Kubo–Bastin approach for the spin Hall conductivity of decorated graphene

Jose H Garcia¹ and Tatiana G Rappoport¹

¹ ICTP South American Institute for Fundamental Research, Instituto de Física Teórica, UNESP-Universidade Estadual Paulista, 01140-070, Sao Paulo, SP, Brazil
² Instituto de Física, Universidade Federal do Río de Janeiro, Caixa Postal 68528, 21941-972 Río de Janeiro RJ, Brazil

E-mail: tgrappoport@if.ufrj.br

Keywords: spin Hall effect, graphene, adatoms

Abstract

Theoretical predictions and recent experimental results suggest one can engineer spin Hall effect in graphene by enhancing the spin–orbit coupling (SOC) in the vicinity of an impurity. We use a Chebyshev expansion of the Kubo–Bastin formula to compute the spin conductivity tensor for a tight-binding model of graphene with randomly distributed impurities absorbed on top of carbon atoms. We model the impurity-induced SOC with a graphene-only Hamiltonian that takes into account three different local contributions: intrinsic, Rashba and pseudospin inversion asymmetry SOCs (Gmitra et al 2013 Phys. Rev. Lett. 110 246602). We show how the spin Hall and longitudinal conductivities depend on the strength of the contributions and the concentration of impurities. Additionally, we calculate the real-space projection of the density of states in the vicinity of the Dirac point for single and multiple impurities and correlate these results with the conductivity calculations.

1. Introduction

Several non-magnetic materials with strong spin–orbit coupling (SOC) present electrically induced transverse spin-currents in the absence of an external magnetic field. This is commonly referred as spin Hall effect (SHE) because of its similarity with the regular charge Hall effect [2–4]. This class of materials may play an important role in spintronics, creating electrically controlled spin-polarized currents in non-magnetic systems, which can be used for spin injection [5].

The SOC in graphene is extremely weak, making the detection of the SHE impossible. However, it has high mobility and long spin relaxation times and it is a good candidate as spin conductor in spintronics [6]. It has been proposed that the functionalization of graphene with adatoms can produce a quantum spin Hall state (QSHE) [7] if the induced SOC has the same symmetry of the intrinsic spin–orbit (ISO) in graphene [8]. The observation of this state is experimentally challenging: adatoms can form clusters, introduce additional SOCs and break symmetries, destroying the topological state [9, 10]. Nevertheless, even without a quantized spin Hall conductivity, it is still possible to use both intrinsic and Rashba SOC to generate SHE in graphene with large spin Hall angles [11–14]. Recent experiments show that different adsorbed adatoms and metallic clusters induce a giant spin–orbit enhancement in graphene, [15–18], opening the possibility to use induced SOCs to create active graphene-based spintronic devices.

It has been reported experimentally that weakly hydrogenated [15] and fluorinated [17] graphene present an enhancement of the SOC of more than one order of magnitude with respect to pristine graphene, giving rise to SHE. The increase in the SOC in light adatoms is attributed to the transformation of the sp² bonds into sp³, breaking the mirror symmetry in graphene and inducing a local SOC [19]. Although the detailed physical mechanism of this enhancement is still unclear, a first step toward its understanding is the minimal effective tight-binding Hamiltonian proposed in [1, 20], where, with the help of group theory, the spin–orbit splitting obtained in DFT calculations is separated into different contributions: the well known ISO and Rashba couplings (RSO) and a novel contribution referred as pseudospin inversion asymmetry (PIA). Other effective tight-binding Hamiltonians that
take into account additional terms and/or deal with the adsorption of atoms in other positions had also been proposed [8, 21, 22].

Recently, we developed a real space implementation of the Kubo formalism to calculate the electronic conductivity tensor of large systems at finite temperatures [23] where we expand the Kubo–Bastin formula [24] in terms of Chebyshev polynomials [25, 26]. In this article, we extend the Kubo–Bastin formula to calculate the spin conductivity tensor and apply this modified Kubo formula to calculate the spin Hall conductivity of graphene decorated with adatoms. We consider a minimal tight-binding Hamiltonian that models the spin–orbit interaction of adatoms sitting at the T-site [1, 20, 27] and we calculate the spin and charge quantum transport of the system. We perform a systematic analysis of the contribution of each term of the effective Hamiltonian to the SHE for different concentrations and couplings. We also examine the real-space local density of states to gain a further insight on these mechanisms.

The article is organized as follows: in section 2 we present the effective tight-binding Hamiltonian for graphene with spin–orbit adatoms sitting at the T-site. In section 3 we discuss our numerical approach to calculate the charge conductivity tensor with the Chebyshev expansion of the Kubo–Bastin formula. We also present its extension to calculate the spin conductivity tensor. In section 4 we present a systematic numerical analysis of the charge and spin conductivity as a function of concentration and SOC and the local density of states for the different types of SOCs. Finally, in section 5 we present our conclusions.

