First Principle Study of Electronic Structure of Gold doped Graphene

By

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Abstract

In this thesis first principle calculations with in density functional theory (DFT) of electronic structure of gold Au doped graphene is studied by using a plane wave pseudopotential method. We used local density approximation (LDA) and generalized gradient approximations (GGA) for the exchange correlation potential. In all calculations, the geometry optimization option was employed in alloying the structure to fully relax. The convergence of the system was checked by calculating total energy versus kinetic energy cutt-off and total energy versus the size of k-points set. Convergence was attained for graphene starting from $41 Ryd$ or $557.6 eV$, hence used to reduce computational cost. A uniform mesh 0f $13 \times 13 \times 1$ k-points was used since it gives a good convergence at a reasonable computational cost providing charge density results and lattice constant of $2.485 \mathring{A}$. From the band structure of graphene the two bands touch each other at K-point. DOS plot also gives neither band gap between conduction and valence bands nor overlapping at the Fermi energy indicating that graphene is semi-conductor. Finally, in the band structure of Au doped graphene built in $13 \times 13 \times 1$ super cell the π/π^* band cross at Fermi level. As clear evidence of the interaction between Au dopant and the graphene, the Fermi level is now moved to the conduction band, and the DOS display a sharp peak at the Fermi level. Therefore, the doping of Au in the graphene makes graphene semi-metallic.

Chapter 1

Introduction

1.1 Graphene and its discovery

Carbon is one of the most abundantly found elements in the earth's crust. In the periodic table carbon lies above the semiconducting elements silicon and germanium. It has many allotropes and each of them has proved to be useful to the mankind. Graphene is one of these allotropes. It is a two-dimensional sheet of sp^2-hybridized carbon. It is a single atom-thick sheet of hexagonally arranged sp^2-bonded carbon atoms. Monolayer (single-layer) graphene is the purest form known and is useful for high-frequency electronics [1, 2].

Graphene is a monolayer of carbon atoms closely packed into a two-dimensional honeycomb lattice with intriguing properties, like high electron mobility about $100,000cm^2/Vs$ at room temperature and high conductivity [3]. Graphene on the other hand has more mechanical strength, flexibility, stiffness that makes it ideal for wearable technologies and also flexible electronics. Graphene is mainly a sheet resistance with a very high transmittance of about 90%. Graphene is the basic material to form nanotube, fullerene and graphite[4]. The unit contains two lattice sites, with a C-C bond length of $1.42\AA$ a lattice parameter of $2.46\AA$.

First-principles calculations and tight-binding modeling [5] show that the valence and conduction bands intersect in a single point at the Fermi level (E_f) (Dirac point), giving rise to a zero-gap semiconducting nature. At the Dirac point the density of states (DOS) approaches to zero and the linear dispersion relation results in zero effective mass. Electrons in graphene thus behave as massless Dirac fermions. The material is expected to be useful particularly for electronic device applications, transistors.

Experimentally graphene has been exfoliated from graphite in 2004 by Novoselov and co-workers [6, 7]. For this discovery they were awarded the Nobel prize in Physics in 2010. Earlier, Smalley and co-workers had discovered fullerenes [8] and Iijima had discovered nano tubes [9], which in principles are graphene sheets rolled up in to cylinders and spheres. These days carbon-based nano structures are important for a wide range of electronic device applications [10]. Graphene layer is one of the most prominent nano scale material currently studied. Graphene had already been studied theoretically in 1947 by Wallace PR [11] as a text book example for calculations in solid state physics and was discovered realistically by the Geim group at the University of Manchester, UK, in 2004. Andre Geim and Konstantin Novoselov were awarded the Nobel Prize in Physics in 2010. Since its successful fabrication in 2004 by micromechanical cleavage of graphite at the University of Manchester, UK, by the group of Geim, it has attracted great interest due to its fascinating properties and a large number of potential applications[12].

1.2 Statement of the Problem

Graphene, a single layer of graphite, has stimulated enormous scientific interest. The interest in graphene is primarily due to its unique (unusual) properties. It was discovered that graphene has high electronic mobility and high charge carrier concentrations which makes graphene an interesting candidate for applications in electronic devices especially nano-scaled devices. The graphene structure is easily accessible and it is cheap to make. Its many unique properties are still not properly understood, and need further investigations. Computer modelling in the past few years has contributed to the understanding of graphene. There is still more effort needed to understand the unique properties of this material. Hopefully, if such challenges are resolved, graphene will find more applications in nano technology. The main aim of this thesis is to investigate electronic structure of graphene and gold doped graphene. All calculations have been performed using the pseudopotential plane wave scf simulation package code within the framework of density functional theory. This work focuses on the following: firstly DFT study of electronic structure of graphene and gold doped graphene. The graphene structures involving different supercell sizes to determine the structural and electronic properties of these different systems. To validate this work, the calculated results are compared with experimental results and other theoretical results obtained previously.

1.3 Objectives of the study

1.3.1 General objectives

The general objective of this work is to study the electronic structure of gold doped graphene by the first principle calculations.

1.3.2 Specific objectives

- To find the kinetics energy cut-offs for the plane wave expansion of the wave functions
- Determine the k-points sampling for the Brillouin zone of the systems.
- Determine the structural properties of the systems such as the equilibrium lattice constant.
- Determine the electronic structure of pure and gold doped graphene, i.e. density of states, band structures and charge densities that give an indication of the nature of the system.

1.4 Significance of the study

The present study of electronic properties on chemically doped graphene, by utilizing quantum ESPRESSO, will provide a basis for nano-related research and innovations based on computing methods, and will serve as a good support for empirical studies in the future.

It is also useful to note that quantum ESPRESSO is a freely accessible package and the technique is cost effective approach.

Chapter 2

REVIEW OF LITERATURE

2.1 Properties of Graphene

Graphene has almost negligible band gap that increases its importance in electronics domain. Though synthesis of graphene is tedious job producing it in large quantities for industrial purposes will reduce the cost and increase the ease of production of graphene. Some of the mechanical properties of graphene are [14]:

- High tensile strength
- High intrinsic strength (about 130GPa)
- High elasticity .

2.1.1 Mechanical Properties

Graphene is very strong, with high tensile strength, elasticity, brittleness and intrinsic strength. With reference to the experiments of Lee and his coworkers, the elastic stiffness of $-2.0TPa$, ultimate tensile strength of $130GPa$ [15].

2.1.2 Chemical Properties:

Graphene is a zero overlap semimetal. In graphene each carbon atom is connected to three other carbon atoms. It has 6 carbon electrons, with four electrons in n shell (outer shell). These four electrons of each carbon atom when bonded with other three carbon atoms having same number of outer shell electrons leave 1 electron freely available. This freely available electron causes conduction to take place. These electrons are commonly known as π-electrons. These are located in between two graphene ultra-thin layers. Thus these π-electrons cause overlapping of π-orbital making the carbon-carbon bond in graphene much stronger [13, 16, 17].

2.1.3 Electrical Properties:

The freely available electrons (pi-electrons) that do not get bonded are the reason for electrical conduction to take place. Graphene thus behaves as a semiconductor just like the Silicon, Germanium and GaAs. But since the cause of conduction in graphene is different from that of other semiconductor materials, it exhibits many unique properties. One such property is the electron mobility. The electron mobility of graphene in its pristine form is more than 100,000 cm2/Vs. The sheet resistance of graphene is about 30 ohms[13, 18]. Since graphene atoms are considered as massless, they behave much similar to photons.

