

FIRST-PRINCIPLES INVESTIGATION OF FUNCTIONALIZATION OF GRAPHENE

A THESIS

SUBMITTED TO THE DEPARTMENT OF PHYSICS

AND THE GRADUATE SCHOOL OF ENGINEERING AND SCIENCE

OF BILKENT UNIVERSITY

IN PARTIAL FULFILLMENT OF THE REQUIREMENTS

FOR THE DEGREE OF

MASTER OF SCIENCE

By

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January, 2013

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ABSTRACT

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M.S. in Physics

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January, 2013

The graphene sheet is a single-atom thick novel material and attracts great interest due to its unique features. However, it is a metallic material with no bandgap, which makes it difficult to integrate in electronic applications. Adatom adsorption is one of the promising ways to make this structure functional. To this end, electronic and structural properties of graphene have been investigated by using density functional theory formalism in order to understand atomic level interaction between halogen adatoms and graphene layer. The most common adatom, hydrogen, has also been studied. In this study, plane-wave, pseudo-potential density functional theory calculations were carried out using generalized gradient approximations for the exchange correlation potential with the Quantum Espresso package. In order to obtain fully relaxed structures, geometry optimization has been performed in all of the calculations. The adatom-graphene system is modelled with a 4×4 graphene supercell. Adsorption energies of halogen adatoms and dimers adsorbed on highly symmetric positions on graphene layer are calculated. Different configurations of adatoms have been tested. Specific properties such as band structure and density of states of these system have been investigated. The results show that a fully covered graphene layer is stable and optimized structures exhibit a band gap of a few eV. The most stable structure among halogen adatoms is the fluorine adsorbed on graphene. It has the highest electronegativity, which is the reason for high electron transfer from the graphene layer. This is the reason of the formation of covalent bonds. Furthermore, the most stable configuration is found to be chair configuration with the halogen atoms alternating in both sides of the layer.

Keywords: graphene, adsorption on graphene, graphane, halogen atoms, DFT, plane-wave pseudo-potential calculations.

ÖZET

GRAFENİN İŞLEVLEŞTİRİLMESİNİN İLK PRENSİP TEKNİKLERİYLE İNCELENMESİ

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Ocak, 2013

Tek atom kalınlığındaki grafen, bilinen ilk iki boyutlu nanomalzemedir ve benzersiz özellikleri nedeniyle oldukça ilgi çekmektedir. Ancak, kimyasal olarak aktif olmayan ve bant boşluğu olmayan bu malzemenin, elektronik uygulamalarda kullanımı zor olmaktadır. Çeşitli atomların grafen üzerine yapışması bu malzemeyi işlevsel hale getirmenin bir yoludur. Bu sebeple atomik boyutta grafen ve halojen atomlarının etkileşimlerini incelemek için, işlevleştirilmiş grafen sisteminin elektronik ve yapısal özellikleri yoğunluk fonksiyonları teorisi kullanılarak irdelenmiştir. Halojen atomlarının yanı sıra, sıkça kullanılan hidrojen atomunun bağlanması da çalışılmıştır. Hesaplamalar, düzlem dalga sanki potansiyel metodu ve genelleştirilmiş gradiyent yaklaşımı kullanılarak Quantum Espresso paketi ile yapılmıştır. Yapışan atom ve grafen sistemi 4×4 periyodik yapıda modellenmiştir. Halojen atomları ve dimer grafenin yüksek simetrideki noktalarına konulup bağlanma enerjileri hesaplanmıştır. Farklı konfigürasyondaki yapılar karşılaştırılarak denenmiştir. Sistemlerin bant diyagramı ve durum yoğunluk özellikleri çıkarılmıştır. Çalışmalar sonucunda, grafen yüzeyine atom bağlanmasının bir kaç elektronvolt büyüklüğünde bant aralığına sahip kararlı yapılar oluşturduğu gözlemlenmiştir. Çalışılan yapıların arasında en kararlısı flor atomlarının bağlandığı sistemdir. Yüksek elektron çekme özelliği bu yapının kovalent bağ oluşturmaya ve kararlı olmasına neden olur. Ayrıca, en kararlı konfigürasyon halojen atomlarının grafenin alt ve üst yüzeyine yapışan durumudur.

Anahtar sözcükler: grafen, grafen üzerinde bağlanma, halojen atomları, yoğunluk fonksiyonları teorisi, düzlem dalga sanki potansiyel hesapları.

Acknowledgement

I would like to direct my special thanks to my supervisor, Professor Oğuz Gülseren for giving me opportunity to work with him, helping me in solving different problems and for his encourage during the period of this work. His willingness to answer every questions I have had and his ability to recognize interesting ideas at an early stage has made this thesis complete. His unfailing support, guidance and excellent discussions are very valuable. I also had great support from my family. I thank them for their understanding and endless love through the duration of my studies.

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Chapter 1

Introduction

Carbon is the building block of life and it is one of the most abundant elements in nature. It was discovered by Lavoisier in 1789 [2] and has many different allotropes such as diamond, graphite, carbon nanotubes and graphene. All carbon allotropes are stable structures because of the hybridization type, which has opened up interesting horizons on carbon-based materials. Its most inert form is

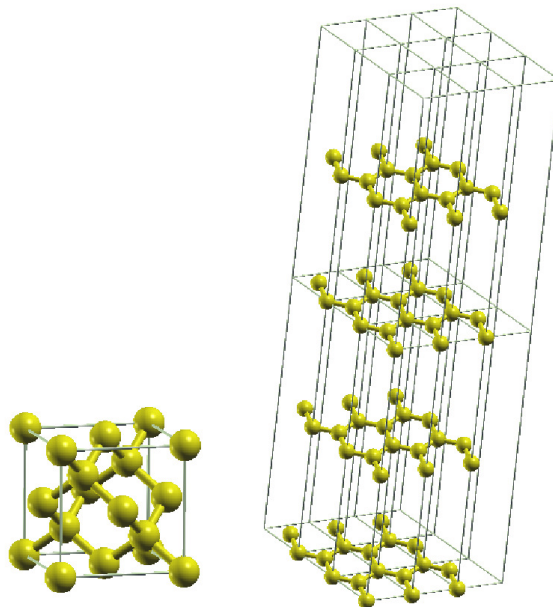


Figure 1.1: Schematic representation of Diamond and Graphite structures .

diamond which has very high thermal conductivity and hardness. Carbon atoms

in diamond structure make tetrahedral bonds. It is an insulating material with a large band gap. It transmits all the spectrum of light which makes it very valuable material in industrial applications.

Graphite is another important carbon structure. Layers of carbon atoms are stacked on each other forming three dimensional structure. These layers are held together by weak van der Waals forces. One of the very first studies of graphite structure is by B.T Kelly in 1981. [3] In this study, the elastic properties of graphite have been reviewed, displacement and irradiation effects of atoms in the graphite structure have been studied in detail.

After the discovery of graphite, it was believed that fabrication of monolayer graphite structure is not possible due to the thermal instability. However, the material called "graphene" was exfoliated in 2004 by Geim and K.S. Novoselov [4, 5]. This monolayer structure has amazing properties and lead researchers to work in quantum relativistic effects and low dimensional physics despite its short history of syntesis. However, this structure is chemically inert and in order to make this material chemically active different approaches have been tried at different levels of sophistication.

Adatom adsorption is a method to make graphene active and has become very popular over the last few years. The primary goal of this thesis is to study theoretically adatom and dimer adsorption on graphene. To this aim, we have investigated structural properties of several atoms and dimers.

This thesis is composed from four chapters. In this chapter, the basics of graphene crystal structure and its place in condensed matter world have been briefly reviewed. Moreover, the important studies on graphene in the scope of tailoring electronic and structural properties have been summarized. The following chapter covers theoretical background of Density Functional Theory (the schemes and approximations that we have used are also explained). Chapter 3 and 4 present the calculations, results and concluding remarks, respectively. Finally, a brief discussion on Quantum Espresso Package [6] is included at the end of the thesis.

1.0.1 The Graphene Structure

Graphene is a two dimensional, one carbon-atom thick material with each C atom forming three bonds with each of its nearest neighbors. It can be considered as a building block of carbon materials of other dimensionalities such as the 0 dimensional bucky ball, 1 dimensional carbon nanotubes and 3 dimensional graphite. It has become very popular over the last few years because it represents

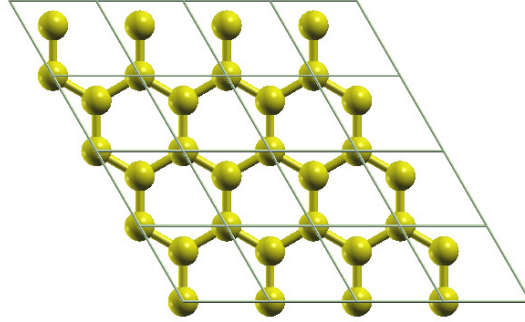


Figure 1.2: *Schematic representation of single layer graphene .*

new type of material which offers a strong ground for applications. [7]

Graphene is the first two-dimensional material with high crystal quality. It was believed that two dimensional materials are thermodynamically unstable and thus can not be used in applications. However, the soft crumbling in the third dimension in graphite made it possible to fabricate this structure.

Graphene has a honeycomb lattice, as shown in figure 1.3 with lattice vectors in real space are given by

$$\mathbf{a}_1 = \frac{a\sqrt{3}}{2}\hat{x} + \frac{a}{2}\hat{y} \quad (1.1)$$

$$\mathbf{a}_2 = \frac{a\sqrt{3}}{2}\hat{x} - \frac{a}{2}\hat{y} \quad (1.2)$$

where $a = \sqrt{3}a_{cc}$ and $a_{cc} = 1.42$ Ångstrom is the carbon-carbon distance in

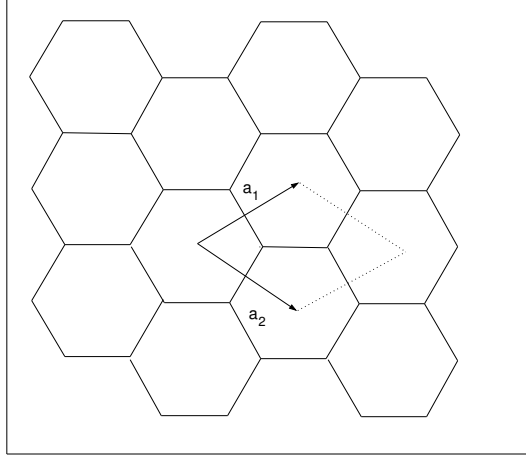


Figure 1.3: *Crystal structure of single layer graphene .*

graphene. Reciprocal lattice vectors in momentum space are given by

$$\mathbf{b}_1 = \frac{b}{2}\hat{x} + \frac{b\sqrt{3}}{2}\hat{y} \quad (1.3)$$

$$\mathbf{b}_2 = \frac{b}{2}\hat{x} - \frac{b\sqrt{3}}{2}\hat{y} \quad (1.4)$$

where $b = \frac{4\pi}{a\sqrt{3}}$.

In contrast to diamond, the carbon atoms in graphitic materials are sp^2 hybridized. Carbon has four valence orbitals ($2s, 2p_x, 2p_y, 2p_z$). Graphene sheet is formed when s , p_x and p_y orbitals are combined forming σ (bonding) and σ^* (antibonding) orbitals. The remaining p_z orbital extends along the z direction on the graphene sheet. The interaction among p_z orbitals creates the delocalized π (bonding) and π^* (antibonding) orbitals [8, 9]. Graphene consists of covalently bonded carbon atoms and this strong binding comes from the σ bonds. However, the fourth valence electron does not contribute to the covalent bond, instead these p_z orbitals form weakly interacting graphene layers. The high symmetry points of the reciprocal space and the band structure for graphene are shown in Figure 1.4 and 1.5 respectively. At low temperatures, cosine like energy band is linear, $E = \hbar v_F k$, and therefore, it also has linear dependence of density of states at the K point. At the edge of the Brillouin zone, these two linearly dispersing bands touch each other. That is called Dirac point and electrons and

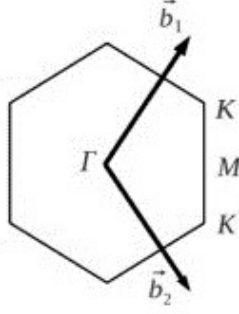


Figure 1.4: *High symmetry points Γ, K, M in reciprocal space .*

holes at the corners of the Brillouin zone have zero effective mass and these are called massless Dirac fermions. This reduction in mass of the fermions is caused by the interaction with the periodic potential of honeycomb lattice. It has the honeycomb shape lattice with two equivalent carbon sublattices. Since each of two sublattices should contribute as two different wavefunctions at Dirac points, they are known as pseudospin and shown by σ in Dirac Hamiltonian [7]

$$\hat{H} = \hbar v_F \begin{pmatrix} 0 & k_x - ik_y \\ k_x + ik_y & 0 \end{pmatrix} = \hbar v_F \vec{\sigma} \cdot \vec{k} \quad (1.5)$$

where $\vec{k}$ is the quasiparticle particle, $\vec{\sigma}$ is the 2D Pauli matrix, v_F plays the role of speed of light. They are 1/2 spin particles (fermions). Moreover, these particles have very high mobility, they have velocity of an effective speed of light ($v_F = 10^6$ m/s) and it is independent of temperature between 10 to 100 K. These charge carriers can travel thousands of interatomic distance before colliding.

This exceptional property of high mobility gives rise to the anomalous quantum Hall effect when they are exposed to magnetic field at high temperatures. Underlying theory of Hall effect is as follows. When the electric current is flowing in the wire in the $\hat{x}$ direction and a magnetic field B_z applied normal to the wire in the $\hat{z}$ direction. An additional electric field normal to both of these fields is created. Hall conductivity is given by $\sigma = \nu \frac{e^2}{h}$. where ν is the filling factor and depending on this constant (integer or fractional) Hall effect is named as integer quantum Hall effect or fractional Hall effect and Hall constant for electron

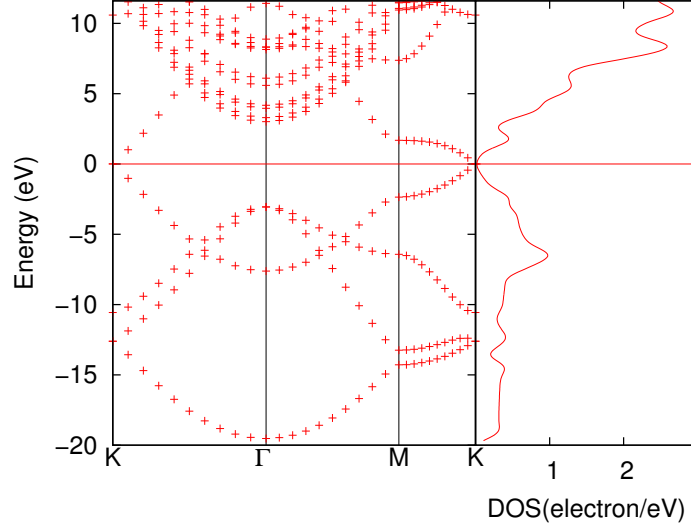


Figure 1.5: *Electronic band structure and density of states of single layer graphene as calculated within DFT formalism.*

is proportional to concentration electrons n_e and given by $R = -\frac{1}{n_e e}$. The same applies to holes with the + sign in front [10].

Quantum Hall effect is observed in two dimensional electron systems and graphene is a suitable candidate for observing the quantum Hall effect because under external magnetic field it has discrete energy levels (Landau Levels) and these levels have large separation [11]. Under a magnetic field, the Landau level at zero energy identifies the difference between hole and electron states. [12]. Longitudinal ρ_{xx} and the Hall component ρ_{xy} of resistivity (ρ) and conductivity (σ) tensors are given by [12]

$$\rho_{xx} = \frac{\sigma_{xx}}{\sigma_{xx}^2 + \sigma_{xy}^2} \quad (1.6)$$

$$\rho_{xy} = \frac{\sigma_{xy}}{\sigma_{xx}^2 + \sigma_{xy}^2} \quad (1.7)$$

Hence, it is clear that conductivity and resistivity never vanish even at the Dirac point where charge carrier changes from electron to hole. Conductivity

for graphene is given by [7]

$$\sigma_{xy} = \frac{\pm 4e^2}{h} \left(N + \frac{1}{2}\right) \quad (1.8)$$

where N denotes the Landau level and 4 comes from the double spin degeneracy. This explains pretty well that graphene's conductivity tensor exhibits neither standard quantum Hall Effect nor fractional Hall effect. It exhibits anomalous quantum Hall effect.

Another very interesting feature of graphene is that it has minimum conductivity and zero resistivity. Since it is a zero band gap semiconductor, the resistivity change is almost zero.

From an experimental point of view, it is not useful for device applications. Indeed, introducing a band gap is an important step to overcome this difficulty. Last but not least, graphene's extraordinary unique features are promising for electronics and photonics. Its charge carriers have unique features. Further, perhaps even greater their mobility remains the same under ambient conditions e.g. by changing electronic structure, by exposing to magnetic field, by doping etc. Therefore, graphene can be used as a transistors. Low switching time is important in order a transistor to be more efficient. Graphenes low resistance contacts is another advantage to reduce the switching time. It might be possible to introduce transistors at THz frequency range by the graphene based electronics [7].

1.0.2 Tailoring Structural and Electronic properties of Graphene

In this section, various theoretical studies will be addressed on tailoring the electronic structure of graphene. There are many different ways to change the crystallographic structure of graphene. In order for graphene to be used in future electronic devices, the Fermi level should be tuned to change graphene from metal to semiconductor. In other words, the band gap should be controllable in this stable and relatively inert material.

One of the most important ways of changing the electronic structure of graphene is doping which can be investigated by changing the number of electrons of the system. Doping can be obtained by several methods such as taking the advantage of supporting substrate, by means of external internal stress and adsorption of proper donors or acceptors.

Graphene on different substrates have been investigated by numerous works. Especially, intercalation of layer of atoms between graphene and its host has been studied in various works. Silicon carbide is one of the most common materials used as a host because graphene grows nearly decoupled from silicon carbide substrate [13]. Then, intercalation by different atoms gives rise the change in the work function due to doping. In a recent study by Sandin *et al.* [13] ab initio calculations have been performed for different intercalation structures for Na in graphene on SiC substrate. They showed that Na electron dopes the graphene and it intercalates in between graphene layer and silicon carbide substrate. In fact, when graphene is grown on the silicon face of this substrate leading to formation of monolayer graphene covalently bonded to the substrate (buffer layer), graphene becomes insulator with a large band gap. However, when they adsorbed Na atoms between the buffer layer and substrate, electron doping was found to increase and work function decreased accordingly. On the other hand, when the Na atom was placed in between the graphene layer and the SiC substrate they observed a shift of the Dirac point but the linear behavior of band structure was observed to remain the same.

The role of the covalent and metallic intercalation of graphene on SiC substrate has been studied by many other scientists. Deretzis *et al.* [14] presented a density functional theory study of hydrogen and lithium intercalation of graphene on SiC substrate. They showed that hydrogen and lithium adsorption causes the buffer layer to be detached from the silicon carbide surface. Hydrogen intercalation gives rise minimal perturbation at the Dirac point while lithium intercalation creates the highly n-doped system with the Dirac cone to shift to the valence band of SiC substrate.

Another hydrogen intercalation study of graphene on SiC substrate is by Hiebel *et al.* [15] and Boukhvalov [16]. They have performed density functional theory calculation for epitaxial graphene on SiC. Boukhvalov observed a small band gap opening by hydrogenization and fluorination of graphene on SiC.

The main goal of these studies is to decrease the strong interaction between buffer layer and SiC. Since it has been shown that first C layer (buffer layer) on SiC displays graphene like structure, intercalation by atoms would lead to electronic structure modification.

Yet another group, Garces *et al.* [17] have pointed out the importance of dielectric material on graphene-based technologies. Although, it is known to be a challenge to deposit dielectric oxide on graphene due to the inert nature of graphene, it enhances the overall graphene device performance.

Dedkov *et al.* [18] studied iron layer intercalation between graphene and nickel (111) surface. Voloshina *et al* [19] have also performed electronic structure calculations to investigate the properties of graphene on ferromagnetic substrate by intercalating metal. They calculated adsorption energy of several systems such as graphene on top of Ni(111) surface, graphene on top of Al (111) surface and intercalation of aluminium layer between graphene and Ni(111) surface. Comparing the results, graphene on nickel surface seems to be more stable than the others. Since Ni is a 3d metal, hybridization is observed between graphene's π and nickel's d states. This interaction has then changed the electronic structure of graphene considerably. It causes shift of graphene's band to higher energies. Graphene on the Ni substrate with aluminium layer intercalation on the other

hand still gives the Dirac point. This system doesn't deviate from the normal electronic structure properties of the graphene layer. Using a metallic substrate without intercalation of any other atom is another promising way in integrated electronics. Xu *et al.* [20] studied the interface structure between graphene and copper (111) and nickel (111) surface. They showed that nickel has much larger cohesive energy than copper. That is due to the strong interaction between open d-orbitals. Andrew *et al.* [21] used crystal copper surface (111), (100) and on both substrate graphene was caused to the shift of Dirac crossing and to open bandgap.

Besides using different kind of materials as a host, there are numerous studies of intrinsic defects on graphene. There are different types of defects such as interstitial defects, vacancy defects, Stone-Wales defects [22]. Li *et al.* [23] emphasized the importance of the vacancy on graphene as a simplest intrinsic defect. They performed ab initio calculations to study defect formation energies. In literature, there are numerous studies on alkaline earth metals on graphene as a hydrogen storage material because they are believed to be very strong adatoms since bulk cohesive energy is quite weak therefore they do not cluster on top of graphene. Thus, Hussain *et al.* [24] have chosen calcium atoms as a dopant for hydrogen storage on graphene. They concluded that binding energy of Ca atoms on graphene is higher than its bulk cohesive energy resulting in the stability of the calcium doped graphene system. On the other hand, band structure of graphene can also be tailored by doping. Attacalite *et al.* [25] have already investigated that for high concentrations of dopants, linearity of bands at Dirac points is broken. In addition to this, they have also estimated that Fermi velocity is also altered by doping. Further, Wu *et al.* [26] introduced different configurations of vacancies in hydrogenated graphene and fluorinated graphene. The resulting structure is chain-like vacancy in both hydrogenated and fluorinated graphene.

The importance of the stress and strain on graphene structure calculations has been pointed out by different groups. In order to transform this inert layer in to a chemically active one, Andres *et al.* [27] studied the effect of tensile stress on σ and π bonds. By performing ab initio study of hydrogen on large clusters and periodic graphene structure. They concluded that stress affects π bonds giving rise

to more strong binding to the adsorbed atoms. Wen *et al* [28] studied graphene crystals over a wide pressure range. They realized that band gap width increases linearly with pressure however, band gap slightly decreases at very high pressures. It is stated that stability of structure is correlated with the band gap i.e. less stable structures have smaller gaps. Thus, graphene crystals are not very stable at very high pressures e.g., 300GPa.

1.0.3 A Brief Survey of the Atomic and Molecular Adsorption on Graphene

Many theoretical studies have been performed in order to understand the interaction between graphene and adsorbed atoms. Researchers have investigated several important schemes to find stable configurations and have reported important properties of these systems such as charge transfer between adatom and graphene, work function difference in the energy band diagram. The main goal of these works is to change hybridization from sp^2 to sp^3 . When the adatom is adsorbed on graphene, the additional electron is localized on p_z like orbital thus is a suitable candidate to form covalent bond along $\hat{z}$ direction. On the other hand, in-plane carbon-carbon bond becomes longer and weakened by keeping the same crystal structure. That means that the structure is on the way to become sp^3 hybridized structure giving rise to opening a bandgap. [27]

In the pioneering work by Sofo *et al.* [29], it has been predicted that hydrogen can be adsorbed on graphene. This structure is called "graphane" and the stability of this structure has also been verified experimentally by Elias *et al.* [30]. In this structure, each carbon atom binds to an additional hydrogen thus changes the structural and electronic properties of the whole system. The resulting stable structures are chair-like and boat-like configurations of graphane. Chair configuration is hydrogen atoms alternating on both sides of graphene and boat like configurations is hydrogen atoms alternating on both sides of graphene in pairs. They obtained the carbon-carbon distance value as 1.52 Å. Boat-like

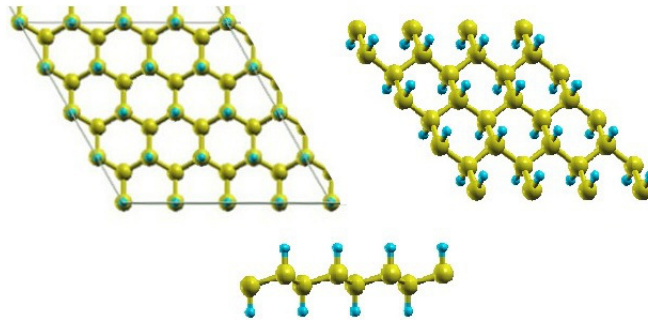


Figure 1.6: *Chair configuration hydrogenated graphene.*

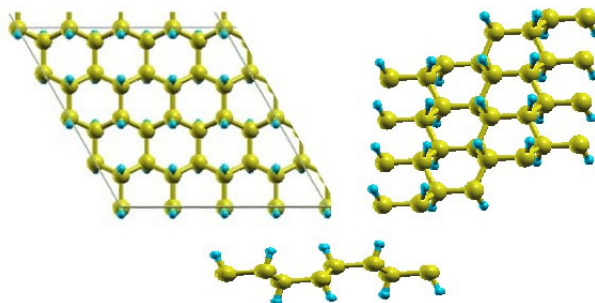


Figure 1.7: *Boat configuration hydrogenated graphene.*

configuration on the other hand, has two different C-C bond length depending on the H-H distance. For both of these structures the C-H distance is $1.1 \text{ \AA}$, which complies with those found in literature. The chair configuration is more stable than the boat configuration. On the other hand, they revealed that boat and chair conformers show semiconducting behavior with band gaps very close to each other, (3.5 eV and 3.7 eV respectively). Charge density analysis shows that charge transfers are from hydrogen to carbon atom. Phonon calculations show that boat configuration has higher frequency than chair one, because of the closer distance of first nearest neighbor hydrogen atoms in boatlike structure. Last but not least, they found chair-like graphane as stable as fluorographene which is the most stable structure in halogen atom adsorption on graphene and graphane is even more stable than graphite and other hydrocarbons such as cyclohexane benzene etc. Although, graphane has a large band gap which makes this structure inappropriate for the applications, hydrogen doping might be a good starting point to tune the bandgap and the density of charge carriers in conduction band.

