Electronic and Spin Transport in Dirac-Like Systems

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This dissertation titled
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**Abstract**

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In this dissertation we study transport properties of graphene within the low energy Dirac approximation. We utilize partial wave scattering methods and relate the scattering matrix elements to physical observables such as the elastic time, transport time, and skewness of scattering. We suggest that experimentally measurable quantities, such as the transport to elastic time ratio, indicate the presence of perturbations that lead to the reduction of symmetries of graphene, as well as spin-orbit interactions. This result relies on the fact that perturbations that leave graphene symmetries untouched, such as potential scatterers, display a constant ratio of transport to elastic times at low energies, making this ratio robust to random scatterer size and strength disorder. We also show that this ratio is not robust to either symmetry breaking perturbations or spin-orbit interactions, as these interactions lead to the ratio deviating from its ideal value. Even though both kinds of perturbations, symmetry breaking and spin-orbit interactions, lead to changes in the ratio, we show that the qualitatively different dependence on energy for each of these perturbations allows the experimental identification and quantification of both effects simultaneously.

We have also shown, in relation to the spin Hall effect detection in graphene, that even though the local enhancement of spin-orbit interactions leads to the appearance of a spin Hall effect signal robust to potential and size disorder, the breaking of effective time reversal symmetry through local perturbations leads to the appearance of a valley Hall effect through skew scattering. This valley skew processes contribute to the non-local resistance that helps quantify the Hall effect. Similarly, we show that multiple potential scatterers with space dependence that breaks parity in graphene, also lead to the
appearance of a valley Hall effect due to the separation of electrons from different valleys in space through skew scattering. These results suggest that measured spin Hall effect in graphene is not robust to the latter perturbations, indicating that this effect may not be completely produced by local enhancement of spin orbit interactions alone, but as suggested before, may be accompanied by a competing valley Hall effect that overestimates the measured effect.

Finally, in the high energy regime we show that long-lived quasi-bound states in graphene gated regions mimic the behavior of whispering gallery modes. In the limit of electron optics, we have also shown how gated regions in graphene are analogous to lenses with variable index of refraction, and that the presence of spin-orbit interactions makes these lenses birefringent, with a degree of birefringence that indicates the strength of the spin-orbit enhancement.
In the loving memory of my father.

To my beloved mother, sisters and brother.
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6.1 NP interface with source of electrons in the n-region positioned at a distance $a$ from the interface. Diverging electron paths in the n region get focused at a point $|n|a$ in the p-region, where $|n|$ is the electronic index of refraction. The position of the focal point can be controlled through the gate $V$. If $|n|a = 0.5a$ then $V = 3E/2$, in order to obtain $n = -0.5$, and change in character of the region from $n$ to $p$, which discards the possibility of $V = E/2$. 
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7.3 a) Differential cross section, $\sigma(\theta)/\max(\sigma(\theta))$, produced by the scattering of an incoming electron along the $x$-axis, with energy $E = 1$ meV, towards two scatterers with equal radii, $a_1 = a_2 = 10$ Å, and equal potentials $V_1 = V_2 = 2$ eV. The two scattering centers symmetrically placed from the global origin along the $x$-axis (see inset in c)), at distance $R_{12}/2 = d_{12}/2 + a_1$ from the global origin. b) Differential cross section for a configuration of two scatterers with the same parameters as in a), but with their centers along the $y$-axis (see inset in d)). c) Scaling of $\max(\sigma(\theta))$ with scatterers separation for the configuration shown in the inset. d) c) Scaling of $\max(\sigma(\theta))$ with scatterers separation for the configuration shown in the inset. Notice that in these two cases, $\sigma(\theta)/2 = \sigma_{\tau\tau}(\theta)$, as $\max(\sigma(\theta))/2 = \max(\sigma_{\tau\tau}(\theta))$, where $\tau = (K, K')$.

7.4 a) Differential cross section, $\sigma_{KK}(\theta)/\max(\sigma_{KK}(\theta))$, produced by scattering of $K$-polarized incident flux along the $x$-axis, with energy $E = 1$ meV, towards two scatterers with radii, $a_1 = a_2 = 10$ Å, and equal potentials $V_1 = V_2 = 2$ eV. The two scatterers centers are along the $x = y$ direction, and symmetrically located about the global origin at a distance $R_{12}/2 = d_{12}/2 + a_1$ (see inset in d)). b) Differential cross section $\sigma_{KK'}(\theta)/\max(\sigma_{KK'}(\theta))$ for same two scatterers as in a), but for a $K'$-polarized electron. c) Differential cross section for a valley unpolarized incident flux, $\sigma(\theta)/\max(\sigma(\theta))$, for the configuration of scatterers in a). d) Scaling of $\max(\sigma(\theta))$ with scatterers separation for the scatterer configuration shown in the inset. Notice the strong angular angular asymmetry for $d_{12} \leq 5a_1$ valley cross sections disappears in $\sigma(\theta)$.
7.5 a) Differential cross section, $\sigma_{KK}(\theta)/\max(\sigma_{KK}(\theta))$, produced by scattering of and incoming $K$-polarized flux, along the $x$-axis, with energy $E = 1$ meV, towards two scatterers with equal radii, $a_1 = a_2 = 10$ Å, but asymmetric potentials $V_1 = -V_2 = 2$ eV. The two scatterers centers are along the $y$-axis, and symmetrically placed at $R_{12}/2 = d_{12}/2 + a_1$ from the global origin (see inset in e)). b) Differential cross section $\sigma_{K'K'}(\theta)/\max(\sigma_{K'K'}(\theta))$ for a configuration of two scatterers with the same parameters as in a), for a $K'$-polarized electron. c) Differential cross section for valley unpolarized incoming flux, $\sigma(\theta)/\max(\sigma(\theta))$ and system as in a). d) Differential cross section, $\sigma(\theta)/\max(\sigma(\theta))$, for scatterers with the same parameters as in a) but with their centers along the $x$-axis, and symmetrically placed at $R_{12}/2$ from the global origin. e) Scaling of $\max(\sigma(\theta))$ with scatterers separation for the scatterer configuration shown in the inset. d) Scaling of $\max(\sigma(\theta))$ with scatterers separation for the scatterer configuration shown in the inset.

7.6 Differential cross section, $\sigma_{KK}(\theta)/\max(\sigma_{KK}(\theta))$, produced by scattering of and incoming, $K$-polarized flux along the $x$-axis, with energy $E = 1$ meV, towards two scatterers with equal radii, $a_1 = a_2 = 10$ Å, but asymmetric potentials $V_1 = -V_2 = 2$ eV. The two scatterers centers are along the $x = y$ direction, and symmetrically placed at $R_{12}/2$ from the global origin (see inset in e)). b) Differential cross section $\sigma_{K'K'}(\theta)/\max(\sigma_{K'K'}(\theta))$ for a configuration of two scatterers with the same parameters as in a), for a $K'$-polarized electron. c) Differential cross section for valley unpolarized incoming flux, $\sigma(\theta)/\max(\sigma(\theta))$, for the configuration of scatterers in a). Scaling of $\max(\sigma(\theta))$ with scatterers separation for the scatterer configuration shown in a). Scaling of $\max(\sigma(\theta))$ with scatterers separation for the scatterer configuration shown in the inset.

7.7 Differential cross section, $\sigma_{KK}(\theta)/\max(\sigma_{KK}(\theta))$, $K$-polarized incoming flux, along the $x$-axis, with energy $E = 1$ meV, towards two scatterers with radii, $a_1/2 = a_2 = 10$ Å, and equal potentials $V_1 = V_2 = 2$ eV. The two scatterers centers are along the $y$-axis, and symmetrically separated from the origin. b) Differential cross section $\sigma_{K'K'}(\theta)/\max(\sigma_{K'K'}(\theta))$ for same configuration as in a) for a $K'$-polarized electron. c) Differential cross section for valley unpolarized flux, $\sigma(\theta)/\max(\sigma(\theta))$, for the configuration of scatterers in a). d) Scaling of $\max(\sigma(\theta))$ with scatterers separation for the scatterer configuration shown in the inset.

7.8 a) Valley skew parameter for a system of two scatterers with $a_1 = a_2 = 10$ Å and $V_1 = V_2 = 2$ eV located at $R_{12}/2 = d_{12}/2 + a_1$ from the global origin, for incoming electrons along the $x$-axis with energy $E = 1$ meV, (inset shows the scatter configuration). b) Valley skew parameter for a system of two scatterers with $a_1 = a_2 = 10$ Å and $V_1 = -V_2 = 2$ eV and located at $R_{12}/2 = d_{12}/2 + a_1$ from the global origin, for incoming electrons along the $x$-axis with an energy $E = 1$ meV. (inset shows the scatter configuration).
7.9 Schematic representations of different configurations of potential scatterers on the underlying graphene lattice. a) This configuration preserves parity in the system, and does not produce skew scattering. b) This configuration breaks parity and leads to the formation of valley currents via skew scattering. Incident currents are assumed along the $x$-axis.
1 INTRODUCTION

Graphene [1], a single layer of carbon atoms is the first, and one of the most intriguing, two-dimensional materials. The discovery of graphene has stimulated numerous theoretical and experimental works [1], opening new doors for promising new technology due to its low dimensionality and high carrier mobility. The low energy band structure and the form of the underlying Hamiltonian are reminiscent of those for massless fermions, usually studied in high-energy physics, with some relevant differences. First, the massless Dirac-like electrons in graphene are constrained to move in two spatial directions. Second, Dirac fermions in graphene originate from a $\mathbf{k} \cdot \mathbf{p}$ expansion around special points in the graphene dispersion, an approximation valid for wave vectors in a disk of radius smaller than the inverse of the lattice spacing. Third, the characteristic velocity of the massless Dirac fermions in graphene is not the speed of light but the Fermi velocity, which is two orders of magnitude smaller than the former. Finally, the geometry of the honeycomb graphene lattice and its symmetries play a crucial role in the existence of massless Dirac fermions at low energies. The latter point made the realization of two dimensional Dirac-like materials possible in artificial systems that mimic and contain the set of symmetries that facilitate the existence of Dirac fermions in graphene at low energies [2–4].

The helical nature of massless Dirac fermions, reflected by the unique parallel/anti-parallel projection of the pseudospin in the direction of motion, makes the electron dynamics in this material interesting. Interesting experiments have confirmed the helical nature of electrons in graphene, including: the observation of what is known as Klein tunneling [5]—the absence of back scattering of normal incident fermions from gated obstacles, the observation of weak antilocalization in graphene [6], and the observation of a constant ratio of transport to elastic times which characterizes Dirac fermion scattering from potential obstacles at low energies [7].
The presence of Dirac fermions in graphene at low energies is compromised by different kinds of disorder naturally present or artificially introduced (artificial decoration). Defects or deformations lead to drastic changes in the helical nature of charge carriers in graphene, as perturbations reduce the set of lattice symmetries that make the existence of massless Dirac fermions in graphene possible in the first place. Symmetry breaking effects in graphene can be described as global or local perturbations to the Dirac Hamiltonian. Effects of these perturbations will lead to different signatures from those expected from helical carriers, as we will explore.

Spintronics [8], is a field of condensed matter that aims to achieve the injection, control and manipulation of electron spins in electronic devices. An important factor in spintronics are spin-orbit interactions, as these interactions allow the manipulation of the electrons spins via electric fields. In graphene, lattice symmetries allow the appearance of a spin-orbit interaction, known as intrinsic [9]. On the other hand, the breaking of \((z \rightarrow -z)\) symmetry of graphene allows for the appearance of the Rashba spin-orbit interaction [9, 10]. Even though symmetry considerations anticipate the appearance of these interactions in graphene, the low atomic number of carbon make for a very weak intrinsic interaction [11]. Similarly, the Rashba spin-orbit interaction generated by electric fields is also somewhat limited [11]. The field of spintronics in graphene has not stopped there, as the decoration [12–16], deposition [17–19], and deformation [20–22] of the graphene lattice lead to sizable enhancement of the spin-orbit interaction in graphene. However, as the methods that lead to the enhancement of spin-orbit interactions in graphene lead also to the reduction of lattice symmetries they also lead to characteristic deviations from ideal behaviour in spin phenomena.

Now, a question of significant importance arises: Can we identify and quantify the effects of symmetry breaking and spin-orbit interactions in graphene via transport measurements? As the reader may expect the answer to this question is yes! The answer
to the question how is what this dissertation addresses. The road to answer that simple
question was paved by important contributions to the field of electronic and spin transport
in Dirac-like systems in general, and in graphene in particular. Our major contribution to
this field rests on gaining a strong theoretical insight on the deep relation between the
symmetries of a given quantum mechanical system and the electronic and spin transport
phenomena that should or should not be displayed in such system. These insights allow
one to suggest experimental measurements to discriminate the symmetries broken by
different perturbations, and also suggest which experimental systems may display a given
physical phenomenon.

We study the effects of symmetry breaking and spin orbit interactions and their
impact on the transport signatures of Dirac fermions in graphene. In Chapter 2, we arrive
at the low energy Dirac Hamiltonian of graphene from the tight binding Hamiltonian, and
investigate the set of symmetries that govern the charge carriers in pristine graphene. We
also show that the appearance of massive terms in the Dirac Hamiltonian reflect the
reduction of symmetries of the pristine case.

In Chapter 3, we introduce the partial wave scattering method for Dirac fermions in
graphene, in the presence of different symmetries and perturbation, from potential and
spin scattering effects. We finally study the different scattering matrix elements of
potential, spin and valley scattering effects.

Chapter 4 is devoted to electronic transport in graphene. We start by analyzing the
case of potential scatterers that do not reduce the lattice symmetries of graphene. We
identify the different scattering regimes, and the unique transport signatures that indicate
the presence of these scatterers. We also show that at relatively high energies electrons in
graphene scattering from potential obstacles mimic the behavior of the well known
whispering-gallery modes. At the end of this chapter we analyze the effects of symmetry
breaking effects, and the way these effects are reflected in the different transport characteristics of graphene.

In Chapter 5, we analyze the effects of potential scatterers and locally enhanced spin-orbit interactions on the transport properties, and provide a method to quantify these interactions via transport measurements. We also show, that in the presence of symmetry breaking and spin-orbit effects, one can extract and quantify both effects simultaneously. Also, we show the set of symmetries that lead to the appearance of the spin Hall effect.

In Chapter 6, we draw analogies between electron scattering in graphene and geometrical optics. We show that circularly gated regions mimic the behavior of a lens with a tunable index of refraction. We show that if the gated region also contains a Rashba spin-orbit interaction, this region will mimic a birefringent lens with indices of refraction that can differentiate different spin components.

In Chapter 7 we study multiple scattering effects in graphene. We show that the arrangements of potential scatterers that lead to parity breaking result into the separation of the scattered valley currents in space. This presents a simple and attractive mechanism to obtain a valley filter.

Finally, in Chapter 8 we conclude by giving a general summary of our results and perspectives of future research directions.
2 **Graphene**

In this chapter we review the tight-binding model of graphene. Then, from the tight-binding Hamiltonian we obtain the effective low energy Dirac Hamiltonian around the corners of the Brillouin zone, known as the $K$ and $K'$, or Dirac points. We then proceed to analyze the symmetries of both the tight-binding and the effective Dirac Hamiltonians, and we obtain explicit forms of the operators that describe time reversal, parity and space inversion. Then, we discuss the appearance of terms that lead to the generation of masses in the Dirac spectrum, and relate them to the breaking of symmetries. Finally, we discuss the form of charge and current density of the Dirac Hamiltonian in graphene.

### 2.1 Tight-Binding Model

Graphene consists of a honeycomb lattice composed of two superimposed triangular sublattices, which are called $A$ and $B$ sublattices (see Fig. 2.1a). Each carbon atom has six electrons: two of them are filling the inner $1s$ shell, the other three take part in forming three $sp^2$ covalent bonds with the neighboring atoms, and the last electron occupies the $\pi$ orbital perpendicular to the plane of the hexagonal arrangement. Since most of the electronic properties of graphene are determined by the electron in the $\pi$ orbital, a single orbital tight-binding model will be a natural choice to describe electron dynamics in this lattice. The tight-binding Hamiltonian reads

$$H_0 = t \sum_{r_A} \sum_j c_B^\dagger(r_A + \delta_j)c_A(r_A) + H.c.,$$

(2.1)

here, $t \approx -2.7$ eV is the hopping parameter between two neighbouring $p_z$ orbitals. The operators $c_\alpha(r_i)$ destroy a $\pi$ orbital electron at site $r_i$, with $\alpha = A, B$ sublattice [23–26]. The sum runs over $r_A$ since the $A$ sites form a Bravais lattice spanned by the basis vectors...
Figure 2.1: a) Graphene honeycomb lattice (top). The A sublattice appears in red, and B in purple. The blue arrows are the $\delta$ vectors connecting the nearest $A - B$ site (bottom). b) A hexagon in the graphene lattice in a) (top) and the corresponding first Brillouin zone (bottom). The red arrows represent the lattice vectors spanning the A sublattice c) Hexagon in the graphene lattice orientation in a) rotated clockwise by $\pi/2$ (top) and the corresponding first Brillouin zone (bottom).

$a_1$ and $a_2$, where

\[
\begin{align*}
    a_1 &= \sqrt{3} a \hat{x}, \\
    a_2 &= \frac{a}{2} \left( \sqrt{3} \hat{x} + 3 \hat{y} \right),
\end{align*}
\]

where $a = 1.42 \, \text{Å}$ is the smallest distance between two carbon atoms. The vectors $\delta_j$ connect the $A$ and $B$ sites (see Fig.2.1a), and are defined as

\[
\delta_{1,2} = \frac{a}{2} \left( \pm \sqrt{3} \hat{x} + \hat{y} \right), \quad \delta_3 = -a \hat{y}.
\]

We should notice that in this description the second nearest neighbour hopping is neglected, since the second nearest neighbour hopping $t'$ is roughly ten times smaller than $t$ [23, 25].
Lattice translation invariance makes the quasi-momentum \( \mathbf{k} = (k_x, k_y) \) a good quantum number, and we can use the Fourier transform of

\[
c_{\alpha}(\mathbf{r}_i) = \frac{1}{\sqrt{N}} \sum_{\mathbf{k} \in \text{BZ}} e^{-i\mathbf{k} \cdot \mathbf{r}_i} c_{\alpha}(\mathbf{k}) ,
\]

where, \( N \) is the total number of sites, \( \alpha = A, B \) is the sublattice index, and the momentum is restricted to the first Brillouin zone (see Fig. 2.1b), BZ. After substituting Eq. 2.4 in 2.1, the Hamiltonian becomes diagonal in momentum and is given by

\[
H_0 = \frac{1}{N} \sum_{\mathbf{k} \in \text{BZ}} \Psi^\dagger(\mathbf{k}) h_0(\mathbf{k}) \Psi(\mathbf{k}) ,
\]

where \( \Psi(\mathbf{k}) = (c_A(\mathbf{k}), c_B(\mathbf{k}))^T \), and the Hamiltonian \( h_0(\mathbf{k}) \) acts on the sublattice pseudospin and reads

\[
h_0(\mathbf{k}) = d_1(\mathbf{k}) \sigma_1 + d_2(\mathbf{k}) \sigma_2
\]

where \( \sigma_1 = \sigma_x, \sigma_2 = \sigma_y \), are Pauli matrices acting on the pseudospin subspace, and

\[
d_1(\mathbf{k}) + id_2(\mathbf{k}) = t \sum_j e^{i\mathbf{k} \cdot \mathbf{\delta}_j}
\]

\( d_1(\mathbf{k}), d_2(\mathbf{k}) \) are real functions of \( \mathbf{k} \), and satisfy \( d_1(\mathbf{k}) = d_1(-\mathbf{k}), d_2(\mathbf{k}) = -d_2(-\mathbf{k}) \),
\( d_1(\mathbf{k}) = d_1(k_x, -k_y), d_2(\mathbf{k}) = -d_2(k_x, -k_y), d_1(\mathbf{k}) = d_1(-k_x, k_y), \) and \( d_2(\mathbf{k}) = d_2(-k_x, k_y) \).

The energy spectrum is given by

\[
E(\mathbf{k}) = \pm |d(\mathbf{k})| = \pm \sqrt{d_1^2(\mathbf{k}) + d_2^2(\mathbf{k})} ,
\]

where \( d(\mathbf{k}) = (d_1(\mathbf{k}), d_2(\mathbf{k})) \), and + and − correspond to the conduction and valence bands, respectively. These bands are symmetric around \( E = 0 \) [23–25, 27–30]. Also, the valence and conduction bands touch at isolated points of the Brillouin zone whenever \( d(\mathbf{k}) = 0 \). There are only two inequivalent points where that happens,

\[
\mathbf{k} = \pm \mathbf{K} = \pm \left( \frac{4\pi}{3 \sqrt{3} a}, 0 \right) ,
\]

and other solutions of \( d(\mathbf{k}) = 0 \) in reciprocal lattice space can be linked to these two points, and by lattice symmetry describe the same physical states [23–25, 27–30].
2.2 Low Energy Dirac Hamiltonian

As we saw in the previous section there are two inequivalent points in the graphene Brillouin zone where the valence and conduction bands touch. These two points are known as the $K$ and $K'$ points, or valleys of graphene [23–25, 27–30]. In order to describe the low energy dynamics we consider the momenta around these points, such that

$$k = \pm K + q,$$

with $q = q_x \hat{x} + q_y \hat{y}$ being a small momentum deviation from $\pm K$. Expanding up to a linear term in momentum $q$, one gets ($\hbar = 1$)

$$H_{0}^{\pm} = v_F \sum_{q \in BZ} \begin{pmatrix} c_{\pm,A}^\dagger(q) & c_{\pm,B}^\dagger(q) \end{pmatrix} \begin{pmatrix} 0 & \pm q_y - iq_x \\ \pm q_y + iq_x & 0 \end{pmatrix} \begin{pmatrix} c_{\pm,A}(q) \\ c_{\pm,B}(q) \end{pmatrix},$$

with $v_F = -3at/2 \approx c/300$, where $c$ is the speed of light, and $+$ and $-$ correspond to the $K$ and $K'$ points respectively. The first quantized four component wave functions describing the pseudospin and valley degrees of freedom satisfy

$$H_D \psi = v_F (\tau_3 \sigma_1 p_x + \sigma_2 p_y) \psi(x) = E \psi(x)$$ (2.11)

in the basis $\psi = (\psi_{K,A}, \psi_{K,B}, \psi_{K',A}, \psi_{K',B})^T$, where $\sigma_\mu, \tau_\mu$, are Pauli matrices that act on the pseudospin and valley degree of freedom respectively, and $p_x = -i \partial_x$ and $p_y = -i \partial_y$. The Hamiltonian in Eq. 2.11 has the form of a Dirac Hamiltonian describing relativistic particles with zero mass around each valley in graphene, where the dispersion of the charge carriers around these points is simply

$$E(k) = \pm v_F |k|,$$ (2.12)

where $k$ is now the momentum around the $K$ and $K'$ points. The properties of the charge carriers around the $K$ and $K'$ points gave them the name of Dirac points of graphene [23–25, 27–30].
We should point out some important considerations that may lead to different forms of the Dirac Hamiltonian in Eq. 2.11. First, spinor representation: In this dissertation, two different basis sets will be considered. The choice of representation is based on the convenience and the details of the problems that will be discussed. The Hamiltonian in Eq. 2.11 is written in what is known as the “normal” basis set. A different basis known as the “chiral” is convenient to use when considering both valleys in graphene [28, 31]. The chiral basis is,  

$$ \psi = (\psi_A, \gamma, \psi_B, \gamma, \psi_B', \gamma')^T $$

and the free Dirac Hamiltonian in this representation becomes

$$ H_D = v_F \alpha \cdot \bar{p}, $$

$$ \alpha_i = \tau_3 \otimes \sigma_i = \begin{pmatrix} \sigma_i & 0 \\ 0 & -\sigma_i \end{pmatrix}, $$

$$ \gamma^5 = \tau_3 \otimes \sigma_0 = \begin{pmatrix} \sigma_0 & 0 \\ 0 & -\sigma_0 \end{pmatrix}, $$

and

$$ \beta = \tau_1 \otimes \sigma_0 = \begin{pmatrix} 0 & \sigma_0 \\ \sigma_0 & 0 \end{pmatrix}, $$

where $\sigma_0$ and $\tau_0$ are $2 \times 2$ identity matrices in the pseudospin and valley spaces, respectively.

An attractive feature of the chiral basis is the similarity of the $\alpha_i, \beta$ and $\gamma^5$ matrices in the three dimensional Dirac equation [32, 33], which satisfy

$$ \{ \alpha_i, \alpha_j \} = 2\delta_{i,j}, $$

$$ [\alpha_i, \gamma^5] = 0, $$

$$ \{ \alpha_i, \beta \} = 0, $$
Another important consideration that not only determines the form of the Dirac equation, but also gives the eigenstates a different character, comes from the orientation of the underlying lattice. In our derivation of the Dirac equation written in the form Eq. 2.11 or 2.13, the underlying lattice orientation is shown in Fig. 2.1b and its corresponding BZ. In this case a Dirac fermion moving along the \(x\) direction moves along the “zigzag chains” composing the hexagonal lattice, while an electron moving along the \(y\) direction moves along the “armchair chains” of the hexagon. A different orientation and a different physical interpretation of the states of the Dirac Hamiltonian is obtained if the orientation of the lattice and the corresponding BZ are like the ones shown in Fig. 2.1c. In that case the effective Dirac Hamiltonian in the “normal” basis becomes

\[
 v_F (\sigma_1 p_x + \tau_3 \sigma_2 p_x) \psi(x) = E \psi(x) ,
\]

and a Dirac fermion moving along the \(y\) direction moves along the zigzag chains composing the hexagonal lattice (while an electron moving along the \(x\) direction is along the armchair chains of the hexagon). All the calculations and results in this dissertation were performed taking the lattice orientation in Fig. 2.1b as the underlying lattice and Eq. 2.11 as the low energy dynamics.

### 2.3 Symmetries and Masses in Graphene

We now discuss three important symmetries in graphene systems, namely time reversal, parity, and space inversion. We also will discuss the appearance of massive terms in the Dirac Hamiltonian, and the relation of these masses to broken symmetries. At the end of this section we will also discuss continuous transformations of the free Dirac Hamiltonian. The ideas in this section follow the presentation in [28, 34, 35].
2.3.1 Spin Independent Symmetries

In this section we define the the time reversal, parity and inversion symmetry operators for graphene in both the tight binding and the low energy Dirac approximation.

The time reversal operator changes the direction of motion, and it leaves the position operator \( \hat{x} \) unchanged, but it changes the sign of the momentum operator \( \hat{p} \) [34, 35]

\[
T \hat{x} T^{-1} = \hat{x}, \quad T \hat{p} T^{-1} = -\hat{p}.
\] (2.23)

The representation of the time reversal operator can be found by looking at the action of time reversal on the commutator of \( \hat{x} \) and \( \hat{p} \),

\[
T[\hat{x}, \hat{p}] T^{-1} = Ti\hbar T^{-1} = -[\hat{x}, \hat{p}] = -i\hbar,
\] (2.24)

so that time reversal operator should satisfy

\[
TiT^{-1} = -i,
\] (2.25)

which means that it should be proportional to the anti-linear complex conjugation operator \( C \). In general the time reversal operator can be represented as

\[
T = UC,
\] (2.26)

where \( U \) is a unitary matrix. Then the square of time reversal reads

\[
T^2 = UCUC = UU^* = U(U^T)^{-1} = \Phi
\] (2.27)

where

\[
\Phi = e^{i\phi} I.
\] (2.28)

Here \( I \) is an identity matrix with the same dimensions as \( U \), since applying time reversal twice to a state should give us back the same state up to a phase. Then

\[
U = \Phi U^T, \quad U^T = U\Phi,
\] (2.29)
then

\[ U = \Phi U \Phi , \quad (2.30) \]

and this only happens if \( \Phi = \pm I \) (\( \phi = n\pi \)), so that \( T^2 = \pm I \).

Let us to analyze the effect of time reversal for “spinless” particles in a lattice. Time reversal leaves the on-site annihilation operator for spinless particles unchanged,

\[ Tc_\alpha(r_j)T^{-1} = c_\alpha(r_j) \quad [34], \]

where \( \alpha \) is an index that does not represent a spin or other angular momentum [34], then

\[ Tc_\alpha(r_j)T^{-1} = \sum_k e^{-ikr_j}c_\alpha(k)T^{-1} = \sum_k e^{ikr_j}c_\alpha(-k) , \quad (2.31) \]

so that the effect of time reversal on the annihilation operator of an spinless electron at momentum \( k \), is to flip the sign of the momentum, \( Tc_\alpha(k)T^{-1} = c_\alpha(-k) \). Then

\[ TH_0T^{-1} = \sum_{k \in BZ} Tc_A^\dagger(k)(d_1(k) - id_2(k))c_B(k)T^{-1} + \]

\[ \sum_{k \in BZ} Tc_B^\dagger(k)(d_1(k) + id_2(k))c_A(k)T^{-1} , \]

\[ = \sum_{k \in BZ} c_A^\dagger(-k)T(d_1(k) - id_2(k))T^{-1}c_B(-k) + \]

\[ c_B^\dagger(-k)T(d_1(k) + id_2(k))T^{-1}c_A(-k) , \]

which can be written as

\[ TH_0T^{-1} = \sum_{k \in BZ} \begin{pmatrix} c_A^\dagger(-k) & c_B^\dagger(-k) \end{pmatrix} \begin{pmatrix} 0 & d_1(k) - id_2(k) \\ d_1(k) + id_2(k) & 0 \end{pmatrix} T^{-1} \begin{pmatrix} c_A(-k) \\ c_B(-k) \end{pmatrix} , \quad (2.32) \]

where the time reversal operator can be defined as \( T = \sigma_0 T = \sigma_0 C \). The Hamiltonian in Eq. 2.6 transforms under time reversal as

\[ Th_0(k)T^{-1} = d_1^\dagger(k)\sigma_1 - d_2^\dagger(k)\sigma_2 = d_1(-k)\sigma_1 + d_2(-k)\sigma_2 = h_0(-k) , \quad (2.33) \]
indicating that $H_0$ is time reversal invariant, as $T H_0 T^{-1} = H_0$ [34]. One should also note that the time reversal operator satisfies $T^2 = 1$, as we are dealing with the spin independent case (spinless particles) in Eq. 2.32 [24, 26, 28].

Now in the case of the continuum representation in Eq. 2.11, applying $T$ to the Dirac Hamiltonian is not sufficient to achieve the time reversal operation, as the spinor contains information about the two valleys located at $k = (\pm K, 0)$, and they need to be exchanged as well. Then in order to define the time reversal operator in the continuum representation in Eq. 2.11, we consider the normal basis, $\psi = (\psi_{A,K}, \psi_{B,K}, \psi_{A,K}', \psi_{B,K}')^T$. Then time reversal in the Dirac representation can be defined as

$$\mathcal{T} = \tau_1 \sigma_0 C , \quad (2.34)$$

and

$$\mathcal{T} H_D \mathcal{T}^{-1} = \tau_1 (-\tau_3 \sigma_1 p_x + \sigma_2 p_y) \tau_1 = H_D \quad (2.35)$$

in the chiral representation the time reversal operator is given by

$$\mathcal{T} = \beta \gamma^5 \alpha_1 C . \quad (2.36)$$

Another symmetry of graphene is what is known in the literature as “effective” time reversal [26]. Effective time reversal reverses both the momentum at each Dirac point and the pseudospin, so that it is defined in the normal basis as

$$\mathcal{T}_1 = i \tau_0 \sigma_2 C \quad (2.37)$$

where

$$\mathcal{T}_1 H_D \mathcal{T}_1^{-1} = \sigma_2 (-\tau_3 \sigma_1 p_x + \sigma_2 p_y) \sigma_2 = H_D , \quad (2.38)$$

in the chiral basis, $\mathcal{T}_1$ is defined as

$$\mathcal{T}_1 = i \gamma^5 \alpha_2 C , \quad (2.39)$$
Notice that $T_1$ is antiunitary ($T_1^2 = -1$), as the pseudospin of the Dirac particles at each cone is transformed as a real spin. It is extremely important to note that effective time reversal symmetry is a symmetry of the Dirac points (the points in the Brillouin zone where the, $H_D$, Dirac representation holds), and not a symmetry of $H_0$ in Eq. 2.5 which describes all the points in the Brillouin zone [26].

Parity in two dimensions is not inversion, but instead is mirror inversion around one of the axes. In order to define the operator that describes parity in graphene, the orientation of the underlying lattice is important, as it determines the axis around which the reflection is applied. In the lattice orientation in Fig. 2.1b, parity takes $(x, y \rightarrow x, -y)$, which leads to the reflection of all the points in the lattice, exchanging $A$ and $B$ (see Fig. 2.1a). Also, parity changes coordinates, $(k_x, k_y \rightarrow k_x, -k_y)$, and $Pc_\alpha(k)P^{-1} = c_\bar{\alpha}(k)$, where $\alpha = (A, B)$ and $\bar{\alpha} = -\alpha$ in the Hamiltonian in Eq. 2.5. The parity operator can be defined as $P = \sigma_1(k_x, k_y \rightarrow k_x, -k_y)$. The Hamiltonian in Eq. 2.6 transforms under parity as

$$Ph_0(k)P^{-1} = d_1(k_x, -k_y)\sigma_1 - d_2(k_x, -k_y)\sigma_2 = h_0(k), \quad (2.40)$$

since $d_2(k_x, -k_y) = -d_2(k)$, and $d_1(k_x, -k_y) = d_1(k)$. Then $H_0$ is invariant under parity as $PH_0P^{-1} = H_0$. Then, parity in two dimensions switches the sublattice index in the spinor while keeping the valley unchanged.