2.1.4 Optical Properties:

Graphene has very good absorption capacity. Even though graphene in pristine form is just 1 atom thick, it has ability to absorb 2.3% of white light. This property is much appreciable considering its size.

2.2 Application of Graphene

Different applications related to graphene, their general lead and requirements[19, 20]:

1. Organic Light Emitting Diode (OLEDs) Graphene

   General lead–Can be used in wearable technologies, since can be folded to a radius of $< 5mm$.

   Requirement–A better control over sheet resistance.

2. Touch Screens

   General lead–Easy to implement compared to nano ribbons.

   Requirement–A better control over contact resistance.

3. E-paper

   General lead–High transmittance of mono layer graphene could provide visibility.

   Requirement–Requires better control of contact resistance.

4. High frequency transistor

   General lead–No manufacturable solution for high-electron-mobility transistor(low noise) after 2021.

   Requirement–Need to achieve current saturation and fT5850GHz, fmax511, 200GHz should be achieved.

5. Tunable fiber mode-locked laser

   General lead–Graphene's wide spectral range.

   Requirement–Requires a cost-effective graphene transferring technology.

6. Optical modulator

   General lead–Graphene could increase operating speed (Si operation bandwidth is currently limited to about 50GHz).

   Requirement–High-quality graphene with low sheet resistance is needed to increase band width to over 100GHz.

7. Batteries

   General lead–Graphene electrodes are used due to their ultra-thin size and flexibility.

   Requirement–It is susceptible to oxidation environment and may not give desired result

2.3 Properties of gold

Gold is shiny yellow soft chemically inert metal. It is ductile and the most malleable of metal, and because of this is usually alloyed to give improved strength and durability. Gold's reflectivity of ultraviolet and visual light rays is low, however, it has high reflectivity of infrared and red wave length. Gold has been used for dentistry and medicine, electronics and computers, medals and awards, decoration and jewelry for ages as it is easy to reshape and it retains its shine also in the long run. However, the modern use of gold includes also electronics, in which the excellent conduction properties and resistance to corrosion via oxidation.

In the case of gold, the atomic 6s states delocalize over the cluster atoms creating a super atom with shell structure. Thus, for example, the electron affinity of gold depends on cluster size. However, gold clusters also have interesting properties that differ from other metal clusters. For example, as Au is heavy metal with high nuclear charge, the kinetic energies of its core electrons are so high that the relativistic effects are significant. These effects lead to contraction of 6s valence orbitals whereas 5d valence orbitals are expanded.

The energy difference between s and d states is decreased and leads to s-d hybridized states. These states are crucial in the bonding between Au atoms and the d character make the bonds highly directional.

However, possibly the most important reason for the modern gold rush in the research during the last two decades has been the discovery that although gold is an inert noble metal as a bulk material, it is catalytically active in cluster form. gold does not only be a catalyst, but it is actually the best one for acetylene hydrochlorination reaction on a carbon support[21].

2.4 General properties of solids

In a metal, the highest occupied band at $0K$ is partially filled with electrons. In a semiconductor at $0K$, the highest occupied band is completely filled with electrons and the next band is completely empty. The separation between the two bands is the band gap E_g.

When an allowed band is completely filled with electrons, the electrons in the band cannot conduct any current. Since electrons are fermions they cannot carry any net current in a filled band since an electron can only move into an empty state. Because of this effect, when we have a material in which a band is completely filled, while the next allowed band is separated in energy and empty, the material has, in principle, infinite resistivity and is an insulator or a semiconductor. The material in which a band is only half full with electrons has a very low resistivity and is a metal.

The band that is normally filled with electrons at $0K$ in semiconductors is called the valence band, while the upper unfilled band is called the conduction band. Semiconductors have zero conductivity at $0K$ and quite low conductivity at finite temperatures, but it is possible to alter their conductivity by orders of magnitude through doping or applied electric potentials. This makes semiconductors useful for active devices [15].

2.4.1 Conductor

There is no forbidden gap between valance band and conduction band. The two bands overlap. Hence even at room temperature, a large number of electrons are available for conduction. So without any additional energy, such metals contain a large number of free electrons and hence called good conductors.

2.4.2 Insulator

There exists large forbidden gap in between conduction band and valance band. Practically it is impossible for an electron to jump from the valance band to conduction band. Hence such material cannot conduct and called insulator. Such materials may conduct only at very high temperatures or if they are subjected to high voltage.

2.4.3 Semiconductor

The forbidden gap in such material is very narrow. Its electronic properties are intermediate between those of metals and insulators. The energy provided by the heat at room temperature is sufficient to lift the electrons from the valance band to conduction band.

2.4.4 semi-metal

A semi-metal is a material with a very small overlap between the bottom of the conduction and the top of the valance band.

Chapter 3

Research Methodology

3.1 Computational methods

In this section deals with the electronic structure calculation methods, which contains the quantum mechanical framework and the Schr$\ddot{o}$dinger equation; Hartree-Fock method, density functional theory, Kohn-Sham equations, exchange-correlation functional, plane wave functions, Brillouin zone sampling, and basis sets.

3.2 Electronic structure calculation

3.2.1 Quantum mechanical approach

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A. Schr$\ddot{o}$dinger equation

To simulate a composite system consisting of N interacting electrons and M nuclei, the many-body wave function $\Psi\ (r_i, R_i)$ is used to describe its quantum state. This wave function Ψ depends on the electronic coordinates r_i and the nuclear coordinates R_i, and is the solution of the time independent Schr$\ddot{o}$dinger equation. Its non-relativistic form can be written as:

$$\hat{H}\Psi = E\Psi \tag{3.2.1}$$

With:

$\hat{H}$: Hamiltonian operator

E: total energy of the system

Ψ: wave function

The Hamiltonian is written as:

$$\hat{H} = \hat{T}_e + \hat{T}_n + \hat{V}_{en} + \hat{V}_{ee} + \hat{V}_{nn} \tag{3.2.2}$$

where

1. Kinetic energy of electrons

$$\hat{T}_e = -\sum_{i=1}^{N} \frac{\hbar^2 \nabla_i^2}{2m_e} \tag{3.2.3}$$

2. Kinetic energy of the nuclei

$$\hat{T}_n = -\sum_{i=1}^{M} \frac{\hbar^2 \nabla_i^2}{2M_n} \tag{3.2.4}$$

3. Attractive energy between electrons and nuclei

$$\hat{V}_{en} = -\sum_{i=1}^{M} \sum_{j=1}^{N} \frac{Z_i e^2}{|\overrightarrow{R}_i - \overrightarrow{r}_j|} \tag{3.2.5}$$

4. Repulsive energy between electrons

$$\hat{V}_{ee} = \frac{1}{2} \sum_{i=1}^{N} \sum_{j>1}^{N} \frac{e^2}{|\overrightarrow{r}_i - \overrightarrow{r}_j|} \tag{3.2.6}$$

5. Repulsive energy between nuclei

$$\hat{V}_{nn} = \frac{1}{2} \sum_{i=1}^{M} \sum_{j>i}^{M} \frac{Z_i Z_j e^2}{|\overrightarrow{R}_i - \overrightarrow{R}_j|} \tag{3.2.7}$$

with:

N: number of electrons

M: number of nucleus atom

r_i: electronic coordinate

R_i: nuclear coordinate

M_n: mass of the nucleus

Z_i: atomic number of the nucleus

m_e : mass of electron

Hence,

The Schr$\ddot{o}$dinger equation can be written as:

$$E\Psi = \Big[-\sum_{i=1}^{N} \frac{\hbar^2\nabla_i^2}{2m_e} - \sum_{i=1}^{M} \frac{\hbar^2\nabla_i^2}{|2M_n|} - \sum_{i=1}^{M}\sum_{j=1}^{N} \frac{Z_i e^2}{|\overrightarrow{R}_i - \overrightarrow{r}_j|} + \frac{1}{2}\sum_{i=1}^{N}\sum_{j>1}^{N} \frac{e^2}{|\overrightarrow{r}_i - \overrightarrow{r}_j|} + \frac{1}{2}\sum_{i=1}^{M}\sum_{j>i}^{M} \frac{Z_i Z_j e^2}{|\overrightarrow{R}_i - \overrightarrow{R}_j|}\Big]\Psi \tag{3.2.8}$$

The above Schr$\ddot{o}$dinger equation is difficult to be solved, therefore to introduce some approximations in order to find an approximate solution of this equation.

B. Born-Oppenheimer approximation

This approximation is based on the fact that the nuclei are much heavier than the electrons (about 1800 times more massive), and the kinetic energy of nuclei are much smaller than the electrons' kinetic energy. Then the nuclear kinetic energy can be neglected when solving the electronic problem. This approximation allows us to dissociate the kinetic energy of the electrons and of the ions, which reduces the difficulties in solving the dynamics of the electrons in a "frozen" nuclei configuration. The potential term V_{nn} also reduces to a constant and we are then left with the kinetic energy of the electrons, the potential energy due to electron-electron interaction, and the potential energy of the electrons in the potential of the nuclei. Therefore, the Hamiltonian operator has only three terms: the kinetic energy of the electrons as well as the electron-electron ($\hat{V}_{ee}$) and the electron-nucleus interactions ($\hat{V}_{ext} = \hat{V}_{en}$). The total wave function then becomes:

$$\hat{H}_{tot}\Psi = E_{tot}\Psi \tag{3.2.9}$$

where

$$\hat{H}_{tot} = \hat{T}_e + \hat{V}_{en} + \hat{V}_{ee} \tag{3.2.10}$$

$$\hat{H}_{tot} = -\sum_{i=1}^{N}\frac{\hbar^2\nabla_i^2}{2m_e} - \sum_{i=1}^{M}\sum_{j=1}^{N}\frac{Z_i e^2}{|\overrightarrow{R}_i - \overrightarrow{r}_j|} + \frac{1}{2}\sum_{i=1}^{N}\sum_{j>1}^{N}\frac{e^2}{|\overrightarrow{r}_i - \overrightarrow{r}_j|} \tag{3.2.11}$$

But it is still difficult to solve this equation, so that more simplifications are needed.

Here $\overrightarrow{r}_i$ and $\overrightarrow{r}_j$ are the coordinates of electron i and j, respectively, and Z_i is the charge of the nucleus at position $\overrightarrow{R}_i$. It is important to note that the kinetic and electron-electron terms depend only on the electron system. Information about the nuclei and their positions is entirely contained in $\hat{V}_{nn}$. The Hamiltonian within the Born-Oppenheimer approximation is much simpler than the original, but still far too difficult to solve. There are several methods to reduce the above equation to an approximate but treatable form. A very important one is the Hartree-Fock method, which is used in quantum chemistry because it performs well for atoms and molecules.

C. Hartree-Fock method

The Hartree-Fock method is introduced to simplify the calculation by calculating the energy of each electron in the averaged static field.

The Fock Hamiltonian can be written as:

$$f_i = -\frac{1}{2}\nabla_i^2 - \sum_{i=1}^{N}\frac{Z_k}{r_{ik}} + V_i^{HF} \tag{3.2.12}$$

WhereV_i^{HF} is Hartree-Fock potential representing the average repulsive potential of one electron to the other $N-1$ electrons.

It can be written as:

$$V_i^{HF}(\vec{\chi}_1) = \sum_{i}^{N}(\hat{J}_i(\vec{\chi}_1) - \hat{K}_i(\hat{\chi}_1)) \tag{3.2.13}$$

Where $\hat{\chi}_1$ is the position of one electron, $\hat{J}_i$ is the coulomb operator, and $\hat{K}_i$ is the exchange contribution to the Hartree-Fock potential. $\hat{J}_i$ is defined as:

$$\hat{J}_i(\hat{\chi}_1) = \int |\chi_j(\vec{\chi}_2)|^2\frac{1}{r_{12}}d\vec{\chi}_2 \tag{3.2.14}$$

and $\hat{K}$ is defined when it is operating on spin orbital:

$$\hat{K}(\hat{\chi}_1)\hat{\chi}_i(\hat{\chi}_i) = \int \chi_j^*(\vec{\chi}_2)\frac{1}{r_{12}}\chi_i(\hat{\chi}_2)d\hat{\chi}_2\chi_i(\vec{\chi}_2) \tag{3.2.15}$$

In this way, the HF potential V_i^{HF} is non-local and depends on the spin orbitals χ_i , which are unknown at first to calculate V_i^{HF}, and a Hartree-Fock Self-Consistent Field (HF-SCF) process is used. An initial set of spin orbitals χ_i is guessed, and used to generate a new V_i^{HF}. Then with this HF potential, new spin orbitals are calculated. This process is repeated until the result meets the criteria of convergence. Since HF method does not consider the dynamic correlation between the electronic movements, the HF energy is above the total energy.

3.2.2 Density functional theory (DFT)

Density Functional Theory (DFT) is one of the most popular, powerful, versatile and successful quantum mechanical modeling methods used to investigate the electronic and structural properties of materials. It was formulated by Hohenberg, Kohn and Sham and aims to describe the ground state properties of many-electron systems in terms of the electronic charge density. Within this approach, the many body problem of interacting electrons in a static external potential is reduced such that one can tackle the problem by non-interacting electrons moving in an effective potential. It is being used for calculating the binding energy of molecules in chemistry and the electronic and phononic band structures of solids in physics. In the present thesis, DFT calculations are performed to investigate the electronic structure of gold doped graphene. Hence, the description of the method and an explanation of its features are necessary for the correct interpretation of the results obtained from band structure calculations.

Density Functional Theory (DFT) does not use the N-body wave functions of the electrons, but the total density of electrons, and uses it as a basic quantity. The electron density is a physical characteristic. When the number of electrons increases, it is easier to be calculated. More importantly, this method overcomes the principal disadvantage of the Hartree-Fock method, which neglects the electron correlation. Hence, DFT improves the calculation accuracy significantly, whereas the exchange part in HF is defined exactly.

A. Hohenberg-Kohn theorems

The conventional formulation of the two theorems of Hohenberg and Kohn is as follows: *Theorem 1*: The non-degenerate ground state electron density ρ_o determines the external potential V_{eA}. Thus the external potential is a well-defined functional of the ground state electron density $V_{eA}[\rho_o]$.

