Spin–orbit coupling in a graphene bilayer and in graphite

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Abstract. The intrinsic spin–orbit interactions in bilayer graphene and in graphite are studied, using a tight binding model and an intra-atomic $\vec{L}\vec{S}$ coupling. The spin–orbit interactions in bilayer graphene and graphite are larger, by about one order of magnitude, than the interactions in single-layer graphene, due to the mixing of $\pi$ and $\sigma$ bands by interlayer hopping. Their values are in the range 0.1–1 K. The spin–orbit coupling opens a gap in bilayer graphene, and also gives rise to two edge modes. The spin–orbit couplings are largest, $\sim 1–4$ K, in orthorhombic graphite, which does not have a center of inversion.

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1. Introduction

The isolation and control of a number of carriers in single- and few-layer graphene flakes \([1, 2]\) has led to a large amount of research activity exploring all aspects of these materials \([3]\). Among others, the application of graphene to spintronic devices \([4]–[10]\) and to spin qubits \([11]–[13]\) is being intensively studied. An understanding of these devices requires a knowledge of the electronic spin–orbit interaction. In principle, this interaction turns single-layer graphene into a topological insulator \([14]\), which shows a bulk gap and edge states at all boundaries. The magnitude of the spin–orbit coupling in single-layer graphene has been studied \([15]–[18]\). The calculated couplings are small, typically below 0.1 K. The observed spin relaxation \([8, 19]\) suggests the existence of stronger mechanisms that lead to the precession of electron spins, like impurities or lattice deformations \([20]–[22]\).

Bilayer graphene is interesting because, among other properties, a gap can be induced by electrostatic means, leading to new ways for the confinement of electrons \([23]\). The spin–orbit interactions that exist in single-layer graphene modulate the gap of a graphene bilayer \([24]\). The unit cell of bilayer graphene contains four carbon atoms, and there are more possible spin–orbit couplings than in single-layer graphene.

In the following we analyze the intrinsic and extrinsic spin–orbit couplings in bilayer graphene, using a tight binding model and describing the relativistic effects responsible for the spin–orbit interaction by an \(\vec{L}\vec{S}\) intra-atomic coupling. We use the similarities between the electronic bands of a graphene bilayer and the bands of three-dimensional graphite with Bernal stacking to generalize the results to the latter.

2. The model

We describe the electronic bands of a graphene bilayer using a tight binding model, with four orbitals, the 2s and the three 2p orbitals, per carbon atom. We consider hoppings between nearest neighbors in the same plane, and nearest neighbors and next-nearest neighbors between adjacent layers, see \([25]\). The couplings between each pair of atoms are parametrized by four hoppings, \(V_{ss}, V_{sp}, V_{pp}^{\pi}\) and \(V_{pp}^{\sigma}\). The model also includes two intra-atomic levels, \(\epsilon_s\) and \(\epsilon_p\), and the intra-atomic spin–orbit coupling

\[
\mathcal{H}_{so} \equiv \Delta_{so} \sum_i \vec{L}_i \vec{S}_i. \tag{1}
\]

The \(\pi\) bands of graphite can be expanded near the corners of the Brillouin zone, and this expansion has been described by a set of parameters \(\gamma_0, \gamma_1, \gamma_2, \gamma_3, \gamma_4, \gamma_5 \) and \(\Delta\) \([26, 27]\). These parameters can be obtained by projecting the full Hamiltonian with four orbitals per atom onto the \(\pi\) orbitals.

In the following, we consider a tight binding Hamiltonian that includes the s and p orbitals at each carbon atom. We neglect the difference between different hoppings between atoms that are next-nearest neighbors in adjacent layers, which are responsible for the difference between the parameters \(\gamma_3\) and \(\gamma_4\) in the parametrization of the \(\pi\) bands of graphite. We also set the difference in onsite energies between the two inequivalent atoms, \(\Delta\), to zero. The parameters \(\gamma_2\) and \(\gamma_5\) are related to hoppings between next-nearest neighbor layers, and they do not play a role in the description of the bilayer. The total number of parameters is 15, although, without loss of generality, we set \(\epsilon_p = 0\). We do not consider hoppings and spin–orbit interactions that include d levels, although they can contribute to the total magnitude of the spin–orbit couplings.

