First-Principles Study of Structural, Electronic and Magnetic Properties of Lithium Doped Hexagonal Boron Nitride Monolayer (h-BN)

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K. Khanal[1], D. Acharya[2], N. Pantha[1, *] and N. P. Adhikari[1]

[1]Central Department of Physics, T. U., Kirtipur, Nepal

[2]Tri-Chandra Multiple Campus, Ghataghar, Kathamandu, Nepal

[*]Corresponding Email: mrnurapati@gmail.com

ABSTRACT

We examine the structural, electronic, and magnetic properties of pure and lithium doped hexagonal boron nitride (h-BN) monolayer using density functional theory (DFT) based on first-principles calculations. Li_B site is more conducive to doping than Li_N site, according to the values of formation energy, which are found to be 13.06 eV and 18.50 eV, respectively. Metallic behavior may be seen in the band structures for both the Li_B site and Li_N in nature. At both sites, the density of states (DOS) is asymmetric for spin-up and spin-down electrons. This suggests that systems with Li doping on h-BN are magnetic.

Keywords: Density functional theory, Hexagonal boron nitride, Lithium atom, Doping.

1. INTRODUCTION

Most people use hexagonal BN (h-BN), a polymorph (The four polymorphic forms of boron nitride, a III-V compound), are rhombohedral (r-BN), hexagonal (h-BN), cubic (c-BN), and wurzite (w-BN) [1], in this chemical world. At low and high temperatures (up to 900 °C, even in an oxidizing atmosphere), it functions well as a lubricant. When the electrical conductivity or chemical reactivity of graphite (an alternate lubricant) would be troublesome, h-BN lubricant is very helpful also at room temperature, hBN's thermal conductivity can reach 751 W/mK, making it a potential filler for materials used in thermal management and heat dissipation in electronic devices [2]. Hexagonal Boron Nitride (hBN) is a layered substance that resembles graphene in terms of structure. It is made up of alternating boron and nitrogen atoms organized in a sp2 bonded network within each layer. In graphene, the binding between the carbon atoms is 1.42 $Å$, whereas the bond between boron and nitrogen is 1.44 $Å$. In contrast to graphene, which has a band gap of zero, hBN has a significant band gap of 5.97 eV like MoS_2, which suggests that it has the potential to be a superior dielectric material. The lattice mismatch between the hBN and graphene is 1.7%. Interestingly, when utilized as a substrate, hBN widens the bandgap in

graphene [3–9]. The most stable kind of boron nitride is hexagonal boron nitride (h-BN). While each layer of BN is held together by weak van der wall forces in a honeycomb lattice, the boron and nitrogen atoms in h-BN are held together by covalent bonding. Because of its similar structural makeup to graphite, it can be referred to as white graphite [7, 8]. We can use h- BN in a variety of electrical domains by doping with various impurities [4].

For the analysis of the atom doped h-BN sheet, spin-polarized density functional theory (DFT) computations using generalized gradient approximation (GGA) was employed. The findings demonstrate that due to the low formation energy, Si impurity is preferred to dope at the boron site of h-BN sheet. The work also demonstrates that silicon atom doping at the B site (SiB) and the N site (SiN) reduces the band gap of h-BN sheets from 4.70 to 1.24 eV and to 0.84 eV, respectively.[10] Similar calculations were used in the investigation of the Be atom doped h- BN sheet structure utilizing VASP and density functional theory (DFT). The minimum band gap was found at the greatest impurity concentration after they altered the dopant concentration in their experiment [11]. Additionally, the first-principles approach can be used to predict magnetic behavior in systems with two doped Li,

Mg, and Na atoms apiece. In this instance, the monolayer boron nitride's (BN) structural, electrical, and magnetic properties were studied after being doped with a number of nonmagnetic metal atoms like Ga, Li, Mg, and Na [12].

