

**Structural and electronic properties of a two-dimensional hybrid  
system of graphene and hexagonal boron nitride:**

**A first-principles study**



**By**

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**Co-supervisor: Dr. Abdulhakeem Bello**

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# **Structural and Electronic Properties of a Two-Dimensional Hybrid System of Graphene and Hexagonal Boron Nitride: A First-Principles Study**

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## **Certification**

This is to certify that the thesis titled “*structural and electronic properties of a two-dimensional hybrid system of graphene and hexagonal boron nitride: a first-principles study*” submitted to the Department of Theoretical and Applied Physics African University of Science and Technology (AUST), Abuja, Nigeria for the award of the master's degree is a record of original research carried out by ***Rabiatu Mahadi***.

## ABSTRACT

Despite the excellent properties of graphene, graphene based electronic devices are yet to be realized, one of the reason for such is the absence of band gap in graphene. Due to its large band gap, hexagonal boron nitride (h-BN) is not suitable for electronic application. Here, we present a new method of tailoring the electronic properties of both graphene and h-BN by making a 2-d hybrid containing both materials. In this study, we investigate the structural and electronic properties of graphene/h-BN lateral hybrid using DFT at different proportions. Our result shows that, as the proportion of h-BN in the hybrid is increased, band gap opens in the range of 0.64 - 1.1 eV. This suggest that our hybrid is semiconducting and can be used for different electronic applications. Even though the structural parameters of the hybrid changes with increasing concentration of h-BN, the formation energy of the hybrid increases as the proportion of h-BN in the hybrid is increased, thus this proposed hybrid is very stable.

## AKNOWLEDGEMENT

I would like to express my deep gratitude to my research supervisors Dr. Okikiola Olaniyan and Dr. Abdulhakeem Bello, for their patience assistance and guidance during this research work. I would like to offer my special thanks to African University of Science and Technology Abuja for sponsoring my master's studies through African development Bank. Finally, I wish to thank my parents' siblings and friends for their support and encouragement throughout my study.

# TABLE OF CONTENTS

Certification .....	ii
ABSTRACT .....	iii
ACKNOWLEDGEMENT .....	iv
TABLE OF CONTENTS .....	v
CHAPTER 1 .....	1
INTRODUCTION .....	1
GRAPHENE .....	1
HEXAGONAL BORON NITRIDE (h-BN) .....	2
AIM AND OBJECTIVES .....	4
Aim .....	4
Objectives .....	4
CHAPTER 2 .....	5
LITERATURE REVIEW .....	5
CHAPTER 3 .....	10
METODOLOGY .....	10
Adiabatic or Born-Oppenheimer approximation .....	12
The Hartree approximation .....	13
DENSITY FUNCTIONAL THEORY .....	16
HOHENBERG KOHN THEOREM .....	16
Exchange-correlation functional .....	18
Local density approximation (LDA) .....	18
Generalized gradient approximation (GGA) .....	18
The Hybrid functionals .....	18
PSEUDOPOTENTIALS .....	20
COMPUTATIONAL DETAILS .....	21
CHAPTER 4 .....	22
RESULT AND DISCUSSION .....	22
CHAPTER 5 .....	32
CONCLUSION AND RECOMMENDATION .....	32
REFERENCES .....	33

# CHAPTER 1

## INTRODUCTION

### GRAPHENE

Graphene is a 2-dimensional material consisting of carbon atoms arranged in a hexagonal lattice. Graphene is the building block of all graphitic materials. It was first isolated from graphite using mechanical exfoliations by Andre Geim and Konstantin Novoselov in 2004. In graphene layers, each carbon atom is bonded with another carbon atom through  $sp^2$  network and one out of plane bond through pi bond, this bonding characteristics are responsible for some of its excellent properties. Graphene has excellent mechanical properties (Bizao, Botari, & Galvao, 2014) and (Papageorgiou, Kinloch, & Young, 2017), electrical properties (Castro Neto, 2010), (A.K & K.S, 2007) and optical properties (Apell, Hanson, & Hägglund, 2012). The most exciting properties are the electronic properties because of the unusual behavior of the charge carriers in graphene namely, high carrier mobility even at room temperature, integer and half integer quantum hall effect, excellent conductivity, chiral transport and so on, (Simpson et al., 2007), (Cooper et al., 2011) and (Morozov et al., 2008). These properties make graphene a perfect candidate for applications in FETs (Mavredakis et al.), super capacitors (Huang, Liang, & Chen,

2012), catalysis (MacHado & Serp, 2012), and many other in optoelectronics and biology.

Band structure calculation has shown that graphene is a semimetal with zero band gap(Wallace, 1947), (Novoselov, Geim, Morozov, & Jiang, 2004). The absence of band gap in graphene makes it difficult to be incorporated in to electronic devices due to its low on/off ratio, hence opening and controlling a band gap in graphene is an important topic with regard to application. Many techniques have be devised to create band gap in graphene, such techniques involved substituting carbon atoms in graphene with heteroatoms, adsorbing molecules on the surface, epitaxial growth of graphene on substrate and so on (Jariwala, Srivastava, & Ajayan, 2011).

### **HEXAGONAL BORON NITRIDE (h-BN)**

Hexagonal boron nitride (h-BN) is quasi in structure to graphene. Hexagonal boron nitride known as white graphene is a 2-D material consisting of alternating nitrogen and boron atoms replacing carbon in hexagonal lattice. It has a smooth and flat surface, chemically and thermally stable. h-BN has similar lattice parameters with graphene, the boron and nitrogen atoms are held together by strong covalent bonds and the layers are bonded by Vander walls forces. It has a wide band gap of about 4.5 to 6 eV (Watanabe, Taniguchi, & Kanda, 2004), (Zhang, Feng, Wang, Yang, & Wang, 2017), this make it an excellent insulator. It has good thermal conductivity



superior than the one used currently (Zheng et al., 2016), low thermal expansion coefficient (Solozhenko & Peun, 1997) and excellent mechanical strength (Falin et al., 2017). In fact (Falin et al., 2017) reported that h-BN mechanical strength is better than that of graphene due to the fact that it doesn't losses its mechanical strength with increasing the number of h-BN layers. h-BN can be used for applications such as substrates and gate dielectrics for 2D electronics applications due the large band gap and excellent thermal conductivity. In addition to this, 2D-hBN based hetero-structures has been reported with a significant improvement in carrier mobility, high on/off ratios, sizable and tunable band gap, this can be used to produced excellent field effect transistors e.g. Graphene/h-BN heterostructure. Furthermore, with the remarkable mechanical properties and excellent thermal conductivity, h-BN nano sheets are considered as one of the promising materials to combine with certain organic polymers for mechanical reinforcement.

## **AIM AND OBJECTIVES**

### **Aim**

To create a stable 2D Nano semiconductor with a tuneable band-gap for nano electronic devices.

### **Objectives**

1. Design a 2D graphene and h-BN lateral nano composite material
2. Investigate the effect of concentration of h-BN in the hybrid
3. Apply the first principle in the framework of DFT method to calculate the stability, structural and electronic properties of the hybrid systems

## CHAPTER 2

### LITERATURE REVIEW

To engineer band gap in graphene, several techniques that include chemical substitution (doping), growing graphene on substrate, and adsorption of molecules on the surface of graphene have been successfully studied. Chemical doping involves replacing carbon atoms in graphene with foreign atoms. There are a lot of theoretical work on single and co doping of graphene with atoms such as N, Be, B, S etc. (Alattas & Schwingenschlögl, 2018) investigate the effects of B and/or N doping on bilayer graphene. They report that B-N pairs hardly modify the band dispersions in bilayer graphene, while opening a substantial band gap (of 70 meV in the case of 2% dopant concentration, for example). For this reason, the paper concluded that co-doping with B-N pairs into bilayer graphene can be used to tune the size of the band gap without critically affecting the band dispersions. (Lee et al., 2019) report that; doping with N and S atoms perturb the bands in graphene and open the band gap at the Dirac points, the energy band shift up above the Fermi level compared to pristine graphene when graphene is doped with three nitrogen atoms around a mono-vacancy defect, which corresponds to p-type nature. On the other hand, the energy bands were increasingly shifted downward below the Fermi level with increasing numbers of S atoms in N/S-co-doped graphene, which results

in n-type behavior. Doping of graphene with atomic impurities at increasing concentration leads to decrease in the cohesive energy of the material, and thus reduced stability. (Reyes García Díaz, Carlos Eduardo Rodríguez García, María Teresa Romero de la Cruz, Víctor Eduardo Comparán Padilla, & Gregorio Hernández Coccoletzi, 2017) reported DFT study on effect of doping and co-doping of graphene with phosphorus and aluminium. Their results shows that; the incorporation of heteroatoms in graphene distorts the unit cell changing angles and lengths of bonds, owing to larger atomic radius of the dopants. Even though the band gap increases with concentration of the dopants but due to the structural deformation induced by the dopant, the stability of graphene is distorted which destroy some of its excellent properties. (Saqlain et al., 2015) performed first-principles DFT calculation to investigate the structural and electronic properties of graphene systems doped with Be and co-doped with Be and B, they have reported that increasing the impurity concentration leads to weakening the bonds due to decrease in cohesive energy of the system.

