

**FIRST PRINCIPLE MODELLING
OF THE FUNDAMENTAL
ELECTRONICS PROPERTIES OF
SINGLE LAYER AND BILAYER
GRAPHENE NANOFLLAKES
MATERIALS**

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FIRST PRINCIPLE MODELLING OF THE FUNDAMENTAL ELECTRONICS PROPERTIES OF SINGLE LAYER AND BILAYER GRAPHENE NANOFLLAKES MATERIALS

By

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ABSTRACT

First principle modelling is computational theoretical modelling used in chemistry, physics and material science to study the nanomaterials electronic properties. Nevertheless, little research has been done on the electronic properties of graphene nanoflakes by using first principle modelling. Therefore, the research aims to investigate the electronic properties of single layer graphene nanoflakes with different shapes by using computational quantum physics modelling which is cost-effective and reliable. The lateral size of the graphene nanoflakes is on the nanoscale and small enough for quantum confinement effect to prevail, which ultimately can lead to an intriguing electronic property that can be studied comprehensively using first principle modelling. Generally, different number of carbon atoms with various shapes of nanoflakes will affect the integrated density of state (IDOS), Fermi energy level and total energy of the scheme. The graphene nanoflakes are studied depending on a detailed theoretical understanding of the electron density wavefunction (the particular are known as first principle or ab initio calculations). The starting point of the framework is to have a model of the basic atomic configuration of the graphene (which has a hexagonal array of carbon atoms). The configuration is then modelled in terms of its electron density by employing the density functional theory (DFT). The computational method applies the first principle method based on Density Functional Theory (DFT) with the aid of Quantum ESPRESSO, a free and open source computer

codes package. Generally, DFT equation $\mathbf{E} = \sum_i^N \epsilon_i - \frac{1}{2} \iint \frac{\rho(\mathbf{r})\rho(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} d\mathbf{r} d\mathbf{r}' + E_{xc}[\rho] - \int v_{xc}(\mathbf{r})\rho(\mathbf{r})d\mathbf{r}$ is used to the study for Fermi energy. We use DFT to investigate electronics properties in graphene nanoflakes with either armchair (AC) and zigzag (ZZ) edges, without passivation and with passivation as well as AA layer configuration and AB layer configuration.

The electronic properties of graphene nanoflakes are greatly influenced by the number of carbon atoms, with and without hydrogen-passivate edges, shape configurations and type of layer configuration. The results show that the Fermi energy of the graphene nanoflakes is increased significantly with the number of carbon atoms. The Fermi energy of the radical rhombus shape graphene nanoflakes with 30 carbon atoms is -0.174 eV per atom and this value is found to increase to -0.110 eV per atom for system that consists of 48 carbon atoms instead. The total energy and integrated density of states are found to have the similar trend as Fermi energy. The total energy of the radical rhombus shape graphene nanoflakes with 30 carbon atoms is -11.22 Ry per atom and this value is further increased to -10.59 Ry per atom when 48 carbon atoms are packed within the honeycomb lattice. An integrated density of states (IDS) for the radical rhombus shape graphene nanoflakes with 48 carbon atoms is found to be significantly higher than 30 carbon atoms as well.

For future works, first principle modelling method will be extended to study the electronic properties of graphene nanoflakes with various shapes (square, hexagonal, triangular, trapezium and rhombus), edges configuration (armchair and zigzag edge) and layers configuration (AA, AB, AAA, ABA, and ABC). In addition, the correlation between the numbers of carbon atoms within the geometry to the Fermi energy of the graphene nanoflakes will be established as well.

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LIST OF SYMBOLS

θ	Angle in Degree
H	Hamiltonian
ψ	Wavefunction
$n(r)$	Charge Density
$V(r)$	Potential
G	Reciprocal Lattice Vector
a_0	Lattice Constant
E_f	Fermi Energy

LIST OF ABBREVIATIONS

AC	Armchair
B88	Becke
BFGS	Broyden Fletcher Goldfard Shanno
BLG	Bilayer Graphene
BO	Born Oppenheimer
BZ	Brillouin Zone
C	Coulomb
CN	Carbon Nitride
DFT	Density Functional Theory
DOS	Density of States
e.m.f	External Magnetic Field
FFT	Fast Fourier Transform
FTI	Fourier Transform Infrared
GE	Gradient Expansion
GGA	Generalized Gradient Approximation
GNRs	Graphene Nanoribbons
GNF	Graphene Nanoflakes
H	Hatree
HED	Homogeneous Electron Gas
HF	Hatree Fock
HK	Hohenberg-Khon
IDS	Integrated Density of States

K.E	Kinetic Energy
KS	Khon Sham
LDA	Local Density Approximation
LED	Light Emitting Diode
LSDA	Local Spin Density Approximation
MBPT	Many Body Perturbation Theory
NDF	Negative Differential Resistance
NEGF	Non Equilibrium Green's Function
PAW	Projector Augmented Wave
PBE	Perdew Burke Ernzerhof of GGA
PDOS	Projected Density of States
PL	Photoluminescence
PWSCF	Plane Wave Self Consistent Field
PW91	Perdew Wang 91 GGA
QE	QUANTUM ESPRESSO
Ry	Rydberg
TB	Tight Binding
TDDFT	Time Dependent Density Functional Theory
TEM	Transmission Electron Microscopy
TF	Thomas Fermi
SCF	Self Consistent Field
SR	Scalar Relativistic
vdW	Van der Waals

UV	Ultraviolet
UV-vis	Ultraviolet and visible
XC	Exchange Correlation
XRD	X-Ray Diffraction
ZZ	Zigzag

CHAPTER 1 INTRODUCTION

1.1 Graphene

Carbon is a group fourteen element and it has a unique flexibility in chemical bonding that can produce various molecules and crystals structures. Carbon consists of four valence electrons that lean to cooperate with each other to provide different types of carbon allotropes. Hence, carbon allotropes differ from the zero-dimensional (0D) is fullerenes [1], one dimensional (1D) is carbon nanotubes [2][3][4][5][6][7][8][9], two dimensional (2D) is graphene [10][11] to three dimensional (3D) is graphite and diamond with various material properties. Different carbon allotropes are shown in Figure 1.2.

Graphite comprises stacks of graphene layers which vdW force is weakly bonding. A lead of pencil is a common graphite example. When we produce stacks of graphene on a sheet of paper, which can also incorporate many layers of graphene. The fundamental building block of graphite materials is graphene. Graphene, the arrangement of a single layer of carbon atoms in two-dimensional (2D) honeycomb lattice, has produced considerable interest in the solid state research community since its first experimental show in 2004. Andre Geim and Konstantin Novoselov from the University of Manchester won the 2010 Nobel Prize in Physics for groundbreaking experiments investigating graphene. Graphene's honeycomb lattice structure has been experimentally observed and shown in Figure 1.1.

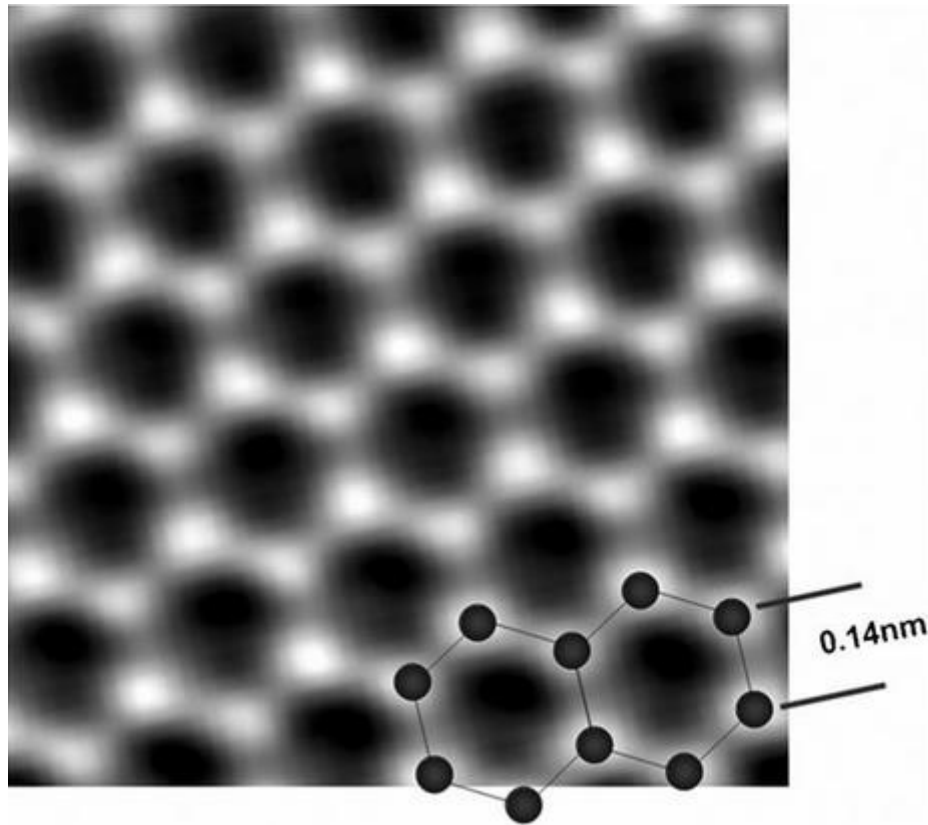


Figure 1.1: Graphene image of transmission electron aberration-corrected microscope (TEAM) showing the carbon atoms and bonds in a honeycomb structure [12].

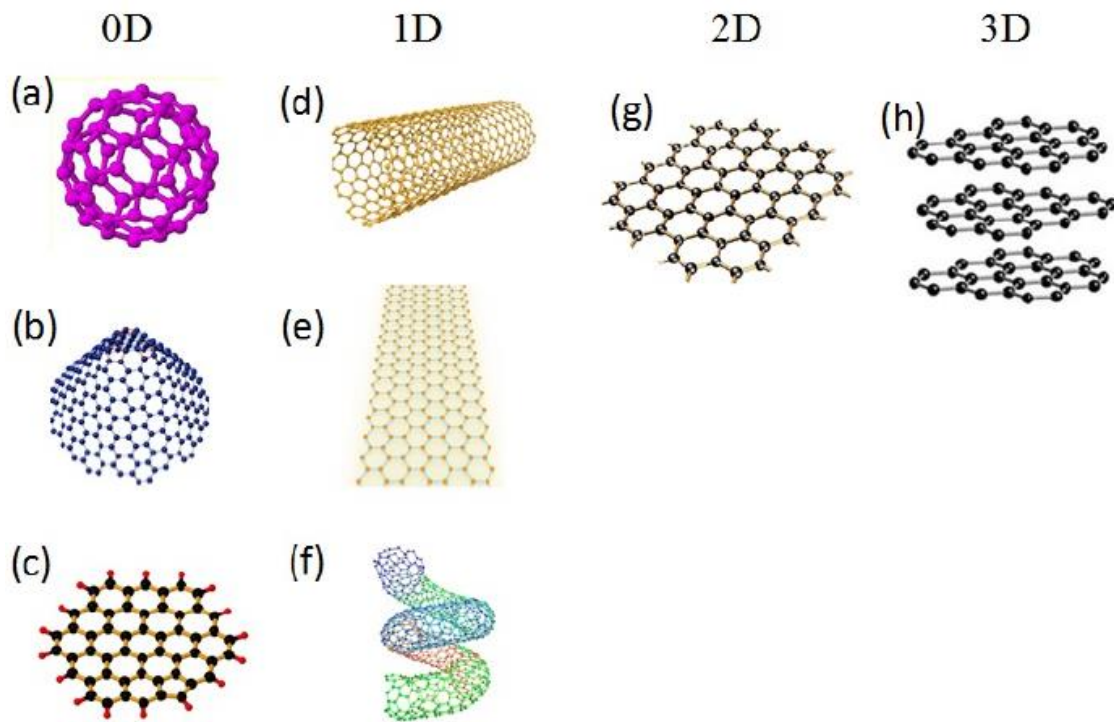


Figure 1.2: Carbon allotropes in different dimensional forms. Fullerene (a) nanocone (nano horn) (b) graphene nanoflake (c) carbon nanotube (d) graphene nanoribbon (e) helicoidal carbon nanotube (f) graphene (g) and graphite (h) [13]

Figure 1.3 shows that zero dimensional (0D) fullerenes are wrapped up the graphene, one dimensional (1D) carbon nanotubes is rolled up the graphene or stacked into three dimensional (3D) graphite. Moreover, graphene can also be made into one dimensional (1D) graphene nanoribbons.

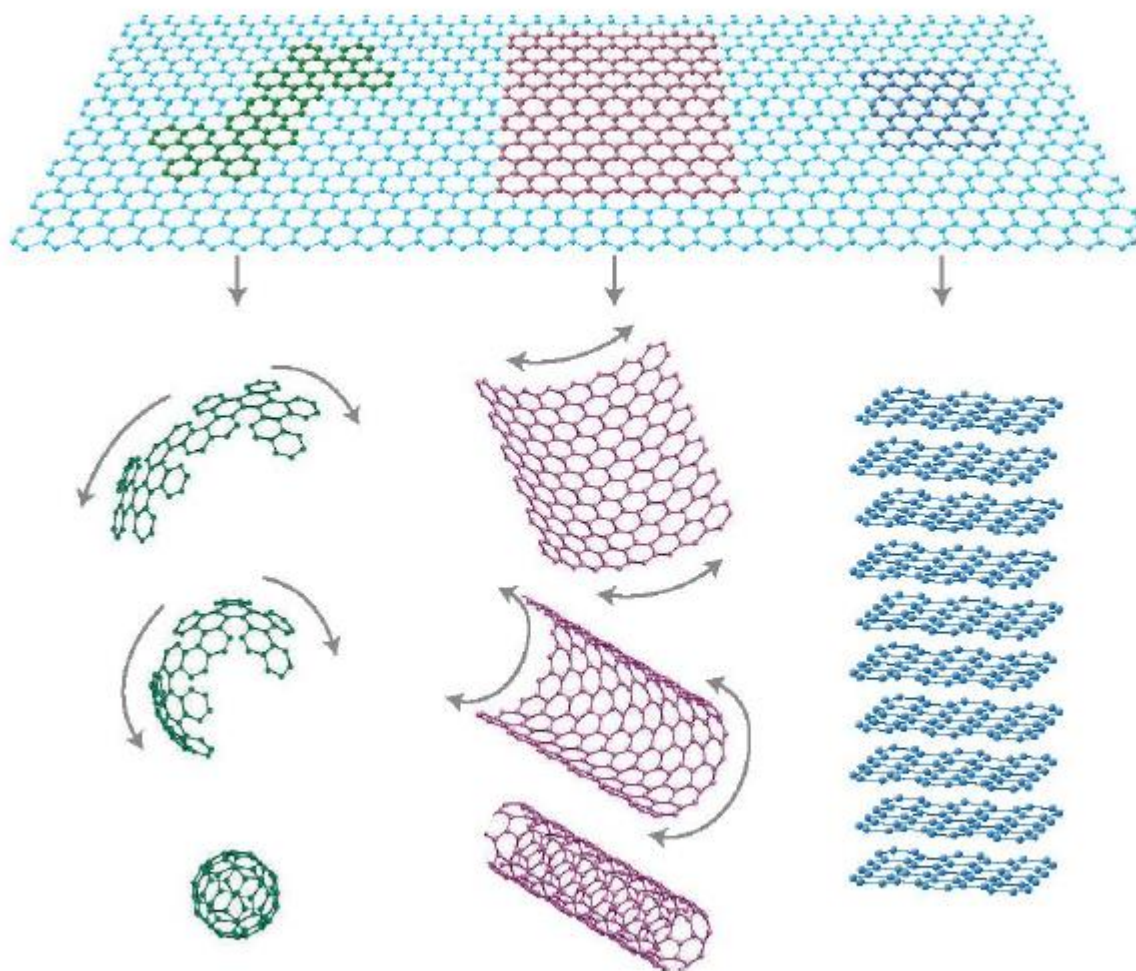


Figure 1.3: Graphene is the basis of the other graphitic carbon allotropes, from left to right: fullerenes (C_{60}), carbon nanotubes, and graphite. [14]

Much work has been conducted to study graphene's electronic properties. In 1947, P.R.Wallace [15] performed band structure calculations using TB approximation for a single layer of graphene, so as to understand the band structure of graphite. From the first-principle approximation approach, he assumed that the interlayer coupling was negligible, thereby indirectly compute the single layer of the graphene band structure. In 2005, two papers appeared that confirmed the existence of

Dirac fermions in a single layer of graphite thus resolving the controversy that had raged for many years. [16][17]. In this thesis, we focus on the theoretical studied of electronic properties with this exciting new material.

1.2 Graphene Arrangement

The direct lattice of graphene: Figure 1.4 shows graphene, a carbon atom honeycomb lattice. The graphene primitive cell is composed of two non-equivalent atoms are A and B. Type A (or B) atoms positions can be generated by using a linear combination of magnitude of a_1 and a_2 , with $|a_1| = |a_2| = a$. For giving

$$\mathbf{A}(n_1, n_2) = n_1 \mathbf{a}_1 + n_2 \mathbf{a}_2, \quad (1.1)$$

$$\mathbf{a}_1 = \left(\frac{\sqrt{3}a}{2}, \frac{a}{2} \right), \mathbf{a}_2 = \left(\frac{\sqrt{3}a}{2}, -\frac{a}{2} \right), \quad (1.2)$$

where n_1 and n_2 are arbitrary integers and $a = 1.42 \text{ \AA}$ is the distance between carbon and carbon.

Each carbon atom (A or B) covalently bonded by its three nearest neighbours and the split between type A(B) and the nearest type B(A) atoms are

$$\mathbf{R}_1 = \left(\frac{a}{\sqrt{3}}, 0 \right), \mathbf{R}_2 = \left(-\frac{a}{2\sqrt{3}}, -\frac{a}{2} \right), \mathbf{R}_3 = \left(-\frac{a}{2\sqrt{3}}, \frac{a}{2} \right), \quad (1.3)$$

With $|\mathbf{R}_1| = |\mathbf{R}_2| = |\mathbf{R}_3| = a_{C-C}$

The reciprocal lattice: Graphene reciprocal lattice also is hexagonal, as shown in Figure 1.4 (b). The reciprocal vectors are provided by

$$\mathbf{b}_1 = \left(\frac{2\pi}{\sqrt{3}a}, \frac{2\pi}{a}\right), \mathbf{b}_2 = \left(\frac{2\pi}{\sqrt{3}a}, \frac{-2\pi}{a}\right), \quad (1.4)$$

with $|\mathbf{b}_1| = |\mathbf{b}_2| = 4\pi / \sqrt{3}a$. The first Brillouin zone is shown in Figure 1.4 by the shaded area and it has length sides $b_{BZ} = |\mathbf{b}_1|/\sqrt{3} = 4\pi / 3a$. The Γ dot is in the central of the Brillouin zone and the magnitudes depicts the position of the another high symmetric dots with respect to the central of the zone are M and k and given by

$$\Gamma_M = \left(\frac{2\pi}{\sqrt{3}a}, 0\right), \Gamma_K = \left(\frac{2\pi}{\sqrt{3}a}, \frac{2\pi}{3a}\right) \quad (1.5)$$

There are three pairs of K- and three pairs of M-points within the Brillouin zone.

In the subsequent section, we will briefly discuss in one-dimensional (1D) graphene, graphene nano-ribbons and zero-dimensional (0D) graphene, graphene nano-flakes.

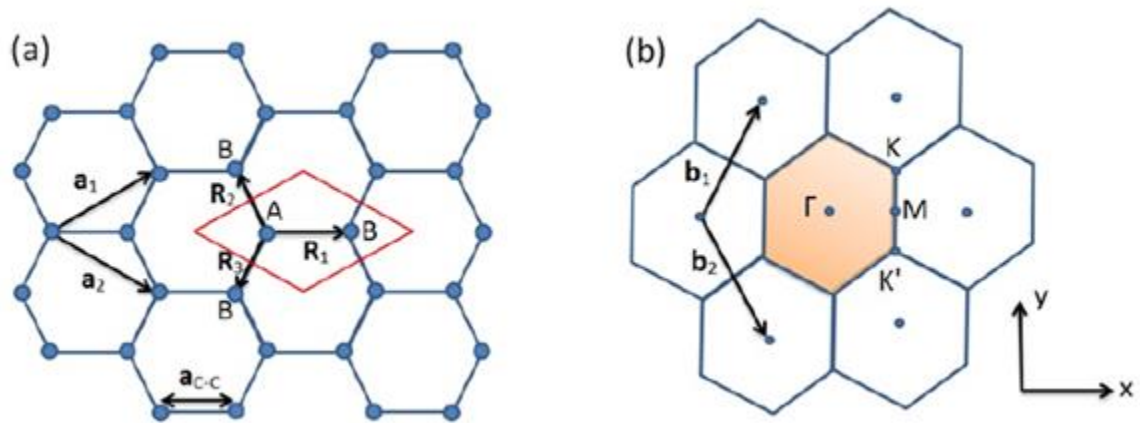


Figure 1.4: (a) The graphene's honeycomb lattice structure. The unit cell contains a pair of carbon atoms denoted as A and B. (b) The first Brillouin Zone is the shadow hexagon with the high

symmetry dots labelled as Γ , M, and K placed at the centre, the core of the lateral and the area of the hexagon, respectively [18].

1.3 Graphene Nanoflakes

Graphene nanoflake (GNF) is a zero dimensional (0D) form of graphene and has excellent potential for different applications, especially as magnetic and electronic devices. The properties can differ from those of two dimensional (2D) and one dimensional (1D) (e.g., nanoribbons) graphene. Small molecular units are fused to make up the bottom-up approach [19][20] while graphene nanoflakes (GNFs) can directly be cut from a large piece of graphene sheet in a top-down method. Large graphene sheets are produced by chemical “unzipping” of carbon nanotubes (CNTs)[21] or micromechanical cleaving of a single graphite crystal [22]. Up to now, there has been little agreement on alternative procedures to make GNFs such as confining a terrain of bulk material by the usage of electrostatic potential. Edges of graphene nanoflakes (GNFs) play a vitally significant part to define electronic and magnetic properties. Additional to edges corners and the effect of defects have a crucial effect that may degrade properties of GNFs but may introduce new properties like magnetism. Because of the finite size of GNFs, defects can control the structure and its properties, depending on their density and size. Recent work on functional groups attached to GNFs has shown that there are new opportunities for technological applications.

It has numerous of graphene nanoflakes material properties has been done with theoretical studied such as electronic properties, magnetic

properties, spin properties and etc. For example, electronic properties of graphene nanodots with the type of edges (AC and ZZ edges) and chemical modifications have been investigated employing DFT [23]. Furthermore, the research extensive from electronic properties to investigate the magnetic properties. The magnetic properties of graphene flakes with arbitrary dimensions have been studied through first principle calculation and has been shown that the net total electron spin of graphene nanoflakes depends strongly on its dimension for the terrain defeat of π bonds [24][25]. To further studied the electron polarization of GNFs has to use Raman spectra. The Raman or infrared spectra can observe vibrational, rotational and other low frequency modes of GNFs, it has lead to understand the GNFs vibrational states [26].

Moreover, the first principle electronic calculations can studied the graphene nanodots in spin properties. From the calculation showed that dot structure can play as fundamental logic gates for high density ultrafast spintronics appliances. It can conduct forecast for those structures will be advantageous in sectors like spintronics, sensors, and transistors [26][26][27].

The theoretical studied has extended to few layer GNFs. Recent developments indicate a renewed interest in few layer GNFs, and they have also been a concern of theoretical and experimental interest. For instance, bilayer GNFs with different band gap in bilayer structures than single layer

GNFs and electrons may cause confinement in potential barriers as opposed to single layer GNFs [28].

The single layer or few layer GNFs has numerous theoretical studied, but still have lack theoretical studied in the fundamental electronic properties. In the thesis, we have focus theoretical studied on the fundamental electronic properties. It can become supportive information in the GNFs application.

1.4 Application of Graphene

Graphene has some excellent physical properties that makes it very appealing for applications, such as room temperature electron mobility $> 1.0 \times 10^5 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ [29], a Young Modulus of 1TPa and intrinsic strength of 130 GPa [30], high thermal conductivity (about $3000 \text{ Wm}^{-1} \text{ K}^{-1}$) [31], optical absorption of precisely $\pi\alpha \approx 2.3\%$ (in the infrared limit, where α is the fine structure constant) [32], complete impermeability to any gases [33], and ability to sustain extremely high densities of electric currents [34]. Graphene may be used for future devices. Moreover, graphene has prospective application for extensive areas, including high speed electronics [35], energy storage [36][37], optical devices [38] and hybrid materials [39].

1.4.1 Energy Storage

At chapter 1.4, we have introduced the graphene material using in energy storage application. Recently there has been renewed attentive in solar cells, as the global energy demand is increasing. The excellent electron

transport, immense carrier strength, and transparency form graphene a prospective candidate for the photovoltaic gadget. Thus small intrinsic optical absorption of graphene, the power conversion efficiency is insufficient for practical purposes [32]. Thus, the gadget would require complex plasmonic improvement configuration to accomplish the desired responsivity. Alternatively, graphene's potential to serve as a translucent electrode in either quantum dots or dye sensitised solar cells has been demonstrated.

A battery is a storage of electrochemical energy and is furnished by the intercalation and deintercalation of lithium ions. In general poor electrical conductivity of the cathode can be overcome by the addition of graphene. Graphene acts as an advanced conductive filler still may give rise to new core shell or sandwich form nanocomposite configuration. The existence of the oxygen containing functional groups increases the interlayer spacing between the graphene sheets to enlarge the accessible exterior for Lithium insertion [40]. Graphene can also remove the significant amount of heat generated by the battery due to its high thermal conductivity.

1.5 The Ab initio Calculation

The ab initio calculation using in the thesis. The Latin word *ab initio* is interpreted as "from scratch". The first principle (*ab initio*) calculation neglect the empirical knowledge except for the physical constant of the

system. Thus, the basic form of an *ab initio* calculation is free parameters and only to include theoretical models, until the quark level.

Until now, this approach has only applied to the form of calculations where they are various types of simplifications and approximations on different levels. Ab initio DFT is the most extensive and widespread approach in solid state physics.

1.6 Computational Physics

Computational physics has implemented the ab initio calculation as a theoretical study to investigate material properties. Materials technologies all but characterise entire eras such as the Stone, Bronze, Iron and Silicon Age. Highly optimised compounds and computer aided development has emerged to understand materials further and shift away from the traditional design of trial and error materials.

Since material properties are related to various scales of length, the range from the tiniest transistor to most extended bridges, computational physics must span many magnitude orders (Figure 1.5). 'Creating' material through computational material design has been hindered by two; First, predicting the most stable material crystal structure is an intricate issue and all other properties are crucially dependent on it. Secondly, the necessity for numerous parameter optimisation means involvement of quantum mechanics and higher computational cost.

A united numerous scale framework developed to serve materials is a major challenge. Various technologies evolution benefit from the work of

materials computational which includes automotive and aerospace, microelectronics, medical applications, hydrogen storage, photovoltaics, batteries and etc.

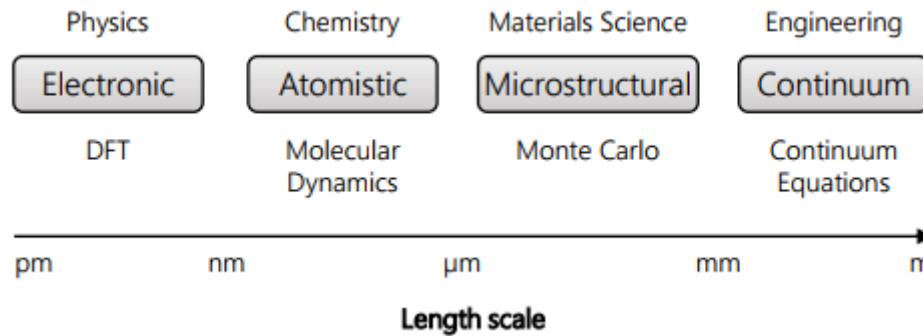


Figure 1.5: Different length scales on materials modelling is affected by computational methods and various scientific disciplines. A novel framework developing for uniting multi-scale modelling remains a challenge.

1.7 Problem Statements

However, there are some theoretical works have been done on the graphene size dependence, there is still unsettling and inconsistency in the results. It is primarily for the insufficient experiment proof on graphene nanoflakes measure dimension structures.

DFT calculations of graphene nanoflakes can be classified into two classifications of formalisms are plane wave basis set and linear combinations of atomic orbitals (LCAO) method. It complies that the former is appropriate for periodical schemes, while the latter is more appropriate for LCAO. Both formalisms were used in the research work to calculate graphene nanoflakes properties. Most of the previous studies of graphene

nanoflakes concentrate on TB approximation. Also, the electronic structure for graphene nanoflakes employing the linear combinations of atomic orbitals (LCAO) method was hardly found in the literature.

1.8 Research Motivation

Among the various unusual physical properties of graphene nanoflakes, present work only concentrate on the fundamental electronic properties of graphene nanoflakes. Graphene nanoflakes (GNFs) are favourable graphene based composites with size controllable, and it can be tailored for various technology applications [28][41][42]. Studies on GNFs have found that they possess unique electronic, optical, and magnetic properties with a tunable bandgap. They can be utilized in solar cells and LED [43]. This thesis aims to explore the fundamental electronic properties of GNFs with various shape and type of layer configuration.

Furthermore, systematic studies of the shape effect and different geometry on the electronic properties of GNFs are rarely reported [44][45]. It leads to a situation whereby the effect of various intrinsic properties of GNFs, like the size, edge termination on the electronic characteristics of this material are still poorly understood. Therefore, it is essential to address these shortcomings to improve the feasibility and viability of GNFs and their use in various scientific and technological applications.

1.9 Aims and Objectives

This thesis aspires to present a comprehensive computational study on GNFs with selective size range employing DFT. The primary objective is to

attain the structural and electronics properties employing DFT, targeting different GNFs shapes and sizes that are rarely reported in the literature. The project aims to employ QE as a cost-effective approach to study GNFs. The research specific objectives are listed as follows.

- I. To evaluate the Fermi energy level in a single layer and bilayer GNFs with various shape (rhombus and trapezium) by employing DFT.
- II. To determine the total energy of single-layer and bilayer graphene for geometry with a different number of atoms and establish a model that can correlate energy and atom numbers.
- III. To model the electronic properties (e.g., the integrated density of states (IDS)) GNFs with different shapes (rhombus and trapezium) and edge configurations (AC and ZZ edges) for single layer and bilayer.

1.10 Outline of the Thesis

The thesis is organised as follows:

CHAPTER 1 is an overview of the project, research problems, and the rationale, objectives, and scope of the project.

Chapter 2 focuses on the literature review for various methods of theoretical studies on graphene and GNFs. This background studies emphasise the graphene electronics properties based on theory and recent studies.

Chapter 3 describes the theoretical background of this research. The computational methodology is fully addressed.

Chapter 4 detailed the methodology of this research. It includes the information about the software used throughout the study, as well as the method utilised to collect, analyse and interpret the data obtained.

Chapter 5 is a result of the discussion. The results obtained is analysed in the respect of total energy and Fermi energy for the graphene flakes with various shapes and the various number of carbon atoms in the geometry.

Chapter 6 is conclusions based on the results obtained and suggestions for future work.

CHAPTER 2 LITERATURE REVIEW

2.1 Background

Graphene layers are the carbon sheets in graphite [46]. Sp^2 (trigonal) hybridization exists in graphite [47], and it has carbon sheets along with chemical bond (covalent and metallic bonding) coexisting in each layer. The stacking layer between carbon sheets known as an AB array, which is distinct from the AB array in a hexagonally closed crystal structure (HCP) is connected with weak vdW interrelation constructed by π delocalized orbital. There are four occupied states which has three Sp^2 orbitals formation σ state and three neighbouring carbon atoms, while the 2p orbital evolve into delocalised π and π^* states that the formation of the valence band (VB) and conduction band (CB). Graphene π and π^* states degraded at the hexagonal Brillouin zone (BZ) corner points (K-points).

