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A QUANTUM ESPRESSO STUDY OF NITROGEN DOPED GRAPHENE USING DENSITY FUNCTIONAL THEORY

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ABSTRACT

Nitrogen doped graphene has attracted attention because of the abundance of nitrogen and high performances of graphene. Graphene is an allotrope of carbon that takes the shape of a plane of sp2-bonded atoms with a molecular bond length of 0.142 nm. Despite the material's unusual characteristics, such as being the thinnest known material but the strongest, and a brilliant conductor of both heat and electricity, it lacks a band gap.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 0.32 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: Graphene, Band Structure, Density of State, Projected Density of State

INTRODUCTION

Since Novoselov, and co-workers pioneered the manufacture of this remarkable two-dimensional substance, graphene has been the subject of intense research (Novoselov et al 2004; Geim and Novoselov, 2007 & Grigorieva et al 2005). Several attempts have recently beenmade to build graphene devices by doping their band gaps (Wang et al 2009; Martins et al 2005 & Ci et al 2010). According to research on doped graphene nanoribbons (Wang et al 2009; Martins et al 2005), n-type or p-type semiconducting graphene can be generated by doping with nitrogen (N) or boron (B). It has been demonstrated experimentally that when graphene is doped with N, the Dirac point in the band structure of graphene tends to shift below the E_F and an energy gap forms at the high-symmetric K-point (Wang *et al.,* 2009).

Ci et al. 2010 recently achieved the creation of a novel two-dimensional nanomaterial in which a few carbon atoms on a graphene sheet are replaced with an equal amount of B and N atoms. The concentration of dopant atoms can be controlled by keeping the B/N ratio constant. This unusual BNC nanomaterial was revealed to have a very narrow gap between its valence and conduction bands, making it semiconducting. Panchakarla et al. also reported the synthesis of BNC materials that are equivalent (Panchkarla et al 2009). The electrical properties of N- and B-doped graphene nanoribbons with armchair edges were also reported (Kaloni et al, 2011). N introduces an impurity level that is higher than the donor level, whereas B introduces an impurity level that is lower than the acceptor level. In contrast to single-walled carbon nanotubes, the impurity level in these systems is neither a donor nor an acceptor. The lowest empty orbital and the highest occupied orbital are used to calculate the donor and acceptor or levels. There are several theoretical ways to introduce gaps in graphene, including oxidation of Mono vacancies in graphene (Kaloni et al, 2011), graphene/boron nitride hetero bilayers (Kaloni et al, 2011 & Fan et al, 2011), F-intercalated graphene on SiC substrate, and bilayer graphene-BN hetero structures. Substitution carbon doping of boron nitride nanosheets, nanoribbons, and nanotubes has been demonstrated experimentally (WeiX et al, 2011). The sp2-hybridized BNC nano-structure, with an equal number of B and N atoms, has been shown to open a limited band gap in experiments (Ci et al. 2010).

Motivated by these recent experimental and theoretical findings, first-principles electronic structure calculations were used based on density functional theory to study the effect of B and N doping, as well as their co-doping, on the electronic characteristics of graphene systems. I this work we report structural ad electronic properties of pure and Nitrogen doped graphene nanosheet simulated from quantum espresso code.

DENSITY FUNCTIONAL THEORY

Density Functional Theory comes when the Schrödinger equations fails to solve the problem of ground state of some element and molecules

$$\hat{H}\Psi = E\,\Psi \qquad (1)$$

where

$$\hat{H} = -\frac{\hbar^2}{2m_e}\sum_i \nabla_i^2 - \sum_{i,I}\frac{Z_I e^2}{|r_i - R_I|} + \frac{1}{2}\sum_{(i\neq j)}\frac{e^2}{|r_i - r_j|} - \sum_I \frac{\hbar^2}{2M_I}\nabla_I^2 + \frac{1}{2}\sum_{I\neq J}\frac{Z_I Z_{J}e^2}{|R_I - R_J|} \qquad (2)$$

were, m_e and M_I represents the electron mass and nuclei mass respectively, r_i and R_I are positions of electron and nuclei. Z_I is charge of nuclei and e is charge of electron.