2. SOC in graphene with adatoms

A minimal tight-binding model for adatoms adsorbed at the T site has been proposed recently [1, 20] where it is considered a Hamiltonian, based on the non-interacting one impurity Anderson Hamiltonian, of the form:

\[
H = H_0 + \sum_\sigma f_\sigma a_\sigma^\dagger a_\sigma + V \sum_\sigma (a_\sigma^\dagger f_\sigma + \text{h.c.}) + H_{SO},
\]

(1)

\(a_\sigma^\dagger\) and \(a_\sigma\) are the creation and annihilation operators of the carbon atom where the adatom is adsorbed, which in this case is defined as belonging to the A sublattice. \(\epsilon_0\) is the energy of the localized state of the adatom and \(f\) is the annihilation operator for the localized electrons. The third term describes the hybridization between the impurity and graphene and \(H_{SO}\) is a graphene only term that takes into account the local modification of the SOC in the presence of the adatom; its form is determined through group theory. The adatom degrees of freedom in the Hamiltonian of equation (1) can be integrated out and in the vicinity of the Dirac point, the impurity acts as a local potential of strength \(\epsilon_1 = -V^2/\epsilon_0\) [28].

The adsorption of adatoms at the T-site locally brakes the sub-lattice and out-of-plane mirror symmetry, allowing the existence of different spin–orbit terms. In [1], DFT calculations of weakly hydrogenated graphene are performed and the data is fitted with the model of equation (1). From this analysis, only three different spin–orbit contributions are necessary to fit the data:

\[
H_{SO} = H_I + H_R + H_{PIA},
\]

(2)

where \(H_{SO}\) is the local intrinsic SOC given by

\[
H_I = \frac{\lambda_I}{\sqrt{3}} \sum_{i,j \in G} |b_{ij}\rangle \langle \delta_{ij}|_\sigma \sigma b_{i\sigma}^\dagger + \text{h.c.},
\]

(3)

\(\lambda_I\) is the strength of the intrinsic SOC, \(G\) represents the set of nearest-neighbors of the carbon atom at the \(R_I\) position where the impurity was adsorbed, \(\delta_{ij}\) is a Pauli matrix acting on the spin \(\sigma\) and \(v_{ij} = \pm 1\) is dictated by the orientation of the hopping process (either clockwise or counterclockwise). \(H_R\) represents a local Rashba coupling that induces spin-flip hopping between the carbon atom at \(R_i\) and its nearest neighbors:

\[
H_R = \frac{2\lambda_R}{3} \sum_{(i,j)\sigma} |a_{i\sigma}^\dagger (\mathbf{\delta} \times \mathbf{d}_{ij})_{\pi,\sigma\sigma} b_{j\sigma} + \text{h.c.},
\]

(4)

where \(d_{ij}\) are the distances from \(R_i\) to the three nearest carbon atoms and \(\lambda_R\) is the strength of the Rashba SOC.

There is a third term that is related to the \(C_{3v}\) symmetry that emerges when an adatom is adsorbed in the top position. It describes spin-flip hoppings between next-nearest neighbors:

\[
H_{PIA} = \frac{2\lambda_{PIA}}{3} \sum_{(i,j)\sigma} |b_{i\sigma}^\dagger (\mathbf{\delta} \times \mathbf{D}_{ij})_{\pi,\sigma\sigma} b_{j\sigma} + \text{h.c.},
\]

(5)

where \(\lambda_{PIA}\) is the strength of the novel SOC. \(H_{PIA}\) is referred as PIA, which originates from the broken sublattice symmetry that makes the sites in A and B sublattices inequivalent in the vicinity of the adatom.

This term basically connects next nearest neighbors site with opposite spins. A schematic visualization of the three terms is given in figure 1. Several T-site adatoms had been examined and these contributions are enough to fit the DFT calculations. However, it is important to notice that the minimum model used to obtain the three different contributions to the SOC does not take into account inter-valley scattering. If inter-valley scattering is also considered, the symmetries of Hamiltonian allow for more contributions to the effective SOC [21, 29].