Graphite consists single sheet of carbon arrangement in a hexagonal lattice and stacked layer in the AB array. The result was a hexagonal lattice per unit cell having dimensions $a=2.46 \text{ \AA}$ and $c=6.71 \text{ \AA}$. The two pairs of carbon atoms with a unit cell are labelled as A, A', B and B' in Figure 2.1. Figure 2.2 have shown A and B atoms on one sheet plane and A' and B' are on another sheet plane which substitutes by half the c-axis spacing of half crystallographic, i.e., $3.35 \text{ \AA}$.

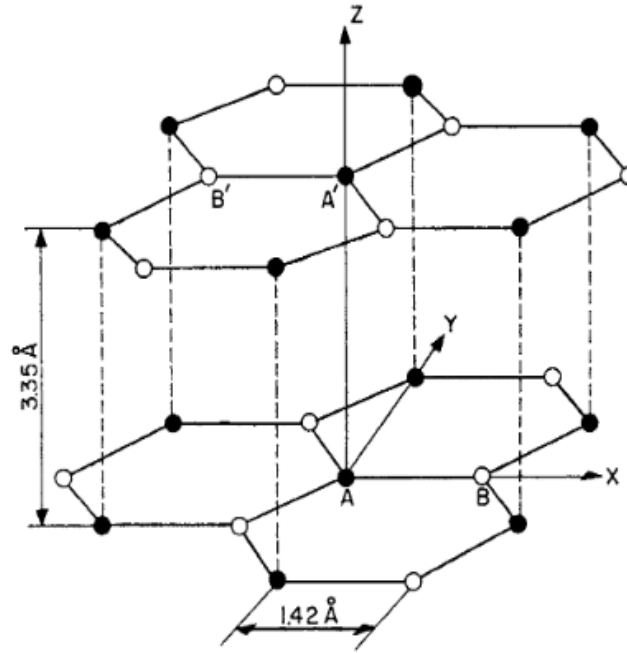


Figure 2.1: Graphite crystal structure. The primary unit cell is having dimensions, $a=2.46 \text{ \AA}$ and $c=6.71 \text{ \AA}$. The in plane bond length is $1.42\text{\AA}$. It has two pairs of carbon atoms in a unit cell, i.e. A, A', B and B'. A and A' atoms shown in right spheres, it has neighbours directly upper and lower in neighbouring sheet planes; atoms B and B', exhibits to make spheres consists neighbours directly upper and lower in sheet planes is $6.71\text{\AA}$. [46]

Figure 2.2 shows the translation vectors of the graphite crystal structure.

$$\vec{a}_1 = a \left(\frac{\sqrt{3}}{2}, -\frac{1}{2}, 0 \right), \quad |\vec{a}_1| = a = 2.46 \text{ \AA}$$

$$\vec{a}_2 = a \left(\frac{\sqrt{3}}{2}, \frac{1}{2}, 0 \right), \quad |\vec{a}_2| = a = 2.46 \text{ \AA}$$

$$\vec{a}_3 = c (0, 0, 1), \quad |\vec{a}_3| = c = 6.71 \text{ \AA}$$

This vector indicated refers to orthonormal coordinates (x, y, and z). It has consist of two types of lattice parameter is interior plane and exterior

plane. The parameter interior plane lattice is $a=\sqrt{3}a_0$, where interior plane nearest neighbour distance is $a=1.42 \text{ \AA}$. The parameter exterior plane lattice is $c=2c_0$, where the gap interval of A and A' atoms on neighbouring layer planes is $c=3.35 \text{ \AA}$. These all values as our ab initio calculation parameter reference.

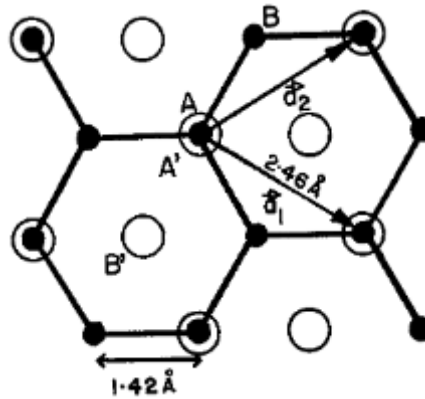


Figure 2.2: Graphite in plane configuration. The sheet plane shows A and B (•) atoms. An atoms of A' and B' (o) positions on the neighbouring sheet plane are also exhibited. The lattice transition variable on a sheet plane are $\vec{a}_1$ and $\vec{a}_2$.

2.2 Single Layer Graphene

A considerable amount of literature on the graphene sheets material properties has been established. The studies include quantum electrodynamics [16], elastic [48], phonon [49], charge [50] and spin transport [51], magnetic [52][53], photonics [54], chemical [55], optoelectronics [56][57], electronic [58][59], mechanical properties[60], thermal [61] and etc. In general, the numerous studies are combinations of experimental work and density functional theory study to focus on

graphene surface electronics properties [62] [63]. Furthermore, graphene surfaces and edges have also been extensively investigated by using TEM. These graphene surface studied are for further understanding and future exploration. Graphene surface studies have concerned the effect of atomic position and atomic bond length parameter. There are several studies have exposed that the atomic position, i.e. the plane gap between adjacent carbon atoms is 1.42 Å [64]. Data from several studies have identified the neighbouring carbon atoms in the plane is 1.42 Å. From the low-dimensional interface study, graphene exhibits complex atomic behaviour at the boundary. The atomic position is one of the ab initio calculation parameters have to be concerned.

2.3 Graphene Nanoflakes (GNFs)

Graphene nanoflakes (GNFs) with finite size can be considered as graphene flakes or molecular subunits [65][66]. As a unique GNF's shape and breadth, the nanoflake shows unusual electronic and magnetic properties. First principle approach (semi-classical) has suggested a method and a standard method that can be proposed to study the electron physics confined in a GNF material. The states close with the distance in the spectrum located between the turning dots is a unique characteristic of classical massless particles. The method used is precise in the system of sizeable angular momentum as well as small radial quantum number [67]. However, this density functional theory approach does not take into account the GNFs electrical properties.

It has shown conclusively that the GNF's electrical properties greatly depend on the flakes shape as well as the structure of the edges. Numerous studies have reported in this context, and most research centred on the commonly encountered geometry such as hexagonal, triangular and spherical [68][69][70]. Also, it has been demonstrated that the topological structure of the edges (ZZ or AC) has crucial effects on the Fermi energy level of the GNF. On top of that, termination at the edges of GNF with a defined active compound such as hydrogen, fluorine, amine functional group (NH_2) is found to be capable of improving the stability of the GNF materials and thus have been widely studied. The below section we discuss various theoretical models of graphene nanoflakes (GNFs) electronics properties. There are numerous of GNFs material properties studies are useful information for GNFs current and future research.

2.3.1 Graphene Nanoflakes Spin Qubits and Charge Qubits

The research reviews the progress of the preparation of GNFs and the operation of spin qubits and charges qubits based on GNFs [71]. Since the graphene material has a relatively light atomic weight resulting in a smaller spin-orbital interaction, and the carbon isotope containing the nuclear spin accounts for only about 1% in the natural world, the ultra-fine interaction (i.e., nuclear spin and electron spin interaction) is weaker, which means graphene has longer spin decoherence time than other materials. Therefore, graphene has promising application in quantum computation and quantum information. The key to the application of spin qubits in the GNFs is the

destruction of valley degeneracy. In the first scenario, the boundary condition is used to destroy valley degeneracy, while in other cases, valley degeneracy destroys by an e.m.f. The spin orbit interrelation effect and hyperfine interrelation on the spin operation introduced in GNFs. GNFs of spin qubit and charge qubit can become a research reference for future study the effect in GNFs shape configuration and layer configuration.

2.3.2 Graphene Nanoflakes Optical Properties

The optical properties are one of the material properties for researchers to studied. From this research, researchers theoretically investigated the changes in the absorption spectra of GNFs in the effected of various gases to demonstrate optical gas sensing feature of GNFs [72]. The gas molecules adsorption like CO₂, N₂, and Ar on GNFs was theoretically studied employing TDDFT calculations. The investigation explored that the UV-Vis absorption spectrum of GNFs undergoes considerable changes in the presence of CO₂ compared to that of N₂ and Ar. In addition to the DOS orbital analyses, the maximum shift of absorption wavelength for CO₂, N₂, and Ar on GNFs was obtained. Comparison with experimental study was made to verify the theoretical result and good agreement between these two is observed. Compares to the electrical property of GNFs, optical properties has been studied and conducted in the gas adsorption process. The tool used in gas adsorption has also paved the way for research in GNFs optical gas sensors. The research has related to GNFs with other chemical passivation focus on

GNFs optical properties. The research have using similar approach with thesis but lack information for fundamental electronic properties study.

2.3.3 Graphene Nanoflakes Electron Transport Properties

Nonequilibrium Green's Function (NEGF) is one of the first principle approach to studied GNFs material properties. Nonequilibrium Green's Function (NEGF) is employed to investigate the influences of phonon scattering on the electron transportation and photocurrent rectangular GNFs with AC edge vary in various breadth. The electron current and photocurrent are first computed to apply the Landauer-Buttiker formalism. The results have shown that electron phonon coupling has three significant influences, first, phonon assisted and resisted influence on the electron transportation and photocurrent, second, increase of band gap in the lack of phonon radiation, and last, increament and reducing of band gap in the existence of phonon radiation. The research used another ab initio calculation different approach from thesis. The research are another explore in different approach and focus on the rectangular GNFs with AC edge electron transport properties. In future, the result can be useful information to study different shape configuration in electron transport properties by using DFT approach.

2.3.4 Graphene Nanoflakes Photoluminescence Properties

The latest material property studied is photoluminescence property. GNFs have also been investigated for its photoluminescence properties. The new photoluminescence system research and development are established for

different technology and engineering applications. Currently, the study is focused on the GNFs dispersion effect in the polyvinyl butyral (PVB) matrix [73]. The GNFs structural and chemical interaction with dispersed PVB composites are studied through with various method such as XRD, FTI, micro-Raman spectroscopy, UV-Vis, and PL. Chemical interaction between the functional groups results in PL quenching at 455 nm. Raman spectroscopy exposed the reduced in strength ratio of D/G affected by GNFs loading wt% in the chemical compound system. The GNFs dispersion and occupied network in the PVB matrix can be verified by using various microscopy devices. The influence of compound electrical conductivity as a temperature function has also been validated. GNFs loading confirms the promising PL properties are prepared the compound system reducing indirect bandgap as a function. Thus, a compound derived from GNFs can be further studied as a membrane for improved PL properties. For future study can include such as other chemical passivation and GNFs layer configuration to investigate the effect in photoluminescence property, it is highly possible to develop a breakthrough study for the technology application.

2.3.5 Fluorinated Graphene Nanoflakes With Luminescent And Paramagnetic Properties

Apart from photoluminescence property, the luminescent and paramagnetic properties are another two material properties in GNFs. The latest technique has been established to composite slightly fluorinated graphene nanoflakes (GNFs-F) via the thermally cut of greatly fluorinated

graphene [74]. The GNFS-F with significant structural deficiency is frangible. For plenty CF_n ($n=2,3$) category direct evaporation closed to the structural deficiency corresponded through the defeat of adjacent Skelton carbon atoms. The fluorinated graphene can be thermal penetrate into GNFS-F by a reasonably consistent nanosize in pyrolysis at 810K. The GNFS-F by a low Fluorinated/Carbon (F/C) atomic ratio of ca. 0.03 has shown excitation wavelength dependent properties by multicolour PL changed from blue to green. Concurrently, F adatoms possibly place at the edges of GNFS-F have great productivity of initiate internal magnetic forces. GNFS-F shows a robust magnetic force due to sp^3 -type deficiency and magnetic ZZ edges. GNFS with multimodal potentials should be of great value in material science. The GNFS-F of luminescent and paramagnetic properties studied in experimental work, the result can use to make a comparison with theoretical work in the future study.

2.3.6 Graphene-Based Nanoflakes $C_{16-x}Si_xH_{10}$ Tuning Optoelectronic Properties

The DFT with MBPT is the combination of first principle calculation. The combination of first principle calculation is the first exist in the GNFS material properties studied. GNFS electronic and optical properties were investigated by employing DFT with MBPT [75]. From pyrene to silicene nanoflakes configurations are vigorously and synthetic stable to show all structures, e.g. formation energy, hardness and electrophilicity. The studied also found to be reactive, which implicit their favourable nature for the feasible conductivity and electronic transportation. The optical and

electronic properties are susceptible to the dimensions and point of the replaced silicon atoms and the magnitude of light polarisation.

Also, quantum containment outcomes produce the CSi graphene nanoflakes exciton binding energy greater than those allotropes. Nanoflake different shapes such as hexagonal GNFs and an UV zone to in view can be customized. The singlet triplet splitting values for the X- and Y-light polarised point out that any structures have an excessive yield of fluorescence quantum contrast to the yield of the conventional semiconductor, which makes them favourable for different application like the LED material and nanomedicine. The combination of the first principle can employ to investigate the effect of various shape GNFs and different layer configuration GNFs in optical and electronic properties for further understanding the GNFs material behaviour.

2.3.7 Triangular and Hexagonal Graphene Nanoflakes

Triangular and hexagonal GNFs structures are the most prominent shapes widely studied [76][77]. Hexagonal and triangular GNFs with AC edges has been investigated by using the TB approach as the initial systematic study [78].

The first principle approach was accomplished to investigate the triangular and hexagonal GNFs for its electrical properties. Dirac equation is solved different boundary conditions and the perpendicular magnetic field of triangular and hexagonal GNFs; the purpose is used to analyse the effect of the dimensions and shape on the energy spectrum. The contrast between

the outcome acquired for graphene dots with ZZ or AC edges, and infinite-mass boundary condition, has shown that the type edges and the choice of boundary conditions have significant influences on the energy spectrum [79].

Moreover, the first principle method has also been utilised to investigate the triangular GNFs electronic properties. It is found that the triangular GNFs with ZZ edge in single particle energy spectrum reveals a shell degraded at the Fermi energy level with degenerate N_{edge} corresponding to the edge dimension. For more significant configurations, the spin depolarisation showed different filling factors would occur. The results were contrasted with the outcome acquired from distinct approximations levels [80]. The lateral size quantisation accessible an energy gap, as well as the broken sublattice symmetry yields of degraded shell states at the Fermi level. The gap closing with the increasing magnetic field is present in all GNFs configurations, regardless of dimension and edge passivation [69]. It has supportive result in the various shape GNFs study. The studied in shape of GNFs structures and edge passivation has related to our research study.

2.3.7.1 Hexagonal Graphene Nanoflakes To Determine Graphene Edge Energy

The different shape GNFs has rapidly developed the various materials properties studied. GNFs are essential for various applications and patterns as well as GNF's shape depending on the boundaries energy [81]. Currently,

numerous approaches have been established for the GNF's preparation by the required borders, dimensions and edge passivation. However, studied on the GNF's properties and their applications are a limitation for these compounds deficiency in pure form. The standard formation enthalpy of the edge is found range within 1 to 6 nm, and an edge carbon atoms enthalpies for AC and ZZ edges are 32.4 and 35.5 kcal mol⁻¹, respectively.

To compare related literature data, the hydrogenated edges standard formation heat content is afar from zero, and the values for AC and ZZ edges are 7.3 and 8.0 kcal mol⁻¹ C, respectively. The hydrogenation for the AC and ZZ edges standard heat content is discovered to be -10.2 and -9.72 eV nm⁻¹, respectively. The research has related to GNFs thermodynamic properties studied, the result showed that the heat content of GNFs with AC and ZZ edges, it is possible to develop thermodynamic properties by using DFT approach in the future.

2.3.7.2 Chemically Functionalized Hexagonal and Triangular Electronic Energy Gap For Graphene Nanoflakes

The chemical functionalized is the edge termination or edge passivation with chemical elements. The research used DFT approach to investigate the total dipole moment and electronic energy gap of chemically functionalised hexagonal and triangular GNFs [82]. It has been found that the energy gap can be efficiently adjusted with various elements or groups in the selected clusters by edge termination. Edge termination with oxygen provides a considerable decrease in the broad energy gap observed in hexagonal GNFs.

The triangular GNFs in edge states and energy gap can also be influenced by fluorine termination. Total dipole moment strongly relies on (i) the graphene quantum dot with dimensions and edge passivation, (ii) group of attached, and (iii) the location to which the chemical groups are attached. Concerning the shape, edge passivation and the group of attached, the chemically modified hexagonal-AC GNFs have the highest total dipole moment. The function relying on the groups of attached, the total dipole can be increment, reduced or removed. The acquired positive binding energy and positive frequencies in the infrared spectra suggest that all the selected clusters are stable under edge functionalisation and passivation with various groups and elements. The research can extend to study the various shape of GNFs in the effect of the total dipole moment and electronic, it can further understanding various shape of GNFs material behaviour. .

2.3.7.3 Triangular Graphene Nanoflakes Electronic and Optical Properties

The researchers investigated the revolution in triangle graphene nanoflakes (TGNFs) electronics and optical properties in response to external strain by employing NEGF formalism combined with DFT calculations [83]. Tunable NDR behaviour was anticipated. External strain can be well tuned to the NDR bias zone, NDR width, and peak to valley ratio. Extensive studied reveals that these distinct properties can be characteristics to the scattering width of the pz orbitals.

In addition, the conductance of TGNFs is very precise to the stress take place, which is favourable for utilisation in nanosensor gadgets. The discovery thus expose the latest method to the production of tunable electronic gadgets depended on GNFs. NEGF formalism combined with DFT calculations is another combination of first principle calculation have been explored. The combination of first principle calculation can become new explore the area for the GNFs material properties study.

2.3.8 Circular Graphene Nanoflakes

Besides the hexagonal and triangular shapes, GNFs with circular structure have affected much interest of study in recent years [84][85][86]. For this system, Dirac-Weyl equation is used to acquire the energy spectrum of circular GNFs and optical absorption in the existence of an e.m.f. The circular GNFs to investigate the energy spectrum and magnetic properties to find out the possible magnetic properties application. The research has excellently explored similar to our study in rhombus and trapezium GNFs.

2.3.8.1 Circular Graphene Nanoflakes Dirac Electrons Properties

Apart from the energy spectrum and magnetic properties of circular GNFs, the circular GNFs extended to studied the Dirac electrons properties to understand the circular GNFs electrons behaviour. Researchers have used a reliable and straightforward finite difference method to solve for the states limited in rotationally symmetric systems by using Dirac equation eigenproblem. The approach sets the boundary condition for the components of the spinor wavefunction at the outer edge of the system

and sweeps the original mesh in search of the energies that meet the boundary conditions inner of flake. The sweep from the edge of the system to the origins allows the applications of a two point finite distinguishing quotient of the first derivative, which prevents the problem of fermion doubling and the aspect of the spurious solutions with rapid wavefunctions oscillations. The boundary condition and the edge passivation has similar material behaviour studied. The GNFs edge passivation can influence the electronics properties behaviour has been discussed in section 5.6; the research has similarly explored with our work.

2.4 Bilayer Graphene

Graphene besides existing in the free condition, though two and more layers configuration can be stacked above each other to become few layers of graphene. For instance, the bilayer graphene (BLG) was found from two sheets has stacked [87]. There are two effective manners to stack two layers. The first is known as AB stacking BLG [88][89] and second is known as AA stacking BLG [90][91]. Supposing of AB stacking BLG, one atom only in the bottom layer lies directly below another atom on the upper layer; the other two atoms are by the hexagon centre in the other layer.

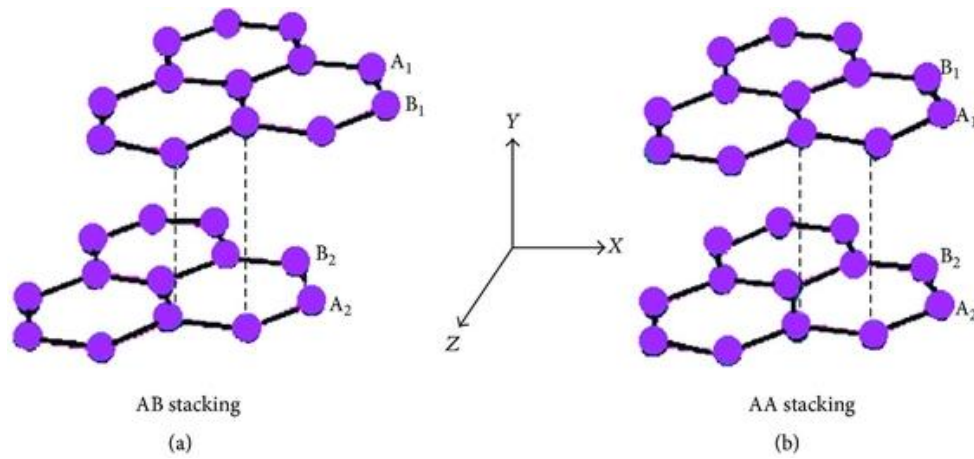


Figure 2.3: Configuration Bilayer graphene: (a) AB stacking and (b) AA stacking

2.4.1 Bilayer Graphene (BLG) Electronic Properties

The BLG has to conduct the study on the electronic properties because still lacking and needs further understanding. The bilayer graphene electronic properties can be analysed using a different theoretical approach. Recently, this view is supported by evaluating bilayer graphene in electronic transmission and conductance via a limitless number of potential barriers. The BLG superlattice with dispersion relation has been evaluated using a periodic possible that place for both layers [92]. For a finite bias, a similar gap also appears. Analytical results on the energy spectrum, conductivity, and the DOS are found to be different compared to single-layer graphene [92]. The electronic properties of bilayer graphene have a small number of study in this area. Our work has involved bilayer GNFs; the research has provided proper analysis as a study reference for our research work to focus on the bilayer GNFs electronic properties.

2.4.2 Electronics Transport and Klein Tunneling Of AA Stacking Bilayer Graphene

The AA stacking layer configuration is one of the bilayer stacking configurations. AA stacking bilayer graphene (AA-BLG) is one of the exciting research for researchers to study. The electronics transport and Klein Tunneling were studied theoretically for AA-BLG enclosed through dielectric substantials [93]. The approach use four bands of continuum models to calculate the probabilities of transmission and reflection through with the corresponding conductances. The results show that the distinct interlayer mass term caused by the dielectric substantials creates a gap in the energy spectrum and pair of the top and bottom Dirac cones in AA-BLG. The cone coupling leads to an asymmetric inter cone transport to the average frequency in the existence of the asymmetric mass term. The AA-BLG gapped energy spectrum has shown electron hole asymmetry that reflected the correlation between intra-cone and inter-cone transport. The results also showed that although Klein tunnelling occurs in gated and biased AA-BLG, interlayer mass term distinct prevents it, and preferably Fabry-Perot resonance appears. The AA-BLG have explored on the electronics transport and Klein tunneling properties, but the AA-BLG did not extend study in the other material properties. The various material properties behaviour of AA-BLGNFs can extend the study in the future.

2.4.3 Magnetic Properties Of AA Stacking Bilayer Graphene Nanoflakes

Besides electronics transport and Klein tunneling of AA-BLG, the magnetic properties of AA-BLGNFs have been aware by the researchers. The researchers also have an interest in exploring the AA stacking bilayer GNFs of the ground state for its magnetic properties [94]. The researchers studied AA stacking bilayer GNFs ground state magnetic properties. The primary model used was the single orbital TB Hamiltonian that was additive by a mean field Hubbard term. DFT approach has been an accomplishment to attain in the discovery. The computational executes for some random and triangular shape of AA stacking bilayer GNFs continually produce an antiferromagnetic direct with a total spin $S=0$ ground state. Even though the calculation results of the Hubbard model is estimable appropriate with Lieb's theorem, predominant crystallographic sublattices were unappropriated to describe calculation results. The result has shown some characteristics including polarisation of local magnetisation, ferromagnetic and antiferromagnetic coupling of vacancies, degeneracies energy spectrum in the system. The magnetic properties of AA-BLGNFs studied have used the DFT approach is similar to our work. For the future study can further explore the various shape of AA and AB layer configuration GNFs with different material properties behaviour such as optical properties, paramagnetic properties, etc.

CHAPTER 3 THEORETICAL BACKGROUND

3.1 Introduction

Even though quantum mechanics furnishes an excellent structure for the non-relativistic interpretation of atoms in a substance, it can solve only a few simple systems, such as hydrogen atom or harmonic oscillator. The mass of realistic techniques escape precise quantum mechanics analysis.

In an ab initio calculation, no experimental variables are required to calculate the electronic configuration properties to a system except for an atomic type, numbers of atoms and their positions. Any theoretical work is considered ab initio if it starts from an established principle directly without any other assumptions based on an empirical model. Ab initio method generally will adopt a reasonable theoretical framework (e.g. quantum mechanics) and is integrated into efficient computer programs to compute the molecules and solid structures for their physical properties. The increase in computer power over past decades has enabled ab initio calculations to be performed on sizeable as well as more realistic techniques, accomplish a scale of accuracy that allows direct comparison with experiments. An ab initio approach that is followed exclusively in this thesis is known as Density Functional Theory (DFT)

This chapter aims to provide a short overview of the Density Functional Theory (DFT).

3.1.1 Hamiltonian

The last century has seen significant efforts to the Schrodinger equation in extensive systems. At the atomistic level, a material system is made up a volume of point-like atomic nuclei and electrons as well as subject to the interaction of Coulomb. An approach is non-relativistic with no external electrical or magnetic fields and the system's total electrical charge is zero. The essential Hamiltonian element consists of potential and kinetic energy, which can be expressed as follows:

$$\hat{H} = \hat{T}_N + \hat{T}_e + \hat{V}_{eN} + \hat{V}_{ee} + \hat{V}_{NN} \quad (1)$$

The starting two terms of that sum act as K.E operants $\hat{T}$ for the nuclei (N) as well as an electron (e), when the final three expressions are potential operators $\hat{V}$ for interaction between different combinations of particle types.

Let Z_i represent the charge and M_i is the nucleus i mass, then let the R_i and r_j be the nucleus i and electron j position, respectively. Subsequently, Hamiltonian components can be expressed as:

$$\hat{T}_N = -\frac{1}{2} \sum_i \frac{1}{M_i} \nabla_{R_i}^2 \quad (2)$$

$$\hat{T}_e = -\frac{1}{2} \sum_i \nabla_{r_i}^2 \quad (3)$$

$$\hat{V}_{eN} = - \sum_{i,j} \frac{Z_i}{|R_i - r_j|} \quad (4)$$

$$\hat{V}_{ee} = + \frac{1}{2} \sum_{i \neq j} \frac{1}{|r_i - r_j|} \quad (5)$$

$$\widehat{V}_{NN} = + \frac{1}{2} \sum_{i \neq j} \frac{Z_i Z_j}{|R_i - R_j|} \quad (6)$$

The position of the nuclei $\{R_1 \dots R_M\}$ and M entity the nuclei total number, are added as variables to system characteristics. In specific, the total energy $E_{\text{tot}}(R_1 \dots R_M)$ can be defined with the similar method as well. Likewise, all other system characteristics are rely on the atomic positions. Following first approximation the solid in Hamiltonian can be written as:

$$\hat{H} = -\frac{1}{2} \sum_i \nabla_{r_i}^2 - \sum_{i,j} \frac{Z_i}{|R_i - r_j|} + \frac{1}{2} \sum_{i \neq j} \frac{1}{|r_i - r_j|} \quad (7)$$

$$i \frac{\partial}{\partial t} \Psi(\{r_i\}, t) = \hat{H} \Psi(\{r_i\}, t) \quad (8)$$

where $\{r_i\}$ is a dimensional coordinates shorthand symbol $r_1 \dots r_m$ of the system of all m electrons. Let the wavefunction be defined as

$$\Psi(\{r_i\}, t) = \Psi(\{r_i\}, t) e^{-iEt} \quad (9)$$

The issue is further decreased with the following time-independent Schrodinger equation:

$$\left(-\frac{1}{2} \sum_i \nabla_{r_i}^2 - \sum_{i,j} \frac{Z_i}{|R_i - r_j|} + \frac{1}{2} \sum_{i \neq j} \frac{1}{|r_i - r_j|} \right) \Psi(\{r_i\}) = E \Psi(\{r_i\}) \quad (10)$$

The many-body wavefunction $\Psi(\{r_i\})$ is a intricate, scale function within multidimensional structure that is extremely hard to compute generally. Hamiltonian act as operant correlate along with the system total energy in the calculation. The limitations of the study is to include over a thousand many-body wave function.

3.1.2 Born-Oppenheimer Approximation (BO)

Born-Oppenheimer approximation (BO) interpreted the many-body Schrodinger equation and it disparages nuclear and movement. This estimation induces two wave equations. An initial equation depicts the electronic movement, which can be determined independently by further estimation to calculate the electronic wavefunction as well as ground state energy. The second equation describes the nuclei's movement. The last outcome is the interpreted Hamiltonian Born-Oppenheimer as depicted in equation (11):

$$\hat{H} = -\frac{\hbar^2}{2m} \sum_i \nabla_i^2 + \frac{1}{2} \sum_{i \neq j} \frac{e^2}{4\pi\epsilon_0 |r_i - r_j|} - \sum_{i,I} \frac{Z_i e^2}{4\pi\epsilon_0 |r_i - R_I|} + \frac{1}{2} \sum_{I \neq J} \frac{Z_I Z_J e^2}{4\pi\epsilon_0 |R_I - R_J|} \quad (11)$$

Born-Oppenheimer Hamiltonian in atomic units with $\hbar = m_e = e = 4\pi\epsilon_0 = 1$ written as:

$$\hat{H} = -\frac{1}{2} \sum_i \nabla_i^2 + \frac{1}{2} \sum_{i \neq j} \frac{1}{|r_i - r_j|} - \sum_{i,I} \frac{Z_i}{|r_i - R_I|} + \frac{1}{2} \sum_{I \neq J} \frac{Z_I Z_J}{|R_I - R_J|} \quad (12)$$

3.1.3 Density Functional Theory

Density Functional Theory (DFT) is among the several different methods that can be used to interpret the Schrodinger equation (others include the HF approach, Moller-Plesset perturbation theory, as well as coupled cluster method). The various approaches share one standard characteristic that depends on the many-body wavefunction is a centre volume. A wavefunction is a complex number and it depends on 3N spatial and the spin variant, where N is the number of electrons in the scheme. These critically restrict the scheme that uses wavefunction depends on the

approach. Specific scheme for hundreds of atoms and large basis sets is apart from the extension for empirical research.

The central DFT idea is to find atomic scheme energy as ground state energy. DFT calculates the energy of ground state of a material scheme, which occurs when the electron of the atoms are in their lowest energy states. Kohn, Hohenberg, and Sham [95] show that the ground state could be discovered by minimising the functional energy, which can be accomplished by finding a self consistent solution to a set of single molecule equations known as the Kohn-Shan (KS) equation.

DFT vary from the wavefunction form on approach since it uses the electron density $\rho(r)$ is the central number. The dominance of employing the electron density by wavefunction is the substantial decreased dimensionality. This allows DFT to be implemented to the substantial huge scheme, hundreds of atoms become feasible.

3.1.3.1 Hohenberg-Kohn Theorem

The latest DFT was constitutional in 1964, which was initiated by Hohenberg and Kohn [96].