Theorem 2: The ground state total energy functional $EV_{eA}[\rho_o]$ reaches its minimal value at the ground state electron density ρ_o corresponding to V_{eA}.

$$E[\rho] \geq E[\rho_o] \tag{3.2.16}$$

for every trial electron density ρ. The ground state total energy functional $EV_{eA}[\rho]$ can be written as

$$EV_{eA}[\rho] =< \Psi|T_e + V_{ee}|\Psi > + < \Psi|V_{eA}|\Psi > \tag{3.2.17}$$

The energy functional $EV_{eA}[\rho]$ for the density ρ corresponding to the particular V_{eA} for any solid gives the ground state energy.

B. The Kohn-Sham equations

The Hohenberg-Kohn theorems show that it is possible to use the ground state density to calculate the physical properties of a system, but it does not tell us a way to find the ground state density. This difficulty is overcome by the Kohn-Sham equations [22]. The correlation energy is defined as part of the total energy absent in the Hartree-Fock solution. This motivates rewriting the total energy $E = T + V$ as

$$EV_{ext}[\rho] = T_0[\rho] + V_H[\rho] + V_{xc}[\rho] + V_{ext}[\rho] \tag{3.2.18}$$

where T_0, V_H, and V_{xc} are the kinetic energy, Hartree potential, and exchange correlation functional, respectively. The corresponding Hamiltonian is called the Kohn-Sham Hamiltonian

$$\hat{H}_{ks} = \hat{T}_0 + \hat{V}_H + \hat{V}_{xc} + \hat{V}_{ext} \tag{3.2.19}$$

. The exchange-correlation potential is given by the functional derivative of the exact ground state density $\hat{V}_{xc} = \frac{\delta E_{xc}[\rho]}{\delta \rho}$.

The Kohn-Sham method is an exact description of the ground state properties of many-electron systems. However, the exchange-correlation functional is unknown and demands further approximations.

3.2.3 Exchange-correlation functional

A. Local-Density Approximations (LDA)

The most widely used approximation to the exchange-correlation functional is the local density approximation (LDA) [22, 23]. In this approximation the exchange-correlation energy is compared to the homogeneous electron gas,

$$E_{xc}^{LDA}[\rho] = \int \rho(\vec{r})\epsilon_{xc}^{hom}(\rho(\vec{r}))d^3(\vec{r}) \tag{3.2.20}$$

where $\epsilon_{xc}^{hom}(\rho(\vec{r}))$ is the exchange-correlation energy density. The many-electron system is divided into infinitesimally small regions located at positions r, each containing a homogeneous interacting electron gas with a constant local densityρ. Particularly, the LDA is exact in the case of constant density, but (surprisingly) also works well in realistic cases. Magnetic materials are modeled using the local spin density approximation, in which the electron density is divided into spin up and spin down densities $(\rho \uparrow (\vec{r})); (\rho \downarrow (\vec{r}))$ with $(\rho(\vec{r})) = (\rho \uparrow (\vec{r})) + (\rho \downarrow (\vec{r}))$. Using the spin polarization $(\zeta(\vec{r})) = \frac{\rho\uparrow(\vec{r})-\rho\downarrow(\vec{r})}{\rho\uparrow(\vec{r})+\rho\downarrow(\vec{r})}$ the above equation takes the form

$$E_{xc}^{LDA}[\rho(\vec{r}), \zeta(\vec{r})] = \int \rho(\vec{r})\epsilon_{xc}^{hom}(\rho(\vec{r})\zeta(\vec{r}))d^3(\vec{r}) \tag{3.2.21}$$

Local-density approximations are important in the construction of more sophisticated approximations to the exchange-correlation energy, such as generalized gradient approximations or hybrid functionals. A desirable property of any approximate exchange-correlation functional is that it reproduce the exact results of the homogeneous electron gas (HEG) for non-varying densities. As such, LDA's are often an explicit component of such functionals.

B. Generalized Gradient Approximations (GGA)

Generalized gradient approximations (GGA) are still local but also take into account the gradient of the density at the same coordinate. where the exchange-correlation functional depends on both the electron density and its gradient $|\nabla\rho(\vec{r})|$ [24, 25]:

$$E_{xc}^{GGA}[\rho(\vec{r})] = \int \rho(\vec{r})\epsilon_{xc}(\rho(\vec{r}), \nabla\rho(\vec{r})d^3(\vec{r}) \tag{3.2.22}$$

In many cases the GGA improves the total energy, structural parameters and binding energies of molecules.

3.3 Bloch's theorem

The Bloch's theorem can be stated as follows: in a periodic solid, the eigenvalues $\Psi_i(r)$ of an electron are given in the form of plane waves times the cell-periodic $g_i(r)$,

$$\Psi_i(r) = e^{ik.r}g_i(r) \tag{3.3.1}$$

The Bloch's theorem introduces wave vectors k which are always in the primitive cell of the reciprocal lattice and satisfy the expression $e^{ik.r} = 1$ for all lattice points. The potential $g_i(r)$ is cell periodic and can be expressed as a fourier expansion of plane waves whose wave vectors are reciprocal lattice vectors of the crystal

$$g_i(r) = \sum_q C_i q e^{iq.r} \tag{3.3.2}$$

Where q is the reciprocal lattice vectors defined by the reciprocal of lattice vector ℓ as follows,

$$q.\ell = 2\pi n \tag{3.3.3}$$

and n is any integer. Now each electronic wave function can be expressed as the sum of all plane waves,

$$\Psi_i(r) = \sum_q c_{i,k+q}e^{i(q+k)r} \tag{3.3.4}$$

The $c_{i,k+q}$ are the coefficients for the plane waves that need to be solved and depend on the kinetic energy cut-off.

3.4 Quantum ESPRESSO

Quantum Espresso is a variety of numerical methods and algorithms aimed at a chemically realistic modeling of materials from the nanoscale upwards, based on the solution of the density functional theory(DFT). It is an integrated suite of computer codes for electronic structure calculations and materials modeling based on DFT, plane waves and pseudo potentials (norm conserving, ultra soft and projector augmented wave) to represent the electron-ion interactions. The ESPRESSO stands for open Source Package for Research in Electronic Structure, Simulation and optimization. The codes are constructed around the use of periodic boundary conditions, which allows for a straight forward treatment of infinite crystalline systems. Quantum espresso can do the following basic computations[26].

1. Calculation of the Kohn-Sham(KS) orbitals and energies for isolated systems, and of their ground state energies.
2. Complete structural optimizations of the microscopic(atomic coordinates) and macroscopic degrees of freedom.
3. Ground state of magnetic or spin polarized systems.
4. Spin orbit coupling and non-collinear magnetism.
5. Density functional perturbation theory(DFPT), to calculate second and third derivatives of the total energy at any orbitary wavelength.
6. Calculation of phonon dispersion, nudged elastic band.

3.4.1 Plane waves

Plane waves are useful and simple for describing the electronic wave function in a periodic system. Because of this reason, to solve the Kohn-Sham equations, we expand the wave function at each k point in terms of plane wave basis. While doing this as a computational technique to simplify the calculation, we can use Fast Fourier Transformation (FFT). But it is impossible to make an expansion with infinite number of plane wave basis set. For this reason, we have to truncate our plane wave expansion. We can define an upper bound for the kinetic energy. Hence, we will only use plane waves which have less kinetic energy than our defined kinetic energy. In order to reduce errors we can increase the cut-off energy [27].

