Theoretical investigations of the structural and electronic properties of boron nitride clusters: DFT comparison of several basis sets

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Abstract. In this present study, Density Functional Theory (DFT) calculations were conducted to study the structural and electronic properties of (1,1), (2,2), (3,3), and (4,4) Boron Nitride (BN) systems. Geometry optimization calculations were carried out to find the stability of BN cluster models. The obtained structural geometries are consistent with that obtained in the previous reported results [1]. The total energies increase when the cluster sizes of BNs increase. For each cluster size of BN, the four total energy values obtained from B3LYP level of theory with employing the basis sets of 6-31++G, 6-31++G**, 6-311++G, and 6-311++G** are close to each. Moreover, our computations revealed that the gap energy values of HOMO-LUMOs in the BN cluster structures have been decreased by following its structure and dimensionality. The calculated HOMO-LUMO gaps are 5.99 eV - 7.68 eV in this study. For the diagrams of molecular electrostatic potential (MEP) surfaces, the regions around the N atoms at the center hold the highest electronegative potential, which can attract more electrons in the BN systems. With a Mulliken population analysis (MPA) scheme, all the boron atoms possess the positive charges, whereas the negative charges were found on the nitrogen atom in the BN systems.

1. Introduction

The chemical formula of boron nitride is BN, with the stoichiometric ratio of B: N = 1:1 [1-9]. It can exit in various configurations, such as diatomic molecule, nanotubes, hexagonal (h-BN), cubic (c-BN), and wurtzite-like (w-BN) crystals. Since the development of BN nanotube applications, various types of BN nanostructured materials have been studied with experimentally and theoretically [1-9]. This is because it may possess a high potential use in nanotechnology application nowadays. BNs not only provide the low dimensions in an isolated environment, it may also possess a large band or HOMO-LUMO gaps, respectively obtained from experimentally and theoretically [7, 8]. Also, the chemical bonding and electronic properties of BNs are well studies recently [2-4, 7, 8]. For example, the theoretical studies on the electronic structures of BN diatomic molecules, h-BN, c-BN, and w-BN crystals. The compositions of BN and carbon are chemical analogues to each other, but their physicochemical properties are very different [2-4, 7, 8]. Moreover, carbon can be metallic in the n-dimensionally structures (n = 1, 2, and 3), while BN is an insulator irrespective of its structure and dimensionality [8]. In 2018, Wolfum and his co-workers studied the influence of oxide glass compounds on the transformation of c-BN materials [9]. The results found that the transformation of
c-BN–glass composites fall in the range between 1100°C and 1575°C. In this present study, we report the structural and electronic properties of BN systems using a DFT method. The findings of geometrical and electronic structures are then given and discussed in the following sections.

2. Computational Methodology
As the most widely used quantum mechanics method, all DFT calculations in this present work were performed using Gaussian 09 software package. Four different cluster sizes of BN models were chosen as the host environment. Figure 1 illustrates the molecular structures of (1,1), (2,2), (3,3), and (4,4) BN cluster models. The geometries of BNs were fully optimized using B3LYP functional with exploiting several basis sets, i.e. 6-31++G, 6-31++G**, 6-311++G, and 6-311++G**. The optimized geometry structures of BN models were then used to calculate the local energy minima. In addition, the equilibrium structures of BNs were also used to determine the electronic parameters, i.e. Frontier molecular orbitals (FMOs), MEP surface, Mulliken atomic charges, and others.

![Figure 1](https://example.com/figure1.png)

**Figure 1.** The optimized structures of (a) (1,1), (b) (2,2), (c) (3,3), and (d) (4,4) BN clusters.

3. Results and Discussion
To examine further the applicability of B3LYP to BN cluster models, the four difference cluster sizes of BNs were chosen in this study by employing several basis sets (i.e. 6-31++G, 6-31++G**, 6-311G, and 6-3111G**). The equilibrium structures of BN clusters are obtained in this study. Following the increase of cluster sizes, the computed bond lengths and bond angles only change slightly. For example, the bond lengths of B-N atoms are determined to be in the range of 1.43Å - 1.46Å, which agrees well with the experiments and earlier reported results (1.45Å) [1]. While the bond-angles of B-N-B and N-B-N atoms fall in the range of 117° - 123°. This is due to all the computational calculations belongs to a small cluster model are carried out in the present work, whereas the experimental results obtained from the experiments are belongs to the bulk system.

