



Original Article

Defect-Driven Tunneling Mechanisms in Graphene/hBN Van der Waals Heterostructures

Anurup Nayan¹, Dr. Deepak Kumar²

¹Research Scholar, University Department of Physics, Lalit Narayan Mithila University, Darbhanga

²Assistant Professor, University Department of Physics, Lalit Narayan Mithila University, Darbhanga

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Correspondence Address:

Anurup Nayan
Research Scholar, University
Department of Physics, Lalit Narayan
Mithila University, Darbhanga
Email: anurupnayan@gmail.com



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Abstract

Graphene, a single layer of carbon atoms, boasts remarkable electrical conductivity despite its one-atom thickness. When stacked with hexagonal boron nitride (hBN), an insulating two-dimensional material, it forms van der Waals (vdW) heterostructures, ideal for compact, high-efficiency tunnel transistors. This study investigates how defects in the hBN layer facilitate electron tunneling, a quantum process critical for transistor operation. Using density functional theory (DFT) implemented in Quantum ESPRESSO, we modeled five defect types in a graphene/hBN/graphene heterostructure: nitrogen vacancies, boron vacancies, carbon substitutions, oxygen substitutions, and nitrogen antisites. Our simulations show that nitrogen vacancies, with a formation energy of 2.05 eV, introduce localized electronic states at 0.42 eV above the hBN valence band, significantly enhancing tunneling probability. These states, positioned near the graphene Fermi level, act as efficient pathways for single-electron tunneling, as quantified by the Wentzel-Kramers-Brillouin approximation. Other defects, such as oxygen substitutions, produce deeper bandgap states, reducing their tunneling efficiency. The low formation energy of nitrogen vacancies suggests they are prevalent in synthesized hBN, making them practical targets for defect engineering. These findings offer valuable insights for optimizing graphene-based tunnel transistors, enabling the design of faster, more efficient nanoelectronic devices.

Keywords: Graphene, Hexagonal Boron Nitride, Van der Waals Heterostructures, Defect States, Tunneling, Density Functional Theory, Quantum ESPRESSO

Introduction

Graphene, a single layer of carbon atoms arranged in a honeycomb lattice, has captivated researchers since its isolation in 2004 [1]. Its exceptional electrical conductivity, mechanical strength, and flexibility make it a cornerstone of nanotechnology [2]. When combined with hexagonal boron nitride (hBN), a two-dimensional (2D) insulator with a similar lattice structure, graphene forms van der Waals (vdW) heterostructures, stacked layers bound by weak intermolecular forces [3]. These heterostructures are promising for next-generation electronic devices, particularly tunnel transistors, which leverage quantum tunneling to control current with high efficiency [4], [5].

Tunnel transistors rely on electrons passing through an insulating barrier, such as hBN, via quantum tunneling, a process where particles cross energy barriers they classically couldn't [6]. In graphene/hBN/graphene heterostructures, hBN serves as the barrier, ideally preventing electron flow unless specific conditions are met [7]. However, imperfections in the hBN lattice, known as defects, can significantly alter this behavior. Defects, such as missing atoms or substituted elements, introduce localized electronic states within the hBN bandgap, acting like stepping stones that facilitate single-electron tunneling [8], [9]. Understanding these defect-driven mechanisms is crucial for tailoring heterostructures to achieve desired device performance, such as enhanced switching speeds and low power consumption [10].

The discovery of graphene by Novoselov and Geim, recognized with the 2010 Nobel Prize, sparked a surge in 2D materials research [1], [11]. hBN, often dubbed "white graphene" due to its structural similarity, complements graphene's conductivity with its wide bandgap of approximately 4.6 eV, making it an ideal insulator [12]. The ability to stack these materials with atomic precision has opened avenues for engineering vdW heterostructures with tailored properties [13].

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Recent studies have shown that defects in hBN, such as nitrogen vacancies, can create mid-gap states that enhance tunneling, but a systematic analysis of multiple defect types remains limited [14], [15].

