



UNIVERSITY OF INDONESIA

**DENSITY FUNCTIONAL THEORY STUDY OF HYDROGENATED
GRAPHENE**

THESIS

Proposed in partial fulfillment of the requirements for the Degree of Master of
Science in Physics, Faculty of Mathematics and Natural Sciences, University of
Indonesia.

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ORIGINALITY

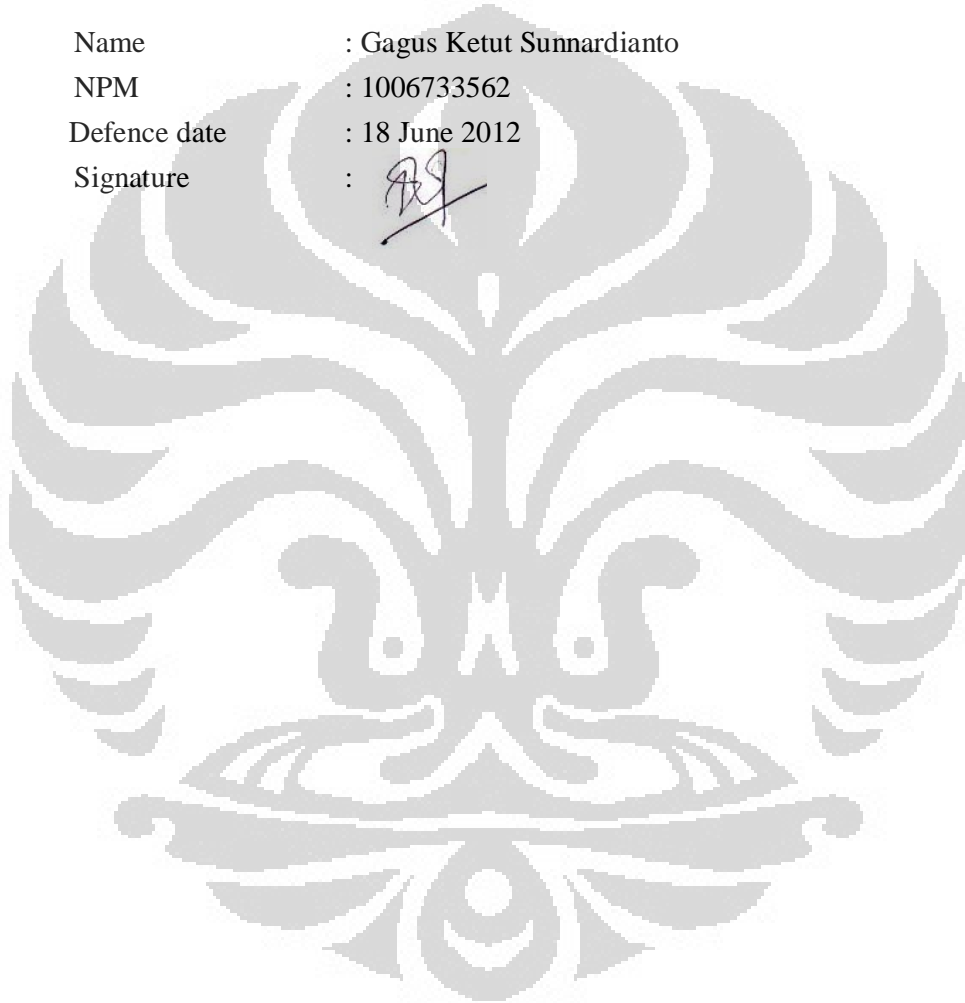
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Cheers,

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ABSTRAK

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Grafena telah diperkirakan memiliki banyak aplikasi karena sifatnya yang unik yang timbul dari dispersi energi linier di sekitar energi Fermi. Meskipun demikian, tidak adanya celah pita membuat grafena tidak dapat berfungsi dengan baik sebagai alat semikonduktor yang merupakan kendala untuk aplikasi elektronik. Oleh karena itu, banyak cara telah diusulkan untuk membuka celah pita pada grafena yaitu penemuan baru dari lembaran grafena yang terhidrogenasi menunjukkan cara yang relatif mudah untuk membuka sebuah celah energi pada grafena. Dalam studi ini, kita mensimulasikan struktur elektronik dari grafena yang terhidrogenasi dalam teori fungsional kerapatan untuk 10 nilai konsentrasi hidrogen. Hasil kami menunjukkan bahwa, grafena menyerap hidrogen dari konsentrasi yang sangat rendah sampai sekitar 96% konsentrasi hidrogen, nilai rapat keadaan di energi Fermi berubah dari nol ke nilai tertentu menimbulkan sifat logam pada grafena terhidrogenasi. Namun, ketika konsentrasi hidrogen mendekati penuh yaitu ketika lebih dari 96% konsentrasi hidrogen, grafena terhidrogenasi mulai terbentuk celah energi kecil, sehingga berubah menjadi semikonduktor.

Kata kunci : teori fungsional kerapatan, rapat keadaan, celah pita, grafena

ABSTRACT

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Graphene has been predicted to possess many applications because of its unique properties arising from its linear energy dispersion around its Fermi energy. Despite this, the absence of band gap which makes graphene unable to function as a semiconductor is a thrill feature for the application to solid state electronic devices. Therefore, many scenarios have been proposed to form a band gap in graphene. Among these, a recent discovery of a hydrogenated graphene sheet suggests a relatively easy way to form an energy gap in graphene. In this study, we have simulated the electronic structure of hydrogenated graphene within the framework of density functional theory for 10 different values of hydrogen concentration. Our results show that, as graphene adsorbs hydrogens from very low concentration up to around 96% of hydrogen coverage, the value of density of states at Fermi energy changes from zero to a finite value, giving rise to a metallic character in the hydrogenated graphene. However, as the hydrogen concentration approaches a full coverage, i.e. when more than 96% of carbon atoms are covered by hydrogens, the hydrogenated graphene starts to form a small energy gap, making it turns into a semiconductor.

Keywords: density functional theory, density of states, band gap, graphene

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CHAPTER 1

INTRODUCTION

1. 1 Research Background

Graphene, as the mother building block of many carbon-based materials has been predicted to possess many applications because of its unique properties primarily related to its two-dimensional shape with single-atom thickness and its linear energy dispersion around its Fermi energy. Graphene can be considered as a single layer of graphite in a structured hexagonal system. Several interesting applications of graphene have been revealed recently. The synthesis of graphene sheets by Novoselov et al opened a new era in nanotechnology [1]. The outstanding properties of graphene make it promising for a variety of applications including hydrogen technology [2]. The experimental realization of graphene monolayer and its weird properties such as the zero effective mass of the electrons and its high Fermi velocity of $\frac{1}{300}$ of the speed of light has triggered many experimental and theoretical activities exploring the magnetic and transport properties [3]. Despite the outstanding properties described above, the absence of band gap in graphene is a thrill feature for the application to solid state electronic devices. Many scenarios have been proposed to make graphene have a band gap. One among the most interesting ones is the recent discovery of a hydrogenated graphene sheet. The advantage of graphene hydrogenation is twofold: to form and tune the band gap, and as a means for storing hydrogen [4]. The functionality of hydrogenated graphene was first predicted by Sofo *et al* [5] on the basis of electronic structure calculation. Recently, hydrogenated graphene is realized by Elias *et al* [6] who demonstrated that the process of hydrogenation is reversible, making the hydrogenated graphene a potential candidate for hydrogenation storage system. In

particular, a fully or nearly fully hydrogenated single layer graphene shows promising semiconductor properties [5].

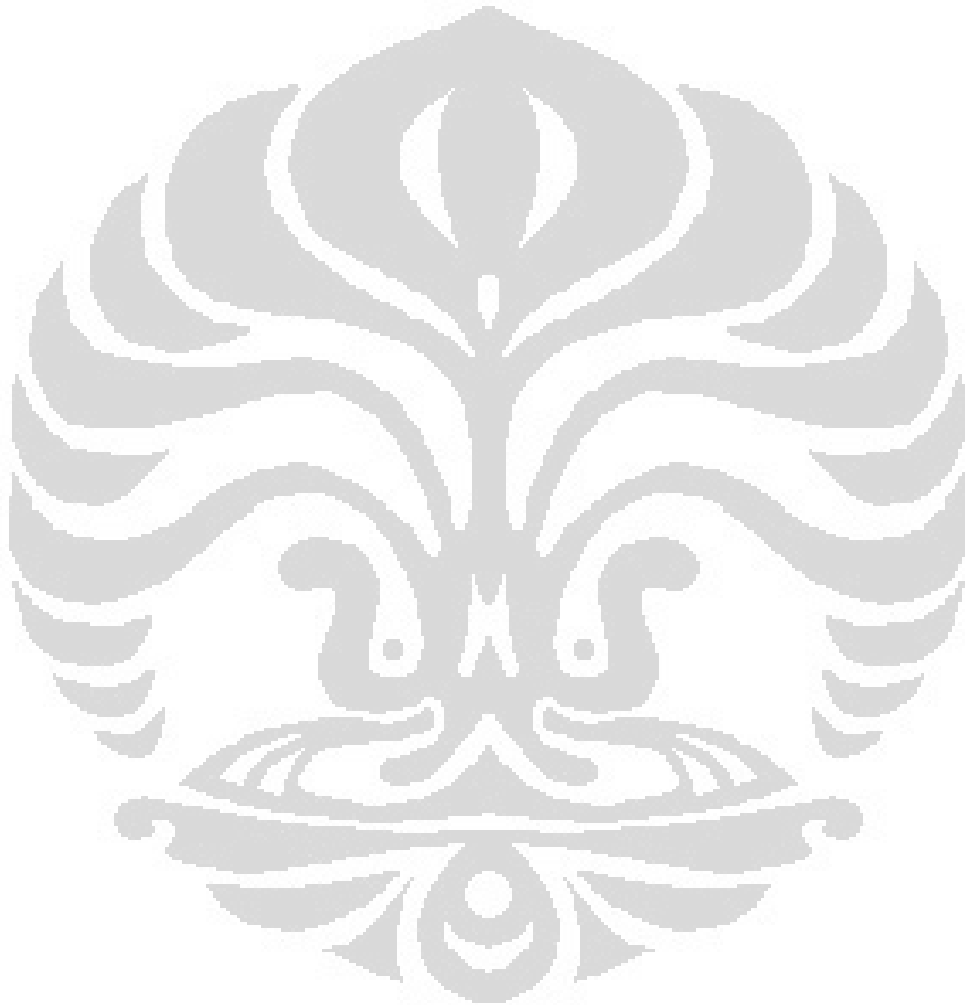
There are a few reports investigating the electronic structure of graphene sheet as a function of hydrogen coverage leading to the opening of a band gap. Most of these studies are restricted to a small percentage of hydrogen atom coverage. Considering the fact that there have been only very few theoretical studies exploring the properties of hydrogenated graphene with high percentage of hydrogen coverage, here we propose to investigate the electronic structure of a hydrogenated graphene sheet as a function of hydrogen coverage ranging from a small to a big number of hydrogen coverage. All my calculations in this work have been performed within the density functional theory (DFT) based first-principles electronic structure calculations using machikaneyama2002 codes [7, 8].