3.4.2 Pseudopotential method

In the pseudopotential method for a solid, one considers the ion cores as a background in which the valence electrons move. These valence electrons actively participate in determining the chemical and physical properties of molecules and solids. This has led to the idea of the pseudo potential method: the interaction between the valence electrons and the ion core is treated with the pseudo potential which allows us to understand why the electron-ion core interaction is apparently so weak. The fact that pseudo potentials are not unique allows the freedom to choose forms that simplify the calculations and the interpretation of the resulting electronic structure.

The coulomb interaction is inversely proportional to the radial distance r. Because of this in the core region of the atom, potential becomes too large when electron is too close to core. The wave functions of valance and core electrons have to be orthogonal. So that plane waves of these valance electrons are oscillating too much. To avoid this we can define a pseudo potential. Instead of considering the potential of all core electrons, we can define a single pseudo potential which can describe the system with a good approximation. Due to this fact large energy cut-offs must be used to include plane waves that oscillate on short wave length scales in real space. This is problematic because the tightly bound core electrons in atoms are associated with wave functions with exactly this kind of oscillation. From a physical point of view, however, core electrons are not especially important in defining chemical bonding and other physical characteristics of materials; these properties are dominated by the less tightly bound valence electrons.

From the earliest developments of plane-wave methods, it was clear that there could be great advantages in calculations that approximated the properties of core electrons in a way that could reduce the number of plane waves necessary in a calculation. The most important approach to reducing the computational burden due to core electrons is to use pseudo potentials. Conceptually, a pseudo potential replaces the electron density from a chosen set of core electrons with a smoothed density chosen to match various important physical and mathematical properties of the true ion core. The properties of the core electrons are then fixed in this approximate fashion in all subsequent calculations; this is the frozen core approximation. Calculations that do not include a frozen core are called all-electron calculations, and they are used much less widely than frozen core methods. Ideally, a pseudo potential is developed by considering an isolated atom of one element, but the resulting pseudo potential can then be used reliably for calculations that place this atom in any chemical environment without further adjustment of the pseudo potential. This desirable property is referred to as the transferability of the pseudo potential.

Current DFT codes typically provide a library of pseudo potentials that includes an entry for each (or at least most) elements in the periodic table. The details of a particular pseudo potential define a minimum energy cut-off that should be used in calculations including atoms associated with that pseudo potential. Pseudo potentials requiring high cut-off energies are said to be hard, while more computationally efficient pseudo potentials with low cut-off energies are soft. The most widely used method of defining pseudo potentials is based on work by Vanderbilt; these are the ultra soft pseudo potentials (USPPs). As their name suggests, these pseudo potentials require substantially lower cut-off energies than alternative approaches. One disadvantage of using USPPs is that the construction of the pseudo potential for each atom requires a number of empirical parameters to be specified. Current DFT codes typically only include USPPs that have been carefully developed and tested, but they do in some cases include multiple USPPs with varying degrees of softness for some elements.

Another frozen core approach that avoids some of the disadvantages of USPPs is the projector augmented-wave (PAW) method originally introduced by Bloch and later adapted for plane-wave calculations by Kresse and Joubert. Kresse and Joubert performed an extensive comparison of USPP, PAW, and all electron calculations for small molecules and extended solids. Their work shows that well-constructed USPPs and the PAW method give results that are essentially identical in many cases and, just as importantly, these results are in good agreement with all-electron calculations. In materials with strong magnetic moments or with atoms that have large differences in electronegativity, the PAW approach gives more reliable results than USPPs [28].

3.4.3 Crystal lattices and cut-off energy

Crystalline solids can be described as a Bravais lattice in which small units are repeated in a periodic array. The units may be atoms, ions or molecules and the crystal may be described as primitive, Wigner-seitz, conventional unit cells etc. This crystalline solid can contain a large number of electrons moving in a field produced by a similarly large number of ions. This large number of electrons is extremely difficult to use in computations. Bloch's theorem is employed to reduce this large number to as little as half the number of electrons in the unit cell of the crystal. In a crystal, the wave function at each k-point can be expanded as a plane wave basis and the convergence of kinetic energy cut-off (E_{cut}) can be obtained. The Fourier coefficients $C_{i,(k+q)}$ with small kinetic energies are large and become small when the kinetic energy increases. The plane wave expansion can be truncated to contain the plane waves that consist of the kinetic energy less than the energy cut-off.

$$\frac{\hbar^2}{2m}|k+q|^2 < E_{cut} \tag{3.4.1}$$

However, the truncation of the plane wave expansion at a small energy cut-off will lead to an error when computing the total energies of the system. This error may decrease when the energy cut-off increases. The expansion of the electronic wave functions in terms of the plane waves basis set allows the Kohn-Sham equations to be represented in a reciprocal space. The electronic wave function expressed in terms of all plane waves equation is substituted into the Kohn-Sham equation and, integrated over the region r, gives the equation

$$\sum_{q'}[\frac{\hbar^2}{2m}|k+q|^2\sigma_{qq'} + V_{ion}(q-q') + V_H(q-q') + V_{xc}(q-q')]C_{i,k+q'} = \epsilon_i C_{i,k+q'} \tag{3.4.2}$$

In this equation the kinetic energy is diagonal and the potentials are expressed in terms of their Fourier components. The Hamiltonian matrix in the square brackets of this equation is diagonal: the size of the matrix was determined by the energy cut-off

$$\frac{\hbar^2}{2m}|k+q|^2 = E_{cut} \tag{3.4.3}$$

3.4.4 k-point sampling

The first Brillouin zone can be mapped out by a continuous set of k-points throughout the region of reciprocal space. These k-points represent the local where the electronic states are found in a solid system. If there is an infinite number of electrons in a solid system there exists an infinite number of k-points in the Brillouin zone. In the calculation, the basis sets are required to represent the wave functions at a finite number of k-points. However, the basis sets calculations are still infinite even if the energy cut-off is chosen to be very small. In the previous section, we discussed Bloch's theorem which enables us to consider a finite number of wave functions in the unit cell at an infinite number of k-points within the Brillouin zone. The electronic states calculated at a set of k-points contribute to the electronic potential of the solid system and are determined by the shape of the Brillouin zone. This is done since the electronic wave functions at the k-points that are close together will be identical, which causes the electronic wave functions to be represented over a region of reciprocal space at a single k-point. This enables us to calculate the electronic potential and the total energy of the solid system at a finite number of k-points. The error occurring during calculations can be made small by choosing a heavier set of k-points in the Brillouin zone. For example, in a metallic system, dense k-points are needed since it is very difficult to define the Fermi surface with a few points. The dense k-points still make the computational time lengthly and still offer a challenge in research[29].

3.4.5 Self consistency

Consider the trial plane-wave function and the pseudo potential approach described in the KS equation. Although the solutions of KS equations provide the ground state charge density, they can not be taken as the desired results because one can obtain a more reliable and stable result by using the charge density which is achieved by iterating the solutions of KS equations. This method is called self-consistent field (SCF) approach. The iterative way is outlined in the following algorithm:

i. Define an initial, trial electron density, $\rho(r)$.

ii. Solve the Kohn Shame quations defined using the trial electron density to find the single-particle wave functions, $\phi(r)$.

iii. Calculate the electron density defined by the Kohn Sham single-particle wave functions from step ii, $\rho_{ks}(r)$.

iv. Compare the calculated electron density, $\rho_{ks}(r)$, with the electron density used in solving the Kohn Sham equations, $\rho(r)$. If the two densities are the same, then this is the ground-state electron density, and it can be used to compute the total energy. If the two densities are different, then the trial electron density must be updated in some way.