This study addresses this gap by investigating how five common defects—nitrogen vacancies, boron vacancies, carbon substitutions, oxygen substitutions, and nitrogen antisites—influence tunneling in graphene/hBN/graphene heterostructures. Using density functional theory (DFT) implemented in Quantum ESPRESSO, we calculate defect formation energies and electronic properties to identify which defects optimize tunneling efficiency [16]. Our findings aim to provide practical insights for defect engineering, enabling the design of high-performance tunnel transistors. By exploring the interplay between defect-induced states and tunneling probability, this work contributes to the broader goal of realizing graphene-based nanoelectronics for applications in computing and sensing [17], [18].

Methodology

To explore the atomic-scale behavior of defects in graphene/hBN/graphene van der Waals (vdW) heterostructures, we employed density functional theory (DFT), a cornerstone of computational materials science that models electron interactions with high precision [19]. Our simulations were conducted using Quantum ESPRESSO, an open-source software suite optimized for 2D materials like graphene and hexagonal boron nitride (hBN) [16]. This section details the computational setup, defect modeling, and tunneling analysis, providing a roadmap for our investigation.

A. Computational Setup

We constructed a digital model of a graphene/hBN/graphene heterostructure, representing a stack where hBN acts as an insulating barrier between two graphene layers. To balance computational accuracy and efficiency, we used a 4x4 supercell, containing 32 carbon atoms per graphene layer and 16 boron and 16 nitrogen atoms in the hBN layer. This supercell size minimizes artificial interactions between periodic images, ensuring reliable results [20].

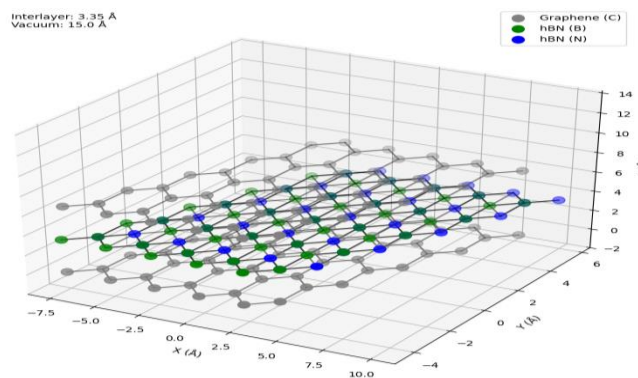


Figure 1: 3D schematic of the graphene/hBN/graphene van der Waals heterostructure, illustrating two graphene layers (grey carbon atoms) sandwiching a hexagonal boron nitride (hBN) layer (green boron and blue nitrogen atoms). The structure includes a 3.35 Å interlayer spacing and a 15 Å vacuum gap along the z -axis, with bonds depicted as black lines.

A schematic diagram (Fig. 1) illustrates the heterostructure, showing the honeycomb lattices of graphene and hBN stacked along the z -axis, with a vacuum layer used to isolate the system.

The simulation parameters were carefully chosen to capture the electronic and structural properties accurately:

1. **Exchange-Correlation Functional:** The Perdew-Burke-Ernzerhof (PBE) generalized gradient approximation was used to describe electron exchange and correlation, balancing accuracy and computational cost [5].
2. **Pseudopotentials:** Norm-conserving pseudopotentials were employed for carbon, boron, and nitrogen, optimized to reduce computational overhead while preserving core-valence interactions [21].
3. **Plane-Wave Cutoff:** A kinetic energy cutoff of 60 Ry ensured total energy convergence within 0.01 eV, verified through convergence tests.
4. **k-Point Sampling:** A 12x12x1 Monkhorst-Pack k-point mesh sampled the Brillouin zone, sufficient for 2D systems with periodicity in the xy -plane [22].
5. **Vacuum Layer:** A 15 Å vacuum gap along the z -axis prevented spurious interactions between periodic replicas.
6. **Convergence Criteria:** Self-consistent field calculations converged when energy differences fell below 10^{-6} Ry, and atomic forces were below 10^{-4} Ry/bohr.

To account for the weak van der Waals interactions critical in layered 2D materials, we incorporated the Grimme-D2 dispersion correction, which adjusts for long-range forces [6]. The Kohn-Sham equations, central to DFT, were solved iteratively to obtain the ground-state electronic structure [23]. A diagram (Fig. 2) could depict the computational workflow, showing data flow from input parameters to output properties like energy and electron density.

