

Band gap calculation of few Arm-Graphene Nano Ribbons

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Abstract—Graphene is a two dimensional material of great interest because of its extraordinary electrical and electronic properties. The main issue with the graphene's band structure is its touching bands, means zero band gap. The graphenenanoribbons can be the new form of the material with some band gap. The report contains the theory of graphene showing some basic electronic properties. The band gap of Armchair & Zigzag nanoribbons having few arms, is calculated here with the help of Mathematica, a simulating tool.

Keywords —Armchair graphenenanoribbon (AGNR), Zigzag graphenenanoribbon (ZGNR), Density of states (DOS)

I. INTRODUCTION

Graphene is a single sheet of carbon atoms detached from graphite, and we all know that graphite is an allotrope of carbon. So graphene exists in two dimensional space. After a long time of wait ultimately the graphene got synthesized in the laboratory. Before the synthesis of graphene, it was a two dimensional abstract material having no real existence. It was just a theory derived very first time by Prof. P. R. Wallace [1]. Interesting fact about the theory is that it was not derived in the name of graphene. The name graphene was given came afterwards. The material was only in theories till 2004 [2]. But A. K. Geim and K. S. Novoselov took the lead in synthesizing graphene and were awarded with Nobel Prize for this. The other interesting fact about graphene is that long back around a century ago, two scientists, Landau and Peierls came up with a proposal that existence of two dimensional crystals is impossible because they were thermodynamically unstable theoretically and it is impossible to see them in reality. That theory pointed out that a divergent contribution of thermal fluctuations in low dimensional crystal lattices, as in case of graphene here, would lead to displacements of atoms in such a way that they will become comparable to interatomic distances at any finite temperature and will disturb the crystallization of two dimensional materials [3].

Graphene got into existence a decade ago and showed this world that two-dimensional materials do exist. It appeared very quickly that this exceptional

material had truly outstanding electronic, electrical, optical and mechanical properties. So it can be used for various applications. Since then, a lot of effort has been devoted not only to the study of graphene but also to its fabrication. Graphene has very interesting properties compared to other materials. Graphene is a one atom thick layer of carbon atoms synthesized from graphite. But as we go from three dimension to two dimension the transport properties and other properties take up a change drastically. The mechanical properties and optical properties of graphene are also far different from the parent material graphite. Behavior and properties of graphene are not only different from graphite but other materials also. It has an unusual band structure as other semiconductors and materials do not. The zero band gap and the relativistic behavior of electrons are responsible for some of these extraordinary properties of graphene. Near the points where band gap is zero the dispersion relation is linear. This linear dispersion relation plays an important role in extraordinary electron transport and unconventional quantum hall effect shown by graphene. On graphene sheet the electrons can travel far long without any scattering, it is a ballistic kind of transport in which the electron pass through and through without very low or no disturbance. There is very low possibility of defects in two dimensional materials like graphene because of the strong atomic bonding. This problem of zero band gap, the graphene has got, is quite hectic for further application of the material. Out of a lot of techniques and methods for the removal of band touching, one is, to confine the material into one dimension and let it be as it was into the other dimension. This new formation of the material is called graphenenanoribbon. Based on their orientation, the graphenenanoribbons have got different names. The transport of electrons takes the different path to travel on graphene basal plane in different nanoribbons.

The synthesis of graphenenanoribbons can be done by epitaxial growth. The growth was carried on the silicon carbide (SiC) substrate and the graphenenanoribbons were patterned onto it by etching. The substrate was heated at a temperature of 1000 °C. During this heating process, the silicon like to move to the edges and gets accumulated on the edges. Thus, in this process, the

graphenenanoribbons get formed. Thegraphenenanoribbons fabricated by this method do not require any further processing. This method gives the nonoribbons of perfect edges[4].

II. ELECTRONIC STRUCTURE OF GRAPHENE

Graphene is a two dimensional material with a honeycomb lattice and a two atom basis. We can represent the lattice by two lattice vectors a_1 and a_2 . The lattice is shown in the Fig.1 (a) below. Fig.1 (a) clearly states that the primitive unit cell of the lattice is a rhombus of edge length a_0 designated by PQRS. The primitive unit cell contains two atoms A and B[1].

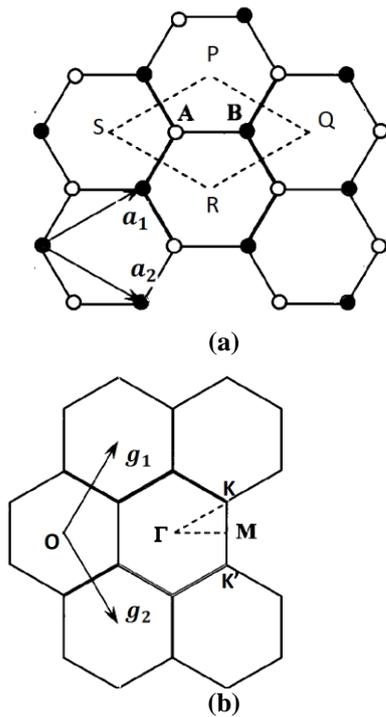


Fig. 1 (a) shows the graphene lattice having primitive lattice vectors a_1 and a_2 . Rhombus PQRS is the primitive unit cell, (b) shows reciprocal lattice of the graphene lattice defined by lattice vectors g_1 and g_2 . The points K and K' are the Dirac points in the reciprocal lattice, this concept of Dirac points will be clear later on.

Taking AB as +ve x axis in two dimensional space, then two primitive vectors of the lattice are given by

$$a_1 = \frac{a_0}{2} \begin{pmatrix} \sqrt{3} \\ 1 \end{pmatrix} \text{ \& } a_2 = \frac{a_0}{2} \begin{pmatrix} \sqrt{3} \\ -1 \end{pmatrix}$$

Here a_0 is the lattice constant having value 2.46 Angstrom.

One can write the g_1 and g_2 as

$$g_1 = \frac{2\pi}{a_0\sqrt{3}} \hat{x} + \frac{2\pi}{a_0} \hat{y} \quad \text{and} \quad g_2 = \frac{2\pi}{a_0\sqrt{3}} \hat{x} - \frac{2\pi}{a_0} \hat{y}$$

These g_1 and g_2 vectors are the reciprocal lattice vectors of graphene reciprocal lattice shown in Fig.1(b).