The first part is proved merely and exquisitely using the reductio ad absurdum principle and derived to the non-degenerate system. Consider the case where electrons are enclosed in a case affected by an external potential $v(r)$, this system's electron density shall be characterised by $v(r)$. If a spare external potential, $v(r)'$ that varies from $v(r)$ by way of a consistent yielding the identical electron density, $\rho(r)$ for the ground state,

we will consist of a pair of distinct Hamiltonians, H and H' with the same ground state electron density but with distinct normalised wavefunction, ϕ as well as ϕ' . The following equation is:

$$E_0 < [\phi' | H | \phi'] = [\phi' | H' | \phi'] + [\phi' | H - H' | \phi'] = E'_0 + \int \rho(r) [v(r) - v(r)'] dr \quad (13)$$

where E_0 as well as E'_0 as ground state energy for H and H' , respectively. E'_0 is,

By summing up the equation (15) and (16), we will obtain

$$E_0 + E'_0 < E'_0 + E_0 \quad (14)$$

Thence, there did not have a pair of distinct external potentials which can allow identical $\rho(r)$. Therefore, $\rho(r)$ is particular determined $V(r)$ with any ground state properties. The energy, E is peculiar is a use of the electron density, $\rho(r)$ is,

$$E[\rho] = T[\rho] + T_{ne}[\rho] + V_{ee}[\rho] = \int \rho(r) v(r) dr + F_{HK}[\rho] \quad (15)$$

$$\text{where} \quad F_{HK}[\rho] = T[\rho] + V_{ee}[\rho] \quad (16)$$

Note here that $F_{HK}[\rho]$ only depends on ρ as well as individual of all external potential $v(r)$. Therefore, $F_{HK}[\rho]$ is a general function of ρ .

The second HK principle shows that the energy of the ground state can be acquired by variation, which diminish the total energy by the exact density of ground state. It can be written as:

$$E_0[\rho_0] \leq E_v[\rho] \quad (17)$$

where $E_v[\rho]$ is the functional energy in equation (18). From the theorem first part, assume that the ground state wavefunction is φ , associated with the electron density is ρ , then ρ solely defines the external potential, $v(r)$. If there is a spare wavefunction, ϕ' different from φ as well as the electron density, ρ' , then it can be derived,

$$[\phi'|\mathbf{H}|\phi'] = \int \rho(r) v(r) dr + F_{HK}[\rho'] = E[\rho'] \geq E[\rho] \quad (18)$$

Thus, an electron density act as the ground state of the electron density when the energy will reach minimal only.

3.1.3.2 Kohn-Sham Theorem

From HK theorem, the ground state energy via minimising the functional energy,

$$E[\rho] = \int \rho(r)v(r)dr + F_{HK}(\rho(r)) \quad (19)$$

While the HK principle provides validation in a theorem that the total energy could be acquired from the density of ground state, it is not yet familiar where to acquire the $\rho(r)$ or $F_{HK}(\rho(r))$.

A one-electron Schrodinger-like equation is the central equation and can be given as:

$$\left(-\frac{1}{2}\nabla^2 + v(r) + \int \frac{\rho(r')}{|r-r'|} dr' + v_{xc}(r)\right)\phi_i = \varepsilon\phi_i \quad (20)$$

KS orbitals are ϕ as well as electron density written as,

$$P(r) = \sum_i^N |\phi_i|^2 \quad (21)$$

Left side equation (20) terms are the noninteracting reference system K.E, the external potential, potential exchange correlation, as well as the Hartree potential, respectively. The ε as KS orbital energy. Also, the potential exchange correlation expressed as,

$$v_{xc}(r) = \frac{\delta E_{xc}[\rho]}{\delta \rho(r)} \quad (22)$$

Exchange-correlation functional is the $E_{xc}[\rho]$. An effective potential (v_{eff}) is,

$$v_{eff} = v(r) + \int \frac{\rho(r')}{|r-r'|} dr' + v_{xc}(r) \quad (23)$$

Rewrite the equation,

$$\left(-\frac{1}{2}\nabla^2 + v_{eff}\right)\phi_i = \varepsilon\phi_i \quad (24)$$

It is an HF-like single molecule equation that must be determined iteratively. Lastly, the resulting density via the total energy to determined

$$E = \sum_i^N \epsilon_i - \frac{1}{2} \int \int \frac{\rho(\mathbf{r})\rho(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} d\mathbf{r} d\mathbf{r}' + E_{xc}[\rho] - \int v_{xc}(\mathbf{r})\rho(\mathbf{r})d\mathbf{r} \quad (25)$$

The v_{eff} depend on $\rho(\mathbf{r})$ via equation (23). The KS equation need be interpreted with self consistent. First, the common approach is to set an initiative approximate of the electron density, build the v_{eff} from the equation (23), as well as next to obtains the orbitals of the KS. The novel density is acquired from equation (21) based on these orbitals, and the system is repeated until convergence is accomplished. Last, the total energy and the final electron density are calculated from the equation (25). Assuming that each expression is known in the functional energy of the KS, we can acquire the exact density of ground state and total energy. Regrettably, there is an anonymous expression, the functional (E_{xc}) of exchange-correlation (xc). E_{xc} comprises the non-classic components of the electron-electron interaction and the real system's K.E and differs from the fictional non-interacting technique. Because E_{xc} is anonymous, it needs to be estimated, which is the focal point of the subsequent section.

The electronic density operates within the KS method allows for a remarkable decrement in the computational requirements involved in quantum calculations. Besides, the KS procedure paved the path for the study of the system that unable to study for the primary ab-initio method (using wave function as an essential variable).

3.1.4 Exchange Correlation Functionals

The success of density functional theory (DFT) has been nurtured by the last decades by the rapidly advancing computational capability and evolution exact exchange correlation functional. An initial fundamental approximation is a Born Oppenheimer approximation in solid state Hamiltonian and the second approximation is exchange-correlation energy functional within DFT.

E_{xc} actually can be determined by using the LDA. It is a simple approximation and written as:

$$E^{xc-LDA}[\rho(r)] = \int \rho(r) \epsilon^{xc-unif}(\rho(r)) d(r) \quad (26)$$

$\epsilon^{xc-unif}$ as homogeneous electron ($\rho(r)$) exchange-correlation energy per particle as well as is appropriated to be identical density as well as constant for electron gas.

$$E_{xc}^{LDA}[n(r,\sigma)] = \int dr n(r,\sigma) \epsilon_{xc}^{hom}(n(r,\sigma)) \quad (27)$$

3.1.5 Local Density Approximation (LDA)

The Local Density Approximation (LDA) already established by Kohn and Sham in [97], estimates the xc-energy density and the xc-energy density of homogeneous electron gas, i.e.

$$E_{xc}^{LDA}[n(r)] = \int dr n(r) \epsilon_{xc}^{hom}(r, [n(r)]) \quad (28)$$

The exchange expression for $\epsilon_{xc}^{hom}(r, [n(r)])$ is accurately known, while the part of the relation is fitted to exact quantum Monte-Carlo simulations.

There are certain parameterization general being the Perdew-Wang [98] and the Perdew-Zunger [99]. Although its accessibility, but broadly utilized particularly in the solid state community.

3.1.6 Generalised Gradient Approximation (GGA)

GGA adds dependence on the LDA

$$E_{xc}^{GGA} = \int dr \epsilon_{xc}^{GGA}(n(r), |\nabla n(r)|) \equiv \int dr \epsilon_{xc}^{unif}(n(r)) F_{xc}(n(r), |\nabla n(r)|) \quad (29)$$

It makes the semi-local functional. Different GGA usually differ in F_{xc} exchange part as well as certain of them have been evolved. GGA functionals are nowadays an usual applied functionals. The standard versions are B88 [100], PW91 [101] as well as PBE [102]. PBE revised versions are widely used, like revPBE [103] and RPBE [104], which are fitted to the database.

3.1.7 Van der Waals (vdW-DF)

Usually, the broadly utilised local and semi-local functionals present an exact depicts of the covalent and ionic chemical bonds. Although, they decline to replicate non local scatter forces, especially vdW interrelation, which are credible to perform a vital character in the case of graphene. VdW-DF [105][106] was developed to an explanation for the vdW interrelation via a non local interaction expression; The functionals take the form

$$E_{xc}^{vdw-DF} = E_x^{revPBE} + E_c^{LDA} + E_c^{nl} \quad (30)$$

Where the revPBE exchange energy is E_x^{vdw-DF} , LDA correlation energy is E_c^{LDA} as well as non local correction is E_c^{nl} and expressed by

$$E_c^{nl} = \frac{1}{2} \int \int n(r_1) n(r_2) \phi(q_1, q_2, r_{12}) dr_1 dr_2 \quad (31)$$

Where $r_{12} = |r_1 - r_2|$ and q_1 and q_2 are values of a universal function $q_0(n(r), |\nabla n(r)|)$. Equation (31) is evaluated efficiently for separate the combination kernel ϕ as well as employing FFT to calculate the potential of self consistent is presented in the reference [107].

3.1.8 Self Consistent Cycle

This method is known as a self consistent field cycle (SCF cycle). It begins by initiate an input density, which is generally an atomic density superposition system.

It can be done by employing the output density as the novel input density,

$$n_{i+1}^{in} = n_i^{in} + \alpha(n_i^{out} - n_i^{in}) \quad (32)$$

where i is the iteration index and where $0 \leq \alpha \leq 1$ is the mixing factor. However, much often such a simple linear scheme is inefficient for good convergence.

In the original approach, it is impractical to figure out the exact self-consistent density with numerical approach. The density distance d_n is,

$$D_n = \frac{1}{\Omega_{cell}} \int_{\Omega_{cell}} d\mathbf{r} (n^{out}(r) - n^{in}(r))^2 \leq d_n^{conv} \quad (33)$$

Where actual vacuum unit cell volume is the Ω_{cell} as well as union achieved when the density distance at the end of self consistent iterative is smaller than d_n^{conv} .

DFT calculation involves guessing the ground state density in the beginning step, and post-DFT is done to find the material physical properties like optical, mechanical, or electronic properties. Post-processing a converged density lead to an equate converged excellent value in each case.

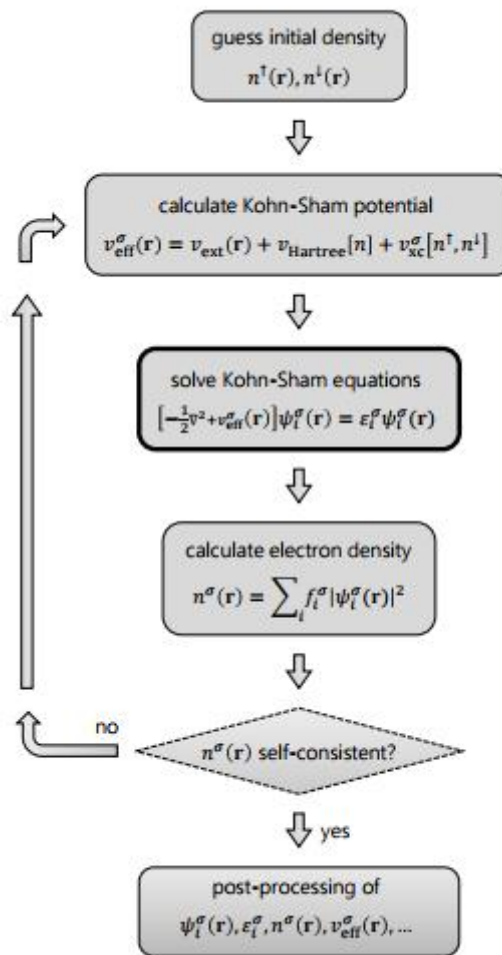


Figure 3.1: The diagram method in an iteration, Kohn- Sham equations self-consistent solution

3.1.9 Total Energy

The total energy is calculated with appropriate functional of exchange-correlation using DFT [96][97]. In the meantime, the exchange correlation energies are evaluated according to the function developed by Hedin and Lundqvist [108].

To express the total energy:

$$E_{\text{total}} = E_{\text{c-c}} + E_{\text{kin}} + E_{\text{e-c}} + E_{\text{e-e}} \quad (34)$$

Accordingly, the KS equation is

$$\left[-\frac{\hbar^2 \nabla^2}{2m} + V_{\text{ion}}(\mathbf{r}) + V_{\text{H}}(\mathbf{r}) + \mu_{\text{xc}}(\mathbf{r}) \right] \psi_i(\mathbf{r}) = \epsilon_i \psi_i(\mathbf{r}) \quad (35)$$

V_{ion} as a total of the ion pseudopotential and V_{H} as Hartree potential for the valence charge density. The KS equation is solved self-consistently.

The charge density, $\rho(\mathbf{r})$ can determine with,

$$\rho(\mathbf{r}) = e \sum_{\epsilon_i < E_F} |\psi_i(\mathbf{r})|^2 \quad (36)$$

$\mu_{\text{xc}}(\mathbf{r})$ as charge density of exchange-correlation potential.

Total of the electron-core, electron-electron interaction energies,

$$E_{\text{kin}} + E_{\text{e-c}} + E_{\text{e-e}} = \sum_{\epsilon_i < E_F} \epsilon_i - \frac{1}{2} \int V_{\text{H}}(\mathbf{r}) P(\mathbf{r}) d\mathbf{r} - \int \mu_{\text{ex}}(\mathbf{r}) P(\mathbf{r}) d\mathbf{r} + \int \epsilon_{\text{xc}}(\mathbf{r}) P(\mathbf{r}) d\mathbf{r} \quad (37)$$

$\int \epsilon_{\text{xc}}(\mathbf{r}) P(\mathbf{r}) d\mathbf{r}$ as an exchange-correlation energy.

3.1.10 Pseudopotentials

As with wavefunction methods, issues like basic sets need to be considered while it arises to the DFT empirical utilisation. In a condensed matter or solid calculations, that will be the type of scheme used by DFT, plane wave basis set is a popular option.

There are generally a pair of initial determinations of the pseudopotential usage. Primary, a weak pseudopotential is used to substitute the potential nucleus core. Secondly is to remove the valence electron wavefunction rapid oscillations in the central part. Figure 3.2 shown that the pseudopotential is weaker than the all electron potential as well as pseudo wavefunction without radial node within the central part. It is required that the pseudopotential and wavefunction coincides with the corresponding all electron system outside the core region.

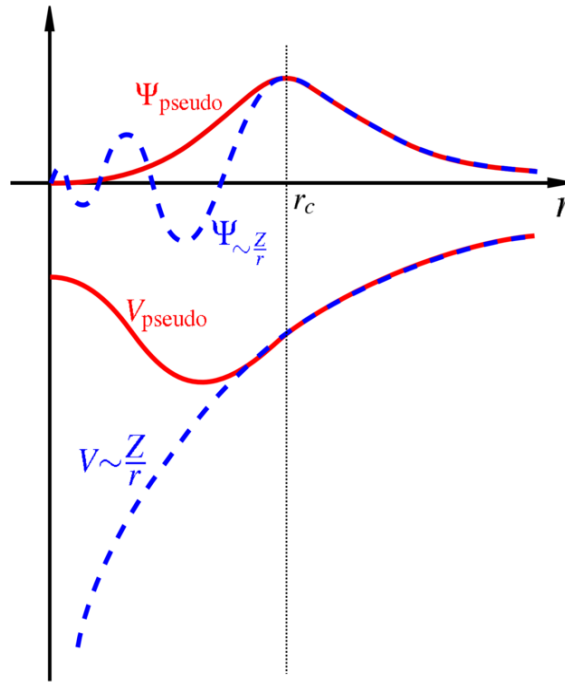


Figure 3.2: Illustrative figure of all electron (blue contours) and pseudopotential (red contours) functions as well as interrelated wavefunctions. The minimal radius at that the values of all-electron, as well as pseudo electron, correspond to r_c [109].

The most usual form of a pseudopotential can be expressed as,

$$V_{ps} = \sum_{lm} |Y_{lm}\rangle V_l(r) \langle Y_{lm}| \quad (38)$$

where Y_{lm} is the spherical harmonics.

An essential class of pseudopotentials is known as the norm conserving pseudopotential. Norm conserving pseudopotentials desire that the all electron and pseudo wavefunction coincide beyond the radius r_c selected as well as combination density within r_c is similar for all electron and pseudo wavefunction ("norm conservation"). Numerous types of norm conserving

pseudopotentials in the ab-initio calculation from distinct authors like Troullier and Martins [110], Kerker [111], Hamann [112], Schluter and Chiang [113], and Vanderbilt [113].

3.2 Plane Wave Basis Sets

DFT calculation involving periodical boundary conditions, plane wave basis sets is employed. Due to the system, Bloch's Theorem [114] is adopted to an extensive number of electronic wavefunctions to a finite number of electronic wave functions. For a periodical crystalline, the potential can thus be expressed as

$$\mathbf{V}(\mathbf{r} + n\mathbf{a}) = \mathbf{V}(\mathbf{r}) \quad (39)$$

Where the lattice vector is $\mathbf{a}$, and an integer is n . Equation (40) the wave function in terms of Bloch's theorem can be expressed as a product of the plane wave $e^{i\mathbf{k}\cdot\mathbf{r}}$ as well as $g_i(\mathbf{r})$

$$\psi_i = e^{i\mathbf{k}\cdot\mathbf{r}} g_i(\mathbf{r}) \quad (40)$$

The $g_i(\mathbf{r})$ the function consists of the identical periodicity as the external potential, $V(\mathbf{r})$ can be written as a Fourier expansion of the plane wave whose variables are reciprocal lattice vectors.

$$g_i(\mathbf{r}) = \sum_{\mathbf{G}} c_{i,(\mathbf{k}+\mathbf{G})} e^{i\mathbf{G}\cdot\mathbf{r}} \quad (41)$$

Where reciprocal lattice vector is the $\mathbf{G}$. Hence, electron wavefunction can be rewritten as a total of all plane waves

$$\psi_i = \sum_{\mathbf{G}} c_{i,(\mathbf{k}+\mathbf{G})} e^{i(\mathbf{k}+\mathbf{G}) \cdot \mathbf{r}} \quad (42)$$

The Fourier coefficient of the plane wave $c_{i,(\mathbf{k}+\mathbf{G})}$ depends on the K.E cut-off. This K.E determines the electronic wave functions expansion in equation (41) that will enable the KS wave functions to be represented in a reciprocal space. The KS wave functions expressed in a plane wave basis are written as

$$\sum_{\mathbf{G}} \left[\frac{\hbar^2}{2m} |\mathbf{k} + \mathbf{G}|^2 \delta_{\mathbf{G},\mathbf{G}'} + \mathbf{V}^{\text{eff}}(\mathbf{G} - \mathbf{G}') \right] c_{i,(\mathbf{k}+\mathbf{G})} = \epsilon_i c_{i,(\mathbf{k}+\mathbf{G})} \quad (43)$$

Where $\delta_{\mathbf{G},\mathbf{G}'}$ is the Kronecker delta indicating that the K.E is diagonal, and all potentials are expressed as a function $\mathbf{V}^{\text{eff}}(\mathbf{G} - \mathbf{G}')$; $\epsilon_{i,j}$ are electronic energies. To solve equation (44) in theory, the plane-wave number must be infinite because of the sum over lattice vector $\mathbf{G}'$. However, the Fourier coefficients $c_{i,(\mathbf{k}+\mathbf{G})}$ for slight K.E are further significant than those with huge K.E.

$$\frac{\hbar^2}{2m} |\mathbf{k} + \mathbf{G}|^2 \leq E_{\text{cut}} \quad (44)$$

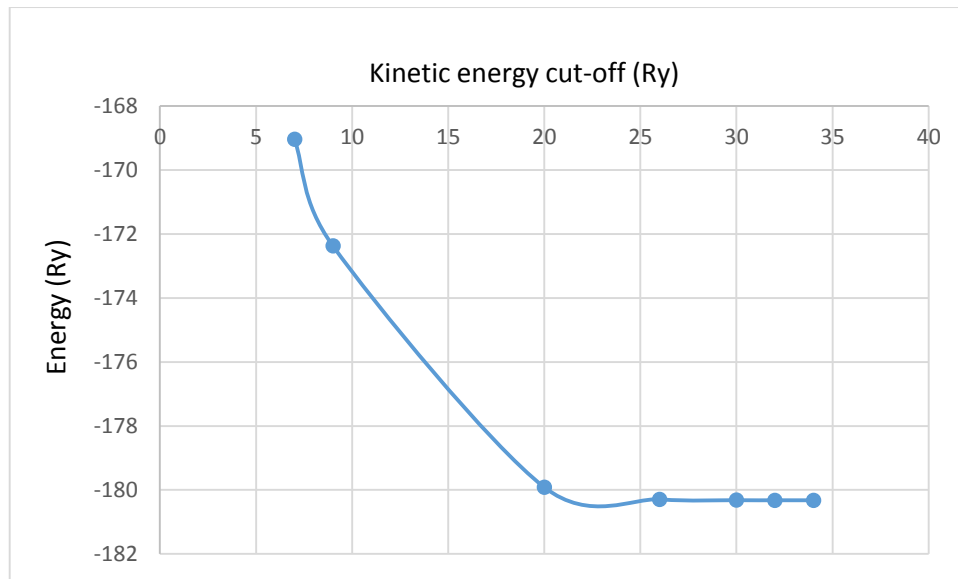


Figure 3.3: The total energy convergence test is a K.E cut off function for 16 atoms hexagonal shape single layer GNFs with AC edge.

Figure 3.3 shows the typical convergent behaviour of total energy as a function of K.E cut-off expressed in Rydberg (Ry). It shows that an error for computing the system total energy can be minimised as the K.E cut-off increases.

3.3 K-points Sampling

The Bloch's theorem outlined in the previous subsection narrative for the expansion of the finite number of wavefunction according to the discrete set of plane waves. However, the expression becomes complicated if the number of the electrons approaches the Avogadro's value order. The reason being that the infinite number of electrons in the scheme means the k-points infinite amount is needed, but in practice the computer can accommodate only finite numbers of k-points.

For minimise the k-points assumed that the electronic wavefunctions nearest to any alternative are same. It will ensure that the wavefunctions be fully interpreted within the part of the reciprocal lattice space at a k-point. Monkhorst and Pack introduced an efficient method in 1976 for k-points sampling at the vicinity of reciprocal space [115].

The chosen set of k-points should sufficiently minimise the error in calculating electric potential and electronic density of a system. In this thesis, k-meshes have been adopted sufficiently enough to achieve a reasonable result. Figure 3.4 shows the k-points convergences test calculations for a fundamental unit of the 16 atoms rhombus shape single layer GNFs with ZZ configuration.

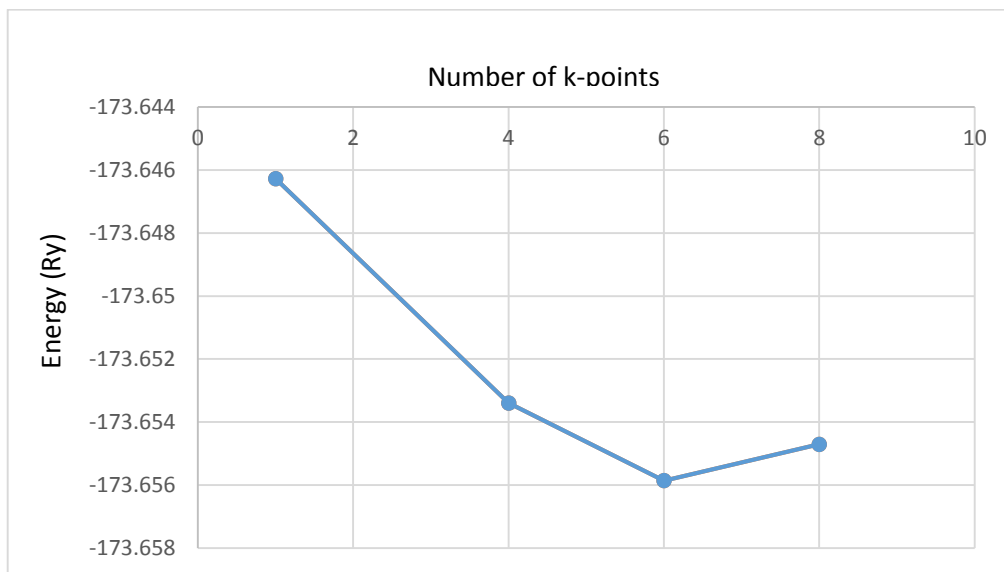


Figure 3.4: The convergence of total energies is a k-points function for a primitive unit of 16 atoms rhombus shape single layer GNFs with the ZZ edge.

CHAPTER 4 METHODOLOGY

4.1 Introduction to Quantum ESPRESSO (QE) Code

Quantum ESPRESSO stands for Open-Source Package for Research in Electronic Structure, Simulation, and Optimization. As the name implies, it is an integrated suite of computer codes for electronic structure estimations as well as materials modelling, depended on the first principle using density functional theory [116]. The code using plane-waves basis and pseudopotential method has been known by scientist community to offer high accuracy in predicting the molecules and crystal structures of various physical properties like magnetic and electronic properties.

It works on both Linux and Windows operating system with at least 64-bit Intel processor. If the system of interest comprises of many atoms, the computational cost can handle on a cluster server. The calculations in this research study are being executed employing a computing resource (University of Nottingham Malaysia HPC Cluster and three units HP Workstation run on parallel version). Visualisation of the stable atomic geometries and charge density obtained from QE were done with a package called XCRYSDEN [117].

4.1.1 Types of Calculations in the Quantum ESPRESSO

Some of the basic types of calculations that the Quantum ESPRESSO package can handle are:

- I. Structural modelling (including crystal surface and molecules equilibrium structures)
- II. Dynamic modelling (ab initio molecular dynamics) either on the electronic ground state (i.e., Born Oppenheimer) or with fictitious electron kinetic energy (Car- Parrinello)
- III. Chemical reactivity and transition path sampling using Nudged Elastic Based Band (NEB) method
- IV. Linear response functions (Vibration and dielectric properties) and some non-linear (Third order force constants and Infrared and Raman (nonresonant) cross section)
- V. Computational microscopy, e.g., Scanning Tunneling Microscopy (STM) images

The plane-wave pseudopotential method implementation in QE has been a success for calculations including periodic system. Within this approach, KS wave function and their solutions can be obtained using an algorithm called the modified broaden method for all k-point in the reciprocal space [118]. For high accuracy calculations at a reduced computational cost, a special k-points called Monkhorst and Pack scheme has been introduced. This scheme utilises the fewest possible k- points capable of sampling the Brillouin zone.

This thesis used the pseudopotential called ultrasoft, and the exchange-correlation treatment has done by the GGA scheme [119]. Near the Brillouin zone sampling techniques developed to consist of the following schemes; Fermi, Methfessel-Paxton, Marzari, Gaussian, and Tetrahedron schemes. In this research work, we use Gaussian and tetrahedron schemes which are usually used on insulators and semiconductor.

4.1.2 Geometry Optimization

The aim of geometry relaxation is to discover an equilibrium position for atoms in molecules or crystal from the initial arbitrary geometric inputs with or without cell constraints. It is achieved through the use of energy and force minimisation techniques at zero kelvin. For a cell constraints case, the atomic relaxation procedure retains the unit cell parameters, while allowing atomic positions to vary. The energy minimisation follows the self-consistent field technique. The forces on the nuclei are calculated from the wave function using Hellman- Feynman theorem. The force on nuclei I with the position R_I is expressed by

$$F_I = -\left\langle \frac{\partial E}{\partial R_I} \right\rangle \quad (45)$$

Where E is the energy. This force minimisation procedure determines the final ground state atoms in an equilibrium position. As most of the computational methods do, QE code uses the first order and second order derivate of BFGS algorithm method in optimization. In first and second order approach can be utilized to achieve lowest total energy as well as the scheme's equilibrium lattice parameter.

4.1.3 Band Structure

The lattice structure has been established, then is to determine the GNFs band structure. To achieved has to build the Brillouin zone of the hexagonal pattern. This is done by adopting the Wigner-Seitz construction approach and construct the Brillouin zone in reciprocal space.

There are some symmetry dots in the Brillouin zone can be employed to sketch the band structure. The equations for the reciprocal vectors and the dots within the Brillouin region employed to sketch the band structure are,

$$\vec{b}_1 = \frac{2\pi}{a\sqrt{3}}(\sqrt{3}\hat{k}_x + \hat{k}_y), \quad (46)$$

$$\vec{b}_2 = \frac{4\pi}{a\sqrt{3}}\hat{k}_y, \quad (47)$$

$$\vec{b}_3 = 2\pi\hat{k}_x \quad (48)$$

which are derived from the equations,

$$\vec{b}_1 = 2\pi \frac{\vec{a}_2 \times \vec{a}_3}{\vec{a}_1 \cdot [\vec{a}_2 \times \vec{a}_3]}, \quad (49)$$

$$\vec{b}_2 = 2\pi \frac{\vec{a}_3 \times \vec{a}_1}{\vec{a}_1 \cdot [\vec{a}_2 \times \vec{a}_3]}, \quad (50)$$

$$\vec{b}_3 = 2\pi \frac{\vec{a}_1 \times \vec{a}_2}{\vec{a}_1 \cdot [\vec{a}_2 \times \vec{a}_3]}, \quad (51)$$

In terms of the cartesian coordinates, any vector in the reciprocal space can be expressed.

The band structure is an energy level's visual representation that the electrons can have inside the solid. These calculations are performed almost entirely within the QE. If the aim is to complete a calculation of band structure, the result will be obtained by calculating an integral over the Brillouin zone of the crystal. Band structure calculation is a post-DFT work, i.e. calculation will start after structure configuration and energy are determined.

4.1.4 Electronic Density Of State

Band structure analysis is derived from density of state (DOS) [114]. In DOS, $g(E)$ in the energy range dE is represented as the electronic state's number per volume Ω in the expressed as energy range $[E, E + dE]$. For a normalised and spin-resolved system, the DOS averaged over a k-space wave vector can be expressed as

$$\begin{aligned} g(E)dE &= \frac{1}{\Omega} \sum_{E_k \in [E, E + dE]} 1 = \frac{2}{(2\pi)^3} \int_{E_k \in [E, E + dE]} dk \\ &= \frac{1}{\pi^2} k^2 dk \end{aligned} \tag{52}$$

The quantity on the equation (52) right-hand side has been deduced using spherical coordinates in the reciprocal space. To corresponding free electron model is given as

$$E_k = \frac{\hbar^2 |k|^2}{2m} = k dk = \frac{m}{\hbar^2} dE, \left(\frac{2mE}{\hbar^2} \right)^{1/2} \quad (53)$$

$$g(E) = \frac{1}{2\pi^2} \left(\frac{2mE}{\hbar^2} \right)^{3/2} \sqrt{E} \quad (54)$$

By employing the concept of electronic band structure calculation with the k-space energy, density of state is

$$\begin{aligned} g(E) &= \frac{1}{\Omega} \sum_{n,k} 2\delta(E - E_k^{(n)}) = \frac{2}{(2\pi)^3} \sum_n \int \delta(E - E_k^{(n)}) dk \\ &= \frac{2}{(2\pi)^3} \sum_n \int_{E_k^{(n)}=E} \frac{1}{|\nabla_k E_k^{(n)}|} dS_k \end{aligned} \quad (55)$$

By integrating the equation (55) closed exterior in the k-space, assuming that $E_k^{(n)}$ is consistent as well as equivalent to E in a two-dimensional S_k gives the DOS. The spherical surface in the energy range E whereas a free electron model is given as

$$|\nabla_k E| = \frac{\hbar^2 k}{m} = \hbar \left(\frac{2E}{m} \right)^{1/2} \quad (56)$$

The subscript n denoted the band index. Equation (56) can also be used to determine the PDOS for individual atoms.

4.2 The Calculations Procedure

1. For the calculation to have ab-initio character, the unit cell parameters of the GNFs rhombus and trapezium were first produced, and the value for total energy is compared with graphite from literatures [120][121]. In this procedure, the types of pseudopotentials and the exchange-

correlation contribution used would be adopted again in the single layer GNFs calculations.