To analyze the stability of BN systems, the results of total and Frontier molecular orbital energies are listed in Table 1. For each cluster size of BN model, we can find that the calculated minimum values of total energies obtained at B3LYP level with employing several basis sets (i.e. 6-31++G, 6-31++G**, 6-311++G, and 6-311++G**) are close to each other. Also, the computed total energies of
### Table 1. Computed total and FMO energies of BN models.

|        | (1,1)       | (2,2)       | (3,3)       | (4,4)       |
|--------|-------------|-------------|-------------|-------------|
| **Total Energy** |            |             |             |             |
| B3LYP/6-31++G      | -6602.31    | -6604.16    | -6603.95    | -6605.53    |
| B3LYP/6-311++G     | -17511.24   | -17515.91   | -17515.47   | -17519.40   |
| B3LYP/6-311++G**   | -32758.60   | -32767.10   | -32766.40   | -32773.51   |
| B3LYP/6-31++G      | -52344.40   | -52357.77   | -52356.76   | -52367.91   |
| **HOMO**          | -7.81       | -7.83       | -7.86       | -7.87       |
| B3LYP/6-31++G      | -7.86       | -7.86       | -7.86       | -7.86       |
| B3LYP/6-311++G     | -7.04       | -7.04       | -7.03       | -7.03       |
| B3LYP/6-311++G**   | -6.99       | -7.04       | -6.98       | -6.98       |
| B3LYP/6-31++G      | -7.03       | -7.04       | -6.98       | -6.98       |
| **LUMO**          | 0.18        | 0.18        | 0.18        | 0.19        |
| B3LYP/6-31++G      | 0.18        | 0.19        | 0.19        | 0.20        |
| B3LYP/6-311++G     | 0.45        | 0.45        | 0.44        | 0.44        |
| B3LYP/6-311++G**   | 0.45        | 0.45        | 0.44        | 0.44        |
| B3LYP/6-31++G      | 0.45        | 0.45        | 0.44        | 0.44        |
| **HOMO-LUMO Gap** | 7.63        | 7.65        | 7.76        | 7.68        |
| B3LYP/6-31++G      | 7.68        | 7.68        | 7.68        | 7.68        |
| B3LYP/6-311++G     | 7.07        | 7.07        | 7.07        | 7.07        |
| B3LYP/6-311++G**   | 7.07        | 7.07        | 7.07        | 7.07        |
| B3LYP/6-31++G      | 7.07        | 7.07        | 7.07        | 7.07        |

**Figure 2.** Electron density diagrams of HOMO for (a) (1,1), (b) (2,2), (c) (3,3), and (d) (4,4) BN systems with employing B3LYP/6-31++G** level of calculation.
BNs increase by following an increase the cluster sizes of BNs. In addition, a similar trend is also observed with the HOMO-LUMO gap. For each cluster size of BN cluster systems, the four energy gap values of HOMO-LUMO obtained from the B3LYP/6-31++G, B3LYP/6-31++G**, B3LYP/6-311++G, and B3LYP/6-311++G** levels of calculations are the same with each other (see Table 1). Overall, the energy gaps of HOMO-LUMOs are predicted to be in the range of 5.99 eV - 7.68 eV,
which agree well to those of earlier reports (i.e. 5 eV - 7 eV) [7, 8]. Furthermore, this computed HOMO-LUMO gap is the most important parameter for a chemical reactivity of BN cluster frameworks. For the optimized BN models as seen as in Figure 2, the highest occupied molecular orbital (HOMO) is mainly composed of 2p orbitals from the N atoms at the center and the edges, respectively. From this analysis; we observed that the electron distributions at the N-edges are stronger than that at the B-edges. While the distributed lowest unoccupied molecular orbital (LUMO) is only localized at the N-edges in the BN systems (see Figure 3). Also, the findings of HOMO and LUMO play an important role in the determination of ionization potential (IP) and the electron affinity (EA) of BNs. Hence, the above results can be concluded that the influences of four different basis sets are small on the calculated parameters of title clusters. The basis set of 6-31++G** is enough to determine the BN models.