Following this study, a year later, it was theoretically verified by Boukhvalov *et al* [31] that the chair-like configuration of graphane is the most favorable structure. The chemisorption energy as a function of hydrogen concentration was calculated. The chair-like conformer was found to experience vertical buckling with around $0.45 \text{ \AA}$ which complies with the experimental buckling value of graphane by Elias *et al.* [30] C-H bond length is around $1.2 \text{ \AA}$ which is consistent with the results of Sofo *et al.* [29].

Strain engineering on reversible hydrogenation of graphene has been suggested

by Pereira *et al.* [32]. Boat and chair configurations with symmetric and antisymmetric structures were considered. The results show that the antisymmetric configuration is energetically more stable. Symmetric configurations displays the sp^2 hybridization of graphene with a band gap of 0.26 eV whereas the antisymmetric configuration gives the value of 3.35 eV for the band gap.

Stability of halogens (F, Cl, Br, I) on graphene have been also studied by Medeiros *et al.* [33]. The graphane structure was also studied for comparison purposes. It was concluded that the chair configuration of graphane is less stable than fluorinated graphene.

Following this, numerous possible configurations of hydrogenated graphene and fluorinated graphene structures has been studied by Leenaerts *et al.* [34]. The results show that the chair configuration of graphane is the most stable structure. In addition to the chair configuration, boat, zigzag and armchair configurations have also been investigated in detail. It is clear that zigzag configuration which has not been studied before Leenaerts et al. is found to be more stable than boat and armchair configurations. The resulting structural and electronic properties of graphane shows that the charge transfer between hydrogen and carbon is very small due to the similar electron affinity of these atoms. Further, band gap value is found to be 3.70 eV for chair graphane.

The comparative analysis of fluorinated and hydronated graphene structures have been performed by Sahin *et al* [35]. Chair configuration of hydrogenated graphene is less stable than fluorinated graphene as in the previously mentioned studies. They have also worked on different decorations of flourine atoms on graphene which is going to be investigated in detail below.

Different than previously held concepts of graphane, nature of single sided hydrogenated graphene has been studied by Subrahmanyam *et al.* [36]. Different concentration with different initial distance of hydrogens at different coverages on graphene have been studied. Consistent with experimental observations, their results indicate that 50 percent coverage gives the most stable structure. For comparison purposes with the other data in table 1, only full coverage with initial hydrogen-carbon distance less than 1.2 Å will be displayed in table 1.

Binding energy values of full coverage of graphane can be seen in table 1.1. In this literature survey, all binding energies are not given as in original paper results. In order to compare with the values given in chapter 3, these binding energy values are adapted to binding energy per bond in primitive unit cell and and the sign convention results from the binding energy calculations.

<i>Structure</i>	<i>Method</i>	<i>Basis</i>	<i>Code</i>	<i>BE(eV)</i>	<i>E_g(eV)</i>	<i>Source</i>
Chair	<i>GGA</i>	<i>PW</i>	<i>CASTEP</i>	-3.280	3.50	[29]
Chair	<i>LDA</i>	<i>PW</i>	<i>PWSCF</i>	-2.847	3.35	[32]
Chair	<i>GGA</i>	<i>PW</i>	<i>VASP</i>	-2.463	3.53	[33]
Chair	<i>GGA</i>	<i>PW</i>	<i>ABINIT</i>	-2.481	3.70	[34]
Chair	<i>LDA</i>	<i>PW</i>	<i>VASP</i>	-2.800	3.42	[35]
Boat	<i>GGA</i>	<i>PW</i>	<i>CASTEP</i>	-3.250	3.70	[29]
Boat	<i>LDA</i>	<i>PW</i>	<i>PWSCF</i>	-1.044	0.26	[32]
Boat	<i>GGA</i>	<i>PW</i>	<i>ABINIT</i>	-2.378	3.61	[34]
Zigzag	<i>GGA</i>	<i>PW</i>	<i>ABINIT</i>	-2.428	3.58	[34]
Armchair	<i>GGA</i>	<i>PW</i>	<i>ABINIT</i>	-2.353	3.61	[34]
Singlesided	<i>GGA</i>	<i>PW</i>	<i>PWSCF</i>	-1.850		[36]

Table 1.1: Literature values of binding energy in Graphane (CH). Binding energy (BE), band gap (E_g)

Adsorption of fluorine on graphene is another promising way to tailor electronic structure of graphene. First principles studies of fluorine have started in 1993 by Charlier *et al* [37]. Fluorine atoms adsorbed on graphite with AA stacking. That means each carbon atoms in each layer have the same position along the z-axis. They studied boat and chair configurations of fluorine atoms and the framework of this calculation results in the binding energy difference of these conformations by 0.145 eV in favour of the chair. As mentioned earlier, Sofo *et al.* [29] have also studied fluorinated graphene, a similar system to graphane. They reported fluorinated graphene to be almost as stable as graphane. Medeiros *et al.* [33] revealed that the repulsion between adsorbate electron clouds causes the C-C-C angles to be distorted which results in sp^3 type behavior. Furthermore, this structure exhibits semiconducting behavior with a bandgap of 3.16 eV.

A comparative study of graphane and fluorinated graphene have been performed by Leenaerts *et al.* [34]. Stability analysis of structures shows that the zigzag configuration is more stable than boat and armchair configurations. The calculations show that boat and chair conformations have high Young modulus which makes these structures quite strong. Overall, the result of this study shows larger values compared to the previously performed experimental works, however, they attribute the reason to the nature of defects in the samples used in experimental studies.

The scope of carbonmonofluoride and graphane has also been investigated by Artyukhov *et al.* [38]. As in the study of Leenaerts *et al.* [34], three different conformations e.g chair boat and zigzag or armchair conformations have been studied which was called chair, bed and washboard or gauche chair, respectively. To avoid confusion, it is referred as the usual names here. For both fluorographene and hydrogenated graphene, armchair configuration turned out to be more stable than zigzag and boat configurations. Considering chair configuration as a reference energy, fluorinated graphene armchair and boat configurations have 0.071 eV and 0.148 eV respective energies per primitive unit cell . In hydrogenated graphene on the other hand, armchair and boat configurations have 0.055 eV and 0.103 eV energies with respect to chair one. The difference between fluorinated graphene and hydrogenated graphene is that fluorinated graphene conformations longer carbon carbon distance in optimized structures because of more electron cloud repulsion in this. Further, C-H and C-F distances are 1.112 Å and 1.382 Å respectively, which in turn leads the approval of previous studies.

In another work, Samarakoon *et al* [39] first principles density functional theory calculations have been performed to understand electronic and structural properties of fluorographene and graphane. They studied so called chair, boat, stirrup and twist boat configurations. Stirrup conformation is such that fluorine atoms alternates on both sides of zigzag direction of carbon atoms whereas in the twist boat configurations are atoms alternates only in zigzag or armchair direction. Comparing these structures, chair configuration is the most stable one, indeed, it is consistent with the other studies. Stirrup conformation is even more stable than boat and twistboat conformation. Fluorinated graphene found to be

more stable than graphane. All the binding energies are in very good agreement with the study of Leeanerts *et al.* [34]. Band gap values are 3.1 eV for the chair conformation and 3.5 eV for the stirrup configurations which are also similar with the previously held experimental and density functional theory based studies.

It has been revealed by Sahin *et al.* [35] that the fluorine atom coverage effects the important properties of the structure. It was found that C_4F , C_2F boat, C_2F chair, CF chair conformations are stable. The important point here is that some of the optimized structures might results in unstable structures such as CF boat conformation. They performed this particular calculations by density functional perturbation theory. Although band gap of the fluorinated graphene structures are ranging from 69 meV to 3 eV, GW_0 approximations have been carried out to correct the gap value because density functional theory calculations is known to underestimate gap values. Hence, CF structure with band gap of 7.49 eV which is in fact a way too large compared to DFT calculation result. However, applying strain to the system results in reduction of band gap value. On the other hand C_2F chair structure exhibits metallic behavior which can be the reason of odd number of electrons in the primitive unit cell. There are several methods to analyze charge transfer. In order to obtain the accurate results with the method they use, they subtract charge density of isolated carbon and fluorine atoms from the resulting value. The resulting charge transfer is from the middle of C-C bond and to F atom. This is a reasonable result considering the electronegativity of fluorine atom compared to carbon atom. Moreover, fully covered chair configuration is nonmagnetic system however, upon vacancy with a single fluorine atom, a magnetic moment in the system is created because of the unpaired π orbitals of that single fluorine atom. This study suggest that concentration of fluorine atom change gives rise to the creation of different structures and some external applications leads possibility to change electronic and elastic properties.

In the experimental side of this work, the very first study of fully covered fluorinated graphene studied by Nair *et al* [40], it has been suggested that fluorinated graphene has bandgap of 3 eV and another work by Robinson *et al* [41] have revealed that single side adsoption creates large band gap at different concentration of flourine atoms on graphene. Recent study by Kwon *et al.* [42] shows

that fluorination on graphene tailor adhesion, friction and charge transport properties of graphene. Friction on graphene is known to arise from flexural phonons, thus functionalization of graphene increases friction. Furthermore, their result revealed that fluorinated graphene has 2.9 eV bandgap which also complies with the theoretical calculation results. In order to verify the experimental results, density functional theory calculation has been performed. They have approved the possibility of single sided fluorination by 25 percent fluorination. Full coverage of fluorine atoms on the other hand, gives that the chair like conformation is the most stable structure. Elastic properties of graphene e.g bending and stiffness constants which is not going to be discussed here in detail, however, calculations result in the increase of frictional forces with fluorination process and that is all about the bending and stiffness constants. Cheng *et al.* [43] showed that through the reduction process of multilayer fluorinated graphene, it is possible to produce conductive material which might be a milestone for fluorine adsorption based graphene and its applications.

<i>Structure</i>	<i>Method</i>	<i>Basis</i>	<i>Code</i>	<i>BE(eV)</i>	<i>E_g(eV)</i>	<i>Source</i>
<i>Chair</i>	<i>GGA</i>	<i>PW</i>	<i>CASTEP</i>	-3.265		[29]
<i>Chair</i>	<i>GGA</i>	<i>PW</i>	<i>VASP</i>	-2.983	3.16	[33]
<i>Chair</i>	<i>LDA</i>	<i>PW</i>	<i>VASP</i>	-3.600	3.60	[35]

Table 1.2: Literature values of binding energy in Fluorographene (CF) Binding energy (BE), band gap (E_g)

Different than previous studies of hydrogenated graphene and fluorinated graphene, members of last three rows of halogens in periodic table i.e. chlorine, bromide and iodine generate very different states when they are adsorbed on graphene. As mentioned earlier, when hydrogen and fluorine adsorbed in the alternating confirmation on graphene, the minimum energy configuration is covalently bonded which was the stability condition. These halogens on the other hand gives two stable configurations with covalently bonded structure and nonbonded structure which has not been investigated yet and will be studied in detail. First

of all, different configurations of halogen atoms on graphene in addition to covalently bonded fluorinated graphene and graphane have been studied by Medeiros *et al.* [33] There are two different configurations as bonded and nonbonded for chlorine, bromide and iodine atoms. Indeed, bonded configuration is not different from fluorinated and hydrogenated graphene whereas in the nonbonded configuration, van der Waals type interaction play an important role. The structural properties of nonbonded system is indeed different than the bonded system. Lattice parameter of nonbonded system is closer than those of bonded system. Increase interaction between carbon atoms with smaller lattice parameter makes corresponding carbon-adsorbate atoms weak enough which tends to behave as van der Waals type interaction. Also, the repulsion between adsorbate atoms which are close to each other, forces adatoms to go away. Further, when the repulsion is compensated by the weak van der Waals interactions, adatom find its equilibrium. Therefore, exchange correlation potential should be approximated by van der Waals density functional theory instead of local density functional theory. Comparing the structural properties of all systems, they revealed that as the atomic radius increases C-C-C angles also increases. In the electronic structure part of the study, it is found that charge transfer depends on halogen polarizability. Since bromide and iodine have higher polarizability charge transfer direction is not the same with the direction of fluorine and chlorine. Another study by Di *et al.* [44] has also investigated graphane like structures i.e. fluorine, chlorine and bromide on graphene. They have calculated chair configuration of these atoms with the full coverage of graphene, the results are shown in table 1.3

Very recent studies in the scope of chlorination performed by Yang *et al.* [45], Ijas *et al.* [46] and Sahin *et al.* [47]. Yang *et al.* [45]. The results in single atom adsorption are shown in table 1.6. Different concentration of chlorine atoms on graphene have also been studied. Unlike hydrogenization, it was found that Cl adatom has two configurations for the full coverage, bonded and nonbonded. Nonbonded configuration is energetically more favorable than bonded configuration which has covalent interaction between them. Double sided chlorination is even more stable than single sided chlorination. Further, single sided 25 percent coverage is the most stable with the binding energy of -1.61 eV.

<i>Atom – Structure</i>	<i>Method</i>	<i>Basis</i>	<i>Code</i>	<i>BE(eV)</i>	<i>E_g(eV)</i>	<i>Source</i>
<i>Cl – Nonbonded</i>	<i>GGA</i>	<i>PW</i>	<i>VASP</i>	-0.669	-	[33]
<i>Cl – Bonded</i>				-0.066	1.53	
<i>Br – Nonbonded</i>	<i>GGA</i>	<i>PW</i>	<i>VASP</i>	-0.080	-	[33]
<i>Br – Bonded</i>				1.255	-	
<i>I – Nonbonded</i>	<i>GGA</i>	<i>PW</i>	<i>VASP</i>	1.265	-	[33]
<i>I – Bonded</i>				2.500	-	
<i>Cl – Bonded</i>	<i>GGA</i>	<i>PW</i>	<i>CASTEP</i>	2.463	1.66	[44]
<i>Br – Bonded</i>	<i>GGA</i>	<i>PW</i>	<i>CASTEP</i>	2.108	-	[44]

Table 1.3: Literature values of binding energy of halogens on graphene. Binding energy (BE), band gap (E_g)

Dimer	Structure	C-dimer Distance	Binding energy(eV)
F_2	<i>Bridge</i>	3.47	-0.214
	<i>Hollow</i>	3.70	-0.187
	<i>Top</i>	3.46	-0.218
Cl_2	<i>Bridge</i>	4.21	-0.208
	<i>Hollow</i>	4.34	-0.193
	<i>Top</i>	4.21	-0.210
Br_2	<i>Bridge</i>	4.51	-0.229
	<i>Hollow</i>	4.67	-0.207
	<i>Top</i>	4.45	-0.214
I_2	<i>Bridge</i>	4.74	-0.375
	<i>Hollow</i>	4.85	-0.352
	<i>Top</i>	4.73	-0.379

Table 1.4: Halogen dimers in perpendicular-to-plane configurations

There are two types of adsorption on graphene. The modes of these adsorption types are known as physisorption and chemisorption. In the case of chemisorption, the nature of bond is covalent or ionic at some level. On the other hand, if the case is physisorption, a weak interaction between adsorbate and graphene takes place. So far, we have reviewed local density functional theory studies which are all about the adsorbates strongly bound on graphene. There is no strong interaction between adsorbate atoms, however if there is any covalently bonded molecules adsorbed on graphene, the structure and its approximation for the exchange correlation potential changes considerably. Local and semilocal density functional theory approximation will have no success to understand such weak behavior between adsorbates and graphene. Hence, a new approximation called

Dimer	Structure	C-dimer Distance	Binding energy(eV)
F_2	<i>Bridge</i>	3.17	-0.231
	<i>Hollow – along $\hat{x}$</i>	3.23	-0.227
	<i>Hollow – along $\hat{y}$</i>	3.24	-0.225
	<i>Hollow – along $\frac{\sqrt{3}}{2}\hat{x}$</i>	3.23	-0.226
	<i>Bridge – along $\hat{y}$</i>	3.26	-0.222
Cl_2	<i>Bridge</i>	3.58	-0.259
	<i>Hollow – along $\hat{x}$</i>	3.65	-0.248
	<i>Hollow – along $\hat{y}$</i>	3.64	-0.249
	<i>Hollow – along $\frac{\sqrt{3}}{2}\hat{x}$</i>	3.65	-0.250
	<i>Bridge – along $\hat{y}$</i>	3.63	-0.251
Br_2	<i>Bridge</i>	3.74	-0.296
	<i>Hollow – along $\hat{x}$</i>	3.77	-0.289
	<i>Hollow – along $\hat{y}$</i>	3.77	-0.287
	<i>Hollow – along $\frac{\sqrt{3}}{2}\hat{x}$</i>	3.77	-0.285
	<i>Bridge – along $\hat{y}$</i>	3.78	-0.288
I_2	<i>Bridge</i>	3.80	-0.523
	<i>Hollow – along $\hat{x}$</i>	3.84	-0.514
	<i>Hollow – along $\hat{y}$</i>	3.83	-0.508
	<i>Hollow – along $\frac{\sqrt{3}}{2}\hat{x}$</i>	3.83	-0.501
	<i>Bridge – along $\hat{y}$</i>	3.81	-0.512

Table 1.5: Halogen dimers in in-plane configurations

van der Waals density functional approach is needed. Further description in this theory can be seen in chapter 2.

In this purpose, adsorption of halogen dimers on graphene has been studied by Rudenko *et al.* [48]. In-plane bridge configuration is the most stable whereas binding energy decreases by increasing the distance of dimer and graphene. However, fluorine dimer at large distances has inversely proportional behavior which shows that this structure has ionic bonding as well. That means that even at large distances electron density might overlap between that of graphene without any need to the van der Waals term. The investigation by only generalized gradient approximation for fluorine dimer also approves the idea that in the absence of van der Waals term, fluorine dimer has still interaction with graphene. Charge transfer analysis also complies with this result. Considerable amount of charge transfer to fluorine dimer is present, it accepts electrons more than iodine and bromide dimer. The corresponding binding energy and relevant distances are shown in table 1.4-1.5. It is clear that there are not so much difference in binding energy of such configurations for in-plane configurations and perpendicular to plane configurations although the binding energy in-plane and perpendicular to plane configurations differ.

<i>Atom</i>	<i>Site</i>	<i>Method</i>	<i>Basis</i>	<i>Code</i>	<i>BE(eV)/atom</i>	<i>Source</i>
<i>F</i>	<i>TOP</i>	<i>GGA</i>	<i>PW</i>	<i>CASTEP</i>	2.273	[44]
<i>F</i>	<i>BRIDGE</i>				1.906	
<i>F</i>	<i>HOLLOW</i>				2.046	
<i>Cl</i>	<i>TOP</i>	<i>GGA</i>	<i>PW</i>	<i>CASTEP</i>	1.025	[44]
<i>Cl</i>	<i>BRIDGE</i>				1.024	
<i>Cl</i>	<i>HOLLOW</i>				1.021	
<i>Br</i>	<i>TOP</i>	<i>GGA</i>	<i>PW</i>	<i>CASTEP</i>	0.769	[44]
<i>Br</i>	<i>BRIDGE</i>				0.767	
<i>Br</i>	<i>HOLLOW</i>				0.764	
<i>Cl</i>	<i>TOP</i>	<i>LDA</i>	<i>PW</i>	<i>VASP</i>	-1.130	[45]
<i>Cl</i>	<i>TOP</i>	<i>GGA</i>			-0.880	
<i>F</i>	<i>TOP</i>	<i>LDA</i>	<i>PW</i>	<i>VASP</i>	-2.570	[45]
<i>Cl</i>	<i>TOP</i>	<i>VDW – DF</i>	<i>PW</i>	<i>FHI – aims</i>	-1.212	[46]
<i>Cl</i>	<i>BRIDGE</i>				-1.210	
<i>Cl</i>	<i>HOLLOW</i>				-1.196	

Table 1.6: Literature values of binding energy of single halogens at different positions. Binding energy (BE)

Until now, we have made literature survey on the full coverage and dimer adsorption on graphene. Another possibility in adsorbed graphene studies is surely to investigate how the single adatom tailor the bonding and structural properties of graphene. For this purpose Di *et al.* [44] changed adatom concentration to understand stable configurations. When there is only one adatom is present, fluorinated graphene is the only chemisorbed structure while chlorinated and bromide structures may only be chemisorbed by full coverage due to adsorbed atom interaction. They tried different high symmetry sites for single fluorine adatom to find its stable position. This is the top side position which gives the smallest fluorine-graphene distance. In the charge density analysis, the charge density overlap has been investigated in fluorine system whereas bromide and iodine has a little overlap in the charge density. Chlorine and bromide adatom exhibits similar adsorption energies. The resulting adsorption energies can be seen in table 1.6.

Amongst the most recent works, one of the noteworthy studies is by Yang *et al.* [45]. The resulting binding energy comparison exhibits that Cl atom prefers top position with 2.53 Å C-Cl distance. They have also performed for single F and H atoms adsorption for comparison purposes. Ijas *et al.* [46] found top position most stable one. In the same way, Sahin *et al.* [47] have also found top position of single Chlorine adatom with the binding energy of 1.16 eV by van der Waals correction. The results are summerized in table 1.6.

Chapter 2

Methodology

2.0.4 Density Functional Theory

Since the 1970's, Density Functional Theory (DFT) has been extensively used for the study of the electronic structure of atoms, molecules and solids, usually with very good agreement with experimental data and in many cases, with relatively low computational cost when compared to other more elaborate methods within many-body theory. The formalism is based on the Hohenberg-Kohn theorem which states that the ground-state energy of the system can be expressed as a functional of the ground-state single-particle density. The theorem, however, does not provide the form of this universal functional, which is unknown and, therefore, approximations have to be made. Within DFT one writes the total energy of the interacting system as a sum of different terms:

$$E[n] = T[n] + \int V_{ion}(\mathbf{r}) n(\mathbf{r}) d^3\mathbf{r} + \frac{1}{2} \int \frac{n(\mathbf{r}) n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d^3\mathbf{r} d^3\mathbf{r}' + E_{xc}[n(\mathbf{r})] . \quad (2.1)$$

Here, $T[n]$ is the kinetic energy of a non-interacting system with the same density n as the fully interacting system, $V_{ion}(\mathbf{r})$ is the electron-ion potential. The third term represents the Coulomb interaction and the term $E_{xc}[n]$ represents the remaining contribution to the total energy. That is the part whose exact form is unknown and which has to be approximated. The first term, kinetic energy is

written as

$$T[n] = -\frac{1}{2} \sum_i \int \varphi_i \nabla^2 \varphi_i^* d^3\mathbf{r} \quad (2.2)$$

The most popular approach within DFT is that due to Kohn and Sham (Kohn-Sham DFT). Here, the problem of a system of interacting electrons is reduced to problem of non-interacting electrons moving in an effective potential which includes the effects of the Coulomb interaction between the electrons. In this approach, the non-interacting energy is calculated exactly from the one-electron orbitals obtained from a set of one-electron Schrödinger-like equations in which the effects of exchange and correlation between the electrons appear in an effective but local one-electron potential. Suppose that we have a number N of non-interacting electrons subject to an external potential. The wave function $\varphi_k(\mathbf{r})$ of these electrons are then obtained from the Kohn-Sham equation. [1]

$$\left(-\frac{1}{2} \nabla^2 + V_{ion}(\mathbf{r}) + V_H(\mathbf{r}) + V_{XC}(\mathbf{r}) \right) \varphi_i(\mathbf{r}) = \epsilon_i \varphi_i(\mathbf{r}) , \quad (2.3)$$

where $V_H(\mathbf{r})$ is the Hartree potential and given by

$$V_H(\mathbf{r}) = \frac{1}{2} \int \frac{n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d^3\mathbf{r}' . \quad (2.4)$$

and exchange-correlation potential, $V_{XC}(\mathbf{r})$ is given by the functional derivative;

$$V_{XC}(\mathbf{r}) = \frac{\delta E_{XC}[n(\mathbf{r})]}{\delta n(\mathbf{r})} \quad (2.5)$$

According to Pauli exclusion principle only one electron is allowed to occupy any single orbital or at most two electrons if we consider spin. We can thus have one spin-up electron and one spin-down electron in every orbital. When we solve this potential, we realize that the lowest total energy is obtained, i.e, the ground state energy, if we put the electrons in the orbitals with the smallest eigenvalues, of course taking due account of the Pauli exclusion principle. This is referred to as the aufbau principle. The total particle density of the N electron system is just the sum of the individual densities $|\varphi_i(\mathbf{r})|^2$ of every electron. Thus,

$$n(\mathbf{r}) = 2 \sum_i |\varphi_i(\mathbf{r})|^2 . \quad (2.6)$$

where factor 2 comes from spin states. Moreover, Hohenberg and Kohn showed that the functional for the total energy is minimized by the correct ground-state

density pertinent to the potential $V(\mathbf{r})$. When we change the external potential $V(\mathbf{r})$ every single orbital being a solution to the Kohn Sham equation will also change. Thus, the density will change too. We can then hope to find an external potential $V(\mathbf{r})$, called the Kohn-Sham potential, such that the particle density becomes identical to the particle density of a fully interacting system of N electrons. One can show that there is a unique potential which yields the exact interacting one-electron density of the system when it is calculated as the sum of the squares of the one-electron orbitals - one for each electron of the system.