2. In the structural optimisation process, a series of convergences calculations are to be carried out to determine the minimum cut-off values. In this series of calculations, the radical, single and dihydrogen terminated of GNFs were to be used.
3. Using the computed lattice constant, a unit cell dimension was then constructed in the QE package. The properties like bond length and total energy for radical triangular and hexagonal nanoflakes were then determined.
4. The various shape of GNFs configurations optimised utilised GGA as parameterisation by Perdew-Burke-Ernzerhof (GGA-PBE). All structural properties (bond lengths, total energy, and Fermi energy) were determined
5. The electronic properties such as the integrated density of state (IDS), using the above-stated pseudopotential of the various configurations were computed and analysed.
6. Part of the novelties of this work is the investigation of the fundamental structural and electronics properties (total energy, Fermi energy, and integrated density of states (IDS)) on the various shape (rhombus and trapezium) of a single layer of GNFs. Therefore, calculations to investigate the various shapes of a single layer of GNFs on the ground state properties were carried out. Firstly, structure without any chemical termination, called radical GNFs was calculated. Secondly, a

single layer of GNFs with hydrogen termination and dihydrogen termination were then carried out. Finally, various shapes (rhombus and trapezium) of bilayer of GNFs configuration (AA and AB configuration) with hydrogen termination and dihydrogen termination were investigated.

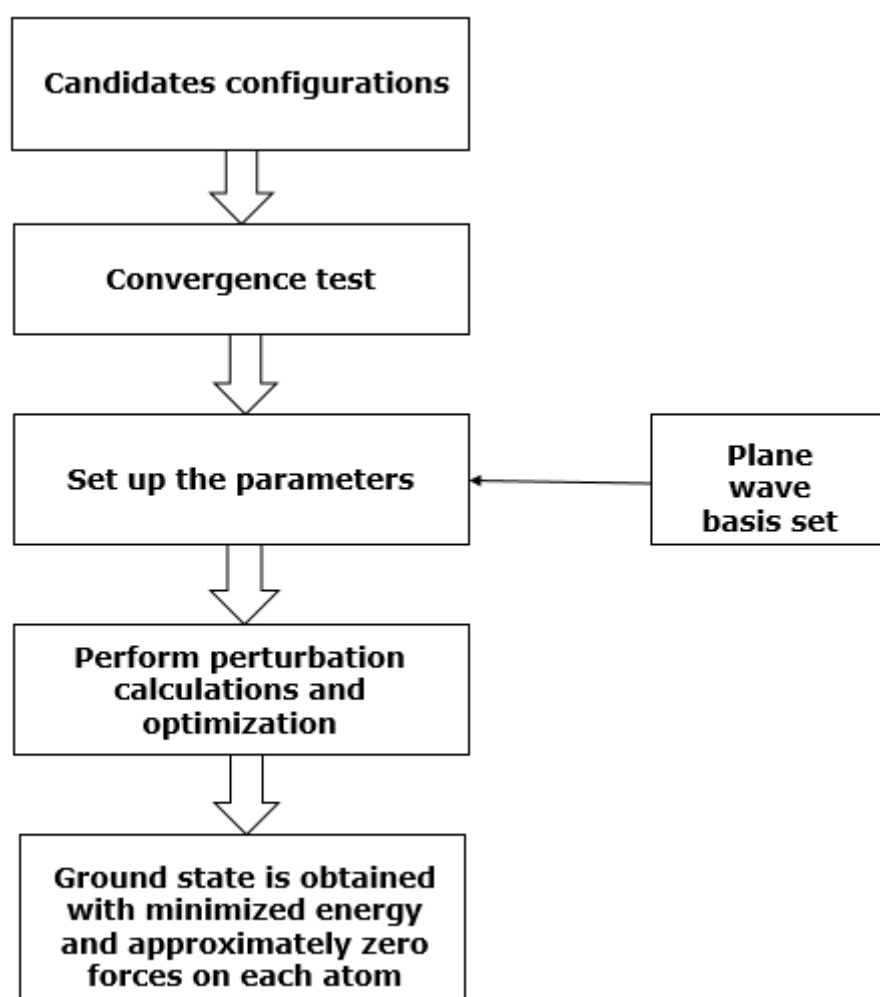
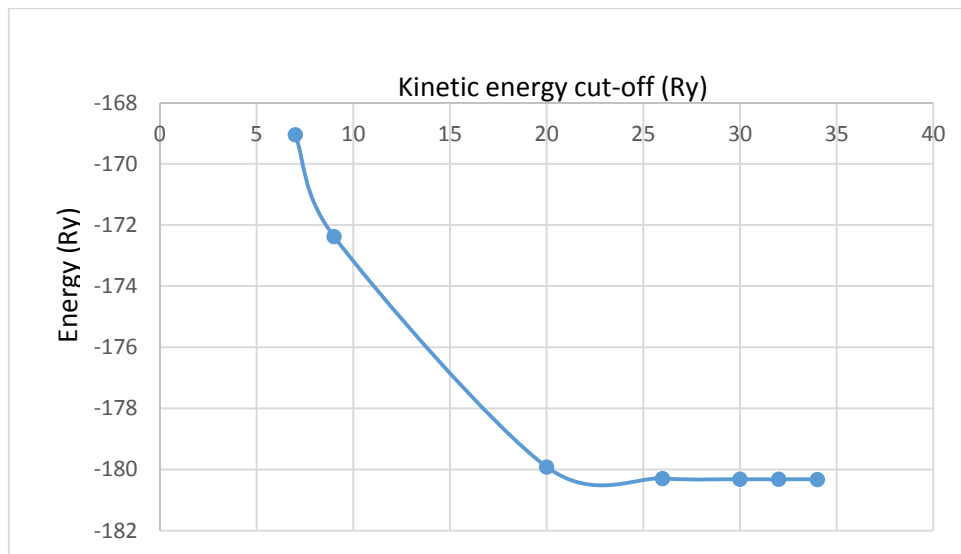


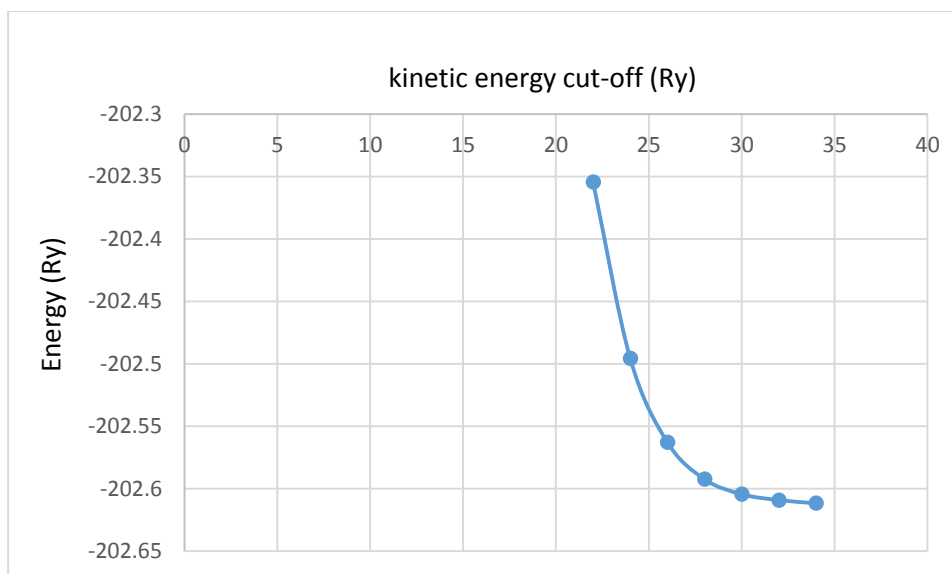
Figure 4.1: Schematic diagram of the DFT calculation procedure (QE package) [122].

4.2.1 Convergences Test

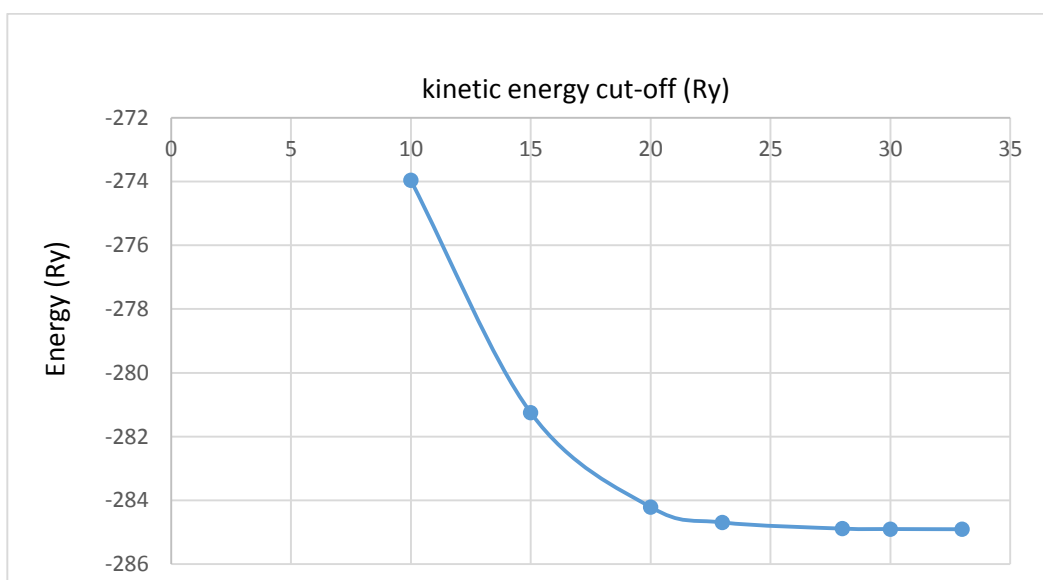
Before the structural optimisation, the kinetic energy cut-off and the number of k-points for sampling the Brillouin zone of the single layer GNFs were determined. In single layer GNFs hexagonal shape with AC and ZZ edge, the smallest number of carbon is 16 and 24 atoms. The results for the total energy versus cut-off for 16 atoms hexagonal shape single layer GNFs with an AC edge is shown in Figure 4.2(a). The 16 atoms hexagonal shape with dihydrogen termination and AC edge is shown in Figure 4.2(b), while 24 atoms hexagonal shape with hydrogen termination and ZZ edge is depicted in Figure 4.2(c), and figure in the last (Figure 4.2(d)) is a 24 atoms hexagonal shape with dihydrogen termination and the AC edge GNFs.



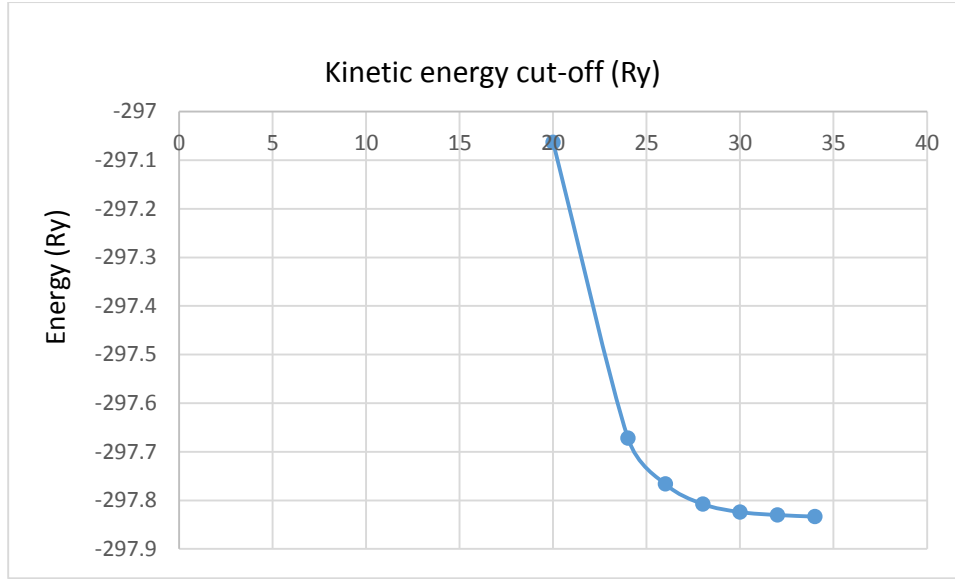
(a) 16 atoms hexagonal shape single layer GNFs with AC edge



(b) 16 atoms hexagonal shape single layer GNFs with dihydrogen termination with AC edge



(c) 24 atoms hexagonal shape single layer GNFs with hydrogen termination with ZZ edge

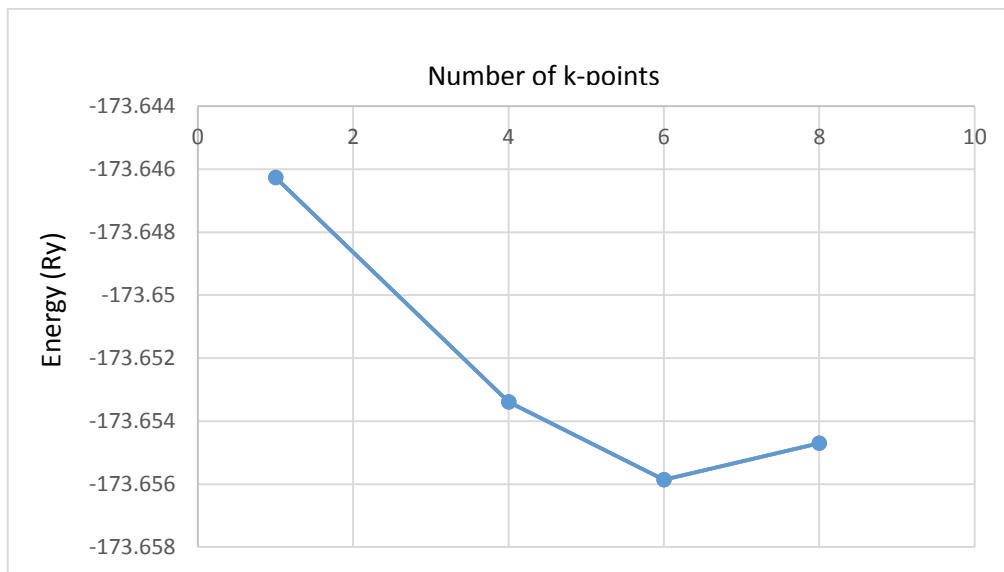


(d) 24 atoms hexagonal shape single layer GNFs with dihydrogen termination with AC edge

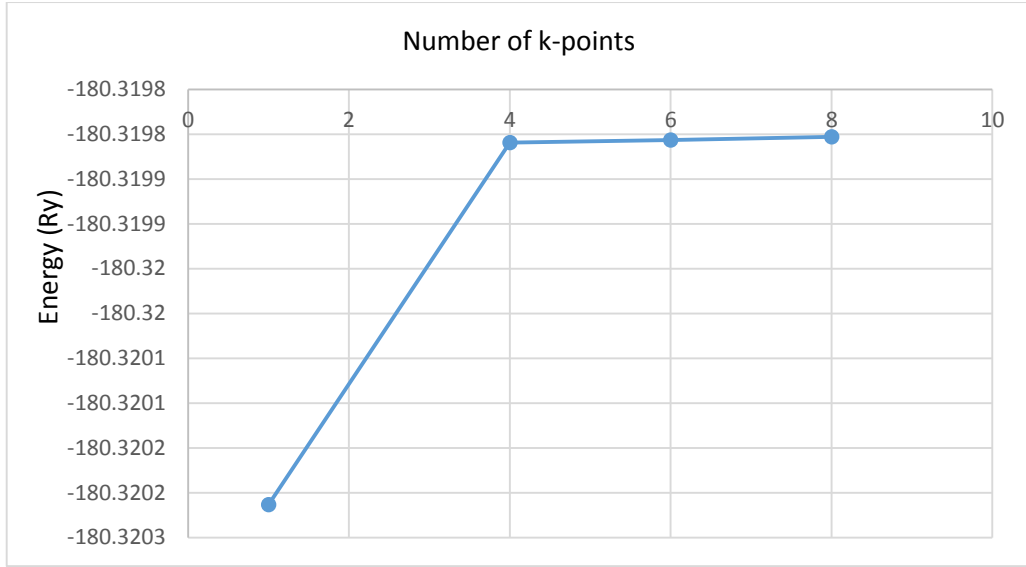
Figure 4.2: (a) The convergence of total energies of 16 atoms hexagonal shape single layer GNFs with AC edge. (b) 16 atoms hexagonal shape single layer GNFs with dihydrogen termination with AC edge (c) 24 atoms hexagonal shape single layer GNFs with hydrogen termination with a ZZ edge (d) 24 atoms hexagonal shape single layer GNFs with dihydrogen termination with AC edge

The cut-off energies for 16 atoms hexagonal shape single layer GNFs with AC edge was found to be between 7-34 Ry. With dihydrogen termination, the cut-off energies were between 22-34 Ry. For 24 atoms hexagonal shape with hydrogen termination and ZZ edge, dihydrogen termination with AC edge, they are 22-34 Ry and 20-34 Ry, respectively. In this respect, the uniform kinetic energy cut-off used in this thesis is 30 Ry and charge density of 150 Ry for both single layer and bilayer GNFs. The

cut-off is found to be within an acceptable limit from DFT related studies. Figure 4.3 shows the results of Brillouin zone sampling for 16 atoms radical rhombus shape single layer GNFs with the ZZ edge. As can be seen, $8 \times 8 \times 1$ is adequate for the calculation. Structural and electronic properties were calculated.



(a)



(b)

Figure 4.3: (a) The convergence of total energy is a k-points function for a primitive unit of 16 atoms rhombus shape single layer GNFs with ZZ edge (upper figure) and (b) 16 atoms rhombus shape single layer GNFs with AC edge (lower figure).

4.3 Single layer Graphene Nanoflakes

The lateral size of GNFs possible to combine with different synthetic groups [20][19] to establish new substance, a pair of homogenous and inhomogenous to GNFs relying on the combination and configurations.

It is feasible to construct nanoflakes (NFs) of alternative aromatic molecules incorporate alternative atoms and alternative plane systems incorporate without any carbon atoms like sheets of boron nitride. It could result to alike more exciting and flexible utilisation applications as well as NFs properties [123].

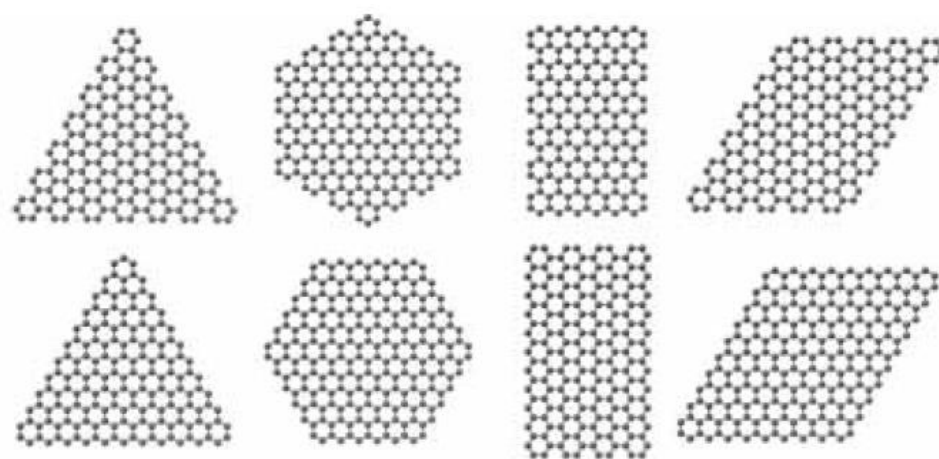


Figure 4.4: Variation of feasible GNFs dimensions that can be constructed with various configurations still always with ZZ and AC edges

4.4 Bilayer Graphene Nanoflakes

In previous research, GNFs with few layers and towering stacks of GNFs from both theoretical and experimental point of view have never been touched [123]. Such configurations may have characteristics that difference, often beneficially, from the single layer GNFs and graphite nanocrystals [124][125]. For example, bilayer GNFs consists of various band gap than single layer GNFs as well as electrons being configurations can be limited to potential barriers as opposed to single layer GNFs [125].

4.5 Graphene Nanoflakes Shape Variations

4.5.1 Graphene Nanoflakes Square And Rectangle

It has been shown the band gap can be easily controlled by adjusting the breadth of the GNFs for square and rectangular shape GNFs [126]. Moreover, a fascinating investigate on GNFs with AC edge has shown that they may be metallic unlike infinite GNRs [127]. Half-metallic states were also predicted in the presence of DFT calculations with ZZ edge [128][23].

The influence of rectangular GNFs doping and passivation by the different atoms and attached groups was also investigate using DFT calculations. The GNFs magnetic and electronic properties can be easily controlled through the particular method [129][130][130][131][132]. It results in the expectation that they may be beneficial applications like spintronics, sensors and transistors.

Several groups have been studied the electronic configuration of a variation of solid formation depended on remarkably regular dimensions

like large triangular, hexagonal, PAHs, and other polygon dimensions, usually called nanodisks [133][134][135][136][137][138]. The outcome reveals that their electronic and magnetic configuration can significantly vary through adjusting the nanodisk dimensions and breadth [123].

4.5.2 Other Shape Variations

Graphene's fascinating magnetic properties emerge from the characteristics of edge states, that implies the feasibility of engineering substances by unusual magnetic properties with employing dimensions, otherwise the natural geometry.

It is usually done using extensive and time-consuming calculations; various methods have been the implication to discover secure orders to anticipate the particular strengths [139][140][141][142][143][144]. These methods consider the radical formation, as well as the configuration of the graphene composition, such as that fact two sublattices A- and B- can interpret the graphene. An approach will be of significant practicality in designing GNF configuration for the ideal magnetic behaviour as an application like spintronics [145][146][147].

CHAPTER 5 VARIOUS SHAPE SINGLE LAYER OF GRAPHENE NANOFLAKES

5.1 Introduction

This chapter discusses the findings of the different shapes of GNFs based on the structural. As mentioned in the previous chapter, various preliminary calculations were carried out to determine the suitable k-points for sampling Brillouin zone, the kinetic energy cut-off for wave function and charge density expansions. Then, different shape structures and edge configurations of GNFs were determined using the converged computational parameters. The results for the mentioned properties are presented in computational detail subsection.

5.2 Circumferential Passivation

Graphene is aquaphobic and hence challenging via solubilise or diffuse in the bulk of liquids, that by many traditional methods limit their secure processing [123]. Therefore, researchers have put reasonable endeavour into searching for chemical functionalization of graphene so that they can be more easily solubilised or diffused, mainly in water. Numerous approaches have been evolved to construct sizeable GNFs (and GMBs or GNRs) much soluble within the solvents diversity like water as well as tetrahydrofuran [148]. One study showed that one could avoid using graphene oxide through the chemical fabrication of graphene [149]. It is crucial as most of the chemical methods used to produce GMBs are metallic and ordinarily abandon numerous deficiency as well as undesirable chemical attached groups. Chemical attached groups like carboxyl epoxy

and hydroxyl are generally utilized for solubilise GNFs within the aqua, as well as long alkyl chains build GNFs soluble with various organic solvents.

Regrettably, numerous approach mechanism heterogenous, an in-stoichiometric functionalized effect that consist of deficiency. As a result, the attached groups themselves modified their properties. All these results are commonly shown to the degenerate of the graphene properties constructed in this way, but in some instances which can be induced to the novel as well as exciting behaviour. For instance, GNFs optical properties may be customised for the use of various chemical attached groups, which may also access the feasibility of employing graphene in optical applications [148].

The first factor considers while investigating pragmatic GNFs is assuming that the GNF is without termination, then edge reconstruction could arise to break aromaticity so deduce the nanoflake total energy. It is obvious in the rightmost configuration in Figure 5.1, in which the edges of the relaxed configuration of non-uniform GNFs induces several types of reconstructions. The GNFs edges perform as an important character in discovering the properties, mainly electronic and magnetic properties. As mentioned in Figure 5.1, graphene has two types of edges, namely ZZ and AC edges. Indicate that the atoms on adverse ZZ edge exist to distinct sublattices between A- and B-. Although, edge state with other types is feasible, assuming that fewer numerous like the reconstructed ZZ as well as AC edges [50][150][151] with those resulting from unconventional "cuttings"

[152], and the corner states where two edges meet. The right-hand side of Figure 5.1 also can see the reconstructed corners in the relaxed structure. GNFs offers the possible by customised the edges states to cleavage GNFs in various shapes, that is flexible than in GNRs and can induce new dominance in the use of GNFs in electronic and magnetic applications.

In the study of hydrogen passivation, passivated carbon atoms absorb (give) the electron part of the hydrogen atom that positively (negatively) charges the hydrogen atoms. It polarises the GNFs with a permanent polarisation. Therefore, the net dipole moment will depend on the shape of the GNFs system. The electronic properties of GNFs originate from unbalancing in charge distribution at the edges.

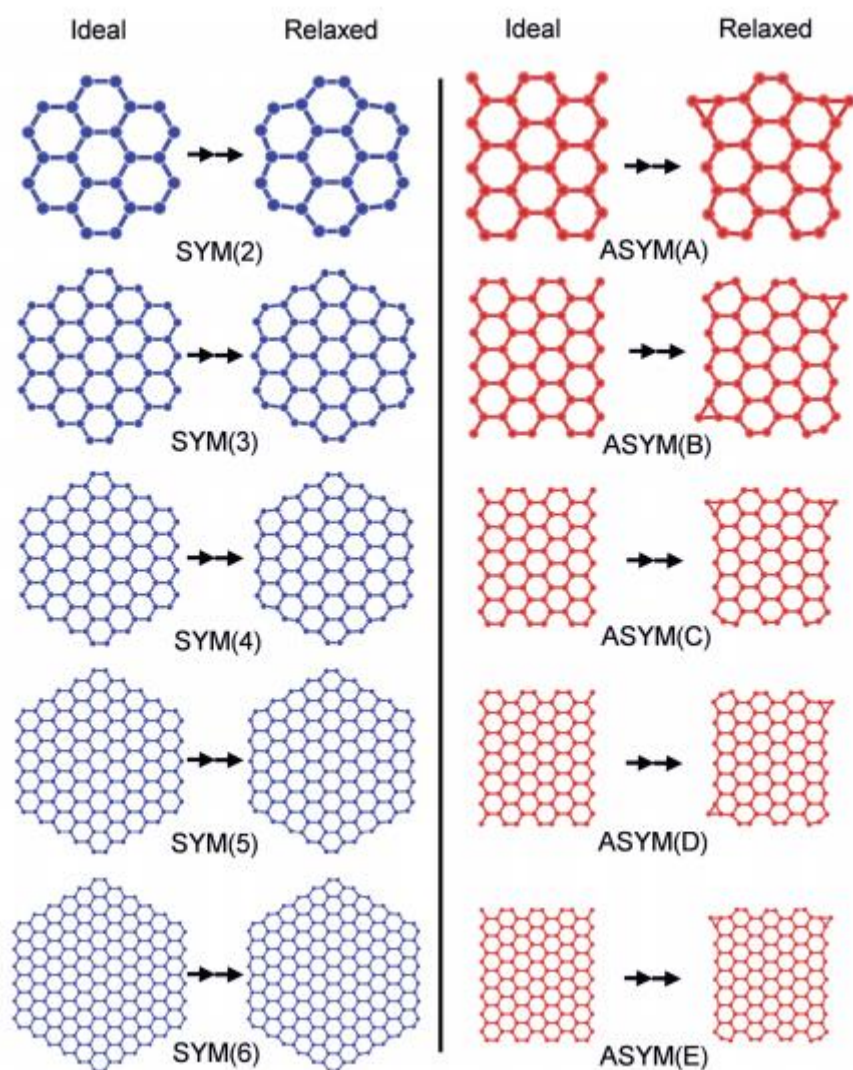


Figure 5.1: For all uniform (SYM) and non-uniform (ASYM) configuration acquired through DFT, the first (ideal) configurations at the left-hand and last relaxed configurations at the right-hand [153].

5.3 Computational Methodology

We used the DFT and a plane wave basis set to perform ab initio calculations. The exchange and correlation are that electron electron interrelation were handled with the Perdew-Zunger scheme's GGA. The carbon and hydrogen atoms electron ion interrelation treated by employing

the ultrasoft pseudopotential. In a plane wave basis set with a K.E cutoff of 30 Ry, the single particle KS wavefunction expanded. KS equations self consistent solutions obtained to using the Monkhorst-Pack set $12 \times 12 \times 4$ k-points in the hexagonal pattern Brillouin zones. The lattice parameter of in plane, $a = 2.45 \text{\AA}$ is in line by values studied [154][155][156] as well as experiment value for bulk graphite [157].

For modelling, we have implemented the single cell approach where the vertical split in the surface direction between the GNFs and their periodic illustrate was appropriated taken as $12.25 \text{\AA}$. After several convergence test calculations, modelling variable have been conservative selected.

5.4 Single Layer Various Shape Graphene Nanoflakes Structural Stability

We conducted convergence test for total energy to determine the kinetic energy before presenting GNFs results. We used $a = 2.45 \text{\AA}$ and $c/a = 2.726$ as lattice constant, Monkhorst-Pack set $12 \times 12 \times 4$ k-points with the identical for carbon ultrasoft pseudopotential as utilized in other simulations of GNFs.

For GNFs, we considered two different structural configurations are ZZ and AC edges. Without hydrogen atoms in the first conformist are alternately terminated with the carbon atoms in the plane. The hydrogen atoms terminated with the carbon atoms on one side only in the second conformist. Hydrogen atoms were terminated on both sides with the carbon atoms in the third conformer.

The graphene nanoflake modelled by a hexagonal unit cell composed of one layer of carbon atoms and a vacuum region of empty layers. It is followed by attaching hydrogen to the GNFs edges. In this way, we have considered the effect of the hydrogen termination in the ZZ/AC edge. GNFs without hydrogen termination (ZZ/AC edge) is shown in Figure 5.2, and we call it radical GNFs and the other is a GNFs with hydrogen termination (ZZ/AC edge) as shown in Figure 5.3. In all cases, self-consistent calculations were done to obtain the equilibrium relaxed structure and the atomic position, when the forces on the atoms were converged to within 1mRy/a.u.

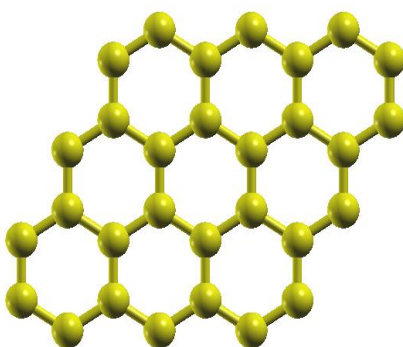


Figure 5.2: 30 atoms Rhombus shape of radical GNFs (ZZ edge)

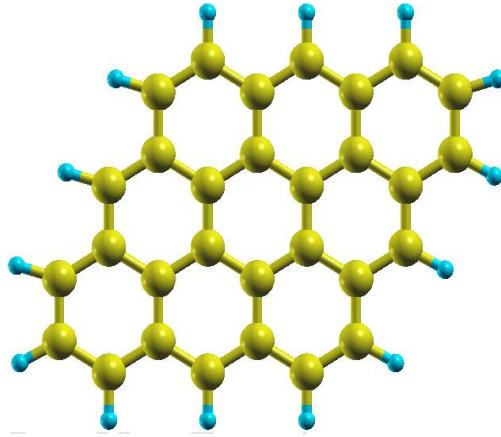


Figure 5.3: 30 atoms Rhombus shape of GNFs with hydrogen termination (ZZ edge)

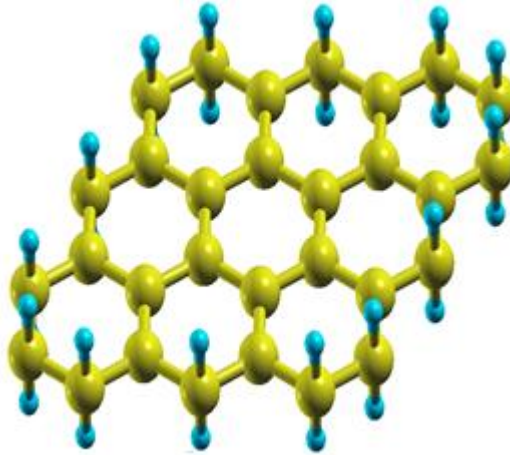


Figure 5.4: 30 atoms Rhombus shape of GNFs with dihydrogen termination (ZZ edge)

As a first step for the geometry optimises, we assumed a graphene sheet attached with hydrogen atoms is $1.1\text{\AA}$ with the carbon atoms. It has discovered the bond length between carbon and carbon is $1.4211\text{\AA}$, it is larger than the bond length between carbon and carbon in the ideal graphene is $1.42\text{\AA}$ and nearly with the bond length between carbon and

carbon in graphite is 1.47Å and diamond is 1.52Å, all computed employing the identical computational variables.