1.2 Research Scope

In this study we have restricted my work to carry out extensive calculations for 10 different hydrogen coverage (10%, 20%, 30%, 40%, 50%, 60%, 70%, 80%, 90%, 96%) on 5x5 supercell of graphene sheet consisting of 50 carbon atoms, within the framework of DFT. In the analysis part, I will focus on the evolution of the density of states with respect to the increase of the hydrogen coverage, in order to understand the change in character of the electric property of hydrogenated graphene as a function of hydrogen coverage.

1.3. Research Objective

The objective of this research is to understand the evolution of the electronic structure of hydrogenated graphene upon hydrogenation and gain some insight in to the way a band gap opens.



CHAPTER 2

THEORETICAL METHOD

In this chapter we will discuss the concept underlying the method of calculation we use to treat the quantum many-body problem, namely the density functional theory (DFT).

2.1 Many Body Hamiltonian

A real quantum many-body problem in condensed matter physics is tremendously complex due to its very large number of constituent particles, hence a very large number of degrees of freedom, interacting with one another and with their complex environment. Due to this very high complexity, there is literally no solution to such a problem one can obtain without any approximation. Thus, here we shall discuss the approximation method we use in this study. To begin with, we can write the time independent Schrödinger equation for a non-relativistic quantum system as the following [10],

$$\hat{H}\psi(\vec{r}_1, \vec{r}_2, \dots, \vec{r}_N, \vec{R}_1, \vec{R}_2, \dots, \vec{R}_M) = E\psi(\vec{r}_1, \vec{r}_2, \dots, \vec{r}_N, \vec{R}_1, \vec{R}_2, \dots, \vec{R}_M) \quad (2.1)$$

where \hat{H} , $\psi(\vec{r}_1, \vec{r}_2, \dots, \vec{r}_N, \vec{R}_1, \vec{R}_2, \dots, \vec{R}_M)$, and E are, respectively, the Hamiltonian, the many-body wave function, and the total energy of the system. A typical many-body Hamiltonian for a system involving electrons and nuclei which interact each other via Coulomb interactions can be written as,

$$\hat{H} = -\frac{1}{2} \sum_{i=1}^N \nabla_i^2 - \frac{1}{2} \sum_{A=1}^M \frac{1}{M_A} \nabla_A^2 - \sum_{i=1}^N \sum_{A=1}^M \frac{Z_A}{r_{iA}} + \sum_{i=1}^N \sum_{j>i}^N \frac{1}{r_{ij}} + \sum_{A=1}^M \sum_{B>1}^M \frac{Z_A Z_B}{R_{AB}} \quad (2.2)$$

with M and N being the number of nuclei and electrons in the system, M_A , Z_A , and R_A the mass, charge, and position of the nuclei, Z_B and R_B the charge and the positions of the electrons. The first two terms of the right hand side is the kinetic energy operators for electrons and nuclei, respectively. The three last terms are the Coulomb interactions between electrons and nuclei, among electrons, and among nuclei. The Schrödinger equation with this Hamiltonian is too difficult to solve analytically. Hence, we need a good approximations for the Hamiltonian, and the many-body wave function, that give the correct physics, and cheap in computation cost.

First approximation to simplify the many-body Hamiltonian (2.2) is by using the Born-Oppenheimer approximation [11]. The difference in the mass of the nuclei and electrons is so large. This allows us to consider the nuclei as nearly stationary compared to the electrons. This way we can consider the total energy of system as a function of particular arrangement of nuclei. Within this approximation the Hamiltonian can be written as (in atomic unit, $\hbar=1$),

$$\hat{H}_{elec} = -\frac{1}{2} \sum_{i=1}^N \nabla_i^2 - \sum_{i=1}^N \sum_{A=1}^M \frac{Z_A}{r_{iA}} + \sum_{i=1}^N \sum_{j>i}^N \frac{1}{r_{ij}} = \hat{T}_e + \hat{V}_{Ne} + \hat{V}_{ee} \quad (2.3)$$

Where all nuclei operators are omitted. However, solving the Schrödinger equation with the above Hamiltonian is still too difficult. In the next sections we will discuss about some techniques to solve the Schrödinger equation with the Hamiltonian of equation (2.3).

2.2 Hartree-Fock Theory

2.2.1 Hartree Approximation

The hardest part in solving the Schrödinger equation with Hamiltonian (2.3) is to treat the electron-electron interactions. This problem can be approximated through the Hartree approximation [12]. In this approximation, the many-body electrons wave function ψ is replaced by a direct product of single particle orbitals, $\psi_i(\vec{x}_i)$,

$$\psi(\vec{r}_1, \vec{r}_2, \dots, \vec{r}_N) = \frac{1}{\sqrt{N!}} \psi_1(\vec{r}_1) \psi_2(\vec{r}_2) \dots \psi_N(\vec{r}_N) \quad (2.4)$$

where $\psi_i(\vec{r})$ consist of a spatial orbital $\phi_k(\vec{r})$ and electronic spin orbitals $\sigma(s) = \alpha(s)$ or $\beta(s)$. However, Hartree approximation does not take into account the exchange interactions since (2.4) does not satisfy the criteria of anti symmetric wave function, which is required by the exclusion principle.

2.2.2 Hartree-Fock Equation

In this approximation, the previous problem where the electrons exchange interactions are ignored is countered by writing the wave function as an anti-symmetrized product of single-particle orbitals [13]. The Hartree-Fock wave function ψ_{HF} can be expressed in the form of Slater determinant [14].

$$\psi_{HF} = \frac{1}{\sqrt{N!}} \begin{vmatrix} \psi_1(\vec{r}_1) & \psi_2(\vec{r}_1) & \dots & \psi_N(\vec{r}_1) \\ \psi_1(\vec{r}_2) & \psi_2(\vec{r}_2) & \dots & \psi_N(\vec{r}_2) \\ \vdots & \vdots & \dots & \vdots \\ \psi_1(\vec{r}_N) & \psi_2(\vec{r}_N) & \dots & \psi_N(\vec{r}_N) \end{vmatrix} \quad (2.5)$$

The orbitals are subjected to the orthonormality constraint, $\int \psi_i^*(\vec{x})\psi_j(\vec{x})d\vec{x} = \delta_{ij}$. The Hartree-Fock energy is evaluated by taking the expectation value of the (2.3) Hamiltonian,

$$\begin{aligned}
 E_{HF} = & \langle \psi_{HF} | \hat{H} | \psi_{HF} \rangle \\
 & \left(\sum_i^N \int \psi_i(\vec{r}) \left(-\frac{1}{2} \nabla^2 + v_{ext}(\vec{r}) \right) \psi_i(\vec{r}) d\vec{r} \right. \\
 & + \frac{1}{2} \sum_i^N \sum_j^N \iint \frac{|\psi_i(\vec{r})|^2 |\psi_j(\vec{r}')|^2}{|\vec{r} - \vec{r}'|} d\vec{r} d\vec{r}' \\
 & \left. - \frac{1}{2} \sum_i^N \sum_j^N \iint \frac{\psi_i(\vec{r}) \psi_i(\vec{r}') \psi_j(\vec{r}) \psi_j(\vec{r}')}{|\vec{r} - \vec{r}'|} \delta_{s_i s_j} d\vec{r} d\vec{r}' \right). \quad (2.6)
 \end{aligned}$$

The last two terms are the Coulomb and the exchange integral. The exchange integral arises from the anti symmetric nature of the Hartree-Fock wavefunction. This integral vanishes if $S_i \neq S_j$.

To obtain the Hartree-Fock ground state energy E_{HF}^0 , we have to minimize (2.6) with respect to the variation of the orbitals, subject to the constraint that the orbitals should remain orthonormal. By using Euler-Lagrange method we will get the Hartree-Fock equations,

$$\begin{aligned}
 & \left(-\frac{1}{2} \nabla^2 + v_{ext}(\vec{r}) + \frac{1}{2} \sum_j^N \int \frac{|\psi_j(\vec{r}')|^2}{|\vec{r} - \vec{r}'|} d\vec{r}' \right) \psi_i(\vec{r}) \\
 & - \frac{1}{2} \sum_j^N \int \frac{\psi_i(\vec{r}') \psi_j(\vec{r}') \psi_j(\vec{r})}{|\vec{r} - \vec{r}'|} \delta_{s_i s_j} d\vec{r}' = \bar{\epsilon}_i \psi_i(\vec{r}) \quad (2.7)
 \end{aligned}$$

This is a nonlinear equation. Hence, in order to solve this, we have to use an iterative process known as self-consistent field procedure. The self-consistent procedure starts with an initial guess for the orbitals, and successive iterations are performed with new orbitals until self-consistent condition is achieved.

The Hartree-Fock theory is not exact because it only uses a single determinant for constructing its electrons wave function. Single determinant is only exact in the case of non-interacting electrons. The error in the Hartree-Fock energy is known as the electron correlation energy and defined as, $E_C = E_0 - E_{HF}$, where E_0 is the exact ground state energy.

2.3 Density Functional Theory

The Density Functional Theory (DFT) is adopted as a tool for the calculation of the electronic structure. A detailed mathematical and physical description of this theory can be found in the Ref [15]. In this method, instead of using the many body wave function, it uses the electronic density $n(\mathbf{r})$ to solve the many-body problems. Hohenberg and Kohn build DFT method based on two theorems. They formally used the electronic density as the central quantity for describing the electron interactions, and from this they derived the exact ground state of the system. In the following section we will describe the Hohenberg-Kohn theorems [16].