III. ENERGY DISPERSION CALCULATION OF GRAPHENE

The dispersion relation (energy vs. reciprocal space vector) for graphene is quite abnormal and is the main cause of very unusual transport properties of graphene. Now we will solve for Eigen values of the system using tight binding model. Graphene is a material with sp_2 hybridised carbons and p_z orbital (π state) and this p_z orbital is completely decoupled from bonding orbitals. So most electronic properties are determined by these loosely bound π states. One can write molecular orbitals as

$$|\chi\rangle = \sum_{j=1}^{N_a} c_{kj} |p_z(r - R_j)\rangle$$

N_a is the no. of atoms and R_j is the position of j_{th} p_z orbital. We have two sublattices one containing A atoms and other one containing B atoms. Now we are defining new notations to represent wave functions at A and B sites.

$$|\chi_{R_j}^A\rangle = |p_z(r - R_j^A)\rangle \quad \text{and} \quad |\chi_{R_j}^B\rangle = |p_z(r - R_j^B)\rangle$$

Now molecular orbitals can be defined as

$$|\Psi_k^A\rangle = \frac{1}{\sqrt{N}} \sum_{j=1}^N |\chi_{R_j}^A\rangle \quad \& \quad |\Psi_k^B\rangle = \frac{1}{\sqrt{N}} \sum_{j=1}^N |\chi_{R_j}^B\rangle$$

Here N is the no. of unit cells[5].

We are using tight binding approximation

$$\langle \chi_{R_i}^A | \chi_{R_j}^B \rangle = 0, \quad \langle \chi_{R_i}^A | \chi_{R_i}^A \rangle = 1, \quad \langle \chi_{R_i}^B | \chi_{R_i}^B \rangle = 1$$

The Hamiltonian matrix **H** and overlap matrix **O** will be given as

$$H = \begin{pmatrix} \langle \psi_k^A | \hat{H} | \psi_k^A \rangle & \langle \psi_k^A | \hat{H} | \psi_k^B \rangle \\ \langle \psi_k^B | \hat{H} | \psi_k^A \rangle & \langle \psi_k^B | \hat{H} | \psi_k^B \rangle \end{pmatrix}$$

$$O = \begin{pmatrix} \langle \psi_k^A | \psi_k^A \rangle & \langle \psi_k^A | \psi_k^B \rangle \\ \langle \psi_k^B | \psi_k^A \rangle & \langle \psi_k^B | \psi_k^B \rangle \end{pmatrix}$$

We can define here $t, w(k)$ and μ as

$$t = -\langle \chi_{R_i}^A | H | \chi_{R_j}^B \rangle, \quad w(k) = \sum_{j=1}^N e^{ik \cdot (R_j - R_0)} \quad \text{and}$$

$$\mu = \langle \chi_{R_i}^A | \chi_{R_j}^B \rangle$$

So our **H** & **O** matrices turn out to be

$$H = \begin{pmatrix} \epsilon & -t \cdot w(k) \\ -t \cdot w^*(k) & \epsilon \end{pmatrix}, \quad O = \begin{pmatrix} 1 & \mu \cdot w(k) \\ \mu \cdot w^*(k) & 1 \end{pmatrix}$$

We need to solve the equation $|H - EO| = 0$, that will give the required energy E

$$\begin{vmatrix} \epsilon - E & -t \cdot w(k) \\ -t \cdot w^*(k) & \epsilon - E \end{vmatrix} = 0$$

Which gives Eigen value as

$$E(k) = \epsilon \pm t \cdot |w(k)|$$

Taking $R_0 = 0$ and three nearest R_j 's, The function $w(k)$ becomes

$$w(k) = e^{\frac{ik_x a_0}{\sqrt{3}}} + 2 \cos\left(\frac{k_y a_0}{2}\right) e^{\frac{-ik_x a_0}{2\sqrt{3}}}$$

function $w(k)$ should be 0 at points where band gap is zero.

This gives, $k_x = \frac{2\pi}{a_0\sqrt{3}}$ and $k_y = \frac{2\pi}{3a_0}$

Taking $\kappa = \mathbf{k} - \mathbf{K}$, here \mathbf{K} is given by, $\mathbf{K} = \frac{2\pi}{3a_0} \begin{pmatrix} \sqrt{3} \\ 1 \end{pmatrix}$
 The Dirac approximation (linear approximation) of $w(\kappa)$ near \mathbf{K} i.e. Near $\kappa = 0$ is

$$|w(\kappa)| = \frac{a_0\sqrt{3}}{2} \sqrt{(\kappa_x^2 + \kappa_y^2)} = \frac{a_0\sqrt{3}}{2} |\kappa|$$

The energy spectrum near \mathbf{K} point is simplified to be

$$E(\kappa) = \pm \hbar v_{df} |\kappa|$$

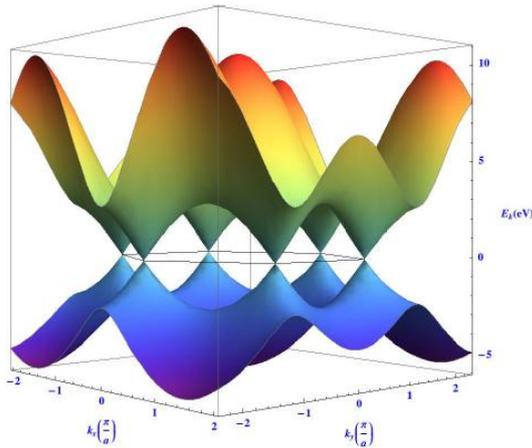


Fig.2 The electronic band structure of graphene [6]

IV. DENSITY OF STATES FOR GRAPHENE

If no. of electronic states in the energy interval E to $E + dE$ are $D(E) dE$ [7]. Then

$$D(E) = 2 \cdot \int \frac{dS}{|\text{grad}_{\kappa}(E)|}$$

$|\mathbf{g}_1 \times \mathbf{g}_2|$ area in reciprocal space contains $= 2$ (k) states

So, unit area in reciprocal space will contain $\frac{(4 \text{ electronic states})}{|\mathbf{g}_1 \times \mathbf{g}_2|}$