Furthermore, we computed the bond length between carbon and hydrogen is 1.1Å same as the hydrocarbon compounds typical bond length (e.g., methane is 1.1Å). We computed the bond length value between carbon and hydrogen also exact with the previously studied results [158]. We discovered that the three carbon atoms bonding and two carbon atoms with single hydrogen atoms bonding angles are 120.001° and 119.995°, respectively, from these calculations. The bond length results between carbon and carbon and the angles of three carbon atoms bonding and two carbon atoms with single hydrogen atoms bonding imply that the GNFs bond similar to sp^3 .

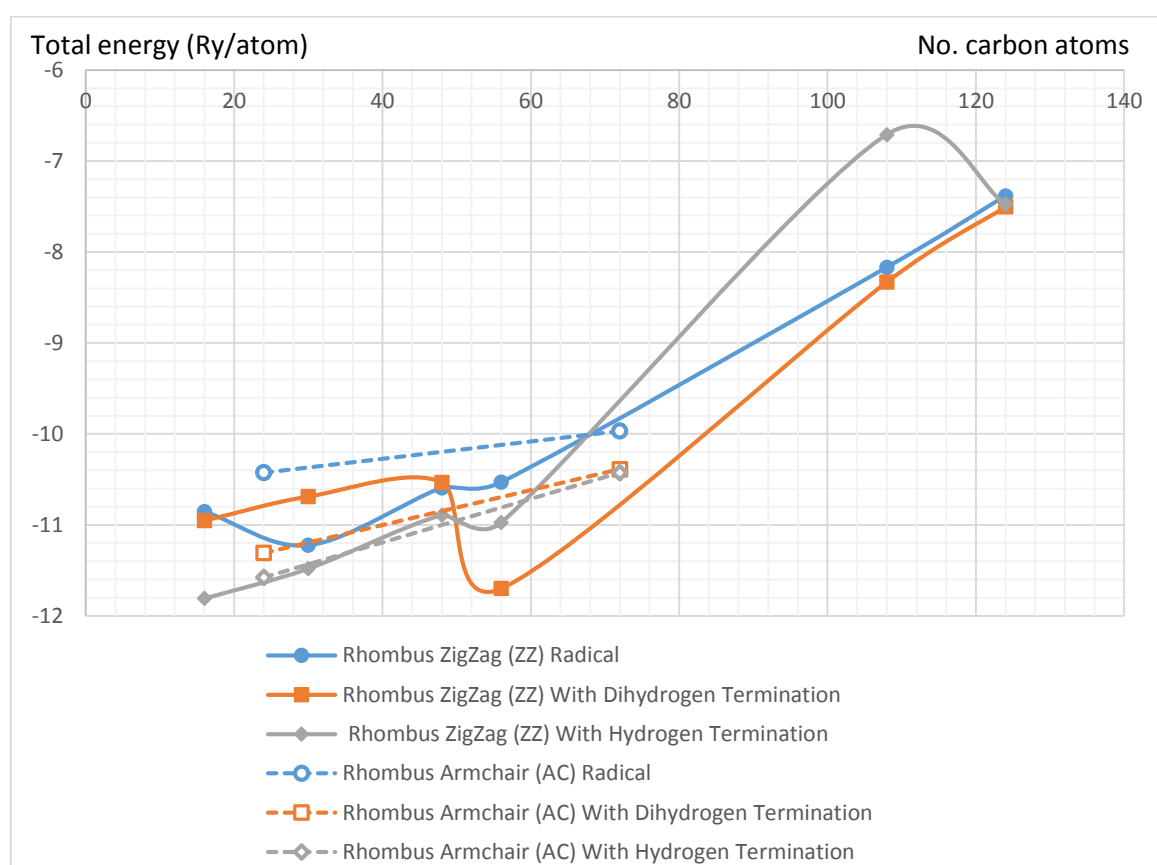
Also, reconstructions usually will occur, as well as aromaticity breaking. The effect on the properties can be varied and depend on the shape of the flakes [159].

5.5 Single Layer Various Shape Graphene Nanoflakes Total Energy

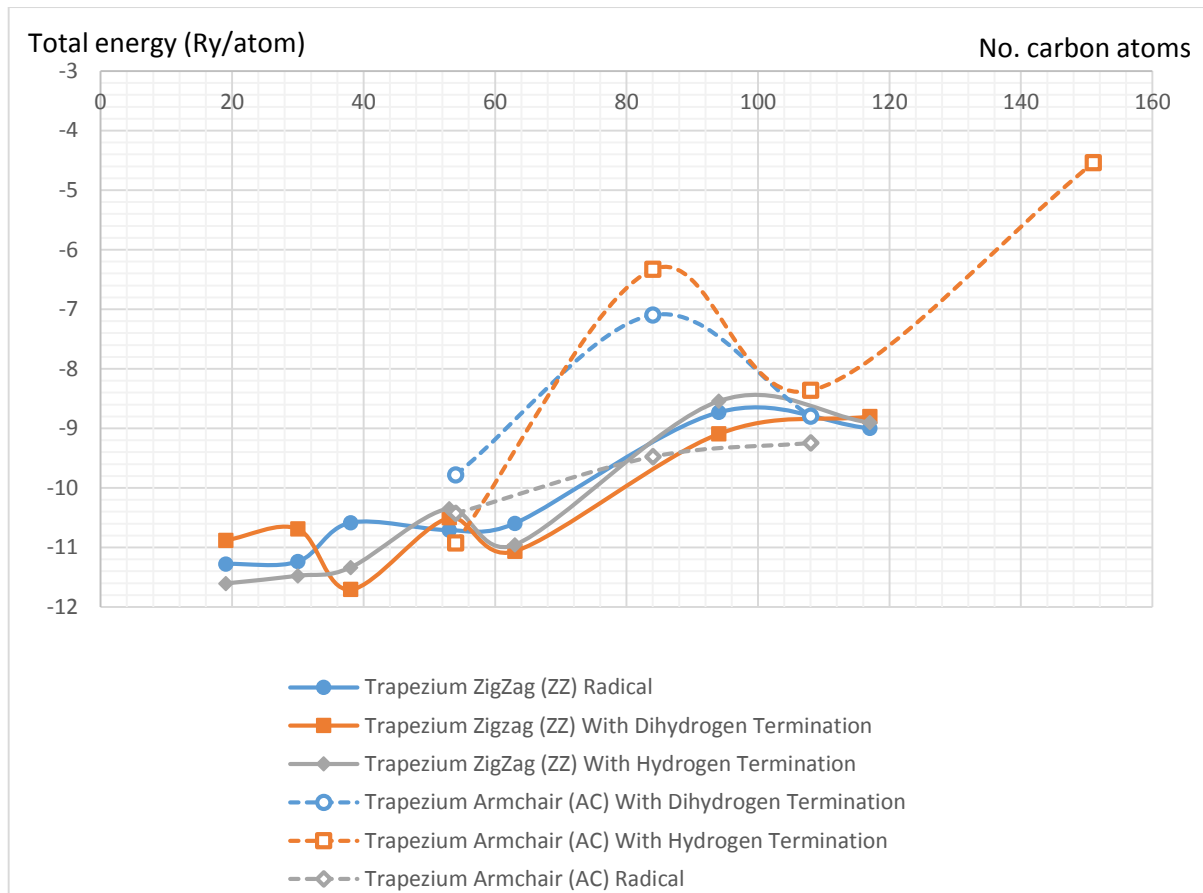
The first element to consider while endeavour to determine the relationship between the fundamental electronics properties and GNFs configuration is that if the edges are unterminated, reformations will happen, shattering the aromaticity and reducing the total energy of flake. The effects may be minimal or quite extreme depending on the shape. Reformations are commonly more critical with a supremely under coordinated feature that differs much from ZZ and AC edges.

In Figure 5.5 have shown GNFs with trapezium shape and rhombus shape are sensitive via the number of carbon atoms and type of edge to the single layer structure. Trapezium and rhombus shape display convergence by enlarging the dimensions, and the total energy is discovered to be independent of the edges type.

For example, 48 carbon atoms of radical rhombus shape GNFs with a ZZ edge, its total energy have slightly higher than 30 carbon atoms. The reason is that while the number of carbon atoms increases, the higher kinetic cutoff is required and minimisation the total energy can be achieved. When higher kinetic cut-off is required, the computational cost is also expected to be increased.



(a)



(b)

Figure 5.5: The total energy (eV) for GNFs with (a) Rhombus and (b) Trapezium shape

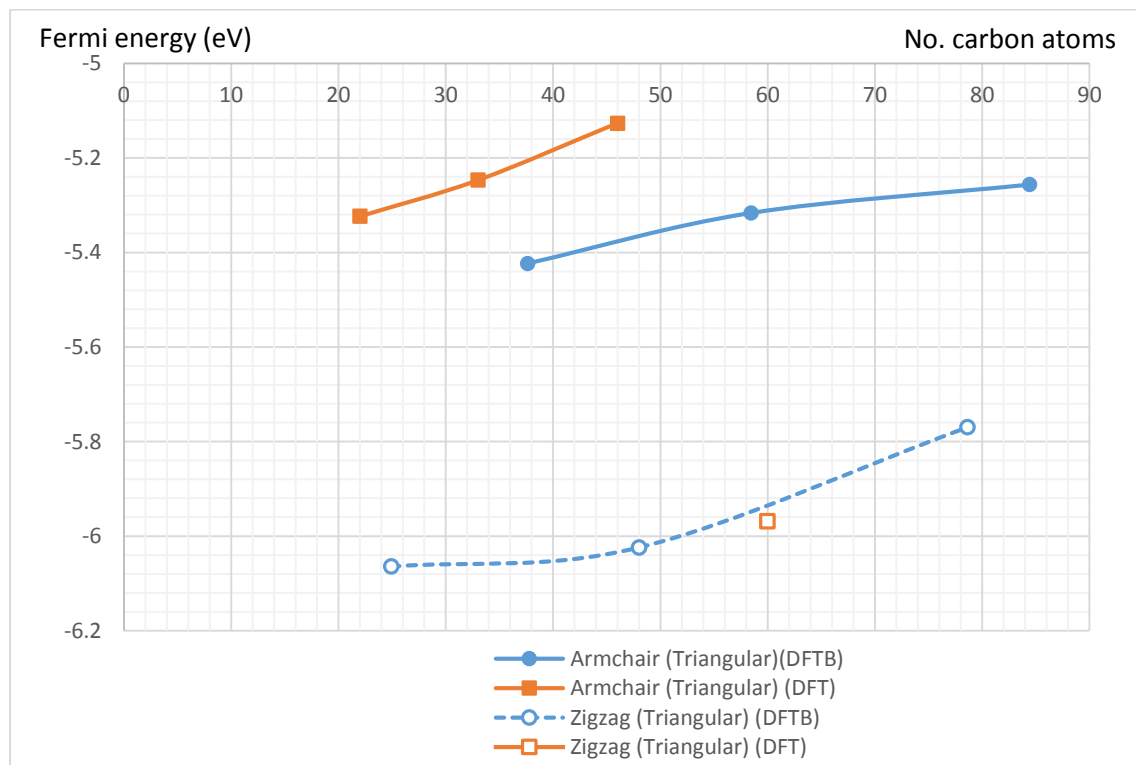
	Radical (Ry/atom)	Hydrogen Termination (Ry/atom)	Dihydrogen Termination (Ry/atom)
Rhombus	-11.2221	-11.4794	-10.6877
Trapezium	-11.2389	-11.4780	-10.6879

Table 1: Comparison of the total energy between 30 atoms Rhombus and Trapezium shape of radical, hydrogen termination and dihydrogen termination GNFs with the ZZ edge

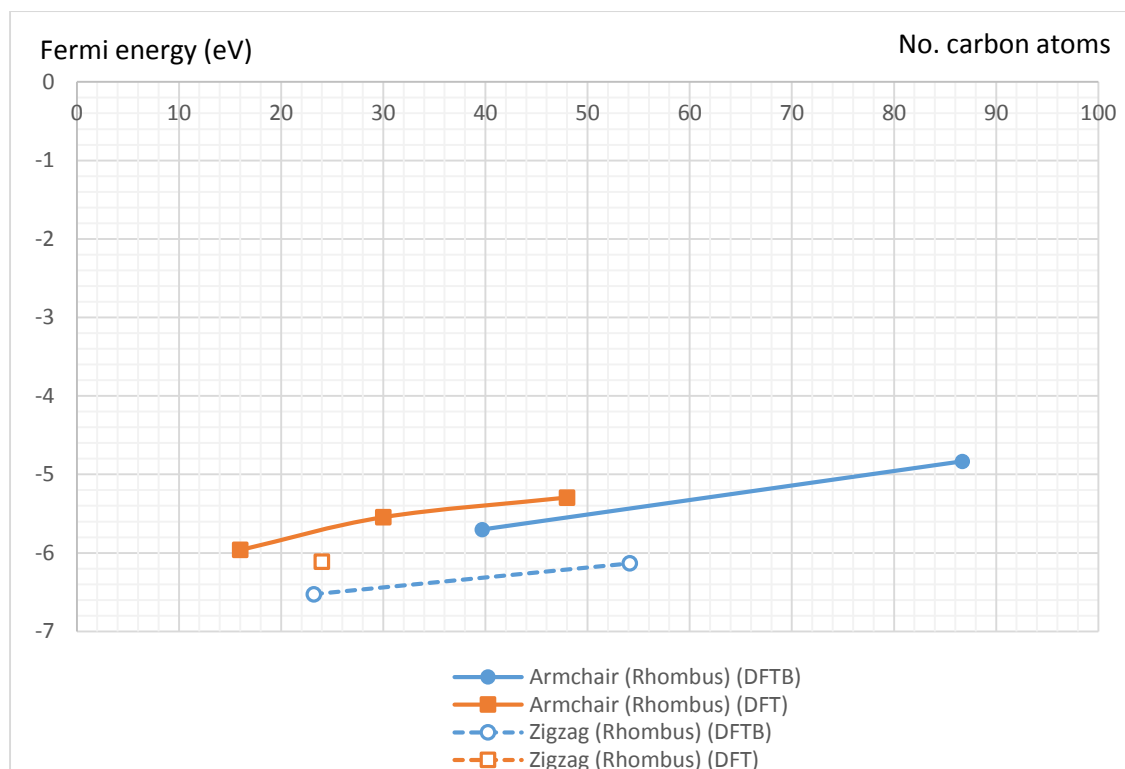
Comparison of the total energy for the rhombus and trapezium shape of GNFs is shown in Table 1. In Table 1, it is shown that the total energy between the trapezium shape of GNFs and rhombus shape of GNFs is a small decimal value in different. Figure 5.5 shows that with an increase in carbon atoms, the total energy decreases.

5.6 Single Layer Various Shape Graphene Nanoflakes in Fermi Energy (E_f)

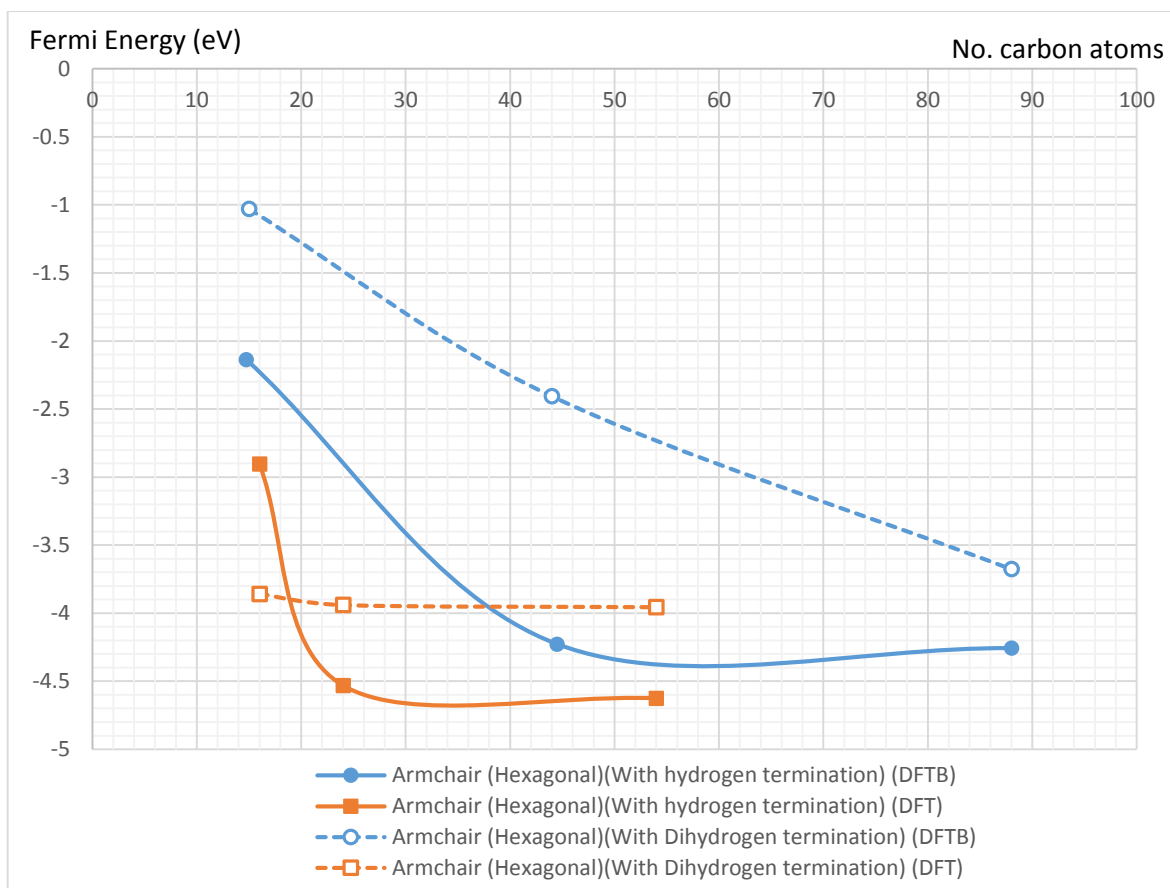
The graphene flakes electronic properties are quantified based on the Fermi level (E_f). For electronic properties of GNFs highly depend on the edge structure [45]. We have reproduced a similar shape configuration to observed the results between using DFTB and DFT.



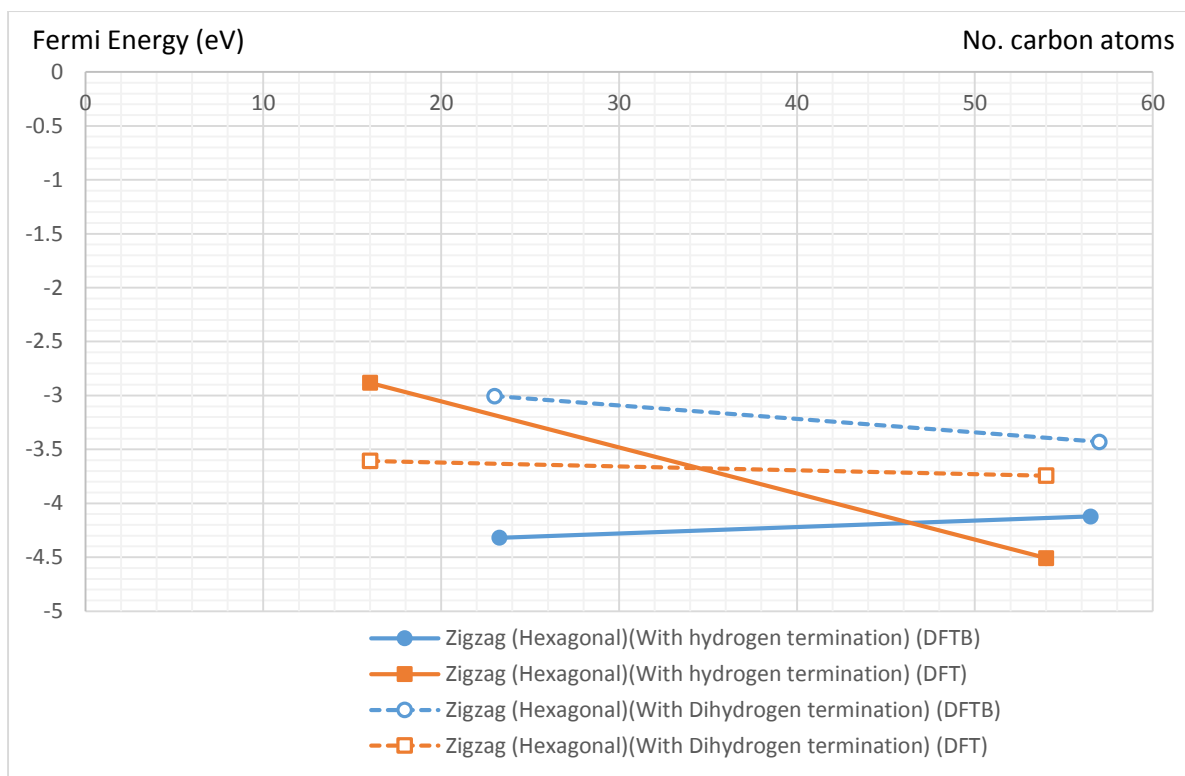
(a)



(b)



(c)



(d)

Figure 5.6: (a) E_f of radical triangular GNFs with AC and ZZ edge by using DFTB and DFT. (b) E_f of radical hexagonal GNFs with AC and ZZ edge by using DFTB and DFT. (c) E_f of AC edge hexagonal GNFs with hydrogen and dihydrogen termination by using DFTB and DFT. (d) E_f of ZZ edge hexagonal GNFs with hydrogen and dihydrogen termination by using DFTB and DFT.

Figure 5.6 (a) shown that the E_f of radical triangular GNFs with an AC edge, the number of carbon atoms between 38 to 84 is -5.4 eV to -5.26 eV by using DFTB approach. The number of carbon atoms between 22 to 46 is -5.3 eV to -5.1 eV by using DFT approach. The E_f of radical triangular GNFs with ZZ edge, the number of carbon atoms between 25 to 79 is -6 eV to -

5.8 eV by using DFTB approach. The E_f for 60 carbon atoms is -5.9 eV by using DFT approach.

Apart from triangular GNFs, the E_f of radical hexagonal GNFs showed in Figure 5.6 (b). The E_f of radical hexagonal GNFs with an AC edge, the number of carbon atoms between 40 to 87 is -5.7 eV to -4.8 eV by using DFTB approach. The number of carbon atoms between 16 to 48 is -5.9 eV to -5.3 eV by using DFT approach. The E_f of radical hexagonal GNFs with a ZZ edge, the number of carbon atoms between 23 to 54 is -6.5 eV to -6.1 eV by using DFTB approach. The E_f for 24 carbon atoms is -6.1 eV by using DFT approach.

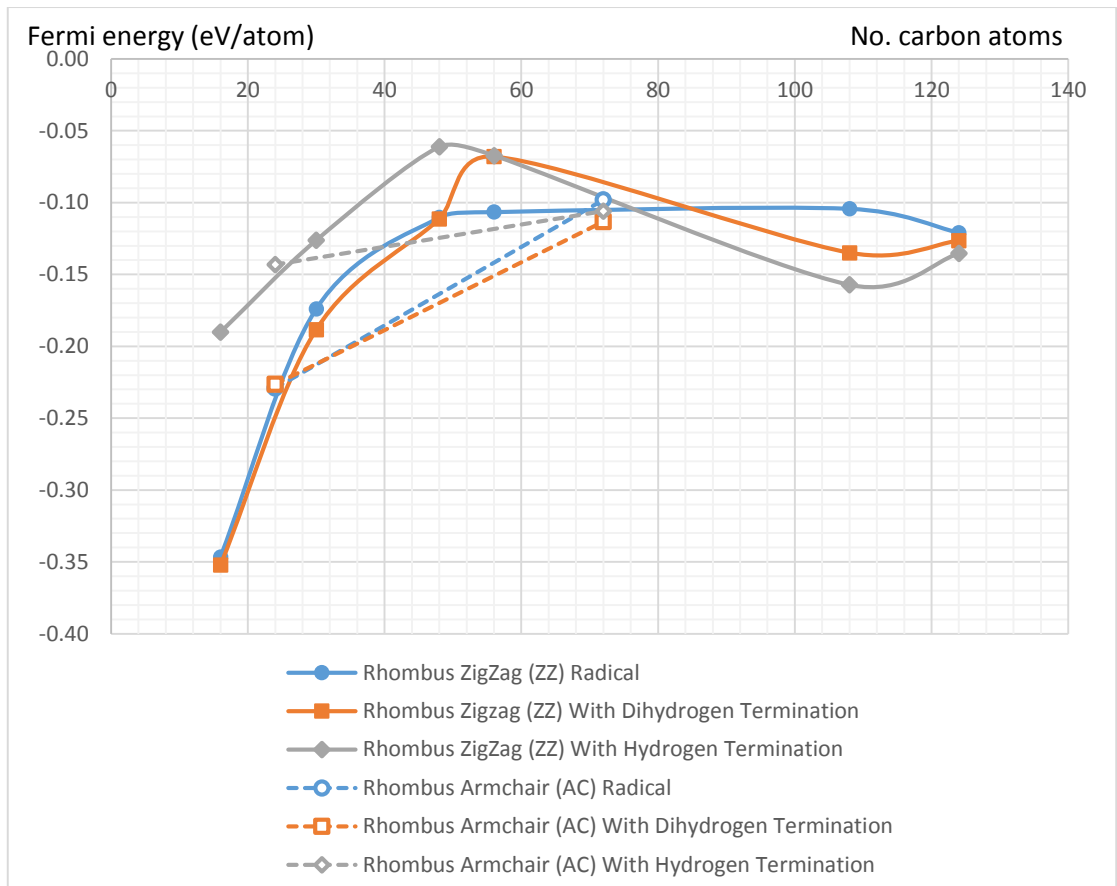
Moreover, E_f of AC edge hexagonal GNFs with hydrogen and dihydrogen termination showed in Figure 5.6 (c). The figure showed that E_f is -2.1 eV to -4.3 eV, the number of carbon atoms between 15 to 88 by using the DFTB approach. The number of carbon atoms between 16 to 54 is -2.9 eV to -4.6 eV by using DFT approach. The E_f of an AC edge hexagonal GNFs with dihydrogen termination, the number of carbon atoms between 15 to 88 is -1.0 eV to -3.7 eV by using DFTB approach. The number of carbon atoms between 16 to 54 is -3.8 eV to -3.9 eV by using DFT approach.

Besides that AC edge, ZZ edge hexagonal GNFs with hydrogen and dihydrogen termination of E_f showed in Figure 5.6 (d). The figure showed that E_f is -4.3 eV to -4.1 eV, the number of carbon atoms between 23 to 57 by using the DFTB approach. The number of carbon atoms between 16 to 54 is -2.8 eV to -4.5 eV by using DFT approach. The E_f of ZZ edge

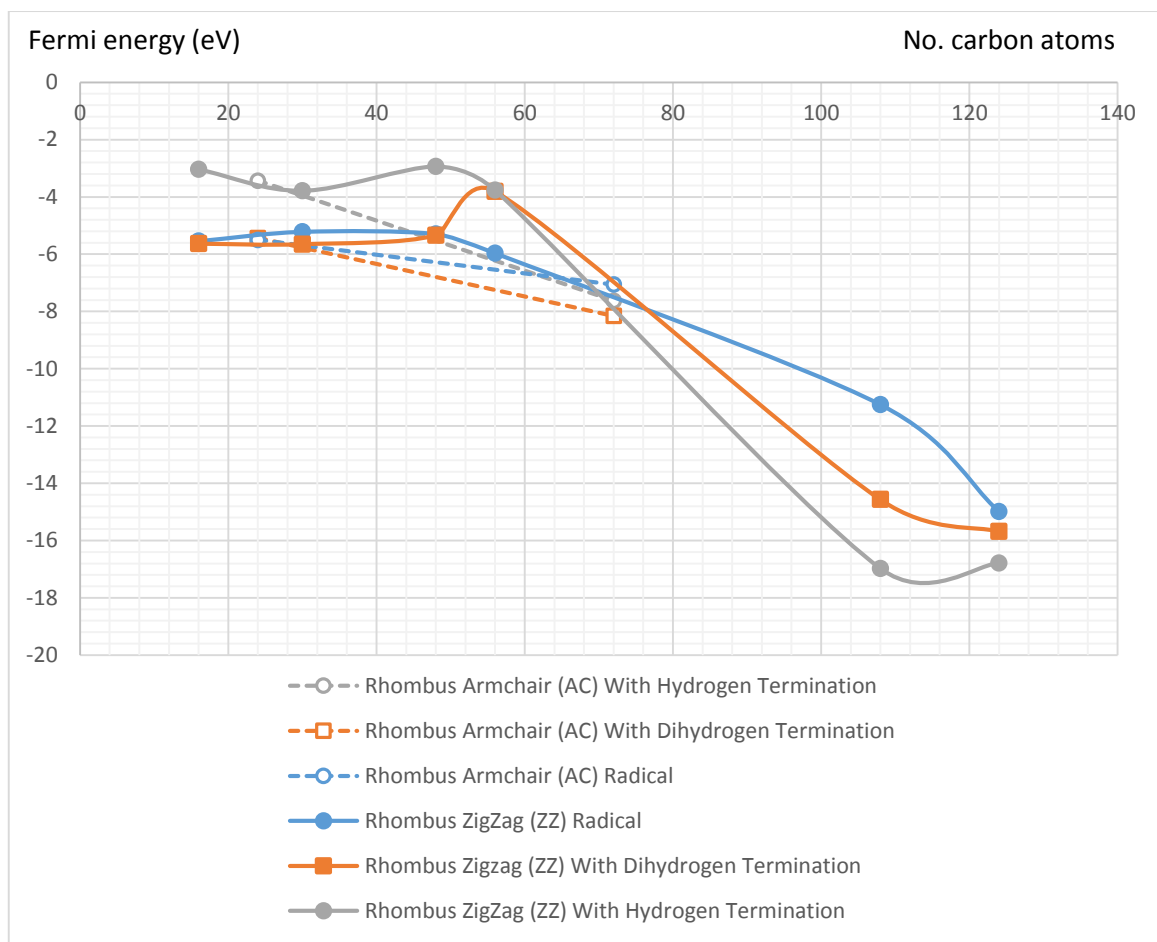
hexagonal GNFs with dihydrogen termination, the number of carbon atoms between 23 to 57 is -3.0 eV to -3.4 eV by using DFTB approach. The number of carbon atoms between 16 to 54 is -3.6 eV to -3.7 eV by using DFT approach. Thus, shape configuration with the number of carbon atoms increase, the Fermi energy have significantly effect.

Furthermore, it is also essential to consider the effect of edge passivation. Hence, the GNFs edge terminated with dihydrogen has possessed higher Fermi energy if compared to radicals, it is shown in Figure 5.7. Also, the energy difference due to the edge reconstruction represents the difference of total energy, which is remarkably influenced by the size and hydrogen (H) atoms density placed on the edge.