The most difficult problem in electronic structure calculations is to deal with electron-electron interactions. Electrons with the same spin should be spatially separated and it reduces the Coulomb energy. This is called exchange energy and it is solved by Hartree-Fock approximation. Furthermore, electrons with opposite spins also repel each other due to Coulomb interactions. Thus, the coulomb energy is reduced at the cost of increasing kinetic energy. The difference between many body energy and calculated Hartree-Fock energy is called correlation energy [1]. The simplest approach to describe exchange-correlation energy is the local-density approximation (LDA) in which the exchange-correlation part of the potential is taken to be the exchange-correlation contribution to the chemical potential of the homogenous but interacting electron gas of a density equal to the local density of the inhomogeneous system. The exchange correlation energy of the inhomogeneous system is calculated by dividing the system into pieces so small that the density in each piece can be considered to be constant and equal to the local density of the inhomogeneous system at that point. The total exchange-correlation energy of the inhomogeneous system is then obtained as the sum of the exchange-correlation energies of these homogenous pieces. Thus,

$$E_{XC}[n] = \int \epsilon_{xc}(n(\mathbf{r})) n(\mathbf{r}) d^3\mathbf{r} , \quad (2.7)$$

where $\epsilon_{xc}(n)$ is the exchange-correlation energy per particle of an homogeneous non-interacting electron gas of density n . The latter quantity is easily obtained by realizing that the solutions to Schrödinger's equation of the gas are just plane waves the densities of which are constant. Minimizing the exchange-correlation expression under the additional constraint of keeping the number of particles

constant yields

$$\frac{\delta E_{XC}(\mathbf{r})}{\delta n(\mathbf{r})} = \frac{[\partial n(\mathbf{r})\epsilon_{XC}(\mathbf{r})]}{\partial n(\mathbf{r})}, \quad (2.8)$$

Then, on top of the LDA, one usually tries to improve matters by adding a number of terms involving local gradients of different orders of the one-electron density. When gradient corrections are added;

$$E_{XC}[n] = \int \epsilon_{xc}(n(\mathbf{r}), |\nabla n(\mathbf{r})|, \dots) d^3\mathbf{r}, \quad (2.9)$$

Although the Kohn-Sham approach leads to the enormous simplification of reducing the interacting many-body problem to an equivalent one-electron problem, one is still forced to solve one-electron Schrödinger equations in realistic three-dimensional systems. In extended systems of low symmetry this is often a formidable task defying the most sophisticated computational machinery.

2.0.4.1 DFT Algorithm

In practice, Kohn-Sham equations are solved numerically by an iterative procedure called self-consistency loop. The process starts with initial guess of the density and creating effective potential and exchange correlation potentials. By solving Kohn-Sham equations, a new density is constructed. It is a cyclic step and in each step, energy is calculated and the process should converge at the ground state energy. If there is geometry optimization, ionic relaxation takes place in the end of each steps. Atoms are moved in the end of each cyclic step. When forces are minimized on the system, the ionic relaxation ends. The diagram of this process is shown in figure 2.1.

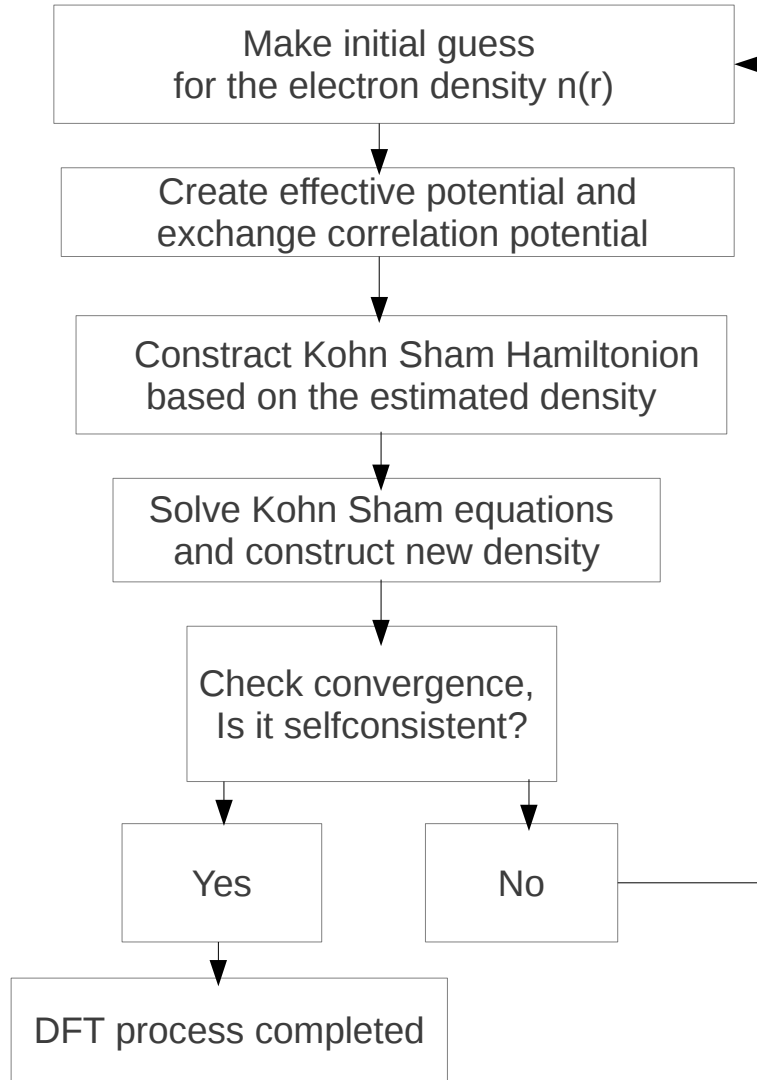


Figure 2.1: *Density Functional Theory Iteration Scheme [1].*

2.0.5 Practical Implementation of the DFT Formalism

There would be a tremendous computational gain if one can reduce the many body problem in to the equivalent noninteracting one electron problem. However, as mentioned in the previous section, one is still forced to solve infinite noninteracting electrons with infinite number of nuclei or ions. Therefore, in standard calculations of physical properties by means of density functional theory, one needs to make some approximations for practical reasons.

2.0.5.1 Crystal Lattice Structure and Bloch Theorem

It is impossible deal with infinite number of electrons in extended system with low symmetry. For instance in solids, there are infinitely many number of electrons nuclei and ions. Therefore, it is beneficial to use crystal structure. Since it has the translational symmetry, periodic boundary conditions makes the process hugely simplified. A crystal structure is defined by the primitive lattice vectors and the coordinates of atoms in a primitive unit cell. The primitive lattice vector is given by

$$\mathbf{R} = n_1 \mathbf{a}_1 + n_2 \mathbf{a}_2 + n_3 \mathbf{a}_3 , \quad (2.10)$$

where n_1, n_2, n_3 are intergers and $\mathbf{a}_1, \mathbf{a}_2, \mathbf{a}_3$ are primitive lattice vectors in real space. In order to describe electronic behavior, one has to work in reciprocal space (also called momentum space). It is inverse space of the real space. [49] The reciprocal lattice vector is given by

$$\mathbf{G} = m_1 \mathbf{b}_1 + m_2 \mathbf{b}_2 + m_3 \mathbf{b}_3 , \quad (2.11)$$

where m_1, m_2, m_3 are intergers and $\mathbf{b}_1, \mathbf{b}_2, \mathbf{b}_3$ are primitive lattice vectors in reciprocal space. Any position vector $\mathbf{R}$ and reciprocal lattice vector $\mathbf{G}$ defines the reciprocal space;

$$\exp(i\mathbf{G}\mathbf{R}) = 1 , \quad (2.12)$$

Translational periodicity of the Brillouin zone allows us to write the potential as ;

$$V(\mathbf{r} + \mathbf{R}) = V(\mathbf{r}) , \quad (2.13)$$

Notice that we write the potential in single particle Hamiltonian. Bloch theorem states that one can write the wave function in a periodic potential in the form of a plane waves times a function with the periodicity of the lattice [1].

$$\psi_i(\mathbf{r}) = \exp(i\mathbf{k}\cdot\mathbf{R}) f_i(\mathbf{r}) , \quad (2.14)$$

where $f_i(\mathbf{r})$ has the full periodicity of the lattice. One can expand this function in terms of discrete plane-wave basis set with reciprocal lattice vectors $\mathbf{G}$

$$f_i(\mathbf{r}) = \sum_{\mathbf{G}} \mathbf{c}_{i,\mathbf{G}} \exp(i\mathbf{G}\cdot\mathbf{R}) , \quad (2.15)$$

where $c_{i,\mathbf{G}}$ are plane wave coefficient. Then we have the wavefunction as

$$\psi_i(\mathbf{r}) = \sum_{\mathbf{G}} c_{i,\mathbf{k}+\mathbf{G}} \exp(i(\mathbf{k} + \mathbf{G}) \cdot \mathbf{R}) , \quad (2.16)$$

Primitive unit cell of the reciprocal space is called Brilloine zone. Usually $\mathbf{k}$ points in the Brilloine zone is sampled such that electronic wavefunctions in $\mathbf{k}$ space is represented by the single $\mathbf{k}$ point. [1] There are several important schemes for $\mathbf{k}$ point sampling. Monkhorst-Pack scheme is very useful and widely used method for $\mathbf{k}$ point sampling. This simple formula proposed by Monkhorst and Pack [50] and defines uniform set of points which is given by

$$\mathbf{k}_{\mathbf{n}_1, \mathbf{n}_2, \mathbf{n}_3} = \sum_i \frac{2n_i - N_i - 1}{2N_i} \mathbf{G}_i , \quad (2.17)$$

where G_i are the primitive lattice vectors of the reciprocal lattice.[51] The choice of $\mathbf{k}$ point depend on the type of crystal structure and it represents uniform grid of the structure. Further, perhaps even greater this formula defines the periodic structure which enables electronic structure calculation easier.

2.0.5.2 Plane Waves

Using plane waves as basis set for the electronic structure calculations have several important aspects. Bloch Theorem is the starting point because this theorem defines the relation of discrete plane wave basis set. It is not possible to expand wave function by using infinite number of plane wave basis set. However, one can reduce this required plane wave basis set by introducing kinetic energy cutoff. Plane waves with smaller kinetic energy is of utmost importance at that point because plane waves smaller than some particular cutoff energy is not going to be taken in to account. It enables easier calculation of energy derivatives and thus very adequete approach for atomic relaxation and etc. Moreover, it introduces periodic boundary conditions to the system and it is easy to make calculation by fourier transformation method. On the other hand, using plane wave basis set might in some cases cause some errors. Especially, they are not enough to define the behavior of core electrons therefore, it only gives accurate results for

the valence electrons and one needs to use help of pseudopotential method for the behavior of core states.

2.0.5.3 Pseudopotentials and PAW

It is very difficult to deal with highly localized states such as core electrons due to strong ionic potential in this region. In the majority of modern electronic structure calculations the nuclear attraction potentials as well as the atomic core electrons are pseudized away and replaced by smooth potentials causing slowly varying densities in the core of the atoms. In this approach, valence states should be orthogonal to the core states. Thus, the standart electron ion interaction is replaced by the smooth pseudopotential in the calculations. Pseudoatomic wavefunctions oscillates slower and that means it requires less number of plane waves. In principle, core electrons are treated as frozen electrons and they have no contribution to the chemical bonds. Therefore, the only contribution comes from valence states. Several important schemes are devised for pseudopotential approximation. In this thesis, the Projector Augmented wave method [52] is always followed and it is one the most important way of treating the rapidly oscillating wavefunction.

2.0.5.4 Van der Waals Interactions

Total potential energy between a pair of neutral atoms or molecules are approximated by Lennard Jones potential which is written as [53]

$$\phi(r) = -4\epsilon \left[\left(\frac{\sigma}{r} \right)^6 - \left(\frac{\sigma}{r} \right)^{12} \right], \quad (2.18)$$

where ϵ is the depth of the potential well, and σ is the distance at which interparticle potential is zero and r is the distance between particles. This potential has two terms, the attractive term which includes van der waals interactions with r^{-6} term and the repulsive term which is proportional to r^{-12} . The latter is associated with the Pauli exclusion principle which states that two fermions can not be in the same state.

Van der Waals interaction, r^{-6} term on the other hand, arises from the long range interaction of electrons in the system. Quantum thermal fluctuations will always induce a dipole even in the neutral atom. The resulting electric field polarizes the other atom with the order of r^{-3} . The interaction is then in the order of r^{-6} . This correlation effect is also known as London dispersion and the resulting are attractive. In electronic structure calculations, this term has often been neglected, however, in the scope of physisorption as mentioned above, van der Waals interactions play an important role. Although it does not care with the sharing of electrons like in covalent bond or ionic bonds, the long range effects of electrons are have also considerable effects. Furthermore, in first principle calculations, it is possible to include C_6 term as an extra term to take care of these long range interactions. As it has been also verified in this thesis, the contribution of van der Waals interactions can not be neglected.

2.0.6 Computational Details

Our calculations have been performed using Quantum Espresso package. [6]. In each electronic step Quantum Espresso calculates the forces on the system and then slightly corrects the initial guess of the density. This procedure continues with number of electronic step until the total electronic energy is minimized. This iteration ends until the change in the energy change of each consecutive selfconsistency step is less than 10^{-4} Rydberg. When the estimated energy error is less than 10^{-6} Rydberg the selfconsistency is achieved.

In order to build the unit cell these hexagonal lattice of carbon structures and corresponding adsorbates system, XCRYSDEN package [54] is used. The system is periodic in three dimensions with 20 Å along $\hat{z}$ axis in order to prevent interactions in this directions. The periodic supercell of 4×4 was used with generalized gradient approximation of Perdew Burke Ernzerhof (PBE) for the exchange correlation energies. For comparison purposes we have also tested local density approximations in some particular systems. Quantum espresso input file overrides the value of exchange correlation type from the pseudopotential part of the code. In the case of physisorption is studied, exchange correlation part

is treated with van der Waals interaction which is implemented in Quantum Espresso package. Plane wave basis set is used with kinetic energy cutoff of 625 eV. Kinetic energy cutoff for the charge density and potential is usually taken to be four times higher than the kinetic energy cutoff for the wavefunctions in order this parameter to be accurately converged. Indeed, testing of this parameters is mandatory for the accurate results.

2.0.6.1 Geometry Optimization and Single Point Energy Calculations

During the geometry optimization, atomic positions are changed until all the forces on the structure becomes less than the convergence parameter. In this thesis, structural optimization is performed using Broyden-Fletcher-Goldfarb-Shanno (BFGS) algorithm. In every iteration, forces and total energy are calculated and atomic positions change in a small distance. We have performed single point energy calculation in order to test some external parameters, such as kpoint convergence, energy cutoff convergency. We have investigated interlayer distance of graphite structure by performing single point energy runs using different approximations. It is important to notice the position of minima, if it exists. The single point energy calculations by local density approximations results in 3.59 Å interlayer distance whereas van der Waals corrections gives 3.69 Å. Generalized gradient approximation doesn't exhibit an energy barrier, thus minimum value of interlayer distance is difficult to obtain. It is already known that generalized gradient approximation tends to overestimate lattice constant although it gives good cohesive energy. In order to investigate the cohesive energy difference by use of different pseudopotential, single energy runs have been performed. Different cut-off energies have been tested for all systems. 500 eV is found to be suitable parameter for both graphite and single layer graphene system. Although higher cut-off energies give lower energies, it doesn't effect the result considerably. The minimum energy lattice constant of single layer graphene is obtained as 2.4662 Å with 1.423 Å C-C distance. Further, k-point convergence test have been performed in order approximations to work well enough. K-points are set according to the Monkhorst-Pack scheme. K-point mesh depends on cell size, hence the k-point convergence tests have been performed for each of the different cells individually. In figure 2.7, it is shown that convergence has been achieved when 225 k-points are used in the calculation.

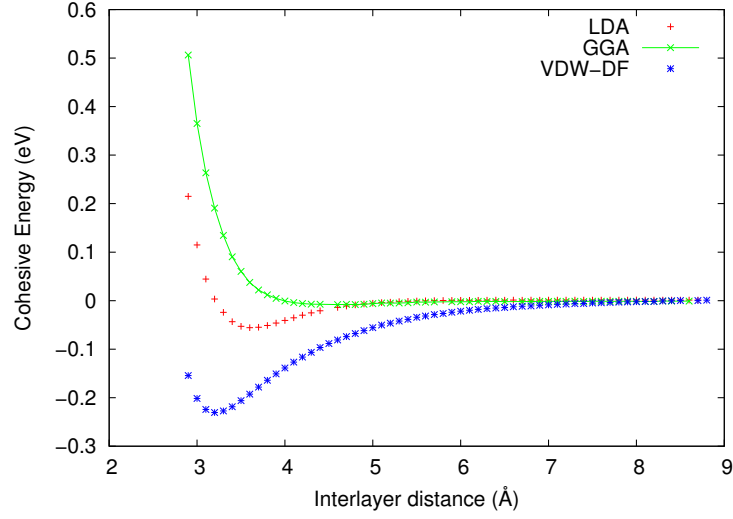


Figure 2.2: Cohesive Energy of AA stacking graphite calculated within Local Density Approximation (red curve) Generalized Gradient Approximation (green curve) and VDW-DF (blue curve)

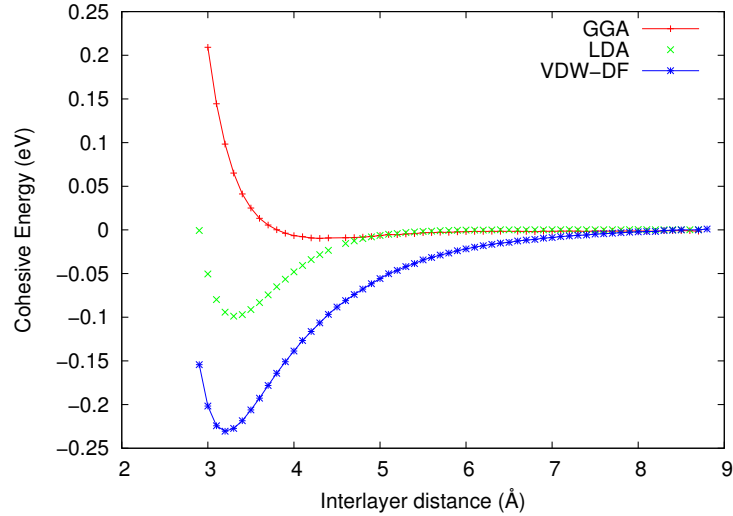


Figure 2.3: Cohesive Energy of AB stacking graphite calculated within PAW Pseudopotential (red curve) and Ultrasoft Pseudopotential (green curve) and VDW-DF (blue curve).

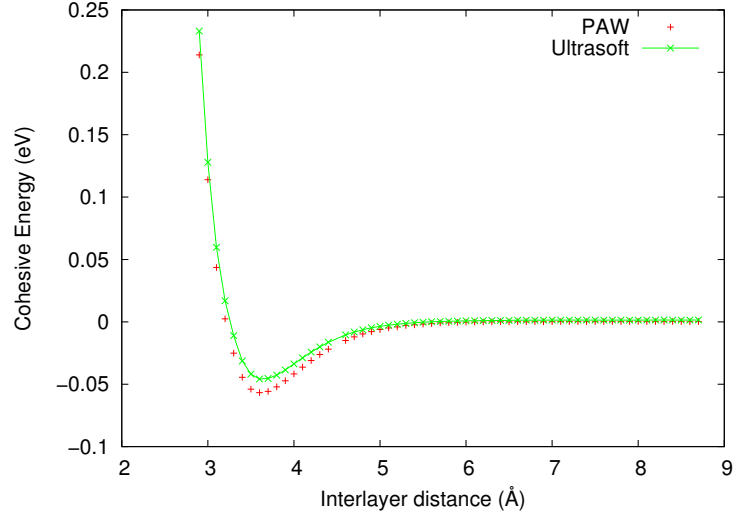


Figure 2.4: Cohesive Energy of AA stacking graphite calculated within PAW Pseudopotential (red curve) and Ultrasoft Pseudopotential (green curve) .

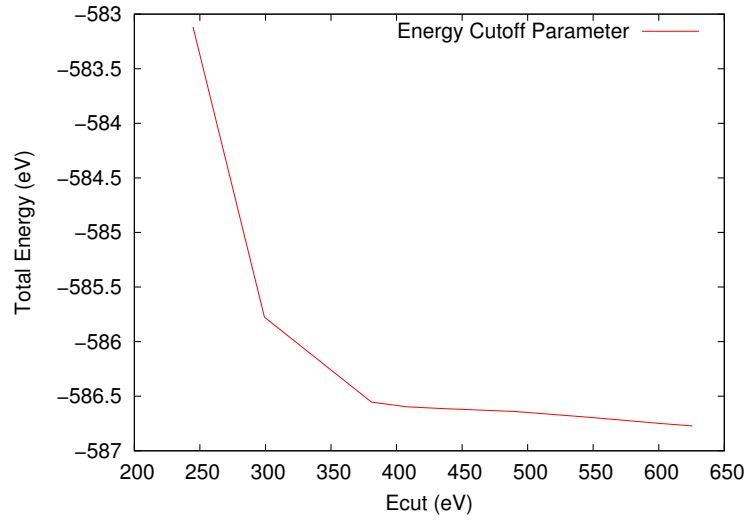


Figure 2.5: Cutoff energy convergence graph of AA stacking graphite.

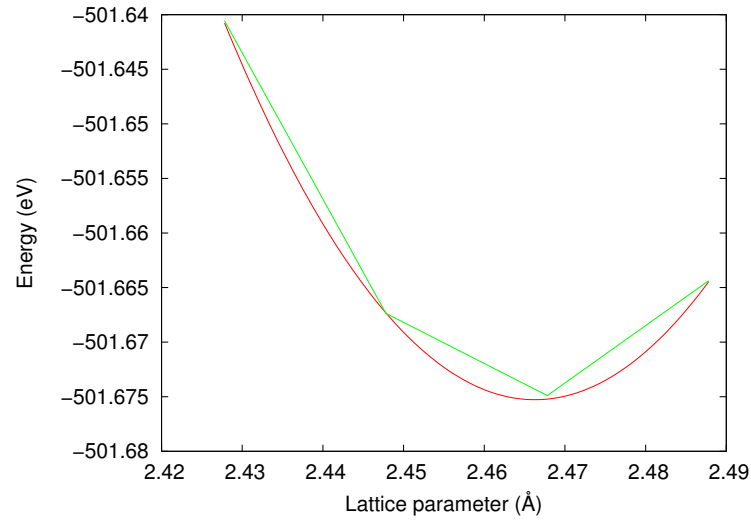


Figure 2.6: *Minimum energy lattice parameter of single layer graphene. $a=2.4662\text{\AA}$*

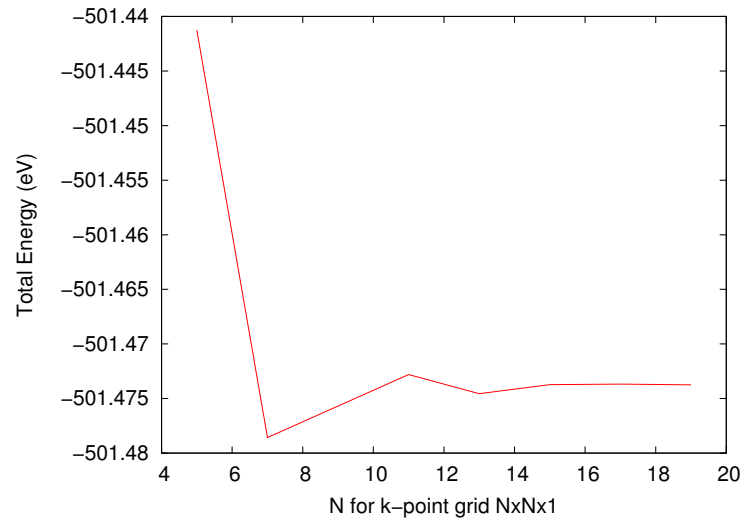


Figure 2.7: *k-point convergence graph of single layer graphene.*

Chapter 3

Results and Discussion

Several researchers have investigated several important schemes to find stable configurations of hydrogen or halogen atoms adsorbed on graphene and have reported important properties of these systems such as charge transfer between adatom and graphene, work function difference in the energy band diagram. The main goal of these works is to change hybridization from sp^2 to sp^3 . When the adatom is adsorbed on graphene, the additional electron is localized on p_z like orbital thus is a suitable candidate to form covalent bond along $\hat{z}$ direction. This results in opening a band gap, which would be enormous distribution for electronic devices. For this purpose, a variety of systems and approximations are investigated which will be useful to understand electronic and structural properties of functionalized graphene. Stability of these systems are investigated by comparing binding energy values.