2.3.1 Hohenberg-Kohn Theorems

P. Hohenberg and W. Kohn [17] formulated the basis of this theory in 1964. Basically these theorems can be applied to any electrons system moving under the influence of an external potential $v_{\text{ext}}(\mathbf{r})$.

Theorem 1

The external potential $v_{ext}(\mathbf{r})$, and hence the total energy, is a unique functional of the electron density $n(\mathbf{r})$.

The energy functional of the system $E[n(\mathbf{r})]$, can be written in terms of external potential as follows,

$$E[n(\vec{r})] = \int n(\vec{r}) v_{ext}(\vec{r}) dr + F[n(\vec{r})] \quad (2.8)$$

Where $F[n(\mathbf{r})]$ is an unknown universal functional of the electronic density $n(\mathbf{r})$. This energy can be expressed as the expectation value of the Hamiltonian. The electronic wave function minimized the expectation value and gives the ground state energy of the system (assuming a non-degenerate ground state),

$$E[n(\vec{r})] = \langle \psi | \hat{H} | \psi \rangle \quad (2.9)$$

Where the Hamiltonian is,

$$\hat{H} = \hat{F} + \hat{V}_{ext}, \quad \hat{F} = \hat{T} + \hat{V}_{ee}.$$

The \hat{F} operator is the same for all N electrons system. Hence, \hat{H} is defined by N and \hat{V}_{ext}

Theorem 2

The ground state energy can be obtained variationally: the density that minimizes the total energy is the exact ground state density.

We have shown that $n(\mathbf{r})$ determines $v_{\text{ext}}(\mathbf{r})$, N and $v_{\text{ext}}(\mathbf{r})$ determine \hat{H} and therefore Ψ . This means that Ψ is a functional of $n(\mathbf{r})$, thus the expectation value of F is also a functional of $n(\mathbf{r})$,

$$F[n(\mathbf{r})] = \langle \Psi | \hat{F} | \Psi \rangle \quad (2.10)$$

The Hohenberg-Kohn theorems are powerful, but they do not give the procedure how to calculate the ground state density. This problem is later solved by the Kohn-Sham equation.

2.3.2 The Kohn-Sham Equation

The Kohn-Sham formulation is mapping the fully interacting electrons system with real interaction potential, into a fictitious non-interacting system, where the electrons moving within an effective ‘Kohn-Sham’ single particle potential [18].

As the first step, consider that the ground state energy of many-electron system can be achieved by minimizing the energy functional (2.8) subject to the constraint that the total number of electrons N must be conserved. This will lead to the Euler equation,

$$\mu = v_{\text{ext}}(\mathbf{r}) + \frac{\delta F[n(\mathbf{r})]}{\delta n(\mathbf{r})} \quad (2.11)$$

Where μ is the Lagrange multiplier associated with constraint of constant N . The main idea of Kohn-Sham is to set the system so that the kinetic energy could be solved exactly. This can be achieved by invoking the non-interacting system of electrons. The ground state wave function of such system can be exactly obtained by using single Slater determinant of single particle orbitals $\psi_i(\mathbf{r}_i)$,

$$\psi_{HF} = \frac{1}{\sqrt{N!}} \begin{vmatrix} \psi_1(\vec{r}_1) & \psi_2(\vec{r}_1) & \dots & \psi_N(\vec{r}_1) \\ \psi_1(\vec{r}_2) & \psi_2(\vec{r}_2) & \dots & \psi_N(\vec{r}_2) \\ \vdots & \vdots & \ddots & \vdots \\ \psi_1(\vec{r}_N) & \psi_2(\vec{r}_N) & \dots & \psi_N(\vec{r}_N) \end{vmatrix}. \quad (2.12)$$

The $F[n(\mathbf{r})]$ functional can be expressed as,

$$F[n(\vec{r})] = T_s[n(\vec{r})] + E_H[n(\vec{r})] + E_{xc}[n(\vec{r})] \quad (2.13)$$

Where $T_s[n(\mathbf{r})]$, and $E_H[n(\mathbf{r})]$ are the Kinetic energy of non-interacting electrons and classical electrostatic of electrons. $E_{xc}[n(\mathbf{r})]$ is the exchange correlation functional which consists of the difference between the exact and non-interacting kinetic energies and also the non-classical electrostatic of electrons. By using this functional, the Euler equation can be written as,

$$\mu = v_{KS}(\mathbf{r}) + \frac{\delta T_s[n(\mathbf{r})]}{\delta n(\mathbf{r})} \quad (2.14)$$

$v_{KS}(\mathbf{r})$ is composed of,

$$V_{KS}(\vec{r}) = V_{ext}(\vec{r}) + V_H(\vec{r}) + V_{xc}(\vec{r}) \quad (2.15)$$

$$V_H = \frac{\delta E_H[n(\vec{r})]}{\delta n(\vec{r})} = \int \frac{n(\vec{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}' \quad (2.16)$$

$$V_{xc} = \frac{\delta Exc[n(\vec{r})]}{\delta n(\vec{r})} \quad (2.17)$$

Equation (2.14) is just an arrangement of (2.11), so the density obtained by solving (2.14) is the same as exact ground state density of (2.11). In practice, the ground state density is obtained by solving N single-particle Schrödinger equations with external potential v_{KS} ,

$$\left[-\frac{1}{2} \nabla^2 + V_{ks}(\vec{r}) \right] \psi_i(\vec{r}) = \epsilon_i \psi_i(\vec{r}) \quad (2.18)$$

ϵ_i are Lagrange multipliers correspond to the orthonormality of the N single-particle states $\psi_i(\mathbf{r})$. The electronic density is constructed from,

$$n(r) = \sum_i^N |\psi_i(r)|^2 \quad (2.19)$$

$T_S[n(r)]$ is written as,

$$T_S[n(r)] = \sum_i^N \langle \psi_i | -\frac{1}{2} \nabla^2 | \psi_i \rangle \quad (2.20)$$

Equations (2.15), (2.18), and (2.19) are known as Kohn-Sham equations. These equations are non-linear equations because the $v_{KS}(r)$ depends on the electronic density $n(r)$. These equations must be solved using self-consistent field procedure like in the Hartree-Fock equations

2.3.3 Spin Polarized and Unpolarised DFT

So far we have studied Kohn Sham DFT, There are two kinds of DFT namely spin polarized DFT and spin unpolarised DFT. In the spin polarized DFT spin orbitals are unrestricted to have the same partial orbitals. It means that the up and down spins are free to have different spatial orbitals $\psi \uparrow(\vec{r})$ and $\psi \downarrow(\vec{r})$ and hence different energies

$$\begin{aligned}\chi \uparrow(\vec{x}) &= \psi \uparrow(\vec{x})\alpha(\omega) \\ \chi \downarrow(\vec{x}) &= \psi \downarrow(\vec{x})\beta(\omega)\end{aligned}\quad (2.21)$$

While in the spin unpolarised DFT spin orbitals where the up (alpha) and down (beta) spins have the same spatial orbitals $\psi(\vec{r})$

$$\begin{aligned}\chi \uparrow(\vec{x}) &= \psi(\vec{x})\alpha(\omega) \\ \chi \downarrow(\vec{x}) &= \psi(\vec{x})\beta(\omega)\end{aligned}\quad (2.22)$$

Where,

$\chi \uparrow(\vec{x}), \chi \downarrow(\vec{x}) =$ Spin orbital,

$\psi(\vec{x}) =$ Spatial orbital,

$\alpha(\omega), \beta(\omega) =$ Spin function

2.3.4 Approximations for the Exchange – Correlation Energy

For the exchange-correlation energy has to be approximated. A rather and remarkably good approximation is the so called local density approximation (LDA), which may be expressed in the form [19]:

$$E_{xc}^{LDA}[n(\vec{r})] = \int n(\vec{r}) \epsilon_{xc}^{LDA}(n(\vec{r})) d\vec{r}\quad (2.23)$$

For a homogeneous interacting electron system with constant density. The exchange part is given by:

$$\varepsilon_x(n) = -\frac{3}{4}e^2\left(\frac{3}{\pi}\right)^{13}n^{13} \quad (2.24)$$

The exchange potential in the Khon-Sham equations follow as

$$v_x(n) = \frac{d}{dn}(n\varepsilon_x(n)) = -e^2\left(\frac{3}{\pi}\right)^{13}n^{13} \quad (2.25)$$

2.4 Graphene

Graphene was discovered in 2004 at the Centre for Mesoscopic and Nanotechnology of the University of Manchester, UK, directed by A K Geim [1]. This new material is the first isolated monoatomic membrane, made solely of carbon atoms arranged in a two-dimensional honeycomb (hexagonal) lattice [20-22]. Graphene is a hexagonal structure with each atom forming 3 bonds with each of its nearest neighbors. Three bonds are known as the σ bonds oriented towards these neighboring atoms and formed from 3 of valence electrons. In the 2Pz state oriented perpendicular to the sheet of graphene forming a conduction π band, this is cause the remarkable electronic properties as consequence of the peculiar band structure of graphene, a zero band gap semiconductor with two linearly dispersing band that touch at the corners of the first Brillouin zone.

2.4.1 Carbon Atoms and Honeycomb Lattice

Graphene is made up of carbon atoms. A carbon atoms has six electrons, occupying the atomic orbitals $1s^2$, $2s^2$, and $2p^2$. The electrons in the $1s^2$ orbital are strongly bounded

and are called core electrons. The four remaining electrons are valence electrons and are distributed to more delocalized orbitals as shown below [23].

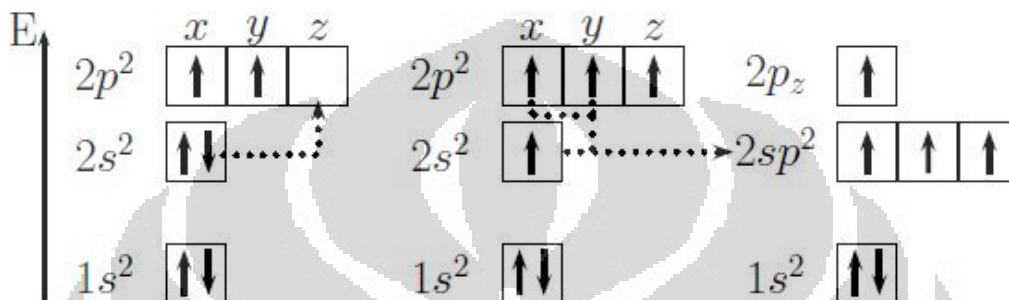


Figure 2.1. Occupation of the atomic orbitals in the hybridization process [23].

