



# First Principle Investigation of Interlayer Interaction, Stacking Order and Layer Number Dependent Structural and Electronic Properties of Multi-Layered Boron Nitride (BN)

Research Article

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**Abstract.** Layered Boron-Nitride (BN) consist of covalent in-plane bonding with van der Waals (vdW) interlayer interactions between layers. In this study, stacking order, interlayer-interaction and layer number dependent structural and electronic properties of multi-layered BN were studied using Density Functional Theory (DFT). The lattice constant, equilibrium interlayer distance and energy band structures for different interlayer distances and the number of layers were computed. The calculated result indicates that interlayer interaction and stacking order in a multi-layer limit could impact on its structural and electronic properties. In addition to this, the calculated energy band structure for the increasing number of layers indicates that as the number of layers increases the bandgap decreases. However, the nature of the bandgap remains direct. Moreover, the Partial Density of State (PDOS) analysis reveals that many contributions of states in the vicinity of Fermi level derived from Boron  $p$ -orbital followed by nitrogen  $p$ -orbital. The findings are bases for experimentalist to control structural and electronic properties of layered materials by manipulating its stacking patterns and layer numbers.

**Keywords.** Density functional theory; Interlayer interaction; Stacking order; Layer number; Energy band structure

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## 1. Introduction

Graphene is the first layered 2D materials mechanically exfoliated from its bulk three Dimension (3D) structure or graphite. Due to its unique thermal, electrical and mechanical properties

graphene has received the attention of researchers in the last few years in the field of condensed matter physics and material sciences [19]. However, graphene is zero gap material (its conduction band minimum and valence band maximum point are overlapped at Dirac point). Thus gap-less nature restricts its application in semiconductor technology like transistor which needs an open band gap [11]. As a result of this, the search for new types of graphene-like layered 2D materials was extended to transition metal dichalcogenides with chemical formula  $\text{MX}_2$ , where M stands transition metal like molybdenum (Mo), tungsten (W), etc. and X stands chalcogen atoms like sulfur (S), Selenium (Se), etc. where discovered [22]. Especially in ML limit, these materials are similar to graphene but the later one is open band semiconductor [12]. Next to  $\text{MX}_2$  family another group of graphene like 2D materials so-called layered boron nitride (BN) was discovered more recently [3]. This new candidate uniquely featured by its exotic opto-electrical properties together with mechanical robustness, thermal stability, and chemical inertness [31]. The crystal structure of BN belong to different forms: hexagonal (h-BN), cubic (c-BN), zinc blend (z-BN), wurtzite (w-BN) and rhombohedra (r-BN) [8]. But, the most stable crystal structure is hexagonal BN [6]. ML h-BN with a direct bandgap (4.7eV) has been fabricated by mechanical exfoliation and chemical vapor deposition [2]. Even though it is similar in geometry to graphene but it has very different chemical and electronic properties contrary: to the black and highly conducting graphene BN is an insulator with a wide band-gap. In addition to this, layered BN has a lot of excellent material characteristics such as high specific surface area and high Young's modulus, and many potential applications in diverse areas such as photo electricity, catalysts, and transistors [27]. It has been reported that the electronic properties of these materials depends on the number of layers and stacking patterns [4] which would be a platform to tune their structural and electronic properties by manipulating the layer number.

It is a well-known fact that as the layer number increases the effect of Van der Waal interaction between these layers comes to exist [18, 21, 28, 32]. However, how structural and electronic properties can be being affected as the number of layers increases are a fresh problem and not yet investigated. In addition to this, the reported magnitude of band-gap and nature of gap(direct/indirect) on going from ML to BL limit varies from author to author [1, 5, 16, 30] which indicates that further investigation is required. As the layer number increases from single (mono) to multi(more than one)not only interlayer interaction between these layers but also how these layers stacked together is another considerable issue [16]. In the current study, we specifically focused on the stacking order and thickness(layer) dependence of the structural and electronic properties of multi-layered BN.