So, no. of states in the in the energy interval E to dE are $= \frac{8\pi\kappa d\kappa}{8\pi^2 / ((a_0)^2 \sqrt{3})}$

$$= \frac{8\pi\kappa d\kappa}{4\pi^2} |\mathbf{a}_1 \times \mathbf{a}_2|$$

No. of states per unit area in the in the energy interval E to dE are $= \frac{2 \kappa d\kappa}{\pi}$

So, density of states, $D(E) = \frac{2E}{\hbar^2 (v_{df})^2 \pi}$, $E > 0$

V. ELECTRICAL CONDUCTIVITY OF ELECTRON IN GRAPHENE

From linearized Boltzmann equation we have

$$e \cdot (\mathbf{v} \cdot \check{\mathbf{E}}) \frac{\partial f_0}{\partial E} = \frac{f - f_0}{\tau}$$

Here f is Fermi distribution function in the electric field, f_0 is the Fermi distribution function without electric field $\check{\mathbf{E}}$ and \mathbf{v} is the velocity of electron [1].

As we know that graphene is isotropic

So, $\sigma_{xx} = \sigma_{yy} = \sigma = \text{conductivity}$

The current density J_{XX} in the x direction will be given by the expression

$$J_{XX} = -2e \int \frac{d^2\kappa}{(2\pi)^2} \delta f v_{xx}, \delta f = f - f_0$$

From above given equation, $f - f_0 = \tau$

$(v_{xx} \cdot \check{\mathbf{E}}) \frac{\partial f_0}{\partial E}$, putting this value in the above equation we get

$$J_{XX} = -2 \cdot e \cdot e \int \frac{d^2\kappa}{(2\pi)^2} \tau \cdot (v_{xx} \cdot \check{\mathbf{E}}) \frac{\partial f_0}{\partial E} v_{xx}$$

From this equation the conductivity expression comes out to be

$$\sigma_{xx} = 2 \cdot e^2 \int \frac{d^2\kappa}{(2\pi)^2} \tau \cdot (v_{xx})^2 \cdot \frac{\partial f_0}{\partial E}$$

$$\sigma_{xx} = -4 \cdot e^2 \int \frac{D(E) dE}{2} \tau \cdot (v_{xx})^2 \cdot \frac{\partial f_0}{\partial E}$$

Using energy dispersion and density of states (DOS) relations, conductivity comes out to be

$$\sigma_{xx} = \frac{4 \cdot e^2 \cdot \tau \cdot k_B \cdot T \cdot \ln(2)}{\pi \hbar^2}$$

VI. METHODS OF PREPARATION OF GRAPHENE

Graphene has become the rising star of research world and different research groups tried to make it with different methods. K.S. Novoselov and A.K. Geim were the first to make it by micromechanical cleavage of bulk graphite and their very first paper got a lot of attention and excited scientists all over the world. This material was immediately seen as the next promising candidate for the current technology to be used in devices. So graphene sheets could be used in classical computer but right now its application in spintronics potentially widened its use for further application. There are different methods to make graphene, but in this report the chemical approaches of graphene production will be elaborated with their advantages as well as their disadvantages. People have used a number of methods of making graphene. Out of them, some are explained here.

A. Micromechanical exfoliation method

This is the method which got the pride of getting graphene very first time in 2004 [2]. Other methods were used after this. In this method, graphene is detached from a graphite crystal using scotch tape, an adhesive tape. After whittling it off the graphite, one generally gets a group of many layer graphene. The single layer graphene is of our importance. By repeated whittling the multiple layer graphene is cleaved into various plics of few layer graphene. Now doing last whittling with a new tape one obtains the flakes of different size. The size ranges from several nanometers to several tens of micrometers for single layer. The absorption rate of single layer graphene is found to be about 2%, but one can see it under a light microscope on SiO₂/Si [8].

B. Epitaxial growth of graphene

One can prepare graphene by heating and cooling the SiC substrate. The lattice structure of Ni and graphene are very similar to each other. Using diffusion method a thin layer of Ni was evaporated on silicon carbide substrate. Carbon got diffused through the nickel layer after heating the substrate and graphene layers are formed on the SiC substrate. The graphene layers obtained were not only single layer but a spectrum of multiple layer graphene was formed. The roll of Ni is very important here because it was very difficult to detach graphene from the substrate without using Ni. One more important thing is that multilayer graphene grows on carbon face of the substrate. There are some disadvantages of this method also. This method is very selective in terms of conditions one apply and this method is very selective in terms of substrate selections also. One does not get a homogeneous layer of graphene using this method. The quality of graphene formed by this method is not as good as that of formed by skotch tape method. The production of large size graphene is not possible by this method. This method is very complex because the requirements of the method are very precise. Requirements of pressure, temperature and heating rate are very tough to match exactly[9].

CVD is one of the mostly used methods of making graphene these days. In this method the metal substrate is heated with the help of plasma or filament and after heating the metal the hydrocarbon gas is exposed to the metal in the chamber. The temperature of heating should be very high i.e. around 1000 °C. Hydrogen and Argon gases are also exposed to the metal. The hydrocarbon gas is decomposed on the surface of the metal and the carbon atoms diffuses into the metal surface. One can control the thickness and size of the graphene layer by controlling the thickness of metal used and by patterning the metal surface. The transfer of the graphene layers can be done by the support of the polymers. Etching the metal substrate, one can stamp the layer on another place[10].

VII. GRAPHENENANORIBBON

The graphenenano-ribbon is another material of interest. The graphenenanoribbons have got different names, based on their orientation, like carbon nanotubes. Unlike the infinite sheet of graphene, spread in two dimensional space, the graphenenano ribbon is limited in one dimension in 2-D space having some atomic length wide width. Nanoribbon is infinite in one dimension but does not go very far in the other dimension.

