Density Functional Theory Study for Structure and Electronic Properties of Graphene and Boron Doped Graphene

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Abstract: For world's energy demand is to be met in the future, engineers and scientists must work on developing methods and materials for storing and producing power. Since the very discovery of this novel material (Graphene) it has piqued the interest of researchers due to its low cost, reduced weight, unique nano-surface patterns, electrical capabilities, magnetic, spintronics and wide variety of industrial applications. Density functional theory method was used to calculate the electronic and structural properties of graphene sheet nano material using the Quantum Espresso Codes and the Xcrysden was used to visualize the structure and was the optimized. The Energy band gap were found to be zero and 0.25 eV respectively for both pure and doped boron graphene sheet. While the formation energy is 0.84eV and 1.5eV for pure and doped graphene. Also for both the total density of state and projected density of state are estimated to be of 0.29 eV and 0.31eV respectively due to effect of doping. Therefore, doping graphene with Boron is an effective approach to open a band gap for carbon-based next generation devices.

Keywords: Graphene, Doping, Formation Energy, Energy Gap, Total Density of State (TDOS), Projected Density of State (PDOS)

1. Introduction

Engineers and scientists must focus on developing technologies and materials for storing and creating power if the world's energy demand is to be met in the future [1]. Researchers are interested in Graphene Sheets (GSs) because of its inexpensive cost, lighter weight, distinctive nano-surface patterns, electrical properties, and wide range of industrial uses, such as gas storage [2-4].

Graphene is a semi-metal or zero gap semiconductor structure. It has incredible electrical and mechanical properties, including: 230,000 cm^2 V^{-1} s^{-1}, high charge carriers (electrons and holes) and a mobility of 230,000 cm^2 V^{-1} s^{-1}. temperature=3000 W m^{-1} K^{-1}, thermal conductivity=3000 W m^{-1} K^{-1}, mechanical conductivity=3000 W m^{-1} K^{-1} with a huge surface area of 2,600 m^2 g^{-1},

stiffness=1 TPa [5]. Graphene is also a type of material with translucent capability of absorbing 2.3 percent of the optical light region. Graphene is a novel two-dimensional carbon allotrope with a monoatomic thick hexagonal (honeycomb) lattice structure with a carbon-carbon spacing of 1.42. In other words, it's a single graphite layer with sp2 properties. Carbon atoms that have been hybridized. Graphene is the fundamental component of all other materials.

Andre K. Geim and Konstantin S. Novoselov were awarded Nobel Prize for "groundbreaking experiments regarding the two-dimensional material graphene". They successfully synthesized free-standing graphene film for the first time by using an effective mechanical exfoliation method with a scotch tape and silicon substrate [6].

Pristine graphene in many potential applications, thead sorption of single atoms [7-14] and molecules [15-26] on the bare grapheme surface has been the subject for different theoretical and experimental investigations due to their promising applications in nanoscale electronics, bioelectronics, gas sensors, and hydrogen storage devices. Among these adsorbates, hydrogen has been considered as one of the most interesting and fantastic candidates. Recently, it has been experimentally reported, using the transmission electron microscopy, that a graphene sheet can be chemically converted into graphane through a hydrogenation process by reacting with atomic hydrogen [16]. This process, however, transforms the zero-gap semiconductor graphene into a wide-gap semiconductor (insulator) graphane. Theoretically reported studies [27, 28] using the density functional scheme, have revealed that the chair like configuration, with hydrogen atoms attached to the carbon atomsin alternative manner, is the energetically most preferable structure for graphane. Sofo*et al.* [28] Have found that the chairlike and boatlike conformers are semiconducting with 3.5 eV and 3.7 eV, respectively. As has been claimed in many literatures [29], future hydrogen-fuel technologies should make use of graphane as hydrogen storage due to its very high hydrogen density. Moreover, thisextremely thin material with a finite band gap is also likely to find its use in many technological and industrial applications. Overall, graphene surface could be successfully used as a base for creating new promising and useful materials, and it would be of quite interest to theoretically investigate the effects of incorporating various molecules into its structure for different technological and industrial applications.