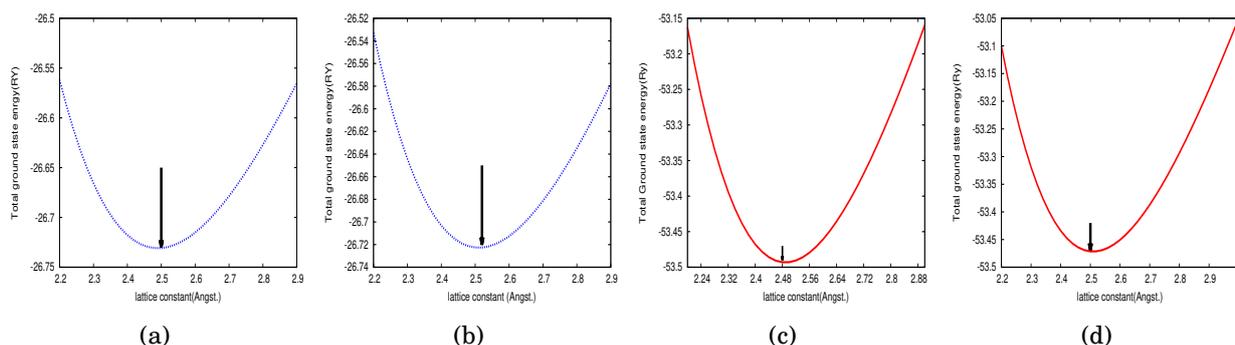
## 2. Computational Details

First-principles electronic structure calculations were performed based on Density Functional Theory (DFT) within Generalized Gradient Approximation (GGA). Ultra-soft Pseudopotentials (UPP) were used to deal with the interaction between valence electrons and the ionic cores [7, 9]. The plane-wave basis set with a certain cutoff energy of 60 Ry was used after performing the convergence test. The atomic positions were optimized until the Hellmann Feynman force acting on each atom becomes less than  $0.05 \text{ eV/\AA}$ . For  $n$  layered BN, where  $n$  is the number of layers and which is greater than two, Grimme DFT-D2 dispersion correction [10, 23–25] was applied to account for the long-range Vander Waals interactions between different layers of bilayers. Integrations over the Brillouin Zone (BZ) were sampled based on a Monk-horst

Pack 2D grid [17] for density calculation. The valance electrons considered in this simulation were Boron (B)  $2s^2 2p^1$  and Nitrogen (N)  $2s^2 2p^3$ . All input structures were visualized using XCrySDen.

### 3. Effect of Interlayer Interaction on Structural Properties of BL BN

After obtaining the converged values of plane wave cut-off energy and  $k$ -points in-plane lattice parameter  $a_x = a_y = a$  was computed for ML and bilayer h-BN. The equilibrium lattice constant (a) was obtained by calculating the total energy for different values of the lattice parameter using both Local Density Approximation (LDA) and Generalized Gradient Approximation (GGA). As shown in Table 1, the calculated lattice parameter for ML h-BN using LDA and GGA are 2.50 Å and 2.52 Å, respectively. While in BL limit the calculated lattice parameters are 2.48 and 2.50 Å, respectively. From these results, it can be concluded that: the calculated lattice parameter for BL (in the presence of interlayer interaction) is less than its counter ML by order of 0.02 Å in both approaches as shown in Figure 1(a-d), which indicates that in the presence of interlayer interaction cause the lattice parameter to shrink. The calculated result is closer to the experimentally observed lattice constant 2.511 Å [14].



**Figure 1.** The calculated equilibrium lattice constants of mono-layer (ML) and bi-layer BN (BL); (a) and (b), ML using LDA and GGA where as (c) and (d) BL using LDA and GGA respectively

On the other hand, the calculated bond length after structural relaxation was found to be 1.399 Å which is slightly less than the reported experimental result (1.455 Å) [26] for detail see Table 1.