The electronic properties of graphene depend on the symmetry, and thus the sites in which impurities are placed play an important role in the modulation of the energy gap. (Rani & Jindal, 2014) reported that when graphene is doped with B/N,

the band gap increases when the dopants are placed at same sub lattice positions, while for BN co doping, the width of band gap increases with distance between B and N atoms. (Saqlain et al., 2015) reported that; the replacement of a single C atom in graphene with a Be atom induces a band-gap of 0.46 eV, and Fermi level shift down which indicates p-type doping. In the case of rectangular doping, an increase in the impurity concentration lead to a linear rise in the band gap. However, an exponential rise (max. value 1.44 eV) was observed for hexagonal doping. Ullah, Hussain, & Sato, 2017 performed electronic structure calculations for graphene doped with B, N, and O at rectangular and hexagonal sites using first-principles density functional theory (DFT). They reported a linear increase in band gap values due to the rectangular doping while an exponential rise in band gaps can be seen due to the hexagonal configuration of the dopants in the graphene. This difference in the band gaps obtained for different configurations is more prominent for O doping, which is comparable to Be doping as these atoms have two electrons more and fewer, respectively, than the C atom. In fact, the value of the band gap obtained from 3 O atoms doped at the hexagonal site is substantially greater than that when 4 O atoms are doped at the rectangular site.

Another method of engineering band gap in graphene is through adsorption of molecules such as H<sub>2</sub>, O<sub>2</sub> and aromatic compounds on the surface of graphene. It is

very important to note that sizable band gap is needed in graphene to increase its on/off ratio so that it can be used for electronic devices without losing its excellent properties. It is found that when molecules are adsorbed on graphene they hybridize graphene from  $sp^2$  to  $sp^3$  (Xu et al., 2018), (Kong, Enders, Rahman, & Dowben, 2014). Electronic properties of graphene are due to the half filled  $\pi$  bands in graphene, hence converting graphene from  $sp^2$  to  $sp^3$  lead to losing some of its excellent properties such as large mobility and excellent conductivity. (Haberer et al., 2010), (Chang, Fan, Li, & Kuo, 2012) have reported a tunable band gap due to adsorption of molecules but the mobility of is very small compared to that of graphene. Hence, it is not applicable for devices where large value of mobility is needed e.g. in FETs. Furthermore, the strong manipulation of graphene electronic structure, including  $p$ - and  $n$ -doping is not possible with molecular adsorbents (Kong et al., 2014). Furthermore, a sizable band gap is reported when graphene is grown on substrates such as SiC, SiO<sub>2</sub>. (Zhou et al., 2007) reported that, when graphene is epitaxially grown on the SiC substrate, a gap of 0.26 eV is produced, they further depict that the band gap is due to interaction between graphene and substrate. (Shemella & Nayak, 2009) have studied the electronic structure of graphene deposited on a SiO<sub>2</sub> surface using DFT. They described that band structure of the graphene monolayer strongly depends on surface characteristics

of the underlying  $\text{SiO}_2$  surface, in such a way that for oxygen-terminated surface, a finite energy band gap 0.52 eV was observed, while the band gap is closed when the oxygen atoms on the substrate are passivated with hydrogen atoms. Band gap obtained from epitaxial growth is non tunable (Berger et al., 2017) hence is not qualified for most of electronic applications.

## CHAPTER 3

### METODOLOGY

The properties of materials are ultimately determined by the interactions of electrons and nuclei, and the fundamental description of those interactions requires quantum mechanics. Assume a situation where we would like to describe the properties of some well-defined collection of atoms. One of the fundamental things we would like to know about these atoms is their energy and, more importantly, how their energy changes if we move the atoms around. To define where an atom is, we need to define both the position of its nucleus and the atom's electrons position. Thus to know all this we used time independent Schrodinger given in equation 1 below.

$$\hat{H}\psi_i = E_i\psi_i \quad \mathbf{1}$$

Where  $\hat{H} = \hat{T} + \hat{V}$  is called **Hamiltonian**

For this system, we treat the atoms composed of valence and core electrons because the valence electrons are the ones responsible for bonding and most of properties of the system, we merge the core electrons and nucleus and called them ions. This lead us to write the  $\hat{H}$  as the sum of the kinetic energy of the ions,



kinetic energy of the electrons, ion-ion interaction, ion-electron interaction, and electron-electron interaction.

$$\hat{H} = -\frac{\hbar^2}{2m_e} \sum_{i=1}^N \nabla_i^2 - \hbar^2 \sum_{I=1}^M \frac{\nabla_I^2}{2M_I} + \frac{1}{2} \sum_{i \neq j}^N \frac{e^2}{|\vec{r}_i - \vec{r}_j|} - \sum_{i=1}^N \sum_{I=1}^M \frac{Z_i e^2}{|\vec{r}_i - \vec{R}_I|} + \frac{1}{2} \sum_{I \neq J}^M \frac{Z_I Z_J e^2}{|\vec{R}_I - \vec{R}_J|} \quad 2$$

We can further expressed  $\hat{H}, \psi$  as;

$$\hat{H} = \hat{T}_{elec} + \hat{T}_{ion} + \hat{V}_{ion-elec} + \hat{V}_{elec-elec} + \hat{V}_{ion-ion}$$

$$\psi_i = \psi_i(\vec{r}_1, \dots, \vec{r}_N, \sigma_1, \dots, \sigma_N; \vec{R}_1, \dots, \vec{R}_M, \delta_1, \dots, \delta_M)$$

Now from Rayleigh-Ritz virational principle expressed in equation 3. If  $\mathbf{Q}$  is an expectation value of a wave function  $\psi$ , then it is always greater than the ground state energy of the wave function, mathematically;

$$\mathbf{Q}(\psi) = \frac{\langle \psi | H | \psi \rangle}{\langle \psi | \psi \rangle} \geq E_o = \psi H \psi / \psi \psi \geq E_o \quad 3$$

Now suppose  $|\psi\rangle$  is expressed in terms of a variable parameter  $\eta$ , then  $\mathbf{Q}$  can be made to get close  $E_o$  by minimizing  $\mathbf{Q}$ , i.e.

$$\frac{\partial \mathbf{Q}}{\partial \eta} = 0 \quad 4$$

Or we can use the method of Lagrange multiplier, i.e.

$$\delta[\langle \psi | H | \psi \rangle - \lambda g] = 0 \quad 5$$

Where  $g$  is Lagrange multiplier. Looking at equation 2, it is very hard to solve because it's a many-body problem; the wave functions has many degrees of freedom as seen above. In addition to this, because we have many electrons in the system the electron- electron interaction is very hard to compute. The solution to this many-body problem within the exact quantum mechanical framework is practically impossible. Hence, we need some valid physical approximations to solve the problem. Some of these meaningful approximations are described as follows.