3. Chebyshev expansion of the Kubo–Bastin formula

The standard Kubo’s formula for the conductivity tensor \(\sigma_{\alpha\beta}(\mu, T)\) is a current–current correlation function [30, 31]
respectively and we can expand the Hamiltonian and velocities operators and the Green functions in the integrand of equation (7) in terms of Chebyshev polynomials using the kernel polynomial method [25, 26]. The first step to approximate the Green’s functions in terms of the Chebyshev polynomials is to rescale the Hamiltonian within the interval $[-\alpha, \alpha]$, with $\alpha \in (0, 1)$ being a given positive parameter. This can be done through the following linear transformation

$$
\hat{H} = \frac{2\alpha}{\Delta E} \left( H - \frac{E^+ + E^-}{2} \right),
$$

$$
\hat{\varepsilon} = \frac{2\alpha}{\Delta E} \left( \varepsilon - \frac{E^+ + E^-}{2} \right),
$$

where $E^-$ and $E^+$ are the minimum and maximum eigenvalue of the spectrum and $\Delta E \equiv E^+ - E^-$. In this article, we choose $\alpha = 0.9$. To estimate the bounds, we apply the power method [34], which is normally used to locate dominant eigenvalues in linear algebra. The rescaled Hamiltonian and energy are represented by $\hat{H}$ and $\hat{\varepsilon}$ respectively and we can expand the rescaled delta and Greens functions by considering their spectral representations $\delta(\hat{\varepsilon} - \hat{H}) = \sum_k |E_k\rangle \langle E_k| \delta(\hat{\varepsilon} - E_k)$ and $G^\pm(\hat{\varepsilon}, \hat{H}) = \sum_k |E_k\rangle \langle E_k| G^\pm(\varepsilon, \hat{H})$ and by expanding their eigenvalues in terms of the Chebyshev polynomials:

$$
\delta(\hat{\varepsilon} - \hat{H}) = \frac{2}{\pi \sqrt{1 - \hat{\varepsilon}^2}} \sum_{m=0}^M g_m \delta_m \frac{T_m(\hat{\varepsilon})}{\delta_m + 1} T_m(\hat{H}),
$$

$$
G^\pm(\hat{\varepsilon}, \hat{H}) = \frac{2i}{\sqrt{1 - \hat{\varepsilon}^2}} \sum_{m=0}^M g_m \hat{\varepsilon}^\pm \arccos(\hat{\varepsilon}) \delta_m \frac{T_m(\hat{\varepsilon})}{\delta_m + 1} T_m(\hat{H}),
$$

where $T_m(x) = \cos[m \arccos(x)]$ is the Chebyshev polynomial of the first kind and order $m$, which is defined according to the recurrence relation $T_m(x) = 2xT_{m-1}(x) - T_{m-2}(x)$. The expansion has a finite number of terms ($M$) and the truncation gives rise to Gibbs oscillations that can be smoothed with the use of a kernel, given by $g_m$. For the numerical results presented here, we use the Jackson kernel [25, 26].

Replacing the expansions above in equation (7) with $\Delta E = E^+ - E^-$, we obtain

$$
\sigma_{\alpha, \beta}(\mu, T) = \frac{i \hbar}{\Omega} \int_0^\infty dt \int_0^{1/\hbar T} d\lambda \langle \hat{\varepsilon}(\mu, T) i\hbar \hat{j}_\alpha(t + i\hbar\lambda) \rangle,
$$

where $\hat{j}_\alpha$ is the electronic current operator in the $\alpha$ direction and $\alpha, \beta = x, y, z, \lambda$ is a temperature-like variable [31]. $\hat{\varepsilon}(\mu, T, H) \equiv 1/(1 + e^{-(\mu N - H)/\hbar T})$ is a density matrix for a given chemical potential $\mu$ and temperature $T$ and $\Omega$ is the volume of the sample. This formula was deduced under very general conditions, requiring only that the electric field is weak enough for the linear response theory to be valid. In many cases, the electron–electron interaction is weak and one can rewrite equation (6) in the non-interacting electron approximation as the Kubo–Bastin formula [24]:

$$
\sigma_{\alpha, \beta}(\mu, T) = \frac{i e^2}{\hbar} \int_{E^-}^{E^+} d\varepsilon f(\varepsilon) \times \text{Tr} \left[ \nu_\alpha \delta(\varepsilon - H) v_\beta \frac{dG^\pm(\varepsilon)}{d\varepsilon} - v_\alpha \frac{dG^\mp(\varepsilon)}{d\varepsilon} v_\beta \delta(\varepsilon - H) \right],
$$

where $H$ and $v_\alpha$ are the non-interacting electron Hamiltonian and velocities operators and $f(\varepsilon)$ is the Fermi–Dirac distribution function for a given chemical potential $\mu$ and temperature $T$. In real space, the velocity operator $v$, can be expressed in terms of the eigenvalues of the position operator $[R_i]$, $i = 1, ... D$ and the Hamiltonian’s matrix elements by using the Heisenberg relation

$$
v = \frac{1}{\iota \hbar} \{ R_{\alpha}, H \} = \frac{1}{\iota \hbar} \sum_{i=1}^D (R_i - R_{\alpha}) H_{\alpha i} [R_i] \langle R_i |. \tag{8}
$$

This particular form is very useful for tight-binding Hamiltonians, where in general the value of matrix elements connecting distant sites is zero.