Different compounds' adsorption on graphene has also been studied. Nakamura et al. [20] and Ito et al. [18] theoretically investigated the structural and electrical properties of oxygen-adsorbed graphene [18]. The adsorption of oxygen molecules onto graphene produces epoxy and ether group phases that are almost bistable, according to their findings. Furthermore, they found that the ether structure is the most energetically preferable for adsorption involving both sides of the sheet, whereas the one-side adsorption structure only appears as a meta-stable phase, with a finite energy gap at the K point that grows as the number of oxygen atoms increases in relation to the number of carbon atoms. The most important charge transfer Leenaerts et al. identified mechanisms for the adsorption of NH_3, NO, and NO_2 onto grapheme [19]. In comparison to the NO molecule, their theoretical results show that NO_2 adsorbates generate a comparatively high doping. Pinto *et al.* [22] used the local density approximation of the density functional theory to explore the chemisorption of the tetrafluoro tetracyanoquinodimethane (F4-TCNQ) molecule on virgin graphene using electronic characteristics.

The F4-TCNQ molecule was found to behave as a p-type dopant for graphene, transferring an estimated charge of 0.3 e/molecule from graphene's highest occupied molecular orbital (HOMO) to the molecule's lowest unoccupied molecular orbital (LUMO). Theory of density functionals. The adsorption of 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) and tetrathiafulvalene (TTF) results in hybridizations between the molecular levels and the graphene valence bands, according to the researchers.

This work will report the density functional theory approach computation on graphenenano sheet for both pure and doped boron. Properties such as energy gap, total density, project density and formation energy were calculated using pseudo potential as implemented in quantum espresso.

2. Computational Details

Ab initio electronic and molecular calculation was performed using quantum Espresso 6.8 code. The code uses plane wave basis set, pseudo potential and density functional theory principle. The name list, (& Control, & System and & Electrons) and Cards (& Atomic_Species, & Atomic_Positions and & K_Points) were selected and optimized. B3lyp exchange correlation was used through out the calculation. The graphene sheet structure was build using virtual nano lab molecular builder and exported as quantum Espresso file. The structure was relaxed and self-consistent-circle (scf) was also performed. The properties; band structure, total density of state, projected density of state and charge density were calculated. However, two atoms were selected from the sheet and replaced with Hydrogen. The sheet was then relaxed and similar properties were calculated and compared with that of pure graphene.

3. Result and Discussion

3.1. Optimize Structure

Geometry optimization using density functional theory (DFT) is done by moving the atoms of a molecule to get the most stable structure with the lowest possible ground state energy.

The graphene and graphene doped Boron structures were optimized and the final structures were shown in figure 1. The structure was build using virtual nanoLab molecular builder and then exported as quantum espresso file. Parameters such as cut off kinetic energy, cut off density and cell dimension were optimized. The optimize structure was viewed using Xcrysden molecular viewer. Similar process was employed and two boron atoms were replaced at the hexagonal ring of the parent benzene.

***Table 1.** Formation Energy.*

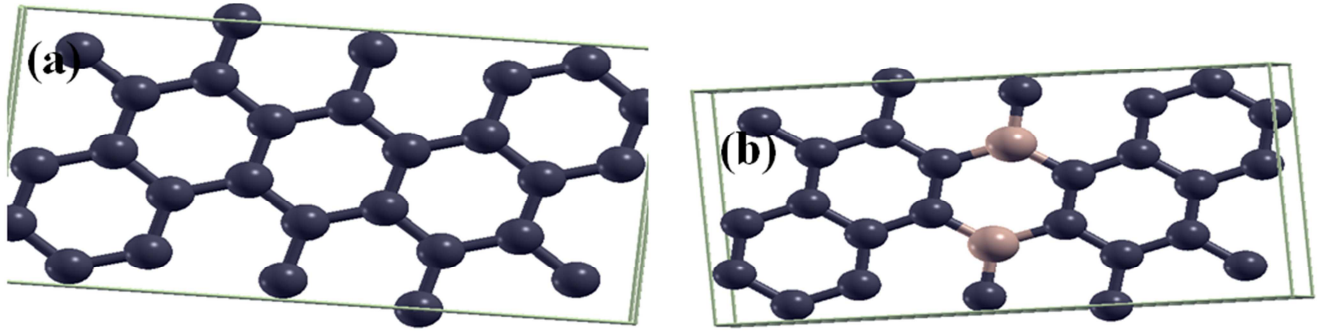| material	Energy (Ry)	Energy (eV)	Energy (free) (Ry)	Energy (eV)	Formation (eV)	ref
pure	-317.21190051	-4315.88934125	-10.81623451	-4382.00	0.84	[31-34,]
dope_B	-306.70105809	-4172.88199286	-5.71876845	-6197.39	1.5	[31, 33, 34]