### **Adiabatic or Born-Oppenheimer approximation**

The adiabatic or Born-Oppenheimer approximation is based on the fact that the nuclei are much heavier than the electrons; hence the velocities of electrons are much higher than that of the nuclei. Thus, the nuclear kinetic energy in the Hamiltonian expression 2 above is negligible. Then equation 2 is modified to give B-O Hamiltonian for electrons of a fixed nuclear configuration  $R$ :

$$\hat{H}_{elec} = -\frac{\hbar^2}{2m_e} \sum_{i=1}^N \nabla_i^2 - \sum_{i=1}^N \sum_{I=1}^M \frac{Z_I e^2}{|\vec{r}_i - \vec{R}_I|} + \frac{1}{2} \sum_{i \neq j}^N \frac{e^2}{|\vec{r}_i - \vec{r}_j|} \quad 6$$

Which can be expressed as

$$\hat{H}_{elec} = \hat{T}_{elec} + \hat{V}_{ion-elec} + \hat{V}_{elec-elec}$$

Thus our Hamiltonian is now a function of position of the electrons only. The nucleus-nucleus interaction is not included because it is a constant for a fixed ionic configuration R. Then our electronic many-body equation, becomes:

$$\hat{H}_{elec}\psi_{elec}(\vec{r}_1, \vec{r}_2, \dots) = E_{elec}\psi_{elec}(\vec{r}_1, \vec{r}_2, \dots)$$

$$E_{tot} = E_{elec} + E_{nucli}$$

But we can see that this doesn't solve the problem, the electron-electron interaction is still there and the wave function has many degrees of freedom. Thus, this led us to look for more approximations.

### **The Hartree approximation**

In this approximation, each electron is treated as an entity and all of these electrons realize a uniform potential known as Hartree potential which replaces electron-electron interaction in equation 6. Hence we can write our Hamiltonian as

$$\hat{H}_{elec}(x_1 \cdots x_n) = \sum_{i=1}^N H(i) + \frac{1}{2} \sum'_{i,j} V(i,j), \text{ Where } V(ij) = V(ji) \quad 7$$

The total wave function is written as the product of the individual electron wave function in such a way that the total wave function is normalized.

$$\psi(x_1 \cdots x_n) = u_1(x_1)u_2(x_2) \cdots u_n(x_n) \quad 8$$

**Which constraint**

$$\int \psi^*(x_1, \dots, x_n) \psi(x_1, \dots, x_n) d\tau = 1 \quad \mathbf{9}$$

Substituting 8 and 9 in 5 we have;

$$\delta[\langle \psi | H | \psi \rangle - \sum_i \lambda_i \int u_i^*(x_i) u_i(x_i) d\tau] = 0 \quad \mathbf{10}$$

Now using 7 and 8 we can write the Schrodinger wave equation for each electron as;

$$\epsilon_k \mathbf{u}_k = \left[ \frac{\nabla^2}{2} - \sum_{I=1}^M \frac{Z_I e^2}{|\vec{r}_k - \vec{R}_I|} + \int \frac{n(r_l)}{|r_k - r_l|} d\tau_l \right] \mathbf{u}_k \quad \mathbf{11}$$

$$\epsilon_k \mathbf{u}_k = [\hat{T}_e + \hat{V}_{ion} + \hat{V}_H] \mathbf{u}_k \quad \mathbf{12}$$

The trial wave function employed in the approximation has no antisymmetric property, as such does not take into account Pauli Exclusion Principle. Moreover, with the approximation, the degree of freedom scales with the size of the system in question. This limit the application of Hartree approximation to solve the problem. To tackle this issue another approximation has to be considered

## The Hartree-Fock (HF) approximation

HF was formulated to correct the failure of Hartree approx., and the difference in the two approaches lies in the trial wave function used. In this approximation, matrix was created such that the wave functions anti symmetrized when electrons change position or become zero when two electrons assume the same position.

$$\psi(\vec{r}_1, \vec{r}_2, \dots, \vec{r}_N) = \frac{1}{\sqrt{N!}} \begin{vmatrix} \phi_1(\vec{r}_1) & \phi_2(\vec{r}_1) & \dots & \phi_N(\vec{r}_1) \\ \phi_1(\vec{r}_2) & \phi_2(\vec{r}_2) & \dots & \phi_N(\vec{r}_2) \\ \cdot & \cdot & \dots & \cdot \\ \cdot & \cdot & \dots & \cdot \\ \cdot & \cdot & \dots & \cdot \\ \phi_1(\vec{r}_N) & \phi_2(\vec{r}_N) & \dots & \phi_N(\vec{r}_N) \end{vmatrix}$$

$$\psi(\vec{r}_1, \vec{r}_2, \dots, \vec{r}_N) = \frac{1}{\sqrt{N!}} \sum_p (-1)^p P \phi_1(\vec{r}_1), \phi_2(\vec{r}_2), \dots, \phi_N(\vec{r}_N) \quad \mathbf{13}$$

Now substituting 13 in 10 and rewriting 12, we have;

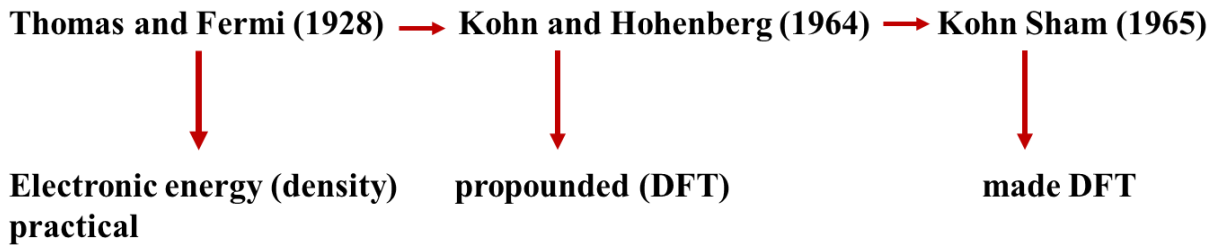
$$\epsilon_i \phi_i = [\hat{T}_e + \hat{V}_H + \hat{V}_{ion}] \phi_i - \frac{1}{2} \sum_{i,j} \int d^3 r' \phi_j^*(\vec{r}') \phi_i(\vec{r}) \frac{1}{|\vec{r} - \vec{r}'|} \phi_i(\vec{r}') \phi_j(\vec{r})$$

This approximation has its own limitations outlined below

- Exchange term makes the equation difficult to solve
- The description of homogenous gases by the equation is limited
- The energy calculation from HF is always greater than ground state energy
- Lack electrons correlation

To overcome this limitation, numerous methods, called post-Hartree-Fock have been formulated. One of these methods is called density functional theory (DFT)

### DENSITY FUNCTIONAL THEORY



### HOHENBERG KOHN THEOREM

- The ground state energy is a unique functional of the electron density  $n(r)$
- The ground state energy is the minimum of this functional, and the density that minimizes the functional is the ground state density

From the first theorem, we can write the functional  $F$  as

$$F[n] = \int dr n(r)V_n(r) + \langle \Psi[n] | T + V_{e-e} | \Psi[n] \rangle$$

Now using 11, we can  $F$  rewrite as

$$E[n] = F[n] = \int dr n(r)V_n(r) - \sum_i \int dr \phi_i^*(r) \frac{\nabla^2}{2} \phi_i(r) +$$

$$\frac{1}{2} \int \int dr dr' \frac{n(r)n(r')}{|r-r'|} + E_{xc}[n] \int dr nrV_{nr}$$

$$\int dr \phi_i^* r \nabla^2 / 2 \phi_i + 1/2 \int \int dr dr' n(r)n(r')/|r-r'| + E_{xc}[n] \quad \mathbf{15}$$

DFT is presently the most widely used method to compute the total energy and electronic structure of matter. The idea behind DFT is that it no longer look for the electron wave function which has many degrees of freedom but its density which depends on only 3-dimention.

Using the second theorem, the ground state density  $\mathbf{n}_o(\mathbf{r})$  can be obtained by;

$$\frac{\delta F[\mathbf{n}]}{\delta \mathbf{n}} \Big|_{\mathbf{n}_o} = \mathbf{0}$$

Using equation 11 and 15 we can have our Kohn sham equation as;

$$\left[ -\frac{1}{2} \nabla^2 + V_n(\mathbf{r}) + V_H(\mathbf{r}) + V_{xc}(\mathbf{r}) \right] \phi_i(\mathbf{r}) = \epsilon_i \phi_i$$

$$V_{xc} = \frac{\delta E_{xc}[\mathbf{n}]}{\delta \mathbf{n}} \Big|_{n(\mathbf{r})}$$

To solve the Kohn–Sham equations, we need to define the Hartree potential, and to define the Hartree potential we need to know the electron density, but to find the electron density, we must know the single-electron wave functions, and to know these wave functions we must solve the Kohn–Sham equations. To break this circle, the problem is usually treated in an iterative way as outlined in the algorithm given the figure below 1.

