Theoretical Study of Electronic Properties of Nanostructures Composed of Blue Phosphorene and Graphene Sheet

Kh N Alnssar1,2*, M R Roknabadi1, M Behdani1, B G Shohany1
1 Department of Physics, Faculty of Science, Ferdowsi University of Mashhad, Iran.
2 Department of Physics, Faculty of Science, Albaath University of Homs, Syria.

Email: khaled.alnssar@mail.um.ac.ir

Abstract. In this study, structural and electronic properties of the single-layer structure of Graphene, the single-layer structure of blue Phosphorene, the two-layer structure of blue Phosphorene/Graphene, the three-layer structure of blue-Phosphorene/Graphene/blue-Phosphorene and the three-layer structure of Graphene/blue-Phosphorene/Graphene have been investigated. The calculations are conducted based on the density functional theory (DFT) and using SIESTA code and generalized gradient approximation (GGA). The results show that the single-layer structure of Graphene reveals quasi-metallic behavior, and the single-layer structure of blue Phosphorene exhibits semiconducting behavior. Two- and three-layer structures of Graphene and blue Phosphorene have a metallic behavior. Total energy and structural stability have also been investigated.

Keywords: Graphene; Blue Phosphorene; Density Functional Theory; SIESTA.

1. Introduction

Graphene refers to a sheet composed of carbon atoms with a regular arrangement. Graphene is a two-dimensional allotrope with a thickness of one carbon atom by SP 2 hybridization that has connected in a hexagonal lattice [1]. For the first time, the Graphene separation was presented by A.K. Geim and K.S. Novoselove [2]. According to their calculations and experiments, the mobility of electrons in pure Graphene is higher than other conductive materials at room temperature, such as gold, silicon, and carbon nanotubes. Since Graphene is a transparent conductor, it can have applications such as touch screens, solar cells, and light panels, in which case, Graphene can replace indium tin oxide (ITO) that is very expensive. Another application of this material is flexible electric and gas sensors. New types of composite materials based on Graphene that are known as high-strength and low-weight can be used in satellite and aerospace industries. Graphene has the excellent conductive property that is why; it is the candidate for the next generation of high-speed transistors [3-6].

Like Graphene, Phosphorus can be prepared as a mono-atomic layer, which is called Phosphorene. Unlike Graphene, Phosphorene has a non-zero band gap and can act like a semiconductor [7-9]. The single-layer structure of black Phosphorus is called black Phosphorene. Phosphorene is predicted to be a serious rival for Graphene, since, unlike Graphene, Phosphorene has band gap. Hultgren et al., were the first to investigate experimentally the structure of black Phosphorus lattice [10]. They found that the crystal structure of black Phosphorus has an orthorhombic structure, and its single cell contains 8 atoms. Black Phosphorus is a direct-band-gap (DBG) semiconductor. The band gap calculated by the researchers is 0.36eV. Black Phosphorus has already attracted great attention due to its adjustable band gap, high mobility of carriers and anisotropic structure [10].

Blue Phosphorene is a single-layer allotrope of phosphorus that, like black Phosphorene, is predicted to be stable. Its primary cell is hexagonal, and unlike black Phosphorene, its structure is isotropic. The band gap obtained according to the ab-initio calculations is about 2eV [11-12]. South Korean researchers in
2015 examined the electronic and magnetic properties of zigzag blue Phosphorene nano-ribbons. They also studied the saturation effect of free bonds of edges with hydrogen and oxygen [12]. The results of their calculations show that these nanoribbons are semiconductor, and by saturation of edge states using hydrogen, destruction of magnetization will occur and the band gap increases up to 1.77eV. In addition, due to the application of external stress, the semiconductor-to-metal transition occurs. Studies have shown that Phosphorene has a high potential for using in Lithium-ion and sodium-ion batteries [19]. Investigating the results of the researchers shows that the activation energy necessary for the sodium diffusion in Phosphorene is less than Graphene, MoS₂ and Silicene. Due to its large surface area and low activation energy, Phosphorene is expected to be used in batteries [13-15].

Given the importance and applications of Phosphorene, in this article, the comparison of structural and electronic properties of the single-layer structure of Graphene, the single-layer structure of blue Phosphorene, the two layers of blue Phosphorene / Graphene, and the three-layer structure of blue Phosphorene and Graphene have been studied.