In the Dirac equation parity is achieved by the operator (written in the “normal” basis)

$$P = \tau_0\sigma_1(x, y \rightarrow x, -y), \quad (2.41)$$

and the Dirac Hamiltonian transforms under parity as

$$PH_DP^{-1} = \sigma_1(\tau_3\sigma_1 p_x - \sigma_2 p_y)\sigma_1 = H_D, \quad (2.42)$$

and in chiral basis parity takes the form

$$P = \gamma^5\alpha(x, y \rightarrow x, -y). \quad (2.43)$$
Inversion symmetry in two dimensions is the combination of two reflections, one around \( x \) and the second one around \( y \) axes, or equivalently a rotation of \( \pi \). Inversion symmetry not only changes, \((x, y) \rightarrow (-x, -y)\) in real space, but it also changes the sublattice space, and rotates the Brillouin zone (see Fig. 2.1b). Parity transforms \((k, -k)\) and \(c_\alpha(k)c_\bar{\alpha}(k) = c_\bar{\alpha}(k)\), where \(\alpha = (A, B)\) and \(\bar{\alpha} = -\alpha\) in the Hamiltonian in Eq. 2.5. The inversion symmetry operator can be written as \(I = \sigma_1(k \rightarrow -k)\). The Hamiltonian in Eq. 2.6 transforms under inversion as

\[
\mathbb{I}h_0(k)\mathbb{I}^{-1} = d_1(-k)\sigma_1 - d_2(-k)\sigma_2 = d_1(k)\sigma_1 + d_2(k)\sigma_2 = h_0(k),
\]

(2.44)

which means that the \(H_0\) in Eq. 2.5 is inversion symmetric, as \(\mathbb{I}H_0\mathbb{I}^{-1} = H_0\).

As one of the lattice reflections changes the sublattice index and the other changes the valley index, the inversion symmetry operator written in the normal representation is defined as

\[
I = \tau_1\sigma_1(x \rightarrow -x, y \rightarrow -y),
\]

(2.45)

and the Dirac Hamiltonian transforms under inversion as

\[
IH_0I^{-1} = \tau_1\sigma_1(-\tau_3\sigma_1p_x - \sigma_2p_y)\tau_1\sigma_1 = H_0,
\]

(2.46)

while in the chiral basis the inversion operator takes the form

\[
I = \beta(x \rightarrow -x, y \rightarrow -y).
\]

(2.47)

### 2.3.2 Masses and Symmetry Breaking

Space-time inversion plays an important role in graphene [24–26, 29]. In order to explore its role, we take a general form of the Hamiltonian, \(H_0\), in Eq. 2.5, such that

\[
h(k) = \sigma_0d_0(k) + \sigma_1d_1(k) + \sigma_2d_2(k) + \sigma_3d_3(k),
\]

(2.48)
where $\sigma_0$ is a $2 \times 2$ identity matrix, $d_1(k)$ and $d_2(k)$ are given in Eq. 2.7, and $d_0(k)$ and $d_3(k)$ are real functions of $k$. The Hamiltonian $h(k)$ transforms under time reversal as

$$Th(k)T^{-1} = \sigma_0 d_0(k) + \sigma_1 d_1(-k) + \sigma_2 d_2(-k) + \sigma_3 d_3(k) ,$$

and $H_0$, in Eq. 2.5, would be time reversal invariant if $d_0(k) = d_0(-k)$ and $d_3(k) = d_3(-k)$.

Under inversion symmetry $h(k)$ becomes

$$\text{I}h(k)\text{I}^{-1} = \sigma_0 d_0(-k) + \sigma_1 d_1(k) + \sigma_2 d_2(k) - \sigma_3 d_3(-k) ,$$

and then $H_0$, in Eq. 2.5, is invariant under space inversion if $d_0(k) = d_0(-k)$ and $d_3(k) = -d_3(-k)$. This means that a perturbation that is proportional to $\sigma_0$ can preserve space and time inversion if it is an even function of $k$. However, a perturbation proportional to $\sigma_3$ can not preserve both symmetries simultaneously.

Consider now, for a generic Dirac Hamiltonian in two spatial dimensions

$$(\vec{\alpha} \cdot \vec{p} + mM)\psi = E\psi ,$$

where $m$ is a real number and $M$ is a matrix. If we apply $\vec{\alpha} \cdot \vec{p}$ to Eq. 2.51, we get

$$\mathbf{p}^2 \psi = \vec{\alpha} \cdot \vec{p}(E - mM)\psi ,$$

where $\mathbf{p}^2 = p_x^2 + p_y^2$. Then the matrix $mM$ leads to the generation of a mass (gap), if $M^2 = I$ and $\{M, \alpha_{1,2}\} = 0$, as Eq. 2.53 would become

$$\mathbf{p}^2 \psi = (E^2 - m^2)\psi ,$$

which is identical to the massive Klein-Gordon equation [28, 32, 33] where particles are characterized by the dispersion, $E = \pm \sqrt{\mathbf{p}^2 + m^2}$. We then get four possible terms that lead to the transformation of the massless graphene Dirac fermions into massive fermions.
These matrices are [28, 31]

\[ M_1 = s\alpha_3, \]
\[ M_2 = \kappa\gamma^5\alpha_3, \]
\[ M_3 = t_1\beta, \]
\[ M_4 = it_2\beta\gamma^5, \]

where \((s, \kappa, t_1, t_2)\) are real parameters. Note that the \(M_3\) and \(M_4\) can be written in a more compact form as \(M = M_3 + M_4 = t\beta e^{i\gamma^5\phi}\), where \(t_1 = t\cos\phi\) and \(t_2 = t\sin\phi\), where \(t\) and \(\phi\) are real.

The matrices satisfy,

\[ [M_1, M_2] = [M_3, M_2] = [M_4, M_2] = 0 \quad (2.54) \]

and any other commutation is non zero; also

\[ \{M_1, M_3\} = \{M_1, M_4\} = \{M_3, M_4\} = 0 \quad (2.55) \]

and any other anti-commutation is non zero. \((M_1, M_3, M_4)\) are called compatible masses, which comes from the additive nature of these masses in the spectrum. Consider a matrix of the form \(A = \sum_i m_i M_i\), with \(m_i\) real, and where each \(M_i\) is involutory (self inverse). If \(A\nu = \lambda\nu\), where \(\lambda\) is an eigenvalue of \(A\) with a corresponding eigenvector \(\nu\), then we have

\[ A (\sum_i m_i M_i) \nu = \left(\sum_j m_j M_j\right) \left(\sum_i m_i M_i\right) \nu = \lambda A\nu \quad (2.56) \]

\[ \left(\sum_i m_i^2 + \sum_{j\neq i} m_j m_i [M_j, M_i]\right) \nu = \lambda A\nu \]

then if the set of matrices \(M_i\) anti-commutes we have

\[ \sum_i m_i^2 \nu = \lambda A\nu = \lambda^2 \nu \quad (2.57) \]

\[ \lambda = \sqrt{\sum_i m_i^2}. \quad (2.58) \]
Therefore the spectrum in the presence of \((M_1, M_3, M_4)\) is given by [28]

\[
E = \pm \sqrt{|p|^2 + s^2 + t_1^2 + t_2^2} = \pm \sqrt{|p|^2 + s^2 + t^2}.
\] (2.59)

Here we should notice an important fact, that the terms that lead to the generation of masses that break either time reversal \(\mathcal{T}\) or inversion symmetry \(\mathcal{I}\). This means that the massless nature of Dirac fermions in graphene is protected by space-time inversion.

The nature of the massless Dirac fermions is characterized by the projection of pseudospin in the direction of the momentum, in what is known as helicity [32, 36]. The Helicity operator takes the form, in chiral basis

\[
\hat{h} = \gamma^5 \hat{\sigma} \cdot \hat{p} = \frac{1}{|\vec{p}|} \begin{pmatrix}
\hat{\sigma} \cdot \hat{p} & 0 \\
0 & \hat{\sigma} \cdot \hat{p}
\end{pmatrix};
\] (2.60)

this operator takes two eigenvalues \(\pm 1\), and the states at \(K\) and \(K'\) are eigenstates of \(\hat{h}\), and they have opposite helicities for fixed \(E\) and \(\vec{p}\).

### 2.3.3 Spin Dependent Symmetries

The discussion above was limited to the spinless case. In the presence of spin-dependent interactions we should modify the time reversal symmetry, as the spin of an electron is reversed with time reversal. The Dirac representation in “normal” basis, \(\psi = (\psi_{A,K,\uparrow}, \psi_{B,K,\uparrow}, \psi_{A,K',\uparrow}, \psi_{B,K',\uparrow}, \psi_{A,K,\downarrow}, \psi_{B,K,\downarrow}, \psi_{A,K',\downarrow}, \psi_{B,K',\downarrow})^T\), results in a time reversal given by

\[
\mathcal{T} = i\sigma_0 \tau_1 s_2 C,
\] (2.61)

where \(s_i\) are the Pauli matrices acting on the spin subspace. Effective time reversal symmetry can be also extended to include spin, and in the normal basis it becomes

\[
\mathcal{T}_1 = \sigma_2 \tau_0 s_2 C.
\] (2.62)

Notice that in the presence of spin, \(\mathcal{T}^2 = -1\), and \(\mathcal{T}_1^2 = 1\). In chiral bases,

\[
\psi = (\psi_{A,K,\uparrow}, \psi_{B,K,\uparrow}, \psi_{B,K',\uparrow}, \psi_{A,K',\uparrow}, \psi_{A,K,\downarrow}, \psi_{B,K,\downarrow}, \psi_{B,K',\downarrow}, \psi_{A,K',\downarrow})^T,
\]
and defining the
corresponding matrices

\[ \mathcal{A}_i = \alpha_i \otimes s_0 = \begin{pmatrix} \alpha_i & 0 \\ 0 & \alpha_i \end{pmatrix}, \quad (2.63) \]

\[ \mathcal{B} = \beta \otimes s_0 = \begin{pmatrix} \beta & 0 \\ 0 & \beta \end{pmatrix}, \quad (2.64) \]

\[ \Gamma^5 = \gamma^5 \otimes s_0 = \begin{pmatrix} \gamma^5 & 0 \\ 0 & \gamma^5 \end{pmatrix}, \quad (2.65) \]

gives operators which operate on the pseudospin and valley degrees of freedom, but leave the spin unchanged, as \( s_0 \) is the identity in spin space. These operators satisfy

\[ \{ \mathcal{A}_i, \mathcal{A}_j \} = 2i \delta_{ij}, \quad (2.66) \]

\[ \{ \mathcal{B}, \mathcal{A}_i \} = 0, \quad (2.67) \]

\[ [\mathcal{A}_i, \Gamma^5] = 0, \quad (2.68) \]

and

\[ \{ \mathcal{B}, \Gamma^5 \} = 0. \quad (2.69) \]

We also define

\[ S_i = s_i \otimes \sigma_0 \otimes \tau_0, \quad (2.70) \]

which act on the spin degree of freedom, with

\[ \{ S_i, S_j \} = 2 \delta_{ij}, \quad (2.71) \]

and commute with \( \mathcal{A}_i, \mathcal{B} \) and \( \Gamma^5 \). In this representation time reversal and effective time reversal are defined as

\[ T = i \mathcal{B} \Gamma^5 \mathcal{A}_1 S_2 C, \quad (2.72) \]

\[ T_1 = \Gamma^5 \mathcal{A}_2 S_2 C. \quad (2.73) \]
One should also notice that unlike the spinless case, the inclusion of spin allows a massive term that preserves both time and space inversion, this term is known as the intrinsic spin-orbit interaction and in the Dirac representation takes the form [9] (note that the tight binding form of this interaction is discussed in [9, 37])

\[ H_{SO} = \Delta_{SO} \tau_3 \sigma_3 s_3 , \quad (2.74) \]

with \([H_{SO}, \mathcal{T}] = [H_{SO}, I] = 0\).

Finally, we want to find the current density and continuity equation for Dirac fermions in graphene. In the chiral representation \((\hbar = 1)\),

\[
- i v_F (\psi^\dagger \alpha_x \partial_x + \psi^\dagger \alpha_y \partial_y) - i \hbar \psi^\dagger \frac{\partial \psi}{\partial t} = 0 , \quad (2.75)
\]

and the hermitian conjugate of Eq. 2.75

\[
i v_F (\partial_x \psi^\dagger \alpha_x \psi + \partial_y \psi^\dagger \alpha_y \psi) + i \hbar \frac{\partial \psi^\dagger}{\partial t} \psi = 0 , \quad (2.76)
\]

subtracting Eq. 2.76 and 2.75, we get

\[
\frac{\partial \rho}{\partial t} + \nabla \cdot \vec{j} = 0 , \quad (2.77)
\]

with

\[
\rho = \psi^\dagger \psi , \quad \vec{j} = v_F (\psi^\dagger \alpha_x \psi, \psi^\dagger \alpha_y \psi) , \quad (2.78)
\]

where \(\rho\) is the charge density and \(\vec{j}\) is the current density. And in the normal basis

\[
\rho = \psi^\dagger \psi , \quad \vec{j} = v_F (\psi^\dagger \tau_x \sigma_x \psi, \psi^\dagger \sigma_y \psi) , \quad (2.79)
\]

This current corresponds to the continuous gauge transformation

\[
\psi \rightarrow e^{i \alpha} \psi , \quad (2.80)
\]
where $\alpha$ is a real number, which leaves Eq. 2.75 invariant. We should notice that there exist another transformation that leaves Eq. 2.75 invariant, and it is given by

$$
\psi \rightarrow e^{i\gamma^5 \phi} \psi,
$$

(2.81)

where $\phi$ is a real number. The transformation in Eq. 2.80 is a global $U(1)$ gauge transformation and it originates from the conservation of electron number in graphene. The transformation in Eq. 2.81, is known as a chiral transformation, and this continuous symmetry is broken as soon as the Dirac points are coupled [28, 32, 33].
3 SCATTERING FORMALISM

In this chapter we present the scattering formalism we will use to analyze the scattering of Dirac fermions in two dimensions. We focus on systems where the perpendicular component of the angular momentum, $J_z$, is conserved. The conservation of angular momentum allows the convenient adoption of the partial wave scattering method, well known for Schrodinger electrons [35, 38, 39], to describe Dirac fermions in two dimensions [36, 40, 41].

First, we are going to show how to determine the scattering phase shift in Dirac systems, and how to relate this phase to the different scattering observables. Second, we study the scattering problem in the context of the scattering matrix, and then proceed to show its relation to the scattering phase shifts and the different cross sections.

We will start our analysis by considering the simple case on which the perturbation to the free Dirac Hamiltonian is a simple potential shift constrained to a circular region in space [36, 42, 43]. Additional degrees of complexity, such as perturbations that include spin orbit interactions and valley mixing effects, will be also analyzed, and the partial wave scattering method will be adapted to include these degrees of freedom [40, 41].

The ideas in this chapter follow the presentation in [35, 36, 38, 44].

3.1 Partial Wave Expansion for Dirac Systems

The Dirac Hamiltonian in Eq. 2.11 describes the dynamics of charge carriers in graphene. A set of possible solutions to this Hamiltonian are the plane wave solutions, $\psi_{\vec{k}}$, with

$$\psi_{\vec{k}} = \begin{pmatrix} e^{-i\theta_k} \\ \text{sgn}(E) \end{pmatrix} e^{ik\cdot r},$$

where $\theta_k = \tan^{-1}(k_x/k_y)$ defines the direction of the wave vector $\vec{k} = (k_x, k_y)$, then for an incoming plane wave along the $x$-axis $\theta_k = 0$. 
If a potential $V$ is present, then this is no longer the case, and we need boundary conditions in order to get the physical solutions of the problem. In order to be able to consider that the scattering solution, $\psi_{\text{scat}}$, is composed from the free plane wave solution, $\psi_{k}$, and a scattered part, $\psi^{+}$, we need to assume that $V$ is spatially restricted (i.e., it vanishes away from a finite region). If we consider the influence of $V$ on the plane wave and its spatial restriction, it will be reasonable to require that the physical real space solution representing $\psi^{+}$, behaves as an outgoing cylindrical wave,

$$\psi^{+}(r, \theta) \xrightarrow{r \to \infty} \hat{f}(r, \theta) e^{ikr} \sqrt{r} \hat{u}_{k_{x}, k_{y}},$$

where $\hat{u}_{k_{x}, k_{y}} = (e^{-i\theta}, \text{sgn}(E))^T$ (in the absence of spin and valley mixing). With this we fix the scattering solution, $\psi_{\text{scat}}$, for wave functions that satisfy the condition in Eq. 3.2. We are then left with the following conditions [38],

$$H \psi_{\text{scat}}(r, \theta) = (H_{0} + V(r, \theta))\psi_{\text{scat}}(r, \theta) = E \psi_{\text{scat}}(r, \theta),$$

where $H_{0} = H_{D}$ (see Eq. 2.11), and

$$\psi_{\text{scat}}(r, \theta) \xrightarrow{r \to \infty} e^{iky \cos \theta} \hat{u}_{k_{x}, k_{y} = 0} + \hat{f}(r, \theta) e^{ikr} \sqrt{r} \hat{u}_{k_{x}, k_{y}},$$

where $\hat{u}_{k_{x}, k_{y} = 0} = (1, \text{sgn}(E))^T$.

The matrix $\hat{f}(r, \theta)$ measures the scattered part of the wave function, its elements represent the allowed mixing process within the spinor components, it vanishes as $V(r, \theta)$ vanishes, and it is called the scattering amplitude.

Now our task is to find the scattering amplitude for systems with different degrees of complexity added to the potential $V$.

In this section, we consider the case where a potential variations with respect to the lattice constant are small, and we approximate this potential by $V(r, \theta) = V_{0}\Theta(R - r)$. In this case the potential does not lead to any valley or spin flipping effects. Here, the Hamiltonian for $r < R$ can be written as
Due to the absence of spin dependent and valley dependent perturbations in the Hamiltonian, one can consider the scattering problem at each valley independently. The Hamiltonian at the $K$ ($\tau_z = 1$ in Eq. 2.11) point is given by

$$H\psi = \begin{pmatrix} V & \nu_F(p_x - ip_y) \\ \nu_F(p_x + ip_y) & V \end{pmatrix} \begin{pmatrix} \psi_{A1} \\ \psi_{B1} \end{pmatrix}.$$  

The conservation of the $z$-component of total angular momentum in the system, $[J_z, H] = 0$, $J_z = L_z + \tau_z \sigma_z / 2$ (written in normal basis, see Sec. 2.2) [36], where $L_z = -i \partial_\theta$ is the orbital angular momentum, allows the eigenstates to be labeled by the corresponding eigenvalue of $J_z$, $J_z \psi_j = (n - \frac{1}{2}) \psi_j$, where $n$ is an integer. We can assume that

$$\psi_{j=n-\frac{1}{2}}(r, \theta) = e^{i\theta} \begin{pmatrix} e^{-i\theta} \phi_A(r) \\ \phi_B(r) \end{pmatrix},$$

and obtain the following radial differential equations for the radial parts of the different spinor components

$$\left(\partial_r + \frac{n}{r}\right) \phi_B(r) = iE \phi_A(r),$$
$$\left(\partial_r - \frac{n-1}{r}\right) \phi_A(r) = iE \phi_B(r),$$

the spinor solutions for $r < R$ in Eq.3.8 are given in terms of Bessel functions; since they should be regular at the origin [45], and we have

$$\psi_{j=n-\frac{1}{2}}(r < R, \theta) = A_n e^{i\theta} \begin{pmatrix} J_{n-1}(k'r) e^{-i\theta} \\ isgn(E - V) J_n(k'r) \end{pmatrix},$$
where \( k' = |E - V| \) and \( A_n \) is a normalization constant. On the other hand, the solutions in the region \( r > R \) can be written as combinations of Bessel and Neumann functions [45], as

\[
\psi_{j=n-\frac{1}{2}}(r > R, \theta) = B_n e^{i\phi} \begin{pmatrix} J_{n-1}(kr) e^{-i\theta} \\ isgn(E)J_n(kr) \end{pmatrix} + C_n e^{i\phi} \begin{pmatrix} N_{n-1}(kr) e^{-i\theta} \\ isgn(E)N_n(kr) \end{pmatrix},
\]

(3.10)

where \( k = |E| \). Now with these solutions in hand we can find the scattering amplitudes generated from the scattering of a plane wave incoming along the \( x \)-axis, by relating these amplitudes to the phase shifts gained due to the scattering process. We use the asymptotic expansion of the Bessel and Neumann functions, and the radial part of the spinor in the asymptotic limit is given by

\[
\phi_{j=n-\frac{1}{2}}(r > R) \underset{r \to \infty}{\longrightarrow} \sqrt{\frac{2}{\pi kr}} \begin{pmatrix} B_n \cos(kr - (n - 1)\pi/2 - \pi/4) + C_n \sin(kr - (n - 1)\pi/2 - \pi/4) \\ isgn(E)(B_n \cos(kr - n\pi/2 - \pi/4) + C_n \sin(kr - n\pi/2 - \pi/4)) \end{pmatrix}
\]

(3.11)

or equivalently,

\[
\phi_n(r > R) \underset{r \to \infty}{\longrightarrow} \sqrt{\frac{2}{\pi kr}} D_n \begin{pmatrix} \cos(kr - (n - 1)\pi/2 - \pi/4 + \delta_n) \\ isgn(E)(\cos(kr - n\pi/2 - \pi/4 + \delta_n)) \end{pmatrix},
\]

(3.12)

where \( \delta_n \) is the phase shift originating from the perturbation \( V \) to the free Hamiltonian.

This phase measures the shift with respect to the incident particle solution; we should note that \( \delta_n \) not only depends on the potential but also on the energy of the incoming particle [35, 38]. The expression in Eq. 3.12 can be written as,

\[
\phi_n(r > R) \underset{r \to \infty}{\longrightarrow} \sqrt{\frac{2}{\pi kr}} D_n \begin{pmatrix} \cos(kr - (n - 1)\pi/2 - \pi/4) \cos(\delta_n) \\ isgn(E)(\cos(kr - n\pi/2 - \pi/4) \cos(\delta_n)) \end{pmatrix} - \begin{pmatrix} \sin(kr - (n - 1)\pi/2 - \pi/4) \sin(\delta_n) \\ \sin(kr - n\pi/2 - \pi/4) \sin(\delta_n) \end{pmatrix}
\]

(3.13)

comparing the contents of Eq. 3.11 and Eq. 3.13, we get

\[
-C_n/B_n = \tan \delta_n.
\]

(3.14)
so we can write the radial solution in Eq. 3.10 as

\[
\phi_n(r > R) = \tilde{A}_n \left\{ \begin{array}{l}
J_{n-1}(kr) - \tan(\delta_n)N_{n-1}(kr) \\
isgn(E)(J_n(kr) - \tan(\delta_n)N_n(kr))
\end{array} \right\},
\tag{3.15}
\]

and \( \tilde{A}_n = A_n \sin \delta_n \).

In order to relate the result in Eq. 3.15 to the scattering of plane waves, we make use of the Jacobi-Anger expansion [45], which allows one to write a plane wave in terms of Bessel functions. An incoming plane wave along \( x \)-axis takes the form,

\[
\psi_\kappa = \sum_{n=-\infty}^{n=\infty} \left( i^{n-1} J_{n-1}(kr) e^{i(n-1)\theta} \right),
\tag{3.16}
\]

then we can write Eq. 3.4 as

\[
\psi_{\text{scat}} \xrightarrow{r \to \infty} \sqrt{\frac{2}{\pi k r}} \left( i^{n-1} \cos(kr - (n-1)\pi/2 - \pi/4)e^{i(n-1)\theta} \right) + \frac{e^{ikr} f_n(\theta)}{\sqrt{r}} \left( e^{-i\theta} \right),
\tag{3.17}
\]

with \( \hat{f}(\theta) = f_n(\theta) I_{2 \times 2} \), where \( I_{2 \times 2} \) is an identity matrix, and compare the latter equation to Eq. 3.12. Equating the coefficients of \( e^{-ikr} \) and \( e^{ikr} \) we get \( D_n = i^{n-1} e^{i\delta_n} \), and

\[
f(\theta) = \frac{1}{\sqrt{2\pi k}} \sum_{n=-\infty}^{n=\infty} f_n e^{i\theta} = \frac{e^{-i\pi/4}}{\sqrt{2\pi k}} \sum_{n=-\infty}^{n=\infty} (e^{2i\delta_n} - 1) e^{i\theta} .
\tag{3.18}
\]

The expression in Eq. 3.18 relates the phase shift gained by the scattering amplitude.

A different approach to find the scattering amplitudes is through the scattering matrix. The scattering matrix, \( S \), is an operator that relates the outgoing and incoming states [38, 39]. The wave function describing the scattering problem can be written with the aid of the \( S \) matrix as

\[
\psi = \psi^{in} + S \psi^{out},
\tag{3.19}
\]

where \( \psi^{in} \) and \( \psi^{out} \) are incoming and outgoing states respectively. When the total angular momentum of the system \( J_z \) is a conserved quantity, the eigenstates can be label according
to the eigenvalues of $J_z$ and similarly the $S$ matrix is block diagonal. It is convenient to express the outgoing and incoming waves in terms of Hankel functions of the first and second kind, due to the conservation of total angular momentum and the circular character of the waves in the system. The scattering of an incoming cylindrical partial wave component can be written as

$$\psi_{n=\frac{j}{2}} = \begin{pmatrix} H_{n-1}^{(2)}(kr)e^{i(n-1)\theta} \\ isg(E)H_{n}^{(2)}(kr)e^{i\theta} \end{pmatrix} + S_n \begin{pmatrix} H_{n-1}^{(1)}(kr)e^{i(n-1)\theta} \\ isg(E)H_{n}^{(1)}(kr)e^{i\theta} \end{pmatrix}.$$ (3.20)

By making use of Eq. 3.4 and the asymptotic expansions of the Hankel functions [45], we can express $\psi_{scat}$ in terms of Hankel functions and the scattering amplitude, such that

$$\psi_{n=\frac{j}{2},scat} = \frac{1}{2} \left\{ \begin{array}{l} H_{n-1}^{(2)}(kr)e^{i(n-1)\theta} \\ isg(E)H_{n}^{(2)}(kr)e^{i\theta} \end{array} \right\} + \frac{1}{2} \left\{ \begin{array}{l} H_{n-1}^{(1)}(kr)e^{i(n-1)\theta} \\ isg(E)H_{n}^{(1)}(kr)e^{i\theta} \end{array} \right\} + \int e^{i\pi/4} f_n \sqrt{\frac{\pi}{2}} \left( \begin{array}{l} H_{n-1}^{(1)}(kr)e^{i(n-1)\theta} \\ isg(E)H_{n}^{(1)}(kr)e^{i\theta} \end{array} \right),$$ (3.21)

and we can relate the $S$ matrix to the scattering amplitude by $\psi_{n} = \alpha_n \psi_{n,scat}$, where $\alpha_n$ is a constant for each partial wave component. Comparing the coefficients of the incoming and outgoing waves in Eq. 3.20 and 3.21, we get $\alpha_n = i^{n-1}/2$ and

$$f_n = \frac{e^{-in/4}}{\sqrt{2\pi k}} (S_n - 1),$$ (3.22)

and consequently

$$f(\theta) = \frac{e^{-in/4}}{\sqrt{2\pi k}} \sum_{n=-\infty}^{n=\infty} (S_n - 1)e^{in\theta}.$$ (3.23)

From Eq. 3.18 and Eq. 4.47, we can relate the $S$ matrix to the scattering phase shift, such that

$$S_n = e^{2i\delta_n}. $$ (3.24)
The scattering matrix has the important property of being unitary, $SS^\dagger = I$, which is a direct reflection of the conservation of probability in a scattering problem [35, 36, 39]. As mentioned before, the scattering matrix, $S$ takes a block diagonal form whenever the angular momentum $J_z$ is a conserved quantity.

After we established the methods to get the scattering amplitudes, we need to relate these to physical observables. A schematic view of a transport experiment is shown in Fig. 3.1. In a transport experiment in two dimensions, one measures the probability flux that penetrates a unit length $dl = rd\theta$ at a distance $r$ from the scatterer center. Here, $d\theta$ is assumed to be infinitesimally small, but in reality it depends on the details of our measurement tool, i.e., sharpness of the scanning tunneling microscope tip, details of electrical contacts, etc.

![Figure 3.1: Schematic representation of a scattering experiment. An incoming flux $\vec{j}_0$ gets scattered by the scattering center (in blue). The detector collects the scattered flux that penetrates the unit length $dl$. The detector is positioned at an angle $\theta$ from the incoming flux axis, and a distance $r$ from the scattering center.](image)

Now one can ask how much of the scattered flux will go through a small length $dl$ subtending an angle $d\theta$ [35]. The quantity that quantifies the latter is given by

$$d\sigma = \frac{\vec{j}_{\text{scat}} \cdot \hat{n} dl}{|\vec{j}_0|} = \frac{\vec{j}_{\text{scat}} \cdot \hat{n} r d\theta}{|\vec{j}_0|},$$

(3.25)

where $\vec{j}_0$ is an incoming flux along the $x$-axis, $\vec{j}_{\text{scat}}$ is the scattered flux, and $\hat{n} = \hat{r}$ is unit vector perpendicular to the length $dl$. Currents in the Dirac Hamiltonian in graphene are given in Eq. 2.79. Also, we know that the spinor that describes the outgoing flux is given
asymptotically by

\[
\psi^+ = \frac{e^{ikr} f_n(\theta)}{\sqrt{r}} \begin{pmatrix} e^{-i\theta} \\ \text{sgn}(E) \end{pmatrix},
\]

then, we have

\[
d\sigma = \frac{\vec{j}_{\text{scat}} \cdot \hat{n} r d\theta}{|\vec{j}_0|} = 2|f(\theta)|^2 \frac{\vec{r} \cdot \hat{n} r d\theta}{2r} = |f(\theta)|^2 d\theta,
\]

then, the differential cross section, \( \sigma(\theta) \), is given by [35, 36, 38]

\[
\sigma(\theta) = \frac{d\sigma}{d\theta} = \frac{1}{2\pi k} \left| \sum_{n=-\infty}^{\infty} (S_n - 1)e^{i\delta_n} \right|^2 = \frac{2}{\pi k} \left| \sum_{n=-\infty}^{\infty} \sin(\delta_n)e^{i\delta_n} \right|^2.
\]

Another important quantity in scattering theory is the total cross section, \( \sigma_t \), which is the differential cross section integrated over the full angular domain. The total “cross section” provides the effective strength of the interaction between the scattering target and the scattered particle [38]. In this case of circularly symmetric scattering centers, the total cross section is given by

\[
\sigma_t = \int_{-\pi}^{\pi} \sigma(\theta)d\theta = \frac{1}{k} \sum_{n=-\infty}^{\infty} |S_n - 1|^2 = \frac{4}{k} \sum_{n=-\infty}^{\infty} \sin^2(\delta_n).
\]

In order to quantify the amount of flux that gets transported with the forward scatter removed, we define the transport cross section as

\[
\sigma_{tr} = \int_{-\pi}^{\pi} (1 - \cos(\theta))\sigma(\theta)d\theta = \sigma_t - \frac{1}{k} \sum_{n=-\infty}^{\infty} \text{Re}(f_n f_{n+1}^*) = \frac{2}{k} \sum_{n=-\infty}^{\infty} \sin^2(\delta_{n+1} - \delta_n),
\]

and in order to quantify how asymmetric is the scattered flux around the axis of the incoming flux, we define the skew cross section as

\[
\sigma_{sk} = \int_{-\pi}^{\pi} \sin(\theta)\sigma(\theta)d\theta = \frac{1}{k} \sum_{n=-\infty}^{\infty} \text{Im}(f_n f_{n+1}^*)
\]

As we will see in the incoming chapters, \( \sigma_t, \sigma_{tr} \) and \( \sigma_{sk} \), will play an important role in the determination of the transport properties of graphene.
3.2 Scattering in the Presence of Spin-Orbit Interactions

In this section, we add one more degree of complexity to the scattering potential \( V(r, \theta) \). As an example we will consider that the perturbation \( V(r, \theta) \) couples the spin degree of freedom due to the presence of spin-orbit interactions (SOIs). An explicit example of this case is the presence of Rashba and/or the intrinsic spin-orbit (see Sec. 5.1 in Ch. 5). The Hamiltonian, in the region enclosing the perturbations, becomes

\[
H_{\tau_z} \psi_{\tau_z} = \begin{pmatrix}
V + \tau_z \Delta_{SO} & v_F(\tau_z p_x - i p_y) & 0 & -i (-\tau_z + 1) \lambda_R \\
v_F(\tau_z p_x + i p_y) & V - \tau_z \Delta_{SO} & i (\tau_z + 1) \lambda_R & 0 \\
0 & -i (\tau_z + 1) \lambda_R & V - \tau_z \Delta_{SO} & v_F(\tau_z p_x - i p_y) \\
i (-\tau_z + 1) \lambda_R & 0 & v_F(\tau_z p_x + i p_y) & V + \tau_z \Delta_{SO}
\end{pmatrix} \begin{pmatrix}
\psi_{\tau_z A \uparrow} \\
\psi_{\tau_z A \downarrow} \\
\psi_{\tau_z B \uparrow} \\
\psi_{\tau_z B \downarrow}
\end{pmatrix},
\]

(3.32)

where we have used normal basis, \( \Delta_{SO} \) is the intrinsic (SOI) and \( \lambda_R \) is the Rashba SOI.

