



Electronic Properties of Two-dimensional Carbon Systems

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A thesis submitted to the Faculty of Science, University of the Witwatersrand,

in fulfilment of the requirements for the degree of Master of Science

School of Physics

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Johannesburg.

15 May 2012

Abstract

Properties of graphene-based nanoelectronic devices are found to be limited by disorder, e.g., vacancies, impurities and ripples on the surface. We investigate the specific effect of defects concentration as well as the structural modulation (ripples) on the electronic properties of layers of graphene-based electronic devices. We show the promise of a possible route for improvement of the current-voltage characteristics by incorporating nitrogen atoms in the defective graphene (which has limited device applications). In this work, we develop the tight-binding model of two-dimensional (2D) carbon and use the recursive Green's function method to study the effect of defects concentration as well as periodic structural disorder (ripples) where it has already been studied using the Dirac Hamiltonian.

The combined effect of vacancies and ripples on the electronic transport of graphene devices was studied. The presence of vacancies results in quasi-localized states at the Fermi energy. This is also found to be common in the presence of ripples, but in that case they are Landau levels originating from the gauge field induced by the ripples. In contrast, resonant states emerge when charged impurities are substituted. The density of these resonances was found to be tunable by controlling the ratio between the impurity-carbon coupling to impurity on-site potential as well as the concentration.

With regard to the mesoscopic phenomena, the system gains zero conductance due to the opening of an energy gap when the ripples as well as vacancies are present. In particular, the transport becomes diffusive rather than ballistic in the case of ripples, which has already been found previously within the Dirac Hamiltonian approach. On the other hand, the impurity enhances the transport properties due to augmentation of the resonant states in the vicinity of the Fermi level. Moreover, the increase of the sample-lead coupling was found to broaden the levels and increase the current by over one order of magnitude. The study shows the possibility of tuning the electronic transport of 2D carbon systems by controlling the structural and topological defects, which can be extended toward the understanding of experimental observations such as enhanced transport properties in 2D graphitic carbon films incorporated with nitrogen.

Declaration

I, the undersigned, declare that this dissertation is my own, unaided work. It is being submitted for the Degree of Master of Science at the University of the Witwatersrand, Johannesburg. It has not been submitted before for any degree or examination at any other University.

A handwritten signature in black ink, appearing to read 'Faris', with a stylized flourish underneath.

Faris Siedahmed Mohammed, 15 May 2012

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1. Introduction

The exceptional experimental breakthrough by the Manchester group in 2004 led to the isolation of the first single layer of the well-known graphite, also known as graphene [1]. The isolated material has shown extraordinary and novel properties due to its unique electronic structure, which has motivated extensive studies to explore the physics behind those properties. The physics of this two-dimensional material is of great importance since it represents the basic building unit for most of the carbon-based materials such as nanotubes, fullerenes and graphite. Thus understanding the properties of graphene will contribute to the understanding of the other materials.

Furthermore, the presence of defects in the two-dimensional material were found to be unavoidable due to the exposure of its surface, and they were found to be crucial in modifying its electronic properties. For example the understanding of the properties of materials such as nitrogen-doped (or equivalently boron-doped) graphene, and amorphous carbon films consisting of sp^2 -clusters in a theoretical basis is of great importance. In particular, nitrogen-doped graphene has been proven to enhance the transport properties [2], but it has not yet been fully revealed from theoretical studies. Therefore, we adapt an approach where we start off with the graphene tight-binding model aiming to understand some of the transport characteristics.

In chapter (2) the properties of graphene are reviewed as well as the development of a tight-binding study of carbon based materials. Chapter (3) is dedicated for the explanation of the Green's function and the recursive Green's function technique, in addition to that, the method used in this study is described. The results on the electronic properties of defected two dimensional carbon are discussed in chapter (4) while the electronic transport is reported in chapter (5).

Finally, a conclusion is presented in chapter (6) which summarizes the important results such as the enhancement of the conductance due to charged impurities, and the increase in the current originating from the broadening of the states.

2. The Electronic Properties of Graphene

Carbon is a very interesting element due to its exceptional physical as well as chemical properties. The location of carbon at the head of the fourth group in the periodic table makes it a unique element. In general, the fourth group elements are neither metals nor insulators, however, carbon is chemically active [3]. In terms of electronic structure, the carbon atom has six electrons distributed as $1s^2$, $2s^2$, and $2p^2$ [4, 5]. These atomic orbitals can hybridize in different forms, for instance, they can hybridize in the form sp^1 , sp^2 and sp^3 . Consequently, carbon can be found in many different stable forms. For example, carbon is the main element in all organic compounds, in all their variety. Moreover, carbon can form covalent bonds and lead to the formation of one of the strongest bonds in nature [3, 5].

The richness of carbon comes from its electronic structure. For the valence shell, $2s^2$, and $2p^2$, four electrons are available to form bonds, while the core electrons, $1s^2$, are not available for any chemical activity. If one considers the low energy configuration of the valence electrons, $2s^2$, $2p_x^1$ and $2p_y^1$, it is noticed that the $2p_z$ orbital is empty. This allows carbon to maximize the number of bonds by forming excited states, resulting in the formation of $2s^1$, $2p_x^1$, $2p_y^1$ and $2p_z^1$ orbitals. Carbon is therefore capable of forming four bonds. To understand the hybridization of carbon atoms, let us consider the compound in fig. (2.1(a)). The carbon atom is surrounded by four hydrogen atoms in this case, meaning that all orbitals have to get mixed in order to form one unpaired electron in each of the four orbitals, so that each hydrogen group donates one electron to the electron pair. However, in this case the s orbital as well as three p orbitals have contributed to the formation of the hybrid orbital known as sp^3 . In terms of geometry, the orbitals arrange themselves in three dimensions such that the repulsive force between them is minimized. The s orbital is spherically symmetric, while the p orbitals have three components, one along each axis (x,y and z). It has two lobes [4], one falls in the positive direction of the axis and the other in the negative one, thus in the case of the sp^3 hybrid, they form a tetrahedral geometry with an angle 109.5° between each orbital.

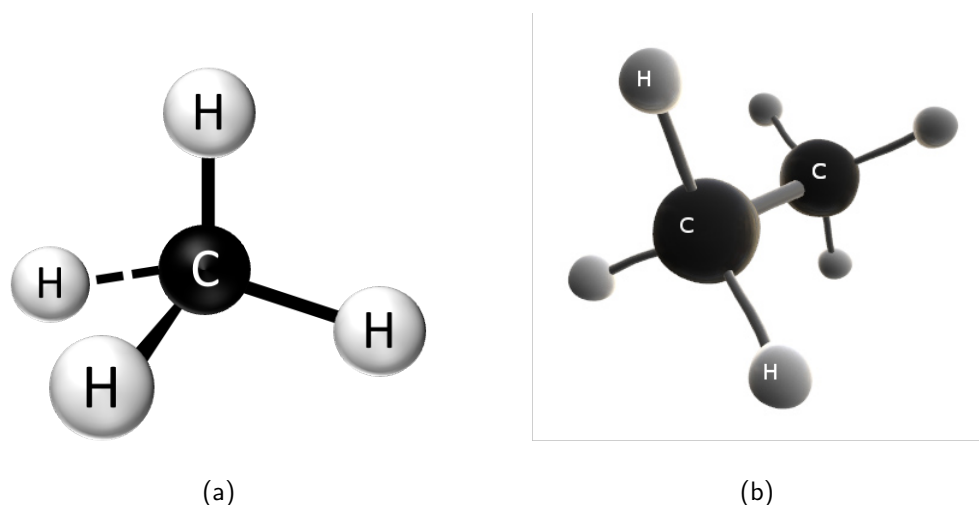


Figure 2.1: (a) The carbon atom in the molecule of methane is the one in the middle (black), while hydrogen atoms are the white ones. The orbitals between the carbon atom and the hydrogen are sp^3 -hybridized, with the geometry of tetrahedral shapes [6]. (b) The molecule of ethane, the carbon atoms are sp^2 -hybridized as indicated in the text. The bond between the two carbon atoms is σ -type one, while the p_z orbital is perpendicular to the plane of the molecule, forming a π -bond (not shown here) [7].

Another example of sp^2 carbon hybridization is ethane. In analogy to the previous example, this time only s , p_x and p_y orbitals get mixed. The p_z orbital has an electron that remains unmixed with the other orbitals, resulting in the formation of a sp^2 hybrid (one s and two p orbitals are contributing). Geometrically, the orbitals arrange themselves to minimize the electric repulsion, forming a trigonal planar geometry with an angle of 120° between the orbitals which lie in the plane, while the p_z orbital remains perpendicular to the plane. Now when sp^2 -hybridized carbon atoms are bonded to each other, the sp^2 orbitals overlap forming the so-called σ bond which is saturated [3, 8], shown in fig. (2.1(b)), the p_z orbitals overlap side by side and form π bond.

The sp^2 hybridization of carbon atoms gives rise to the lattice geometry as well as the structural flexibility and the optical properties [8]. In terms of electronic structure, the saturated σ bond formed by the overlap of the sp^2 hybrid forms a deep valence band that does not contribute to the electronic properties. The π bond is formed when the half-filled p_z orbitals bind covalently. Most of the electronic properties of graphene, which will be discussed in the following section, are described by these electrons [9, 5].

2.1 Electrons in Graphene

Although it was argued that the presence of truly two dimensional (2D) layers of graphene would not be possible since the system would be thermodynamically unstable [5, 10], the breakthrough achieved by the Manchester group [1] opened the door for an intensive study of the new material. The importance of studying graphene emerges from the fact that it forms the basic building block for many carbon-based materials such as the three-dimensional graphite (see fig. (2.2(b))) which is formed by stacking of graphene layers. The one-dimensional nanotubes [4] which are formed by rolling the graphene along a certain direction, and fullerenes [11], which are considered to be zero-dimensional materials, are formed by introducing pentagons, which in turn produce positive curvatures on the surface. Thus understanding the properties of graphene will contribute to the study of several carbon-based materials.

Before proceeding, one has to understand the geometry of the graphene lattice. The graphene unit cell is bi-atomic since it contains two non-equivalent sublattices A (white) and B (coloured) as shown in fig. (2.3), with lattice separation $a_o = 1.42 \text{ \AA}$. The choice of the bi-atomic unit cell arises from the honeycomb lattice which does not form a Bravais lattice, i.e., one cannot build the lattice by considering one atom as basis, thus by considering the basis to have two atoms the lattice reduces to a hexagonal lattice with unit vectors $\hat{a}_1$ and $\hat{a}_2$ as shown in the left panel of fig. (2.3). Therefore, the Brillouin zone, BZ, in the reciprocal space has the geometry shown in the right panel of fig. (2.3) with four high symmetry points Γ , M , K and K' , where K and K' are non-equivalent to each other [5].

In general, half-filled bands play a fundamental role in the physics of strongly correlated systems, such as transition metal oxides. The reason behind this is that the electrons in half-filled bands are tightly bound and they have large Coulomb energies which lead to collective effects [14]. P. R. Wallace was the first to study the band structure of graphene [15] and showed its semi-metallic behaviour. Although nobody had thought about graphene particularly at that time, Wallace's realization helped him in understanding the properties of graphite, which was widely used in nuclear reactors as a moderator. Tremendous progress was made by McClure in 1957 [16], Slonczewski and Weiss in 1958 [17] which resulted in the model known as the Slonczewski-Weiss-McClure (SWM) band structure of graphite. The SWM model was successful in describing

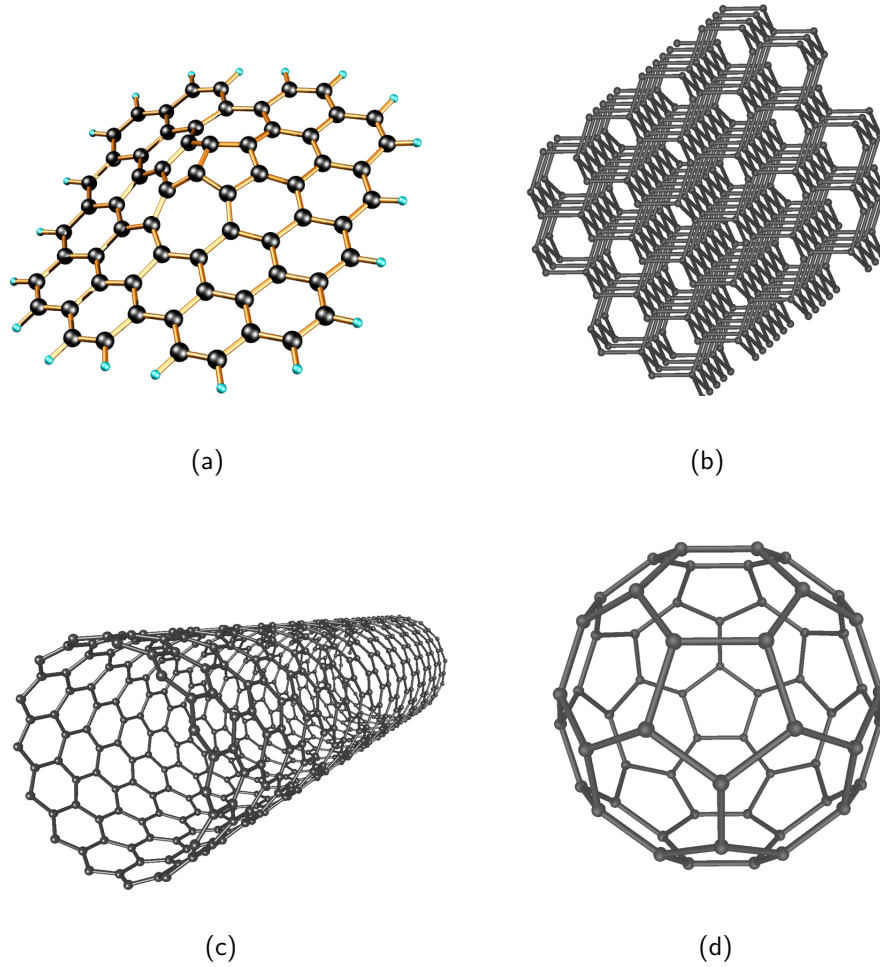


Figure 2.2: Some of the different geometries formed from graphene. (a) A single graphene sheet [12], in (b) a few stacks of graphene are shown forming the well-known graphite. (c) and (d) show the structure of a single walled nanotube and a fullerene respectively [13].

experimental data [18, 19, 20, 21, 22, 23]. The model was modified recently by incorporating the many body effect of the van der Waals-like interaction [24], which is important only when studying multi-layered graphene.

The study of graphene using the tight-binding has revealed interesting properties in addition to the semi-metallic behaviour. The dispersion relation shows linearity around the non-equivalent points, which means that the low energy excitations (electrons and holes) behave as massless chiral Dirac fermions [25]. Hence, the non-equivalent points are termed Dirac points. Moreover, the situation is also similar to that of massless Dirac fermions presented in quantum electrodynamics (QED)

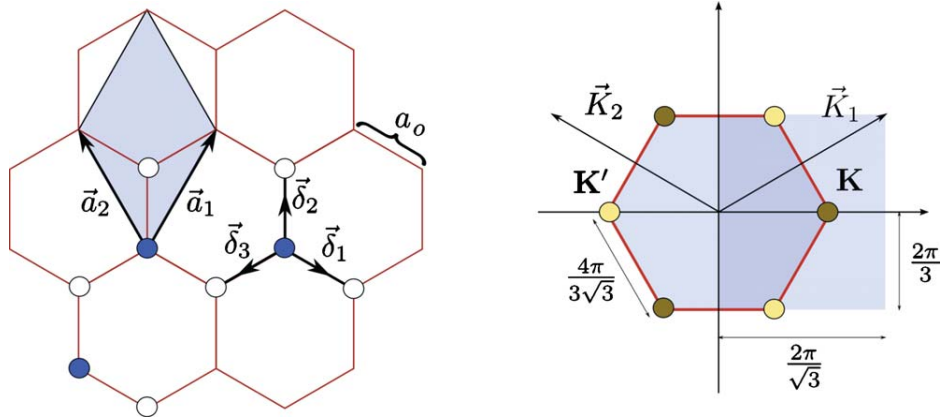


Figure 2.3: The left panel shows the graphene lattice in real space. Each primitive unit cell has two inequivalent sublattices A and B, the white circles correspond to the sublattice A while the coloured one corresponds to sublattice B. The right panel is a representation of the first Brillouin zone 1BZ in the reciprocal space. The 1BZ has six corners with two inequivalent points labelled K and K' . These two points are also given the term Dirac points. Taken from ref. [8].

except that the electrons in graphene have a velocity v_F which is 300 times smaller than the speed of light [26, 27, 28].

Interesting behaviour is observed when graphene is subjected to a magnetic field [29, 30], for example, phenomena such as the experimentally observed anomalous integer quantum Hall effect (IQHE) [31]. Moreover, the IQHE can be observed at room temperature since the cyclotron energy is high due to the relativistic speed at which the electrons propagate [32].

Another fingerprint of Dirac fermions is their ability to transmit through a potential confinement with a probability equal to one, which is known as the Klein paradox [28], hence they become insensitive to an external electrostatic potential. Moreover, it leads to the appearance of the Zitterbewegung phenomenon [33, 34, 35]. Therefore, the study of graphene-based systems under the application of an external electrostatic potential is vital since such potentials can be formed by any kind of disorder in the material, where it is noted that the presence of such disorder is unavoidable in all solids and it influences the electronic properties, as will be explained in the following section.

On the microscopic level, graphene has shown unusual properties due to the boundary conditions that the wave function is restricted to at the edges [36, 37, 30, 38]. Considering the edges

in the sample shown in fig. (2.4), one can see that graphene can have the edges along the y-axis with dangling atoms, while the edge along the x-axis is called the armchair arrangement. Another arrangement can be achieved by moving the sites labelled A_1, A_5, A_9 and A_{13} to the end after sites B_4, B_8, B_{12} and B_{16} , and it is known as zigzag edges. These names are just visualizations of their geometry. However, the properties of electronic transport along a certain axis is drastically different from the other direction. For example, at zigzag edges, surface states as well as resonances are created which are not found in the case of the armchair edges [5]. Moreover, quantities such as the conductance in graphene samples are found to be highly sensitive to the boundary conditions satisfied by the wave function. As an example, when a sample is coupled to conducting leads, the boundary conditions have to be chosen in such a way that the transport is limited to one direction. In other words, if the leads are attached to the edge along the y-axis (the lead on the left hand side is connected to the source while the one on the right is connected to the drain), that means the electrons have to flow from the source along the x-axis to reach the other end of the sample (drain). Thus the transport along the y-axis is forbidden, which is incorporated in terms of the boundary conditions as reflecting boundary conditions or the hard wall boundary conditions. Furthermore, superconductivity effects, such as supercurrent flow and Andreev processes characteristic of the superconducting proximity effect, can show up when superconducting contacts are coupled to a graphene sample [39].

Beside all the features mentioned previously, graphene has a high crystalline quality, high mobility [40], and tunable electronic properties under the application of gate voltage or by considering multilayer structures [1]. Moreover, it shows both spin and valley degrees of freedom, which allows for the manufacture of spintronic [41, 42] as well as valleytronic devices [43]. So from the technological point of view, graphene is a promising candidate for the backbone of future electronic devices.

2.2 Defects in Graphene

The defects in real solids have different forms and they vary from vacancies (due to the removal of ions), impurities (presence of extra charged ions) and atomic dislocations. The vacancies as

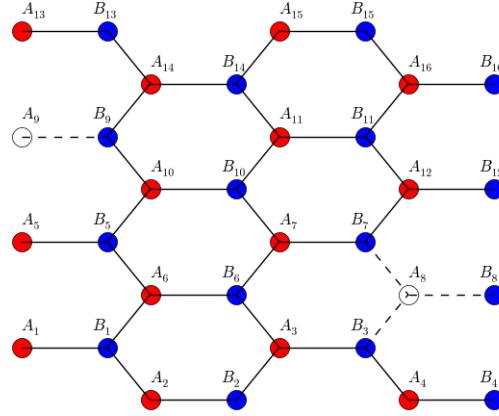


Figure 2.4: A lattice of 16 primitive unit cells is depicted. Sublattice A is the circles with red colour while the blue circles represent the sublattice B. The white circles represent the defects in the cell as will be explained in the following chapter.

well as impurities are responsible for most of the observed electrical as well as optical properties, while the dislocation of atoms has a more prominent effect on the mechanical properties [44]. The focus will be on vacancies and impurities as they have a stronger influence on the electronic properties.

However, ideal graphene structures have been found in the so-called amorphous carbon films, a-C [45]. The properties of a-C have been investigated intensely, although its electronic structure has not been fully described. On the other hand, the incorporation of nitrogen in carbon films was found to enhance the electrical properties remarkably [46, 47]. Furthermore, the presence of nitrogen impurities in π -conjugated systems such as graphene and carbon nanotubes results in functionalization [48] as well as structural changes [49, 50]. More importantly, nitrogen-doped carbon provides more control over the electronic properties and influences the magnetic properties as well [51].

Given the impossibility of avoiding defects in solids, a theory by Hohenberg-Mermin-Wagner [52, 53] involving some simple calculations of the Gibbs free energy of a system, shows that as few defects as possible should be present in any solid in order to minimize the free energy. Moreover,

the interplay between the dimensionality of the system and the thermodynamic equilibrium has a very important role in forming surface defects, where the energy required to form one of those defects at the thermal equilibrium is proportional to the linear dimensions of the sample [44]. In the case of graphene, the surface exposure is another factor that gives rise to formation of defects. In addition to that the presence of phonons plays a similar role [54] in creating surface defects as well as topological defects such as edge states [55] and Stone-Wales type [56]. The latter type of defects is of great importance in sp^2 -bonded carbon materials since they result in many kinds of topological defects in all carbon nanostructures. In graphene, they were found to influence the electronic structure and consequently the electronic transport, see ref. [57] and the references therein.

The realisation of the importance of defects in graphene particularly and solids in general has led scientists to investigate the effect of defects, both experimentally and the theoretically. For instance, techniques such as irradiation were used in order to create artificial defects in samples of graphene [58, 59]. Intense theoretical studies were carried out by different groups around the world to model defects and develop a theoretical understanding of the experimental results (see [60] and the references therein). Appreciable progress has been made since the first isolation of this noble material.

However, in a previous work [60], situations where a carbon atom is removed, and a vacancy is created or a charged impurity is substituted were considered. Numerical calculations were performed using the tight-binding model [9, 5] and the recursive Green's function technique [61, 62] which are also employed in this work to study the electronic properties of defective 2D carbon systems. In the presence of vacancies, it was found that new states are formed at the Fermi level [63]. Analysis of the inverse participation ratio (IPR) has revealed that those states are localised at the Fermi level, while they are quasi-localised (centred about the vacant site) when the particle-hole symmetry is broken [60]. As a consequence, a gap opens near the Dirac points introducing the possibility of controlling the electronic properties using applied voltage.

From a theoretical point of view, wave functions with large amplitudes at zero eigenenergies, called zero modes, arise when considering the propagation of the wave in a medium with unusual topological defects, which are vacancies in this study. Such a situation shows up in different

fields of physics for example field theories (where applications in the chiral symmetry breaking in (1+1)-space-time QED have been shown), anti-phase boundaries in narrow-gap semiconductors, edge states in nano-graphite ribbon junctions and many other examples in many different fields as reported in ref. [5] and the references therein.

Furthermore, if one thinks of a simple 2D bipartite lattice ¹, then quantum particles hopping between the sites of the lattice with a link disorder can be influenced by the appearance of those zero modes, which is also known as the Dyson's stochastic model. Moreover, the presence of zero modes is linked to a theory in linear algebra as discussed in ref. [64, 60].

In the case of graphene, an analytical form for the wave function associated with zero eigenvalues was found [63], where the wave function decays as the electrons move away from the vacancy site. However, the position of the newly-created states is exactly at the Fermi level, which has a very interesting consequence in the topological sense; the states have to be localized at one lattice site. When the particle-hole symmetry is broken, two effects take place, the first one is broadening of the states created at the Fermi level, and the second one is shifting the peak position by an amount that is approximately equal to the value of the second nearest hopping energy [60] (usually given by the symbol t').

The second kind of defects, as mentioned previously, are impurities or charged particles. In fact boron as well as nitrogen are the common impurities in carbon allotropes. The difference between an impurity and a vacancy in terms of the tight-binding method is that, the vacancy does not couple to the nearest neighbours. On the other hand the impurity couples to its nearest neighbour [60, 50] with a coupling (hopping) energy which is different from the one between carbon sites due to the difference in the radii of the foreign atoms.

Another important feature of graphene is that it shares the properties of thin membranes [54] which are considered to be a third kind of defect [65, 66]. Curvatures in graphene are induced by many factors; for instance graphene layers are usually placed on a SiO₂ substrate [67, 68] which leads to observations of ripples through scanning tunnelling microscopy (STM) [69, 68]. Moreover, the ripples were also observed using transmission electron microscopy (TEM) [65] in a suspended

¹A bipartite lattice is a lattice that can be formed by merging two lattices together. Graphene as an example can be formed by merging two triangular lattices as shown in the left panel of fig. (2.3).

layer of graphene. With regard to the effect of the substrate, it was also reported that imaging graphene using a single electron transistor (SET) [70] showed electron-hole inhomogeneity limiting the transport. Such interpretation of this charge inhomogeneity is due to the remote effect of charged impurities on the substrate as suggested in ref. [71, 72], which is also considered as a key factor in effecting the transport properties of graphene. However, recent microscopic calculations showed that the curvature on the graphene surface may act as an additional source of the charge inhomogeneity. In addition to this, the problem of Dirac fermions moving on a curved surface is analogous to problems in quantum gravity [73].

More interestingly, soft membranes gain energy due to bending, which might come from suspension on a solvent [74, 54], but since graphene is an electronic membrane, extra energies have to be taken into account such as the elastic free energy that accounts for energies due to van der Waals forces, which may appear between the sample and the substrate as attractive or repulsive forces, and also the energy that may arise from a surface tension [75]. Therefore, all these properties make graphene the first electronic membrane to be attached to leads and characterized.

To understand the effect of the corrugation on the electronic structure of graphene, one can think of an ideal layer of graphene where sp^2 orbitals are aligned to the xy -plane, while p_z orbitals are perpendicular to this plane. Then, curvature introduced to the system spoils the ideal picture of the orthogonal orbitals locally. For instance, when considering the first ideal scenario, the sp^2 orbital is not hybridized with the p_z orbitals, but in the second case, one infers that p_z is no longer perpendicular to the sp^2 orbitals of the nearest p_z orbital, see fig. (2.5). Thus it is convenient to redefine the hopping integrals (energies); instead of having one constant value t for the hopping between all sites in the cell, it is replaced with a hopping energy $\tilde{t} = t + \delta t$ where δt is a correction that depends on the local curvature.

