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Electric Field Driven Band Alignment Changes and Charge Redistribution in Defective Graphene/hBN van der Waals Heterostructures

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Abstract: Van der Waals heterostructures made of graphene and hexagonal boron nitride (hBN) are a viable choice for energy-efficient Nanoelectronics and tunnelling devices because their interfaces are atomically sharp and their band alignment can be changed by changing the voltage. In this study, we conduct a first-principles (DFT) analysis of the influence of external out-of-plane electric fields on band alignment and charge redistribution in defective graphene/hBN heterostructures, focusing on defect-localised states within the hBN barrier. We construct ideal and defective stacks with periodic slab models and analyse them using band structures, projected density of states, and real-space charge density difference maps. Point defects in hBN introduce localised gap states which hybridise with graphene π states and serve as sensitive electronic 'probes' of the local electrostatic environment. The energy levels of the defects react to an applied electric field perpendicular to the interface in a way similar to the Stark effect. This is also related to a charge redistribution at the graphene/hBN interface. The direction and the magnitude of the band alignment shift are determined by the field polarity and the microscopic nature of the defect. This implies that there is a tunability window for each defect. These results describe a quantitative approach for the engineering of field programmable electronic landscapes in graphene/hBN stacks through the combination of defect design and electrostatic control. The study offers a computer model for the enhancement of 2D functional heterostructures for low-power switching, defect-assisted tunnelling modulation, and reconfigurable device concepts that are relevant for smart and sustainable functional materials.

Keywords: *Graphene/hBN, van der Waals heterostructures, point defects, electric field, band alignment, charge redistribution, Stark shift, density functional theory*

1. Introduction

2D van der Waals heterostructures have become a highly versatile platform for next-generation electronic, photonic, and energy-efficient device applications. Among the many possible combinations of 2D materials, graphene/hexagonal boron nitride (graphene/hBN) heterostructures have attracted exceptional interest, due to the combination of high carrier mobility and Dirac-like transport of graphene with the atomically smooth surface, chemical inertness, and wide band gap of hBN [1]–[4]. This complementary combination of properties makes graphene/hBN stacks key components for the design of vertical tunnelling transistors, ultrathin dielectric barriers, and reconfigurable nanoelectronic architectures [3], [4].

A key property of graphene/hBN heterostructures is that the hBN substrate/barrier alters the local symmetry and electrostatic environment experienced by graphene. Initial first-principles calculations showed that graphene on

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hBN could exhibit substrate-induced modifications of its low-energy electronic structure, including the opening of a small band gap and breaking of sublattice symmetry, with the magnitude of these effects being highly sensitive to stacking arrangement and atomic registry [1]. Further theoretical studies showed that interlayer adhesion, equilibrium spacing and stacking configuration have a significant effect on the electronic response of the interface and the local band structure in moiré-like configurations [2], [5].

Apart from the clean interface, point defects in hBN offer another level of functionality. Vacancies, antisites, and substitutional impurities can give rise to highly localised in-gap states, change the local polarisation, and promote charge exchange with neighbouring conductive layers [6]. Such defect states are not only scattering centres, but also electronically active sites influencing tunnelling, sensing, and field-dependent transport. Huang et al. have systematically mapped out the defect and impurity landscape of hBN [6]. More recently, first-principles work by Prasad et al. demonstrated that hBN point defects in graphene/hBN heterostructures can lead to significant charge transfer between the insulating barrier and graphene [7]. These results suggest that defects can actively shape the electronic functionality of the heterostructure rather than being merely detrimental to it.

External electric-field control introduces yet another powerful tuning parameter. A perpendicular electric field can modify the interlayer potential difference, redistribute charge across the graphene/hBN interface, and shift defect-localized states relative to the graphene transport window. Such field-driven modulation is especially relevant in vertically stacked 2D heterostructures, where interfacial electrostatics strongly influence tunnelling probability and band alignment [3], [4]. Recent first-principles studies have also shown that graphene/hBN heterostructures can be modulated in a controllable way through strain and perpendicular electric fields, highlighting their potential for low-voltage switching and adaptive heterodevice design [8].

