ELECTRONIC PROPERTIES OF GRAPHENE AND BORON NITRITE
NANORIBBON JUNCTIONS

A Thesis
Presented to
The Graduate Faculty of The University of Akron

In Partial Fulfillment
of the Requirements for the Degree
Master of Science

Gihan Uthpala Panapitiya
December, 2013
Graphene, the most recently extracted allotrope of carbon has attracted the interest of the scientific community, due to its remarkable electronic properties. Even though the two dimensional undoped graphene is considered as a semiconductor without a band gap, its one dimensional counterpart, graphene nanoribbons, which are stripes of graphene with nanometer sized widths[1], posses a tunable band gap which depends on their widths. In this study, we mainly investigate the electronic properties of structures constructed using graphene nanoribbons to find the relationship between their band gaps and the corresponding structural and geometrical properties. The electronic band structures of both monolayer and bi-layer cross-like junctions are modeled using the $\pi$ orbital tight binding method. It is shown that for a given structure, the shapes of the energy bands near the Fermi level depend on the dimensions of the structure to a considerable extent. Further, it is proven that the structural dimensions and the number of atoms on the zigzag edges of the nanoribbons have a significant effect on the magnitude of the direct band gap. This computational experiment is also extended to study the Boron Nitride-Boron Nitride and graphene-Boron Nitride bi-layer nano structures. It is shown that the patterns of band gap changes in Graphene-Boron Nitride bi-layer systems with respect to certain geometrical pa-
parameters are similar to that in graphene-graphene systems. The results of this study provides a basis to fine tune the band gaps of monolayer and bi-layer junctions.
Foremost, I would like to sincerely thank my advisor Dr. Alper Buldum for the continuous guidance given to me throughout the period of this master’s research. He was always available for my questions which I think was the main reason which motivated me in the right direction and challenged me to come up with an improved output for this computational experiment.

Secondly, my wholehearted gratitude goes to Dr. Sergei F. Lyuksyutov and Dr. David Perry, who are the other two members of my thesis committee for being very supportive in completing this study.

Finally, I am deeply grateful to my father, mother and my wife for their constant encouragement and the mental support given to me in the times when the things were tough and hard for me.
# TABLE OF CONTENTS

<table>
<thead>
<tr>
<th>LIST OF TABLES</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>LIST OF FIGURES</td>
<td>ix</td>
</tr>
</tbody>
</table>

## CHAPTER

I. INTRODUCTION .............................................. 1

1.1 Graphene .............................................. 1

1.2 The electronic structure of graphene ................. 2

1.3 Graphene nanoribbons (GNRs) .......................... 5

II. METHODOLOGY .............................................. 9

2.1 The tight binding method .............................. 9

III. RESULTS .................................................. 20

3.1 Armchair graphene nanoribbon junction ................ 21

3.2 Zigzag nanoribbon junction ............................ 32

3.3 Armchair bi-layer nanoribbon junction structure ...... 38

3.4 Zigzag bi-layer nanoribbon structure ................ 54

3.5 Results for the Boron Nitride bilayer structures .... 70

IV. GRAPHENE-BORON NITRIDE BILAYER STRUCTURES ............. 73

4.1 Electronic properties of the graphene-Boron Nitride bilayer structures 73
## LIST OF TABLES

<table>
<thead>
<tr>
<th>Table</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.1 The number of edge atoms along the vertical edge of the horizontal arm for an armchair junction</td>
<td>23</td>
</tr>
<tr>
<td>3.2 The number of atoms along the horizontal edge of the vertical ribbon and the corresponding form for a zigzag bi-layer structure</td>
<td>66</td>
</tr>
</tbody>
</table>
## LIST OF FIGURES

<table>
<thead>
<tr>
<th>Figure</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.1</td>
<td>2</td>
</tr>
<tr>
<td>1.2</td>
<td>3</td>
</tr>
<tr>
<td>1.3</td>
<td>4</td>
</tr>
<tr>
<td>1.4</td>
<td>6</td>
</tr>
<tr>
<td>1.5</td>
<td>8</td>
</tr>
<tr>
<td>2.1</td>
<td>17</td>
</tr>
<tr>
<td>2.2</td>
<td>18</td>
</tr>
<tr>
<td>3.1</td>
<td>22</td>
</tr>
<tr>
<td>3.2</td>
<td>23</td>
</tr>
<tr>
<td>3.3</td>
<td>25</td>
</tr>
<tr>
<td>3.4</td>
<td>26</td>
</tr>
<tr>
<td>3.5</td>
<td>27</td>
</tr>
</tbody>
</table>
3.6  (a) The same plot for DOS as shown in 3.5 (d) except that the number of line segments considered is 5000; (b) an enlarged portion near \( DOS = 0 \) point ............... 28

3.7  The band gap versus the horizontal length of the vertical arm .... 29

3.8  Band diagrams with respect to the \( \vec{k}_x \) direction for the first four cases in Fig. 3.7 .................................................. 30

3.9  Band diagrams with respect to the \( \vec{k}_y \) direction for the first four cases in Fig. 3.7 .................................................. 31

3.10 (a) Three dimensional valence and conduction energy surfaces and the (b) corresponding DOS for case 1 ......................... 32

3.11  The structure of a zigzag nanoribbon junction .................... 33

3.12  Band gap with respect to the vertical length of the horizontal arm ... 33

3.13 (a) Three dimensional valence and conduction energy surfaces and the (b) corresponding DOS for case 1 in Fig. 3.12 ............... 34

3.14  Band gap with respect to the horizontal length of the vertical arm (the number of atoms along the horizontal zigzag edge for each case is mentioned as a subscript) ......................... 35

3.15  Energy band diagrams with respect to \( \vec{k}_y \) direction for the zigzag junction corresponding to the cases in Fig. 3.14 .................... 36

3.16  \( E(\vec{k}_x, \vec{k}_y) \) (only the valence and the conduction energy surfaces are shown) for the cases (a) 1 and (b) 3; Density of states for the cases (c) 1 and (d) 3 in Fig. 3.14 ............................... 37

3.17  Band gap with respect to the total horizontal length of a zigzag nanoribbon junction .................................................. 38

3.18  The structure of a bilayer armchair junction ....................... 39

3.19  Four types of atoms considered for the tight binding analysis .... 40

3.20  Band gap versus the (a) vertical length of the horizontal ribbon of an armchair bi-layer structure and (b) width of an armchair graphene nanoribbon ............................................ 40
3.21 Energy band diagrams with respect to the $\vec{k}_x$ wave vectors for the cases (a)1 and (b)2 in Fig. 3.20 ........................................ 41

3.22 Energy band diagrams with respect to the $\vec{k}_y$ wave vectors for the cases (a)1 and (b)2 in Fig. 3.20 ........................................ 42

3.23 Energy as a function of $\vec{k}_x$ and $\vec{k}_y$ (a) 1 and (b)2; density of states for the cases (a) 1 and (b) 2 in Fig. 3.20 ........................................ 43

3.24 The change in the band gap with respect to the vertical length of the horizontal ribbon in the absence of inter-layer interactions for the same 10 cases considered in Fig. 3.20 (a) ........................................ 44

3.25 Band gap versus the horizontal length of the horizontal ribbon ........................................ 45

3.26 (a)Energy bands with respect to the (a) $\vec{k}_x$ direction and (b) $\vec{k}_y$ direction, (c)Density of states and the (d) three dimensional band structure for case 1 in Fig. 3.25 ........................................ 46

3.27 Band gap versus the vertical length of the vertical ribbon ........................................ 47

3.28 Energy bands with respect to the $\vec{k}_x$ direction for the cases (a) 1, (b)2 and (c) 3 in Fig. 3.30 ........................................ 48

3.29 Energy bands with respect to the $\vec{k}_y$ direction for the cases, (a) 1 and (b) 2 and (c) 3 in Fig. 3.30 ........................................ 49

3.30 Three dimensional band structures for the cases (a) 1 , (b)2 and (c) 3 in Fig. 3.30 ........................................ 50

3.31 Density of states for the cases (a)1 and (b)7 in Fig. 3.30 ........................................ 51

3.32 Band gap versus the horizontal length of the vertical ribbon ........................................ 51

3.33 Three dimensional energy surfaces for cases (a)1 , (b)5 and (c)8 in Fig. 3.32 ........................................ 52

