Special Conference Edition, April, 2022
http://dx.doi.org/10.4314/bajopas.v13i1.71S

Bayero Journal of Pure and Applied Sciences, 13(1): 471 - 477
ISSN 2006 – 6996

DFT CALCULATION FOR ADATOM ADSORPTION ON GRAPHENE MONOLAYER USING QUANTUM ESPRESSO CODE

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ABSTRACT
Doping has been shown to cause significant electronic structure perturbation, resulting in the formation of mind-gap states in semiconductors. Since the beginning of 2005, research in this area has literally exploded, resulting in an ever-increasing number of papers devoted to graphene and its unique properties. Quantum Espresso was used to investigate the structural and electronic properties of graphene nanosheet. It was observed that pure graphene produces zero energy gap while 0.773eV when the hydrogen atom was doped. Different patterns were observed in Total Density of State (TDOS) and Projected Density of State (PDOS) due to the doping effect.
Keywords: Band Structure, Density of State, Projected Density of State and Graphene,

INTRODUCTION

Research has shown that doping can strongly perturb the electronic structure, leading to the formation of mind-gap states in semiconductors since the beginning of 2005 advancement in this area has obviously exploded, producing an increasingly growing numbers of papers concerning graphene and its unique properties (Ahmed, Mansur & Sisa, 2022).

Graphene is a monolaer of carbon atoms, tightly bounded in a hexagonal honeycomb lattice. It is an allotrope of carbon (fig.1) in the form of a plane of sp2- bonded atoms with a molecular bond length of 0.142 nm (Wang, Ma & Sun, 2017).

. Despite the unique qualities of this material such as the thinnest known material but yet the strongest and a superb conductor of both heat and electricity it doesn't have a band gap (can't be switched off), researchers are now working on the rectification of this shortcoming.

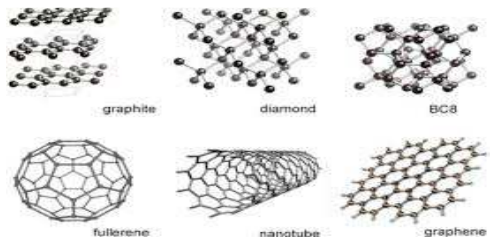


Figure 1. Allotrope of Carbon

The combination of graphene with other materials like metals, semiconductors, polymers and even biomaterials change the properties of graphene(J & M L, 2009) another process that can alter the properties of materials is doping (Thakur, Borah & Adhikary, 2018) e.g., hydrogen adsorption on graphene (Marsusi, Drummond & Verstraete, 2019) also (Wang et al. 2017) Have also shown the possibility of band opening with the adsorption of fluorination of graphene, with these motivations in mind we studied hydrogenation of graphene using density functional theory approach.

DFT (Hohenberg & Kohn, 1964; Kohn & Sham, 1965) is commonly employed in the study of electronic structure of semiconductors (John Chris &Van, 2013).

Functional such as the local density approximation (LDA) and the generalized gradient approximation (GGA) have been used in producing accurate results for many structural and energetic properties. Even though DFT have some limitations for the prediction of accurate vacancy formation energies in transition metals (Ivanovskaya, A.Zobelli,Teillet-Billy, Rougeau & Briddon, 2010).

