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## The Study of Graphene Band Gap Using Hartree Fock Method in Molecular Scale

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### ABSTRACT

Graphene is known as an advanced material that has good electrical conductivity and heat conductivity. To understand the nature of graphene it is necessary to calculate the energy, band gap and vibrate frequency at the nanoscale. One method that can be used is the ab initio calculation using the Hartree-Fock method. In this research, we performed a computational study of the electronic properties of grapheme within RHF/STO-3G basis set in different cluster molecules. From this study we get band gap for graphene in ab initio level, have a consistent value around zero. Using ab initio method, we can obtain a deeper understanding about the graphene behaviour at the molecular scale.

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### Introduction

Graphene is an allotrope of carbon in the form of thin flat sheets in which each carbon atom has a sp<sup>2</sup> bond and is tightly packed in the form of a crystal lattice like a honeycomb [1]. It can be seen as an atomic-scale net consisting of carbon atoms and their bonds. Graphene has good electrical conductivity, high charge carrier mobility (230,000 cm<sup>2</sup>/Vs) with 2.3% light absorbability, high thermal conductivity (3000 W/mK), the highest tensile strength (130 GPa), and the largest surface area (2600 m<sup>2</sup>/g) [2]. The superiority of the properties of graphene is graphene has the potential to be applied to a variety of electronic devices including solar cells, touch screens, lasers, and others. Another property of graphene is the zero band energy gap that

we call Dirac point in graphene [3]. For this reason, understanding the electrical properties of graphene is very important to study. We can understand the electrical properties of graphene by understanding the properties in molecular scale.

Besides experiments [4], graphene's electrical properties can be determined by using molecular modeling. There are several levels of theory used in molecular modeling, such as Hartree Fock (HF), Density Function Theory, Quantum Semi-empiric, Molecular Dynamics, and Molecular Mechanics [5, 6]. HF theoretical calculation for graphene have been conducted in some papers [7, 8]. HF theory is the best level of theory with high accuracy for simple molecular modeling and is suitable for calculating properties near molecular ground states. In HF, the instantaneous Columbic electron–electron repulsion is not specifically taken into account and only its average effect is included in the calculation [9].

Therefore, this study aims is to determine the electrical properties of graphene structures on a molecular scale by analyzing total energy, band gap, and IR spectrum. The method used here is the Restricted Hartree-Fock (RHF) method, where the orbitals are double occupied by electrons [10].

### **Experimental Method**

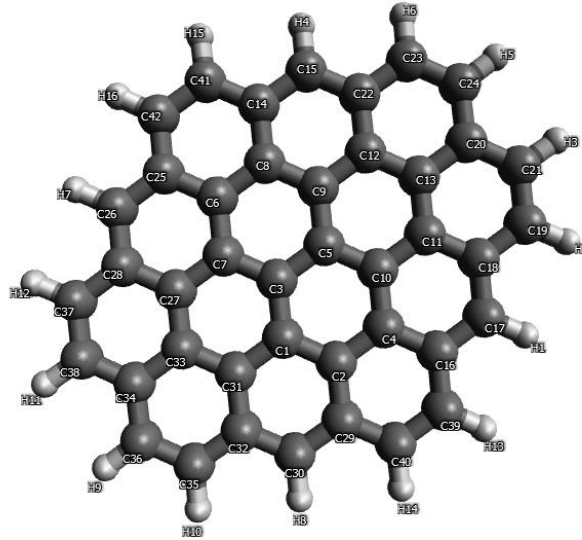
The equipment used in this type of computational research is a set of PCs / Laptops. While the software used is Avogadro which functions to model molecular images, Notepad ++ 7.6.1 as a text editor, Firefly 8.2.0 [11] to analyze molecules created using RHF, and WxMacMolpt to visualize band gap characteristics.

The calculation of energy, energy band, and graphene frequency at the nanoscale in this study uses the ab initio calculation method, which uses the Restricted Hartree-Fock / STO-3G basis set method which is large enough to explain all the electrons in the group. The initial geometry of these molecules was built using Avogadro with a different number of cells for each input file unit. The model is optimized by molecular mechanical methods using universal force fields (UFF) which automatically work in Avogadro [12].

Each input file that has been made is analyzed one by one using Firefly and the help of the command prompt as a compiler. Each cell has two different input files, one input file for analyzing single point molecular energy and the other for molecular frequencies. If the input file has finished processing/running using the help of Firefly 8.2.0 as a compiler, an output file is obtained. In the output file can be read the total energy value. While energy bands are obtained from the characteristics of graphene in WxMacMolpt by first analyzing orbitals to get the lowest Unoccupied Molecular Orbital (LUMO) and Highest Occupied Molecular Orbital (HOMO) values. Energy band values are calculated using the LUMO and HOMO difference values [13]. The difference values of HOMO and LUMO also can show the stability of the molecules [14].