3.34 Density of states for the cases (a)1 , (b)5 and (c)8 in Fig. 3.32 ........................................ 53

3.35 Unit cell of a zigzag bi-layer graphene nanoribbon structure ........................................ 55

3.36 Band gap versus the vertical length of the horizontal ribbon ........................................ 55

3.37 The four types of band structure cross sections with respect to $\vec{k}_x$ direction for the cases, (a) 1,(b) 4 (c) 5 and (d) 7 in Fig. 3.36 ........................................ 56
3.38 The band structure cross section with respect to $\vec{k}_y$ direction for case 1 in Fig. 3.39 ................................. 57
3.39 The three dimensional band structures for the cases, (a) 1 (b) 4 (c) 5 and (d) 7 in Fig. 3.39 ................................. 58
3.40 Density of states for the cases (a) 1, (b) 4, (c) 5 and (d) 7 in Fig. 3.39 ................................. 59
3.41 Band gap versus the horizontal length of the horizontal ribbon ......... 60
3.42 Band structures with respect to $k_x$ direction for the the cases (a) 1, (b) 2, (c) 3, (d) 8 and (e)9 in Fig. 3.41 ................................. 61
3.43 Three dimensional band structures for the the cases (a) 1, (b) 2, (c) 3, and (d) 8 and (e)9 in Fig. 3.41 ................................. 62
3.44 Density of states for the cases (a) 1, (b) 2, (c) 3, (d) 8, and (e) 9 in Fig. 3.41 ................................. 63
3.45 Band gap versus the Horizontal length of the Horizontal ribbon .......... 64
3.46 Band diagrams with respect to (a) $\vec{k}_x$ direction, (b) $\vec{k}_y$ direction, (c) density of states and (d) the three dimensional band structure for case 1 in Fig. 3.45 ................................. 65
3.47 Band gap versus the horizontal length of the horizontal ribbon .......... 66
3.48 Energy band diagrams with respect to $k_x$ directions for the cases (a) 1, (b) 2, (c) 3 and (d) 6 in Fig. 3.47 ................................. 67
3.49 Energy band diagrams with respect to $k_y$ directions for the cases (a) 1, (b) 2, (b) 3 and (d) 6 in Fig. 3.47 ................................. 68
3.50 $E(k_x, k_y)$ for the cases (a) 1 and (b) 3 in Fig. 3.47 ................................. 69
3.51 Density of states for the cases (a) 1 and (b) 3 in Fig. 3.47 ................................. 69
3.52 A comparison of the band gaps of the Graphene Boron Nitride armchair bi-layer structures ........................................ 71
3.53 A comparison of the band gaps of the Graphene Boron Nitride zigzag bi-layer structures ........................................ 72
4.1 Atoms in the graphene-BN bi-layer junction ................................. 75
<table>
<thead>
<tr>
<th>Section</th>
<th>Title</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>4.2</td>
<td>A comparison between the band gap curves for Graphene-Graphene and Graphene-Boron Nitride armchair bi-layer structures</td>
<td>76</td>
</tr>
<tr>
<td>4.3</td>
<td>A comparison between the band gap curves for Graphene-Graphene and Graphene-Boron Nitride armchair bi-layer structures</td>
<td>77</td>
</tr>
<tr>
<td>4.4</td>
<td>Band gap versus the (a)horizontal length of the horizontal ribbon and the (b)horizontal length of the vertical ribbon for a graphene BN zigzag bi-layer structure</td>
<td>78</td>
</tr>
</tbody>
</table>
CHAPTER I

INTRODUCTION

1.1 Graphene

Graphene is a two dimensional allotrope of graphite. Even though it had attracted the interest of theoretical physicists since late 1940s [2], little attention had been given to find ways of extracting it from three dimensional graphite. This is because it had been popularly believed that two dimensional graphite was thermodynamically unstable based on the arguments of Landau and Peierls [3]. However with the successful attempts of Geim and Novosolov in extracting graphene from graphite in 2004 [4], an unprecedented rise in the research activities took place in graphene, owing to the previously predicted remarkable properties of this new material. Among these properties are high charge carrier mobility [3] of upto $200,000 cm^2/Vs$ [5], high crystal quality [3] and high thermal conductivity [6]. Two main ways of producing graphene are micromechanical cleavage or mechanical exfoliation where graphene layers are repeatedly peeled off from three-dimensional graphite using adhesive tape [3] and epitaxial growth through thermal decomposition on SiC [7].
1.2 The electronic structure of graphene

The carbon atoms in graphene are bonded to each other with $\sigma$ bonds creating a two dimensional honeycomb structure. The carbon orbitals which participate in these bonds are $sp^2$ hybridized. The steps of this hybridization process are depicted in figure 1.1. It is clear that out of the four outer shell (valence) electrons only three occupy the $sp^2$ hybridized orbitals. This leaves one electron in a $p$ orbital which does not participate in the covalent bonds. However, these electrons make $\pi$ bonds with that of their neighboring carbon atoms creating a cloud of electrons hovering above and below the plane of the $\sigma$ bonds. It is these electrons which contribute greatly in determining the electronic properties of graphene.

![Figure 1.1: sp\(^2\) hybridization of Carbon orbitals](image)

The lattice vectors of graphene are given by,

$$\vec{a}_1 = \left( \frac{\sqrt{3}}{2} a, \frac{a}{2} \right), \quad \vec{a}_2 = \left( \frac{\sqrt{3}}{2} a, -\frac{a}{2} \right),$$  \hspace{1cm} (1.1)
and the corresponding reciprocal lattice vectors are,

\[
\vec{b}_1 = \left( \frac{2\pi}{\sqrt{3}a}, \frac{2\pi}{a} \right), \quad \vec{b}_2 = \left( \frac{2\pi}{\sqrt{3}a}, -\frac{2\pi}{a} \right).
\]

Here, \( a \) is the magnitude of either \( \vec{a}_1 \) or \( \vec{a}_2 \) vectors which is about 2.46 Angstroms. These lattice vectors are shown in figure 1.2.

Figure 1.2: (a) Real space lattice vectors of graphene. (b) Reciprocal space lattice vectors and the symmetry points of graphene.

A notable electronic property of graphene is that the electrons behave like mass-less Dirac Fermions close to the non-equivalent K points (Figs: 1.2 (b) and 1.3 (a)) for the undoped graphene, due to the linear dispersion relation of the energy bands with respect to the wave vector \( \vec{k} \) (Fig: 1.3 (a)) at the vicinity of these points. These six corners of the first Brillouin zone of graphene are also called Dirac points or charge neutrality points [8].

3
Figure 1.3: (a) $\pi$ and $\pi^*$ energy bands and the (b) density of states of graphene.
As it is shown in the figure 1.3 (b), strictly two dimensional graphene is a zero gap semiconductor with the density of states vanishing at the Fermi level. This is not a favorable feature when it comes to using graphene in the semiconducting industry to make use of it’s remarkable properties. However thanks to the numerous experimental and theoretical studies of various research groups, it has been found that a band gap can be introduced in graphene by changing it’s structural properties. Few ways of doing this are, cutting a graphene sheet into ribbons, adding different edge atoms and substituting different impurity atoms in few regions of the ribbon. The next section is devoted to present a detailed description of graphene nanoribbons which will most likely replace the semiconducting components of the next generation electronic devices.

1.3 Graphene nanoribbons (GNRs)

A graphene nanoribbon can be considered as a part of a graphene sheet, which is periodic in only one direction. These one dimensional structures can be produced by cutting mechanically exfoliated two dimensional graphene, deposition of nanotubes or diamonds, or by patterning epitaxially grown graphenes [10]. Graphene nanoribbons fall into two distinct categories based on the shape of their edges, namely armchair and zigzag. The atomic structures of armchair and zigzag nanoribbons are shown in figure 1.4. There are different conventions to define a nanoribbon based on the number of atoms along it’s width. The one adopted in this work is shown in figure 1.4, where both armchair and zigzag nanoribbons are defined by the number of carbon atoms.
along the width of the nanoribbon. This is compatible with the popular convention for the armchair nanoribbons where they have been defined by the number of dimer lines (two carbon atoms) [11], meanwhile, in most of the previous works on zigzag nanoribbons, they have been defined by the number of zigzag lines (E.g.; [11]), which is half the number of atoms along the width. However, since only armchair nanoribbons exhibit different behaviors based on the number of edge atoms \( N \), it will not be confusing when this number is used to relate the properties of complex nanoribbon structures which have also been defined by the convention shown in figure 1.4 (a). The armchair and zigzag nanoribbons will thus be named as N-aGNRs and N-zGNRs respectively in this study.

Figure 1.5 shows band structures and densities of states of armchair and zigzag nanoribbons. Of the armchair ribbons the one with eight edge atoms is clearly metallic and the other has a band gap of about 1.3732 eVs.

![Diagram](image-url)

Figure 1.4: Atomic structures of (a) armchair and (b) zigzag nanoribbons (the respective unit cells are also indicated)
There has been numerous studies on the energy band gaps, electron transport properties and magnetic properties of these structures ([12, 13, 14, 15]). For example, the dependence of the band gap on the width of the nanoribbon has been well studied by previous works [16]. These studies show that an armchair nanoribbon can either be metallic or semiconducting depending on the width of the nanoribbon [16] whereas the zigzag nanoribbons have proven to be metallic, regardless of the ribbon width [16]. In particular, the armchair nanoribbons have been studied by dividing them to three categories based on the value of $N$. The first nearest neighbor tight binding calculations show that if $N$ is of the form $3n + 2$, where $n$ is an integer starting from 1, the corresponding armchair nanoribbon is metallic and when $N$ takes the form of either $3n$ or $3n + 1$, the ribbon happens to show no band gap between the valence and the conduction bands. However, it has been shown that when the band structures obtained with the third nearest neighbor tight binding method, a band gap appears also in the cases where the number of edge atoms is of the form $3n + 2$ [11]. Both first and third nearest neighbor studies further reveal that the Fermi level occurs exactly at the energy = 0 eV level.

