Ab Initio DFT Study of Band Gap of Armchair and Zigzag Graphenes

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Abstract. Graphene sheet is a single-atom thick material and attracts great interest due to its extraordinary physical properties, but it has zero bandgap. At the boundary of graphene sheet, two types of stable edges were the zigzag edge and armchair edge. The electronic states of graphene largely depend on the edge structures. In this research, we used Quantum ESPRESSO package to calculate the band gap of armchair and zigzag graphene due to the increase of their number of cells. The results show that the graphene band gaps are influenced by the number of cells in the armchair and zigzag configuration.

1. Introduction
Graphene is made from carbon atoms arranged on a honeycomb structured by hexagons form. The structure flexibility of graphene is reflected in its electronic properties. The sp² hybridization between planar structure with a formation of a ρ bond between carbon atoms are separated by 1.42 Angstrom [1]. The theory of graphene has been established in 1947 as a first step to understand the electronics properties of graphite 3D. But it has predicted theoretically that 2D material is impossible to be grown. In 2004, Andre Geim and Novoselov exfoliate the graphene for the first time and they have received the 2010 Nobel Prize in Physics for their work on graphene research. The tight binding calculation of graphene shows that its conduction and valence band touch at Dirac points in the Brillouin Zone where energy dispersion are linear with respect to momentum [2]. Graphene has a potential as a nanotechnology material and can change the soft matter and the 2D material. Graphene can be used as a transparent conducting layer, sensor, supercapacitor, solar cell, but it has zero bandgap [3].

Nanographene have an important edge geometry dependence on their electronic structures. The are two stable configurations of graphene, armchair and zigzag configuration. The armchair and zigzag configurations are fundamental edges configurations, and there are clear different between armchair and zigzag configuration. The gap can be tuned by changing the ribbon width in graphene nanoribbon [4].

In this research, we study the band gap of armchair and zigzag graphene. We study the influence of increase the number of cells in armchair and zigzag graphene to the band gap of graphene using Quantum ESPRESSO package. Quantum ESPRESSO is the open source code always used for electronic calculations based on density functional theory (DFT), or many-body perturbation theory, using plane-wave basis sets and pseudopotentials [5].
2. Experimental

Description of the Coulomb’s interaction between nuclei and electron is needed to calculate the band gap and density of states. Researcher usually solve this problem by using Hartree-Fock method. Since 1970’s, density functional theory (DFT) has been extensively used for the calculations of electronic structure of atoms, molecules, and solids. The formalism is based on the Hohenberg-Kohn theorem [6], which states that the ground-state energy of system can be expressed as a functional of the ground-state of a single-particle density.

The main problem for calculating the electronic structure is to find the energy, that can be written in Schrödinger equation for certain Hamiltonian:

$$\hat{H} = \hat{T} + \hat{V}$$  \hspace{1cm} (1)

In solid case, we calculate the Coulomb interaction between nuclei and electron. We can write 3 types of interaction: nucleus-nucleus interaction, nucleus-electron interaction, and electron-electron interaction.

$$\hat{H} = \sum_{i} \frac{\hbar^2}{2m_i} \hat{p}_i^2 + \frac{\hbar^2}{2m_e} \sum_{i} \hat{p}_i^2 + \sum_{i \neq j} \frac{e^2}{8\pi\varepsilon_e |\vec{r}_i - \vec{r}_j|} + \sum_{i} \sum_{j} \frac{e^2}{4\pi\varepsilon_e |\vec{R}_i - \vec{r}_i|} + \sum_{i \neq j} \frac{1}{8\pi\varepsilon_e |\vec{r}_i - \vec{r}_j|}$$  \hspace{1cm} (2)

Depend on Born-Oppenheimer approximation, we can have a nucleus with fixed position than we can neglect the kinetic energy.

$$\hat{H} = \frac{1}{2} \sum_{i} \hat{p}_i^2 + \sum_{i \neq j} \frac{1}{2 |\vec{r}_i - \vec{r}_j|} + \sum_{i} \sum_{j} \frac{e^2}{4\pi\varepsilon_e |\vec{R}_i - \vec{r}_i|}$$  \hspace{1cm} (3)

In 1929, Hartree proposed that the electron system can be characterized by the electron density, which is given by the sum of all electrons at a point \( \vec{r} \).

$$n(\vec{r}) = \sum_{i=1}^{N_e} \delta(\vec{r} - \vec{r}_i)$$  \hspace{1cm} (4)