In terms of the Dirac Hamiltonian formalism, which is the approach followed in most previous works [75, 77, 76], the curvature induces local gauge fields [78] that have two components; one scalar called the electrochemical potential, and the other one called the vector potential. The gauge fields in carbon-based systems like carbon nanotubes lead to suppression of weak localization [79, 80] as well as anomalies in the density of states [81]. Details of the computational method of $\tilde{t}$ as well as the relation between Slater-Koster formalism (tight-binding formalism),

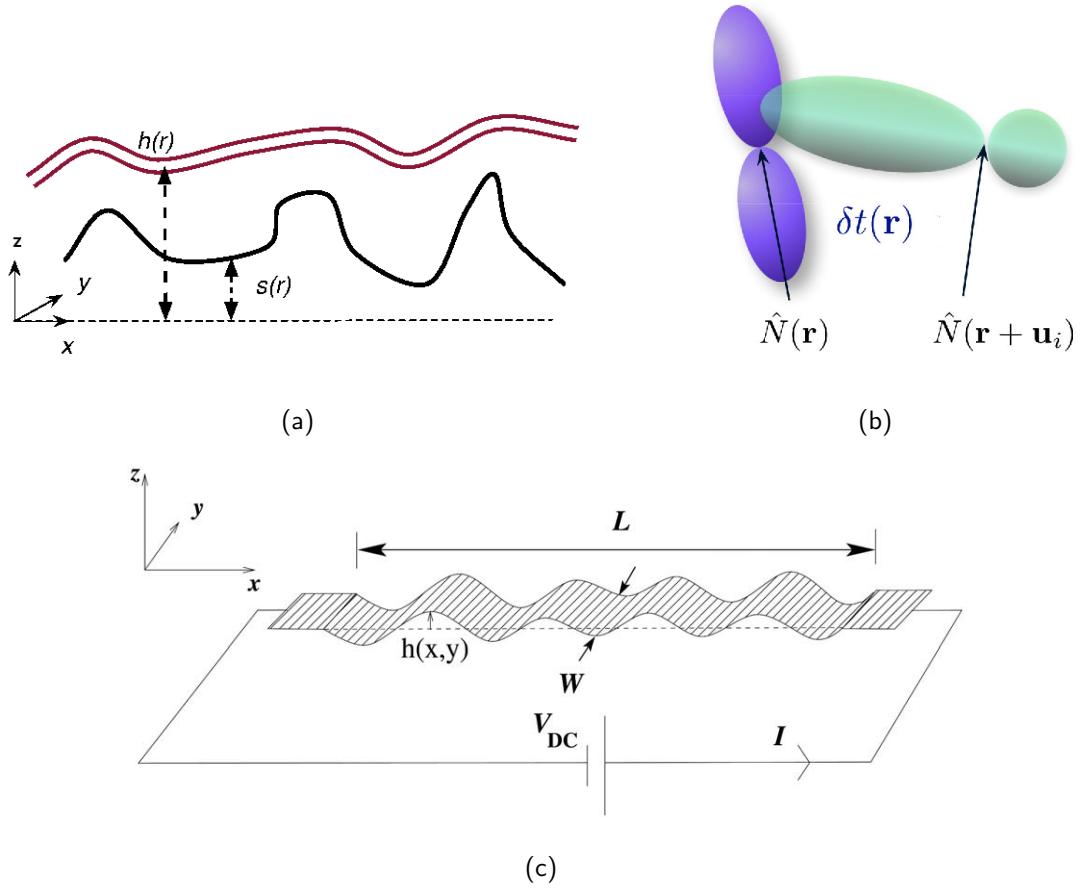


Figure 2.5: The figure shows a corrugated surface and two p_z orbitals that belong to a certain primitive unit cell, (a) the substrate (black solid line at the middle) is at height $s(r)$ measured relative to the reference axis showed with dashed line at the bottom, while the graphene layer is placed on top of the substrate (red solid line) and it at height $h(r)$ relative to the reference axis. (b) The re-overlap between the orbitals due to ripples on the surface which depends on the norms at the atoms positions $\hat{N}(r)$ and $\hat{N}(r + u_i)$, where r is the position of the atom to the left and u_i is the nearest neighbours vector. It results in a correction δt , taken from ref. [75]. (c) is a diagram that shown a corrugated graphene-based device [76].

and how gauge fields with two components arise are discussed in chapter (3).

Furthermore, another interesting feature in graphene is the vibrational modes (phonons). In graphene there are off-plane modes [54], and they are considered as another cause of bending, accounting for the lack of long range order which results in the formation of wrinkles as well as a crumpling effect.

In the following chapter the methodology used is explained, the Green's function, the graphene tight-binding and the computation of potential matrices are discussed.

3. Green Function and the Tight-binding Method

3.1 Green Function

Green's function [82] is a general function used to solve a system of inhomogeneous differential equation of the form

$$[z - H(r, r')] G(r, r'; E) = \delta(r - r'), \quad (3.1)$$

where $H(r, r')$ is an inhomogeneous operator, z is a complex variable that consists of a real component E and imaginary one η that tends to zero, $\delta(r - r')$ is the Dirac delta function. The function $G(r, r'; E)$ is Green's function that satisfies specific boundary conditions imposed on r as well as r' . In the situation we are handling, the differential operator is a tight-binding Hamiltonian that is discussed in the following section, however, the Hamiltonian H is a hermitian operator that results in an eigenvalue problem defined as

$$H |\Phi_n\rangle = \varepsilon_n |\Phi_n\rangle, \quad (3.2)$$

such that ε_n is the eigenvalue associated with the eigenstate $|\Phi_n\rangle$, which form a complete set of orthonormal eigenstate,

$$\begin{aligned} \langle \Phi_n | \Phi_{n'} \rangle &= \delta_{n,n'} \\ \sum_n |\Phi_n\rangle \langle \Phi_n| &= \mathbb{I}, \end{aligned} \quad (3.3)$$

and $\mathbb{I}$ is the identity operator. Then, the operator in eq. (3.1) reads

$$G(r, r'; E) = \lim_{\eta \rightarrow 0^+} \frac{1}{E - H(r, r') + i\eta}. \quad (3.4)$$

Applying the identity operator defined in eq. (3.3) from the left and the right of the operator defined above, then we obtain

$$G(r, r'; E) = \sum_n \frac{|\Phi_n\rangle \langle \Phi_n|}{E - \varepsilon_n + i\eta}, \quad (3.5)$$

where ε_n is the eigenvalue corresponding to state $|\Phi_n\rangle$. The expansion above is referred to as the eigenstates expansion. The sum runs over all the states whether they belong to discrete or continuous states. Moreover, the function $G(r, r'; E)$ is called the retarded Green's function. By changing the sign of η to $-\eta$, we obtain the advanced Green's function [82, 83]. If the retarded function as well as the advanced Green's function are relabelled so that the retarded becomes $G^r(r, r'; E)$ and the advanced $G^a(r, r'; E)$, then

$$G^a(r, r'; E) = [G^r(r, r'; E)]^\dagger, \quad (3.6)$$

where $\dagger$ stands for the hermitian conjugate. Furthermore, the operator defined in eq. (3.4) can be written in a different form using the identity

$$\lim_{\eta \rightarrow 0} \frac{1}{H^* \pm i\eta} = \mathbb{P} \frac{1}{H^*} \mp i\pi\delta(H^*), \quad (3.7)$$

where $\mathbb{P}$ is the principal value [84], H^* represents the terms $E - H$. In fact, the identity above is of a great importance due to its use in defining some of the physical properties such as the density of states (DOS) as it shall be explained. Proof of the identity can be found in ref. [82]

3.1.1 Green's Function in Perturbation Theory

Green's functions are widely used in mathematics as well as in different aspects of theoretical physics. One of the most important fields where Green's functions are implemented is a perturbative approach of the field theories, particularly the many particle physics [85, 83, 86, 87]. In real life problems the eigenvalue problem that corresponds to some Hamiltonian is not as simple as in eq. (3.2), usually it contains some potentials that make it impossible to find an analytical solution, i.e., the eigenstates that satisfy the equation involves the solution of a complicated system of a partial differential equation. Thus, a perturbative approach will be suitable for solving such equations.

Assume a system described by the Hamiltonian

$$H = H_0 + V, \quad (3.8)$$

where H_0 is the non-perturbed Hamiltonian, and V is the potential which is assumed to be small compared to H_0 . The eigenfunctions $|\Phi_0\rangle$ as well as the associated eigenenergies ε_0 that

correspond to the non-perturbed Hamiltonian are assumed to be known, then one can expand the Green's function as [82, 83]

$$\begin{aligned}
 G^r &= \frac{1}{E - H + i\eta} = \frac{1}{E - H_o - V + i\eta} \\
 &= \frac{1}{E - H_o + i\eta} \left(\frac{1}{1 - \frac{V}{E - H_o + i\eta}} \right) \\
 &= \frac{G_o}{1 - G_o V},
 \end{aligned} \tag{3.9}$$

where the term $(1 - G_o V)^{-1}$ can be expanded as a geometric series [84] since V is considered to be much smaller than H_o , thus

$$G_o = G_o + G_o V G_o + G_o V G_o V G_o + \dots \tag{3.10}$$

The terms in the expansion in eq. (3.10) are physically meaningful. In terms of Feynman diagrams, each term represents a specific interaction. Details of this method are found in ref. [86, 87, 88]. Following the approach of ref. [82] the T-matrix ($T(E)$) is defined as

$$T(E) = V + V G_o V + V G_o V G_o V + \dots, \tag{3.11}$$

now substitute $T(E)$ in eq. (3.10), then we obtain

$$G(E) = G_o(E) + G_o(E) T(E) G_o(E), \tag{3.12}$$

which is the key equation used throughout this work to find $G(E)$.

3.2 Tight-binding Formalism

Electrons in a solid can be described by the free electron model [44]. However, this model has some limitations due to the fact that the spacing distance between the atoms is comparable to the length of the wavefunction of the corresponding atoms, which indeed mean they have to overlap. Such overlap of the wavefunctions lead to correction in the potential felt by the electron. Thus, instead of completely free electrons, a system of interacting electrons has to be used; tight-binding method deals with such a situation where atoms are not completely isolated.

In terms of atomic orbitals [89], one notes that most of the transport, thermal, optical and mechanical properties are specified by the outer shell electrons. Moreover, they are more likely to overlap with electrons from other atoms, while inner orbitals are less likely to overlap. However, the tight-binding approximation provides a good tool to study electronic properties of partially filled d-shells of transition metals as well as insulators on the basis of the outer shell electrons [44].

In contradiction to the free electron point of view, tight-binding method assumes that the electron bound states are well localized, which requires the state to decay as one moves one lattice distance. The later condition is also necessary since one deals with a system that satisfies some kind of translation symmetry. In other words, the tight-binding Hamiltonian can be constructed by considering only atoms in the basic unit cell, and therefore the Bloch theorem applies.

In a Schrödinger-like form [44], tight-binding Hamiltonian H_{tb} is expressed as a sum of two parts,

$$H_{tb} = H_a + \Delta U \quad (3.13)$$

where H_a is a free electron Hamiltonian and ΔU is a potential that accounts for the overlap between the wavefunctions, and it has the same periodicity as the lattice. However, the state $\Psi_n(r)$ as well as $\Psi_n(r \pm R)$, where R is any Bravais lattice vector, has to be an eigenstate for both H_a and ΔU . Furthermore, it should yield N eigenenergies, where N is the number of the basis in the unit cell. It is worth noting here that ΔU vanishes when $\Psi_n(r)$ does not and vice versa.

Having the eigenstate $\Psi_n(r)$ calculated, then Bloch theorem requires

$$\Psi_n(r + R) = e^{ik \cdot R} \Psi_n(r) \quad (3.14)$$

and the total wavefunction $\Psi_{nk}(r)$ is expressed as a linear combination of all Bloch states,

$$\Psi_{nk}(r) = \sum_R e^{ik \cdot R} \Psi_n(r - R) \quad (3.15)$$

where k is a point in the reciprocal space that belongs to the first Brillouin zone, 1BZ. The values of k are usually specified through appropriate boundary conditions depending on the nature of the system. In our case, the Born-Von Karman boundary condition is used unless it is specified. The Born-Von Karman boundary condition assumes that the wavefunction is periodic [44]. In

other words, a one dimensional sample that has a length L can be constructed by translation of the unit cell along a certain direction N times, thus $L = Na$, where a is the lattice vector. Then the boundary conditions requires the wave to be periodic at the boundaries, so

$$\Psi_n(r) = \Psi_n(r + L) \quad (3.16)$$

$$= e^{ik \cdot Na} \Psi_n(r) \quad (3.17)$$

$$(3.18)$$

then the exponential factor has to be equal to one at the boundaries, then $k = \frac{n\pi}{N}$ where n is an integer that takes values between $-N$ and N , and all the values obtained for k fall in 1BZ.

The techniques to obtain the allowed values of k were in the focus of scientific research for a while due to its importance in the computational work, for example, some methods can be found in ref. [90, 91, 92]. In the calculations performed here, a grid generated by applying the approach described by Monkhorst and Pack in ref. [91] is used. To create the grid, assume that the translation vectors that describe a two-dimensional reciprocal lattice are $\hat{a}$ and $\hat{b}$, then an equally spaced mesh is generated using the relation

$$k = u_i \hat{a} + u_j \hat{b}, \quad (3.19)$$

where $u_{i(j)}$ is given by

$$u_i(j) = \frac{2i(j) - q_{i(j)} - 1}{2q_{i(j)}}, \quad (3.20)$$

where $q_{i(j)}$ is the number of k-points in the direction of $i(j)$, and $i(j)$ is an integer that takes discrete values between 1 and $q_{i(j)}$. The grid described in eq. (3.19) has $q_i \times q_j$ points and the points in the direction of a specific unit vector are obtained assuming periodic boundary conditions. For reflecting boundary conditions the k-vector has to be shifted by a factor of $\pm\pi\hat{a}(\hat{b})$, however, in the situation where reflecting boundary conditions are used, we added the factor so eq. (3.20) becomes

$$u_i(j) = \frac{2i(j) - q_{i(j)}}{2q_{i(j)}}, \quad (3.21)$$

which is used in the description of the transport in a direction perpendicular to the direction of the electron motion. It is worth noting that when the boundaries are assumed to be hard (reflecting), the weight factor assigned to each point in the grid is changed due to the shift. The

weight of these points originates from the symmetry operations at each point, which then leads to elimination of some of the points and facilitates the use of the irreducible Brillouin zone to perform integrals. However, to overcome this in the shifted grid, each point is considered to have weight equal to one, and no symmetry operations are considered. Hence, all the points in the Brillouin zone are used to perform the integral instead of using special points with weight factors.

3.3 Second Quantization

The equation (3.13) is a many body problem which is not easy to solve. Moreover, it is computationally expensive. Thus, reformulation of the equation (3.13) might solve part of the difficulty and reduce the computational cost.

Furthermore, the construction of a many-body wavefunction requires accounting for the nature of the described particles. If they form a system of fermions, that means the wavefunction has to be antisymmetric and the particles are subjected to Pauli exclusion principle, while a system of bosons has to have a symmetric wavefunction. However, quantum states are represented in the Hilbert space. For dealing with particles such as electrons (fermions), the state can only accommodate one particle. Thus to expand the Hilbert space to accommodate more states [93], the tensor is used,

$$H^N = H \otimes H \otimes \dots \otimes H. \quad (3.22)$$

For instance, if a particles a and b are located in states $|1\rangle$ and $|2\rangle$ respectively, the state that contains both particles, $|\Psi\rangle$ can be expressed as a linear combination of the product [94]

$$|\Psi\rangle = \alpha |1\rangle \otimes |2\rangle \pm \beta |2\rangle \otimes |1\rangle, \quad (3.23)$$

where the first term represents the probability of finding the particle a in state $|1\rangle$ and b in $|2\rangle$, while the second term represents the probability of finding a in state $|2\rangle$ and b in $|1\rangle$. The sign between the two terms specifies the nature of the particles; positive sign means the wavefunction is symmetric and the described particles are bosons, the negative sign means that the particles are fermions and thus the wavefunction is antisymmetric. Moreover, for a system of a large number

of fermions, the wavefunction can be put in the Slater determinant [93],

$$\Psi = \frac{1}{\sqrt{N!}} \det \begin{bmatrix} \Phi_{k1}(r_1) & \Phi_{k1}(r_2) & \cdots & \Phi_{k1}(r_N) \\ \vdots & \vdots & \ddots & \vdots \\ \Phi_{kN}(r_1) & \Phi_{kN}(r_2) & \cdots & \Phi_{kN}(r_N) \end{bmatrix} \quad (3.24)$$

Another formalism which can be used instead of the Slater determinant is the occupation number formalism [86, 94]. In this representation, the wavefunction is replaced by one ket that contains all possible states, such that

$$|\Psi\rangle_{l,m} = |0, 0, \dots, 1, \dots, 0, 1, 0, 0\rangle, \quad (3.25)$$

where the first 1 in the ket on the right hand side corresponds to the state l while the second 1 corresponds to the state m . The 0's indicate that there is no particle in the state, and the 1's indicate that the states are occupied with one particle, which is the maximum number allowed in the case of fermions. When the ket describes bosons, there might exist numbers greater than one since it is allowed to have more than one particle in the state. But indeed the number of particles in the states does not have to exceed the total number of particles in the system.

Now, to accommodate the states with particles (create particles) or evacuate (annihilate) particles, the vacuum state $|0\rangle$ has to be introduced, so

$$|0\rangle = |0, 0, \dots, 0\rangle \quad (3.26)$$

to create the state $|\Psi\rangle_{l,m}$ given in eq. (3.25) the creation operators $a_l^\dagger$ and $a_m^\dagger$ are used such that $a_l^\dagger$ will create a fermionic state l , and $a_m^\dagger$ will do the same thing and produce the state m ,

$$a_l^\dagger |0\rangle = |0, 0, \dots, 1, \dots, 0, 0, 0\rangle \quad (3.27)$$

$$a_l^\dagger a_m^\dagger |0\rangle = |0, 0, \dots, 1, \dots, 0, 1, 0, 0\rangle \quad (3.28)$$

$$= |\Psi\rangle_{l,m}. \quad (3.29)$$

But due to the antisymmetric nature of fermionic states, the product $a_l^\dagger a_m^\dagger$ has to be equal to $-a_m^\dagger a_l^\dagger$, thus

$$(a_l^\dagger a_m^\dagger + a_m^\dagger a_l^\dagger) |0\rangle = 0 \quad (3.30)$$

so $(a_l^\dagger a_m^\dagger + a_m^\dagger a_l^\dagger) = 0$ which holds for the conjugate (annihilation) operators a_l and a_m . Moreover, the anti-commutation relation for fermionic states reads [94]

$$a_l^{(\dagger)} a_m^{(\dagger)} + a_m^{(\dagger)} a_l^{(\dagger)} = \{a_l^{(\dagger)}, a_m^{(\dagger)}\} \quad (3.31)$$

$$a_l a_m^\dagger + a_m^\dagger a_l = \{a_l, a_m^\dagger\} \quad (3.32)$$

$$= \delta_{lm} \quad (3.33)$$

For bosonic operators, $b_l^{(\dagger)}$ and $b_m^{(\dagger)}$, the commutation relations are

$$b_l^{(\dagger)} b_m^{(\dagger)} - b_m^{(\dagger)} b_l^{(\dagger)} = [b_l^{(\dagger)}, b_m^{(\dagger)}] = 0 \quad (3.34)$$

$$b_l b_m^\dagger + b_m^\dagger b_l = [b_l, b_m^\dagger] = \delta_{lm} \quad (3.35)$$

However, irrespective of the nature of the described particles, the states $|n_1, n_2, \dots\rangle$ has to form a complete set of orthonormal eigenstates, so

$$\langle \dots, n'_2, n'_1 | n_1, n_2, \dots \rangle = \delta_{n_1 n'_1} \delta_{n_2 n'_2} \dots \quad (3.36)$$

$$\sum_n |\dots, n'_2, n'_1\rangle \langle n_1, n_2, \dots| = \mathbb{I} \quad (3.37)$$

where n corresponds to all states and $\mathbb{I}$ is the identity matrix. Moreover, the states $\langle n_1, n_2, \dots|$ is constructed from the vacuum state $\langle 0|$ as

$$\langle n_1, n_2, \dots| = \frac{a_1^\dagger}{\sqrt{n_1!}} \frac{a_2^\dagger}{\sqrt{n_2!}} \dots \langle 0|. \quad (3.38)$$

3.3.1 Second Quantization of Observables

In the language of the second quantization, the Schrödinger wavefunction is raised to the level of an operator, and hence it is treated on the same footing as all other operators such as the momentum operator. To construct the quantum operators, say the kinetic energy operator T , usually it is constructed using [82, 85, 87, 94]

$$T = \int d^n x \Psi^*(x) \left[-\frac{\hbar^2}{2m} \nabla^2 \right] \Psi(x) \quad (3.39)$$

where n is the number of degrees of freedom. However, in the language of second quantization T becomes

$$\hat{T} = \int d^n x \hat{\Psi}^\dagger(x) \left[-\frac{\hbar^2}{2m} \nabla^2 \right] \hat{\Psi}(x). \quad (3.40)$$

Note that the field operators were derived by quantization of the single body wavefunction. Philosophically, the idea of the second quantization is not as clear as it seems, however, if one starts with the one particle wavefunction $|\Psi\rangle$, it can be expanded in any complete set of basis as

$$|\Psi\rangle = \sum_n |n\rangle \langle n | \Psi \rangle \quad (3.41)$$

$$= \sum_n |n\rangle \Psi_n \quad (3.42)$$

and then $|\Psi_n|^2 = P_n$ is the probability of finding the particle in state n . The Schrödinger equation then reads [85, 94]

$$i\hbar \partial_t |\Psi\rangle = \hat{H} |\Psi\rangle, \quad (3.43)$$

expanding in complete sets of basis m and n

$$i\hbar \dot{\Psi}_n = \sum_m \langle n | \hat{H} | m \rangle \Psi_m, \quad (3.44)$$

which also holds for the complex conjugate with a negative sign preceding the sum

$$i\hbar \dot{\Psi}_n^\dagger = - \sum_m \langle n | \hat{H} | m \rangle \Psi_m^\dagger, \quad (3.45)$$

where the dot above $|\Psi\rangle$ indicates the time derivative of the projected state. Then the expectation value of energy $\langle H \rangle$ is given by

$$\langle H \rangle = \sum_{m,n} \Psi_m^\dagger \Psi_n \langle n | \hat{H} | m \rangle. \quad (3.46)$$

Thus, it follows from the basic formalism of quantum mechanics

$$\dot{\Psi}_m = -\frac{i}{\hbar} \frac{\partial H}{\partial \Psi_m^\dagger} \quad (3.47)$$

$$i\hbar \dot{\Psi}_m^\dagger = -\frac{\partial H}{\partial \Psi_m}, \quad (3.48)$$

where equation (3.47) is equivalent to $\dot{q} = \frac{\partial H}{\partial p}$ in the Hamiltonian formalism of classical mechanics, and equation (3.48) is equivalent to $\dot{p} = -\frac{\partial H}{\partial q}$ where q and p are the position and momentum coordinates respectively. Eq. (3.47) and (3.48) lead to

$$\{\Psi_n, i\hbar\Psi_n^\dagger\} \equiv \{q_n, p_n\}, \quad (3.49)$$

the canonical coordinates. However, for second quantization, the wavefunction is replaced by with field operator so that

$$i\hbar [\hat{\Psi}_n, \hat{\Psi}_m^\dagger] = i\hbar\delta_{nm}, \quad (3.50)$$

then the Hamiltonian reads

$$\hat{H} = \sum_{n,m} \hat{\Psi}_n^\dagger \hat{\Psi}_m \langle n | \hat{H} | m \rangle. \quad (3.51)$$

It is noted that the Hamiltonian obtained previously is achieved using the single particle field operator. For many particles the sum running over n and m in equation (3.51) has to be expanded so it considers all states, and the anticommutation relation has to be used instead of commutation in the case of the fermions, see ref. [94] for detailed review.

Fields as creation-annihilation operators:

As in the quantum mechanical harmonic oscillator, the number operator $\hat{n}_i$ is given by

$$\hat{n}_i = a_i^\dagger a_i, \quad (3.52)$$

then the total number of particles $\hat{N}$ is given by the sum over all states i . For fields, the same relation in eq. (3.52) as well as all commutation relations are defined analogously to the harmonic oscillator,

$$\begin{aligned} [\hat{N}_i, \hat{\Psi}_i^{(\dagger)}] &= [\hat{n}_i, \hat{\Psi}_i^{(\dagger)}] \\ &= \mp \hat{\Psi}_i^{(\dagger)}, \end{aligned} \quad (3.53)$$

where the sign is negative when annihilation operator is used [94].

The many body wavefunction can be written in the form

$$\begin{aligned} |n_1, n_2, \dots, n_i\rangle &= \prod_i \frac{(\hat{\Psi}_i^\dagger)^{n_i}}{\sqrt{n_i!}} |0\rangle & \text{Bosons} \\ |n_1, n_2, \dots, n_i\rangle &= \prod_i (\hat{\Psi}_i^\dagger)^{n_i} |0\rangle & \text{Fermions} \end{aligned} \quad (3.54)$$

where eq. (3.54) is divided by the square root of $n_i!$ since the permutation of particles does not make any difference in the many-body boson wavefunction.

3.4 Graphene Tight-Binding

As mentioned in the previous section, the tight-binding approximation is the most suitable approach to describe the band structure of localized orbitals. In carbon materials the valence electrons are the π electrons, which are found to be localized. Moreover, the bands associated with those orbitals are mainly responsible for the transport phenomena since they fall at the vicinity of the Fermi level [4, 9, 15], thus modelling the problem in terms of the tight-binding method should yield deep insight into the electronic transport in such systems.

However, in order to construct the Hamiltonian, a set of basis has to be chosen which is $|n\rangle$ and $|m\rangle$ in eq. (3.51). However, two kinds of Bloch waves are usually used in the literature [44]; plane waves as well as atomic orbitals. In both cases the chosen waves have to satisfy the Bloch theorem,

$$T_{a_i} \Psi_o = e^{ik \cdot a_i} \Psi_o \quad (3.55)$$

where T_{a_i} is the lattice translation operator and a_i is the translation vector, and i specifies the dimensionality of the crystal, i.e., if the crystal is in one dimension then a_i has one component ($i = 1$) and so on. The most commonly used form of Ψ_o is a linear combination of plane waves. The usage of this kind of waves has the advantage of the ease of performing integrations and getting analytical forms. Also it has high numerical accuracy depending on the number of plane waves used. In spite of all those advantages, plane waves have limitations since they have large computational scale, and it is difficult to relate them to atomic orbitals [44].

On the other hand, atomic orbitals are based on the i -th atomic orbital in the unit cell, then the Bloch functions are written as

$$\Phi_i(\vec{k}, \vec{r}) = \frac{1}{\sqrt{N}} \sum_{\vec{R}} e^{i\vec{k} \cdot \vec{R}} \Phi_i(\vec{r} - \vec{R}) \quad (3.56)$$

where the index i varies from 1 to n , and n is the number of basis per unit cell. However, the advantage of using atomic orbitals is that, the number of basis compared to plane waves is small. Furthermore they can be used to derive formulae for many of the physical properties [95].

The use of atomic orbitals has also disadvantages due to the fact that they are assumed to be localized at the atom sites, so they do not describe the inter-atomic distance. The full wavefunction $\Psi_j(\vec{k}, \vec{r})$ is, however, constructed as a linear combination of $\Phi_i(\vec{k}, \vec{r})$,

$$\Psi_j(\vec{k}, \vec{r}) = \sum_{i=1}^n C_{ji}(\vec{k}) \Phi_i(\vec{k}, \vec{r}) \quad (3.57)$$

where the coefficients $C_{ji}(\vec{k})$ are to be determined using optimization methods [96], so that the energy of the system is minimized. However, details of the way the coefficients are specified is beyond the scope of this work.