2. Calculation Method

Structural relaxations and electronic properties of the single-layer structure of Graphene, the single-layer structure of blue Phosphorene, the two-layer structure of blue Phosphorene / Graphene, and the three-layer structure of blue Phosphorene / Graphene / blue Phosphorene, and the three-layer structure of Graphene / blue Phosphorene / Graphene have been studied based in the density functional theory and using the computational package of SIESTA (Spanish Initiative for Electronic Simulation with Thousands of Atoms) based on the linear combination of localized atomic orbitals [16]. In the simulations conducted to describe the exchange- correlation functional of electron-electron interaction, the generalized gradient approximation (GGA-PBE) has been used [17]. After the structural relaxations, the force applied to each atom is less than 0.01eV/Å.

2.1. Single-Layer Structure of Graphene

Monkhorst Pack method was used to describe Brillouin zone. For the single-layer structure of Graphene, the optimum number of k points of 20 × 20 × 1 and the optimal cutoff energy of 200 Ry were used in the calculations. A large enough vacuum layer (5 Å) is considered to avoid interacting with adjacent structures. The optimized lattice constants for the single-layer structure of Graphene are plotted in Figure 1. As shown in the Figure, the optimized lattice constants of the single-layer structure of Graphene are:

\[ a_1 = 2.46 \text{ Å}, a_{2x} = 1.23 \text{ Å}, a_{2y} = 2.13 \text{Å}\]

2.2. Single-Layer Structure of Blue Phosphorene

For the single-layer structure of blue Phosphorene, the optimum number of k points of 10 × 10 × 1 and optimal cutoff energy of 160 Ry were used in the calculations. A large enough vacuum layer (7 Å) is considered to avoid interacting with adjacent structures. According to Figure 2, the optimized lattice constants for the single-layer of blue Phosphorene are:

\[ a_1 = 3.4 \text{ Å}, a_{2x} = 1.9 \text{ Å}, a_{2y} = 2.9 \text{ Å}\]

2.3. Two-Layer Structure of Blue Phosphorene / Graphene

For the two-layer structure of blue Phosphorene / Graphene, the optimum number of k points of 25 × 25 × 1 and optimal cutoff energy of 150 Ry were used in the calculations. As shown in Figure 3, by optimizing the distance between two layers, it was selected to be 3.388 Å, and after relaxations, the distance between two layers equal to 3.448 Å was obtained. A large enough vacuum layer (12 Å) is considered to avoid interacting with adjacent structures. According to Figure 4, the optimized lattice constants for the two-layer structure of blue Phosphorene / Graphene are:
2.4. Three-Layer Structure of Graphene / Blue Phosphorene / Graphene
For the three-layer structure of Graphene / blue Phosphorene / Graphene, the optimum number of k points of $25 \times 25 \times 1$ and optimal cutoff energy of 150 Ry were used in the calculations. A large enough vacuum layer (15 Å) is considered to avoid interacting with adjacent structures. In the three-layer structure of Graphene / blue Phosphorene / Graphene, the distance between two layers after optimization was 3.378 Å (Figure 5), and after relaxation, the value of 3.412 Å was obtained. According to Figure 6, the optimized lattice constants for the three-layer structure of Graphene / blue Phosphorene / Graphene are:

\[ a_1 = 2.4 \text{ Å}, \quad a_{2x} = 1.43 \text{ Å}, \quad a_{2y} = 9.94 \text{ Å} \]

![Graphene](image1.png)

**Figure 1.** The optimized lattice constants for the single-layer structure of Graphene.
Figure 2. The optimized lattice constants for the single-layer of blue Phosphorene.

Figure 3. Optimizing the distance between two layers.
Figure 4. The optimized lattice constants for the two-layer structure of blue Phosphorene / Graphene.

Figure 5. Optimization of the distance between two layers of Graphene / blue Phosphorene / Graphene.
2.5. Three-Layer Structure of Blue Phosphorene / Graphene / Blue Phosphorene
Like before, for the three-layer structure of blue Phosphorene / Graphene / blue Phosphorene, the optimum number of k points of $25 \times 25 \times 1$ and the optimum cutoff energy of 150 Ry were obtained. A large enough vacuum layer (12 Å) is considered to avoid interacting with adjacent structures. In the three-layer structure of blue Phosphorene / Graphene / blue Phosphorene, the distance between two layers after optimization was 3.378 Å and after relaxation, the value of 3.435 Å was obtained. The optimized lattice constants for the three-layer structure of blue Phosphorene / Graphene / blue Phosphorene similar to those of Graphene / blue Phosphorene / Graphene are:

$a_1 = 2.4 \, \text{Å}, \ a_{2x} = 1.43 \, \text{Å}, \ a_{xy} = 9.94 \, \text{Å}$

![Graph](image.png)

Figure 6. The optimized lattice constants for the three-layer structure of Graphene / blue Phosphorene / Graphene.