3.1 Calculation of Binding Energy

Binding energies are calculated using

$$E_B = E_{ad-gra} - E_{gra} - nE_{ad} , \quad (3.1)$$

where E_{ad-gra} , E_{gra} , E_{ad} is the total energy of adatom-graphene system, total energy of isolated graphene layer and total energy of isolated adatom respectively. n is number of adatom. Negative binding energies indicate that the structure is more stable than those with positive binding energy. Formation energy of the system is calculated as

$$E_F = E_{dim-gra} - E_{gra} - E_{dim} , \quad (3.2)$$

where $E_{dim-gra}$, E_{gra} , E_{dim} is the total energy of dimer-graphene system, total energy of isolated graphene layer and total energy of isolated dimer molecule respectively. In this thesis, atomic and molecular adsorption of several systems are studied. Calculated reference value of atomic radii, the bond length, atomic and dimer energies in a cubic box with a length of 20 Å of numerous dimers are summerized in table 2.1. Generalized gradient approximation with PAW pseudopotentials are used for the calculations. Energy cutoff parameter is chosen with the convergency achievement.

<i>Atom</i>	<i>CovalentRadii(Å)</i>	<i>BL(Å)</i>	<i>DE(eV)</i>	<i>AE(eV)</i>	<i>BE(eV)</i>
H_2	0.37	0.7500	-31.72878	-12.67309	-6.382
F_2	0.71	1.4288	-1611.02611	-803.98705	-3.050
Cl_2	0.99	1.9988	-2157.75291	-1077.39971	-2.953
Br_2	1.14	2.3145	-5558.63688	-2778.13267	-2.371
I_2	1.33	2.6910	-10305.98974	-5151.98777	-2.014

Table 3.1: Reference Energy Values for Different Elements. Bond length (BL), dimer energy (DE), atomic energy (AE), binding energy (BE)

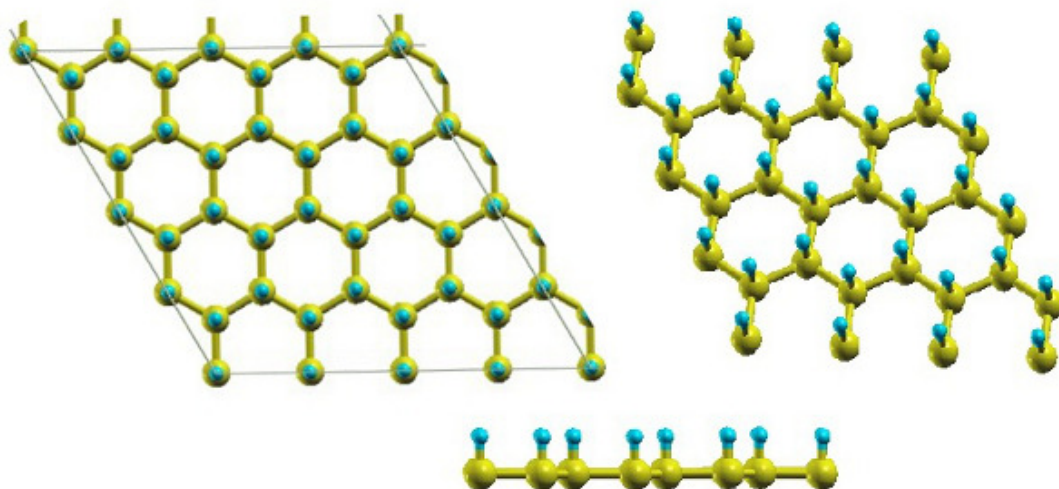


Figure 3.1: *Single sided hydrogenated graphene.*

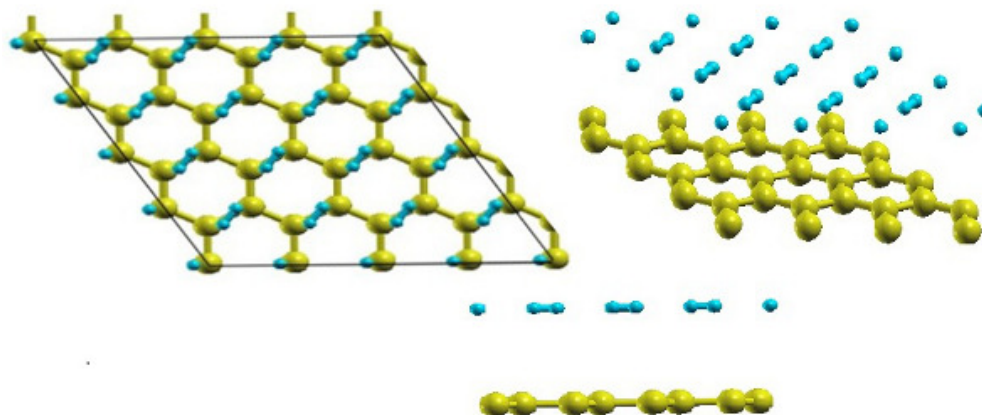


Figure 3.2: *Dimer hydrogen adsorbed graphene.*

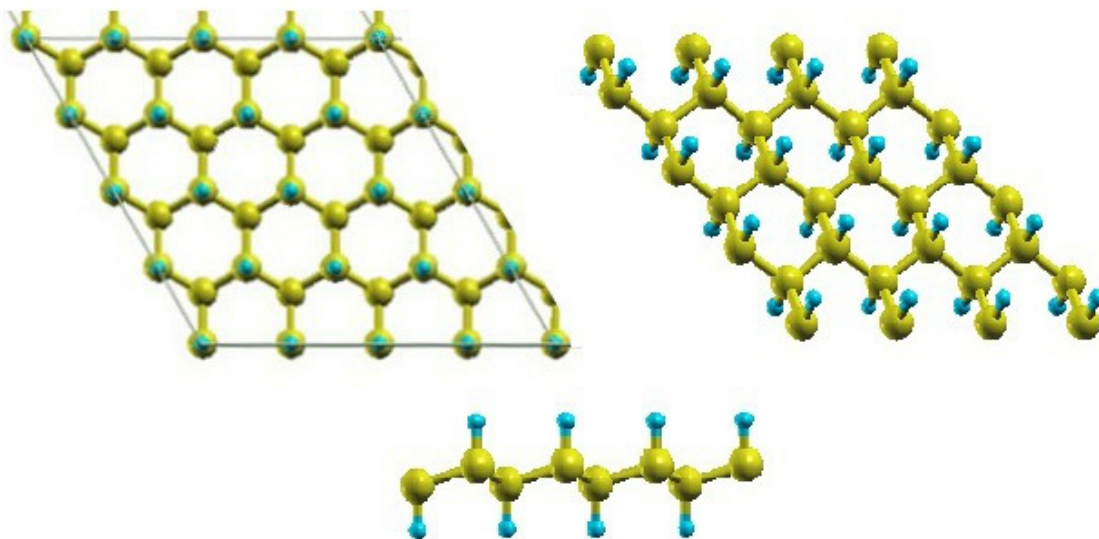


Figure 3.3: *Chair configuration hydrogenated graphene.*

3.2 Hydrogen Adsorption

We begin with hydrogenated graphene called "graphane" [29] which is to our knowledge one among the very first studied adsorbate on single layer graphene for band gap engineering through chemical modification. Hydrocarbons are simplest commonly found organic compounds of nature. Sofo *et al.*, found that graphane is two dimensional covalently bonded hydrocarbon. There are numerous studies on graphane, hence, the results reported here can be compared with the previous works. Attachment of the hydrogen atoms leads each carbon atoms of graphene to make an additional bond giving rise to change in hybridization by crumpling the structure. Starting with fully covered single sided hydrogenated graphene structure, different configurations of graphane have been studied. The relaxation process have been performed and minimum energy lattice constant has been obtained. The unit cell of the graphene sheet is 4×4 since it is not possible to perform all configurations in a smaller unit cell. Energy cutoff parameter is set to 625 eV. Results are summarized in table 3.1.

The results show that the lattice parameter is longer than the lattice parameter of single layer graphene. The behavior for smaller lattice constant is

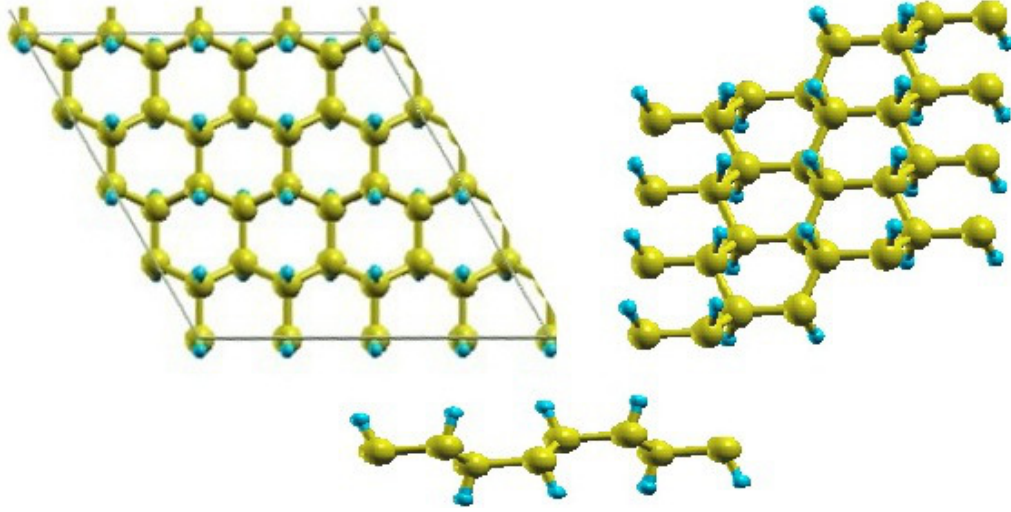


Figure 3.4: *Boat configuration hydrogenated graphene.*

<i>Configuration</i>	<i>a</i>	<i>C_h</i>	<i>d_{C-C}</i>	<i>d_{C-H}</i>	<i>d_{H-H}</i>	<i>θ_{C-C-H}</i>	<i>BE/bond</i>	<i>E_g</i>
Single sided	2.83	0.020	1.637	1.074	1.636	90.20	-1.570	1.257
Dimer adsorbed	2.49	0.000	1.413	3.351	0.730	90.00	-5.985	-
Chair	2.54	0.463	1.537	1.109	2.520	107.03	-3.286	3.352
Boat	2.50	0.647	1.531	1.104	2.202	107.09	-3.181	3.233
Zigzag	2.44	1.035	1.585	1.106	2.242	105.11	-3.108	2.784
Armchair	2.42	1.090	1.551	1.102	2.179	106.28	-3.102	

Table 3.2: Calculated structural properties and binding energy of different configurations of graphane: lattice constant (*a*)(Å), buckling (*C_h*) (Å), distance between C atoms, H-C atoms and H atoms are (*d_{C-C}*), (*d_{C-H}*), (*d_{H-H}*) (Å) respectively. Angle between carbon and hydrogen atoms (*θ_{C-C-H}*), binding energy per bond (BE)(eV), Energy gap (*E_g*) (eV), formation energy of dimer adsorbed: 0.375 eV.

different. Strong covalent character of carbon-carbon bond makes corresponding carbon-hydrogen interactions weaker. Furthermore, since hydrogen atoms becomes closer, they form dimer molecule and escape. This result has led us to study hydrogen dimer molecules on top of graphene layer. Indeed, van der Waals interaction plays important role for the present interaction, therefore, we used vdW functional for the exchange correlation part of the total energy as opposed to the previous case that has been performed with generalized gradient approximation. It seems dimer molecule adsorption on graphene gives more stable structure when compared to the binding energy of previous calculation. However, formation energy of this structure is 0.375 eV which indicates instability.

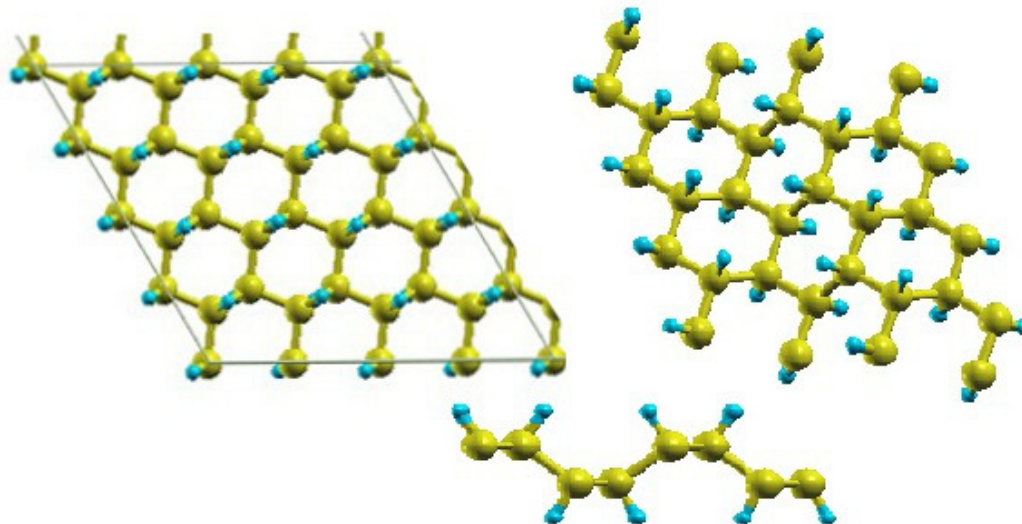


Figure 3.5: *Zigzag configuration hydrogenated graphene.*

Other configurations we have studied referred as chair, boat, zigzag and armchair configurations. In chair configuration, hydrogen atoms alternate in two sides of graphene layer, whereas in boat configurations hydrogens alteranate in pairs. Zigzag and armchair configurations forms bond like a chain in different directions. Furthermore, chair configuration is the most stable structure, with the calculated C-C bond length 1.5379 Å. It is now useful to compare the bond lengths and the bond angles with the diamond structure. Diamond has sp^3 hybridization with the carbon-carbon distance of 1.54 Å and 109.5° whereas graphene structure has sp^2 hybridization with the carbon-carbon bond of around 1.42 Å as mentioned in the previous chapters. Hydrogen atom forms covalent bond with carbon atom thus it changes hybridization from sp^2 to sp^3 . That means that the resulting structure is in the middle between graphene and diamond structure. This results in opening a band gap. Band structure of numerous configurations and corresponding density of states 1×1 and 4×4 unit cell is given in figure 3.9-3.10. It is important to notice bands are folded for different supercells. For all the supercells highest point of the valence band and lowest of the conduction band at Γ point. However, linearity of the bands disappeared. Uppermost occupied band is clearly doubly degenerate. Furthermore, there are degeneracies at the zone edges. Although this degeneracy appears in single layer graphene as well, there is an energy shift in this case. Hydrogen atom has one electron and there is a charge transfer from

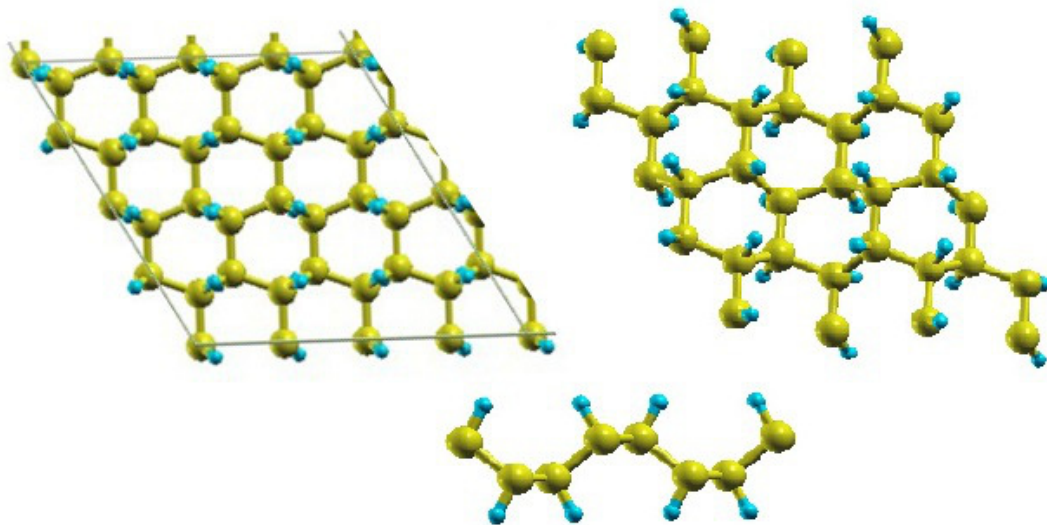


Figure 3.6: *Armchair configuration hydrogenated graphene.*

hydrogen atom to graphene layer. For the dimer adsorption on graphene, electronic band structure indicates zero gap nature. There is overlap between Dirac points and fermi level.

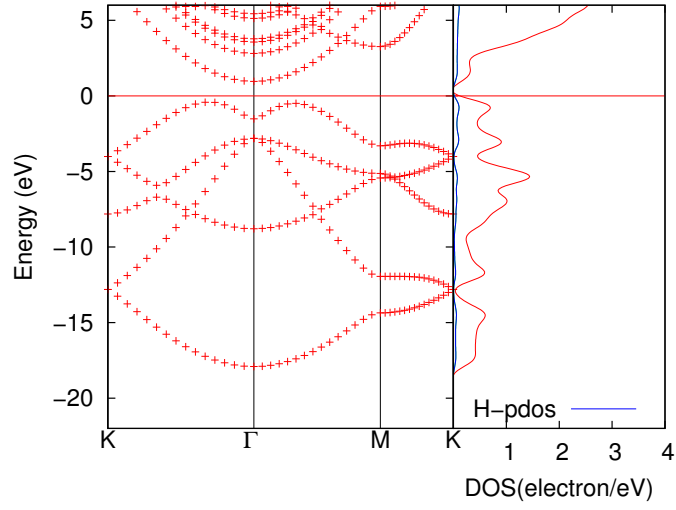


Figure 3.7: *Band structure and density of states of singleside configuration hydrogenated graphene of 1×1 unit cell.*

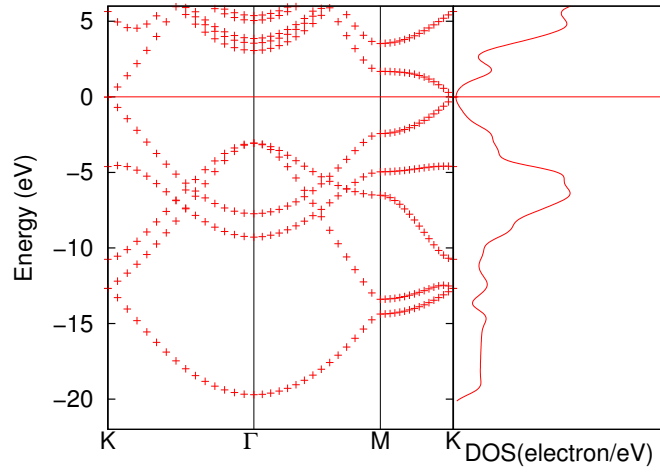


Figure 3.8: *Band structure and density of states of dimer adsorbed hydrogenated graphene of 1×1 unit cell.*

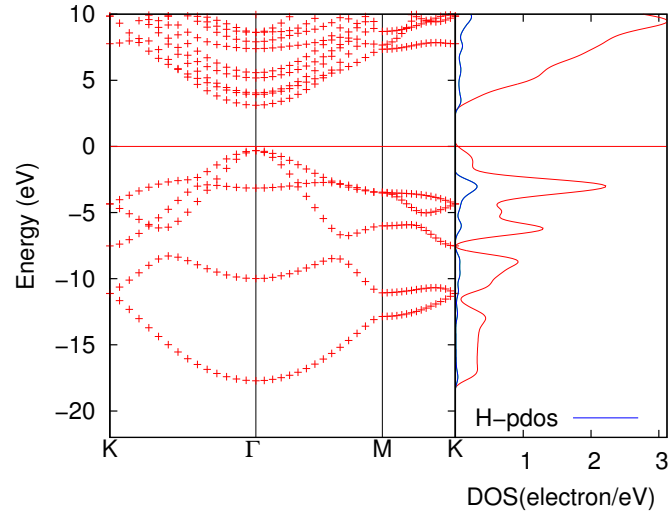


Figure 3.9: *Band structure and density of states of chair configuration hydrogenated graphene of 1×1 unit cell.*

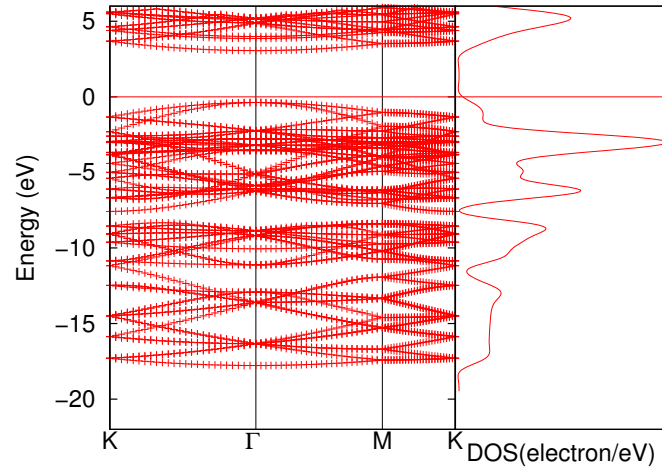


Figure 3.10: *Band structure and density of states of chair configuration hydrogenated graphene of 4×4 unit cell.*

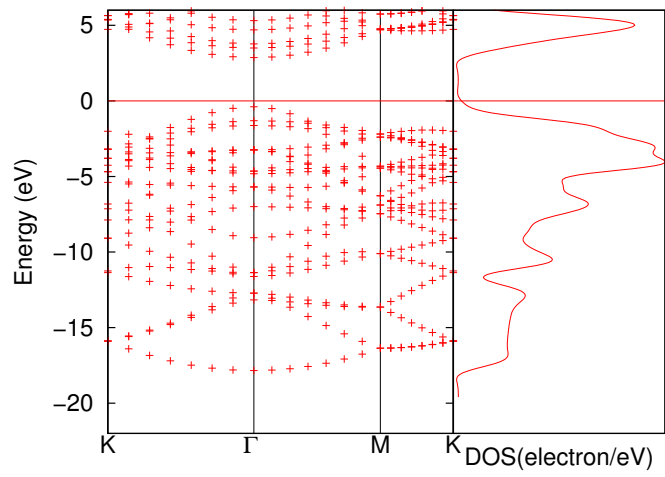


Figure 3.11: *Band structure and density of states of boat configuration hydrogenated graphene of 2×2 unit cell.*

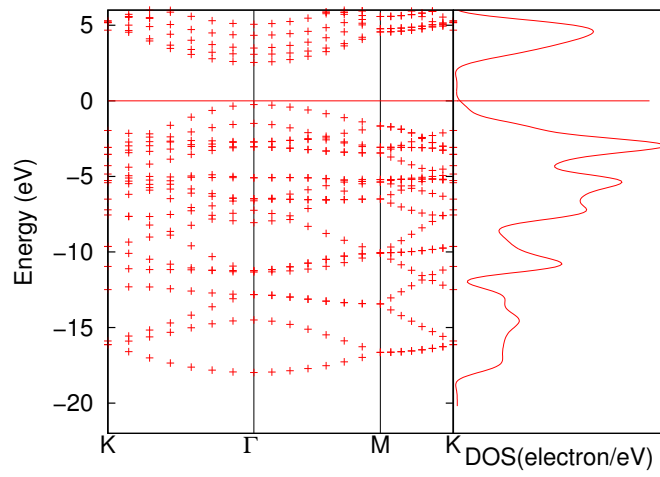


Figure 3.12: *Band structure and density of states of zigzag configuration hydrogenated graphene of 2×2 unit cell.*

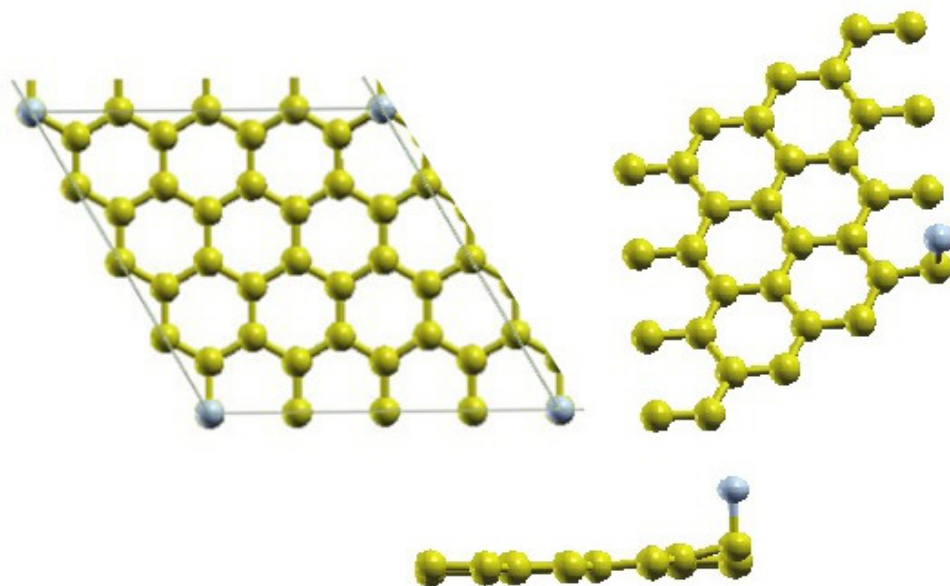


Figure 3.13: *Single F adsoption on top of the carbon atom on graphene.*

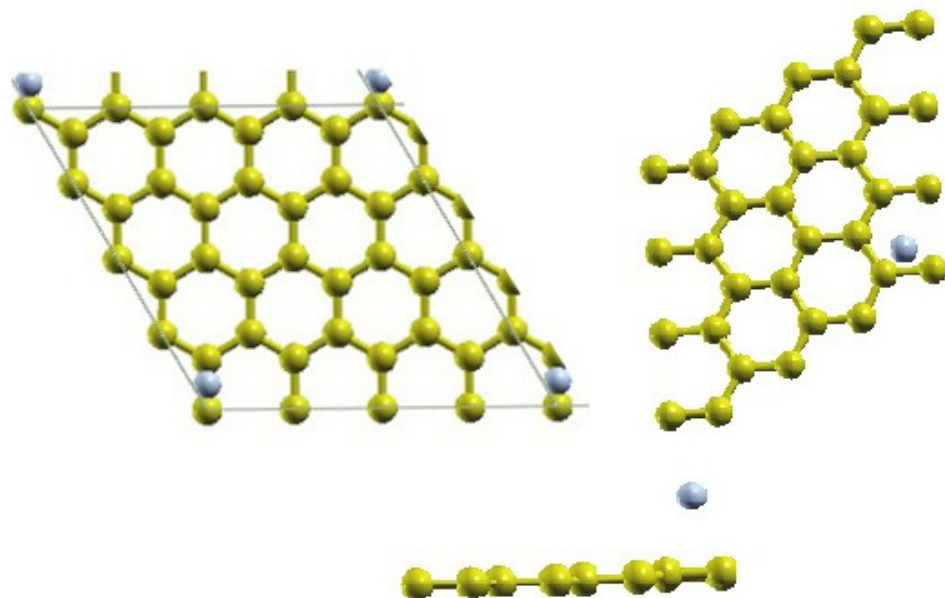


Figure 3.14: *Single F adsoption in the middle of carbon-carbon bond on graphene.*

