STRUCTURAL AND ELECTRONIC PROPERTIES OF BLUE PHOSPHORENE NANORIBBONS

Dissertation Submitted to the Central University of Punjab

For the award of

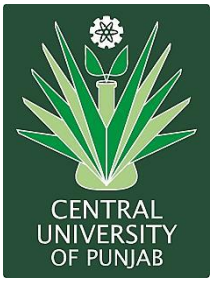
Master of Philosophy

In

Center for Physical Sciences

By
Ram Swaroop

Supervisor
Dr. Ashok Kumar



Centre for Physical Sciences
School of Basic and Applied Sciences
Central University of Punjab, Bathinda

June, 2016

CERTIFICATE

I declare that the dissertation entitled "STRUCTURAL AND ELECTRONIC PROPERTIES OF BLUE PHOSPHORENE NANORIBBONS" has been prepared by me under the guidance of Dr. Ashok Kumar, Assistant Professor, Center for Physical Sciences, School of Basic and Applied Sciences, Central University of Punjab. No part of this dissertation has formed the basis for the award of any degree or fellowship previously.

RAM SWAROOP
Centre for Physical Sciences,
School of Basic and Applied Sciences,
Central University of Punjab, Bathinda - 151001.
Date:

CERTIFICATE

I certify that RAM SWAROOP has prepared his dissertation entitled "STRUCTURAL AND ELECTRONIC PROPERTIES OF BLUE PHOSPHORENE NANORIBBONS", for the award of M.Phil. degree of the Central University of Punjab, under my guidance. He has carried out this work at the Centre for Physical Sciences, School of Basis and Applied Sciences, Central University of Punjab.

Dr. Ashok Kumar
Centre for Physical Sciences,
School of Basis and Applied Sciences,
Central University of Punjab, Bathinda – 151001.
Date:

ABSTRACT

Structural and Electronic Properties of Blue Phosphorene Nanoribbons

Name of the student: Ram Swaroop

Registration number: CUPB/M.Phil./SBAS/PMS/2014-15/07

Degree for which submitted: Master of Philosophy (M.Phil.)

Name of supervisor: Dr. Ashok Kumar

Name of centre: Physical Sciences

Name of school: Basic and Applied Sciences

Key words: Blue Phosphorene, Passivation, APNR, ZPNR, Density Functional Theory, Siesta,

Experimental discovery of graphene has opened up the door for the researcher in the field of 2D materials. After the successful synthesis of the graphene, new classes of the 2D material are emerging. Phosphorene, single layer of Phosphorous atoms, is one of those materials which was recently discovered in year 2014. In present study, we have focused on the Blue-Phosphorene nanoribbons which is one of the stable allotrope of phosphorene. Our DFT-based calculations suggest the electronic properties of blue phosphorene nanoribbons to have strong dependence on the edge structure. The passivation plays important role in the electronic properties of the Blue Phosphorene nanoribbons. In our work, we have also performed the calculations for mechanical strength, width and strain depended electronic properties of the Blue Phosphorene nanoribbons. It was found that the zigzag phosphorene nanoribbon (ZPNR) possess more mechanical strength than the armchair phosphorene nanoribbon (APNR). The electronic band gap is found to be inversely proportional to the width of the nanoribbons. On applying mechanical strain, the band gap the nanoribbon decreases and at specific high value of strain semiconductor to metallic transition occur. Our results may finds applications in Nanoelectronic devices based on the phosphorene based nanoribbons.

Ram Swaroop Dr. Ashok Kumar

Papers Published

1. Swaroop, R., Bhatia, P., & Kumar, A., “Electronic properties and mechanical strength of β-phosphorene nanoribbon”, AIP Conference Proceedings, 2016, vol. **1728**, pp. 020600.

2. Bhatia, P., Swaroop, R., & Kumar, A., “Shape-dependent electronic properties of blue phosphorene nano-flakes”, AIP Conference Proceedings, 2016, vol. **1728**, pp. 020598.

Papers Submitted to journal

1. Ram Swaroop, Pradeep Bhatia and Ashok Kumar. “Electronic and Optical properties of Ultra Narrow Width of Blue Phosphorene Nanoribbons”.

2. Pradeep Bhatia, Ram Swaroop and Ashok Kumar. “Edge and Shape Dependent Electronic and Optical Properties of β-phosphorene Nanoflakes”.

ACKNOWLEDGEMENTS

First of all, I would like to thanks my thesis supervisor **Dr. Ashok Kumar** for the valuable guidance during the course of the work. I really appreciate him for his help, guidance, discussion, patience with me and encouragement. Without his mentorship, this work could not have been completed. It was a great experience to work and learn so many things from him both as a guide and as human being. I have gained much in my professional skills and capability to face future challenges in my career. Thank you very much.

This dissertation could not have been possible without the help of **Dr. A.L. Sharma**, **OIC & Dr. R. S. Deven, CoC**, Centre for Physical Sciences, Central University of Punjab and other faculty members of the Centre for their encouragement, insightful comments and hard questions. The library and the computer facility of the university have been vital.

I would also show gratitude to our Vice-Chancellor **Prof. (Dr.) R.K Kohli** and Dean of Academic Affairs **Prof. (Dr.) P. Ramarao** without their constant help, support and encouragement; this dissertation would not have been possible.

I express my deep gratitude and sincere thanks to **Dr. Koushik Giri** for allowing me to perform computational work in his laboratory. **Harpreet Singh** also deserve my special thanks, for the help at different stages during the completion of the course work.

I thank my CUPB friends **Ms. Chandni Devi, Ms. Anjna Devi, Ms. Geeta Sachdeva, Ms. Priya Thakur, Mr. Pradeep Bhatia, Mr. Devendra, Mr. Chandra Kumar, Mr. Gurdhir Singh** and all in CUP, Bathinda who all are helped me in my research work.

Last but not least; I thank my **parents,** brother and my friends and other who helped me anonymously in completing this research work successfully. I have no words to express thanks to my parents for their love, blessing and always being with me for every small step of the way.

Finally, I would also like to extend my whole-hearted thanks to all my teacher for their encouragement and blessings.

Above all I thank Almighty GOD for giving me the courage to move on.

Ram Swaroop

TABLE OF CONTENTS

Sr. No.	Contents	Page number
	Chapter 1: Introduction	
1.1	Introduction	1
1.2	Motivation of the Work	2
1.3	objective	3
1.4	Outline of Thesis	3
1.5	Low Dimensional Materials	4
1.6	Layered Materials	5
1.6.1	Method for Extracting 2D Materials	5
1.7	Graphene	6
1.7.1	Two Dimensional (2D) Nanostructures Analogous to Graphene	8
1.8	Phosphorene	9
1.8.1	Allotropes of Phosphorene	11
	Chapter 2 : Review of Literature	
2	Literature Review	13
	Chapter 3:Theoretical and Computational Formulation	

3.1	Theoretical Formulation	24
3.2	Born-Oppenheimer Approximation	25
3.3	Hartree Approximation	25
3.4	Hartree-Fock Approximation	26
3.5	Exchange Energy	26
3.6	Correlation Energy	27
3.7	Density functional theory	27
3.7.1	Hohenberg-Kohn Theorems	28
3.8	Computational Method	29
3.8.1	Basis Sets	31
3.8.2	Atomic Orbital Basis Sets	31
3.8.3	Plane Wave Basis Sets	33
3.8.4	Pseudopotential	34
3.8.5	Calculation with SIESTA	35
3.8.6	Band structure	35
	Chapter 4:Results and Discussions	
4.1	Computational Details	37

4.2	Edge Effect on the Electronic Properties of Blue Phosphorene Nanoribbons	37
4.3	Role of passivation with Hydrogen-atom on Blue-Phosphorene nano –ribbons	38
4.4	Effect of width on the Electronic properties of APNR and ZPNR	40
4.4.1	Hydrogenated Edge Structures of Phosphorene: Effect of Width	41
4.5	Mechanical Strength of APNR and ZPNR	45
4.6	Variation in band gap with strain of APNR and ZPNR	47
	Chapter 5: Summary and Conclusions	
5.1	Summary	50
5.2	Future Scope of Research	51
5.3	Future Application of Phosphorene Ribbons	51
	References	53

LIST OF TABLES

Table Number	Table Description	Page No.
1.	Shows the different code which are based on DFT	33

LIST OF FIGURES

Figure Number	Description of figures	Page No.
1.1	The pictorial representation of Low Dimensional Materials.	2
1.2	Monolayer honeycomb structure of graphene.	3
1.3	Different structural forms that can be built up from graphene.	10
1.4	Top view (A) and Side view (B) of Black-Phosphorene.	34
1.5	Different allotropes of Black-Phosphorene.	40
3.1	Algorithm for the Density Functional Theory.	43
3.2	All electron (AE) and pseudo (PS) wave function and potentials.	43
4.1	Top and side view of APNR and ZPNR for the width n = 12.	38
4.2	Electronic band structure and DOS for APNR and ZPNR.	39
4.3	Top and side view of the passivated of APNR and ZPNR.	39
4.4	Band structures and DOS for the H-APNR and H-ZPNR.	40
4.5	Effect of width on band gap for APNR, ZPNR, H-APNR, and H-ZPNR.	40
4.6	Band structures for APNR for width n = 2 to width n=12.	42
4.7	Band structures for H-APNR for width n = 2 to width n=12.	43
4.8	Band structures for ZPNR for width n = 2 to width n=12.	44
4.9	Band structures for H-ZPNR for width n = 2 to width n=12.	44
4.10	Stress versus strain curve for APNR and H-APNR.	46
4.11	Mechanical strength for the ZPNR and H-ZPNR.	46
4.12	Variation in band gap with applied value of strain in APNR and H-APNR.	48
4.13	Variation in band gap with applied value of strain in ZPNR and H-ZPNR.	48

4.14	Band structures for APNR and H-APNR for different values of strain.	49
4.15	Band structures for ZPNR and H-ZPNR for different values of strain.	49

LIST OF ABBREVIATIONS

Sr. No.	Full Form	Abbreviation
1	Zero Dimensional	0D
2	One Dimensional	1D
3	Two Dimensional	2D
4	Three Dimensional	3D
5	Density Functional Theory	DFT
6	Arm- Chair Blue-Phosphorene nanoribbons	APNR
7	Hydrogenated- Arm- Chair Blue-Phosphorene nanoribbons	H-APNR
8	Zigzag Blue-Phosphorene nanoribbons	ZPNR
9	Hydrogenated- Zigzag Blue-Phosphorene nanoribbons	H-ZPNR
10	Spanish Initiative for Electronic Simulations with Thousands of Atoms	Siesta

LIST OF SYMBOLES

Sr. No.	Full Form	Symbol
1	Beta	B
2	Angstrom	Å
3	Electron-volt	eV

Chapter 1: Introduction

This chapter furnishes a brief introduction of two dimensional (2D) materials. It is organized as follows: The initial part of this chapter specifies the general aim and objectives of the research work and the outline of the thesis. The middle sections contain a general description of introduction and history of the graphene and other 2D materials. The last part is specifically focused on classification of phosphorene, a recently emerged 2D material and its properties and possible applications.

1.1 Introduction

The 19^{th} century is known as the golden period in the field of the scientific research and development. The various researches during this period give us excellent application that changes the means of today's life. The researchers are continuing to developing new applications which are playing vital role in the current scientific scenario. With the passage of time development take place in each and every field of science including solid state physics and materials science.

The various properties of the materials are strongly affected by their crystal structure, and this crystal structure exists in nature with lowest energy state. The change in the crystal structure of the material means change in the various properties of the material such as electronic, magnetic and optical properties. Here we are going to discuss the properties of the two dimensional (2D) material that provides us the various excellent application in our modern days life. With the passage of time the study of material form bulk to nano scale reached with excellent results, and the result shows that properties of nano scaled material are excellent than that of bulk state, which signifies the importance of the study of nano science (Cao et al., 2004).

As a result of reduced size of materials and change in the electronic, magnetic, and optical properties, the size of various electronic circuits get reduced that gives electronic devices a new shape. Nano size structured was like a dream in many years back, but now days it is true and possible to make the devices using nano structures. Nano scale structures can be made by two basic approaches i.e. TOP-DOWN and BOTTOM-UP, which gives the concept of low dimensions materials to come into existence.

1.2 Motivation of the Work

Nano science play very important role in present days, there are so many application available in present days which are based on the nano-technology. Let's take an example of the computer, the size of the first computer was very large about equal to the dimension of the two room set, but now a days the size of the computer has been reduced as small as wrist watch. Now a days, the various properties of the material can be changed when we move form bulk to nano scale and these properties of the material leads us to the modern technology i.e. nanotechnology.

Nanotechnology or nano scale science deals with the study of matter at the nano scale, generally taken the 1 to 100 nm range. The nanotechnology deal with the invention and application of physical, chemical, and biological system at nanometer scales. Nanoparticles are considered to be the building blocks for nanotechnology. The nanomaterial's have the ability to display enhanced physical, dielectric, optical, electrical and mechanical properties. The physical properties depend on the nature, shape and dimension of the nano-materials as well as the composite made up from them. The composite materials also hold mechanical, electrical, optical properties which are very valuable (Alda, et al., 2005) (Chau et al., 2005)

Nano materials have number of applications and these applications cover different domains in the world of science and technology. Optically, electrically and anisotropic nature of the nanomaterial have the ability to change the means and way of thinking about the electronic devices today and we can also say that the sharp boundary of technology of the electronics lies in the development of the 2D layered materials.

At present time the 2D layered material have its own importance in the field of electronic industry with the successful discovery of world's first 2D material i.e. Graphene. It is just the startup for new evolution in field of the electronic as well as optoelectronic devices; this new technology will be faster and much more effective as comparison to that of older electronic technology. After the graphene, there are new classes of the 2D materials which are coming into existence and now a days the phosphorene is emerging one of the best 2D material which come into existence in 2014 with various stable allotropic form that has motivated us to

study its electronic properties in various novel forms such as nano ribbons. Although, phosphorene has been studied by various researcher, but a novel allotropic form i.e. blue phosphorene in ribbon form remain untouched part in the literature. Therefore, in the present thesis we have studied the novel form of phosphorene with quasi one dimensional (1D) nano ribbons.

1.3 Objective

- Study the Edge Depended Electronic Properties of Blue Phosphorene Nanoribbons.
- Study the Effect of Passivation on Electronic Properties of the Blue Phosphorene Nanoribbons.
- Study the Effect of Width on Electronic Properties of the Blue Phosphorene Nanoribbons.
- Study of the Mechanical Properties of the Blue Phosphorene Nanoribbons.
- Study of the Effect of Applied Strain on the Electronic Properties of Blue-Phosphorene Nanoribbons.

1.4 Outline of Thesis

This work is aimed at studying the electronic properties of the blue phosphorene nanoribbon. The effect of width and mechanical strain has also been studied. The thesis has been organized as follows:

- **Chapter 1** provides a general overview of the topic. Beginning with the low dimensional materials and there types. The introduction of the first 2D material of the world and the various classes of the 2D material and then finally brief introduction of Phosphorene.

- **Chapter 2** provides the literature review of phosphorene, the current topic of the thesis, from a broader perspective.

- **Chapter 3** briefly explains the theoretical background and computational methods used to study in the thesis. The elements of Density Functional

Theory (DFT) have been briefly described. The overview of the practical implementation of DFT for computer based calculations is also given.

- **Chapter 4** explains the results and discussion of the electronic properties of phosphorene nanoribbons. The effect of width and mechanical strain in the electronic band gap of blue phosphorene nanoribbons are also discussed in details.

- **Chapter 5** includes the summary and future scope of the work.

1.5 Low Dimensional Materials:

Low dimensional materials can be categorised as given in Fig. 1.1 along with three dimensional (3D) bulk counterparts. There are lot of devices which we are using in our daily life such as mobile phones, our digital watch, computers, laptops etc. which uses the applications of the low dimensional materials.

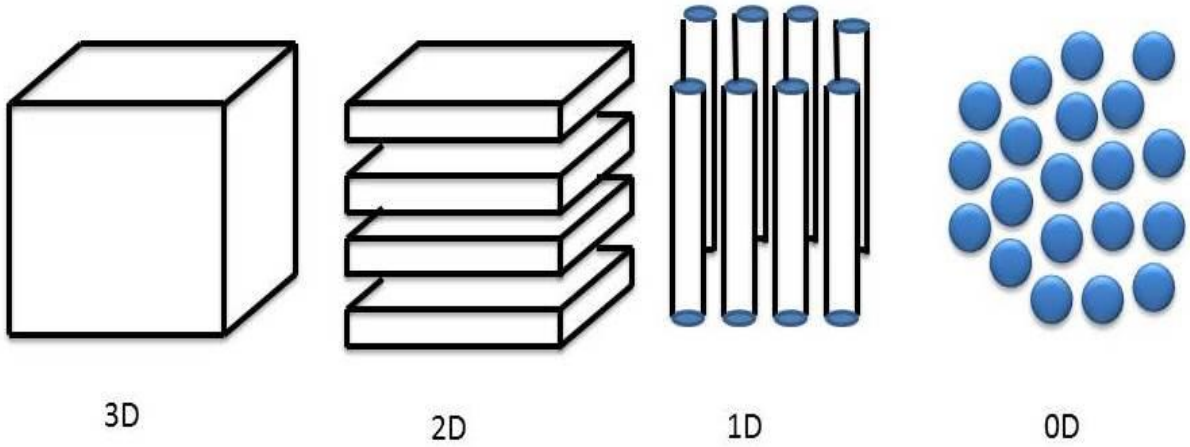


Figure 1.1:-The pictorial representation of Low Dimensional Materials.

These low dimension materials enhance the carrier mobility in the transistor as a result of which faster switching with low power consumption. The low dimensional materials offer excellent electrical, optical and transport properties.

When we characterize these materials then bulk materials come under the categories of the 3D materials meaning to say that all three dimensions are of the order greater than 100 nm. If we reduce the one dimension out of the three dimension up to the nano scale the resultant material is 2D material which is also known as the quantum well, and if we reduce the two dimension of the material up

to the nano scale out of three dimension, the resulting material is one dimension which is also known as the quantum wire. If we reduce all three dimensions of the materials up to nano scale the resulting material is quantum dot.

Here our topic of interest is 2D/1D material as it name itself suggest that it is a single layer/strip of the material, and the extraction of these material is only possible if these exist in layered form. So it is necessary to understand what the layered materials are. So first of all we need to pay attention about the layered material and how they are different as comparison to other materials.