Since the energy difference between the 2s and the 2p level is much smaller than their binding energy, the wave functions of these four electrons can mix up easily, in a process called hybridization [23]. From that picture show that three states lie in the xy-plane. These so called σ states form covalent bonds with their neighbors and give rise to the hexagonal lattice structure of graphene. The remaining state is the $2p_z$ orbital. It is named π state and is aligned in the z-direction. Electron in this state are weakly bonded and can hop easily between neighboring atoms. They are therefore relevant for the transport properties, and we will even consider the π states only when calculating electronic properties of graphene.

CHAPTER III

CALCULATION METHOD

3.1 Software and Hardware

The software used for this study is Machikaneyama2002, made and provided by Prof. Hisazumi Akai of Osaka University, Japan. This software is installed on linux operating system and used in accordance with the procedure given in reference [8, 9].

3.2 Machikaneyama2002

Machikaneyama is a software package used for first-principles calculation within the framework of local density approximation of density functional theory (DFT). The package has been in continuous development since 1970 and this development still continues till today. It is written in Fortran 77. It may be best for use on linux platform where a FORTRAN compiler is installed. It can be used for either serial computing running on a PC, or a parallel computing on a computer cluster or a supercomputer. In this software package the density of states is obtained directly by using Green's function. The eigenfunction ϕ_n of the Schrödinger equation $H\phi = E\phi$ which associated with the eigenvalue E_n and Green's function of the system satisfy

$$H\phi_n = E_n\phi_n$$

$$[E - H]G(\vec{r}, \vec{r}') = \delta(\vec{r} - \vec{r}')$$

Expanding $G(\vec{r}, \vec{r}')$ into ϕ_n with the expansion coefficients $G_n(\vec{r}')$,

$$G(\vec{r}, \vec{r}') = \sum_n G_n(\vec{r}')\phi_n(\vec{r})$$

and multiplying it by $(E - H)$ from the left, we obtain

$$(E - H)G(\vec{r}, \vec{r}') = \sum_n G_n(\vec{r}') (E - H)\phi_n(\vec{r})$$

$$= \delta(\vec{r} - \vec{r}')$$

Multiplying by ϕ_m^* and the volume integration leads to

$$G_n(\vec{r}') = \phi_n^*(\vec{r}') / (E - E_n)$$

Therefore,

$$G(\vec{r}, \vec{r}') = \sum_n \frac{\phi_n^*(\vec{r}')\phi_n(\vec{r})}{E - E_n}$$

Is obtained. With an identity

$$\frac{1}{x + i\varepsilon} = P. \frac{1}{x} - i\pi\delta(x),$$

$$G(\vec{r}, \vec{r}') = \sum_n \frac{\phi_n^*(\vec{r}')\phi_n(\vec{r})}{E + i\varepsilon - E_n}$$

$$G(\vec{r}, \vec{r}') = P. \sum_n \frac{\phi_n^*(\vec{r}')\phi_n(\vec{r})}{E - E_n} - i\pi \sum_n \delta(E - E_n) \phi_n^*(\vec{r}')\phi_n(\vec{r})$$

$$\text{DOS } n(E) = -\frac{1}{\pi} \text{Im} \int d^3\vec{r} G(\vec{r}, \vec{r}, E)$$

3. 3 Calculation Method

The Density Functional Theory is adopted as a tool for the calculation of the electronic structure. The main goal of a first principles computational method is to calculate the material properties as precisely as possible by solving the electronic Schrödinger equation, given the chemical composition and the geometrical structure of the system. By this means, these methods do not make use of any empirical information. However, the problem of solving Schrödinger equation to find the quantum ground state

description of the electrons in a solid system is correlated to many-electron problems, which can be solved only approximately. Density Functional Theory is now one of the most widely used methods to solve many-electron problems. It is an exact theory for weakly interacting electron systems by means of mapping the many-electron problem into an approximate single electron picture.

3.4 Mechanism

3.4.1 Structural optimization

For reaching the stable condition of graphene, the geometry structure of graphene have to be optimized first. The bond length of C-C and lattice parameter of graphene are found by varying the distance between two carbon atoms in hexagonal configuration. The exact bond length is the most stable position. It will be achieved when the total energy reaches the most negative value. Theoretical result by Nugraha et al [24] using density functional theory (DFT) as shown below:

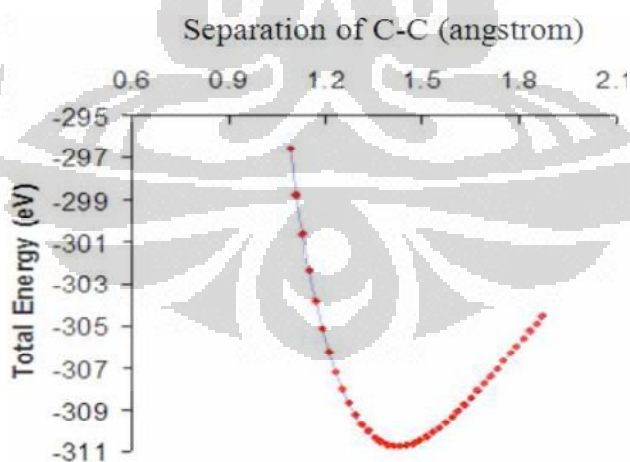


Figure 3.1. The curve of total energy as a function of separation distance between two atoms [24].

The graphs shows the curve of total energy as a function of separation distance between carbon-carbon bonds in graphene. It is found that the bond length of C-C in the graphene system is about 1.42 Å, which is consistent with the experimental result 1.415 Å by A. Ubbelohde *et al* [25]

3.4.2 Binding energy calculation

Regarding the binding energy between hydrogen atom and graphene. Several theoretical investigation have been carried out for the binding energy between hydrogen atom and graphene. They calculated by employing:

$$E_{\text{bind}} = E_{C-X} - E_C - E_X$$

Where E_{C-X} represents the total energy of the graphene-X system (X refers to H), E_X is the energy of isolated X atom and E_C is the total energy of graphene. The exact bond length has been achieved when the binding energy reaches the most negative value

The value of the C-H binding energy from several theoretical investigation are Casolo *et al* [26], their result for a single H adsorption the C-H binding energy is 0.97 Å, Boukhvalov *et al* [27] the C-H binding energy is 1.22 Å, Pablo *et al* [28] the C-H binding energy is 1.1 Å, Zhou *et al* [29] the C-H binding energy is 1.1 Å, Jorge *et al* [30] the C-H binding energy is 1.1 Å. Therefore we used 1.1 Å for the C-H binding energy is similar in typical of hydrocarbon compounds.

3.4.3 Hydrogenated graphene

The graphene structure used in hydrogenated graphene study is 5x5 supercell of graphene sheet consisting of 50 carbon atoms. Hydrogen atom was placed on the top site.

3.4.4 Density of states calculation

Before calculating the density of states of hydrogenated graphene by 10%, 20%, 30%, 40%, 50%, 60%, 70%, 80%, 90% and 96% hydrogen coverage, we calculated the density of states of pure graphene first. To calculate the density of states of hydrogenated graphene, we used 5x5 supercell of graphene sheet consisting of 50 carbon atoms and located hydrogen on top of carbon atom.

3.4.5 DFT (Density functional theory) algorithm

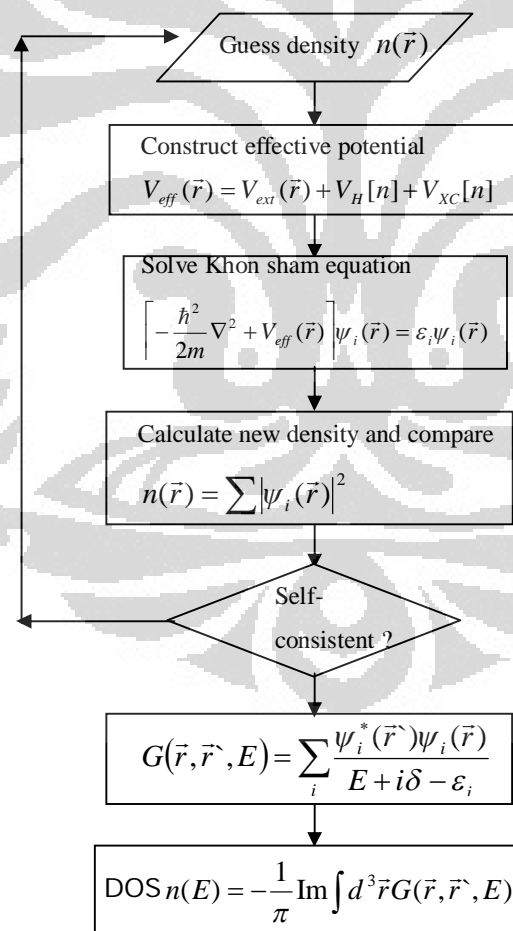


Figure 3.2 Density functional theory (DFT) algorithm

CHAPTER IV

RESULT AND DISCUSSION

In this chapter, we discuss about the density of states of pure graphene and hydrogenated graphene.

4.1 Density of states of pure graphene

The result of density of states of pure graphene

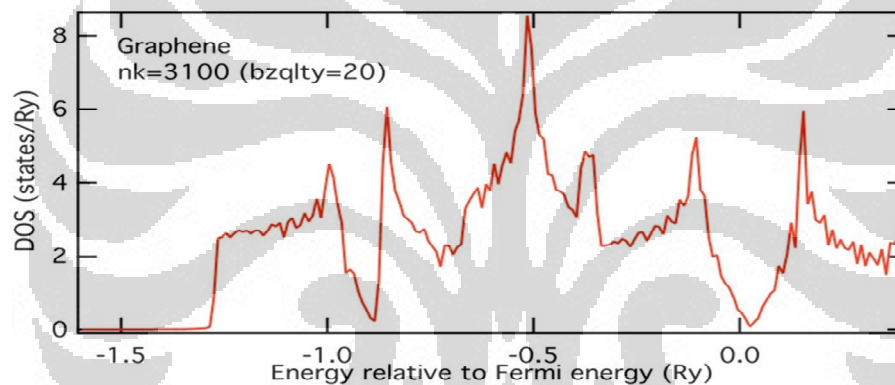


Figure 4.1. Density of states of pure graphene.