The purpose of this study is to computationally study the energy band gaps and the corresponding densities of states of different two dimensional structures, constructed using graphene nanoribbons. This is important primarily because the band gap engineering plays a considerable role in determining the usage of graphene nanoribbons in nanoscale semiconductor devices [17] such as field effect transistors.
Figure 1.5: (a) Energy bands and the density of states of graphene nanoribbons; (a) 6-aGNR band structure, (b) 6-aGNR DOS, (c) 8-aGNR band structure, (d) 8-aGNR DOS, (e) 12-zGNR band structure, (f) 12-zGNR DOS.
CHAPTER II

METHODOLOGY

2.1 The tight binding method

A detailed description of the principles of the general tight binding method can be found in [18] while a very clear explanation on the implementation of the tight binding method for carbon nano-structures is given in [19].

A main assumption of the tight binding method is that the ionic potential of a crystal is strong and an electron captured by an ion, stays bound to it for a long time before escaping to the neighboring ion. The state function of this electron, which is not affected by the potential of other atoms is therefore similar to that of an atomic orbital.

If an atomic orbital with an energy $E_j$ is centered at the $j^{th}$ atom, the wave function of the whole crystal can be described as a linear combination of the wave functions of all such atoms in the crystal, as shown in the equation 2.1.

$$\Psi(\vec{k},\vec{r}) = \frac{1}{\sqrt{N}} \sum_{j=1}^{N} e^{i\vec{k} \cdot \vec{R}_j} \phi_n(\vec{r}) , \quad (n = 1, 2,...,m) \quad (2.1)$$

Here $\vec{R}_j$ is the vector specifying the position of the $j^{th}$ atom in the crystal and $\phi_n(\vec{r} - \vec{R}_j)$ is the $n^{th}$ atomic orbital centered at the $j^{th}$ atom. The term, $\frac{1}{\sqrt{N}}$ in this
equation ensures that the wave function, \( \Psi_j(\vec{k}, \vec{r}) \) is normalized to unity. As proven in (2.2), the wave function given in equation (2.1) satisfies the Bloch’s theorem. This is essential in order to account for the translational symmetry of the unit cell in the directions of the lattice vectors of the crystal.

\[
\Psi(\vec{k}, \vec{r} + \vec{a}) = \frac{1}{N} \sum_{j=1}^{N} e^{i \vec{k} \cdot \vec{R}_j} \phi_n(\vec{r} - \vec{R}_j) = e^{i \vec{k} \cdot \vec{a}} \Psi(\vec{k}, \vec{r}) \tag{2.2}
\]

It is also clear by the equation (2.3) that the near the center of the \( j^{th} \) atom the function \( \Psi(\vec{k}, \vec{r}) \) reduces to,

\[
\Psi(\vec{k}, \vec{r}) \approx e^{i \vec{k} \cdot \vec{r}} \phi_n(\vec{r} - \vec{R}_j) \sim \phi_n(\vec{r} - \vec{R}_j) \tag{2.3}
\]

This shows that at the close vicinity the \( j^{th} \) atom, the crystal orbital can be considered very similar to the atomic orbital.

Since we now know the form of the wave function of the crystal, we are in a position to find the energy of the crystal, which is given by,

\[
E(\vec{k}) = \langle \Psi(\vec{k}, \vec{r}) | H | \Psi(\vec{k}, \vec{r}) \rangle. \tag{2.4}
\]

Here, \( H \) is the Hamiltonian.

Using the equation 2.1, the expression for the energy becomes,

\[
E(\vec{k}) = \frac{1}{N} \sum_{j,j'} e^{i \vec{k} \cdot (\vec{R}_j - \vec{R}_{j'})} \langle \phi_n(\vec{r} - \vec{R}_j) | H | \phi_n(\vec{r} - \vec{R}_{j'}) \rangle \tag{2.5}
\]
By setting $\vec{R}_j' = 0$, and after some further manipulations the equation 2.5 can be reduced to,

$$E(k) = \langle \phi_n(\vec{r})|H|\phi_n(\vec{r}) \rangle + \sum_j e^{i\vec{k}\cdot\vec{R}_j} \langle \phi_n(\vec{r})|H|\phi_n(\vec{r} - \vec{R}_j) \rangle \quad (2.6)$$

Note that this equation, expresses the energy in terms of the on site energy (first term on the right hand side) and the energy coming from the electron’s interaction with all the other atoms (second term on the right hand side).

A specific value for the energy can be obtained by substituting the expression for the Hamiltonian of the electron which can be written as the sum of the kinetic and the potential energy.

$$H = -\frac{\hbar^2}{2m_0} \frac{d^2}{dr^2} + V(\vec{r}), \quad (2.7)$$

where $V(\vec{r})$ is the crystal potential which can be approximated as the sum of the potential of the atom which is at the origin($v(\vec{r})$) and the potential due to the rest of the atoms in the crystal($V'(\vec{r})$). Therefore,

$$V(\vec{r}) = v(\vec{r}) + V'(\vec{r}) \quad (2.8)$$

Using these two expressions, we are now in a position to rewrite the two parts on the right hand side of the equation 2.6 as,

$$\langle \phi_n(\vec{r})|H|\phi_n(\vec{r}) \rangle = \langle \phi_n(\vec{r})| - \frac{\hbar^2}{2m_0} \frac{d^2}{dr^2} + v(\vec{r})|\phi_n(\vec{r}) \rangle + \langle \phi_n(\vec{r})|V'(\vec{r})|\phi_n(\vec{r} - \vec{R}_j) \rangle \quad (2.9)$$
\[
\sum_j e^{i\vec{k}\cdot\vec{R}_j} \langle \phi_n(\vec{r}) | H | \phi_n(\vec{r} - \vec{a}) \rangle = \sum_j e^{i\vec{k}\cdot\vec{R}_j} \langle \phi_n(\vec{r}) | - \frac{\hbar^2}{2m_0} \frac{d^2}{dr^2} + v(\vec{r} - \vec{a}) | \phi_n(\vec{r} - \vec{a}) \rangle + \langle \phi_n(\vec{r}) | V'(\vec{r} - \vec{a}) | \phi_n(\vec{r}) \rangle \quad (2.10)
\]

Here, \( a \) is the distance to the first nearest neighbor atoms.

The first term in the right hand side of equation 2.9 is the energy of the atom itself(\( E_n \)) and the second term is a small constant for a given crystal which can be evaluated as,

\[
\beta = - \int \phi_n^*(\vec{r}) V'(\vec{r}) \phi_n(\vec{r}) dr \quad (2.11)
\]

This term is also often ignored in the tight binding calculations. The first term in the right of equation 2.10 is a negligible quantity due to the assumption that the wave functions centered around neighboring atoms have no overlap with each other. Therefore this term can be ignored. The second term in the right is another constant which has popularly been equated in the literature to the Greek letter \( \gamma \).

\[
\gamma = - \int \phi_n^*(\vec{r}) V'(\vec{r} - \vec{a}) \phi_n(\vec{r}) dr \quad (2.12)
\]

Gathering all these terms together a simplified version of the equation 2.6 can be written as,

\[
E(\vec{k}) = E_n - \beta - \gamma \sum_j e^{i\vec{k}\cdot\vec{R}_j} \quad (2.13)
\]
This expression for the energy can also be obtained using the tight binding Hamiltonian matrix and the overlap integral matrix as outlined in [19]. This is in fact the desired method when the unit cell of a structure contains many atomic orbitals. These Hamiltonian matrix elements $H_{nn'}(\vec{k}, \vec{r})$ and the overlap matrix elements $S_{nn'}(\vec{k}, \vec{r})$ are defined as,

$$H_{nn'}(\vec{k}, \vec{r}) = \langle \Psi_n | H | \Psi_{n'} \rangle$$  \hspace{1cm} (2.14)

$$S_{nn'}(\vec{k}, \vec{r}) = \langle \Psi_n | \Psi_{n'} \rangle \hspace{0.5cm} (n, n' = 1, 2, \ldots, m),$$  \hspace{1cm} (2.15)

where $m$ is the number of atoms in the unit cell. These matrix elements specify the interaction between the $n$ and $n'$ atomic orbitals. The energy eigenvalues are then obtained by solving the equation,

$$\text{det}[H - ES] = 0$$  \hspace{1cm} (2.16)