C. Chemical Vapor Deposition (CVD) method

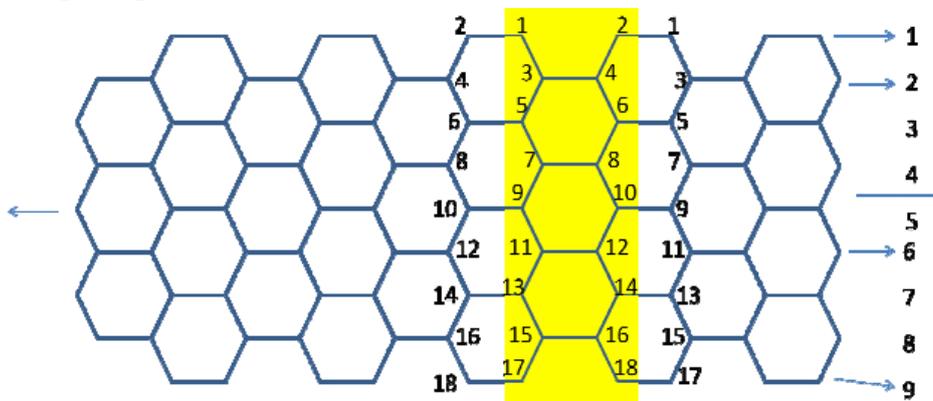


Fig. 3(a) Arm chair graphenenano-ribbon

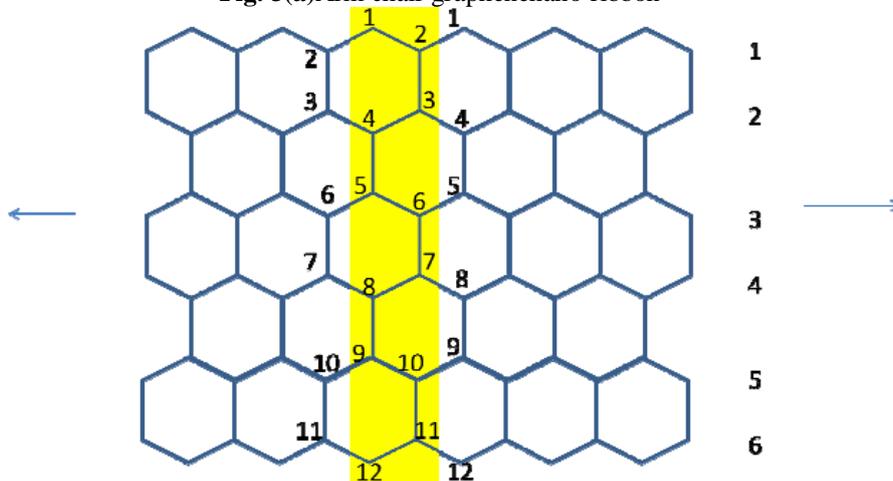


Fig. 3(b) Zigzag graphenenanoribbon

VIII. BAND STRUCTURE SOLUTION FOR THE GRAPHENENANO RIBBONS

The two Hamiltonian matrices regarding arm chair nano ribbons and zigzag nano ribbons are defined below.

For arm chair nano ribbons the Hamiltonian will be defined as[11],

$$H_{m,m'} = \begin{cases} t e^{-ik_x b}, & \text{for } m' = m + 1, \text{ if } m \text{ is odd} \\ t e^{-ik_x b/2}, & \text{for } m' = m + 1, \text{ if } m \text{ is even} \\ t e^{-ik_x b/2}, & \text{for } m' = m + 3, \text{ if } m \text{ is odd} \end{cases}$$

For, zigzag nano ribbons the Hamiltonian will be defined as[11],

$$H_{m,m'} = \begin{cases} 2t \cos \frac{k_x a}{2}, & \text{for } m' = m + 1, \text{ if } m \text{ is odd} \\ t, & \text{for } m' = m + 1, \text{ if } m \text{ is even} \\ 0, & \text{for all others} \end{cases}$$

The parameter 't' is the hopping term having value 2.5 eV. The parameters b & a are the lattice parameters having values 4.2 nm (3 × 1.42 nm) & 2.42 nm (3^{1/2} × 1.42 nm) respectively.

One set of all the 8 matrices is solved taking above Hamiltonians into account.

The matrices are solved in Mathematica to get eigenvalues & E vs k graphs were plotted.