## **Exchange-correlation functional**

The exchange-correlation term ( $E_{xc}[\mathbf{n}]$ ) is the energy contribution from the quantum effects not included in the Coulomb repulsion and the single-particle kinetic energy. The exact form of this expression is unknown. The commonly used approximations to determine the exchange correlation energy include the local density approximation (LDA), generalized gradient approximation (GGA), and hybrid functional. These approximations are describe below.

### **Local density approximation (LDA)**

- Failed to predict accurately electronic properties of semiconductors such as band gaps
- Underestimation of lattice parameters
- Overestimation of cohesive energy and modulus of solids

### **Generalized gradient approximation (GGA)**

- Usually gives better result than LDA
- Slightly underestimate the band-gap of semiconductors

### **The Hybrid functionals**

- Hybrid functional gives accurate band gap of semiconductors but computationally



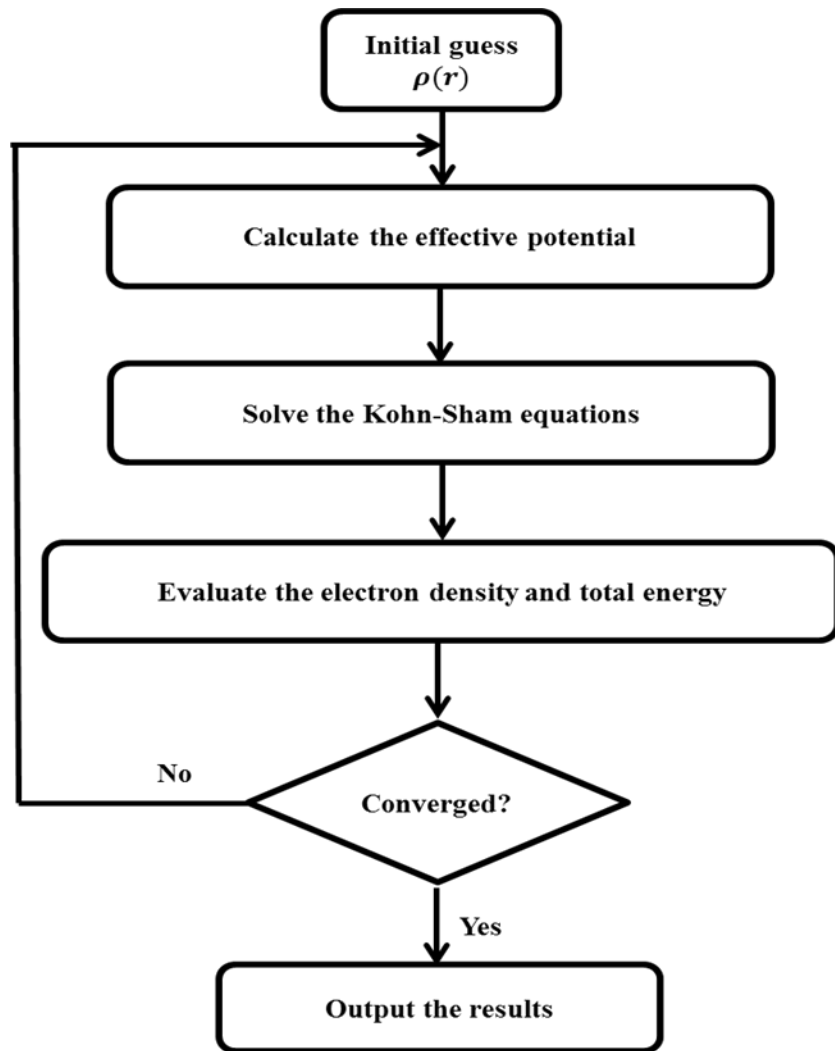
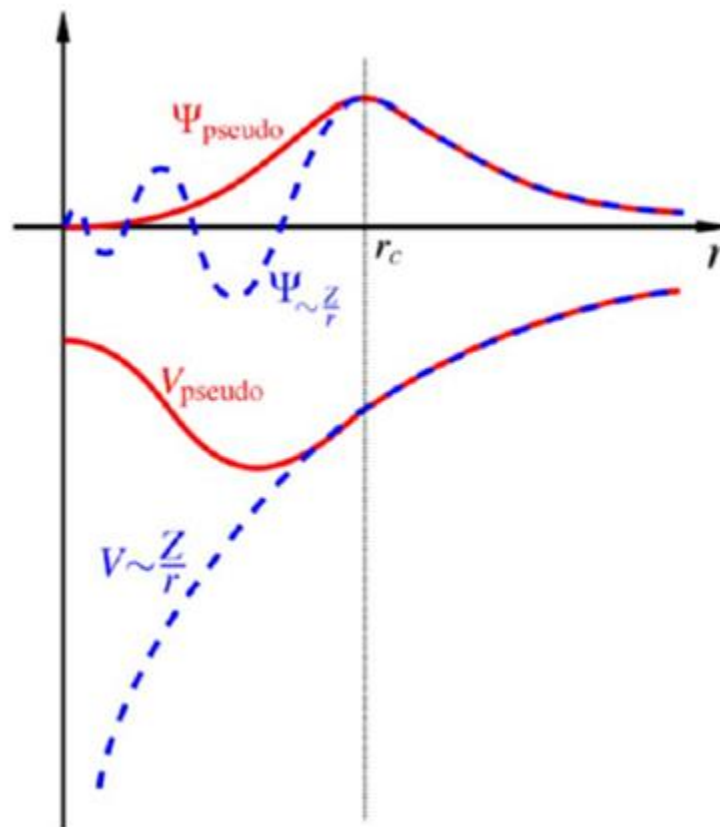


Figure 1 flow chart for iterative algorithm used in DFT

This process is aided using software such as VASP, Quantum Espresso, CASTEP, Abinit, etc

## PSEUDOPOTENTIALS

The electron-ion interaction is described in terms of pseudopotential. Pseudopotentials explain the apparent weak interaction between the active electrons and the ion cores in solids and provide great efficiency in the computation of the properties of real materials. Pseudopotentials eliminate the core electrons from the problem and allow the use of significantly simpler basis sets (e.g. plane waves or uniform real-space grids). They are of different types such as norm conservatives, ultra-soft, projected-augmented wave (PAW)



**Figure 2.** Pseudopotential as a function of atomic radii

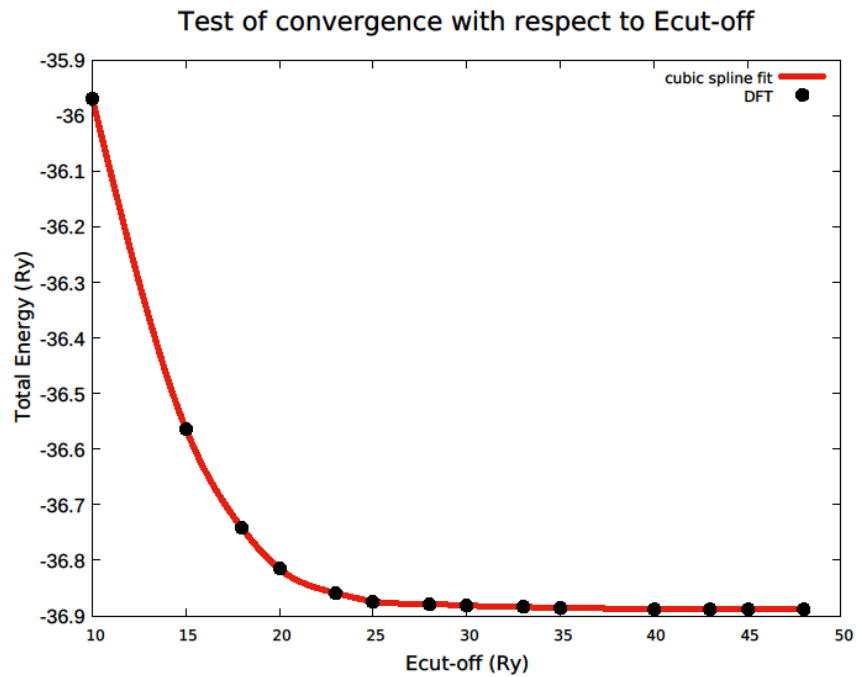
## COMPUTATIONAL DETAILS

DFT calculations were carried out using the PWscf (Plane Wave self-consistent field) code of the Quantum ESPRESSO package. In these calculations, we use a plane wave basis set and projected augmented wave (PAW) pseudopotential to represent the interaction between ionic cores and valence electrons. Exchange-correlation energies are treated within the generalized gradient approximation (GGA) with the PBE (Perdew-Burke-Ernzerhof) parameterization. We test the convergence due to  $E_{\text{cut}}$  and k points, used energy cutoff of 40 Ry for the plane wave basis. The 2D layer of graphene was simulated using a supercell geometry; we used a supercell size of  $6 \times 6 \times 1$  unit cells, containing 72 carbon atoms. To analyze the electronic properties we calculated the band structure. We used the same computational details for hexagonal boron nitride and obtain its band structure, and design a hybrid containing h-BN and graphene and optimized the hybrid to obtain the band structure. The concentration of h-BN was varied in the hybrid and band structure as well as formation energies for each hybrid was determined.