1.6 Layered Materials

As its name suggest that material that exist in bulk form but arranged layer by layer, known as the layered materials. For example the graphene which is extracted from the graphite which exists in layered form. In graphite, in-plan C-C bonding is stronger and in between the layers there are weak Vander Waal forces of interaction. C-C bonding among carbon atoms is stronger than that of Vander waal interaction as a result of which the layer of graphene can easily extracted from the graphite and this single layer of graphite is known as the graphene. For the extraction of these single layers from the layered material there are different techniques that can be used. We have discussed these techniques briefly below:

1.6.1 Method for Extracting 2D Materials

The first step toward the study of 2D material is the extraction from bulk crystal. We need to understand the extraction process of the 2D layer or their fabrication methods.

- **Mechanical Exfoliation:**

  Mechanical exfoliation technique is the one of the best technique for obtaining the pristine form of the 2D material. In mechanical exfoliation technique, separation of 2D layer is take place with the help of applied mechanical force that results into the pristine 2D monolayer. This technique was widely used in the case of graphene and other 2D material (Novoselov et al., 2004), (Balendhran et al., 2013), (Novoselov et al., 2005). The simplest example of the technique is the exfoliation of the graphene 2D layer with the help of adhesive tape in 2004.

- **Chemical Exfoliation:-**

  The chemical exfoliation technique is basic technique for the growth of 2D layers. In this technique the growth of the required material take place on the other material which act as the substrate with the help of chemical process popularly known as Chemical Vapour Deposition (CVD) method. For example the silicene nano ribbons from the 'Ag' substrate can be extended up to the monolayer form (Dávila et al., 2012) (Tritsaris et al., 2013).

- **Liquid Exfoliation:**

  Mechanical and chemical exfoliation technique is used to obtain the 2D layer in small amounts while the liquid exfoliation technique is useful to obtain the 2D layer in large scale. In liquid exfoliation technique the material is disperse in the organic solvent with nearly similar surface energy which is nearer to material surface energy as a result of which the barrier is reduced and the layers are detach form the crystal. After this the ultrasound bath for the hundreds of hour or a voltage is applied then after the dispersion of the solution will be centrifuged in order to dispose of the thicker flakes.

Above are the three basic technique for the exfoliation of the 2D layer form the layered material, form these basic technique we are also learn that mechanical and chemical exfoliation techniques are basically used for the laboratory purpose and for the large amount of production of 2D material generally the liquid exfoliation technique is followed. After the successful exfoliation of the world's first 2D layer from the graphite which is popularly known as the graphene, it become the first 2D crystal of the world in 2004 and simplest technique used for this purpose in adhesive tape method (mechanical exfoliation). The study of this 2D crystal reveals new idea in the field of electronic as well as in tuneable electronic industries.

1.7 Graphene

The single layer of C atoms i.e. graphene in represented in Fig: 1.2. Graphene has hexagonal planer structure which is also known as honeycomb like structure. Graphene can be regarded as the mother of all 2D materials. We can form 1D

nanotube, wires or ribbons, 0D Fullerene-like structures and 3D (bulk) structures from 2D layers as shown in Fig: 1.3. Therefore, 2D materials are the universal building block of the other materials.

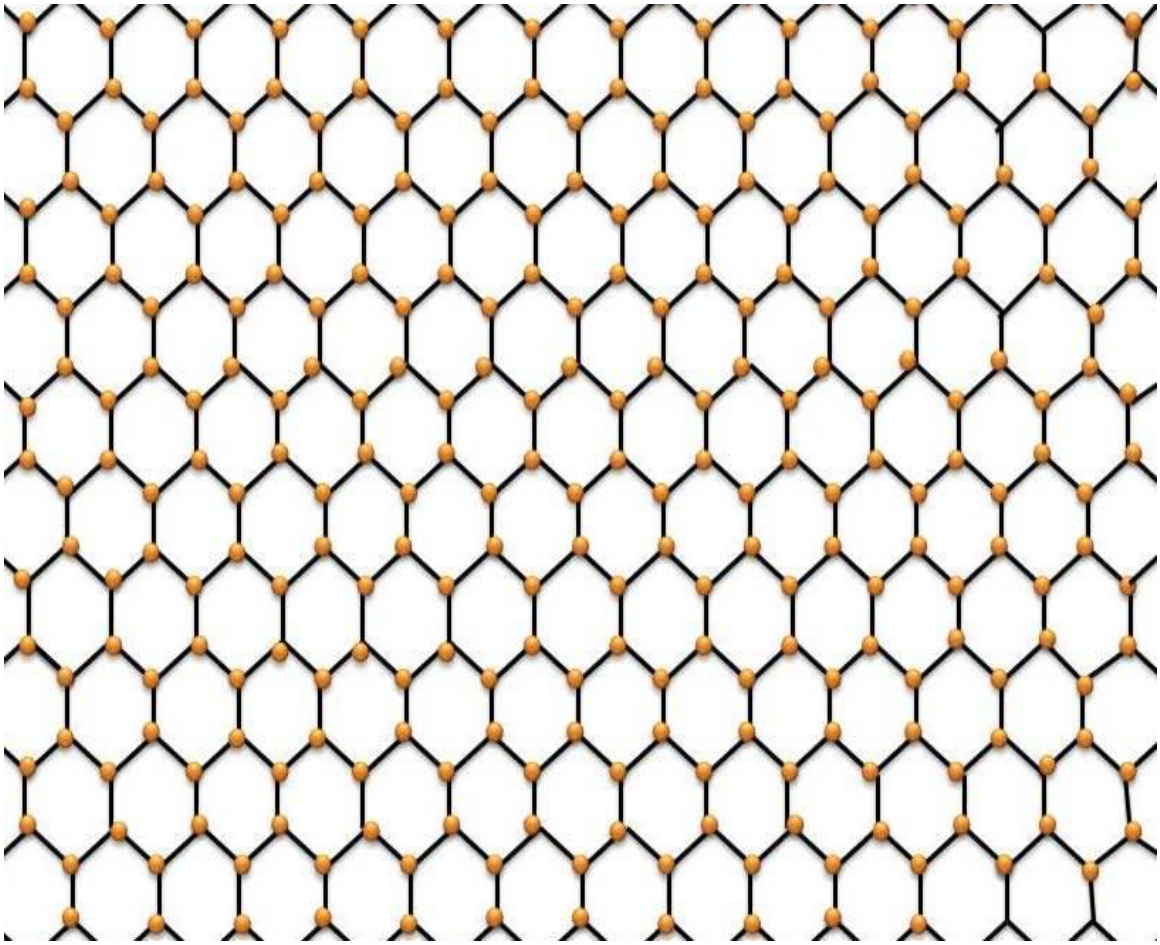


Figure 1.2: Monolayer honeycomb structure of graphene.

It is not only the size but also the dimensionality that is the most important parameters when determining material properties. This particularly applies to the case of sp^2 carbon materials, where 0D fullerenes (example of quantum dot), 1D nanotubes (which is one dimensional materials), 2D graphene(two dimensional material) and 3D graphite (which is 3D material) exhibit very different properties.
Also when it comes to analysing the chronological order of the findings of the different dimensional forms of a given material, the case of carbon is a representative example. Graphite has been known since the sixteenth century and has been widely used in industry for steel-making process, as brake lining or as dry lubricant. But it was not until because the discovery of fullerenes greatly

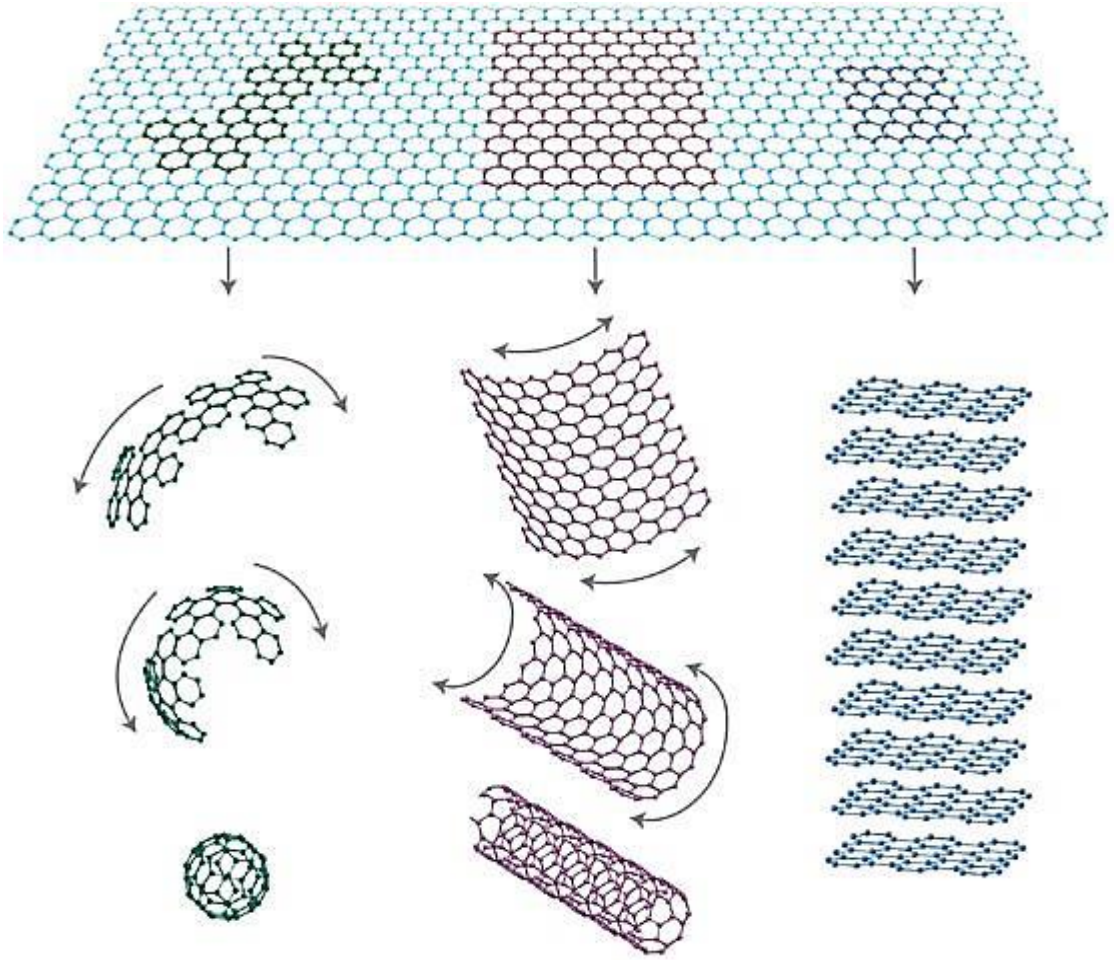


Figure 1.3:-Different structural forms that can be built up from graphene (Geim et al., 2007)

expanded the number of known carbon allotropes and also plug the idea of 1D form i.e. carbon nanotubes, which were first demonstrated in 1991 (Lijima S., 1991)

1.7.1 Two Dimensional (2D) Nanostructures Analogous to Graphene

After the successful discovery of graphene, the scientist and researchers started taking interest in the search of other 2D material and now it has become wide interest research area, as a result of which there are number of 2D material coming into existence likewise graphene, which are given below:

- **Silicene:**

  In 2007 a new 2D material comes into play known as Silicene which is two dimensional atomic layer of Si atoms. The various electronic properties of

the silicene are similar like graphene but the basic difference in between the graphene and silicene is in the structure. Graphene has the planer honeycomb structure whereas silicene also exists in hexagonal honeycomb structure but possess buckling in the atomic planes in z-direction (Takeda et al., 1994) (Guzmán-Verri et al., 2007)

- **Germanene:**

  In 2014 new 2D material which is known as Germanene came into play. Germanene is 2D layer of germanium atoms; the formation process of this material is similar like that of graphene. On the basis of first principles calculation, it is found that Germanene have no band gap but it can be induced with help of passivation with H-atom. Also it is useful for the formation of field effect transistors (Dávila et al., 2014).

- **Borophene:**

  Borophene the next 2D material which come into existence as a allotrope of boron in 2014. The interesting thing about this 2D material is that it contains 36 atoms in its one unit and arranged in 2D sheet which contains a hexagonal hole in the middle (Piazza et al., 2014).

- **Phosphorene:**

  As above we discuss the different classes of 2D material which are discovered after the successful discovery of graphene, next 2D material is Phosphorene which also our research topic. To know about the Phosphorene in details, it is necessary to know about the origin of phosphorene, which is the 2D layer of Black Phosphorus.

1.8 Phosphorene

Phosphorus was discovered in 1669 by Hennig Brand. At that time researcher had not given much attention because of the toxicity and its structural instability (Chou et al., 2001). With the passage of time, first allotrope of the Phosphorus came into existence in 1960 which is popularly known as Black Phosphorus. Phosphorene is Discovered in 2014 by the Ye group (Liu et al., 2014) which is the atomic layer of

P atoms as shown in Fig.1.4. The researchers start paying attention toward the Phosphorene due to its unique properties like high carrier mobility, tuneable band gap which make it useful in optoelectronics (Li et al., 2014) (Qiao et al., 2014). The extraction technique for the phosphorene is commonly the same mechanical exfoliation which was used to extract graphene from graphite crystal (Liu et.al., 2014). Also with the help of liquid exfoliation technique we can also achieve the Phosphorene layers but this technique is useful for large scale production purpose only (Brent et al., 2014).

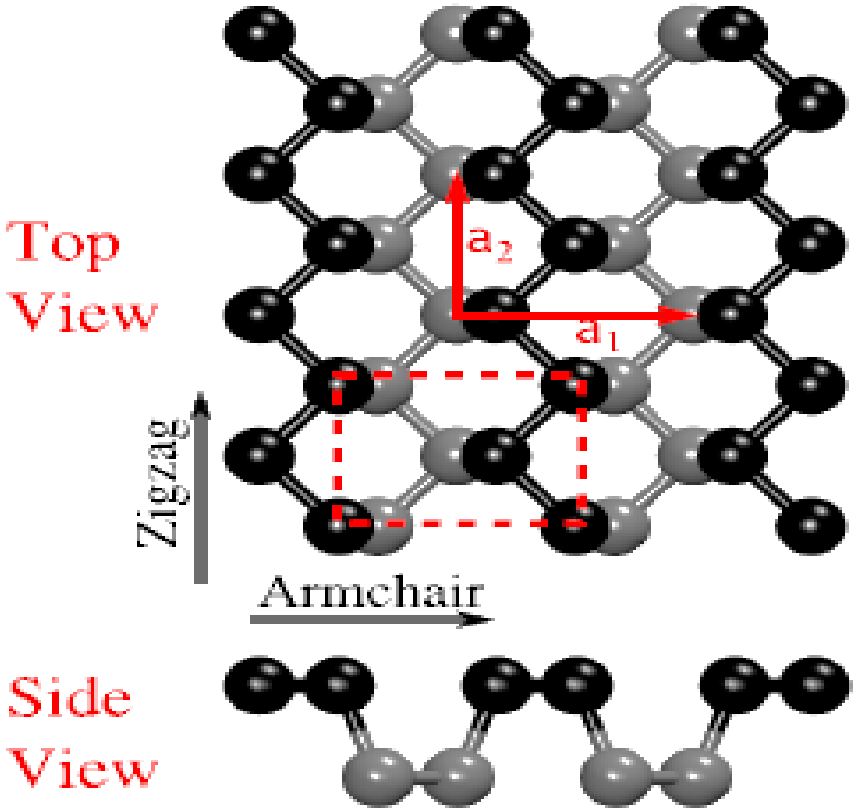


Figure 1.4:- Top view (A) and Side view (B) of Black-Phosphorene (Jain et al., 2015)

First time Black phosphorene is obtain with the help of scotch tape method, after this the phosphorene that produced with the help of adhesive tape was placed on the Si substrate. After this the cleaning process had been taken place with the acetone or with the alcohol as a result of which the unwanted residue of tape is successfully removed from the 'Si' substrate and a phosphorene layer is

left of the substrate. In the next step heating the complete sample about of 200^0C take place to remove residue of the solvent.

Now come to its structural properties, phosphorene possess the puckered structure and the layers of the phosphorene is held together by Vander Waal interaction and within the layers there is strong covalent bonds between the P-P atoms. In the various studies on the band gap of the phosphorene revels that the thickness matters, a monolayer of the phosphorene have direct band gap of order of 1.88 eV and in bulk state its band gap is of order of 0.3 eV (Guo et al., 2015)

1.8.1 Allotropes of Phosphorene:

As we know that any crystal structure for the material always acquires the minimum energy where the maximum stability of the structure takes place. In case of phosphorene there are four basic stable allotropic forms which are black phosphorene (α), Blue phosphorene (β), Gamma-phosphorene (γ) and Delta-phosphorene (δ) as shown in Fig. 1.5. The common thing lies in these structure is that all the structures have sp^3-hybridization. But the difference is that their electronic properties are different, they show different band gap values. Here in our work we have focused on the graphene-like structure of phosphorene i.e. blue phosphorene (Guan et al., 2014).

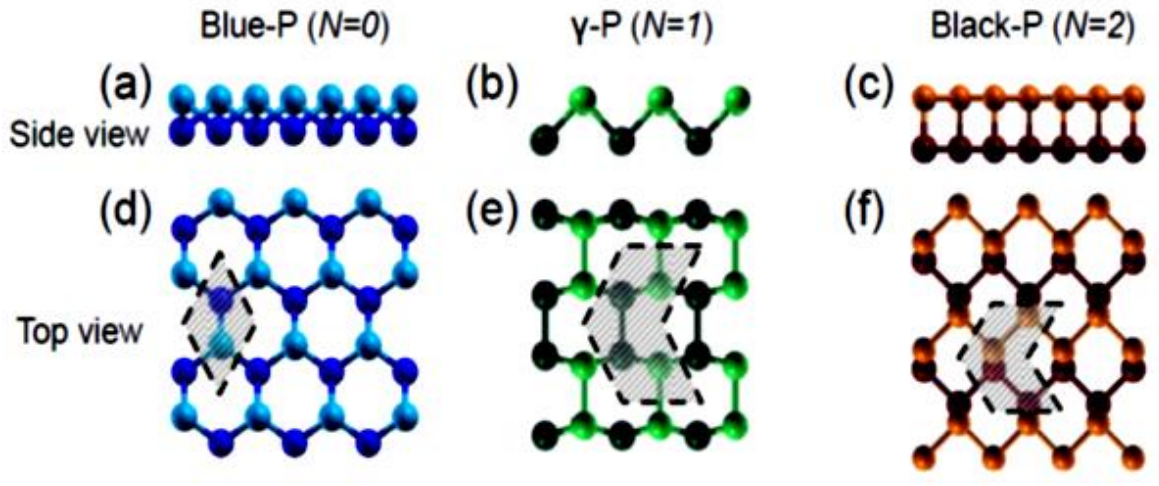


Figure 1.5: Different allotropes of Black-Phosphorene (Guan et al., 2014)

It is important to note that unlike graphene, blue phosphorene has buckled structure similar to silicene. As we discussed previously that dimensionality plays an important role to describe the properties of any materials, we have specifically

focused on the quasi one dimensional (1D) nano ribbon of silicone-like phosphorene to study the electronic properties of the nano ribbons. Our study also includes the effect of the mechanical strain on the electronic properties of the blue phosphorene nano ribbon. And also studied its mechanical strength of the nano ribbon for its maximum width (n) i.e. for n = 12 for the both of the edge configuration i.e. armchair nano ribbon (APNR) and zigzag nano ribbon (ZPNR).

