

EFFECTS OF VACANCY DEFECTS ON MONOLAYER HBN: A DENSITY FUNCTIONAL THEORY STUDY

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Received September 5, 2026. Revised September 25, 2026. Accepted September 30, 2026.

Abstract. Density functional theory (DFT) calculations were performed to investigate the structural and electronic properties of pristine monolayer hexagonal boron nitride (hBN) containing neutral B and N vacancies. Both types of vacancies preserve the overall planar configuration of the monolayer but induce distinct local structural reconstructions. The N vacancy slightly elongates the neighboring B–N bonds, whereas the B vacancy causes bond contraction accompanied by angular distortion. The calculated vacancy removal energies indicate that V_N@hBN is energetically more favorable than V_B@hBN. Notably, both the vacancies introduce localized in-gap states and induce spin-dependent electronic properties. In V_B@hBN, these states predominantly originate from the px- and py- orbitals of the three N atoms surrounding the vacancy, whereas those of V_N@hBN are primarily associated with the pz- orbitals. These findings demonstrate that vacancy defects can effectively modulate the electronic structure and spin properties of monolayer hBN.

Keywords: monolayer hBN, nitrogen vacancy, boron vacancy, electronic structure, projected density of states (PDOS), DFT.

1. Introduction

The rapid development of nanotechnology has stimulated considerable interest in two-dimensional (2D) materials because their reduced dimensionality gives rise to electronic, optical, and mechanical properties that differ markedly from those of their bulk counterparts. Among these materials, monolayer hexagonal boron nitride (hBN) is distinguished by its high thermal and chemical stability, mechanical strength, atomically flat surface, and wide band gap. These characteristics make hBN attractive for dielectric, optoelectronic, sensing, and nanoscale device applications [1]-[5]. However, its wide band gap limits the direct use of pristine hBN in active electronic applications.

Several approaches have been proposed to modify the electronic properties of monolayer hBN, including adsorption, chemical functionalization, substitutional doping,

and defect engineering [6]-[8]. Among them, vacancy engineering is particularly important because B and N vacancies may form during synthesis or be generated by irradiation and thermal treatment. Removal of B or N atoms disrupts the surrounding B–N bonding network and produces under-coordinated neighboring atoms, resulting in local structural reconstruction and vacancy-induced electronic states within the pristine band gap.

Previous theoretical studies have investigated the stability, migration, magnetism, and general electronic effects of vacancies in hBN. In investigating vacancy stability and migration, A. Zobelli *et al.* [6] showed that the nitrogen vacancy is more stable than the boron vacancy. Ryou *et al.* [7] realized that vacancies in hBN monolayer tend to form a triangular shape, with structures depending on the vacancy size. In addition, using first-principles calculations, Liu *et al.* indicated that vacancy defects can induce magnetism in hBN sheets [8]. Their PDOS analysis also indicated that the valence-band maximum (VBM) and conduction-band minimum (CBM) of pristine hBN sheets are predominantly derived from the pz- orbitals, whereas the px-, py- orbitals contribute mainly to lower-energy valence states. Similarly, Asif *et al.* reported that the VBM and CBM of pristine hBN originate primarily from the pz- orbitals of N and B atoms [9]. These studies provide an important reference for the orbital character of pristine hBN. However, they do not clarify how vacancies redistribute the electronic states between the atoms surrounding the defect and the remaining lattice. In the present work, these two atomic groups are analyzed separately for the systems containing neutral B and N vacancies, enabling direct identification and comparison of the atomic and orbital origins of the valence-band maximum (VBM), conduction-band minimum (CBM), and vacancy-induced states near the Fermi level. This comparison further reveals how the identity of the removed atom governs the local structural reconstruction and spin-dependent electronic response of monolayer hBN.