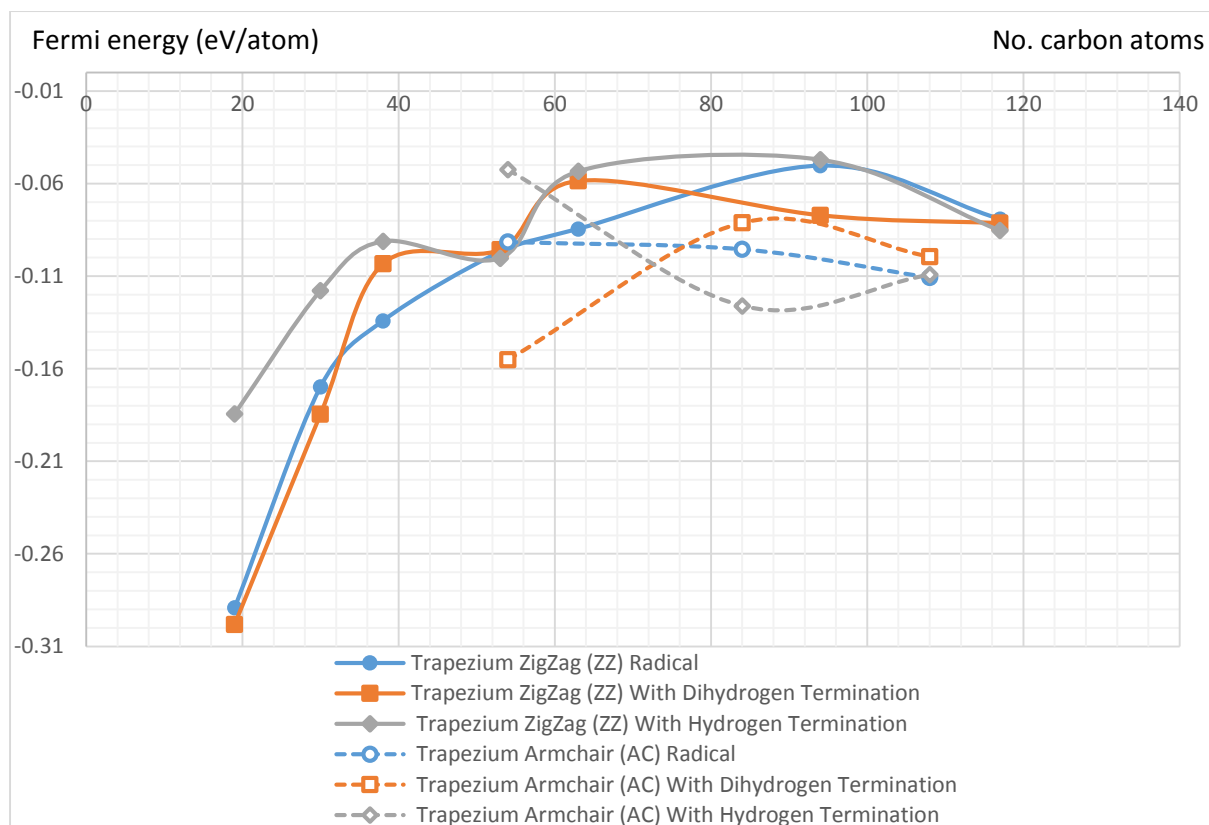
The Fermi energy (E_f) has an essential influence on the configuration affinity and other chemicals and molecules [45]. Figure 5.7 illustrates the Fermi energy of the GNFs with rhombus and trapezium shape. Figure 5.7 (a) and (b), radical rhombus shape GNFs with zigzag edge between the smallest (16) and largest number (124) of carbon atoms, E_f in 16 carbon atoms is -5.55 eV (-0.347 eV/atom) and 124 carbon atoms is -14.99 eV (-0.12 eV/atom). E_f is also effect by the number of carbon atoms.



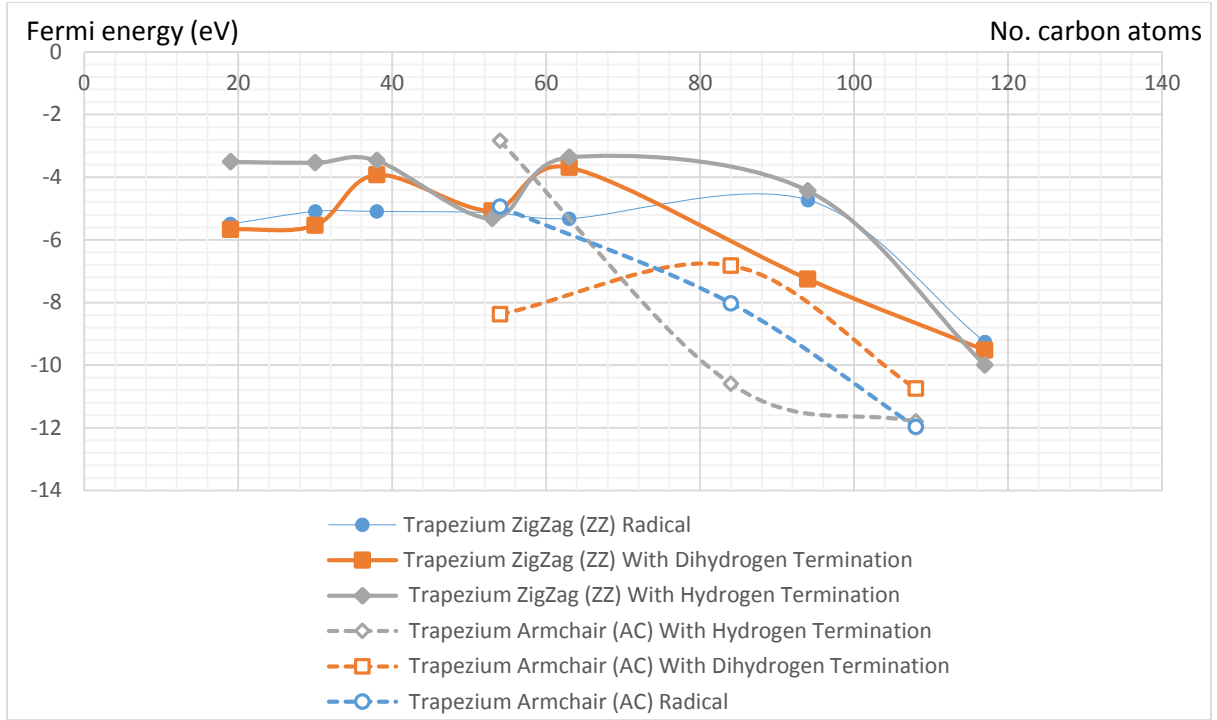
(a)



(b)



(c)



(d)

Figure 5.7: The Fermi energy (E_f) level for GNFs with (a) Rhombus shape (eV/atom), (b) Rhombus shape (eV), (c) Trapezium shape (eV/atom) and (d) Trapezium shape (eV/atom)

E_f is influenced by the GNFs structures after interaction with other materials. The size of carbon atoms as well as edge terminations will affect the E_f . As refer to Figure 5.7, The E_f of single layer rhombus GNFs ZZ edge with hydrogen termination is higher than the radical rhombus GNFs ZZ edge.

Otherwise, Figure 5.7 (b) shows that trapezium GNFs with hydrogen termination have a slightly higher E_f as compared to radical GNFs.

	Radical (eV/atom)	Hydrogen Termination (eV/atom)	Dihydrogen Termination (eV/atom)
Rhombus	-0.174	-0.126	-0.188
Trapezium	-0.170	-0.118	-0.185

Table 2: Comparison of the Fermi energy between 30 atoms Rhombus and Trapezium radical, hydrogen termination and dihydrogen termination with the ZZ edge

Table 2 shows a comparison between the same number of carbon atoms with a ZZ edge but two different shapes. E_f of rhombus and trapezium of GNFs with hydrogen termination is higher than the radical and dihydrogen termination. It has the trigonal and hexagonal shape of GNFs studied by using DFTB [45][160]. E_f comparison between DFTB and DFT approach is relatively different because both approach algorithms are different.

These results show that GNFs with various electronic configurations can be evolved by deliberate adjustment of structural criterion, as evidenced in the trapezium and rhombus shape of GNFs. Perhaps it is relatively challenging to have absolute control over the specific shapes of graphene flakes to be produced, the edge passivation as well as chemical functionalization controlled technique are developed and can apply in structure/ property engineering [20][19][148][161][162].

5.7 Bilayer Graphene Nanoflakes

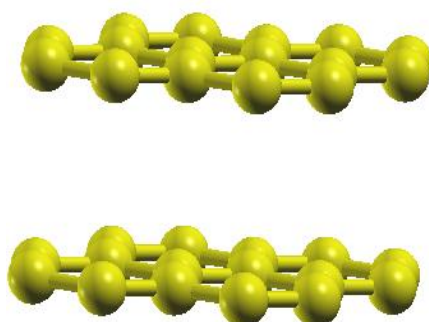
This section discusses the results of the stable geometries of bilayer GNFs based on the structural and electronic properties and the influence of variant stacking layer configuration such as AA stacking and AB stacking layer configuration. As mentioned in Chapter 4, various preliminary calculations were carried out to determine the suitable k-points for examine Brillouin region and the K.E cut-off for the wavefunction. Then, the equilibrium structures of AA stacking bilayer GNFs configuration and AB stacking bilayer GNFs configuration were all determined using the fully converged computational parameters. Calculations were then subsequently carried out to determine the stable geometries, electronic properties of AA stacking bilayer GNFs configuration and AB stacking bilayer GNFs configuration with hydrogen termination.

5.8 Computational Methodology

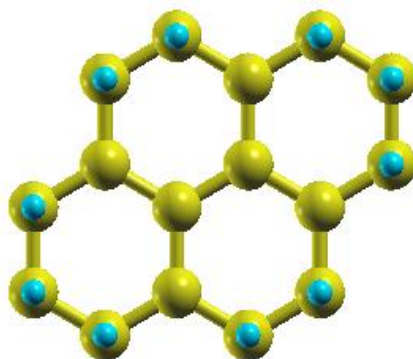
All calculation was carried out within the DFT framework [97] as implemented in the QE code [122]. The electron electron interrelation was conducted using GGA as parameterised by the PBE exchange correlation scheme [119]. Ultrasoft pseudopotentials were utilised for carbon (C) and hydrogen (H) atoms to treat electron ion core interrelation. The plane wave basis set for K.E cut-off of 30 Ry is selected. $8 \times 8 \times 1$ Monkhorst-Pack k-point meshes are employed in 2D Brillouin zone (BZ) integration in the self consistent calculation. The DOS was acquired using a denser set of $13 \times 13 \times 1$ k-points [115].



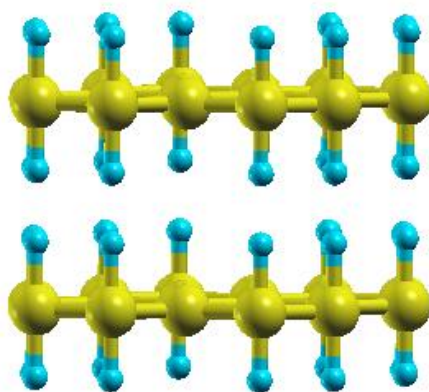
(a) AA Bernal Rhombus shape of bilayer radical GNFs (Top View)



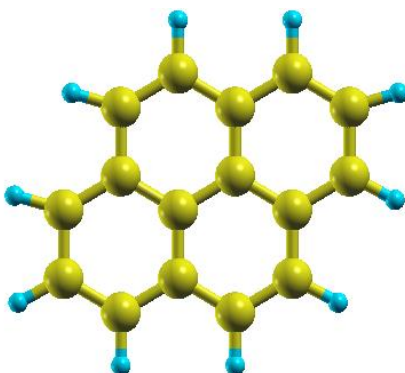
(b) AA Bernal Rhombus shape of bilayer radical GNFs (Side View)



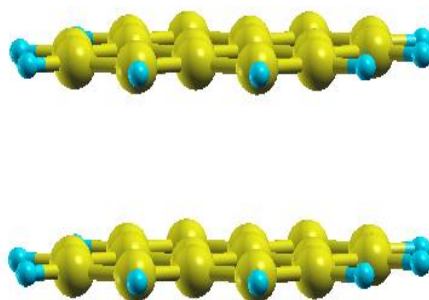
(c) AA Bernal Rhombus shape of bilayer GNFs with dihydrogen termination (Top View)



(d) AA Bernal Rhombus shape of bilayer GNFs with dihydrogen termination (Side View)



(e) AA Bernal Rhombus shape of bilayer GNFs with hydrogen termination (Top View)



(f) AA Bernal Rhombus shape of bilayer GNFs with hydrogen termination (Side View)

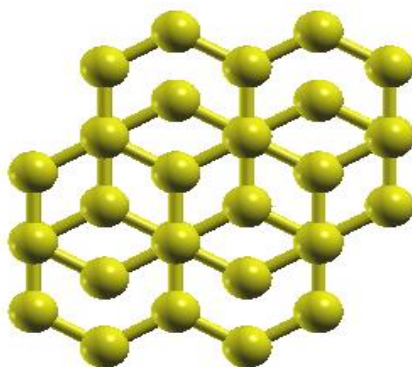
Figure 5.8: (a) AA Bernal Rhombus shape of bilayer radical GNFs (Top View), (b) AA Bernal Rhombus shape of bilayer radical GNFs (Side View), (c) AA Bernal Rhombus shape of bilayer GNFs with dihydrogen termination (Top View) (d) AA Bernal Rhombus shape of bilayer GNFs with dihydrogen termination (Side View) (e) AA Bernal Rhombus shape of bilayer GNFs with hydrogen termination (Top View) (f) AA Bernal Rhombus shape of bilayer GNFs with hydrogen termination (Side View)

5.9 Bilayer Various Shape Graphene Nanoflakes Structural Stability

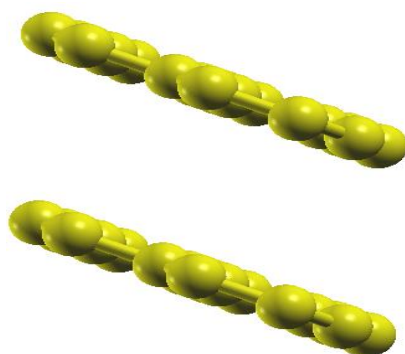
The first element that must be considered is to analyse the relationships between physical properties and GNFs structure.

Based on our calculation, the smallest number of carbon atoms, 16 carbon atoms with a ZZ edge has an average bond length between carbon and carbon is $1.42 \pm 0.011 \text{ \AA}$, as well as an infinite graphene membrane bond length between carbon and carbon was found to be $1.42 \text{ \AA}$. Figure 5.9 shows the AB Bernal bilayer GNFs with trapezium and rhombus shape.

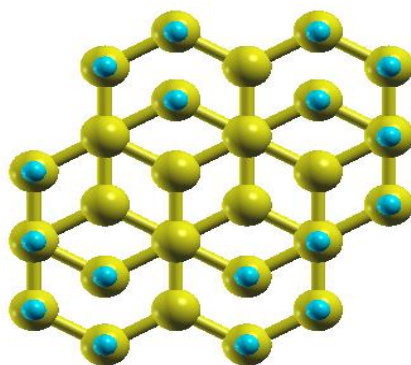
Graphene can form a layered configuration in each layer the carbon atoms are arranged in a hexagonal unit cell as well as stacked layers in the AB sequence [163]. It resulted in a hexagonal pattern with dimensions of $a=2.46\text{\AA}$ and $c=6.71\text{\AA}$ [164]. In Figure 5.9 yellow colour on the plane of top layer plane and bottom layer replaced by the c-axis spacing of half crystallographic, i.e., $3.35\text{\AA}$. It is unchanged in bond length with different geometry as well as with AC and ZZ edges.



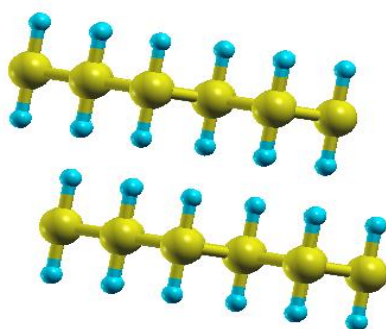
(g) AB Bernal Rhombus shape of bilayer radical GNFs (Top View)



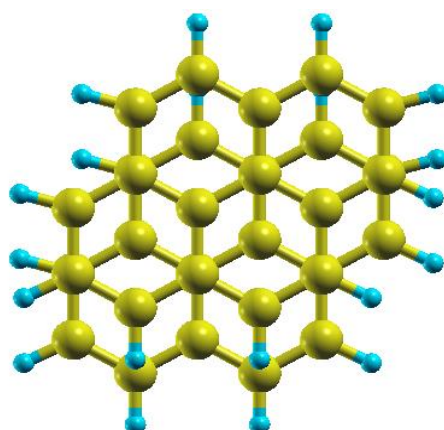
(h) AB Bernal Rhombus shape of bilayer radical GNFs (Side View)



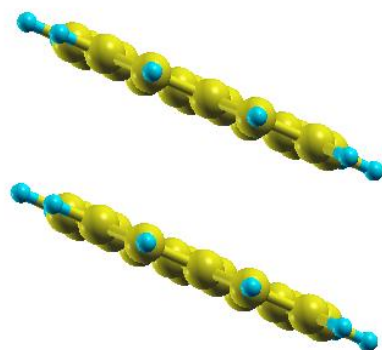
(i) AB Bernal Rhombus shape of bilayer GNFs with dihydrogen termination (Top View)



(j) AB Bernal Rhombus shape of bilayer GNFs with dihydrogen termination



(k) AB Bernal Rhombus shape of bilayer GNFs with hydrogen termination (Top View)



(l) AB Bernal Rhombus shape of bilayer GNFs with hydrogen termination (Side View)

Figure 5.9: AB Bernal Rhombus shape of bilayer GNFs with ZZ edge.

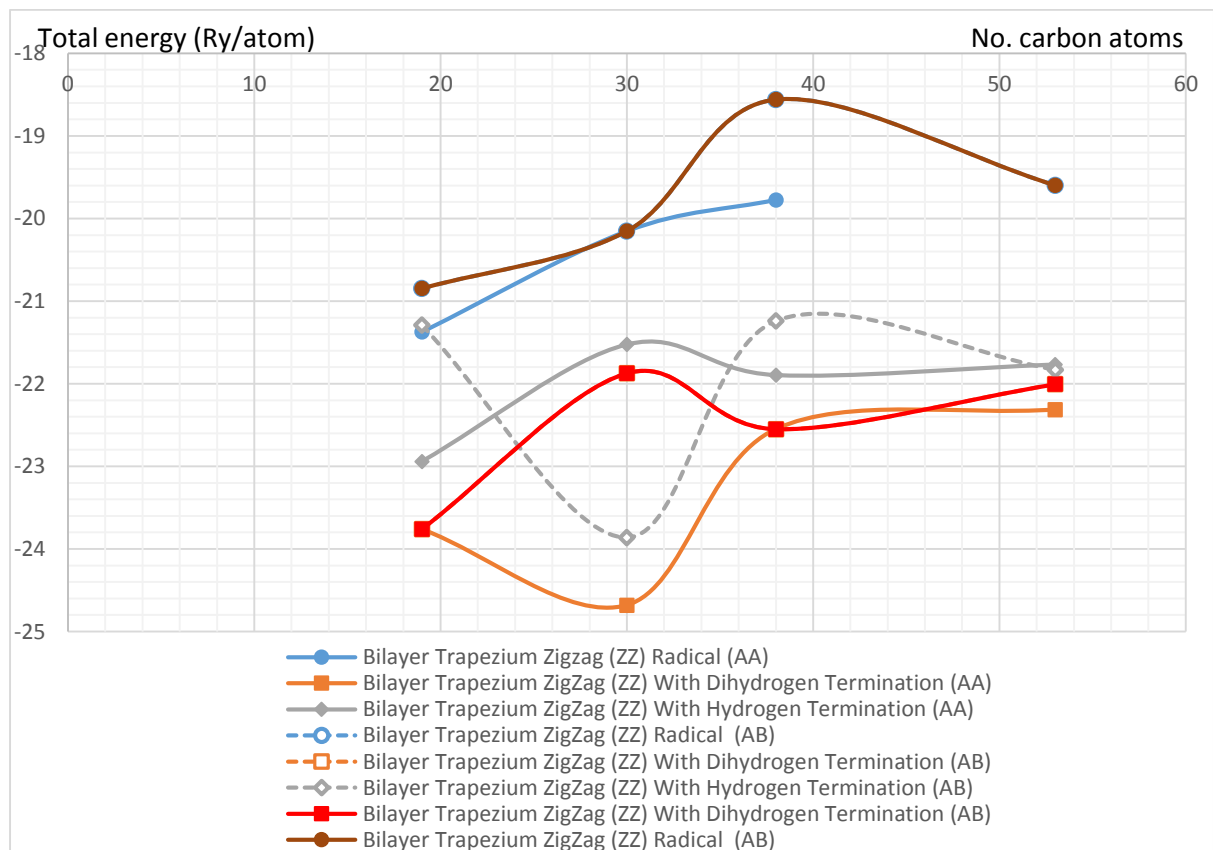
(g) AB Bernal Rhombus shape of bilayer radical GNFs (Top View), (h) AB Bernal Rhombus shape of bilayer radical GNFs (Side View), (i) AB Bernal Rhombus shape of bilayer GNFs with dihydrogen termination (Top View), (j) AB Bernal Rhombus shape of bilayer GNFs with dihydrogen termination (Side View), (k) AB Bernal Rhombus shape of bilayer GNFs with hydrogen termination (Top View) and (l) AB Bernal Rhombus shape of bilayer GNFs with hydrogen termination (Side View)

5.10 The Total Energy of Bilayer Graphene Nanoflakes

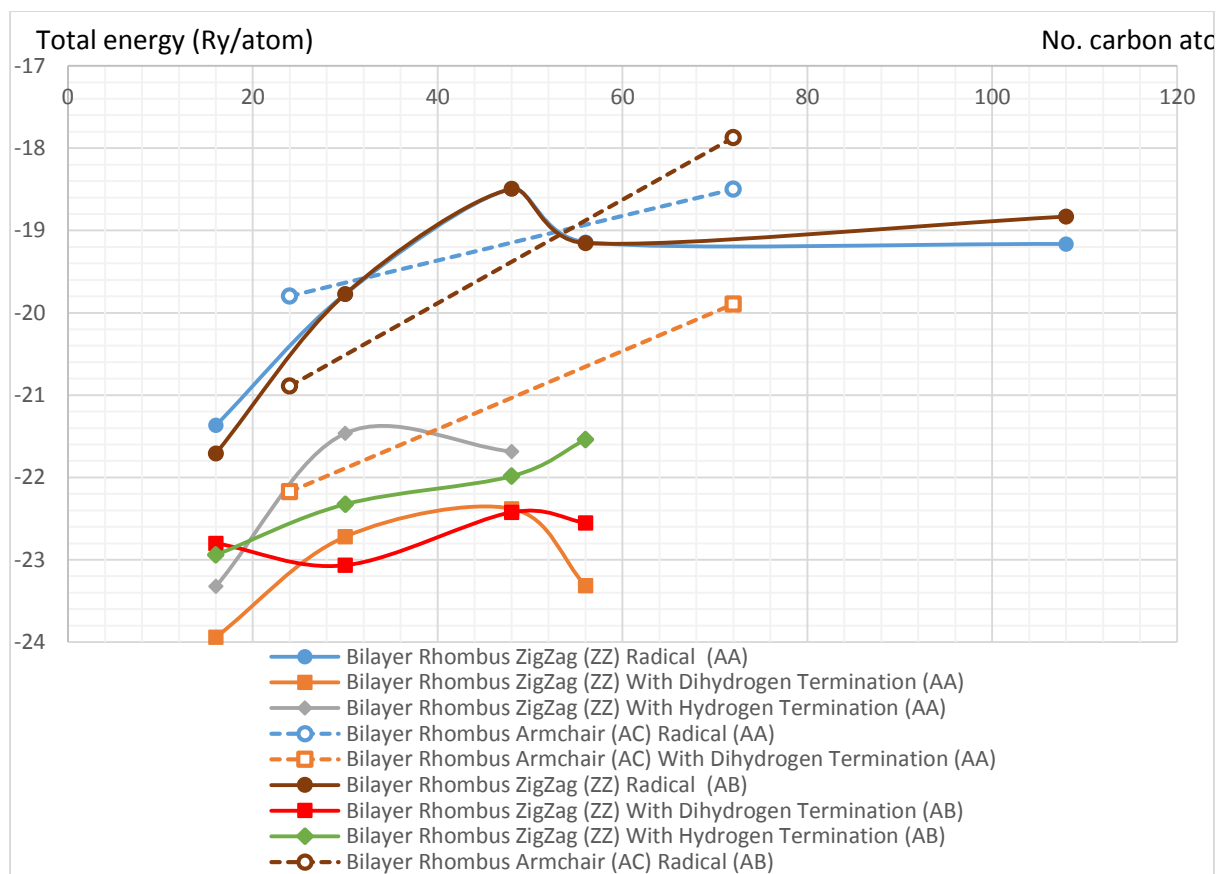
There are two types of stacking configuration, first is AA bilayer stacking configuration and second is AB bilayer stacking configuration. Based on the layer stacking structure, the effects can be minimal, or quite extreme.

The AA and AB layer stacking configuration of rhombus and trapezium shape are more solid, i.e. lower in total energy than single layer rhombus and trapezium GNFs.

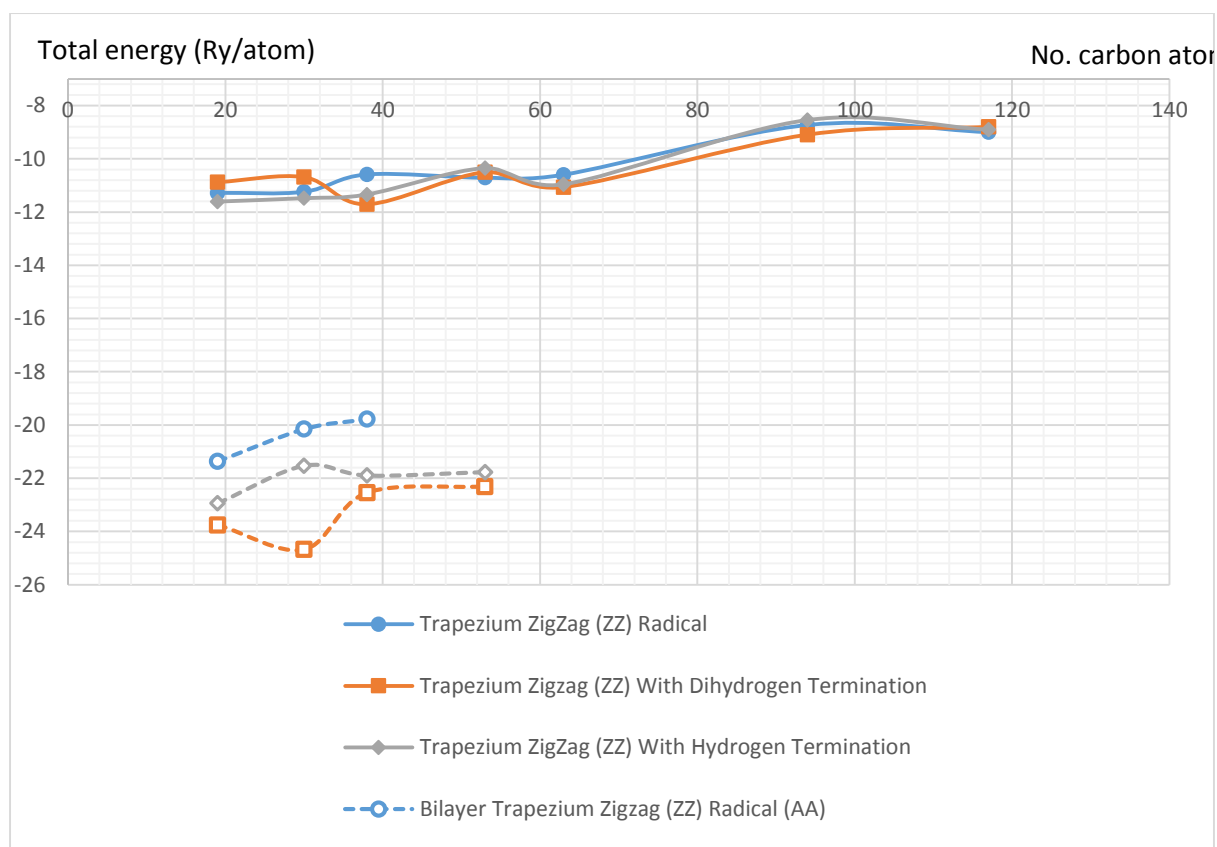
For instance, AA bilayer configuration 56 carbon atoms radical rhombus shape GNFs with a ZZ edge are -19.141 Ry/atom; its total energy has slightly lower than AB bilayer configuration 56 carbon atoms rhombus shape of bilayer GNFs with hydrogen termination with a ZZ edge are -19.154 Ry/atom. The results show that the two types of layer stacking configuration have affected the total energy with and without hydrogen termination and with hydrogen/dihydrogen termination, the number of carbon atoms, type of edge and passivation termination.



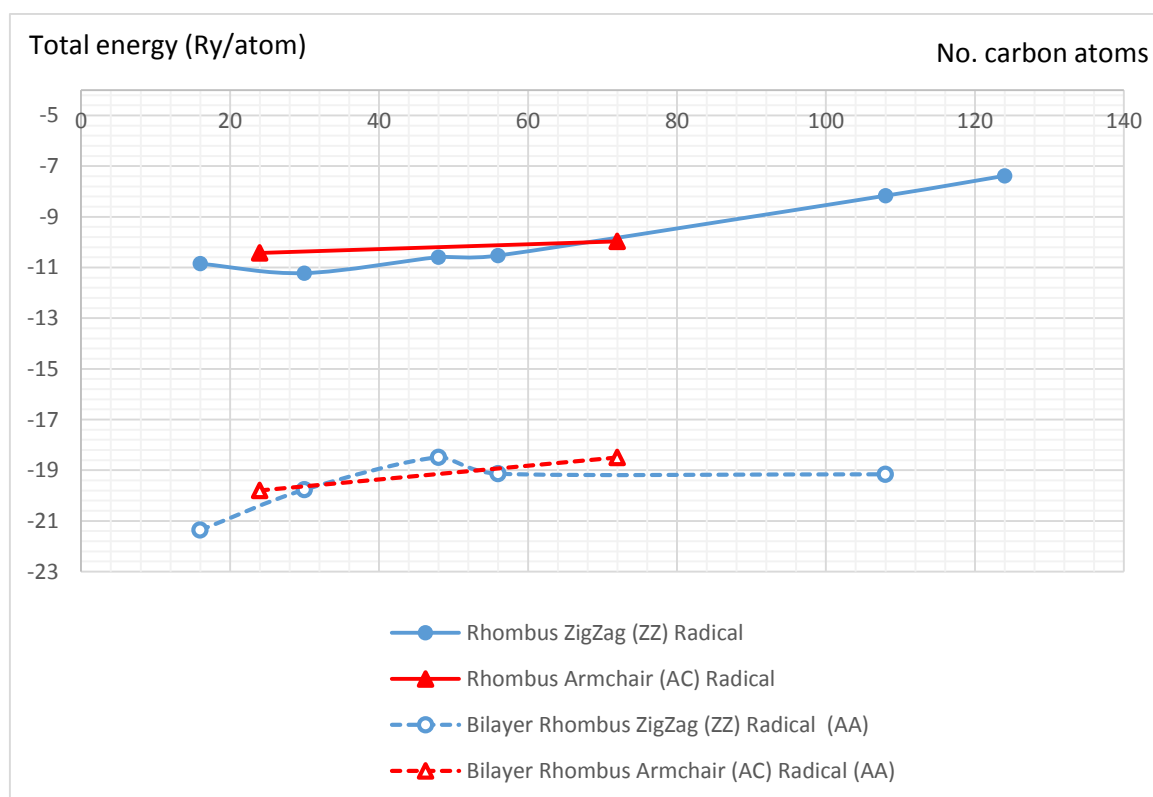
(a)



(b)



(c)



(d)

Figure 5.10: Comparison of the total energy of the single layer and bilayer of GNFs. (a) Trapezium shape of AA and AB bilayer configuration with hydrogen termination and dihydrogen termination (b) Rhombus shape of AA and AB bilayer configuration with hydrogen termination and dihydrogen termination (c) Trapezium shape of AA bilayer configuration and single layer configuration and (d) Rhombus shape of AA bilayer configuration and single layer configuration

		Radical (Ry/atom)	Hydrogen Termination (Ry/atom)	Dihydrogen Termination (Ry/atom)
Rhombus	AA	-19.772	-21.464	-22.720
	AB	-19.772	-22.325	-23.067
Trapezium	AA	-20.153	-21.525	-24.681
	AB	-20.152	-23.863	-21.873

Table 3: Comparison of the total energy between 30 atoms Rhombus and Trapezium radical, hydrogen termination and dihydrogen termination with the ZZ edge between bilayer configuration of AA and AB

The total energy for the bilayer stacking configuration of AA and AB configuration of rhombus and trapezium shape are compared in Table 3. In Table 3, the total energy GNFs without hydrogen termination are higher than hydrogen termination and dihydrogen termination. The interaction exists between the carbon layers is vdW interaction. The interaction between the interlayers is an essential element in explaining the observed results.