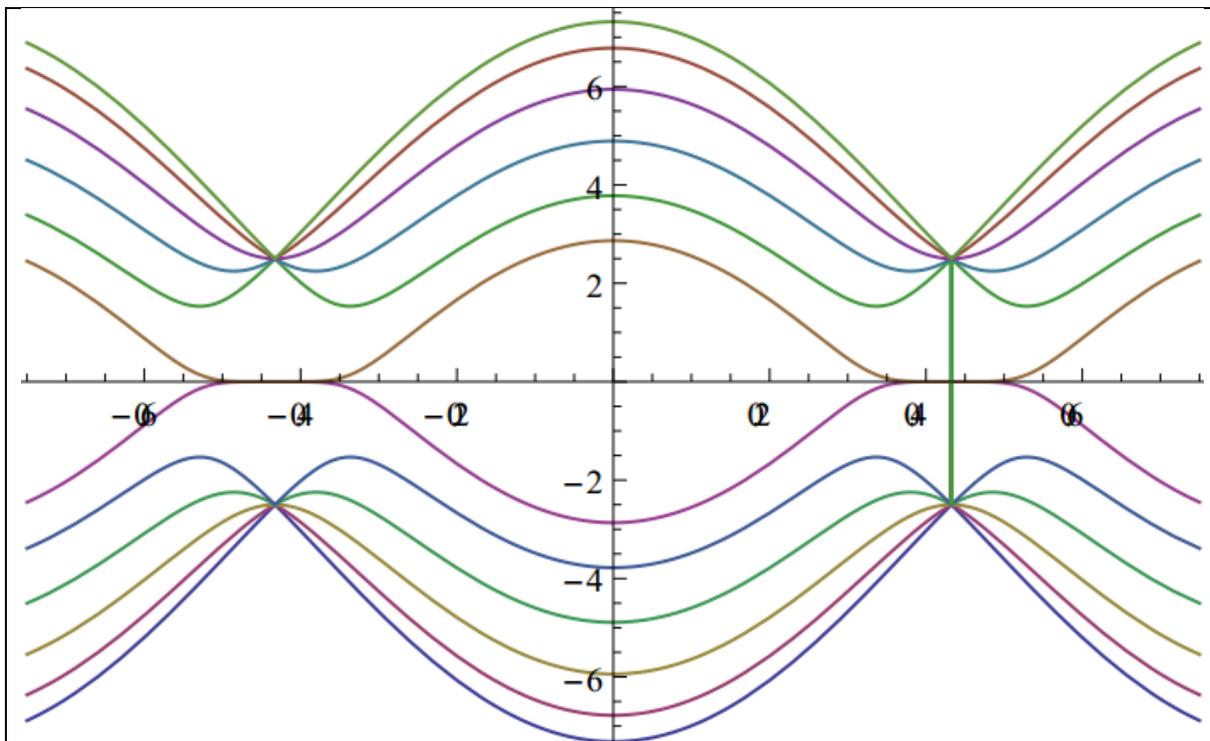


Fig. 4(a) Band structure of 6-Zigzag graphene nano-ribbon

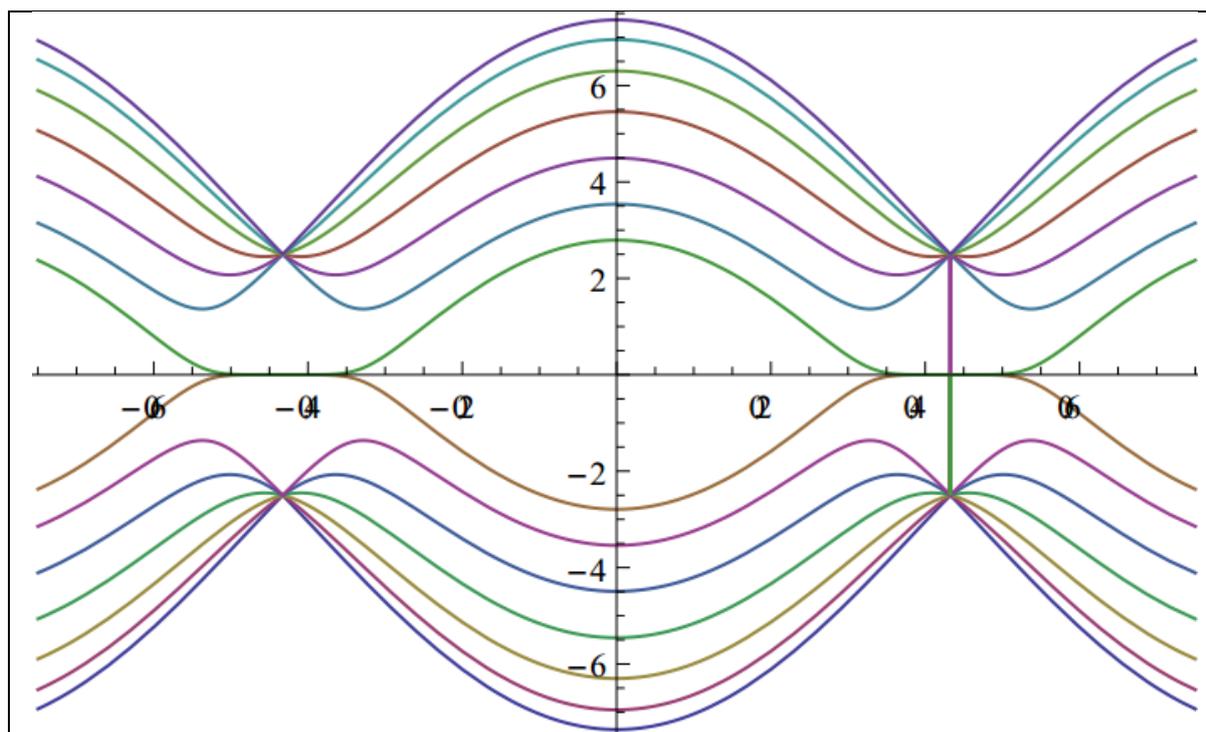