Pristine graphene in many potential applications, the adsorption of single atoms (Jean-Paul & Francois, 2020; Chen, Feng & Li, 2011; Chan, Neaton & Cohen, 2008 ; Farjam & Rafii-Tabar, 2009 ; Han, Özylmaz, Zhang & Kim, 2007 ; Hao, Zhou, Duan,Wu & Gu, 2006 ; Li, Wang, Zhang, Lee & Dai, 2008 ; Mao, Yuan & Zhong, 2008 ; Medeiros, Mota, Mascarenhas & Castilho, 2010 ; Yang, 2009) and molecules (Duplock, Scheffler & Lindan, 2004; Elias, Nair, Mohiuddin, Morozov, Blake, Halsall, Ferrari, Boukhvalov, Katsnelson, Geim & Novoselov, 2009; Giannozzi, Car & Scoles, 2003; Ito, Nakamura & Natori, 2008; Leenaerts, Partoens & Peeters, 2008; Nakamura, Ito & Natori, 2008; Novoselov, Geim, Morozov, Jiang, Zhang, Dubonos & Firsov, 2004 ; Pinto, Jones, Goss, Briddon, 2009 ; Kengo & Akira, 2011; Yoshitaka, 2015; Yan,Wang & Wang, 2004; Monika & Anurag, 2021) on the bare graphene 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. Using transmission electron microscopy, it was recently demonstrated that a graphene sheet may be chemically transformed into graphane by a hydrogenation process by interacting with atomic hydrogen (Duplock *et al,* 2004). This process, however, transforms the zero-gap semiconductor graphene into a wide-gap semiconductor (insulator) graphane. Theoretically reported studies(Jiayu, Yuan & Giannozzi, 2009 ; Sachs, 1963) using the density functional scheme, have revealed that the chairlike configuration, with hydrogen atoms attached to the carbon atoms in alternative manner, is the energetically most preferable structure for graphane. With 3.5 eV and 3.7 eV, respectively (Monika & Anurag, 2021) discovered that the chairlike and boatlike conformers are semiconducting. Because of its extremely high hydrogen density, graphane should be used as hydrogen storage in future hydrogen-fuel technologies, according to various publications (Sachs, 1963). Furthermore, this ultra-thin material with a limited band gap is expected to be used in a wide range of technical and industrial applications. Overall, graphene surface might be effectively utilized as a platform for generating new promising and useful materials, and theoretically investigating the impacts of adding other molecules into its structure for various technical and commercial applications would be of great interest.

Different compounds' adsorption on graphene has also been studied (Nakamura et al. 2008) and (Ito *et al,* 2008) theoretically investigated the structural and electrical properties of oxygen-adsorbed graphene. The adsorption of oxygen molecules onto graphene produces epoxy and ether group phases that are almost bistable, according to their findings. They also discovered that for adsorption involving both sides of the sheet, the ether structure is the most energetically preferable, 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 essential charge transfer processes for the adsorption of NH3, NO, and NO2 onto graphene were found by (Leenaerts *et al,* 2009). Their theoretical calculations demonstrate that NO2 adsorbates create a disproportionately high amount of doping when compared to NO molecules. Pinto *et al, 2009* used the local density approximation of the density functional theory to explore the chemisorption of the tetrafluorotetracyanoquinodimethane(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.

understanding the working principle on how doped hydrogen works on the graphene sheet to enables it used as hydrogen storage tanks is very essential in order to improve the storing performance This work will report the DFT approach computation on graphene nano sheet for both pure and doped hydrogen. Properties such as energy gap, total density, project density and formation energy were calculated using pseudo potential as implemented in quantum espresso.

Computational Details

In this study we used the QUANTUM ESPRESSO CODEs 6.8 version, which is an integrated suite of Open-Source computer codes for electronic-structure calculations and materials modeling at the nanoscale. It is based on density-functional theory, plane waves, and pseudopotentials.. 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 total energies (scf) were also performed. The properties; band structure, total density of state, projected density of state and charge density were also calculated. However, two atoms were selected from the graphene sheet and replaced with Hydrogen. The sheet was then relaxed and similar properties were calculated and compared with that of pure graphene.

RESULTS AND DISCUSSION

Optimize structure

The optimized geometries and formation energies of graphene and graphene doped hydrogen structures were optimized within the plane wave pseudopotential DFT framework using the Quantum ESPRESSO CODE and the final structures were shown in figure 2 &3

Formation Energy

(a)

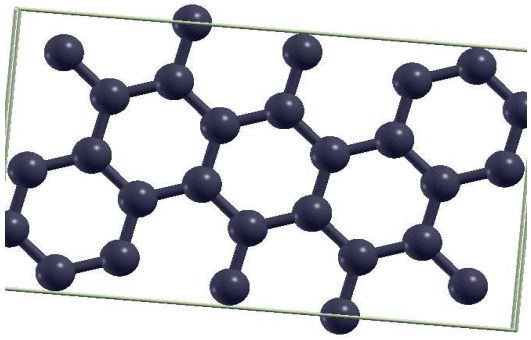


Figure 2. Pure Graphene

(b)