Our team used calculations based on density functional theory (DFT) to examine the electronic and magnetic characteristics of the nickel-doped h-BN sheet system. It has been discovered that a location rich in boron is more suited for doping with low formation energy. The novel systems become magnetic after doping. They exhibit semi-conducting and half-metallic properties after Ni is doped at various places [13]. By doping h-BN with various impurities, it has been discovered that we can use it in a number of electronic applications. Lithium, the third element on the periodic table, is represented by the letter Li and has the electrical configuration [He] $2s^1$. It is an alkali metal that belongs to group I of the periodic table and is soft, white, and silvery. In our study, a Li atom is added to the 2D surface of the h-BN via a replacement method.

2. CALCULATION METHODS

The structural, magnetic, and electronic properties of pure h-BN sheet and Li doped h-BN sheet have been investigated using first principles calculations based on density functional theory (DFT) and the Quantum ESPRESSO code [14–19]. The electronic exchange and correction effect has been incorporated into our system using the generalized gradient approximation (GGA), which was created by the scientists Perdew, Burke, and Emzerhof (PBE) [20]. The complex effects of the mobility of the core (i.e. non-valence) electrons and ions were replaced by Ultrasoft Pseudopotentials (USPPs) from the official site of quantum-ESPRESSO. [18]

To prevent interaction between the layers of h-BN in the z-direction, a vacuum of 20 Å was used. The system was allowed to relax using the Broyden-Fletcher-Goldfarb-Shanno (BFGS) scheme until the total energy change was less than 10^{-4} Ry between two successive "scf" steps and each component of

force acting was less than 10^{-3} Ry/Bohrs in order to obtain the geometrically optimal system [21]. We employed a K-point mesh of 8×8×1 for the 4 × 4 h - BN supercell computations of the relaxation calculations. We have selected the charge density cutoff energy value of 450 Ry and the wave function cutoff energy value of 45 Ry using the convergence test. We calculated the lattice parameter for a 4×4 supercell using these numbers, and the result was 4.74 Å. Additionally, we employed the Marzarri-Vanderbilt (m–v) cold smearing technique with a narrow width of 0.001 Ry [22]. Moreover, the "david" diagonalization method was selected, with a mixing factor of 0.7 for self-consistency. In this section, we go over the h-BN sheets' geometrical structure, formation energy, band structure, density of states, and magnetic characteristics.

3. RESULTS AND DISCUSSION

In this section, we go over the h-BN sheets' geometrical structure, formation energy, band structure, density of states, and magnetic characteristics. The most stable form of boron nitride is hexagonal boron nitride, which has alternating boron and nitrogen atoms arranged in a honeycomb lattice within each layer. The layers are held together by weak van der waals forces, while the boron and nitrogen atoms are bound by strong covalent bonds (Fig. 1 and Fig. 2). The structural characteristics of Fig. 1 and Fig. 2 are shown in the table below.

3.1 Geometrical structure and formation energy
3.1.1 Pure h-BN

The most stable form of boron nitride is hexagonal boron nitride, which has alternating boron and nitrogen atoms arranged in a honeycomb lattice within each layer. The layers are held together by weak van der waals forces, while the boron and nitrogen atoms are bound by strong covalent bonds (Fig. 1 and Fig. 2) [4]. The structural characteristics of Fig. 1 and Fig. 2 are shown in the table below.

Table 1: Structural Parameters of Relaxed System

Primitive Cell (2 atoms)	Lattice Parameter	a = b = 2.51 Å, c = 20.02 Å
	B -N bond length	1.45 Å
4 × 4 supercell (32 atoms)	Lattice Parameters	a = b = 10.03 Å, c = 20 Å
	B – N bond lengths	1.44 Å
	N – B -N bond angles	120^0
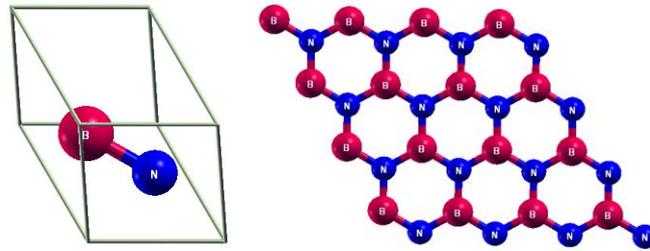
Fig. 1: Unit cell of h-BN Fig. 2: 4×4 supercell of h-BN (Red = Boron and Blue =Nitrogen).