Chapter 4

Results and Discussion

Before presenting any results, it is important to ensure that the system is in equilibrium. One way to do this is to minimize the energy and calculate the equilibrium parameters of the system that corresponds to the minimum energy. Therefore, the convergence of the system is checked by calculating total energy versus kinetic energy cut-off and total energy versus the size of the Monkhorst-Pack k-points set.

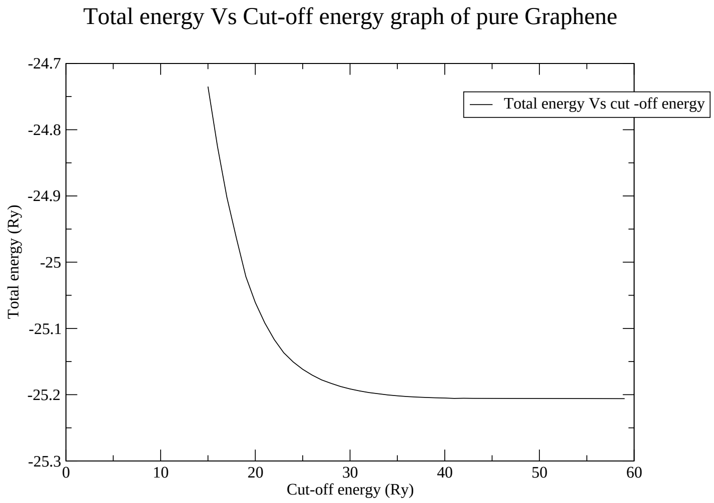

Figure 4.1: Total energy of graphene with a lattice constant of $2.46\mathring{A}$ using $4 \times 4 \times 1$ k-points as a function of the cut-off energy.

Figure 4.1 shows computed total energy of graphene with respect to the cut-off energy.

Higher cut-off energies give marginally lower energies giving nearly starting from $41Ryd$ or $557.6eV$. However the differences become very small and do not effect the accuracy of the results. Therefore, we choose $41Ryd$ or $557.6eV$ cut-off energy to reduce computational cost.

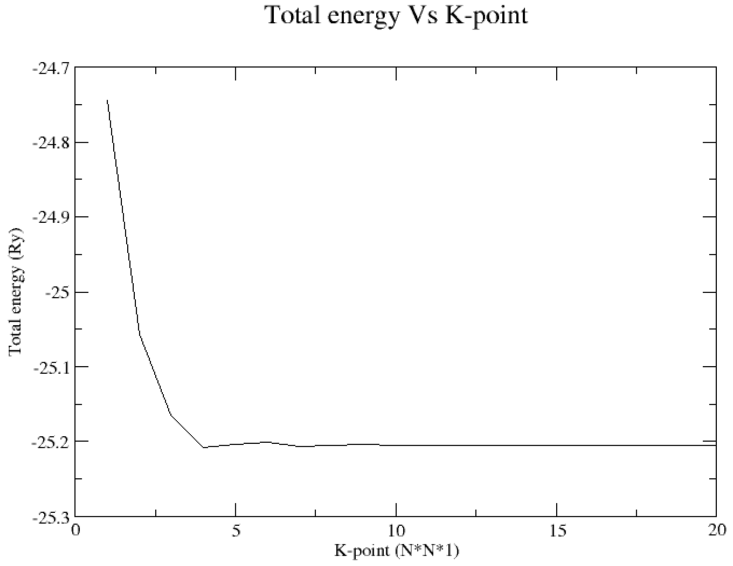

Figure 4.2: Total energies for graphene with a lattice constant of $2.46\mathring{A}$ and $E_{cut} = 557.6eV$ as a function of the parameter n in the choices of the Monkhorst-Pack k-points

The convergence of the computed total energy of graphene as a function of the parameter n in the choices of the Monkhorst-Pack k-points set is shown in Figure 4.2, When $n \geq 13$, the total energy of graphene seems to be (almost) independent of the number of k points. More specifically the variation in the energy as n varies in the range of $13 \leq n \leq 36$ is less than $10.4Ryd$ or $141.44eV$. For smaller numbers of k-points, however, the energy varies considerably as the number of k-point is changed. I used a uniform mesh of $13 \times 13 \times 1$ of k-points since it gives good convergence at a reasonable computational cost. Because of the quasi two-dimensional structure of graphene, we use the $13 \times 13 \times 1$ grid. We found that the $13 \times 13 \times 1$ grid provides a slightly better sampling for calculations of charge density results for graphene.

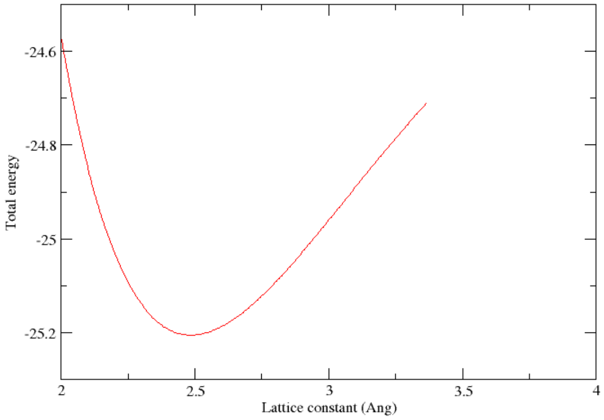

Figure 4.3: Total energy of graphene with Ecut=41 Ryd or 557.6eV and 13 × 13 × 1 k-points as a function of the lattice parameter, a.

For $E_{cut} = 557.6eV$ and the k-mesh $13 \times 13 \times 1$ the variation of total energy with a few values of the lattice constant a is shown in Figure 4.3. Following standard practice [33] we fitted the results to the cubic sp line curve and thus determined the equilibrium lattice constant at 2.46Å corresponding to the lowest energy value. To verify that this determined value a is accurate, we made total energy calculations for a large number of a values in the range $2.00 - 3.465$ Å. The results are shown in Figure 4.3 With in the numerical noise of calculated values we note that energy minimum occurs for $a = 2.485\mathring{A}$. Thus, we establish that the error margin in our numerical estimate is 0.025 Å. Therefore, we quote our numerical estimate of a as $a = (2.460 \pm 0.025)\mathring{A}$. In terms of k-integration, insulators and semiconductors are well-behaved in the sense that the density of states goes to zero smoothly before the gap and the integration of a smooth function usually does not cause problems. For metals on the other hand, resolution of functions to be integrated in plane waves can be very hard and the functions need first to be multiplied by a sharp Fermi occupation.