2.1.1 The tight binding method for graphene

As mentioned before, graphene has a unit cell with two atoms. Therefore in formulating an expression for the energy dispersion in graphene using the $\pi$-orbital tight binding method, two basis wave functions centered at these two atoms should be considered. The Hamiltonian of an infinite two dimensional graphene sheet can be viewed as a 2 by 2 matrix, of which the matrix elements are given by,
\[ H(\vec{k}) = \begin{pmatrix} \epsilon & \gamma_0 f(\vec{k}) \\ \gamma_0 f(\vec{k})^* & \epsilon \end{pmatrix} \] (2.17)

where \( \gamma_0 \) is the first nearest neighbor hopping integral and \( \epsilon \) is the on site energy for \( 2p_z \) energy level of Carbon. \( f(\vec{k}) \) is the summation of \( e^{i\vec{k} \cdot \vec{R}} \) terms for the nearest neighbor atoms and \( f(\vec{k})^* \) is it’s complex conjugate.

\[ f(\vec{k}) = \gamma_0 (e^{ik_xa/\sqrt{3}} + e^{-i(k_xa/2\sqrt{3}+k_ya/2)} + e^{-i(k_xa/2\sqrt{3}−k_ya/2)}) \] (2.18)

The matrix \( S(\vec{k}) \) can also be constructed in a similar way (Eq. 2.19). Here, \( s \) is the nearest neighbor hopping integral for graphene which takes a constant value around 0.129 [19].

\[ S(\vec{k}) = \begin{pmatrix} 1 & f(\vec{k}) \\ f(\vec{k})^* & 1 \end{pmatrix} \] (2.19)

In almost all the previous tight binding studies of graphene, the value of \( s \) has been considered to be zero. Thus the condition to obtain the energy eigenvalues becomes,

\[ \det[H - EI] = 0 \] (2.20)
where $I$ is the identity matrix. This approach has also adapted in this work as it reduces the computational effort by a large factor and the results obtained in this study will be comparable with the other similar ones.

Density of states

The density of states corresponding to a given set of eigenvalues is calculated using the standard expression given by[20],

$$D(E) = -\frac{1}{\pi} \text{Im} \int_{1^{\text{st}} BZ} \frac{d\vec{k}}{E - E(\vec{k}) + i\eta}$$

(2.21)

where $\eta$ is a very small real number.

2.1.2 The tight binding method for graphene nanoribbons and complex nanoribbon structures

The process of constructing the tight binding Hamiltonian for a nanoribbon is done in a similar way to that of the infinite graphene. The only difference is that in the case of a nanoribbon the unit cell considered can contain many atoms depending on the width of the ribbon. The other difference is that the unit cell of a nanoribbon is periodic only in one direction. Thus, the Brillouin zone is also in one dimension. As an example, the tight binding Hamiltonian for an armchair graphene nanoribbon with $N = 3$ can be constructed as follows,
In this case, \( k \) is a reciprocal lattice vector component only in the \( k_x \) direction.

As a summary, the process of constructing the tight binding Hamiltonian matrix for any complex structure like that are shown in figure 2.1 is outlined as follows.

1. Model the real space unit cell of the structure using an appropriate coordinate system.

2. Number each atom in the unit cell in a convenient way.

3. Identify the periodicity of the structure and construct additional unit cells surrounding the main one in order to apply the periodic boundary conditions. For example, if the unit cell is periodic only in one direction, two other unit cells left and right to the main unit cell are adequate. However if the periodicity extends to two dimensions, eight surrounding unit cells have to be considered.
4. Find the nearest (second or third nearest) neighbor atoms of each atom as required.

5. Determine the path(s) in the first Brillouin zone along which the eigenvalues are sought and divide the selected path to a specific number of equally spaced $k$ points.

6. Construct the tight binding Hamiltonian matrix for each $k$ point and find the energy eigenvalues. There will be $N$ number of eigenvalues corresponding to a $N \times N$ Hamiltonian matrix.

This formalism can also be extended to bi-layer structures. However in this case, apart from the in-plane hopping parameters, inter-plane hopping integral values should also be considered when constructing the tight binding Hamiltonian.
Figure 2.2: AB Bernal stacked bilayer graphene. Atom types 1 and 2 are in the top layer whereas the types 3 and 4 are in the bottom layer. The solid rectangle marks the unit cell of this structure.

In this study, the two layers in the bi-layer graphene are arranged according to the AB Bernal stacking configuration (see Fig. 2.2). According to this configuration, the type 3 atoms of one layer are located directly above the type 2 atoms of the other layer. The other possible stacking configuration for graphene is the AA stacking configuration where the type 3 atoms are placed directly on top of the type 1 atoms. The tight binding Hamiltonian matrix for the AB Bernal stacked bi-layer graphene can be written as,

$$H(\vec{k}) = \begin{pmatrix}
\epsilon & \gamma_0 f(\vec{k}) & \gamma_5 f(\vec{k}) & \gamma_4 f(\vec{k})^* \\
\gamma_0 f(\vec{k})^* & \epsilon & \gamma_3 & \gamma_5 f(\vec{k}) \\
\gamma_5 f(\vec{k})^* & \gamma_3 & \epsilon & \gamma_0 f(\vec{k}) \\
\gamma_4 f(\vec{k}) & \gamma_5 f(\vec{k})^* & \gamma_0 f(\vec{k})^* & \epsilon
\end{pmatrix}$$

(2.23)
where $\gamma_3$ is the hopping energy between 2 and 3 whereas $\gamma_4$ is the hopping energy between 1 and 4 atom types [21]. The electronic transitions between the atom types of 2 and 4 or 1 and 3 correspond to the same value of $\gamma_5$ [21] since they experience the same effect due to their neighboring atomic orbital environments.
CHAPTER III

RESULTS

This chapter presents the results regarding the band structures and the densities of states of graphene and Boron Nitride nanoribbon junctions and investigates the dependence of the structural parameters on the band gaps of these structures. Boron Nitride is one of the two dimensional materials which can be produced by the method of micromechanical cleavage [22]. One of the reasons to test the electronic properties of Boron Nitride nanoribbons was because of the capability to create graphene-Boron Nitride bi-layer junctions, due to the structural similarity of Boron Nitride to graphene (the carbon-carbon and Boron Nitride-Boron Nitride bond lengths in the two materials differ by only about 0.03 Å). All the structures were modeled computationally using the Cartesian coordinate system and the real and reciprocal space structural parameters required to find the tight binding Hamiltonian for each system were fed into a computer program to find the corresponding energy eigenvalues. All the computer programs were written with the Fortran computer language.

All the monolayer and bi-layer structures studied in this chapter posses rectangular real space lattices. Therefore, the first Brillouin zone of these structures is a rectangle of the dimension $2\pi/L_x \times 2\pi/L_y$, where $L_x$ and $L_y$ are the periodic lengths of the real space lattice.
The band gap for a particular structure was obtained by finding the minimum direct energy gap between the valence and the conduction bands. Three cross sections of the three dimensional band structure were investigated to find this minimum value; from $-\pi/L_x$ to $\pi/L_x$ with $k_y = 0$, from $-\pi/L_y$ to $\pi/L_y$ with $k_x = 0$ and along the diagonal of the rectangular Brillouin zone. In the following sections, the two dimensional bands obtained for $-\pi/L_x$ to $\pi/L_x$ and $-\pi/L_y$ to $\pi/L_y$ will be called as $\vec{k}_x$ cross section and $\vec{k}_y$ cross section band structures for brevity. These $\vec{k}_x$ and $\vec{k}_y$ lengths are in the units of $1/\text{Å}$. In the graphs which shows the variation of the band gap with respect to a particular structural parameter the label G-G and BN-BN stand for Graphene-Graphene ribbons and Boron Nitride - Boron Nitride ribbons respectively.

Only five energy bands which lie in the vicinity of the Fermi level are displayed in every two dimensional band structure presented in the following sections. Three of them, which are plotted with dark dotted lines lie below the Fermi level whereas the other three drawn with thin lines lie above the Fermi level.

3.1 Armchair graphene nanoribbon junction

An armchair graphene nanoribbon junction can be constructed by cutting out rectangular pieces from the corners of a larger rectangular armchair nanoribbon. The band gap was calculated using the tight binding method, for different structural parameters to observe the corresponding changes.
The horizontal length of the vertical ribbon and the vertical length of the horizontal ribbon of the structure (Fig. 3.1) were progressively changed and the resulting band gaps were recorded.