In addition, the influences of basis sets on BNs show a very small effect on the results of MEP and MPA. Figure 4 presents the MEP diagrams of BN models using DFT/B3LYP/6-31++G** level of theory. The optimized result shows that the regions around H atoms at N-edges possess the most positive electrostatic potential, while the most electronegative is found in the region around N atoms at the center. These findings obtained are quite consistent with Mulliken atomic charge distributions in this present work. Based on the scheme of MPA, all the boron atoms have positive charge values, while the nitrogen atomic charges found to be negative, as shown in Figure 5. Moreover, the DFT computations revealed that the N atoms at the center hold the highest negative charge in the title clusters. The charges of N atoms increase by following the cluster sizes of BN models increase.

![Figure 4.](image)

**Figure 4.** MEP diagrams of BN models using DFT/B3LYP/6-31++G** level of theory.

![Figure 5.](image)

**Figure 5.** Optimized Mulliken atomic charge distributions of (a) (1,1), (b) (2,2), (c) (3,3), and (d) (4,4) BN structures using DFT/B3LYP/6-31++G** level of theory.

4. **Summary**

In this study, we have investigated the structural geometries and total energies to examine the stability of BN clusters by employing DFT/B3LYP level and several basis set (i.e. 6-31++G, 6-31++G**, 6-311++G, and 6-311++G**). According to the data, the total energies of each cluster sizes of BNs are close to each other, with employing B3LYP/6-31++G, B3LYP/6-31++G**, B3LYP/6-311++G, and B3LYP/6-311++G** levels of calculations. The computed gap values of HOMO-LUMO are found to be in good agreement with experiments. For BN cluster models, all the B atoms have positive charge values, and N atoms possess the negative charges, respectively.
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References
[1] Pease R S 1952 An X-ray study of boron nitride Acta Crsyt. 5, p. 356-361.
[2] Hou S Shen Z Zhang J Zhao X and Xue Z 2004 Ab initio calculations on the open end of single-walled BN nanotubes Chem. Phys. Lett. 393, p. 179-183.
[3] Xu Y N and Ching W Y 1993 Electronic, optical, and structural properties of some wurtzite crystals Phys Rev. B 48, 7, p. 4335-4351.
[4] Enyashin A N and Ivanovskii A L 2011 Graphene-like BN allotropes: Structural and electronic properties from DFTB calculations Chem. Phys. Lett. 509, p. 143-147.
[5] Kang C Cha E Patel M D Wu H F and Choi W 2016 Three-Dimensional Carbon Nanostructures for Advanced Lithium-Ion Batteries J. Carbon Res. 2, 4, p. 23-48.
[6] Esrafili M D 2017 N2O reduction over a fullerene-like boron nitride nanocage: A DFT study Phys. Lett. 381, p. 2085-2091.
[7] Li H Zhu S Zhang M Wu P Pang J Zhu W Jiang W and Li H 2017 Tuning the Chemical Hardness of Boron Nitride Nanosheets by Doping Carbon for Enhanced Adsorption Capacity ACS Omega 2, p. 5385-5394.
[8] Saeid O and Mozhdeh L D 2017 The effects of different Minnesota functionals on the sensitivity of boron nitride nanocluster to nitrogen dioxide Chem. Phys. Lett. 680, p. 22-27.
[9] Wolfrum A K Matthey B Michaelis A and Herrmann M 2018 On the Stability of c-BN-Reinforcing Particles in Ceramic Matrix Materials Materials 11, p. 255-271.