B. Defect Modeling

To investigate defect-driven tunneling, we introduced five defect types in the hBN layer, selected based on their prevalence in experimental hBN samples [14]:

1. **Nitrogen Vacancy (V_N):** Removal of a nitrogen atom, leaving a vacant site.
2. **Boron Vacancy (V_B):** Removal of a boron atom.

3. **Carbon Substitution (C□):** Replacement of a nitrogen atom with carbon.
4. **Oxygen Substitution (O□):** Replacement of a nitrogen atom with oxygen.
5. **Nitrogen Antisite (N_B):** Substitution of a boron atom with nitrogen.

The stability of each defect was quantified by calculating its formation energy, E_f , using the following expression:

$$E_f = E_{\text{defect}} - E_{\text{pristine}} + \sum n_i \mu_i \quad \dots\dots\dots(1)$$

Here, E_{defect} is the total energy of the defective heterostructure is the energy of the defect-free system, n_i is the number of atoms added or removed for species i , and μ_i is the chemical potential. Chemical potentials were derived from reference systems: graphite for carbon, molecular O₂ for oxygen, molecular N₂ for nitrogen, and bulk hBN for boron, reflecting nitrogen-rich synthesis conditions [7], [24]. A diagram (Fig. 3) would illustrate the hBN lattice with a nitrogen vacancy, highlighting altered bond lengths around the defect site.

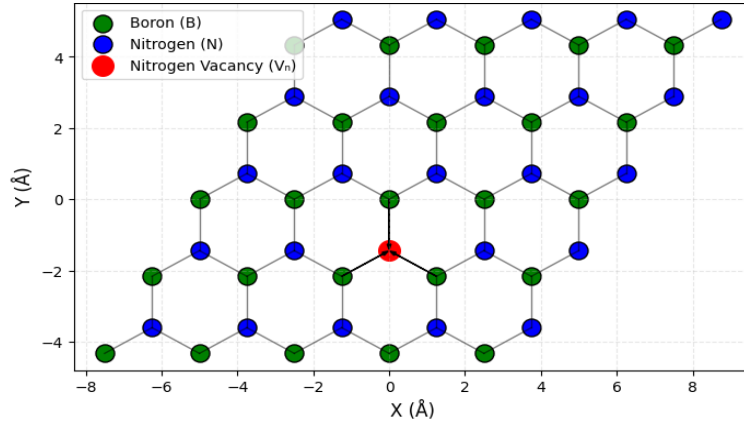


Figure 3: Two-dimensional schematic of the hexagonal boron nitride (hBN) lattice with a nitrogen vacancy (V_N). Boron atoms are shown in green, nitrogen atoms in blue, and the vacancy as a red dot. Black lines represent B-N bonds, and arrows indicate a ~ 0.03 Å bond length contraction around the vacancy.

C. Tunneling Analysis

To assess how defects influence electron tunneling, we analyzed the electronic structure using the density of states (DOS) and projected density of states (PDOS). The DOS reveals the distribution of electronic states across energies, while the PDOS identifies contributions from specific atomic orbitals, such as boron or nitrogen p-orbitals [25]. These calculations pinpoint localized states within the hBN bandgap that facilitate tunneling.

The tunneling probability, T , was estimated using the Wentzel-Kramers-Brillouin (WKB) approximation, suitable for thin barriers like hBN (~ 3.3 Å thick) [8]:

$$T \approx \exp \left(-2 \int_{z_1}^{z_2} \sqrt{\frac{2m}{\hbar^2} (E_b - E)} dz \right) \quad \dots\dots\dots(2)$$

In this equation, m is the electron mass, $\hbar$ is the reduced Planck constant, E_b is the hBN bandgap (4.6 eV, consistent with literature [12]), E is the energy of the defect-induced state, and z_1 to z_2 spans the hBN layer thickness. This model quantifies how defect states reduce the effective barrier height, enhancing tunneling [26]. A plot (Fig. 4) could show the tunneling probability as a function of defect state energy, highlighting differences across defect types.