Figure 1. Optimize structure (a) Pure Graphene (b) Boron doped Graphene.

The formation energy was computed using the following expression to determine the most stable structure [32].

$$E_f = E_{tot} - (M_c\mu_c + M_B\mu_B) \qquad (1)$$

Where E_f, $E_{tot}M_c$, M_B are Energy of formation, Total energy of defective, Number of carbon atom, Number of atom in Boron respectively and μ_C and μ_B are chemical potential of atoms that was substituted. The table 1 above shows the formation energies calculated for both pure and doped Boron in electron volt. It was observed that the formation energy of doped Boron is greater than that of pure graphene and it implies that pure graphene is more stable and hence the electron hole flows is more than that of the doped. The result obtained was in agreement with the literature [31-34].

3.2. Band Structure (BS)

One of the main reasons graphene is likely to be the material of choice for future nano devices is because of its high electron mobility.
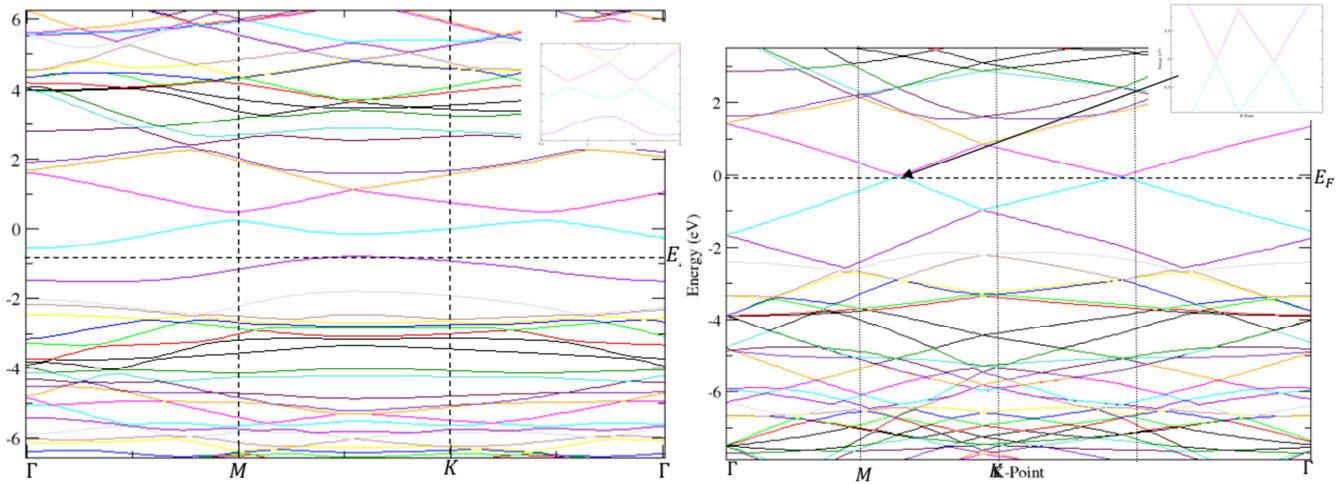

Figure 2. Band structure (a) Pure Graphene Sheet and (b) Doped Boron Graphene Sheet.

We can expect a lot of graphene applications for low gate voltage for electrons and holes in the device because of its enormous mobility. Furthermore, due of the carbon atoms, graphene has a high thermal conductivity, a high Young's modulus, and a low weight. Adsorption of atoms or molecules on graphene influences the electronic characteristics of graphene primarily through the orbitals, due to the two-dimensional nature of graphene. As a result, the graphene doping effect is extremely intriguing.