5.11 Bilayer Graphene Nanoflakes Effect of Circumferential Passivation in Fermi Level (E_f)

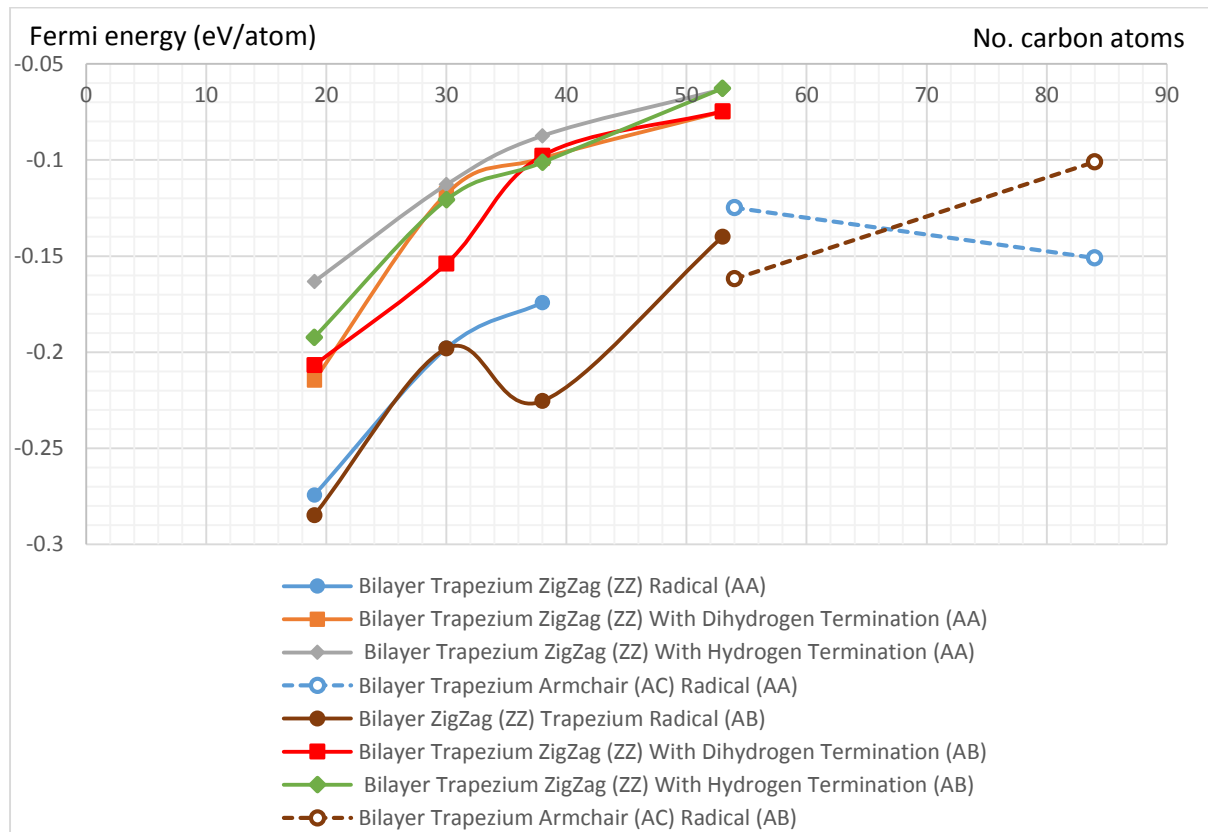
Fermi level (E_f) is responsive to dimension, edge type and terminations type. The Fermi level (E_f) also influenced by the amount of layer. Figure 5.11 (a) and (b) shows the E_f for AA and AB bilayer stacking configuration. Figure 5.11 (c) and (d) compares between the single layer and AA bilayer stacking configuration.

The Fermi energy (E_f) for the AA and AB bilayer stacking configuration without termination is found to be different slightly. For example, the E_f for AA bilayer stacking configuration of 24 atoms radical rhombus shape with an AC edge is -0.231 eV/atom and while for AA bilayer stacking with 16 atoms with a ZZ edge is -0.319 eV/atom.

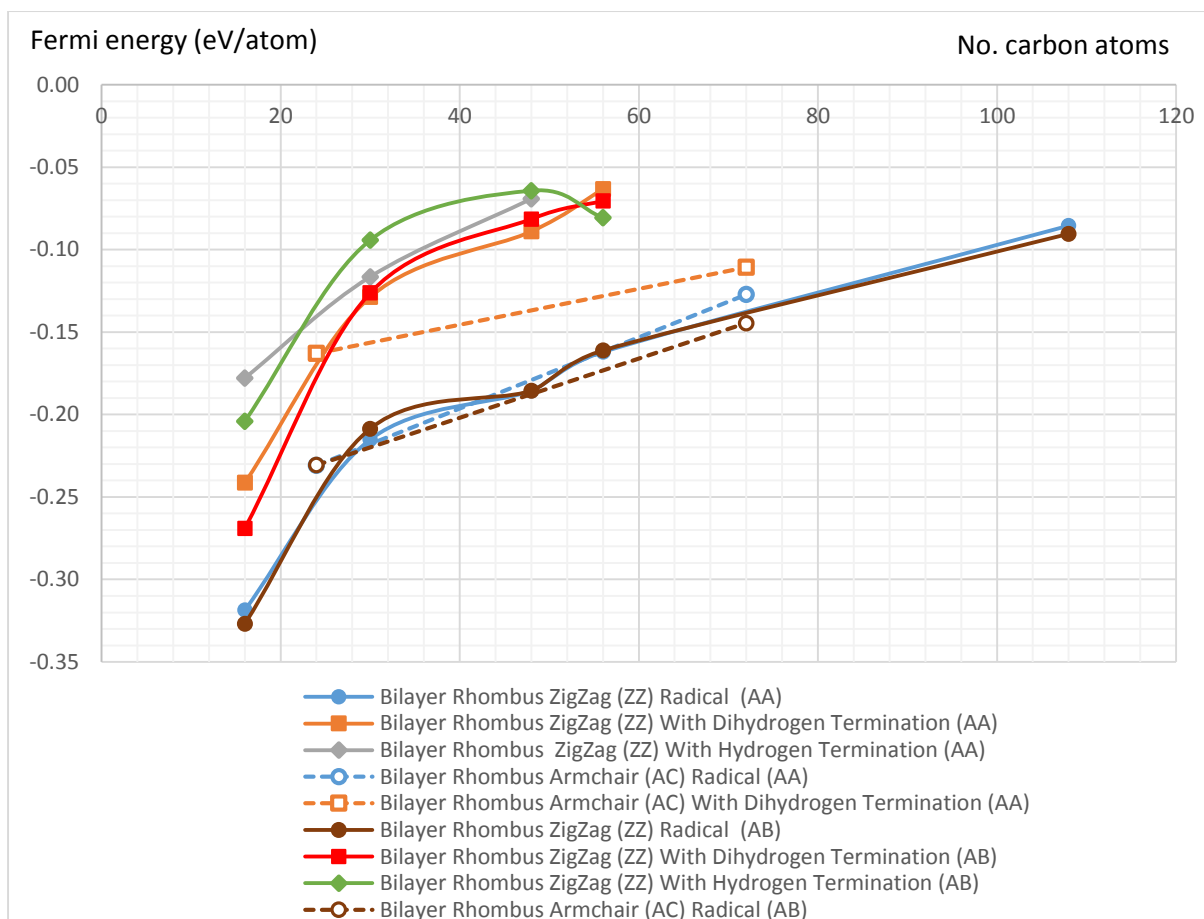
Similarly, E_f is slightly different between the AC and ZZ edge with termination, due to the differences in edge type as well as the weakening of dangling bonds. On top of that, a similar observation is recorded where for AA bilayer stacking configuration of 30 atoms of rhombus shape with ZZ is -0.215 eV/atom while AA bilayer stacking configuration 30 atoms of a trapezium with ZZ is -0.198 eV/atom. However, E_f is found significantly different between the GNFs with and without termination; It is found that termination can efficiently lower in E_f compare to radical due to the high dangling bonds by the hydrogen termination [165][166]. For instance, AA bilayer stacking configuration 16 atoms of trapezium shape of GNFs ZZ edge with hydrogen termination is -0.178 eV/atom while for a system

without hydrogen termination, the values increased to -0.319 eV/atom. In summary, the results show that for bilayer of rhombus and trapezium GNFs, the Fermi energies are dependent on the edge pattern (AC and ZZ edge), the sizing of carbon atoms and most significantly the hydrogen termination.

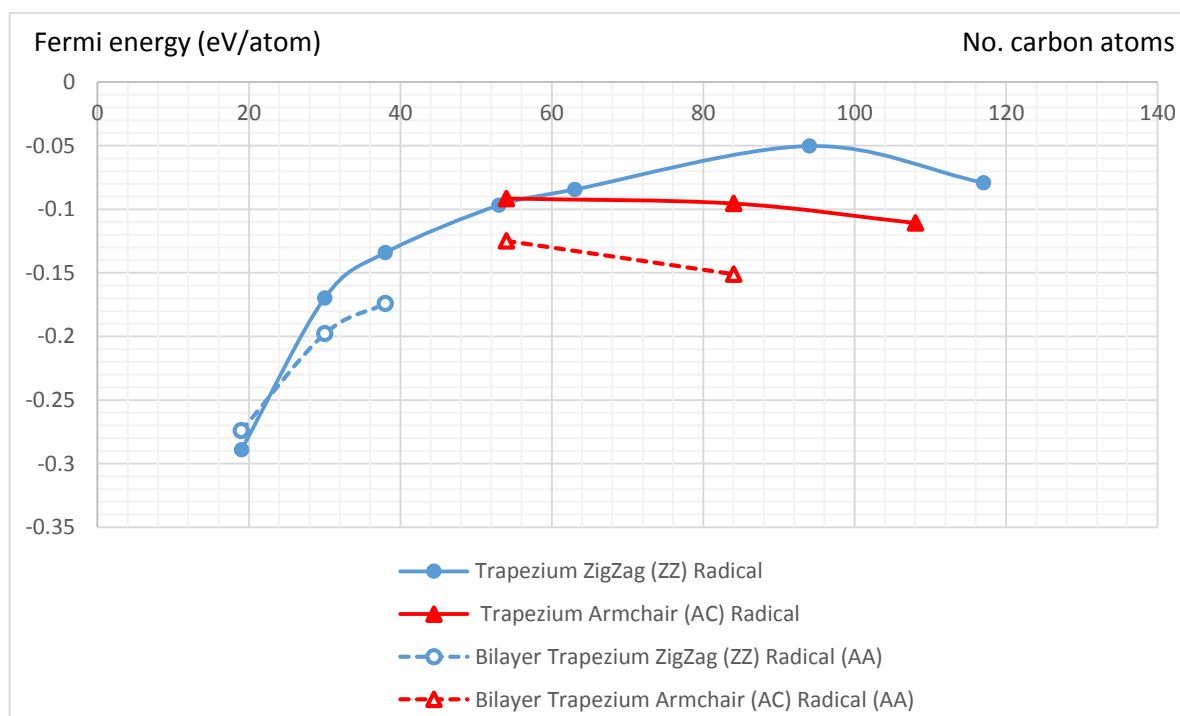
In GNFs, electronic properties are highly depend on the edge configurations, and hence essential to consider the effect of edge passivation.



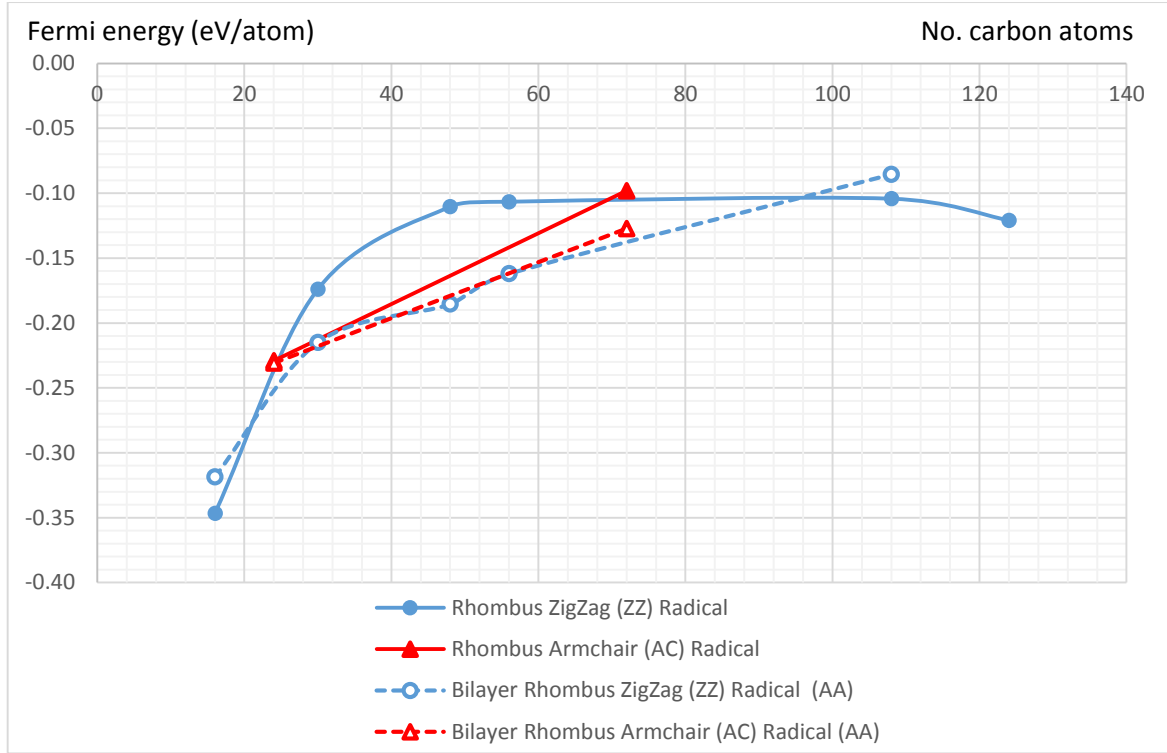
(a)



(b)



(c)



(d)

Figure 5.11: Comparison of the energy of the Fermi level (E_f) between single layer and bilayer of GNFs. (a) Trapezium shape of AA and AB layer configuration with hydrogen termination and dihydrogen termination (b) Rhombus shape of AA and AB layer configuration with hydrogen termination and dihydrogen termination (c) Trapezium shape of AA layer configuration and single layer configuration and (d) Rhombus shape of AA layer configuration and single layer configuration

		Radical (eV/atom)	Hydrogen Termination (eV/atom)	Dihydrogen Termination (eV/atom)
Rhombus	AA	-0.215	-0.117	-0.129
	AB	-0.209	-0.126	-0.094
Trapezium	AA	-0.198	-0.113	-0.118
	AB	-0.198	-0.121	-0.154

Table 4: Comparison of the Fermi energy between 30 atoms Rhombus and Trapezium radical, hydrogen termination and dihydrogen termination with the ZZ edge between bilayer configuration of AA and AB

The Fermi energy for the bilayer stacking configuration is shown in Table 4. In Table 4, we notice that the total energy of trapezium and rhombus shape without hydrogen termination is lower than hydrogen termination and dihydrogen termination. Thus, the Fermi energy bilayer configuration of AA and AB stacking configuration of rhombus and trapezium shape of GNFs is affected by edge type and chemical passivation termination.

5.12 Single Layer Graphene Nanoflakes Integrated Density of States (IDS)

In rhombus shape of GNFs, the edge types are dependable in the sizes but different between sets.

For additional information on the electronic configuration of the rhombus shape of GNFs, the integrated density of states (IDS) presented for the AC and ZZ edges in Figure 5.12.

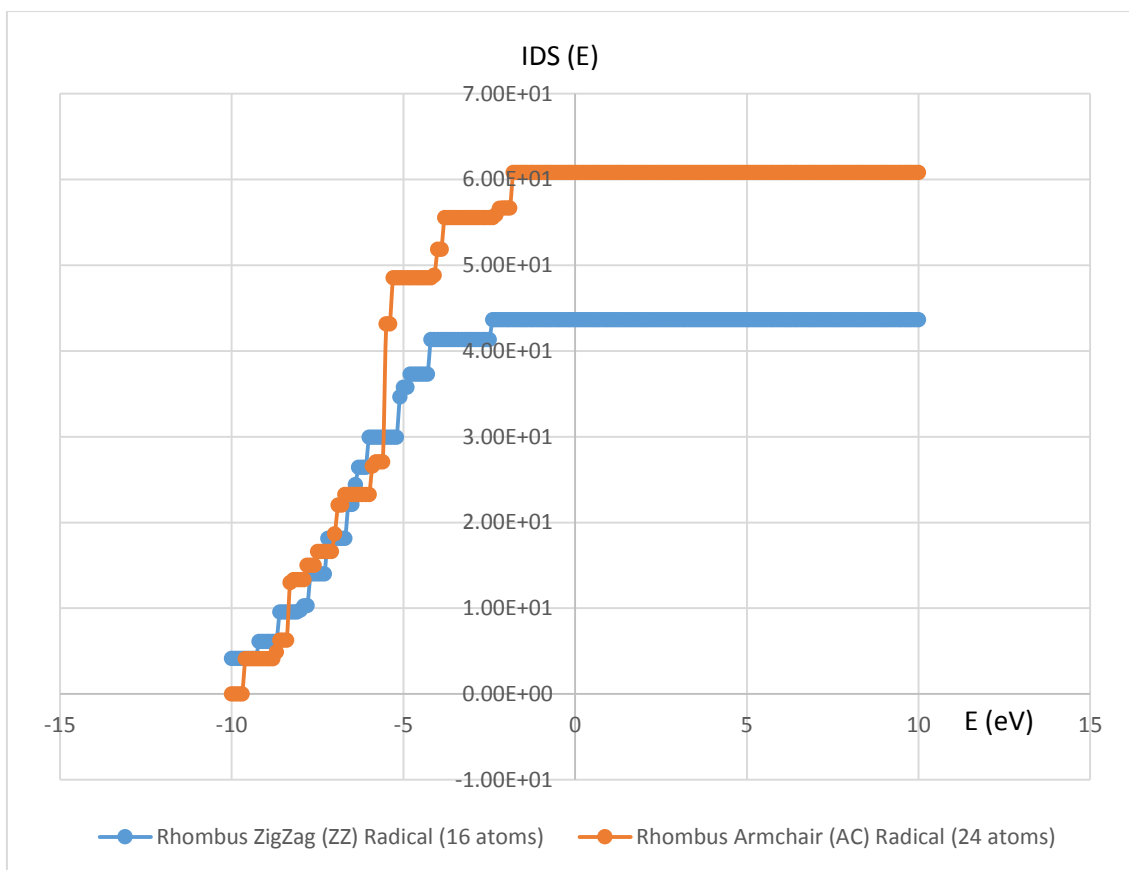
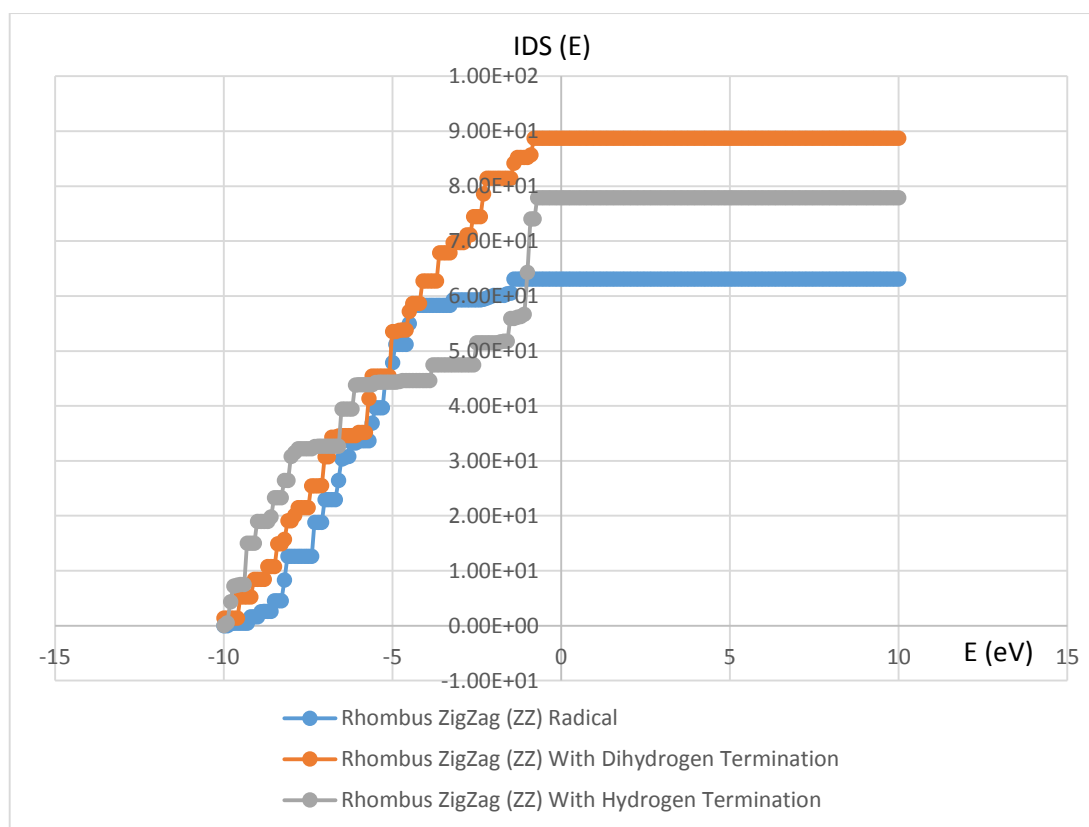
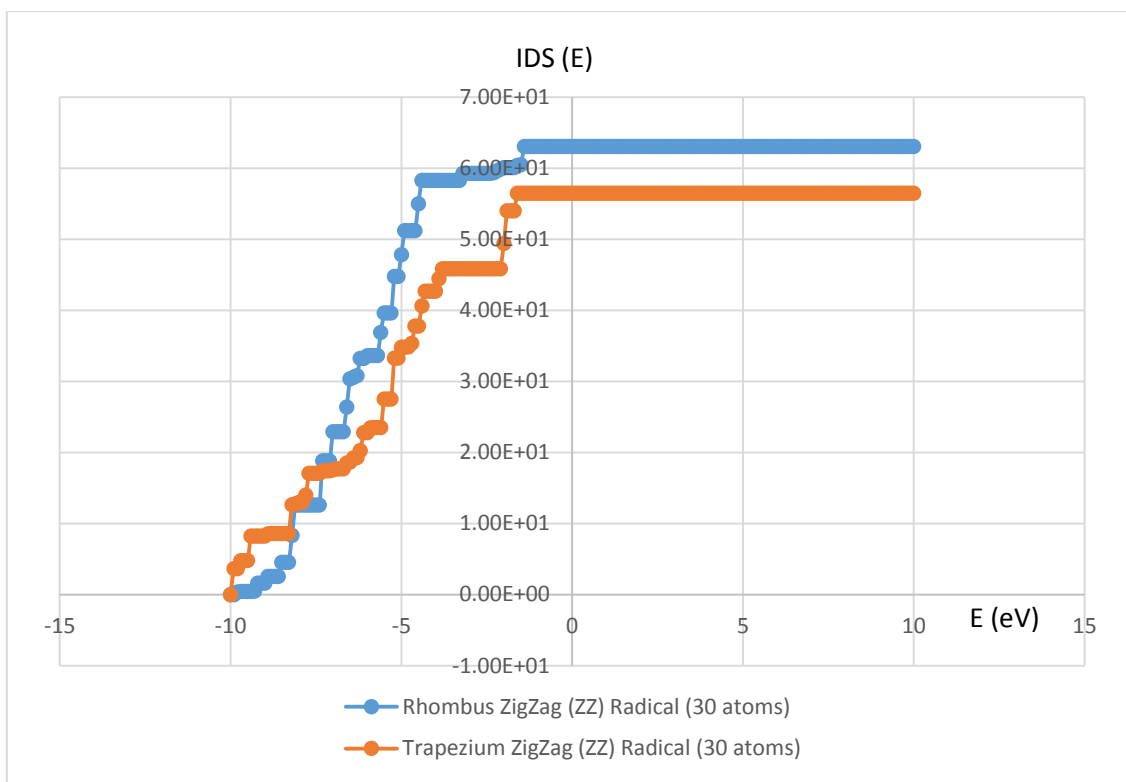


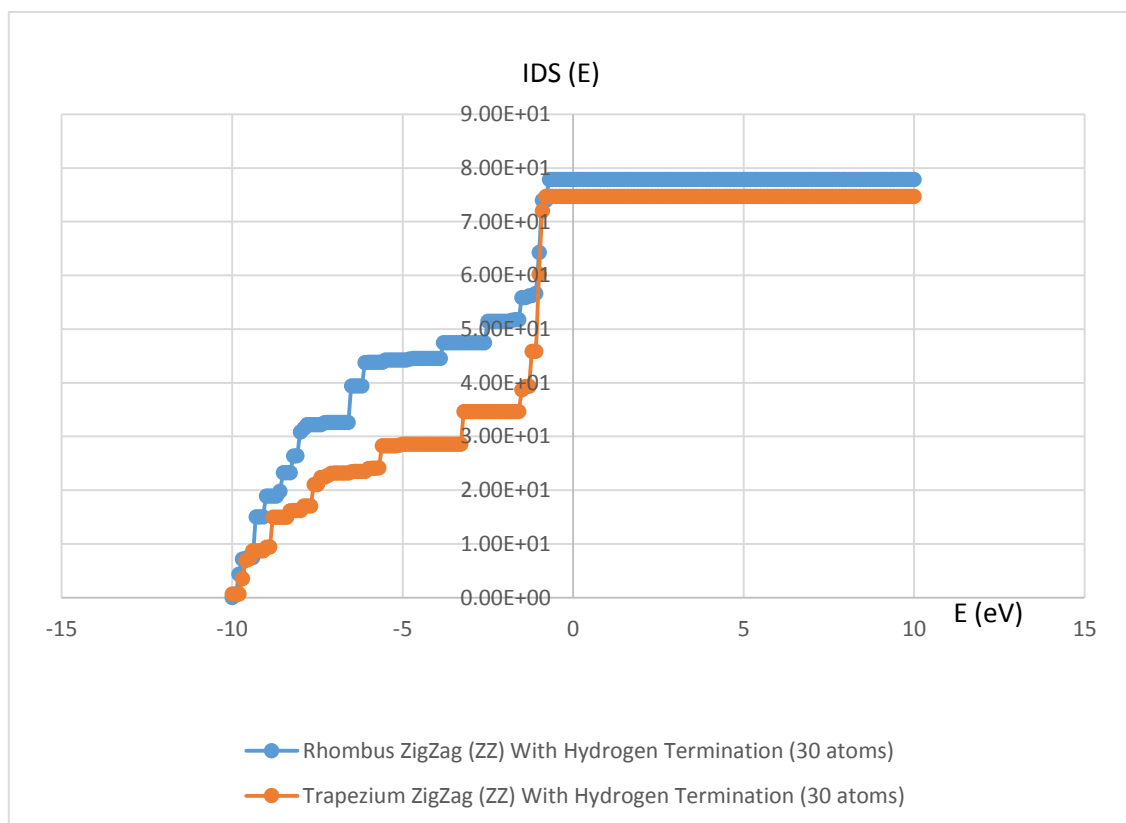
Figure 5.12: IDS of the Rhombus shape of AC edge radicals with 24 carbon atoms and the ZZ edge radicals with 16 carbon atoms



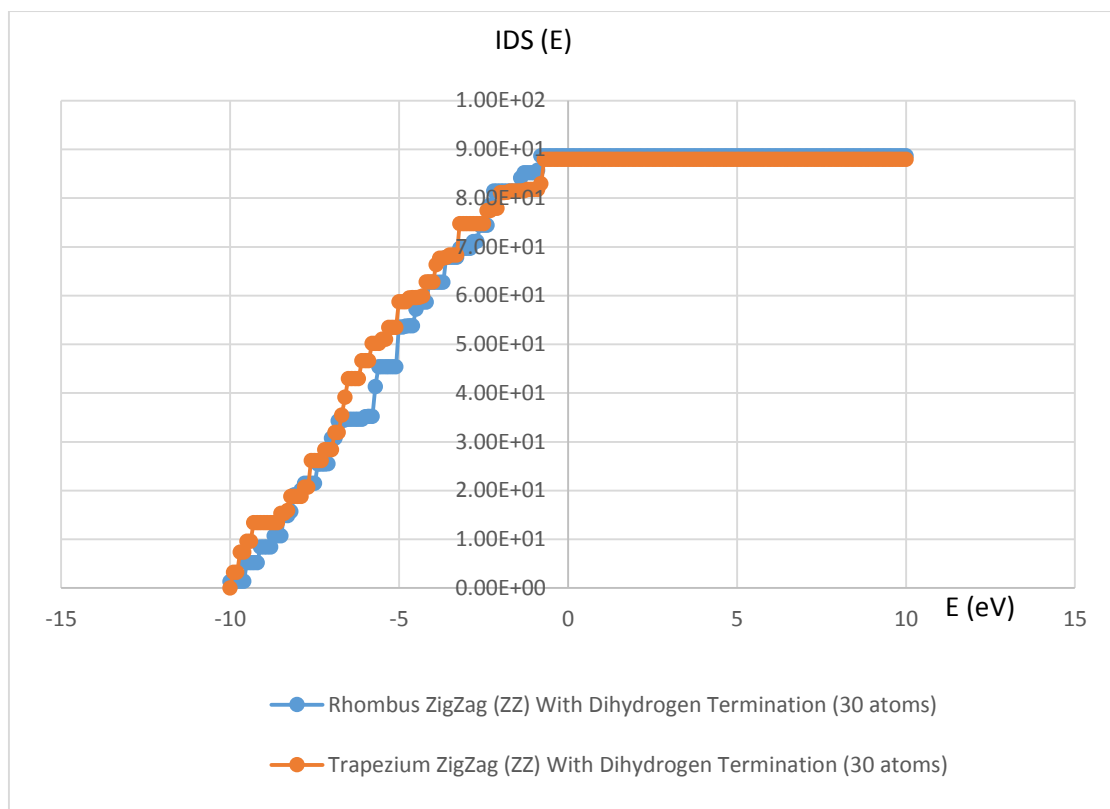
(a)



(b)



(c)



(d)

Figure 5.13: IDS GNFs, comparing (a) the C_{30} Rhombus shape of GNFs ZZ edge with radical, hydrogen termination and dihydrogen termination. (b) the C_{30} Rhombus and Trapezium ZZ edge with radical (bare) GNFs. (c) The C_{30} Rhombus and Trapezium ZZ edge with hydrogen termination GNFs and (d) the C_{30} and Rhombus and Trapezium ZZ edge with dihydrogen termination GNFs.