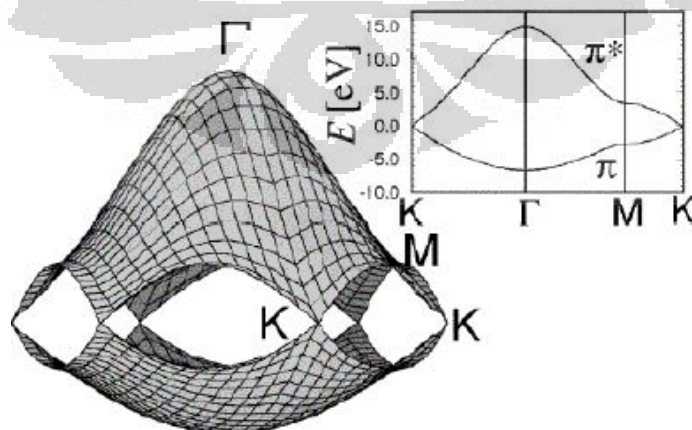
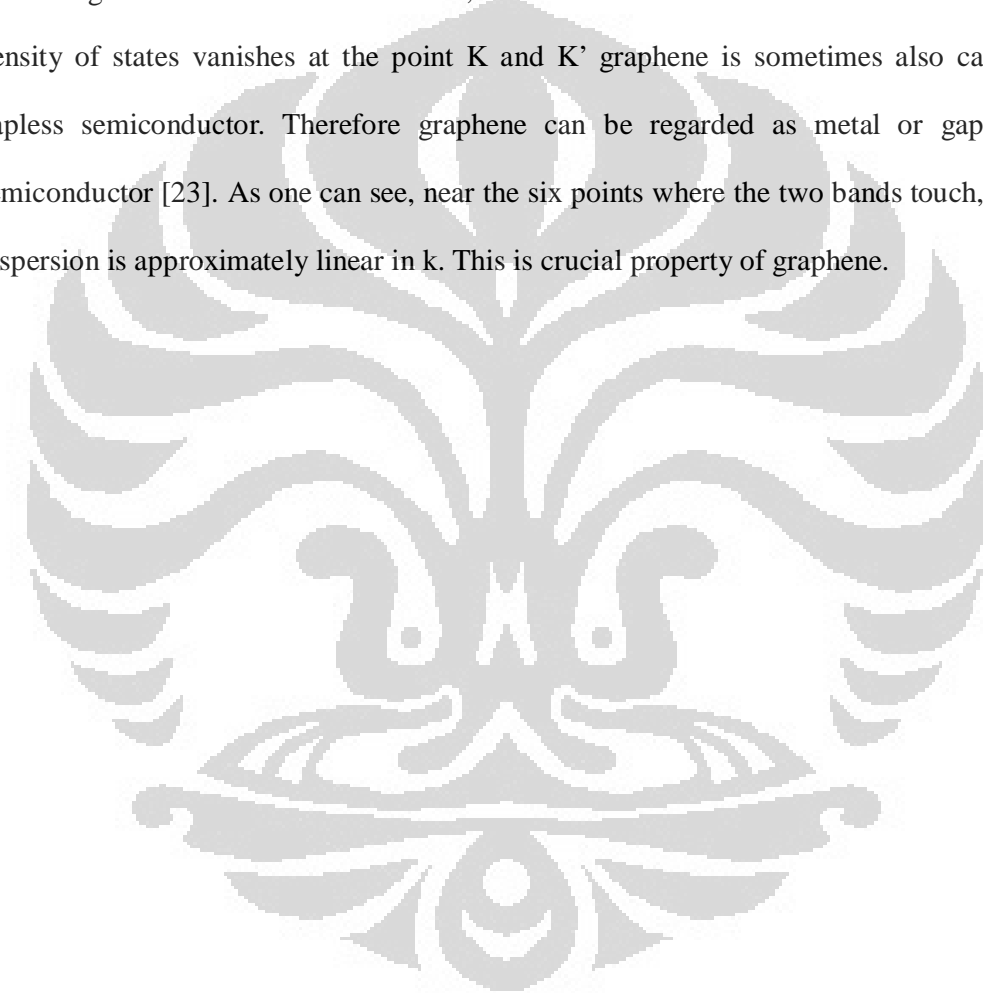


Figure 4.2. Band structure of 2D graphene [31]

As can be seen the density of states of pure graphene that we have already calculated. It shows the conduction and the valence bands cross at the Fermi level. Therefore graphene has no gap and is consequently a metal. However, from the band structure as can be seen that the valence band and the conduction band touch at six points, located at the edges of the first Brillouin zone, which were denoted K and K'. Due to the density of states vanishes at the point K and K' graphene is sometimes also called gapless semiconductor. Therefore graphene can be regarded as metal or gapless semiconductor [23]. As one can see, near the six points where the two bands touch, the dispersion is approximately linear in k . This is crucial property of graphene.



4.2 Density of States of Hydrogenated Graphene (10%H, 20%H, 30%H, 40%H, 50%H, 60%H, 70%H, 80%H, 90%H, 96%H)

Density of states of hydrogenated graphene calculated using spin polarized density functional theory (DFT) calculation. The upper and lower halves of the graph represent up and down spins respectively. The Fermi energy is taken at 0 and marked by a solid vertical line.