**Table 1.** The calculated lattice constant using LDA and GGA DFT approximation for monolayer (ML) and bilayer (BL) boron nitride (BN)

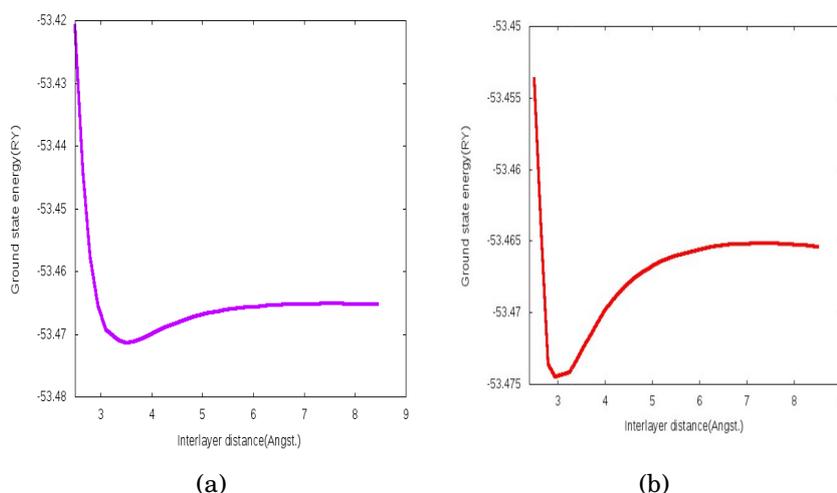
System	Calculated result (Å)	DFT approximation
ML BN	2.50	LDA
ML BN	2.52	GGA
BL BN	2.48	LDA
BL BN	2.50	GGA

## 4. Interlayer and Stacking Order Dependent Electronic Properties of Bilayer(BL) h-BN

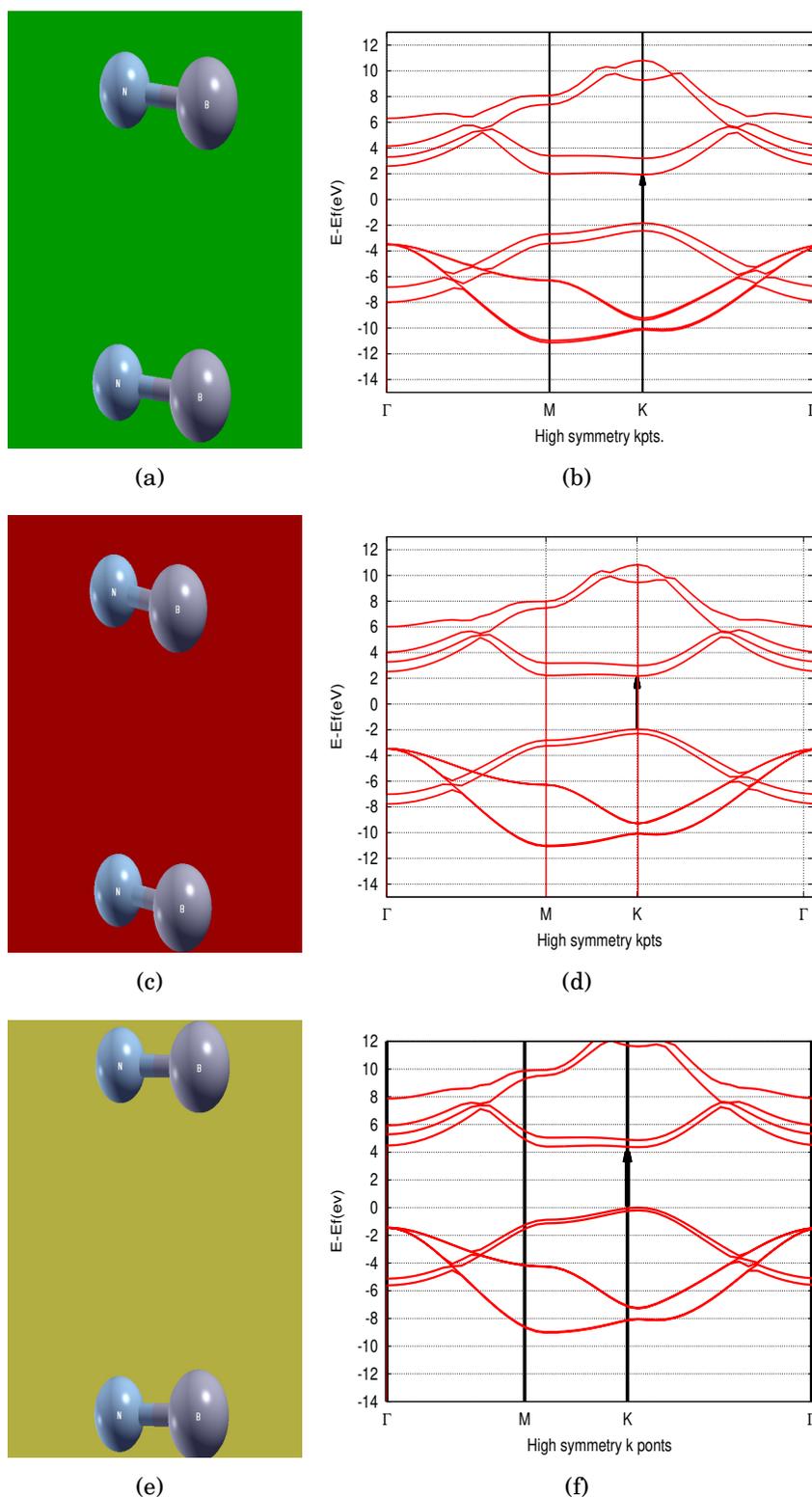
### 4.1 Stacking Order Dependent Interlayer Interaction and Band Structure in Bilayer h-BN