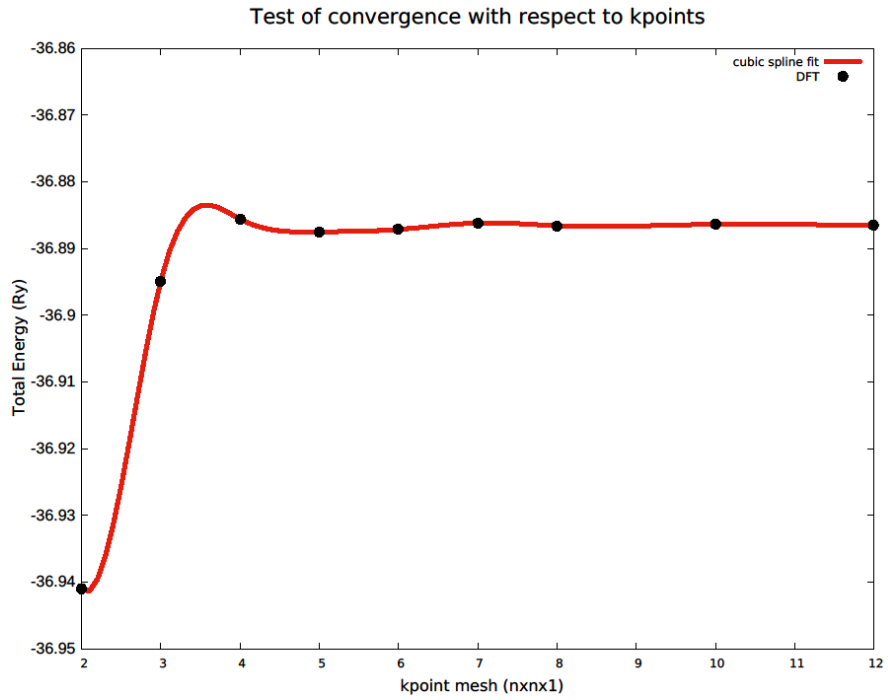
## CHAPTER 4

### RESULT AND DISCUSSION

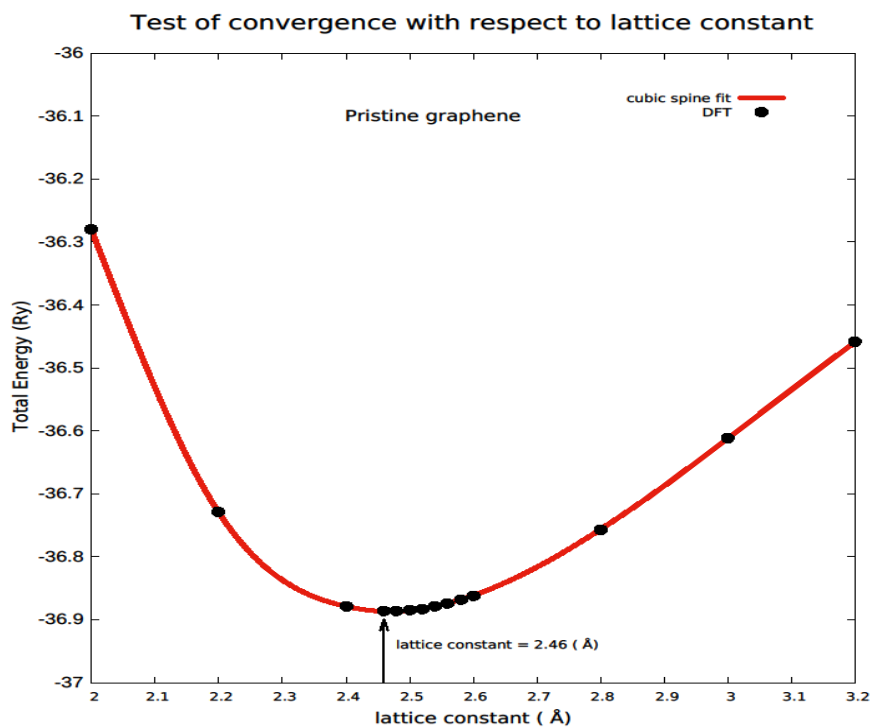
Below are the result of our findings. The optimized structures and self-consistent calculations and convergence of  $E_{\text{cut}}$  and k points are shown in figure 4.1 and 4.2 below respectively. We observe that the total energy converges from the  $E_{\text{cut}}$  value of 40, and k points value of  $5 \times 5 \times 1$ .



**Figure 4.1:** test of convergence with respect to  $E_{\text{cut}}$ -off in graphene



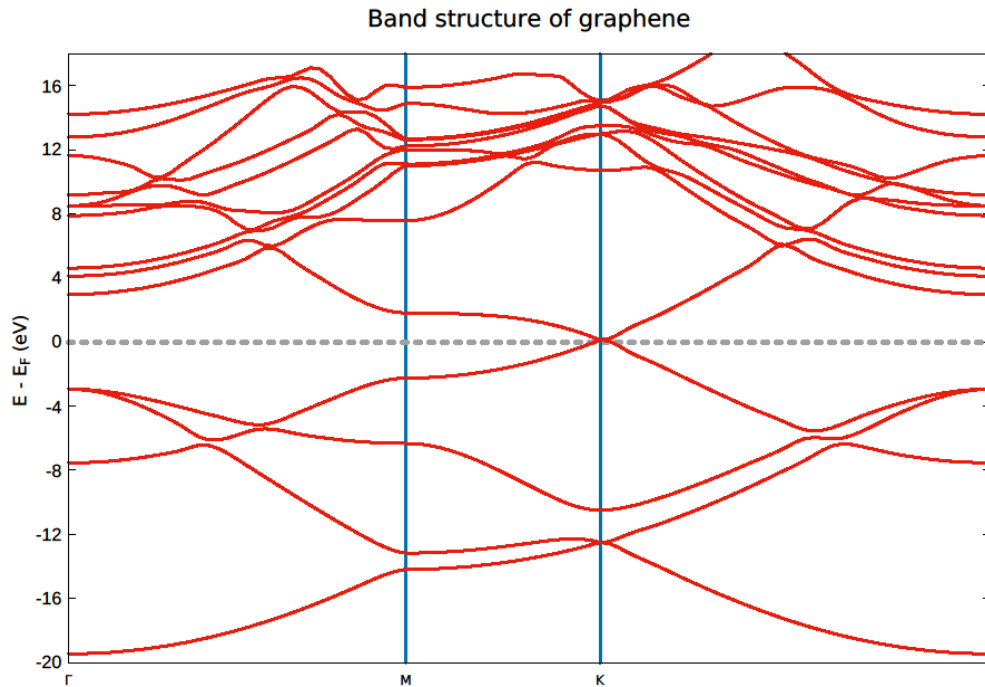
**Figure 4.2:** top of this page; test of convergence with respect to kpoint in graphene