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Table 1. Nonzero tight binding parameters, in eV, used in the model. The
hoppings are taken from [29, 30], and the spin–orbit coupling from [31].
Superindices 0, 1 and 2 correspond to atoms in the same layer nearest-neighbors
in different layers, and next nearest neighbors in different layers.

| Parameter       | Value  |
|-----------------|--------|
| $\epsilon_s$    | -7.3   |
| $V_{ss}$        | 2.66   |
| $V_{sp}$        | 4.98   |
| $V_{ss\pi}$     | 2.66   |
| $V_{pp\sigma}$  | -6.38  |
| $V_{pp\pi}$     | 0.4    |
| $V_{pp\sigma}$  | 0.4    |
| $V_{pp\pi}$     | -0.4   |
| $\Delta_{so}$   | 0.02   |

The effects mediated by d orbitals do not change the order of magnitude of the
couplings in single-layer graphene, and their contribution to interlayer effects should be small.

The main contribution to the effective spin–orbit at the Fermi level due to the interlayer
coupling is due to the hoppings between p orbitals in next-nearest neighbor atoms in
different layers. This interaction gives rise to parameters $\gamma_3$ and $\gamma_4$ in the parametrization of the $\pi$ bands
in graphite. For simplicity, we will neglect couplings between s and p orbitals in neighboring
layers (note that the s orbitals do not play a role in the intra-atomic spin–orbit coupling). The
nonzero hoppings used in this work are listed in table 1. The parameter defined as $V_{pp\pi}$
is the nearest-neighbor hopping commonly used to describe the conduction and valence bands in
graphene.

The Hamiltonian can be written as a $32 \times 32$ matrix for each lattice wavevector. We define
an effective Hamiltonian acting on the $\pi$, or $p_z$, orbitals, by projecting out the rest of the orbitals:

$$\mathcal{H}_\pi^{\text{eff}} \equiv \mathcal{H}_\pi + \mathcal{H}_{\pi\sigma} (\omega - \mathcal{H}_{\sigma\sigma})^{-1} \mathcal{H}_{\sigma\pi}. \quad (2)$$

We isolate the effect of the spin–orbit coupling by defining

$$\mathcal{H}_\pi^{\text{so}}(\mathbf{k}) \equiv \mathcal{H}_\pi^{\text{eff}}(\Delta_{so}) - \mathcal{H}_\pi^{\text{eff}}(\Delta_{so} = 0). \quad (3)$$

Note that $\mathcal{H}_\pi^{\text{so}}$ depends on the energy, $\omega$.

We analyze $\mathcal{H}_\pi^{\text{so}}$ at the K and K' points. The two matrices have a total of 16 entries, which
can be labeled by specifying the sublattice, layer, spin and valley. We define operators that
modify each of these degrees of freedom using the Pauli matrices $\hat{\sigma}$, $\hat{\mu}$, $\hat{s}$ and $\hat{\tau}$. The unit cell is
described in figure 1.

The Hamiltonian has inversion and time reversal symmetry, and it is also invariant under
rotations by 120°. These symmetries are defined by the operators

$$\mathcal{I} \equiv \sigma_x \mu_x \tau_z,$$

$$\mathcal{T} \equiv i s_y \tau_z \mathcal{K},$$

$$\mathcal{C}_{120°} \equiv \left( -\frac{1}{2} + i \frac{\sqrt{3}}{2} s_z \right) \left( -\frac{1}{2} - i \frac{\sqrt{3}}{2} \tau_z \mu_z \right) \left( -\frac{1}{2} + i \frac{\sqrt{3}}{2} \tau_z \sigma_z \right),$$

where $\mathcal{K}$ is complex conjugation.

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Figure 1. Unit cell of a graphene bilayer. Labels A and B define the two sublattices in each layer, while subscripts 1 and 2 define the layers.

Figure 2. Dependence on energy of the spin–orbit couplings, as defined in equation (5).