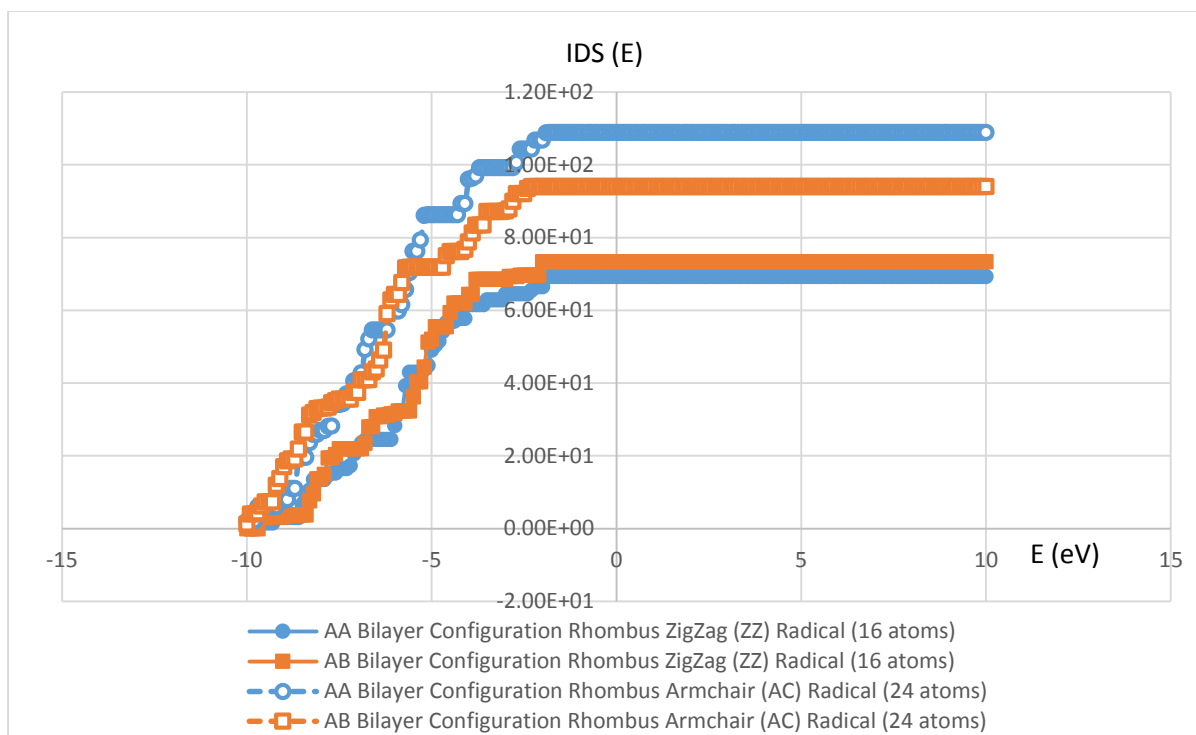
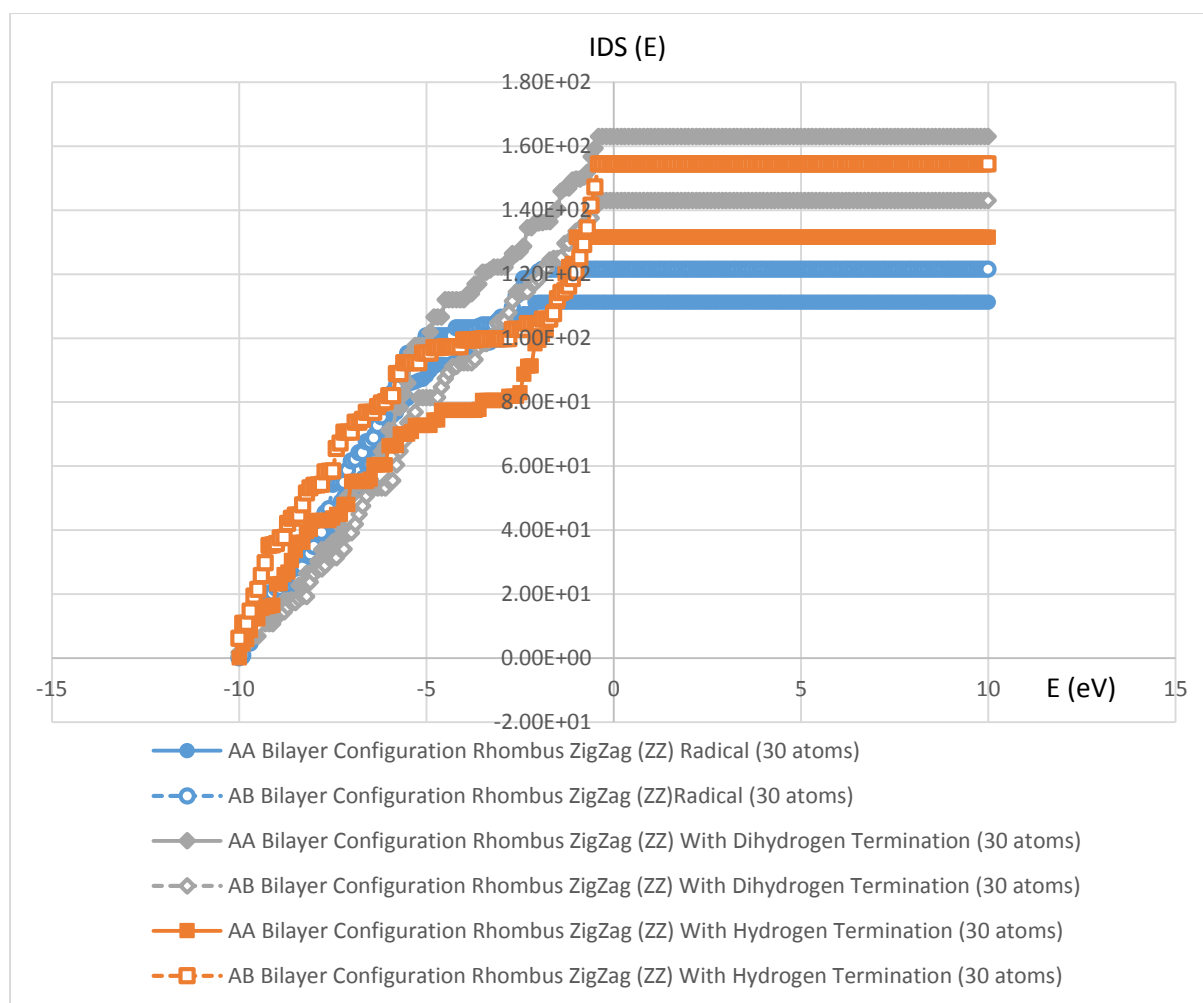
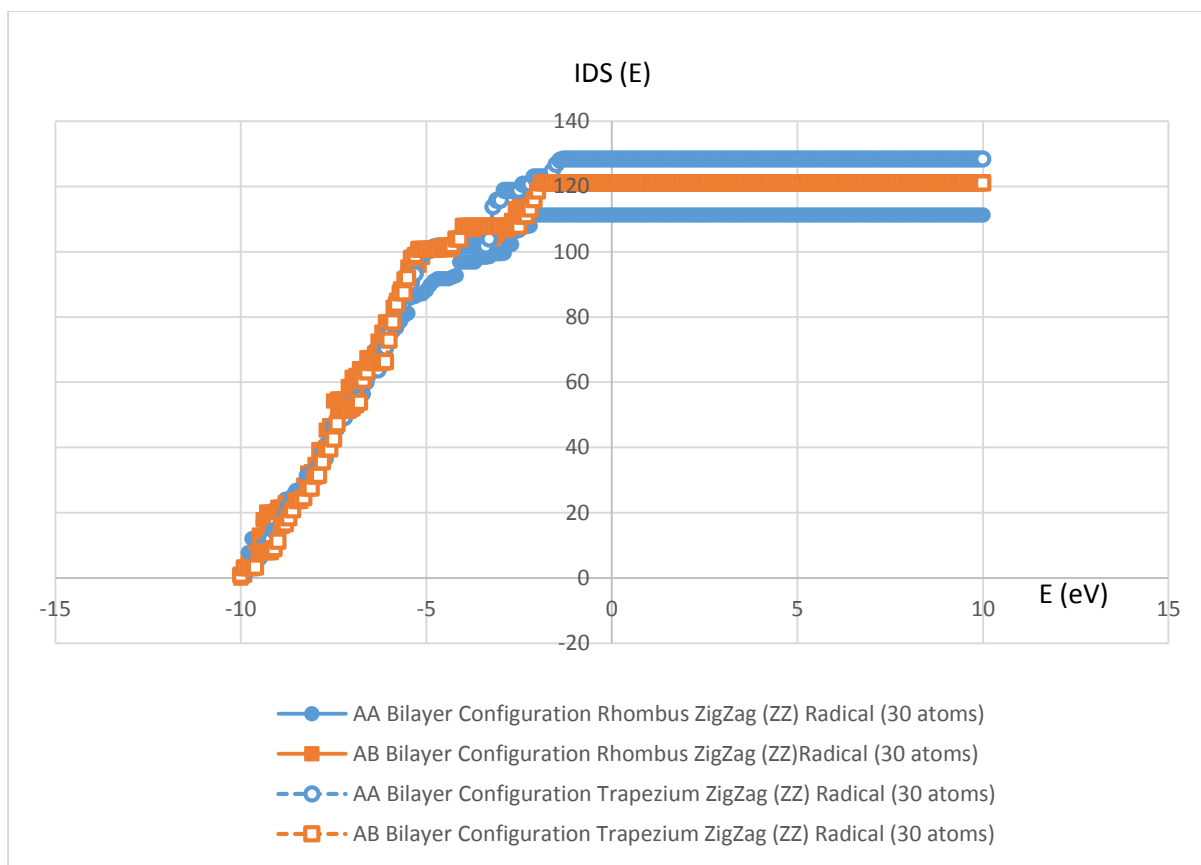


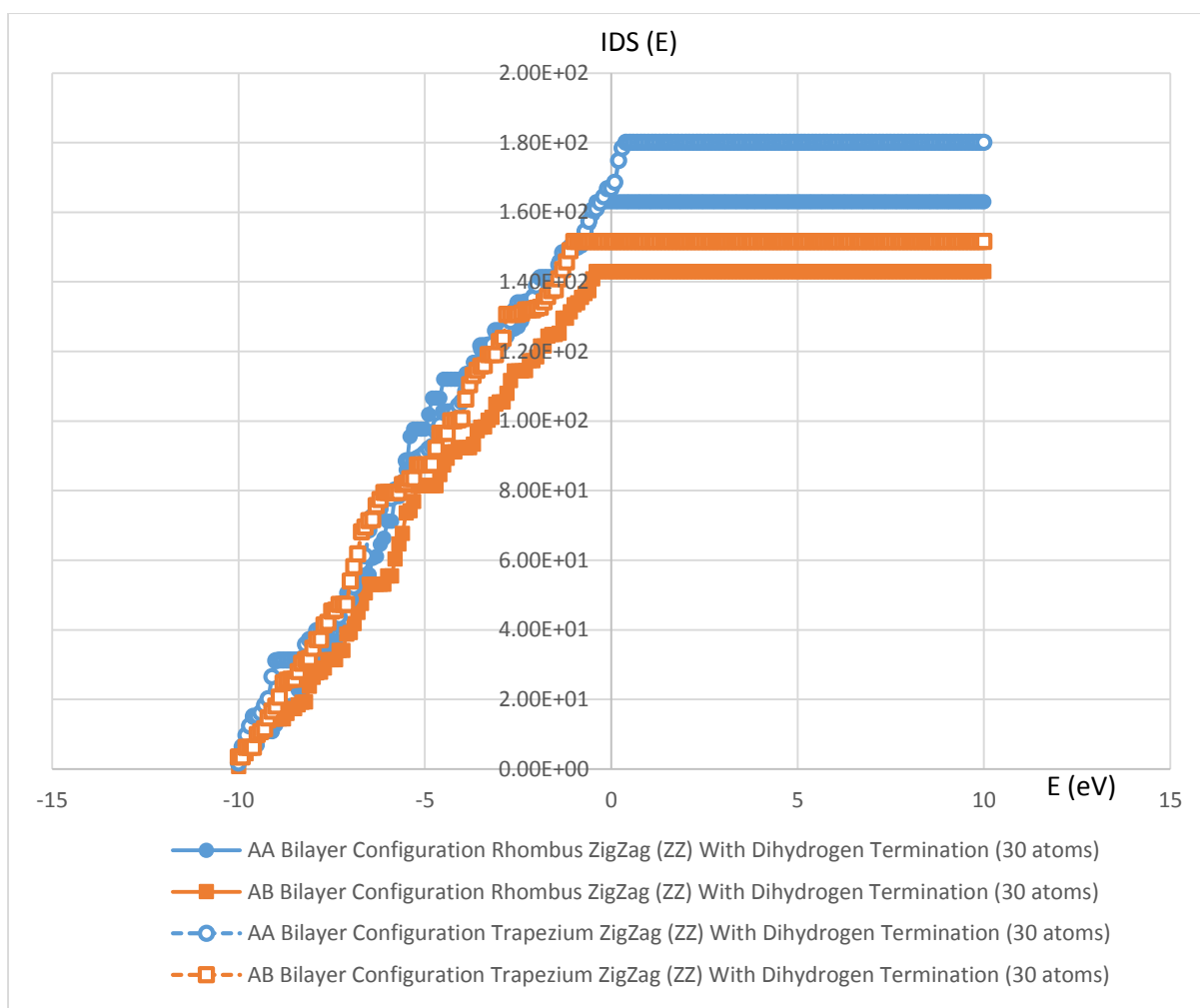
Figure 5.14: IDS of the AA and AB Bilayer configuration Rhombus shape AC edge radicals with 24 carbon atoms and the ZZ edge radicals with 16 carbon atoms



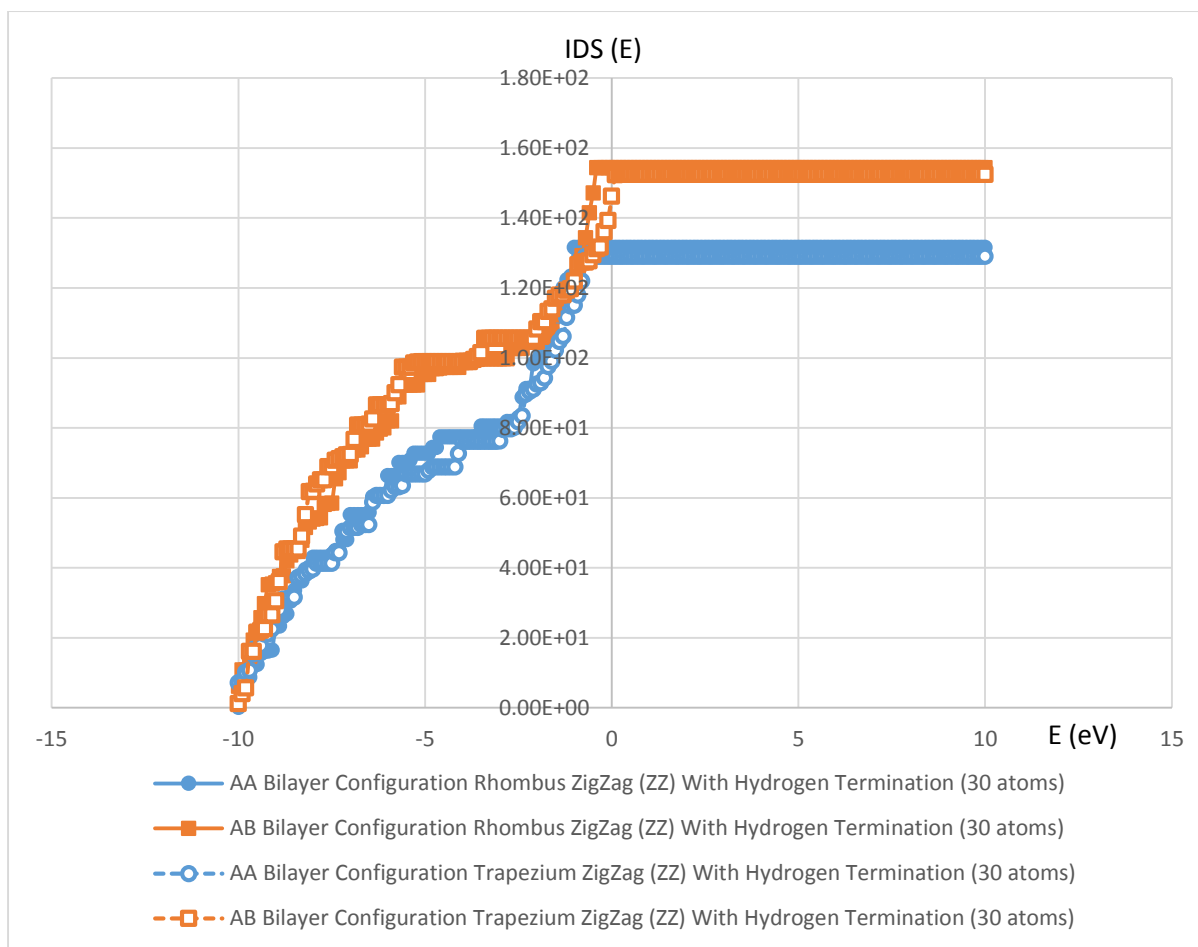
(a)



(b)



(c)



(d)

Figure 5.15: IDS of AA and AB Bilayer configuration of GNFs, comparing (a) the C₃₀ Rhombus shape of GNFs ZZ edge with radical, hydrogen termination and dihydrogen termination. (b) the C₃₀ Rhombus and Trapezium ZZ edge with radial (bare) GNFs. (c) The C₃₀ Rhombus and Trapezium ZZ edge with hydrogen termination GNFs and (d) the C₃₀ and Rhombus and Trapezium ZZ edge with dihydrogen termination GNFs.

Figure 5.12 has two set data point; 16 carbon atoms radical rhombus shape of GNFs with a ZZ edge and 24 carbon atoms radical rhombus shape

of GNFs with an AC edge. The IDS for radical, hydrogen termination and dihydrogen termination ZZ-C₃₀ configurations are compared in Figure 5.13(a). The IDS energy in 24 carbon atoms radical rhombus shape is higher than 16 carbon atoms radical rhombus shape.

Furthermore, the IDS for radical, hydrogen termination and dihydrogen termination ZZ-C₃₀ structures are compared in Figure 5.13(b)–(d), respectively. Figure 5.13 (b)–(d) compares between rhombus and trapezium shape of GNFs, where trapezium shape has IDS higher than rhombus shape. A comparison of the results reveals that the difference in the IDS can reliably attribute to the number of layers, various shape and the different edges.

CHAPTER 6 CONCLUSIONS AND FUTURE WORK

This chapter summarises the results acquired from the current analysis and highlights the project major discoveries. In addition, suggestions and recommendations for future research can be accomplished are provided as well to further understanding the GNFs fundamental electronic properties with various shapes.

6.1 Conclusions

When GNFs increase the number of carbon atoms and different shape, the resultant atomic configuration exhibits different shape structure and size dependence.

This thesis endeavour to conduct a comprehensive study on selected shapes (rhombus and trapezium) of GNFs and the size up to 100 carbon atoms. To studied the different shapes of GNFs that rarely reported previously, the number of carbon atoms from 16 to 100 are selectively chosen to be used in the current research study. The project aims to study the GNFs structural and electronic properties, i.e. (1) total energy, (2) Fermi energy, and (3) integrated density of states (IDS). The integrated density of state (IDS) is an essential physical information in graphene material analysis, particularly in the atomistic system theoretical study.

In the thesis, the first principle density functional theory (DFT) is adopted to aquire GNFs geometries. The applicability of DFT in studying the GNFs properties within the framework of GGA and LDA model is adopted, by using the PAW potentials as the analysis parameter. The code used in

this thesis is known as QE, which is made by the CNR-INFM DEMOCRITOS National Simulation Center in Trieste (Italy). Concurrently, various aspects of DFT have been employed to explore the fundamental electronics properties of GNFs with various structural shapes, namely rhombus and trapezium, in the order of ascending in the number of carbon atoms.

QE is a free and open source software that can be employed to conduct first principle calculation based on the DFT. DFT is widely used to evaluate important intrinsic properties of materials, such as equilibrium geometry, quantum energy levels, optoelectronic properties, vibrational properties, IR spectrum, etc. Therefore, the DFT computational strategy utilized in this thesis provided a suitable and practical path, with accurate calculation on the quantum energy level of graphene nanomaterial. As a measure to verify whether the density functional theory (DFT) produces reliable value, in this thesis has undertaken different research and comparison against the available structures studied in the literature. In summary, the comparative study of total energy results indicates that many of the structures obtained from this work are in great understanding with those obtained from the literature, while others are similar [121][167].

The structural effects of GNFs on its quantum energy level have been reported in this thesis. The findings add to the understanding of fundamental electronic properties. These structural-dependant behaviours have notably been reported in the literature, as evidenced by a complete literature search when this thesis work. This study adds to the body of

expertise on the shape and edge effects of graphene nanomaterial associated with the fundamentals of electronic properties. However, some limitations need to be considered. For instance, the total energy of the single layer and bilayer GNFs.

The present work has also explicitly demonstrated that graphene nanoflakes structural and electronic properties are size dependent. The plots of size-dependence electronic properties of single layer GNFs are shown in Figure 5.1–Figure 5.15. The results dictate the significance of three important aspects like total energy, Fermi energy and integrated density of States (IDS). From the modelling analysis, it shows that the Fermi energy of GNFs is greatly influenced by the shape configuration, number of carbon atoms, with and without hydrogen passivation as well as edge configurations. Although the shape and edge configuration is an essential part of the electronic properties, but chemical passivating the edges will readily remove any shape depend on advantage. Hydrogenated and dihydrogenated GNFs are two systems that has be used to study the fundamental electronics properties.

In addition, DFT calculations have been carried out to investigate the bilayer GNFs with different shapes and edges (AC and ZZ). The edge effect as well as the shapes of GNFs are discovered to have a robust effect on the electronic properties, particularly in total energy, Fermi energy and integrated density of states (IDS).

In conclusion, the objectives of this research have achieved. The thesis has provided a detailed technical description on evaluating the fundamental quantum levels of graphene material using the DFT.

6.2 Future Work

Based on the results and observations we recommend the following for future works.

1. Further research is needed to better understand the fundamental electronic properties like HOMO-LUMO, cohesive energy, and binding energy, the density of states (DOS), total energy and Fermi energy of GNFs in triangular, hexagonal, rhombus and trapezium shapes shall be conducted.
2. An implication of these findings are is not only for single layer and bilayer GNFs in different shapes, trilayer/ multilayer GNFs in different shapes shall be studied fundamental electronics properties thoroughly as well.
3. The findings of this study have some significant implications that future research should concentrate on various number of layers of GNFs in different shapes with hydrogen termination, fluorine termination, di-hydrogen termination and di-fluorine termination to study the various fundamental electronic properties.

4. Finally, future works can be carried on the magnetic and optical properties of GNFs with different number of layers and different dimensions with hydrogen termination, fluorine termination, di-hydrogen termination and di-fluorine termination.

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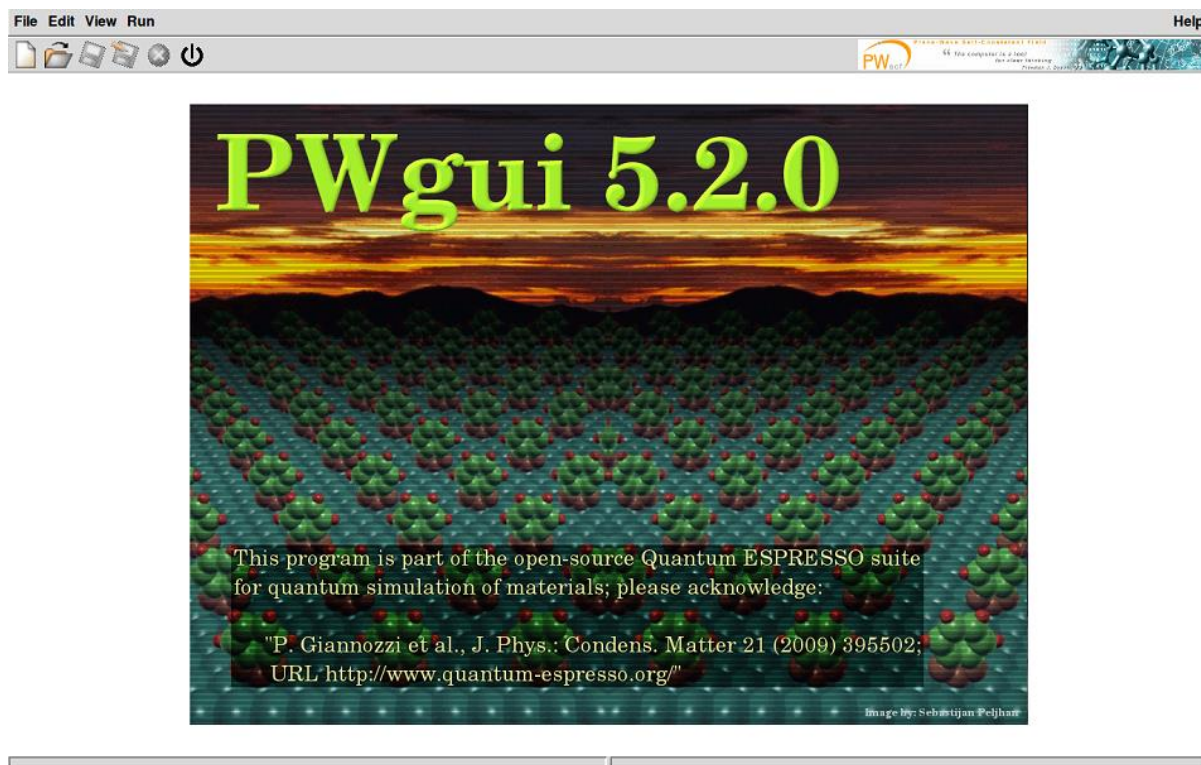
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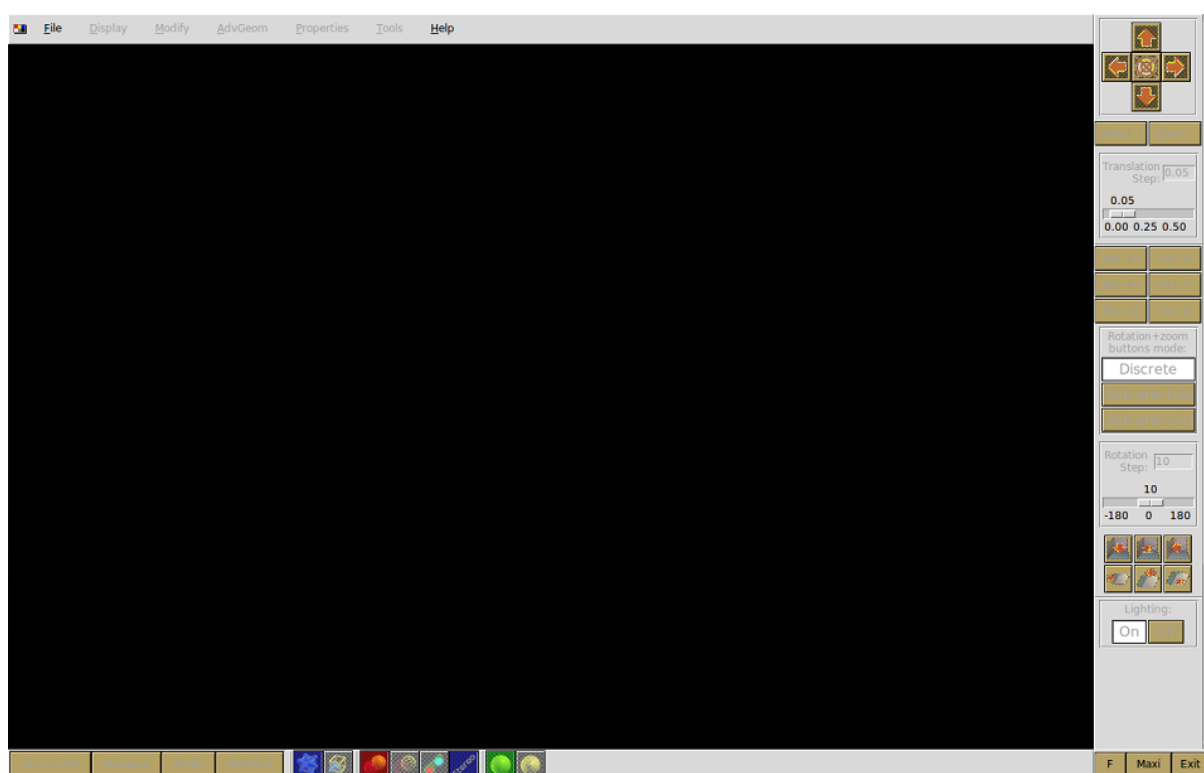
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APPENDIX

QUANTUM ESPRESSO PWgui: A PWscf's GUI



QUANTUM ESPRESSO XCrySDen



QUANTUM ESPRESSO self consistent

&CONTROL

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    pseudo_dir = '/home/user/Desktop/espresso-5.3.0/pseudo/' ,  
    prefix = 'GNFH16atoms' ,  
    disk_io = 'high' ,  
    verbosity = 'high' ,
```

/

&SYSTEM

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    celldm(1) = 23.30 ,  
    celldm(3) = 4.65 ,  
    nat = 16 ,  
    ntyp = 1 ,  
    ecutwfc = 30.0 ,  
    ecutrho = 120.0 ,  
    occupations = 'smearing' ,  
    degauss = 0.01 ,  
    smearing = 'methfessel-paxton' ,
```

/

&ELECTRONS

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    conv_thr = 1.0d-8 ,  
    mixing_beta = 0.7 ,
```

/

ATOMIC_SPECIES

C 12.07010 C.pbe-van_ak.UPF

ATOMIC_POSITIONS angstrom

C	1.230600000	2.131500000	0.000000000
C	2.461200000	1.421000000	0.000000000
C	1.230600000	3.552500000	0.000000000
C	0.000000000	4.263000000	0.000000000
C	1.230600000	6.394500000	0.000000000
C	0.000000000	5.684000000	0.000000000
C	1.230600000	7.815500000	0.000000000
C	2.461200000	8.526000000	0.000000000
C	3.691900000	2.131500000	0.000000000
C	3.691900000	3.552500000	0.000000000
C	2.461200000	4.263000000	0.000000000
C	3.691900000	6.394500000	0.000000000
C	2.461200000	5.684000000	0.000000000
C	3.691900000	7.815500000	0.000000000
C	4.922500000	4.263000000	0.000000000
C	4.922500000	5.684000000	0.000000000

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QUANTUM ESPRESSO Non self consistent

&CONTROL

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prefix = 'GNFH16atoms' ,  
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verbosity = 'high' ,
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/

&SYSTEM

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celldm(3) = 4.65,  
nat = 16,  
ntyp = 1,  
ecutwfc = 30.0 ,  
ecutrho = 120.0 ,  
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degauss = 0.01 ,  
smearing = 'methfessel-paxton' ,
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/

&ELECTRONS

```
conv_thr = 1.0d-8 ,  
mixing_beta = 0.7 ,
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/

ATOMIC_SPECIES

C 12.07010 C.pbe-van_ak.UPF

ATOMIC_POSITIONS angstrom

C	1.230600000	2.131500000	0.000000000
C	2.461200000	1.421000000	0.000000000
C	1.230600000	3.552500000	0.000000000
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C	4.922500000	5.684000000	0.000000000

K_POINTS automatic
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QUANTUM ESPRESSO DOS

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ngauss = 0,
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