To find the equilibrium interlayer distance (the distance between two ML) of BL h-BN, the total ground state energy was calculated for different values of interlayer distance using AA and AB stacking. Here, AA stacking means that a geometry having Boron-atom in one layer is over Boron atom of the other layer as shown the left side of Figure 3 while AB stacking Boron atom of one layer is over Nitrogen atom in another layer.

The calculated equilibrium interlayer distance for AA stacking was 3.40 Å closer to experimental value 3.33 Å [33] but in AB stacking it was found to be 3.25 Å is slightly less than that of AA stacking for detail see Figure 2(a-b). The calculated energy band-gap for both cases are also different in magnitude order of 0.1 Å see Table 2. From our previous report, we have also reported such a kind of properties in bilayer MoS<sub>2</sub> [15]. Some of the authors argue that the nature of the band-gap becomes indirect when the layer number increases from ML to BL. Others also reporting such a large band-gap around 6 eV [20]. To resolve this issue the energy band structures were calculated for ML and BL BN. BL phase, the band structures are calculated not only at equilibrium interlayer distance but also for different interlayer distance (by varying the interlayer distance from its equilibrium point in the step of 0.3 Å). As shown from Table 2 and Figure 3(a-f) the nature of the band-gap remains direct (the conduction band minimum and valence band maximum points are located at the same high symmetry *k*-points) of h-BN but the band-gap suppresses by order of 1 eV on going from ML limit to BL see Table 2. It is also found that as the distance between the layers (interlayer distance) increases from equilibrium its point the band-gap also increases see Table 2. In other words, as interlayer distances increase the system becomes more likely insulators see Figure 3(a-f). Therefore, the electronic properties depend on stacking order and inter-layer distances since the band gaps are the decisive parameter to control material properties.



**Figure 2.** The calculated total energy versus equilibrium interlayer distance: (a) for AA stacking, (b) AB stacking



**Figure 3.** The input structures and band structures of bilayer h-BN for different values of interlayer distances: (a) and (b) input structure and the calculated band structure at equilibrium interlayer distance (3.25 Å), (c) and (d) input structure and the calculated band structure at interlayer distance 3.55 Å whereas (e) and (f) indicate input structure and the calculated band structure at interlayer distance 3.85 Å. Here energy zero levels indicate the Fermi level

**Table 2.** The calculated inter layer distance, and energy band gap for monolayer (ML) and bilayer (BL) h-boron nitride (BN)