3.1.1 Changing the vertical length of the horizontal arm of the nanoribbon junction

The change in the band gap, when the vertical length of the horizontal arm is increased is shown in figure 3.2 (a). The band gap does not increase monotonically, instead it shows some oscillations. It was found that the drops in the band gap occur when the number of atoms along the vertical edge of the horizontal ribbon is of the form $3n$, where $n$ is an integer starting from 1. A rich variety of band structures were observed for this case and the first four $k_x$ and $k_y$ cross sections are depicted in the figures 3.3 and 3.4 respectively. Table 3.1 presents these forms of the edge atoms for each case considered in figure 3.2 (a).
Table 3.1: The number of edge atoms along the vertical edge of the horizontal arm for an armchair junction

<table>
<thead>
<tr>
<th>Case</th>
<th>Number of edge atoms</th>
<th>Form</th>
<th>Case</th>
<th>Number of edge atoms</th>
<th>Form</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>9</td>
<td>$3n$</td>
<td>6</td>
<td>29</td>
<td>$3n + 2$</td>
</tr>
<tr>
<td>2</td>
<td>13</td>
<td>$3n+1$</td>
<td>7</td>
<td>33</td>
<td>$3n$</td>
</tr>
<tr>
<td>3</td>
<td>17</td>
<td>$3n+2$</td>
<td>8</td>
<td>37</td>
<td>$3n+1$</td>
</tr>
<tr>
<td>4</td>
<td>21</td>
<td>$3n$</td>
<td>9</td>
<td>41</td>
<td>$3n+2$</td>
</tr>
<tr>
<td>5</td>
<td>25</td>
<td>$3n+1$</td>
<td>10</td>
<td>45</td>
<td>$3n$</td>
</tr>
</tbody>
</table>

Figure 3.2: The band gap versus the vertical length of the horizontal part (a) and the horizontal arm (b)

After further analysis it was revealed that these drops occur only if the number of edge atoms is odd and of the form $3n$. Figure 3.2 (b) shows a graph where
the number of edge atoms are changed as 9, 10, 11, 13, 14, 15, 17, 18. It is clear that only when the this number is 9, 21 and 33, the reductions in the band gap occur. It should be noted that the appearance of the horizontal arm depends on the oddness and the evenness of the number of edge atoms. The number of edge atoms in the structures corresponding to the results shown in figure 3.2 (a), was only allowed to be odd and the band gaps in figure 3.2 (b) correspond to the structures where the number of edge atoms could either be odd or even. When this number is even, the atoms in the the upper horizontal edge of the horizontal arm are bonded with just a single bond. This could be the reason for not observing a gradual increase in the band gaps in this case.

The reason why a noticeable change in the band gap was not detected for the cases 9 and 10 was because the vertical length of the horizontal arms of these junctions are very large compared to the vertical length of the vertical arms. This means that these structures are almost similar to that of a nanoribbon. Thus, it can be deduced that since an armchair nanoribbon with $N = 41$ is clearly metallic, the junction in case 9 could also be influenced by this nature of nanoribbons, which reduces it’s band gap.

Three dimensional valence and conduction energy surfaces and the corresponding density of states for the cases 1 and 2 in figure 3.2 (a) are depicted in 3.5).
Figure 3.3: Here, (a) through (d) shows electronic band structures of cases 1 through 4 in $k_x$ direction.
Figure 3.4: Here, (a) through (d) shows electronic band structures of cases 1 through 4 in $\vec{k}_y$ direction.
Figure 3.5: $E(\vec{k}_x, \vec{k}_y)$ (only the valence and the conduction energy surfaces are shown) for the cases 1 and 2 are shown in (a) and (b) respectively; Density of states for the cases 1 and 2 are shown in (c) and (d) respectively
Figure 3.6: (a) The same plot for DOS as shown in 3.5 (d) except that the number of line segments considered is 5000; (b) an enlarged portion near $DOS = 0$ point

A note on the density of states

It should be mentioned that to observe the small band gaps in the density of states graph, the energy range should be split to a large number of line segments. A density of states plot obtained for case 2 by dividing the energy range into 5000 segments is shown in figure 3.6 whereas the plots in figure 3.5 were drawn by considering 500 line segments. When figure 3.5 (d) is compared with this graph, it is clear that the information about the distribution of the energy densities are lost in figure 3.6. Due to this reason, only 500 line segments were considered for the density of states plots presented in this study since the band gap could be accurately obtained from the energy band diagrams.
3.1.2 Changing the horizontal length of the vertical arm of the nanoribbon junction

Changing the horizontal length of the vertical part of the junction seems to have very noticeable effects on the band gap (Fig. 3.7). The band gap was observed to drop abruptly to negligible values when this length was increased beyond a particular value. For the cases considered in this experiment, this value was found to be around 15 Å.

![Figure 3.7: The band gap versus the horizontal length of the vertical arm](image)

Figures 3.8 and 3.9 present the first four band structures plotted with respect to the \( \vec{k}_x \) and \( \vec{k}_y \) wave vectors in the first Brillouin zone. A wide variety in the shapes of the bands was observed near the Fermi level as in the case for changing the vertical length of the horizontal arm.
Figure 3.8: Band diagrams with respect to the $\vec{k}_x$ direction for the first four cases in Fig. 3.7
Figure 3.9: Band diagrams with respect to the $\vec{k}_y$ direction for the first four cases in Fig. 3.7
3.2 Zigzag nanoribbon junction

The energy bands and the density of states of a structure which can be obtained by cutting four rectangular parts from a rectangular zigzag graphene sheet are studied in this section. As shown in figure 3.11, two parameters, vertical length of the horizontal part and the horizontal length of the vertical part were changed to observe the corresponding changes in the band gap.

A drastic drop in the band gap was detected when the vertical length of the horizontal ribbon was changed within the range from 7 Å to 40 Å. This behavior of the band gap is shown in figure 3.12. Very negligible band gaps were detected between the conduction and the valence bands when this vertical length was increased beyond 15 Å. It is therefore evident that very little vertical lengths for the horizontal part is required in order to get significantly large band gaps for this structure.
Figure 3.11: The structure of a zigzag nanoribbon junction

Figure 3.12: Band gap with respect to the vertical length of the horizontal arm
Figure 3.13: (a) Three dimensional valence and conduction energy surfaces and the (b) corresponding DOS for case 1 in Fig. 3.12

Changing the horizontal length of the vertical part of the junction on the other hand has the effect of gradual and monotonic increase in the band gap as shown in the figure (3.14). However clear drops in the band gap has occurred for the cases 10 and 13. The structure for case 13 is almost like a nanoribbon with an armchair edge in the \( \vec{y} \) direction and a zigzag edge in the \( \vec{x} \) direction. This fact is also proven by the \( \vec{k}_y \) cross section of the band structure for this case (Fig. 3.15 (f)). The number of edge atoms along the zigzag edge is 56 which is of the form \( 3n + 2 \) with \( n = 18 \). It is clear that the band gap of this structure is affected by the metallic nature of the armchair nanoribbons. This argument can also be applied to explain the sudden deviation observed for the junction for case 10. It is also observed that when the number of edge atoms were of the form \( 3n \), some particularities in the band structure could occur (Figs. 3.15 (c) and (e)). Further, these changes in the band structure were noticeable, for structures with a relatively large number of atoms.
Figure 3.14 shows the relationship between the band gap and the increasing horizontal length of the vertical part. The corresponding band structures are shown in figure 3.15.

The three dimensional band structures and the corresponding density of states for the cases 1 and 3 in figure 3.14 are shown in figure 3.16. For case 1, the direct band gap occurs on the planes through $k_y = \pm \pi/L_y$, whereas for case 3 it occurs on the planes through $k_x = \pm \pi/L_x$.

It was also found out that when the total horizontal length of the junction is increased, while keeping every other parameter fixed, the band gap decreases. This behavior is shown in figure 3.17.
Figure 3.15: Energy band diagrams with respect to $\vec{k}_y$ direction for the zigzag junction corresponding to the cases in Fig. 3.14
Figure 3.16: \(E(\vec{k}_x, \vec{k}_y)\)(only the valence and the conduction energy surfaces are shown) for the cases (a) 1 and (b) 3; Density of states for the cases (c) 1 and (d) 3 in Fig. 3.14
Figure 3.17: Band gap with respect to the total horizontal length of a zigzag nanoribbon junction

3.3 Armchair bi-layer nanoribbon junction structure

This structure can be realized by placing one nanoribbon on top of another, rotated by 90 degrees with respect to the other. The perpendicular distance between the two ribbons were chosen to be 3.35 Å in accordance with the inter-layer distance of bi-layer graphene stacks. There are two possible ways of arranging these two ribbons, namely AB and AA stacked configurations.

In an AB stacked graphene bi-layer system, the unit cell consists of four atoms as depicted in figure 3.19. As in the case of the graphene bi-layer configuration, each atom is distinguished by one of four numbers, 1,2,3 and 4. The two sub-lattice atoms in the vertical ribbon are given the labels 1 and 2, whereas those of the horizontal ribbon are assigned with 3 and 4. There are four parameters that can be changed, with respect to which, the corresponding variations in the band gap can be
detected. These are the horizontal length of the horizontal ribbon, vertical length of the horizontal ribbon, horizontal length of the vertical ribbon and the vertical length of the vertical ribbon.

The inter-layer hopping parameters considered in this work are, $\gamma_3 = 0.364 \, eV$, $\gamma_4 = 0.319 \, eV$ and $\gamma_5 = 0.177 \, eV$. $\gamma_3$ is the hopping integral between the 2 and 3 atom types; $\gamma_4$ between 1 and 4 and $\gamma_5$ is between 1 and 3 or 2 and 4 ([21]).