2. Computational method and model

All calculations were performed with the Vienna Ab Initio Simulation Package (VASP) [10]. The interaction between valence electrons and ionic cores was treated using projector augmented-wave potentials. Spin-polarized DFT calculations were used for the study of vacancy-containing systems. Geometry optimizations and electronic structure calculations for monolayers were performed using the PBE functional [11], [12]. The plane-wave kinetic-energy cutoff was set to 550 eV. Geometry optimizations were performed until the Hellmann-Feynman force acting on each atom was smaller than 0.001 eV/Å°. In all our calculations, the convergence for energy is set to 10^{-6} eV. The Brillouin zone is sampled by an $8 \times 8 \times 1$ *k*-point mesh within the Monkhorst–Pack scheme for relaxation. For the density of states (DOS), a denser *K*-point grid of $48 \times 48 \times 1$ was used. A vacuum thickness of 12 Å was chosen to avoid artificial interlayer interactions. A dipole correction normal to the layer was applied to reduce artifacts from periodic boundary conditions.

For bulk hBN, in order to account for the possible dispersion interactions existing between layers in bulk hBN, four density functionals (optPBE-vdW [13], optB88-vdW [14], optB86b-vdW [15], and DFT-D3-vdW [16]) were examined. The optimized optPBE-vdW bulk structure was chosen. hBN sheet was derived from the bulk structure optimized via the optPBE-vdW functional. Monolayer vacancy models were then generated by

removing a single B or N atom from a pristine 4×4 supercell (16 B and 16 N atoms). This approach establishes a periodic defect system with a finite concentration of 3.125% (6.25% relative to the specific sublattice) instead of an isolated vacancy in the dilute limit. To ensure consistent comparison, identical supercell constraints and computational settings were applied to both defect configurations.

The vacancy removal energy for each vacancy defect, E_{v_X} , was evaluated as

$$E_{V_X} = (E_{V_X@hBN} + E_X) - E_{hBN} \quad (1.1)$$

Here, $E_{V_X@hBN}$, E_{hBN} , and E_X are the total energies of the vacancy-containing system, pristine supercell hBN, and an isolated atom, respectively.

3. Result and discussion

3.1. Molecular structures and vacancy removal energies

Pristine bulk hBN in the AA' stacking configuration was optimized with the optPBE-vdW functional. The obtained result showed in Table 1.

Table 1. Some structural parameters of bulk hBN

Structural parameter	Calculated value (Å)	Experimental value (Å) [17]	Deviation (%)
a = b	2.517	2.504	0.52
r _{BN}	1.453	1.440	0.90

Here, the deviation between the calculated and experimental values was determined using the following expression:

$$Deviation(\%) = \left| \frac{calculated_value - experimental_value}{experimental_value} \right| \times 100\% \quad (1.2)$$

The lattice constants of pristine monolayer hBN were determined to be $a = b = 2.517$ Å. This value is in good agreement with the experimental value of 2.504 Å [17], corresponding to a deviation of only 0.52 %. Moreover, the calculated B–N bond length of 1.453 Å is also consistent with the experimental value of 1.440 Å. These minimal deviations (both below 1%) demonstrate the reliability of the chosen computational methodology.

Pristine monolayer hBN and hBN sheets containing a nitrogen vacancy or a boron vacancy are denoted as hBN, $V_N@hBN$, and $V_B@hBN$, respectively. Optimized hBN, $V_N@hBN$, and $V_B@hBN$ are shown in Figure 1.



Figure 1. Optimized structures of $V_N@hBN$ (a) and $V_B@hBN$ (b)

Nitrogen and boron atoms are represented by blue and pink spheres, respectively

Removing one N atom leaves three neighboring B atoms under-coordinated, as shown in Figure 1a. To elucidate the structural changes induced by the nitrogen vacancy, the selected B–N bond lengths, bond angles, and dihedral angle of pristine hBN were compared with those of the V_N@hBN system. The corresponding structural parameters are summarized in Table 2.