3.1.2 Li-doped h-BN

Figure 3 depicts the optimum defective system after lithium is doped at either the boron site or the nitrogen site of h-BN. We can observe changes in the structural characteristics of the defective system as a result of the transfer of charges from impurity atoms after optimizing the Li_B and Li_N defects on h-BN sheets. Below are the tables for structural parameters for both defective systems:

Table 2: Structural Parameters for Li_B Defected System

Structural details of Li doped 4×4 h – BN sheet at B site	
N – Li – N bond angles	120^0
N – Li bond lengths	1.69 Å
Nearest neighbor B – N – B bond angles	126.86^0
Nearest neighbor B – N bond length	1.38 Å

Table 3: Structural Parameters for Li_N Defected System

Structural details of Li doped 4×4 h–BN sheet at N site	
B – Li – B bond angles	120^0
B – Li bond lengths	1.72 Å
Nearest neighbor N – B – N bond angles	137.14^0
Nearest neighbor B – N bond length	1.40 Å

The average bond length between Ni and Li is modified to 1.69 Å in the case of the Li_B defect (Fig. 3a). The h-BN layer has no effect on the vertical height of Li. Similar to this, the average bond length (B-Li) is adjusted to 1.72 Å in the case of the Li_N defect (Fig. 3b).

(a)   (b)
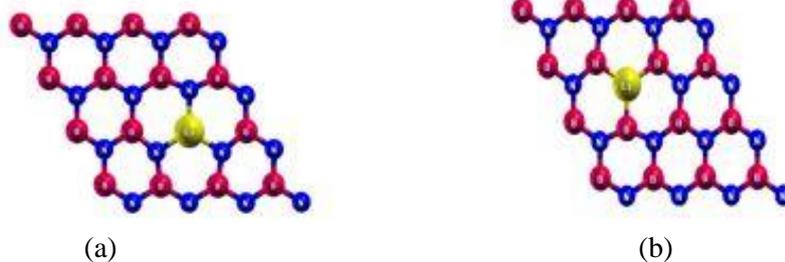
Fig. 2: Optimized structure after relaxation (a) when B is replaced by Li (Li_B) (b) when N is replaced by Li (Li_N).

We must compute the formation energies for both systems in order to verify the stability of the defective systems. The following is the formula to calculate defect formation energy (E_F):

$$E_F = (E_{Li} - E_p) - (E_1 - E_2)$$

Where E_1 is the energy of a single Li atom and E_2 is the energy of a single free B or N atom, E_{Li} is the total energy of the Li-doped h-BN sheet, E_p is the total energy of the pristine h-BN sheet. The energy numbers are accounted for per supercell because all computations were done in a 4×4 h-BN supercell. According to the calculations, the formation energies for the Li_B and Li_N defects are respectively 13.06 and 18.50 eV. This demonstrates that due to low formation energy, boron defects are simpler to produce than nitrogen defects.

3.2 Electronic and magnetic properties

3.2.1 Pure h-BN

We calculated the band structure for the 4 by 4 pristine h- BN sheet using spin-polarized calculations, as shown in figure 4. The conduction band and valance band are separated by 4.64 eV in this case. The obtained band gap value, which ranges from 3.0 eV to 7.5 eV, is in line with the earlier findings. After setting it to zero, the Fermi level is seen as a horizontal, dotted blue line. Furthermore, there is no magnetic moment for pure h-BN sheet because the PDOS plot for the electronic spin of electrons in figure 5 is symmetrically distributed.
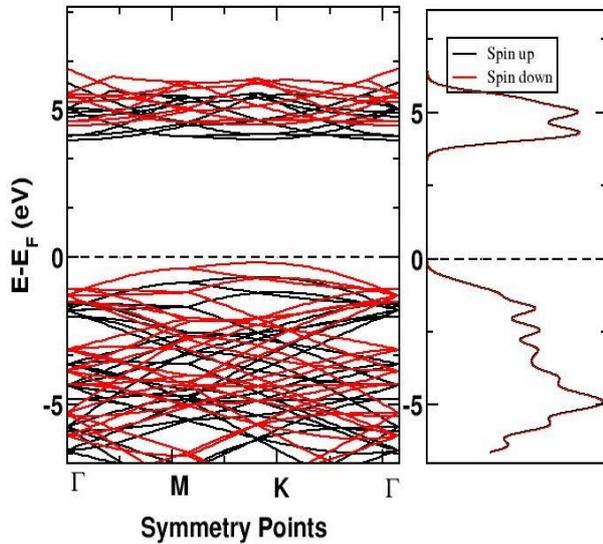
Fig. 3: Band structures and density of state for Pristine h-BN sheet.