![The structure of a bilayer armchair junction](image)

**Figure 3.18: The structure of a bilayer armchair junction**

### 3.3.1 Changing the vertical length of the horizontal ribbon

The energy bands plotted with respect to $k_x$ direction show variations from the flat structure when the number of atoms along the vertical edge of the horizont
Figure 3.19: Four types of atoms considered for the tight binding analysis.

Figure 3.20: Band gap versus the (a) vertical length of the horizontal ribbon of an armchair bi-layer structure and (b) width of an armchair graphene nanoribbon.
tal ribbon($N$) is of the form $3n + 2$ (see Fig. 3.21 (b)). The value of $N$ for each case shown in Fig. 3.20 (a) is indicated as a subscript to the case number and the $N$ (number of atoms along the width of an armchair nanoribbon) for the armchair nanoribbon was varied in the same way (Fig. 3.20 (b)). These peaks at $k_x = 0$ are therefore due to the metallic nature of the armchair nanoribbons. Thus these band structures can be categorized into two main groups based on their $\vec{k}_x$ cross sections near the Fermi level. A better understanding of the band structure can be obtained by plotting $E(k_x, k_y)$ in three dimensions, which shows that the bands are almost flat when viewed from $\vec{k}_y$ direction.

![Energy band diagrams](image)

Figure 3.21: Energy band diagrams with respect to the $k_x$ wave vectors for the cases (a)1 and (b)2 in Fig. 3.20

As evident from figure 3.20 (a), the band gap increases with the increasing vertical length of the horizontally placed armchair ribbon. Interestingly, this behavior is not in agreement with the band gap variations observed in a semi-infinite armchair
Figure 3.22: Energy band diagrams with respect to the $\vec{k}_y$ wave vectors for the cases (a) 1 and (b) 2 in Fig. 3.20

The band gap decreases with the increasing nanoribbon width (see Fig. 3.20 (b)).

A difference between the density of states for the cases with $N$ of the form $3n + 2$ and the others was also observed. As shown in figures 3.23 (c) and (d), the DOS for the cases of the former type are generally characterized by relatively higher energy densities than that of the latter (where $N$ is of the form $3n$ or $3n + 1$).

It was also found out that the energy eigenvalues strongly depend on the inter-layer electron interactions. This fact was tested by re-doing the calculations by setting the inter-layer hopping integral equal to zero. It was revealed that the band gaps were in the order of $10^{-16}$ when $N$ was of the form $3n + 2$ and $10^{-7}$ in the all the other cases (see Fig. 3.24).
Figure 3.23: Energy as a function of $\vec{k}_x$ and $\vec{k}_y$ (a) 1 and (b) 2; density of states for the cases (a) 1 and (b) 2 in Fig. 3.20
Figure 3.24: The change in the band gap with respect to the vertical length of the horizontal ribbon in the absence of inter-layer interactions for the same 10 cases considered in Fig. 3.20 (a)

3.3.2 Changing the horizontal length of the horizontal ribbon

It is evident from figure 3.25 that as the horizontal length is increased, the band gap decreases almost linearly. However, these changes are not significant. Doubling the horizontal length has only reduced the band gap approximately by $2.8 \times 10^{-8}$, which is a reduction of about 0.9%. These results were obtained for structures where the vertical length of the horizontal ribbon, vertical and horizontal lengths of the vertical ribbon were kept fixed at 11.1 Å, 33.2 Å and 11.4 Å respectively. It should be noted that changing this length, does not increase the inter-layer interaction area. Therefore the effect on the band gap should come from the interaction energies of the electrons in the horizontal ribbon. However inter-layer interactions also plays an important role in producing these band gaps. This was confirmed by repeating the calculations without taking into account the inter-layer interactions, which resulted
in negligible band gaps. The constant inter-layer interaction area could also be the cause for the identical band structures detected near the Fermi level.

Figure 3.25: Band gap versus the horizontal length of the horizontal ribbon

When $E(k_x, k_y)$ is examined, it reveals that the band gaps for all these structures were located on the plane that passes through the points $k_x = \pm \pi / L_x$, $k_y = 0$.

3.3.3 Changing the vertical length of the vertical ribbon

The effect of changing the vertical length of the vertical armchair ribbon is shown in figure 3.27. The band gap decreases with the increasing vertical length, in accordance with the results for the armchair nanoribbons. It is however interesting for not observing ups and downs in the band gap curve, even though the atoms on the vertical edge were arranged according to the zigzag formation just like the zigzag edge atoms in the horizontal ribbon. Meanwhile, the band structures can be categorized into two
Figure 3.26: (a) Energy bands with respect to the $(a) \vec{k}_x$ direction and (b) $\vec{k}_y$ direction, (c) Density of states and the (d) three dimensional band structure for case 1 in Fig. 3.25.
groups based on the shapes of the valence and conduction energy bands. For the cases 3,5,7,9,11,13, these bands looked similar to the one shown in figure 3.30 (c) and the band gaps were located through the points of $k_x = \pm \pi / L_x, k_y = 0$. On the other hand, the band gaps for the cases 2,4,6,8,10,12 were located at the four corners of the first Brillouin zone. Even though the energy surfaces for case 1 were found to posses some features of case 3,5..etc, it also had some distinctive characteristics as shown in figure 3.30 (a).

![Band gap versus the vertical length of the vertical ribbon](image-url)

**Figure 3.27:** Band gap versus the vertical length of the vertical ribbon

The density of states were not observed to contain distinctive features based on the number of edge atoms. Figure 3.31 depicts the band structures for the cases 1 and 7. The maximum density for the cases 1 to 6 is about 0.2 whereas for the cases 7 to 10 this value drops to about 0.14.
Figure 3.28: Energy bands with respect to the $\vec{k}_x$ direction for the cases (a) 1, (b) 2 and (c) 3 in Fig. 3.30
Figure 3.29: Energy bands with respect to the $\vec{ky}$ direction for the cases, (a) 1 and (b) 2 and (c) 3 in Fig. 3.30
Figure 3.30: Three dimensional band structures for the cases (a) 1, (b) 2 and (c) 3 in Fig. 3.30
3.3.4 Changing the horizontal length of the vertical ribbon

The effect on the band gap when the horizontal length of the vertical ribbon of the bi-layer structure was changed is considered in this section.
The band gap decreases with respect to the increasing horizontal length of the horizontal ribbon. These reductions can be due to the increasing inter-layer interaction area, as without the inter-layer interactions these structures have very negligible band gaps.

Figure 3.33: Three dimensional energy surfaces for cases (a)1 , (b)5 and (c)8 in Fig. 3.32

The three dimensional valence and conduction energy surfaces obtained for this case were found to evolve gradually from the one shown in figure 3.33 (a) to 3.33 (c). The location where the direct band gap occurs had also shifted from the four
Figure 3.34: Density of states for the cases (a)1, (b)5 and (c)8 in Fig. 3.32
corners of the first Brillouin zone in cases 1 to 4, to the middle of the Brillouin zone in case 5 to 10. The density of states for the three cases in figure 3.34 are depicted in figure 3.34

3.4 Zigzag bi-layer nanoribbon structure

This structure is realized by placing two zigzag nanoribbons on top of each other, with one of them being rotated by 90 degrees with respect to the other. There are again four parameters that can be changed. The way these parameters (horizontal length of the horizontal ribbon, vertical length of the horizontal ribbon, horizontal length) are selected is shown in Figure 3.35.

3.4.1 Changing the vertical length of the horizontal ribbon

The band gap exhibits an exponential type decrease with respect to the increasing vertical length of the horizontal ribbon of the structure. Four different types of band structures were detected based their shapes with respect to \( k_x \) direction for this case as shown in figure 3.37. The \( E(\vec{k}_x, \vec{k}_y) \) shown in figure 3.39 explains the reason for getting flat cross sections for the band structures with respect to \( k_y \) direction. The density of states obtained for the these four types are presented in figure 3.40.

Band gaps in these structures could occur either at the four corners of the first Brillouin zone or on the plane through \( \vec{k}_x = 0 \). For example, for the cases 3 and 4 the band gaps were found in the corners where as for others, they were most likely to be present close to the \( \vec{k}_x = 0, \vec{k}_y = \pm \pi/L_y \) points.
Figure 3.35: Unit cell of a zigzag bi-layer graphene nanoribbon structure

Figure 3.36: Band gap versus the vertical length of the horizontal ribbon
Figure 3.37: The four types of band structure cross sections with respect to $\vec{k}_x$ direction for the cases, (a) 1, (b) 4 (c) 5 and (d) 7 in Fig. 3.36
Figure 3.38: The band structure cross section with respect to $\vec{k}_y$ direction for case 1 in Fig. 3.39

3.4.2 Changing the horizontal length of the horizontal ribbon

The relationship between the band gap and the increasing horizontal length of the horizontal ribbon is shown in figure 3.41. Increasing the horizontal length of the horizontal ribbon also has the effect of reducing the resultant band gap as was the case with increasing it’s vertical length. Even though it was expected to detect differences in the band structure when the number of zigzag edge atoms of the horizontal ribbon was of the form $3n + 2$, such peculiarities were not observed. Five different types of band structures were recognized, simply by comparing their shapes near the Fermi level when the energy eigen values were plotted against the $\vec{k}_x$ wave vector values in the first Brillouin zone (see Fig. 3.42).