Here we start by assuming that the incoming flux has a given spin \( s = \uparrow \), then the asymptotic form of the wave function becomes

\[
\psi_{\text{scat}} \xrightarrow{r \to \infty} e^{ikr \cos \theta} \hat{u}_{\uparrow, k_x, k_y} + \frac{\tilde{f}_{\uparrow \uparrow}(\theta)}{\sqrt{r}} e^{ikr} \hat{u}_{\uparrow, k_x, k_y} + \frac{\tilde{f}_{\uparrow \downarrow}(\theta)}{\sqrt{r}} e^{ikr} \hat{u}_{\downarrow, k_x, k_y},
\]

(3.33)

where \( \hat{u}_{\uparrow, k_x, k_y} = (1, \text{sgn}(E), 0, 0)^T \), \( \hat{u}_{\uparrow, k_x, k_y} = (e^{-i\theta}, \text{sgn}(E), 0, 0)^T \) and \( \hat{u}_{\downarrow, k_x, k_y} = (0, 0, 1, \text{sgn}(E) e^{i\theta})^T \).

In the case of conservation of total angular momentum \( J_z = -i \partial_\theta + \tau_z \sigma_z/2 + \sigma_z/2 \), the eigenfunctions can be labeled by the eigenvalues of \( J_z \), \( J_z \psi_n = n \psi_n \), with \( n \) integer. Then we can use the asymptotic forms of the Hankel functions in order to express Eq. 3.33 for
an spin $s = \uparrow$ as incoming spin, such that

$$\psi^{\alpha}_{n,\text{scat}} = \int_{-\theta}^{\theta} \psi^{\alpha}_{n} | \uparrow \rangle + i^{n-1} \frac{1}{2} \left( \begin{array}{c} H^{(2)}_{n-1}(kr)e^{i(n-1)\theta} \\ \text{sgn}(E)H^{(2)}_{n}(kr)e^{i\theta} \end{array} \right) \left| \uparrow \right\rangle + i^{n-1} \frac{1}{2} \left( \begin{array}{c} H^{(1)}_{n-1}(kr)e^{i(n-1)\theta} \\ \text{sgn}(E)H^{(1)}_{n}(kr)e^{i\theta} \end{array} \right) \left| \uparrow \right\rangle + f_{n,\uparrow\uparrow} \sqrt{\frac{\pi k}{2}} e^{i\pi/4} \left( \begin{array}{c} H^{(1)}_{n-1}(kr)e^{i\theta} \\ \text{sgn}(E)H^{(1)}_{n}(kr)e^{i\theta} \end{array} \right) \left| \downarrow \right\rangle.$$  

We also know that the wavefunction describing the scattering of single incoming cylindrical partial wave component with a spin up, is given by

$$\psi_{n} = \left( \begin{array}{c} H^{(2)}_{n-1}(kr)e^{i(n-1)\theta} \\ \text{sgn}(E)H^{(2)}_{n}(kr)e^{i\theta} \end{array} \right) \left| \uparrow \right\rangle + S_{n,\uparrow\uparrow} \left( \begin{array}{c} H^{(1)}_{n-1}(kr)e^{i(n-1)\theta} \\ \text{sgn}(E)H^{(1)}_{n}(kr)e^{i\theta} \end{array} \right) \left| \uparrow \right\rangle + S_{n,\uparrow\downarrow} \left( \begin{array}{c} H^{(1)}_{n}(kr)e^{i\theta} \\ \text{sgn}(E)H^{(1)}_{n+1}(kr)e^{i(n+1)\theta} \end{array} \right) \left| \downarrow \right\rangle,$$  

and we can relate the $S$ matrix to the scattering amplitude by $\psi_{n} = \alpha_{n}\psi^{\alpha}_{n,\text{scat}}$, with $\alpha_{n} = i^{n-1}/2$, and

$$f_{n,\uparrow\uparrow} = \frac{e^{-i\pi/4}}{\sqrt{2\pi k}}(S_{n,\uparrow\uparrow} - 1)$$  

$$f_{n,\uparrow\downarrow} = -\frac{ie^{-i\pi/4}}{\sqrt{2\pi k}}S_{n,\uparrow\downarrow}.$$

Similarly, the problem can be analyzed for an incoming spin $s = \downarrow$. In this case we get

$$f_{n,\downarrow\downarrow} = \frac{e^{-i\pi/4}}{\sqrt{2\pi k}}(S_{n,\downarrow\downarrow} - 1)$$  

$$f_{n,\downarrow\uparrow} = \frac{ie^{-i\pi/4}}{\sqrt{2\pi k}}S_{n,\downarrow\uparrow}.$$

In this case the $S$ matrix becomes block diagonal, and the components of each block reflect the spin-mixing and spin-preserving effects of the different scattering process [40, 41].
In this case we also find the cross sections for the different scattering processes

\[
\sigma_{ss'}(\theta) = \frac{1}{2\pi k} \left| \sum_n f_{n,ss'} e^{i n \theta} \right|^2 ,
\]

\[
\sigma_{t,ss'} = \frac{1}{k} \sum_n |f_{n,ss'}|^2 ,
\]

\[
\sigma_{tr,ss'} = \sigma_{t,ss'} - \frac{1}{k} \sum_n \text{Re} \left( f_{n,ss'} f_{n+1,ss'}^* \right) ,
\]

and

\[
\sigma_{sk,ss'} = \frac{1}{k} \sum_n \text{Im} \left( f_{n,ss'} f_{n+1,ss'}^* \right) ,
\]

while the cross sections are given by the sum over all different processes, for an initial state with equal amplitudes in both spins

\[
\sigma(\theta) = \sum_{ss'} \sigma_{ss'}(\theta) ,
\]

\[
\sigma_t = \sum_{ss'} \sigma_{ss'} ,
\]

\[
\sigma_{tr} = \sum_{ss'} \sigma_{tr,ss'} ,
\]

and

\[
\sigma_{sk} = \sum_{ss'} \sigma_{sk,ss'} .
\]

with these quantities at hand, one can characterize the influence of SOIs on the dynamics and transport properties of Dirac fermions, as it is going to clarified in the incoming chapters.

### 3.3 Scattering in the Case of Spin and Valley Mixing

One more degree of complexity to the problem of Dirac fermion scattering in graphene could arise from the mixing between the two valleys of graphene (see Sec. 4.2 in Ch. 4 and Sec. 5.2 in Ch. 5). Then if the perturbation, \( V(r, \theta) \), leads to potential scattering,
spin, and valley mixing, one can express the asymptotic form of the wave function for an incoming electron with a spin $\uparrow$ and in the $K$ in chiral basis valley as

$$\psi_{\text{scat}} \xrightarrow{r \to \infty} e^{ikr \cos \theta} \hat{u}_{K,\uparrow,k_x,0} + \frac{f_{KK,\uparrow}(\theta)}{\sqrt{r}} e^{ikr} \hat{u}_{K,\uparrow,k_x,k_y} + \frac{f_{KK,\uparrow}(\theta)}{\sqrt{r}} e^{ikr} \hat{u}_{K,\downarrow,k_x,k_y} + \frac{f_{KK',\uparrow}(\theta)}{\sqrt{r}} e^{ikr} \hat{u}_{K',\uparrow,k_x,k_y}, \quad (3.46)$$

where, $\hat{u}_{K,\uparrow,k_x,0} = (1, \text{sgn}(E), 0, \ldots, 0)^T$, $\hat{u}_{K,\uparrow,k_x,k_y} = (e^{-i\theta}, \text{sgn}(E), 0, \ldots, 0)^T$, $\hat{u}_{K',\uparrow,k_x,k_y} = (0, 0, 1, \text{sgn}(E)e^{i\theta}, 0, \ldots, 0)^T$, $\hat{u}_{K',\downarrow,k_x,k_y} = (0, \ldots, 0, -1, \text{sgn}(E)e^{-i\theta}, 0, \ldots, 0)^T$, and $\hat{u}_{K',\downarrow,k_x,k_y} = (0, \ldots, 0, -e^{i\theta}, \text{sgn}(E))^T$.

Now if the total angular momentum $J_z$ is conserved, we can express $\psi_{\text{scat}}$ in terms of incoming and outgoing Hankel functions, such that
and the problem can be expressed in terms of the $S$ matrix as,

$$
\psi_n = \left( \begin{array}{c} H_n^{(2)}(kr)e^{i(n-1)\theta} \\ \text{isgn}(E)H_n^{(2)}(kr)e^{i\theta} \end{array} \right) |K \uparrow\rangle + S_{n, KK, \uparrow\uparrow} \left( \begin{array}{c} H_n^{(1)}(kr)e^{i(n-1)\theta} \\ \text{isgn}(E)H_n^{(1)}(kr)e^{i\theta} \end{array} \right) |K \uparrow\rangle + 
\begin{aligned}
S_{n, KK, \uparrow\downarrow} \left( \begin{array}{c} H_n^{(1)}(kr)e^{i\theta} \\ \text{isgn}(E)H_n^{(1)}(kr)e^{i(n+1)\theta} \end{array} \right) |K \downarrow\rangle \\
S_{n, KK', \uparrow\uparrow} \left( \begin{array}{c} -iH_n^{(1)}(kr)e^{i\theta} \\ \text{sgn}(E)H_n^{(1)}(kr)e^{i(n+1)\theta} \end{array} \right) |K', \uparrow\rangle \\
S_{n, KK', \uparrow\downarrow} \left( \begin{array}{c} -iH_n^{(1)}(kr)e^{i(n+1)\theta} \\ \text{sgn}(E)H_n^{(1)}(kr)e^{i\theta} \end{array} \right) |K', \downarrow\rangle,
\end{aligned}
$$

and by setting $\psi_{n, \text{scat}} = \alpha_n \psi_n$, we get $\alpha_n = i^{n-1}/2$, and

$$
\begin{aligned}
f_{n, KK, \uparrow\uparrow} &= \frac{e^{-in/4}}{\sqrt{2\pi k}} \left( S_{n, KK, \uparrow\uparrow} - 1 \right) \\
f_{n, KK, \uparrow\downarrow} &= \frac{-ie^{-in/4}}{\sqrt{2\pi k}} S_{n, KK, \uparrow\downarrow} \\
f_{n, KK', \uparrow\uparrow} &= \frac{-ie^{-in/4}}{\sqrt{2\pi k}} S_{n, KK', \uparrow\uparrow} \\
f_{n, KK', \uparrow\downarrow} &= \frac{e^{-in/4}}{\sqrt{2\pi k}} S_{n, KK', \uparrow\downarrow}.
\end{aligned}
$$

A similar way, is we start with an incoming flux in the $K'$ valley and with $\uparrow$ spin we have

$$
\begin{aligned}
f_{n, K', \uparrow\uparrow} &= \frac{e^{-in/4}}{\sqrt{2\pi k}} \left( S_{n, K', \uparrow\uparrow} - 1 \right) \\
f_{n, K', \uparrow\downarrow} &= \frac{-ie^{-in/4}}{\sqrt{2\pi k}} S_{n, K', \uparrow\downarrow} \\
f_{n, K'K, \uparrow\uparrow} &= \frac{ie^{-in/4}}{\sqrt{2\pi k}} S_{n, K'K, \uparrow\uparrow} \\
f_{n, K'K, \uparrow\downarrow} &= \frac{e^{-in/4}}{\sqrt{2\pi k}} S_{n, K'K, \uparrow\downarrow},
\end{aligned}
$$
for an incoming flux in the $K$ valley and with ↓ spin we have

\[ f_{n,KK,\downarrow \downarrow} = \frac{e^{-in/4}}{\sqrt{2\pi k}} (S_{n,KK,\downarrow \downarrow} - 1) \]

\[ f_{n,KK,\downarrow \uparrow} = \frac{ie^{-in/4}}{\sqrt{2\pi k}} S_{n,KK,\downarrow \uparrow} \]

\[ f_{n,KK',\downarrow \downarrow} = \frac{-ie^{-n/4}}{\sqrt{2\pi k}} S_{n,KK',\downarrow \downarrow} \]

\[ f_{n,KK',\downarrow \uparrow} = \frac{e^{-in/4}}{\sqrt{2\pi k}} S_{n,KK',\downarrow \uparrow} . \]

Finally for an incoming flux in the $K'$ valley and with ↓ spin we get

\[ f_{n,K'K',\downarrow \downarrow} = \frac{e^{-in/4}}{\sqrt{2\pi k}} (S_{n,K'K',\downarrow \downarrow} - 1) \]

\[ f_{n,K'K',\downarrow \uparrow} = \frac{-ie^{-n/4}}{\sqrt{2\pi k}} S_{n,K'K',\downarrow \uparrow} \]

\[ f_{n,K'K',\downarrow \downarrow} = \frac{ie^{-in/4}}{\sqrt{2\pi k}} S_{n,K'K',\downarrow \downarrow} \]

\[ f_{n,K'K',\downarrow \uparrow} = \frac{e^{-in/4}}{\sqrt{2\pi k}} S_{n,K'K',\downarrow \uparrow} . \]

Now, with the scattering amplitudes in hand we can obtain the different cross sections for the various scattering process, such that

\[ \sigma_{\tau\tau',ss'} (\theta) = \frac{1}{2\pi k} \left| \sum_n f_{n,\tau\tau',ss'} e^{in\theta} \right|^2 , \]

\[ \sigma_{1,\tau\tau',ss'} = \frac{1}{k} \sum_n \left| f_{n,\tau\tau',ss'} \right|^2 , \]

\[ \sigma_{\tau,\tau',ss'} = \sigma_{1,\tau\tau',ss'} - \frac{1}{k} \sum_n \text{Re} \left( f_{n,\tau\tau',ss'} f^*_{n+1,\tau\tau',ss'} \right) , \]

and

\[ \sigma_{sk,\tau\tau',ss'} = \frac{1}{k} \sum_n \text{Im} \left( f_{n,\tau\tau',ss'} f^*_{n+1,\tau\tau',ss'} \right) , \]

and the cross sections are given by the sum over all different process, as

\[ \sigma (\theta) = \sum_{\tau\tau',ss'} \sigma_{\tau\tau',ss'} (\theta) , \]
\[
\sigma_t = \sum_{\tau \tau', ss'} \sigma_{\tau \tau', ss'} , \quad (3.56)
\]
\[
\sigma_{tr} = \sum_{\tau \tau', ss'} \sigma_{tr, \tau \tau', ss'} , \quad (3.57)
\]
and
\[
\sigma_{sk} = \sum_{\tau \tau', ss'} \sigma_{sk, \tau \tau', ss'} . \quad (3.58)
\]

The determination of these quantities, will allow us to characterize the effects of spin and valley mixing on the different transport properties in graphene samples displaying these perturbations, as will be shown in the incoming chapters.

### 3.4 Length Scales

It is important to notice that in order to use the Dirac approximation of charged carriers in graphene, see Ch. 2, the length scales, \( R \), of all perturbations affecting the pristine system should be larger than the distance between two carbon atoms, \( a \). The Fermi energy of charged carriers in graphene also determines another length scale, the de Broglie wavelength, given by \( \lambda = \frac{2\pi \hbar v_F}{E_F} \). Then in order to be able to use the dilute limit of scattering where the scattering from multiple impurities is incoherent, then the distance between two impurities, \( d \), should be larger than \( \lambda \). Furthermore, the length scales of the sample, \( L \), should be larger than the distance between two impurities. Therefore in the case where \( kR < 1 \), which is analyzed in Ch. 4 and Ch. 5, the conditions on the lengths scales of the system are given by

\[
a < 2\pi R < \frac{2\pi \hbar v_F}{E} < d < L . \quad (3.59)
\]
4 Impurity Characterization and Effects of Symmetry Breaking on Electronic Transport in Graphene

In this chapter we show that potential scatterers in graphene can be classified according to their cross section into three main categories: “small cross section scatterers”, “resonant scatterers” and “unitary scatterers”. We also show that the ratio of transport to elastic times at low carrier concentrations takes a characteristic value of 2 for potential scatterers, and that ratio reflects the highly anisotropic character of electron scattering in graphene. We also show that the photo-controllable graphene/azobenzene/gold sandwiches lead to the local doping of graphene and display unitary resonances associated with the appearance of quasi-bound states, where these states mimic the classical phenomenon of whispering gallery modes. Finally, we show that in the presence of disorder that leads to the reduction of the symmetries of graphene, the characteristic ratio of transport to elastic times changes from its value of 2 and becomes closer to 1. This indicates a higher degree of isotropy in the scattering due to the appearance of back scattering. We also show that the absence of skew scattering in graphene systems is protected by effective time reversal, and that the perturbations that break this symmetry will lead to a non-vanishing valley skewness, which leads to the formation of the valley Hall effect. The main results of this chapter have been reported in [41, 43, 46]

4.1 Short Range Scatterers, and Their Scattering Regimes

Adsorbed impurities [47, 48], as well as lattice vacancies and other local defects in the lattice [49] provide natural short-range scattering centers known as resonant scatterers, due to the resonant character of their total cross section, as we are going to show in this section. Sources of resonant scatterers are also organic groups [50], clusters of impurities [42], or even artificially controlled metallic islands deposited on the surface
of graphene [51]. Extensive work has identified the existence of resonant scatterers as the main mechanism limiting carrier mobility in graphene samples [50, 52, 53]. These conclusions are supported by the insensitivity to screening effects provided by the different substrates used [54, 55], and by the independence of the ratio of the transport to elastic times to the carrier concentration [7]. Experiments performed by Monteverde et al. [7] used the transport ($\tau_{tr}$) and elastic ($\tau_e$) scattering times extracted from magnetotransport measurements to probe the nature of the impurities in single and bilayer graphene. The ratio of these two characteristic times, $\xi = \tau_{tr}/\tau_e$, describes at low Fermi energies (low carrier concentration) the degree of angular anisotropy of the scattering process, offering an interesting insight on the type of impurities present in samples. One should comment that other work argues that carrier mobility in graphene is mainly limited by long range scattering from charged impurities [56–59], also related to the formation of electron-hole puddles [25, 54, 57, 60].

In the presence of short range scatterers, that do not lead to valley mixing, the Hamiltonian of the system at the $K$ point, in normal basis in Eq. 2.11,

$$H = H_0 + V\Theta(R - r) \ ,$$  \hspace{1cm} (4.1)

where $H_0$ is given in Eq. 2.11 (with $\hbar v_F \approx 6.6$ eV Å), and $\Theta$ is the Heaviside function determining the radius $R$ of the region.

Here we use the scattering formalism described in Ch.3 (see Sec. 3.1), where we obtained (Eq. 3.18)

$$f_n = \frac{e^{-in\pi/4}}{\sqrt{2\pi k}} (S_n - 1) \ ,$$  \hspace{1cm} (4.2)

and in this in this case

$$S_n = -\frac{aH^{(2)}_n(kR)J_{n-1}(k'R) + a'H^{(2)}_{n-1}(kR)J_n(k'R)}{aH^{(1)}_n(kR)J_{n-1}(k'R) + a'H^{(1)}_{n-1}(kR)J_n(k'R)} \ ,$$  \hspace{1cm} (4.3)

with, $j = n - 1/2$ is the total angular momentum, $k = |E|/(\hbar v_F)$, $k' = |E - V|/(\hbar v_F)$, $a = 1$, and $a' = \text{sgn}(E/(E - V))$. 

As \( f_n \propto S_n - 1 \), and \( S_n = S_{-(n-1)} \), this leads to equal weights in the scattering amplitude for the \( n \) and \(-(n-1)\) (\( j \) and \(-j\)) channels, and therefore the total suppression of back scattering.

This latter result can be clearly obtained from the differential cross section

\[
\sigma(\theta) = \frac{2}{\pi k} \left| \sum_{n \geq 0} e^{i\theta/2} (S_n - 1) \cos \left( \frac{(2n + 1)\theta}{2} \right) \right|^2 ,
\]

(4.4)

Notice that \( \sigma(\pi) = 0 \), while it takes its maximum value at \( \sigma(0) \), indicating that the scattering process is predominantly forward, strongly anisotropic, with fully suppressed backscattering. This anisotropy reflects the nature of the massless helical particles in graphene [33].

At low carrier concentration \((kR \ll 1)\), the lowest total angular momenta channels \((j = \pm \frac{1}{2})\), which correspond to \( n = 0 \) and \( n = 1 \) will be the dominant channels in scattering. In this limit we find

\[
S_0 \approx S_1 \approx 1 + i\pi \left( \frac{aJ_0(k'R)}{a'kRJ_1(k'R)} + \ln(e'kR) + i\frac{\pi}{2} \right)^{-1};
\]

(4.5)

this expression [7, 36] uses the asymptotic behavior of the Hankel functions [45], where \( \gamma \approx 0.58 \) is the Euler-Mascheroni constant.

The differential cross section \( \sigma(\theta) \), explicitly displays the anisotropy of the scattering; the transport cross section \( \sigma_{tr} \), is related to the transport mean free time, \( \tau_{tr}^{-1} = n_{imp}v_F\sigma_{tr} \); and the total cross section \( \sigma_t \), is related to the elastic scattering time, \( \tau_e^{-1} = n_{imp}v_F\sigma_t \), where \( n_{imp} \) is the impurity concentration in the sample.

Short range scatterers are categorized according to the total cross section they produce [7] (as shown in Fig. 4.1): “Small cross section scatterers”, “Medium cross section scatterers” are referred in the literature also as resonant scatterers, and the “large total cross section scatterers” or “unitary” [61, 62].
Figure 4.1: Total cross section as a function of $V$, for an incoming electron along the $x$-axis with $kR = 1.5 \times 10^{-3}$. Scatterers belonging to the blue shaded region are small cross section scatterers. Scatterers in the red shaded region are resonant scatterers. The unitary scattering regime happens for a very specific value of $V$ and $R$ as it is shown by the green line.

From Eq. 4.5 we notice three different regimes of scattering [7]; first, small cross section (off-resonant) scatterers where,

$$\frac{\sigma_t}{2} \simeq \sigma_{tr} \simeq kR^2 \left( \frac{\pi J_1(k'R)}{J_0(k'R)} \right)^2; \quad (4.6)$$

the medium cross section (resonant) scatterers, where

$$\frac{\sigma_t}{2} \simeq \sigma_{tr} \simeq \frac{\pi^2}{k \ln^2(e^{\gamma}kR)}; \quad (4.7)$$

and the large cross section (unitary) scatterers, where

$$\frac{\sigma_t}{2} \simeq \sigma_{tr} \simeq \frac{4}{k}. \quad (4.8)$$

The scattering of massless Dirac fermions in graphene from short range potential scatterers results in $\xi \simeq 2$, for all $V$ and $R$, as long as the carrier density is small, $kR \ll 1$. 
This ratio is fully determined by the number and equal weights of the angular momentum channels contributing to the scattering process, where the relations between the different scattering channels are determined by the conservation laws, as will be shown in the following sections (see Sec. 4.2). The differential cross section, Eq. 4.4, reflects the absence of back scattering in any of these regimes, confirming that this ratio provides a good measure of anisotropy in the scattering process, due to the helical nature of the scattered charged carriers in graphene [7].

Therefore, the ratio of transport to elastic scattering times, which are determined in experiments via magneto-conductance measurements can give insights into the nature of the dominant scattering mechanism in graphene samples. In the experiment performed in [7] these times were measured as a function of carrier concentration for single layer graphene and a ratio $\xi = 1.8 \pm 0.2$ was obtained, which suggested that the main source of scattering in the samples analyzed were short range scatterers. It should be also noticed that $\xi \approx 2$, for all $V$ and $R$, as long as the carrier density is small, $kR \ll 1$ [7], a result that is protected from the disorder in the potential strength and random sizes of the scatterers. In the next section, we explore the symmetries that lead to this protection, and the perturbations that may lead to the deviation of this ratio from its ideal value of 2.

4.1.1 Optically Controllable Quasi-Bound States in Graphene

In this section we are going to show that electron scattering from potential obstacles, at high energies ($kR > 1$), leads to the formation of quasi-bound states that mimic the well known whispering gallery modes. In the previous section we have shown that Dirac fermions in graphene are insensitive to potential scatterers. The insensitivity to these scatterers is reflected through the highly anisotropic differential cross section, in Eq.4.4, which indicates that electrons with finite energies will be mostly transmitted forward with no back scattering. This makes the electrostatic confinement of Dirac fermions with a
non-zero energy in graphene an impossible task. However, in analogy with the MIT bag model, it was proposed that Dirac fermions in graphene can be bound in a circularly gated region at zero energy [63]. Even though this proposal seems to satisfy the purpose of electrostatically confining electrons in graphene, it remains experimentally challenging, as it relies on the fact that the carrier concentrations are exactly zero.

As mentioned in the previous section, according to the their total cross section, potential scatterers display three main scattering regimes. In this section we will focus on the unitary resonant limit, as this limit is associated with the appearance of relatively long lived states known as quasi-bound states.

![Figure 4.2](image-url)

Figure 4.2: a) Schematic representation of graphene-azobenzene-gold sandwich before shining u.v. light. b) Schematic representation of graphene-azobenzene-gold sandwich after shining u.v. light.

In the experiment preformed by Margapoti et al. [43], they made use of photo-sensitive molecules, known as azobenzene, in order to control the electronic properties of graphene. The experimental setup consisted of a gold substrate, on which the azobenzene molecules were sulfur terminated in order to get attached to the gold substrate, and afterwards a single layer graphene sheet was deposited on top of the attached molecules, as shown in Fig. 4.2a. When u.v. light is shined on the graphene-azobenzene-gold sandwich, the azobenzene molecules change their
configuration from trans (standing up), to cis (bent). This optically induced photo-isomerization and the consequent length reduction of the molecule from 1.90 nm to 1.45 nm, are accompanied with a significant change of the dipole moment[64, 65].

A conductive atom force microscope was used to determine the topography of the samples and the current as a function of bias voltage, an schematic setup of the experiment is shown in Fig. 4.3a. The change in the dependence of the current on the bias voltage between the trans and cis configurations in shown in Fig. 4.3, the topography of the sample before shining u.v. in Fig. 4.3d, and the current was measured at the red circled area in Fig. 4.3c

Figure 4.3: a) Schematic representation of c-AFM measurement on the graphene-azobenzene/Au hybrid with the azobenzene molecule in trans and cis configurations. b), I-V characteristics in trans-configuration before illumination (blue trace), in cis- configurations after switching with UV-light (red trace) and after switching back to the trans-configuration (green trace) following white light illumination. c), Typical current topography over a 200 × 200 nm area at a fixed bias voltage of 10 mV with the mSAM in the trans-configuration. The red spot indicates the position of the AFM-cantilever when the I-V was performed. The current compliance used for all measurements was set to 20 nA., topographical image of b). d) Topographic image of the sample. (Courtesy of Margapoti et al. [43]).
Fig. 4.3b,c and d provide important evidence that helps describe the underlaying physical phenomenon in this system. First, the difference in the current patterns between trans and cis suggest that the change in the dipole moment of the molecules plays an important role in the local gating (change of carrier concentration) in given areas of the sample. The current map in Fig. 4.3c and the topographic image of the sample before illumination in Fig.4.3d reveal terraces with rings of high current, delineating the grains of the underlying Au-electrode when deposited on glass substrate.

![Graph showing current versus bias voltage](image)

**Figure 4.4:** a) I-V characteristics measured on several positions of the sample. Colour of the I-V traces corresponds to the position on the current map recorded at fixed bias of 10 mV when the molecules are in cis-configuration, b). The switching of the molecules has been carried out by illuminating the sample with 360 nm lamp over a 30 min time scan. c) I-V traces recorded consecutively in up-down sweeps over an entire 2 sec time. Each trace is vertically shifted for clarity; the arrow indicates bias sweep direction. The resonance peaks are slightly shifted by few millivolts with respect to the previous cycle. (Courtesy of Margapoti *et al.* [43]).

The final and most significant component that helped us establish the simple model that describes the electron dynamics in the system comes from Fig. 4.4 which shows equally spaced resonances in the $I - V$ curves over scanned regions as a function of bias voltage, and these peaks shift by a few millivolts as a function of time in a given region.

With this information at hand, we simulate the effect of local gating, via the 2D Dirac equation with a potential perturbation for a circular region. The circular region is an approximation of the areas formed in the graphene-azobenzene/Au hybrid system. The
potential perturbation can be described over a finite-sized circular region as in Eq. 4.1. Assuming the potential to be smooth such that it does not cause intervalley scattering, one can treat the problem at each Dirac point independently [41, 42].

Utilizing a partial mode-$j$ decomposition in Ch. 3 (see Sec. 3.1), one can obtain the phase shifts gained for each angular momentum channel [36]

$$
\tan \delta_j(E, V) = \frac{J_{j-1/2}(kR)J_{j+1/2}(k'R) - \zeta J_{j+1/2}(kR)J_{j-1/2}(k'R)}{N_{j-1/2}(kR)J_{j+1/2}(k'R) - \zeta N_{j+1/2}(kR)J_{j-1/2}(k'R)},
$$

where $\zeta = \text{sgn}((E - V)E)$.

The phase shifts can be directly related to differential, total and transport cross sections, which reveal different aspects of the scattering processes, including the formation of quasi-bound states in the scattering region.

The total cross section in terms of phase shifts is given in Eq. 3.28, is shown in Fig. 4.5, in a local potential versus bias map for this system. High amplitude peaks in this map signal the presence of resonances in the scattering as marked by the white crosses (at $VR/hv_F = 22.1$), indicating the formation of periodic quasi-bound states in the gated region with finite life time characterized by the width of the peak. The quasi-bound states can be seen as circulating inside the gated region, avoiding Klein tunneling for a finite time, given their scattering from the potential boundary at non-normal angles of incidence, as shown in Fig. 4.5c.

For high energies, these shape resonances would mimic the classical whispering gallery modes inside the region defined by the potential. In that limit, one can understand the near-constant energy spacing between consecutive resonances, as the characteristic wavelength $\lambda \approx 2\pi R/n$, so that $k_n = 2\pi/\lambda$ which would yield

$$
\Delta E = hv_F(k_{n+1} - k_n) = hv_F/R.
$$

For $\Delta E \approx 100\text{meV}$, we estimate $R \approx 7\text{nm}$ (given that $hv_F \approx 6.6\text{ eV} \cdot \text{Å}$). Similarly, in other regions of the sample where the characteristic spacing between the resonant peaks is
Figure 4.5: a) Map of total cross section, $\sigma_{\text{Total}}$, for circular gated region of radius $R$, as function of gate potential $V$ and electron energy $E$ in units of $\hbar v_F/R$ ($\sigma_{\text{Total}}$ scaled by $k = ER/\hbar v_F$). Nearly periodic peaks in $E$ at constant $V$ are shape resonances with consecutive peaks characterized by $\Delta E \approx \hbar v_F/R$. b) Line trace of total cross section as a function of $ER/\hbar v_F \propto V_{\text{Bias}}$, for $VR/\hbar v_F = 22.1$ with thermal broadening corresponding to room temperature. The peaks are nearly equally spaced after the thermal broadening (nearly periodic resonances correspond to the white crosses in panel a). c) Spatial amplitude map of a typical resonance at $ER/\hbar v_F = -10.2$ for $VR/\hbar v_F = 22.1$ (leftmost white cross in panel a and leftmost peak in panel b), resonant peaks in the cross section result in spatial amplitudes increasingly bounded to the perimeter of the circular gate region as $|E|$ increases, similarly to well-known whispering gallery modes.

Notice that the thermal broadening $\approx 25\text{meV}$ appears to be the dominant factor controlling the resonance line widths, suggesting that the injected electrons propagate ballistically over the characteristic length scales explored in the experiment. The effects of thermal broadening can be estimated by the convolution of the total cross section at zero temperature and a normalized distribution function; for simplicity, we use a gaussian function, $g(x, s) = e^{-x^2/2s^2}/s \sqrt{2\pi}$, with thermal width $s = k_B T \approx 25 \text{meV}$, such that

$$\sigma_{\text{Total}}(V_{\text{Bias}}, T) = \int_{-\infty}^{\infty} \sigma_{\text{Total}}(E, 0) g(E - V_{\text{Bias}}, k_B T) \, dE.$$  

(4.11)
Sample results of this convolution are shown in Fig. 4.5b, for the $\sigma_{\text{Total}}(E, 0)$ shown in Fig. 4.5a.

In this section we have presented a simple model that explains the electronic properties obtained from graphene-azobenzene-gold sandwiches. The equally spaced resonances displayed after illumination indicate the appearance of quasi-bound states in graphene due to the gating produced by the change in the dipole moment of the molecules. The regions on which the azobenzene molecules exist are determined by the terraces produced by the gold substrate, and from our calculations we were able to estimate an average size of $7\text{nm}$. The quasi-bound states in these regions mimic the classical whispering gallery modes, in that the electrons in these states can be seen as circulating inside the potential region, avoiding Klein tunneling for a finite time. This hybrid assembly allows for possible in situ modification of scattering potentials on graphene using a convenient method - simply illuminating to change the conformation of the proximal azobenzene in a controllable fashion.

### 4.2 Symmetry Breaking Effects on Electronic Transport in Graphene

The helical nature of the massless Dirac particles in pristine graphene gives rise to interesting phenomena, such as Klein tunneling [5], and the observation of weak anti-localization in this material [6]. However, it has been shown that the transport properties of graphene strongly depend on the nature, symmetries and concentration of the impurities present in typical samples [6, 7, 66–75]. Perturbations from impurities may belong to different symmetry classes. As such, they could either enhance or weaken the signatures expected from the helical nature of the scatterers of graphene and drastically modify the electronic and spin transport properties.