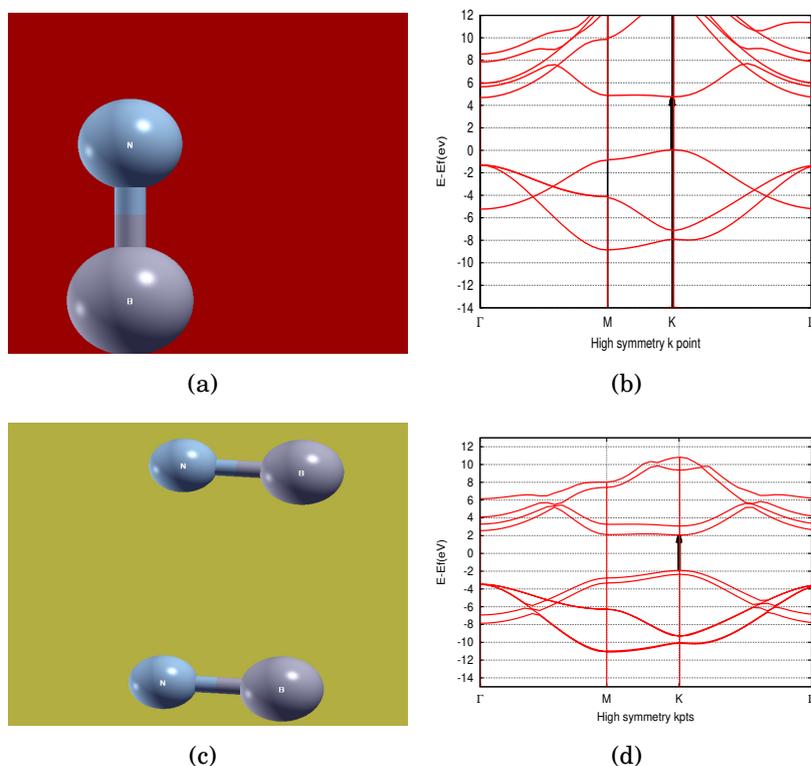
System	Interlayer distance (Å)	Stacking order	Calculated band gap(eV)	Nature of the gap	Method
ML BN	-	-	4.7	Direct	GGA
BL BN	3.25	AA	3.7	Direct	GGA
BL BN	3.50	AB	3.8	Direct	GGA
BL BN	3.85	AB	3.9	Direct	GGA

#### 4.2 Layer Number(n)dependent Band Structure in h-Boron Nitride (BN)

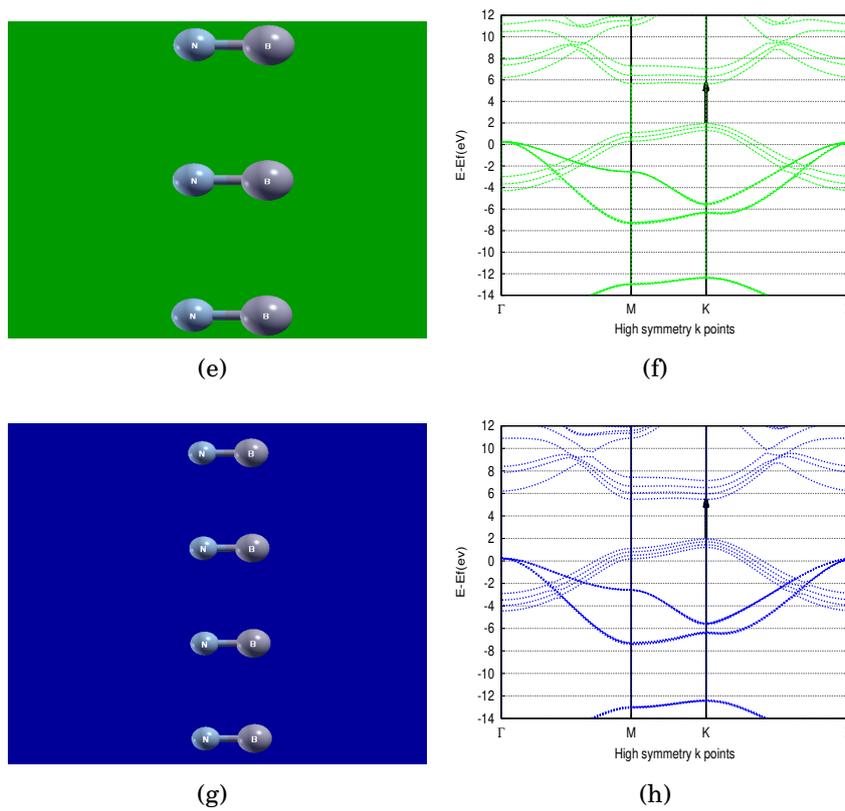
To understand how the band structure and energy band-gap depends on the number of layer, the energy band structures were calculated for  $n$ -BN by varying  $n$  from 1 to 4. As shown from Table 3 the bandgap decrease as the number of layers increase. However, the nature of the band-gap remains direct see Figure 4(a-h) and hence unlike MoS<sub>2</sub> with an indirect band-gap for multi-layer limit, multi-layered h-BN has more applicable than its counter ML limit due to the tunable energy band-gap.