As it is evident from the three dimensional band structures, the band gaps can either be found to be located in the four corners or on the plane through $\vec{k}_x = 0$.
Figure 3.39: The three dimensional band structures for the cases, (a) 1 (b) 4 (c) 5 and (d) 7 in Fig. 3.39
Figure 3.40: Density of states for the cases (a) 1, (b) 4, (c) 5 and (d) 7 in Fig. 3.39
3.4.3 Changing the vertical length of the vertical ribbon

Figure 3.45 shows how the band gap changes with respect to the changes in the vertical length of the vertical ribbon of a zigzag bi-layer structure. Unlike for the previous two cases considered for the horizontal ribbon, the band gap increases with the increasing vertical length of the vertical ribbon, even though the rate of increase decreases. For about 192% increase in the vertical length, the band gap increase was detected only to be about 1.2%. The energy band diagrams with respect to $\vec{k}_x$ and $\vec{k}_y$ directions are shown in the figure 3.46. The shapes of the bands were found to be independent of the vertical length and the number of edge atoms and the valence and conduction energy surfaces were detected to possess the same appearance as shown in the figure 3.46 (d). This figure also helps to determine the location where the direct
Figure 3.42: Band structures with respect to $k_x$ direction for the cases (a) 1, (b) 2, (c) 3, (d) 8 and (e) 9 in Fig. 3.41
Figure 3.43: Three dimensional band structures for the cases (a) 1, (b) 2, (c) 3, and (d) 8 and (e) 9 in Fig. 3.41.
Figure 3.44: Density of states for the cases (a) 1, (b) 2, (c) 3, (d) 8, and (e) 9 in Fig. 3.41
Figure 3.45: Band gap versus the Horizontal length of the Horizontal ribbon

band gap occurs as the four corners of the first Brillouin zone.

3.4.4 Changing the horizontal length of the vertical ribbon

It is clear from figure 3.47 that there are drops in the band gap for the cases 6 and 9. These cases correspond to the instances where the number of edge atoms along the horizontal edge of the vertical ribbon ($N$) happens to be of the form $3n + 2$ (see table 3.2). This is an expected result since this behavior for the band gaps was also observed in armchair bi-layer structures.

The metallic influence on the bands is clear in the $\vec{k}_y$ cross sections of the band structures 3.49. Further, figure 3.50 gives a precise idea about the abnormality of the bands which lie on the plane through $\vec{k}_y = 0$. 
Figure 3.46: Band diagrams with respect to (a) $\vec{k}_x$ direction, (b) $\vec{k}_y$ direction, (c) density of states and (d) the three dimensional band structure for case 1 in Fig. 3.45
Figure 3.47: Band gap versus the horizontal length of the horizontal ribbon

Table 3.2: The number of atoms along the horizontal edge of the vertical ribbon and the corresponding form for a zigzag bi-layer structure

<table>
<thead>
<tr>
<th>Case</th>
<th>Number of edge atoms</th>
<th>Form</th>
<th>Case</th>
<th>Number of edge atoms</th>
<th>Form</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>10</td>
<td>3n+1</td>
<td>7</td>
<td>22</td>
<td>3n+1</td>
</tr>
<tr>
<td>2</td>
<td>12</td>
<td>3n</td>
<td>8</td>
<td>24</td>
<td>3n</td>
</tr>
<tr>
<td>3</td>
<td>14</td>
<td>3n+2</td>
<td>9</td>
<td>26</td>
<td>3n+2</td>
</tr>
<tr>
<td>4</td>
<td>16</td>
<td>3n+1</td>
<td>10</td>
<td>28</td>
<td>3n+1</td>
</tr>
<tr>
<td>5</td>
<td>18</td>
<td>3n</td>
<td>11</td>
<td>30</td>
<td>3n</td>
</tr>
<tr>
<td>6</td>
<td>20</td>
<td>3n+2</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Figure 3.48: Energy band diagrams with respect to $\vec{k}_x$ directions for the cases (a) 1, (b) 2, (c) 3 and (d) 6 in Fig. 3.47
Figure 3.49: Energy band diagrams with respect to $\vec{k}_y$ directions for the cases (a) 1, (b) 2, (b) 3 and (d) 6 in Fig. 3.47
Figure 3.50: $E(k_x, k_y)$ for the cases (a) 1 and (b) 3 in Fig. 3.47

Figure 3.51: Density of states for the cases (a) 1 and (b) 3 in Fig. 3.47
3.5 Results for the Boron Nitride bilayer structures

This section is dedicated to compare the band gaps obtained for the Boron Nitride (BN) bi-layer structures with that of the corresponding results for the graphene structures. Figures 3.52 and 3.53 depict these comparisons made for the armchair and zigzag bi-layer structures respectively.

These BN junctions are structurally identical to the graphene bi-layer junctions except for the bond length and the inter-layer distance. The length between two Boron Nitride atoms is about 1.45 Å. This in turn results in a difference in the nearest neighbor hopping parameter when compared with graphene. The hopping integral for nearest neighbor atoms in BN is about 2.37 eV [22]. The inter-layer distance has been shown to have a dependence on the stacking configuration [22]. For AB Bernal stacking considered in this work, this distance is about 3.57 Å.

3.5.1 Electronic properties

The clearly evident fact when the results in the figures 3.52 and 3.53 are examined, is that in general the band gaps corresponding to BN structures are higher than that of the graphene ones. Apart from this the changes in the band gaps with respect to structural parameters are almost identical. However, more oscillations were observed in the band gap with respect to the vertical length of the vertical ribbon for the BN-BN structure than that for the Graphene-Graphene one (see Fig. 3.52 (c)).
Figure 3.52: A comparison of the band gaps of the Graphene Boron Nitride armchair bi-layer structures
Figure 3.53: A comparison of the band gaps of the Graphene Boron Nitride zigzag bi-layer structures
CHAPTER IV

GRAPHENE-BORON NITRIDE BILAYER STRUCTURES

4.1 Electronic properties of the graphene-Boron Nitride bilayer structures

The changes in band gaps observed in the BN bi-layer structures motivated us to study the electronic properties of graphene - BN bi-layer junctions. The geometries of these structures are same as for the ones considered in the graphene or BN bi-layer junctions considered in the previous sections, except for the fact that the two constituting ribbons are graphene and BN. The inter-layer distance between the ribbons was chosen as 3.35 Å.

There are few things that need to be careful about when applying the tight binding method for these structures, due to the differences in the bond lengths of graphene and BN. The most important of these is the difficulty to perfectly stack the two layers according to the AA or AB stacking configuration. As shown in figure 4.1 it is not possible to arrange the two layers so that the type 2 atoms are directly on top of the type 3 atoms. This could result in, up to seven inter layer nearest neighbor atoms whereas there are only six in the case of graphene-graphene or BN-BN bilayer structures. The hopping integrals associated with these inter layer atoms with different inter-layer distances and angles were not readily available in the
literature. Therefore a method had to be found to approximately determine these values. One can use the relationship given in equation 4.1 to calculate the hopping integral for two parallel nanotubes [19].

$$\gamma = -W \sum_{i',j'} \cos(\theta_{i',j'}) e^{(\alpha-r_{i',j'})/\delta}$$  \hspace{1cm} (4.1)

Here, $W$ is the inter-tube coupling strength with an optimal value of $\gamma_0/8$, $\theta$ is the angle between the two $\pi$-orbitals $i'$ and $j'$ and $\alpha$ and $\delta$ are parameters that describes the inter-tube distance dependence. $r$ is the distance between the two atoms $i'$ and $j'$. The parameters of this equation were modified so that it correctly gave the hopping parameters $\gamma_3$ and $\gamma_1$ for bi-layer graphene. It should be noted that this equation doesn’t take into account the differences in the orbital environment for electron transitions between inter-layer atoms. Therefore the $\gamma$ values obtained using this equation only depend on the distance and the angle between the atoms.

In figures 4.2 and 4.3 we compare three sets of results for armchair and zigzag bi-layer nanoribbon junctions. Since the results presented in Chap. 3 were obtained using different inter layer hopping integrals than the ones calculated from the equation (4.1), a reasonable comparison was not thought to be possible between the Graphen-Graphene bi-layer results in chapter 3 and the Graphene - BN bilayer results. Therefore the band gap variations were recalculated for Graphene-Graphene structures using equation (4.1) and the resultant band gap curves are labeled as G-G(2) in the figures 4.2 and 4.3. The results obtained in chapter 3 are also shown on the same graphs which are labeled as G-G(1).
Figure 4.1: Atoms in the graphene-BN bi-layer junction

It is evident that the results in Chap. 3 are in good agreement with those obtained using equation (4.1) for Graphene-Graphene structures.