Table 2. Selected bond lengths and angles of pristine hBN and V_N@hBN

Structural parameter	V_N@hBN	hBN	Structural parameter	V_N@hBN	hBN
B1-N4 (Å)	1.465	1.453	B3-N8 (Å)	1.465	1.453
B2-N5 (Å)	1.465	1.453	B3-N9 (Å)	1.465	1.453
B2-N6 (Å)	1.465	1.453	(B1-N4-B10) angle (°)	120.02	120.00
B2-N7 (Å)	1.465	1.453	(N4-N5-B3-B2) angle (°)	0.00	0.00

Inspection of Table 2 indicates that representative B–N bonds near the N vacancy elongate by 0.012 Å, from 1.453 to 1.465 Å. The redistribution of forces and electronic density around the vacancy causes a slight adjustment of the remaining B–N bonds in the defect region. In contrast to the change in bond length, the angular distortion is negligible. The B1–N4–B10 angle increases only slightly from 120.00° to 120.02°, indicating that the hexagonal arrangement is largely preserved. Furthermore, the N4–N5–B3–B2 dihedral angle remains unchanged after structural optimization. Therefore, the defective monolayer retains its planar configuration.

Table 3. Selected bond lengths and angles of V_B@hBN

Structural parameter	V_B@hBN	Structural parameter	V_B@hBN
N1-B4 (Å)	1.453	N3-B8 (Å)	1.453
N1-B5 (Å)	1.453	N3-B9 (Å)	1.453
N2-B6 (Å)	1.453	(N1-B4-N10) angle (°)	120.00
N2-B7 (Å)	1.453	(B4-B5-N3-N2) angle (°)	0.00

For V_B@hBN (Figure 1b), analysis of structural parameters reported that representative B–N bonds around the B vacancy contract from 1.453 to 1.410 Å, a decrease of 0.043 Å (Table 3). Meanwhile, N–B–N angle increases from 120° to 123.68°, representing a change of 3.68°. This angular expansion indicates that the atoms surrounding the vacancy undergo an in-plane rearrangement to minimize the total energy of the defective structure. The B4–B5–N3–N2 dihedral angle remains 0.00°, confirming that the monolayer stays planar despite the stronger in-plane reconstruction.

Table 4. Calculated removal energy of the vacancies

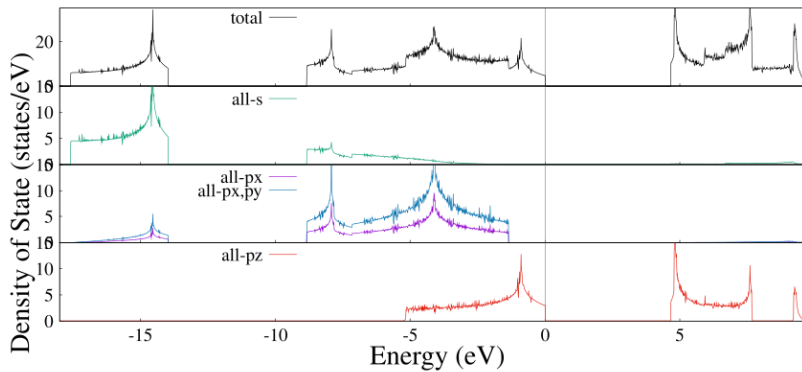
Structure	$E_{V_X@hBN}$ (eV)	E_X (eV)	E_{hBN} (eV)	E_{V_X} (eV)
V_N@hBN	-265.554	-3.124	-281.697	13.019
V_B@hBN	-264.989	-0.348	-281.697	16.360

In comparison with the undistorted pristine sheet, V_B@hBN causes substantial bond contraction and angular expansion, whereas V_N@hBN causes only slight bond elongation and negligible angular changes. Both defective systems remain planar. Furthermore, inspection of vacancy removal energy (Table 4) demonstrated that both defects show positive removal energies. Therefore, vacancy formation is energetically less favorable than in pristine hBN. Additionally, the vacancy removal energy of V_N@hBN is 3.341 eV lower than that of V_B@hBN. It indicated that the formation of an N vacancy is energetically more favorable than that of a B vacancy, which is in good agreement with the previous paper [6].

3.2. Electronic properties

The electronic properties of hBN, V_N@hBN, and V_B@hBN were investigated using the total density of states (DOS) and projected density of states (PDOS). For the defective systems, the three atoms directly surrounding the vacancy were treated separately from the remaining atoms to identify the localized vacancy states.