Chapter 2: Literature Review

This chapter furnishes a literature review of 2D materials including graphene. Specifically, phosphorene and its studied properties till date have been reviewed. Around the world, various research groups have made attempts to improve the charge carrier, electronic band gap and mechanical properties of the phosphorene.

- **Novoselov et al. (2005),** they demonstrated the existence of 2D atomic crystals with the simple mechanical exfoliation technique and found that 2D material is stable at room temperature. 2D materials can be easily made with the help of adhesive tape method. For industry point of view other method like liquid exfoliation technique can be used to fabricate 2D sheets at large scale.

- **Berger et al. (2006),** they studied the growth of ultrathin graphite on the silicon substrate. Form the designed sample it is found that the transport properties are closely related to carbon nanotube which are governs by the single graphite sheet i.e. the monolayer of graphene sheet. Also they show the quantum confinement of electrons and found the phase coherence lengths beyond 1 micrometer at 4 K and carrier mobility's 2.5 m^2/Vs.

- **Novoselov et al. (2007),** they studied that graphene has zero band gap with linear energy spectrum. Single layer graphene is 2D massless Dirac fermion system that is of crucial importance for the understanding unusual electronic properties such as an anomalous quantum hall effect, absence of Anderson localisation etc.

- **Kyle et al. (2009),** they performed DFT calculations for the study of electronic properties of graphene. In their study they found that electronic band gap varies with the edges of graphene. Different edge construction of graphene provides the different electronic band gap.

- **Köpf et al. (2014),** they demonstrated the method for growing the single crystal of black phosphorus by short way transport reaction from red phosphorus by applying a mineralization approach. In their work they found one of the cheapest and fastest effective growth of single crystal of black phosphorus.

- **Brent et al. (2014),** in their work they introduced the method for the liquid exfoliation for the black phosphorus in N-methyl-2-pyrrolidone with the help of which three to five layers of the phosphorene are formed. And also provide the conclusion that with this methodology a sheet of the phosphorene layer can also be prepared.

- **Castellanos-Gomez et al. (2014),** they demonstrated the new technique for mechanically exfoliation for the phosphorene. In their technique, they use the Nitto tape instead of adhesive tape so that the problem of unwanted residue of adhesive tape is overcome. With the help of Nitto tape the cleavage of the phosphorene take place and then tape is pressed against a poly-dimethilsiloxane (PDMS) based substrate and peeled off rapidly, as a result of which pure form of black phosphorene get achieved.

- **Han et al. (2014),** they investigated the optical and electronic properties of the few layers of the phosphorene, and found that the electronic band gap of the phosphorene directly depends upon the number of phosphorene layers. The value of band gap in monolayer phosphorene is larger than that of bulk phosphorus. In monolayer, the band gap is in the range of 0.31-0.36 eV

- **Fengnian et al. (2014),** they showed the higher carrier mobility in black phosphorene layers along with anisotropic nature of the layers with narrow band gap. In their study they found that the phosphorene act as good agent for the formation of the optoelectronic devices, sensors and transistor technology.

- **Hugh et al. (2014),** they studied that the electronic mobility is the key indicator of device quality. In their study they mention that black phosphorus layers have an anisotropic structure and having uniqueness among 2D layers. The layers are bucked in nature with two planes mutually perpendicular directions with zigzag and armchair edges. The anisotropy has the strong impact on the electronic properties of the materials.

- **Koenig et al. (2014),** they studied that phosphorene is also layered material like as graphene and can also be obtain with the help of mechanical exfoliation technique similar to graphene. Their study also includes the carrier mobility and they found that at room temperature mobility is up to 300 cm^2/Vs and drain current modulation of over 10^3. On-off ratio exceeded 10^5 and device exhibits both electron and hole conduction.

- **Rodin et al. (2014),** they demonstrated the first principles calculations of monolayer phosphorene and it is found that there is direct or nearly direct semiconducting band gap which can be tuned by mechanical strain. Apart from the strain dependency of the band gap in phosphorene layers, the structural modification comes into existence with the applied stain.

- **Buscema et al. (2014),** in their study they found that phosphorene layers possess high carrier mobility with semiconducting band gap of ~ 2.0 eV and also the electronic band gap varies as a function of width. For the formation of field effect transistor there is requirement of the thickness of the phosphorene layers about 3 nm to 8 nm.

- **Qiao et al. (2014),** in their study they found that the black phosphorene is promising candidate for the future electronic as well as optoelectronics. They studied the electronic behaviour of five phosphorene layers and found that band gap decreases from 1.51eV for a monolayer to 0.59 eV for five layers. Also they found that phosphorene possess higher hole mobilities than other 2D layers.

- **Li et al. (2014),** they studied the potential application of the black phosphorene in their study and found that a reliable transistor performance can be achieved at the room temperature in a sample with drain current modulation. They demonstrated with their work that the 2D material is emerged as a class of materials that may give best contribution in the future electronic technology.

- **Li et al. (2014),** they performed the density functional theory simulation for the phosphorene layer in their work by investigating the electronic properties of six phosphorene layers and found that the band gap depends upon the layers thickness or number of phosphorene layers. Lattice constant for the phosphorene layer increases with the increase in number of phosphorene layers. The electronic band gap change from 0.5 to 1.6 eV with layer thickness. Also strain plays very important role in the band gap modulation. Biaxial and uniaxial strain significantly influences the electronic properties. The band gap continuously modified by strain from zero to 1.97eV, which may results into the promising material for the solar cell applications.

- **Hu et al. (2014),** by using density functional theory they also studied the electronic and properties of the monolayer and bilayer phosphorene under uniaxial strain, and they found that under the continue strain on the monolayer results into the structural change in the monolayer of phosphorene from pucker structure to a flat hexagonal planer structure at 29% strain. Also under the tensile strain the band gap increases for both monolayer and bilayer.

- **Peng et al. (2014),** by using first principles calculations they provided the detail analysis of two-dimensional phosphorene and conclude that: band gap of the 2D phosphorene has direct to indirect gap transitions with strain; the band gap calculated with the conventional approach of density functional theory is nearly same as that obtained with hybrid functional method; carrier effective masses of the electron and hole in the armchair direction are an order of magnitude smaller that of zigzag direction which

means that the armchair edges are more favourable for the charge carrier transport.

- **Çakır et al. (2014),** they studied the effect of strain on the electronic transport properties and optical properties of phosphorene. In their research work they found that the carrier conductivity is highly anisotropic and strongly depend on the amount of applied strain. They also found that variation in the electronic band gap is due to the many body effect, and the exciton binding become prominent when the dimensionality is reduced of the thin layers. Strain engineering act as an effective agent for the tuning the optical response and electrical conductivity.

- **Peng et al. (2014),** they performed the density functional theory based calculations to study the chemical scissors effects on the phosphorene. They found that H, Cl, OH and F act as a good agent rather than O, S, and Se for the chemical scissor due to the strong bonding with the P-atom.

- **Guo et al. (2014),** they performed the ab initio calculations to study the electronic properties of phosphorene nano ribbon and single wall phosphorene nanotube. It is found that zigzag edge phosphorene nano ribbons are metallic while arm chair nano ribbons are semiconducting in nature. Arm-chair and zigzag edge nano ribbons along with single wall phosphorene nanotube are semiconducting in nature with direct band gap. The multilayer phosphorene layers are semiconducting with their band gap which gets modified with layer thickness.

- **Han et al. (2014),** studied the arm-chair, diagonal and zigzag phosphorene nano ribbons by using density functional based code and they found that in case of zigzag phosphorene nano ribbon the quantum size effect is more than other edge ribbons. Increases in the band gap take place from 1.4 eV to 2.6 eV when the width is reduced from 26 to 6 Å. When the strain is applied it leads to increase in electron effective mass at 8% strain in the case of arm-chair edge while zigzag edge phosphorene nano ribbon show increase in hole effective mass at 3% strain.

- **Tran et al. (2014),** with the help of density functional theory they demonstrated electronic and optical responses of phosphorene nano ribbon. In their calculations they showed that band gap can be enhanced by the quantum confinement, and carriers of phosphorene behave as relativistic particles along the armchair direction. In case of optical response of arm-chair and zigzag nano ribbon both the ribbons exhibit a nearly direct band gap while armchair nano ribbon have strong optical excitations as compare to zigzag nano ribbons.

- **Ramasubramaniam et al. (2014),** they presented the density functional theory calculations of the thermodynamic and electronic properties of phosphorene nano ribbons with and without passivation. The calculated phase diagram identifies energetically preferred edges as a function of temperature and hydrogen partial pressure. They also found that phosphorene ribbon which is passivated with hydrogen show semiconducting behaviour and the band gap decreases with the increase in the width of ribbon. They showed in their work that electronic properties of phosphorene nano ribbon is controlled by the edge termination by processing the condition of the temperature and hydrogen partial pressure.

- **Peng et al. (2014),** they studied the effect of edges which are passivated with the various functional groups and in their study they found that zigzag phosphorene nano ribbons show semiconductor as well as metallic behaviour. On the other hand, arm-chair phosphorene nano ribbons show semiconducting properties. The conduction band maxima and valance band maxima for the different edge functional groups are contributed by the intrinsic electronic states of non-edge phosphorus atoms and edge species have negligible contribution on their wave functions.

- **Li et al. (2014),** they demonstrated the systematic study of the electronic and edge stability of the phosphorene nano ribbons with passivation and without passivation. The edges of phosphorene nano ribbon show diverse electronic properties without passivation. The ribbons become stable on the saturation of dangling bonds. It is found that the passivated edges show minimum energy values than as comparison to the unpassivated edges of

the phosphorene nano ribbons. They also conclude that passivated edges of the phosphorene nano ribbons can act as the promising candidates for the applications in the electronic and photonic devices.

- **Guan et al. (2014),** they studied the black phosphorene and discuss about the other allotropes of the phosphorene via Blue-Phosphorene or beta-phosphorene, Gamma- phosphorene and Delta phosphorene. Out of these three allotropes, blue Phosphorene is more approaching for the stability like as black phosphorene and remaining are less stable as comparison to blue phosphorene. Although these are the allotropes of the phosphorene, but shows different electronic properties from each other which make it more interesting candidate in field of electronics. Also Blue Phosphorene has sp^3 hybridization as like the black phosphorene.

- **Xie et al. (2014),** they performed the first principles calculations for the blue phosphorene nano ribbons and present the quantum confinement effect mechanism for the band gap as a function of the width of blue phosphorene nano ribbons. In their work they use hydrogen passivated and unpassivated ribbons in both arm chair and zigzag form. Both types of ribbons show the semiconducting behaviour on decreasing the width.

- **Li et al. (2014),** they performed the first principles calculations for the Dirac cones in the phosphorene and come along with the conclusion that phosphorus atoms have potentially bringing about many intriguing phenomenon related to its Dirac fermions, which is different than from the graphene.

- **Dai et al. (2014),** they performed the first principles calculations to investigate the electronic properties of the bilayer phosphorene with different staking order and found that the direct band gap can be varied from 0.78 to 1.04 eV with the three different stacking orders. Also they found that when the monolayer of the MoS_2 is superimposed with stacked layer of the phosphorene , the resulting tri layer can be acts as effective material for the solar cell material with hetero junction alignment, and the power conversion efficiencies is predicted to be approximately 18% or 16%.

- **Kou et al. (2014),** on the basis of various properties like electronic, optical and mechanical properties of the phosphorene, they describe phosphorene as prominent candidate for the various applications such as transistor technology due to high carrier mobilities. Also it can act as an active candidate Li battery because the Li atoms strongly bind with phosphorus atom in the cationic state which is useful for the development of the futuristic Li ion batteries.

- **Kou et al. (2014),** they studied the structural, electronic and transport properties of monolayer phosphorene with adsorption of gas molecules CO, NH_3, NO and NO_2. In their study they found that the gas molecules bind with the phosphorene which means phosphorene show sensitivity for these gas molecules. Also due to this behaviour of the phosphorene electronic band structure also gets influenced and alter the transport properties of the phosphorene. Such sensitivity and selectivity for the gas adsorption make phosphorene a desirable as best gas sensor.

- **Zhao et al. (2014),** they performed the first principles calculations based on density functional theory and investigated the adsorption and diffusion of Li atom on the phosphorene monolayer and bilayer. It is found that phosphorene undergo a transition from semiconducting to metallic upon the lithiation, as a result of which additional electric conductivity come into play. And the binding of the Li atoms is stronger in the case of the bilayers than as comparison to the monolayer. Theoretical capacity of the monolayer is about the 432.79 mAh/g which is larger than that of anodes which is generally used in the Li ion batteries.

- **Zhang et al. (2015),** they studied that phosphorene acts as good agent for the electronic industry due to its finite band gaps and anisotropic electronic mobility. By make use of first principles calculations they also studied the effect of strain on the sheet and found that anisotropic conductance can be controlled by using strain conditions i.e. biaxial or uniaxial strain. And the also found that conducting direction can be rotated by 90^0 with the applied strain.

- **Ju et al. (2015),** they studied the black phosphorene and effect of the biaxial strain on its band gap. In their work they use five layers of phosphorene. To perform this work they use the density functional theory and found that with the applied strain the band gap can be modified. Without strain the ground state was found to be semiconductor. The biaxial tensile strain does not affect essentially the electronic properties of the system, but when the compressive strain is applied the ground state of the few phosphorene is turns into the metals.

- **Ge et al. (2015),** in their work they investigated the effect on electron-phonon coupling and superconductivity in case of monolayer of phosphorene by making use of first principles calculations They found the main contribution to electron-phonon coupling at low frequency optical phonon modes. The strain act as an agent which enhances the electron phonon coupling.

- **Hu et al. (2015),** they studied the compressive strain and in-plane strain on the phosphorene and found that with the applied strain up to its maximum strength, deformation in the structure of the phosphorene come into play, and also the electronic properties get also changed with the applied magnitude of the strain which is useful for the device engineering.

- **Owens et al. (2015),** they employed the density functional theory to calculate the electronic properties of the phosphorene nano ribbons as a function of wave vector. Because of the anisotropic and layered nature of the black phosphorus, the monolayer can be achieved and the electronic properties show strong dependence on the direction of cutting the nano ribbons. Their calculations also predicts that the ground state of unit cell is a triplet which shows that ribbons are made of triplet unit cell which is ferromagnetic semiconductors.

- **Wu et al. (2015),** they studied the electronic and transport properties of the phosphorene nano ribbons by density functional theory and Greens function's approach and found a giant stark effect in the Phosphorene nano ribbon. Their study also includes the transport channels in phosphorene

nano ribbons via the calculations of the current density and local electron transmission pathway. They found under the low bias that carrier transport channels are located in the interior of both armchair and zigzag phosphorene nano ribbons.

- **Sun et al. (2015),** they performed the first principles calculations to study the geometric, magnetic and electronic properties of non-metallic atom like B, C, N, O, F on Blue Phosphorene. The non-metallic atoms that are attached with the blue phosphorene are highly stable and show the direct band gap semiconductor behaviour with approximated band gap of order of 1.5 eV. Also the magnetic nature gets induced in the layer when C and O atom are attached with blue phosphorene.

- **Aierken et al. (2015),** they studied the lattice thermal properties of the black and blue phosphorene by making use of first principles calculations based on the quasi-harmonic approximation approach. They use black and blue phosphorene allotropes. Blue phosphorene is isotropic in nature while the black phosphorene is anisotropic in nature. From their calculations they predict that black phosphorene has highly anisotropic thermal properties in comparison to blue phosphorene and their linear thermal expansion coefficient along the zigzag and armchair direction differ up to 20% in black phosphorene. The arm chair phosphorene are more expandable than as comparison to zigzag phosphorene and biaxial expansion of the blue phosphorene under finite temperature.

- **Hu et al. (2015),** they investigated the magnetic and electronic properties of the blue phosphorene nano ribbon by make use of the density functional theory, in their calculations they found that electronic properties of the blue phosphorene nano ribbons depend on their width. Zigzag ribbons display the intra edge antiferromagnetic ground state with a semiconducting band gap of the order of 0.35 eV but with the passivation this effect gets vanishes. Also the band gap of the passivated zigzag phosphorene nano ribbons is about 1.77 eV which is almost equal to band gap of monolayer of blue phosphorene nano ribbon. Passivation with O atom shows that the

antiferromagnetic state, beside both unpassivated and O-passivated zigzag blue phosphorene nano ribbon preserved almost the same band gap.

- **Aierken et al. (2015),** they demonstrated the advantage of the blue phosphorene nanotube in order to make the small nanotubes. For this purpose they create the five different types of the defect lines in various combinations for the formation of the phosphorene nanotubes. In their study they found that the armchair faceted phosphorene nanotubes have the similar formation energy than the recently proposed multiphase faceted phosphorene nanotubes but they have variety of structures.

- **Zhang et al. (2016),** they performed the first principles calculations and study the effect of different edge passivated with various groups or atoms. The results show that carrier mobility of the passivated phosphorene nano ribbon is very sensitive to the passivated group, but this property is also strongly dependent on the orientation of the phosphorene nano ribbons. Passivated armchair nano ribbons have larger carrier mobility than zigzag phosphorene nano ribbons.

Chapter 3: Theoretical Background and Computational Method

In this chapter, theoretical background for solving multi electron system and various approximations necessary to solve many-body Hamiltonian have been discussed. The development of the Density Functional Theory (DFT) and its practical implementation are briefly discussed.

The base of the various properties of the material is its electrons and nuclei or we can also say that the properties of the material depend on the interactions of their electrons and nuclei. In the history of science, various methods have been developed to predict the properties of the materials (Ziman et al., 1972), out of these methods Density Functional Theory (DFT) (Kohn et al., 1965), (Martin et al., 2004) is one of the important method. With computational technique, we can implements the structural and chemical composition of the given material.