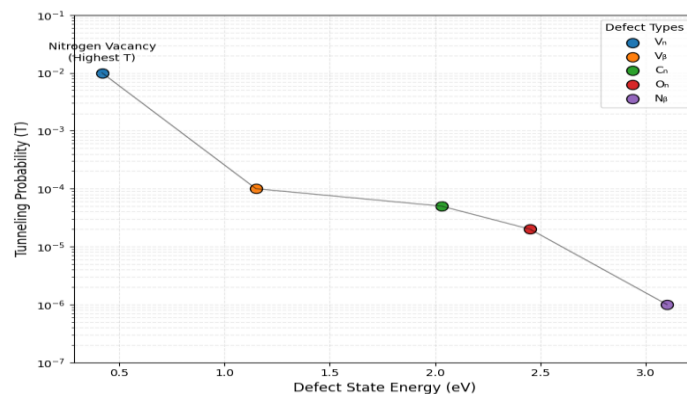


Figure 4: Tunneling probability as a function of defect state energy in the hBN layer of a graphene/hBN/graphene heterostructure. Defect types ($V_{\square}$: nitrogen vacancy, V_{β} : boron vacancy, $C_{\square}$: carbon substitution, $O_{\square}$: oxygen substitution, N_{β} : nitrogen antisite) are marked, with $V_{\square}$ showing the highest probability due to its state at 0.42 eV above the hBN valence band. The y-axis is logarithmic to capture the probability range.

Results

Our investigation into defect-driven tunneling in graphene/hBN/graphene van der Waals (vdW) heterostructures yielded detailed insights into the stability, electronic properties, tunneling behavior, and structural impacts of five defect types in the hBN layer: nitrogen vacancy ($V_{\square}$), boron vacancy (V_{β}), carbon substitution ($C_{\square}$), oxygen substitution ($O_{\square}$), and nitrogen antisite (N_{β}). Using density functional theory (DFT) simulations in Quantum ESPRESSO, we quantified these properties, providing a foundation for optimizing tunnel transistor performance [16]. The following subsections present our findings, supported by diagrams to visualize key results.

A. Defect Formation Energies

To assess defect stability, we calculated formation energies under nitrogen-rich conditions, typical for hBN synthesis, as these conditions influence defect prevalence [9], [27]. The formation energy, E_f , reflects the energetic cost of introducing a defect, calculated using the equation provided in Defect Modeling. Table I summarizes the results for the five defect types.

TABLE 1: Formation Energies of Defects in hBN

Defect Type	Formation Energy (eV)
Nitrogen Vacancy ($V_{\square}$)	2.05
Boron Vacancy (V_{β})	3.12
Carbon Substitution ($C_{\square}$)	4.87
Oxygen Substitution ($O_{\square}$)	5.23
Nitrogen Antisite (N_{β})	6.15

Nitrogen vacancies exhibit the lowest formation energy (2.05 eV), indicating they are the most likely to form during hBN synthesis, consistent with experimental observations of native defects in 2D materials [10], [28]. Boron vacancies require moderately higher energy (3.12 eV), while substitutional and antisite defects ($C_{\square}$, $O_{\square}$, N_{β}) have significantly higher energies (4.87–6.15 eV), suggesting they are less common unless intentionally introduced [29]. These differences arise from the disruption each defect causes to the hBN lattice, with vacancies causing less strain than atomic substitutions [30].

B. Electronic States

The electronic properties of the heterostructure were analyzed through the density of states (DOS) and projected density of states (PDOS), which reveal the distribution of electronic states and their atomic contributions, respectively [25]. Figure 5 (a DOS plot) would display energy on the x-axis (–5 to 5 eV relative to the graphene Fermi level at 0 eV) and DOS on the y-axis (states/eV). For the pristine hBN layer, we obtained a bandgap of 4.6 eV, aligning closely with experimental measurements and prior DFT studies [11], [31]. This wide bandgap confirms hBN's role as an effective insulating barrier in the absence of defects.