The contributions of several electron orbitals close to the Fermi level are displayed in the (PDOS) density of states (Fig. 5). According to the illustration, the orbitals close to the Fermi level are made up of the 2s and 2p orbitals of the boron atom as well as the 2p orbital of the nitrogen atom.
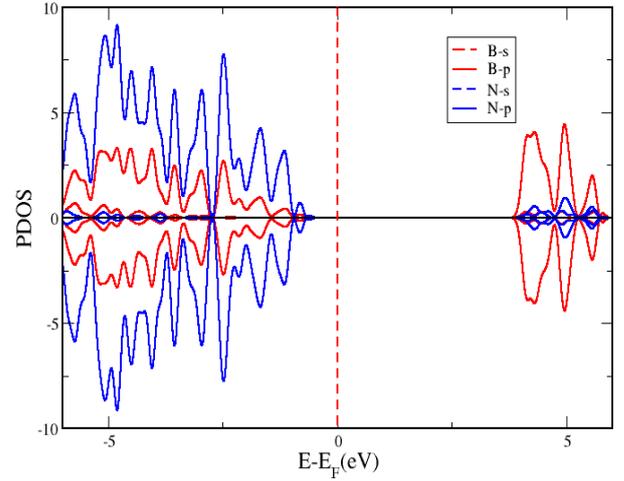
Fig. 4: Projected density of states (PDOS) of pristine h-BN.