**Table 3.** The calculated layer number ( $n$ ) dependent band gap in h-Boron nitride (BN)

System	Number of layer ( $n$ )	Calculated band gap (eV)	Nature of the gap
BN	1	4.7	Direct
BN	2	4	Direct
BN	3	3.7	Direct
BN	4.	3.5	Direct



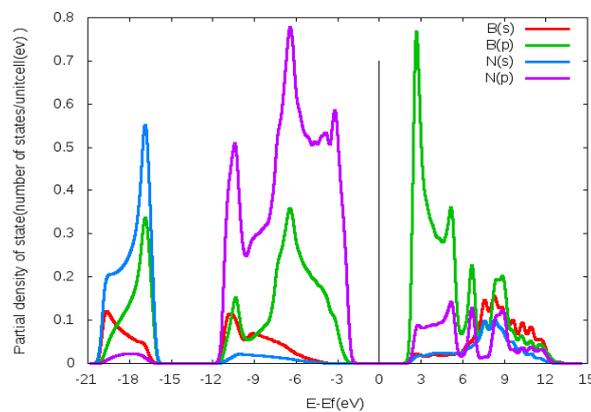
(Contd. Figure 4)



**Figure 4.** The input structures and energy band structures of n-BN: (a) and (b) input structure and the calculated band structure of ML( $n = 1$ ), (c) and (d) input structure and the calculated band structure for  $n = 2$ (bilayer), (e) and (f) input structure and the calculated band structure for  $n = 3$ . Whereas (g) and (h) are indicated input structure and calculated energy band structure for  $n = 4$  respectively

### 4.3 Density of States

To understand how the state is distributed and to this to get a clear understanding of which orbitals are more contributing to the electronic properties (state near the Fermi surface). The Partial Density of States (PDOS) was plotted. As shown in Figure 5, many contributions for the state in the vicinity of the Fermi level are derived from Nitrogen  $p$  orbital followed by Boron  $p$  orbital.



**Figure 5.** The calculated Partial Density of State (PDOS) in monolayer BN. Here energy zero indicates the Fermi level

## 5. Conclusion

The effect of interlayer interaction, stacking order and increasing layer number on the structural and electronic properties of multi-layered BN were studied using DFT. Based on this calculation it is concluded that: interlayer interaction and stacking patterns (how two layers stacked together) in multi-layer BN can affect its structural and electronic properties. As the interlayer distance increases from its equilibrium point the energy band gap decreases. But as the number of layers increases the band-gap decreases. The nature of the energy band-gap remains direct in both scenarios. The findings are critical to controlling the structural and electronic properties of layered materials by manipulating layer numbers and stacking patterns without application of external perturbation.

## Data Availability

The data used to support the findings of this study are available from the corresponding author upon request.

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## Competing Interests

The authors declare that they have no competing interests.

## Authors' Contributions

All the authors contributed significantly in writing this article. The authors read and approved the final manuscript.

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