Our method, presented in [23] and applied to quantum transport calculations of different solid state systems [14, 32, 33] consists in expanding the Green’s functions in the integrand of equation (7) in terms of Chebyshev polynomials using the kernel polynomial method [25, 26].
\[ \sigma_{\alpha \beta} (\mathbf{T}, \mathbf{J}) = \frac{4e^2}{\pi \Omega} \int_{-1}^{1} \frac{d\xi}{(1 - \xi^2)^2} \sum_{m,n} \Gamma_{mn}(\xi) \mu_{mn}^{\alpha \beta} \] (12)

\[ \mu_{mn}^{\alpha \beta} \] are the expansion moments of the polynomial expansion and \( \Gamma_{mn}(\xi) \) are the expansion functions. The moments

\[ \mu_{mn}^{\alpha \beta} \equiv \frac{\delta_m \delta_n}{(1 + \delta_m)(1 + \delta_n)} \text{Tr} [\mathbf{v}_n T_{m}(\mathbf{H}) \mathbf{v}_j T_{n}(\mathbf{H})] \] (13)

do not depend on the energy. Since \( \mu_{mn}^{\alpha \beta} \) involves products of polynomial expansions of the Hamiltonian, its calculation is responsible for most of the computational cost. On the other hand, \( \Gamma_{mn}(\xi) \) is a scalar that is energy dependent but independent of the Hamiltonian and is given by

\[ \Gamma_{mn}(\xi) \equiv [ (\xi - i \sqrt{1 - \xi^2}) e^{-i \arccos(\xi)} T_m(\xi) + (\xi + i \sqrt{1 - \xi^2}) e^{-i \arccos(\xi)} T_n(\xi)] . \] (14)

As shown in equation (12), once the coefficients \( \mu_{mn}^{\alpha \beta} \) are determined, we can obtain the conductivities for all temperatures and chemical potentials without repeating the most time-consuming part of the calculation [35]. Moreover, the recursive relations between Chebyshev polynomials lead to a recursive multiplication of sparse Hamiltonian matrices that can be performed in a very efficient way in GPUs [36, 37]. Instead of the full calculation of traces, we use self-averaging properties, normally used in Monte-Carlo calculations, to replace the trace in the calculation of \( \mu_{mn}^{\alpha \beta} \). With this method, known as random phases vector approximation [25, 26, 38], we construct a set of \( R \ll N \) complex vectors

\[ |r \rangle \equiv (\xi_1^+, \ldots, \xi_N^+) , \quad r = 1, \ldots, R, \] (15)

with dimension equal to \( N \) and whose elements \( \xi_i^+ \) are drawn from a probabilistic distribution with the following characteristics:

\[ \langle \xi_i \rangle = 0 , \quad \langle \xi_i \xi_j \rangle = \delta_{i\gamma} \delta_{ij} \] (16)

where \( \langle \ldots \rangle \) is the statistical average. The trace can be calculated as the average expected value of this random vector and the convergence of the approximation \( \delta_R \) as function of the number of random vectors \( R \) follows a relation of the type

\[ \delta_R \propto (DR)^{-1/2} . \] (17)

Therefore, for large systems we can obtain the same accuracy with less random vectors. Moreover, the fact that the accuracy depends on \( DR \) instead of only \( R \) is useful because the convergence rate can be tested for small systems and the results can be extrapolated to obtain the adequate \( R \) for higher \( D \) without having to perform the set of numerical simulations required to perform the convergence analysis. The conductivities are averaged over several disorder realizations, \( S \), with \( R \) random vectors for each of them. Because of the self-averaging properties of large systems, the product \( SR \) is the main defining factor of the accuracy of the trace operation. For more details about the convergence of the conductivity as a function of \( SR \), see the supplementary information of [23].

3.1. The Kubo–Bastin formula for spin-conductivity

The Kubo–Bastin formula presented in [23], was derived for spinless non-interacting electrons. To study the SHE numerically, it is necessary to extend this formula to calculate the spin Hall conductivity \( \sigma_{sH} \). This was done in details in [39] by replacing the first velocity operator in equation (7) by the spin-current operator \( \mathbf{j}_s \) defined as:

\[ \mathbf{j}_s = \frac{1}{2\Omega} \{ \mathbf{s}_\gamma , \mathbf{v}_\gamma \} , \] (18)

where \( s_\gamma \) is the spin operator and \( \gamma = x, y, z \). This substitution leads to the following Kubo–Bastin formula for spin-conductivity [39]:

\[ \sigma_{s,H,\gamma}^{\alpha \beta} = i e \hbar \int_{-\infty}^{\infty} dx \frac{df (x)}{dx} \times \text{Tr} \left\{ \mathbf{j}_s^2 \delta (x - H) \mathbf{v}_\gamma \frac{dG^{\gamma \gamma} (x)}{dx} \right. \\
\left. - \mathbf{j}_s^2 \frac{dG^{\gamma \gamma} (x)}{dx} \mathbf{v}_\gamma \delta (x - H) \right\} . \] (19)