Here, going beyond the single-valley Dirac treatment [41], we study the scattering properties of Dirac fermions from adatoms or imperfections on graphene, as they may
lead to the reduction of lattice symmetries. Through a symmetry analysis and considering intra- and inter-valley processes, we are able to identify the constants of motion for different situations. We further examine the constraints imposed by these conserved quantities on the scattering matrix and the observable consequences on transport experiments.

We focus in particular on the ratio of transport to elastic times, \( \xi = \tau_t / \tau_e \), and its dependence on carrier concentration, which was previously studied for systems where SOIs were locally enhanced, and no additional local symmetry breaking effects were considered [41]. We find that this ratio depends strongly on the microscopic potential perturbations, which make \( \xi \) deviate from its characteristic low-energy value of 2 [41]. This deviation depends on the carrier concentration and strength of the symmetry breaking, as well as on the local potential shift produced by the impurities. As backscattering becomes stronger, the ratio takes a value closer to 1 (the limit for massive Schrödinger particles). Finally, from the symmetries of the scattering matrix, we show which systems may display non-zero valley transport skewness (skew scattering), and lead to the appearance of the valley Hall effect.

We further illustrate the impact of the symmetry considerations described above for typical graphene samples. Throughout the discussion of the different perturbations, we present numerical results for the anticipated dependence of \( \xi \) and skewness to different effects, by analyzing the results for a random impurity distribution. This allows us to gain insights into the contribution of different effects to various measurable quantities.

In order to analyze the effects of symmetry breaking on the dynamics of Dirac fermions in graphene, we first consider the Hamiltonian

\[
H = H_0 + V_T ,
\]

(4.12)

where \( H_0 \) is the pristine graphene Hamiltonian in chiral basis, Eq. 2.13.
Here we define, $V_T$, as the set of time reversal invariant perturbations [66, 68, 69, 72],

$$[V_T, \mathcal{T}] = 0 ,$$  \hspace{1cm} (4.13)

where $\mathcal{T}$ is the time reversal operator, Eq. 2.35. Additionally, the helicity operator in Eq. 2.60, indicates the pseudo-spin projection in the direction of momentum [28, 32], with

$$\left[ H_0, \hat{h} \right] = 0 ,$$  \hspace{1cm} (4.14)

and

$$\{\mathcal{T}, \hat{h} \} = 0 .$$  \hspace{1cm} (4.15)

The conservation of total angular momentum in a system in which perturbations $V_T$ are present requires

$$\left[ H, J_z \right] = 0 ,$$  \hspace{1cm} (4.16)

where

$$J_z = -i \partial_\theta + \frac{1}{2} \gamma^5 \alpha_3 .$$  \hspace{1cm} (4.17)

In systems where the spatial dependence of the perturbations has circular symmetry, such as the simple form $H = H_0 + V_T \Theta(R - r)$, there exist a subset of time reversal invariant interactions that conserve the total angular momentum,

$$V_{T,J} \subset V_T .$$  \hspace{1cm} (4.18)

This set can be shown to be composed of the elements [28, 31, 66–70, 72–74, 76, 77]

$$V_{T,J} = \{vI, s\alpha_3, t\beta e^{i\gamma^5 \phi} \} ,$$  \hspace{1cm} (4.19)

where $v$, $s$, $t$ and $\phi$ are real parameters. Notice that with the exception of $vI$, the $V_{T,J}$ generate gaps in the spectrum and are referred to as “massive terms” [28] (see Sec. 2.3.2 in Ch. 2). The $v$ term describes a constant local potential shift caused by the adatoms, while the $s$ term describes a staggered potential effect some perturbations may add, where
the A and B sites are affected differently. The $t$ terms describe a hopping modulation amplitude caused by the adatoms/defects, where $\phi$ describes the angle of dimerization of the resulting deformation, as in a Kekulé pattern [28, 31, 76].

One can also define the subset

$$V_{T,J,h} \subset V_{T,J} ,$$

for perturbations that in addition to commuting with $T$ and $J_z$, also commute with the helicity operator $\hat{h}$, and find that

$$V_{T,J,h} = \{ vI, t\beta e^{i\gamma \phi} \} .$$

In these cases the eigenstates of the Hamiltonian,

$$H = H_0 + V_{T,J,h} ,$$

can be identified by corresponding quantum numbers, such that

$$\hat{h}\psi_{\pm,j} = \pm\psi_{\pm,j}$$

(as $\hat{h}^2 = 1$), and

$$J_z\psi_{\pm,j} = j\psi_{\pm,j} ,$$

where $j$ is half-integer. One can also find an additional operator

$$\mathcal{T}_1 = ie^{-i\gamma \phi} \gamma^5 \alpha_2 C ,$$

such that $\mathcal{T}_1^2 = -1$,

$$[\mathcal{T}_1, H] = [\mathcal{T}_1, \hat{h}] = 0 ,$$

while

$$\{\mathcal{T}_1, J_z\} = 0 .$$

$\mathcal{T}_1$ can be seen as a combination of a chiral rotation and the effective time reversal operator in each Dirac point [26, 28, 36, 63] (see Eq. 2.39 and 2.81). This operator
together with the time reversal operator $T$, relate the states with angular momentum $j$ and $-j$, which can be chosen such that

$$T_1 \psi_{\pm,j} = \pm (-1)^j \psi_{\mp,-j}, \quad (4.28)$$

and

$$T \psi_{\pm,j} = \mp (-1)^{j+\frac{1}{2}} \psi_{\mp,-j}. \quad (4.29)$$

These eigenstates can be represented with the help of the (helicity) projection operators $P_{\pm} = (1 \mp \gamma^5)/2$, so that a general eigenstate of the Hamiltonian can be written as

$$\psi = P_+ \psi + P_- \psi \quad (4.30)$$

with $[\hat{h}, P_{\pm}] = 0$ and $\hat{h}(P_{\pm} \psi) = \pm P_{\pm} \psi$. In addition, for a partial wave component we have

$$T_1 \psi_j = T_1 P_+ \psi_j + T_1 P_- \psi_j$$

$$= (-1)^j (P_+ - P_-) \psi_{-j}$$

$$= (-1)^j \gamma^5 \psi_{-j}. \quad (4.31)$$

Similarly, for the operator $T$, one gets

$$T \psi_j = (-1)^{j+\frac{1}{2}} \gamma^5 \psi_{-j}. \quad (4.32)$$

Conservation of total angular momentum allows one to use the $j$ block-diagonal character of the scattering matrix. The lack of valley mixing in the area outside the potential perturbation region, $r > R$, enables the determination of the scattering amplitudes between the $+$ and $-$ (or correspondingly $K$ and $K'$) states for each $j$ block. The scattering of a single partial wave $j$ can be written in terms of incoming $\psi_j^{in}$ and outgoing $\psi_j^{out}$ radial eigenstates of the free Hamiltonian,

$$\psi_j = \psi_j^{in} + S_j \psi_j^{out}, \quad (4.33)$$
where,

\[
S_j = \begin{pmatrix} \hat{S}_{++j} & \hat{S}_{+-j} \\ \hat{S}_{-+j} & \hat{S}_{--j} \end{pmatrix},
\]

(4.34)

\[
\hat{S}_j = S_{\tau\tau^{'},j} \sigma_0,
\]

where \(\tau, \tau' = \pm\). Unitarity of \(\hat{S}\) requires

\[
\hat{S}_j \hat{S}_j^\dagger = I,
\]

(4.35)

since the \(S\) matrix takes a block diagonal form.

Symmetry under the operators \(T_1\) and \(T\) determine relations between the \(j\) and \(-j\) blocks, such that

\[
T_1 \psi_j = T_1 \psi_j^{in} + T_1 S_j T_1^{-1} T_1 \psi_j^{out}
\]

(4.36)

or

\[
\psi_{-j} = \psi_{-j}^{out} + \gamma^5 T_1 S_j T_1^{-1} \gamma^5 \psi_{-j}^{in}.
\]

(4.37)

Comparison with the \(-j\) wave component,

\[
\psi_{-j} = \psi_{-j}^{in} + S_{-j} \psi_{-j}^{out},
\]

(4.38)

results in the following condition for \(S_j\),

\[
\gamma^5 T_1 S_j T_1^{-1} \gamma^5 = S_{-j}^*,
\]

(4.39)

or equivalently,

\[
\begin{pmatrix} \hat{S}_{++j} & -\hat{S}_{+-j} e^{2i\phi} \\ -\hat{S}_{-+j} e^{-2i\phi} & \hat{S}_{--j} \end{pmatrix} = \begin{pmatrix} \hat{S}_{++-j} & \hat{S}_{+-j} \\ \hat{S}_{-+j} & \hat{S}_{--j} \end{pmatrix}.
\]

(4.40)

Similarly, symmetries under \(T\) result in

\[
\gamma^5 T S_j T^{-1} \gamma^5 = S_{-j}^*.
\]

(4.41)
or

\[
\begin{pmatrix}
\hat{S}_{--}, j & -\hat{S}_{-+}, j \\
-\hat{S}_{+-}, j & \hat{S}_{++}, j
\end{pmatrix} =
\begin{pmatrix}
S_{++}, j & S_{+-}, j \\
S_{-+}, j & S_{--}, j
\end{pmatrix},
\]

(4.42)

with the resulting relations

\[
S_{\tau\tau}, j = S_{\tau\tau}, -j = S_{\bar{\tau}\bar{\tau}, -j} = S_{\bar{\tau}\bar{\tau}, j},
\]

(4.43)

\[
S_{\bar{\tau}\bar{\tau}, j} = -S_{\tau\tau, -j}e^{-2i\tau\phi} = S_{\bar{\tau}\bar{\tau}, j}e^{-2i\tau\phi} = -S_{\tau\tau, -j},
\]

where \( \bar{\tau} = -\tau \).

The amplitudes and corresponding cross sections can be obtained by direct comparison of the far field forms of the incoming and scattered waves in Eq. 4.33 (see Sec. 3.3). The scattering amplitudes in each \( j \)-block are given by [35]

\[
f_j = \frac{e^{-i\pi/4}}{\sqrt{2\pi k}} \begin{pmatrix}
(\hat{S}_{++}, j - 1) & -i\hat{S}_{+-}, j \\
i\hat{S}_{-+}, j & (\hat{S}_{--}, j - 1)
\end{pmatrix}
\]

(4.44)

and related to different cross sections in Eq. 3.8, 3.52, 3.53 and 3.54, with the spin index omitted in the expressions of the cross sections, we similarly define the valley averaged quantities in Eq. 3.55, 3.43, 3.44 and 3.58 (spin index omitted).

For a circularly symmetric region where

\[
H = H_0 + V_{T, J, h}
\]

(4.45)

for \( r < R \), and

\[
H = H_0
\]

(4.46)

for \( r > R \), ensures that the set of relations in Eq. 4.43 are satisfied, so that

\[
f_{\tau\tau}, j = f_{\tau\tau, -j} = f_{\bar{\tau}\bar{\tau}, -j} = f_{\bar{\tau}\bar{\tau}, j},
\]

(4.47)

\[
f_{\tau\tau, j} = -f_{\tau\tau, -j}e^{-2i\tau\phi} = f_{\bar{\tau}\bar{\tau}, j}e^{-2i\tau\phi} = -f_{\tau\tau, -j}.
\]
Consequently,

\[
\sum_{j=\pm \infty}^{\infty} f_{\tau \tau, j} e^{ij\theta} = \sum_{j\geq\frac{1}{2}} 2f_{\tau \tau, j} \cos(j\theta), \tag{4.48}
\]

\[
\sum_{j=\pm \infty}^{\infty} f_{\tau \bar{\tau}, j} e^{ij\theta} = \sum_{j\geq\frac{1}{2}} 2if_{\tau \bar{\tau}, j} \sin(j\theta),
\]

which results in

\[
\sigma_{\tau \tau}(\theta) = \frac{2}{\pi k} \left| \sum_{j\geq\frac{1}{2}} f_{\tau \tau, j} \cos j\theta \right|^2, \tag{4.49}
\]

\[
\sigma_{\tau \bar{\tau}}(\theta) = \frac{2}{\pi k} \left| \sum_{j\geq\frac{1}{2}} f_{\tau \bar{\tau}, j} \sin j\theta \right|^2,
\]

\[
\sigma(\theta) = \sum_{\tau, \bar{\tau}} \sigma_{\tau \tau}(\theta).
\]

Notice that the differential cross sections for valley-preserving processes, \(\sigma_{\tau \tau}(\theta)\), display a maximum at \(\theta = 0\), and vanish at \(\theta = \pi\) (which signals the absence of backscattering). The situation is reversed for the valley-flipping cross sections, \(\sigma_{\tau \bar{\tau}}\), which display a maximum at \(\theta = \pi\), and vanish at \(\theta = 0\). It is then clear that any backscattering in the system is caused solely by valley flipping events.

The scattering matrix elements are naturally related to experimentally measurable quantities via the total, transport and skew cross sections. The transport cross section \(\sigma_{tr}\) is related to the transport time, and the total cross section \(\sigma_t\) to the elastic scattering time (see previous Sec. 4.1). We like to emphasize that the ratio

\[
\xi = \frac{\tau_{tr}}{\tau_e} = \frac{\sigma_t}{\sigma_{tr}} \tag{4.50}
\]

reflects the degree of angular isotropy in the scattering processes, [7, 41, 71] with \(\xi = 1\) in the fully isotropic (massive) limit at low energies. The skew cross section \(\sigma_{sk}\), quantifies the asymmetry of the scattering about the electron’s direction of incidence, and it is related to the appearance of Hall currents, as characterized through the skew parameter [78]

\[
\gamma = \frac{\tau_{tr}}{\tau_{sk}} = \frac{\sigma_{sk}}{\sigma_{tr}}. \tag{4.51}
\]
The form of the differential cross section in Eq. 4.49 results in no skewness, since it is symmetric about the $x$-axis ($\theta = 0$), yielding null skew cross sections, since

$$
\sum_{j=-\infty}^{\infty} f_{\tau\tau,j} f_{\tau\tau,j+1}^* = |f_{\tau\tau,\frac{1}{2}}|^2 + \sum_{j\geq \frac{1}{2}} 2\text{Re}(f_{\tau\tau,j} f_{\tau\tau,j+1}^*),
$$

$$
\sum_{j=-\infty}^{\infty} f_{\tau\bar{\tau},j} f_{\tau\bar{\tau},j+1}^* = -|f_{\tau\bar{\tau},\frac{1}{2}}|^2 + \sum_{j\geq 1} 2\text{Re}(f_{\tau\bar{\tau},j} f_{\tau\bar{\tau},j+1}^*),
$$

(4.52)

which results in

$$
\sum_{j=-\infty}^{\infty} \text{Im}(f_{\tau\tau,j} f_{\tau\tau,j+1}^*) = 0,
$$

$$
\sum_{j=-\infty}^{\infty} \text{Im}(f_{\tau\bar{\tau},j} f_{\tau\bar{\tau},j+1}^*) = 0.
$$

(4.53)

Now, when $kR \ll 1$, the only scattering channels with non vanishing amplitudes are $j = \pm \frac{1}{2}$, and the ratio of transport to elastic times becomes

$$
\xi = \frac{\tau_{tr}}{\tau_e} = \frac{\sigma_t}{\sigma_{tr}} = \frac{\sum_{\tau\tau'} \sigma_{t,\tau\tau'}}{\sum_{\tau\tau'} \sigma_{tr,\tau\tau'}},
$$

(4.54)

where,

$$
\sigma_{t,\tau\tau} \approx 2 \frac{2}{k} |f_{\tau\tau,\frac{1}{2}}|^2 = 2\sigma_{tr,\tau\tau},
$$

$$
\sigma_{t,\bar{\tau}\tau} \approx 2 \frac{2}{k} |f_{\bar{\tau}\tau,\frac{1}{2}}|^2,
$$

$$
\sigma_{tr,\tau\tau} \approx 3 \frac{3}{k} |f_{\tau\bar{\tau},\frac{1}{2}}|^2,
$$

$$
\sigma_{sk,\tau\tau} = \sigma_{sk,\bar{\tau}\tau} = 0.
$$

(4.55)

This yields

$$
\xi = \frac{\sigma_t}{\sigma_{tr}} = \frac{2 \left(|f_{++\frac{1}{2}}|^2 + |f_{+-\frac{1}{2}}|^2 \right)}{|f_{++\frac{1}{2}}|^2 + 3|f_{+-\frac{1}{2}}|^2}.
$$

(4.56)

Remote charge impurities lead to a local change in the carrier concentration in their area of influence and a local change of the Fermi momentum in that region. These impurities can then be described in the continuum model by the perturbation $\nu I$, which
respects all the symmetries of the graphene lattice and belongs to the $A_1$ representation of
the $C_{6\nu}$ point group [66, 74]. This shift does not lead to valley mixing and from Eq. 4.56
(as $f_{\tau\tau',1} = 0$) one finds $\xi = 2$ for $kR \ll 1$, regardless of the value of $v$, as has been
experimentally shown [7, 71]. This is a direct consequence and signature of the anisotropy
and predominant forward scattering in graphene.

Some impurities may generate a staggered potential that differentiates between the $A$
and $B$ sites, as mentioned above, with a perturbation described by $s\alpha_3$ in the continuum
model. This term reduces the point symmetries of the lattice (belongs to the $B_2$
representation of $C_{6\nu}$), and although it does not mix valleys, it opens a gap.

In the presence of interactions that belong to the set $V_{T,J}$, the conditions on the
scattering matrix elements are those resulting only from time reversal symmetry, such that
they are reduced to those in 4.42,

$$S_{\tau\tau,j} = S_{\tau\tau,-j}, \quad (4.57)$$
$$S_{\tau\tau,j} = -S_{\tau\tau,-j},$$
$$S_{\tilde{\tau}\tilde{\tau},j} = -S_{\tilde{\tau}\tilde{\tau},-j},$$

and correspondingly,

$$f_{\tau\tau,j} = f_{\tau\tau,-j}, \quad (4.58)$$
$$f_{\tau\tau,j} = -f_{\tau\tau,-j},$$
$$f_{\tilde{\tau}\tilde{\tau},j} = -f_{\tilde{\tau}\tilde{\tau},-j}.$$

These relations cannot guarantee 4.52 and 4.53, so that for example $\sum_{j=-\infty}^{\infty} Im(f_{\tau\tau,j}f_{\tau\tau,j+1}^*)$
is not identically zero by symmetry; instead, its value depends on the details of the
perturbations in the Hamiltonian. As a consequence, one can write

\[ \sigma_{t,\bar{t}t} = \sigma_{t,\bar{t}t}, \]
\[ \sigma_{t,\bar{t}t} = \sigma_{t,\bar{t}t}, \]
\[ \sigma_{sk,\bar{t}t} = -\sigma_{sk,\bar{t}t}, \]
\[ \sigma_{t,\bar{t}t} = \sigma_{t,\bar{t}t}, \]
\[ \sigma_{t,\bar{t}t} = \sigma_{t,\bar{t}t}, \]
\[ \sigma_{sk,\bar{t}t} = -\sigma_{sk,\bar{t}t} = 0. \] (4.59)

The presence of \( s \neq 0 \) not only affects the ratio of scattering times \( \xi \), but also results in a non-zero skew cross section (Eq. 4.59), given that

\[ \sigma_{sk,\bar{t}t} = -\sigma_{sk,\bar{t}t} \] (4.60)

and

\[ \sigma_{sk,\bar{t}t} = 0, \] (4.61)

and the corresponding appearance of a valley Hall effect [79]. This effect is associated with the appearance of transverse valley currents, which can be characterized by a valley Hall angle

\[ \Theta_{VH} = \frac{j_{VH}}{J_x}. \] (4.62)

At zero temperature the valley Hall angle is equal to the valley skewness, in the absence of side-jump effects [46, 78],

\[ \gamma_V = \frac{1}{2}(\gamma_K - \gamma_{K'}). \] (4.63)

This effect is found to be robust to the introduction of a non-zero \( t \) valley-mixing perturbation. Note that in the case of valley polarized incident currents, \( \gamma = \gamma_V \), leading to the appearance of Hall voltages due to the accumulation of charge on the sample edges.

For impurities that accommodate on the center of the hexagon, as is the case of Ca and Al atoms [80], for a substrate with a periodicity commensurate with graphene [70],
and for ‘Kekulé’ distortions with zero dimerization angle [70], the perturbation terms can be described by \( \text{Re}(t\beta e^{i\gamma \phi}) \approx t\beta \); this does not break point symmetries of graphene (belongs to the \( A_1 \) representation of \( C_{6v} \)) but breaks translational invariance, which leads to vanishing Dirac points and the opening of a gap [70]. Other hexagon-centered impurities [28, 76, 80], lead to more general perturbations with \( \phi \neq 0 \), as described by \( t\beta e^{i\gamma \phi} \) (in the \( B_1 \) representation of \( C_{6v} \)), which also open a gap in the spectrum. The presence of these interactions is reflected in particular through the deviation of \( \xi \) away from 2 at low energies, as we will describe in detail below.

![Figure 4.6: Numerical calculation of the transport to elastic time ratio \( \xi \), for a set of 500 randomly sized impurities, where \((5 \leq R \leq 15) \text{Å}\), and \( v = 2\text{eV} \), for systems with \( \Delta \) raising from 0 to 0.5 eV; as indicated in the legend, for symmetry breaking effects described by \( t \) and \( s \), where \( \Delta = \sqrt{t^2 + s^2} \). Notice \( \xi \) deviates from the value of 2 by nearly a constant value at large energies, and reaches its minimum at/near zero energy. Inset: Dependence of \( \xi \) on \( \Delta / |E - v| \) for fixed values of \( v \) and \( E = 60\text{meV} \).](image-url)
In the presence of $t$ and $s$ perturbations, $\xi$ not only depends on these parameters but also on the value of $v$. Since $\{\alpha_3, \beta e^{i\gamma^5} \phi \} = 0$, and as $\alpha_i, \beta$, and $\gamma^5$ are self-inverse (involutory), and obey $\{\beta, \alpha_i \} = \{\alpha_3, \alpha_i \} = 0$, the local spectrum shows a gap of $2\Delta$,

$$k = \sqrt{(E - v)^2 - \Delta^2},$$

(4.64)

where

$$\Delta^2 = s^2 + t^2.$$  

(4.65)

When the potential shift generated by the impurity is such that $|E - v| \gg |\Delta|$, one recovers the linear (ultra-relativistic regime), $k \approx |E - v| + O(\Delta^2/|E - v|)$, and the effect of $\Delta$ is minimal on the scattering amplitudes; this leads to $f_{rr, \pm \frac{1}{2}} \approx 0$, as well as to $f_{rr, \pm \frac{1}{2}} \approx f_{rr, -\frac{1}{2}}$, and consequently $\xi \approx 2$, even when $s$ and $t$ may be nonzero. $\Delta$ should then be comparable to the local kinetic energy, $\Delta \approx |E - v|$, in order to have a noticeable effect. In this limit the valley-flipping contributions are non negligible, with $f_{rr, \frac{1}{2}} \neq f_{rr, -\frac{1}{2}}$, and the ratio $\xi$ exhibits a large drop at low carrier concentrations, as can be seen in Fig. 4.6.

It should be noted that although the ratio $\xi$ has similar dependence on energy in the presence of $s$ or $t$, the mechanisms by which the scattering isotropy is enhanced are different. In the presence of $t\beta e^{i\gamma^5} \phi$, the isotropy is achieved through valley-flip processes that acquire an amplitude comparable to the valley preserving processes as $|t|/|E - v| \to 1$, leading to $\xi \approx 1$ in Eq. 4.56. In the case of the staggered perturbation, the isotropy is enhanced by the decay in amplitude of one of the two available scattering channels (e.g. $f_{rr, \frac{1}{2}} \to 0$ while $f_{rr, -\frac{1}{2}} \neq 0$ at the K point) as $|s|/|E - v| \to 1$, at each valley independently [41].

It is then clear that as graphene is perturbed by adatoms or deformations, and different symmetry breaking terms appear in the Hamiltonian, many of the dynamical electronic properties will change depending on details of the specific terms. In particular, the ratio $\xi$ will generically deviate from its value of 2 as the massless nature of free
graphene quasiparticles is affected by these perturbations. The appearance of backscattering becomes increasingly important for stronger perturbations and can be detected by different transport measurements.

In the experiments by Monteverde et al., [7] graphene was deposited on SiO$_2$, and a ratio of transport to elastic times $\xi \approx 1.8$ was observed. The lowest carrier concentration for which $\xi$ is reported corresponds to $E \approx 100$ meV. The effects of substrate and impurities are more likely to be symmetry breaking, with a staggered $s$, and/or hopping modulation $t$, character. Assuming this to be the case, and comparing with the results of Fig. 7.1, we estimate the value of $\Delta/v$ (with $\Delta = \sqrt{t^2 + s^2}$) to be $\Delta/v \approx 1/7$, or $\Delta \approx 300$meV – not an unreasonable estimate of the staggered perturbation strength.

In this section we have seen that the ratio $\xi$ is not robust to symmetry breaking effects, where these effects lead to its deviation from the ideal value of 2 to the value of 1 in the case of strong symmetry breaking. Moreover, we have seen that perturbations that lead to the breaking of effective time reversal lead to the appearance of a non-zero valley skewness, which leads to the appearance of transverse valley currents, and eventually the formation of a Hall voltages in the case of valley polarized injection, or signatures in four probe experiments [12, 13].
5 Spin Orbit Active Impurity Characterization and Effects of Symmetry Breaking on Spin Transport in Graphene

In this chapter we present an analysis of scattering by defects in graphene in the presence of spin-orbit interactions (SOIs). A characteristic constant ratio ($\approx 2$) of the transport to elastic times for massless electrons signals the anisotropy of the scattering, as discussed in Ch. 4. We show that SOIs lead to a drastic decrease of this ratio, especially at low carrier concentrations, while the scattering becomes increasingly isotropic. As the strength of the SOI determines the energy (carrier concentration) where this drop is more evident, this effect could help evaluate these interactions through transport measurements in graphene systems with enhanced spin-orbit coupling. Additionally, we present an analysis based on symmetry considerations and examine the impact on the scattering matrix for graphene systems containing defects that enhance spin-orbit interactions, while conserving the electronic total angular momentum. We show that the appearance and dominance of skew scattering, and the related observation of valley and/or spin Hall effect in decorated graphene samples, suggests the set of symmetries that adatom perturbations should satisfy. We further show that detailed measurements of the transport and elastic times as function of carrier concentration make it possible to not only extract the strength of the spin-orbit interaction, as suggested before, but also obtain the amplitude of the symmetry breaking terms introduced. To examine how different terms would affect measurements, we also present calculations for typical random distributions of impurities with different perturbations, illustrating the detailed energy dependence of different observables. The main results of this chapter have been reported in [41, 46].
5.1 Spin-Orbit Interactions and Isotropic Scattering in Graphene

The importance of graphene on transport devices also motivates the identification and understanding of spin dynamics [81] as an important element in the development of spintronics. In graphene, interface or bulk broken symmetries allow for the existence of two kinds of spin orbit interaction (SOIs) that affect spin dynamics in different ways [9]. The hexagonal arrangement of carbon atoms allows an intrinsic SOI that respects lattice symmetries and can be seen to arise from the atomic SO coupling. This generates a gap in the spectrum, a mass term in the Dirac equation with sign depending on the spin, pseudospin and Dirac valley [11, 82]. An inversion asymmetry in graphene could also generate an extrinsic Rashba SOI, resulting from the effect of substrates, impurities generating $sp^3$ distortions—such as hydrogen, fluorine or gold—perpendicular electric fields, or lattice corrugations [14, 18, 19, 21, 22, 83].

Here, we will show that the presence of SOIs leads to an important transformation of scattering processes in graphene, from highly anisotropic (zero backscattering) to more or fully isotropic at low energies, depending on the strength of these interactions. We show that the Rashba SOI results in the appearance of new unitary resonances for short-range scatterers, whenever Rashba coupling is comparable to the Fermi energy. These findings suggest that transport experiments performed at low carrier concentration could unveil the local enhancement of the Rashba interaction produced by impurities, lattice corrugations, or substrate effects, and provide a direct measurement of its strength.

We consider the presence of intrinsic SOI affecting the carriers throughout the graphene system, while an extrinsic scatterer generates a local potential obstacle and corresponding Rashba SOI; the Hamiltonian for this system, written in normal basis, Eq. 2.11, close to the Dirac points is then given by

$$ H = H_0 + H_V + H_{SO} + H_R, $$

(5.1)
where $H_0$ describes Dirac fermions in graphene is given in Eq. 2.11 with $\hbar = 1$, $H_{SO} = \Delta_{SO} \tau_z s_z$ is the intrinsic SOI, $H_V = V \Theta(R - r)$ is the scattering potential characterized by strength $V$ over a region $r < R$, and $H_R = \lambda_R (\tau_z \sigma_x s_y - s_x \sigma_y) \Theta(R - r)$ is the Rashba SOI [9] over the same region. $\Delta_{SO}$ and $\lambda_R$ are the strengths of intrinsic and Rashba interactions, and $\Theta$ is the Heaviside function. The characteristic size of the scatterers is assumed to be much larger than the lattice spacing in graphene for the continuum Dirac description of graphene to be appropriate, and to neglect intervalley scattering [25, 84], although this effect will be discussed in Sec. 5.2 (notice that Eq. 5.1 can be written in a matrix form as in Eq. 3.32).

The analytical solution of the real space Dirac equation is facilitated by the adoption of the standard basis set, and the circular symmetry of the potentials. Then, $[J_z, H] = 0$, where $J_z = L_z + s_z/2 + \tau_z \sigma_z / 2$, and $L_z = -i \partial_\theta$ is the orbital angular momentum. This allows the energy eigenstates to be labeled by the corresponding eigenvalue $J_z \psi_j = j \psi_j$ ($j$ is an integer here unlike the spinless case), and allows one to write four linear coupled differential equations for the different components [40, 85, 86]. The solution to these equations in $r < R$, reads

$$\psi_n(r, \theta) = T_j^+ e^{ij\theta} \begin{pmatrix} J_{j-1}(k_+ r) e^{-i\theta} \\ ia_+ J_j(k_+ r) \\ -a_+ J_{j+1}(k_+ r) e^{i\theta} \end{pmatrix} + T_n^- e^{ij\theta} \begin{pmatrix} J_{j-1}(k_- r) e^{-i\theta} \\ ia_- J_j(k_- r) \\ a_- J_{j+1}(k_- r) e^{i\theta} \end{pmatrix}, \quad (5.2)$$

where $T_j^\pm$ are normalization constants, $a_\pm = (E - V - \Delta_{SO}) / (v_F k_\pm)$, $k_\pm = \sqrt{(E - V \pm \lambda_R)^2 - (\Delta_{SO} \pm \lambda_R)^2} / v_F$ are the wave numbers in the presence of the Rashba and intrinsic SOIs [87], with $E$ representing the energy of the state, and $J_j$ are Bessel functions regular at the origin.
The analytical form of the spinors allows one to use a partial wave decomposition to study the scattering of an incoming flux of electrons along the \( x \)-direction [36], as it is discussed in Ch. 3 (see Sec. 3.2). In this case the different scattering matrix elements \( S_{j,ss} \) and \( S_{j,\bar{s}s} \), where \( s = (\uparrow, \downarrow) = (1, -1) \), are found from the boundary conditions. For an incoming flux with spin up and down components given by \( c_1 \) and \( c_2 \), respectively, and including both the intrinsic and Rashba SOI at the \( K \) point, the boundary conditions can be written as

\[
\begin{pmatrix}
H^{(1)}_{j-1} & 0 & -J_{j-1}(k R) & -J_{j-1}(k R) \\
aH^{(1)}_{j} & 0 & -a_+J_{j}(k R) & -a_-J_{j}(k R) \\
0 & aH^{(1)}_{j} & a_+J_{j}(k R) & -a_-J_{j}(k R) \\
0 & H^{(1)}_{j+1} & J_{j+1}(k R) & -J_{j+1}(k R)
\end{pmatrix}
\begin{pmatrix}
c_1S_{j,\uparrow\uparrow} + c_2S_{n,\downarrow\uparrow} \\
c_1S_{j,\downarrow\uparrow} + c_2S_{n,\downarrow\downarrow} \\
c_1aH_{j} \equiv c_2aH_{j} \\
c_2H^{(2)}_{j+1}
\end{pmatrix},
\] (5.3)

where \( H^{(1),(2)} \) are Hankel functions of the first and second kind and are all evaluated at \( kR \) (heretofore omitted for simplicity), \( a = (E - \Delta_{SO})/\nu_F k \), \( k = \sqrt{E^2 - \Delta_{SO}^2/\nu_F} \), and \( |c_1|^2 + |c_2|^2 = 1 \), \( (|c_1|^2 = 1 \) for an incoming spin up, for example).