3.1 Theoretical Formulation

It is possible to solve the one electron system easily with the help of Schrödinger equation, but when we move from one electron system to multi electron system it is difficult to solve these problems with the help of Schrodinger equation. This is because the increase in the number of interaction terms like electron-electron, electron-nuclei, etc. even when we increase the number of atom in the system nuclei-nuclei interaction terms also comes into play. These multi interaction term are very difficult to solve with the help of Schrödinger equation. Thus here we requires to addition of some extra term in the Schrödinger's equation so that these multi electron or multi atom system are solved effectively.
The many-body Hamiltonian can be represented as:

$$H = -\frac{\hbar^2}{2m_e}\sum_i \nabla_i^2 - \frac{\hbar^2}{2m_I}\sum_I \nabla_I^2 - \sum\frac{Z_I e^2}{|r_i - R_i|} + \frac{1}{2}\sum\frac{e^2}{|r_i - R_J|} + \frac{1}{2}\sum_i'\frac{Z_I Z_J e^2}{|r_J - R_J|} \quad \ldots\ldots\ldots\ldots (3.1)$$

Where m_e and m_I represent the electron mass and mass of the nuclei respectively, r_i and R_i are positions of electron and nuclei. Z_I is charge of nuclei and $'e'$ is charge of electron. The first and second terms are the kinetic energies of the electrons and nuclei, respectively. The third term describes the Coulomb

attraction between nuclei and electrons. The fourth and fifth terms describe the electron-electron and nucleus-nucleus Coulomb repulsion, respectively. Since the real Hamiltonian of solids consists of electrons and nuclei of the order of 10^{23}, the problem is impossible to solve. So we need new approximations to make the many-body problem solvable. Now above equation represents the modified Hamiltonian by make use it we can solve the multi atom problems but it is still too complex to solve the problem. Now to make it more-simpler the various approximations are used to solve the complexity of the Hamiltonian. These approximations are discussed below:-

3.2 Born-Oppenheimer approximation

In multi electron system the wave function is comprise of the electronic and nuclei, the nuclei velocity can be neglected in comparison to the velocity of the electron. And nuclei-nuclei repulsion interaction can be considered as the constant. After the implementation of the above idea the nuclei interaction term is removed from the total Hamiltonian. And the remaining terms in the Hamiltonian describe the motion of electron of the fix nuclear charge which is known as the electronic Hamiltonian. Now if we have the N electron moving in external potential (V_{ext}) of the fixed nuclei than the electronic Hamiltonian is

$$H = -\frac{1}{2}\sum \nabla_i^2 + \sum_i V_{ext}(r_i) + \frac{1}{2}\sum_{ij}{}' \frac{1}{r_{ij}} \quad \ldots\ldots\ldots (3.2)$$

3.3 Hartree Approximation

Hartree make the another approximation for the more simplification of the multi atom Hamiltonian which is known as Hartree approximation (Hartree. 1928). According the Hartree approximation each electron in the system is consider as independent entity, interaction with the another electron is an average way. Thus the electron is considering the independent entity; therefor the total energy is approximated as the sum of the n number of the one electron energies.

$$E = E_1 + E_2 + E_3 + \ldots\ldots\ldots\ldots\ldots + E_n$$

And the n-electron wave function can be simply approximated as the product of n numbers of independent one-electron wave functions:

$$\psi(r_1, r_2, r_3, \ldots\ldots, r_n) = \psi_1(r_1)\psi_2(r_2)\psi_3(r_3)\ldots\ldots\ldots \psi_n(r_n) \ldots\ldots (3.3)$$

The biggest drawback in Hartree method is that it does not satisfy the basic principles of quantum mechanics which must be followed by electrons due to its spin. Hartree method violates the Pauli exclusion principle. In addition, the exchange and correlation energies are neglected.

3.4 Hartree-Fock Approximation

The Hartree-Fock approximation is viewed as the basis or foundation for more accurate approximation involving correlation between electrons. Within the Hartree- Fock approximation, the many body electrons satisfies anti-symmetry rule. The total wave function of the system can be treated as a single Slater determinant of independent electrons.

$$\psi_{HF} = \frac{1}{\sqrt{n!}} \begin{vmatrix} \psi_1(x_1,\sigma_1) & \psi_1(x_2,\sigma_2) & .. & .. & \psi_1(x_n,\sigma_n) \\ \psi_2(x_1,\sigma_1) & \psi_2(x_2,\sigma_2) & .. & .. & \psi_2(x_n,\sigma_n) \\ \vdots & \vdots & & \vdots & \vdots \\ \vdots & \vdots & & \vdots & \vdots \\ \psi_n(x_1,\sigma_1) & \psi_n(x_2,\sigma_2) & .. & .. & \psi_n(x_n,\sigma_n) \end{vmatrix}$$

Where each wave function represents the single particle spins orbital.

3.5 Exchange Energy

To understand the Exchange energy first of all we need to understand what is antisymmetry of wave function. Antisymmetric nature of wave function means the electron that have the same spin are spatially separated by obeying the Pauli exclusion principle, as a result of which less overlapping of the electron densities around the electron which leads to the less electron-electron repulsion energy and decrease in the total energy. This reduction in energy due to the antisymmetry is known as the exchange energy and therefore need to add an exchange term in

the Hartree- Fock approximation. This exchange energy is the sum of the integrals as a function of single particle orbitals.

$$E_x = -\frac{1}{2}\sum_{ij}^{n} \iint \frac{\Phi_i^*(r)\Phi_j^*(r')\Phi_i(r')\Phi_j(r)}{|r-r'|}\ dr\ dr' \quad \ldots\ldots\ldots\ldots\ldots (3.4)$$

The above expression calculates the exact exchange energy and the negative sign show that it is attractive and therefore reduction in total energy.

3.6 Correlation Energy

Correlation energy term is defined as the difference between the many body energy of the system and the total energy of the system calculated by the Hartree Fock approximation. Hartree-Fock approximation does not include the correlation effect. According to the Hartree-Fock approximation electrons are moving in the average potential field of all the other electrons. The instantaneous influence of electrons that come close together at some point is not taken into account. Electrons repel each other due to same sign of charge, and they tend to stay away from each other.

Their motion, therefore, is correlated, and this correlation reduces the energy of the system because it also reduces the electron-electron repulsion. The Hartree-Fock wave function does not account for this correlation and, therefore, produces an energy that is too high. It is extremely difficult to calculate the correlation energy of a complex system because correlation affects both kinetic and potential energies. Thus an approximation is required to solve this problem. The first quantitative form of the correlation of homogeneous electron gas was proposed by Wigner (Wigner 1938) and first calculations are performed in 1957 by Gell-Mann and Breuckner (Gell-Mann et al., 1957).

3.7 Density functional theory

To solve the multi electron system various implementation take place in the Schrödinger equation so that it is easier to solve the multi electron system which is of 3N coordinates system. The Hartree-Fock method was able to simplify the calculations keeping them parameter free, but limitation is that it is applicable to small systems only up to number of atom of order of tens only. It means problem occurring again for large number of systems, then breakthrough finally happen

when Hohenberg give two theorems which is concerning about the electron density and energy functional in 1964 (Hohenberg et al., 1964) and after the gap of one year Kohn and Sham came with scheme which is now popularly known as Density Functional Theory (Kohn et al., 1965).

In Density Functional theory instead of using single electrons they uses the density term as a main variable $\rho(r)$ to solve the multi electron system, as result of which computational effort drastically changes to the level of practical use for big molecules, solids and real materials. Additionally, correlation energy in HF method also got accounted within DFT.

3.7.1 Hohenberg-Kohn Theorems

Hohenberg and Kohn give the two theorems which is very useful, according to these theorem if we know about the density of system then we can determine the all ground state properties of the system, and the total ground state energy of many electron system is functional of the density. Therefore, if we know the electron density functional, we can know the total energy of the system. These two theorems are discussed below:

- **Hohenberg-Kohn First Theorem**

  According to first theorem "the external potential and hence the total energy is a unique functional of the electron density" and hence the energy functional can be written in term of external potential.

$$E[\rho(r)] = \int \rho(r) V_{ext}(r)\, dr + F[\rho(r)] \quad \ldots\ldots\ldots\ldots (3.5)$$

  Where F [$\rho(\mathbf{r})$] is an unknown and is a functional of the electron density.

  And Hamiltonian for this system is known as:

$$\hat{\mathcal{H}} = V_{ext} + \hat{F} \quad \ldots\ldots\ldots (3.6)$$

  Where '$\mathcal{H}'$ represents the electronic Hamiltonian.

- **Hohenberg-Kohn Second Theorem**

  Hohenberg-Kohn second theorem gives the information about the functional. The electron density which minimizes the energy of the overall functional is the true electron density corresponding to the full solutions of

the Schrödinger equations. Second theorem of the Hohenberg-Kohn is also known as the Hohenberg-Kohn variational theorem because this theorem provides the energy variational principle (Hohenberg, P et al., 1964).

These two theorem act as the basic foundation of the Density Functional Theory after the implementation of these two theorems it is possible to solve the multi electron system effectively and efficiently for large number of real materials, because after the implementation of these two theorems computational work drastically decrease.

3.8 Computational Method

Now after the development of the Density Functional Theory, it has to be practically implemented. For this, it is necessary to develop the algorithm followed by the development of the computer code. Currently we have number of computational code available commercially as well as in open source. Using this code, researcher performs the Density Functional Theory calculations and studies the various properties of the material which like electronic, magnetic, optical, strength of material, also variation in various properties when different condition is applied to the system, and these conditions are like, temperature, strain, increasing the number of atom of the system. With the passage of time, the development in Density functional theory take place and implemented in computer codes so that we can predict the more accurate properties of the materials.

With the help of computer simulation we are able to idealized model of physical system which we want to study, for this purpose we need to specify the algorithm. Given below in Fig. 3.1 is the flowchart of the algorithm used to implement the density functional theory. The computer system simulates the physical system and defines the computer experiment. Computer simulation technique acts as a bridge between the laboratory experiment and idealized model that has no laboratory counterpart.

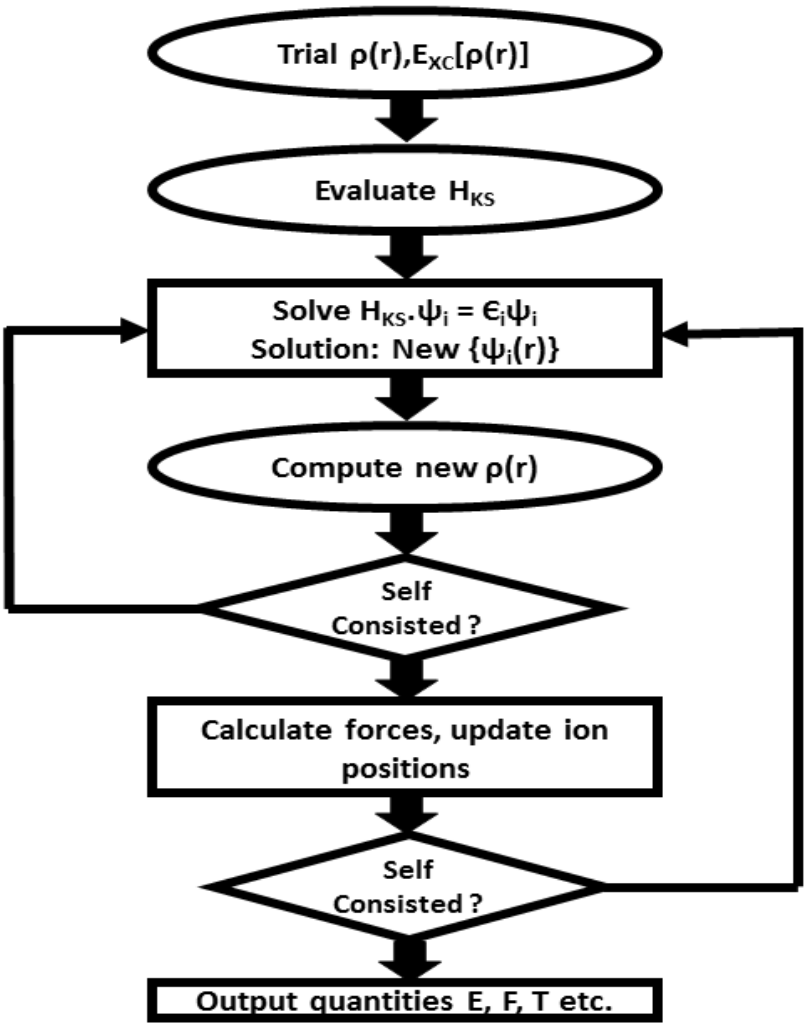


Figure 3.1: Algorithm for the Density Functional Theory

Simulation studies are performed not on the real world system but on a model of the system created for the purpose of studying certain system dynamics and characteristics. Due to the increasing power of computer technology, we are able to get the desired results in less time. In our research work to perform the First Principles calculations in computer system first we follow the algorithm for the DFT with the help of different codes. The basic description of the code is illustrated below:

As we discuss in Hohenberg Kohn theorem that if we know the ground state energy of system than we are able to calculate the various properties of the systems. So our first aim is to predict the ground state density for the system. To do this we have to predict a trial wave function for corresponding density of the

system. And solve it for the Hohenberg Kohn system, and then predict the value of ground state density. If the predicted ground state density is not consistent with the trial density, system performs the calculations once again to predict the ground state density. If the predicted ground state density is consistent with actual ground state density of the system than calculations moves forward. And we perform the calculations for various properties of the system. The procedure is described in fig. 3.1

In our research work we deal with the DFT based computer simulation by using software. And we know that Density Functional Theory is completely based on the Kohn-Sham equations, and the electron wave function of Kohn-Sham wave function is represented by a linear combination of basis set orbital. These basis sets may be made from localized atomic orbitals, plane wave or some mixed basis sets which is specified in different DFT based computer codes.

3.8.1 Basis Sets

Kohn-Sham equations can be solved by expanding them in the linear combination of known simple functions or basis set orbitals as shown in following equation

$$\psi_i(r) = \sum_{\mu=1}^{p} \phi_\mu(r) \quad \ldots\ldots\ldots\ldots (3.7)$$

In the above equation $\Phi_\mu(r)$ is the basis set. This basis set generally used are of two types that are it may be atomic orbital basis set or plane wave basis set. Whereas $c_{i\mu}$ are the coefficients of basis set functions (Kresse, G et al., 1996)

3.8.2 Atomic Orbital Basis Sets

To solve the electronic structure problem within the framework of DFT or Hartree-Fock approaches, it need to choose the mathematical representation for one electron orbital and therefor, require an atom centred basis set. But the problem associated with it is not sufficient to represent accurate atomic orbital by using the single basis set, which mean we requires a set of basis function (Sánchez-Portal et al., 1996)(Junquera et al., 2001). Now to deal with the electron-ion interaction,

we need to choose the solution of pseudo-atomic problem because the columbic potential is replaced with the pseudopotential. These pseudo-atomic orbitals provide an optimal representation of the orbitals close to the theory. On the basis of size, the numerical value of orbitals can be defined as:

- **Single zeta basis set:** single zeta basis set has one single radial function per angular momentum channel. Single zeta basis which is also known as minimal basis set are accurate for isolated atoms they are not flexible enough to describe the molecular system where electrons participate in chemical bonding and become polarized.

- **Double zeta basis set:** In double zeta basis set, one additional set per orbital is considered to increase the accuracy.

- **Double zeta polarized basis set:** To account for polarization3 effects, the set of basis functions of the first angular momentum that is occupied in the isolated atom has to be included. Thus when DZ basis set is supplemented with polarization function it becomes a double zeta polarization basis set.

Main reason behind using these atomic orbital as basis set is to reduce time and memory requirement at the cost of accuracy. Atomic orbital basis sets, as the name indicate describe atoms, even with few orbitals. They are numerical atomic-like orbitals of finite range and corresponding to chemical picture. The atomic-cantered orbital have its intensity mainly on a local point and is well fitted to orbitals around individual atoms in the real space. The equation given below describes the atomic orbital basis set

$$\phi_{I.lmn}(r) \ = \phi_{l.lmn}(|r_I|) \quad \mathrm{Y}_{lm}(r_I) \ \ldots\ldots\ldots (3.8)$$

Where $\mathrm{Y}_{lm}(r_I)$ are represents the spherical harmonics and l,m represent the angular momentum and $\phi_{l.lmn}(|r_I|)$ are radial function. For each value of l, one can have the multiple radial functions labeled by n, which means for singal zeta basis set n =1, and for double zeta n = 1,2 etc. For example in the case of carbon the single zeta basis set consists of single s which means we have l=0, m

= 1,0,1 corresponding to the four valence electrons. This basis can be expanded by five polarization d orbitals (l = 2, m = 2, 1, 0, +1, +2) and denoted by single zeta polarization.

3.8.3 Plane Wave Basis Sets

In plane-waves basis sets plane waves are the basis functions in reciprocal space. All functions in the basis are mutually orthogonal means they are not associated with any particular atom. Due to that reason they are independent of atomic positions. Plane-wave basis functions do not exhibit basis-set superposition error and there results can be improved by increasing plane waves. They are naturally periodic and therefore mainly useful in calculations involving periodic boundary conditions.

$$\Phi_{\mu}(r) = \frac{1}{\sqrt{\Omega}} e^{iG_{\alpha}.r} \quad \ldots\ldots\ldots (3.9)$$

Where G is a vector of reciprocal lattice. Depending upon different basis sets many simulation packages like VASP (Blöchl et al., 1994) , WEIN2K (Blaha et al., 2001), Elk, SIESTA, CASTE etc. have been developed to solve Kohn-Sham equations. Depending on the different basis sets many simulation packages are which are listed on below table:

Table 1: Shows the comparison of different DFT code in terms of potential and basis sets.

Codes	Potentials	Basis Sets
VASP	Pseudopotential	Plane-waves
WEIN2K	Full-potential	Plane-waves + atomic orbital
ELK	Full-potential	Plane-waves
SIESTA	Pseudopotential	Atomic orbitals
CASTEP	Pseudopotential	Plane-waves
Quntum Expresso	Pseudopotential	Plane-waves

Depending of the problem we can choose the simulation package to deal with the problem or for different types of basis and potentials.

3.8.4 Pseudopotential

Pseudopotential is also known as an effective potential to take care about electron-ion interactions. As we all know that in case of solids, various kinds of bonding occur due to the participation of the valence electrons alone while core electrons and nuclei play passive role. Though in principle, exact potential should include all the contributions.