3. Results and Discussion
3.1. Single-Layer Structure of Graphene
The geometric structure of Graphene single-layer is depicted in Figure 7 from the top and the side view. Investigating the relaxed structure shows that Graphene has a non-bending two-dimensional structure. The length of carbon-carbon bonds of 1.43 Å was obtained. The band structure and the total density of states of Graphene single-layer were calculated, that is plotted in Figure 8. Fermi energy is placed at zero
point. As shown in the Figure, Graphene has a quasi-metallic behavior. The results of the study of structural and electronic properties are in agreement with other reports [18, 19].

![Graphene structure](image1)

**Figure 7.** The single-layer geometric structure of Graphene in from the top and the side view.

![Band structure and total density of states](image2)

**Figure 8.** The band structure and total density of states of single-layer of Graphene.

3.2. **Single-Layer Structure of Blue Phosphorene**

The single-layer geometric structure of blue Phosphorene is shown after relaxation in Figure 9 from the top and the side view. Investigating the relaxed structure shows that blue Phosphorene has a quasi-sheet structure. The bending value of the structure is 1.24 Å and the length of phosphorus-phosphorus bonds of 2.28 Å was obtained. The results of the study of structural properties are in agreement with other reports [20].

In the next step, the band structure and the total density of states of the single-layer structure of blue Phosphorene were calculated, that is plotted in Figure 10. Fermi energy is placed at zero point. As shown in the Figure, blue Phosphorene has semiconductor behavior and an indirect band gap of 1.94 eV, which is consistent with the results of other researchers [21].
Figure 9. The geometric structure of blue Phosphorene single-layer after relaxation from the top and the side view.

Figure 10. The band structure and the total density of states of the single-layer structure of blue Phosphorene.

3.3. Two-Layer Structure of Blue Phosphorene / Graphene
A super cell consisting of 14 atoms (8 carbon atoms and 6 phosphorus atoms) was considered to simulate the two-layer structure of blue Phosphorene / Graphene. The geometric structure of blue Phosphorene / Graphene after relaxation is depicted in Figure 11 from the top (a) and the side view (b). Investigating the relaxed structure shows that bending value of blue Phosphorene sheet in this structure was 1.26 Å, which is not significantly different from that of the single-layer structure. The length of phosphorus-phosphorus bond is 2.28 Å. The length of carbon-carbon bond in Graphene sheet is 1.5 Å.

The band structure and total density of states of the two-layer structure of blue Phosphorene / Graphene are plotted in Figure 12. Fermi energy is selected at the zero point. As shown in the Figure, Fermi level is cut by several bands, so that the two-layer structure of blue Phosphorene / Graphene exhibit the metallic behavior. The band structure and total density of states are consistent. At zero energy (Fermi energy) the density of states is opposite to zero which confirms the metallic behavior of this structure.
Figure 11. The geometric structure of blue Phosphorene / Graphene after relaxation from the top (a) and the side view (b).

Figure 12. The band structure and the total density of states of the two-layer structure of blue Phosphorene / Graphene.

3.4. Three-Layer Structure of Blue Phosphorene / Graphene / Blue Phosphorene
A super cell consisting of 20 atoms (8 carbon atoms and 12 phosphorus atoms) was considered to simulate the three-layer structure of blue Phosphorene / Graphene / blue Phosphorene. The three-layer geometric structure of blue Phosphorene / Graphene / blue Phosphorene is shown in Figure 13 from the top (a) and the side view (b). Investigating the relaxed structure shows that the bending value of blue Phosphorene sheet in the structure is 1.35 Å, which is not significantly different from that of single-layer structure. The length of phosphorus-phosphorus bonds has not changed. In Graphene sheet, the length of the carbon-carbon bonds has slightly changed (1.51 Å).

The band structure and the total density of states of the three-layer structure of blue Phosphorene / Graphene / blue Phosphorene are plotted in Figure 14. Fermi energy is selected at the zero point. As shown in the Figure, several bands cut the Fermi level, so the three-layer structure of blue Phosphorene / Graphene / blue Phosphorene exhibits a metallic behavior.
3.5. Three-Layer Structure of Graphene / Blue Phosphorene / Graphene