**Figure 4.3:** bottom of this graph test of convergence with respect to lattice parameter in graphene.

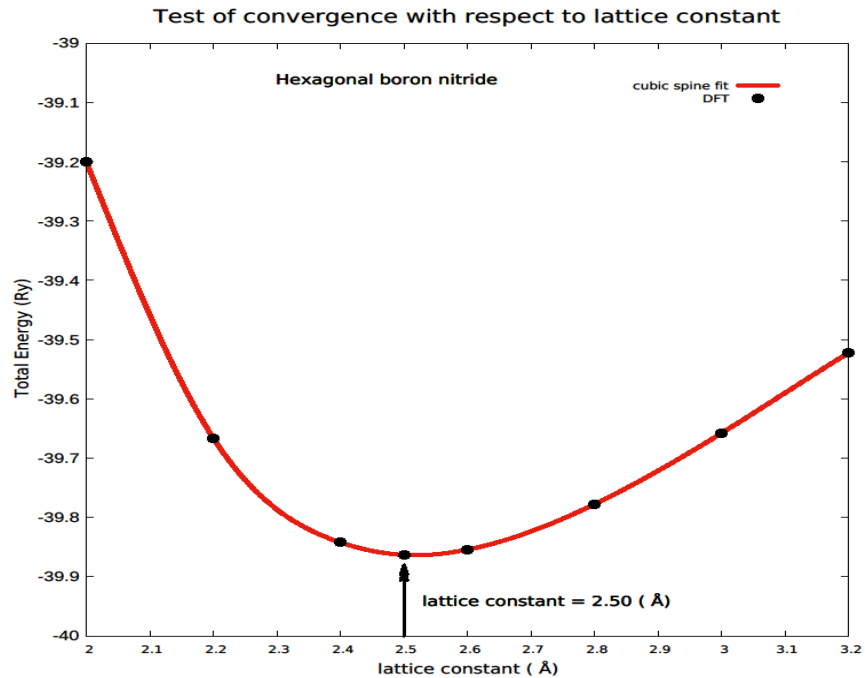
To ensure that the parameters used for the calculation are accurate respective to the system under consideration, we check convergence due to lattice parameter for graphene and we were able to obtain the minimum lattice parameter with respect to the total energy to be 2.46 as observed in figure 3 above. Surprisingly, the calculated lattice parameter for graphene is in agreement with theoretical and experimental lattice parameter for graphene (Hill, Hallmark, McNeese, Blue, & Ross, 2009). Using our proposed system we calculate the band structure of

graphene as seen in figure 4.4, and the result confirmed that graphene is a semi-metal with zero band gap.



**Figure 4.4:** band structure of graphene

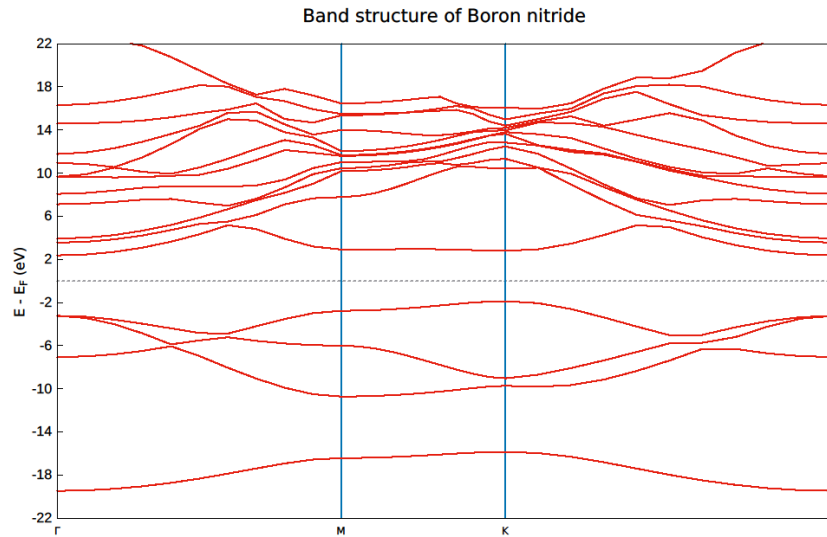
Using the same parameters for graphene in our calculations, we optimised hexagonal boron nitride(h-BN) and check convergence of total energy due to lattice parameter of the system. Interestingly, the minimum lattice parameter corresponding to total energy obtained was 2.50 which is in agreement with some theoretical result (Mukhopadhyay & Behera, 2013) and (Ooi, Rajan, Gottlieb, Catherine, & Adams, 2006), as shown in figure 4.5 below.



**Figure 4.5:** test of convergence with respect to lattice constant in h-BN

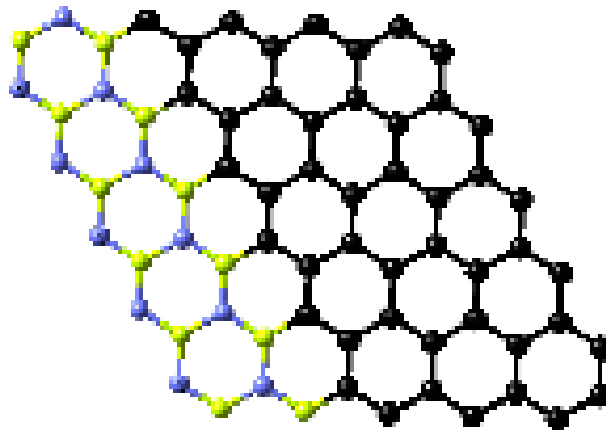
We used this optimised system and calculated the electronic band structure of h-BN of h-BN. From our calculation, we a band gap of 5.0 eV was obtained which is between the range of band gap values obtained theoretically and experimentally for h-BN; 3.6-7.0 eV





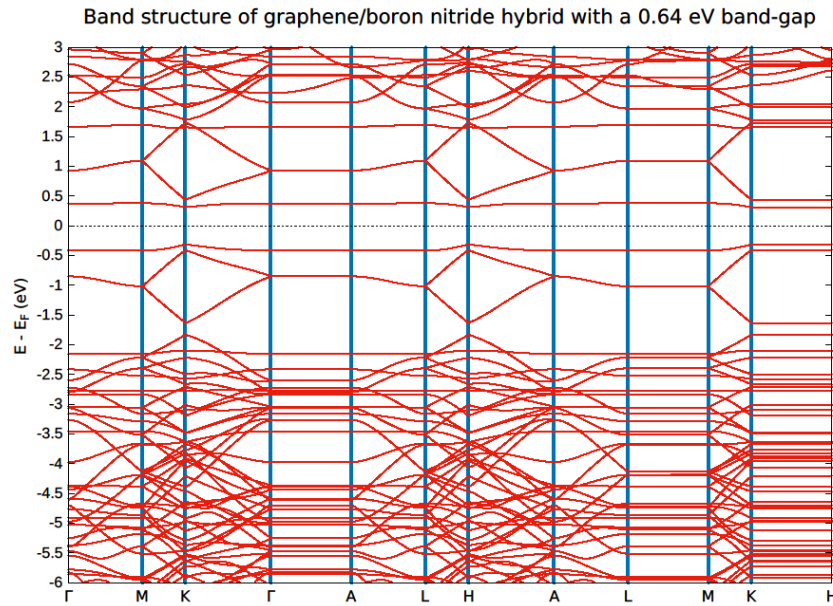
**Figure 4.6:** band structure of hexagonal boron nitride (h-BN)

To investigate the effect of hexagonal boron nitride on electronic and structural properties of h-BN, we made a hybrid consisting of graphene and hexagonal boron nitride. In this hybrid, we vary the concentration of h-BN, optimized the structure, calculate the electronic band structure and formation energy.

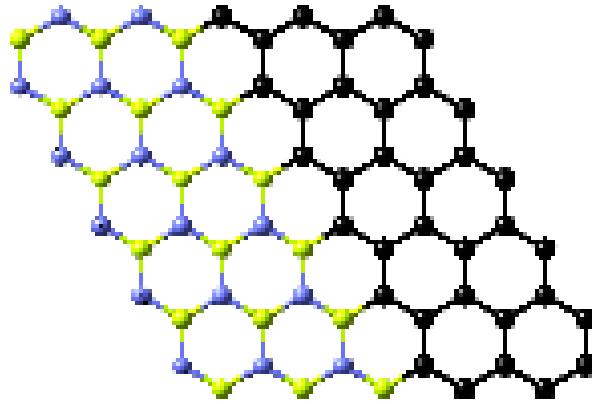


**Figure 4.7:** hybrid of 2 zig-zag strand of h-BN and 4 zig-zag strand of graphene

During the formation of the 2 zig-zag strand of h-BN and the 4 zig-zag strand of graphene (figure 4.7), a structural shift is observed with a lattice parameter of 2.47 Å and bond length of 1.43 Å. For the h-BN a lattice parameter of 2.51 Å and bond length remain the same. From the figure we observe a band gap of ~0.64 eV interestingly, the formation energy of the hybrid is -21.86 eV/unit cell which shows that the hybrid is stable.