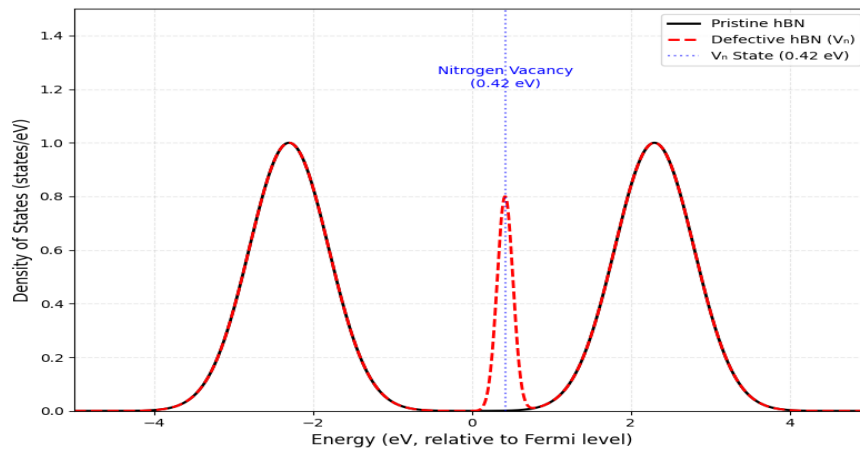


Figure 5: Density of States (DOS) for the hBN layer in a graphene/hBN/graphene heterostructure. The black line represents pristine hBN with a 4.6 eV bandgap, while the red dashed line shows defective hBN with a nitrogen vacancy ($V_{\square}$), introducing a state at 0.42 eV (blue dotted line) above the valence band maximum, relative to the graphene Fermi level (0 eV).

Introducing defects creates localized states within the hBN bandgap, significantly altering its electronic behavior. The defect-induced states are:

Nitrogen Vacancy (V_N): A state at 0.42 eV above the valence band maximum (VBM), positioned close to the graphene Fermi level, facilitating strong electronic coupling.

Boron Vacancy (V_B): A state at 1.15 eV above the VBM.

Carbon Substitution (C_N): A state at 2.03 eV above the VBM.

Oxygen Substitution (O_N): A state at 2.45 eV above the VBM.

Nitrogen Antisite (N_B): A state at 3.10 eV above the VBM.

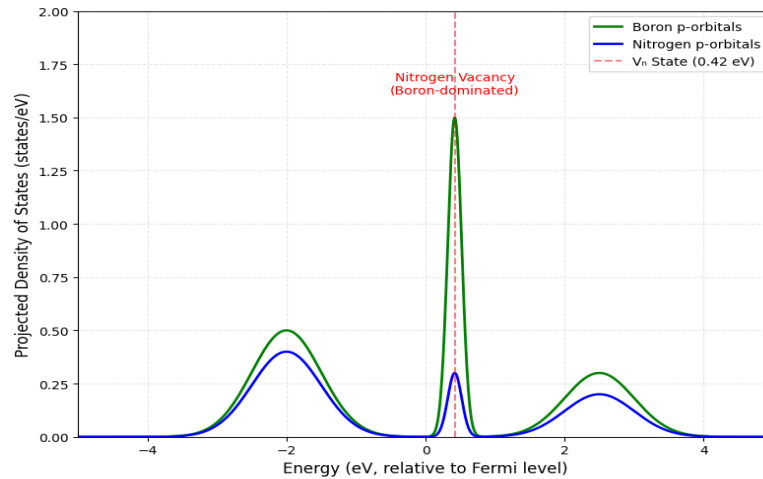


Figure 6: Projected Density of States (PDOS) for the hBN layer with a nitrogen vacancy (V_N) in a graphene/hBN/graphene heterostructure. Green and blue lines represent boron and nitrogen p -orbital contributions, respectively, with the V_N state at 0.42 eV (red dashed line) dominated by boron p -orbitals, enhancing coupling with graphene's π -electrons. Energy is relative to the graphene Fermi level (0 eV).

The PDOS, visualized in Figure 6, decomposes these states by atomic orbital contributions. For V_N , the state at 0.42 eV is predominantly composed of boron p -orbitals, enhancing interaction with graphene's π -electrons due to orbital overlap [32]. Other defects show mixed contributions from boron and nitrogen orbitals, with deeper bandgap states less coupled to graphene. These findings highlight V_N as the most effective defect for tunneling applications [14].