Then, the Chebyshev approximation can be performed in an analogous way as the one described in [23], by modifying the moments

\[ \mu_{mn}^{\alpha \beta} \rightarrow \mu_{mn}^{\alpha \beta, \gamma} = \text{Tr} [T_{m}(H) \mathbf{j}_s^2 T_{n}(H) \mathbf{v}_\gamma] . \] (20)

A generalized Kubo formula for spin transport can also be obtained using non-abelian fields, which consider also external fields acting on the spin [40]. However for the present purpose, the spin Kubo–Bastin formula is adequate.

4. Numerical calculations

To gain an insight into the effect of the locally induced SOC in the spin and charge conductivities of graphene, it is necessary to analyze the role of the three different contributions of the SOC separately, that are referred here as ISO, RSO and PIA impurities. In this section, we perform a systematic analysis of the spin and charge conductivities of graphene in the presence of randomly distributed spin–orbit impurities as a function of the impurity concentration and the intensity of the coupling of each of the three contributions. For the numerical calculations, we consider a honeycomb lattice with \( D = 2 \times N \times N \) with \( N = 200 \) sites with periodic boundary conditions. For the statistical analysis we use \( R = 20 \) random vectors and \( S > 40 \) disorder realizations such that \( SR > 800 \), necessary to achieve the convergence of the conductivities in the region of interest (for details, see supplementary information of [23]). All the conductivity calculations were performed using the same temperature \( T = 0.01 \). The systematic analysis as a function of the strength of the coupling was performed considering
different values of the SOC at a fixed concentration of adatoms \( x = 0.2 \). For simplicity, we do not take into account any local potential in the carbon site where the adatom is located.

We begin our analysis by considering the effect of \( H_I \). In figure 2 we show the KPM numerical calculations with \( M = 1600 \) moments for a honeycomb lattice decorated with a random distribution of pure intrinsic adatoms \((\lambda_R = \lambda_{\text{PIA}} = 0)\). The density of states is shown in figure 2(c) where the presence of a band gap is observed. This gap translates into a region of zero longitudinal conductivity, shown in figure 2(a). For this concentration, the value of the gap follows the following relation

\[
\Delta_{\text{ISO}} \propto x \lambda_I,
\]

which is consistent with Kane and Mele [7] model rescaled by the concentration and agrees with previous numerical calculations [23, 32]. For intensities below \( \lambda_I = 0.1t \), the gaps close due to the effect of the temperature. In figure 2(b) we can see that inside the gap, the system presents a quantized spin Hall conductivity as expected from Kane and Mele model. However, we observe that a robust spin Hall conductivity still persists outside the gapped region, a fact that can be important in experiments where the strength of the coupling can be seen in figure 2(f) where the presence of the band gap is observed. This gap translates into a region of zero longitudinal conductivity, shown in figure 2(a). For this concentration, the value of the gap follows the following relation

\[
\Delta_{\text{ISO}} \propto x \lambda_I,
\]

which is consistent with Kane and Mele [7] model rescaled by the concentration and agrees with previous numerical calculations [23, 32]. For intensities below \( \lambda_I = 0.1t \), the gaps close due to the effect of the temperature. In figure 2(b) we can see that inside the gap, the system presents a quantized spin Hall conductivity as expected from Kane and Mele model. However, we observe that a robust spin Hall conductivity still persists outside the gapped region, a fact that can be important in experiments where the strength of the ISO coupling is usually small and the gap is closed by disorder and/or temperature.

In figure 3, the same analysis is performed for a fixed coupling strength and different concentrations. For these values of concentration, the behavior is similar to the previous case. One can see a topological gap whose size scales as \( \Delta_I \propto x \lambda_I \), with a robust spin Hall conductivity outside the gap. In experiments, the concentration is much smaller than the ones considered here, and this linear scaling of the gap with concentration might change below some critical concentration. However, the robust spin Hall conductivity for both low concentration and weak coupling, even in the absence of the topological gap, may play an important role in experimental results.