The transport properties in graphene are specified by the π -electrons [5], thus the Hamiltonian will be constructed using π orbitals. To formulate the Hamiltonian, the unit cell has to be defined in two dimensions as shown in fig. (2.3). The graphene lattice in real space is represented by two basic vectors $\hat{a}_1$ and $\hat{a}_2$ as follow,

$$\begin{aligned} \hat{a}_1 &= \left(\frac{\sqrt{3}}{2}, \frac{1}{2} \right) a_0, \\ \hat{a}_2 &= \left(\frac{\sqrt{3}}{2}, -\frac{1}{2} \right) a_0, \end{aligned} \quad (3.58)$$

where a_0 is the interatomic separation between the carbon atoms in the unit cell. It is also termed the lattice constant, its value is 1.42 Å [4]. The Bravais lattice vectors $\hat{a}_1$ and $\hat{a}_2$ are written in such a way that the first element of the corresponding bracket is the x-component, while the second is the y-component.

The reciprocal lattice unit vectors $\hat{b}_1$ and $\hat{b}_2$ are constructed using the real space lattice vectors

using the relations [44],

$$\hat{b}_1 = 2\pi \frac{\hat{a}_2 \times \hat{a}_3}{\hat{a}_1 \cdot (\hat{a}_2 \times \hat{a}_3)},$$

$$\hat{b}_2 = 2\pi \frac{\hat{a}_3 \times \hat{a}_1}{\hat{a}_1 \cdot (\hat{a}_2 \times \hat{a}_3)},$$

where $\hat{a}_1 \cdot (\hat{a}_2 \times \hat{a}_3)$ (the denominator) is the volume of the unit cell in real space, and the vector $\hat{a}_3$ is taken to be perpendicular to both $\hat{a}_1$ and $\hat{a}_2$ with length equal to the unit. Thus,

$$\hat{b}_1 = \frac{2\pi}{a_0} \left(\frac{1}{\sqrt{3}}, 1 \right), \quad (3.59)$$

$$\hat{b}_2 = \frac{2\pi}{a_0} \left(\frac{1}{\sqrt{3}}, -1 \right). \quad (3.60)$$

As noted in chapter (2), the graphene unit cell is bi-atomic, i.e it has two atoms per unit lattice point, hence, the lattice point in the reciprocal space, k , can be specified in two ways. The first method assumes that one point per unit cell is considered as the center of Bloch functions and the basis, which have two p_z orbitals, are centred at each site of the unit cell, but they have the same phase factor k . The second way assumes that the Bloch functions are centred at the atom positions, and the phase is also specified by the atom position. Throughout this work only the first method is considered as explained in sec. (3.2).

Now, one proceeds and constructs the Hamiltonian using the atomic orbitals, as stated before, only the p_z orbitals are considered, so, the Hamiltonian that describes the bi-atomic unit cell is a 2×2 matrix. The element H_0^{11} corresponds to the local energy (on-site energy) at site A , while H_0^{22} is the on-site energy at sublattice B , and they are given by

$$H_0^{11(22)} = \left\langle \Phi_i^{A(B)} \left| \hat{H}_0 \right| \Phi_i^{A(B)} \right\rangle$$

$$= \varepsilon^{A(B)} \quad (3.61)$$

where the index i corresponds to Bloch state at site i . When the overlap between the wave-functions is extended to include second nearest neighbours coupling, the element $H_0^{11(22)}$ has to include extra terms that belong to coupling between site A (B) in the unit cell studied and site A (B) in second nearest unit cell, then the Hamiltonian yields,

$$H_0^{11(22)} = \left\langle \Phi_i^{A(B)} \left| \hat{H}_0 \right| \Phi_i^{A(B)} \right\rangle + \sum_j \left\langle \Phi_i^{A(B)} \left| \hat{H}_0 \right| \Phi_j^{A(B)} \right\rangle$$

$$= \varepsilon^{A(B)} + t' f(\vec{k}) \quad (3.62)$$

where the sum in the second term runs over all the Bloch states j localized at sites A (B) in the second nearest neighbours unit cells. The constant t' represents the hopping energy between those sites, and it is given by

$$t' = \left\langle \Phi_i^{A(B)} \left| \hat{H}_o \right| \Phi_i^{A'(B')} \right\rangle. \quad (3.63)$$

where the prime on A (B) indicates that the site belongs to second nearest neighbours. The function $f(\vec{k})$ contains information on the geometry of the lattice. However, as depicted in fig (2.3) the unit cells labelled j 's are identical to the one labelled i , thus one can construct any wavefunction locally at the cell labelled i , and then multiply the same wavefunction by a phase factor $e^{i\vec{k} \cdot \vec{R}}$ where $\vec{R}$ is the translation vector in real space between the cells i and j ¹. For instance, one can obtain the phase shifts $e^{i\vec{k} \cdot \vec{a}_1}$ and $e^{-i\vec{k} \cdot \vec{a}_1}$ for cells translated by vector a_1 and $-a_1$ respectively. However, following the same methodology, the function $f(\vec{k})$ is constructed as follow,

$$\begin{aligned} \sum_j \left\langle \Phi_i^{A(B)} \left| \hat{H}_o \right| \Phi_j^{A(B)} \right\rangle &= t' \sum_j e^{i\vec{k} \cdot \vec{R}_j} \\ &= 2t' \left(\cos(\vec{k} \cdot \vec{a}_1) + \cos(\vec{k} \cdot \vec{a}_2) + \cos(\vec{k} \cdot (\vec{a}_2 - \vec{a}_1)) \right) \end{aligned} \quad (3.64)$$

Following the same procedure, the off-diagonal elements $H_o^{12(21)}$ correspond to coupling site A (B) to site B (A). The matrix element is given by

$$\begin{aligned} H_o^{12} &= \left\langle \Phi_i^A \left| \hat{H}_o \right| \Phi_j^B \right\rangle \\ &= tg(\vec{k}) \end{aligned} \quad (3.65)$$

where the constant t represents the overlap energy between the orbitals at site A and site B that belongs to a nearest neighbour. In analogy to the relation in equation (3.63), t is given as

$$\begin{aligned} t &= \left\langle \Phi_i^A \left| \hat{H}_o \right| \Phi_i^{B'} \right\rangle, \\ &= \left\langle \Phi_i^B \left| \hat{H}_o \right| \Phi_i^{A'} \right\rangle, \end{aligned} \quad (3.66)$$

where the prime over B indicates that it belongs to nearest neighbours unit cell. The function $g(\vec{k})$ contains all the phase factors, and it is given by

$$g(\vec{k}) = \sum_j e^{i\vec{k} \cdot \vec{R}_j}, \quad (3.67)$$

¹It is actually Bloch theorem [44].

where the sum runs over j , all nearest neighbours vectors $\vec{R}_j$, and in analogy to what we did to obtain $f(\vec{k})$, $g(\vec{k})$ reads

$$g(\vec{k}) = 1 + e^{-i\vec{k} \cdot \vec{a}_1} + e^{-i\vec{k} \cdot \vec{a}_2}. \quad (3.68)$$

The element H_o^{21} is the complex conjugate of H_o^{12} . The conjugation arises from the geometry of the lattice since the element H_o^{21} corresponds to the coupling between B and A in a nearest neighbour cell, thus all the translation vectors are in opposite directions to those of the element H_o^{12} . The overlap energy is the same as defined in equation (3.66). However, the value of t varies from -2.5 to -3 eV [4, 5], where intermediate value is considered (-2.7 eV) for the calculations performed in this work. Moreover, the on-site energies, ε^A and ε^B , were taken to be zero for ideal graphene. Thus, combining all the matrix elements together, The Hamiltonian matrix yields

$$H_o = \begin{pmatrix} t'f(\vec{k}) & tg(\vec{k}) \\ tg^\dagger(\vec{k}) & t'f(\vec{k}) \end{pmatrix}. \quad (3.69)$$

To represent the matrix in equation (3.69), we simplify the notation such that the ket $|\Phi_i\rangle$ reads $|i\rangle$. Then, the path followed to construct the second-quantized tight-binding Hamiltonian can also be followed here,

$$H_o = \sum_i t' |i\rangle \langle i + \Delta| + \sum_i t |i\rangle \langle i + \delta| \quad (3.70)$$

where the first term is the second nearest neighbour coupling, and $i + \Delta$ indicates states localized at second nearest neighbours, while the second term represents the nearest neighbours coupling, and $i + \delta$ is states at nearest neighbours. The term that represents the on-site energy is dropped out since the energy is zero. Note that the sum in all these terms runs over all sublattices in the unit cell.

Now the Hamiltonian in equation (3.70) is rewritten in terms of creation-annihilation operators, so

$$H_o = t' \sum_i a_i^\dagger a_{i+\Delta} + b_i^\dagger b_{i+\Delta} + t \sum_i a_i^\dagger b_{i+\Delta} + H.c, \quad (3.71)$$

where $a_i^\dagger$ (a_i), $b_i^\dagger$ (b_i) are the creation (annihilation) operators at site A and B respectively. $H.c$ is the complex conjugate of the term $\sum_i a_i^\dagger b_{i+\Delta}$, which has to be taken into account since the second

term in the equation takes care of creating one electronic state at sublattice A and annihilate one at sublattice B , and hence, the complex conjugate considers the other case where states are created at sublattice B and destroyed at A .

The Hamiltonian in eq. (3.71) involves the second nearest neighbour coupling, which has certain consequences for the electronic structure of graphene. In the model developed by Wallace [15], the second nearest coupling was not taken into account, and the tight-binding Hamiltonian with first nearest neighbour coupling only is considered to be sufficient. However, the consideration of the second and third nearest neighbours coupling was found to be important for the case of the graphene. It has been shown that to compare the band structure obtained using first principle calculations with that achieved by the tight-binding approximation, it is necessary to include higher order coupling between nearest neighbour, see ref. [9] and the references therein. Moreover, modelling the nanotubes requires accounting for this kind of parametrization since the curvature of the surface results in overlap between the orbitals of second and third nearest neighbours [89, 4].

To incorporate the potential induced by defects, and to have freedom in controlling the percentage of those defects in the sample, the size of the unit cell to work with has to be increased. In other words, more electrons have to be considered in the model rather than just two electrons.

3.5 The Large unit Cell

The physics of any system is independent of the number of the basis chosen [44]. Hence, for this purpose, a large unit cell (LUC) that contains sixteen basic unit cell (bi-atomic unit cell) is chosen as depicted in fig. (2.4). The basic translation vectors, $\hat{a}_x$ and $\hat{a}_y$, that build up the lattice are defined as

$$\begin{aligned}\hat{a}_x &= (6, 0) a_0, \\ \hat{a}_y &= (0, 4\sqrt{3}) a_0.\end{aligned}\tag{3.72}$$

Note that the choice of those unit vectors is not unique, but the choice of vectors that lie along the x and y coordinates is more convenient in terms of computation. Now, the reciprocal space

unit vectors are constructed using equation (3.59),

$$\begin{aligned}\hat{b}_1 &= \left(\frac{1}{2\sqrt{3}}, 0 \right) \frac{\pi}{a_0}, \\ \hat{b}_2 &= \left(0, \frac{1}{3} \right) \frac{\pi}{a_0}.\end{aligned}\tag{3.73}$$

The Brillouin zone is the Wigner-Sietz cell [44] of the lattice defined by the vectors in equation (3.73). Thus the Brillouin zone is constructed by bisecting the vectors that connect a single point in the reciprocal lattice to its nearest neighbours, and then draw lines that pass through the bisections (planes in the case of 3D lattices), and normal to the reciprocal lattice vectors.

3.5.1 Tight-Binding of LUC

The tight-binding Hamiltonian that corresponds to the unit cell depicted in fig. (2.4), is constructed following the same methodology used in constructing the matrix in eq. (3.69). However, the Hilbert space is expanded so one can accommodate more electrons in the states. The Hamiltonian matrix of the LUC H_o has the form

$$H_o = \begin{pmatrix} \varepsilon_A & t_{AB} \\ t_{BA} & \varepsilon_B \end{pmatrix},\tag{3.74}$$

where the matrix H_o is 32×32 . The sub-matrices ε_A and ε_B are 16×16 matrices and they correspond to the on site energy as indicated in the subscript. The off-diagonal elements t_{AB} and t_{BA} in the matrix in eq (3.74) correspond to submatrices that contain the coupling constants between sublattices A-B and B-A respectively.

Constructing the matrix elements in eq (3.74) is not straightforward as in eq (3.69). However, in order to achieve this, we define an auxiliary matrix, L , that has dimensions 16×16 . The matrix is actually a mathematical view of the unit cell shown in fig. (2.4). Thus each basic unit cell is represented by an element in the matrix, and this element is a matrix that has the dimension 1×3 . To specify the position of this element in the matrix, we treat the unit cell as a matrix, the first row is the most bottom one, the second row in the second from bottom and so on. For the columns, the first column is the one at the left while the second one is the second from the left. Thus the position that correspond to the cell labelled 10 should fall in the interception of the third row and second column.

To construct the elements of the matrix L_1 , let us consider the basic unit cell with labels A_{10} and B_{10} , the site A_{10} is coupled to site B_5 along the vector $-\hat{a}_1$, site B_9 along the vector $-\hat{a}_2$ and site B_{10} along the vector $\delta_0 = a_0(1, 0)$. Now the element that correspond to the cell labelled 10 is given by the matrix $[5, 9, 10]$, where each number indicates the label of the site B coupled to A_{10} as explained. In the Hamiltonian matrix, the wave interference between those sites does not result in any phase factor since all atoms belong to the same large unit cell.

Moreover, we consider the element that corresponds to the cell labelled 5 which falls in the interception of the second row with the first column. The sublattice A_5 is coupled to sublattice B_8 along $-\hat{a}_1$, coupled to sublattice B_{12} along $-\hat{a}_2$ and site B_5 along the vector $\delta_0 = a_0(1, 0)$, and the element becomes $[8, 12, 5]$. But it is worth noting that the wave interference along the vectors $-\hat{a}_1$ and $-\hat{a}_2$ results in a phase factor $e^{-i\hat{k} \cdot \hat{a}_x}$ since the sublattices B_8 and B_{12} are shifted by one vector $-\hat{a}_x$. The auxiliary matrix that contains the second nearest neighbour labels, L_2 , is constructed in the same way L_1 was constructed.

3.6 Defect Potential

As stated before, the existence of ideal solids is not physical, thus the study of defects in solids is of a great importance since they influence the electronic properties of the solids. However, different defects have different effects, for instance, the presence of vacancies in a solid will act as scattering centres [5, 60]. In the following sections, the potentials induced by the defects are discussed.

3.6.1 Vacancies

If one site of the lattice at position r_i is substituted by a vacancy, this will result in a local potential of the form $V_i\delta(r - r_i)$, and hence the electron is not allowed to hop from and to the vacancy site. The potential induced by the vacancy V_v in a second quantized form reads

$$V_v = \sum_l V_A^l a_l^\dagger a_l + \sum_m V_B^m b_m^\dagger b_m, \quad (3.75)$$

where the sum runs over all sites l and m that have vacancies substituted. The potentials are labelled V_A^l and V_B^m to indicate that the vacancy is substituted in sublattice A and B respectively. However, in all the calculations performed in this work, only the situation where the vacancy is substituted in sublattice A , and the potential V_A^l is taken to be constant, thus the vacancy potential becomes

$$V_v = V_A \sum_l a_l^\dagger a_l. \quad (3.76)$$

3.6.2 Impurities

The case of the impurity is slightly different from the later case. The impurity is equivalent to substituting one sublattice or more with another atom, so in addition to the on-site energy, an electronic bond will couple the impurity to its nearest carbon atom, so the electrons are allowed to hop to and from the site where the impurity is substituted, but the value of the hopping energy differs from the one used for the carbon atoms. In the calculations done in this work, all impurities are substituted in sublattice A , which indeed means that the potential used in eq. (3.76) has to be modified by including terms that count for coupling the impurity to its nearest neighbours, so the impurity potential reads,

$$V_i = V_A \sum_l a_l^\dagger a_l + t_p \sum_l a_l^\dagger b_{l+\delta} + H.c, \quad (3.77)$$

where t_p is the carbon-impurity coupling, $H.c$ is the complex conjugate of the second term in the equation and it takes care of coupling the sublattice B to the impurity site, while the second term handles the coupling between the impurity and nearest neighbours of carbon atoms. The potential is different from the one used in ref. [60] since it contains on-site potential so it represents a more realistic picture of a situation where a foreign atom such as boron or nitrogen with local potential higher or deeper than the one used for carbon.

The effect of the on-site energy was investigated in ref. [60] where it was found that the spectral weight increases by increasing the local energy of the defect. On the other hand, the coupling energy between the nearest neighbours is found to have a prominent effect in the vicinity of the Fermi energy, the higher the coupling energy, the closer the states to $E = 0$ eV.

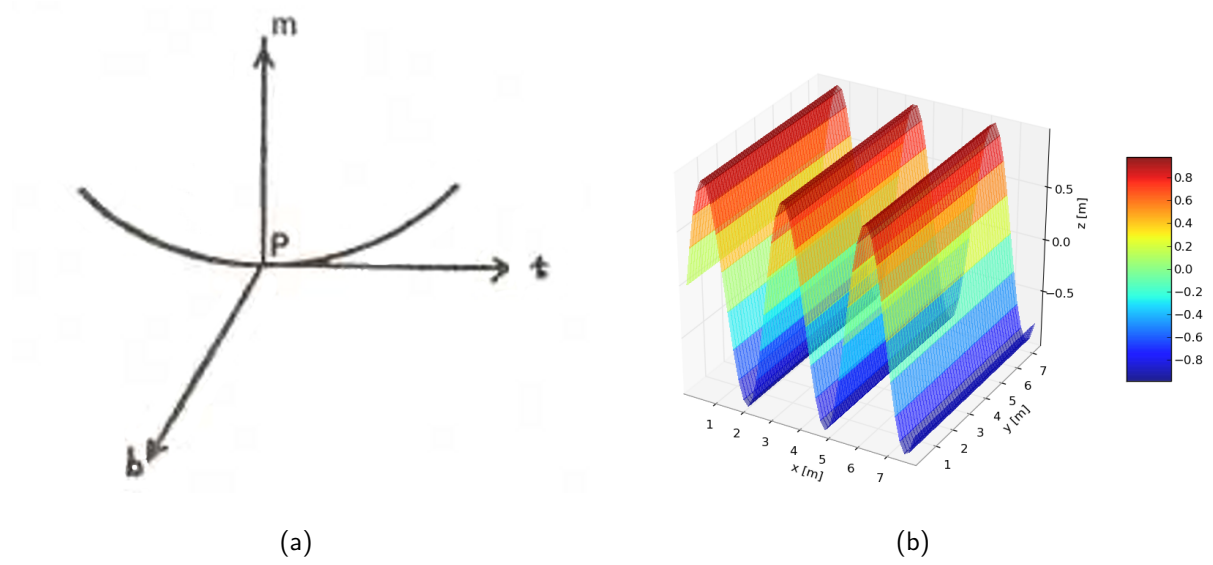


Figure 3.1: (a) A curved surface where the three vectors needed to define the curvature are shown at the point p [97]. (b) A surface with ripples that have certain amplitude h and frequency ω , i.e, the surface obeys specific sinusoidal equation, $z = h \sin(\omega x)$.

3.7 Corrugation

In pure 2D graphene, the presence of completely pure massless fermions is impossible due to the fact that graphene is placed on a substrate [71, 72]. The importance of studying the rippling in graphene is vital from the fundamental point of view as well as the practical side. Moreover, the presence of ripples on the suspended layer of graphene has been observed experimentally using the TEM as discussed in chapter (2). Thus, the study of corrugation in graphene becomes necessary since it plays a crucial role when it comes to fabricating devices where the quality control is required. Moreover, the observation of ripples in the 2D graphene makes graphene the first electronic membranes where the statistical mechanics [54] of membranes plays a major role, as it has been an important branch of soft condensed matter, thus graphene will be the first electronic membrane subjected to direct probes. Further discussions on the properties of corrugated graphene can be found in sec. (2.2) and the references therein. Here, the mathematical formalism for the potential associated with ripples is to be discussed.

The study of thin membranes is extensively used in the biological systems such as lipid membranes and cells [54]. However, the curvature of a surface is defined as the relative change between the

tangent vector at some point, say p , with respect to the change in arc length, δs , as it tends to zero. Thus, for a flat surface, the curvature has to be zero since there is no relative change between those two quantities, while the curvature gains a negative sign when the curvature is convex, then the tangent has to be below the curvature, and visa versa when the curvature is concave. Furthermore, to describe the curvature at some point on a surface, three unit vectors have to be defined as in fig. (3.1(a)), details of the computing those vectors are beyond the scope of the work but good review can be found in ref. [97].

3.7.1 Curvature and Electronic Structure

The effect of finite curvature can be understood within the tight-binding formalism [96]. However, the finite curvature causes the atomic orbitals to rearrange. Initially, the π orbitals are completely perpendicular to the plane of the σ orbitals, and hence no overlap between π and σ takes place. But the curvature causes the π orbitals to be misaligned, and then form an angle $\Theta \neq 90^\circ$ with the σ orbitals. Thus the $\pi - \sigma$ mixing leads to a modification in the nearest neighbours hopping energy by an amount Δt , thus, a potential V_c will arise, which will simply add the term

$$V_c = \Delta t \sum_j a_j^\dagger b_{j+\delta} + H.c \quad (3.78)$$

to the Hamiltonian in eq. (3.71), where all symbols have the usual meanings. However the as explained before, the product of the operators $a_j^\dagger b_{j+\delta}$ will result in a phase factor that depends on the position r of the concerned atoms, i.e. the phase will be 1 if the atom is coupled to a site that belongs to the same LUC while it will be $e^{\pm i k \cdot a_j}$ if the site belongs to the nearest cell.

In general the off-diagonal elements potential defined in the tight-binding Hamiltonian (eq. (3.78)) in the case where the ideal graphene is considered will result in a phase factor $e^{\pm k \cdot a}$. This phase has two components; one real and the other one is imaginary. Hence when the low energy spectrum is considered by expanding the Hamiltonian around the Dirac point, K and K' , two potentials will emerge [75, 77, 76]. The potential associated with the real part is called the scalar field or the electrochemical potential while the one resulting from the imaginary part is called the vector potential, thus in terms of the Dirac Hamiltonian the corrugation potential can be expressed as a gauge field.

The approach to find the hopping energies between lattice sites was originally developed by Slater and Koster [89, 98]. However, the formula to calculate Δt in corrugated graphene has already been found analytically in previous work [76], but the potential found was expanded around the non equivalent corners of the 1BZ, which yields the gauge field as discussed above. In the following, we make use of the formula while detailed derivation is found in ref. [76],

$$\tilde{t} = v_{pp\pi} n_1 \cdot n_2 + (v_{pp\sigma} - v_{pp\pi}) \left(\frac{(n_1 \cdot d)(n_2 \cdot d)}{d^2} \right) \quad (3.79)$$

where $\tilde{t}$ is the modified hopping energy, d is the vector between nearest (second nearest) neighbours after corrugation, $v_{pp\pi}$ and $v_{pp\sigma}$ are the energies of the π and σ orbitals respectively. Hence Δt is given by $\tilde{t} - t$. The norms are then calculated using the Monge's form [97] of the surface equation, i.e., the form

$$z = f(x, y) \quad (3.80)$$

is used. n_1 and n_2 represent the norms at positions of neighbouring atoms in the lattice labelled 1 and 2 respectively. So by using eq. (3.80) the norm at a position of an atom labelled i (n_i) is

$$n_i = \frac{\nabla f(x_i, y_i)}{|\nabla f(x_i, y_i)|}, \quad (3.81)$$

where the norm is a vector that has a dimension normal to the surface at position (x_i, y_i) with length equal to the unit.

3.8 Leads Self Energy

Prior characterization of any material, it has to be sandwiched between conducting leads that inject and receive electrons into the system. However, the effect of leads is remarkable on the observed properties due to their broadening effect on the electronic states inside the sample [99].

To account for the lead effect on a sample, the Hamiltonian that represents the lead (H_L) has to be included as well as another Hamiltonian (H_C) that represents the coupling at the boundaries between the lead and the sample. Now, if a finite lead is used, then the plane wave inside the lead will encounter some scattering from the sample boundaries which will result in interference between incident and reflecting waves. Therefore to reduce the effect of the reflection, the leads

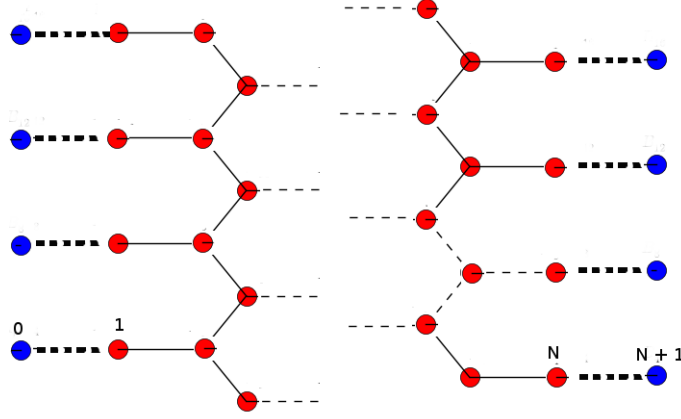


Figure 3.2: Atoms of the lead (blue circles) are connected to dangling carbon atoms (red circles) in a sample of graphene. The dashed line inside the sample represents extension of the sample, while the thick-dashed line represents the coupling between the outer layer atoms of graphene with those of the lead.

have to be extended along the direction of the motion of electrons to be infinite. The infinite dimensionality of the lead will result in a Hamiltonian matrix with infinite dimensions as well, which in turn gives rise to some computation difficulty.

However, to overcome the difficulties due to the matrix size, the Hamiltonian matrix is given by the self-energies [99]. Consider the Hamiltonian,

$$H = H_S + H_C + H_L, \quad (3.82)$$

which describes systems such as the one depicted in fig. (3.2). The subscripts S , C and L stand for the sample, coupling and lead respectively. To find the retarded propagator $\tilde{G}$ that corresponds to the Hamiltonian in eq. (3.82), the technique developed in numerical methods [99] to deal with such kind of matrices, so

$$\tilde{G} = \begin{pmatrix} G_l & G_{l-s} \\ G_{s-l} & G_s \end{pmatrix} = \begin{pmatrix} E + i\eta - H_L & H_C \\ H_C^\dagger & E + i\eta - H_S \end{pmatrix}^{-1}. \quad (3.83)$$

From the identity $H.\tilde{G} = \mathbb{I}$, it follows,

$$(E + i\eta + H_L).G_{l-s} + H_C.G_s = 0, \quad (3.84)$$

therefore,

$$G_{l-s} = -\frac{H_C.G_s}{E + i\eta - H_L} = -g_l.H_C.G_s, \quad (3.85)$$

where g_l is the lead Green's function. Also,

$$H_C^\dagger.G_{l-s} + (E + i\eta - H_C).G_s = \mathbb{I}, \quad (3.86)$$

then by substituting eq. (3.85) in eq. (3.86),

$$\begin{aligned} G_s &= \frac{1}{(E + i\eta - H_s - H_C^\dagger.g_l.H_C)} \\ &= \frac{1}{(E + i\eta - H_s - \Sigma_L)}, \end{aligned} \quad (3.87)$$

where $\Sigma_L = H_C^\dagger.g_l.H_C$ is the self energy associated with the leads, and the subscript L indicates the left lead since it is the one considered at the beginning. Note that the structure of the matrix H_C is special in the sense that all its elements are zeros except for adjacent sites between the sample outer layer and the lead one, thus, the self energy reduces to

$$\Sigma_L = t_C^2 g_L, \quad (3.88)$$

where t_C is the coupling integral in the matrix H_C . Before proceeding in the calculation of the matrix elements of leads self energy, the issue of edges has to be addressed. As discussed in chapter (2), graphene has two different types of geometries at the edges; zigzag and armchair. In addition to that, in fig. (3.2) the edge along the y-axis is neither zigzag nor armchair, it is rather dangling carbon atoms. In fact the edges are considered to be an additional source of defects [100]. Particularly, the zigzag edge as well as the dangling atoms are likely to experience edge-reconstruction which may also depend on the leads attached to the sample (see ref. [101, 102] and the references therein for further details). However, in this work the effect of the edges is overcome through the incorporation of periodic boundary conditions as discussed earlier this chapter.