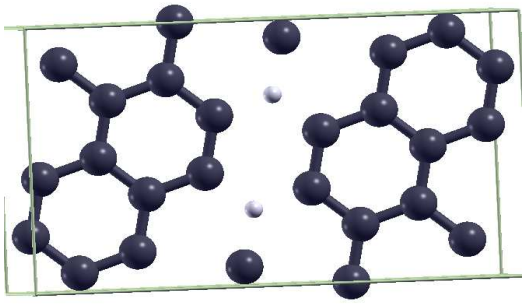


Figure 3. Hydrogen Doped Graphene

Material	Energy(Ry)	Energy(eV)	Energy(free)(Ry)	Energy(eV)	Formation (eV)	Ref
Pure Graphene	-317.212	-4315.889	-10.816	-147.162	0.32	Yoshitaka, 2015
Dope_H	-296.232	-4030.452	-1.015	-13.811	0.84	Yoshitaka, 2015

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

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

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 Hydrogen respectively and μ_C and $\mu_B$are chemical potential of atoms that was substituted. The table 1 shows the formation energies calculated for both pure and doped Hydrogen in electron volt. It was observed that the formation energy of doped Hydrogen 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 were in agreement with the literature (Ahmed, Mansur & Sisa, 2022).

Band Structure

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. 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 4(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 (Yoshitaka, 2015).

Studies had shown that the graphene band structure is very sensitive to deformations of any kind. As noted before, there is a clear evidence that upon partial hydrogenation the bandgap of graphene is likely to open. As can be seen in the Fig 4. The electronic band structure of graphene and hydrogen doped graphene structure were computed and it was found that the energy gap of pure graphene and Hydrogen doped graphene are zero eV and 0.773 eV respectively.

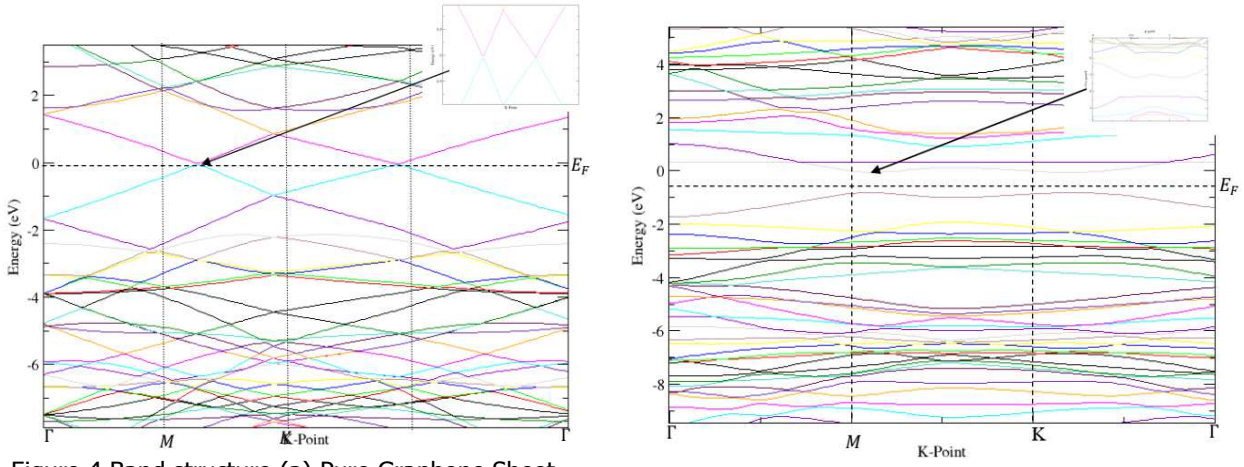
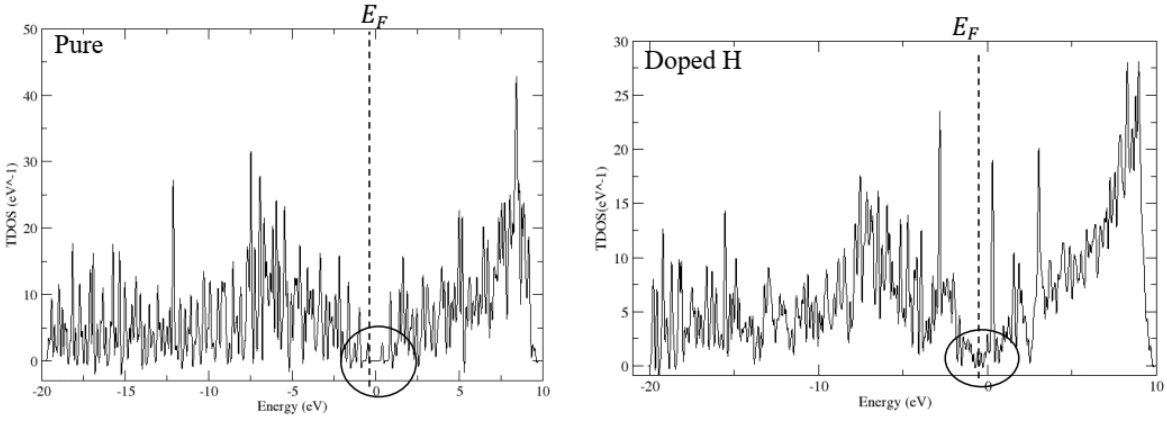