3.2.2 Doping of h-BN by Li at B site (Li_B)

Figure 6 depicts the band structure of the h-BN system doped with lithium atoms. It demonstrates that the bands from the valence band and conduction band have both reached the Fermi level but have not yet passed it. The system is therefore partially metallic. In this instance, the Fermi energy is discovered to be -4.0272 eV. The DOS plot is also asymmetrical, indicating the presence of magnetic behavior. The total magnetization of the defective system is discovered to be 2.09 Bohr magnetron. as a result of redistribution of charge density in the system. According to the projected density of states (PDOS) calculations, the 2p orbitals of the nitrogen and boron atoms, as well as the 2s orbitals of the lithium atom, all contribute significantly to the region near the Fermi level.
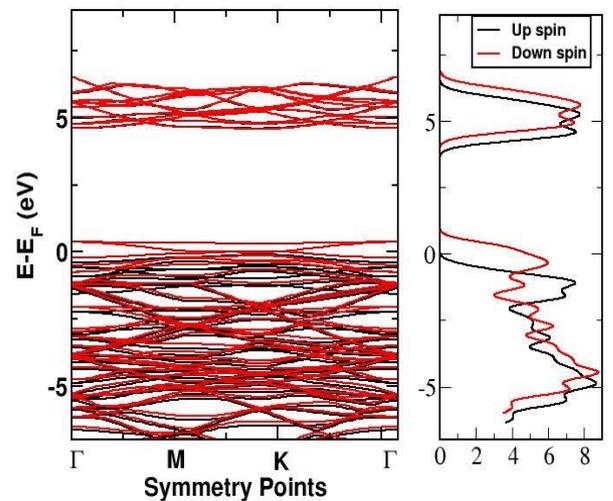
Fig. 5: Band structures and density of state for Li_B defected h-BN sheet.
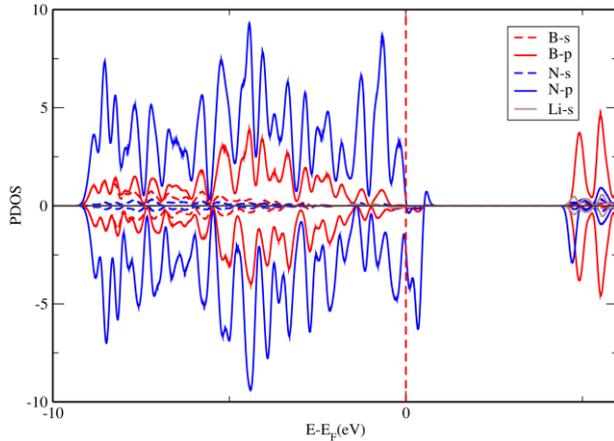
Fig. 6: Projected density of states (PDOS) for Li$_B$ defected h -BN system.
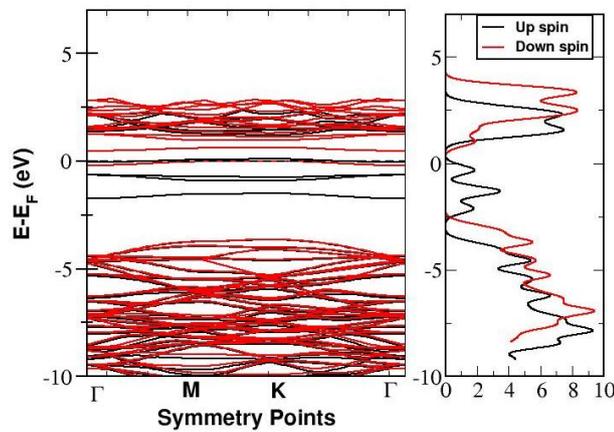
Fig. 7: Band structures and density of state for Li$_N$ defected h-BN sheet.
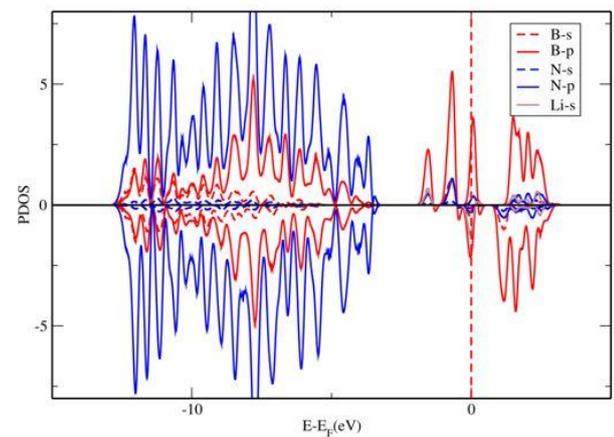
Fig. 8: Projected density of states (PDOS) for Li$_N$ defected h -BN.

3.2.3 Doping of h-BN by Li atom at N site (Li$_N$)

Fig. 8 depicts the band structure for a lithium atom doped at the nitrogen position of an h-BN sheet. It demonstrates that the bands from the conduction band are descending and crossing the Fermi level, giving the system its metallic nature. This is caused by the charge being transferred from the Li atom. In this instance, the Fermi energy is discovered to be -0.8143 eV. Additionally, the nature of the DOS is asymmetric, which suggests that the system is magnetic. Figure 11 shows the observed value of total magnetization to be 2.55 μ_B. Fig. 8's PDOS plot illustrates the importance of the 2p orbitals of the boron and nitrogen atoms, as well as the 2s orbitals of the lithium atom close to the Fermi level.

4. CONCLUSIONS

In conclusion, we have investigated the electronic and magnetic characteristics of Li doped h-BN sheet using density-functional theory methods of computation. Due to its low formation energy, the boron site is more appropriate for doping than the nitrogen site. Lithium atom doping results in Li$_N$'s bond length being longer than Li$_B$'s. Additionally, doped systems are magnetic whereas unadulterated h-BN is not. The band structures of the Li doped systems demonstrate that the metallic behavior of the Li$_B$ defected system is half that of the Li$_N$ defected system.

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