The computation of Σ_L in terms of g_l is rather complicated unless one avoids considering the entire matrix since it is of infinite dimensions. However, this difficulty is lifted by assuming

the lead can be modelled by using a lattice that obeys certain symmetries such as the one for graphene. Now, let us assume that each atom in the lead is coupled to only one atom in the sample and visa versa, with noting that the second nearest coupling between carbon atoms and lead atoms is taken to be zero. Thus one can assume the existence of a 2D square lattice with mono-atomic basis. It has translation vectors $\hat{\alpha}$ and $\hat{\beta}$ that translate an atom along the x-axis and y-axis respectively. The magnitude of both vectors has to be chosen carefully so that each atom in the lead is aligned with only one atom in the sample, i.e., the translation vectors have a magnitude of $\sqrt{3}a_0$, and they are defined as

$$\begin{aligned}\hat{\alpha} &= (1, 0)\sqrt{3}a_0 \\ \hat{\beta} &= (0, 1)\sqrt{3}a_0.\end{aligned}\tag{3.89}$$

Then, following the same procedure described in sec. (3.4), we introduce the effective hopping between the lead lattice sites t_L , then the Hamiltonian that describes the system reduces to a 2×2 matrix,

$$H_L = \begin{pmatrix} \epsilon & 2t_L \cos(k_x\alpha) + 2t_L \cos(k_y\beta) \\ 2t_L \cos(k_x\alpha) + 2t_L \cos(k_y\beta) & \epsilon \end{pmatrix},\tag{3.90}$$

where the parameters have their usual meaning, and it yields a dispersion relation

$$\varepsilon(k_x, k_y) = \epsilon \pm 2t_L (\cos(k_x\alpha) + \cos(k_y\beta)),\tag{3.91}$$

for simplicity, usually the on-site energy ϵ is taken as zero.

The Green's function g_l that corresponds to the Hamiltonian in eq. (3.90) is defined as a function of the energy E ,

$$g_l = \frac{1}{E - H_L + i\eta},\tag{3.92}$$

which can be expanded by using a complete set of complete basis $|k\rangle$ as explained in sec. (2.1);

$$g_l = \sum_k^{\text{1BZ}} \frac{|k\rangle \langle k|}{E - \varepsilon(k_x, k_y) + i\eta}.\tag{3.93}$$

Now, from the above definition, specifying the elements of the propagator requires to sum over all states that fall in 1BZ. However, there is no interest in all the elements of the matrix, the interest

is focused only on elements that correspond to coupling between neighbours, i.e., off-diagonal elements. Thus, the element that corresponds to coupling site n to m is given by

$$\langle n | g_L | m \rangle = \sum_k \frac{\langle n | k \rangle \langle k | m \rangle}{E - \varepsilon(k_x, k_y) + i\eta}. \quad (3.94)$$

Expanding the state $|k\rangle$ into two components using tensor product, so $|k\rangle = |k_x\rangle \otimes |k_y\rangle = |k_x k_y\rangle$, where the states k_x is chosen so that it satisfies the periodic boundary conditions. On the other hand, some restrictions are imposed on k_y so the wave along its direction satisfies reflecting boundary condition. The physical meaning of this restriction originates from the fact that electrons are not transported along the y-axis, thus the wavefunction has to reflect from the boundaries and the values are obtained through eq. (3.19). Now using the expansion above, eq. (3.94) yields

$$\begin{aligned} \langle n | g_L | m \rangle &= \sum_{k_x, k_y} \frac{\langle n_x n_y | k_x k_y \rangle \langle k_x k_y | m_x m_y \rangle}{E - \varepsilon(k_x, k_y) + i\eta} \\ &= \sum_{k_x} \sum_{k_y} \frac{\langle n_x | k_x \rangle \langle k_x | m_x \rangle}{E - \varepsilon(k_x, k_y) + i\eta} \langle n_y | k_y \rangle \langle k_y | m_y \rangle. \end{aligned} \quad (3.95)$$

It follows from the discussion in sec. (3.4), that the product $\langle n_x | k_x \rangle \langle k_x | m_x \rangle$ should result in a phase shift given by $e^{ik_x \alpha (n_x - m_x)}$, and similarly $\langle n_y | k_y \rangle \langle k_y | m_y \rangle = e^{ik_y \beta (n_y - m_y)}$. Plugging those results in eq. (3.95), one obtains

$$\langle n | g_L | m \rangle = \sum_{k_x} \sum_{k_y} \frac{e^{ik_x \alpha (n_x - m_x)}}{E - \varepsilon(k_x, k_y) + i\eta} e^{ik_y \beta (n_y - m_y)}. \quad (3.96)$$

But from the fact that the lead is extended to the infinity along the x-axis, it requires replacing the summation over k_x by an integral, so

$$\sum_{k_x} \longrightarrow \frac{\Omega}{2\pi N} \int_{-\frac{\pi}{\alpha}}^{\frac{\pi}{\alpha}} dk_x, \quad (3.97)$$

where $\frac{\Omega}{N}$ is volume (length in this case) of the 1BZ. Thus eq. (3.96) reads

$$\langle n | g_L | m \rangle = \frac{\Omega}{2\pi N} \sum_{k_y} e^{ik_y \beta (n_y - m_y)} \int_{-\frac{\pi}{\alpha}}^{\frac{\pi}{\alpha}} \frac{e^{ik_x \alpha (n_x - m_x)}}{E - \varepsilon(k_x, k_y) + i\eta} dk_x. \quad (3.98)$$

The task now is to evaluate the integral in eq. (3.98) analytically. However, the integral can be written in a simpler form as

$$\begin{aligned} \int_{-\frac{\pi}{\alpha}}^{\frac{\pi}{\alpha}} \frac{e^{ik_x \alpha(n_x - m_x)}}{E - \varepsilon(k_x, k_y) + i\eta} dk_x &= \int_{-\frac{\pi}{\alpha}}^{\frac{\pi}{\alpha}} \frac{e^{ik_x \alpha(n_x - m_x)}}{E - (2t_L \cos(k_x \alpha) + 2t_L \cos(k_y \beta)) + i\eta} dk_x \\ &= \frac{1}{t_L} \int_{-\frac{\pi}{\alpha}}^{\frac{\pi}{\alpha}} \frac{e^{ik_x \alpha(n_x - m_x)}}{E_J - 2 \cos(k_x \alpha)} dk_x, \end{aligned} \quad (3.99)$$

where $E_J = \frac{1}{t_L} (E - 2t_L \cos(k_y \beta) + i\eta)$. Then, we change the variables so that $n_x - m_x = \lambda = n_x - m_x$, and $k_x \alpha = \theta$, the integral then yields

$$\frac{1}{t_L} \int_{-\frac{\pi}{\alpha}}^{\frac{\pi}{\alpha}} \frac{e^{ik_x \alpha(n_x - m_x)}}{E_J - 2 \cos(k_x \alpha)} dk_x = \frac{1}{t_L \alpha} \int_{-\pi}^{\pi} \frac{e^{i\theta \lambda}}{E_J - 2 \cos \theta} d\theta. \quad (3.100)$$

Substitute

$$\cos \theta = \frac{e^{i\theta} + e^{-i\theta}}{2} = \frac{z + z^{-1}}{2}, \quad (3.101)$$

thus

$$\begin{aligned} \frac{1}{t_L \alpha} \int_{-\pi}^{\pi} \frac{e^{i\theta \lambda}}{E_J - 2 \cos \theta} d\theta &= \frac{-i}{t_L \alpha} \oint \frac{z^{\lambda-1}}{E_J - (z + z^{-1})} dz \\ &= \frac{i}{t_L \alpha} \oint \frac{z^{\lambda}}{z^2 - zE_J + 1} dz, \end{aligned} \quad (3.102)$$

where the integral in eq. (3.102) has two poles at $z_1 = \frac{1}{2} (E_J + \sqrt{E_J^2 - 1})$ and $z_2 = \frac{1}{2} (E_J - \sqrt{E_J^2 - 1})$, thus can be written in the form

$$\frac{i}{t_L \alpha} \oint \frac{z^{\lambda}}{z^2 - zE_J + 1} dz = \frac{i}{t_L \alpha} \oint \frac{z^{\lambda}}{\left(z - \left(E'_J + \sqrt{E_J'^2 - 1}\right)\right) \left(z - \left(E'_J - \sqrt{E_J'^2 - 1}\right)\right)} dz, \quad (3.103)$$

where the $\frac{1}{2}$ factor is absorbed in E'_J . Hence, following the methods of the complex analysis, namely the residue theorem [84], the above integrals reduces to the sum of the residuals, R_j , around the poles (singularities),

$$\oint f(z) dz = 2\pi i \sum_j R_j, \quad (3.104)$$

where R_j is the residual at the pole z_j . However, the evaluation of the residuals R_j depends on the degree of the pole. Fortunately, the poles encountered here are of first order, i.e., none of the poles has a doubled value or results from solving something that looks like $(z - a)^s$, where a is the pole and s does not equal to the unit. Thus the residuals are calculated straight forward from the relation

$$R_j = \lim_{z \rightarrow z_j} ((z - z_j)f(z)), \quad (3.105)$$

where $f(z)$ is the function to be integrated. Thus the two residuals R_1 and R_2 are obtained as

$$\begin{aligned} R_1 &= \frac{\left(E'_J + \sqrt{E_J'^2 - 1}\right)^\lambda}{2\sqrt{E_J'^2 - 1}}, \\ R_2 &= \frac{\left(E'_J - \sqrt{E_J'^2 - 1}\right)^\lambda}{-2\sqrt{E_J'^2 - 1}}. \end{aligned} \quad (3.106)$$

Now the integral in eq. (3.102) reads

$$\begin{aligned} \frac{i}{t_L \alpha} \oint \frac{z^\lambda}{z^2 - zE_J + 1} dz &= \frac{2\pi}{t_L \alpha} (R_1 + R_2) \\ &= \frac{-\pi}{t_L \alpha} \frac{1}{\sqrt{E_J'^2 - 1}} \left[\left(E'_J + \sqrt{E_J'^2 - 1}\right)^\lambda - \left(E'_J - \sqrt{E_J'^2 - 1}\right)^\lambda \right]. \end{aligned} \quad (3.107)$$

To find λ , it actually depends on labels of the atoms coupled to one site. For instance, if one considers the cell shown in fig. (3.2), the atom labelled 1 (N) is coupled to the one labelled 0 (N+1) and visa versa, thus λ has to be equal to ± 1 depending on the direction considered. In other words, if coupling of the left lead is considered, that basically means the atoms belong to boundaries of the sample and fall to the right of the lead require λ to be equal to -1, while those on the left of the lead require λ to be +1. In the same sense, if second order coupling is considered in the lead, then λ has to be equal to ± 2 , which is not considered the lead Hamiltonian (3.90). So, the result in eq. (3.107) becomes

$$\frac{-\pi}{t_L \alpha} \frac{1}{\sqrt{E_J'^2 - 1}} \left[\left(E'_J + \sqrt{E_J'^2 - 1}\right)^\lambda - \left(E'_J - \sqrt{E_J'^2 - 1}\right)^\lambda \right] = \frac{\pm 2\pi}{t_L \alpha}, \quad (3.108)$$

where the sign is + when $\lambda = -1$ (left lead) and - when $\lambda = +1$ (right lead). Substituting

the expression obtained above in eq. (3.98), we deduce that

$$\langle n | g_l | m \rangle = \pm \frac{1}{t_L} \sum_{k_y} e^{\mp i k_y \beta}, \quad (3.109)$$

where the factor $\frac{2\pi}{\alpha}$ is cancelled with $\frac{\Omega}{2\pi N}$.

To find the elements of the self energy matrix, the result in eq. (3.109) is substituted in eq. (3.88), then the element Σ_i that correspond to coupling between adjacent sites yields

$$\Sigma_i = \pm t_e \sum_{k_y} e^{\mp i k_y \beta}, \quad (3.110)$$

where the new parameter t_e is introduced as a result of dividing $\frac{t_C^2}{t_L}$.

The self energy matrix is simply defined by introducing a matrix that has the same dimensions as the Hamiltonian, and all its element are zeros except some entries in the diagonal since the leads are replaced with their effect on atoms at outer layer of the sample. From figs. (3.2 and 2.4), the leads are coupled to the sites labelled $A_{1,5,9,13}$ from the left, while they are coupled to sites $B_{4,8,12,16}$ from the right. Therefore, the diagonal elements corresponding to the coupled sites will be replaced by Σ_i .

3.9 The Physical Quantities and Green's Function

Information about measurable quantities such as the density of states (DOS) and the current are obtained from the wavefunction since it plays the role of the information carrier. On the other hand, Green's function carries the same kind of information although it is defined differently from the way the wavefunction is defined. In this section the density of states as well as the transmission coefficients (T) are given in terms of the propagator [99].

3.9.1 Density of States

The density of states (DOS) is defined as the number of electronic states at certain energy per unit area (volume). Thus DOS has a sharp peak at certain energies. Mathematically, it is defined

as [44]

$$\text{DOS} = \sum_i \delta(E - \varepsilon_i), \quad (3.111)$$

which means that DOS has a sharp peak when the energy is equal to ε_i . But note that the Green's function can also be defined in terms of the identity in eq. (3.7), so that one can redefine the delta function $\delta(E - \varepsilon_i)$ as the imaginary part of Green's function divided by $-\pi$. In terms of matrices, the matrix $A(E)$ is defined by

$$A = -\frac{1}{\pi} \text{Im} [G(E)], \quad (3.112)$$

where it is called the spectral matrix and it gives the energy resolution between two points in the system [99]. For instance, if a system consists of three particles and hence is described by a 3×3 matrix, then the particles are labelled as 1, 2 and 3, thus the element A_{13} in the spectral matrix corresponds to the energy resolution between the particles 1 and 3. Similarly, the element A_{11} is the local density of states at the position of particle 1, actually when a sample is studied by a scanning tunnelling microscope (STM), it measures LDOS of the electrons. So, the total DOS can be constructed as a sum of the diagonal elements which is the trace of the matrix,

$$\text{DOS} = -\frac{1}{\pi} \text{Tr} (\text{Im} [G(E)]), \quad (3.113)$$

which is an invariant quantity since it is given in terms of the matrix trace.

3.9.2 Transmission Coefficients

Another quantity of great importance in the field of quantum transport is the transmission coefficients. It is calculated in many different ways; the most popular one is the T-matrix approach which assumes that plane waves are used to construct the basis. The wavefunction in this case consists of two plane waves; one is transmitted while the other is reflected, thus the transmission probability for the electron to tunnel through a barrier is given as a ratio of the amplitude of the transmitted wave to the reflected one. This approach is not appropriate in the case we are handling, so another technique that relates the Green's function to the transmission probability is required [99, 82].

We avoid detailed derivation of the mathematical relation between Green's function and transmission. However, the transmission coefficient as a function of energy ($T(E)$) is given by

$$T(E) = \text{Tr} (\Gamma_L G(E) \Gamma_R G^\dagger(E)), \quad (3.114)$$

where Γ_L (Γ_R) is the imaginary part of the self energy of the left (right) lead, and $\dagger$ indicates the hermitian conjugate of the operator, see ref. [82] for a detailed derivation.

The conductance $G_e(E)$ in a sample is obtained through the Landauer-Büttiker formalism [103],

$$G_e(E) = \frac{e^2}{h} T(E), \quad (3.115)$$

where e is the electron charge and h is Planck constant. It is noted that some authors write the constant $\frac{e^2}{h}$ with extra factor of 2 to include the degeneracy arising from the electron spin. Following the procedure described in ref. [99], the current flowing in the sample, I , is given by

$$I(\mu) = \frac{e}{h} \int_{-\infty}^{\infty} T(E) [f_L(E, \mu) - f_R(E, \mu)] dE \quad (3.116)$$

where μ is the chemical potential of in the leads and it is related to the applied bias V by the relation $\mu = \frac{1}{2}eV$ [103]. f is the Fermi distribution function for the leads,

$$f(E, \mu) = \frac{1}{e^{(E \pm \mu)/k_B \theta_T} + 1}, \quad (3.117)$$

where k_B is Boltzmann constant and θ_T is the temperature. When the sign is $+$, it means the distribution is for the left lead f_L (source), while the negative sign stands for the right lead f_R (drain).

4. Density of States in Defected Graphene

In this chapter we present the results for the electronic density of states (DOS) in disordered graphene. This chapter is divided into two main sections; the first one discusses the electronic properties in disordered graphene (vacancies as well as impurities), while in the second one the effect of the rippling on a sheet of graphene is reported.

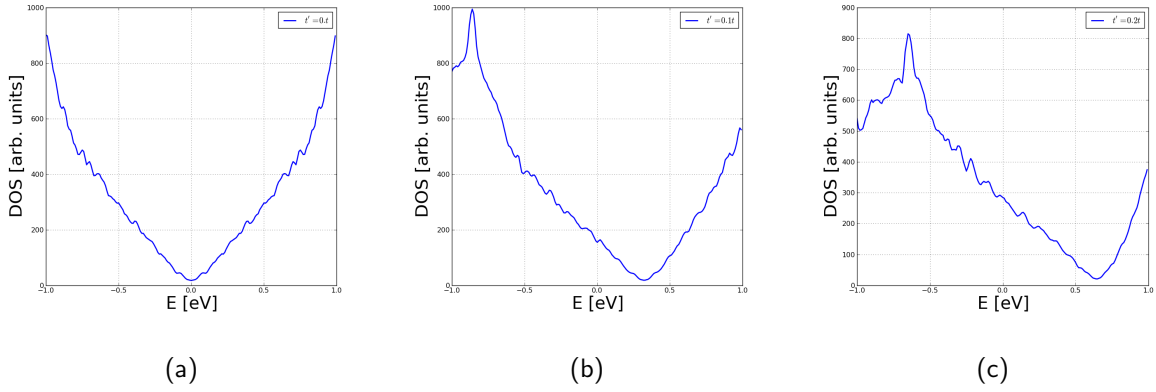


Figure 4.1: Density of states in pure graphene: (a) The particle-hole symmetry is not broken in this case, i.e. the electron is only allowed to hop to the nearest neighbouring carbon atoms, (b) The electron is allowed to hop to second nearest carbon atoms which means the particle-hole symmetry is no longer maintained, the hopping energy, t' , is taken to be $0.1t$ in (b) while it is $0.2t$ in (c).

Although a convergence test shows that the solution is well converged for a grid of 70×70 k-points, the DOS is calculated for a sheet of graphene using a grid that has 103×103 k-points along each axis of symmetry. The points are generated using the Monkhorst-Pack algorithm [91] explained in eq. (3.20). The energy is taken to be in the range $[-1, 1]$ which is the low energy regime. In an ideal sheet of graphene, the overall picture for the case where the second nearest hopping energy is considered to be zero shows linearity around the Fermi energy (0 eV), see fig. (4.1(a)). Despite the fact that it is not precisely linear; the fluctuation observed is due to numerical oscillations arising from the integral over the 1BZ, so extra k-points points in the grid should yield a smoother curve. The DOS at the Fermi level equals zero where the chemical

potential crosses the Dirac points, so ideal graphene is said to be metallic [15, 1, 8]. The linearity of the spectrum around this point indicates that the dispersion relation is linear in the momentum which is similar to the dispersion obtained for relativistic particles satisfying the massless Dirac equation [25]. On the other hand, the particle-hole symmetry is considered to be broken when $t' \neq 0$, as shown in figs. (4.1(b) and 4.1(c)), the position of the point where the DOS is zero (Fermi level) is shifted to the right with an amount approximately equal to the second nearest hopping energy [60]. For instance, the Fermi level in fig. (4.1(b)) is shifted by 0.3 eV while the shift in fig. (4.1(c)) is 0.6 eV which are approximately of the order of the hopping energy to second nearest neighbours.

4.1 Disordered Graphene

As the sublattice is substituted with a foreign atom the electronic properties are influenced. However, the defects considered include vacancies as well as impurities. The way the defect is defined depends on its potential; the vacancy is considered as a high (deep) potential center located at one of the lattice sites. The impurity is formed by substituting one site in the lattice with a foreign atom (adsorbed impurities) so a new coupling parameter has to be taken into account in addition to the on-site potential (see chapter (3) for discussion). The concentration of the impurity is calculated using the relation $\frac{N_i}{N}$ where N_i is the number of the impurities per unit cell, and N is the total number of atoms in the unit cell which is 32 as shown in fig. (2.4). Generally, two scenarios are considered: in the first one the particle-hole symmetry is not broken, so the second-nearest hopping energy is taken as zero. In the second case the particle-hole symmetry is broken (which is common in bipartite lattices [60]) and two values for the hopping energy t' are investigated, $t' = 0.1t$ and $t' = 0.2t$.

4.1.1 Vacancies

In this case a vacancy is substituted on one site of the lattice, particularly A sublattice as indicated in the potential defined in eq. (3.76). The DOS is calculated for five different vacancy concentrations; 3.125%, 6.25% , 9.375%, 12.5% and 15.625% which corresponds to numbers

of 1, 2, 3, 4 and 5 vacancies respectively in each unit cell. For each configuration, the DOS is averaged over five arbitrary configurations.

Particle-Hole Symmetry

In figs. (4.2), in each panel the DOS was calculated using two different boundary conditions, i.e., periodic boundary conditions (Born-von Karman boundary conditions) and hard wall boundary conditions where the wave is forced to reflect from the boundaries. At all the vacancy concentrations there is an obvious formation of new states located at the Fermi level, which is understood as the formation of a new band at the Fermi energy. To understand the nature of the new states, different boundary conditions are applied since the localized states are insensitive to the change of boundary conditions [104] while other delocalized states are sensitive. The Fermi energy states tend to be quasi-localized as can be seen in figs. (4.2(a)-4.2(e)) where the DOS plotted in a dashed green line are obtained through the hard wall boundary conditions, while the DOS plotted in a solid blue line are obtained through the periodic boundary conditions. The states are said to be quasi-localized since the change of boundary conditions will not cause them to disappear or change their shape, but they yield different peak intensities.

The states at the Fermi level increase as the concentration of the vacancies increases (see fig. (4.2(f))). To understand this we refer to a theorem discussed in ref. [60], which states that the number of zero modes (zero eigenenergies) in a bipartite lattice is proportional to the number of the vacancies substituted. The theorem is also linked to another theory in linear algebra called rank-nullity theorem [64]. The zero modes are basically wavefunctions with high amplitudes at energies equal to zero. They arise when two sublattices are inequivalent to each other, in other words, the lattice of graphene has carbon atoms only, when a vacancy is present, the lattice symmetry breaks, that causes the symmetry to break. The solution of a Hamiltonian using exact diagonalization methods will result in zero eigenvalues which correspond to non-normalizable eigenfunctions [63], hence a sharp peak is observed at the Fermi level.

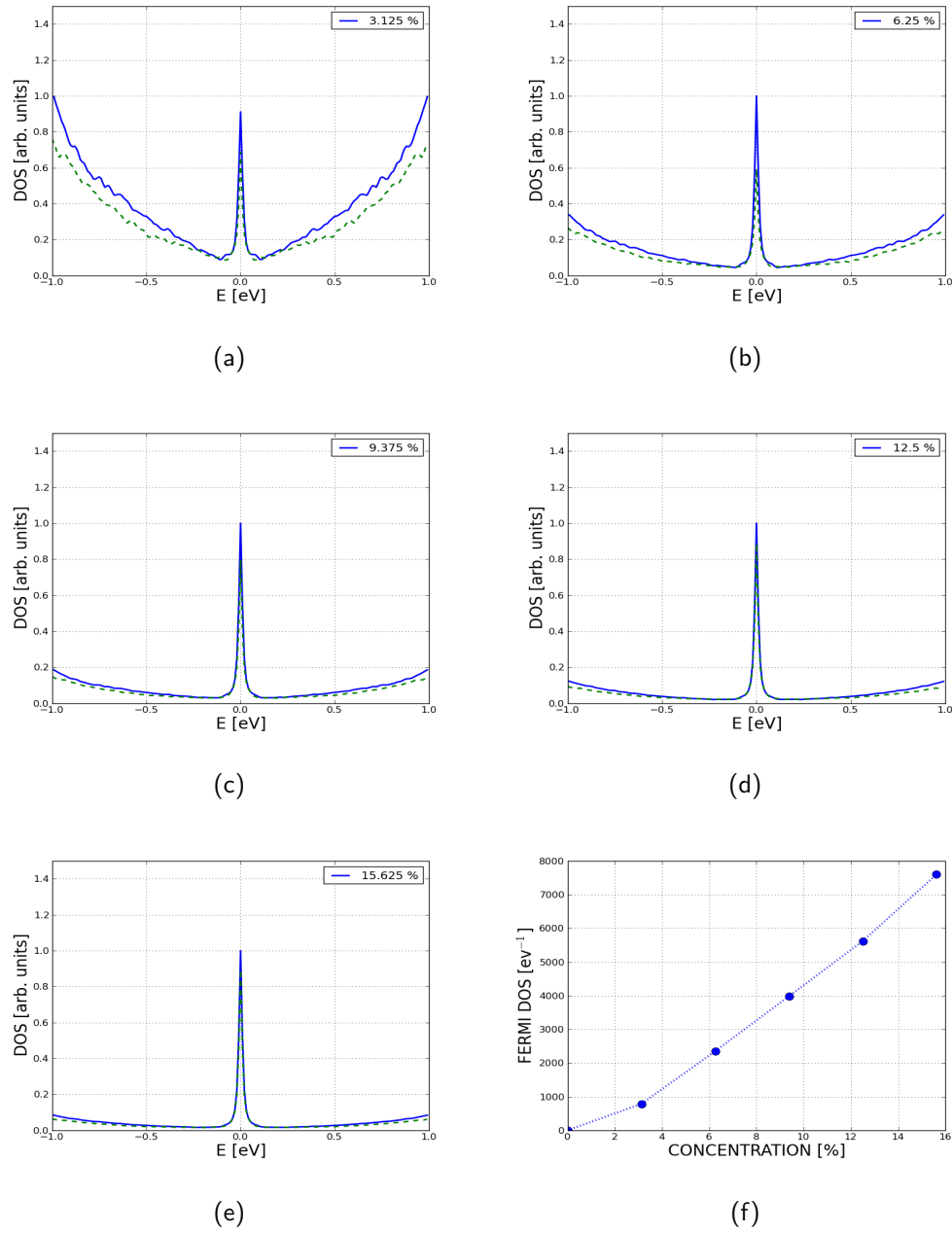


Figure 4.2: The DOS (in arbitrary units) is calculated around the Fermi level for different vacancy concentrations. Each window contains two plots; the solid blue line is the DOS obtained by applying periodic boundary conditions, while the dashed green line is the DOS obtained by using reflecting boundary conditions. In panel (f) the behaviour of the DOS at the Fermi level as a function of the vacancy concentration is plotted.