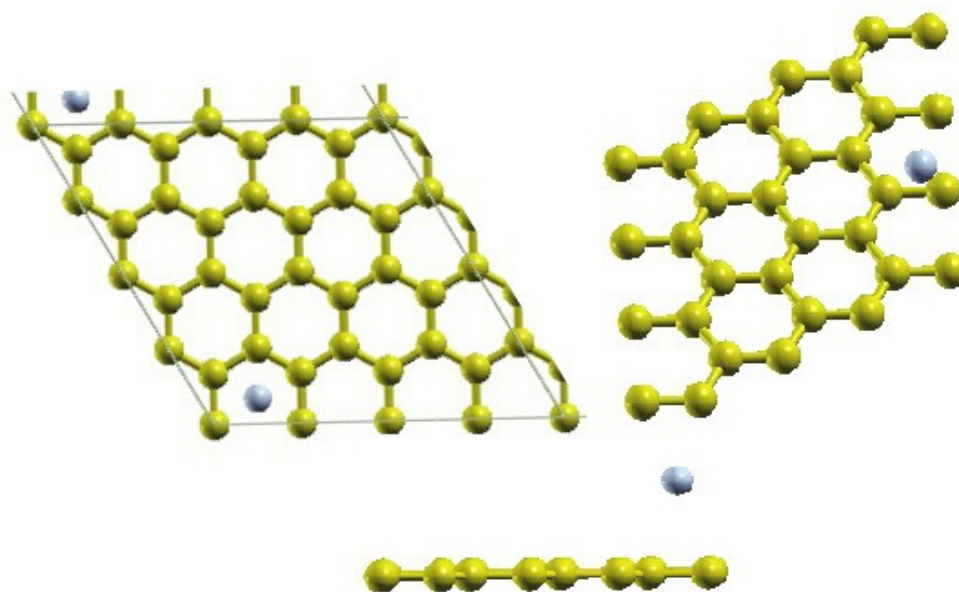


Figure 3.15: *Single F adsorption in the middle of hexagon on graphene.*

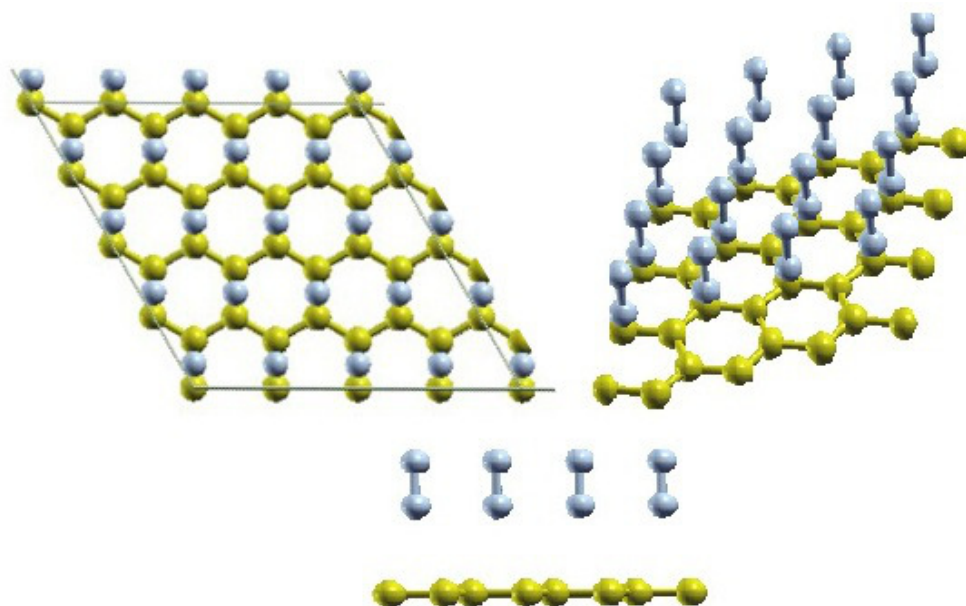


Figure 3.16: *F_2 adsorption in the middle of the carbon-carbon bond on graphene.*

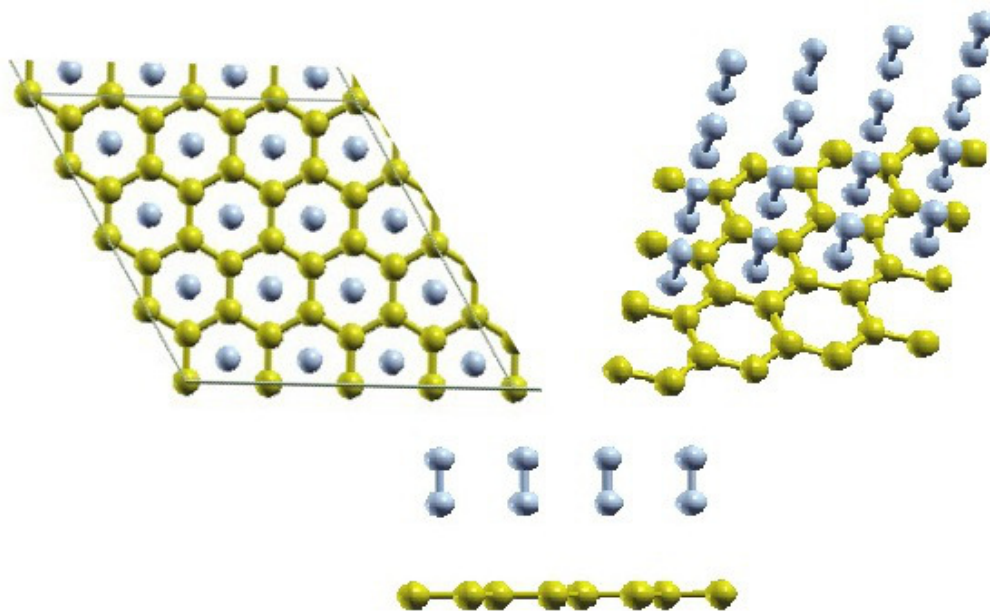


Figure 3.17: F_2 adsorption in the middle of hexagon on graphene .

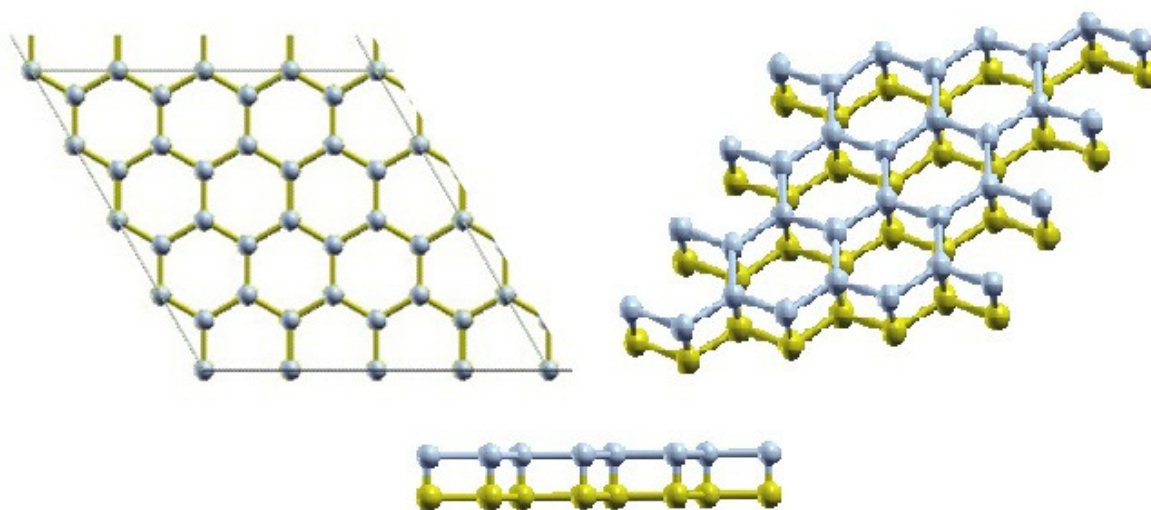


Figure 3.18: Single sided fluorinated graphene.

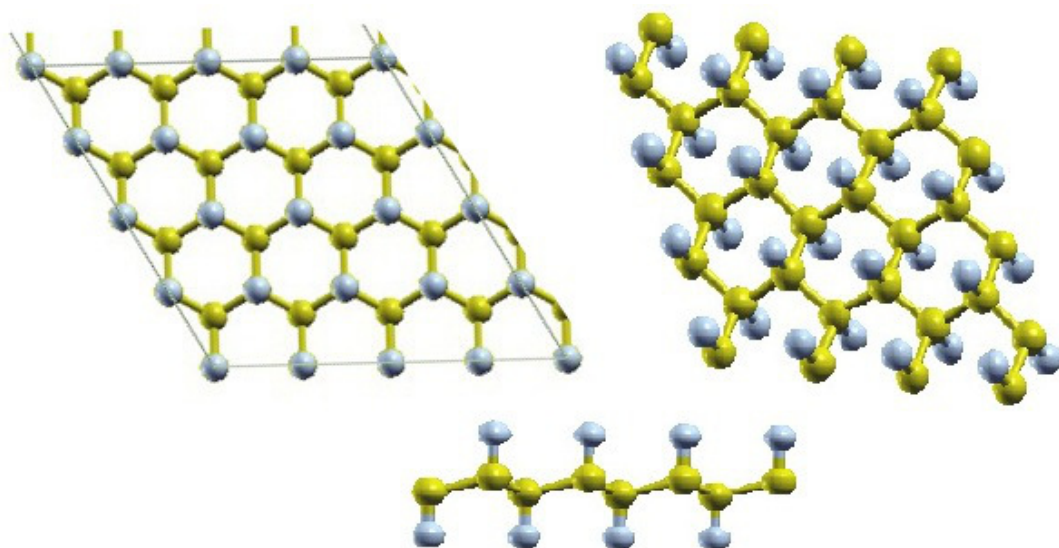


Figure 3.19: *Chair configuration of fluorinated graphene.*

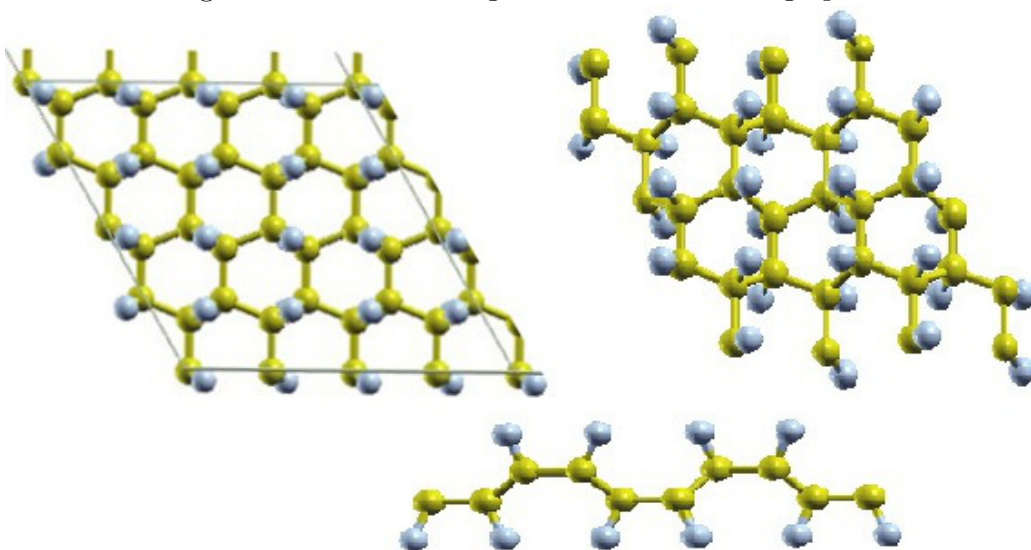


Figure 3.20: *Armchair configuration of fluorinated graphene.*

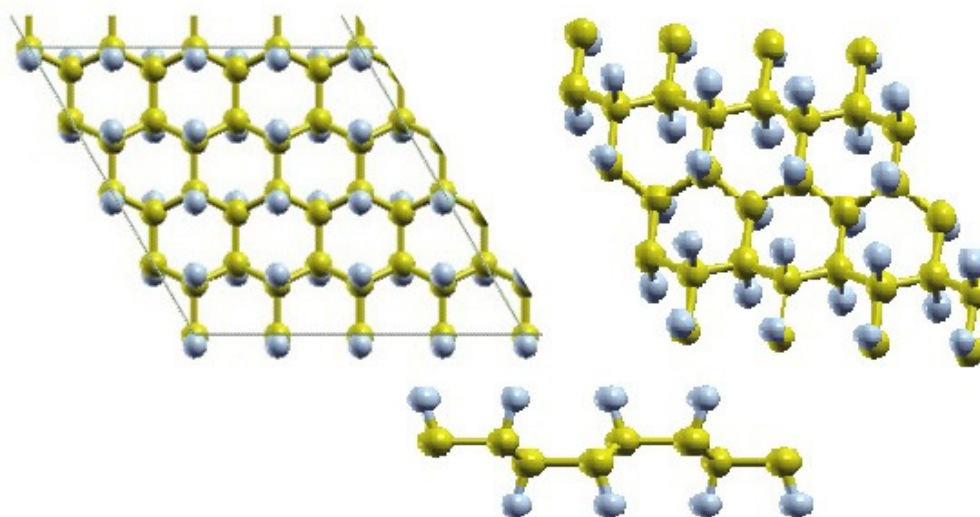


Figure 3.21: *Boat configuration of fluorinated graphene.*

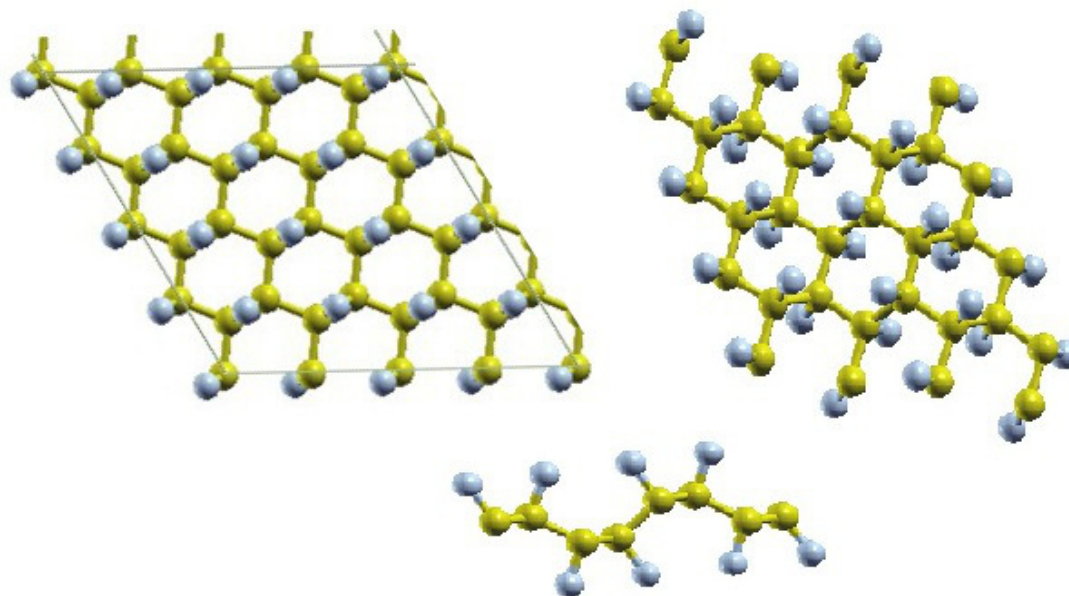


Figure 3.22: *Zigzag configuration of fluorinated graphene.*

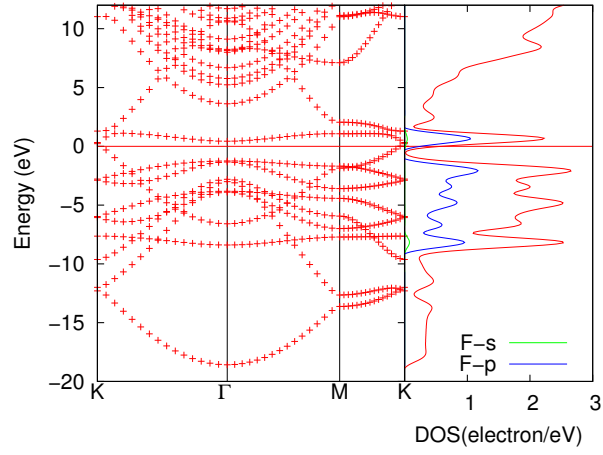


Figure 3.23: *Band structure and density of states of top side dimer fluorinated graphene of 1×1 unit cell.*

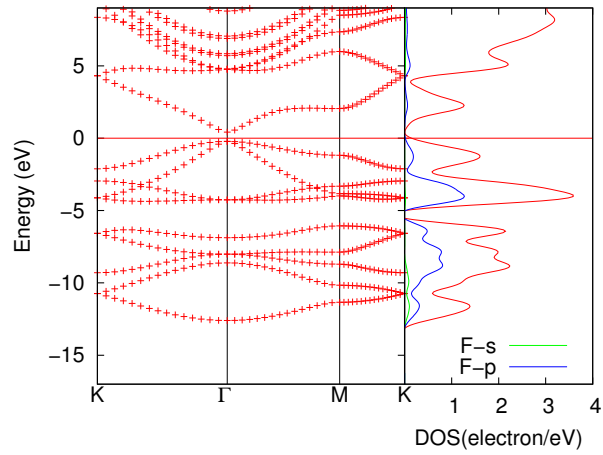


Figure 3.24: *Band structure and density of states of singleside configuration fluorinated graphene of 1×1 unit cell.*

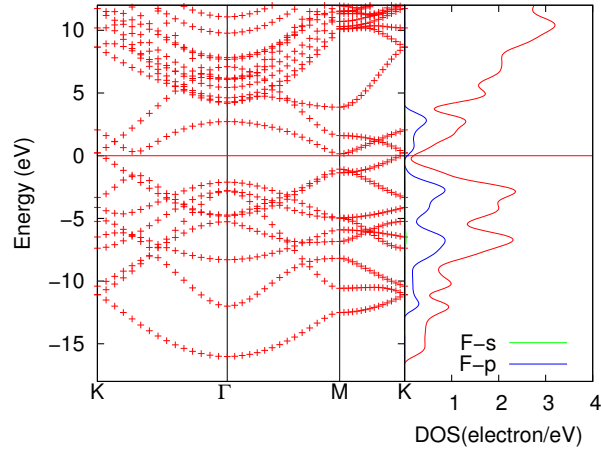


Figure 3.25: *Band structure and density of states of singleside dimer fluorinated graphene of 1×1 unit cell.*

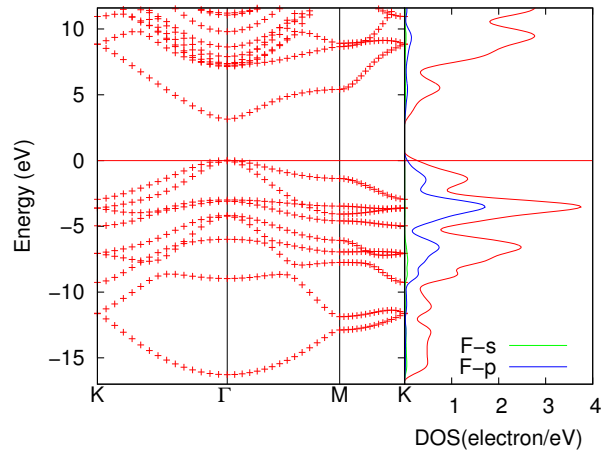


Figure 3.26: *Band structure and density of states of chair configuration fluorinated graphene of 1×1 unit cell.*

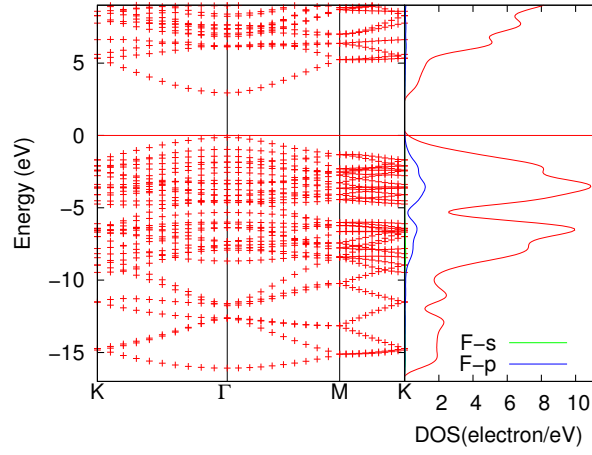


Figure 3.27: *Band structure and density of states of boat configuration fluorinated graphene of 2×2 unit cell.*

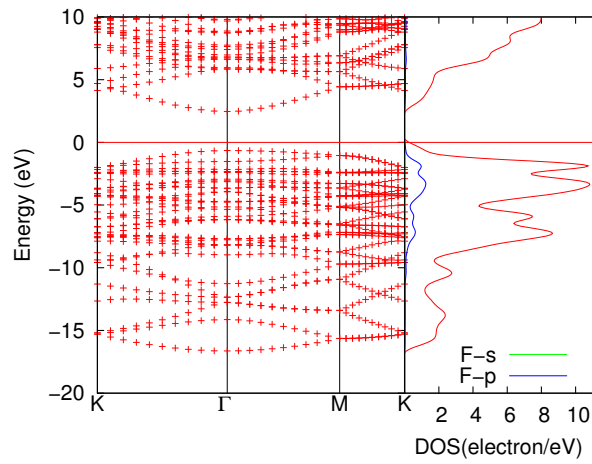


Figure 3.28: *Band structure and density of states of zigzag configuration fluorinated graphene of 2×2 unit cell.*

3.3 Fluorine Adsorption

<i>System</i>	<i>a</i>	<i>C_h</i>	<i>d_{C-C}</i>	<i>d_{C-F}</i>	<i>d_{F-F}</i>	<i>θ_{C-C-F}</i>	<i>BE/bond</i>
TOP	2.46	0.3200	1.482	1.547	9.864	102.47	-2.194
BRIDGE	2.46	0.000	1.439	2.132	9.864	70.25	-1.851
HOLLOW	2.46	0.000	1.423	2.813	9.864	75.35	-1.726

Table 3.3: Calculated structural properties and binding energy of single fluorine adsorption at different high symmetry points of graphene: lattice constant (*a*) (Å), buckling (*C_h*) (Å), distance between carbon atoms, fluorine-carbon atoms, fluorine atoms are given (*d_{C-C}*), (*d_{C-F}*), (*d_{F-F}*) respectively (Å). Angle between carbon and fluorine atoms (*θ_{C-C-F}*) and binding energy per bond (BE)(eV)

Next, graphene fluoride configurations are examined. Fluorine atom has very high electronegativity, hence, it is worth studying various coverage and configurations. The optimized configurations are schematically depicted in figure 3.13-3.22. The first configuration is the single fluorine adsorption on graphene surface. Fluorine adatom prefers top side on graphene surface. The adsorption energy of the top side is -2.194 eV with an adatom height of 1.547 Å. This is the largest adsorption energy and smallest height among those of three sides. Fluorine atom forms covalent bond with carbon atoms.