The possible spin-dependent terms that respect these symmetries were listed in [32], in connection with the equivalent problem of three-dimensional Bernal graphite (see below). In the notation described above, they can be written as

\[ H_{\text{so}}^{\text{bilayer}} = \lambda_1 \sigma_z \tau_z s_z + \lambda_2 \mu_z \tau_z s_z + \lambda_3 \mu_z \left( \sigma_y s_x - \tau_z \sigma_z s_y \right) + \lambda_4 \sigma_z \left( \mu_y s_x + \tau_z \mu_z s_y \right) \]

The first term describes the intrinsic spin–orbit coupling in single-layer graphene. The other three, which involve the matrices \( \mu_i \), are specific to bilayer graphene. The term proportional to \( \lambda_3 \) can be viewed as a Rashba coupling with opposite signs in the two layers.

3. Results

3.1. Bilayer graphene

The energy dependence of the four couplings in equation (5) is shown in figure 2. The values of the couplings scale linearly with \( \Delta_{\text{so}} \). This dependence can be understood by treating the
next-nearest neighbor interlayer coupling and the intra-atomic spin–orbit coupling as a perturbation. The spin–orbit coupling splits the spin-up and spin-down states of the $\sigma$ bands in the two layers. The interlayer couplings couple the $\pi$ band in one layer to the $\sigma$ band in the other layer. Their value is of order $\gamma_3$. The $\pi$ states are shifted by

$$\delta\epsilon_{\pi\pm} \sim \pm \frac{\gamma_3^2}{\epsilon_{\sigma\pm}^0} \Delta_{so} \left( \frac{\gamma_3}{\epsilon_{\sigma}^0} \right)^2,$$

(6)

where $\epsilon_{\sigma}^0$ is an average value of a level in the $\sigma$ band.

The model gives for the only intrinsic spin–orbit coupling in single-layer graphene the value

$$|\lambda_{SLG}^1| = 0.0065 \text{ meV}.$$

(7)

This coupling depends quadratically on $\Delta_{so}$, $\delta\epsilon_{\pi\pm} \sim \pm \Delta_{so}^2 / \epsilon_{\sigma}^0$ [15].

The band dispersion of bilayer graphene at low energies, in the absence of spin–orbit couplings, is given by four Dirac cones, because of trigonal warping effects associated with $\gamma_3$ [23]. Hence, we must consider the couplings for wavevectors $\mathbf{k}$ slightly away from the $K$ and $K'$ points. We have checked that the dependence of the couplings $\lambda_i$ on momentum, in the range where trigonal warping is relevant, is comparable to the changes with energy shown in figure 2.

A gap, $E_g$, between the two layers breaks inversion symmetry and can lead to new couplings. The calculations show no new coupling greater than $10^{-6} \text{meV}$ for gaps in the range $-0.1 \text{eV} \leq E_g \leq 0.1 \text{eV}$. The dependence of the couplings on the value of the gap is shown in figure 3. This calculation considers only the effect in the shift of the electrostatic potential between the two layers. The existence also of an electric field will mix the $p_z$ and $s$ orbitals within each atom, leading to a Rashba term similar to the one induced in single-layer graphene [15, 16].

The effect of $\lambda_1$ is to open a gap of opposite sign in the two valleys for each value of $s_z$. The system will become a topological insulator [14, 33]. The number of edge states is two, that is, even. The spin Hall conductivity is equal to two quantum units of conductance. A perturbation that preserves time reversal invariance can hybridize the edge modes and open a gap. Such perturbation should be of the form $\tau_x s_y$.
Figure 4. Dependence on momentum perpendicular to the layers in Bernal graphite of the spin–orbit couplings, as defined in equation (5).

The terms with $\lambda_3$ and $\lambda_4$ describe spin flip hoppings that involve a site coupled to the other layer by the parameter $\gamma_1$. The amplitude of the wavefunctions at these sites is suppressed at low energies [23]. The shifts induced by $\lambda_3$ and $\lambda_4$ in the low-energy electronic levels will be of order $\lambda_2^3/\gamma_1$, $\lambda_2^4/\gamma_1$.