The scattering amplitude matrix is given by

\[
\hat{f}(\theta) = \frac{e^{-i\theta/4}}{i\sqrt{2\pi k}} \sum_j \begin{pmatrix} f_{j,\uparrow\uparrow} & f_{j,\downarrow\uparrow} \\ f_{j,\uparrow\downarrow} & f_{j,\downarrow\downarrow} \end{pmatrix} e^{i\delta_j},
\] (5.4)

where \( f_{j,ss} \) and \( f_{j,\bar{s}s} \), with \( \bar{s} = -s \), are given in Eq. 3.36 and 3.37. Conservation of flux for each channel of angular momentum (unitarity of \( S \)), imposes the condition

\[ |S_{j,ss}|^2 + |S_{j,\bar{s}s}|^2 = 1 \],

so that one can relate the scattering amplitudes to the phase shifts gained during the scattering process by \( S_{j,ss} \equiv e^{2i\delta_{j,ss}} \cos \delta_{n,ss} \) and \( S_{j,\bar{s}s} \equiv \sin \delta_{j,ss} \), where \( \delta_{j,ss} \) is the phase for spin preserving processes and \( \delta_{j,\bar{s}s} \) is conveniently defined for spin-flipping events [40, 85, 86]. The differential cross section \( \sigma(\theta) \), the transport cross section \( \sigma_T \) and the total cross section \( \sigma_T \), are given in Eq. 3.42, 3.44 and 3.43, respectively.
5.1.1 Intrinsic-SOI

Graphene systems with uniform intrinsic SOI, $\Delta_S O \neq 0$, represent a rich opportunity to explore topological effects. An example of such a system is predicted by appropriate deposition of heavy metal atoms on graphene [15]. In those cases, the eigenstates no longer have a well-defined pseudo-helicity, due to the carrier mass generated by the SOI; notice however that although this mass is spin-dependent, it does not cause intravalley spin-flip processes, and the scattering can still be analyzed in terms of independent spins. The broken helicity, however, results in $S_{j,ss} \neq S_{-(j-1),ss}$. However, effective time reversal symmetry [26] (see 4.2 in Ch. 4) imposes the relations $f_{j,ss} = f_{-j,\bar{s}s}$, and $f_{j,s\bar{s}} = f_{-j,\bar{s}s}$, and since spin mixing is not produced by the intrinsic SOI, we have $S_{j,ss} = S_{-j,\bar{s}s} = 0$.

Figure 5.1: Polar plots of differential cross section, normalized to its maximum, for different values of the intrinsic spin orbit interaction, $\Delta_{SO}$; here $ER/(\hbar v_F) = 8 \times 10^{-3}$ and $VR/(\hbar v_F) = 1.5$. Top inset: $\sigma_{max}(\theta)$, which increases as $1/(k \ln^2(kR))$ for $\Delta_{SO}/E \approx 1$, sets the scale used in the polar plots. Bottom inset: Dependence of $\xi = \sigma_i/\sigma_T = \tau_T/\tau_e$ vs. $\Delta_{SO}/E$. Notice that $\sigma(\theta)/\sigma_{max}$ and $\xi$ do not depend on the value of $V$ in this regime; $V$ only determines the amplitude of $\sigma_{max}$ in the top inset.
As one could suspect, the isotropy of the scattering process depends on the ratio of $\Delta_{SO}/E$, as shown in Fig. 5.1: the scattering is anisotropic—with absence of back scattering—for $\Delta_{SO} = 0$, while it becomes increasingly isotropic with larger $\Delta_{SO}/E$, and for $\Delta_{SO} \approx E$, the scattering is equally probable in all directions.

As mentioned above, the effect of the intrinsic SOI is the generation of a mass dependent on pseudo-spin, spin and valley, which does not result in spin-flipping processes, as it can be seen from $H_{SO} = \Delta_{so}\sigma_z s_z \tau_z$. In this case, $k = \sqrt{E^2 - \Delta_{SO}^2/(v_F)}$, $k_\pm = k' = \sqrt{(E - V)^2 - \Delta_{SO}^2/v_F}$, and $a = \frac{E - \Delta_{so} v_F}{v_F k'}$, leading to $T^+_j = T^-_j$.

$S_{j,\bar{s}} = 0$, and $S_{j,\uparrow\uparrow} = S_{-(j-1),\downarrow\downarrow}$, as expected from effective time reversal symmetry [26] (see 5.2 for details of derivation). However the mass term induced by the intrinsic SOI results in $S_{j,\uparrow\uparrow} \neq S_{-(j-1),\downarrow\downarrow}$ (for $c_1 = 1$), where

$$S_{j,\uparrow\uparrow} = \frac{aH_j^{(2)} J_{j-1}(k'R) - a'H_{j-1}^{(2)} J_j(k'R)}{aH_j^{(1)} J_{j-1}(k'R) - a'H_{j-1}^{(1)} J_j(k'R)}.$$  \hspace{1cm} (5.5)

Notice that the mass term leads to inequivalent weights for the different spinor components (i.e. $|a| \neq |a'| \neq 1$), as helicity is not a good quantum number anymore. This leads to the transformation of the scattering process from anisotropic to isotropic depending on the carrier concentration (or Fermi energy). At higher carrier concentrations, $E \gg \Delta_{SO}$, we have $a \approx \text{sgn}(E)$ and $a' \approx \text{sgn}(E - V)$ (the “ultra-relativistic limit”), resulting in $S_{j,\uparrow\uparrow} \approx S_{-(j-1),\downarrow\downarrow}$, and the different scattering regimes described above. However, it is clear that at lower energies $a \neq a' \neq 1$, leading to $S_{j,\uparrow\uparrow} \neq S_{-(j-1),\downarrow\downarrow}$; This leads to an enhancement in the isotropy of the scattering process, which will be dominated by one spinor component in this range of energies.

In the case $E \approx \Delta_{SO}$, but such that $kR \ll 1$, the asymptotic forms of the Hankel functions [45] allow one to obtain

$$S_{0,ss} \simeq 1 + \theta(k^2R^2)$$  \hspace{1cm} (5.6)
and

\[ S_{1,\uparrow\uparrow} \approx S_{-1,\downarrow\downarrow} \approx 1 + \frac{\pi}{\ln(e^{\gamma}kR)} + \vartheta(k^2 R^2), \]  
(5.7)

leading to

\[ \sigma_{t,ss} = \sigma_{tr,ss} \approx \frac{\pi^2}{k \ln^2(e^{\gamma}kR)} + \vartheta(kR^2); \]  
(5.8)

with \( \xi \equiv \sigma_t/\sigma_{tr} = 1 \). Therefore, the presence of the intrinsic SOI leads to the variation of \( \xi \) from \( \approx 2 \) for “high” concentrations, \( E \gg \Delta_{SO} \), to \( \approx 1 \) for “low” carrier concentrations. This last regime yields isotropic scattering and the onset of backscattering, which is a characteristic of massive particles at low energies [33, 88]. The ratio \( 1 < \xi < 2 \) is found to be proportional to the carrier concentration in the presence of intrinsic SOI, with \( \xi \approx 1 \) at low carrier concentrations; in other words, one of the spinor components dominates the scattering process in this energy range and leads to a fully isotropic differential scattering cross section.

As \( \Delta_{SO} \) determines the energy scale for which the isotropy would play a larger role, the exploration of decorated graphene samples would be an interesting system in which to test these results [15].

### 5.1.1.1 Space Dependent Intrinsic SOI

The case of space dependent intrinsic SOI could arise from external factors, such as the non uniform decoration of graphene with heavy adatoms [15]. In order to simulate such a case we have considered \( H = H_o + H_V + H_{SO} \), where \( H_{SO} = \Delta_{SO} \sigma_z \tau_z \Theta(R - r) \), and \( H_V = V\Theta(R - r) \). The analytical form of \( S_{j,\uparrow\uparrow} \) for this case could be easily obtained from Eq. 5.5, by replacing \( k = \sqrt{E^2 - \Delta_{SO}^2/v_F} \rightarrow |E|/v_F \) and \( a = (E - \Delta_{SO})/(v_F k) \rightarrow \text{sgn}(E) \).

As shown in Fig. 5.2, the presence of intrinsic SOI results in the displacement and decrease of the resonant peak from its original resonant value and height. This is due to the imbalance in the scattering channels as the intrinsic SOI increases. Moreover, the ratio \( \xi = \tau_{rr}/\tau_e \) deviates from the expected value of 2, and becomes \( \sim 1 \) at values of
Figure 5.2: Total cross section as function of the scattering potential shift $V$, with $kR = 1.5 \times 10^{-3}$, for different values of the intrinsic SOI (non-zero only in the region $r \leq R$). Inset: Dependence of $\xi = \sigma_{t}/\sigma_{tr} = \tau_{tr}/\tau_{e}$ vs. $\Delta_{SO}/|E - V|$. Notice that $\xi \geq 1.9$ for large resonant $V$ values.

$\Delta_{SO}/|E - V| \sim 1$, as shown in the inset of Fig. 5.2. Therefore, the detection of non negligible effects of the intrinsic SOI in $\xi$ becomes not only dependent on the values of $\Delta_{SO}$ produced but also on the potential shift produced by the adatoms.

5.1.2 Graphene with Rashba SOI

We now analyze the case of graphene samples containing scattering centers that also produce Rashba interactions [13, 14, 18, 19], $\Delta_{SO} \ll \lambda_{R} \neq 0$. This requires a detailed analysis of the spin dependent scattering processes. When $kR \ll 1$, we have two contributing channels, depending on the spin of the incoming particle ($j = 0, 1$ for spin up, and $j = 0, -1$ for spin down), similar to the case discussed above for $\Delta_{SO} \neq 0$. Effective time reversal symmetry within the Dirac cone allows one to study the scattering of a given spin without loss of generality [26].
The presence of Rashba SOI leads to spin-flip processes in graphene due to the nontrivial coupling of momentum, spin and pseudo-spin of the charge carriers in graphene. In this case of $\lambda_R \neq 0$ and $\Delta_{SO} = 0$, we have $k = |E|/v_F$, $k_\pm = \sqrt{(E - V)^2 \pm 2\lambda_R(E - V)/v_F}$, and $a_\pm = \frac{E - V}{v_F k_\pm}$, leading to $T^+_j \neq T^-_j$, $S_{j,\uparrow\uparrow} = S_{j,\downarrow\downarrow} \neq 0$, and $S_{j,\uparrow\downarrow} = S_{j,\downarrow\uparrow}$, where

$$S_{j,\uparrow\uparrow} = -\frac{H^{(2)}_{j+1}H^{(1)}_j X_j + H^{(2)}_j H^{(1)}_{j+1} Y_j - H^{(2)}_j H^{(1)}_j Z_j - 2H^{(2)}_{j+1}H^{(1)}_{j} Q_j}{H^{(1)}_{j+1}H^{(1)}_j X_j + H^{(1)}_j H^{(1)}_{j+1} Y_j - H^{(1)}_j H^{(1)}_j Z_j - 2H^{(1)}_{j+1}H^{(1)}_{j} Q_j},$$

(5.9)

and

$$S_{j,\uparrow\downarrow} = \frac{\text{W}(H^{(1)}_{j+1}, H^{(2)}_{j-1}) M_j}{H^{(1)}_{j+1}H^{(1)}_j X_j + H^{(1)}_j H^{(1)}_{j+1} Y_j - H^{(1)}_j H^{(1)}_j Z_j - 2H^{(1)}_{j+1}H^{(1)}_{j} Q_j},$$

(5.10)

where

$$X_j = a_+ J_j(k,R) J_{j+1}(k,R) + a_- J_{j+1}(k,R) J_j(k,R),$$

$$Y_j = a_+ J_j(k,R) J_{j-1}(k,R) + a_- J_{j-1}(k,R) J_j(k,R),$$

$$Z_j = J_{j+1}(k,R) J_{j+1}(k,R) + J_{j-1}(k,R) J_{j-1}(k,R),$$

$$Q_j = a_+ a_- J_0(k,R) J_0(k,R),$$

$$M_j = a_+ J_j(k,R) J_{j+1}(k,R) - a_- J_{j+1}(k,R) J_j(k,R),$$

(5.11)

and $\text{W}(H^{(1)}_j(x), H^{(2)}_j(x)) = H^{(1)}_j(x) H^{(2)}_j(x) - H^{(1)}_j(x) H^{(2)}_{j+1}(x)$ is the Wronskian [45].

Now we analyze the case of $kR \ll 1$ and $\lambda_R > E$, and focus on the behavior of the angular momentum channels $j = 0$ and $j = \pm 1$, since they are the main contributing channels in this limit, other channels having negligible contribution. Using the asymptotic expansion of the Hankel functions, we get

$$S_{0,ss} \simeq 1 + \frac{i\pi}{2} \sum_{\mu = \pm} \left( \frac{a_\mu J_0(k_\mu R)}{kR J_1(k_\mu R)} + \ln(e^{i\gamma kR}) + \frac{i\pi}{2} \right)^{-1},$$

(5.12)

$$S_{0,\uparrow\downarrow} \simeq \frac{i\pi}{2} \sum_{\mu = \pm} \mu \left( \frac{a_\mu J_0(k_\mu R)}{kR J_1(k_\mu R)} + \ln(e^{i\gamma kR}) + \frac{i\pi}{2} \right)^{-1},$$

(5.13)

$$S_{1,\uparrow\uparrow} \simeq S_{-1,\downarrow\downarrow} \simeq 1 + i\pi \left( \frac{X_0}{2kR Q_1} + \ln(e^{i\gamma kR}) + \frac{i\pi}{2} \right)^{-1},$$

(5.14)
and $S_{\pm 1,\uparrow \uparrow} \approx 0$. Notice that the $s\bar{s}$ (spin-flip) processes are only determined by the $j = 0$ channel, which leads to $\sigma_{t,ss} = \sigma_{tr,ss}$, where $\bar{s} = -s$.

Setting $\lambda_R = 0$ in Eq. 5.13, leads to vanishing amplitudes for the spin-flip amplitudes, as well as $S_{0,\uparrow \uparrow} = S_{1,\uparrow \uparrow}$ while $S_{0,\uparrow \downarrow} = S_{-1,\uparrow \downarrow}$ in Eqs. 5.12-5.14, as mentioned above.

From the scattering amplitudes in Eqs. 5.12–5.14, it is clear that we have three different scattering regimes that not only could be distinguished by the dependence of the cross section on the carrier concentration but also through the isotropy ratio

$$\xi_R = (\sigma_{t,\uparrow \uparrow} + \sigma_{t,\downarrow \downarrow})/(\sigma_{tr,\uparrow \uparrow} + \sigma_{tr,\downarrow \downarrow}).$$

The off-resonant regime requires the non-logarithmic terms in the denominators of Eqs. 5.12–5.14 to be the dominant factors

$$\sigma_{t,ss} \approx \left[ \left( \frac{\pi X_0}{2Q_0} \right)^2 + \left( \frac{2\pi Q_1}{X_0} \right)^2 \right] kR^2,$$

$$\sigma_{tr,ss} \approx \sigma_{t,ss} - \left( \frac{Q_1}{Q_0} \right) \frac{\pi^2 kR^2}{2Q_0},$$

$$\sigma_{t,s\bar{s}} \approx \sigma_{tr,s\bar{s}} \approx \left( \frac{\pi M_0}{2Q_0} \right)^2 kR^2. \quad (5.15)$$

This leads to a relatively small deviation of $\xi_R$ from the value of 2 since the channels $j = 0$ and $j = \pm 1$ are contributing with relatively small weights to the $ss$ (spin-preserving) process.

The resonant scattering regime in this case occurs for three different conditions. Two of these occur when $J_0(k_\pi R) = 0$, so that the $j = 0$ channel for both $ss$ and $s\bar{s}$ are dominated by the logarithmic term, while the $j = \pm 1$ is still dominated by the non-logarithmic terms (keep in mind that $\lambda_R > E$), leading to
The unitary resonant regime is also achieved when \( X_0 = 0 \), which leads to logarithmic resonances of the \( j = \pm 1 \) channel in \( ss \) processes, while the \( j = 0 \) channel is off-resonance for the \( ss \) and \( s\bar{s} \) processes, such that

\[
\sigma_{t,ss} \simeq \frac{\pi^2}{4k \ln^2(e^\gamma kR)} + \frac{\pi^2 RJ_1(k_R R)}{2a_+ J_0(k_R R) \ln(e^\gamma kR)} + \left[ \left( \frac{2\pi Q_1}{X_0} \right)^2 + \left( \frac{\pi J_1(k_R R)}{2a_+ J_0(k_R R)} \right)^2 \right] kR^2 , 
\]

\[
\sigma_{tr,ss} \simeq \sigma_{t,ss} - \frac{\pi^2 Q_1 R}{X_0 \ln(e^\gamma kR)} - \frac{\pi^2 Q_1 J_1(k_R R) kR^2}{X_0 a_+ J_0(k_R R)} , 
\]

\[
\sigma_{t,s\bar{s}} \simeq \sigma_{tr,s\bar{s}} \simeq \frac{\pi^2}{4k \ln^2(e^\gamma kR)} \mp \frac{\pi^2 RJ_1(k_R R)}{2a_+ J_0(k_R R) \ln(e^\gamma kR)} + \left( \frac{\pi J_1(k_R R)}{2a_+ J_0(k_R R)} \right)^2 kR^2 , 
\]

resulting in a significant drop of \( \xi_R \) from 2 to 1. This deviation at lower energies, with \( \xi_R \) becoming closer to 1, arises from the dominance of the terms \( \propto 1/(k \ln(kR)) \) in both the transport and total cross sections, which makes them equal. Notice that the resonant regime is also satisfied for three different conditions, first when \( a_+ J_0(k_R R) + \ln(e^\gamma kR) = 0 \), which leads to unitary resonance in the \( j = 0 \) channel for both the \( ss \) and \( s\bar{s} \) processes, such that

\[\sigma_{t,ss} \simeq \frac{\pi^2}{k \ln^2(e^\gamma kR)} + \left( \frac{\pi X_0}{2Q_0} \right)^2 kR^2 , \]

\[\sigma_{tr,ss} \simeq \sigma_{t,ss} - \frac{\pi^2 RX_0}{2Q_0 \ln(e^\gamma kR)} , \]

\[\sigma_{t,s\bar{s}} \simeq \sigma_{tr,s\bar{s}} \simeq \left( \frac{\pi M_0}{2Q_0} \right)^2 kR^2 , \]

leading to a noticeable a deviation of \( \xi_R \) from 2, especially at low energies.

The unitary resonant regime is also satisfied for three different conditions, first when

\[
\frac{a_+ J_0(k_R R)}{kR J_1(k_R R)} + \ln(e^\gamma kR) = 0 ,
\]

which leads to unitary resonance in the \( j = 0 \) channel for both the \( ss \) and \( s\bar{s} \) processes, such that

\[
\sigma_{t,ss} \simeq \frac{1}{k} + \frac{\pi J_1(k_R R)}{a_+ J_0(k_R R)} + \left[ \left( \frac{2\pi Q_1}{X_0} \right)^2 + \left( \frac{\pi J_1(k_R R)}{2a_+ J_0(k_R R)} \right)^2 \right] kR^2 , 
\]

\[
\sigma_{tr,ss} \simeq \sigma_t - \frac{2\pi Q_1 R}{X_0} - \frac{\pi^2 Q_1 J_1(k_R R) kR^2}{a_+ J_0(k_R R) X_0} , 
\]

\[
\sigma_{t,s\bar{s}} \simeq \sigma_{tr,s\bar{s}} \simeq \frac{1}{k} \mp \frac{\pi J_1(k_R R)}{a_+ J_0(k_R R)} + \left( \frac{\pi J_1(k_R R)}{2a_+ J_0(k_R R)} \right)^2 kR^2 . \]
Also, when \( \frac{X_0}{2kQ_0} + \ln(e^{e^kR}) = 0 \), we have a unitary resonance in the \( j = \pm 1 \) channel, leading to

\[
\sigma_{t,ss} \approx \frac{4}{k} + \left( \frac{\pi X_0}{2Q_0} \right)^2 kR^2,
\]
\[
\sigma_{tr,ss} \approx \sigma_t - \frac{\pi X_0 R}{Q_0},
\]
\[
\sigma_{t,s\bar{s}} \approx \sigma_{tr,s\bar{s}} \approx \left( \frac{\pi M_0}{2Q_0} \right)^2 kR^2.
\]

(5.19)

In all cases of the unitary regime we have \( \xi_R \approx 1 \), since the terms \( \propto 1/k \) are dominant in both the total and transport cross sections.

Figure 5.3: a) Total cross section for spin-preserving processes as function of the scattering potential shift \( V \), for different values of the Rashba SOI, with \( kR = 1.5 \times 10^{-3} \) and \( \Delta_{SO} = 0 \). Inset: Total cross section for spin-flip processes. b) The ratio \( \xi_R = (\sigma_{t,\uparrow\uparrow} + \sigma_{t,\downarrow\downarrow})/(\sigma_{tr,\uparrow\uparrow} + \sigma_{tr,\downarrow\downarrow}) \) for different values of Rashba SOI (legend as in a). Notice \( \xi_R = 1 \) at \( \sigma_t \) resonances.

Curves of total cross section vs. scattering potential strength \( V \) are shown in Fig. 5.3a for \( kR \ll 1 \), and different values of the Rashba SOI interaction, \( \lambda_R \).

Figure 5.3a shows how the location and number of resonances change in the presence of Rashba SOIs. The resonances at \( \chi' = \chi_0 \pm \lambda_R R/\hbar v_F \) for both \( \sigma_{t,ss} \) and \( \sigma_{t,s\bar{s}} \), can be identified as resonances of the \( n = 0 \) channel, while the resonance at
\( \chi' \approx \chi_0 + \theta((\lambda_R R / (h v_F))^2) \) can be identified as coming from the \( j = 1 (-1) \) for \( s = \uparrow (\downarrow) \) incoming spin, where \( \chi_0 \) is the location of the unitary resonance in the absence of SOIs.

Similarly, Fig. 5.3b demonstrates that the scattering isotropy at resonant values is different from the case of no SOI, by showing that the ratio \( \xi_R = (\sigma_{t,\uparrow\uparrow} + \sigma_{t,\uparrow\downarrow}) / (\sigma_{tr,\uparrow\uparrow} + \sigma_{tr,\uparrow\downarrow}) \) takes on different values in the different regimes, being \( \xi_R \approx 1 \) for unitary resonances, \( 1 < \xi_R < 2 \) for medium scatterers, and \( \xi_R \approx 2 \) when off-resonance. This qualitative difference arises from the fact that the scattering amplitudes of the two contributing channels are not equal for all the scattering regimes, in contrast to the case of scattering in the absence of the Rashba interaction, where \( \xi \approx 2 \) for all regimes, off- and on-resonance.

Figure 5.4: The ratio \( \xi_R \) for 500 randomly sized impurities in the range of \( 5\text{Å} \leq R \leq 8\text{Å} \), for different values of the Rashba coupling and \( V = 2\text{eV} \), as a function of carrier energy. Notice a clear drop of \( \xi_R \) from 2 for \( E < \lambda_R / 2 \). Inset: \( \xi_R \) as function of Rashba coupling for different energies.

To further explore the consequences of this SOI-dependent behavior on transport experiments [7, 71], we consider a random distribution of scatterers in a typical graphene
sample. The distribution is assumed to be of low-density, as we ignore multiple scattering
events. Moreover, as the parameter in the theory is $VR$, we assume a random distribution
for that quantity in the range 1.5 to 2.4 (in units of $\hbar v_F$). For a fixed value $V \approx 2\text{eV}$, for
example, this would correspond to a variation in $R$ from $\approx 5$ to 8 Å, not unlike those
considered before [7, 14]. We revisit this connection to experiments in Sec. 5.2 The results
of such averaging procedure are shown in Fig. 5.4, where

$$\xi_R = \frac{\langle \sigma_{t,\uparrow\uparrow} + \sigma_{t,\downarrow\downarrow} \rangle}{\langle \sigma_{t,\uparrow\uparrow} + \sigma_{t,\downarrow\downarrow} \rangle}$$

is shown as function of (Fermi) energy for different
values of the Rashba SOI strength $\lambda_R$, while $V = 2\text{eV}$ is kept fixed. Notice that the range
of $E$ in the figure satisfies $kR < 0.24$ for all values shown and can therefore be understood
in terms of the analytical expansions above—however, the curves shown are obtained from
a full numerical evaluation of the different cross sections that consider multiple channels.
As one would expect, as the energy (or carrier density) increases, the ratio $\xi_R$ approaches
the anisotropic, effectively SOI-free limit, $\approx 2$, while at low energies, $\xi_R$ approaches the
isotropic scattering limit of 1. The drop occurs for a characteristic energy given by $\lambda_R$,
with $\xi_R \approx 1.8$ for $E \approx \lambda_R/2$; this condition can be traced back to the shifting resonances of
the $j = 0$ channel under Rashba SOI. One can also analyze the dependence of $\xi_R$ on the
Rashba coupling for different carrier densities (energies), as shown in the inset of Fig. 5.4.
It is evident that the effect of a small Rashba coupling is more pronounced at lower
energies.

From the preceding analysis, it appears that the experimental evaluation of the
transport to elastic times ratio at low carrier densities would be able to provide an
alternative measure of the effective Rashba SOI present, as produced by impurities and
defects, either intrinsic or purposely introduced. Such careful experiments have already
explored this ratio [7], and as the carrier density has been reduced down to $E \approx 100\text{meV}$, it
appears the induced Rashba SOI in those samples was well below that number (i.e.,
$\lambda_R < 200\text{meV}$), since $\xi_R \approx 2$ over the entire range explored. We believe it would be
interesting to repeat those experiments in systems with higher mobility, such as graphene on boron nitride substrates, which may allow reaching even lower carrier densities without large inhomogeneities. Considering that in systems with adatoms the expected SOI is $\lambda_R \approx 10\text{meV}$ [13, 14, 18], this requires rather low carrier densities, such as those attained on boron nitride substrates [89, 90].

5.1.2.1 Uniform Intrinsic and Rashba SOI

As before, the $S_{j,ss'}$ matrix elements determining the scattering process are obtained by solving the linear set of equations (5.3) above. Here we maintain a constant carrier concentration, i.e., constant $kR$, while changing $\Delta_{SO}$.

In the top panels of Fig. 5.5, we notice that the effect of increasing intrinsic SOI is to shift the $V$ location at which the resonant conditions are satisfied. Moreover, since the carrier concentration $kR$ is kept constant for different values of $\Delta_{SO}$, one notices that an increase in $\Delta_{SO}$ leads to the reduction of the ratio $\lambda_R/E$. As mentioned in the case with $\Delta_{SO} = 0$, the splitting and clear appearance of peaks caused by the Rashba SOI is more pronounced when $\lambda_R$ and $E$ are comparable; this effect leads to the recombination of the resonance peaks at large values of $\Delta_{SO}$, and the decrease of amplitudes of the spin-flip cross sections. Notice moreover that the points at which the isotropic scattering is pronounced shift while increasing $\Delta_{SO}$: this leads to an enhancement of the isotropy in the scattering process for given values of $\lambda_R/E$, when compared to the case in which $\Delta_{SO} = 0$. In this case, the deviation of $\xi_R$ from 2 can in general indicate the combined effect of both SOIs. To extract the strength of each interaction independently, one imagines that spin polarized measurements would be required (see also Sec. 4.2).

5.1.2.2 Rashba and Space Dependent Intrinsic SOI

Here we consider $H = H_o + H_V + H_{SO} + H_R$, where $H_{SO} = \Delta_{SO}\sigma_z\tau_zs_z\Theta(R - r)$, $H_V = V\Theta(R - r)$, and $H_R = \lambda_R(\tau_z\sigma_zs_y - s_x\sigma_y)\Theta(R - r)$. In this case, the analytical form of
Figure 5.5: Top Left: Total cross section for spin-preserving processes as function of the scattering potential shift $V$, for different values of the intrinsic SOI, where $kR = 1.5 \times 10^{-3}$, and $\lambda_R / (\hbar v_F) = 20kR$. Top Right: Total cross section for spin-flip processes as function of the scattering potential shift $V$, for different values of the intrinsic SOI. Bottom: The ratio $\xi_{R} = (\sigma_{t, \uparrow \uparrow} + \sigma_{t, \uparrow \downarrow}) / (\sigma_{tr, \uparrow \uparrow} + \sigma_{tr, \uparrow \downarrow})$ for different values of the intrinsic SOI. All labels are as in the top left panel.

$S_{n,ss'}$ can be obtained from Eqs. (14)-(15) by changing $k_{\pm}$ and $a_{\pm}$ to

$$k_{\pm} = \sqrt{(E - V \pm \lambda_R)^2 - (\Delta_{SO} \pm \lambda_R)^2 / v_F}$$ and $$a_{\pm} = (E - V - \Delta_{SO}) / (v_F k_{\pm}).$$

As shown in Fig. 5.6, the effect of the intrinsic SOI in this case is limited to a shift of the resonant peaks. This is due the presence of the potential shift $V$, that sets the energy inside the obstacle at values that are approximately linear in momentum. Similarly we notice that the ratio $\xi_{R}$ displays a similar behavior as in the case of $\Delta_{SO} = 0$, with shifts in its isotropic values due to the presence of $\Delta_{SO}$. It is interesting to notice that the shift in the first (left) resonant peak is not monotonic. This effect is due to the fundamental change
in the dispersion relation of the $k_-$ branch, as it changes from quadratic to linear at
\[ \Delta_{SO} = \lambda_R, \]
and a gap is generated in the spectrum as \[ \Delta_{SO} > \lambda_R \] [87].

In this section we have shown that SOIs in graphene lead to clear signatures in the
scattering processes and therefore to observable consequences in electronic transport. The
drop in value of the ratio of transport to elastic times from its known value of \( \approx 2 \) reflects
the presence of SOI, with the ratio dropping to \( \approx 1 \) as \( E_F \) falls close to the SOI energy
scale. We have also shown qualitative changes in the number and nature of resonances

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Figure 5.6: Top Left: Total cross section for spin-preserving processes as function of the
scattering potential shift \( V \), for different values of the intrinsic SOI, where \( kR = 1.5 \times 10^{-3} \),
and \( \lambda_R/(\hbar v_F) = 100kR \). Top Right: Non monotonic shift in the first (left) resonance due
to the effects of \( \Delta_{SO} \). Bottom Left: Total cross section for spin-flip processes as function of
the scattering potential shift \( V \), for different values of the intrinsic SOI. Bottom Right: The
ratio \( \xi_R = (\sigma_{t,\uparrow\uparrow} + \sigma_{t,\uparrow\downarrow})/(\sigma_{tr,\uparrow\uparrow} + \sigma_{tr,\uparrow\downarrow}) \) for different values of the intrinsic SOI. All labels
are as in the top left panel.
produced in scattering due to impurities and the Rashba SOI they induce. Three different regimes of scattering can be distinguished based on the levels of isotropy they produce, with the isotropy becoming more pronounced at low carrier concentrations. Measuring the ratio of scattering times with precision at low carrier densities should enable the experimental characterization of impurity-induced spin-orbit interactions.

5.2 Symmetry Breaking Effects on Spin transport in Graphene

The ability to manipulate and control the electronic and spin properties of graphene and related materials by decoration [12–14, 78], stacking [91, 92], intercalation [17–19, 93, 94] and distortion [20–22, 31, 76, 77, 80, 95, 96] may also lead to important technological advances. Methods that rely on the artificial functionalization of graphene could lead to sizable enhancement of SOIs. Successful examples of these methods include the intercalation of gold atoms between graphene and the Ni substrate [17–19], weak hydrogenation [13, 14], and the deposition of large copper or gold nanoparticles [12]. Other approaches are also promising, including externally induced curvature of samples [20–22], decoration with heavy adatoms such as thallium and indium [15, 16], and the deposition of graphene on the surface of a strong topological material [93]. These methods have achieved or project the enhancement of SOI of up to several tens of meV, leading to clear measurable effects on the electron dynamics [14, 40, 41, 75, 78, 85, 86].

The methods used to enhance SOIs in graphene require the presence of adatoms or local defects/deformations that accommodate on the graphene lattice in different ways. These perturbations introduce additional effects from the lattice symmetries they may break. The enhancement of intrinsic and/or Rashba SOIs on the dynamics of electrons in graphene has been analyzed for the most part in the framework of a single-valley Dirac description [14, 41, 42, 78]. In that limit–valid for potential scatterers with large
characteristic spatial variation compared to the lattice constant—the scattering preserves helicity, it is predominantly forward, and gives rise to Klein-tunneling, as mentioned above [7, 41, 71]. If the scattering centers lead to enhancement of Rashba and/or intrinsic SOIs, the electronic scattering has been shown to become increasingly isotropic [41]. This scattering could also lead to spin Hall effect via enhanced skew scattering close to the resonant regime [12, 13, 78].

We further study the effects symmetry breaking perturbations may produce on the detection of Rashba and intrinsic SOIs. The dependence of $\xi$ on carrier concentration in the presence of Rashba SOI is shown to be qualitatively different for different symmetry breaking terms in the perturbation. Systematic experimental studies of $\xi$ in given graphene systems would allow the identification and simultaneous evaluation of the relative strengths of the different perturbations. Finally, from the symmetries of the scattering matrix, we show which systems may display non-zero valley and/or spin transport skewness (skew scattering). In particular, we find that disorder that is not invariant under “effective time reversal” leads to a reduction of spin skew scattering, due to the enhancement of valley skew scattering; this allows one to identify what kind of decorated system will display skew scattering and may result in the appearance of valley and/or spin Hall effect.

We further illustrate the impact of the symmetry considerations described above for typical graphene samples. Throughout the discussion of the different perturbations, we present numerical results for the anticipated dependence of $\xi$ and skewness to different effects, by analyzing the results for a random impurity distribution. This allows us to gain insights into the contribution of different effects to various measurable quantities.
5.2.1 Symmetry Considerations and Constrains on Spin Transport

In the presence of spin-orbit interactions (SOIs) we consider the extended representation in Ch. 2 (see Sec. 2.3.3), and the corresponding matrices in Eq. 2.63. In this representation, the time reversal [97], helicity operator, and total angular momentum are defined as

\[ T = i \Gamma^5 \mathcal{A}_1 S_2 C, \]  
\[ \hat{h} = \Gamma^5 \mathcal{A} \cdot \vec{k}/k, \]  
\[ J_z = -i \partial_\theta + \Gamma^5 \mathcal{A}_3/2 + S_3/2, \]

with \( J_z \) having integer eigenvalues, \( T^2 = -1 \), and \( \{T, J_z\} = 0 \). Similarly, one can define

\[ T_1 = e^{-i \Gamma^5 \phi} \Gamma^5 \mathcal{A}_2 S_2 C, \]

with \( T_1^2 = 1 \), and satisfying

\[ \{T_1, J_z\} = 0. \]

In this representation, the set of spin dependent interactions that conserve total angular momentum is found to be

\[ V_{SO}^{T,J} = \{\lambda_R (A_1 S_2 - A_2 S_1), \lambda (A_2 S_2 + A_1 S_1), \Delta_{SO} \Gamma^5 A_3 S_3, \Delta_S \Gamma^5 S_3\}, \]

all with real coefficients.