<i>System</i>	<i>a</i>	<i>C_h</i>	<i>d_{C-C}</i>	<i>d_{C-F}</i>	<i>d_{F-F}</i>	<i>θ_{C-C-F}</i>	<i>BE/bond</i>	<i>DE</i>	<i>E_g</i>
TOP	2.53	0.000	1.463	3.056	1.450	90.00	-1.820	1.025	-
BRIDGE	2.53	0.000	1.462	2.984	1.452	75.76	-1.822	1.023	-
HOLLOW	2.53	0.000	1.463	3.320	1.448	75.32	-1.808	1.037	-
Singleside	3.51	0.000	2.030	1.310	2.032	90.00	0.103	-	-
Chair	2.60	0.4912	1.582	1.376	2.605	108.07	-2.832	-	2.944
Boat	2.62	0.6315	1.587	1.370	2.241	107.46	-2.674	-	2.980
Zigzag	2.53	0.9953	1.597	1.381	2.437	104.28	-2.699	-	2.740
Armchair	2.57	0.9947	1.575	1.371	2.207	105.63	-2.566	-	

Table 3.4: Calculated structural properties and binding energy of different configurations of graphene fluoride: lattice constant (*a*) (Å), buckling (*C_h*) (Å), distance between carbon atoms, fluorine-carbon atoms, fluorine atoms are given (*d_{C-C}*), (*d_{C-F}*), (*d_{F-F}*) respectively (Å). Angle between carbon and fluorine atoms (*θ_{C-C-F}*), binding energy per bond (BE)(eV), dimer energy (DE)(eV) and Band Gap (*E_g*)(eV)

Then, dimer molecules adsorption on graphene have been studied. The optimal adsorption positions on graphene surface are determined and binding energies are calculated. The results show that adsorption energy and adatom heights are very similar to each other for different adsorption sides. Still, bridge side is more favorable with 2 meV difference. Furthermore, final F-F bond distance is around 1.45 Å. The resulting C-F distance shows that there is a van der Waals interaction present between fluorine dimer and carbon atoms. Also, full coverage of fluorine atoms on graphene are considered. The structure called fluorographene in which carbon atoms alternates on top and bottom sides of the graphene layer is the most stable structure. Indeed, graphene planar surface are buckled and carbon-carbon bond length increased. The angle between graphene surface and adsorbed atom is around 109°. Hence, it is obvious that fluorographene is sp^3 like rehybridized. Moreover, the binding energy of boat configuration slightly less than chair configuration which is due to F-F repulsion. Finally, zigzag configuration is found to be more stable than armchair configuration.

3.4 Chlorine Adsorption

<i>System</i>	<i>a</i>	<i>C_h</i>	<i>d_{C-C}</i>	<i>d_{C-Cl}</i>	<i>d_{Cl-Cl}</i>	<i>θ_{C-C-Cl}</i>	<i>BE/bond</i>
TOP	2.46	0.000	1.423	3.234	9.864	89.79	-1.103
BRIDGE	2.46	0.000	1.424	3.294	9.864	77.52	-1.101
HOLLOW	2.46	0.000	1.423	3.535	9.864	78.39	-1.102

Table 3.5: Calculated structural properties and binding energy of single chlorine adsorption at different high symmetry points of graphene: lattice constant (*a*) (Å), buckling (*C_h*) (Å), distance between carbon atoms, chlorine-carbon atoms, chlorine atoms are given (*d_{C-C}*), (*d_{C-Cl}*), (*d_{Cl-Cl}*) respectively (Å). Angle between carbon and fluorine atoms (*θ_{C-C-Cl}*) and binding energy per bond (BE)(eV)

Third system is chlorinated graphene. Again, three different positions of single and dimer chlorine atoms has been considered i.e top, bridge and hollow. Binding energies at different sides appears to be rather similar. This is due to relatively large radius of chlorine atom compared to fluorine. It has very large lattice constant for single side adsorption. For smaller lattice constant, the stronger carbon-carbon bond makes corresponding carbon-chlorine bond weaker, hence chlorine atoms form layer structure. The dimer adsorption doesn't give different binding energies at different positions. However, it forms chlorine layers with the distance 3.9 Å between them. Only the top side adsorption is presented in table 3.6. For the full coverage of chlorine, the chair configuration exhibits different behavior than chair configuration of fluorinated graphene.

<i>System</i>	<i>a</i>	<i>C_h</i>	<i>d_{C-C}</i>	<i>d_{C-Cl}</i>	<i>d_{Cl-Cl}</i>	<i>θ_{C-C-Cl}</i>	<i>BE/bond</i>	<i>DE</i>	<i>E_g</i>
TOP	2.59	0.000	1.499	4.112	3.970	90.19	-0.632	1.587	-
Singleside	5.19	0.000	2.995	1.651	3.000	90.03	2.827	-	-
NB Chair	2.60	0.000	1.501	3.722	2.594	90.00	-0.472	-	-
Chair	2.91	0.5079	1.755	1.750	2.910	106.79	-0.030	-	1.908
Boat	3.02	0.6242	1.748	1.718	2.577	106.97	0.365	-	0.930

Table 3.6: Calculated structural properties and binding energy of different configurations of chlorinated graphene : lattice constant (*a*) (Å), buckling (*C_h*) (Å), distance between carbon atoms, chlorine-carbon atoms, chlorine atoms are given (*d_{C-C}*), (*d_{C-Cl}*), (*d_{Cl-Cl}*) respectively (Å). Angle between carbon and fluorine atoms (*θ_{C-C-Cl}*) and binding energy per bond (BE)(eV), Band Gap (*E_g*) (eV)

There are two stable configurations in chair structure, referred as, nonbonded

and bonded. For smaller lattice constant, chlorine atoms exhibit nonbonded stable configurations. The repulsion between nonbonded atoms and carbon atoms are compensated with van der Waals forces, as a result, atoms reach their equilibrium position. In the bonded system on the other hand, there is a strong covalent character, because carbon-chlorine bond is stronger. Boat configuration gives positive binding energy value, therefore it is not stable configuration. Zigzag and armchair initial configurations form completely different lattice, therefore graphene layer doesn't remain in its original honeycomb shape. Band structure calculations show that chlorine adsorption results in energy gap for chair and boat conformations.

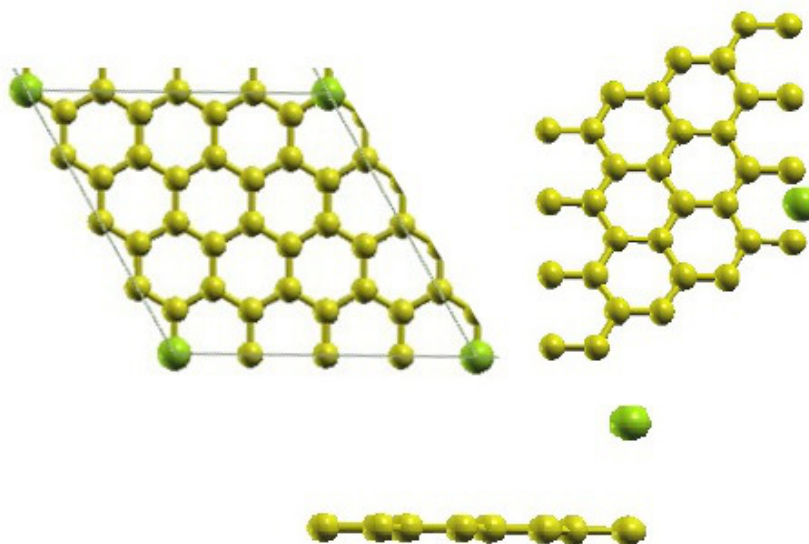


Figure 3.29: *Single chlorine adsorption on top of carbon atom on graphene.*

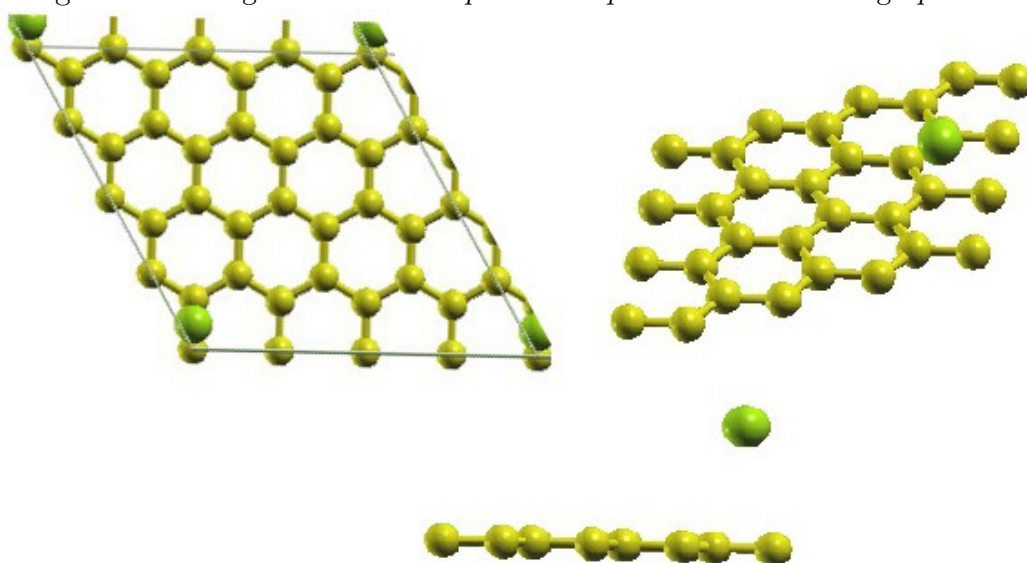
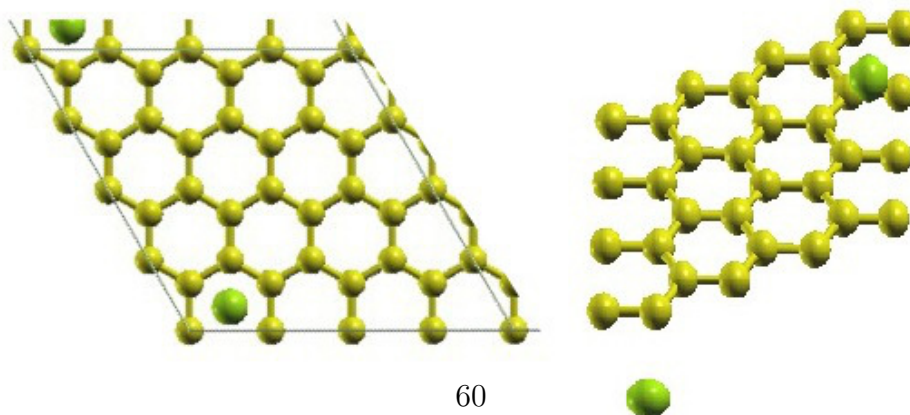


Figure 3.30: *Single chlorine adsorption in the middle of carbon-carbon bond on graphene.*



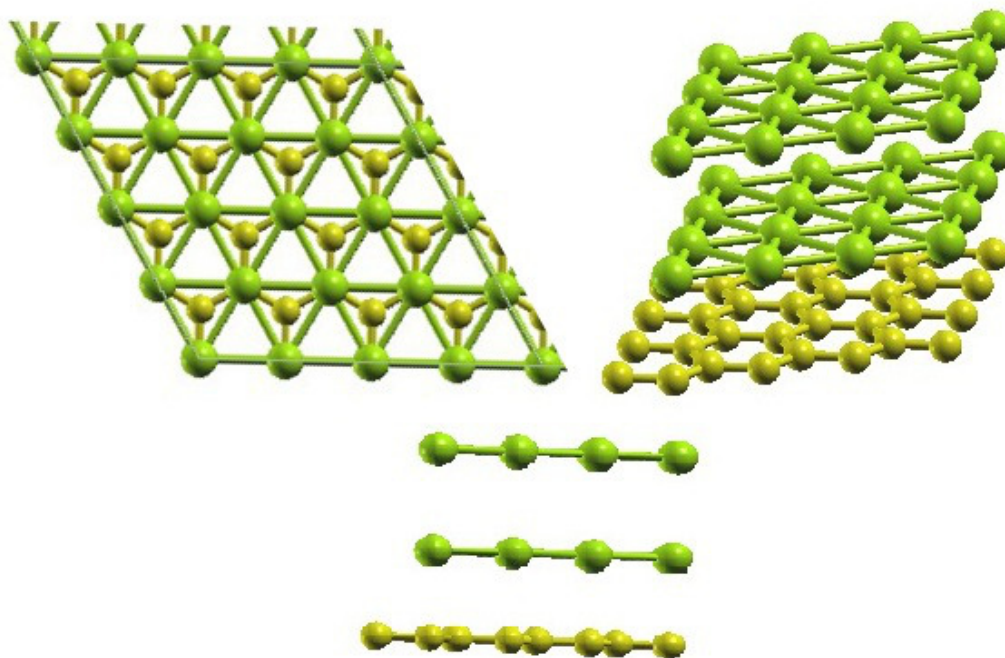


Figure 3.32: Cl_2 adsorption on top of carbon atom on graphene.

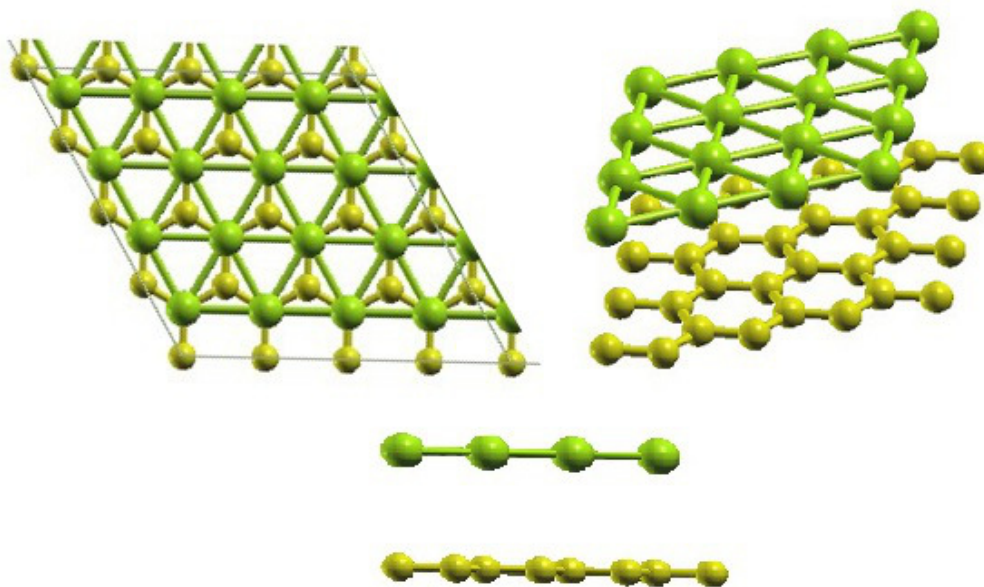


Figure 3.33: 50 percent singlesided coverage of Cl atoms on graphene.

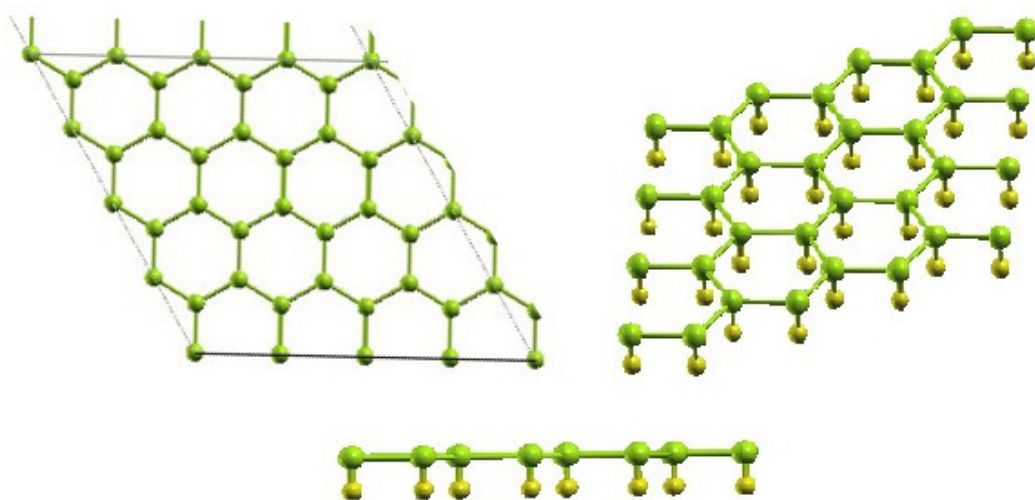


Figure 3.34: *Single sided chlorinated graphene.*

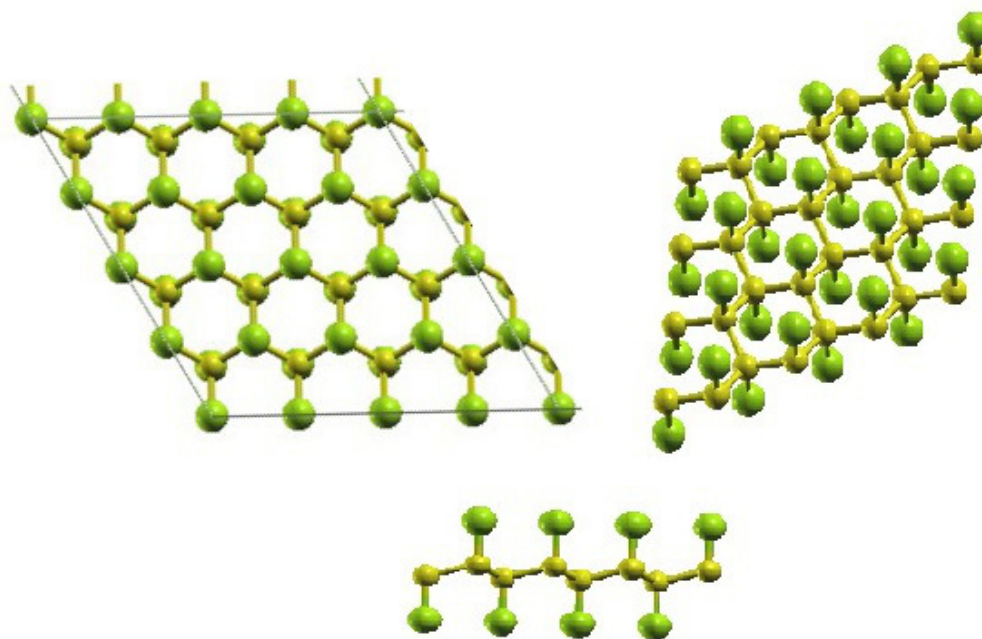


Figure 3.35: *Chair configuration of chlorinated graphene.*

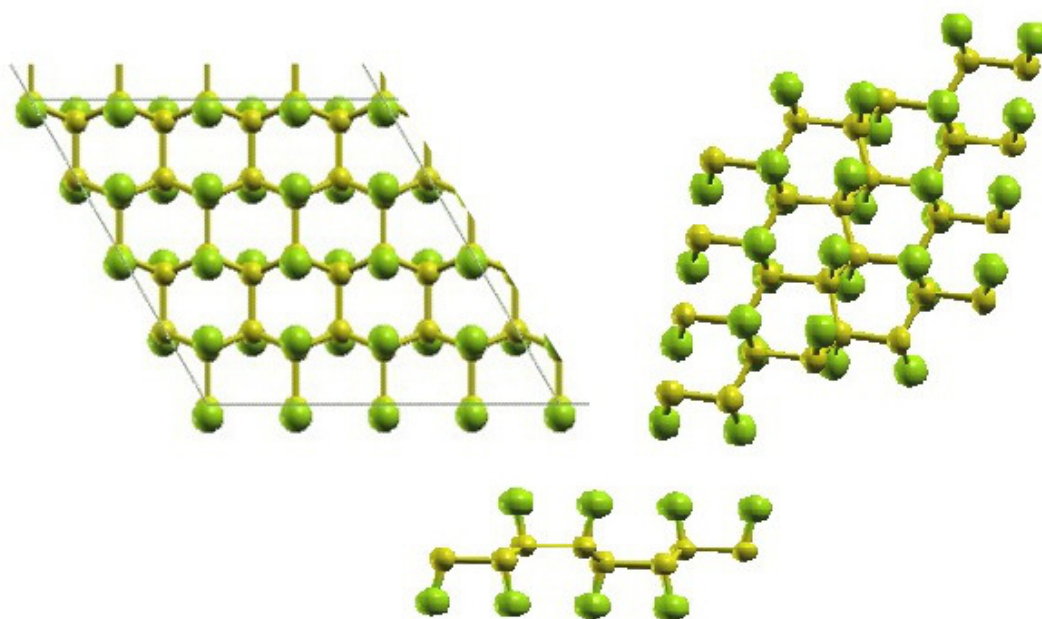


Figure 3.36: *Boat configuration of chlorinated graphene.*

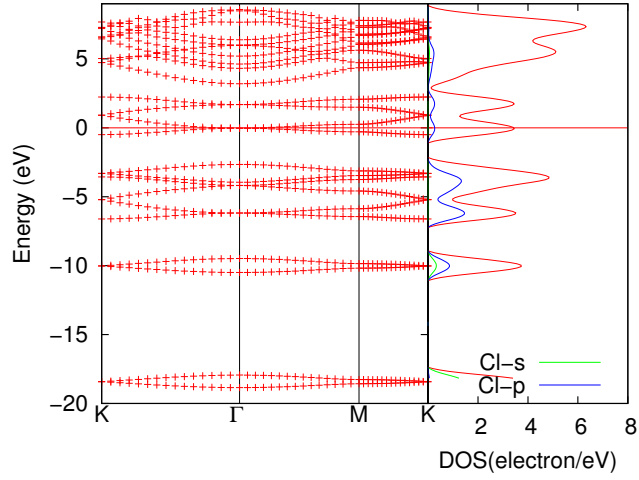


Figure 3.37: *Band structure and density of states of singleside configuration chlorinated graphene of 1×1 unit cell.*

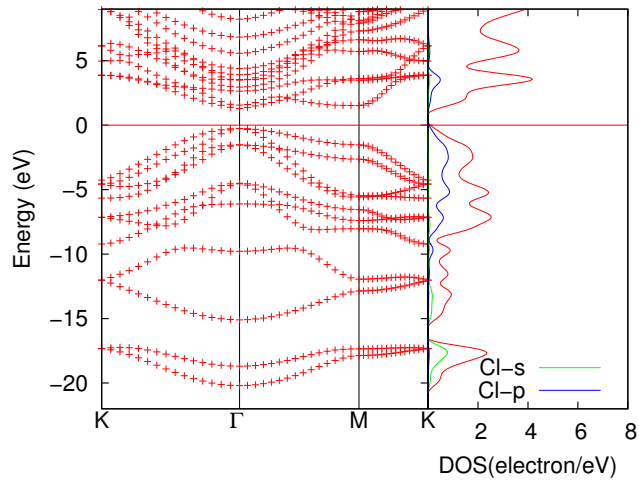


Figure 3.38: *Band structure and density of states of chair configuration chlorinated graphene of 1×1 unit cell.*

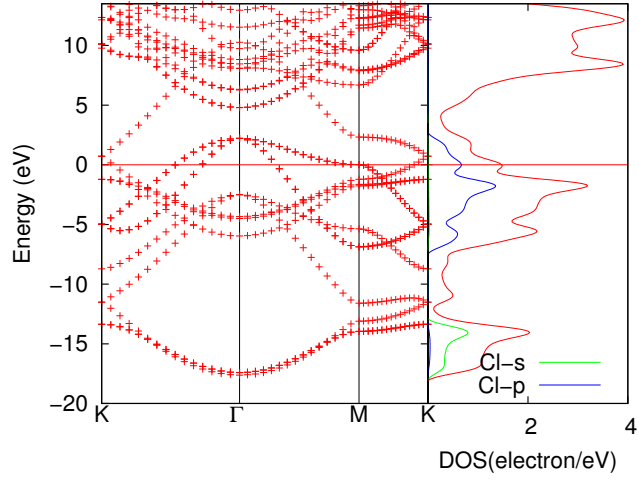


Figure 3.39: *Band structure and density of states of nonbonded chair configuration chlorinated graphene of 1×1 unit cell.*

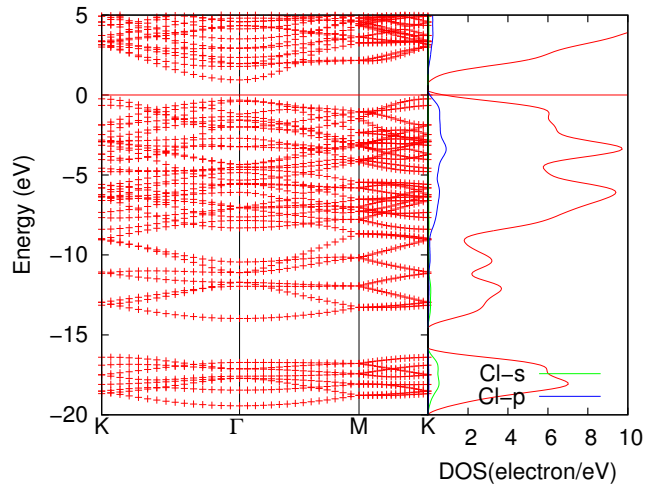


Figure 3.40: *Band structure and density of states of boat configuration chlorinated graphene of 2×2 unit cell.*

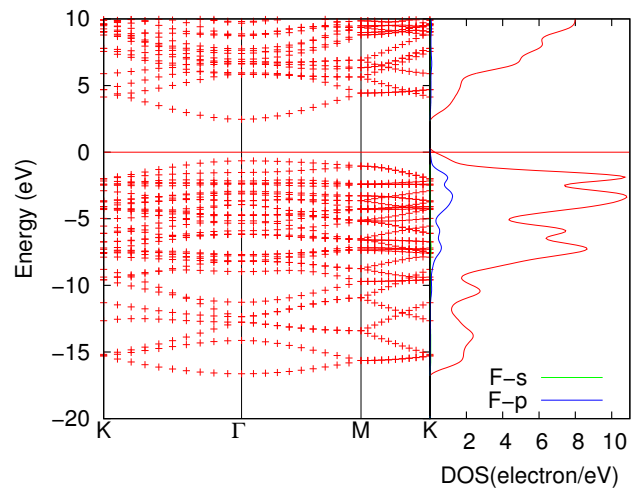


Figure 3.41: *Band structure and density of states of zigzag configuration chlorinated graphene of 2×2 unit cell.*

3.5 Bromide Adsorption

<i>System</i>	<i>a</i>	<i>C_h</i>	<i>d_{C-C}</i>	<i>d_{C-Br}</i>	<i>d_{Br-Br}</i>	<i>BE/bond</i>
TOP	2.46	0.00	1.423	3.445	9.84	-0.871
BRIDGE	2.46	0.00	1.424	3.509	9.84	-0.871
HOLLOW	2.46	0.00	1.423	3.731	9.84	-0.871

Table 3.7: Calculated structural properties and binding energy of single bromide adsorption at different high symmetry points of graphene: different configurations of bromide-graphene: lattice constant (*a*) (Å), buckling (*C_h*) (Å), distance between carbon atoms, bromide-carbon atoms, bromide atoms are given (*d_{C-C}*), (*d_{C-Br}*), (*d_{Br-Br}*) respectively (Å). and binding energy per bond (BE)(eV)

<i>System</i>	<i>a</i>	<i>C_h</i>	<i>d_{C-C}</i>	<i>d_{C-Br}</i>	<i>d_{Br-Br}</i>	<i>θ_{C-C-Br}</i>	<i>BE/bond</i>	<i>DE</i>	<i>E_g</i>
TOP	2.72	0.0000	1.574	3.864	4.071	90.0	0.219	2.435	-
Singleside	5.75	0.0000	3.319	1.827	3.320	90.0	3.743	-	-
NB Chair	2.72	0.0000	1.570	3.906	2.7207	90.0	0.225	-	-
Chair	3.10	0.4961	1.861	1.924	3.108	105.4	1.364	-	-
Boat	3.24	0.5645	1.828	1.907	2.776	104.6	1.741	-	-

Table 3.8: Calculated structural properties and binding energy of different configurations of bromide-graphene: lattice constant (*a*) (Å), buckling (*C_h*) (Å), distance between carbon atoms, bromide-carbon atoms, bromide atoms are given (*d_{C-C}*), (*d_{C-Br}*), (*d_{Br-Br}*) respectively (Å). Angle between carbon and bromide atoms (*θ_{C-C-Cl}*), binding energy per bond (BE)(eV), dimer energy (DE) (eV), Band Gap (*E_g*) (eV)

The same configurations have been tested for bromide adsorption. Single bromide adsorption on graphene doesn't exhibit any difference in binding energies. For the full coverage of bromide the results of 4×4 unit cell are presented in table 3.8. For the full coverage of dimer bromide molecules, there is no difference in the binding energy at different high symmetry sides. After the structures are fully relaxed, the second atom on dimer molecule escapes and bromide atoms form layer structure. Bromide adsorption also exhibits non-bonded chair configuration like in the case of chlorographene. Again, chair configuration is the most favorable structure compared to the other configurations. However, bromide graphene does not exhibit stability. Indeed, it has higher radius and this shows that the expected final carbon-adsorbate bond length to be higher. Zigzag and armchair configurations of bromide atoms deformed the graphene structure, thus resulted

in different structure. Moreover, there is no gap in the band structure in figures 3.37-3.41.