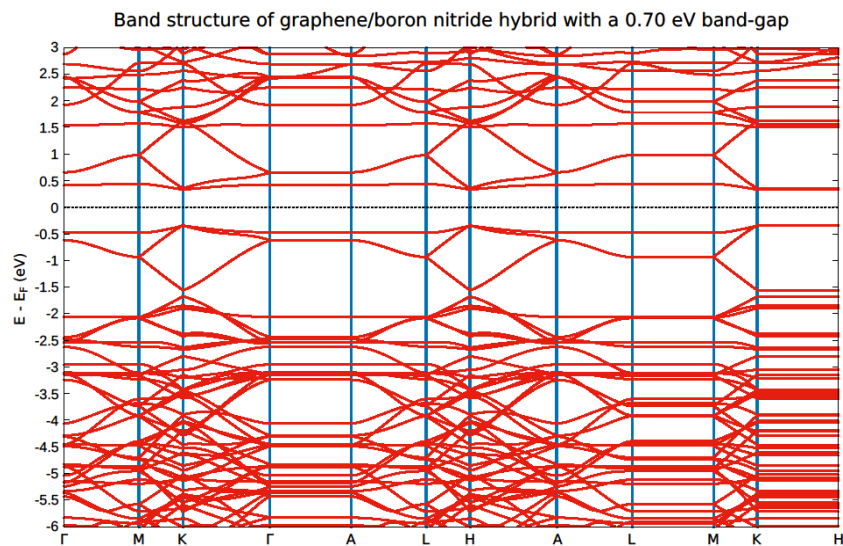


**Figure 4.8:** band structure of h-BN/ graphene hybrid

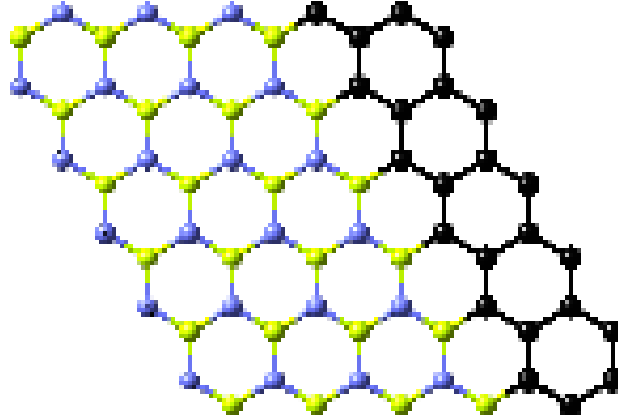


**Figure 4.9:** hybrid of 2 zig-zag strand of h-BN and 4 zig-zag strand of graphene

When have an equal proportion of h-BN and graphene (figure 4.9), Similar structural shift is observed with a lattice parameter and bond length same as that of 2 zig-zag strand of h-BN and 4 zig-zag strand of graphene. From figure 4.10, we observed a band gap of  $\sim 0.7\text{eV}$ . In this case, the formation energy increases to -36.817 eV/ unit cell.



**Figure 4.10:** band structure h-BN/graphene hybrid



**Figure 4.11:** hybrid of 4 zig-zag strand of h-BN and 2 zig-zag strand of graphene

The concentration of h-BN was increased to 4 zig-zag and graphene to 2 zig-zag strand, (figure 4.11), the structure shift with graphene having a lattice parameter of 2.48 Å and bond length of 1.43 Å and h-BN having a lattice parameter and bond length same as in the cases above. From figure 4.12 below, we observed that the band structure indicates a band gap of about 1.1 eV with the formation energy of the hybrid further increases to -52.300 eV/unit cell which shows that the hybrid become more stable as the concentration of h-BN is increasing.

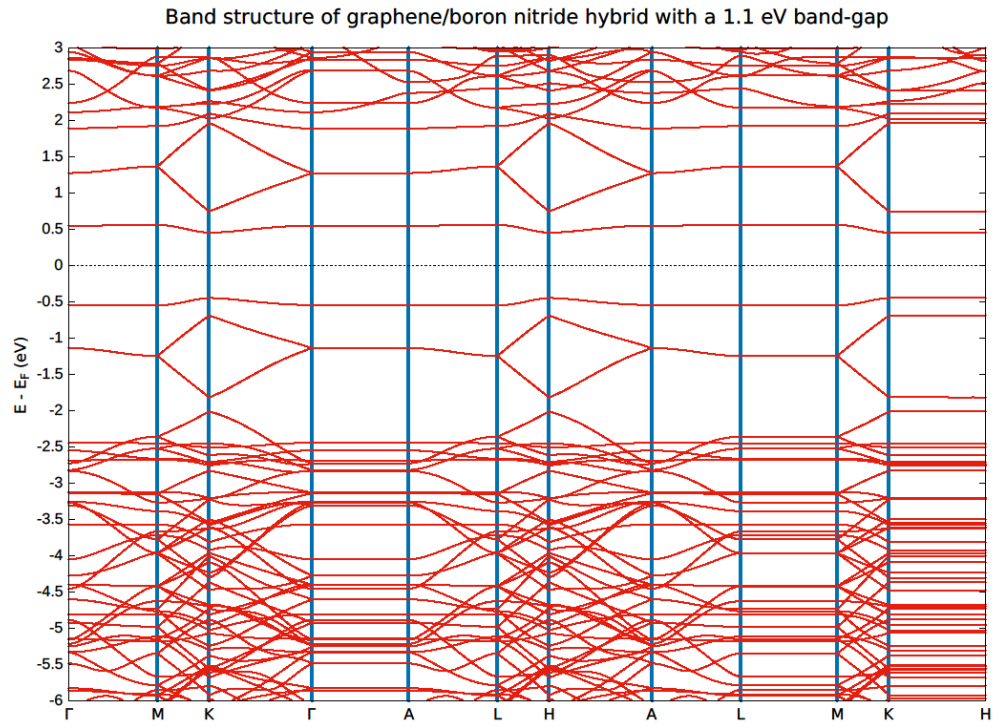


figure 4.12 : band structure of h-BN/graphene hybrid

## CHAPTER 5

### CONCLUSION AND RECOMMENDATION

We have used DFT to investigate the geometry and electronic structures of graphene/hexagonal boron nitride hybrid. The result of the study shows that the system is a semiconductor with a tunable band gap within 0.64 – 1.1 eV. This range of band gap of the material makes it applicable in a wide range of electronic application. Furthermore, our result reveals a new a technique of transforming both graphene and h-BN to a semiconductor by combining the two systems to form a lateral heterostructure. Moreover, our technique of transforming graphene and h-BN to a semiconductor suggested in this study leads to preservation of the hexagonal lattice of the constituent systems as seen in the result above. In addition to this, the result of the formation energies suggest that the hybrid system is very stable. For future study, would recommend that hybrid functionals (such as HSE06) should be used as exchange correlation function because HSE06 usually gives accurate band gap of semiconductors.

## REFERENCES

A.K, G., & K.S, N. (2007). The rise of graphene. *Nature Materials*, 6, 183–191.

Alattas, M., & Schwingenschlögl, U. (2018). Band Gap Control in Bilayer Graphene by Co-Doping with B-N Pairs. *Scientific Reports*, 8(1), 1–6.

<https://doi.org/10.1038/s41598-018-35671-2>

Apell, S. P., Hanson, G. W., & Hägglund, C. (2012). *High optical absorption in graphene*. Retrieved from <http://arxiv.org/abs/1201.3071>

Berger, C., Conrad, E., Heer, W. De, Berger, C., Conrad, E., Heer, W. De, ...

Subvolume, B. (2017). *Epigraphene : epitaxial graphene on silicon carbide To cite this version :*

Bizao, R. A., Botari, T., & Galvao, D. S. (2014). Mechanical properties of graphene nanowiggles. *Materials Research Society Symposium Proceedings*, 1658(January), 14–18. <https://doi.org/10.1557/opl.2014.402>

Castro Neto, A. H. (2010). Lecture 5: Graphene: Electronic band structure and Dirac fermions. *Nature Materials*, 769, 183.