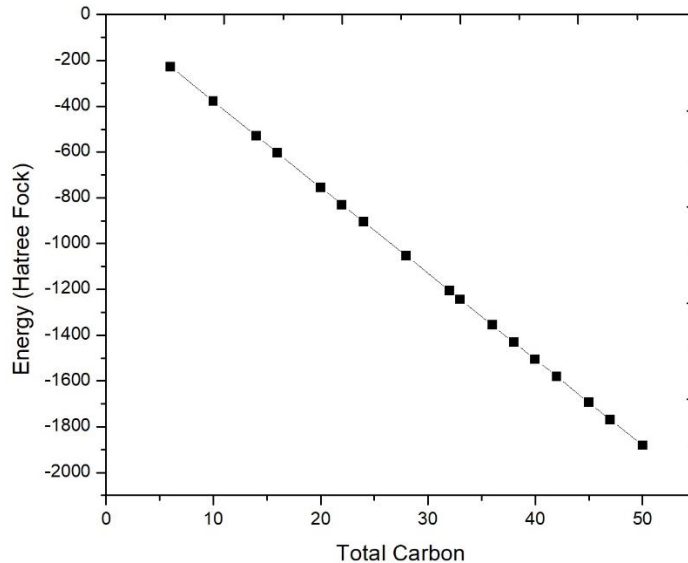
### **Result and Discussion**

Equilibrium geometry from graphene has been obtained using universal force fields (UFF) in Avogadro applications. In Figure 1, it appears optimize geometry for graphene with 42 carbon, where carbon free electrons bind to hydrogen.



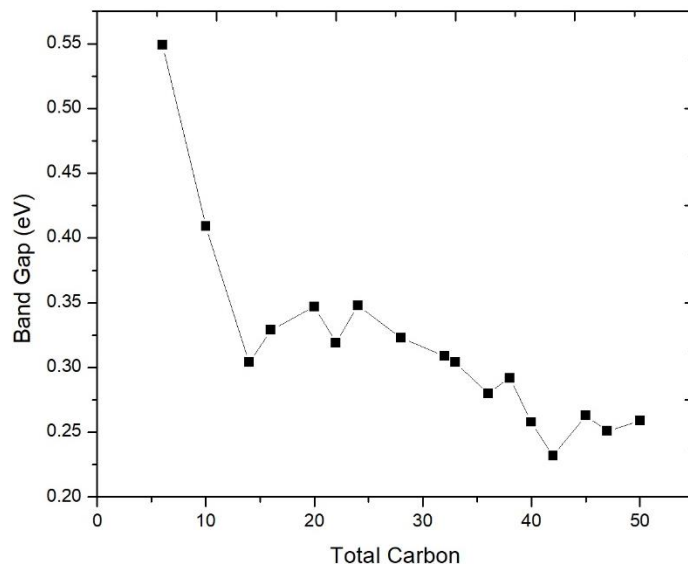
**Figure 1.** Graphene structure with 42 carbon atoms

The total energy of the optimized atomic structure is calculated using the ab initio hartree fock method on the basis of the STO-3G set. It appears that with the increase of carbon atoms the total energy of the structure gets negative because we multiply the atom constituent in molecules.



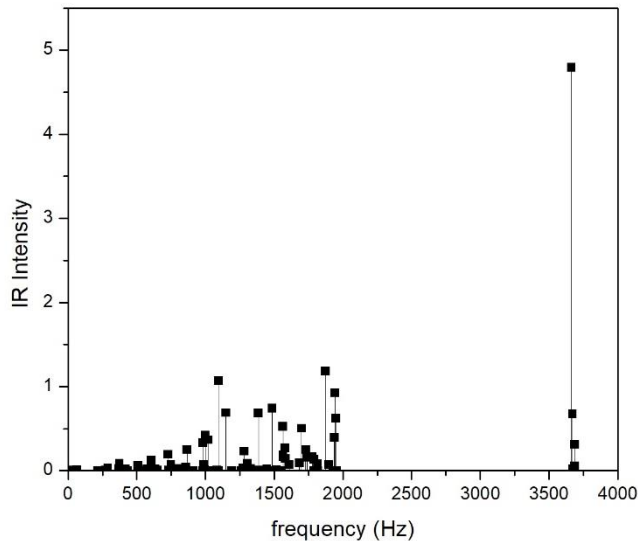
**Figure 2.** Total Energy calculation results with different numbers of carbon

Unlike the total energy, the band gap calculation does not follow a straight curve, but overall it appears that the band gap decreases with the addition of carbon atoms. The biggest band gap is at 6 carbon and the lowest is at 42 carbon. In this study we counted up to 50 carbons. This value is in accordance with the theory that the larger the molecular size, the smaller the band gap. Besides that, the electron Coulomb potential reduces the repulsion between valence and conduction band electrons leads to a band gap reduction. The large energy band gap in the 6 carbon structure is due to the quantum size effect.



**Figure 3.** The band gap results from different cluster of atom carbon

While for frequency calculations from data of geometry optimization, we get infrared absorption spectrum predictions that can provide information about the vibrational movements of molecules and are used to identify compounds and study their structure. This intensity are in  $\text{Debye}^2/\text{amu}\cdot\text{\AA}^2$ . The results calculated from changes in molecular dipoles using hessian calculation.



**Figure 4.** The calculated IR spectrum in different frequency for 42 carbon atoms

Band gap energy is related to photon energy transition from valence band to conduction band. Strong infrared intensity at longer wavelengths, associated with the generation of phonons, and weaker intensity caused by multi-phonon absorption processes. It is appears that the more complex the structure, the higher the intensity of infrared that appears. Optical properties of graphene has a very broad band optical absorption, where the infrared absorption are related to

thermodynamic equilibrium. At thermodynamic equilibrium, the infrared energy can be described by the Stefan–Boltzmann law.

### Conclusion

The total energy, band gap, and IR spectra characteristics of graphene have been successfully calculated using the ab initio and restricted hartree fock methods. The results of band gap calculations using this methods are for the 6 atom C structure the width of the energy band is 0.54 eV and the smallest band gap is 0.23 eV for the 42 atom C structure.

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