In Figure 4.4 (A) unit cell of graphene and (B) translational asymmetric unit of graphene. The parameter set to be $a = 2.485\mathring{A}$ in the plane (a is the crystal lattice

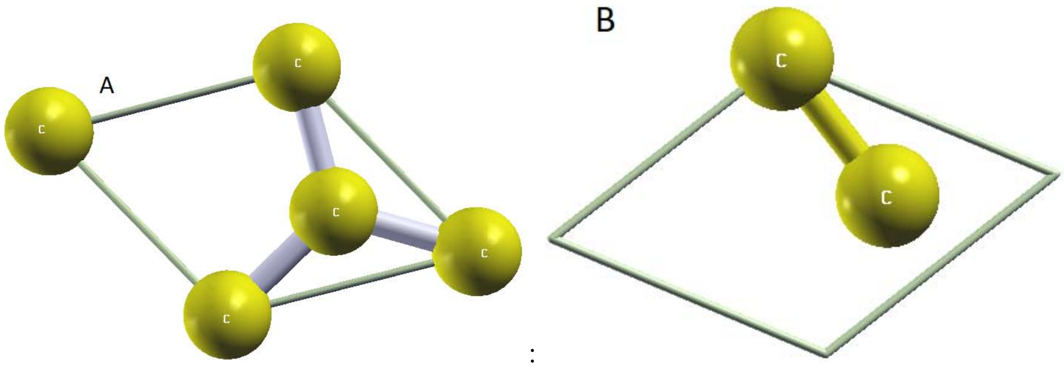

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Figure 4.4: (A) unit cell of graphene, (B) translational asymmetric unit of graphene.

constant). The C-C bond length is 1.4347$\mathring{A}$. The calculations were performed in the framework of DFT with the local density approximation (LDA) and ultra soft pseudo potentials. Because generalized gradient approximation (GGA) calculations give essentially no bonding between graphene planes and lead to excessively large values of C [30].

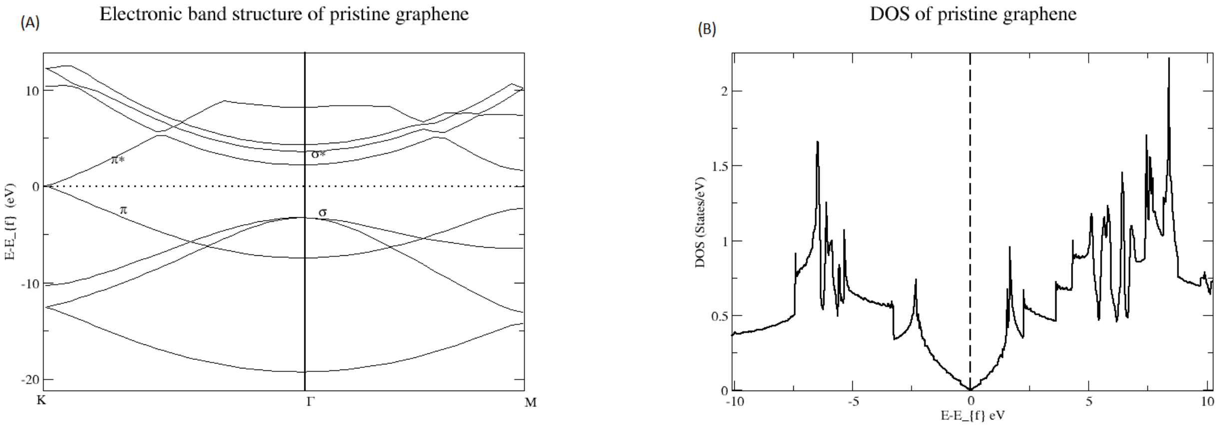

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Figure 4.5: (A)Electronic band structure of pristine graphene at the direction of $K\Gamma M$ and (B) Density of state for pristine graphene

Figure 4.5(A) shows the band structure of graphene. Apparently the two bands touch together at K point and this indicates that the graphene is semi-conductor, which is consistent with the conclusion in the literature [31]. The electron dispersion curves in

Figure 4.5 the π and π^* bonds, formed by the combination of the p orbital of the two basis of C atoms per primitive hexagonal unit cell, are degenerate at the K point of the Brillouin zone and Fermi level. The dispersion around the K point is linear for both electron and hole bands. The electron occupies the p orbital which overlaps with p electron of neighboring Carbon atom to form π-bond. This electron has higher energy than that of electrons which form the σ bonds, and are delocalized over the entire lattice. The electronic properties of graphene are determined by these delocalized electrons.

Figure 4.5(B) gives the total density of states of pure graphene. We notice that the DOS plot gives no band gap between conduction and valence bands (no band gap but also no overlap between conduction and valence band) at the Fermi energy. This property was also revealed by Wallace et al. [32]. This absence of band gap is caused by the joining of conduction and valence bands at the bottom of the Fermi energy at the Γ-point of the Brillouin zone. Theoretically, a zero band gap reveals that the pure graphene is semi-conductor.

4.1 Electronic structure calculation for Au doped graphene

Figure 4.6unit cell of final relaxed configurations Au doped graphene to construct a 13×13×1 supercell structure.

The supercell parameters are set to be the same as $a = b = 8.874\mathring{A}$ in the x y-plane (a and b refer to the crystal lattice constants). The relaxed Au-C bond length in the perfect bilayer graphene is 1.432Å. The calculations were performed in the framework of DFT with the local density approximation (LDA) and ultrasoft pseudopotentials.

Figure 4.7 shows the band structure of Au doped graphene built in 13×13×1 super cell. The π/π^* band crossing of the pure graphene is disturbed by the presence of Au impurity. As clear evidence of the interaction between Au dopant and the graphene, the Fermi level is now moved to the conduction band, making the graphene semi-metallic. Especially in the region above or below the Fermi level, the bands have noticeable modifications by the Au dopant. Detailed analysis indicate that the band of E_f at gamma is localized on Au in s-orbital but around K point (just below E_f) is localized on graphene. The corresponding

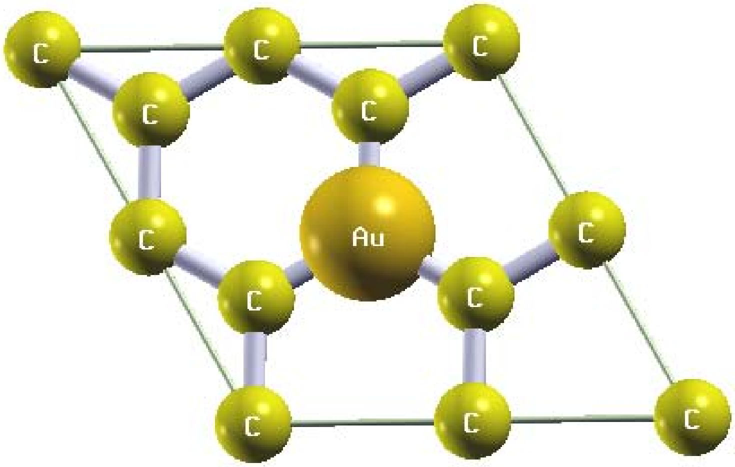

Figure 4.6: unit cell of final relaxed configurations Au doped graphene

DOS in figure 4.8 display a sharp peak at the Fermi level. Therefore, the doping of Au in the graphene makes graphene semi-metallic. Figure 4.9 displays the comparison of DOS of Au doped graphene and pristine graphene. In this graph the highest peak of Au doped graphene at the fermi level shows that Au doped graphene is more metallic than pristine graphene.

Distributions of charge density on plane that pass through the carbon atoms in the graphene and Au atom are shown in figure 4.10. In the Au-doped graphene electrons around the Au atom in graphene show localized characteristics. According to Castro et al [33] addressed the character of vacancy-induced electronic states in bilayer graphene. They demonstrated that the wave function was quasi-localized in one layer and totally delocalized in the other. They commented that the delocalization was due to the spread of the wave function in the opposite layer where the vacancy resided.