Particle-Hole Symmetry Breaking

In the case where the picture of particle-hole symmetry is spoiled by introducing a non-zero second nearest neighbour hopping energy t' , the most prominent feature is the shift in the Fermi energy and as a consequence the states at the level are shifted to the right with an amount approximately equal to the hopping energy between second nearest neighbours, see figs. (4.3, 4.4).

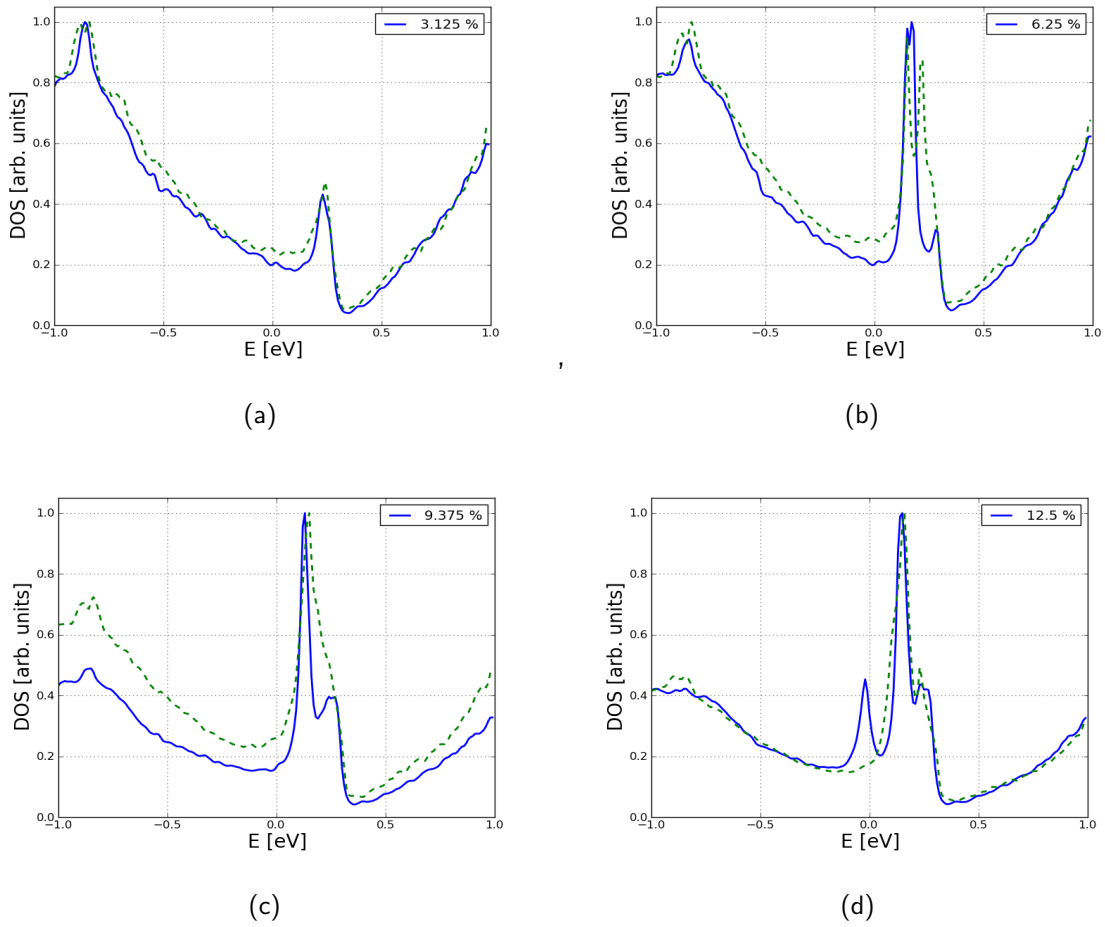


Figure 4.3: DOS for disordered graphene (arbitrary units) in the case where second nearest hopping is allowed, $t' = 0.1t$. Each window contains a plot of the DOS at different concentrations as shown in the labels. The boundary conditions used to obtain the results plotted in the blue solid line are periodic boundary conditions while the green dashed line is obtained through aperiodic boundaries.

Unlike the case where the particle-hole symmetry is maintained, more than one state is observed around the main state as shown in figs. (4.3, 4.4). Changing the boundary conditions satisfied

by the propagator shows that the new states around the main localized state are quasi localized in nature as shown by the dashed green line in all windows in figs. (4.3, 4.4).

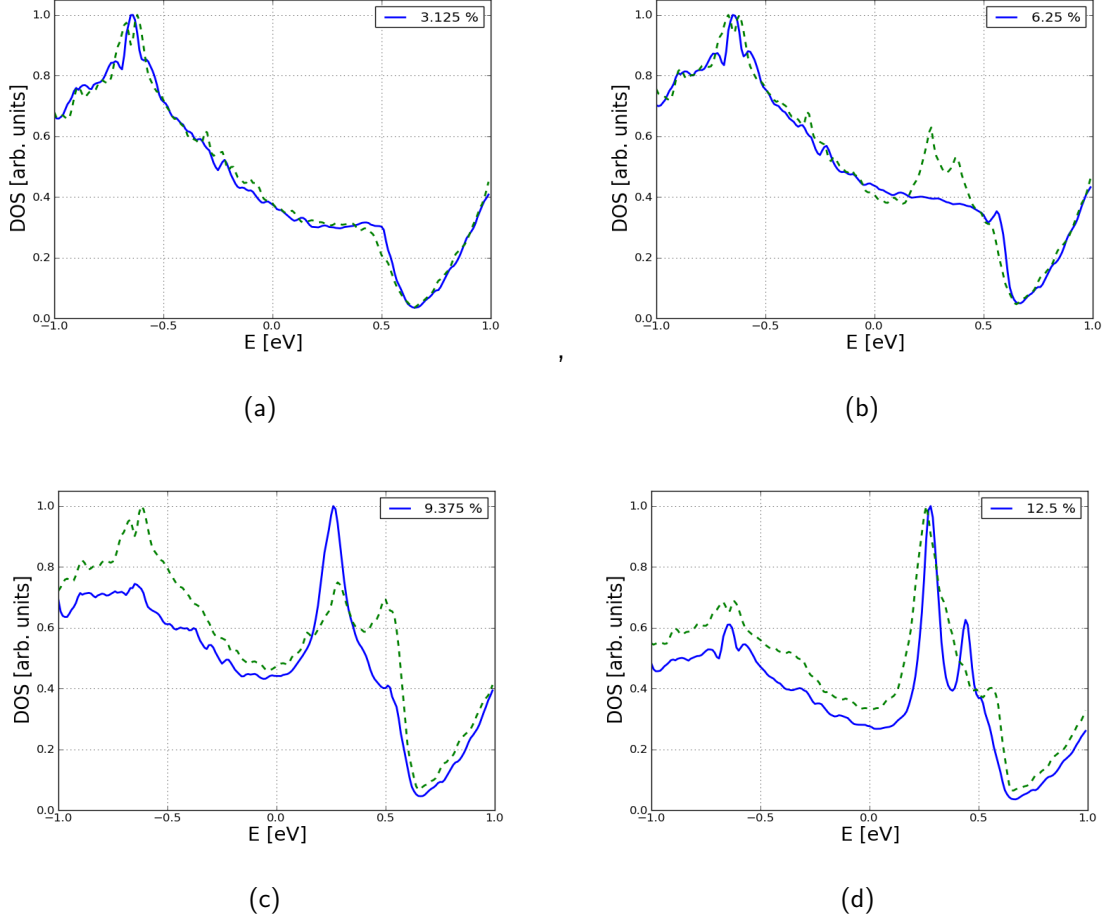


Figure 4.4: DOS for disordered graphene (arbitrary units) in the case where second nearest hopping is allowed, $t' = 0.2t$. Each window contains a plot for DOS at different concentration as shown in the labels. The boundary conditions used to obtain the results plotted in blue solid line are periodic boundary conditions while the green dashed is obtained through aperiodic boundaries.

Furthermore, at low concentrations where the second nearest neighbour hopping energy equals $0.1t$, see figs. (4.3(a), 4.3(b)), the main localized states at the Fermi energy split, and the states tend to spread more rather than localize as in the case where $t' = 0$. In addition, when the second nearest coupling increases to $0.2t$, the density of states around $E \sim 0.6$ eV becomes more flat. The reason could be related to the fact that the localized states arise from the presence of scatterers in the lattice, hence by allowing the electron to hop to equivalent sites of the lattice,

i.e., $t' \neq 0$, it propagates easily without feeling a strong influence of the scatterers. Therefore by increasing the concentration of the scatterers, see figs. (4.4(c) and 4.4(d)) it becomes more difficult to propagate through the lattice without experiencing multiple scattering processes, so at higher concentrations more localized states appear.

4.1.2 Impurities

In the case of the impurity, its orbitals hybridize with the nearest carbon atoms since it is assumed that impurities are adsorbed at one site of the lattice, the distance between any two impurities is relatively large so the overlap of impurity wave functions need not be considered. Hence the coupling parameter has to be modified locally, so it becomes t_p as defined in eq. (3.77). The effect of the impurity takes place very close to the Fermi energy (the on-site potential is taken to be -2.5 eV, which is equivalent to the potential of nitrogen atoms measured relative to the potential of carbon atoms [105]) and it can be extrapolated by comparison with the effect of the vacancy. The DOS was calculated for a sheet of graphene where different impurity concentrations are considered as indicated in the labels of figs. (4.5 - 4.6). As in the case of the vacancy, two scenarios are considered; in the first one the particle-hole symmetry is not broken while in the second one the picture is disturbed by defining non-zero values for the second nearest neighbours hopping energy. In each scenario two hopping energies between the impurity site and the nearest carbon atoms are studied at different concentrations.

Particle-Hole Symmetry

In fig. (4.5) the DOS (in arbitrary units) is plotted as a function of the energy E . In each panel, the DOS plots are obtained at the same concentration for two different impurity-carbon coupling energy as indicated in the labels on the figures.

As mentioned in sec. (4.1.1) the presence of vacancies gives rise to the formation of quasi-localized states at the Fermi-level. However, the case of the impurity differs from the vacancy in two aspects; firstly, the potential at the vacancy site is large compared to the potential of surrounding atoms, see ref. [60]. Secondly, the hopping is forbidden to and from the site where

the vacancy is located. Thus the impurity corresponds to a more realistic situation where oxygen, hydrogen or nitrogen atoms can be adsorbed on the surface of graphene, so the orbitals hybridize to form new bonds, and consequently new states are formed. To extrapolate from the situation of the vacancy when it is coupled to the nearest neighbours, then the electrons are allowed to tunnel through the potential barrier at the vacancy location. Hence the localized states formed at the Fermi level diminish gradually as the coupling constant decreases (the absolute value increases since t_p is negative).

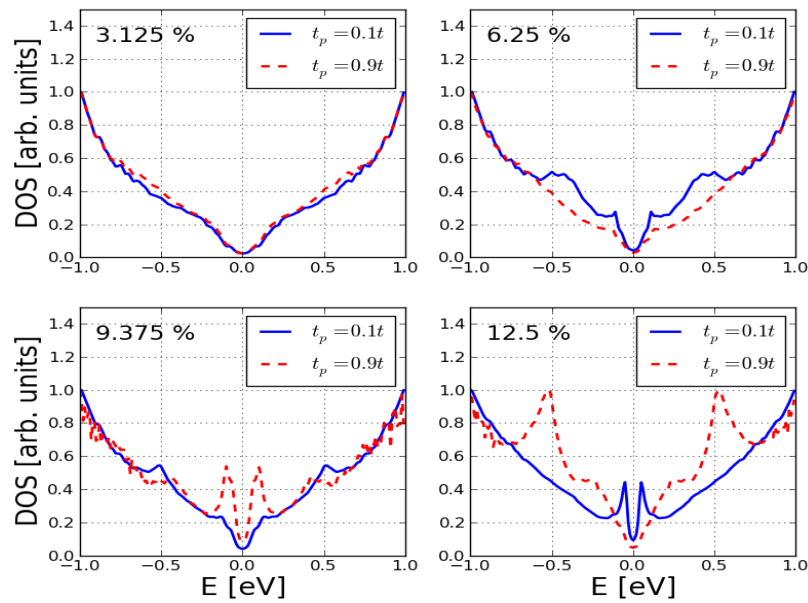
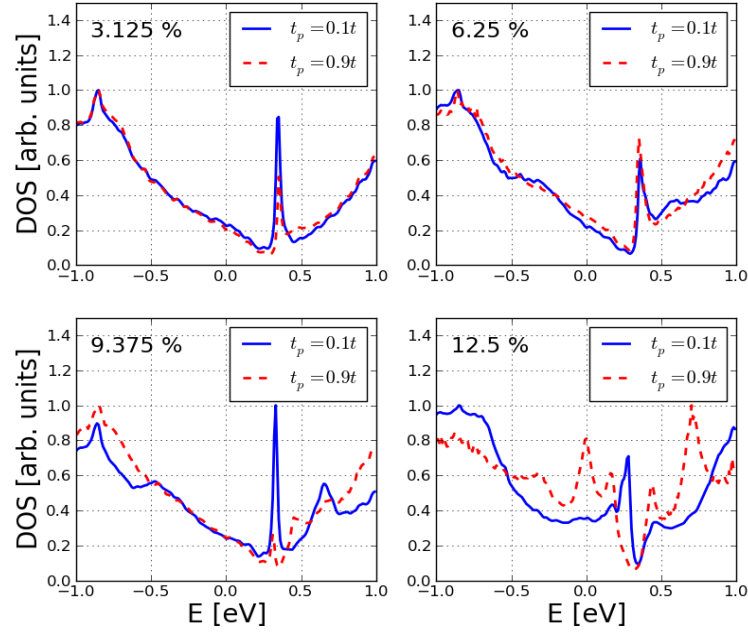


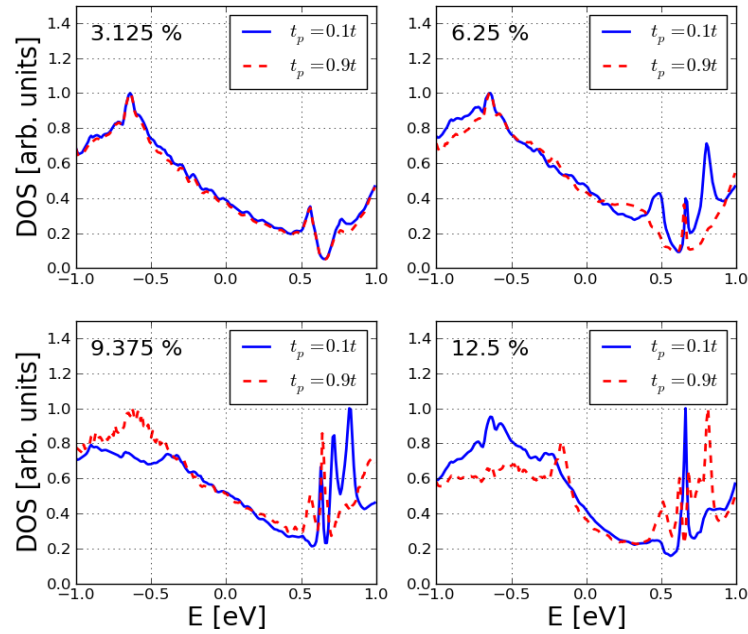
Figure 4.5: The DOS (arbitrary units) for non-diagonal impurities that have on-site potential equivalent to nitrogen's. It is coupled to its nearest neighbours by two different coupling energies; $t_p = 0.1t$ (plotted in blue solid line) and $0.9t$ (red dashed line). The figure at the top-right is plotted for impurity concentration = 3.125 %, the top-left is for 6.25 %, while the bottom-left is for 9.375 %, and the last one is for 12.5 %.

In fig. (4.5), it can be seen that the DOS at $E = 0$ eV approaches zero, but it loses the linearity around the Fermi level (Dirac fermions fingerprint), which is understood as a splitting of the states, hence it gains back the symmetrical features. But in general at low concentrations, the peaks are not pronounced due to the relatively low intensity of the original localized states formed by the vacancy, see fig. (4.2). As the concentration increases, the sharpness of the observed peaks increases especially when $t_p = 0.9t$.

Particle-Hole Symmetry Breaking



(a)



(b)

Figure 4.6: DOS in the case where second nearest hopping is allowed, (a) $t' = 0.1t$, and $t' = 0.2t$ in (b). Each window contains a plot for the DOS at different concentrations as shown in the labels.

When the second nearest interaction is turned on, the Fermi level is displaced by an amount approximately equal to the coupling parameter t' . Similarly to the situation shown in figs. (4.3 and 4.4), new resonance peaks show up around the energy $E \sim t'$ even at low concentrations as shown in figs. (4.6(a) and 4.6(b)).

Moreover, the number of the resonant states around $E \sim t'$ is enhanced as the impurity concentration increases regardless of the value of t_p , but it is important to stress that the DOS is sensitive to concentration and the number of configurations used when averaging (only 5 different configurations are considered), and this is the reason for the variation in the intensities of the peaks from one concentration to the other.

4.2 Electronic States in Rippled Graphene

The presence of ripples as well as wrinkles on a sheet of graphene is unavoidable due to the reasons discussed previously in sec. (3.7). They lead to the appearance of the off-plane modes which requires the modification of the hopping energies. The modification of the hopping parameters depends on the local curvature, thus by using eq. (3.79), the coupling energy $\tilde{t}$ is calculated, then Δt is found locally by subtracting t from $\tilde{t}$. The potential matrix with ripples incorporated is constructed following the same technique developed in sec. (3.5). Then the Green's function is found recursively.

In contrast to the usual approach in studying corrugation on graphene by using the Dirac Hamiltonian [76, 77, 106], this study focuses on the effect of rippling on a sheet of graphene within tight-binding formalism, as we investigate the effect of periodic ripples on the electronic state, it is assumed that the substrate is periodic along the x-axis. The ripple has a frequency ω , while the height (sometimes referred to as the amplitude) is h . The surface obey a certain sinusoidal equation which can be written in Monge's form [97], i.e.,

$$\begin{aligned} z(x, y) &= f(x, y) \\ &= h \sin(\omega x). \end{aligned} \tag{4.1}$$

The tested amplitudes are $h = 0.001$, $h = 0.01$ and $h = 0.05$ nm, where we choose h so that $h < a_o$ ($a_o = 1.42$ Å). At each amplitude the effect of four different values of ω is explored. The

rippled surfaces used for the study are plotted in fig. (4.7) where the panels (4.7(a),4.7(b),4.7(c) and 4.7(d)) shows the surface when $\omega = 0.33 \times 10^9$, 0.25×10^9 , 0.2×10^9 and $0.125 \times 10^9 \text{ m}^{-1}$ respectively.

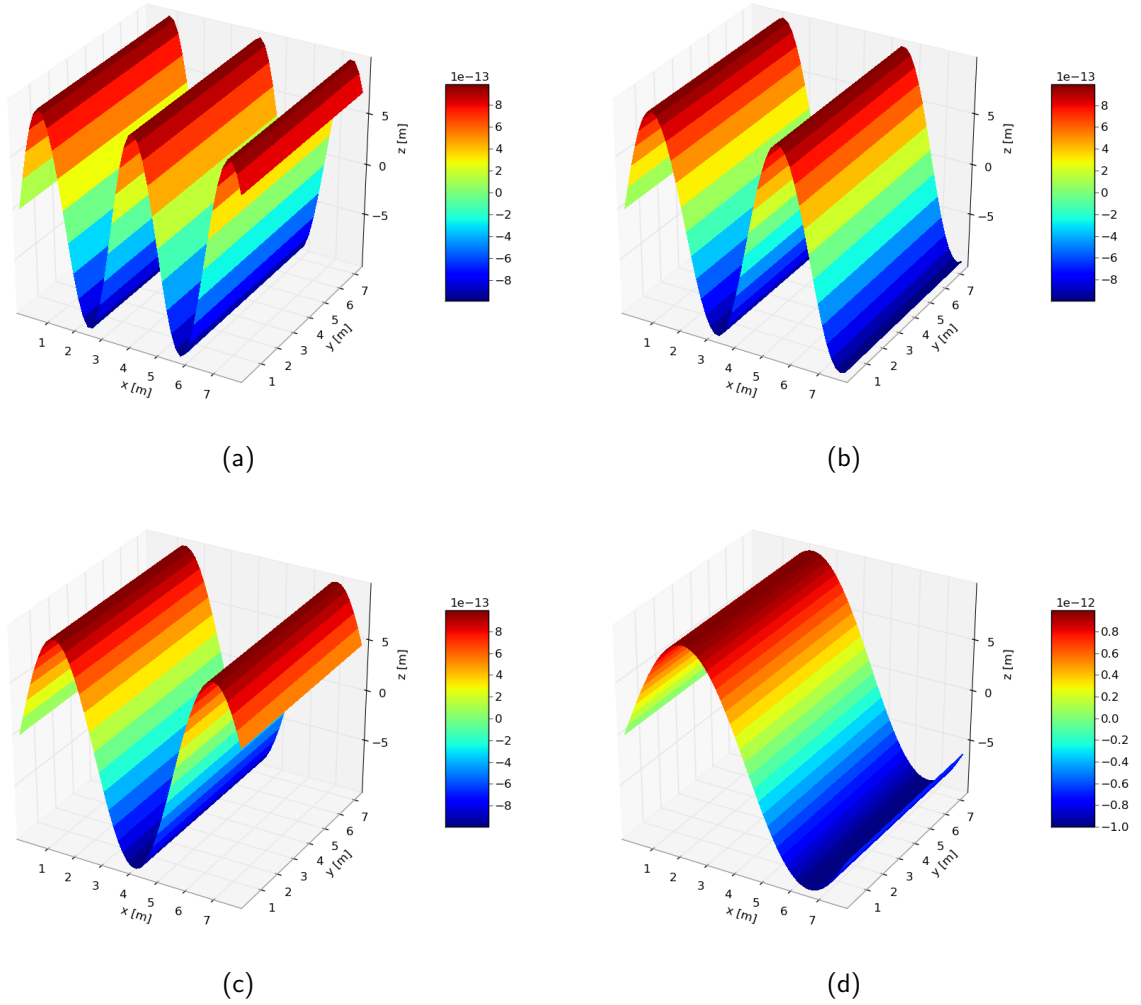


Figure 4.7: In all windows only one value for the height (amplitude) is plotted while the four different values for the frequency (ω) used to perform the calculations are shown, (a) $\omega = 0.33 \times 10^9 \text{ m}^{-1}$, (b) $\omega = 0.25 \times 10^9 \text{ m}^{-1}$, $\omega = 0.2 \times 10^9 \text{ m}^{-1}$, and $\omega = 0.125 \times 10^9 \text{ m}^{-1}$.

In fig. (4.8) The normalized DOS is plotted for all different values of ω as well as $\hbar$. It is noted that the plotted values are shifted along the y-axis by 0.1 for each value, i.e., the blue-solid line plotted at the bottom is not shifted, the red-dashed line is shifted by 0.1 from the blue, while the green-dotted line is shifted by 0.1 from the red one, so the differences can be observed.

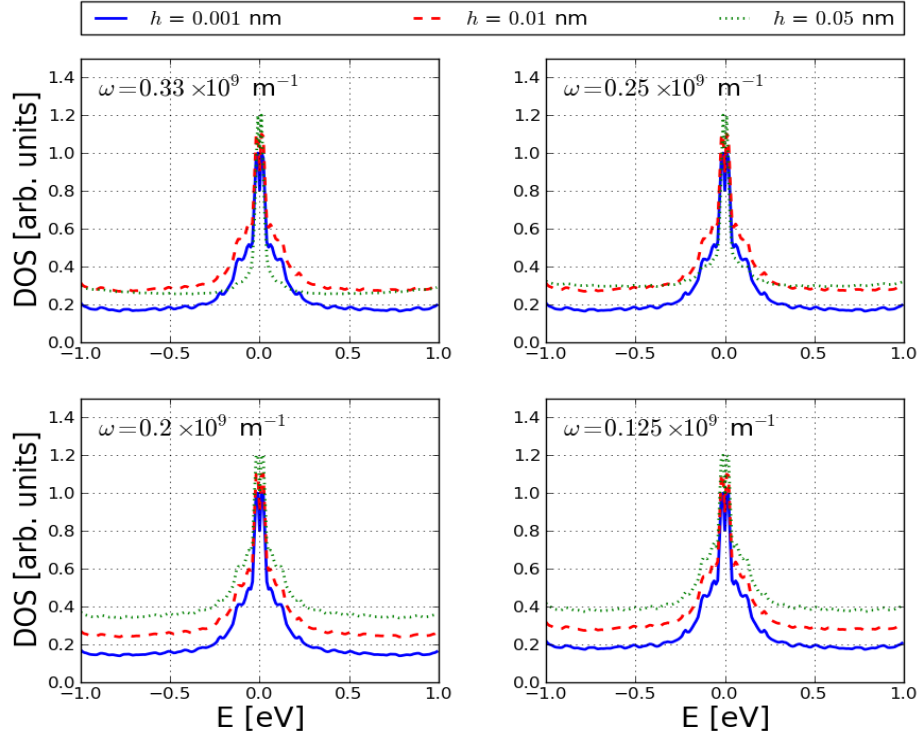


Figure 4.8: DOS at the Fermi level for rippled graphene. In each window DOS is plotted for different amplitudes at the same frequency.

The investigated density of state has shown the same behaviour with slight differences. However, the main effect of the rippling is the formation of quasi-localized states around the Fermi level as shown in fig. (4.8). Although the scatterers are absent in this case, the localized states are formed again at the Fermi energy. The same effect was found to be present when the system is subjected to an effective magnetic field which induces gauge fields that change the phase of the electrons between the two inequivalent corners in the Brillouin zone [106]. Moreover, the states at the Fermi level are of great importance due to the fact that when the effective magnetic length resulting from the gauge field induced by the ripples becomes comparable to the ripple size, Landau levels emerge in the region where the field is slowly changing [30], and that is why the change is observed only at energies close to the Fermi energy. Furthermore, the midgap states are not expected to be suppressed by presence of charged impurities associated with ripples [25].

4.3 Summary

The electronic properties in defected two-dimensional 2D carbon are studied in terms of the tight-binding Hamiltonian and the aid of recursive methods to solve the Green's functions. Two situations were considered; in the first one the vacancy is considered to be substituted in one sublattice, in the second one the situation was considered for the non-diagonal impurity where two impurity-carbon couplings are considered ($t_p = 0.1t$ and $0.9t$). To overcome the effect of the position dependence of the calculated DOS, it was averaged over five arbitrary configurations.