The wave function for free electron in periodic crystal can be expanded in plane waves, if potential is smooth, then it can be treated as perturbation as a result of which it leads to nearly free electron model. Thus we conclude that plane wave expansion of wave function in real crystal is difficult proposition and hence avoided. Therefore, we need an effective potential because density functional theory for practical calculations we need to solve Kohn-Sham equations numerically and the solutions of Kohn-Sham equations depends upon the treatment of electron nuclear interactions. To reduce the numerical cost in Density Functional Theory implementations the strong Coulomb potential is replaced by effective external potential $V_{ext}(r)$ which is also known as Pseudopotential.

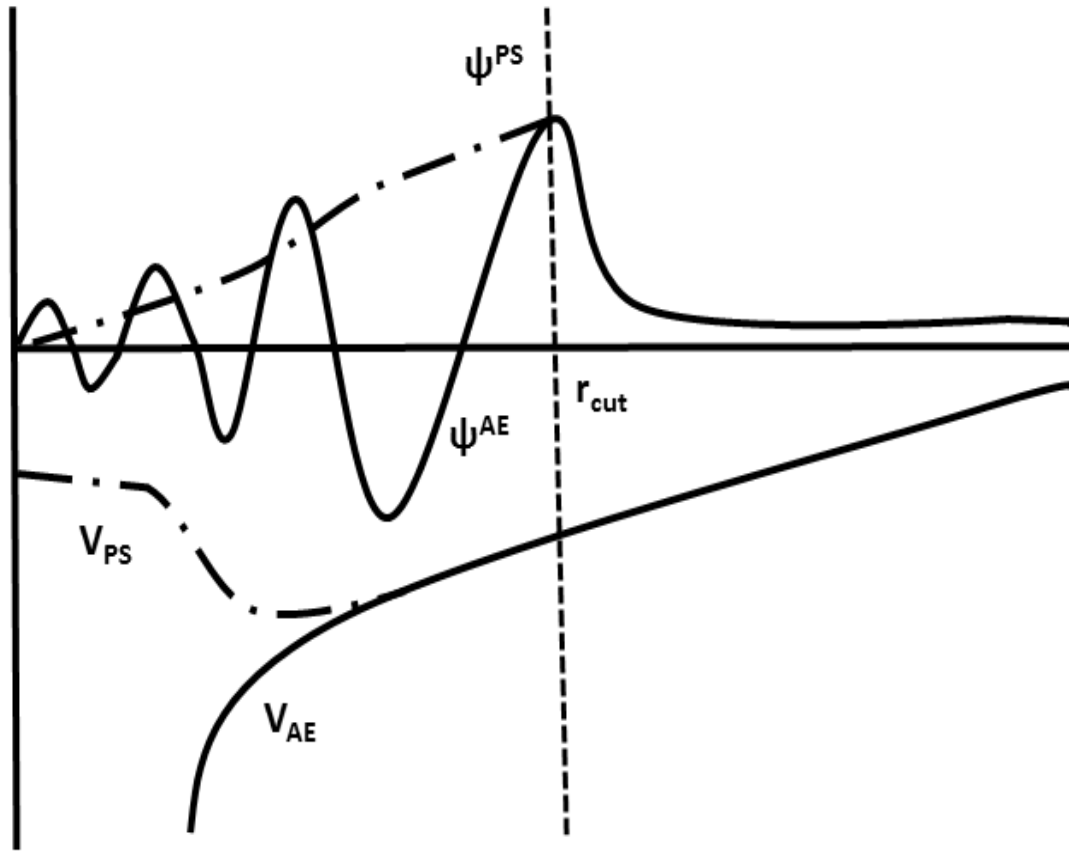


Figure 3.2: All electron (AE) and pseudo (PS) wave function and potentials.

3.8.5 Calculation with SIESTA *(Spanish Initiative for Electronic Simulations with Thousands of Atoms)*:

SIESTA is one of the DFT based package which used DFT implemented in it. In Siesta code, which is being used in the present thesis, is both method and computer program implementation to perform efficient electronic structure calculations for the molecules and solids. Siesta's efficiency comes from the use of strictly localized basis sets of atomic orbitals (Soler et al., 2002). Important advantage of Siesta code is that it can be tuned in wide range from quick exploratory calculations to highly accurate simulations over traditional plane wave techniques.

Siesta is effective code which is very use full for the study of low dimensional materials because the presence of vacuum does not involve as extra computational cost as in the case of plane wave approaches. With the help of siesta code, we are able to make study of various properties of the material like structural, electronic magnetic optical, and transport properties. In siesta code structural optimization is done by conjugate gradients (number of CG modes) and after the relaxation of the structure of the material we are able to calculate the various properties of the material as per our requirements.

In our work with the help of siesta code we have obtained the electronic properties of the layered blue-phosphorene nano ribbon. We have also study the effect on the band structure when the width of the blue-phosphorene nano ribbon is increased. The computational technical parameters used for the calculations are described in the next chapter.

3.8.6 Band structure

As we know that for the case of periodic potential wave function can be expressed in the form of Bloch functions.

$$\psi_k(r) = u_k(r)e^{ikr} \quad \ldots\ldots\ldots (3.10)$$

Here $u_k(r)$ is a periodic function in space with the same periodicity as the super cell. The Eigen function $\psi(r)$ of Hamiltonian is can be expressed as sum of Bloch function:

$$\psi(r) = \sum_k A_K \psi_K(r) = \sum_k e^{ikr}\, u_k(r) \ldots\ldots\ldots\ldots (3.11)$$

Where A_k are constants. Therefor the one electron wave function can be indexed by the 'k'. Thus a plot for one electron is

$$H_e\psi_n(r) = E_n\psi_n(r) \ldots\ldots\ldots (3.12)$$

where H_e is one electron Hamiltonian versus K is shown the electronic band structure of the crystal.

The Monkhorst-Pack sampling of Brillion zone is common technique of numerical calculation of electronic bands. With the help of this method, some special points in the Brillion zone get generated and integration weight provide the efficient means of integrating periodic function in k-space. Accuracy of integration is depending upon the choice of integration grid. This technique allows the sampling of the entire Brillion zone.

Chapter 4: Results and Discussion

This chapter includes the results and discussion of the Density Functional Theory based calculations of blue phosphorene nanoribbons. The first part of this chapter describe the computational details of the calculations, and in the subsequent parts the electronic properties of different edge structures in nano ribbon configurations (with and without passivation) are presented. The mechanical strength and the effect of mechanical strain on the electronic properties of various configurations of nanoribbons are also discussed.

4.1 Computational Details:

To perform Density Functional Theory calculations for the Blue-Phosphorene nano ribbons, firstly we modeled the APNR and ZPNR with the help of GDIS MOLECULE MODELLER. We have used the SIESTA (Spanish Initiative for Electronic Simulations with Thousands of Atoms) Packages to perform DFT calculations. A Troullier Martin norm- conserving Pseudopotential is used for calculations to treat electron-nuclei interaction (Troullier. N et al., 1991) Also the exchange and correlation energies are treated within the generalized gradient approximation (GGA) with PBE parameterization.

We perform our calculations by choosing the reciprocal space which is sampled by grid of 10×1×1 k-points. Numerical atomic orbitals basis sets with double zeta polarization (DZP) are used to expand Kohn-Sham orbitals. Minimization of energy has been performed using conjugate gradients (CG) technique. The forces on each atom were less than 0.01eV/ Å. After the minimization, fully relax coordinate are used to calculate electronic structure. The mesh cut-off energy used to calculate the Hamiltonian exchange and correlation energy was chosen 450 Ry. The distance between the periodic images in non-periodic direction of ribbons is kept more than 10 Å to avoid the mutual interaction between images.

4.2 Edge Effect on the Electronic Properties of Blue Phosphorene Nanoribbons.

In our DFT based calculations we found that electronic properties of the Blue-Phosphorene nanoribbon are edge depended. In our research work we have

taken two edge configurations APNR and ZPNR. To demonstrate the dependence of edges on the electronic properties, we choose the nano ribbons having width n=12 for both cases. Here 'n' show the width of nano ribbons for different values shown in Fig. 4.1.

Since here we are performing the calculations for the APNR and ZPNR for the electronic band structures which is shown in Fig.4.2. From the electronic band structure of the APNR and ZPNR it is found that, for the same width of nanoribbons, they shows the different band gap. In our calculations it is found that in APNR the band gap is found of the order of 1.16 eV and in the case of ZPNR the band gap is the order of 0.58 eV. These results show the edge dependency of the Blue-Phosphorene nanoribbons for their electronic properties.

4.3 Role of passivation with Hydrogen-atom on Blue-Phosphorene nano - ribbons.

Edge passivation of the blue phosphorene nanoribbon plays important role in the electronic properties of the nano ribbons. It is found that attachment of the different functional group changes the electronic properties of the nanoribbons (Peng et al., 2014). In our research work passivation take place with Hydrogen atom and it is found band gap increases with passivation with Hydrogen atom.

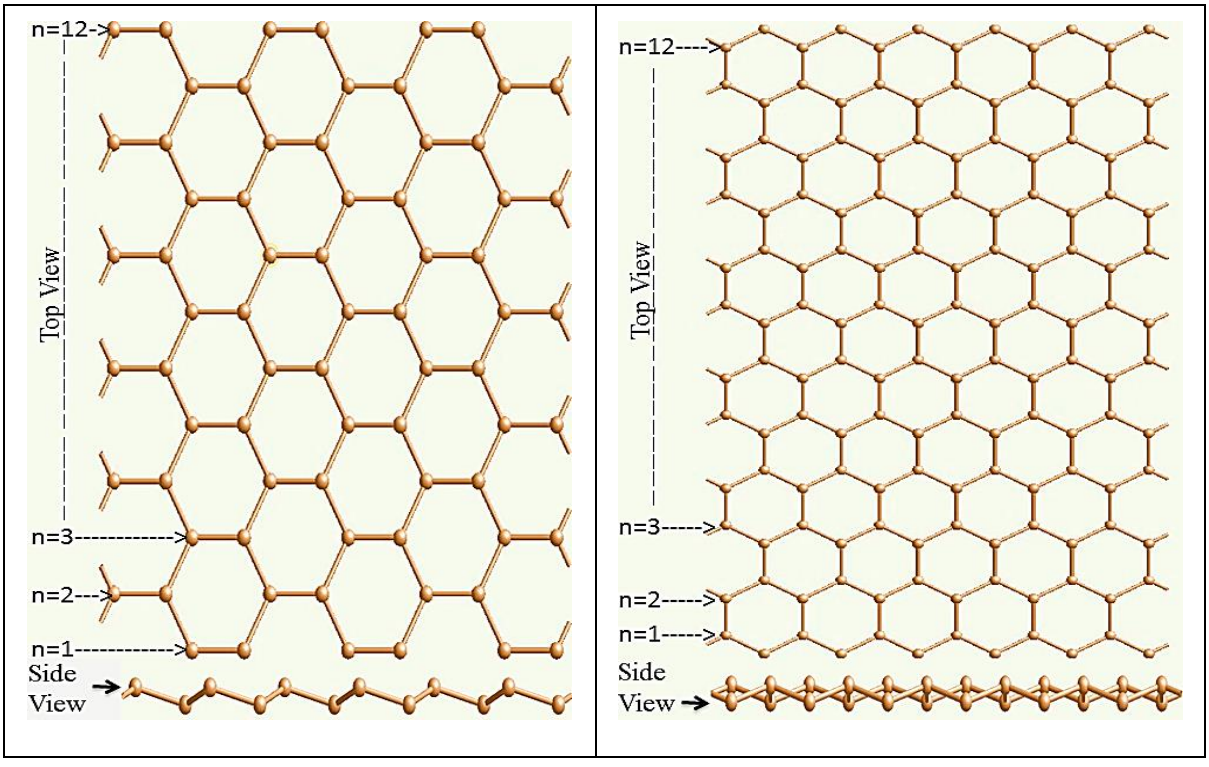


Figure 4.1: Top and side view of APNR and ZPNR for the width n = 12

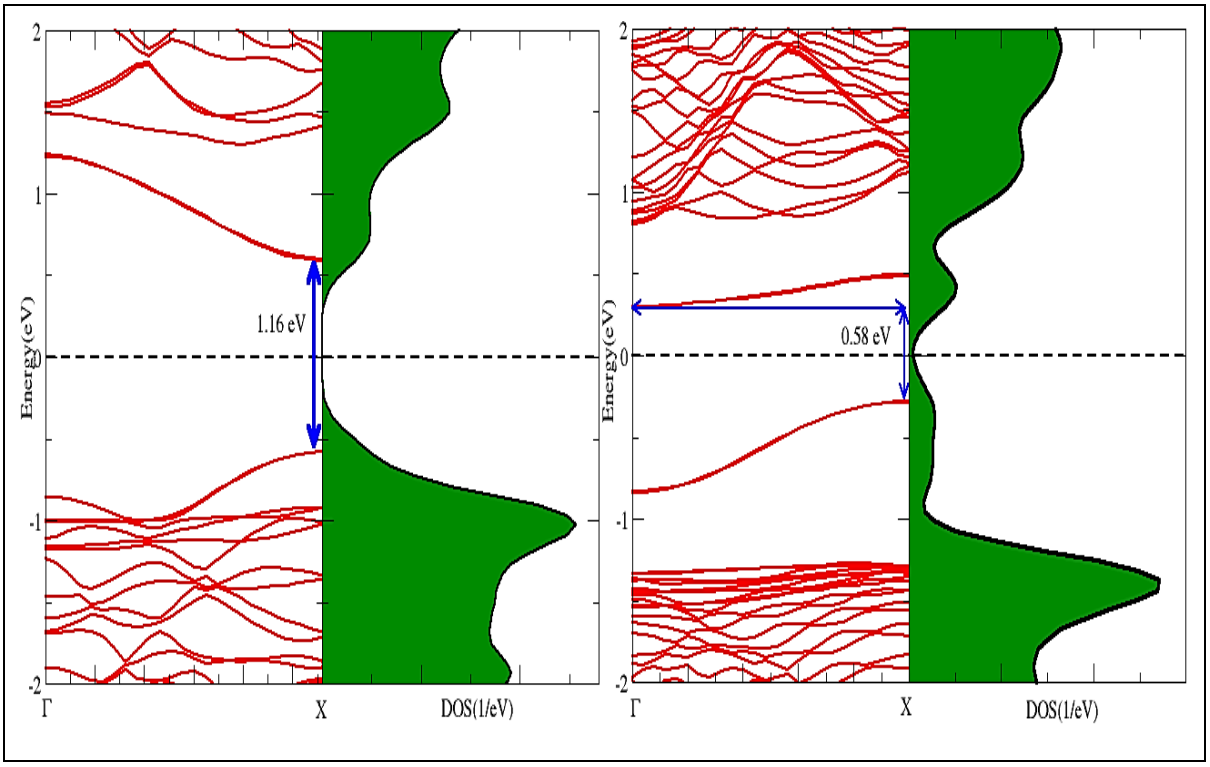


Figure 4.2: Electronic band structure and DOS for APNR and ZPNR.

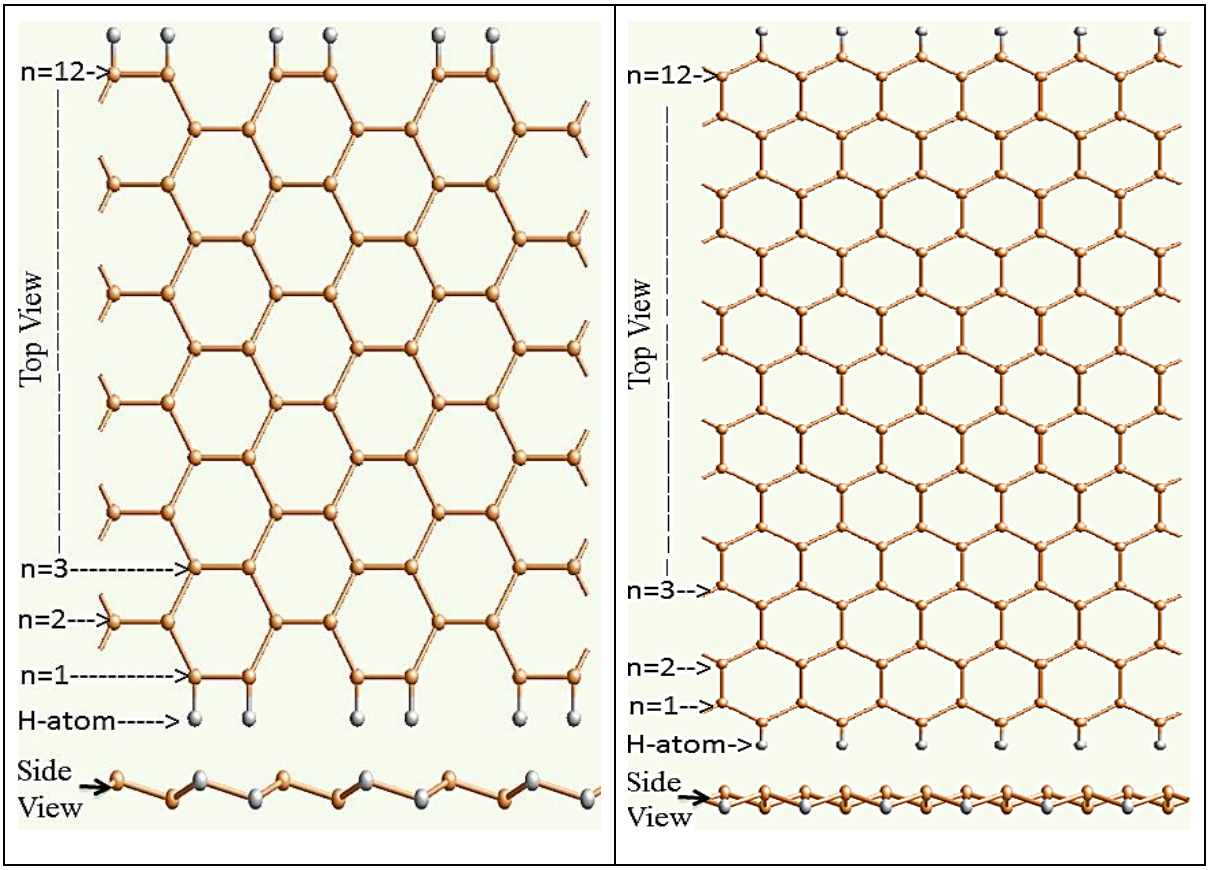


Figure 4.3: Top and side view of the passivated of APNR and ZPNR

The band gap for the APNR changes from the 1.16 eV to 2.18 eV and in the case of the ZPNR band gap changes from 0.58 eV to 2.04 eV after the passivation. This is because after the passivation dangling bond is replaced with covalent bond as a result of which redistribution of the atomic orbitals takes place, which leads to the change in band gap of the nanoribbons. Passivated APNR and ZPNR for the width n=12 with Hydrogen atoms are shown in Fig 4.3 and respective band structures with the passivation for the both of the edge configurations are shown in the Fig: 4.4.