3.2.1. Electronic properties of pristine hBN

**Figure 2. DOS and PDOS of pristine 2D hBN**

The Fermi level is set to 0 eV

Pristine monolayer hBN exhibits a band gap of 4.654 eV, which is in agreement with previous literatures [9], [18]. This result confirms the insulating character of hBN. The PDOS shows that the s-orbitals contribute mainly to the deep valence region, approximately from -17 to -10 eV, and have negligible contributions near the band edges. Meanwhile, the px- and py- orbitals contribute primarily to the σ -bonding states within the valence band. In contrast, the pz- orbitals dominate the states close to both the VBM and CBM. These states correspond predominantly to the occupied π and unoccupied π^* bands formed by the out of plane pz- orbitals of B and N atoms. These findings are in good agreement with previous studies [7], [9].

3.2.2. Electronic properties of V_B@hBN

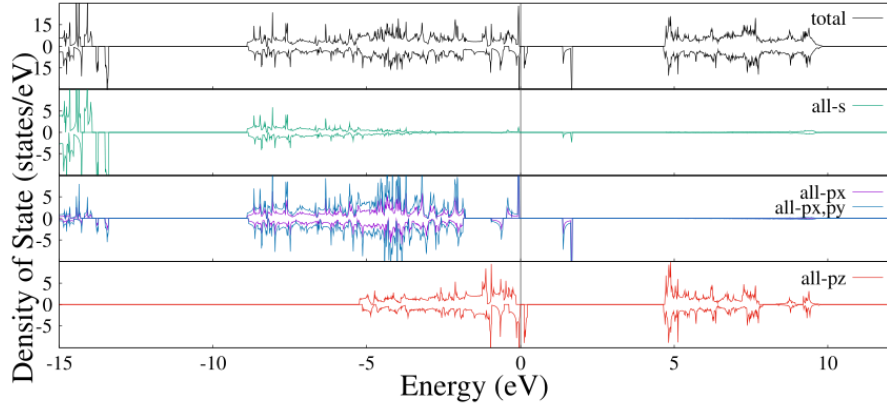


Figure 3. DOS and PDOS of V_B@hBN

Positive and negative values represent the spin-up and spin-down channels, respectively, and the Fermi level is set to 0 eV

Inspection of Figure 3 indicates that V_B@hBN shows a more pronounced asymmetry between the two spin channels. The calculated spin-up band gap is 4.683 eV, which is only 0.029 eV larger than that of pristine hBN (4.654 eV). Therefore, the B vacancy does not significantly alter electronic properties in this spin channel. In the spin-down channel, several defect-induced peaks emerge within the pristine bandgap at approximately 0.03 eV and 1.65 eV. Specifically, the narrow peak at 0.03 eV originates from out-of-plane pz-states, whereas the broader peaks at higher energy are predominantly driven by the in-plane px-, py- orbitals. These newly introduced states significantly narrow the effective electronic gap to 0.030 eV, clearly confirming a spin-polarized electronic structure. Therefore, removal of a B atom breaks three B–N bonds and leaves three under-coordinated N atoms. The unsaturated orbitals of these atoms form localized dangling-bond states within the pristine band gap. The unequal occupation of these localized states in the two spin channels produces states near the Fermi level and a spin-dependent narrowing of the electronic gap. To clarify their atomic and orbital origins, the contributions from the three N atoms surrounding the vacancy are analyzed separately from those of the remaining lattice (Figure 4).

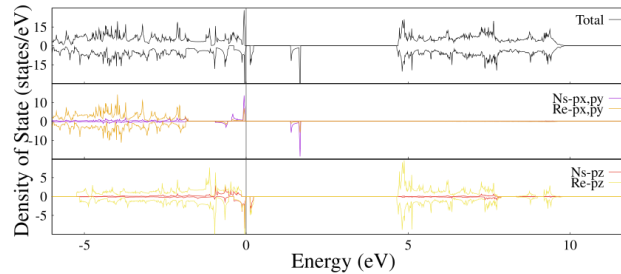


Figure 4. PDOS of V_B@hBN

The three N atoms directly surrounding the B vacancy are denoted by Ns, while Re represents all remaining atoms. The Fermi level is set to 0 eV

According to the PDOS, the narrow peak near the Fermi level (0.03 eV) possesses pz- character, whereas the broader peaks at 1.65 eV are dominated by the px-, py- orbitals of Ns. These in-plane states are directly associated with the dangling σ bonds. Meanwhile, the px- and py- orbitals of Re are mainly distributed throughout the deep valence band. Thus, the localized in-gap states are mainly associated with the px- and py-orbitals of the under-coordinated N atoms surrounding the vacancy.