Fig. 4(b) Band structure of 7-Zigzag graphene nano-ribbon

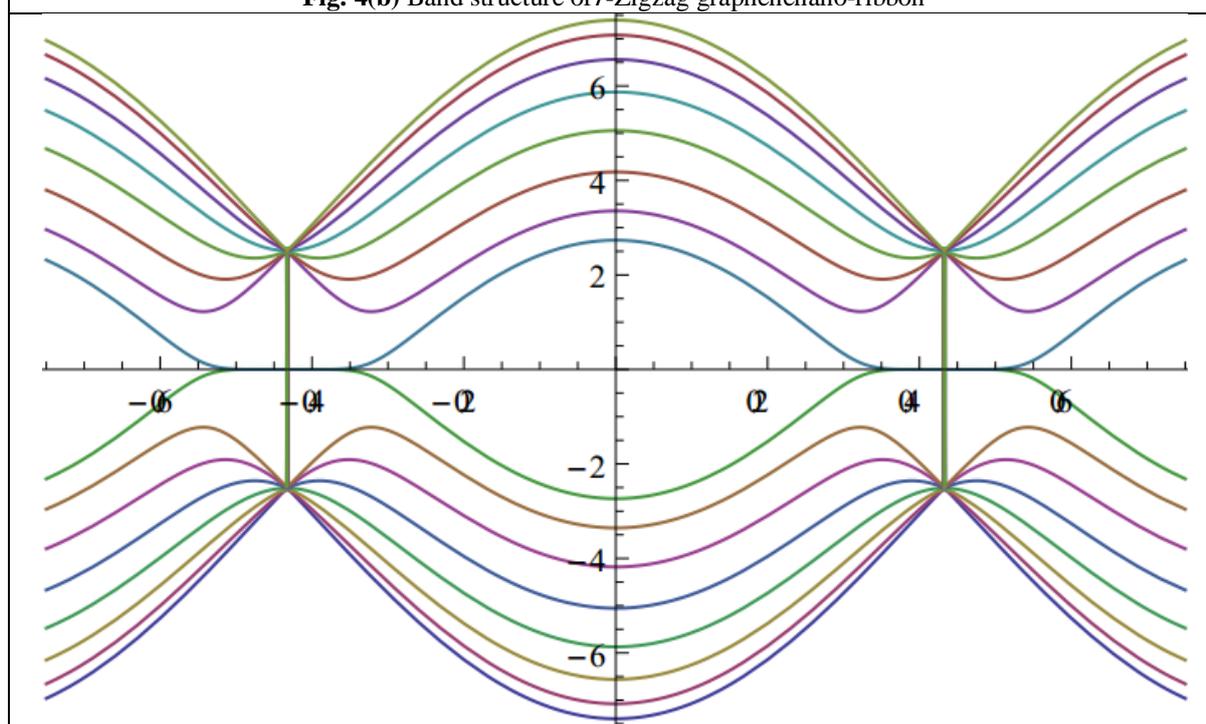
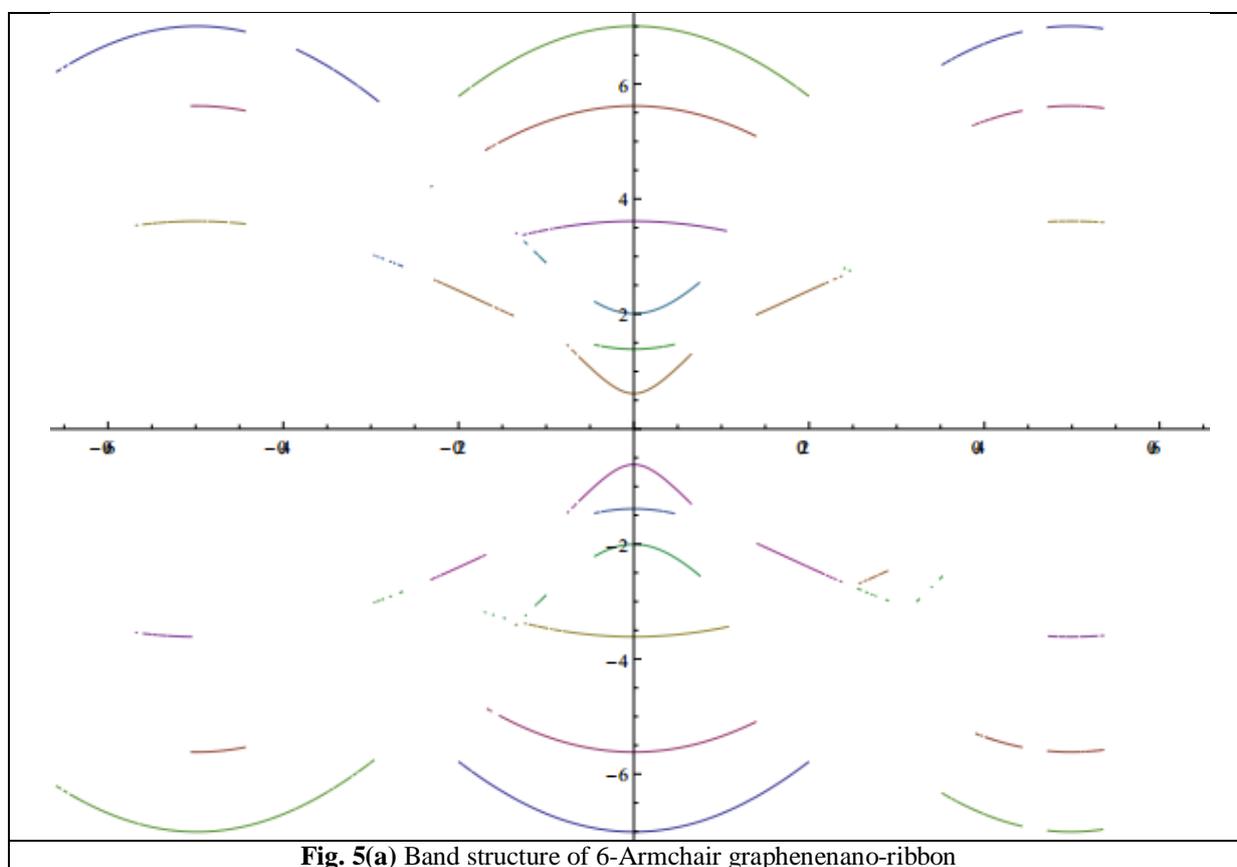
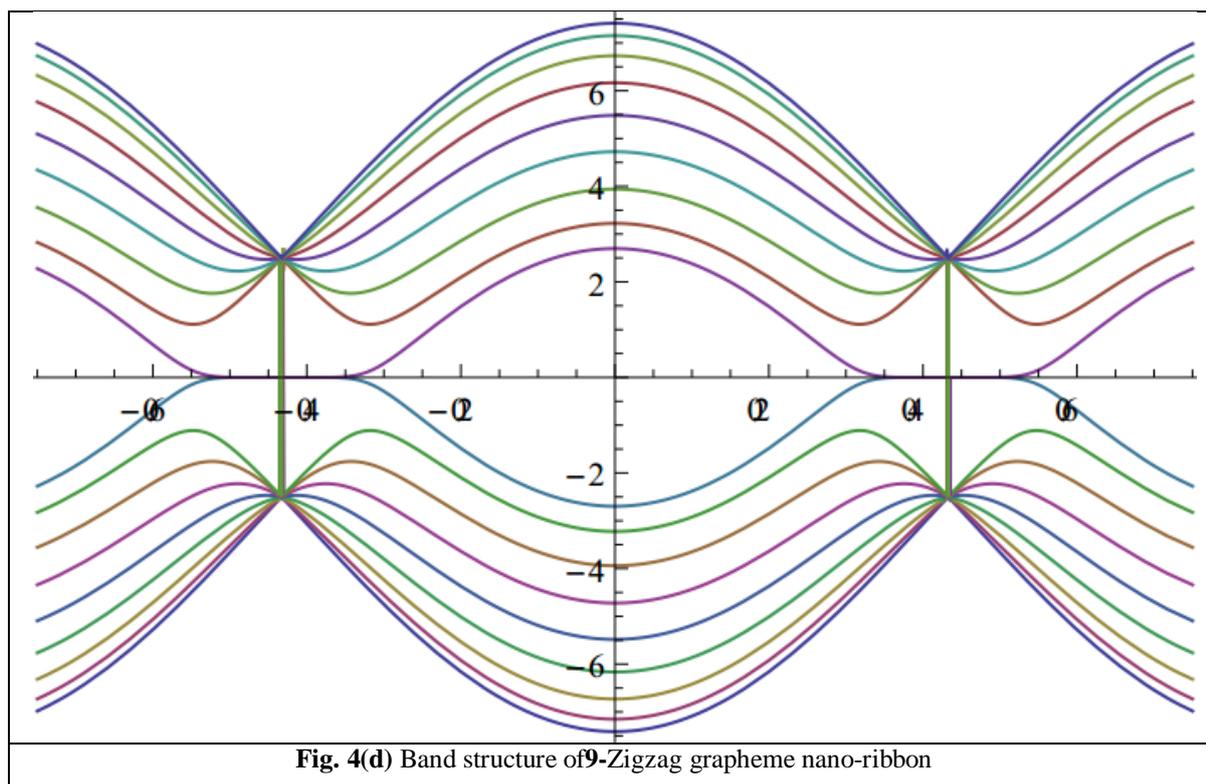