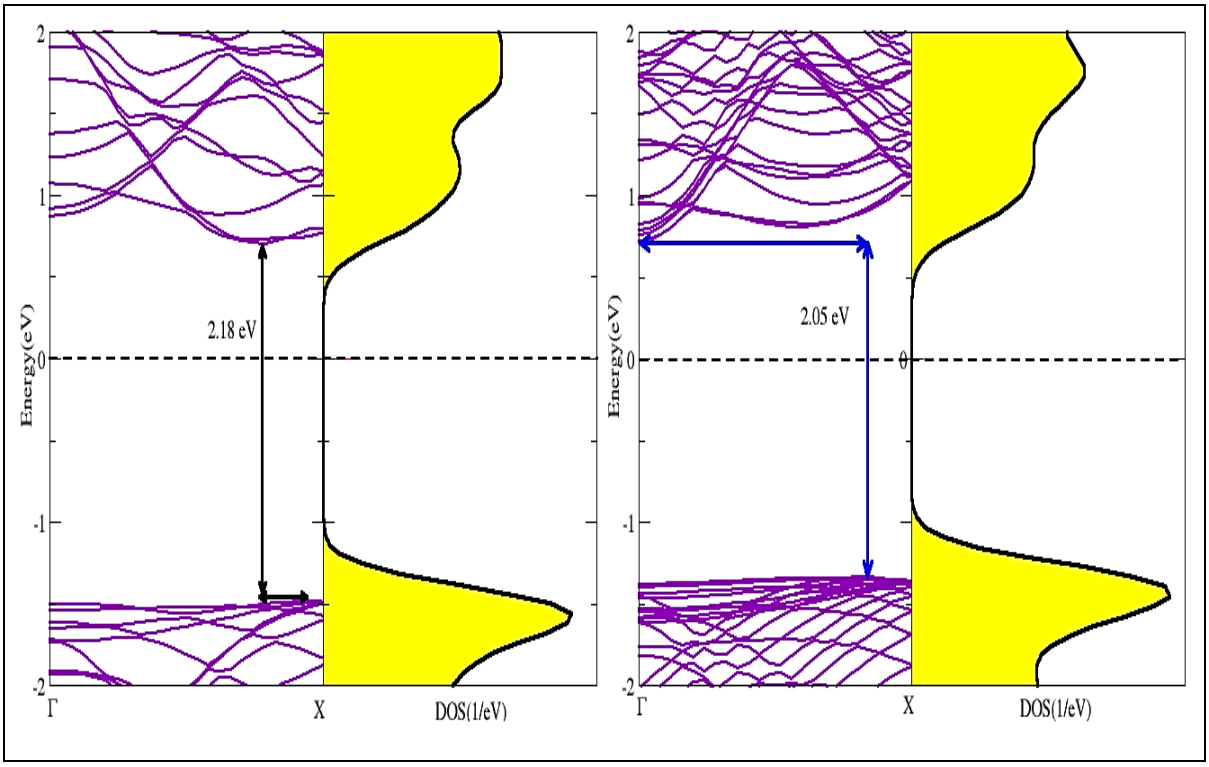


Figure 4.4: Band structures and DOS for the H-APNR and H-ZPNR.

4.4 Effect of width on the Electronic properties of APNR and ZPNR

Since both of the ribbons have the edge dependent properties, as a result of which they shows different band structure for the same width. Now in the next step we studied the effect of width on the electronic properties of the Blue-Phosphorene nanoribbons. For this purpose we models the Blue-Phosphorene nanoribbons of different widths (from n = 2 to n = 12) for both of the edge configurations. Calculations for the different width of Blue Phosphorene nanoribbons for the both of edge configurations show the interesting results which are shown in Fig 4.5.

- **Effect of width on APNR**

  With the increase in width the band gap of Blue Phosphorene nanoribbons initially increases when we move from n = 2 to n = 4. When we further increase in the width of the nanoribbons the band gap starts decreasing. Width dependency of the band gap is shown in Fig 4.5. After reaching to the particular value of n=10 width the electronic band gap of the APNR is approaches to constant values.

- **Effect of width on ZPNR**

  In case of the ZPNR the band gap of the nanoribbons is also varying with the width initially from n = 2 to n = 5 and for the remaining width values band gap increases and attains constant values for the rest of the width value for the ZPNR as shown in Fig.4.5.

4.4.1 Hydrogenated Edge Structures of Phosphorene: Effect of Width

After the passivation of APNR and ZPNR, the band gap in the electronic band structure increases for the both of the edge configurations. Here we perform the passivation process for the different width of the nanoribbons from n = 2 to n= 12 for both APNR and ZPNR as shown in band structure (Fig.4.5)

- **Effect of width on H-APNR**

  Our results shows that passivation increase the band gap of the H-APNR. But with the increasing in width of the nanoribbons the band gap starts decreasing as shown in Fig 4.5 in case of H-APNR the band gap starts decreasing with the width.

- **Effect of width on H-ZPNR**

  Similar results are obtained for the H-ZPNR. The band gap increases due to the passivation with hydrogen atom as compared to unpassivated case, while increasing the width of ribbons, the band gap decreases continuously as shown in Fig: 4.5.

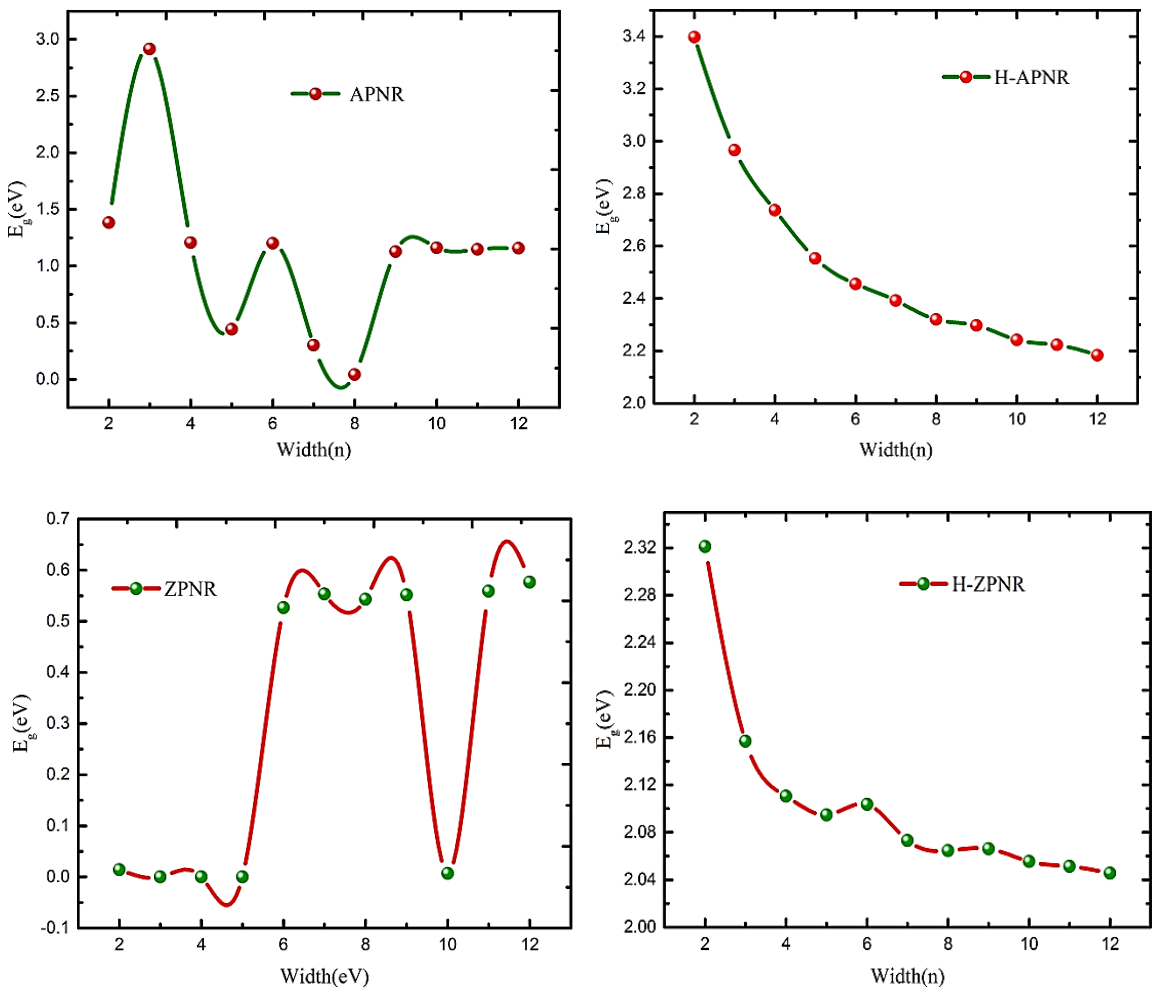


Figure 4.5: Effect of width on band gap for APNR, ZPNR, H-APNR, and H-ZPNR.

Thus from above results we found that the band gap of the blue Phosphorene nanoribbons decreased with the increase in the width of the Blue Phosphorene nanoribbons. It can be concluded that the band gap is inversely proportional to the width of the Blue Phosphorene nanoribbons. The band structure diagrams for the APNR, ZPNR, H-APNR and H-ZPNR are shown in Fig: 4.6, 4.7, 4.8, and in 4.9 respectively. Form the figures, it is clearly evident that electronic band gap of unpassivated nanoribbons show oscillatory behaviour for ultra-narrow width and after attaining the specific value of width electronic band gap attain a constant value. On the other hand, with passivation of edges by hydrogen atoms, opening the band for the both of edge configurations have been achieved. Additionally, when the width of nanoribbons was increased along with the passivation the band gap show decrease in magnitude.

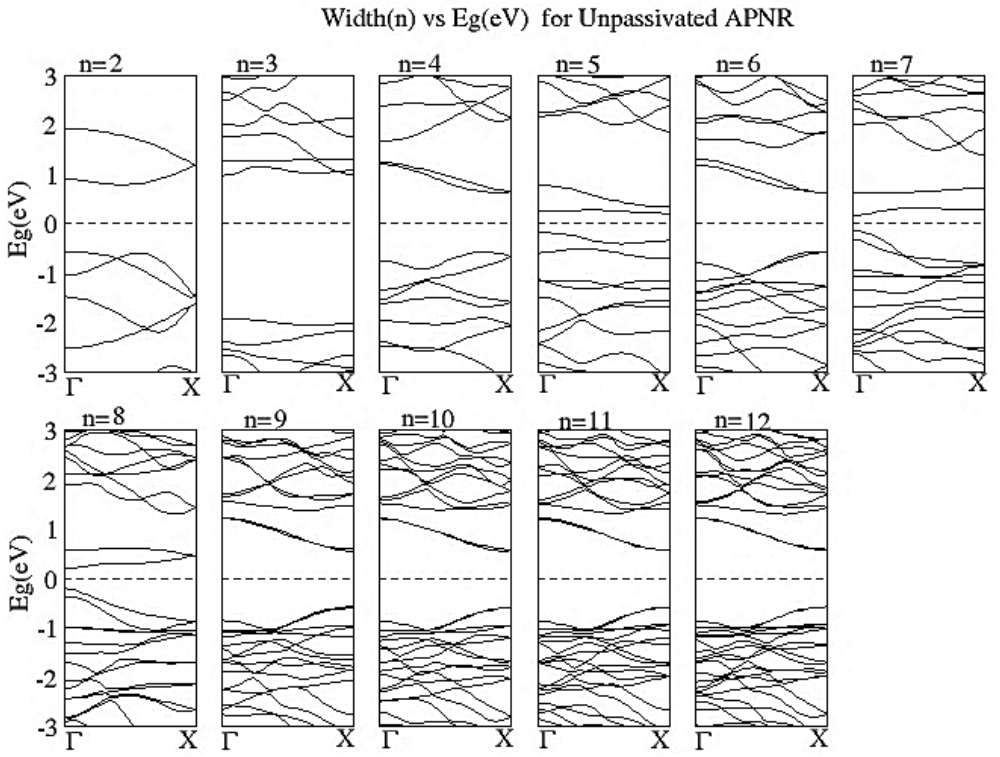


Figure 4.6: Band structures for APNR for width n = 2 to width n=12.

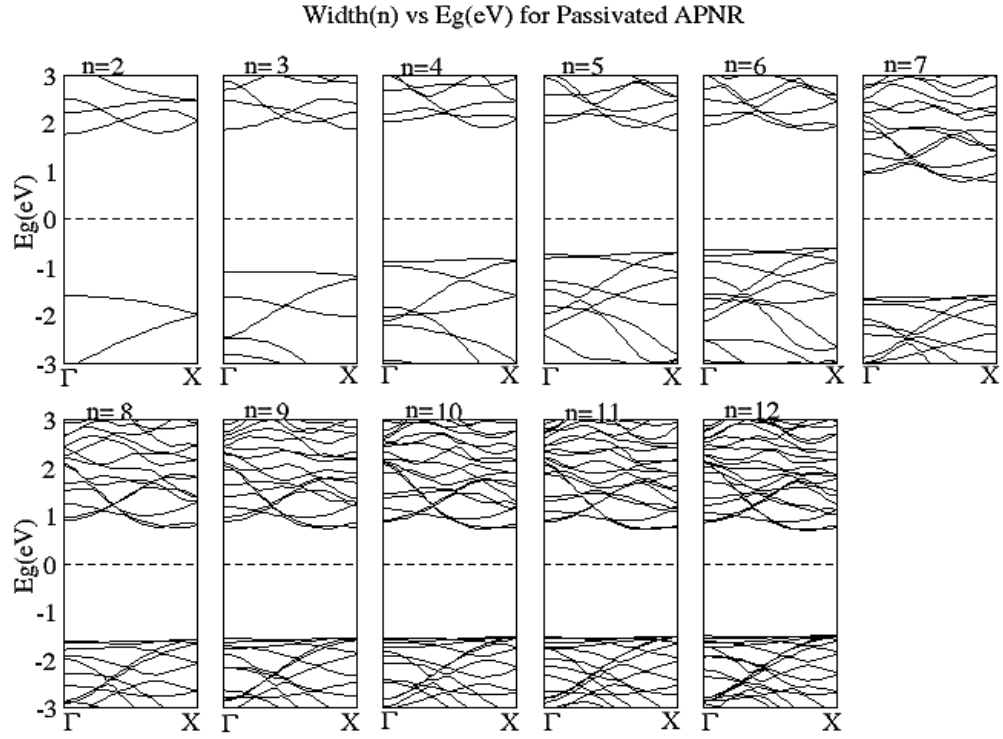


Figure 4.7: Band structures for H-APNR for width n = 2 to width n=12.

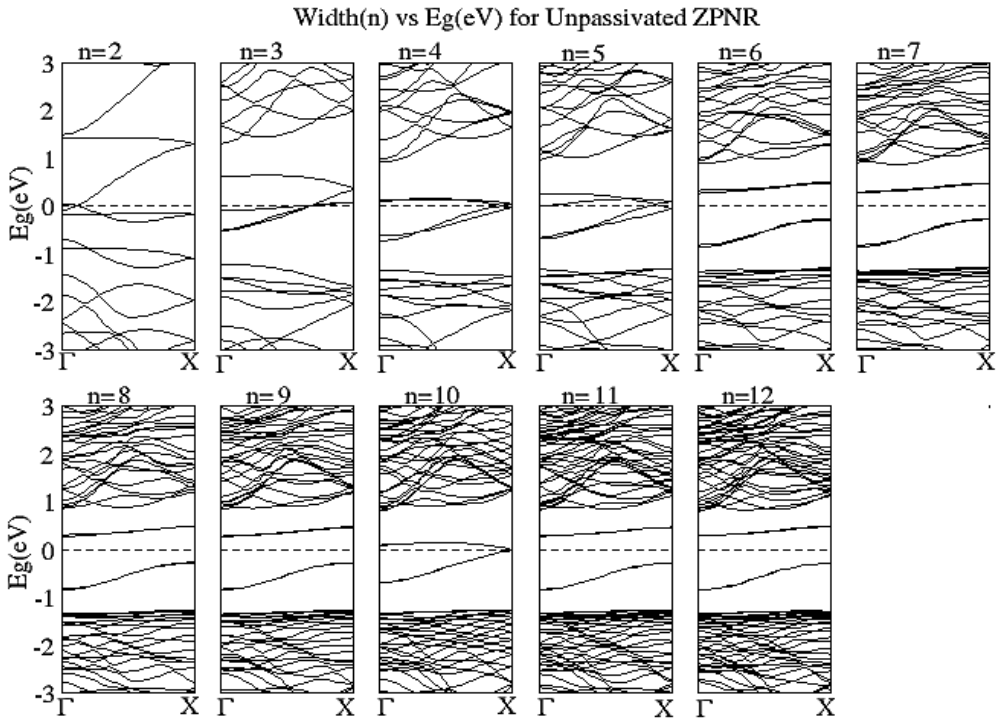


Figure 4.8: Band structures for ZPNR for width n = 2 to width n=12.