3.2.3. Electronic properties of V_N@hBN

Removing an N atom from hBN breaks the spin degeneracy of pristine hBN (Fig. 5). The two spin channels exhibit markedly different band gaps: the spin-up channel has a gap of 1.707 eV, whereas the spin-down channel has a gap of 3.1432 eV. In comparison with pristine hBN, these values correspond to reductions of approximately 63.3% and 32.5%, respectively. The much smaller spin-up gap demonstrates that V_N@hBN strongly modifies the low-energy electronic excitations of hBN.

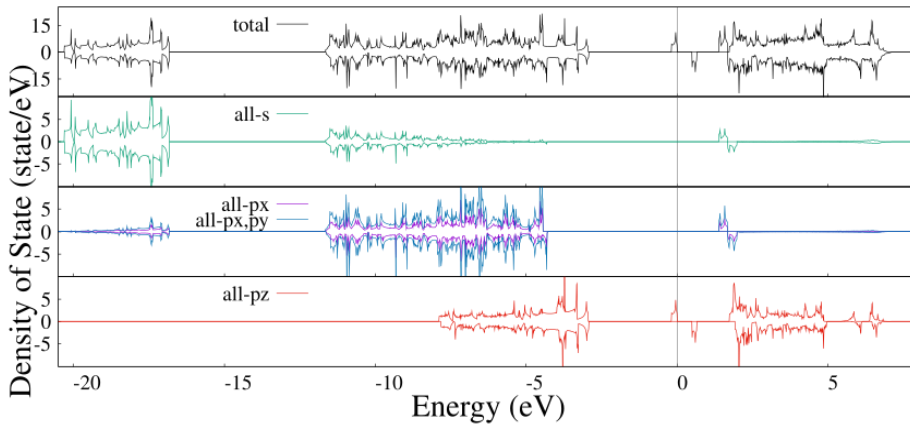


Figure 5. DOS and PDOS of V_N@hBN

The Fermi level is set to 0 eV

In the deep valence region, approximately from -20 to -17 eV, the DOS is dominated by the s-orbitals, with only weak contributions from the px- and py- orbitals and an almost negligible pz- component. These strongly bonding s-derived states lie far below the Fermi level and therefore have little direct influence on the near-gap electronic properties. Between approximately -13 and -8 eV, the increasing contributions from the px- and py- orbitals, together with the remaining s- component, reflect the sp^2 -hybridized states that form the in-plane B–N σ -bonding network. In the upper valence region, approximately from -8 to -3 eV, the contribution of the s-orbitals becomes very small, while the px-, py-, pz- components dominate. At the same time, the pz- contribution becomes increasingly pronounced toward the upper edge of the valence band. Therefore, the VBM is expected to possess substantial pz- character associated with the occupied π states of the hBN lattice. At higher conduction energies, approximately from 2 to 6 eV, the DOS is dominated by the pz-orbitals, with smaller contributions from the px-, py- and almost negligible contributions from s-orbitals. These states are mainly associated with the π^* conduction bands rather than strongly localized vacancy states.

To identify the atomic origins of the vacancy-induced states, the atoms were divided into two groups for the PDOS analysis: the three B atoms directly surrounding the N vacancy (Bs) and the remaining atoms (Re), as shown in Figure 6.