It was found that for the vacancies quasi-localized states form at the Fermi energy. This is found to be similar to what was reported in ref. [60] where lower concentrations were assumed. The nature of those states was confirmed to be localized by imposing reflecting boundary conditions on the propagator, and the DOS did not show any drastic changes. It was also found that increasing the vacancies concentrations increases the number of states as expected when considering the rank-nullity theorem in linear algebra [60]. The breaking of the particle-hole symmetry in the electronic states was found to shift the electronic states along the energy axis by an amount approximately equal to t' which was also proven to exist using the rigid band theorem [107]. Moreover, it causes the quasi-localized states to split forming more of them around the main peak located at $E \sim t'$, which weakens the localization, our findings are similar to those in ref. [60, 108]. The property of the localization in this case was also confirmed by forcing the boundaries to satisfy reflecting boundaries. It is worth noting that our findings can be reliable in explaining some of the experimentally-observed magnetism induced by vacancies at relatively high concentrations [58, 59] and also proven to exist using *ab initio* calculations [109, 110].

The substitution of a charged (particle) was found to suppress the localized state created by the presence of vacancies, but at high impurity concentrations, new extended states form around the Fermi level. Moreover, in comparing our results with those reported in ref. [60], it is necessary to note that in the previous work the on-site potential of the impurity is considered to be zero, thus no localized states are formed at the Fermi energy. However, for a carbon-impurity coupling close to the values tested in this thesis, the DOS showed similar peaks at the vicinity of the Fermi energy. In ref. [108] the DOS was calculated to a system of impurities similar to ours, they showed that at high concentrations new states emerge around $E = 0$ eV. In addition to

this, the sharpness and the number of the states is proportional to the concentration as well as the coupling strength between the impurity and the carbon atoms. The effect of the particle-hole symmetry is found to be the same as in the case of the vacancy with noting that the states are extended. Thus it is predictable that such states enhance the transport properties rather than effecting them negatively.

The ripples are present on the suspended graphene as well as the ones on a substrate. In the study performed, it is assumed that the surface of graphene has periodic ripples with frequency ω and amplitude h , which is small compared to the lattice constant a_o . The effect of the ripples on the graphene electronic states has been studied within Dirac Hamiltonian, but we try to provide a different perspective using the tight-binding formalism, which requires the change of the hopping energies according to local curvature. It was found that the ripples have the same effect as an applied magnetic field since it results in midgap, Landau levels localized at the Fermi level. Thus it is noted that the effective magnetic length of the electrons is comparable to the ripple size [106].

5. Electronic Transport in Defective Graphene

Graphene has shown interesting properties in the mesoscopic regime as indicated in chapter (3) and the references therein. The transport has different characteristic depending on many factors, for instance, the direction in which the transport is considered yields different properties (whether zigzag direction or armchair). Moreover, they are extremely sensitive to the change of boundary conditions as well as the way the leads are attached to the sample.

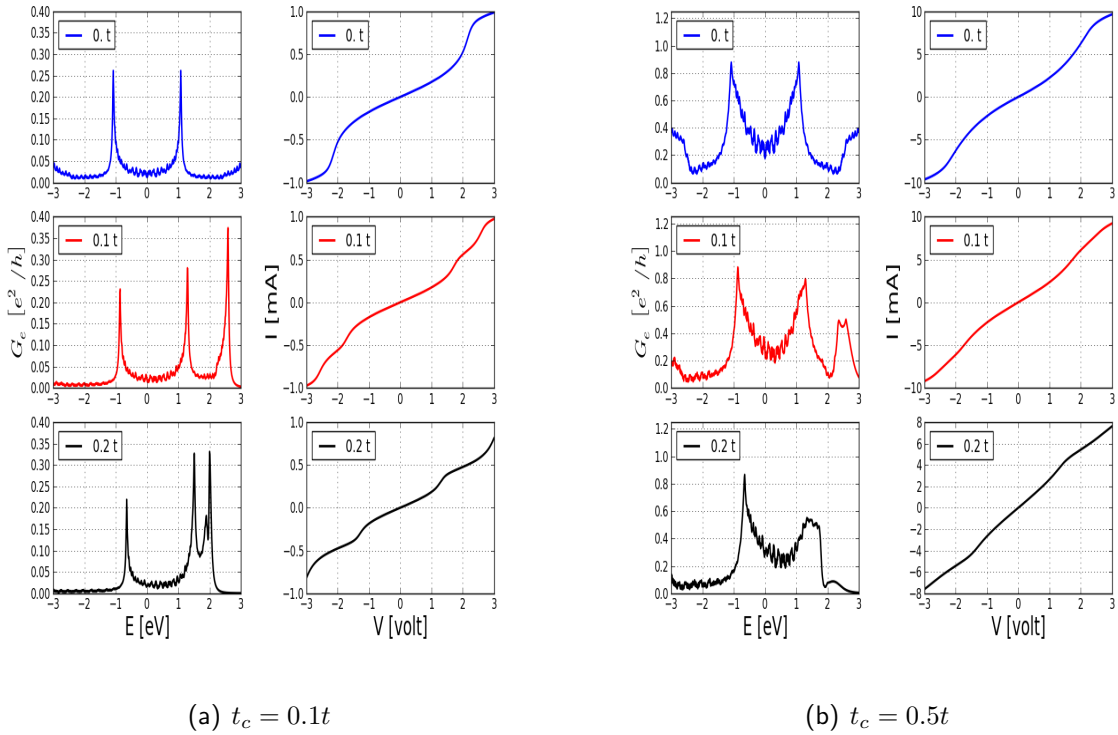


Figure 5.1: Conductances as well as current for an ideal sheet of graphene for the cases where second nearest hopping is allowed, (a) the topmost figure is the conductance (left panels) in units of $\frac{e^2}{h}$ for the case $t' = 0$ while the current is to the right. The panel in the middle is the case where $t' = 0.1t$ and the bottom one is $t' = 0.2t$. The sample-lead coupling is $0.1t$. (b) The same functions plotted in (a) are plotted again for sample-lead coupling $0.5t$.

In the model adapted, the transport is studied along only one direction (armchair) where hard wall boundary conditions are implemented in a direction perpendicular to the transport direction. The leads are assumed to be perfect (no presence of defects) and they are infinite. They are modelled using the approach described in sec. (3.8) where they are replaced by self-energies given in terms of effective coupling t_c as in eq. (3.110). The conductances are calculated using eq. (3.114) which is basically the transmission coefficients, so it has to be multiplied by $\frac{e^2}{h}$. The equilibrium currents are calculated within the Landauer-Büttiker formula [99] as given in eq. (3.116). The effective coupling constant between the leads and the sample t_c is considered to be $t_c = 0.1t$ and $t_c = 0.5t$.

The sections are organised as follows: a brief description of the case of the ideal graphene is reported first, then the case of the vacancy is discussed and followed by the situation of the substitutional impurity. Finally, the effect of ripples on graphene is studied briefly.

For the weak sample-leads coupling ($t_c = 0.1t$), the conductance is found to be non-vanishing (even for $t_c = 0.5t$) at the Fermi energy (which means the energy gap is zero), then it increases slowly for low energies. At $E = \pm 1$ eV and $t' = 0$ it has two sharp, symmetrical peaks with intensities 0.3 in units of $\frac{e^2}{h}$. When the second nearest hopping energy is changed to $0.1t$, the position of the resonance peaks is shifted to the right along the energy axis with amount approximately equal to t' (~ -0.3 eV). Generally it behaves in a similar manner as the DOS does (see chapter (4)), for instance, the conductance loses its symmetric nature around the Fermi energy which originates from the breaking of the particle-hole symmetry. In fig. (5.1(a)), the positions of the peaks is shifted by $E \sim 0.3$ eV which equals approximately t' . Moreover, a new resonant peak appears at $E \sim 3$ eV indicating the development of Lifshitz tails at the band edge associated with increase of disorder [60] due to the overlap of the wavefunctions between the second nearest neighbour carbon atoms. For $t' = 0.2t$, the main peak is displaced to a position $E \sim 1.5$ eV which is approximately equal to t' . Also a resonant peak is observed at $E \sim 2$ eV. This means when the second nearest neighbour coupling increases the peaks tend to merge in one peak, which is also observed in the DOS [5].

When the sample-leads coupling is high ($t_c = 0.5t$) the broadening of the resonant peaks in the conductance is observed for all cases. The reason behind this is that for an ideal system the

states are discrete (represented by delta functions), which means that the lifetime of an electron in those states is infinite. When the system is coupled to leads the levels become broader, so they start to overlap with each other, and hence they are not discrete. As a consequence, the lifetime of the electron in a specific level becomes shorter [99]. The broadening of the states depends on the strength of the coupling, i.e., the stronger the coupling the more the states are broadened, which indeed enhances the transport. However, in fig. (5.1(b)), it is observed that the conductance increases faster at low energies than it does in fig. (5.1(a)). At $t' = 0$, the conductance has the same resonance peaks (shown in the top panel of fig. (5.1(b))) located at $E = \pm 1$ eV but with higher intensity (~ 0.9 in units of $\frac{e^2}{h}$ compared to 0.3 in fig. (5.1(a))). When the second nearest neighbour interaction is turned on, the conductance peaks are displaced along the energy axis as in the situation discussed above. It is noted that when $t' = 0.1t$, the peak observed at $E \sim 3$ eV in the middle panel of fig. (5.1(a)) is also observed in fig. (5.1(b)) with a comparable height since it is only associated with second nearest neighbour hopping, but it is broader. As the second nearest hopping energy t' reaches $0.2t$, the peaks at energies ~ 1.5 eV and 2 eV are merged into one peak as shown in the bottom panel of fig. (5.1(b)). In contrast to the situation where $t' = 0.1t$, the resonance associated with second nearest neighbour hopping is also present here, but since it appears at energy close enough to the shifted peak (at $E \sim 1.5$ eV) it gets merged with it. Its effect is clear in suppressing the peak to a value of approximately 0.5 in units of $\frac{e^2}{h}$ rather than 0.9. This has its origin from the superposition of two Lorentzian peaks into one broader peak.

Generally, the equilibrium currents have shown linearity. It is shown in the top-right window of fig. (5.1(a)) as well as (5.1(b)) that the current is linear for low bias (V) with a sudden jump at $V \sim 2$ eV, which means at this bias the chemical potential in the leads coincides with one of the resonant states ($E = 1$ eV in this case). Comparing the sharpness of those jumps in the current, it is noticed that it is smoother for $t_c = 0.5t$ (see fig. (5.1(b))) which is a reflection of the broadening of the energy states.

For non-zero second nearest hopping energies, the same trend is observed in addition to symmetric jumps for both the negative and the positive bias. To understand this further, in the second-left window in fig. (5.1(a)), a little jump is observed at bias approximately equal to 1.6 eV, and it

corresponds to the resonance peak observed at energy 0.8 eV, and the same argument holds for the rest of the results. But it is noted that the jumps are smoothed out because of the broadening of the electronic states.

5.1 Disordered Graphene

A sheet of graphene with defects (described in sec (3.6)) is assumed to be sandwiched between two infinite, perfect leads coupled to it by an effective coupling t_c as described previously. The defects considered here are the vacancies as well as the impurities.

5.1.1 Vacancies

The effect of the vacancy in the density of states is seen by the presence of the quasi-localized states at the Fermi level as reported in chapter (4). Thus, it is not expected to see any resonance in the conductance since localized states do not contribute to the transport, in fact they affect the transport negatively while resonant states have a greater effect on transport.

Particle-Hole Symmetry

As can be seen in fig. (5.2(a) and 5.2(c)), the conductance differs from the conductance in fig. (5.1) by the asymmetry present in addition to the suppression of the relatively high value achieved in the case of the ideal sheet of graphene, see fig. (5.1). This is caused by the scattering induced by the presence of the vacancy potential in the lattice, so, as the concentration of the vacancies increases, the probability of multiple scattering processes increases as well, therefore, the conductance decreases as shown in the panels of fig. (5.2(a)). Moreover, the conductance at $E = 0$ eV for low vacancy concentration (3.125 %) has a non-zero value (see the top-right panel of fig. (5.2(a)) and (5.2(c))) which is also observed in the case of ideal graphene, while it is zero at the same energy for higher concentrations (which indicates the formation of disorder-induced energy gap), see fig. (5.1(a) and 5.1(b)).

The increase of the coupling energy between the leads and the sample results in the broadening

of the energy levels [99], thus, instead of observing a sharp peak at a certain energy one observes a broader peak. The sharp peak becomes wider and has a high intensity since the electron can propagate between the states easily and the lifetime is shorter than the case where the coupling parameter is relatively low, see the conductance shown in fig. (5.2(c)).

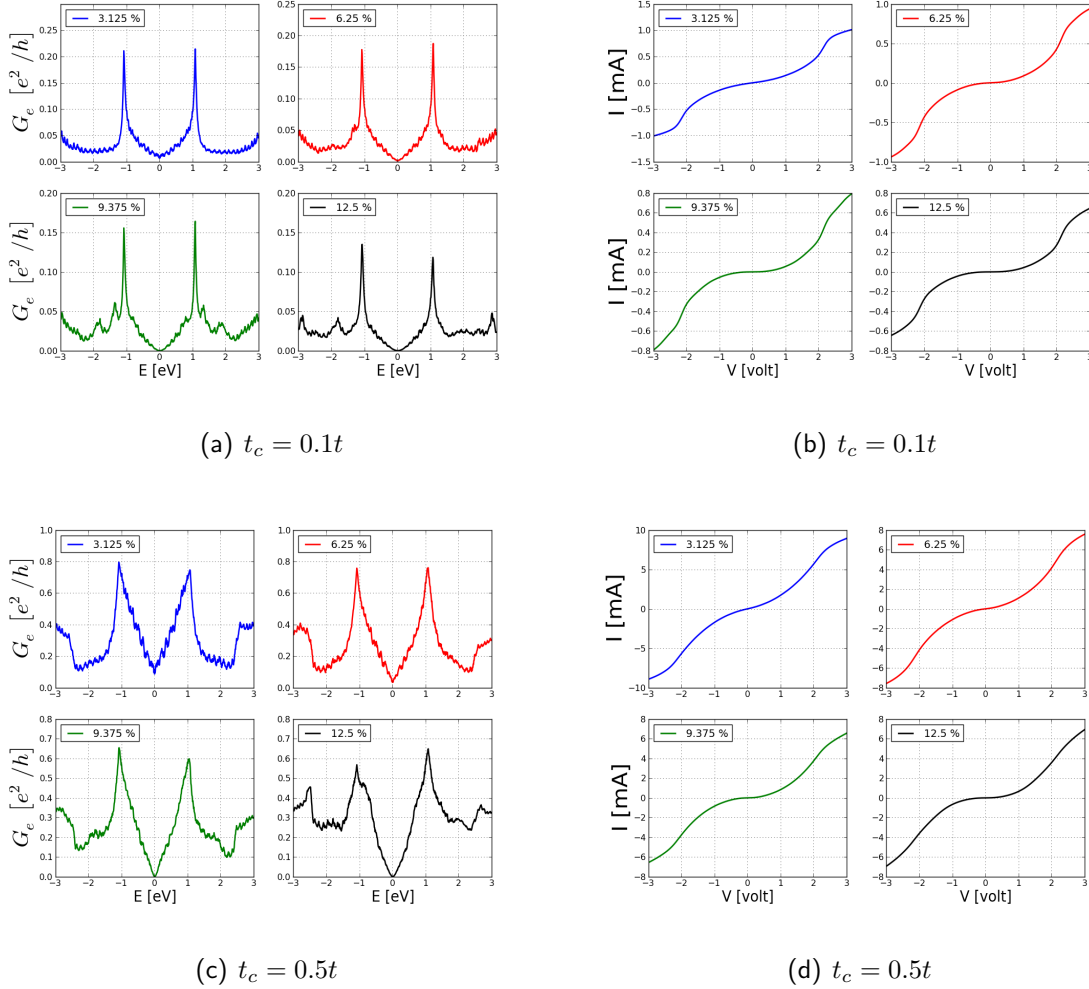


Figure 5.2: The conductances and the corresponding current-voltage characteristics for different vacancy concentration.

The behaviour of the equilibrium current observed in figs. (5.2(b) and 5.2(d)) is the same as in fig. (5.1); in general, it is linear. However, it can be noticed that for low bias, and high vacancy concentration (6.25 % to 12.5 %), the system shows more resistance and the current tends to an exponential function (fig. (5.1)), while it is linear in the low concentration regime as shown

in the top-right panels of figs. (5.2(b) and 5.2(d)).

The behaviour observed for exponential currents can be understood in terms of the corresponding conductances. For instance, at low concentrations (3.125 %) the conductance has a non-zero value at zero energy, hence the resistance which is inversely proportional to the conductance is not extremely large, and it is even smaller in the situation where $t_c = 0.5t$. At high concentrations the conductance is zero at $E = 0$ eV, hence the resistance tends to infinity, therefore, the current is suppressed exponentially.

Particle-Hole Symmetry Breaking

The disturbance of the particle-hole symmetry by setting the second nearest neighbour hopping energy t' to a non-zero value will result in the usual effect of displacing the resonance peaks along the energy axis by an amount close to t' . Furthermore, it results in new resonances at energies close to 3 eV (figs. (5.3(a) and 5.3(c))) as discussed in the previous section. The intensity of the peaks is found to be reduced as the concentration increases, which supports our previous argument about the scattering processes causing the amplitude of conductance peaks to decrease with the increase of vacancies. However the effect is more pronounced on peaks located at high, positive energies as seen clearly in figs. (5.3(d), 5.4(a) and 5.4(c)). It is important to note that the conductance depends on the configuration of the vacancies, so the reported values are averaged over five arbitrary configurations.

The current has shown behaviour similar to the features discussed above when the particle-hole symmetry is not broken. But it is important to stress that at low bias the current is linear when the corresponding conductance is non-vanishing at low energies, while it is exponential when the corresponding conductance is zero or approaching zero at the Fermi energy. In other words, the system tends to show more resistance at low bias when the conductance is zero at the Fermi energy, while it is less resisting for non-zero conductances, see figs (5.3 and 5.4).

The increase of the sample-lead coupling also leads to the increase of the current produced; when the coupling energy increases from $0.1t$ to $0.5t$ the current is enhanced by approximately a factor of 10 as it can be seen in figs. (5.3(b)-5.3(d) and 5.4(b)-5.4(d)).

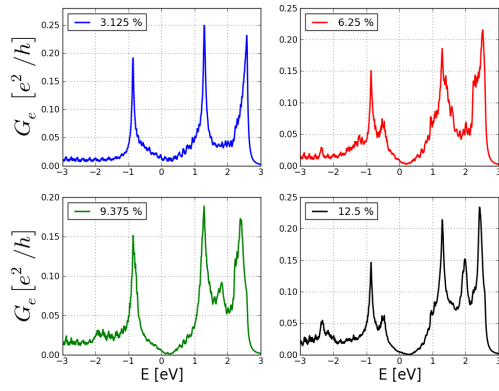
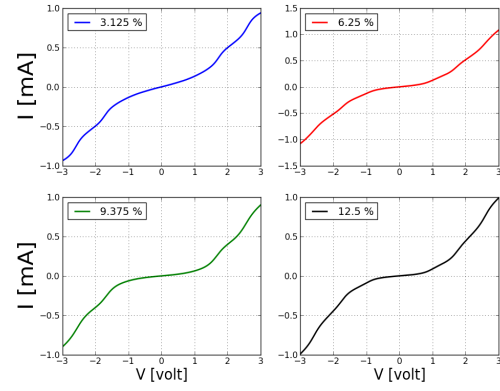
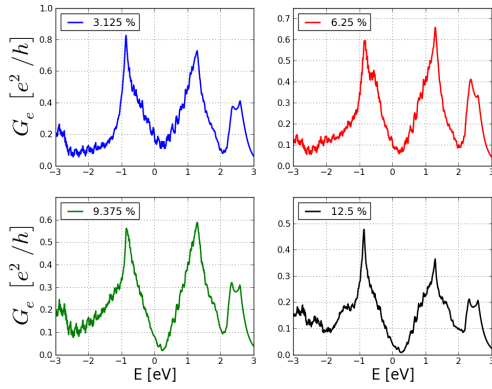
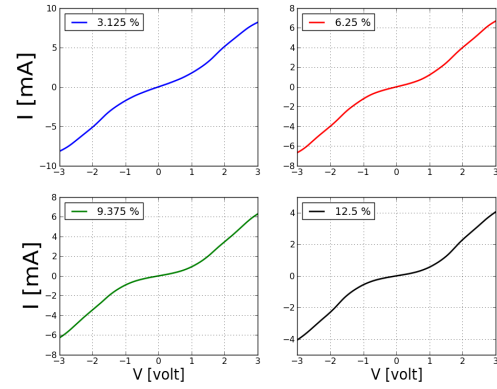
(a) $t_c = 0.1t$ (b) $t_c = 0.1t$ (c) $t_c = 0.5t$ (d) $t_c = 0.5t$

Figure 5.3: G_e and the corresponding currents when $t' = 0.1t$, where each window represents different concentration of vacancies.

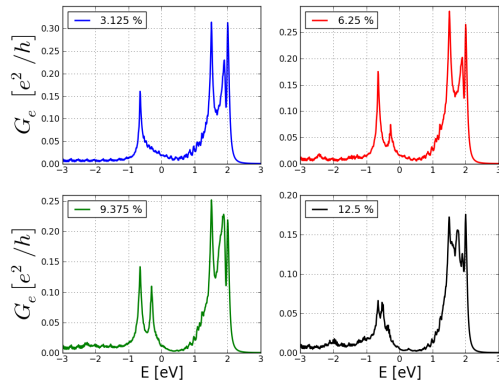
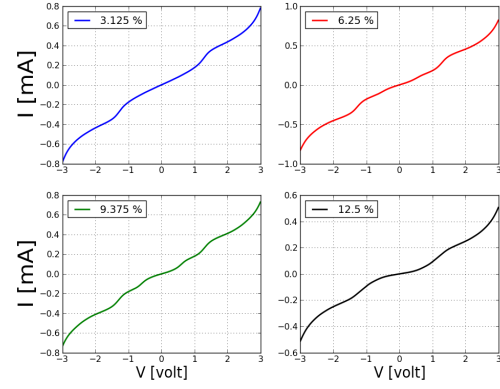
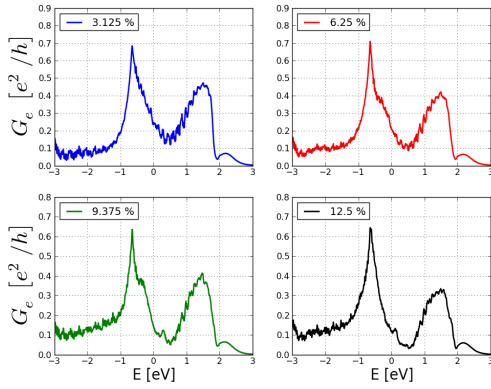
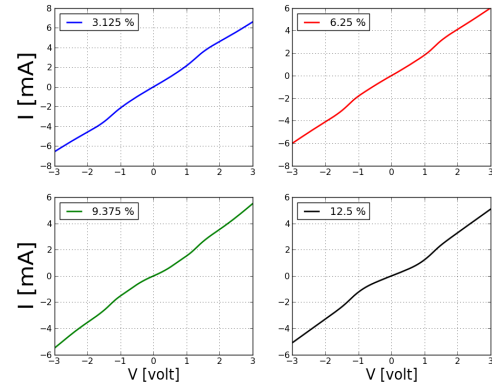
(a) $t_c = 0.1t$ (b) $t_c = 0.1t$ (c) $t_c = 0.5t$ (d) $t_c = 0.5t$

Figure 5.4: The conductances in the units of $\frac{e^2}{h}$ as well as the corresponding currents for different vacancy concentrations. The second nearest neighbour coupling t' is $0.2t$.

5.1.2 Impurities

The impurity is the substitution of a foreign atom in the location of one of the lattice sites as discussed in sec. (3.6.2) where its orbitals have to overlap with those of the nearest neighbour atoms. In the cases investigated here, the impurity has local potential $V_p = -2.5$ eV which is the potential induced by the presence of nitrogen atoms in the carbon-based structure [105]. It is coupled to the nearest carbon atoms with coupling energies t_p equal to $0.1t$ and $0.9t$ where the first is considered as a low value while the latter is the high (extreme) value. The importance of the study of impurities originates from the fact that the surface of graphene can adsorb several species, but nitrogenated graphene has shown interesting physical as well as chemical properties, (see sec. (2.2) and the references therein), hence modelling the problem will shed light on many of the measured properties from theoretical aspects.

However, The impurity in general results in resonance peaks [60] depending on the concentration as well as the coupling energy. In this section we report the effect of the impurity on the transport properties where the sample is attached to the leads with coupling energy taken to be $0.1t$ in one case and $0.5t$ in the other one.

Particle-Hole Symmetry

As the vacancy is replaced by an impurity, the electrons can then tunnel through the potential barrier caused by the impurity. On the other hand, resonant states show up at the vicinity of the Fermi energy, which enhances the conductance of the system. The number of those peaks in the conductance depends on the concentration of the impurities as well as the coupling between the impurity and its nearest neighbours.

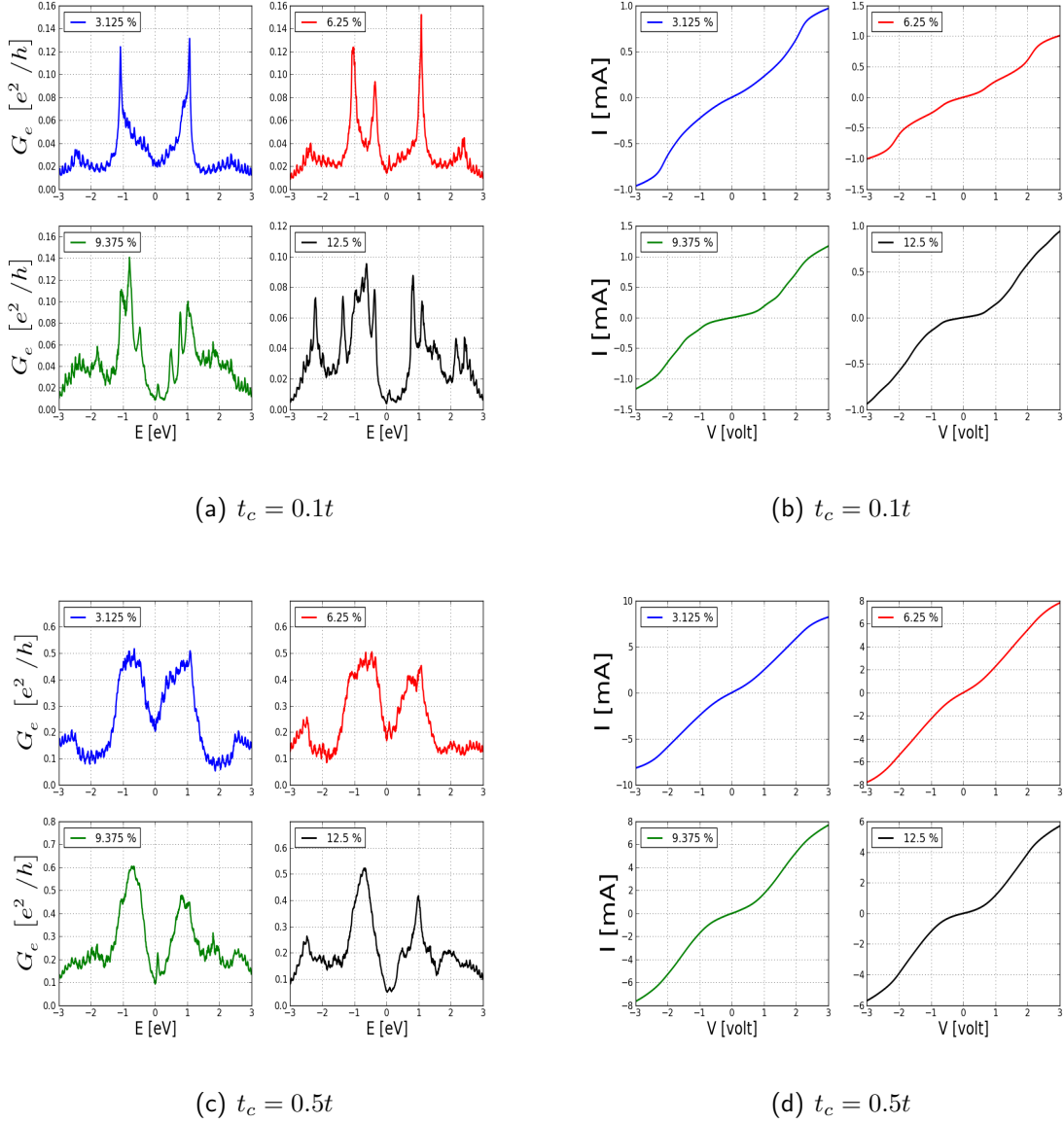


Figure 5.5: The conductance and the current for a sample with impurities coupled to the nearest neighbour carbon atoms with coupling energy equal to $0.1t$, and different concentrations.