Chang, C. H., Fan, X., Li, L. J., & Kuo, J. L. (2012). Band gap tuning of graphene by adsorption of aromatic molecules. *Journal of Physical Chemistry C*, 116(25), 13788–13794. <https://doi.org/10.1021/jp302293p>

Cooper, D. R., D’Anjou, B., Ghattamaneni, N., Harack, B., Hilke, M., Horth, A., ...

Yu, V. (2011). *Experimental review of graphene*. 2012.

<https://doi.org/10.5402/2012/501686>

Falin, A., Cai, Q., Santos, E. J. G., Scullion, D., Qian, D., Zhang, R., ... Li, L. H. (2017).

Mechanical properties of atomically thin boron nitride and the role of interlayer interactions. *Nature Communications*, 8, 1–9.

<https://doi.org/10.1038/ncomms15815>

Haberer, D., Vyalikh, D. V., Taioli, S., Dora, B., Farjam, M., Fink, J., ... Grüneis, A.

(2010). Tunable band gap in hydrogenated quasi-free-standing graphene.

*Nano Letters*, 10(9), 3360–3366. <https://doi.org/10.1021/nl101066m>

Hill, M. J., Hallmark, C. J., McNeese, M., Blue, N., & Ross, M. W. (2009). Crystal

Structure of Graphite , Graphene and Silicon. *Physics for Solid State*

*Applications*, 2, 730. Retrieved from

<http://community.wvu.edu/~miholcomb/graphene.pdf>

Huang, Y., Liang, J., & Chen, Y. (2012). An overview of the applications of

graphene-based materials in supercapacitors. *Small*, 8(12), 1805–1834.

<https://doi.org/10.1002/sml.201102635>

Jariwala, D., Srivastava, A., & Ajayan, P. M. (2011). Graphene Synthesis and Band

Gap Opening. *Journal of Nanoscience and Nanotechnology*, 11(8), 6621–6641.

<https://doi.org/10.1166/jnn.2011.5001>



Kong, L., Enders, A., Rahman, T. S., & Dowben, P. A. (2014). Molecular adsorption on graphene. *Journal of Physics Condensed Matter*, 26(44).

<https://doi.org/10.1088/0953-8984/26/44/443001>

Lee, J., Kwon, S., Kwon, S., Cho, M., Kim, K., Han, T., & Lee, S. (2019). Tunable Electronic Properties of Nitrogen and Sulfur Doped Graphene: Density Functional Theory Approach. *Nanomaterials*, 9(2), 268.

<https://doi.org/10.3390/nano9020268>

MacHado, B. F., & Serp, P. (2012). Graphene-based materials for catalysis. *Catalysis Science and Technology*, 2(1), 54–75.

<https://doi.org/10.1039/c1cy00361e>

Mavredakis, N., Wei, W., Pallecchi, E., Vignaud, D., Happy, H., & Garcia, R. (n.d.). *Velocity Saturation effect on Low Frequency Noise in short channel Single Layer Graphene FETs*. 19–22.

Morozov, S. V., Novoselov, K. S., Katsnelson, M. I., Schedin, F., Elias, D. C., Jaszczak, J. A., & Geim, A. K. (2008). Giant intrinsic carrier mobilities in graphene and its bilayer. *Physical Review Letters*, 100(1), 11–14.

<https://doi.org/10.1103/PhysRevLett.100.016602>

Mukhopadhyay, G., & Behera, H. (2013). *Emerging Two-dimensional Materials: graphene and its other structural analogues*. (December 2010), 1–12.

Retrieved from <http://arxiv.org/abs/1306.0809>

Novoselov, K. S., Geim, A. K., Morozov, S. V., & Jiang, D. (2004). *Electric Field Effect in Atomically Thin Carbon Films*. *306*(October), 666–669.

Ooi, N., Rajan, V., Gottlieb, J., Catherine, Y., & Adams, J. B. (2006). Structural properties of hexagonal boron nitride. *Modelling and Simulation in Materials Science and Engineering*, *14*(3), 515–535. <https://doi.org/10.1088/0965-0393/14/3/012>

Papageorgiou, D. G., Kinloch, I. A., & Young, R. J. (2017). Mechanical properties of graphene and graphene-based nanocomposites. *Progress in Materials Science*, *90*, 75–127. <https://doi.org/10.1016/j.pmatsci.2017.07.004>

Rani, P., & Jindal, V. K. (2014). A DFT study of B, N and BN doped graphene. *Materials Research Society Symposium Proceedings*, *1701*, 1–6. <https://doi.org/10.1557/opl.2014.538>

Reyes García Díaz, Carlos Eduardo Rodríguez García, María Teresa Romero de la Cruz, Víctor Eduardo Comparán Padilla, & Gregorio Hernández Cocolletzi. (2017). Ab Initio Study of Aluminum-Phosphorus Co-doped Graphene. *Journal of Physical Science and Application*, *7*(1). <https://doi.org/10.17265/2159-5348/2017.01.001>

Saqlain, M. A., Ullah, S., Syed, W., Leenaerts, O., Hussain, A., Karim, A., & Ahmad,

- I. (2015). Band-gap tuning of graphene by Be doping and Be, B co-doping: a DFT study. *RSC Advances*, 5(69), 55762–55773.  
<https://doi.org/10.1039/c5ra08061d>
- Shemella, P., & Nayak, S. K. (2009). Electronic structure and band-gap modulation of graphene via substrate surface chemistry. *Applied Physics Letters*, 94(3).  
<https://doi.org/10.1063/1.3070238>
- Simpson, Novoselov, K. S., Simpson, D., Derna, Jiang, Z., Zhang, Y., ... Geim, A. K. (2007). Room-Temperature Quantum Hall Effect in Graphene. *Science*, 315(5817), 1379. <https://doi.org/10.1126/science.1137201>
- Solozhenko, V. L., & Peun, T. (1997). Compression and thermal expansion of hexagonal graphite-like boron nitride up to 7 GPa and 1800 K. *Journal of Physics and Chemistry of Solids*, 58(9), 1321–1323.  
[https://doi.org/10.1016/S0022-3697\(97\)00037-1](https://doi.org/10.1016/S0022-3697(97)00037-1)
- Ullah, S., Hussain, A., & Sato, F. (2017). Rectangular and hexagonal doping of graphene with B, N, and O: a DFT study. *RSC Advances*, 7(26), 16064–16068.  
<https://doi.org/10.1039/c6ra28837e>
- Wallace, P. R. (1947). The band theory of graphite. *Physical Review*, 71(9), 622–634. <https://doi.org/10.1103/PhysRev.71.622>
- Watanabe, K., Taniguchi, T., & Kanda, H. (2004). Direct-bandgap properties and

evidence for ultraviolet lasing of hexagonal boron nitride single crystal.

*Nature Materials*, 3(6), 404–409. <https://doi.org/10.1038/nmat1134>

Xu, X., Liu, C., Sun, Z., Cao, T., Zhang, Z., Wang, E., ... Liu, K. (2018). Interfacial engineering in graphene bandgap. *Chemical Society Reviews*, 47(9), 3059–3099. <https://doi.org/10.1039/c7cs00836h>

Zhang, K., Feng, Y., Wang, F., Yang, Z., & Wang, J. (2017). Two dimensional hexagonal boron nitride (2D-hBN): Synthesis, properties and applications. *Journal of Materials Chemistry C*, 5(46), 11992–12022. <https://doi.org/10.1039/c7tc04300g>

Zheng, J. C., Zhang, L., Kretinin, A. V., Morozov, S. V., Wang, Y. B., Wang, T., ... Novoselov, K. S. (2016). High thermal conductivity of hexagonal boron nitride laminates. *2D Materials*, 3(1), 1–6. <https://doi.org/10.1088/2053-1583/3/1/011004>

Zhou, S. Y., Gweon, G. H., Fedorov, A. V., First, P. N., De Heer, W. A., Lee, D. H., ... Lanzara, A. (2007). Substrate-induced bandgap opening in epitaxial graphene. *Nature Materials*, 6(10), 770–775. <https://doi.org/10.1038/nmat2003>