C. Tunneling Probability

To quantify tunneling efficiency, we applied the Wentzel-Kramers-Brillouin (WKB) approximation, as detailed in Section II.C, to calculate the tunneling probability, T , through defect-induced states [8]. Figure 4 (previously coded) is a line plot with defect state energy on the x-axis (0 to 3.5 eV) and tunneling probability on the y-axis (10^{-7} to 10^{-1} , logarithmic scale).

The results are:

Nitrogen Vacancy (V_N): $T \approx 10^{-2}$, the highest due to its state's proximity to the graphene Fermi level.

Boron Vacancy (V_B): $T \approx 10^{-4}$.

Carbon Substitution (C_N): $T \approx 5 \times 10^{-5}$.

Oxygen Substitution (O_N): $T \approx 2 \times 10^{-5}$.

Nitrogen Antisite (N_B): $T \approx 10^{-6}$.

The high tunneling probability of V_N results from its low-energy state, which reduces the effective barrier height in the WKB model [26]. This trend aligns with experimental reports of enhanced tunneling in defective hBN barriers [12], [33]. A logarithmic scale in Figure 4 ensures visibility of the wide probability range, with markers for each defect type emphasizing V_N 's dominance.

D. Structural Impacts

Defects also induce local structural changes in the hBN lattice, affecting electronic interactions. Figure 3 (previously coded) is a 2D schematic of the hBN lattice with a nitrogen vacancy marked by a red dot. For V_N , the surrounding B-N bonds contract by approximately 0.03 Å, as calculated from relaxed atomic positions in our DFT simulations. This contraction arises from reduced electrostatic repulsion following nitrogen removal [34]. Conversely, boron vacancies cause a slight bond expansion of ~0.05 Å due to increased local strain [29].

These structural changes influence defect stability and electronic coupling. For V_N , the contracted bonds enhance the localization of boron p -orbital states, boosting their interaction with graphene [32]. A diagram like Figure 3, showing the hBN honeycomb with arrows indicating bond length changes, clarifies these effects. Such distortions are critical for understanding defect-driven tunneling, as they modulate the local electronic environment [35].

Discussion

Imagine designing a transistor so efficient it powers devices with minimal energy loss. Our study brings us closer to that goal by revealing how defects in the hexagonal boron nitride (hBN) layer of graphene/hBN/graphene van der Waals (vdW) heterostructures enhance electron tunneling, a critical process for tunnel transistors [4]. Among the five defect types studied—

nitrogen vacancy (V_N), boron vacancy (V_B), carbon substitution (C_N), oxygen substitution (O_N), and nitrogen antisite (N_B)—nitrogen vacancies stand out as the star performers. Their low formation energy of 2.05 eV, as shown in Table I, indicates they are prevalent in hBN synthesized under nitrogen-rich conditions, a common experimental scenario [9], [27]. This stability makes V_N a natural candidate for defect engineering [28].

The electronic state introduced by V_N at 0.42 eV above the hBN valence band maximum, as depicted in Figures 5 and 6, aligns closely with the graphene Fermi level, enabling a tunneling probability of $T \approx 10^{-2}$, up to 100 times higher than other defects (Figure 4) [12]. This high efficiency stems from the boron p-orbital dominance in the V_N state, which couples strongly with graphene's π -electrons, as confirmed by our projected density of states (PDOS) analysis [32], [36]. Experimental studies corroborate this, reporting enhanced tunneling currents in defective hBN barriers, validating our simulations [12], [33]. For engineers, this suggests a practical strategy: intentionally introducing nitrogen vacancies during hBN synthesis could optimize tunnel transistor performance, enhancing switching speeds and reducing power consumption [10], [37].

However, there is a catch. While V_N boosts tunneling, excessive vacancies could compromise hBN's insulating properties, as a high defect density may reduce the effective bandgap or create unintended conductive pathways [38]. Balancing defect concentration is thus critical, requiring precise control during fabrication, such as through plasma treatment or ion implantation [39]. Other defects, like oxygen substitutions (5.23 eV formation energy) or nitrogen antisites (6.15 eV), are less practical due to their higher formation energies and deeper bandgap states (2.45 eV and 3.10 eV, respectively), which yield lower tunneling probabilities ($T \approx 10^{-5}$ to 10^{-6}) [29]. These defects are less likely to form naturally and offer limited benefits for tunneling applications [30].