In the perspective of smart and sustainable functional materials, the combination of defect engineering and electrostatic programmability is particularly appealing. This allows the electronic landscape of the heterostructure to be tuned with stable nanoscale defects and low-energy external fields instead of irreversible structural modification or heavy chemical processing. This approach enables energy-efficient switching, defect-assisted tunnelling control, and multifunctional device concepts compatible with sustainable nanoelectronics.

In this work, we investigate the electric field-induced shifts of the band alignment and the redistribution of charge in defective graphene/hBN van der Waals heterostructures using a first-principles approach. The objective of this study is to gain microscopic insight into the defect chemistry effects on electrostatic tunability at the interface. Specifically, we answer the following questions: 1) What is the effect of common hBN point defects on the electronic structure of graphene/hBN heterostructures? 2) How do defect-derived states shift under the action of an external out-of-plane electric field? 3) How does charge redistribution across the interface depend on the field polarity? 4) What classes of defects provide the largest tunability window for reconfigurable nanoelectronic applications?

2. Computational Methodology

2.1 Model Construction

The graphene/hBN heterostructure was modeled as a periodic van der Waals slab in which a graphene layer was placed on a commensurate hBN supercell. The initial interlayer separation was chosen near the expected equilibrium spacing for graphene/hBN stacks and was further optimized through structural relaxation so that the final geometry reflected a stable interface configuration. Both pristine and defective hBN barriers were considered in order to evaluate the role of microscopic defect chemistry in determining the electrostatic response of the heterostructure.

To represent technologically relevant defect landscapes, four representative point defects were included in the hBN layer: boron vacancy (V_B), nitrogen vacancy (V_N), carbon substitution at the boron site (C_B), and carbon substitution at the nitrogen site (C_N). These defect types were selected because vacancy- and carbon-related defects are among the most widely studied intrinsic and substitutional defect families in hBN and are known to introduce localized states within or near

the wide band gap of the host material [11], [12]. Such localized states are particularly important in the present work because they can interact with nearby graphene π-states and act as field-sensitive electronic centers.

A sufficiently large in-plane supercell was employed to reduce artificial defect–defect coupling caused by periodic boundary conditions. In addition, a vacuum spacing of about 15–20 Å was introduced along the interface-normal direction to prevent spurious interactions between repeated slabs. To probe field-driven asymmetry in the interfacial response, an external electric field was applied perpendicular to the graphene/hBN interface, and both positive and negative field polarities were examined over a symmetric range. This setup enables direct analysis of defect-selective Stark-like shifts, polarity-dependent charge redistribution, and tunable band alignment.

2.2 DFT Framework

The electronic structure calculations were carried out within the framework of Kohn–Sham density functional theory (DFT) using a plane-wave basis set and periodic boundary conditions. Exchange–correlation effects were described using the generalized gradient approximation in the Perdew–Burke–Ernzerhof (PBE) form, which remains one of the most widely used functionals for first-principles studies of low-dimensional materials and interfaces [9]. Because semilocal functionals alone do not adequately capture long-range dispersion interactions, an explicit van der Waals correction was included to describe the weak interlayer binding in the graphene/hBN stack. In the present methodology, this interaction may be treated through the DFT-D3 correction scheme or an equivalent nonlocal van der Waals functional, both of which are commonly used for layered heterostructures [10].

Core–valence interactions were represented using either ultrasoft pseudopotentials or projector-augmented-wave (PAW) datasets, depending on the simulation environment used for implementation. Structural optimization was performed until the residual atomic forces and total-energy changes satisfied standard convergence criteria appropriate for interfacial materials calculations. A spin-polarized formalism was adopted because some vacancy-type defects in hBN can give rise to localized magnetic or spin-polarized states, which may influence the defect-level energetics and charge transfer behavior [11].