The changes in the band gap with respect to the horizontal length of the horizontal ribbon and the vertical length of the vertical ribbon in a graphene - BN bi-layer structure seem to follow the same trend which was observed for a graphene-graphene bilayer junction. However an apparent discrepancy can be seen between the band gap variations with respect to the horizontal length of the vertical ribbon for these two structures (see Fig. 4.2 (d)), where the band gap for graphene-BN junction clearly increases with the increasing horizontal length, which is in contrast with the corresponding variations for graphene-graphene structure. The results also show an increase in the band gap when the vertical length of the horizontal ribbon is increased.
Figure 4.2: A comparison between the band gap curves for Graphene-Graphene and Graphene-Boron Nitride armchair bi-layer structures.
Figure 4.3: A comparison between the band gap curves for Graphene-Graphene and Graphene-Boron Nitride armchair bi-layer structures
(Fig. 4.2 (a)) upto about 18 Å which agrees with the results for graphene-graphene junctions.

Results for the graphene-BN zigzag bi-layer junction predict that the band gap changes with respect to the vertical length of the horizontal ribbon and the vertical length of the vertical length (Figs. 4.3 (a) and (c)) are similar to those obtained for a graphene-graphene junction. For other two cases (4.3 (b) and (d)) the variations in the band gap for graphene-BN are not clearly detectable since these changes take place within a range which is very small when compared with the range in which the energy values for graphene-graphene junction are plotted. In figures 4.4 (a) and (b), the band gaps for only graphene-BN are plotted which gives a better picture.

Figure 4.4: Band gap versus the (a) horizontal length of the horizontal ribbon and the (b) horizontal length of the vertical ribbon for a graphene-BN zigzag bi-layer structure.
CHAPTER V
CONCLUSION

This study focused on electronic properties of nanoribbon structures which could be used as conducting channels in two perpendicular directions, while investigating the dependence of the band gaps on their respective structural and geometrical properties. Single layer nanoribbon junctions and bi-layer cross like structures have been mainly studied. The study was also extended to estimate the electronic properties of Boron Nitride-Boron Nitride and graphene-Boron Nitride bi-layer structures.

Vertical length of the horizontal arm, horizontal length of the vertical arm, total vertical length and the total horizontal length were the four structural parameters changed in armchair and zigzag monolayer junctions in order to study the corresponding band gap changes. These junctions were obtained by cutting out pieces from either armchair or zigzag rectangular nanoribbons.

In the case of bi-layer structures, the parameters changed were the vertical and horizontal lengths of the horizontal ribbon and the vertical and horizontal lengths of the vertical ribbon. Two nanoribbons of the same type(either zigzag or armchair) were placed on top of each other such that the compound structure makes a cross-like junction. The distance between the ribbons was chosen as 3.35 Å in the case of graphene and 3.57 Å in the case of Boron Nitride(BN) bi-layer nanoribbon.
structures. Unlike in monolayer junctions, these bi-layer junctions allow the electrons to hop between the neighboring layers which was also studied in this work. The inter-layer hopping parameters were readily available in the literature for graphene stacks which were used in developing the computer model for this work. These parameters ($\gamma_3, \gamma_4, \gamma_5, \gamma_6$) take into account not only the distance and the angle between the atomic orbitals but also the effects on the electron transitions due to the distribution of the neighboring $\pi$ orbitals.

However, when it comes to modeling Boron Nitride bi-layer structures, only one hopping parameter ($\gamma_3$), which corresponds to the electron transfers between the orbitals which make a zero degree angle with each other was found. The other parameters were found by multiplying the corresponding graphene parameters by the ratio, ($\gamma_{3BN}/\gamma_{3Graphene}$). This can be considered as a valid manipulation, since the bond lengths of graphene and BN differ by a very small amount (0.03 Å). In fact there are some previous studies which have considered the bond length of BN to be equal to that of graphene. However, as it was proven in this work the band gaps obtained for BN structures are somewhat higher than the corresponding values for graphene.

The results of this computational study illustrates that changing the geometrical and structural properties of the nanoribbon structures have a considerable effect on their band gaps. In some cases the changes in the band gaps were smooth, monotonic and proportional to the magnitude of the geometric property with respect to which they were studied, while in others these changes are either drastic or oscillatory.
For example the band gaps were observed to drop to negligible values when the horizontal length of the vertical arm of an armchair junction and the vertical length of the horizontal arm of a zigzag nanoribbon was increased. On the other hand when the vertical length of the horizontal arm of an armchair junction and the horizontal length of the vertical arm of a zigzag junction were increased the band gaps exhibited a somewhat oscillatory but an obvious growth. An interesting conclusion can be made from these results if the real space unit cell for this structure is examined. It is clear that on both occasions when an increase in the band gap is detected, the atoms along the edge of which the length is increased are arranged according to the zigzag formation. The other obvious conclusion is that whenever the length increases happen in the arms such that the number of atoms along the armchair edge are increased, sudden band gap drops can be expected. It was further noticed that when these edge atoms were of the form $3N$ with $N$ being an integer value, sudden drops could occur in the band gap variations for armchair nanoribbon junctions. For zigzag junctions this kind of deviations were observed when the number of edge atoms took the form $3N + 2$. However, this relationship was not found for the cases where the horizontal length of the vertical ribbon was less than 38 Å.

Significant oscillations in the band gap curve were also found when the band gaps were plotted with respect to the vertical length of the horizontal ribbon in an armchair bi-layer structure (for both graphene-graphene and BN-BN). Apart from this the energy surfaces, in particular the conduction ones in each structure, where the number of zigzag edge atoms were of the form $3n + 2$ were found to have delta function...
like peaks when viewed from the $k_y$ direction. Similar appearance in energy surfaces were also observed when the band diagrams were obtained by varying the vertical length of the vertical ribbon in an armchair bi-layer and the horizontal length of the vertical ribbon in a zigzag bi-layer. These findings prove that an effect on the direct band gap of a complex nanoribbon structure is highly possible when the number of atoms along a zigzag edge of this structure are subjected to a change. It should also be mentioned that this effect was not found for the horizontally placed ribbon of a zigzag structure.

A comparison between the band gap curves for graphene-graphene and BN-BN bi-layer structures were made and the results showed that the band gap changing patterns are similar to a significant extent in all the eight cases studied. The magnitudes of the band gaps produced by BN-BN structures, however were found to be generally higher than those obtained for graphene-graphene ones.

The results for the graphene - Boron Nitride bi-layer structures showed that apart for two cases for the armchair (changing the horizontal length of the horizontal ribbon and horizontal length of the vertical ribbon) structure and two for the zigzag structure (changing the vertical length of the horizontal ribbon and the vertical length of the vertical ribbon), the band gap variations were not in much agreement with the trends observed for the graphene-graphene bi-layer structures. More tests should be performed by extending the range of in which the geometric dimensions of the nanoribbons are changes in order to better understand the behavior of the band gaps. The results obtained for this novel structure in this study generally predicts
that the band gaps are lower than the ones found for graphene and Boron Nitride
bi-layer junctions.

It should also be mentioned that slight errors in the position of the atoms in
the graphene-BN structure were noticed due to the rounding off of the real numbers in
Fortran. The effect of this error was detected to increase with the increasing number
of atoms in a particular structure. Therefore as an improvement, the usage of the
double precision numbers is suggested to mitigate the influence of this rounding off
error.

Suggestions for future studies

A wide variety of computational experiments can be performed on these mono-layer
and bi-layer junctions simply by using the tight binding method which is not com-
putationally expensive as the other ab-initio methods. Even though there are slight
differences between the results produced by these two methods, the tight binding
method gives an accurate understanding about the band structures and the density
of states which is generally in good agreement with the experimental results.

The third nearest neighbor tight binding method can be used to repeat this
study which will help to refine the already obtained results. Even though the com-
puter programs capable of taking into account upto third nearest neighbor interac-
tions were also developed as part of this study, results were not obtained using them
due to the lack of time.
The other experimental possibility is to computationally subject these structures to a perpendicular magnetic field and study the resultant changes in the band structures. The effect of an magnetic field on the energy bands have been shown in a number of previous studies for infinite graphene sheets and nanoribbons. In the references [13, 14, 23, 24] a spatially modulated magnetic field for monolayer and bi-layer nanoribbons which have produced interesting results.

The electrical conductivity of these structures is another important property which plays a vital role when it comes to integrate them in practical devices.

Adding impurity atoms to these structures and creating defects are another two research alternatives. These can also be coupled with changing the angle with respect to which the two constituting ribbons in bi-layer structures are oriented.

As a final remark, I believe that the results of this study which provide the basic grounds to manipulate and fine tune the band gaps of cross-like monolayer and bi-layer junctions should also be experimentally tested which could pave the way to successfully integrate these structures in practical semiconducting devices.
BIBLIOGRAPHY