Born-Oppenheimer approximation is the early approximation used to solve the Hamiltonian by considering the fact that the nuclei can not move as much as electron due to its heavy mass. Thus, the kinetic energy of nuclei term was omitted from the Hamiltonian equation and the new Hamiltonian is given by

$$\hat{H} = -\frac{\hbar^2}{2m_e}\sum_i \nabla_i^2 + \frac{1}{2}\sum_{(i\neq j)}\frac{e^2}{|r_i - r_j|} + V_{R\alpha}^{ext}(r_i) \qquad (3)$$

Even after omitting the nuclei terms in old Hamiltonian, still the electrons are in theorder of 10^{23} making an exact solution impossible. Therefore, a new approximation is necessary, to solve the Hamiltonian whereby considering number of independent particles (electrons) or by other variables as input (Hohenberg and W. Kohn, 1964).

The DFT is a method in which the single-particle density is used to solve the many-body problem using the Kohn-Sham equations. P. Hohenberg and W. Kohn proposed this in 1964. The total energy is a density-dependent function. As a result, all of the system's features may be thought of as distinct functions of the ground state density. In comparison to other quantum chemical approaches, the number of degrees of freedom has been greatly reduced, allowing for faster computations. As a result, DFT has emerged as a key technique for calculating electronic structure in condensed matter, as well as for quantitative analyses of molecules and other finite systems. Much of today's methods for treating electrons in atoms, molecules, clusters, surfaces, adsorbates, and bulk are based on the classic work of W. Kohn and L. J. Shamin1965 and have become the basis of much of today's methods for treating electrons in atoms, molecules, clusters, surfaces, adsorbates, and bulk.

Based on the H-K theorems, Kohn-Sham proposed a new way to solving multiple electron systems [15]. In an external potential, total energy is functional of $V_{ext}(r)$ and can be

$$E[\rho(r)] = T[\rho(r)] + \int V_{ext}(r)d^3r + E_{ee}[\rho(r)] \qquad (4)$$

$$E_{ee}[\rho(r) = \iint \frac{\rho(r)\rho(r')}{|r-r'|} d^3rd^3r' + E_{xe}[\rho(r)] \qquad (5)$$

The first term is the kinetic energy $T[\rho(r)]$, the second term is electron-electron potential and the last term contributes for both classical and non-classical exchange behind the mean field theory. To solve the Kohn and Sham equations, it is assumed that for an interacting system describing the equation, there is a reference non interacting system with ground state density same as interacting system (Hohenberg and W. Kohn, 1964). The equation for the reference system can be written as

$$H_{eff}|\Psi_i\rangle = [-\sum_i \nabla_i^2 + V_{eff}[\rho(r)]|\Psi_i\rangle \qquad (6)$$

Then, the kinetic energy of this system is

$$T_{eff}[\rho(r)] = \sum_i n_i \epsilon_i - V_{eff}[\rho(r)] \qquad (7)$$

The new pseudo kinetic energy in the form of exchange correlation energy functional $E_{xe}[\rho(r)]$ can be written as

$$E_{xe}[\rho(r)] = T[\rho(r)] - T_{eff}[\rho(r)] + E_{xe}[\rho(r)] \qquad (8)$$

Inserting the new exchange correlation functional into total energy system and deriving the new total energy of the non interacting system which is in potential with respect to $\rho(r)$conserving the density,

$$\int \rho(r)dr = N \qquad (9)$$

where N is the total number of electrons. Solving the above 2 equations (6 and 7) we will obtain final Kohn-Sham equation. The one-electron Schrodinger like equation which is moving in a potential $V_{eff}$is

$$\epsilon_i\Psi_i(r) = [-\nabla^2 + V_{eff}[\rho(r)]]\Psi_i(r) \qquad (10)$$

and we get the final ground state energy given by

$$E_o = \sum_i n_i \epsilon_i \iint \frac{2\rho(r')}{\delta p(r')} d^3r' + E_{zc}[\rho(r)(11)$$

where E_{xc} is the exchange-correlation potential which is unknown? So, if we know the exact functional of E_{xc}, then, we know the exact solution of the many electrons system. No analytical solution has been made to solve the Kohn-Sham equations. So we need more approximations to solve such a difficult and complicated equations.The new approximations such as Local Density Approximation (LDA)

$$E_{XC}^{LSDA}[n^{\downarrow}, n^{\uparrow}] = \int d^3rn(r)\, \varepsilon_{XC}^{hom}(n^{\uparrow}(r), n^{\downarrow}(r)) \qquad (12)$$

$$\delta E_{XC}[n] = \sum_\sigma \int dr \left[\varepsilon_{XC}^{hom} + n\,\frac{de_{XC}^{hom}}{dn^\sigma}\right] dn(r,\sigma) \qquad (13)$$

and Generalised Gradient Approximations are implemented analytically and solve many difficult of DFT.

$$\delta E_{XC}[n] = \sum_\sigma \int dr \left[\varepsilon_{XC} + n\frac{d\varepsilon_{XC}}{dn^\sigma} + n\frac{d\varepsilon_{XC}}{d\nabla n^\sigma}\right] dn(r,\sigma) \qquad (14)$$

$$\delta E_{XC}[n] = \left[\varepsilon_{XC} + n\frac{d\varepsilon_{XC}}{dn^\sigma} + n\frac{d\varepsilon_{XC}}{d\nabla n^\sigma}\right]_{r,\sigma} \qquad (15)$$

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.