The band is linear near the point, as shown in figure 2(a), hence the effective mass of the electron in the bands is almost zero. Because the band structure around the point is comparable to the massless Dirac particle as predicted in the solution of the relativistic Dirac equation, this point is called a "Dirac point" and are very important especially in the physics of graphene, the Dirac point is crucial. Because of this property, electron mobility in graphene is extremely high. The theoretical mobility forecast is 1000 times greater than silicon, while the empirically observed mobility is at least 100 times greater [30].

When compared with the doped Boron figure 2(b) it was found that the doping increases the energy gap to about 0.25 eV and this can imply that the properties mentioned above are reduced to some reasonable quantities.
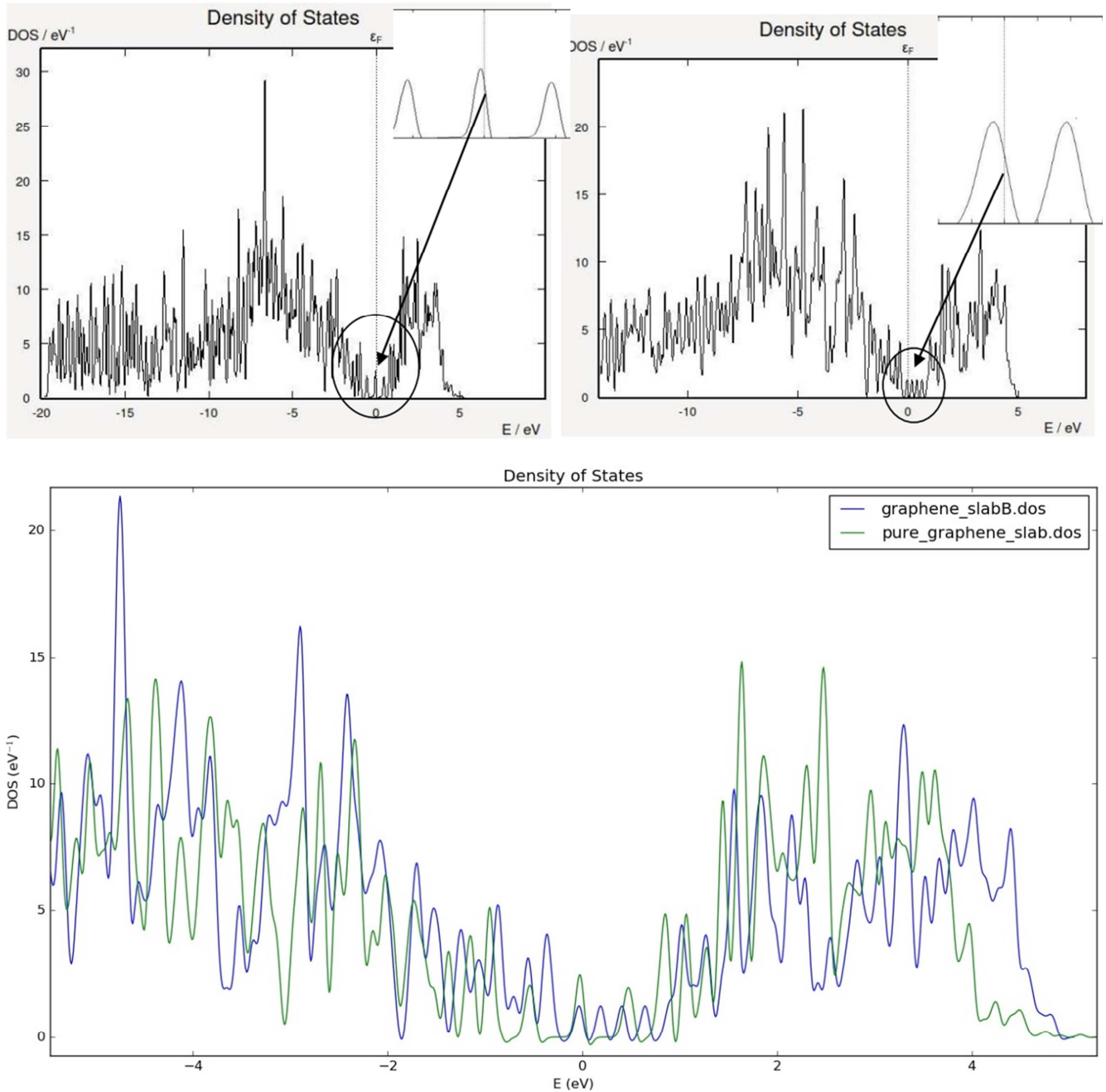
Figure 3. The Total Density of State of (a) Pure Graphene (b) Doped Boron.(c) Comparision between pure and doped Graphene. Bet.