Our analysis for a distribution of pure Rashba spin–orbit impurities \((\lambda_I = \lambda_{\text{PIA}} = 0)\) as a function of the strength of the coupling can be seen in figure 4, where we keep the concentration fixed \((x = 0.2)\). In the density of states shown in figure 4(c), we notice the presence of new states at the neutrality point. These states produce a slight increase in the minimum of the longitudinal conductivity for increasing values of the SOC, as can be seen in panel 4(a). At the same time, the Rashba coupling strongly suppresses the longitudinal conductivity away from the charge neutrality point, decreasing the mobility of graphene. As expected, the spin Hall conductivity changes signs with the energy and it is zero at the Dirac point (see figure 4(b)). However in the vicinity of the \( E = 0 \) there is a rapid increase of the spin Hall conductivity that saturates at \( \pm e/(2\pi) \), which is consistent with analytical calculations for the SHE in graphene with homogeneous RSO [41]. The transition from negative to positive spin Hall conductivity as a function of the chemical potential gets more abrupt for weak \( \lambda_R \). Surprisingly, this translates into an increase of the SHE in the vicinity of the neutrality point for decreasing values of \( \lambda_R \), as shown in figure 4(d). RSO breaks the spin degeneracy and there are two non-degenerate bands for electrons at the Dirac point. For the case of \( x = 1 \), the sharp increase of the spin Hall conductivity occurs at energies of the order of the Rashba splitting between the bands at energy scales where the DOS presents the contribution of a single band. A similar behavior is
seen for $x = 0.2$ with the Rashba splitting scaled with the concentration.

In figure 5 we show the results as a function of the concentration, fixing the RSO coupling in $\lambda_{RSO} = 0.4t$. Again, the conductivity minima increases progressively for increasing concentrations (see figure 5(a)). The dependence of the spin Hall conductivity with concentration is shown in figure 5(b), where we see a rapid increase in the spin Hall conductivity in the vicinity of the Dirac point when the concentration is reduced. Furthermore, figure 5(d) indicates a dependency of $1/x$ for the spin Hall conductivity at a fixed chemical potential close to the neutrality point up to $x = 0.05$. This suggests that the spin Hall conductivity generated by Rashba must be extremely relevant in experiments: it is larger for low concentrations and weak Rashba SOC, as it is expected for graphene with adatoms. However, lower concentrations of impurities, not accessible in the present analysis, may affect the SHE in a different way and modify the dependency with $x$. 

Figure 3. Graphene decorated with a random distribution of ISO-impurities ($\lambda_E = \lambda_{PIA} = 0$) sitting at the $T$-site. $D = 2 \times 200 \times 200$ sites, $\lambda_I = 0.4t$ and $M = 1600$. (a) Longitudinal conductivity (b) spin Hall conductivity as a function of the chemical potential for increasing values of the concentration $x$. (c) Density of state (d) spin Hall conductivity as a function of the concentration for different values of the Fermi energy: (black) $0.02t$, (red) $0.05t$, (blue) $0.1t$.

Figure 4. Graphene decorated with a random distribution of RSO-impurities ($\lambda_I = \lambda_{PIA} = 0$) sitting at the $T$-site. $D = 2 \times 200 \times 200$ sites, concentration of $x = 0.2$ and $M = 800$. (a) Longitudinal conductivity and (b) spin Hall conductivity as a function of the chemical potential for increasing values of the intensity of the ISO coupling. (c) Density of state (d) spin Hall conductivity as a function of the spin–orbit intensity for different values of the Fermi energy: (black) $0.05t$, (red) $0.1t$, (blue) $0.5t$. 

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Figure 6 presents the results for pure PIA impurities ($\lambda_l = \lambda_R = 0$) for increasing SOC with $x = 0.2$ and $M = 800$. In the density of states, shown in figure 6(c), we can see the emergence of new states in the vicinity of the Dirac point. These new states translate in a decrease of the electronic mobility (see figure 6(a)). Figure 6(b), displays the spin Hall conductivity that has a maximum at high energies with a value that depends directly on the coupling intensity. In figure 6(d) we show the behavior of the spin Hall conductivity in the vicinity of the neutrality point. In contrast with the RSO, for PIA, the spin Hall conductivity increases with the coupling strength and it is small (tending to zero) in the low coupling regime.

Finally, we consider $\lambda_{PIA} = 0.4t$ and display the results as a function of the concentration $x$ (figure 7). In the density of states shown in figure 7(c), we can see again the presence of new states in the vicinity of the Fermi energy, which also generate a decrease in the longitudinal conductivity (see figure 7(a)). In figure 7(b) one can see that the spin Hall conductivity quickly reaches a maxima at high energy as a function of the
concentration. Near the neutrality point, the behavior is shown in Figure 7(d), where the spin Hall conductivity increases with concentration and tends to zero for small concentrations. Our results show that PIA induces new localized states in the vicinity of the neutrality point. They also indicate that the SHE induced by PIA must be negligible under realistic experimental conditions were the SOC is weak and the concentrations are small.