Hohenberg-Kohn theorem leads to energy

$$E[n] = \langle \psi[n] | \hat{H} | \psi[n] \rangle = F_{HK}[n] + \int d^3r V_{ext}(\vec{r}) n(\vec{r})$$  \hspace{1cm} (5)

where \( F_{HK} \) as Hohenberg-Kohn functional denoted as:

$$F_{HK}[n] = \langle \psi[n] | \hat{T} + \hat{V} | \psi[n] \rangle$$  \hspace{1cm} (6)

In 1965, Kohn-Sham [7] assumed that the ground state of the original system is equal to the ground state density of some chosen non-interacting systems. Thus we can write
In this work, the first step to obtain the structure of graphene system is to generate a single layer graphene. We use graphite CIF file to generate an armchair and zigzag graphene through VESTA and ASE Python. The band gap and density of states (DOS) are obtained through planewave DFT calculations in Quantum ESPRESSO package. Exchange-correlation (XC) potential is approximated by PBE-GGA, and k-points are chosen to be “automatic” for self-consistent field (SCF) and non-self consistent field calculation (NSCF), and chosen to be “crystal_b” for band and DOS calculation, where the k-point were generated by using XCRYSDEN. The pseudopotential is taken from Kresse-Joubert PAW algorithm [8]. In this research we are not doing a relax calculation since we only need a band gap and DOS. To obtain these two results, the SCF calculation is considered more efficient. After calculating the SCF, we calculate the NSCF as a prequel to the projected DOS. After calculating the NSCF, we calculate the band gap and DOS of armchair and zigzag graphene.

3. Results and Discussion

3.1. Armchair graphene

3.1.1. Band gap and Fermi energy

![Figure 1. Band gap and Fermi energy.](image)

For different number of cells in armchair graphene (Figure 1), the Fermi energy decrease when the number of cells increase, the Fermi energies are -4.766 eV, -5.067 eV and -5.284 eV, respectively for 4, 10 and 19 number of cells. For its band gap, the value is 0.310 eV for 4 cells, increase to 0.490 eV for 10 cells and decrease to 0.180 eV for 19 cells. We can see from this result that the band gap value is oscillating, but the value is between 0.0 and 0.5 eV.

3.1.2. Density of states

The density of states of the system describes the number of states per an interval of energy at each energy level available to occupied.
Figure 2. DOS for 4 cells. Figure 3. DOS for 10 cells. Figure 4. DOS for 19 cells.

Figure 2, 3 and 4 are all the total density of states of armchair graphene. The Fermi energy is shown by the vertical line in each curve. As we see from these density of states curves, we can say that the armchair graphene is metal-like, since there is no gap in each density of states curve. The total density of states curve shows the antisymmetric between spin up and spin down, indicates that the armchair graphene is paramagnetic-like [9,10].

3.2. Zigzag graphene
3.2.1. Band gap and Fermi energy

Figure 5. Band gap and Fermi energy.

For different number of cells in zigzag graphene, the Fermi energy increase from -5.065 eV to -4.332 eV for 6 to 10 number of cells but decrease to -4.675 eV when the number of cells increased to 15. For spin up band gap, the band gap increased when the number of cells is increased. When we use 6 cells, the gap is 0.161 eV, increase to 0.419 eV for 10 cells, and then 0.455 eV for 15 cells. We can see from these results that the band gap of zigzag graphene is between 0.0 eV and 0.5 eV.
3.2.2. Density of states

![Figure 6. DOS for 6 cells.](image1)

![Figure 7. DOS for 15 cells.](image2)

![Figure 8. DOS for 15 cells.](image3)

Figure 6, 7, and 8 are the density of states of zigzag graphene. From the overall of the density of states curves, it is seen that the zigzag graphene is paramagnetic-like. Since there is no gap shown in these density of states curves, then the zigzag graphene is metal-like material.

4. Conclusion

Based on the results above, one can say that there is an influence between the number of cells and the band gap of armchair and zigzag graphene. For armchair graphene, the band gap is oscillating when we increase the number of cells, but the band gap is increase when we increase the number of cells for zigzag graphene. The value of armchair and zigzag band gap not more than 0.5 eV. From DOS calculation, one can say that these two types of graphene are paramagnetic-like.

Acknowledgement

This work is supported by Republic of Indonesia Ministry of Research, Technology and Higher Education (127/SP2H/PTNBH/DRPM/2018).

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