10% Hydrogen coverage

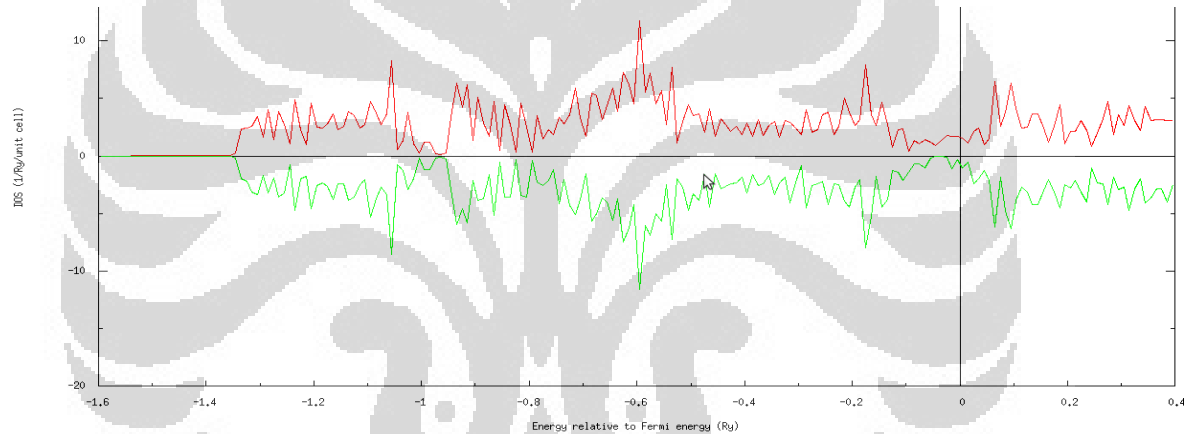


Figure 4.3. DOS of 10% hydrogen coverage

20% hydrogen coverage

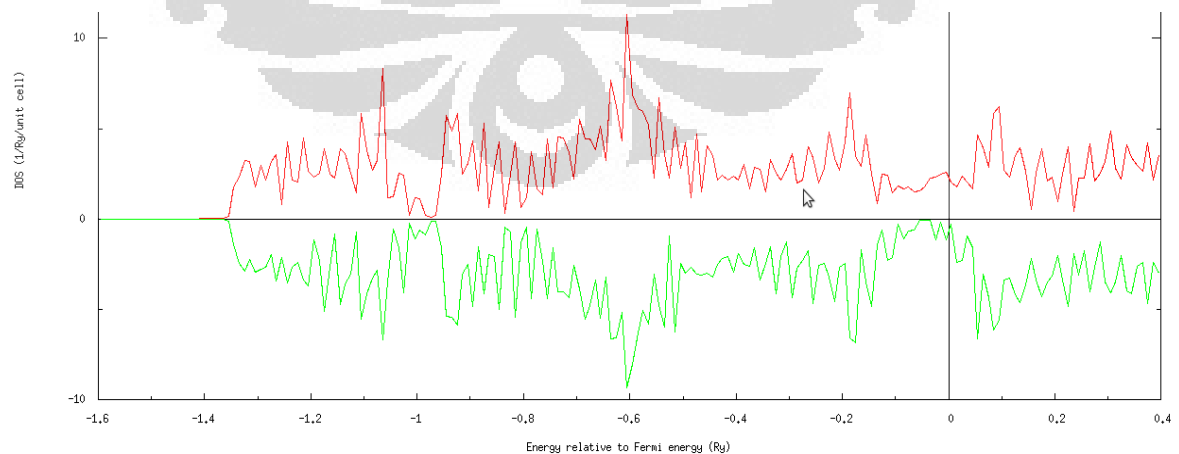


Figure 4.4. DOS of 20% hydrogen coverage

30% Hydrogen coverage

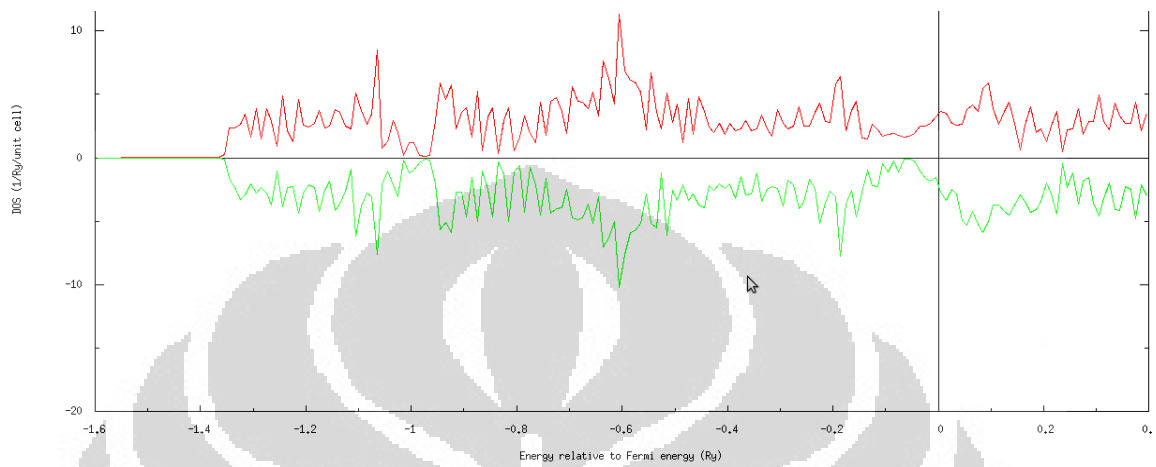


Figure 4.5. DOS of 30% hydrogen coverage

40% Hydrogen coverage

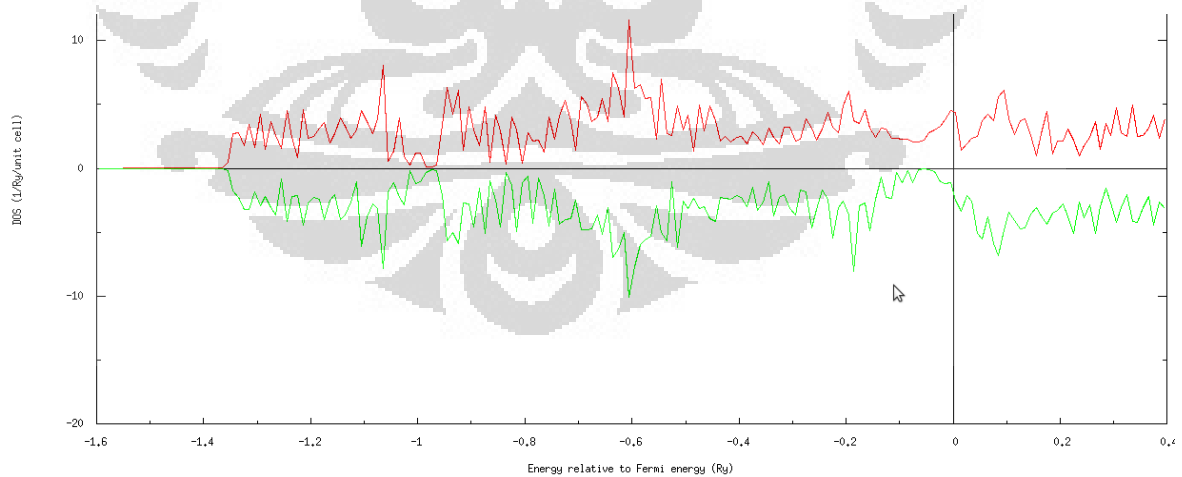


Figure 4.6. DOS of 40% hydrogen coverage

50% Hydrogen coverage

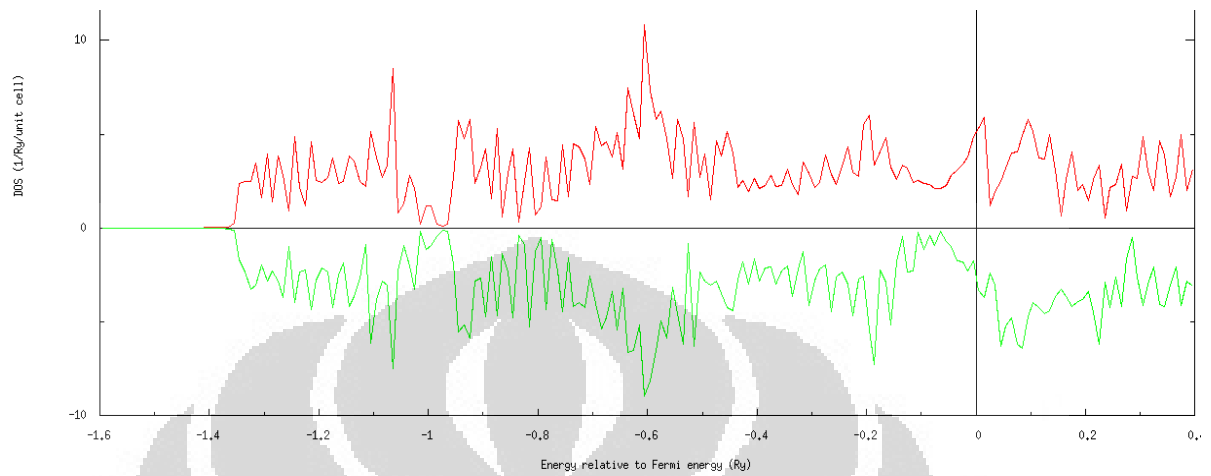


Figure 4.7. DOS of 50% hydrogen coverage

60% Hydrogen coverage

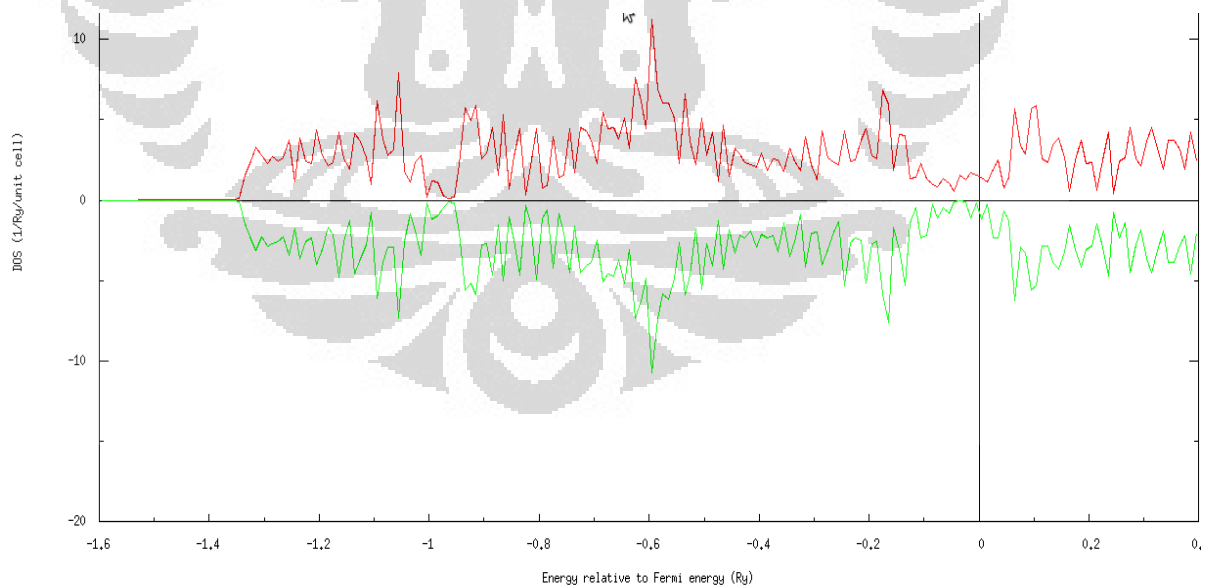


Figure 4.8. DOS of 60% hydrogen coverage

70% Hydrogen coverage

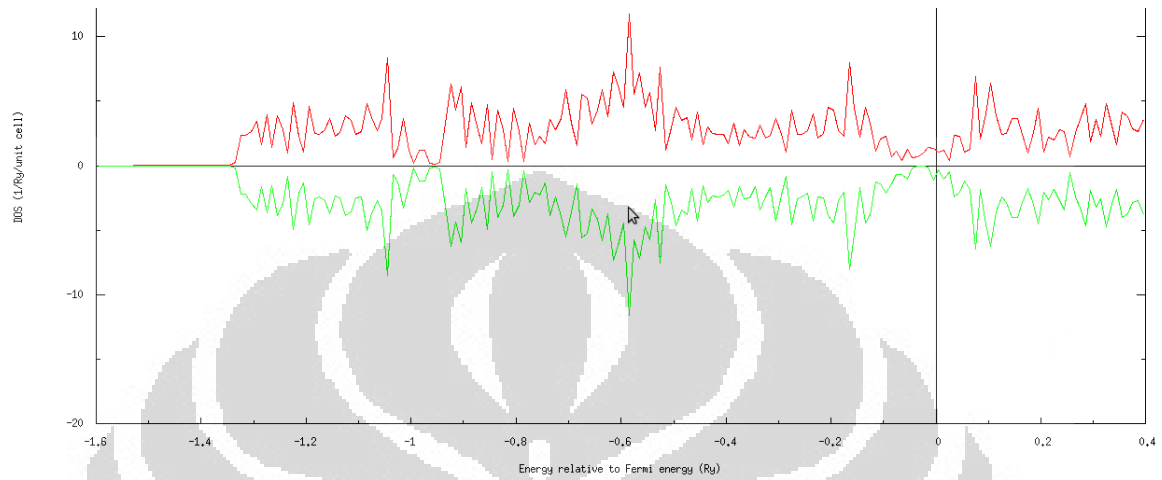


Figure 4.9. DOS of 70% hydrogen coverage

80% Hydrogen coverage

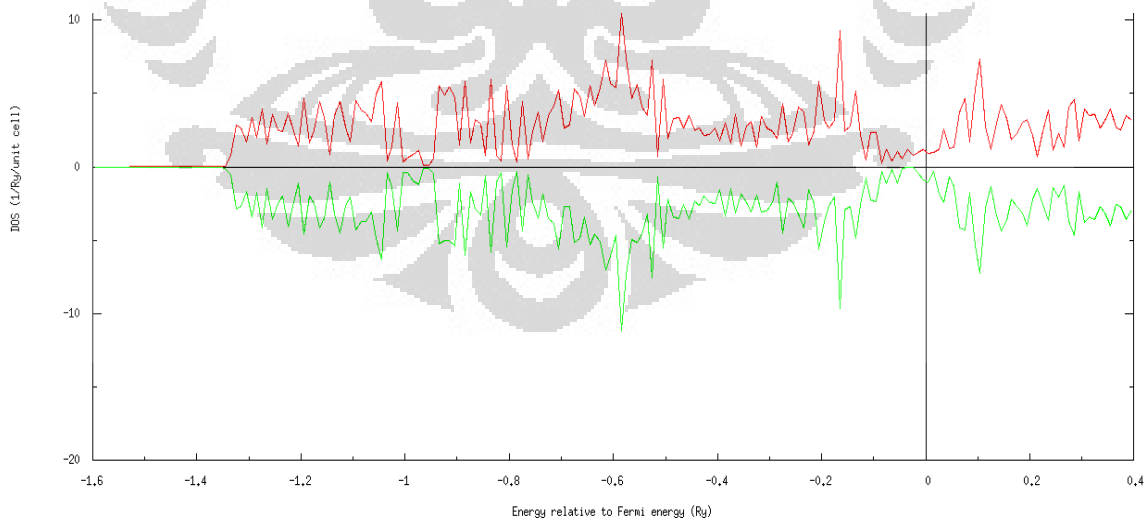


Figure 4.10. DOS of 80% hydrogen coverage

90% Hydrogen coverage

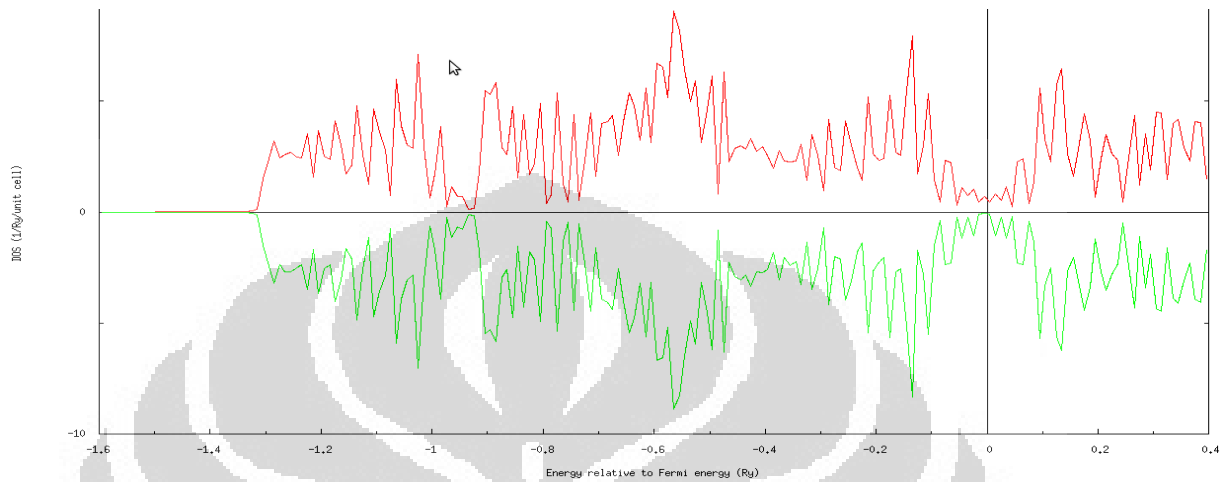


Figure 4.11. DOS of 90% hydrogen coverage

96% Hydrogen coverage

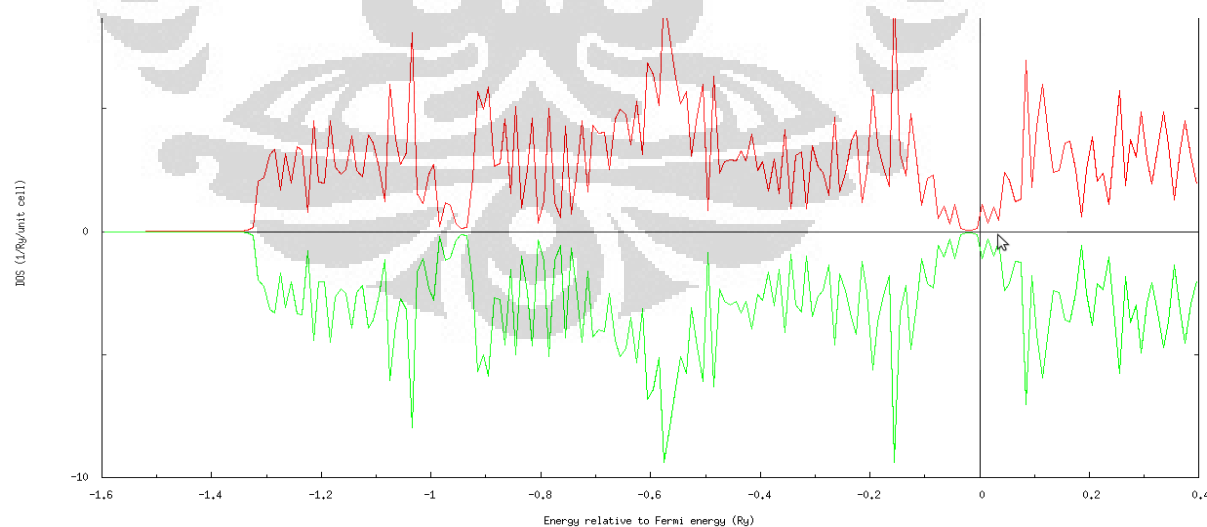


Figure 4.12. DOS of 96% hydrogen coverage

4.2.1 Density of States at Fermi level

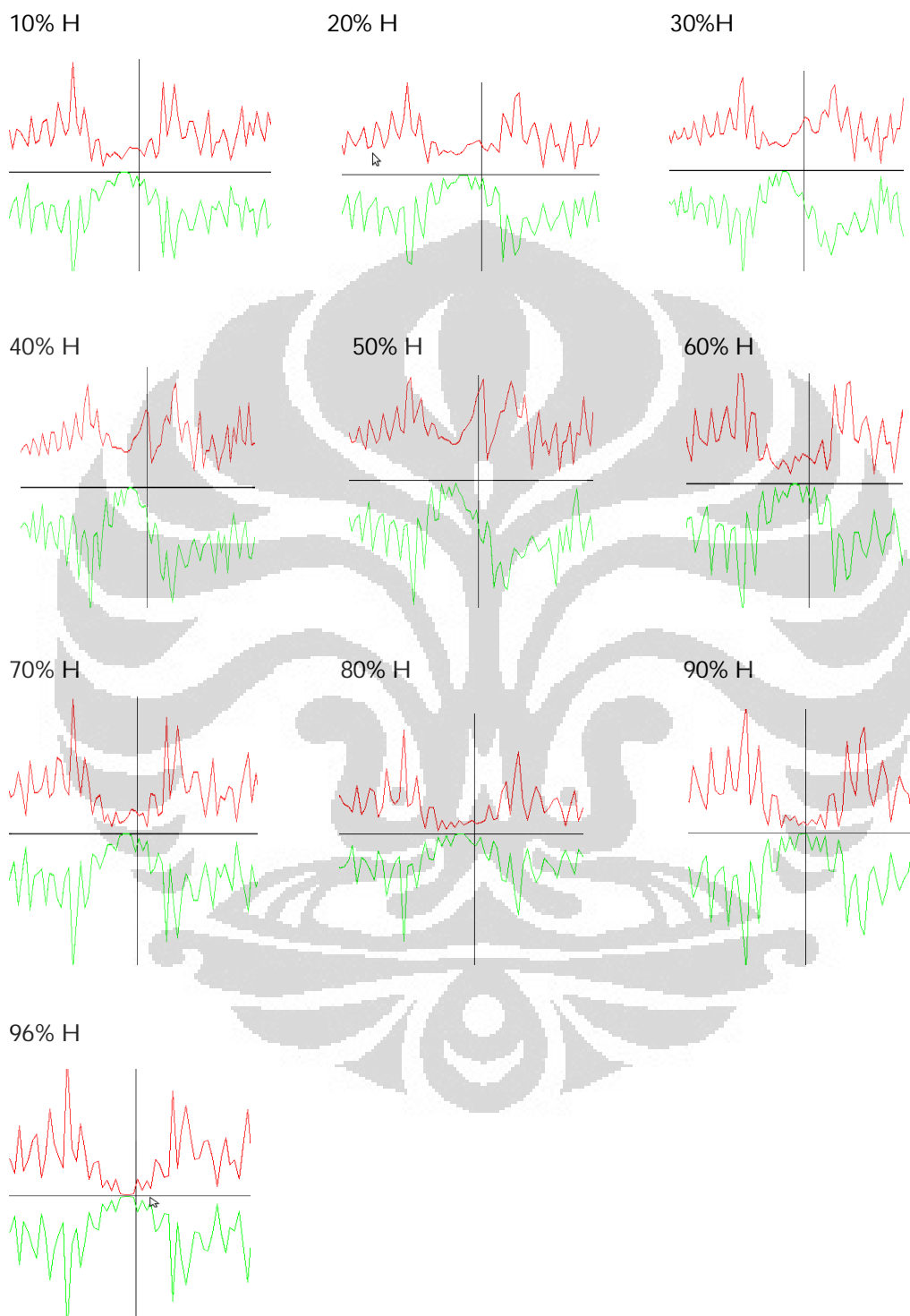


Figure 4.13 DOS around the Fermi level

As can be seen that in the 10%-50% hydrogen coverage DOS at the Fermi level is increase while >60% hydrogen coverage is decrease. When hydrogen atoms are placed on top site of carbon atoms, electron of hydrogen are delocalized with electron of Pz orbitals on hydrogenated carbon atoms and electron of Pz orbitals on bare carbon atoms are localized making finite DOS at the Fermi level. Based on the site projected DOS