For many spintronic applications, the spin Hall angle $\gamma_{\text{SH}} = \sigma_{\text{sH}}/\sigma_{xx}$, which is the ratio between the spin Hall conductivity and the longitudinal conductivity, is the most relevant parameter. Here, we opted to present systematic analysis in terms of the spin Hall conductivity because $\gamma_{\text{SH}}$ is often used for metals but does not have a physical meaning in the case of a topological insulator, where $\sigma_{xx} = 0$. For easy comparison with experimental analysis, we show in Figure 8 $\gamma_{\text{SH}}$ for the different contributions in the limit of weak coupling and low impurity concentration, such that the system with ISO impurities is metallic. We can see that $\gamma_{\text{SH}}$ is extremely large for ISO impurities. This is a result of the zero temperature spin–orbit induced gap. RSO also give rise to large $\gamma_{\text{SH}}$. However, for experimental conditions, where the SOCs range from 1 to 200 meV and the concentrations are of the order of $x = 0.01$, we expect a decrease of $\gamma_{\text{SH}}$ for ISO, as the system becomes more and more metallic, while $\gamma_{\text{SH}}$ for RSO has a tendency to increase in the vicinity of the Dirac point: the spin Hall conductivity is very large in that limit while, for low energies, the longitudinal conductivity is not substantially affected by the impurities.

To better understand how the three SOCs affect the electronic properties of graphene, we computed the local density of states LDOS in real-space $p_\rho(\varepsilon)$:

$$p_\rho(\varepsilon) \equiv \langle R_\rho \mid \delta (\varepsilon - H) \mid R_\rho \rangle = \mp \frac{1}{\pi} \text{Im} \{G_{\rho\rho}(\varepsilon)\}.$$

(21)

Following the definition above, $p_\rho(\varepsilon)$ can be considered as the number of available states, for a given
energy, at a given lattice site. It can also be expressed as a Chebyshev series and computed numerically\[42].

Figures 9(a)–(c) display the effect of an isolated adatom. We can see that the symmetry of each coupling, presented in figure 1, has a characteristic fingerprint in the local density of states.

Additionally, RSO and ISO couplings have a weak effect on the LDOS with variations of the order of 2\% with respect to the mean value. The deviations on the LDOS due to these two terms extends over three lattice constants and there is a reduction of the LDOS at the adsorption site accompanied by an increment of the LDOS in nearest and next–next nearest neighbors. This behavior indicate that the new states created by RSO and ISO impurities are extended. On the other hand, PIA has a different behavior: the effect on the LDOS is very localized, covering a region of only a single lattice constant, with a variation of the LDOS of the order of 20\%.

In figures 9(d)–(f) we show the effects of a distribution of adatoms for a concentration of $x = 0.2$. We can see that for RSO and ISO impurities, there are small variations of the LDOS at extended regions, which support the previous results where extended states were predicted. For PIA, there are small regions with a concentrated LDOS which is consistent with the picture of states that are more localized.

5. Summary

We presented an extension of the Chebyshev expansion of the Kubo–Bastin formula to calculate the spin Hall conductivity at finite temperature. We applied it to study the spin and charge transport resulting from adsorbed adatoms that induce SOC in graphene. We considered a minimal tight-binding model with three different SOC terms and performed a systematic
analysis of the quantum transport for each of them in terms of concentration and coupling strength.

For the intrinsic SOC, where the appearance of a QSHE is expected, we observed a linear dependence of the size of the gap with the concentration of atoms, for all cases considered here. We also showed the presence of robust spin Hall conductivity outside the topological gap. We found that Rashba induces robust spin Hall conductivity for low concentrations and weak coupling which is an important limit to compare with experimental results. Conversely, PIA tends to localize electrons and does not contribute to the spin Hall conductivity in the low concentration and weak coupling limit. In conclusion, both intrinsic and Rashba SOCs should be relevant in the regime of parameters that are typically found in experiments. Furthermore, even at finite temperatures and in the presence of disorder, they can give rise to non-quantized but sizable spin Hall conductivities.

Acknowledgments

TGR acknowledges the financial support of the Brazilian agency CNPq (Grants No. 477877/2013-3 and 307705/2013-7) and The Royal Society (UK) through a Newton Advanced Fellowship. JHG is grateful to Prof Alexandre Rocha for hosting him in IFT where this work was completed and also acknowledges the financial support of the Sao Paulo Research Foundation (FAPESP) under grants 2011/11973-4 and 2015/09434-9.