The operators \( T \) and \( T_1 \) allow us to relate the states with \( j \) and \(-j\); here one can write

\[ \psi_j = (J_{j-1} e^{-i\theta}, iJ_j, J_j e^{-i\theta}, -iJ_j, J_j, iJ_{j+1} e^{i\theta}, J_j, -iJ_{j+1} e^{i\theta}) T e^{i\theta}, \]

where \( J_l(kr) \) are Bessel functions [41].

In the presence of SO interactions, an incident state could be projected into valley and spin subspaces with the aid of the corresponding projection operators, given by

\[ P_\pm = (1 \pm \Gamma^5)/2 \]  
\[ P_{\uparrow/\downarrow} = (1 \pm S_z)/2. \]

A general eigenstate of \( H_0 \) can then be written as

\[ \psi = P_+(P_{\uparrow} + P_{\downarrow}) \psi + P_-(P_{\uparrow} + P_{\downarrow}) \psi. \]
The partial wave components can be chosen to satisfy \( T_1 P_\pm P_\psi = \pm(-1)^j P_\pm P_\psi \) and \( T P_\pm P_\psi = \mp(-1)^{j+\frac{1}{2}} P_\pm P_\psi \). Consequently

\[
T_1 \psi_j = (-1)^j (P_+(P_\uparrow + P_\downarrow)\psi_{-j} - P_-(P_\uparrow + P_\downarrow))\psi_{-j},
\]

\[= (-1)^j \Gamma^5 \psi_{-j} \tag{5.27}
\]

and

\[
T \psi_j = (-1)^{j+\frac{1}{2}} (P_+(P_\uparrow + P_\downarrow)\psi_{-j} - P_-(P_\uparrow + P_\downarrow))\psi_{-j},
\]

\[= (-1)^{j+\frac{1}{2}} \Gamma^5 \psi_{-j} \tag{5.28}
\]

As before, the incoming and outgoing partial waves describing the scattering problem can be written as

\[
\psi_j = \psi^{in}_j + S_j \psi^{out}_j. \tag{5.29}
\]

In this case, the scattering matrix can be written in terms of \( 4 \times 4 \), \( S_j \)-blocks, with elements \( S_{\tau\tau, ss', j} \). By applying the operator \( T_1 \) to Eq. 5.29, we get

\[
\Gamma^5 T_1 S_j T_1^{-1} \Gamma^5 = S^\dagger_{-j}, \tag{5.30}
\]

and by applying \( T \) we get

\[
\Gamma^5 T S_j T^{-1} \Gamma^5 = S^\dagger_{-j}. \tag{5.31}
\]

From these conditions and unitarity of \( S_j \) we have,

\[
S_{\tau\tau, ss, j} = S_{\bar{\tau}\bar{\tau}, \bar{s}\bar{s}, j} = S_{\tau\tau, \bar{s}\bar{s}, -j} \tag{5.32}
\]

\[
S_{\tau\tau, ss, j} = -S_{\tau\tau, \bar{s}\bar{s}, -j} = -S_{\bar{\tau}\bar{\tau}, s\bar{s}, j} e^{2ir\phi}
\]

\[
S_{\bar{\tau}\bar{\tau}, s\bar{s}, j} = S_{\tau\tau, \bar{s}\bar{s}, -j} = -S_{\bar{\tau}\bar{\tau}, s\bar{s}, -j} e^{2ir\phi} = -S_{\tau\tau, s\bar{s}, -j} e^{2ir\phi}
\]

\[
S_{\tau\tau, \bar{s}\bar{s}, j} = S_{\bar{\tau}\bar{\tau}, s\bar{s}, -j} = -S_{\tau\tau, s\bar{s}, -j} e^{2ir\phi}.
\]

The scattering amplitudes are given in Eq. 3.3–3.50, the different cross sections for the various scattering processes are given in Eq. 3.51–3.54, and the different cross sections are
given in Eq. 3.55, 3.56, 3.57 and 3.58. These quantities help define the ratio of transport to elastic times in the presence of SOI,

\[ \xi_{SO} = \frac{\sum_{T,T',S,S'} \sigma_{T,T',S,S'}}{\sum_{T,T',S,S'} \sigma_{Tr,T',S,S'}} \]  \hspace{1cm} (5.33)

and skew parameter

\[ \gamma_s = \frac{1}{2} (\gamma_{\uparrow} - \gamma_{\downarrow}) \]  \hspace{1cm} (5.34)

\[ \gamma_s = \frac{\sum_{T,T',S,S'} \sigma_{sk,T,T',S,S'}}{\sum_{T,T',S,S'} \sigma_{Tr,T',S,S'}} \]

For interactions commuting with \( T \) and \( T_1 \), we have the relations

\[ \sum_{j=-\infty}^{\infty} f_{\tau,ss,j} f_{\tau,ss,j+1}^* = (\sum_{j=-\infty}^{\infty} f_{\tau,\bar{s}s,j} f_{\bar{\tau},\bar{s}s,j+1}^*)^* = \] \hspace{1cm} (5.35)

\[ (\sum_{j=-\infty}^{\infty} f_{\tau,\bar{s}s,j} f_{\bar{\tau},\bar{s}s,j+1}^*)^* = \sum_{j=-\infty}^{\infty} f_{\tau,ss,j} f_{\bar{\tau},ss,j+1}^* \]

\[ \sum_{j=-\infty}^{\infty} f_{\tau,ss,j} f_{\tau,ss,j+1}^* = \sum_{j=-\infty}^{\infty} f_{\tau,\bar{s}s,j} f_{\bar{\tau},\bar{s}s,j+1}^* \]

\[ (\sum_{j=-\infty}^{\infty} f_{\tau,\bar{s}s,j} f_{\bar{\tau},\bar{s}s,j+1}^*)^* = (\sum_{j=-\infty}^{\infty} f_{\tau,ss,j} f_{\bar{\tau},ss,j+1}^*)^* \]

\[ \sum_{j=-\infty}^{\infty} \text{Im}(f_{\tau',ss,j} f_{\bar{\tau}',ss,j+1}^*) = \sum_{j=-\infty}^{\infty} \text{Im}(f_{\tau',\bar{s}s,j} f_{\bar{\tau}',\bar{s}s,j+1}^*) = 0 \]

and consequently,

\[ \sigma_{T,T,ss} = \sigma_{T,T,\bar{s}s} = \sigma_{T,\bar{T},ss} = \sigma_{T,\bar{T},\bar{s}s} \]  \hspace{1cm} (5.36)

\[ \sigma_{Tr,T,ss} = \sigma_{Tr,T,\bar{s}s} = \sigma_{Tr,\bar{T},ss} = \sigma_{Tr,\bar{T},\bar{s}s} \]

\[ \sigma_{sk,T,ss} = -\sigma_{sk,T,\bar{s}s} = -\sigma_{sk,\bar{T},ss} = \sigma_{sk,\bar{T},\bar{s}s} \]

\[ \sigma_{T,T,\bar{s}s} = \sigma_{T,\bar{T},ss} = \sigma_{T,\bar{T},\bar{s}s} = \sigma_{T,T,\bar{s}s} \]

\[ \sigma_{Tr,T,\bar{s}s} = \sigma_{Tr,T,ss} = \sigma_{Tr,\bar{T},ss} = \sigma_{Tr,\bar{T},\bar{s}s} \]

\[ \sigma_{sk,T,\bar{s}s} = -\sigma_{sk,T,ss} = -\sigma_{sk,\bar{T},ss} = \sigma_{sk,\bar{T},\bar{s}s} \]

\[ \sigma_{T,T',s\bar{s}} = \sigma_{T,T',\bar{s}s} \]

\[ \sigma_{Tr,T',s\bar{s}} = \sigma_{Tr,T',\bar{s}s} \]

\[ \sigma_{sk,T',s\bar{s}} = \sigma_{sk,T',\bar{s}s} = 0 \]
In the case where the perturbations present do not commute with $T_1$, instead of 5.36 we have

\begin{align*}
\sigma_{t,t',s,s} &= \sigma_{t,t',s,s}, \\
\sigma_{t',t,s,s} &= \sigma_{t',t,s,s}, \\
\sigma_{sk,t,s,s} &= -\sigma_{sk,t,s,s}, \\
\sigma_{t,t,s,s} &= \sigma_{t,t,s,s}, \\
\sigma_{t',t,s,s} &= \sigma_{t',t,s,s}, \\
\sigma_{sk,t',s,s} &= -\sigma_{sk,t',s,s}, \\
\sigma_{sk,t',s,s} &= \sigma_{sk,t',s,s} = 0.
\end{align*}

(5.37)

It should be noted that the SO terms $\lambda_R$ and $\lambda$ do not lead to a gap opening; instead they break the spin degeneracy by doubling the bands for a fixed energy, such that

\[ k_{\pm} = \sqrt{(E - v)^2 \pm 2\Upsilon(E - v)}, \]

(5.38)

where

\[ \Upsilon = \sqrt{\lambda_R^2 + \lambda^2}. \]

(5.39)

These interactions split the low energy resonant peaks corresponding to $j = 0$ and $j = \pm 1$ channels whenever $\Upsilon > 2E$ [41], and produce a noticeable drop in the ratio of cross sections at low carrier concentrations ($E < \Upsilon$),

\[ \xi_{SO} = \frac{\sum_{t't's's'} t_{t't's's'} \sigma_{t't's's'}}{\sum_{t't's's'} \sigma_{t't's's'}}, \]

(5.40)

as shown in Fig. 5.7b.

The spin independent terms lead also to a variation of $\xi_{SO}$ at low energies, although with a different dependence on the carrier concentration, as shown in Fig. 5.7a. Therefore, in the presence of $\lambda_R$, $\lambda$, $t$ and $s$ terms one can determine the value of $\Upsilon$ and the ratio $\Delta/v$ from the behavior of $\xi_{SO}$ with Fermi energy, as illustrated in Fig. 5.7b.
Figure 5.7: Numerical calculation of the transport to elastic time ratio $\xi$ ($\xi_{SO}$ in the presence of SOIs), for a set of 500 randomly sized impurities, where $(5 \leq R \leq 15)\text{Å}$, and $v = 2\text{eV}$, for the following systems: a) In the presence of symmetry breaking effects described by $t$ and $s$, $s$ and $t$ are defined in Eq. 4.19, notice $\xi$ deviates from the value of 2 by nearly a constant value at large energies, and reaches its minimum at/near zero energy. Inset: Dependence of $\xi$ on $\Delta = \sqrt{t^2 + s^2}$ for fixed values of $v$ and $E = 60\text{meV}$. b) Effects of $t$ and $s$ on $\xi_{SO}$ in the presence of a Rashba interaction $\lambda_R = 20\text{meV}$. Notice the sharp drop of $\xi_{SO}$ at $E \rightarrow 0$ due to the Rashba interaction. The deviation from 2 at high energies is due to $t$ and $s$, allowing the quantification of their amplitudes. Horizontal dashed lines correspond to the value $\xi_{SO}$ for given $t$ and $s$ in the inset of a); the vertical dashed line shows the value of $\lambda_R$; $\xi_{SO}$ drops rapidly for $E < \lambda_R$. c) Effects of $t$ and $s$ on $\xi_{SO}$ in the presence of intrinsic SOI, $\Delta_{SO} = v/10$. Notice that $\xi_{SO}$ has a similar behavior as a), indicating that the simultaneous extraction of intrinsic SOI and the symmetry breaking amplitudes $t$ and $s$ from $\xi_{SO}$ is not feasible.

The intrinsic SOI ($\Delta_{SO}$) does not commute with $T_1$ and does not cause spin flips, but opens a gap, and leads to a reduction of $\xi_{SO}$, such that $\xi_{SO} \rightarrow 1$ as $\Delta_{SO}/|E - v| \rightarrow 1$. 


However, the gap generated by $\Delta_{SO}$ is incompatible with the gaps generated by $t$ and $s$, since these interactions do not anticommute with the intrinsic SOI. [28] In this case, the effect of the intrinsic SOI can not be distinguished from symmetry breaking effects in samples through measurements of the ratio $\xi_{SO}$. In the presence of $\Delta_{SO}$ and with no symmetry breaking terms ($t = s = 0$), the dependence of $\xi_{SO}(E)$ on the different values of $\Delta_{SO}$ are qualitatively similar to those in Fig. 5.7a. It is the case that the simultaneous presence of $\Delta_{SO}$, $t$ and $s$ will lead to an overestimation of $\Delta_{SO}$ from $\xi_{SO}$ measurements, due to the similar deviation caused by $t$ and $s$, as shown in Fig. 5.7c.

### 5.2.2 Skew Scattering and Spin Hall Effect

An alternative method to measure the strength of SOIs in graphene was introduced recently by Ferreira et al. [78]. The method exploits the skew character of scattering in the presence of locally enhanced SOIs. In this section, we study effects produced by dimerization perturbations such as $tB e^{i\Gamma \phi}$, and staggered sublattice symmetry breaking, and how they influence skew scattering and the possible determination of the SOI parameters from transport experiments.

In the absence of valley mixing effects or sublattice symmetry breaking, the $V_{T,J}^{SO}$ perturbations commute with both $T$ and $T_1$, as mentioned above. The symmetries of the scattering matrix result in $\sigma_{sk,rr\uparrow\uparrow} = -\sigma_{sk,rr\downarrow\downarrow}$ and $\sigma_{sk,rr\uparrow\downarrow} = -\sigma_{sk,rr\downarrow\uparrow} = 0$. This indicates that carriers with opposite spin are scattered in opposite directions, which would lead to their accumulation on the sample edges and the appearance of a spin Hall effect signal [78].

One way to quantify this effect is through the ratio of the skew to transport cross section for each spin projection, $\gamma_{\uparrow}$ and $\gamma_{\downarrow}$, and define the spin transport skewness $\gamma_s$ in Eq. 5.34. The spin skewness $\gamma_s$ considers all processes resulting in spin asymmetries; it is enhanced through resonant scattering, and fully characterizes the spin Hall angle at zero
temperature,
\[ \theta_{SH} = \lim_{T \to 0} \frac{\mathcal{J}_H}{\mathcal{J}_x} = \gamma_S, \tag{5.41} \]
in the absence of side-jump effects [78]. In the absence of valley mixing or sublattice symmetry breaking, the skew parameters for each spin are equal in magnitude and opposite in sign, leading to \( \gamma_S = \gamma_\uparrow \). This effect was recently observed in graphene samples in which the SOI was enhanced through the deposition of large copper or gold nanoparticles [12], and in weakly hydrogenated samples, and found to yield rather strong spin Hall effect signals [13].

In the presence of valley mixing, \( t\mathcal{B}_e^{\tau_3} \), in addition to SOI terms, both \( \mathcal{T} \) and \( \mathcal{T}_1 \) commute with the Hamiltonian, resulting in the following relations,
\[ \sigma_{sk,\tau\tau,ss} = -\sigma_{sk,\tau\tau,\bar{s}s} = -\sigma_{sk,\bar{\tau}\bar{\tau},ss} = \sigma_{sk,\bar{\tau}\bar{\tau},\bar{s}s} = \sigma_{sk,\tau\tau',\bar{s}s} = 0, \]
as well as a nonzero value of the skew parameter \( \gamma \); its dependence on the valley mixing strength, \( t \), as a function of carrier concentration is illustrated in Fig. 5.8a.

However, in the presence of a staggered perturbation \( s\mathcal{A}_3 \), the Hamiltonian does not commute with the operator \( \mathcal{T}_1 \). This reduces the set of conditions imposed on the skew cross section elements, so that the relation between \( \sigma_{sk,\tau\tau,ss} \) and \( \sigma_{sk,\tau\tau,\bar{s}s} \) depends on the staggered parameter \( s \) (see Eqs. 5.37 and 5.34). A nonzero \( s \) leads to a reduction of \( \gamma_S \) and the corresponding transverse spin currents. Figure 5.8b shows the energy dependence of \( \gamma_S \) for different values of the staggered perturbation \( s \) in the system of Fig. 5.8a. For increasing values of \( s \) the spin skew parameter \( \gamma_S \) decreases and eventually vanishes for large \( s \) values. In Fig. 5.8c we show the effect of \( s \) on a sample of randomly sized impurities. We notice that the spin Hall effect is robust to impurity size disorder, but it is not to staggered potential perturbations; \( \gamma_S \) decreases with increasing values of \( s \), eventually vanishing for all Fermi energies. It is also interesting that the presence of \( s \) leads to a non-zero valley skewness, \( \gamma_V \), which would then result in a valley Hall effect, accumulating carriers from different valleys to different edges of the sample. Figure 5.8d
Figure 5.8: a) Spin skew parameter $\gamma_S$ as function of energy for different values of $t$ in a system with $\Delta_{SO} = 25\text{meV}$, $v = 2\text{eV}$ and $R = 6\text{Å}$. Even for large values of $t$ the skew scattering persists, as expected from symmetry arguments. b) Map of spin skew parameter $\gamma_S$ vs symmetry breaking staggered interaction $s$ and energy (carrier concentration) $E$, for $\Delta_{SO}$, $v$ and $R$ as in a). Notice that for large values of $s$ the skew parameter $\gamma \to 0$, showing that skew scattering is not robust to this kind of perturbation. c) Spin skew parameter dependence on $s$ for a set of 2000 randomly sized impurities ($3 \leq R \leq 9$Å, for values of $v$ and $\Delta_{SO}$ as in a). This shows the robustness of skew scattering to random impurity size, but not under $s$ perturbations. d) Valley skew parameter dependence on $s$ for the same set of random impurities and $s$ values in (c). Note that in systems with $s > \Delta_{SO}$, it is generally the case that $|\gamma_V| > |\gamma_S|$ (notice different vertical scales). Both $\gamma_S$ and $\gamma_V$ vanish away from the resonant regime, as it is the case for $s/\Delta_{SO} = 80$.

shows the dependence of $\gamma_V$ on energy and $s$ strength, for a random impurity configuration, reflecting a relatively large value of $\gamma_V$ for sizable $s$, while $\gamma_S$ is much
smaller. At high values of $s$, however, the resonance conditions are offset and both $\gamma_V$ and $\gamma_S$ are small in the energy range shown.

We emphasize that spin Hall effect appears and it is enhanced close to the resonant scattering regime [78], due to the presence of centrosymmetric impurities that enhance SOIs (and produce also a local potential shift). This effect is robust to impurity size and potential disorder [78], as well as to perturbations that lead to valley mixing in the form $iBe^{i\Gamma\phi}$. Notice also that close to resonance, both the spin and valley Hall effects are enhanced, but become negligible far away from resonance, as is the case for $s/\Delta_{SO} = 80$ in Fig. 5.8c and d. The competition between these two effects can be schematically illustrated as in Fig. 5.9: the spin Hall effect generated by skew scattering is not robust to a staggered potential, as this leads to a non-zero valley skewness. The latter reduces spin accumulation on the sample edges, while enhancing the valley contrast.

Figure 5.9: Schematic representation of spatial separation of spins and valleys through skew scattering due to different perturbations. SOI perturbations act as a spin splitter while leaving the valleys unaffected. The skew character of the scattering remains unaffected in the presence of $V_{T1}$. In contrast, the presence perturbations that belong to $V_{TJ}$ and do not commute with $T_1$, such as the staggered potential $s$, resulting in valley skewness. In this case the perturbation acts as a valley splitter, while leaving the spin unaffected. In the presence of a staggered potential and SOIs, spin skewness will be reduced, depending on the strength of the staggered effects.
5.3 Comparison to Experimental Measurements

In light of our results and examination of symmetry breaking effects, let us consider recent experimental results on decorated graphene.

In the experiments by Marchenko et al. [19], Rashba interaction was enhanced through the intercalation of gold atoms between graphene and the Ni substrate. The value of the Rashba interaction was found to depend on the detailed position of the gold atoms with respect to the graphene sample. For samples exhibiting a Rashba interaction of $\sim 70\text{meV}$, gold atoms were located in the center of all the hexagon; for $\sim 60\text{meV}$, the gold atoms were in the center of non consecutive hexagons; and for $\sim 7\text{meV}$, the gold atoms were on top of carbon locations. Each of these arrangements can be seen to generate different symmetry breaking terms, in addition to the enhanced SOI. In the case of hexagon-centered gold atoms one expects the perturbation to be dominated by $t$ and $v$, as these terms possess the symmetries of this specific arrangement. In the cases of 60 and 7meV, one can expect the symmetry breaking to be described by $\{t, s, v\}$ and $\{s, v\}$, respectively. In those cases, the detection and quantification of the Rashba SOI based on transport and elastic times not only allows one to quantify the strength of the Rashba interaction but also to obtain an estimate of the additional parameters of the Hamiltonian (see Fig. 5.7b).

For example, in the case of a Rashba interaction $\lambda_R = 20\text{meV}$, we notice a sharp drop in the ratio $\xi_{SO}$ for a Fermi energy around this value (indicated by a dashed vertical line) in Fig. 5.7b. For values of energy larger than 20meV, the ratio displays a nearly constant value, slightly shifted down from the value of 2 (as indicated by horizontal dashed lines in Fig. 5.7b), with an asymptotic value dependent on the value of $\Delta/v$.

The decoration of graphene with heavy adatoms positioned at the center of hexagons leads to the enhancement of intrinsic SOI [15]. The detection and quantification of this interaction through transport measurements becomes masked by symmetry breaking
effects, as shown in Fig. 5.7c. This would lead to overestimation of $\Delta_{SO}$ from measurements of $\xi_{SO}$ with varying Fermi energy. This suggests that different measurements, such as spin Hall effect (SHE) should be used in conjunction in order to fully characterize the role of the adatom perturbation.

Skew scattering and the resulting SHE represents an alternative method of quantification of SOIs. The physisorption of nanoparticles on the surface of graphene may be expected to produce a potential shift $\nu$ and enhanced SOIs with no additional symmetry breaking effects, given their large size when compared to the graphene lattice constant, leading to more accurate quantification of the SOIs [12]. Intrinsic SOI enhanced by heavy adatoms [15], may be characterized through this method. One can expect staggered effects to be weak in these samples, $s \ll \Delta_{SO}$, so that skew scattering would be an important contribution to the SHE.

Our results are also in general agreement with the theoretical analysis by Pachoud et al. [75], who examine the different low-energy perturbations arising from different adatom locations on the graphene lattice. They notice that the Hall effects produced from hexagon centered or on-top adatoms are of different character. For the hexagon centered position they expect a pure spin Hall effect, in agreement with the symmetry constraints presented in our work. Moreover, for on-top positions it was suggested that if the adatom number of on-$A$ and on-$B$ types is different, a Hall effect may be observed. This is in agreement with our results for the staggered potential perturbation and the corresponding appearance of a valley Hall effect, which could eventually yield a charge Hall effect for valley polarized currents.

In hydrogenated samples, where the Rashba interaction is enhanced due to $sp^3$ deformations [13, 48], the non-local resistance was seen to be independent of carrier concentration. This suggested that skew scattering was negligible, and the appearance of SHE was attributed to the side-jump mechanism [13]. The weak contribution of the skew
scattering in this kind of sample, however, may also be due to the presence of strong symmetry breaking effects that reduce the conditions for the appearance of SHE, such as a strong staggered perturbation, $s \gg \lambda_R$. This regime would result in a negligible spin skew parameter, as shown in Fig. 5.8c, due to the dominance of the valley skewness. The persistence of SHE would further suggest that side jump effects are robust to this kind of perturbations, and/or that the phenomenon observed should consider the role of valley skewness in the non local resistance. It would be interesting to carry out a detailed study of this issue in the future.

Finally, in connection with the experiments by Monteverde et al. [7], a more complete conclusion about the factor playing important roles in this experiment can be drawn based on the analysis of this section. As discussed in the previous section, $\xi$ did not display a sharp drop below the value of 2 until the experimental minimum $E$ considered; we can safely consider that the value of any Rashba SOI is lower than $\approx 200$ meV, if present [41]. It is interesting to notice that sample A in their Fig. 3 exhibits a drop in the value of $\xi$ for both polarities near the minimum carrier density, suggesting the presence of Rashba SOI in that sample. We can also neglect the intrinsic SOI in pristine graphene [11], and it being unlikely enhanced by the SiO$_2$ substrate [15]. As mentioned in Ch. 4, the effects of substrate and impurities are more likely to be symmetry breaking, with an estimated strength, from Fig. 5.7b, of $\Delta/v \approx 1/7$, or $\Delta \approx 300$meV.

5.3.1 Summary

In this section we have studied how symmetry breaking effects lead to the appearance of backscattering in graphene, which is reflected among other things on the deviation of the transport to elastic time ratio $\xi$ from its ideal value of 2 at low carrier concentrations. We have also considered that perturbations introduced by adatoms in graphene lead to the enhancement of Rashba-like interactions, in addition to various symmetry breaking
effects. In many situations, we find it is possible to detect and separately quantify the SOI and the symmetry breaking amplitudes through measurements of the ratio of transport and energy relaxation times, $\xi$, as function of carrier concentration. This separability of contributions becomes a challenging task if the SOI enhancement has an intrinsic character, however. In that case, the dependence of $\xi$ on carrier concentration for SOI and symmetry breaking interactions is quite similar, obstructing the extraction of each effect independently. Finally, we discussed that nonzero spin and/or valley skew parameters, $\gamma_S$ and $\gamma_V$, are expected for certain adatoms. This allows the detection of both Rashba and intrinsic SOIs in the presence of valley mixing effects, even when the transport times ratio may not give definitive answers. For adatoms that enhance SOIs and break sublattice symmetry, we find a reduction of $\gamma_S$, which vanishes in systems where the staggered perturbation is larger than the SOI amplitude. As a consequence, the SOI strength would be masked by sublattice symmetry breaking, and the appearance of a valley Hall effect.
6 Birefringent Electron Optics

In this chapter we show that a circular gate- or doping-controlled region in the presence of Rashba spin-orbit interaction in graphene may indeed behave as a Veselago electronic lens but with two different indices of refraction. We demonstrate that this birefringence results in complex caustic patterns for a circular gate, selective focusing of different spins, and the possible direct measurement of the Rashba coupling strength in scanning probe experiments. Some of the results in this chapter have been reported in [40].

6.1 Electron Optics

Electron optics exploits the analogies between rays in geometrical optics and electron trajectories, leading to interesting insights and potential applications.

In geometrical optics, transparent interfaces, such as lenses and prisms are used to manipulate and control the rays paths. Rays in geometrical optics are analogous to the classical trajectories of electrons, where the electron de Broglie waves can interfere. Following the analogies between rays in geometrical optics and electrons, one can suggest that interfaces in materials may aid the manipulation and control of electron paths. If we take semiconductors as an example, interfaces in these materials have played an important role, through interfaces of semiconductors with different charges, in what is known as PN junctions. The depletion region that forms at these interfaces, rules out semiconductors PN junctions as a potential candidate for the precise manipulation of electrons paths.

From this perspective graphene is one of the most promising candidates for electron optics. The low energy dispersion of electrons in graphene is centered near two inequivalent points in the Brillouin zone, the $K$ and $K'$ or Dirac points [1, 25]. The “massless” nature of electrons results in novel phenomena such as the Klein paradox [5, 25, 98, 99], which leads to full transparency of a sharp gated interface for normal
incident electrons, and a high probability of transmission for incoming electrons with finite angles. The linear dispersion of electrons is also evocative of photons, prompting a number of proposals and experiments to probe optical analogs with charge carriers [100], aided in great measure by the high electron mobility in this unique material. In fact, the transparency of barriers and ability to gate regions of the system to change the sign of carriers can lead to the use of graphene gate-controlled interfaces as electronic lenses that follow Snell’s law with negative index of refraction and allow the implementation of electronic analogues of Veselago optics [101–103]. These intrinsic properties of graphene, and the recent experiments that have demonstrated gate tunability, make the study of electron optics on graphene viable and controllable[99, 104, 105].

In the following sections, we are going to explore the theory behind electron optics in graphene, and the effects of spin orbit interactions in the manipulation of electronic paths, and the new features and improvements these interactions introduce to electron optics.

### 6.2 Veselago Lens in Graphene

The Fermi energy of pristine graphene is at the point of degeneracy of both bands, and the states at this energy correspond to the Dirac states at opposite corners of the hexagonal Brillouin zone (see Ch. 2). The group velocity of the eigenstates with a momentum \( k \) measured from the Dirac points, is given by

\[
V_{g,x} = \frac{1}{\hbar} \nabla_{k} E = \frac{\partial E}{\partial(hk_x)} \hat{x} + \frac{\partial E}{\partial(hk_y)} \hat{y} = \pm v_F \frac{(k_x \hat{x} + k_y \hat{y})}{|k|},
\]

where \( \pm \) represent the conduction and the valence bands. In order to control the electron and hole character of the antiparticles in graphene one can make use of gating techniques [99, 104, 105]. Possible techniques make use of top and bottom gates, as gates move the Fermi level away from the point of degeneracy of the conduction and valence bands, and sets the Fermi energy at \( E_F = E \). An effective PN junction can be made by setting the gate
over a region where the Fermi energy is lowered to $E'_F = E - V$, where $V > E$ [102]. Now if we have a source of electrons approaching the PN junction from the $n$-side, with a group velocity $V_C$, let us focus on the ray incoming to the interface with an angle $\theta_c$, and at group velocity $\vec{V}_{g,+} = v_F(\cos(\theta_c), \sin(\theta_c))$, and the wave vector $\vec{k} = |k|(\cos(\theta_c), \sin(\theta_c))$. Part of this electron ray will get reflected at the interface with a group velocity $\vec{V}'_{g,+} = v_F(-\cos(\theta_c), \sin(\theta_c))$, and a wave vector $\vec{k}' = |k'|(-\cos(\theta_c), -\sin(\theta_c))$. A part of this ray will get transmitted into the $p$-region with a group velocity $\vec{V}_{g,-} = v_F(\cos(\theta_v), \sin(\theta_v))$, and wave vector $\vec{k}' = |k'|(-\cos(\theta_v), -\sin(\theta_v))$. Since the component of the momentum along the interface is conserved, we get the electronic analog of Snell’s law

$$|k| \sin(\theta_c) = -|k'| \sin(\theta_v) \quad (6.2)$$

$$\frac{\sin(\theta_c)}{\sin(\theta_v)} = \frac{-|k'|}{|k|} = \frac{-|E - V|}{|E|} \equiv n,$$

here $n$ is the index of refraction, where we have used the relativistic dispersion of the massless particles in this definition. $n$ is negative, and it focuses divergent rays in to a focal point [102], in what is known as a Veselago lens [101], as is shown in Fig. 6.1.

This phenomenon becomes more interesting in a circular geometry, as this geometry allows patterns similar to the optical caustics which develop by light refraction through a shaped medium, and belong to a class of cusps in catastrophe theory [40, 106].

To study these effects, we consider a graphene sheet with a circular gate potential (or corresponding doping/intercalation profile) covering an area of radius $R$, where the electric field (or doping) reverses the carrier character from electron to hole.

The Hamiltonian of the system has the form $H = H_o + H_V$, where $H_o/\hbar v_F = \sigma_x k_x + \sigma_y k_y$ describes free electrons in graphene with momentum $\vec{k} = (k_x, k_y)$ away from the $K$ point. $H_V = V\Theta(R - r)$ represents the gated or doped region of strength $V$. We are interested in Rashba regions with $R \gg a$, where $a$ is the lattice constant of graphene, in order to adopt the continuum description of graphene.
Source of electrons  Focal Point

\[ \theta_c \quad \theta_v \]

\[ |n|a \]

\[ a \]

\[ n \rightarrow p \]

\[ |n|a \]

\[ \text{Figure 6.1: NP interface with source of electrons in the n-region positioned at a distance } a \text{ from the interface. Diverging electron paths in the n-region get focused at a point } |n|a \text{ in the p-region, where } |n| \text{ is the electronic index of refraction. The position of the focal point can be controlled through the gate } V. \text{ If } |n|a = 0.5a \text{ then } V = 3E/2, \text{ in order to obtain } n = -0.5, \text{ and change in character of the region from } n \text{ to } p, \text{ which discards the possibility of } V = E/2. \]

In order to study the scattering problem, described in Fig. 6.2a, we use the scattering matrix method, described Sec. 3.1 of Ch. 3. Here the scattering matrix elements are determined by the boundary condition

\[
\begin{pmatrix}
H^{(1)}_{n-1}(kR) & -J_{n-1}(k'R) \\
H^{(1)}_n(kR) & -J_n(k'R)
\end{pmatrix}
\begin{pmatrix}
S_n \\
T_n
\end{pmatrix}
=
-\begin{pmatrix}
H^{(2)}_{n-1}(kR) \\
H^{(2)}_n(kR)
\end{pmatrix},
\]

(6.3)

where \( T_n \) are the transmission parameters for each partial wave. The determination of \( T_n \) and \( S_n \), allows us to determine the wave functions over the entire system.