Figure 4 Band structure (a) Pure Graphene Sheet and (b) Doped Boron Graphene Sheet

Total Density of State

Figure 5. The Total Density of State of (a) Pure Graphene (b) Doped Hydrogen



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 (Yoshitaka,

2015). As reported in the literature (Jean-Paul & Francois, 2020) Graphene is Sp2 state material. Figure 4 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 6.

Projected Density of State

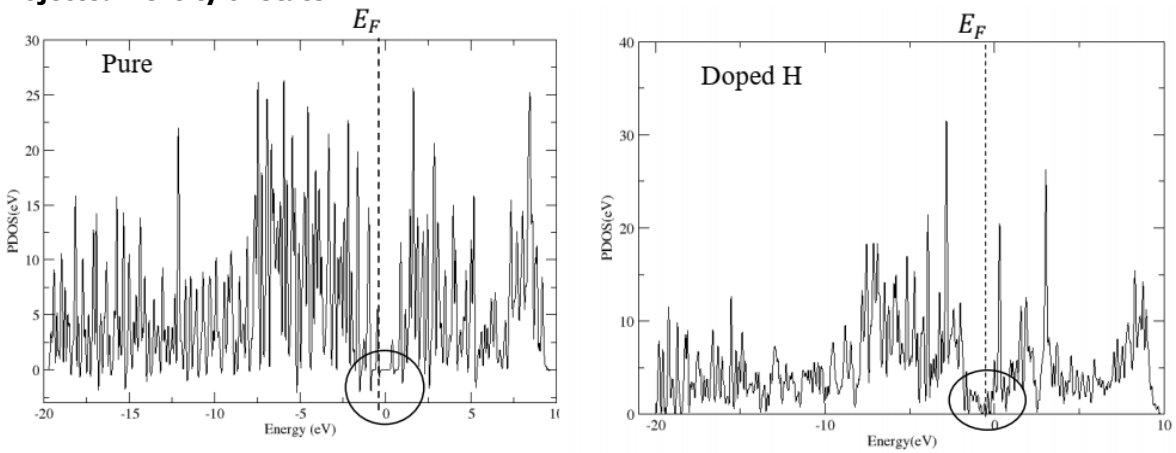


Figure 4. The Projected Density of State of (a) Pure Graphene (b) Doped Hydrogen

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. 0.773 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 semiconductive 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 (Jean-Paul & Francois, 2020).

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