3.2. Bulk graphite

The Hamiltonian of bulk graphite with Bernal stacking can be reduced to a set of bilayer Hamiltonians with interlayer hoppings that depend on the momentum along the direction perpendicular to the layers, $k_z$. In the following we neglect the (small) hoppings that describe hoppings between next-nearest neighbor layers, $\gamma_2$ and $\gamma_5$, and the energy shift $\Delta$ between atoms in different sublattices. At the $K$ and $K'$ points of the three-dimensional Brillouin zone ($2k_zc = 0$, where $c$ is the interlayer distance), the Hamiltonian is that of a single bilayer where the value of all interlayer hoppings is doubled. At the $H$ and $H'$ points, where $2k_zc = \pi$, the Hamiltonian reduces to two decoupled layers, and in the intermediate cases the interlayer couplings are multiplied by $|2\cos(k_zc)|$. Carrying out the calculations described in the previous section, $k_z$-dependent effective couplings, $\lambda_i(k_z)$, can be defined. These couplings are shown in figure 4. The results for bilayer graphene correspond to $k_zc = 2\pi/3$, $4\pi/3$. The layers are decoupled for $k_zc = \pi$. In this case, the only coupling is $\lambda_1$, which gives the coupling for a single layer, given in equation (7).

The significant dispersion as a function of momentum parallel to the layers shown in figure 4 implies the existence of spin-dependent hoppings between layers in different unit cells. This is consistent with the analysis that showed that the spin–orbit coupling in a bilayer has a contribution from interlayer hopping, see equation (6).

The spin–orbit couplings can be larger in bulk graphite than in a graphene bilayer. The bands in Bernal graphite do not have electron–hole symmetry. The shift in Fermi energy with respect to Dirac energy is about $E_F \approx 20 \text{meV} \gg \lambda_1, \lambda_3$ [34]. Hence, the spin–orbit coupling is not strong enough to open a gap throughout the entire Fermi surface, and graphite will not become an insulator.
A similar analysis applies to rhombohedral graphite, which is characterized by the stacking sequence $ABCABC\ldots$ [35]. The electronic structure of this allotrope at low energies differs markedly from Bernal graphite [36, 37], and it can be a model for stacking defects [36]–[38]. If hoppings beyond nearest-neighbor layers are neglected, the Hamiltonian can be reduced to an effective one-layer Hamiltonian where all sites and all layers are equivalent. The only nonzero spin–orbit couplings are

$$\mathcal{H}_{\text{romb}}^{\text{so}} = \lambda_1 \sigma_z \tau_z s_z + \lambda_4 \sigma_z \left( \mu_y s_x + \mu_x s_y \right),$$

where we use the same notation as in the case of a bilayer. Unlike the case for Bernal stacking, the couplings do not have a significant dependence on the momentum perpendicular to the layers, $k_z$ (figure 5).

$$\lambda_1^{\text{romb}} = 0.022\,\text{meV},$$
$$\lambda_4^{\text{romb}} = 0.483\,\text{meV}.$$  

The largest coupling involves interlayer hopping, and it is of the same order as in Bernal graphite.

4. Conclusions

We have studied the intrinsic spin–orbit interactions in a graphene bilayer and in graphite. We assume that the origin of the couplings is the intra-atomic $\vec{L}\vec{S}$ interaction, and we use a tight binding model that includes the 2s and 2p atomic orbitals.

The intrinsic spin–orbit couplings in a graphene bilayer and in graphite are about one order of magnitude larger than in single-layer graphene, due to mixing between the $\pi$ and $\sigma$ bands by interlayer hoppings. Still, these couplings are typically of order 0.01–0.1 meV, that is, 0.1–5 K.

Bilayer graphene becomes an insulator with an even number of edge states. These states can be mixed by perturbations that do not break time reversal symmetry. These perturbations can only arise from local impurities with strong spin–orbit coupling, as a spin flip process and intervalley scattering are required.

The interplay of spin–orbit coupling and interlayer hopping leads to spin-dependent hopping terms.
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Note added. Since this work was released, related work has been posted; see [39, 40].

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