0 & \Pi + 2\tau^{-1}_{asy}
\end{pmatrix}
\]

\[
\Pi = D (i \nabla + 2 e \vec{A} / \hbar c)^2 + \tau^{-1}_e,
\]

\[
\tau^{-1}_{so} = \tau^{-1}_e + \tau^{-1}_{asy}.
\]

After matrix inversion,

\[
C^0_{0,2} = \frac{1}{\Pi + 2\tau^{-1}_{asy}}
\]

where the limit \( \epsilon_z \rightarrow \infty \) of large Zeeman energy essentially means that \( \epsilon_z \gg \hbar \tau^{-1}_{so} \).

In the absence of in-plane field, \( \epsilon_z = 0 \), the low-field magnetoresistance Eqs. [59] is given by

\[
\Delta \rho = \frac{e^2 \rho^2}{2\pi \hbar} \left( F(\vec{B}_z) - F\left(\frac{B_z}{B_\phi + B_{asy}}\right) - 2F\left(\frac{B_z}{B_{asy} + B_{so}}\right)\right),
\]

\[
B_{asy} = \frac{\hbar c}{4D\tau^{-1}_{asy}}, \quad B_{so} = \frac{\hbar c}{4D\tau^{-1}_{so}}.
\]
This result shows that for \( z \to -z \) symmetric SO coupling (\( B_{\text{asy}} = 0 \)), in-plane field partially restores weak localization at the lowest temperatures lifting the limitation of \( \tau_{\phi} \) discussed above. In contrast, for \( z \to -z \) asymmetric SO coupling, in-plane field changes weak anti-localization into a suppressed weak localization behavior. The low-field magnetoresistance calculated using Eq. 8 for intermediate values of \( \epsilon_z \) is plotted in Fig. 1 for \( z \to -z \) symmetric (left) and asymmetric (right) SO scattering.

To summarize, among the two extremes of SO coupling in graphene, \( z \to -z \) symmetric and \( z \to -z \) asymmetric, the manifestation of the latter in quantum transport resembles that observed in a 2D electron gas in GaAs/AlGaAs heterostructures, whereas the former is peculiar for graphene. Experimentally, the effect of \( z \to -z \) symmetric SO coupling can be taken for a decoherence time “saturation” (\( \tau_{\phi}(T \to 0) \to \tau_{\text{sym}} \)) at low temperatures. Unlike inelastic decoherence, such saturation can be partially lifted by electron Zeeman splitting induced by a strong in-plane magnetic field making the negative magnetoresistance \( \Delta \rho(B_z) \) sharper when \( \tau_{\phi}^{-1}(T \to 0) \to 0 \). It is necessary to mention that a similar behavior of weak localization magnetoresistance should be expected in magnetically contaminated conductors 20. Spin-flip scattering of electrons from localized spins leads to saturation of \( \tau_{\phi} \) at the value of the spin-relaxation time whereas in-plane field freezes local moments thus suppressing spin-flip scattering of electrons and restoring the full size of the weak localization effect. However, the size of the in-plane field lifting the “saturation” of \( \tau_{\phi} \) in these two cases is different: polarization of magnetic impurities requires \( \mu_B B_{\|} > kT \) whereas the suppression of the effect of \( z \to -z \) symmetric SO coupling occurs when \( \mu_B B_{\|} > \hbar \tau_{\text{sym}}^{-1} \).

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\[
\Delta \rho = \frac{e^2 \rho^2}{2\hbar} \left[ F \left( \frac{B_z}{B_\phi + B_{\text{asy}}} \right) + F \left( \frac{B_z}{B_\phi + B_{\text{asy}}} \right) \right].
\]

\[ \text{FIG. 1: The low-field magnetoresistivity in the presence of } \]
\[ z \to -z \text{ symmetric (left) or asymmetric (right) SO scattering, as compared to the absence of SO scattering (lower dashed curves). Solid curves show the influence of SO scattering, } \]
\[ \tau_{\text{sym}} = 25 \tau_{\phi}^{-1} \text{ and } \tau_{\text{asy}} = 25 \tau_{\phi}^{-1}, \text{ respectively, with Zeeman energy } \epsilon_z = 0 \text{ (top) to } \epsilon_z \gg \tau_{\phi}^{-1} \text{ (bottom).} \]
(1971).

[23] R. J. Elliott, Phys. Rev. 96, 266 (1954); Y. Yafet, in Solid State Physics, edited by F. Seitz and D. Turnbull (Academic, New York, 1963), Vol. 14.

[24] I. L. Aleiner and V. I. Fal’ko, Phys. Rev. Lett. 87, 256801 (2001).

[25] D. M. Zumbühl et al., Phys. Rev. Lett. 89, 276803 (2002).

[26] F. Pierre et al., Phys. Rev. B 68, 085413 (2003).