For instance, the conductance for low concentrations (3.125 % and 6.25 %) shown in fig. (5.5(a)) has a non-vanishing conductance at $E = 0$ eV, and one resonant peak at energy $E \sim -0.3$ eV for concentration 6.25 %. As the concentration is increased to 9.375 % and 12.5 %, the conductance at the Fermi level becomes zero, but the amplitude of the resonance peak remains the same when compared with those of low concentration as seen in the bottom panel of fig. (5.5(a)).

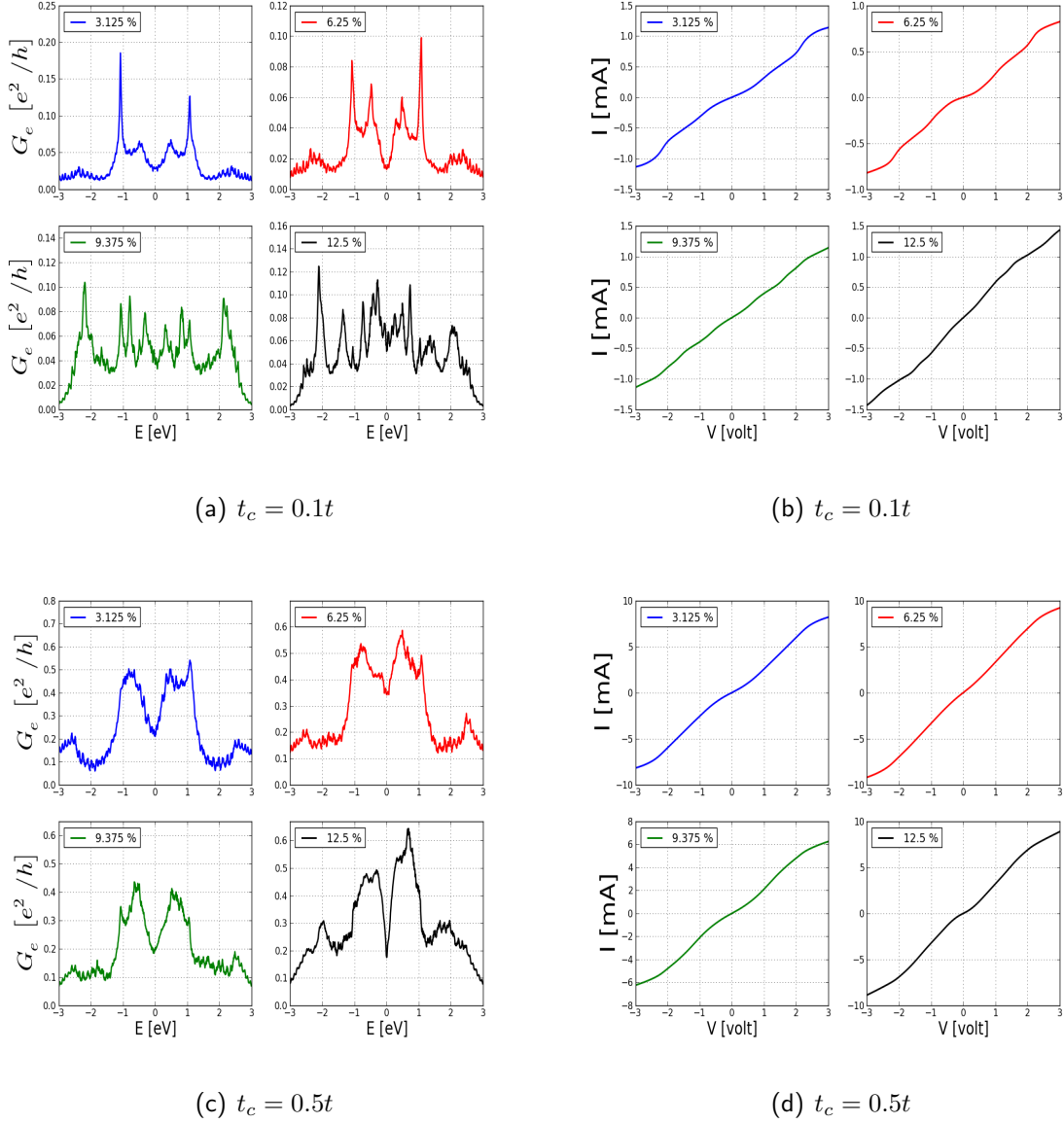


Figure 5.6: The conductance in units of $\frac{e^2}{h}$ and the corresponding current-voltage characteristics. The impurities-carbon coupling $t_p = 0.9t$.

When the coupling energy increases to $0.9t$, the conductance at low concentration does not show that much of a change (see the top panels of fig. (5.6(a))) but at high concentration, new resonances emerge at the vicinity of the Fermi level which has a remarkable influence on the transport properties. When the sample-lead coupling is increased, the levels overlap and hence for resonances occurring in a narrow range of energies get absorbed in one large peak as shown

in figs. (5.5(c) and 5.6(c)).

In conclusion, a quick comparison between the influence of vacancies and the impurities shows a remarkable enhancement in the conductance when the impurity is substituted.

Particle-Hole Symmetry Breaking

The main observation when the particle-hole symmetry is broken is the asymmetric conductance as shown in figs. (5.7(a), 5.9(a), 5.8(a) and 5.10(a)). When the lead sample coupling is increased, all the peaks get absorbed into the two main peaks centred around $E = \pm 1$ eV due to the effect of the level broadening as in all the cases discussed previously.

The current obtained in this case is also similar to the current obtained previously when the vacancy is considered. The current-voltage characteristics do not change drastically. In addition to this the current has a step-like change when the bias multiplied by the electron charge is approximately as twice as the resonance energy in the corresponding conductance. However, when the electron is allowed to hop to the next nearest neighbour the current loses this feature. As the coupling between the sample and the lead is increased, the current value increases by approximately one order of magnitude, and tends to be more linear as shown in figs. (5.7(d) - 5.10(d)).

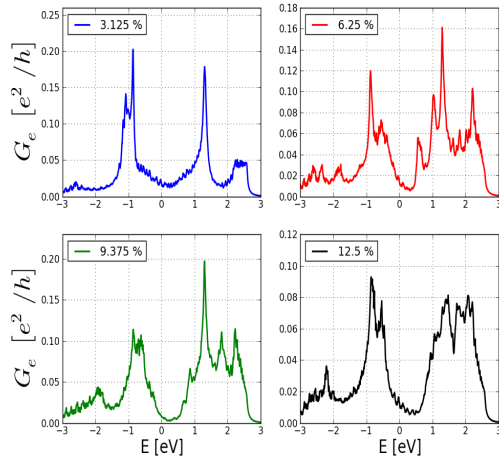
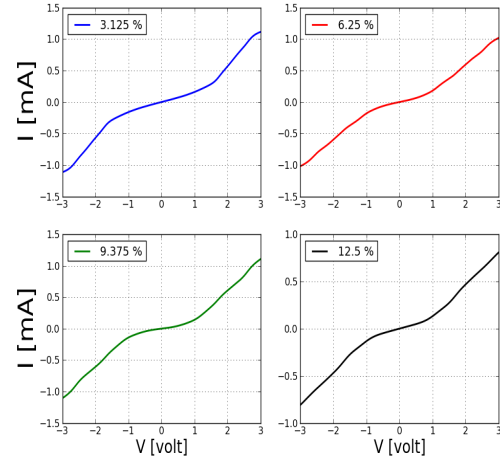
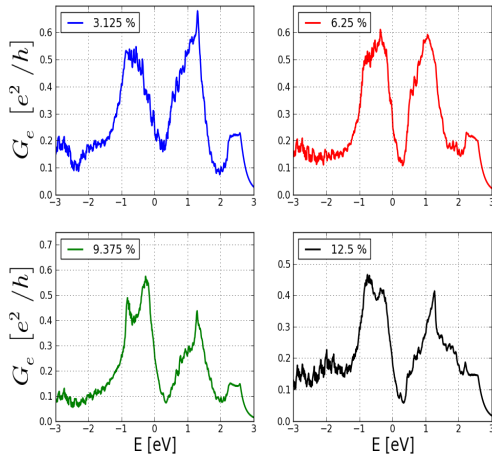
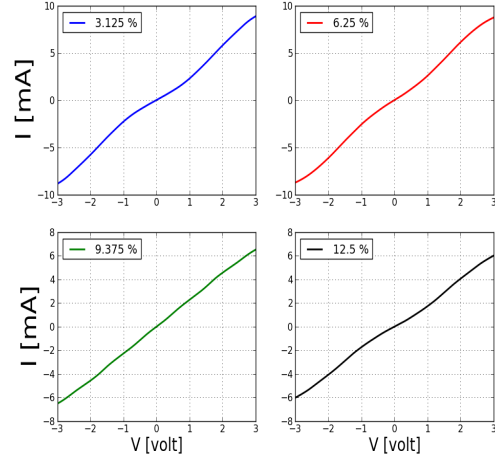
(a) $t_c = 0.1t$ (b) $t_c = 0.1t$ (c) $t_c = 0.5t$ (d) $t_c = 0.5t$

Figure 5.7: G_e and the corresponding currents for a sample with different impurity concentrations coupled to the nearest carbon atoms by $t_p = 0.1t$. The second nearest neighbours hopping energy $t' = 0.1t$.

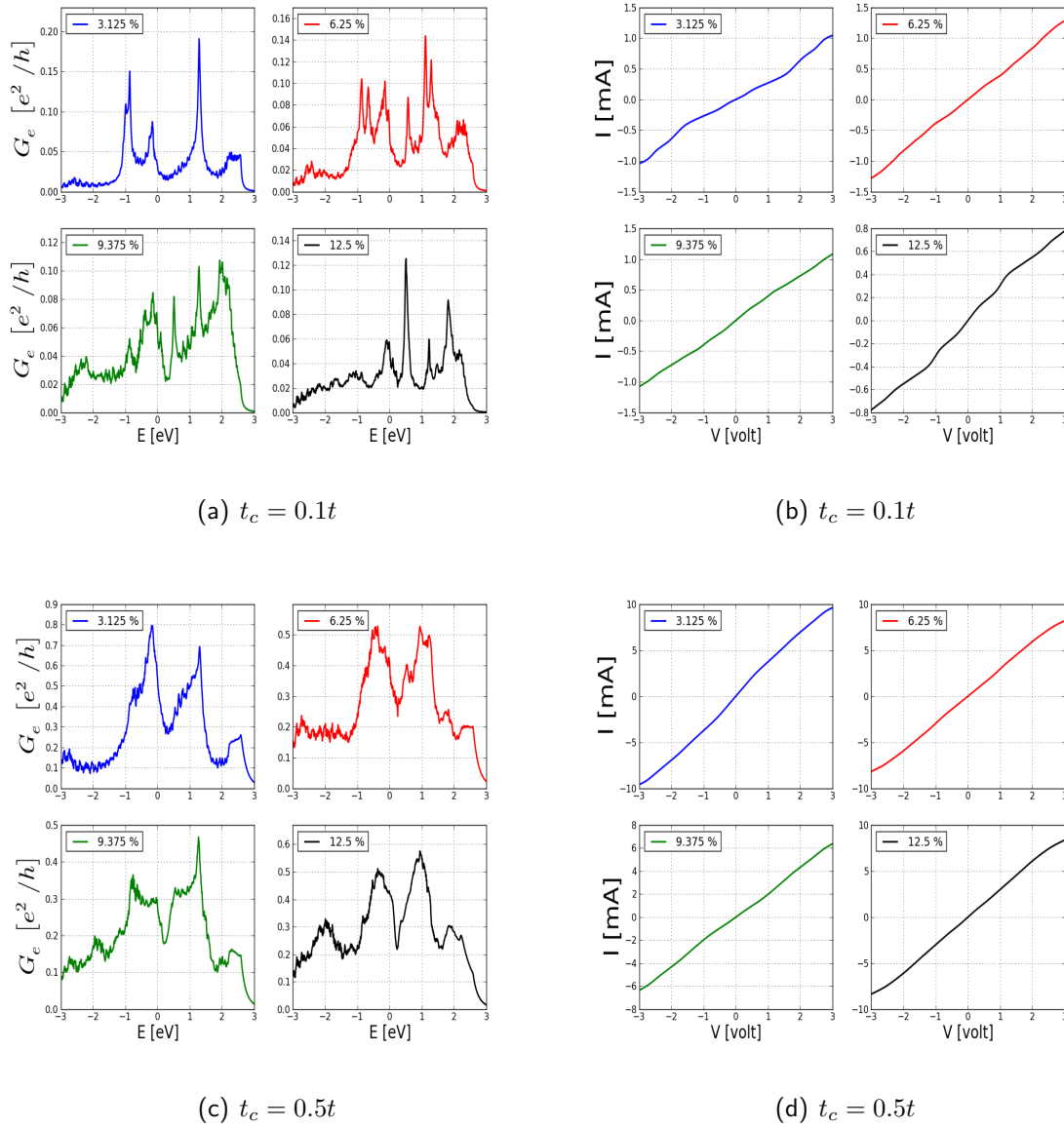


Figure 5.8: The conductance and the corresponding currents for a sample with impurities (different concentrations) coupled to the nearest carbon atoms with $t_p = 0.9t$. The second nearest neighbour coupling $t' = 0.1t$.

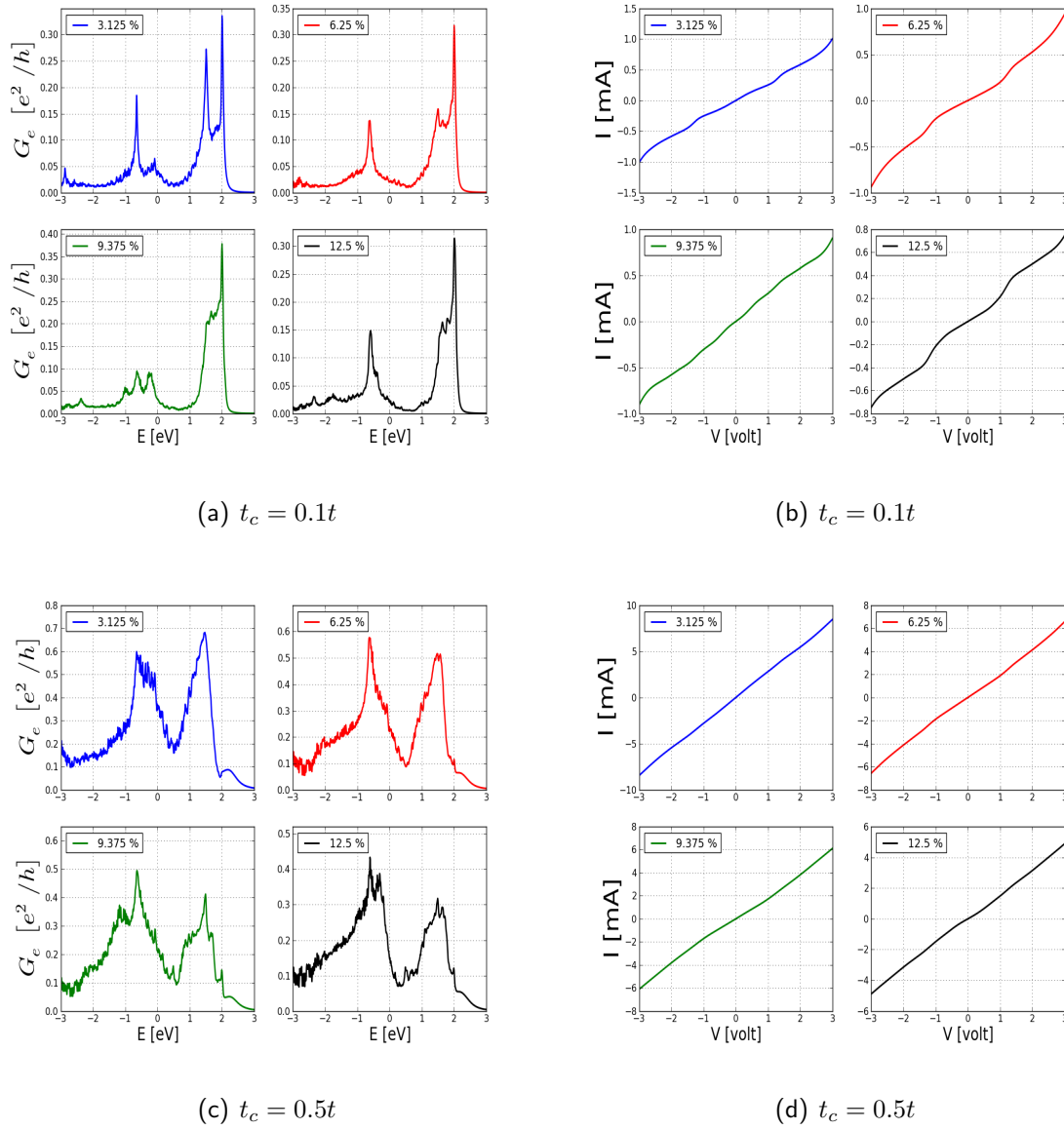


Figure 5.9: The conductance as well as the corresponding current different impurity concentrations incorporated in graphene. The impurity-carbon coupling is $0.1t$ while the second nearest hopping energy is $t' = 0.1t$.

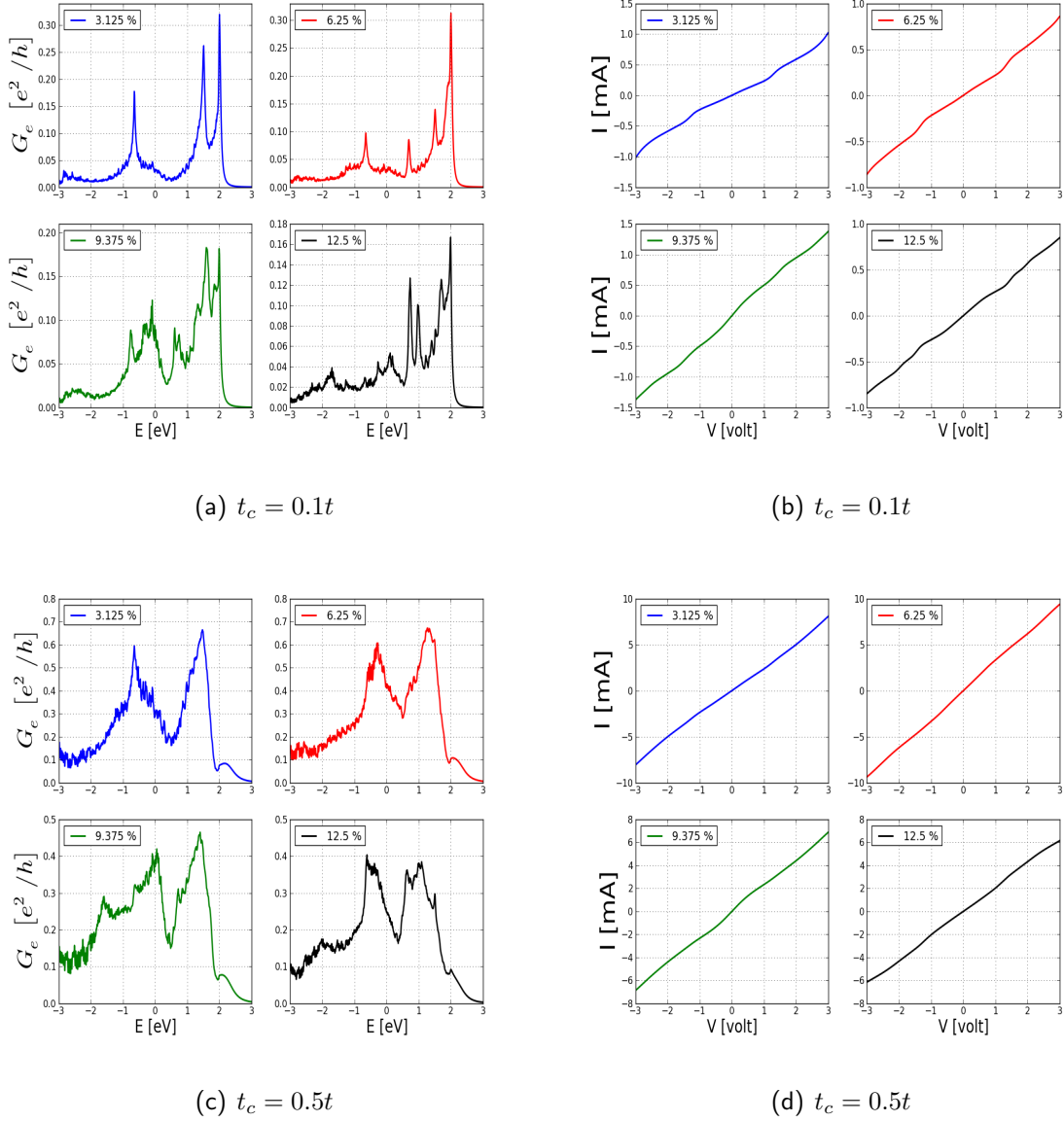


Figure 5.10: The conductance in units of $\frac{e^2}{h}$ and the corresponding current for impurities (different concentrations) coupled to the nearest carbon atoms with $t_p = 0.9t$. The second nearest neighbour coupling $t' = 0.2t$.

5.2 Transport in Rippled Graphene

The presence of corrugations in a sheet of graphene is unavoidable and it is of great interest since it creates localized Landau levels at zero energy as discussed in chapter (4). It is noted that the rippled sheet of graphene is assumed to be attached to perfect, semi-infinite leads with

effective coupling t_c . The ripples are assumed to have frequency, ω , and height h where the values considered are the same as those used in sec. (4.2). The conductance is modelled in terms of a tight-binding formalism whereas previous studies have modelled it with the Dirac Hamiltonian for low energies only [77, 76, 75, 106].

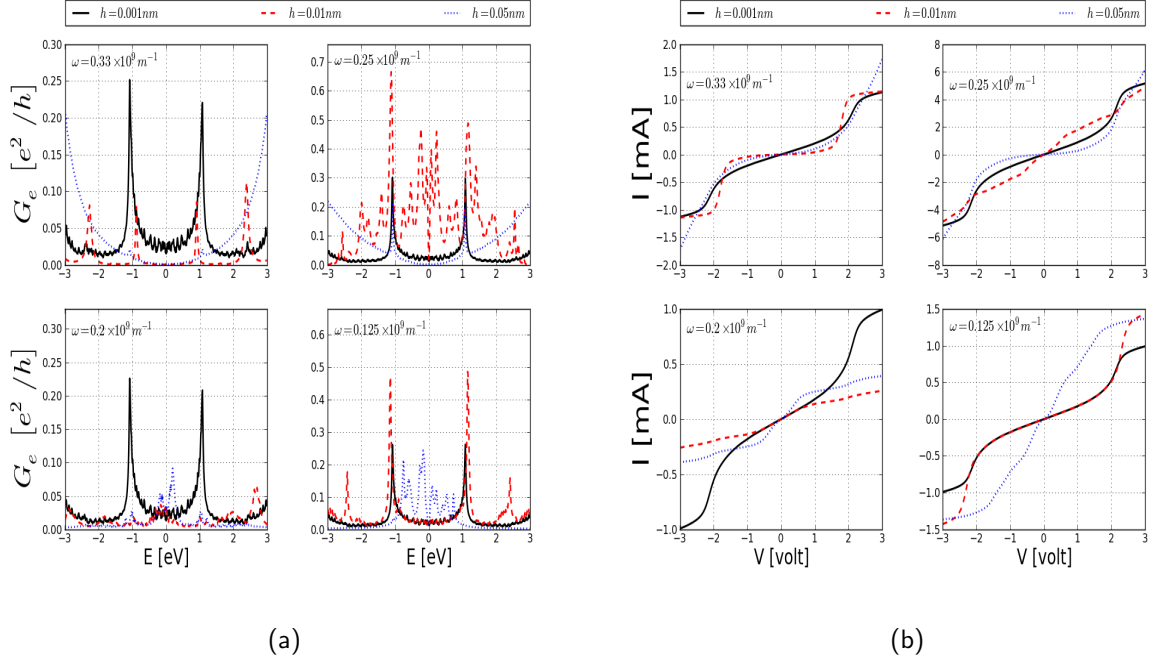


Figure 5.11: G_e in units of $\frac{e^2}{h}$ and the corresponding current-voltage characteristics for a rippled sheet of graphene when $t_c = 0.1t$. In each window the conductance is plotted in linear scale for a specific frequency and different heights as indicated in the labels. (a) In the top-left and right windows the conductance corresponding to $h = 0.05$ nm (blue-dotted line) is scaled up by a factor of 10^6 . The bottom-left window, the blue-dotted line ($h = 0.05$ nm) is scaled up 10 times. (b) The current corresponding to $h = 0.05$ nm (blue-dotted line) in the top panels is multiplied by 10^7 . In the top-left window the current corresponding to $h = 0.01$ nm (red-dashed line) is scaled up 10 times while the black solid line in the top-right panel ($h = 0.001$ nm) is scaled up 5 times. The current corresponding to $h = 0.05$ nm is scaled up by a factor of 10.

Two scenarios are considered in the study, so one can gain some understanding of the transport properties under extreme conditions. The first scenario assumes the presence of ripples only on ideal graphene, while the second accounts for the presence of vacancies on the rippled graphene. Breaking particle-hole symmetry and non-diagonal impurities are not considered in this study.

In figs. (5.11(a)) the conductance (G_e) is plotted as a function of energy E . Each panel corresponds to a situation where a different frequency (ω) is considered as indicated in the figure. For ripple amplitude $h = 0.001$ nm the conductance is comparable to ideal graphene shown in the top-left window of fig. (5.1(a)) in terms of the presence of two symmetric peaks at $E \sim 1$ eV and a non-vanishing conductance at $E = 0$ eV. The reason for this is that the amplitude is small compared to the lattice spacing ($a_o = 1.42$ Å) so the overlap between the π and σ orbitals of neighbouring atoms in such a configuration is weak and the electrons do not feel a significant change in the hopping energies. As the ripple height increases to $h = 0.01$ nm, the conductance becomes very sensitive to any change in frequency. In the top-right window of fig. (5.1(a)) for $\omega = 0.25 \times 10^9$ m⁻¹, resonant states are observed in the vicinity of the Fermi energy which indicates that the ripples act as potential barriers with height proportional to the height of the ripple and width proportional to the frequency which results in effective resonant states. In the bottom-left panel of the same figure where $\omega = 0.2 \times 10^9$ m⁻¹, suppression of the conductance occurs due to the formation of a wide barrier which causes the electronic wavefunction to decay rapidly. As the frequency decreases, the height becomes insignificant, as can be seen in the bottom-right window of fig. (5.1(a)) where the extreme rippling has completely suppressed the conductance. On the other hand, at low frequencies weak resonances appear at low energies.