for hydrogenated carbon atoms and bare carbon atoms that DOS at the Fermi level is determined by electron in Pz orbitals of bare carbon atoms so that in the 60% hydrogen coverage, it means consist of 30 hydrogen atom randomly are placed on top site of 50 carbon atoms so that there are 30 hydrogenated carbon atoms and 20 bare carbon atoms. The number of bare carbon atoms less than hydrogenated carbon atoms, therefore DOS at the Fermi level is decrease. In the 70%, 80% hydrogen coverage DOS at the Fermi level have the same pattern with 60% that is DOS at the Fermi level is decrease because of subtraction the number of bare carbon atoms so that DOS at the Fermi level is decrease close to zero. Especially in the 90% hydrogen coverage shows half-metallic feature that is metallic in spin up band but semiconductor in spin down band, to analyze why in the 90% hydrogen coverage is half metallic are needed additional data like site projected DOS, isosurface for charge density, etc. Further studies are needed in order to understand that in the 90% hydrogen coverage shows half-metallic behaviour. It will be better to use a large supercell and running on parallel computer. In the 96% hydrogen coverage means that the system consists of 48 hydrogen atoms are placed on top site of carbon atoms, in other word, there are 48 hydrogenated carbon atoms and 2 bare carbon atoms. As we have know based on the site projected DOS that DOS at the Fermi level caused by electron of Pz orbitals on bare carbon atoms. Due to the number of bare carbon atoms just two bare carbon atoms, therefore DOS at the Fermi level is zero.