References

[1] Gmitra M, Kochan D and Fabian J 2013 Phys. Rev. Lett. 110 246602
[2] Dyakonov M I and Khaetskii A V 2008 Spin Hall effect Spin Physics in Semiconductors (Berlin: Springer) pp 211–43
[3] Kato Y K, Myers R C, Gossard A C and Awschalom D D 2004 Science 306 1910
[4] Sih V, Myers R C, Kato Y K, Lau W H, Gossard A C and Awschalom D D 2005 Nat. Phys. 1 31
[5] Jungwirth T, Wunderlich J and Olejnik K 2012 Nat. Mater. 11 382
[6] Han W, Kawakami R K, Gmitra M and Fabian J 2014 Nat. Nanotechnol. 9 794
[7] Kane C L and Mele E J 2005 Phys. Rev. Lett. 95 226801
[8] Weeks C G, Hu J, Alicea J, Franz M and Wu R 2011 Phys. Rev. X 1 021001
[9] Jiang H, Qiao Z, Liu H, Shi J and Niu Q 2012 Phys. Rev. Lett. 109 116803
[10] Cresti A, Van Tuan D, Soriano D, Cummings A W and Roche S 2014 Phys. Rev. Lett. 113 246603
[11] Ferreira A, Rappoport T G, Cazalilla M A and Castro Neto A H 2014 Phys. Rev. Lett. 112 066601
[12] Milletari M and Ferreira A 2016 arXiv:1601.08076 [cond-mat.mes-hall]
[13] Huang C, Chong Y D and Cazalilla M A 2016 arXiv:1603.08107 [cond-mat.mes-hall]
[14] Van Tuan D, Marmolejo-Tejada J M, Waintal X, Nikolic B K and Roche S 2016 arXiv:1603.03870 [cond-mat.mes-hall]
[15] Balakrishnan J, Kok Wai Koon G, Jaiswal M, Castro Neto A H and Ozyilmaz B 2013 Nat. Phys. 9 284
[16] Balakrishnan J et al 2014 Nat. Commun. 5 4748
[17] Avsar A, Lee J H, Koon G K W and Ozyilmaz B 2015 2D Mater. 2 044009
[18] Calleja F et al 2015 Nat. Phys. 11 43
[19] Castro Neto A H and Guinea F 2009 Phys. Rev. Lett. 103 026804
[20] Irmer S, Frank T, Putz S, Gmitra M, Kochan D and Fabian J 2015 Phys. Rev. B 91 115141
[21] Pachoud A, Ferreira A, Ozyilmaz B and Castro Neto A H 2014 Phys. Rev. B 90 035443
[22] Brey L 2015 Phys. Rev. B 92 235444
[23] Garcia J H, Covaci I and Rappoport T G 2015 Phys. Rev. Lett. 114 6602
[24] Bastin a, Lewiner C, Betbeder-matibet O and Nozieres P 1971 J. Phys. Chem. Solids 32 1811
[25] Silver R, Roeder H, Voter A and Kress J 1996 J. Comput. Phys. 124 115
[26] Weilea A, Wellein G, Alvermann A and Fehske H 2006 Rev. Mod. Phys. 78 275
[27] Konschuh S, Gmitra M and Fabian J 2010 Phys. Rev. B 82 245412
[28] Uchoa B, Yang L, Tsiat S W, Peres N M R and Castro Neto A H 2009 Phys. Rev. Lett. 103 206804
[29] Asmar M M and Ulloa S E 2015 Phys. Rev. B 91 165407
[30] Kubo R 1957 J. Phys. Soc. Japan 12 570
[31] Mahan G D 2000 Many–Particle Physics (Berlin: Springer)
[32] Liu Z, Zhu M and Zheng Y 2015 Phys. Rev. B 92 245438
[33] Yuan S, Katsnelson M I and Roldán R 2015 arXiv:1512.06345 [cond-mat.mes-hall]
[34] Kincaid D R and Cheney E W 2002 Numerical Analysis: Mathematics of Scientific Computing vol 2 (Providence, RI: American Mathematical Society)
[35] Weisse A 2004 Eur. Phys. J. B 40 125
[36] Covaci I, Peeters F and Berciu M 2010 Phys. Rev. Lett. 105 167006
[37] Harju A, Sirol T, Canova F, Hakala S and Rantalaaho T 2013 Computational physics on graphics processing units Applied Parallel and Scientific Computing: 11th Int. Conf. Para 2012 (Helsinki, Finland, 10–13 June 2012) (Berlin: Springer) pp 3–26 revised selected papers
[38] Iitaka T and Ebisuzaki T 2004 Phys. Rev. E 69 057701
[39] Yang M F and Chang M C 2006 Phys. Rev. B 73 073304
[40] Jin P Q and Li Y Q 2006 Phys. Rev. B 74 085315
[41] Dyrdal A, Dugaev V K and Barnaś J 2009 Phys. Rev. B 80 155444
[42] Garcia J H, Uchoa B, Covaci I and Rappoport T G 2013 Phys. Rev. B 90 085425