A super cell consisting of 22 atoms (16 carbon atoms and 6 phosphorus atoms) was considered to simulate the three-layer structure of Graphene / blue Phosphorene / Graphene. The three-layer geometric structure of Graphene/ blue Phosphorene / Graphene after relaxation is depicted in Figure 15 from the top (a) and the side view (b). Investigating the relaxed structure shows that the bending value of blue Phosphorene sheet in the structure is equal to 1.38 Å, which has increased compared with other structures studied. The length of phosphorus-phosphorus bonds is 2.3 Å. The length of the carbon-carbon bonds in the Graphene sheet has also slightly increased. The band structure and the total density of states of Graphene / blue Phosphorene / Graphene three-layer are plotted in Figure 16. Fermi energy is selected at the zero point. As shown in the Figure, in this state, similar to the two-layer and three-layer structures studied, several bands cut the Fermi level, so the three-layer structure of Graphene / blue Phosphorene / Graphene also exhibit a metallic behavior.
3.6. Comparison of Total Energy
In Table 1, the total energy of the single-layer structure of Graphene, the single-layer structure of blue Phosphorene, the two-layer structure of blue Phosphorene / Graphene, the three-layer structure of blue Phosphorene / Graphene / blue Phosphorene, and the three-layer structure of Graphene / blue Phosphorene / Graphene have been compared. As shown in the Table, the total energy of the three-layer structure of Graphene / blue Phosphorene / Graphene is more negative, so this structure is more stable compared to other compounds studied.

Table 1. The total energy of the studied structures.

| Structure                                      | Total energy (eV) |
|------------------------------------------------|------------------|
| Single-layer Graphene                          | -324.533         |
| Single-layer Blue phosphorene                  | -416.845         |
| Two-layer Graphene/Blue phosphorene            | -2543.744        |
| Three-layer Blue phosphorene/Graphene/Blue phosphorene | -3792.77         |
| Three-layer Graphene/Blue phosphorene/Graphene | -3839.1          |

4. Conclusion
In this research, the single-layer structure of Graphene, the single-layer structure of Blue Phosphorene, the two-layer structure of Blue Phosphorene / Graphene, the three-layer structure of Blue Phosphorene / Graphene / Blue Phosphorene, and the three-layer structure of Graphene / Blue Phosphorene / Graphene have been investigated using SIESTA code in the framework of density functional theory and using the generalized gradient approximation. The results show that the Graphene sheet in all structures studied is in a non-bending status and the bond length of carbon-carbon in the two-layer and three-layer structures slightly increases. Blue Phosphorene sheet has a quasi-sheet structure in all compounds. The bending value of blue Phosphorene also slightly increases in the two-layer and three-layer structures, and the bond length of phosphorus-phosphorus is similar to that of single-layer structure. Investigating the band structure and density of states shows that single-layer structure of Graphene exhibits a quasi-metallic behavior, but the single-layer structure of blue Phosphorene exhibits semiconductor behavior. Two-layer and three-layer structures of Blue Phosphorene and Graphene have the metallic behavior. The results show that the total energy of three-layer structure of Graphene / Blue Phosphorene / Graphene is more negative than other structures studied, therefore, this structure is more stable compared to other compounds.

5. References:
[1] Petrov A G and Rotkin S V, 2004 Physical Review B 70 3.
[2] Novoselov K S, 2004 science 306 5696.
[3] Taghioskou M, 2009 Materials today 12 10.
[4] Shohany B G, Roknabadi M R and Kompany A, 2016 Physica E 84 146.
[5] Dresselhaus MS, 2009 materials today 12 21.
[6] Shohany B G, Roknabadi M R and Kompany A, 2016 Commun. Theor. Phys. 65 99.
[7] Jain A and McGaughey A J, 2015 Scientific reports 10 5.
[8] Shohany B G, Roknabadi M R and Kompany A, 2018 Computational Materials Science 144 280.
[9] Mak K F, 2010 Physical review letters 105 13.
[10] Hultgren R, Gingrich N and Warren B, 1935 Journal of Chemical Physics 3 6.
[11] Du Y, 2015 Scientific reports 5 8921.
[12] Popov I, Seifert G and Tománek D, 2012 Physical review letters 108 15.
[13] Li Y, 2018 Journal of Materials Chemistry A 7 2.
[14] Ding Y and Wang Y, 2015 J. Phys. Chem. C 119 10610.
[15] Kulish V, Malyi O, Persson C, Wu P, 2015 Physical Chemistry Chemical Physics 17 21.
[16] Soler J M, Artacho E, Gale J D, García A, Junquera J, Ordejón P, Sánchez-Portal D, 2002 J. Phys. Cond. Matt. 14 2745.
[17] Perdew J P, Burke K, Ernzerhof M, 1996 Phys. Rev. Lett. 77 3865.
[18] Li L, 2014 Nature Nanotechnology 9 372.
[19] Pollak E, Geng B, Jeon K J, Lucas I T, Richardson T J, Wang F and Kostecki R, 2010 Nano Lett. 10 3386.
[20] Hu T and Hong J, 2015 Journal of Applied Physics 118 054301.
[21] Ding Y and Wang Y, 2015 J. Phys. Chem. C 119 10610.