4.3. Site Projected DOS for Hydrogenated and Bare Carbon Sites

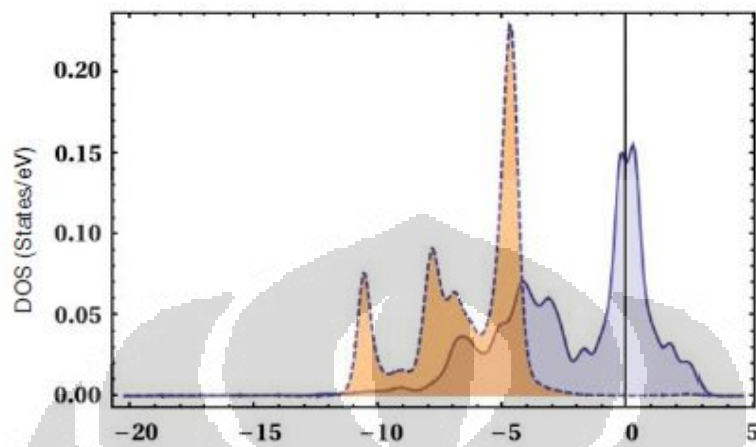


Figure 4.14. Site projected DOS for hydrogenated carbon sites (dotted line) and bare carbon sites (continuous line) for hydrogen coverage of 40% [32].

This is the graph of the site projected DOS for hydrogenated carbon sites (dotted line) and bare carbon sites (continuous line) for hydrogen coverage of 40%. Almost all the contribution of DOS value at Fermi level comes from the Pz which has been shown in the figure. Note that only bare carbon atoms contribute to the DOS at the Fermi level. This graph brings out the difference between the local electronic structure of the bare carbon atoms and the hydrogenated carbon atoms. The contribution around the Fermi level comes from the Pz orbitals of bare carbon atoms only. Upon hydrogenation, only bare carbon atoms contribute to the DOS at Fermi energy. As can be seen that the energy of hydrogenated carbon atoms lower than bare carbon atoms because the hydrogenated carbon atoms have sp^3 hybridization while the bare carbon atoms have sp^2 hybridization, therefore the hydrogenated carbon atoms have lower energy than the bare carbon atoms. This graph (the difference between the local electronic structure of the bare carbon atoms and the hydrogenated carbon atoms) will be used as reference.

4.4 Variation of the DOS at the Fermi level

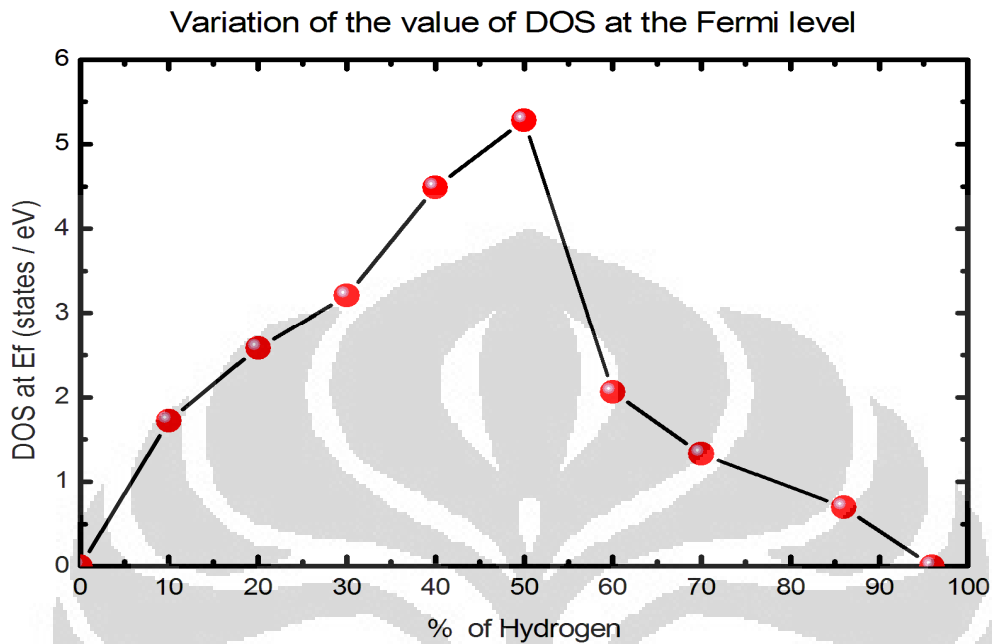


Figure 4.15. Variation of the value of DOS at the Fermi level as a function of hydrogen coverage

This graph shows the value of DOS at the Fermi level, from 0% up to 50% hydrogen coverage, the value of DOS at the Fermi level is increase. It may be underlined that the states around the Fermi level giving a finite DOS show that the system is metallic. The decline seen after 50% hydrogen coverage because of the subtraction in the number of bare carbon atoms. Especially for above 70% hydrogen coverage the value of DOS at Fermi level is decrease close to zero and in 96% hydrogen coverage the value of DOS at the Fermi level is zero, in other words, the band gap is opened. This is in agreement with experiment result by Balog *et al* [33] that is hydrogen atom populate all of the sites, the size distribution of the bare carbon graphene regions becomes narrower and the gap attains a well-defined value. For 10%-50% hydrogen coverage is consistent with Chandrachud *et al* [32] but for >70% hydrogen coverage is different because we

still presence used 5x5 supercell while they used 6x6 and 7x7 supercell. Hydrogen adsorption dependence on the periodic supercell size [34].

4.4.1 Analyzing Variation of the value of DOS at Fermi level

As can be seen on the graph of density of states (DOS) by 10%, 20%, 30%, 40%, 50% hydrogen coverage. As the hydrogen coverage increase there is significant increase in the value of DOS at the Fermi level, this rise is due to the process of hydrogenation is accompanied by the change in the geometry. The effect of H adsorption are breaking π bonds and producing additional σ bond [20]. Thus, the DOS is modified by additional localized $\sigma - P_z$ bonds between the hydrogen and carbon. In addition, hydrogenation of graphene pulls the carbon atom out of the plane breaking the symmetry of pure graphene. The carbon atoms shift in the z direction because its orbital hybridization changes from sp^2 to sp^3 to make the formation of the covalent bond possible. Therefore as the hydrogen coverage increase, in spin up there is significant increase in the value of DOS at the Fermi level. Here is the illustration of the change geometry of graphene induced by hydrogen atom.

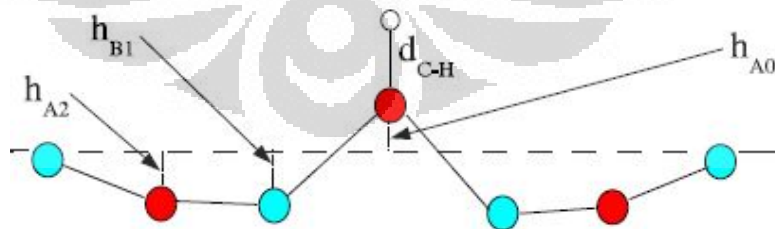


Figure 4.16. Picture of local distortions of graphene as chemisorption of single hydrogen atom [27]

As can be seen that the structural distortions of graphene sheet. Chemisorption of hydrogen by A_0 carbon atom induces its shift up perpendicular to the plane, together with shifts of atoms B_1 and A_2 in the opposite direction because of transition from sp^2 to sp^3 hybridization causes the structural distortions of graphene sheet. The H atoms form local sp^3 hybridization between hydrogen and carbon atoms, which causes local distortion of the graphene sheet [35].

4.4.2 Half Metallic and Semiconductor Behaviour

In the 90% hydrogen coverage. It shows characteristic feature of half metallic, that is metallic in spin-up band but semiconductor for spin-down band. While in the 96% hydrogen coverage is semiconductor which is in agreement with experiment result by Elias *et al* [6] showed that the temperature dependent resistivity of hydrogenated graphene shows that the higher temperature cause the resistivity is decrease, it may be emphasized that is shows semiconductor behavior. The band gap is opened because:

1. As the concentration increases further (90% and 96%), in the 96% hydrogen coverage means that the systems consist of 48 hydrogenated carbon atoms and 2 bare carbon atoms so that there are too few bare carbon atoms available for the formation of delocalized π bonds. The value of DOS approaches zero and a band gap is opened. It seems to be in agreement with the experimental results by Balog *et al* [33], they combined Scanning Tunneling Microscopy (STM) and Angle-Resolved Photoemission Spectroscopy (ARPES) experiments showed that the adsorption of atomic hydrogen of graphene grown on an Ir substrate produces a band gap opening in graphene, the width gap is coverage dependent and the gap opening is indeed due to a confinement effect in the residual bare graphene regions[33]

2. In pure graphene, the each carbon atom is sp^2 bonded with three planar σ bonds. This leaves an unpaired P_z orbital empty which is perpendicular to the plane. A set of π bond orbitals give rise to weird conductivity in graphene. Now, when graphene is hydrogenated, these unpaired p_z orbitals which is hold the important role for conduction will be slightly broken (will be reduced), hence a band gap slightly open up.



CHAPTER V

CONCLUSION

In this study, within the DFT calculations, we are able to show the evolution of the density of states of hydrogenated graphene as a function of hydrogen coverage. Density functional investigations have revealed some novel features of metallic-semiconductor. As the hydrogen coverage increases, graphene with metallic character turns first in to half metallic, finally turns in to semiconductor. Hydrogenated graphene for low concentration hydrogen ($\leq 50\%$) is metallic and very high concentration region where most of the carbon atoms are hydrogenated give rise a small gap (semiconductor).

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