In order to compare electron trajectories to rays in geometrical optics, we need to have \( kR \gg 1 \) and \( k'R \gg 1 \), which for a given obstacle of size \( R \) and potential shift \( V \) requires a carrier concentration \( n_i \) for \( E = E_F = \sqrt{\pi n_i}/(\hbar v_F) \) [7, 25].

As it is shown in Fig. 6.2b and Fig. 6.2d, notice that the convergence of electronic paths inside the scattering region leads to the formation of caustics and cusps. These interesting electronic patterns can be understood in terms of geometrical optics, and characterized by a negative index of refraction \( n = -|E - V|/|E| \) [102]. For an incident
Figure 6.2: a) Electron flux in graphene coming along the $x$-direction onto a circular gate potential covering an area of radius $R$. b) Three dimensional map of $|\psi|^2$ near and inside gated region. The electronic patterns produced inside the gated region are analogous to those produced by the refraction of light in a circular Veselago lens. Linear electronic dispersion (center left inset), and in this case, $kR = 300$ (electron) and $k'/R = 300$ (hole). High intensity maxima correspond to caustics with $p = 1$ ($x < 0$) and $p = 2$ ($x > 0$), where $p - 1$ is the number of internal reflections. $x/R$ and $y/R$ coordinates. c) In the presence of Rashba spin orbit interaction the electronic dispersion in the gated region is modified, so that scattering particles have access to two different wave numbers (center right inset). Scattering produces electronic patterns as shown in the three dimensional map $|\psi|^2$, with $kR = 300$, $VR/\hbar v_F = 600$, $\lambda R/\hbar v_F = 100$, for $\uparrow$-spin incoming flux. The $p = 1$ and $p = 2$ caustics and cusps are doubled, associated with states of different chirality in graphene. The pattern can be described by the refraction from a medium with two indices, $n_{\pm}$. Here, the degree of birefringence is $\Delta n = n_- - n_+ = 0.71$. The dual pattern persists even for spin-unpolarized incidence. d) and e) Probability density patterns (scale bar shows log of $|\psi|^2$ amplitudes) near and inside gated region centered at $(x, y) = (0, 0)$. d) Corresponds to b). e) corresponds to c).
electron flux along the $x$-direction, the position of the cusps produced inside a circular gated region can be shown to be given by

$$x_{	ext{cusp}} = \frac{(-1)^p}{|n| - 1 + 2p},$$

(6.4)

for $p - 1$ internal reflections of the ray inside the region [103].

In order to realize a system, such as the one suggested in Fig. 6.2b, where $kR = 300$, and $k'R = 300$, and assuming experimentally feasible carrier concentrations, $n_i \approx 0.5 \times 10^{12} cm^{-2}$, which result in $E_F = 80$ meV, yields that the value of the gate potential should be set at $V = 160$ meV, and require $R \geq 250$ nm [40].

Recent experiments have demonstrated gate tunability, which makes the study of electron optics on graphene viable and controllable [99, 104, 105]. This makes the manipulation of paths of electrons possible. This kind of interface acts as a lens, that converges parallel incoming electronic paths, and focuses them into caustics and cusps, where the location of these points of convergence depend on the index of refraction of the lens, through laws identical to those in geometrical optics. In this case the index of refraction $n$ is negative, and represents the electronic realization of the Veselago lens. Moreover, imaging of the patterns resulting from the electron flow through these nanoscale structures can be achieved through STM [107, 108] or other scanning probe techniques [109, 110].

### 6.3 Birefringent Veselago Lens in Graphene

The study of spin transport properties of suspended and deposited graphene is rapidly becoming an important area of research [40, 41]. Experiments have achieved spin polarized injection of electrons and measured spin valve effects [111–113], spin polarized currents with long coherence lengths in suspended graphene [81], and shorter coherence lengths for deposited samples or samples containing impurities that enhance spin orbit effects [83, 114], such as hydrogen or gold [14, 18]. An important ingredient determining
the carrier spin dynamics in this and other materials is the spin orbit interaction (SOI). Here, we focus on the effects of the Rashba SOI in the spin dynamics of carriers away from the neutrality point as the spin-orbit interaction can be controlled by external factors [11, 40].

Optical birefringence in materials results from crystal anisotropies which are manifested as different group velocities for different polarizations of the propagating light in the material. Here, we show that an equivalent phenomenon to optical birefringence in electron optics is feasible in two dimensional graphene, which in essence reflects the intrinsic crystal structure even at large electronic wavelengths. The effect requires the presence of Rashba spin-orbit interaction, where the different group velocities depend on the chirality of the electronic states, mimicking the light polarization dependence of the group velocities in optical birefringent materials.

To study these effects, we consider a graphene sheet with a circular gate potential (or corresponding doping/intercalation profile) covering an area of radius $R$, where the electric field (or doping) reverses the carrier character from electron to hole and also generates a Rashba SOI of strength $\lambda_R$, as shown in Fig. 6.2c and Fig. 6.2d.

The Hamiltonian of the system is given in Eq. 3.32, for the region $r < R$, setting $\Delta_{SO} = 0$, and in the region $r > R$ takes the form in Eq. 2.11. The real space solutions to the Hamiltonian in the region $r < R$ are given in Eq. 5.2, by setting $\Delta_{SO} = 0$.

As described in Sec. 3.2 of Ch. 3, the scattering of an incident flux of electrons on the gated obstacle is studied through a spin-dependent generalization of the partial wave component method [36, 40]. The scattering matrix elements are found through the boundary value problem in Eq. 5.3.

These relations allow the direct evaluation of wave functions inside and outside the Rashba region, depending on the incident energy, momentum and spin content of the incident flux, as well as system parameters. The momentum outside the scattering region
is given by $k = E/\hbar v_F$, while the momentum inside takes two different values, $k_\pm = \sqrt{(E - V)^2 \pm 2\lambda_R(E - V)/\hbar v_F}$, for the given energy $E$, due to the presence of the Rashba SOI (see Fig. 6.2).

In a system with Rashba SOI the two wave numbers for a given energy allow for two refraction indices, associated with the two chiral solutions of the Dirac equation,

$$n_\pm = -k_\pm/k.$$ \hspace{1cm} (6.5)

Correspondingly, the optical analogue results in two different cusp locations (see Fig. 6.2c and e) given by

$$x_{cusp}^\pm = \frac{(-1)^p}{|n_\pm| - 1 + 2p}.$$ \hspace{1cm} (6.6)

As we will see below, this simple description is borne out by the full quantum calculation of the scattering patterns. We should emphasize that despite the optical analogy, birefringence here has a clear quantum mechanical spinful origin, as the group velocity and built in phases of the different chiral states are different due to the presence of the Rashba interaction.

The presence of the Rashba interaction causes the spin of the incoming electron to precess as it travels along the scattering region, there oscillations in the amplitudes of the spin components of the wave function are known as Rashba oscillations. As is shown in Fig. 6.3 and 6.4, the spatial frequency of these oscillations depends on the values of $\lambda_R$ values: shorter precession wavelength for larger $\lambda_R$.

For small Rashba coupling, the wavelength of these oscillations is comparable to the size of the gated region, leading to the presence of different spins over large areas of the scattering disk. Fig. 6.3a,b shows the wave functions inside and outside the scattering region for spin up and down components for $\lambda_R R/\hbar v_F = 3$; take notice these are results for spin-up incidence. Notice that both spin components display caustics inside the scattering region. Moreover, one observes that the wave function around the caustics has a net spin
Figure 6.3: a) Probability density patterns (scale bars show log of amplitudes, normalized to incident flux) resulting from the scattering of incoming $\uparrow$-spin electron wave along the $x$-direction with $kR = 300$, in the presence of a gate potential $VR/\hbar v_F = 600$, and Rashba coupling $\lambda_R R/\hbar v_F = 3$. This arrangement leads to a system with a small degree of birefringence $\Delta n = n_- - n_+ = 0.02$. a) The spin-preserving component $|\psi_{\uparrow\uparrow}|^2$ and b) spin-flip component $|\psi_{\uparrow\downarrow}|^2$ display Rashba oscillations with a wavelength covering a large region of the scattering target, due to the small $\lambda_R$. c) Total wave function $|\psi|^2 = |\psi_{\uparrow\uparrow}|^2 + |\psi_{\uparrow\downarrow}|^2$, displays caustics and cusps that remain almost unchanged from the case in which the Rashba interaction is absent. d) Net spin $\eta \sim |\psi_{\uparrow\uparrow}|^2 - |\psi_{\uparrow\downarrow}|^2$ quantifies the predominance of a given spin in different regions of the system. The large wavelength of Rashba oscillations leads to a cusp at $x \approx -0.5$ with a net $\downarrow$-spin (blue) while the annular region near $x \approx 0$ has a net $\uparrow$-spin (red).

content, as shown by

$$\eta = \text{sgn}(\Delta)|\log_{10}(|\Delta|)|$$,  \hspace{1cm} (6.7)$$

where $\Delta = |\psi_{\uparrow\uparrow}|^2 - |\psi_{\uparrow\downarrow}|^2$, in Figure 6.3d. For this set of parameters, the $p = 1$ caustic ($x < 0$) is predominantly spin-down, while the $p = 2$ caustic ($x > 0$) is predominantly spin-up. The total wave function, $|\psi|^2 = |\psi_{\uparrow\uparrow}|^2 + |\psi_{\uparrow\downarrow}|^2$ shows no major changes due to the
Rashba SOI, since $\lambda_R$ is small and the two different wave numbers are nearly equal,

$$k_- - k_+ \approx 2\lambda_R/\hbar v_F,$$

see Figure 6.3c. Correspondingly, the two indices are also very similar, $n_- - n_+ = 0.02$, and the pattern of caustics and cusps is essentially unchanged from the $\lambda_R = 0$ case.

For larger values of the Rashba interaction the oscillations become even sharper, with shorter wavelength, and their number inside the gated region is approximately $\lambda_R R/2\hbar v_F$ for both spins. The larger value of $\lambda_R$ leads to two very different wave numbers inside the scattering region, $k_{\pm}$, different group velocities for the charge carriers, and different indices $n_{\pm}$. In the case of $\lambda_R R/\hbar v_F = 30$, Figure 6.4, we notice a clear doubling of the cusps, especially evident in panel c for the total wave function. Moreover, the cusp positions are in agreement with the anticipated values shown by Eq. (6.6), as one can easily verify.

In order to be able to observe the suggested electronic birefringence, we first need to recall the set of assumptions in our model. We have first assumed a semi-classical limit, with $kR \gg 1$ and $k_{\pm} R \gg 1$; second, we have assumed the absence of intervalley scattering ($K$ to $K'$), which requires that the characteristic length of potential change must be much larger than the lattice constant. These two requirements introduce constraints on the values of the Fermi energy of the incoming electron flux, the gate voltage, and the size of the gated region. Recent experiments have reported values of the Rashba interaction in the range 10-100meV for graphene samples grown on Ni and intercalated with Au atoms [17]. This coupling is 2-3 orders larger than the spatially random spin orbit generated by intrinsic ripples in graphene. [21] Assuming possible values of these parameters in experiments as $E = 80meV$, corresponding to carrier concentration $n_c \approx 0.5 \times 10^{12}cm^{-2}$, $V = 200meV$, and $\lambda_R = 10meV$, would require $R \geq 1000nm$ and lead to $n_- - n_+ \geq 0.24$.

This allows the observation of the patterns shown in Figure 6.4c, and its clear detection in scanning probe experiments, as $|x_{cusp}^+ - x_{cusp}^-| \geq 42nm$. We should also notice that although
Figure 6.4: Wave function maps (scale bar show log of amplitudes; normalization to incident flux) similar to those in Figure 6.3 but for larger $\lambda_R$. Here, $kR = 250$, $VR/\hbar v_F = 600$ and $\lambda_R R/\hbar v_F = 30$. This arrangement leads to a system with a degree of birefringence $\Delta n = n_- - n_+ = 0.24$. The different energy of the incoming wave leads to modified positions of caustics and cusps. a) $|\psi_{\uparrow\uparrow}|^2$ and b) $|\psi_{\uparrow\downarrow}|^2$ show clearer and sharper Rashba oscillations with shorter wavelength. Notice that the number of oscillations inside the gated region is approximately $\lambda_R R/2\hbar v_F = 15$ for both spins, as shown by the rings around the main cusp. c) The total wave function, $|\psi|^2$, displays clear duplicate sets of caustics and cusps manifesting the birefringent character of the scattering, due to the large Rashba interaction and associated different group velocities. d) The net spin $\eta$, shows variation of the two spin components along the the different cusps and caustics.

we have used spin-polarized injection in our calculations, to expose the spin character of the caustic pattern, this is not a necessary ingredient to observe the birefringence.

Unpolarized electron injection will obviously erase the net spin structures we have discussed. However, the appearance of duplicate caustics and cusps would persist and result in an identical spatial structure of the total wave function to the ones shown above. Similarly, $K-K'$ coupling would preserve the duplicate caustic pattern, although with
decreased contrast, as the enhanced backscattering would reduce the overall transparency of the region.

The concept of birefringent electron optics established here can lead to important consequences in experiments and applications. For example, using guiding gates [100] over graphene samples grown on Ni[111], or creating a suitable spatial pattern of gold intercalation, one could design a birefringent waveguide with two different critical angles ($\theta_{\pm} = \sin^{-1}(k_{\pm}/k)$) for the two orthogonal chiral states of the system, leading to the independent propagation of chiral states, with the corresponding spatial modulation of the spin components [115].
7 Multiple Scattering Effects on Electron Transport of Dirac Fermions in Two Dimensions

7.1 Introduction

The excellent electronic properties and the different degrees of freedom that graphene offers [25] makes it a promising candidate for a variety of electronic applications. The arrangement of carbon atoms in a hexagonal lattice, results in a low energy spectrum characterized by linear dispersion cones residing at opposite corners of the Brillouin zone. These points, hosting massless Dirac fermions at low energies, are known as the valleys or the Dirac points of graphene, and represent an additional degree of freedom for electrons in this material, besides its pseudo-spin and spin. In analogy with the field of spintronics which aims to access and control the spin degree of freedom in electronic devices [8], the field of valleytronics [116–127], aims to access and utilize the valley degree of freedom. Not only graphene, but also other two dimensional materials, such as transition metal dichalcogenides [91, 92], are potential candidates for new promising applications in valleytronics.

In order to control the valley degree of freedom, it is important to be able to differentiate between the two valleys via controllable perturbations that affect the pristine form of graphene, and result in the desired phenomenon of valley filtering. Following the analogy with spintronics, many proposals have demonstrated the valley counterpart of the spin valve [116]. It has been shown that valley polarized currents can be obtained in a quantum point contact made of graphene, where its narrow region is zigzag terminated [116, 125]. Other methods rely on the use of local real magnetic fields, via magnetic barriers[121], pseudo magnetic fields introduced by locally straining graphene [126, 127], and by using time-dependent lattice vibration and optical phonon modes [124]. Suitable sample deposition can also result in the appearance of valley
filtered currents, as is the case for graphene on $hBN$ [128], or by depositing adatoms on graphene that lead to the local enhancement of a staggered potential [46, 122, 123]. Not only artificially tailored systems can result in valley filtering, but also naturally occurring line defects that arise due to the growth process of graphene on different materials, such as grain boundaries, can in principle act as valley filters [117–120, 129, 130].

Functionalization of graphene makes this material a strong candidate for a versatile group of electronic, spintronic and now valleytronic applications. Some functionalization methods relying on the deposition of graphene on substrates lead to a tailored and controlled doping of this material. For example, deposition of graphene on pillar-superlattice arrays, which may in principle result in the patterned doping of the graphene sheet, where the doping pattern is controlled by the substrate underneath [131, 132]. Similarly, it has been experimentally shown that graphene-azobenzene-Au sandwiches result in photo-controllable gated regions extending over few $nms$ [43] (see 4.1). It has been shown that adatoms such as $Sn$ [51], $Au$, $Cu$ [12], and transition metals [133], tend to form clusters when deposited on graphene. The presence of these clusters not only affects the mobility of electrons in graphene samples [42], but may also introduce unexpected effects through the scattering of Dirac fermions in graphene, due to shape irregularities and/or spatial distribution of the clusters.

In Ch. 4 and 5, we have seen the effects of perturbations belonging to different symmetry classes on the electronic and spin transport of Dirac fermions in two dimensions. It was shown that the perturbations that do not preserve effective time reversal act as a valley filter [46]. The analysis of the scattering produced by these perturbations was performed in the dilute impurity concentration limit, where the scattering cross sections of largely separated impurities is given by the addition of the cross sections for single impurities. However, the case is very different for perturbations that are separated by short distances, specially if their spatial distribution leads to the reduction of graphene
symmetries, as the role of symmetry breaking together with the effects of multiple scattering may lead to drastic changes on the transport signatures of the system.

In order to obtain a clear understanding of the effects of symmetry breaking, reflected through multiple scattering, and the interesting physical phenomena that they may produce, we study the scattering of Dirac fermions from a set of individually centrosymmetric scattering regions which break lattice symmetries collectively. In order to study these effects we first generalize the partial wave method in the presence of multiple centrosymmetric scatterers.

We specifically study the effects of symmetries on the scattering signatures of time reversal invariant systems. We focus on the role played by parity conservation in these systems, the constrains that the conservation of this symmetry requires on impurities distribution, and the corresponding scattering properties. We show that for a set of impurities distributed in such a way that parity is a conserved quantity, the constrains imposed by parity conservation on the scattering matrix dictate the absence of skew scattering. Moreover, if the scatterers have a space dependence that leads to the breaking of parity in the system, skew scattering becomes non-zero, and its has opposite signs for opposite valleys, acting as a valley splitter, and leads to the appearance of the valley Hall effect [128].

In order to have a better quantitative idea of the importance of parity breaking effects and their impact on the transport properties of Dirac-like systems such as graphene, we focus on the example of two potential scatterers. We quantify the skew scattering parameter in this case and analyze its dependence on the location of the two scatterers relative to each other and their relative sizes.
7.2 Symmetry Constraints and Multiple Scattering Effects

In this section we analyze the symmetry constrains on Dirac fermion dynamics in the presence of multiple scatterers. As, it was shown in Ch. 4, a single scatterer can break the symmetries that protect the appearance of the phenomena expected from Dirac fermions in graphene [46], and result into even more interesting effects, such as valley splitting through skew scattering, and the valley Hall effect. In the presence of multiple scatterers, not only the symmetries that each individual scatterer matter, but also the spatial distribution that this scatterers have will play an important role.

Here we use the chiral basis, where $H_0$ is given in Eq. 2.13, then let us assume that the perturbation to the Hamiltonian is given by

$$V(x, y) = \sum_i c_i a_i V_i(x, y), \quad (7.1)$$

where, $a_i$ are the elements in the set of operators allowed by time reversal symmetry in the Dirac Hamiltonian, $V_T$, with $c_i$ being the perturbation strength, $V(x, y)$ is an arbitrary function of space, and $c_i \in R$. Note that out of 16 possible spin independent perturbations to the Dirac Hamiltonian one can form the set $V_T$ including all the possible time reversal invariant perturbations [46, 69]

$$V_T = \{I, \beta, i\beta\gamma^5, \alpha_3, \gamma^5\alpha_1, i\beta\alpha_1, \beta\gamma^5\alpha_1, \alpha_2, \beta\alpha_2, i\beta\gamma^5\alpha_2\}, \quad (7.2)$$

and $[a_i, T] = 0$, where the time reversal operator $T$ is given in Eq. 2.35.

As discussed in Ch. 2, parity in two dimensions is a mirror symmetry, such as $y \rightarrow -y$ and $x \rightarrow x$, and it is not inversion symmetry, $r \rightarrow -r$ [27], and the form of the parity operator depends on the original orientation of the lattice. In this chapter as in the previous ones, we have chosen the lattice orientation in Fig. 2.1a and b, for which the parity operator is given by Eq. 2.43. Now, we can divide the set of elements in $V_T$, into two subsets, the first one composed of elements that commute with both time reversal and
parity, $E_{T,P}$, and the ones that only commute with time reversal, $O_{T,P}$, and anti-commute with parity, to find

$$E_{T,P} = \{ I, \gamma^5 \alpha_1, \beta \gamma^5 \alpha_1, \beta, i \beta \alpha_1, i \beta \gamma^5 \} ,$$

$$O_{T,P} = \{ \alpha_3, i \beta \gamma^5 \alpha_2, \beta \alpha_2, \alpha_2 \} .$$

We can write the Hamiltonian in the presence of time reversal invariant perturbations $V_T$ as

$$H = H_0 + \sum_i \lambda_i e_i f_i(x,y) + \sum_j \delta_j o_j g_j(x,y) ,$$

where $e_i \in E_{T,P}$, $o_i \in O_{T,P}$, and $\lambda_i$, $\delta_i$ represent the strengths of the perturbations. Now, we require that the Hamiltonian be invariant under a parity transformation, such that

$$\mathcal{P} H \mathcal{P}^{-1} = \mathcal{P}(H_0 + \sum_i \lambda_i e_i f_i(x,y) + \sum_j \delta_j o_j g_j(x,y)) \mathcal{P}^{-1}$$

$$= H_0 + \sum_i \lambda_i e_i f_i(x,-y) - \sum_j \delta_j o_j g_j(x,-y) = H .$$

This clearly requires the functions $f_i(x,y)$ and $g_j(x,y)$ to satisfy

$$f_i(x,y) = f_i(x,-y) ,$$

and

$$g_i(x,y) = -g_i(x,-y) .$$

Now, with these conditions on the spatial dependence of perturbations to the free Dirac Hamiltonian, let us assume that the Hamiltonian is indeed time reversal and parity invariant. Let us now assume an incoming circular wave approaches the scattering region containing the set of time reversal and parity invariant perturbations. The wave function in the range where the perturbation vanishes is described by incoming and outgoing eigenstates of the free Hamiltonian, $H_0 \psi = E \psi$, and can be written as

$$\psi_j = \psi_j^{(-)} + \sum_l \hat{S}_{jl} \psi_l^{(+)} ,$$
where $j$ and $l$ are half integers, and

Consider $P_{\pm} = (1 \pm \gamma^5)/2$, are the projectors into the valley space $((+, -) = (K, K'))$

\[ P(P_{\pm} \psi) = \pm P_{\pm} \psi, \quad (7.9) \]

so that we get Eq. 4.30, we have

\[ P\psi_j = PP_+ \psi_j + PP_- \psi_j \]
\[ = (-1)^j (P_+ - P_-) \psi_{-j} \]
\[ = (-1)^j \gamma^5 \psi_{-j}. \quad (7.10) \]

From this expression, notice that the effect of the parity operator on the spinor $\psi_j$ is equivalent to the effect of the effective time reversal operator $T_1$ introduced in Ch. 4 (see Eq. 4.31). Then if we apply the parity operator on the state $\psi_j$ in Eq. 7.8, we have

\[ P\psi_j = P\psi_j^{(-)} + \sum_l P\hat{S}_{jl} P^{-1} P\psi_l^{(+)} , \quad (7.11) \]
\[ (-1)^j \gamma^5 \psi_{-j} = (-1)^j \gamma^5 \psi_{-j}^{(-)} + \sum_l P\hat{S}_{jl} P^{-1} (-1)^j \gamma^5 \psi_l^{(+)} , \]
\[ \psi_{-j} = \psi_{-j}^{(-)} + \sum_l (-1)^{l+j} \gamma^5 P\hat{S}_{jl} P^{-1} \gamma^5 \psi_{l}^{(+)} . \]

By comparing Eq. 7.11 to the scattering of a circular wave of angular momentum $-j$,

\[ \psi_{-j} = \psi_{-j}^{(-)} + \sum_q \hat{S}_{-jq} \psi_q^{(+)} , \quad (7.12) \]

we get

\[ (-1)^{l+j} \gamma^5 P\hat{S}_{jl} P^{-1} \gamma^5 = \hat{S}_{-j-l} . \quad (7.13) \]
Now, we can also get the effect of the time reversal operator on the scattering matrix. The time reversal operator in Eq. 2.35, such that (see Eq. 4.32)

\[
\mathcal{T} \psi_j = \mathcal{T} \psi_j^{(-)} + \sum_l T \hat{S} \mathcal{T}^{-1} \mathcal{T} \psi_l^{(+)},
\]

\[
(-1)^{j+\frac{1}{2}} \gamma^5 \psi_{-j} = (-1)^{j+\frac{1}{2}} \gamma^5 \psi_{-j}^{(+)},
\]

\[
\psi_{-j} = \psi_{-j}^{(+)} + \sum_l (-1)^{j+\frac{1}{2}} \gamma^5 T \hat{S} \mathcal{T}^{-1} \gamma^5 \psi_{-l}^{(-)},
\]

(7.14)

(7.15)

Comparing Eq. 7.14 to Eq. 7.12, we get

\[
(-1)^{j+\frac{1}{2}} \gamma^5 \hat{S} \mathcal{T}^{-1} \gamma^5 = \hat{S}^{\dagger}_{-l-j},
\]

(7.16)

with the aid of the unitarity of the scattering matrix.

Now with the constraints of time reversal symmetry and parity on the scattering matrix, and correspondingly on the Dirac fermion dynamics, we are going to analyze the differences in the scattering properties of parity preserving and parity breaking systems. The system that we will analyze consists of multiple potential centrosymmetric scatterers distributed in space. The Hamiltonian describing graphene in the presence of these scatterers is given by

\[
H = H_0 + \sum_{l=1}^{N} \hat{V}_l \Theta(R_l - r_l),
\]

(7.17)

where, \( \hat{V}_l = V_l \sigma_0 \otimes \tau_0 \), \( V_l \) is the strength of the \( l \)-th potential scatterer, \( N \) is the total number of scatterers, \( \Theta \) is a Heaviside step function, \( r_l = \sqrt{(x - x_l)^2 + (y - y_l)^2}, (x_l, y_l) \) defines the center of the scatterer \( l \) with radius \( R_l \). Now, with this simple model in mind, we are going to introduce the multiple scattering formalism.

### 7.3 Formalism

In order to study the problem of multiple centrosymmetric scatterers we need to consider the following important components; the global coordinate of the system,
origin $O$ and a position vectors $\mathbf{r} = (x, y)$ defined with respect to $O$. A local coordinate system for each scatterer $i$, with a local origin $O_i$ located at $\mathbf{b}_i$ from the global origin $O$, and radius $R_i$. The position vector from the global origin to a point $P$ can be expressed in terms of the local position vector and the location of the scatterer $i$, such that $\mathbf{r} = \mathbf{r}_i + \mathbf{b}_i$, where $(x_i, y_i) = (r_i \cos \theta_i, r_i \sin \theta_i)$ and $\theta_i = \tan^{-1} \left( \frac{x_i}{y_i} \right)$, as shown in Fig. 7.1.

![Figure 7.1: The global and local coordinate systems for a two scatterer system. The local origins are defined from the center of the scatterers $i$ and $l$.](image)

Another important component of the multiple scattering formalism is the ability to express the wave functions of the problem at any given point $P$ in terms of the local coordinate system of a scatterer $i$. This is made possible by the local conservation of total angular momentum around each scatterer,

$$J_{\omega} = -i \partial_{\theta_i} + \frac{1}{2} \gamma^5 \alpha_3,$$

which makes it possible to label the eigenstates around these scatterers by their local angular momentum, such that $J_{\omega} \psi_j(r_i, \theta_i) = j \psi_j(r_i, \theta_i)$, where $j = (n - 1/2)$, with $n$ integer. The ability to express the wave functions at any point $P$ in terms of the local coordinate of a given scatterer, is achieved via addition theorems, which in this case are known as Graf’s addition theorems [45].
An incoming plane along the \( x_l \) axis and at point \( P \), can be expressed in the local coordinate system of scatterer \( i \), by using the Graf’s addition theorem as

\[
e^{ikr_i \cos \theta_l} = \sum_{n=-\infty}^{\infty} \sum_{m=-\infty}^{\infty} i^n J_m(kb) e^{im \epsilon} J_{-m}(kr_i) e^{in \epsilon} \tag{7.19}
\]

\[
e^{ikr_i \cos \theta_l} = \sum_{n=-\infty}^{\infty} \sum_{m=-\infty}^{\infty} i^n J_{-m}(kb) e^{im \epsilon} J_m(kr_i) e^{in \epsilon} \tag{7.19}
\]

where, \( j, m \) are integers, with respect to scatterer \( i \), \( \epsilon_{il} \) is the relative angle between the scatterer \( i \) and \( l \), and is given by \( \epsilon = \tan^{-1}\left(\frac{y_l - y_i}{x_l - x_i}\right) \), and \( \vec{b}_l - \vec{b}_i = \vec{R}_{il} = \vec{b}_{il} - \vec{R}_{li} \), is the distance between these two scatterers.

Similarly, the Hankel function of the first and second kind, take an asymptotic form representing incoming and outgoing waves, such that

\[
H_n^{(1/2)}(kr) \propto e^{\pm ikr} \frac{e^{\pm\sqrt{r}}}{\sqrt{r}}. \tag{7.20}
\]

Then, an outgoing wave expressed in the local coordinates of scatterer \( i \) can be expressed in terms of the local coordinates of \( l \), as facilitated by Graf’s theorem for Hankel functions,

\[
H_n^{(1/2)}(kr) e^{i\theta_l} = \sum_{m=-\infty}^{\infty} H_{n-m}^{(1/2)}(kb) e^{i(n-m)\epsilon} J_{-m}(kr) e^{i\theta_l} \tag{7.21}
\]

for \( r_i < b \), and

\[
H_n^{(1/2)}(kr) e^{i\theta_l} = \sum_{m=-\infty}^{\infty} J_{n-m}(kb) e^{i(n-m)\epsilon} H_{m}^{(1/2)}(kr) e^{i\theta_l} \tag{7.22}
\]

for \( r_i > b \), and

In the case of two or more centrosymmetric scattering centers, the proper combination of local angular momentum conservation and addition rules, facilitate the study of this problem. The combination of these two methods result into an infinite system of simultaneous algebraic equations, that lead to the exact solution of this problem, through the determination of the different scattering matrix elements [134].
As in the single scatterer problem, we assume plane wave incoming towards the scattering region, which in this case is composed of $N$ scattering centers with radii $\{R_1, R_2, \cdots, R_N\}$; additionally, we assume that far away from the scattering region the wave will recover its asymptotic form, which should be consistent with the correct set of boundary conditions. Also, the continuity of the wave function in and out the different scattering regions allows the determination of the different scattering matrix elements, and through the far field matching one is able to find the different amplitudes of the problem.