3.3. Total Density of State (DOS)

The density of states (DOS) is the number of distinct states that electrons are allowed to occupy at a given energy level, i.e., the number of electron states per unit volume per unit energy. This function determines bulk properties of conductive substances such as specific heat, paramagnetic susceptibility, and other transport phenomena. DOS calculations can be used to calculate the general distribution of states as a function of energy in semi-conductors, as well as the spacing between energy bands [35]. As reported in the literature [5], Graphene is Sp2 state material. Figure 3 shows that there are a greater number of states and increase in intensity in the doped and then that of pure graphene this is due to the effect of doping and hence the state may likely shift completely to P.

However, the projected density of state account for the contribution of each with respect to the state. It was observed that introduction of doped to the Graphene sheet decreases the activity of the states in all the states which when compared with pure graphene the states are less as shown in figure 4.
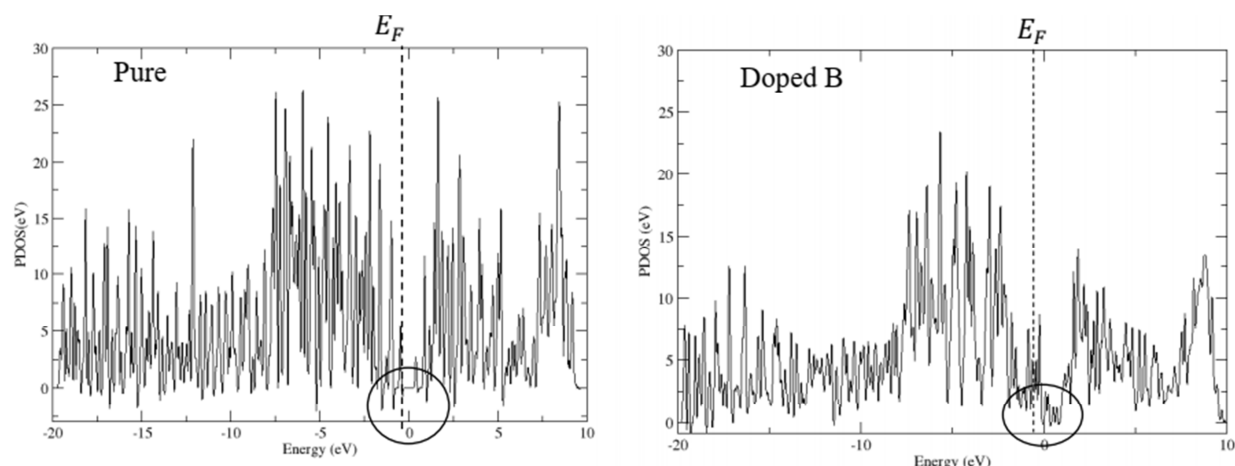
3.4. Projected Density of State (PDOS)

Figure 4. *The Projected Density of State for (a) Pure Graphene (b) Doped Boron.*

4. Conclusion

Density functional theory method as implement in Quantum Espresso was use to investigate the effect of doping on graphene sheet. The study accounts the optimization of parameters, energy gap, total density of state and projected density of state of both pure and boron doped graphene. It was found that pure graphene has zero energy gap which shows its metallic properties of the material. 0.25 eV was observed when the boron atom is introduces at some selected site. Also the doping shows less stability of the sheet and signals the semi conductive properties of the material as reported by literatures. However the work shows that small number of doped Boron can easily change the structural properties of the sheet which is contrary to the literature [31-34].

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