RESULT AND DISCUSSION

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 Nitrogen 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.

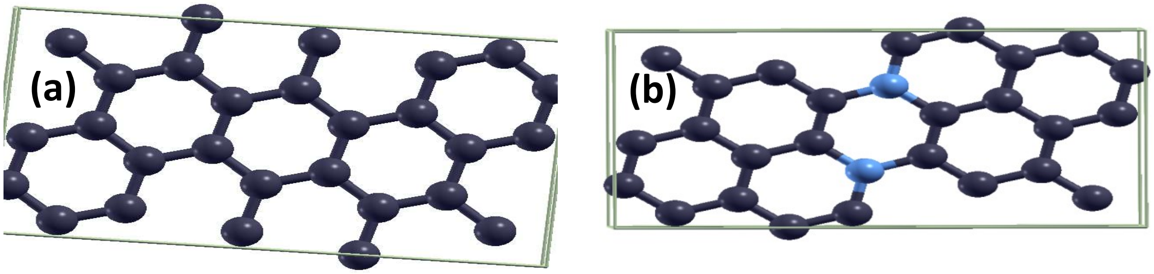

Figure 1: optimize structure (a) Pure Graphene (b) Nitrogen doped Graphene

Formation Energy

Material	Energy(Ry)	Energy(eV)	Energy(free)(Ry)	Energy(eV)	Formation (eV)
Pure	-317.21190051	-4315.88934125	-10.81623451	-147.16242095	0.84
Dope_N	-333.97678508	-4543.98729882	-839.098	-11416.5	0.32

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 atoms in Nitrogen 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 Nitrogen in electron volt. It was observed that the formation energy of doped Nitrogen 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 (Yoshitaka, 2015;Yan, 2004; Monika, 2021 & Jiayu, 2009)

Band Structure

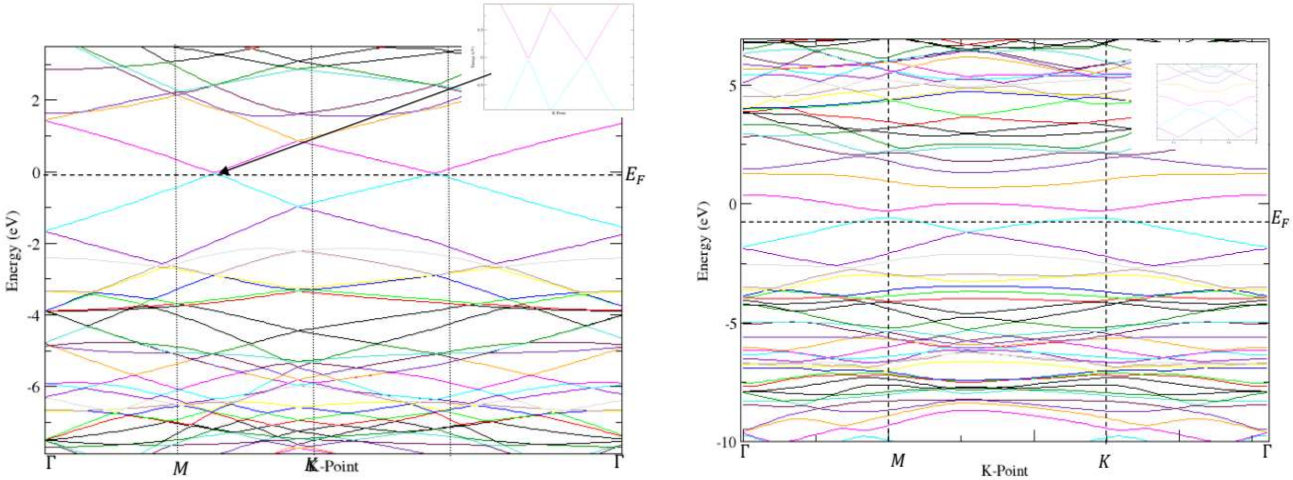

Figure 2: Band structure (a) Pure Graphene Sheet and (b) Doped Nitrogen Graphene Sheet

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 to 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 (Sachs, 1963).