The equilibrium current for $\omega = 0.33 \times 10^9$ m⁻¹ shows that for a high ripple amplitude the system is insulating (the current corresponding to $h = 0.05$ nm shown in the top-right window of fig. (5.11(b)) is scaled up by a factor of 10^7 , and the one for $h = 0.01$ nm is multiplied by 10 in order to be able to observe the features), while it is semi-metallic for low amplitude ($h = 0.001$ nm). In general, due to the change in the ripple parameters (amplitude and frequency), and consequently the conductance, the current-voltage characteristics change as well. Thus the current for high amplitudes and frequencies shows that the system is insulating and the corresponding currents are small (see the caption of fig. (5.11(b)) for scaling factors). However, as the frequency tends to have small values, the system becomes semiconducting as can be seen in the bottom-right panel of fig. (5.11(b)).

5.2.1 Vacancies on Rippled Graphene

The vacancy as an additional source of defects contributes to the gap opening at the Fermi level as well as the absence of symmetry in the conductance peaks at $E \sim 1$ eV, which is also observed clearly in fig. (5.12(a)) for low sample-lead coupling. As the ripple height increases, the rippling dominates the transport. In fig. (5.13(a)) when the amplitude is $h = 0.01$ nm, the conductance exhibits resonant states at high energy ($E \sim 3$ eV), see top-left panel of the figure. As the frequency decreases ($\omega = 0.25 \times 10^9$ m⁻¹ - see the top-right panel) these resonances shift toward low energies. These states are associated with the ripples and they change due to any change in the height or the amplitudes. They are produced due to interference effects between the waves transmitted and those reflected from the quantum barriers formed by the ripples. A similar situation where resonant states are formed due to interference effects is reported in a system of graphene quantum dots [111]. On the other hand increasing t_c from $0.1t$ to $0.5t$ results in a broader peaks as discussed in the previous section, see fig. (5.12(c)). Moreover, resonant states associated with ripples merge into one peak (figs. (5.13(c)) and (5.14(c))) where the most prominent feature in this case is the presence of asymmetry in the conductance peak, which induces charge inhomogeneity as suggested previously [71, 72].

The effect of the vacancy becomes significant for low frequencies (the bottom panel), for instance, in the bottom-left window, the low vacancy concentration (black solid line) does not influence the conductance, and the resonant states associated with ripples dominate. However, as the vacancy concentration increases, they play a central role in suppressing these resonances and restore the original peaks associated with planar graphene. Under the extreme condition where $h = 0.05$ nm (figs. (5.14(a)) and (5.14(c))), the vacancies do not play an important role in influencing the transport. The conductance for high frequencies (top panels) is suppressed and no resonant states are observed. When the ripple frequency decreases, the resonant states appear at relatively high energy (the bottom-left panel), and they shift to lower energies as the frequency decreases further (bottom-right window).

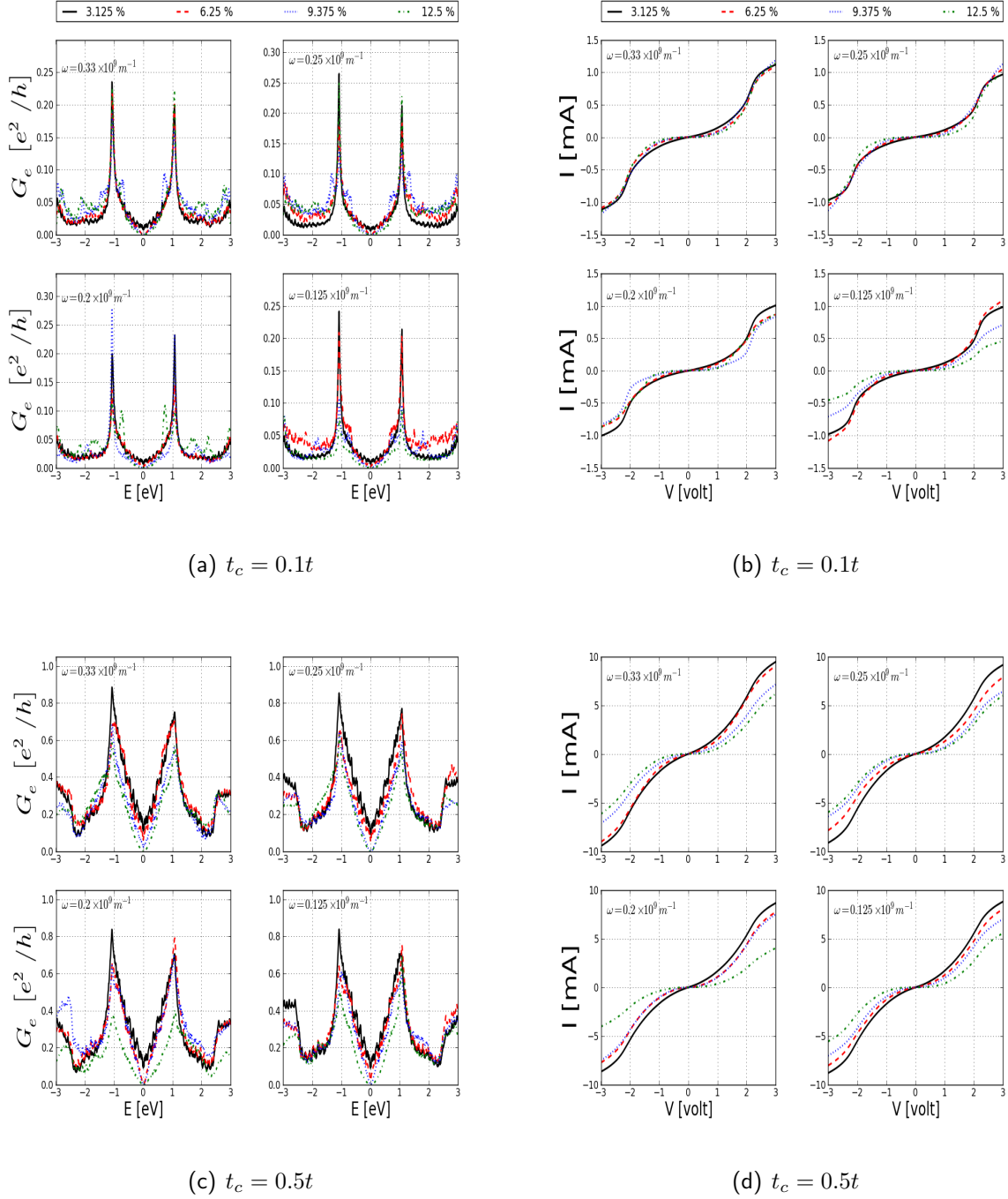


Figure 5.12: The conductance as well as the current-voltage characteristics for rippled graphene ($h = 0.001 \text{ nm}$) with vacancies considered. In each window the conductance (current) is plotted for certain frequency ω and different concentrations as indicated in the label.

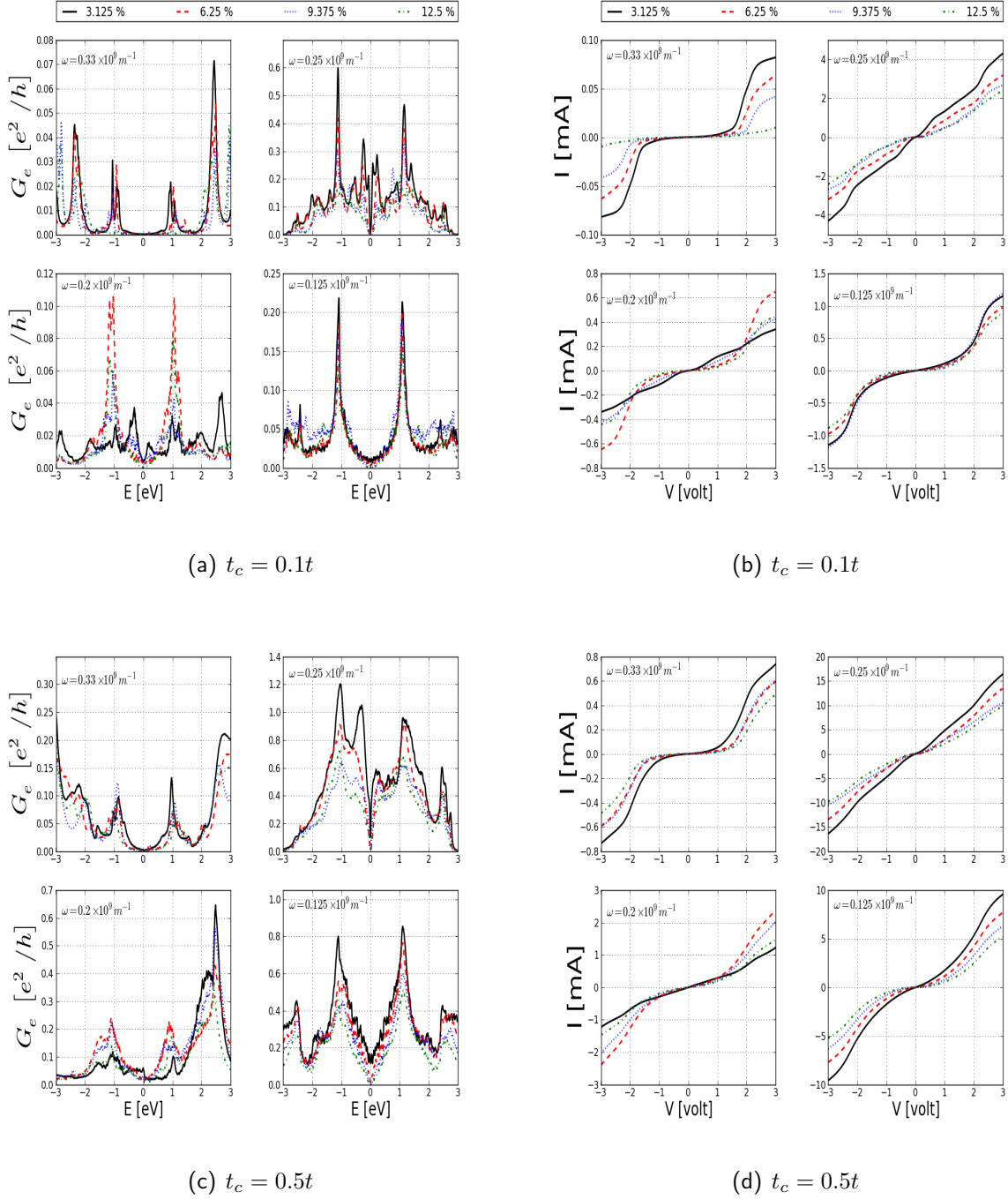


Figure 5.13: The conductance as well as the current-voltage characteristics for rippled graphene ($h = 0.01 \text{ nm}$) with vacancies considered. In each window the conductance (current) is plotted for certain frequency ω and different concentrations as indicated in the label.

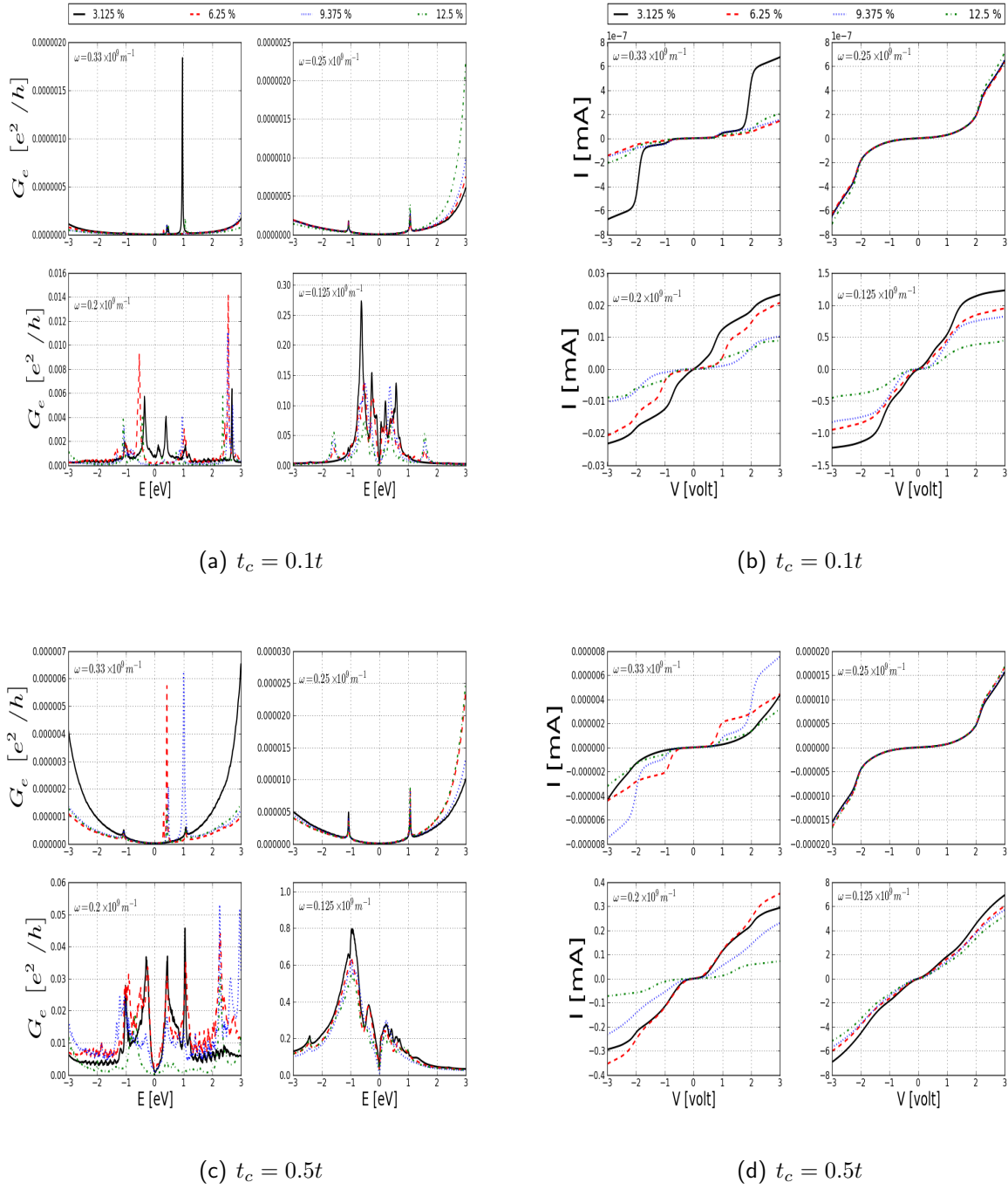


Figure 5.14: The conductance as well as the current-voltage characteristics for rippled graphene ($h = 0.05 \text{ nm}$) with vacancies considered. In each window the conductance (current) is plotted for certain frequency ω and different concentrations as indicated in the label.

The current-voltage characteristics show that the system is insulating for extreme conditions as discussed previously (see the top panels of figs. (5.14(b)), (5.14(d)), and the top-left window of

fig. (5.13(b))). Semiconducting for low amplitudes and frequencies (figs. (5.12(b)), (5.12(d)), bottom-right and top-left panels of figs. (5.13(b)) and (5.13(d)) respectively) where the current tends to be exponential. It is important to note that in some conditions (usually intermediate frequencies and amplitudes) where the resonant states in the corresponding conductance shift toward low energies, the system behaves as a semi-metallic, see the top-right, bottom-left windows of fig. (5.13(b)), the bottom panels of fig. (5.14(b)) and (5.14(d)).

5.3 Summary

A sample of graphene is assumed to be placed between two semi-infinite, perfect leads, and the transport is studied along the armchair direction (considered to be the direction along which the leads are infinite). The leads were modelled in terms of a tight-binding Hamiltonian and their effect was represented by self-energies. The conductance as well as the equilibrium currents were calculated. It is noted that in the case of the defects, the conductance was found by averaging over five arbitrary configurations.

For ideal graphene sheets, the conductance was found to have the two symmetrical peaks that correspond to states located at energies $E = \pm 1$ eV in the graphene. The sharpness of the peaks and the amplitude depends on the coupling energy between the lead and the sample, whereas the high values cause the states to be broader. Furthermore, it has non-vanishing conductance at zero energy supporting the presence of a zero energy gap at the Brillouin zone corners existing in flat, perfect graphene [5]. Breaking the particle-hole symmetry results in a shift in the resonances similar to the one experienced by the density of states, and approximately equal to t' .

The vacancies have a negative effect on the conductance from two aspects, firstly they result in the presence of asymmetric peaks rather than the symmetric ones observed in the ideal graphene, secondly, they suppress the amplitudes to lower values. Moreover, as the vacancy concentration increases, the conductance becomes zero at low energies. When impurities substitute the vacancy, new resonances emerge which indicates the presence of new resonant states around the Fermi energy in addition to the existence of the original peaks at $E = \pm 1$ eV. The number of the resonances is proportional to the impurity concentration and strength of the coupling between

the impurity and its nearest neighbour carbon atoms. When the particle-hole symmetry is broken, the same effect observed previously is observed again. Also, the increase of the sample-lead coupling merges the resonances within a narrow range of energies into one peak centred around the maxima. The transport under the influence of the vacancies was studied in several articles [111, 112, 113] within different approaches. However, in all the situations studied previously specific situations were considered (for instance graphene quantum dots is investigated in [111], boron-nitrogen doping in trigonal graphene in [112] and graphene nanoribbons in [113]), while in our case the average effect of defects (vacancies and impurities) is studied, thus our results show some differences compared to others.

The interplay between height and the frequency of the ripple plays a central role in influencing the transport properties in graphene. It was found that for very small heights there is no remarkable effect on the conductance except that the gap opens at $E = 0$ eV. Previous *ab initio* calculations for transport in graphene under extreme conditions reported similar effect [114] although they assumed a step-like corrugation which makes the graphene semiconducting rather than semi-metallic. For relatively high amplitudes and frequencies, resonant states appear at high energies, as the frequency becomes smaller, those states shift toward the Fermi level resulting in a semi-metallic state. Extreme rippling results in a complete suppression of the conductance leading to a transition to an insulating regime.

The equilibrium current is found to correlate with the corresponding conductance. In other words, the current shows a tendency to linearity which supports the metallic nature of the two-dimensional carbon, where the conductance is non vanishing at $E = 0$ eV, while in the case of the vacancy, the current is exponential at low energies which is indicated by the zero conductance at the Fermi energy. In addition to that, when the coupling between the sample and the leads is increased from $0.1t$ to $0.5t$, the resonant states become broader, thus the current is approximately one order of magnitude greater than the first case. It is noted that the formula used in calculating the current (eq. (3.116)) has some limitations since it does not take into account the voltage drop across the sample. However, calculations performed on a system subjected to the same conditions using the non-zero bias transmission coefficients showed the possibility of achieving negative differential resistance as well as rectifying behaviour [115].

6. Conclusion

The unusual properties of graphene [1, 116, 8] motivated scientists and engineers to pursue the study of this material intensively. The observed properties of solids are influenced by the presence of defects such as vacancies and impurities. In graphene those defects exist due to surface exposure and in some studies defects have intentionally been induced [58, 59] to study their properties. Furthermore, due to its low dimensionality, it acts as a soft electronic membrane, so it forms ripples which act as additional sources of defects [77, 76, 75].

In this work the electronic as well as the transport properties were studied for disordered graphene within the tight-binding formalism. Green's functions were solved using recursive methods [82]. A lattice of 32 sites was used to model the problem, where the vacancies and impurities were located at one site of the lattice. The on-site potential (which is the potential of the nitrogen measured relatively to that of carbon atoms [105]) of the defects was taken to be -2.5 eV. The impurities were assumed to be coupled to the nearest neighbour carbon atoms - two coupling energies were used in this study, $t_p = 0.1t$ and $t_p = 0.9t$, where t is the hopping energy between the carbon atoms in the ideal honeycomb lattice of graphene and it equals -2.7 eV.

It was found that the presence of the vacancy results in quasi localized states at the Fermi level [60] where the nature of the states was investigated through the change of the boundary conditions from symmetric to asymmetric. When the impurity is present it was found that the localized states formed by vacancies split into a set of new resonant states in the vicinity of the Fermi level. The sharpness and the number of the peaks is enhanced as the concentration increases. Furthermore, as the coupling between the impurity and its nearest neighbour carbon atoms increases, more resonances show up due to the formation of new bands. The latter picture is of great importance since it corresponds to situations where atoms like hydrogen, boron or nitrogen are adsorbed on the surface, which has been experimentally proven to have improved properties over the ideal graphene [117, 2].

Allowing the electron to hop to second nearest neighbours breaks the lattice symmetry, however, it affects the states by displacing them along the energy axis by an amount approximately equal to the hopping constant between second nearest neighbours t' . In addition to that, it causes

the states formed by vacancies as well as impurities to split and get smeared around the second nearest neighbour hopping energy t' , which has a positive effect on the electronic transport.

In the mesoscopic regime, a sample was assumed to be sandwiched between two ideal semi-infinite leads, and the transport along the armchair direction is investigated. They were modelled using a mono atomic unit cell in order to construct their corresponding tight-binding Hamiltonian. Then their self-energies were found by following the approach described in ref. [99], where hard wall boundary conditions were imposed in the direction perpendicular to the transport direction. The transport is explored for two effective coupling energies t_c between the sample and the leads; $t_c = 0.1t$ and $t_c = 0.5t$.

In the ideal sheet of graphene it was found that only two symmetric, sharp resonance peaks exist at energies $E = \pm 1$ eV at coupling $t_c = 0.1t$. The case of the vacancy has shown similar resonances but the peaks were asymmetric since the vacancy was substituted in one sublattice. When the impurity is considered, resonance peaks appear around the Fermi energy which enhances the transport remarkably. The number of peaks is sensitive to the coupling between the impurity and its nearest neighbour carbon atoms and the concentration of the impurities, hence, the higher the coupling, the more the resonances are observed. Furthermore, the intensity of the peaks increases due to the increase in the sample-leads coupling, but it is noted that when the coupling is increased from $0.1t$ to $0.5t$ the states become broader, and most of the resonance peaks merge into the two main peaks centred around $E = \pm 1$ eV. Moreover, when the second order coupling is considered, the main feature is the shift of the peaks in the energy axis by an amount approximately equal to t' . Also, in the case of the vacancy the localized states split, giving rise to the observation of new resonances at energies around t' .

The equilibrium current was calculated within the Landauer-Büttiker formula [99] where zero-bias transmission was used. The main observation was that the current is linear in ideal graphene sheets which was observed previously [1], and supports the metallic nature of graphene. The presence of a vacancy influences the characteristics of the current due to the scattering of electrons from the vacancy potential. As the concentration of the vacancies increases, the current tends to be exponential since the corresponding conductance is zero at the Fermi energy (which indicates a disorder-induced energy gap), while it is linear for bias greater than 2 V. A remarkable

enhancement on the calculated current is realised when the impurity is considered. It results in new resonances in the conductance which occur around the Fermi level. These new peaks play a crucial role in modifying the behaviour of the current from exponential to linear at low bias. The change in the conductance, and consequently the current becomes pronounced at high impurity-carbon coupling as well as high concentrations. The second nearest neighbour interaction shifts the resonance energies in the conductance with a shift consequently appearing in the current-voltage characteristics. Moreover, the increase in the coupling energy between the sample and the leads changes the transport properties since the electronic states become broader rather than sharp resonances. Although finer details of resonances get washed out by high sample-lead coupling, the broadening of the states makes the average lifetime of an electron in a state much shorter. Thus increasing the effective sample-leads coupling enhances the current by approximately one order of magnitude. This in principle shows the possibility of controlling the transport properties in two dimensional carbon.

Unlike previous work [77, 76, 75] where the Dirac Hamiltonian was employed to model the corrugation problem, the effect of rippling was modelled within the Slater-Koster formalism [89], where the change in hopping energies due to the overlap between σ and π orbitals was calculated based on the local curvature [76]. It was found that the ripples have a stronger effect than the vacancies since the ripples act as scattering centres when the electron propagates through the corrugated sheet. The localized, midgap states were found to be similar to those which emerge when the system is subjected to a magnetic field (creates Landau levels) [106]. With regard to the transport properties, the effect of the ripples was found to be more pronounced than the vacancies. From the conductance it was predicted that the corrugations cause a gap to open which changes the transport from ballistic to diffusive regime (has been predicted by using Dirac Hamiltonian [118]). Furthermore, the ripples with relatively low height and high frequency results in resonant states at high energies, as the frequency decreases the states move toward low energies, while extreme rippling suppresses the conductance. From the observations, one can conclude that the ripples results in quantum-well-like structure leading to the possibility of observing negative differential resistance due to the gap opening.

The study of the defects in graphene-based materials is a very important field especially for the

purpose of fabricating devices since this material forms the basis for a wide range of carbon materials. Moreover, the disorder plays a central role in all the observed properties, in particular, the magnetic properties. Hence, a further extension of the work would focus more on the properties of corrugated surfaces, and the localization of the states due to that. In addition, the magnetic properties and the role of electron-electron interaction, which play a key role in explaining some of the observations such as the fractional quantum Hall effect.

Acknowledgements

First of all, I thank ALLAH for the uncountable granted blessings and his mercy.

I sincerely thank my supervisor Professor Somnath Bhattacharyya for giving me the opportunity to be one of his students, working with him was a great experience for life, and I learnt a lot during the period I worked under his supervision. The research office at the university of the Witwatersrand represented in its director Mr. Iain Burns, and the African institute for mathematical sciences for funding the research.

I would like to thank Professor Alex Quandt for his patience in answering my questions and providing me with very useful textbooks.

I am also grateful to the members our wonderful group, Dr. Michael Katkov for his useful discussions, Dr. Dmitry Churochkin, George Chimowa, Ross McIntosh, Siphephile Ncube, Christopher Coleman and Charles Sandrock for his tolerance in helping me with the technical problems.

Special thank you to the members of School of Physics, University of the Witwatersrand, specially head of school, Professor Joao Rodrigues, the postgraduate coordinator, Professor Daniel Joubert, and Professor Robert de Mello Koch for being supportive.

I also want to take the opportunity to express respect to Professor Joubert's students, M. P. Molepo and M. Suleiman for giving part of their busy time for discussion. I would like to thank all the friends and the colleagues who had directly or indirectly made a contribution to the work.

I would like to express my gratitude to all of those who have been supporting and encouraging the development of science in Africa in general and AIMS in particular. Many thanks to Professor Neil Toruk, AIMS founder, Professor Fritz Hahne, the former director of AIMS, Professor Barry Green, the current director, and all the rest of AIMS community.

Finally I thank my parents especially my beloved mother for encouraging me through the difficult times and providing me with warmth and infinite love, and I would like to dedicate this thesis to her.

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