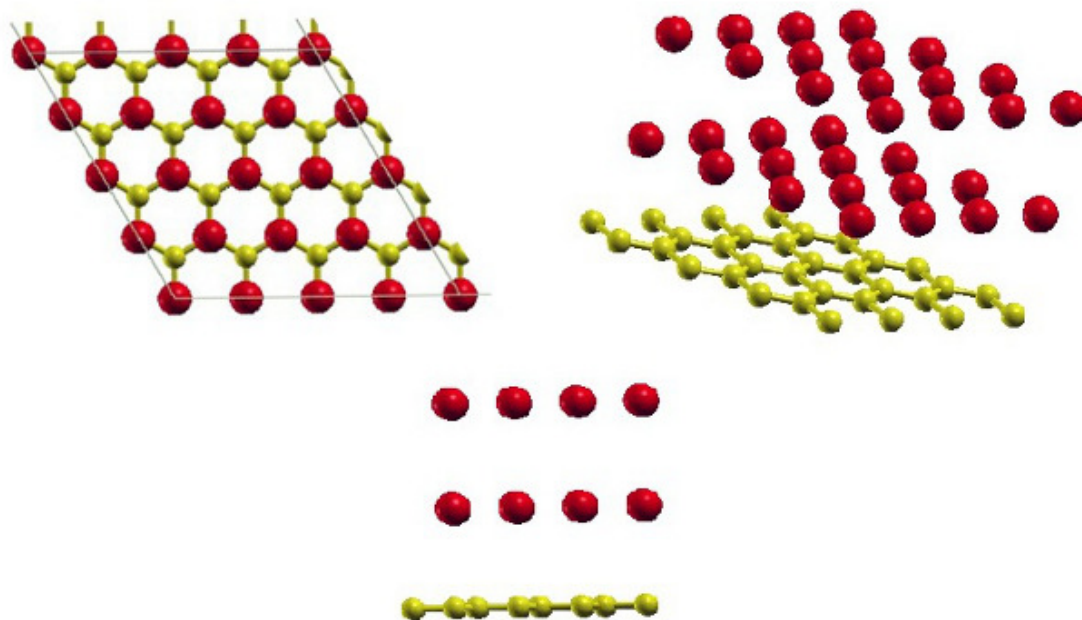


Figure 3.42: Br_2 adsorption on top of carbon atom on graphene.

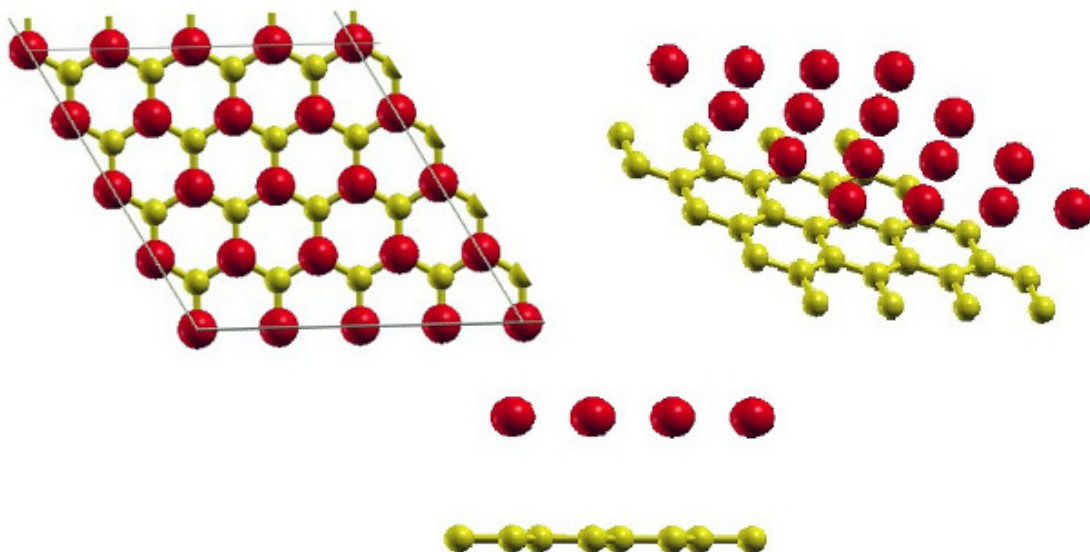


Figure 3.43: Half coverage singlesided coverage of Br atoms on graphene.

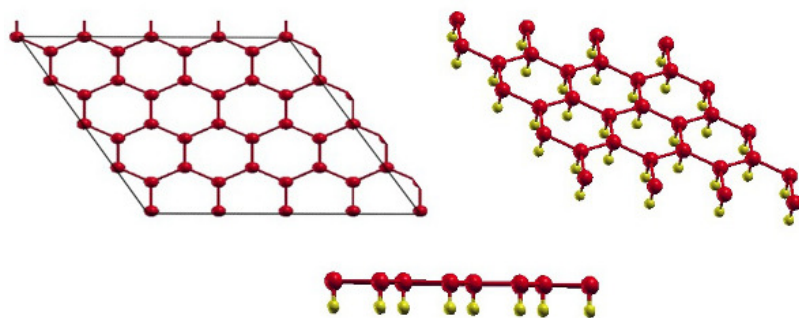


Figure 3.44: *Single sided bromide graphene.*

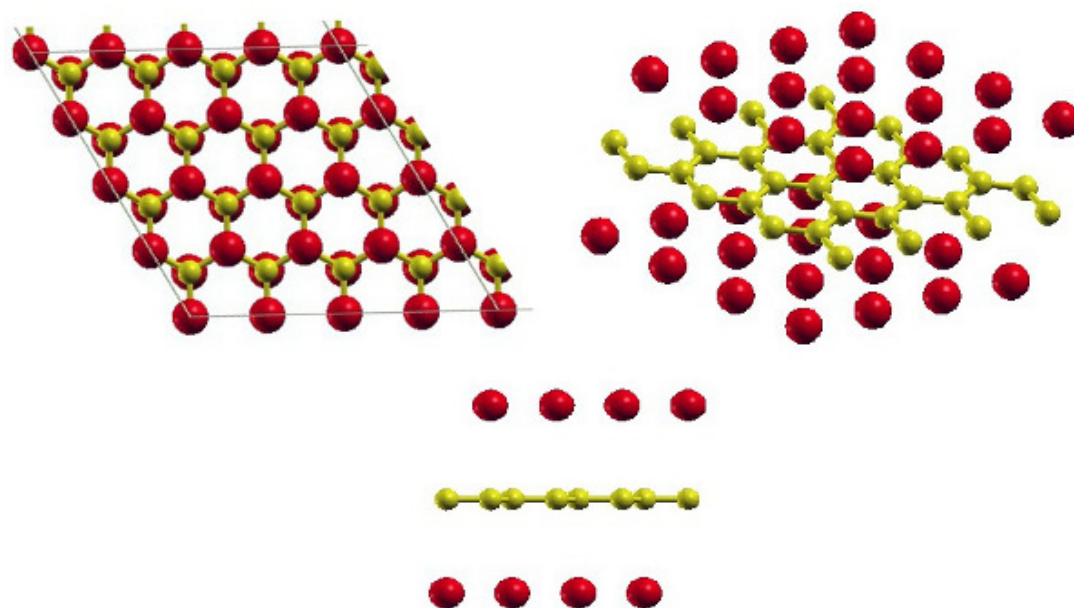


Figure 3.45: *Nonbonded chair configuration of bromide graphene.*

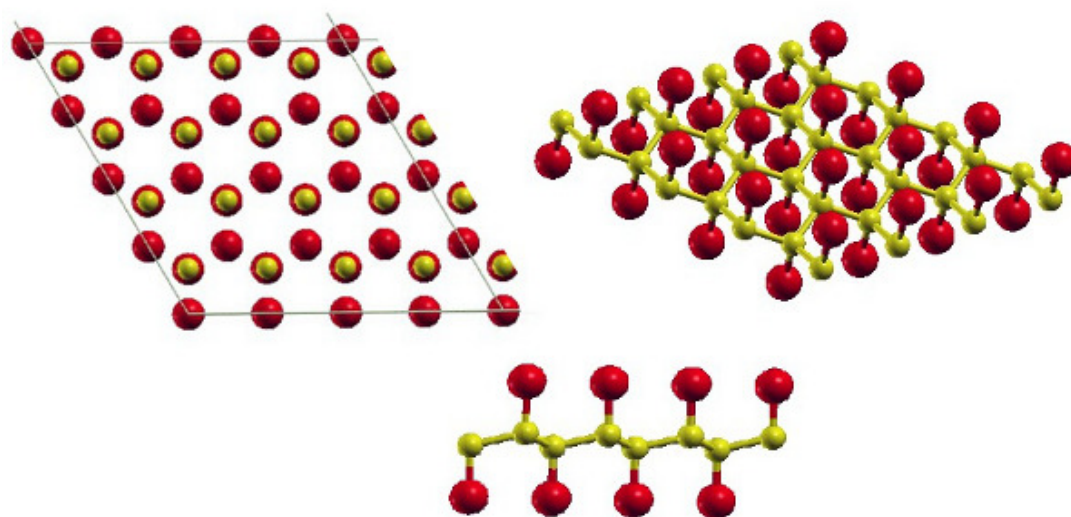


Figure 3.46: *Chair configuration of bromide graphene.*

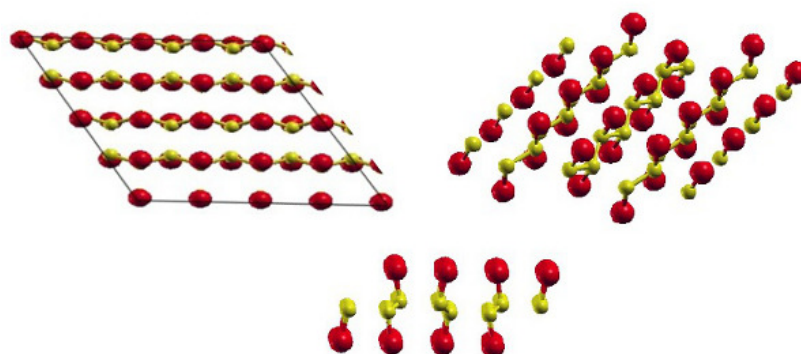


Figure 3.47: *Boat configuration of bromide graphene.*

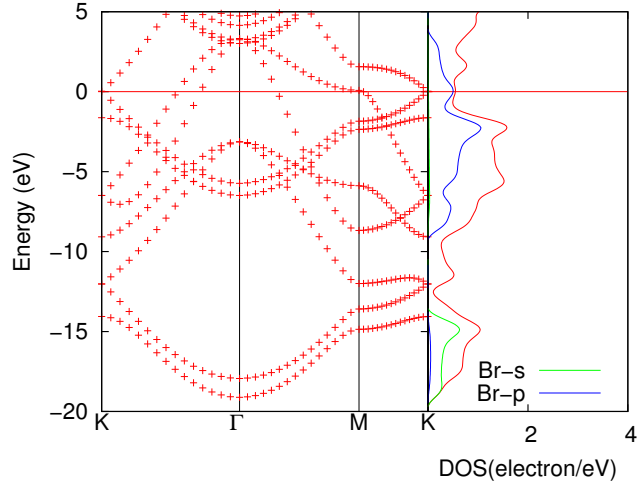


Figure 3.48: *Band structure and density of states of singleside monolayer half coverage bromide graphene of 1×1 unit cell.*

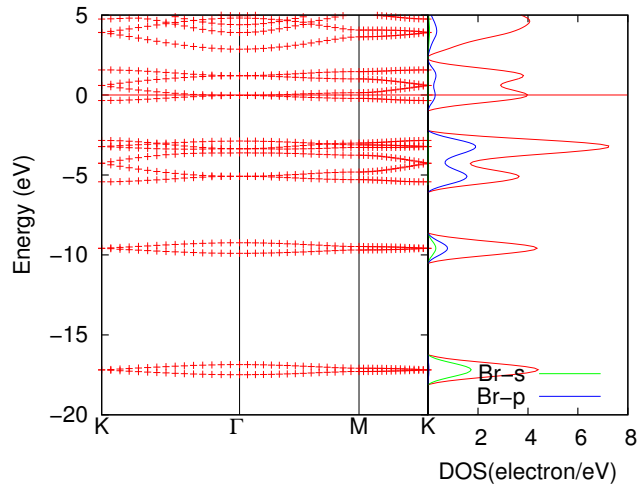


Figure 3.49: *Band structure and density of states of singleside configuration bromide graphene of 1×1 unit cell.*

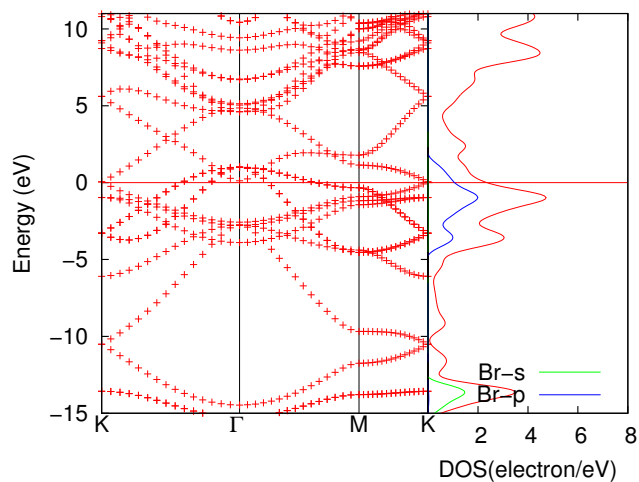


Figure 3.50: *Band structure and density of states of nonbonded chair configuration bromide graphene of 1×1 unit cell.*

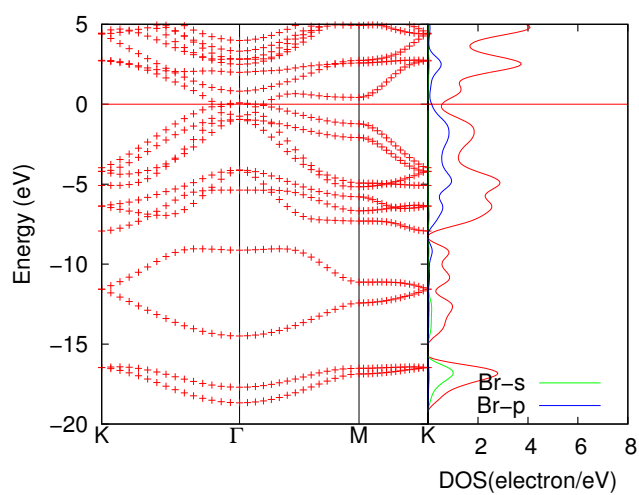


Figure 3.51: *Band structure and density of states of chair configuration bromide graphene of 1×1 unit cell.*

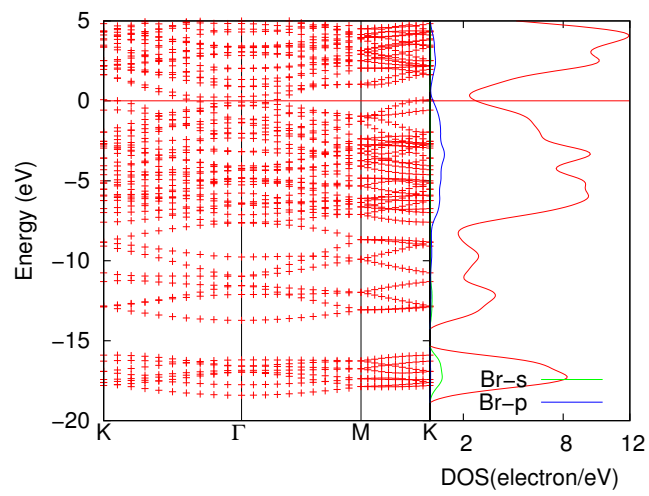


Figure 3.52: *Band structure and density of states of boat configuration bromide graphene of 2×2 unit cell.*

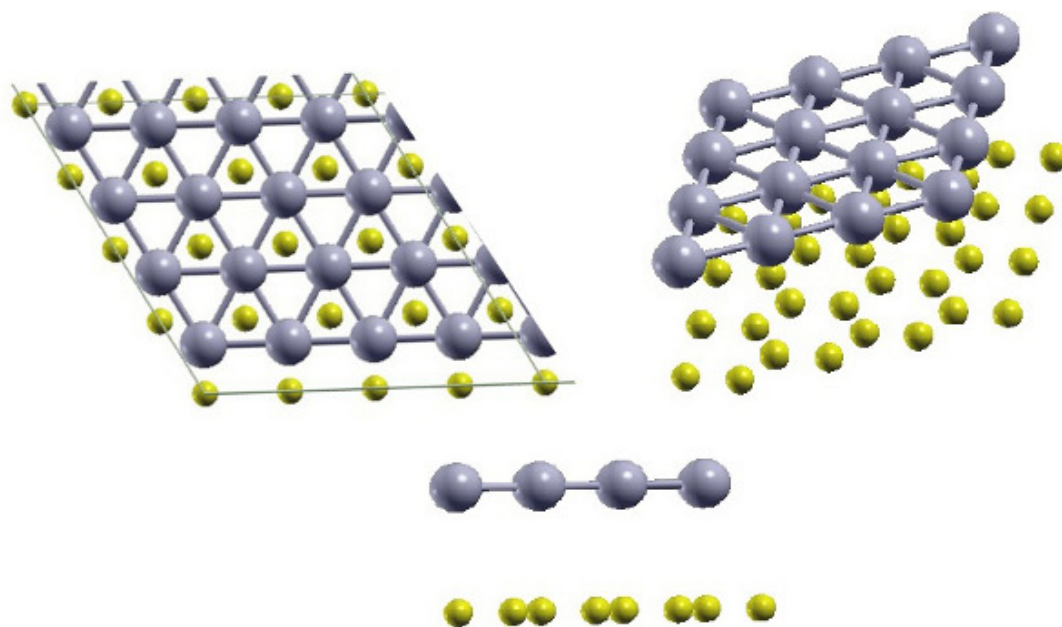


Figure 3.53: *Half coverage singlesided coverage of I atoms on graphene.*

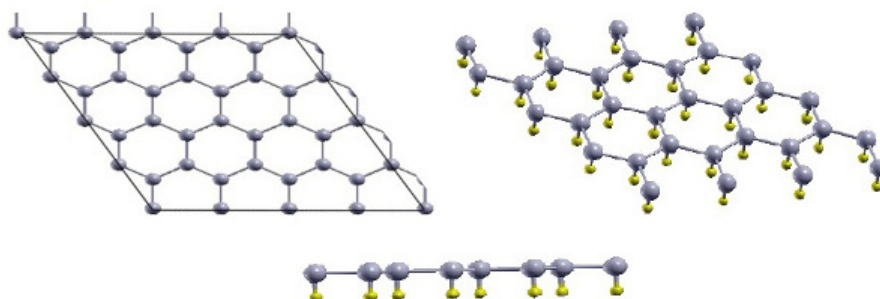


Figure 3.54: *Single sided iodine graphene.*

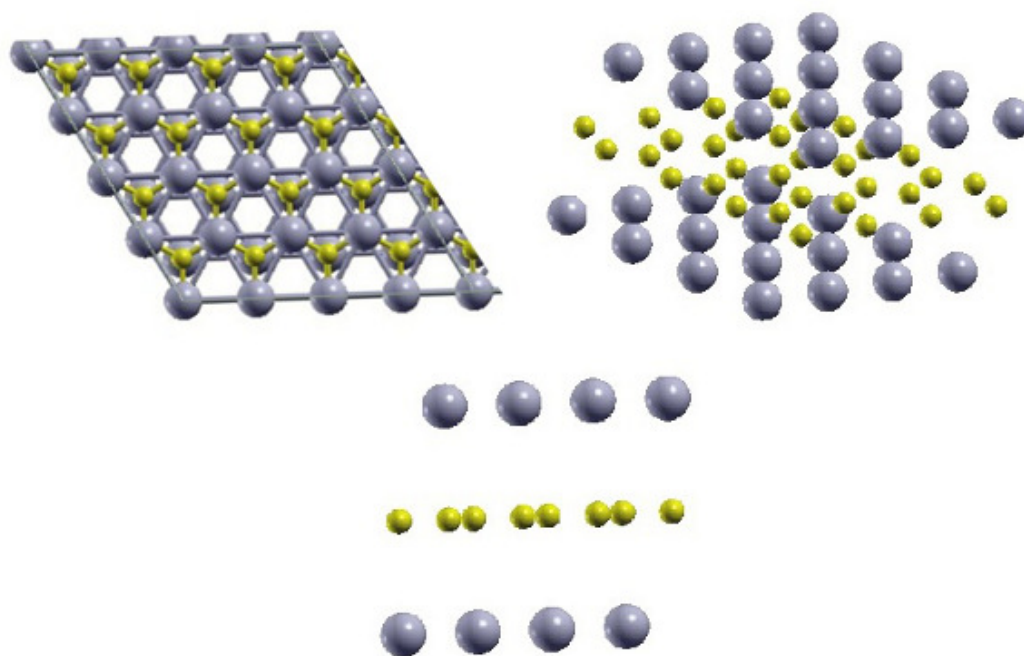


Figure 3.55: *Nonbonded chair configuration of iodine graphene.*

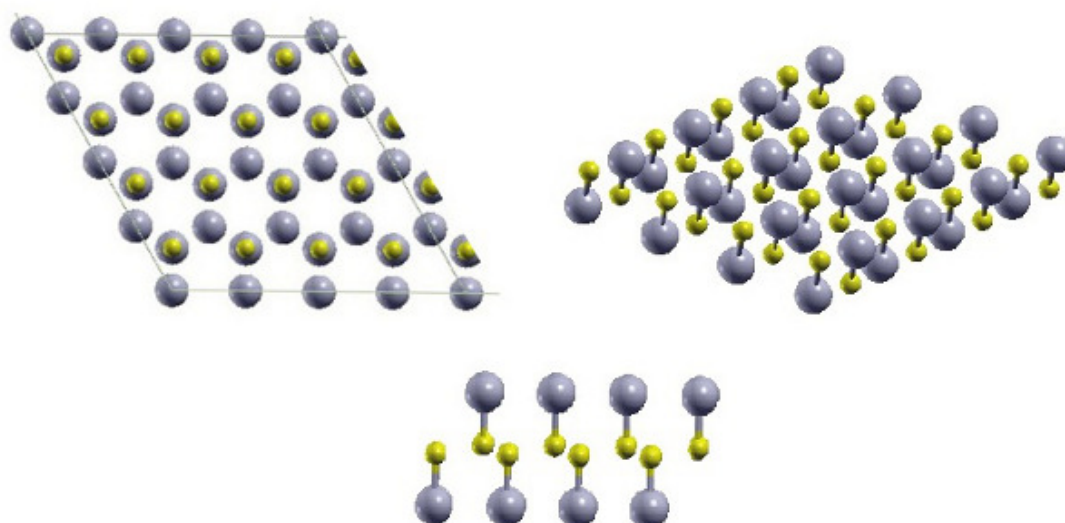


Figure 3.56: *Chair configuration of iodine graphene.*

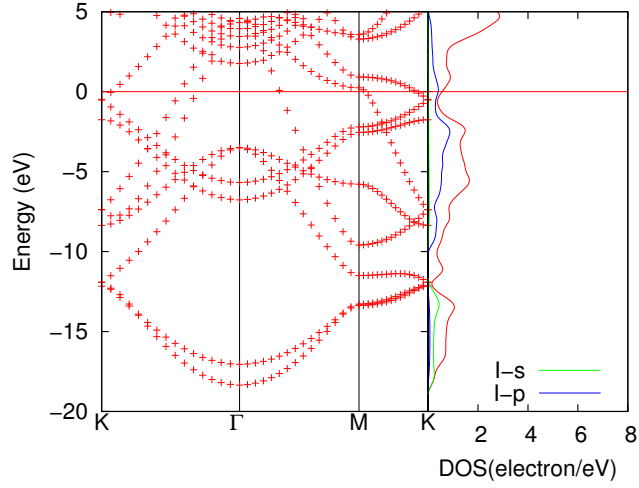


Figure 3.57: *Band structure and density of states of singleside monolayer half coverage iodine graphene of 1×1 unit cell.*