Fig. 4(c) Band structure of 8-Zigzag graphene nano-ribbon



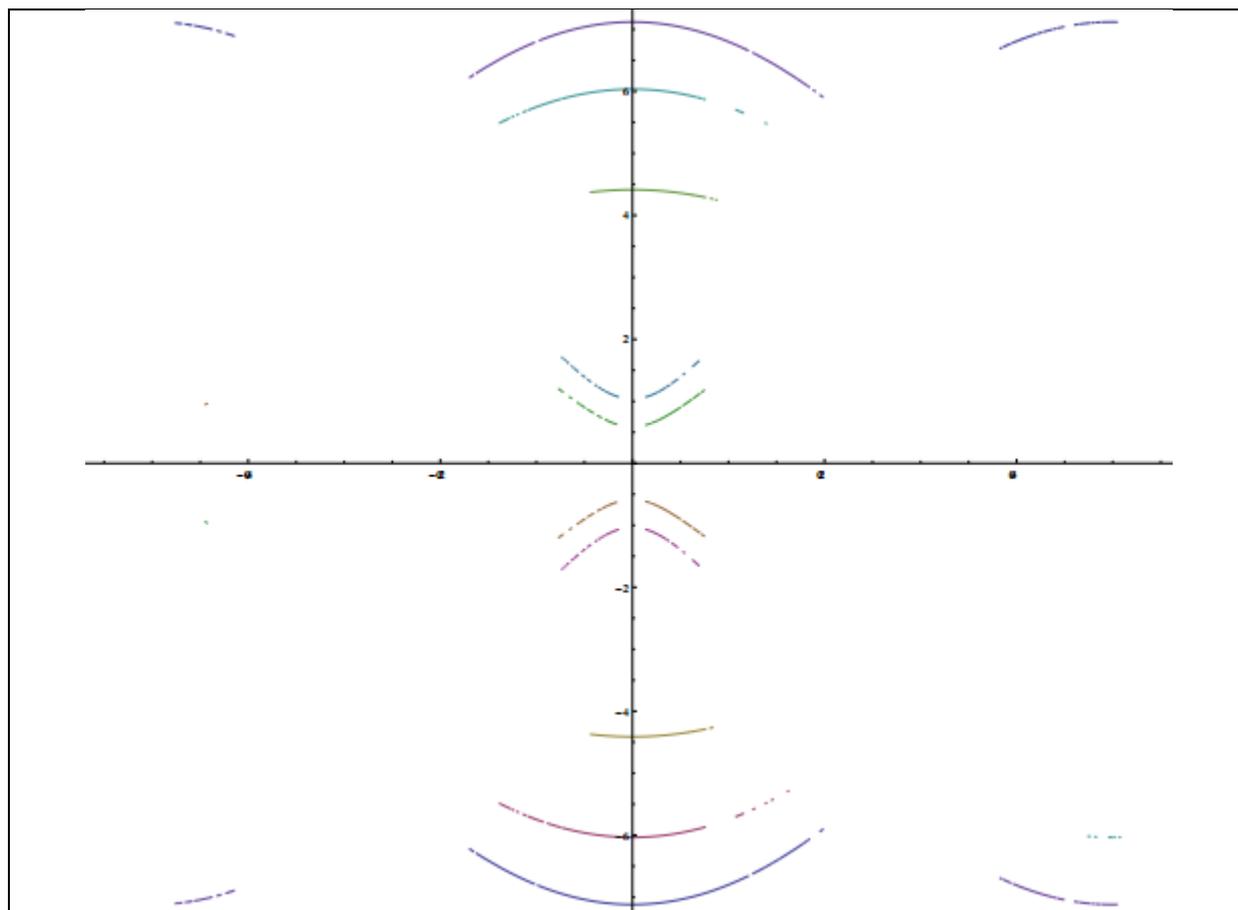


Fig. 5(b) Band structure of 7- Armchair graphene nano-ribbon

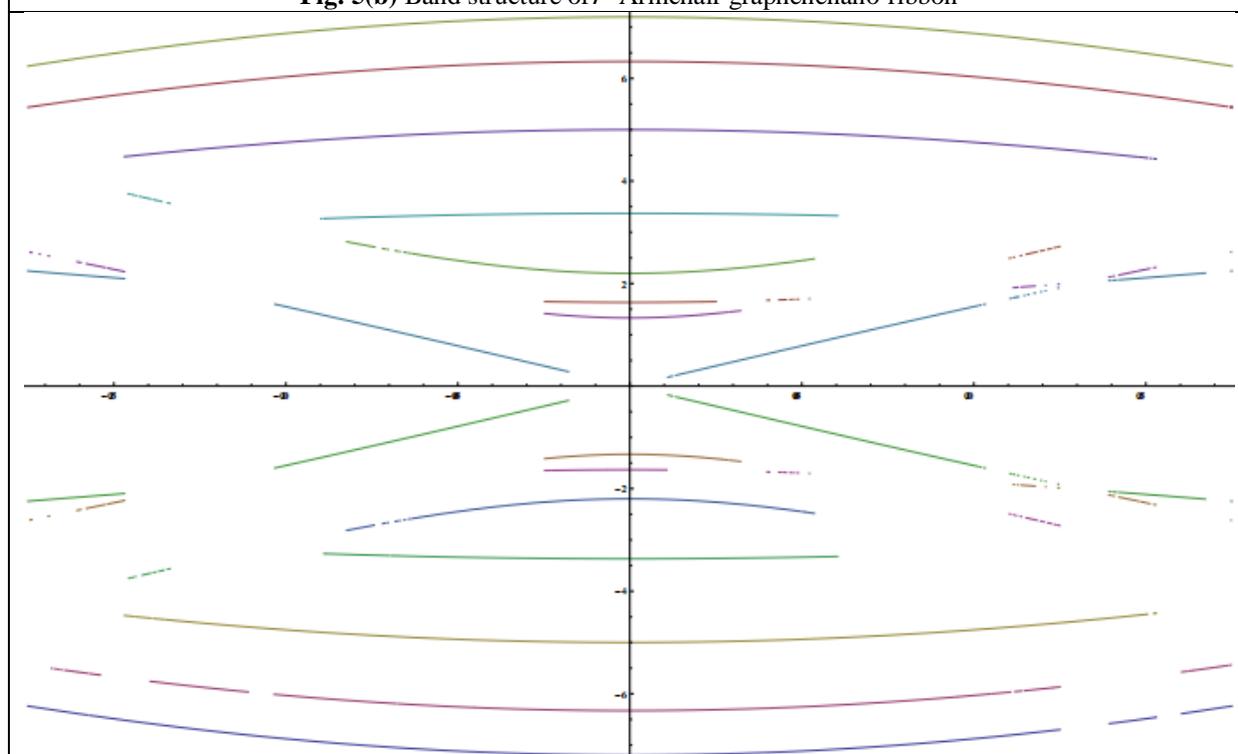


Fig. 5(c) Band structure of 8- Armchair graphene nano-ribbon

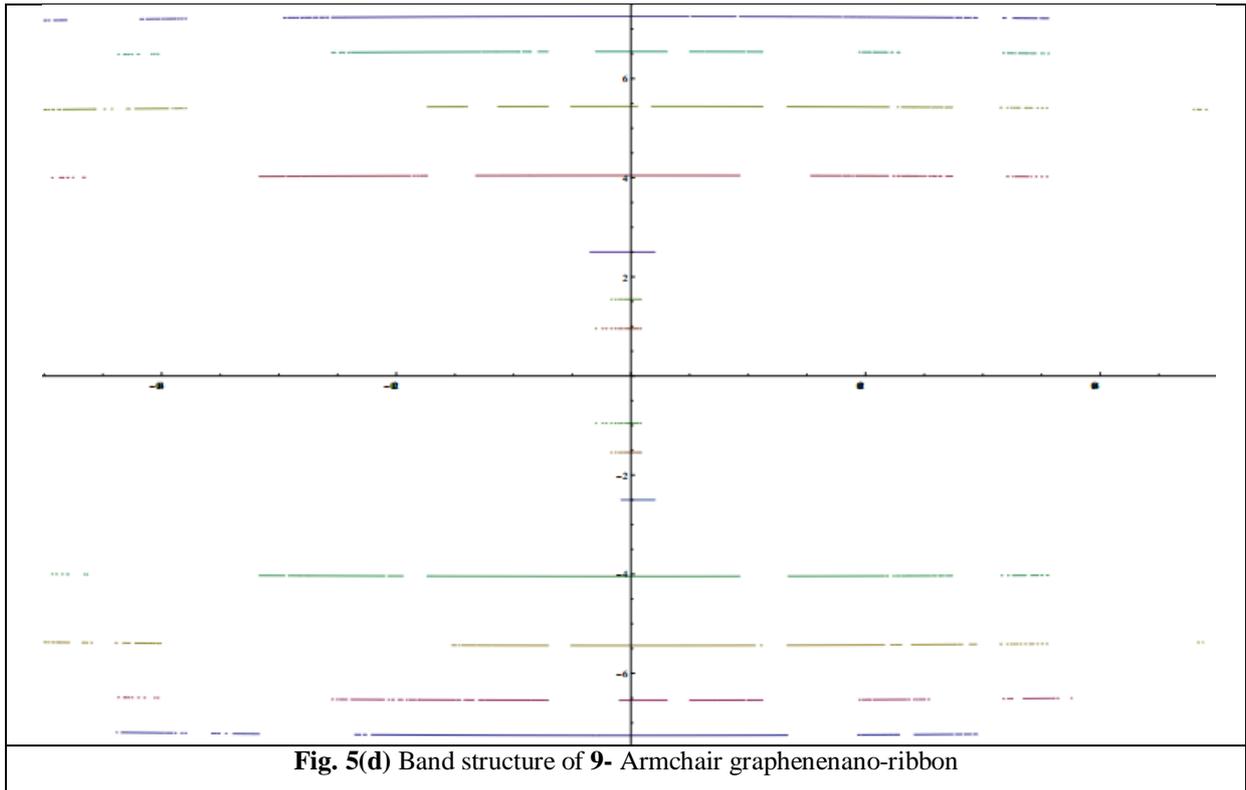


Fig. 5(d) Band structure of 9- Armchair graphene nano-ribbon

IX. RESULTS&DISCUSSIONS

In the plots, 4(a) to 5(d), the Y axis is the energy axis having measurements in electron-volt(eV).The valence band and conduction band are touching in case of Zigzag nanoribbons, so no band gap is there. The zigzag nanoribbons did not show any band gap opening and zero band gap of the graphene got continued. The armchair nanoribbons did show the band gap opening. The band gap in case of Arm chair nanoribbons is observed and listed below.

N-AGNR	Bandgap
6-AGNR	1.24 eV
7-AGNR	1.14 eV
8-AGNR	0.00 eV
9-AGNR	0.88 eV

One thing is very clear from this computation of the band structure of the nanoribbons, that some armchair nanoribbons can be very useful for future application.

X. SUMMARY

The graphenenano-ribbon is a strip of the two dimensional material graphene. The stripes are termed as armchair nanoribbon or zigzag naoribbon based on the orientation of the strip means how they got cut out from the graphene sheet. The transport of

electron is different in both the nanoribbons. In the present report the electronic theory of graphene is presented with all derivations required. The band structure calculation of the nanoribbons is done with the help of Mathematica based on tight binding formulation. The computational code was developed in Mathematica and band diagrams for 6,7,8,9 Armchair nanoribbons& 6,7,8,9 Zigzag nanoribbons were obtained by simulating the code in Mathematica.

The armchair nanoribbons showed up some band gap while the zigzag nanoribbons showed no band gap.

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