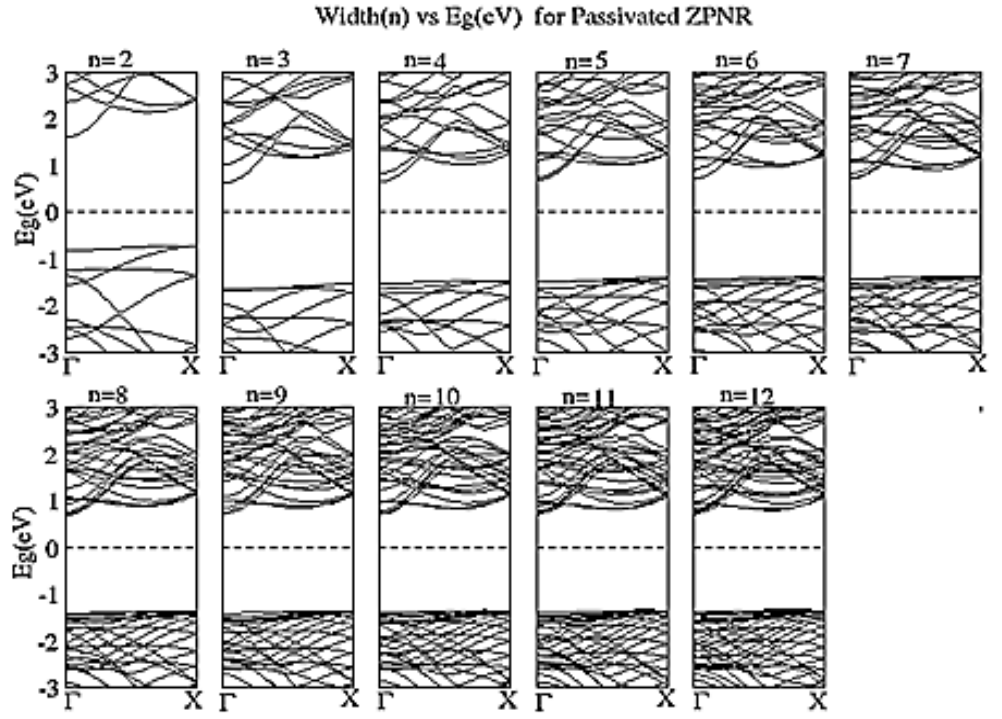


Figure 4.9: Band structures for H-ZPNR for width n = 2 to width n=12.

4.5 Mechanical Strength of APNR and ZPNR

In our research work we have also evaluated the mechanical strength of the Blue-Phosphorene nanoribbons. We applied the various values of strain in both edge configurations for the width n = 12. Since every crystal structure exist at its lowest energy state and corresponding periodic distance of unit cell in the crystal is known as the lattice constant of the crystal. Thus variation in the lattice constant of the crystal produces the strain in the complete structure. In our work, we apply the outward strain in the nanoribbon for the both of the edge configuration. To perform this we add the small percentage value of strain in the lattice constant value and produce the outward strain in the nanoribbon for the both of edge configurations and then perform the DFT calculations for the respective value of applied strain and evaluate the stress tensor as an output parameter.

Since our specific purpose of applying the strain is to find out the mechanical strength of the both of edge configuration. Thus this process is carried out until the value of stress tensor increases accordingly, after reaching its maximum value stress tensor it starts decreasing which means ribbons starts breaks at particular value of strain/stress. Thus the maximum value of stress at given strain is known as mechanical strength of the nanoribbon. Mechanical strength for the both of the edge configurations are discussed as below:

- **Mechanical properties for APNR and H-APNR:**

  In case of APNR for width n = 12, different value of strain is applied up to breaking strength of the Arm-chair Phosphorene nanoribbon (2% to 22%), and it is found that the mechanical strength of the APNR and H-APNR are 2.95 GPa and 2.89 GPa, which shows that the mechanical strength of the APNR and H-APNR are almost same as shown in Fig. 4.10.

- **Mechanical properties of ZPNR and H-ZPNR**

  In case of ZPNR for width n = 12, different value of strain is applied up to breaking strength of the Arm-Chair Phosphorene nanoribbon (2% to 28%), and it is found that the mechanical strength of the ZPNR and H-ZPNR are 2.99 GPa and 2.95 GPa, which shows that the mechanical strength of the ZPNR and H-ZPNR are almost same as shown in Fig. 4.11.

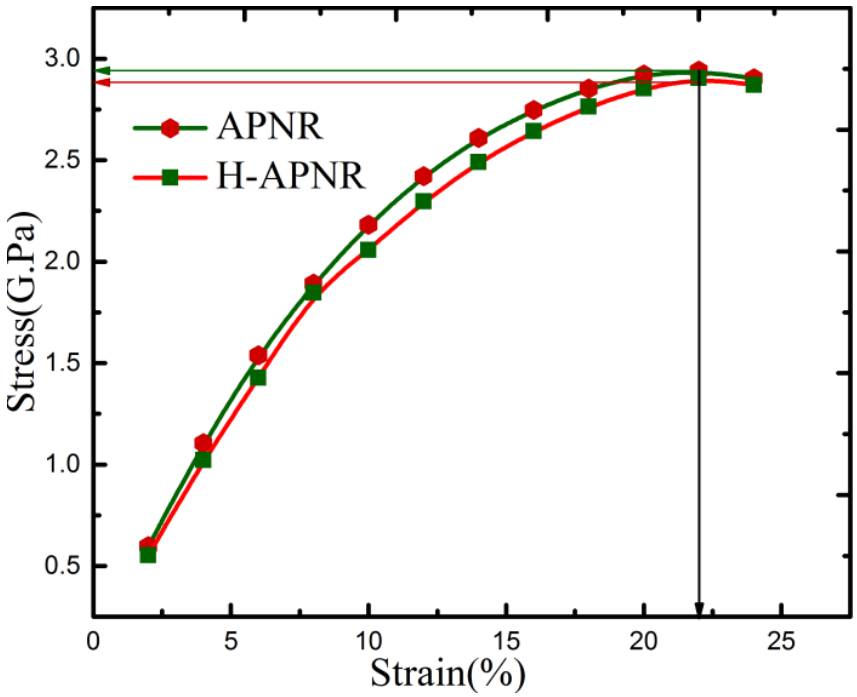


Figure 4.10: Stress versus strain curve for APNR and H-APNR.

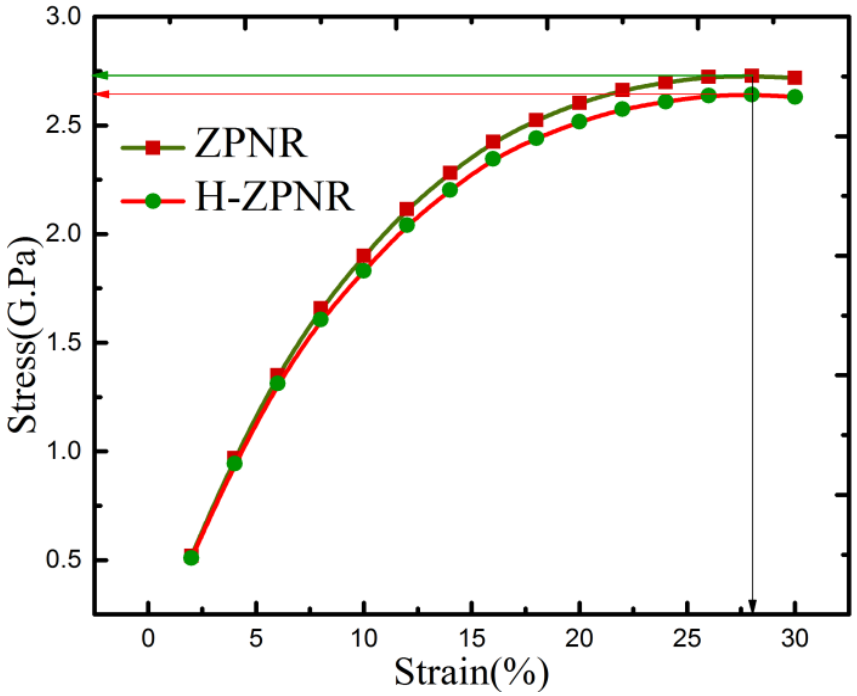


Figure 4.11: Mechanical strength for the ZPNR and H-ZPNR.

From the study of the Mechanical strength of the Blue-Phosphorene nanoribbons for both of the edge configuration we found that the mechanical strength of the APNR and ZPNR are almost same for the both of the edge configurations. And we

found that effect of the passivation doesn't change the mechanical strength of the nanoribbons in large extent.

4.6 Variation in band gap with strain of APNR and ZPNR

Now at last we studied the effect of in-plan strains on the electronic properties of various nanoribbons. For this purpose we choose the Blue Phosphorene nanoribbon having width n = 12 in the both of the edge configurations i.e. APNR and ZPNR. Effect of the strain for the both the edge configurations are discussed below.

- **Effect of strain on APNR and H-APNR**

  In case of the APNR and H-APNR the value of band gap is of the order of 1.16 eV and 2.18 eV for the width n = 12. At this value of width we apply the various values of the strain up to its maximum value i.e. from 2% to 22%. Form our electronic structure calculations it is found that with the applied each value of strain for APNR and H-APNR the band gap value starts decreasing in the both APNR and H-APNR. Variation in band gap with applied strain is shown in Fig.: 4.12.

- **Effect of strain on ZPNR and H-ZPNR**

  In case of the ZPNR and H-ZPNR the value of band gap is of the order of 1.16 eV and 2.18 eV for the width n = 12. At this value of width, we applied the various values of strain up to its maximum value i.e. from 2% to 28%. Form our calculations; it is found that with the applied each value of strain for ZPNR and H-ZPNR the band gap value starts decreasing, for the both of the case of ZPNR and H-ZPNR. Variation in band gap with applied strain as shown in Fig. 4.13.

From the above discussion it is found that with the applied value of the strain for the both of the edge configuration, the value of the band gap decreases. This is due to the fact that with the every applied value of strain structural deformation takes place that leads to the redistribution of atomic orbitals. The electronic band structures for the different values of strain are shown in Fig. 4.14, 4.15 respectively.

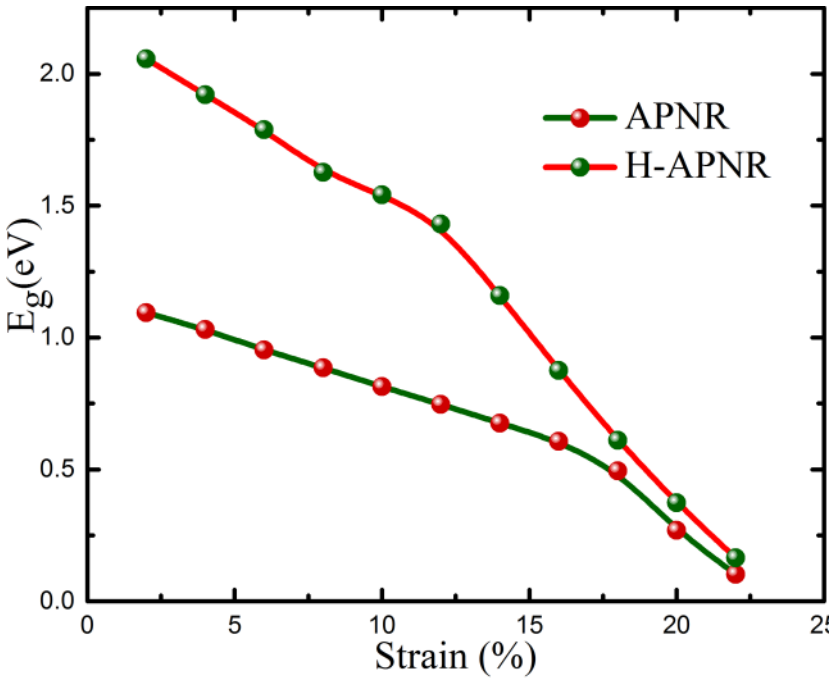


Figure 4.12: Variation in band gap with applied value of strain in APNR and H-APNR.

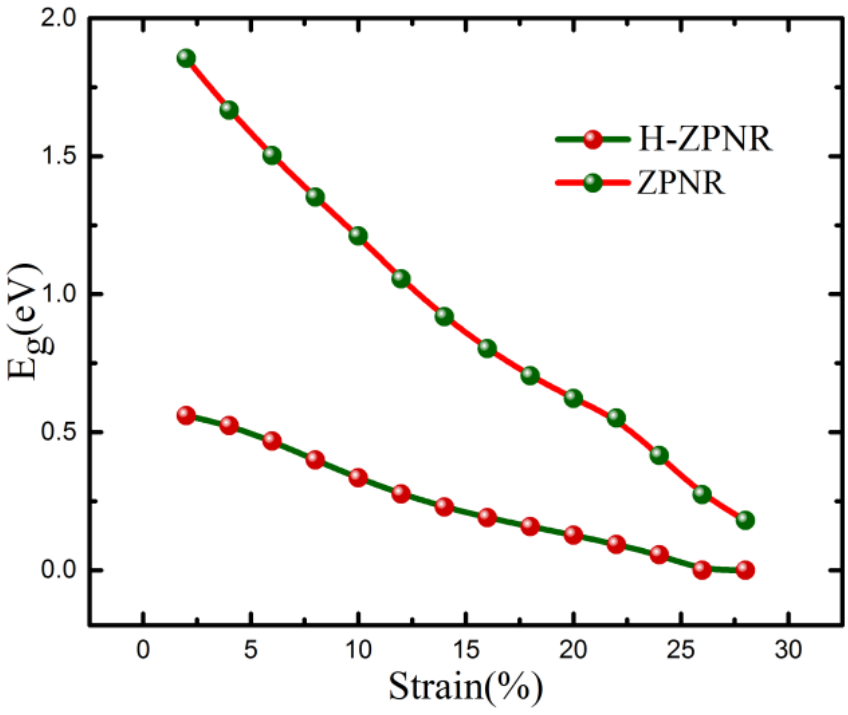


Figure 4.13: Variation in band gap with applied value of strain in ZPNR and H-ZPNR.

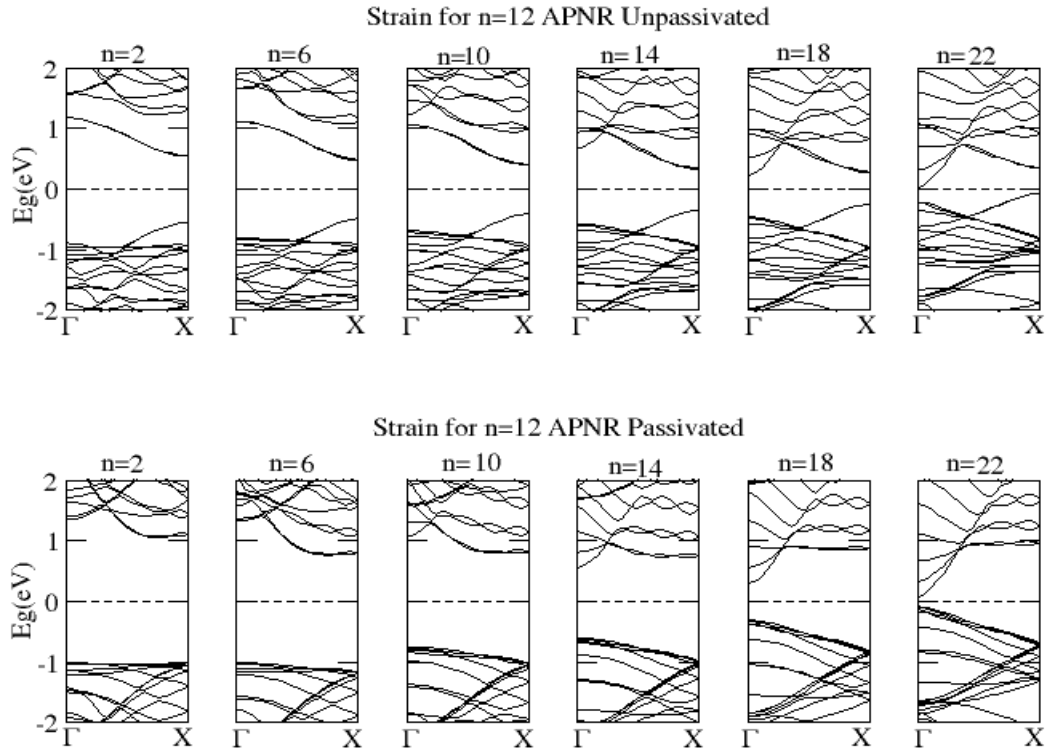


Figure 4.14: Band structures for APNR and H-APNR for different values of strain.

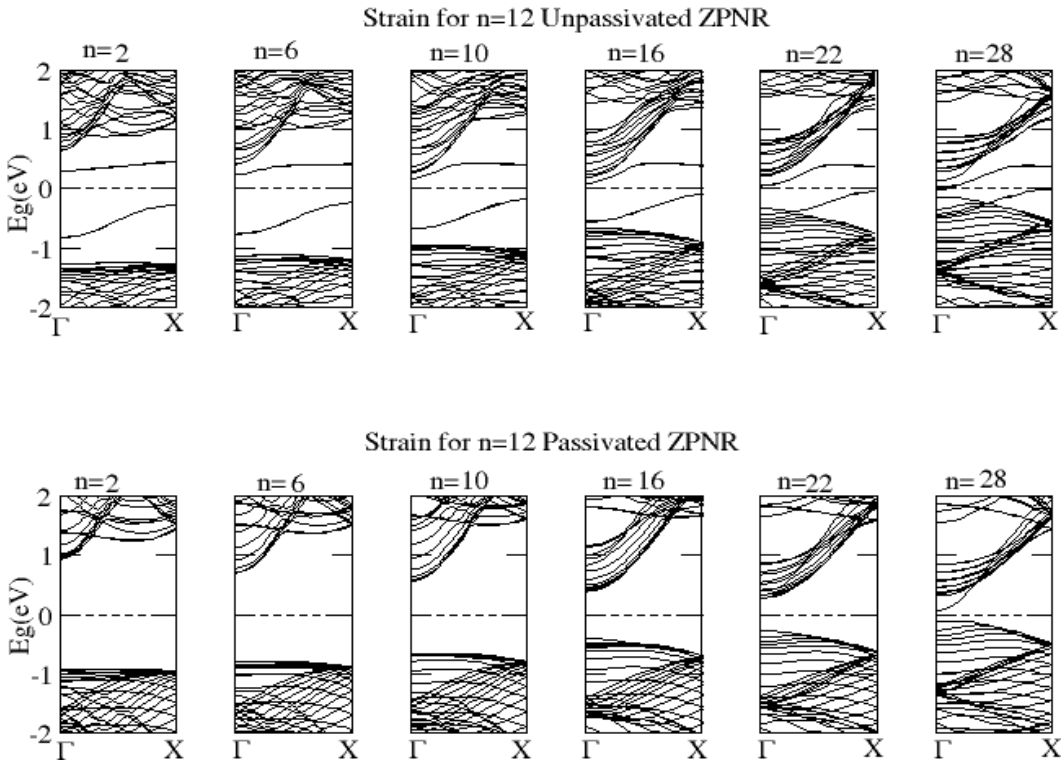


Figure 4.15: Band structures for ZPNR and H-ZPNR for different values of strain.

Chapter 5: Summary and Conclusions

This chapter includes the brief summary and conclusions of the results. First part of this chapter contains the summary which describes the output of DFT calculations for various nanoribbons configurations. Second parts of this chapter describe the future scope and applications of the research work.