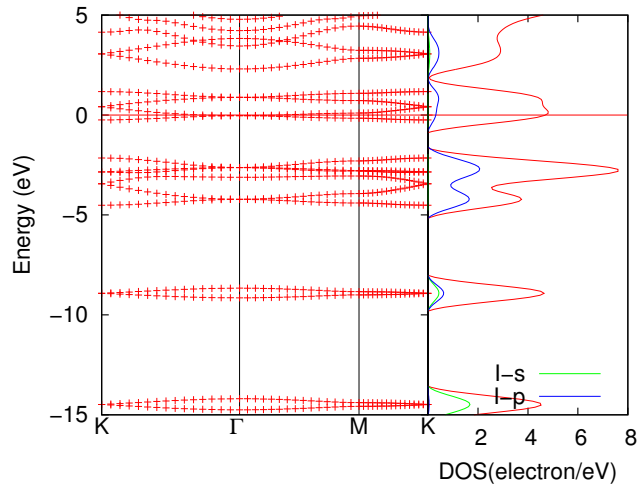


Figure 3.58: *Band structure and density of states of singleside configuration iodine graphene of 1×1 unit cell.*

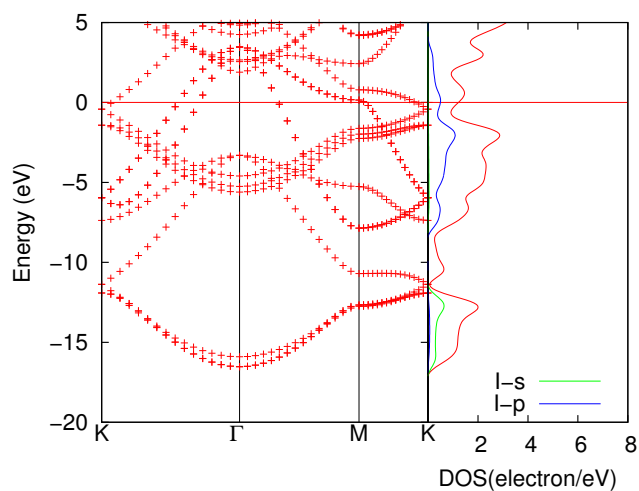


Figure 3.59: *Band structure and density of states of nonbonded chair configuration iodine graphene of 1×1 unit cell.*

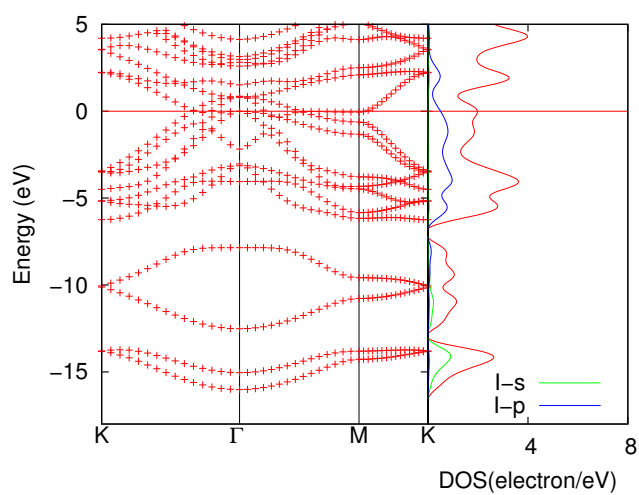


Figure 3.60: *Band structure and density of states of chair configuration iodine graphene of 1×1 unit cell.*

3.6 Iodine Adsorption

<i>System</i>	<i>a</i>	<i>C_h</i>	<i>d_{C-C}</i>	<i>d_{C-I}</i>	<i>d_{I-I}</i>	<i>BE/bond</i>
TOP	2.46	0.000	1.423	3.717	9.84	-0.669
BRIDGE	2.46	0.000	1.424	3.786	9.84	-0.670
HOLLOW	2.46	0.000	1.423	3.968	9.84	-0.670

Table 3.9: Calculated structural properties and binding energy of single iodine adsorption at different high symmetry points of graphene: different configurations of iodine-graphene: lattice constant (*a*) (Å), buckling (*C_h*) (Å), distance between carbon atoms, iodine-carbon atoms, iodine atoms are given (*d_{C-C}*), (*d_{C-Br}*), (*d_{Br-Br}*) respectively (Å). Angle between carbon and iodine atoms (θ_{C-C-I}) and binding energy per bond (BE)(eV)

<i>System</i>	<i>a</i>	<i>C_h</i>	<i>d_{C-C}</i>	<i>d_{C-I}</i>	<i>d_{I-I}</i>	θ_{C-C-I}	<i>BE/bond</i>	<i>E_g</i>
Singleside	6.40	0.000	3.700	2.030	3.7014	-	4.445	-
NB Chair	2.96	0.000	1.707	4.000	2.960	-	1.594	-
Chair	3.39	0.4294	1.998	2.61	3.392	102.47	2.623	-

Table 3.10: Calculated structural properties and binding energy of different configurations of iodine-graphene: lattice constant (*a*) (Å), buckling (*C_h*) (Å), distance between carbon atoms, iodine-carbon atoms, iodine atoms are given (*d_{C-C}*), (*d_{C-I}*), (*d_{I-I}*) respectively (Å). Angle between carbon and iodine atoms (θ_{C-C-I}), binding energy per bond (BE)(eV), dimer energy (DE) (eV), Band Gap (*E_g*) (eV)

Iodine is the largest atom in halogen columns, thus larger initial bond length was set in order to be able to perform relaxation. As in the previous cases, single atom adsorption results in stable structure with -0.67 eV. However, binding energy does not differ at different high symmetry sides. Full iodine coverage in chair configuration results in a very large lattice constant. Furthermore, boat, zigzag and armchair configurations of iodine atoms deformed graphene's honeycomb structure. Possible configurations of iodine adsorption can be seen in figures 3.53-3.56. Moreover, iodine dimer adsorption gives 2.748 eV bonding energy. Overall, this structure is not stable and corresponding band structures show that there is no energy gap in these structures.

Chapter 4

Conclusions

The functionalization of graphene by hydrogen or halogen atoms has been investigated by plane-wave pseudo-potential calculations based on density functional theory. It has been investigated that the structures of full coverage of fluorinated graphene and hydrogenated graphene have similar structures. The fourth valence electrons of carbon atoms participate covalent bonds. π bands are removed in the electronic band structure of adsorbed graphene system leading to opening a band gap. In these adsorbed systems every carbon atom forms 4 bonds thus, they change the sp^2 graphene structure to sp^3 by increasing the bond lengths and decreasing bond angles of graphene structure. Fluorine is the lightest atom among halogen atoms. Stability decreases as the radius of atoms increase and weakening in electronegativity. Heavier compounds like chlorine, bromide and iodine atoms exhibit ionic bonding and they do not exhibit very high and strong binding. It is also clear from the adatom heights in these structures, i.e. 3-4 Å which shows that binding is not covalent type. For the single adatom adsorption only the fluorine atom is chemically adsorbed on graphene. Chlorine single adatom on the other hand, exhibits physisorption which shows that chlorine and graphene interacts weakly. Dimer molecules are found to be relaxed around 3.3 Å which suggests that no bond formation between dimers and carbon atoms of graphene. Therefore, graphene keeps its original planar structure. For the full coverage, chair configuration is the most stable structure for all of the systems. Moreover,

boat configuration is the second highest among the most stable structure. Smaller binding energy results from repulsion of the smaller F-F distance positioned on the same side. For armchair and zigzag configurations there is a considerable alteration in the planar structure of graphene. The resulting bromide-graphene and iodine-graphene system exhibits positive binding energy, consequently it is difficult to use these systems in electronic application, large amount of energy is required in order to obtain efficient materials. Overall, halogen atoms are useful for technological applications, adsorption of these atoms in various configurations tailor electronic structure of graphene. Therefore, these systems are very promising candidates for the future technologies.

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Appendix A

Quantum Espresso Package

Quantum espresso is an open source package under the terms of General Public License for the electronic structure calculations. Density functional theory and its approximations are all implemented in this program which enables calculation of quantum mechanical systems. Hence, it is very practical for crystal structure and surface structure calculations which are the main tool of quantum chemistry measurements. Quantum espresso package is written mostly in Fortran 95 and C and Fortran 77. Parallelization is also possible by MPI (message passing interface) libraries [6] which reduces computational cost considerably.

Gianozzi *et al.* [6] implemented many different concepts in the code. These useful implementations are ground state energy calculation of Kohn Sham orbitals, pseudopotential approximations for the exchange correlation potentials, supercell approach, structural optimization schemes, ab initio molecular dynamics schemes, calculation of magnetic systems, density functional perturbation theory calculations etc. It has several different codes in it which are devoted for different type of calculations. These codes are called PWscf, CP, PHonon, Atomic, PWcond, GIPAW, XSPECTRA, Wannier90, PostProc, PWggu.

Three namelists control, system and electrons should be present in the input file. Control should indicate flux of the calculations whereas system namelist defines the structural and electronic properties of the system. Electrons namelist

on the other hand, exhibits which algorithms to be used for the self consistent solutions. Other mandatory fields are input cards which are shown in last three titles called atomic species, atomic positions and kpoints. Atomic species defines which type of the atomic species, pseudopotential are used. Atomic positions build the crystal lattice structure and k points part is used for the brillouin zone integration in the reciprocal space. In order to run this input file one must type `pw.x < inputfile > outputfile`.

```

&control
  calculation='relax'
  restart_mode='from_scratch',
  prefix='hydrogenatedgraphene',
  tstress = .true.
  tprnfor = .true.
  nstep = 1000
/
&system
 ibrav=4
a=2.44781
c=20
nat=4
ecutwfc=46.
ecutrho=201.
ntyp=2
nosym=.TRUE.
occupations='smearing',
smearing='methfessel-paxton',
degauss=0.05
/
&electrons
  electron_maxstep =1000
/
&ions
  ion_dynamics = 'bfgs'
/
ATOMIC_SPECIES
C 12. C.pbe-paw_kj.UPF 1
H 1.007825035 H.pbe-kjpaw.UPF 1
ATOMIC_POSITIONS {crystal}
C 0.000344000 0.000000000 0.500000000 1 1 1
C 0.333345677 0.666745456 0.500000000 1 1 1
H 0.000000000 0.000445464 0.555000000 1 1 1
H 0.339399033 0.666666666 0.555000000 1 1 1
K_POINTS {automatic}
11 11 1 0 0 0

```

"1*1oneside2.44781.in" 38L, 758C 1,1 All

Figure A.1: *Quantum Espresso input file sample.*

```

Program PWSCF v.5.0      starts on 12Sep2012 at 19: 2:40

This program is part of the open-source Quantum ESPRESSO suite
for quantum simulation of materials; please cite
  P. Giannozzi et al., J. Phys.:Condens. Matter 21 395502 (2009);
  URL: http://www.quantum-espresso.org/,
in publications or presentations arising from this work. More details at
http://www.quantum-espresso.org/quote.php

Parallel version (MPI), running on 12 processors
R & G space division: proc/pool = 12

Current dimensions of program PWSCF are:
Max number of different atomic species (ntypx) = 10
Max number of k-points (npk) = 40000
Max angular momentum in pseudopotentials (lmaxx) = 3
Waiting for input...
Reading input from standard input

Subspace diagonalization in iterative solution of the eigenvalue problem:
scalapack distributed-memory algorithm (size of sub-group: 2* 2 procs)

Parallelization info
-----
sticks:  dense  smooth  PW  G-vecs:  dense  smooth  PW
Min      25      22      7      2809    2442    495
Max      26      23      8      2825    2466    530
Sum      301     265     91     33783   29383   6091

bravais-lattice index = 4
lattice parameter (alat) = 4.6257 a.u.
unit-cell volume = 700.3460 (a.u.)^3
number of atoms/cell = 4
Number of atomic types = 2
38,6 Top

number of Kohn-Sham states= 9
kinetic-energy cutoff = 46.0000 Ry
charge density cutoff = 201.0000 Ry
convergence threshold = 1.0E-06
mixing beta = 0.7000
number of iterations used = 8 plain mixing
Exchange-correlation = SLA PW PBX PBC ( 1 4 3 4 0)
EXX-fraction = 0.00
nstep = 1000

celldm(1)= 4.625691 celldm(2)= 0.000000 celldm(3)= 8.170569
celldm(4)= 0.000000 celldm(5)= 0.000000 celldm(6)= 0.000000

crystal axes: (cart. coord. in units of alat)
a(1) = ( 1.000000 0.000000 0.000000 )
a(2) = ( -0.500000 0.866025 0.000000 )
a(3) = ( 0.000000 0.000000 8.170569 )

reciprocal axes: (cart. coord. in units 2 pi/alat)
b(1) = ( 1.000000 0.577350 0.000000 )
b(2) = ( 0.000000 1.154701 0.000000 )
b(3) = ( 0.000000 0.000000 0.122390 )

PseudoPot. # 1 for C read from file:
/home/ykorknaz/espresso/pseudo/c.pbe-paw_kj.UPF
MD5 check sum: 94bccd327f0fc7800919d2118d753d63
Pseudo is Projector augmented-wave + core cor, Zval = 4.0
Generated using "atomic" code by A. Dal Corso (Quantum ESPRESSO distribution)
Shape of augmentation charge: BESSEL
Using radial grid of 1073 points, 4 beta functions with:
l(1) = 0
l(2) = 0
l(3) = 1
l(4) = 1
Q(r) pseudotized with 0 coefficients
77,0-1 0%

```

Figure A.2: Quantum Espresso output file sample.

```
/home/ykorknaz/espresso/pseudo/H.pbe-kjpaw.UPF
MDS check sum: b6732a8c2b51919c45a22ac3ed50cb01
Pseudo ls Projector augmented-wave, Zval = 1.0
Generated using 'atomic' code by A. Dal Corso (espresso distribution)
Shape of augmentation charge: PSQ
Using radial grid of 929 points, 2 beta functions with:
    l(1) = 0
    l(2) = 0
Q(r) pseudized with 0 coefficients

atomic species  valence  mass      pseudopotential
C                4.00    12.00000    C( 1.00)
H                 1.00     1.00783    H( 1.00)

No symmetry found

cartesian axes

site n.      atom      positions (alat units)
1            C      tau( 1) = ( 0.0003440  0.0000000  4.0852844 )
2            C      tau( 2) = ( -0.0000271  0.5774185  4.0852844 )
3            H      tau( 3) = ( -0.0002227  0.0003858  4.5346657 )
4            H      tau( 4) = ( 0.0060657   0.5773503  4.5346657 )

number of k points= 61 Methfessel-Paxton smearing, width (Ry)= 0.0500
cart. coord. in units 2pi/alat
k( 1) = ( 0.0000000  0.0000000  0.0000000), wk = 0.0165289
k( 2) = ( 0.0000000  0.1049728  0.0000000), wk = 0.0330579
k( 3) = ( 0.0000000  0.2099456  0.0000000), wk = 0.0330579
k( 4) = ( 0.0000000  0.3149183  0.0000000), wk = 0.0330579
k( 5) = ( 0.0000000  0.4198911  0.0000000), wk = 0.0330579
k( 6) = ( 0.0000000  0.5248639  0.0000000), wk = 0.0330579
k( 7) = ( 0.0909091  0.0524864  0.0000000), wk = 0.0330579
k( 8) = ( 0.0909091  0.1574592  0.0000000), wk = 0.0330579
k( 9) = ( 0.0909091  0.2624319  0.0000000), wk = 0.0330579
117,6 0%
k( 10) = ( 0.0909091  0.3674047  0.0000000), wk = 0.0330579
k( 11) = ( 0.0909091  0.4723775  0.0000000), wk = 0.0330579
k( 12) = ( 0.0909091  0.5773503  0.0000000), wk = 0.0330579
k( 13) = ( 0.0909091 -0.4723775  0.0000000), wk = 0.0330579
k( 14) = ( 0.0909091 -0.3674047  0.0000000), wk = 0.0330579
k( 15) = ( 0.0909091 -0.2624319  0.0000000), wk = 0.0330579
k( 16) = ( 0.0909091 -0.1574592  0.0000000), wk = 0.0330579
k( 17) = ( 0.0909091 -0.0524864  0.0000000), wk = 0.0330579
k( 18) = ( 0.1818182  0.1049728  0.0000000), wk = 0.0330579
k( 19) = ( 0.1818182  0.2099456  0.0000000), wk = 0.0330579
k( 20) = ( 0.1818182  0.3149183  0.0000000), wk = 0.0330579
k( 21) = ( 0.1818182  0.4198911  0.0000000), wk = 0.0330579
k( 22) = ( 0.1818182  0.5248639  0.0000000), wk = 0.0330579
k( 23) = ( 0.1818182  0.6298367  0.0000000), wk = 0.0330579
k( 24) = ( 0.1818182 -0.4198911  0.0000000), wk = 0.0330579
k( 25) = ( 0.1818182 -0.3149183  0.0000000), wk = 0.0330579
k( 26) = ( 0.1818182 -0.2099456  0.0000000), wk = 0.0330579
k( 27) = ( 0.1818182 -0.1049728  0.0000000), wk = 0.0330579
k( 28) = ( 0.1818182  0.0000000  0.0000000), wk = 0.0330579
k( 29) = ( 0.2727273  0.1574592  0.0000000), wk = 0.0330579
k( 30) = ( 0.2727273  0.2624319  0.0000000), wk = 0.0330579
k( 31) = ( 0.2727273  0.3674047  0.0000000), wk = 0.0330579
k( 32) = ( 0.2727273  0.4723775  0.0000000), wk = 0.0330579
k( 33) = ( 0.2727273  0.5773503  0.0000000), wk = 0.0330579
k( 34) = ( 0.2727273  0.6823230  0.0000000), wk = 0.0330579
k( 35) = ( 0.2727273 -0.3674047  0.0000000), wk = 0.0330579
k( 36) = ( 0.2727273 -0.2624319  0.0000000), wk = 0.0330579
k( 37) = ( 0.2727273 -0.1574592  0.0000000), wk = 0.0330579
k( 38) = ( 0.2727273 -0.0524864  0.0000000), wk = 0.0330579
k( 39) = ( 0.2727273  0.0524864  0.0000000), wk = 0.0330579
k( 40) = ( 0.3636364  0.2099456  0.0000000), wk = 0.0330579
k( 41) = ( 0.3636364  0.3149183  0.0000000), wk = 0.0330579
k( 42) = ( 0.3636364  0.4198911  0.0000000), wk = 0.0330579
k( 43) = ( 0.3636364  0.5248639  0.0000000), wk = 0.0330579
k( 44) = ( 0.3636364  0.6298367  0.0000000), wk = 0.0330579
k( 45) = ( 0.3636364  0.7348094  0.0000000), wk = 0.0330579
k( 46) = ( 0.3636364 -0.3149183  0.0000000), wk = 0.0330579
k( 47) = ( 0.3636364 -0.2099456  0.0000000), wk = 0.0330579
155,6 1%
k( 47) = ( 0.3636364 -0.2099456  0.0000000), wk = 0.0330579
k( 48) = ( 0.3636364 -0.1049728  0.0000000), wk = 0.0330579
k( 49) = ( 0.3636364  0.0000000  0.0000000), wk = 0.0330579
k( 50) = ( 0.3636364  0.1049728  0.0000000), wk = 0.0330579
k( 51) = ( 0.4545455  0.2624319  0.0000000), wk = 0.0330579
k( 52) = ( 0.4545455  0.3674047  0.0000000), wk = 0.0330579
k( 53) = ( 0.4545455  0.4723775  0.0000000), wk = 0.0330579
k( 54) = ( 0.4545455  0.5773503  0.0000000), wk = 0.0330579
k( 55) = ( 0.4545455  0.6823230  0.0000000), wk = 0.0330579
k( 56) = ( 0.4545455  0.7872958  0.0000000), wk = 0.0330579
k( 57) = ( 0.4545455 -0.2624319  0.0000000), wk = 0.0330579
k( 58) = ( 0.4545455 -0.1574592  0.0000000), wk = 0.0330579
k( 59) = ( 0.4545455 -0.0524864  0.0000000), wk = 0.0330579
k( 60) = ( 0.4545455  0.0524864  0.0000000), wk = 0.0330579
k( 61) = ( 0.4545455  0.1574592  0.0000000), wk = 0.0330579

Dense grid: 33783 G-vectors FFT dimensions: ( 24, 24, 180)
Smooth grid: 29383 G-vectors FFT dimensions: ( 20, 20, 180)

Largest allocated arrays est. size (Mb) dimensions
Kohn-Shan Wavefunctions 0.05 Mb ( 343, 9)
NL pseudopotentials 0.10 Mb ( 343, 20)
Each V/rho on FFT grid 0.13 Mb ( 8640)
Each G-vector array 0.02 Mb ( 2825)
G-vector shells 0.01 Mb ( 1125)
Largest temporary arrays est. size (Mb) dimensions
Auxiliary wavefunctions 0.19 Mb ( 343, 36)
Each subspace H/S matrix 0.00 Mb ( 18, 18)
Each <psi_l|beta_j> matrix 0.00 Mb ( 20, 9)
Arrays for rho mixing 1.05 Mb ( 8640, 8)

Check: negative/imaginary core charge= -0.000003 0.000000
Initial potential from superposition of free atoms
Check: negative starting charge= -0.000322

starting charge 9.99990, renormalised to 10.00000
155,6 1%
```

```

End of BFGS Geometry Optimization

Final energy = -39.1952274920 Ry
Begin final coordinates
ATOMIC_POSITIONS (crystal)
C      0.009105701  0.000573978  0.336002648
C      0.342409330  0.067284312  0.336003995
H     -0.176390162 -0.027787254  0.718978927
H      0.497903841  0.693706550  0.719014429
End final coordinates

Writing output data file hydrogenatedgraphene.save

init_run      :    0.48s CPU    0.69s WALL (    1 calls)
electrons     :   184.78s CPU  307.80s WALL (   18 calls)
update_pot    :    2.81s CPU    3.69s WALL (   17 calls)
forces        :    2.35s CPU    3.15s WALL (   18 calls)
stress        :    4.89s CPU    6.43s WALL (   18 calls)

Called by init_run:
wfcinit       :    0.30s CPU    0.44s WALL (    1 calls)
potinit       :    0.08s CPU    0.12s WALL (    1 calls)

Called by electrons:
c_bands       :   162.17s CPU  278.15s WALL (  123 calls)
sum_band      :   15.18s CPU   19.97s WALL (   123 calls)
v_of_rho      :    1.12s CPU    1.49s WALL (   141 calls)
newd          :    0.64s CPU    0.79s WALL (   141 calls)
mtx_rho       :    1.23s CPU    1.41s WALL (   123 calls)

Called by c_bands:
init_us_2     :    2.25s CPU    2.29s WALL (  18300 calls)
cegtg         :   158.93s CPU  224.06s WALL (   7503 calls)

Called by *egterg:
init_us_2     :    2.25s CPU    2.29s WALL (  18300 calls)
cegtg         :   158.93s CPU  224.06s WALL (   7503 calls)

Called by *egterg:
h_psi         :   93.73s CPU   137.02s WALL (  46663 calls)
s_psi         :   2.40s CPU    2.37s WALL (  46663 calls)
g_psi         :   1.87s CPU    1.85s WALL (  39099 calls)
cdiaghg       :   38.68s CPU   52.37s WALL (  45565 calls)

Called by h_psi:
add_vuspsi    :    2.35s CPU    2.41s WALL (  46663 calls)

General routines
calbec        :    5.18s CPU    8.61s WALL (  57399 calls)
fft           :    1.30s CPU    2.81s WALL (   2651 calls)
ffts          :    0.08s CPU    0.09s WALL (    264 calls)
fftw          :   90.39s CPU   135.59s WALL ( 559157 calls)
interpolate   :    0.26s CPU    0.28s WALL (    264 calls)
davcio        :    0.36s CPU   51.63s WALL (  25803 calls)

Parallel routines
fft_scatter   :   42.21s CPU   88.35s WALL ( 562072 calls)
EXX routines

PAW routines
PAW_pot       :    3.73s CPU    4.35s WALL (   158 calls)
PAW_ddot      :    1.01s CPU    1.18s WALL (   1010 calls)

PWSCF         : 3m19.14s CPU  5m26.65s WALL

This run was terminated on: 19: 8: 7 12Sep2012

=====
JOB DONE.
=====
8600,1 Bot

```

Figure A.3: *Quantum Espresso* output file sample.