Furthermore, as can be seen in figure 4.10 the Au-C interaction features larger values of the charge density between the doped Au atom and the carbon atoms indicating a clear covalent-bonding character.

The projected partial density of states (PDOS) and total density of state (TDOS) for the Au doped graphene are shown in figure 4.11.In the occupied region the highest peaks at the fermi level owing to the p orbital of graphene are observed for Au doped

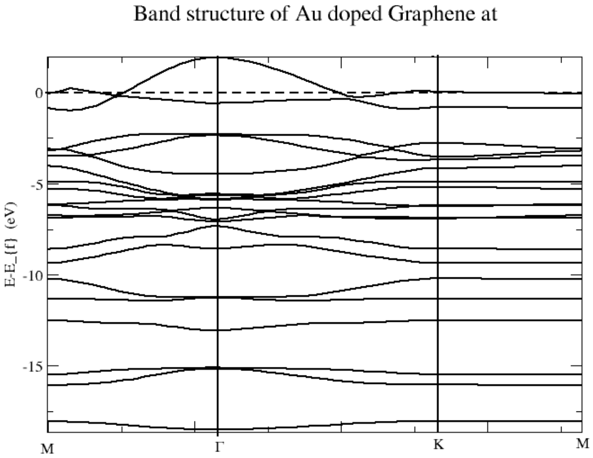

Figure 4.7: Electronic band structure of Au doped graphene at the direction of $M\Gamma KM$.

graphene structures.The density of states above the Fermi level is dominated by p orbitals of C atom while p orbitals from C and Au atoms have almost same contributions. For the C-Au-doped graphene systems, figure 4.11, shows that orbital hybridization can be observed near Fermi energy, which can possibly exhibit metallic properties. The density of state at the Fermi level has mainly dominant contributions from P orbital of Au and C atom.

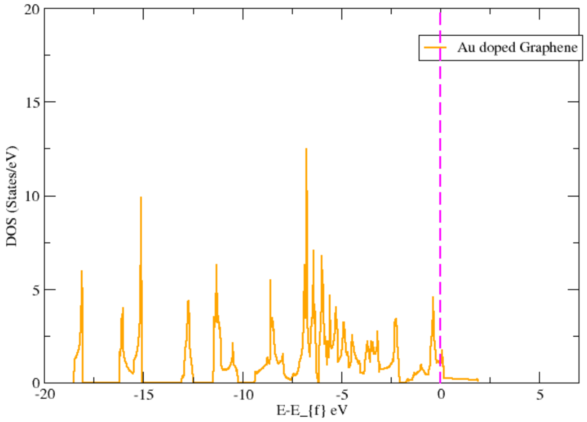

Figure 4.8: Density of state for Au doped graphene.

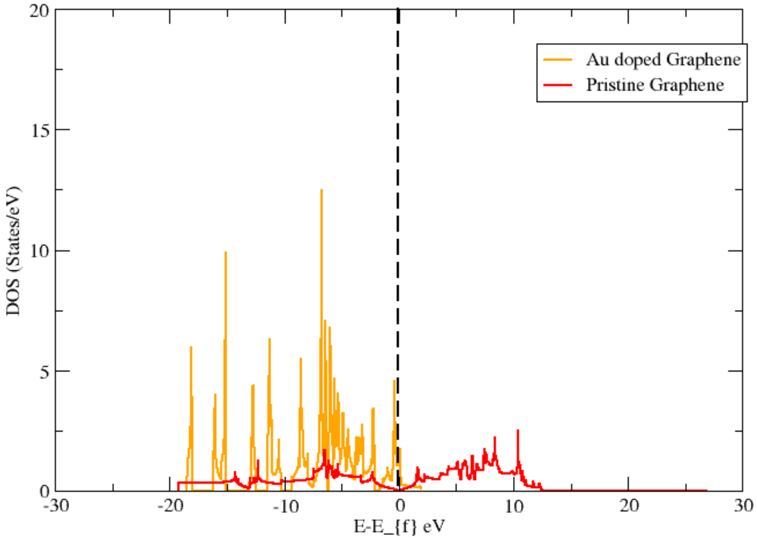

Figure 4.9: DOS of Au doped graphene and pristine graphene

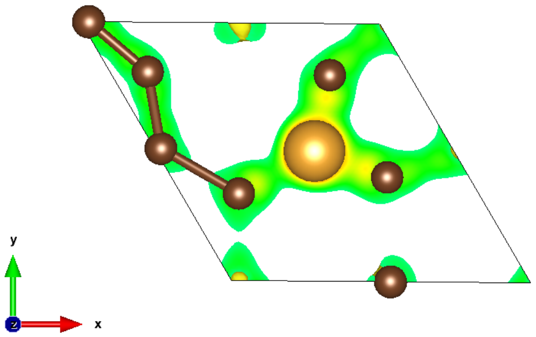

Figure 4.10: The charge density isoface of graphene.

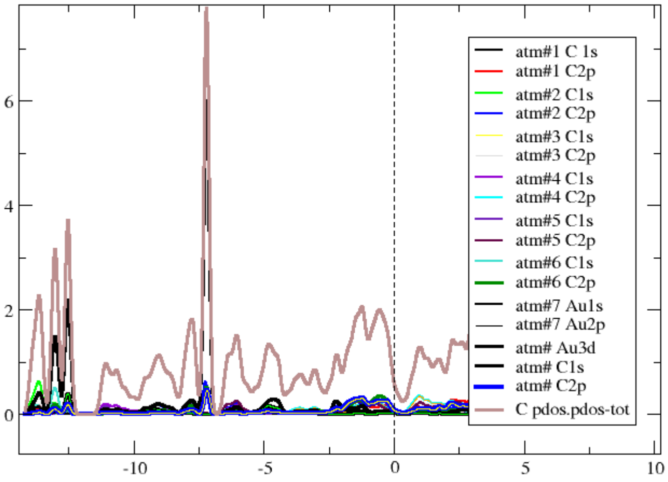

Figure 4.11: TDOS and PDOS of Au doped graphene.

Chapter 5

CONCLUSION

We presented plane wave pseudopotential calculations to investigate the electronic structure of Au doped graphene, using the density functional theory within the local approximation and observe a transition of graphene from semi-metal to metal by doping. The values of doping energy of Au at different sites of graphene suggest that the top site is the most favorable site for doping on graphene sheet. The equilibrium distance of Au atom from the surface of graphene sheet, calculated in $13 \times 13 \times 1$ supercell of graphene, is found to be $1.432A^o$ and the value agrees well with the previously reported data.

The band structure analysis of the pure graphene and Au doped graphene systems shows that conduction and valence band meet exactly at the Fermi level in the former case. This reiterates that the pure graphene is zero band gap semi-conductor. The study also reveals that the conduction band and valence band overlap upon the doping of Au atom.

Investigation of the density of states (DOS) of pure graphene confirms its semi-metallic nature. Au Doped system, however, indicate that the Au doped graphene could be semi-metallic.

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DECLARATION

I hereby declare that this MSc thesis is my original work and has not been presented for a degree in any other universities, and that all sources of material used for the project have been duly acknowledged.

Name: Beletu Zeleke

Signature: ________________

This research thesis has been submitted to for examination with my approval as university advisor.

Name: Dr. Chernet Amente
Signature: ________________

Place and date of submission:

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