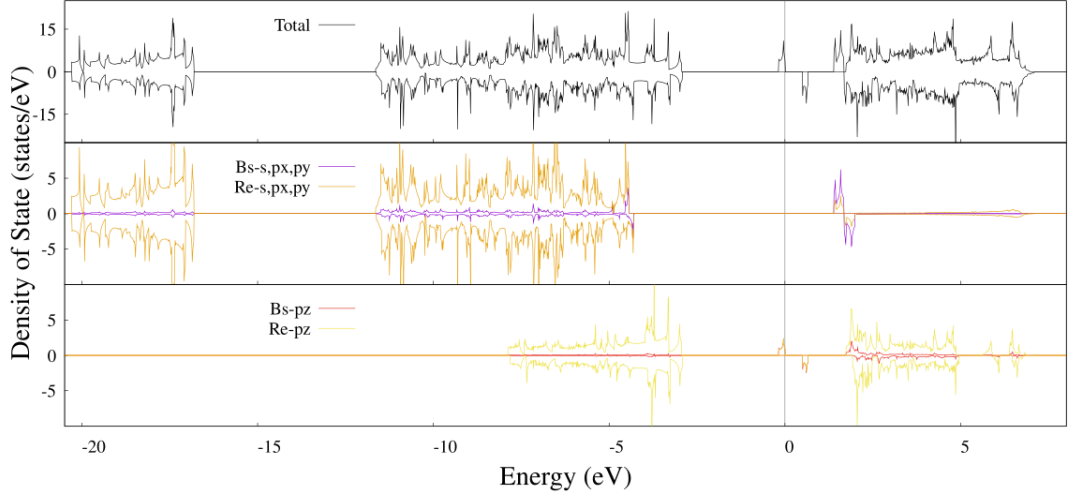


Figure 6. PDOS of $V_N@hBN$

The three B atoms adjacent to $V_N@hBN$ are denoted by Bs, whereas Re stands for the remaining atoms. The Fermi level is set to 0 eV

It can be seen that the upper valence-band states approaching the VBM are dominated by the pz- orbitals. This indicates that the VBM retains the extended π bonding character of the hBN lattice and is distributed mainly over atoms away from the vacancy. Furthermore, the pz-orbitals of Bs make the main contribution to the defect states at approximately 0.75 eV above the Fermi level. The appearance of the pz- states of the Bs inside the original band gap shows that removal of the N atom introduces new localized electronic levels between the VBM and CBM. Their position close to the Fermi level means that they are particularly important for the low-energy electronic and spin properties of $V_N@hBN$. Near the CBM, sharp peaks in the combined s-, px-, and py-orbitals of the Bs contributions occur at approximately 1.55 eV and 1.92 eV for spin up and spin down channels, respectively. At approximately the same energy, both Bs-pz and Re-pz components are also present. Therefore, the CBM cannot be assigned to a single orbital or atomic group. Instead, it has a mixed character.

4. Conclusions

In summary, DFT calculations reveal that neutral boron and nitrogen vacancies effectively modulate the electronic and spin properties of monolayer hBN. Although both defects maintain the planar monolayer configuration, they induce contrasting local structural reconstructions: a distinct bond contraction in $V_B@hBN$ versus a slight bond elongation in $V_N@hBN$. The fundamental differences among these systems lie in their defect-induced electronic structure. In $V_B@hBN$, the localized in-gap states originate

predominantly from the px- and py- orbitals of neighboring nitrogen atoms. Conversely, the in-gap states in V_N@hBN are dominated by pz- orbitals near the Fermi level, leading to a more pronounced bandgap modification and a stronger spin-splitting effect compared to the B-vacancy system.

Note for contributor:

- Short bio: Tran Thi Thoa and Hoang Van Hung are lecturers at Hanoi National University of Education, Vietnam. Nguyen Phuong Linh and Nguyen Thi Khanh Linh are chemistry alumni of Hanoi National University of Education, Vietnam. Vu Thi Huong Giang is a researcher.

- Author's contributions: Tran Thi Thoa: supervision & editing; Nguyen Phuong Linh: conceptualization, data analysis; Nguyen Thi Khanh Linh: methodology, data analysis; Vu Thi Huong Giang: writing; Hoang Van Hung: review.

Conflict of interest: The authors declare no conflict of interest.

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