In order to obtain a simultaneous set of linear equations that determine the scattering coefficients, one needs to express the continuity of the wave functions at the boundary of the different scatterers in the problem. We consider an incoming circular wave (global coordinate system), and the outgoing waves from the different scattering centers, as shown in Fig. 7.2, such that

$$\psi^\ast(r) = \sum_{n=-\infty}^{\infty} \left( \begin{array}{c} H_{n-1}^{(2)}(kr) e^{i(m-1)\theta} \\ i\text{sgn}(E) H_n^{(2)}(kr) e^{im\theta} \end{array} \right),$$

(7.23)
and

$$\psi_{\text{in}}(r_1, r_2, \cdots, r_N) = \sum_{l=1}^{N} \sum_{n=-\infty}^{\infty} S_l^n \left( \begin{array}{c} H_{n-1}^{(1)}(kr_l)e^{i(n-1)\theta_l} \\ \text{isgn}(E)H_n^{(1)}(kr_l)e^{i\theta_l} \end{array} \right).$$

(7.24)

Then the wave function expressed in terms of the local coordinate of a impurity \(i\), is given by

$$\psi(r_i) = \sum_n \sum_m \left( \begin{array}{c} \xi_{n-1,m}^2(kb_{0i})J_n(kr_i)e^{i\theta_l} \\ \text{isgn}(E)\xi_{n,m}^2(kb_{0i})J_n(kr_i)e^{i\theta_l} \end{array} \right) + \sum_{l \neq i} \sum_n \sum_m S_m^n \left( \begin{array}{c} \xi_{n-1,m}^1(kR_{li})J_n(kr_i)e^{i\theta_l} \\ \text{isgn}(E)\xi_{n,m}^1(kR_{li})J_n(kr_i)e^{i\theta_l} \end{array} \right) + \sum_{n=-\infty}^{\infty} S_n^l \left( \begin{array}{c} H_{n-1}^{(1)}(kr_i)e^{i(n-1)\theta_l} \\ \text{isgn}(E)H_n^{(1)}(kr_i)e^{i\theta_l} \end{array} \right),$$

(7.25)

for \(r_i < R_{li}\), where, \(R_{li} = b_i - b_l\), \(r_i = r_l + R_{li}, \epsilon_{li} = \tan^{-1}\left(\frac{y_i-y_l}{x_i-x_l}\right), \) and

$$\xi_{1/2}^1(kx_{li}, \epsilon_{li}) = H_{n-m}^{(1/2)}(kR_{li})e^{i(n-m)\epsilon_{li}} \quad \text{if} \quad i \neq l.$$  

(7.26)

Also, Eq. 7.25 can be written as

$$\psi(r_i) = \sum_n \sum_m \left( \begin{array}{c} \xi_{m,n-1}^2(kb_{0i})J_{n-1}(kr_i)e^{i(n-1)\theta_l} \\ \text{isgn}(E)\xi_{m,n}^2(kb_{0i})J_{n}(kr_i)e^{i\theta_l} \end{array} \right) + \sum_{l \neq i} \sum_n \sum_m S_m^n \left( \begin{array}{c} \xi_{m,n-1}^1(kR_{li})J_{n-1}(kr_i)e^{i(n-1)\theta_l} \\ \text{isgn}(E)\xi_{m,n}^1(kR_{li})J_{n}(kr_i)e^{i\theta_l} \end{array} \right) + \sum_{n=-\infty}^{\infty} S_n^l \left( \begin{array}{c} H_{n-1}^{(1)}(kr_i)e^{i(n-1)\theta_l} \\ \text{isgn}(E)H_n^{(1)}(kr_i)e^{i\theta_l} \end{array} \right).$$

(7.27)

The wave function in the area defined by \(\Theta(r_l - R_l)\), should be regular at the local origin \(O_l\), and it is given by

$$\psi_{\text{in}} = \sum_{n=-\infty}^{\infty} A_n^l \left( \begin{array}{c} J_{n-1}(kr_l)e^{i(n-1)\theta_l} \\ \text{isgn}(E - V)J_n(kr_l)e^{i\theta_l} \end{array} \right).$$

(7.28)
Matching the total fields present in the vicinity of the scatterer \(i\) at the boundary \(r_i = R_i\), for a given \(n\), can be written as,

\[
\sum_m \xi_{m,n}^2 (k b_0i) + \sum_{l \neq i} \sum_{m=-\infty}^{\infty} S_m^l \xi_{m,n-1}^1 (k R_i) + S_n^l \frac{H_n^{(1)}(kr_i)}{J_{n-1}(kr_i)} = A_n^l \frac{J_{n-1}(k'_ri)}{J_{n}(kr_i)},
\]

\[
\sum_m \xi_{m,n}^2 (k b_0i) + \sum_{l \neq i} \sum_{m=-\infty}^{\infty} S_m^l \xi_{m,n}^1 (k R_i) + S_n^l \frac{H_n^{(1)}(kr_i)}{J_{n}(kr_i)} = \text{sgn} \left( \frac{E-V}{E} \right) A_n^l \frac{J_{n}(k'_ri)}{J_{n}(kr_i)} \]

(7.29)

and by applying the boundary condition on \(N\) scatterers we get \(2N\) equations for each \(n\), so that in total we get \(4N \max|n|\) equations, allowing us to find all the unknowns of the problem. However since we are interested in the scattering matrix elements we can reduce the set of equations by half, such that

\[
\sum_m \xi_{m,n-1}^2 (k b_0i) + \sum_{l \neq i} \sum_{m=-\infty}^{\infty} S_m^l \xi_{m,n-1}^1 (k R_i) + S_n^l \frac{H_n^{(1)}(kr_i)}{J_{n-1}(kr_i)} = \text{sgn} \left( \frac{E-V}{E} \right) A_n^l \frac{J_{n-1}(k'_ri)J_n(kr_i)}{J_{n}(k'_ri)J_{n}(kr_i)},
\]

\[
S_n^l \left( \frac{H_{n-1}^{(1)}(kr_i)}{J_{n-1}(kr_i)} - \text{sgn} \left( \frac{E-V}{E} \right) \frac{J_{n-1}(k'_ri)}{J_{n}(kr_i)} \right) + \sum_{l \neq i} \sum_{m=-\infty}^{\infty} S_m^l \left( \xi_{m,n-1}^1 (k R_i) - \xi_{m,n}^1 (k R_i) \right)
\]

\[
= \sum_m \left( \text{sgn} \left( \frac{E-V}{E} \right) \frac{J_{n-1}(k'_ri)J_n(kr_i)}{J_{n}(k'_ri)J_{n}(kr_i)} \right) \xi_{m,n}^2 (k b_0i) - \xi_{m,n-1}^2 (k b_0i),
\]

(7.30)

where \(\text{sgn} \left( \frac{E-V}{E} \right) \frac{J_{n-1}(k'_ri)J_n(kr_i)}{J_{n}(k'_ri)J_{n}(kr_i)}\), makes the total number of equations \(2N(\max|n|)\).

The boundary value problem can be represented in a matrix form as \(MX = Y\), where

\[
X^T = \begin{pmatrix} S_{n-1}^1 & S_n^1 & \ldots & S_{n-1}^2 & S_n^2 & \ldots & S_{n-1}^N & S_n^N & \ldots \end{pmatrix}
\]

\[
Y^T = \begin{pmatrix} \ldots \xi_{n-1}(k_1b_01) \xi_n(k_1b_01) \ldots \xi_{n-1}(k_2b_02) \xi_n(k_2b_02) \ldots \xi_{n-1}(k_Nb_0N) \xi_n(k_Nb_0N) \ldots \end{pmatrix}
\]

where \(\xi_n(k_i b_0i) = \sum_m \left( \xi_{n}^2 \xi_{m,n}^2 (k b_0i) - \xi_{m,n-1}^2 (k b_0i) \right)\), with this choice of the vectors \(X\) and \(Y\), the matrix \(M\) takes the form:
where the matrices $D$ and $O$, are given by

$$D_{\mu\nu}^i = \left( \begin{array}{c} H_{n-1}(kr_i) \\ J_{n-1}(kr_i) \end{array} \right) - \left( \begin{array}{c} H_{m-1}(kr_i) \\ J_{m}(kr_i) \end{array} \right) \delta_{\mu\nu}$$

(7.33)

and

$$O_{\mu\nu}^i = \sum_{l} S_{l}^1 (kR_{li}) - \sum_{l} S_{l}^1 (kR_{li})$$

(7.34)

Solving the inversion problem $X = M^{-1}Y$, for all $n$ and $m$, we are able to find the $S^l$ coefficients, allowing the determination of scattering observables.

In order to obtain physical observables, we need to work on the global set of coordinates. Let $r$ be the position vector with respect to the global origin $O$, and $\theta$ the polar angle defined in this coordinate system. Then, one can make use of the far field produced by an incoming plane wave along the global $x$-axis is given in Eq. 3.4, obtained by the asymptotic forms of the Hankel functions in Eq. 3.21 (see 3.1).

We need to express the wave function in Eq. 7.25, in the global coordinate system, in order to obtain the wave function outside the scatterers. Using Graf’s addition theorems we get

$$\psi = \sum_{n'} \left[ \begin{array}{c} H_{n'-1}^{(2)}(kr)e^{i(n'-1)\theta} \\ isgn(E)H_{n'}^{(2)}(kr)e^{in'\theta} \end{array} \right] + \sum_{m} S_{n'm} \left[ \begin{array}{c} H_{m-1}^{(1)}(kr)e^{i(m-1)\theta} \\ isgn(E)H_{m}^{(1)}(kr)e^{im\theta} \end{array} \right]$$

(7.35)

where

$$S_{n'm} = \sum_{l} S_{n'm}^l J_{m-n'}(kb\theta)e^{i(m-n')\theta}$$

(7.36)
then by using orthogonality of the angular functions, in Eq. ?? and 7.36, we get

\[ \alpha_n \psi_n = \psi_{\text{out},n}, \]

where \( \alpha_n = \frac{i^{n-1}}{2}, \) and

\[ f(\theta) = \frac{e^{-i\pi/4}}{\sqrt{2\pi k}} \sum_n (S_n - 1)e^{i\theta} = \frac{e^{-i\pi/4}}{\sqrt{2\pi k}} \sum_n f_n e^{i\theta}, \quad (7.37) \]

where

\[ S_n = \sum_m S_{nm} = \sum_m \sum_l S_{n}^l J_{m-n}(kb_0)e^{i(m-n)e_0}. \quad (7.38) \]

From here we proceed to find the different cross sections, and the effects of multiple scattering, using the relations in Eq. 3.28, 3.29, 3.30 and 3.31 (see 3.1).

### 7.4 Multiple Scattering Signatures on Electronic Transport

In Sec. 7.2, we have discussed the effects and constraints imposed by parity and time reversal conservation in a Dirac system in two dimensions. The multiple scattering formalism in Sec. 7.3 allows us to study the effects of symmetry breaking caused by the spatial distribution of nearby scatterers in the sample. As an example of these effects we will study two scatterers with local origins at \((x_1, y_1)\) and \((x_2, y_2)\), radii \(a_1\) and \(a_2\), and potential strengths \(V_1\) and \(V_2\).

We start by analyzing the differential cross sections of different configurations. First, we consider the case where \(a_1 = a_2 = a\), and \(V_1 = V_2 = V\). In Fig. 7.3, where \(\theta_{01} = -\theta_{02} = (0, \pi/2)\), the differential cross section \(\sigma(\theta) = \sum_{rr'} \sigma_{rr'}(\theta)\) displays the same angular dependence as the cross section for the different valleys, \(\sigma_{rr}(\theta) = \sigma_{r'r}(\theta)\), and no asymmetry around the incoming direction of the flux. However, a more interesting case arises, when \(\epsilon_{01} = -\epsilon_{02} = \pi/4\), as shown in Fig. 7.4. The differential cross section has no angular asymmetry around the incoming flux axis, but this results include the addition of two asymmetric cross sections corresponding to the different valleys; this effect is larger for closely spaced scatterers. Notice that \(\sigma_{rr}(\theta) = \sigma_{r'r}(\theta),\) which indicates an interesting spatial separation of the scattered valley currents.
Figure 7.3: a) Differential cross section, $\sigma(\theta)/\max(\sigma(\theta))$, produced by the scattering of an incoming electron along the $x$-axis, with energy $E = 1$ meV, towards two scatterers with equal radii, $a_1 = a_2 = 10$ Å, and equal potentials $V_1 = V_2 = 2$ eV. The two scattering centers symmetrically placed from the global origin along the $x$-axis (see inset in (c)), at distance $R_{12}/2 = d_{12}/2 + a_1$ from the global origin. b) Differential cross section for a configuration of two scatterers with the same parameters as in a), but with their centers along the $y$-axis (see inset in d)). c) Scaling of $\max(\sigma(\theta))$ with scatterers separation for the configuration shown in the inset. d) Scaling of $\max(\sigma(\theta))$ with scatterers separation for the configuration shown in the inset. Notice that in these two cases, $\sigma(\theta)/2 = \sigma_{\tau\tau}(\theta)$, as $\max(\sigma(\theta))/2 = \max(\sigma_{\tau\tau}(\theta))$, where $\tau = (K, K')$.

In the case of $a_1 = a_2 = a$, but asymmetric potentials $V_1 = -V_2 = V$, we notice that the differential cross section $\sigma(\theta)$ does not display any angular asymmetry around the axis of incidence. When $\varepsilon_{01} = -\varepsilon_{02} = 0$, the differential cross section for different valleys are equal and do not display asymmetry around the $x$ axis. However, in contrast to the case where the potential are equal in magnitude and sign, we notice that there is asymmetric response for a larger set of potential configurations. For example, when $\varepsilon_{01} = -\varepsilon_{02} = \pi/2$
Figure 7.4: a) Differential cross section, $\sigma_{KK}(\theta)/\max(\sigma_{KK}(\theta))$, produced by scattering of $K$-polarized incident flux along the $x$-axis, with energy $E = 1$ meV, towards two scatterers with radii, $a_1 = a_2 = 10$ Å, and equal potentials $V_1 = V_2 = 2$ eV. The two scatterers centers are along the $x = y$ direction, and symmetrically located about the global origin at a distance $R_{12}/2 = d_{12}/2 + a_1$ (see inset in d). b) Differential cross section $\sigma_{K'K'}(\theta)/\max(\sigma_{K'K'}(\theta))$ for same two scatterers as in a), but for a $K'$-polarized electron. c) Differential cross section for a valley unpolarized incident flux, $\sigma(\theta)/\max(\sigma(\theta))$, for the configuration of scatterers in a). d) Scaling of $\max(\sigma(\theta))$ with scatterers separation for the scatterer configuration shown in the inset. Notice the strong angular angular asymmetry for $d_{12} \leq 5a_1$ valley cross sections disappears in $\sigma(\theta)$.

(Fig. 7.5) and $\epsilon_{01} = -\epsilon_{02} = \pi/4$ (Fig. 7.6) the differential cross section for different valleys displays a strong asymmetry around the $x$ axis, that would lead to their spatial separation, and obey $\sigma_{rr}(\theta) = \sigma_{rr}(-\theta)$. This asymmetry is larger when the scatterers are close, and eventually vanishes large separations, as it is shown in Figs. 7.5 and 7.6.
Figure 7.5: a) Differential cross section, $\sigma_{KK}(\theta)/\max(\sigma_{KK}(\theta))$, produced by scattering of and incoming $K$-polarized flux, along the $x$-axis, with energy $E = 1$ meV, towards two scatterers with equal radii, $a_1 = a_2 = 10$ Å, but asymmetric potentials $V_1 = -V_2 = 2$ eV. The two scatterers centers are along the $y$-axis, and symmetrically placed at $R_{12}/2 = d_{12}/2 + a_1$ from the global origin (see inset in e)). b) Differential cross section $\sigma_{K'K'}(\theta)/\max(\sigma_{K'K'}(\theta))$ for a configuration of two scatterers with the same parameters as in a), for a $K'$-polarized electron. c) Differential cross section for valley unpolarized incoming flux, $\sigma(\theta)/\max(\sigma(\theta))$ and system as in a). d) Differential cross section, $\sigma(\theta)/\max(\sigma(\theta))$, for scatterers with the same parameters as in a) but with their centers along the $x$-axis, and symmetrically placed at $R_{12}/2$ from the global origin. e) Scaling of $\max(\sigma(\theta))$ with scatterers separation for the scatterer configuration shown in the inset. d) Scaling of $\max(\sigma(\theta))$ with scatterers separation for the scatterer configuration shown in the inset.
Figure 7.6: Differential cross section, $\sigma_{KK}(\theta)/\max(\sigma_{KK}(\theta))$, produced by scattering of and incoming, $K$-polarized flux along the $x$-axis, with energy $E = 1$ meV, towards two scatterers with equal radii, $a_1 = a_2 = 10$ Å, but asymmetric potentials $V_1 = -V_2 = 2$ eV. The two scatterers centers are along the $x = y$ direction, and symmetrically placed at $R_{12}/2$ from the global origin (see inset in e)). b) Differential cross section $\sigma_{K'K'}(\theta)/\max(\sigma_{K'K'}(\theta))$ for a configuration of two scatterers with the same parameters as in a), but for a $K'$-polarized electron. c) Differential cross section for valley unpolarized incoming flux, $\sigma(\theta)/\max(\sigma(\theta))$, for the configuration of scatterers in a). Scaling of $\max(\sigma(\theta))$ with scatterers separation for the scatterer configuration shown in the inset. d) Scaling of $\max(\sigma(\theta))$ with scatterers separation for the scatterer configuration shown in the inset.

A qualitatively similar case is obtained when $a_1/2 = a_2 = a$, and $V_1 = V_2 = V$, which exhibits asymmetric differential cross sections around the $x$ axis for different valleys, when $\epsilon_{01} = -\epsilon_{02} = \pi/2$, as it is shown in Fig 7.7.

The differential cross sections for these different cases indicate that there is a fundamental difference whenever the scattered valley currents are spatially separated through scattering. The critical difference between these cases is parity conservation. As
we saw in Sec 7.2, parity and time reversal conservation impose conditions on the scattering matrix elements, and consequently constraints on the carriers dynamics, Eq. 7.13 and 7.16, for parity and time reversal, respectively. In Sec. 7.3 we obtained an expression for the scattering matrix of a system with many scatterers, Eq. 7.36, in terms of the local scattering matrix elements for each impurity. Using these relations we get
\[ \gamma^5 \mathcal{P} S_{jq} \mathcal{P}^{-1} \gamma^5 = S_{-j-q}, \quad (7.39) \]

\[ \alpha_x S_{jq} \alpha_x = \quad , \]

or

\[
\begin{pmatrix}
\hat{S}_{jq,++} & \hat{S}_{jq,+-} \\
\hat{S}_{jq,-+} & \hat{S}_{jq,--}
\end{pmatrix}
\begin{pmatrix}
\hat{S}_{-j-q,++} & \hat{S}_{-j-q,+-} \\
\hat{S}_{-j-q,-+} & \hat{S}_{-j-q,--}
\end{pmatrix}.
\]

(7.40)

Similarly, from time reversal symmetry we obtain

\[ \gamma^5 \mathcal{T} S_{jq} \mathcal{T}^{-1} \gamma^5 = S_{-j-q}^\dagger, \quad (7.41) \]

\[
\begin{pmatrix}
\hat{S}_{jq,--} & -\hat{S}_{jq,+-} \\
-\hat{S}_{jq,++} & \hat{S}_{jq,++}
\end{pmatrix}
\begin{pmatrix}
\hat{S}_{-j-q,--} & \hat{S}_{-j-q,+-} \\
\hat{S}_{-j-q,++} & \hat{S}_{-j-q,++}
\end{pmatrix},
\]

where

\[ S_{j,\tau\tau'} = \sum_q \sum_l S_{j,\tau\tau'}^l J_{q-j}(kb_l) e^{iq-k\epsilon}, \quad (7.42) \]

these conditions, in addition to the unitarity of the scattering matrix, result in

\[ f_{j,\tau\tau} = f_{-j,\tau\tau} \quad (7.43) \]

\[ f_{j,\tau\bar{\tau}} = -f_{-j,\tau\bar{\tau}} \]

\[ f_{j,\bar{\tau}\tau} = f_{-j,\bar{\tau}\tau} \]

\[ f_{j,\bar{\tau}\bar{\tau}} = -f_{-j,\bar{\tau}\bar{\tau}}, \]

where the dependence of the scattering amplitudes on the scattering matrix elements is given in Eq. 4.34 in Ch. 4.

As described in Ch. 3, the quantity that measures the asymmetry of the scattered waves around of the incoming flux axis is the skew cross section,

\[ \sigma_{sk,\tau\tau'} = \frac{1}{k} \sum_j \text{Im}(f_{j,\tau\tau} f_{j+1,\tau\tau'}^*). \quad (7.44) \]
With the help of Eq. 7.43, we get

$$
\sum_j f_{j,\tau\tau} f_{j+1,\tau\tau}^* = |f_{1/2,\tau\tau}|^2 + \sum_{j \geq 1/2} \text{Re}(f_{j,\tau\tau} f_{j+1,\tau\tau}^*) ,
$$

(7.45)

and

$$
\sum_j f_{j,\tau\bar{\tau}} f_{j+1,\tau\bar{\tau}}^* = -|f_{1/2,\tau\bar{\tau}}|^2 + \sum_{j \geq 1/2} \text{Re}(f_{j,\tau\bar{\tau}} f_{j+1,\tau\bar{\tau}}^*) ,
$$

(7.46)

which indicates that the skew cross section for all scattering processes is zero,

$$
\sigma_{sk,\tau\tau} = 0 \ [\text{parity preserved}] .
$$

(7.47)

This regime is in fact achieved in the model of two scatterers whenever the spatial dependence is such that it is invariant under the reflection around $x$-axis, as is noticed in Fig. 7.3. However lacking parity conservation, the conditions on the scattering amplitudes are reduced to those resulting from only time reversal and unitarity,

$$
f_{j,\tau\tau} = f_{-j,\tau\bar{\tau}}
$$

(7.48)

$$
f_{j,\tau\bar{\tau}} = -f_{-j,\tau\tau}
$$

$$
f_{j,\tau\tau} = -f_{-j,\tau\bar{\tau}} .
$$

These relations result in the valley-flip processes having zero skew cross sections,

$$
\sigma_{sk,\tau\bar{\tau}} = 0 ,
$$

(7.49)

while the valley-preserving processes are related by

$$
\sigma_{sk,\tau\tau} = -\sigma_{sk,\tau\bar{\tau}} \ [\text{no parity}] ,
$$

(7.50)

which indicates the splitting of valley currents in real space.

The non-vanishing skew cross section is associated with the appearance of transverse valley currents that are characterized by a valley Hall angle

$$
\Theta_{VH} = \frac{j_{yH}}{j_x} ;
$$

(7.51)
at zero temperature the valley Hall angle is given by \[46, 78\]

\[
\Theta_{VH} = \gamma_V = \frac{1}{2}(\gamma_K - \gamma_K'),
\] (7.52)

where \(\gamma_V\) is the valley skew parameter (skewness), and it is given by

\[
\gamma_V = \frac{\sum_{\tau'} \sigma_{sk,\tau'\tau}}{\sum_{\tau'} \sigma_{tr,\tau'\tau}}.
\] (7.53)

From the relations in Eq. 7.45 and 7.46, we notice that

\[
\sigma_{tr,\tau\tau} = \sigma_{tr,\bar{\tau}\bar{\tau}},
\] (7.54)

\[
\sigma_{tr,\tau\bar{\tau}} = \sigma_{tr,\bar{\tau}\tau},
\]

and consequently we have

\[
\gamma_K = -\gamma_K',
\] (7.55)

\[
\gamma_V = \gamma_K.
\]

This result suggests that for valley polarized fluxes, we will have the appearance of a Hall effect, and the corresponding accumulation of charge at sample edges, and Hall voltages.

In the two target problem in Fig 7.8a, the skew parameter becomes zero for configurations where parity is preserved, at \(\varepsilon_{01} = 0, \pm \pi/2, \pm \pi\), as expected from symmetry arguments. Moreover we notice that the skew parameter decreases as the distance between the scatterers increases and eventually vanishes for large distances, as the single scatterer limit is approximately restored. One should also notice that the sign of the skew parameter alternates every \(\pi/2\), and takes of course identical values for equivalent configurations.

The case is different in Fig. 7.8b, as the only parity preserving configuration is at \(\varepsilon_{01} = 0\), where the skew parameter vanishes. The arrangements of maximum skewness are present at \(\varepsilon_{01} = \pm \pi/2\), and the skew parameter changes sign around zero with a period of \(\pi\).
Figure 7.8: a) Valley skew parameter for a system of two scatterers with $a_1 = a_2 = 10 \text{ Å}$ and $V_1 = V_2 = 2$ eV located at $R_{12}/2 = d_{12}/2 + a_1$ from the global origin, for incoming electrons along the $x$-axis with energy $E = 1$ meV. (inset shows the scatter configuration). b) Valley skew parameter for a system of two scatterers with $a_1 = a_2 = 10 \text{ Å}$ and $V_1 = -V_2 = 2$ eV and located at $R_{12}/2 = d_{12}/2 + a_1$ from the global origin, for incoming electrons along the $x$-axis with an energy $E = 1$ meV. (inset shows the scatter configuration).

Notice that in the cases discussed above, if the scatterers were considered in the dilute limit, far away from one another, the scattering events would be independent and additive, resulting in no skewness in the system, as the total Hamiltonian will commute with the parity operator. This limit is evident for $d_{12} \gg 1$ in Fig. 7.8, with different decay lengths. Notice that, in these cases, parity breaking was solely arising from the spatial arrangement of the scatterers, and is the result of multiple scattering effects.

It should be emphasized that the skewness and consequently the valley Hall effect can result in systems even in the dilute limit, if the form of the interaction does not commute with the parity operator. As shown in Ch. 4, a system that results in a staggered potential, $s\alpha_3$, displays non-zero valley skewness.
From the discussion above, notice that valley filtering can be achieved in experimental setups in which the potential scatterers are closely distributed in a way that breaks parity, as shown in the schematic in Fig. 7.9. These realizations of close by potential scatterers can be achieved in systems where deposited adatoms form clusters that break parity, or in artificially tailored systems where the graphene sample is decorated with potential scatterers in such a way that parity breaking effects can be reflected through multiple scattering effects.

It should be noted that in systems of clusters of impurities, where the distance between clusters is large, the scattering of electrons from a cluster to the next are essentially independent, and the total skewness of the system maybe reduced from the single cluster picture, as the skewness gained by the scattering from a cluster can be inverted by the next cluster. This averaging of the skew parameter due to the randomness in clusters irregularities, suggests that skew scattering and valley filtering can be better achieved in experiments with a higher degree of control over the potential arrangements [43, 131, 132]. Similarly, in systems where parity can be broken in the single scatterer picture, due to the presence of impurities that locally enhance a perturbation that does not preserve parity even if it was symmetrically distributed in space, the appearance of valley filtering and the valley Hall effect via skew scattering will persist, even in the presence of randomly sized regions containing the interaction, as it was shown in [46].

Recent experiments have shown the appearance of the spin Hall effect in graphene [12]. In these samples, spin orbit interactions were enhanced through the deposition of Au and Cu adatoms, that attached to graphene through physisorption, which tend to form clusters. These clusters are irregular in shape, and can be close to each other, which may indicate that parity breaking effects have a contribution, through valley skewness, to the measured non local resistance. In addition, parity breaking effects reflected through multiple scattering effect, may also introduce perturbations that lead to a valley Hall
effect, due to the enhancement of a staggered perturbation. The presence of perturbations that lead to the formation of both spin and valley Hall effects, result in a non local resistance. The nature of the currents that accumulate on the edges of the samples are determined by a competition between interaction that cause spin or valley splitting.

In conclusion, we have studied the effects of parity breaking on the transport properties of graphene. These effects, in the case of multiple centrosymmetric scatterers, are reflected through multiple scattering effects, and lead to the formation of valley Hall effects, as the system of multiple scatterers that breaks parity acts as a valley filter. The experimental observation of a valley Hall effect (valley splitter) in systems of multiple potential scatterers, can be achieved in systems with adatoms that form clusters, if not dramatically reduced by shape irregularity averaging. However, systems where the location and distance of the potential scatterers is artificially controlled, or in which the deposited adatoms introduce perturbations that break parity at the single scatterer limit, are better candidates for the observation of the valley Hall effect. Finally, as parity breaking effects are reflected by the appearance of valley skewness and the consequent formation of the valley Hall effect, the non local resistance reported in decorated graphene
systems, may not be completely a result of spin skewness, as reported recently [12].
Consequently transport experiments will likely be needed to fully identify the nature of
the non local resistance of the non vanishing skewness in these or other systems, as
discussed in Ch. 5 [46].
8 Outlook and Perspectives

In this dissertation we have studied the effects of symmetry-breaking and spin-orbit interactions on electron dynamics in graphene. In Chapter 2, starting with a tight-binding model, we were able to obtain the effective low energy Dirac approximation that describes carriers in graphene, and determine the symmetries that govern the motion of these carriers. The scattering matrix method adopted in Chapter 3 allowed us to proceed and analyze the scattering of massless fermions in graphene systems with different degrees of complexity.

An important point in Chapter 4 was to realize that measurable transport quantities, in this case the transport to elastic time ratio at low energy or skew scattering, take unique values constrained by the symmetries that the system preserves. Realizing this point helped to answer the question that we had in mind since the beginning: how can we identify and quantify the effects of symmetry breaking and spin-orbit interactions in graphene via transport measurements? We have shown in Chapter 4 that the presence of impurities or deformations that lead to the reduction of symmetries in the graphene lattice can be detected and quantified through the deviation of the transport to elastic time ratio from its ideal value at low energies. Additionally we have shown that breaking effective time reversal in graphene systems leads to the appearance of skew scattering, and the consequent separation of electrons from different valleys in real space.

Similarly, in Chapter 5, we have shown that the presence of spin orbit interactions in graphene also lead to the the changes in the transport to elastic time ratio. However, the dependence of the deviation of this ratio in the presence of spin-orbit interactions as a function of carrier density is qualitatively different from the deviation produced by symmetry breaking effects, which allows one to extract both effects simultaneously from detailed measurements of this ratio. We have also shown that the presence of spin-orbit interactions in graphene leads to the appearance of skew scattering that leads to the
separation of electrons with different spins in space, and the appearance of the spin Hall effect. This effect can be reduced in the presence of symmetry breaking perturbations that break effective time reversal, as they lead to the formation of a competing valley Hall effect.

The effects of potential gated regions at high energies include the appearance of whispering gallery modes, which reflects the presence of long-lived quasi-bound states, as discussed in Chapter 4. Similarly, potential gated regions in graphene play the role of lenses with tunable indices in electron optics, and the presence of spin-orbit interactions makes these lenses birefringent. This leads to the doubling of caustics and cusps formed in circular potential regions, allowing the measurement of the interactions responsible for this doubling, as it was shown in Chapter 6.

In Chapter 7 we showed the effects of parity breaking in systems of multiple scatterers. We show that they are reflected through the appearance of skew scattering, which causes electrons from different valleys to separate in real space, and presents an attractive and simple proposal for the achievement of a valley splitter in graphene based electronics.

The important relation between symmetries and electronic and spin transport properties of Dirac-like systems drawn out in this dissertation, and the concepts and techniques learned along the way, have opened new doors for future research directions, some of which we will try to summarize below.

The global enhancement of symmetry breaking effects presents an interesting direction of research in graphene. It has been experimentally shown that the deposition of graphene on hexagonal boron nitride, $hBN$, leads to the formation of topological valley currents at the edges, due to the global modification of the dispersion relation of the combined system [128]. This proposal, suggests the possible realization of a spin Hall insulator in layered graphene systems, where topological spin currents are anticipated [9].
The proposed system of study is composed of a layer of graphene deposited on another two dimensional material, such as $\text{MoS}_2$, which is a host to electrons of opposite spins at different $K$ points in the valence band, due to the presence of an intrinsic spin-orbit interaction in this material. The analysis of the band structure formed in the combined system would allow an effective model describing the low energy electrons, and we suggest that by tuning a relative gate voltage on the two layers, one may be able to observe topological phase transitions in the system, and to find a range of tunable parameters on which the topological insulating phase can be achieved in the system.

The observation of a two dimensional material with a single Dirac cone (2D Dirac semimetal) has not been achieved yet. However, methods of intercalation present a promising opportunity. The proposal in [135] shows that the intercalation of a regular insulator between topological insulating layers provides a system that can be tuned into a 3D Dirac semi-metal. Following this proposal, and encouraged by the experimental observation of topological valley currents [128], we propose that a $\text{hBN}$-graphene-$\text{hBN}$ super-lattice presents a system where hybridization between different edge states can lead to the formation of a two dimensional Dirac semimetal. The proposed system can be tuned through the width of the $\text{hBN}$-graphene layers, and the width of the $\text{hBN}$ separating $\text{hBN}$-graphene hybrid.

Many questions, related to transport on the surface of topological insulators remain of great interest. It has been experimentally shown, that the surface states of a 3D topological insulator are not easily localized [136], and the effects of magnetic and strong Coulomb scatterers on the localization on these surface remain important open questions [137]. A similar approach to that followed in this dissertation can be adopted in order to get deeper insights on the expected phenomena in systems with magnetic impurities. A first step on the understanding of the effects of strong Coulomb scatters can be done through the analysis of the two body problem on the surface of these materials,
where the properties of these states can give a first insight on the modification of the
nature of the carriers on these materials due to strong Coulomb interaction.

Finally, we have seen how this honeycomb arrangement of carbon atoms known as
graphene can offer a rich ground for both theoretical and applied physics. We hope that
this modest theoretical contribution will give a clear guideline for both theorists and
experimentalists on the detection and quantification of the effects of perturbations in
graphene systems. We also wish that future researchers, theorists and experimentalists
alike, will find this proposal interesting enough to test, improve, and finally perfect.

    Our job in physics is to see things simply, to understand a great many
complicated phenomena in a unified way, in terms of a few simple
principles... (Steven Weinberg) [138].
REFERENCES


APPENDIX: LIST OF PUBLICATIONS AND PRESENTATIONS

A.1 List of Publications, Work in Progress and Presentations

A.1.1 Publications


A.1.2 Work in Progress

- **Mahmoud M. Asmar** and Sergio E. Ulloa, *Multiple Scattering of Dirac Fermions in Two Dimensions*.

A.2 PRESENTATIONS

Oral Presentations

• Multiple Scattering of Dirac Fermions in Two Dimensions. **Mahmoud M. Asmar** and Sergio E. Ulloa, APS March meeting, Denver, Colorado, USA, March 2014.

• Inter-Valley Scattering and Spin Transport in Graphene. **Mahmoud M. Asmar** and Sergio E. Ulloa, APS March meeting, Denver, Colorado, USA, March 2014.

• Effects of Spin Orbit Interactions on Electronic Transport in Graphene. **Mahmoud M. Asmar** and Sergio E. Ulloa, Helmholtz Zentrum Berlin, Germany, June 2013.

• Spin Orbit Interactions and Isotropic Transport in Graphene. **Mahmoud M. Asmar** and Sergio E. Ulloa, Dahlem Center for Complex Quantum Systems and Fachbereich Physik, Freie Universitat Berlin, Germany, June 2013.


• Probing Spin Orbit Interaction in Single Layer Graphene Via Electronic Transport. **Mahmoud M. Asmar** and Sergio E. Ulloa, APS March meeting, Baltimore, Maryland, USA, March 2013.

• Rashba Spin Orbit Interaction and Birefringent Electron Optics in Graphene. **Mahmoud M. Asmar** and Sergio E. Ulloa, APS March meeting, Baltimore, Maryland, USA, March 2013.

• Probing Spin Orbit Interactions Via Electronic Transport in Graphene. **Mahmoud M. Asmar** and Sergio E. Ulloa, Physics department colloquium at the Federal University of São Carlos, São Carlos, São Paulo, Brazil, December 2012.

• Effects of Spin Orbit Interactions on Resonant Scatters in Graphene Systems. **Mahmoud M. Asmar** and Sergio E. Ulloa, APS March meeting, Boston, Massachusetts, USA, March 2012.

• *Electric and Spin Transport Properties of Graphene.* **Mahmoud M. Asmar** and Sergio E. Ulloa, Physics department colloquium at the National University of Colombia, Bogotá, Colombia, July 2011.

• *Spin Dependent Scattering from Gated Potential Obstacles in Graphene Systems.* **Mahmoud M. Asmar** and Sergio E. Ulloa, APS March meeting, Dallas, Texas, USA, March 2011.

**Posters**


• *Spin Dependent Scattering in Graphene Systems.* **Mahmoud M. Asmar** and Sergio E. Ulloa, Graphene Week, Chemnitz, Germany 2-7 June 2013.