5.1 Summary

In the present Dissertation work, the electronic properties of the Blue-Phosphorene nanoribbons for the both of edge configuration APNR and ZPNR are investigated. The entire study can be summarized as follows:

- Electronic properties of the Blue-Phosphorene nano ribbons are found to be edge dependent. Variation in the electronic band structure take place with the two different edge configurations.

- Passivation plays important role in the electronic properties of the Blue-Phosphorene nanoribbons. Passivation with Hydrogen atom of the Blue-Phosphorene nanoribbon changes band gap of both the edge configurations i.e. APNR and ZPNR.

- Electronic properties of the Blue-Phosphorene nano ribbon are width dependent. With the increase in width, variation in band gap come into play up to the specific width, after attaining the specific value of width, the band gap approaches to constant value.

- Ultra-narrow width of APNR and ZPNR shows oscillatory behaviour in the electronic band structure for specific values of width and attains a constant band gap when width of the nanoribbon is increased further for both of the edge configurations.

- Passivation opens up the electronic band gap, however, by increasing the width of nanoribbon electronic band gap show decrease in the magnitude.

- Mechanical strength of the Blue-Phosphorene nanoribbons is different for the different edge configuration. It is found that mechanical strength of the APNR and H-APNR are 2.95 GPa and 2.89 GPa. In the case of ZPNR and H-ZPNR, the mechanical strength is found to be 2.99 GPa and 2.95 GPa respectively.

- Maximum mechanical strength for the APNR and H-APNR is found at 22% of applied strain.

- Maximum mechanical strength for the ZPNR and H-ZPNR is found at 28% of applied strain.

- Strain acts as an effective agent for modification in the electronic band structure. It is found that with applied value of mechanical strain, semiconductor to metal transition takes place at specific high value for both of the edge configuration with and without passivation.

5.2 Future Scope of Research

The study of the 2D materials is just the beginning of new era of science, and the study of the Blue Phosphorene is in its initial stage. There are lot of study of Blue Phosphorene nanoribbons is still pending. In addition, other allotropes such as Gamma-Phosphorene and Delta-Phosphorene still need to explore. For example, along with nanoribbons, the study of monolayers of Blue-Phosphorene and their thickness depended properties need to be studied in details which may be useful for the future electronic and optoelectronic applications.

5.3 Future Application of Phosphorene Nanoribbons

- **Transistor**

  Since transistor technology play very important role in electronic industry, with the help of blue phosphorene monolayers or nanoribbons which has inherent band gap, it may be useful in transistor technology.

- **Tunable electronics**

  Since the band gap of the phosphorene ribbons have width and edge dependence which means the variation in band gap may be useful for future tunable electronic devices.

- **Flexibility**

  Phosphorene ribbons possess the good mechanical strength which make it a promising candidate for the flexible electronic devices.

- **Solar cell material**

  Phosphorene layers acts as good candidates in solar cell materials. The power conversion efficiency for a monolayer MoS_2/AA stacked bilayer phosphorene and MoS_2/AA stacked bilayer phosphorene has been found to possess as high as 18% and 16 %, respectively in recent studies. Our results of phosphorene nanoribbons also suggest that the studied ribbons and their hetero-structures may have promising applications in solar cells.

References

Aierken,Y.,Cakır, D.,Sevik,C.,and Peeters ,F.M.(2015).Thermal properties of black and blue phosphorene from a first-principles quasiharmonic approach. Physical Review B, 92(8), 081408.

Aierken, Y.,Leenaerts, O.,and Peeters, F.M.(2015).Defect-induced faceted blue phosphorene nanotubes. Physical Review B, 92(10), 104104.

Alda, J., Rico-García, J. M., López-Alonso, J. M., & Boreman, G. (2005). Optical antennas for nano-photonic applications. Nanotechnology, 16(5), S230

Balendhran, S., Walia, S., Nili, H., Ou, J. Z., Zhuiykov, S., Kaner, R. B., and Kalantar-zadeh, K. (2013). Two-dimensional molybdenum trioxide and dichalcogenides. Advanced Functional Materials, 23(32), 3952-3970.

Berger, C., Song, Z., Li, X., Wu, X., Brown, N., Naud, C., and Conrad, E. H. (2006). Electronic confinement and coherence in patterned epitaxial graphene. Science, 312(5777), 1191-1196.

Blaha, P., Schwarz, K., Madsen, G. K. H., Kvasnicka, D., and Luitz, J. (2001). wien2k. An augmented plane wave local orbitals program for calculating crystal properties.

Blochl, P. E. (1994). Projector augmented-wave method. Physical Review B, 50(24), 17953.

Brent, J. R., Savjani, N., Lewis, E. A., Haigh, S. J., Lewis, D. J., and O'Brien, P. (2014). Production of few-layer phosphorene by liquid exfoliation of black phosphorus. Chemical Communications, 50(87), 13338-13341.

Buscema, M., Groenendijk, D. J., Blanter, S. I., Steele, G. A., van der Zant, H. S., and Castellanos-Gomez, A. (2014). Fast and broad band photoresponse of few-layer black phosphorus field-effect transistors. Nano letters, 14(6), 3347-3352.

Çakır, D., Sahin, H., and Peeters, F. M. (2014). Tuning of the electronic and optical properties of single-layer black phosphorus by strain. Physical Review B, 90(20), 20542.

Castellanos-Gomez, A., Vicarelli, L., Prada, E., Island, J. O., Narasimha-Acharya, K. L., Blanter, S. I., and Zandbergen, H. W. (2014). Isolation and characterization of few-layer black phosphorus. 2 Dimensional Materials, 1(2), 025001.

Cao, G. (2004). Synthesis, Properties and Applications. Imperial college press, London.

Chau, R., Datta, S., Doczy, M., Doyle, B., Jin, B., Kavalieros, J.,and Radosavljevic, M. (2005). Benchmarking nanotechnology for high-performance and low-power logic transistor applications. Nanotechnology, IEEE Transactions on, 4(2), 153-158.

Chou, T. D., Lee, T. W., Chen, S. L., Tung, Y. M., Dai, N. T., Chen, S. G., and Wang, H. J. (2001). The management of white phosphorus burns. Burns, 27(5), 492-497.

Churchill, H. O., and Jarillo-Herrero, P. (2014). Two-dimensional crystals: Phosphorus joins the family. Nature nanotechnology, 9(5), 330-331.

Dai, J., and Zeng, X. C. (2014). Bilayer phosphorene: effect of stacking order on bandgap and its potential applications in thin-film solar cells. The Journal of Physical Chemistry Letters, 5(7), 1289-1293.

Dávila, M. E., Marele, A., De Padova, P., Montero, I., Hennies, F., Pietzsch, A., and Le Lay, G. (2012). Comparative structural and electronic studies of hydrogen interaction with isolated versus ordered silicon nanoribbons grown on Ag (110). Nanotechnology, 23(38), 385703.

Dávila, M. E., Xian, L., Cahangirov, S., Rubio, A., and Le Lay, G. (2014). Germanene: a novel two-dimensional germanium allotrope akin to graphene and silicene. New Journal of Physics, 16(9), 095002.

Ge, Y., Wan, W., Yang, F., and Yao, Y. (2015). The strain effect on superconductivity in phosphorene: a first-principles prediction. New Journal of Physics, 17(3), 035008.

Gell-Mann, M., and Brueckner, K. A. (1957). Correlation energy of an electron gas at high density. Physical Review, 106(2), 364.

Guan, J., Zhu, Z., and Tománek, D. (2014). Tiling phosphorene. ACS nano, 8(12), 12763-12768.

Guan, J., Zhu, Z., and Tomanek, D. (2014). Tiling phosphorene. ACS nano, 8(12), 12763-12768.

Guo, H., Lu, N., Dai, J., Wu, X., and Zeng, X. C. (2014). Phosphorene nanoribbons, phosphorus nanotubes, and van der Waals multilayers. The Journal of Physical Chemistry C, 118(25), 14051-14059.

Guo, Z., Zhang, H., Lu, S., Wang, Z., Tang, S., Shao, J., and Chu, P. K. (2015). From Black Phosphorus to Phosphorene: Basic Solvent Exfoliation, Evolution of Raman Scattering, and Applications to Ultrafast Photonics. Advanced Functional Materials, 25(45), 6996-7002.

Guzmán-Verri, G. G., and Voon, L. L. Y. (2007). Electronic structure of silicon-based nanostructures. Physical Review B, 76(7), 075131.

Han, X., Morgan Stewart, H., Shevlin, S. A., Catlow, C. R. A., and Guo, Z. X. (2014). Strain and orientation modulated bandgaps and effective masses of phosphorene nanoribbons. Nano letters, 14(8), 4607-4614.

Hartree, D. R. (1928). The wave mechanics of an atom with a non-Coulomb central field. Part I Theory and methods. In Mathematical Proceedings of the Cambridge Philosophical Society (Vol. 24, No. 01, pp. 89-110). Cambridge University Press.

Hohenberg, P., and Kohn, W. (1964). Inhomogeneous electron gas. Physical review, 136(3B), B864.

Hu, T., and Dong, J. (2015). Structural phase transitions of phosphorene induced by applied strains. Physical Review B, 92(6), 064114.

Hu, T., and Hong, J. (2015). Electronic structure and magnetic properties of zigzag blue phosphorene nanoribbons. Journal of Applied Physics, 118(5), 054301.

Hu, T., Han, Y., and Dong, J. (2014). Mechanical and electronic properties of monolayer and bilayer phosphorene under uniaxial and isotropic strains.Nanotechnology, 25(45), 455703.

Jain, A., and Mcgaughey, A. J. (2015). Strongly anisotropic in-plane thermal transport in single-layer black phosphorene. Scientific reports, 5.

Ju, W., Li, T., Wang, H., Yong, Y., and Sun, J. (2015). Strain-induced semiconductor to metal transition in few-layer black phosphorus from first principles. Chemical Physics Letters, 622, 109-114.

Junquera, J., Paz, Ó., Sánchez-Portal, D., & Artacho, E. (2001). Numerical atomic orbitals for linear-scaling calculations. Physical Review B, 64(23), 235111.

Koenig, S. P., Doganov, R. A., Schmidt, H., Neto, A. C., and Oezyilmaz, B. (2014). Electric field effect in ultrathin black phosphorus. Applied Physics Letters, 104(10), 103106.

Kohn, W., and Sham, L. J. (1965). Self-consistent equations including exchange and correlation effects. Physical review, 140(4A), A1133.

Kohn, W., and Sham, L. J. (1965). Self-consistent equations including exchange and correlation effects. Physical review, 140(4A), A1133.

Köpf, M., Eckstein, N., Pfister, D., Grotz, C., Krüger, I., Greiwe, M., and Nilges, T. (2014). Access and in situ growth of phosphorene-precursor black phosphorus. Journal of Crystal Growth, 405, 6-10.

Kou, L., Chen, C., and Smith, S. C. (2015). Phosphorene: fabrication, properties, and applications. The journal of physical chemistry letters, 6(14), 2794-2805.

Kou, L., Frauenheim, T., and Chen, C. (2014). Phosphorene as a superior gas sensor: Selective adsorption and distinct I–V response. The Journal of Physical Chemistry Letters, 5(15), 2675-2681.

Kresse, G., and Furthmüller, J. (1996). Efficient iterative schemes for ab initio total-energy calculations using a plane-wave basis set. Physical Review B,54(16), 11169

Li, L., Yu, Y., Ye, G. J., Ge, Q., Ou, X., Wu, H., and Zhang, Y. (2014). Black phosphorus field-effect transistors. Nature nanotechnology, 9(5), 372-377.

Li, L., Yu, Y., Ye, G. J., Ge, Q., Ou, X., Wu, H., and Zhang, Y. (2014). Black phosphorus field-effect transistors. Nature nanotechnology, 9(5), 372-377.

Li, W., Zhang, G., and Zhang, Y. W. (2014). Electronic properties of edge-hydrogenated phosphorene nanoribbons: A first-principles study. The Journal of Physical Chemistry C, 118(38), 22368-22372.

Li, Y., and Chen, X. (2014). Dirac fermions in blue-phosphorus. 2D Materials,1(3), 031002.

Li, Y., Yang, S., and Li, J. (2014). Modulation of the electronic properties of ultrathin black phosphorus by strain and electrical field. The Journal of Physical Chemistry C, 118(41), 23970-23976.

Liu, H., Neal, A. T., Zhu, Z., Luo, Z., Xu, X., Tománek, D., and Ye, P. D. (2014). Phosphorene: an unexplored 2D semiconductor with a high hole mobility. ACS nano, 8(4), 4033-4041.

Liu, H., Neal, A. T., Zhu, Z., Luo, Z., Xu, X., Tománek, D., and Ye, P. D. (2014). Phosphorene: an unexplored 2D semiconductor with a high hole mobility. ACS nano, 8(4), 4033-4041.

Lijima, S. (1991). Helical microtubules of graphitic carbon. nature, 354(6348), 56-58.

Martin, R. M. (2004). Electronic structure: basic theory and practical methods. Cambridge university press.

Novoselov, K. S., Geim, A. K., Morozov, S. V., Jiang, D., Zhang, Y., Dubonos, S. A., and Firsov, A. A. (2004). Electric field effect in atomically thin carbon films.

science, 306(5696), 666-669.

Novoselov, K. S., Jiang, D., Schedin, F., Booth, T. J., Khotkevich, V. V., Morozov, S. V., and Geim, A. K. (2005). Two-dimensional atomic crystals.Proceedings of the National Academy of Sciences of the United States of America, 102(30), 10451-10453.

Novoselov, K. S., Jiang, D., Schedin, F., Booth, T. J., Khotkevich, V. V., Morozov, S. V., and Geim, A. K. (2005). Two-dimensional atomic crystals.Proceedings of the National Academy of Sciences of the United States of America, 102(30), 10451-10453.

Novoselov, K. S., Morozov, S. V., Mohinddin, T. M. G., Ponomarenko, L. A., Elias, D. C., Yang, R., and Giesbers, J. (2007). Electronic properties of graphene. Physica Status Solidi-B-Basic Solid State Physics, 244(11), 4106-4111.

Owens, F. J. (2015). Electronic structure of phosphorene nanoribbons. Solid State Communications, 223, 37-39.

Peng, X., and Wei, Q. (2014). Chemical scissors cut phosphorene nanostructures. Materials Research Express, 1(4), 045041.

Peng, X., Copple, A., and Wei, Q. (2014). Edge effects on the electronic properties of phosphorene nanoribbons. Journal of Applied Physics, 116(14), 144301.

Peng, X., Wei, Q., and Copple, A. (2014). Strain-engineered direct-indirect band gap transition and its mechanism in two-dimensional phosphorene. Physical Review B, 90(8), 085402.

Piazza, Z. A., Hu, H. S., Li, W. L., Zhao, Y. F., Li, J., and Wang, L. S. (2014). Planar hexagonal B36 as a potential basis for extended single-atom layer boron sheets. Nature communications, 5.

Qiao, J., Kong, X., Hu, Z. X., Yang, F., and Ji, W. (2014). High-mobility transport anisotropy and linear dichroism in few-layer black phosphorus. Nature communications, 5

Qiao, J., Kong, X., Hu, Z. X., Yang, F., and Ji, W. (2014). High-mobility transport anisotropy and linear dichroism in few-layer black phosphorus.Nature communications, 5.

Ramasubramaniam, A., and Muniz, A. R. (2014). Ab initio studies of thermodynamic and electronic properties of phosphorene nanoribbons.Physical Review B, 90(8), 085424.

Ritter, K. A., and Lyding, J. W. (2009). The influence of edge structure on the electronic properties of graphene quantum dots and nanoribbons. Nature materials, 8(3), 235-242.

Rodin, A. S., Carvalho, A., and Neto, A. C. (2014). Strain-induced gap modification in black phosphorus. Physical review letters, 112(17), 176801.

Sánchez-Portal, D., Artacho, E., & Soler, J. M. (1996). Analysis of atomic orbital basis sets from the projection of plane-wave results. Journal of Physics: Condensed Matter, 8(21), 3859

Soler, J. M., Artacho, E., Gale, J. D., García, A., Junquera, J., Ordejon, P., and Sánchez-Portal, D. (2002). The SIESTA method for ab initio order-N materials simulation. Journal of Physics: Condensed Matter, 14(11), 2745.

Sun, M., Tang, W., Ren, Q., Wang, S. K., Yu, J., and Du, Y. (2015). A first-principles study of light non-metallic atom substituted blue phosphorene. Applied Surface Science, 356, 110-114.

Takeda, K., and Shiraishi, K. (1994). Theoretical possibility of stage corrugation in Si and Ge analogs of graphite. Physical Review B, 50(20), 14916.

Tran, V., and Yang, L. (2014). Scaling laws for the band gap and optical response of phosphorene nanoribbons. Physical Review B, 89(24), 245407.

Tritsaris, G. A., Kaxiras, E., Meng, S., and Wang, E. (2013). Adsorption and diffusion of lithium on layered silicon for Li-ion storage. Nano letters, 13(5), 2258-2263.

Troullier, N., & Martins, J. L. (1991). Efficient pseudopotentials for plane-wave calculations. Physical review B, 43(3), 1993.

Wigner, E. (1938). Effects of the electron interaction on the energy levels of electrons in metals. Transactions of the Faraday Society, 34, 678-685.

Wu, Q., Shen, L., Yang, M., Cai, Y., Huang, Z., and Feng, Y. P. (2015). Electronic and transport properties of phosphorene nanoribbons. Physical Review B, 92(3), 035436.

Xia, F., Wang, H., and Jia, Y. (2014). Rediscovering black phosphorus as an anisotropic layered material for optoelectronics and electronics. Nature communications, 5.

Xie, J., Si, M. S., Yang, D. Z., Zhang, Z. Y., and Xue, D. S. (2014). A theoretical study of blue phosphorene nanoribbons based on first-principles calculations. Journal of Applied Physics, 116(7), 073704.

Zhang, W., Ye, C., Bi, L., Yang, Z., and Zhou, R. (2015). Wetting and Diffusion of Water on Pristine and Strained Phosphorene. arXiv preprint arXiv:1512.02116.

Zhang, X., Li, Q., Xu, B., Wan, B., Yin, J., and Wan, X. G. (2016). Tuning carrier mobility of phosphorene nanoribbons by edge passivation and strain. Physics Letters A, 380(4), 614-620.

Zhao, S., Kang, W., and Xue, J. (2014). The potential application of phosphorene as an anode material in Li-ion batteries. Journal of Materials Chemistry A, 2(44), 19046-19052.

Ziman, J. M. (1972). Principles of the Theory of Solids. Cambridge university press.