When compared with the doped Nitrogen figure 2(b) it was found that the doping increases the energy gap to about 0.32 eV and this can imply that the properties mentioned above are reduced to some reasonable quantities.

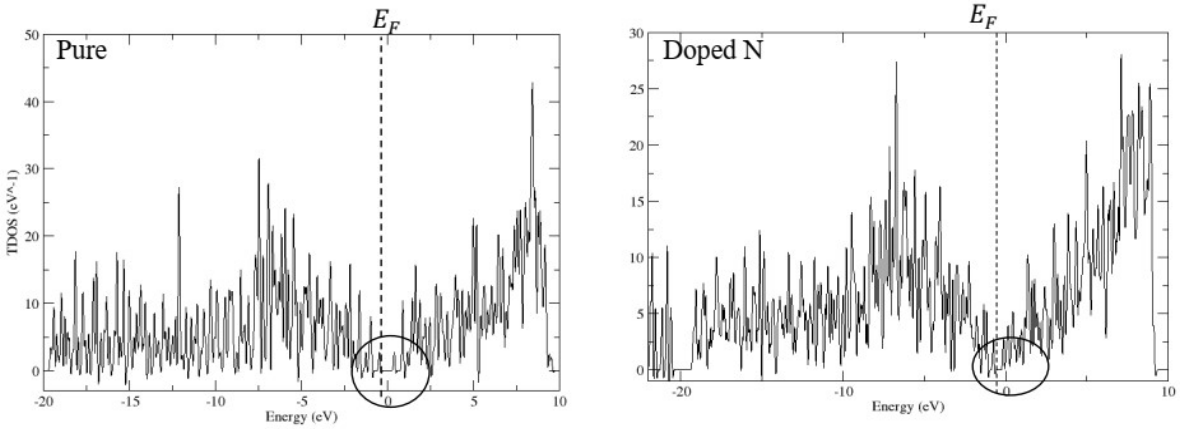

Figure 3: The Total Density of State of (a) Pure Graphene (b) Doped Nitrogen

Total Density of State

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 (Sachs, 1963). As reported in the literature (Martins et al 2005), 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.

Projected Density of State

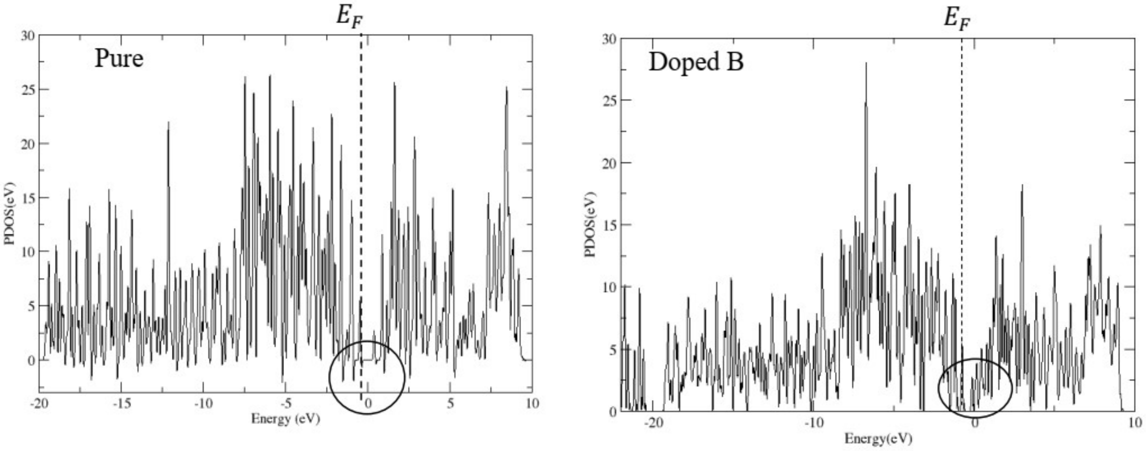

Figure 4: The Projected Density of State of (a) Pure Graphene (b) Doped Boron

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 Nitrogen doped graphene. It was found that pure graphene has zero energy gap which shows its metallic properties of the material. 0.32 eV was observed when the Nitrogen 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 can easily change the structural properties of the sheet which is contrary to the literature (Monika, 2021).

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