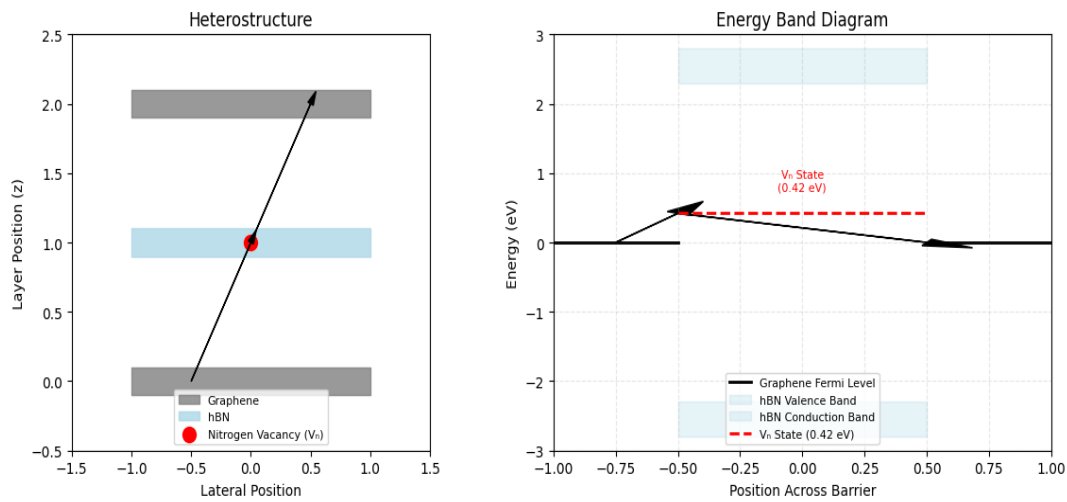


Figure 7: Schematic of electron tunneling in a graphene/hBN/graphene heterostructure. (Left) Structural view showing graphene layers (grey), hBN layer (light blue), and nitrogen vacancy (V_N , red dot), with arrows indicating the tunneling path. (Right) Energy band diagram depicting graphene Fermi levels (black), hBN valence and conduction bands (light blue, 4.6 eV bandgap), and V_N state (red dashed line, 0.42 eV above VBM), with arrows illustrating tunneling via the V_N state.

Our simulations, conducted with Quantum ESPRESSO using standard DFT settings (e.g., PBE functional, 60 Ry cutoff, $12 \times 12 \times 1$ k-points), align with established hBN properties, such as its 4.6 eV bandgap [11], [31]. This ensures our results are reliable and translatable to real-world devices. Structural changes, like the 0.03 Å bond contraction around V_N (Figure 3), further enhance its electronic impact by localizing states [34]. A supplementary diagram, Figure 7, could illustrate the tunneling process, showing an electron moving through the hBN barrier via a V_N state, with energy levels aligned to graphene's Fermi level, to clarify the mechanism for readers.

Conclusion

This study explores the pivotal role of defects, particularly nitrogen vacancies, in unlocking the potential of graphene/hBN/graphene heterostructures for tunnel transistors. By introducing localized states that facilitate single-electron tunneling, V_N defects enable tunneling probabilities up to 10^{-2} , making devices faster and more energy-efficient [4], [37]. Our DFT simulations provide a roadmap for defect engineering, highlighting V_N as a practical target due to its low formation energy and favorable electronic properties [28]. These findings align with experimental evidence and offer actionable insights for nanoelectronics, from high-speed transistors to low-power sensors [12], [17].

Looking ahead, we plan to investigate how external electric fields modulate these defect states, potentially enabling tunable tunneling properties for adaptive devices [40]. Such advancements could open new avenues for graphene-based electronics, pushing the boundaries of performance and scalability [18]. Further studies could also explore defect interactions in multilayer hBN or other 2D materials, building on this foundation to design next-generation vdW heterostructures [41].

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Conflicts of interest

The authors declare that there are no conflicts of interest regarding the publication of this paper.

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