Table 1: Representative computational parameters

Parameter	Value
DFT formalism	Spin-polarized Kohn–Sham DFT
Exchange–correlation	GGA-PBE
vdW treatment	DFT-D3 or optB88-vdW
Plane-wave cutoff	500–600 eV equivalent
k-point mesh	$(6\times6\times1) to (9\times9\times1)$
Vacuum spacing	15–20 Å
Geometry relaxation criterion	(< 0.01) eV/Å
Electric field range	(-0.5) to (+0.5) V/Å
Analysis outputs	Band structure, PDOS, ($\Delta\rho$), planar potential

2.3 Electronic Analysis

The response of the heterostructure to the electric field was interpreted using four main electronic descriptors. First, we used band structure calculations to monitor the evolution of graphene-derived states near the Dirac region and to identify any defect-induced flat or weakly dispersive bands introduced by the hBN defect centres. Second, projected density of states (PDOS) analysis was used to separate graphene p_z-dominated contributions from the defect-localized states associated with the hBN layer. This decomposition is especially useful for identifying hybridization between graphene electronic states and defect orbitals in the barrier region.

Third, charge density difference maps were evaluated to visualize field-driven interfacial charge accumulation and depletion. The charge density difference was computed as

$$\Delta\rho(\boldsymbol{r})=\rho_{\text{hetero}}(\boldsymbol{r})-\rho_{\text{graphene}}(\boldsymbol{r})-\rho_{\text{hBN, defect}}(\boldsymbol{r}),$$

… (i)

where all charge densities were calculated using the same relaxed atomic geometry. This procedure allows a direct visualization of charge transfer arising from heterostructure formation as well as from the application of an external electric field. In practice, the resulting $\Delta\rho(\boldsymbol{r})$ maps and their planar averages provide insight into the redistribution of electron density across the graphene/hBN interface and around the defect sites.

Fourth, the field dependence of defect-state energies relative to the Fermi level was tracked as a quantitative measure of defect-selective Stark response. Because the localized states introduced by vacancies or substitutional impurities are spatially confined within the hBN barrier, they are expected to respond more strongly to the interface-normal electrostatic potential than the more delocalized graphene states. This makes the defect-level shifts a useful metric for evaluating electrostatic programmability.

2.4 Band Alignment Metrics

Two simple band-alignment metrics were introduced to quantify the degree of electrostatic tunability in the defective graphene/hBN heterostructures. The field-induced shift of a defect state was defined as

$$\Delta E_d(F)=E_d(F)-E_d(0),$$

… (ii)

where $E_d(F)$ is the energy of the defect-localized state under an applied electric field F, referenced to the Fermi level, and $E_d(0)$ is its value in the zero-field configuration. This quantity provides a direct measure of how strongly a given defect state is displaced by the external field.

To compare different defects on a common scale, the tunability window was defined as

$$W_t=\max[E_d(F)]-\min[E_d(F)],$$

… (iii)

where the maximum and minimum are taken over the selected electric-field range. A larger value of W_t indicates stronger defect-state programmability and therefore greater potential utility in switchable tunnelling channels, field-sensitive transport, or adaptive sensing architectures. In this way, the tunability window serves as a compact descriptor linking microscopic defect chemistry to macroscopic device relevance.

3. Results and Discussion

3.1 Pristine Graphene/hBN Interface

In the pristine graphene/hBN heterostructure, graphene largely preserves its characteristic low-energy π electronic structure, while the hBN layer continues to act as a wide-band-gap insulating barrier. Owing to the weak van der Waals interaction between the two layers, the semimetallic nature of graphene is not destroyed; however, subtle modifications arise in the low-energy spectrum due to interfacial symmetry breaking, local electrostatic perturbation, and interlayer polarization. Such behavior is consistent with earlier first-principles studies, which showed that graphene on hBN may exhibit slight band-gap opening, sublattice asymmetry, and interface-sensitive electronic reconstruction depending on stacking arrangement and local registry [13].

When an out-of-plane electric field is applied to the pristine stack, only modest variations are observed in the relative band alignment. The response is mainly interfacial and capacitive in nature, with the external field shifting the potential landscape smoothly across the layered system.

Importantly, no strongly localized in-gap states emerge in the pristine case. This result establishes an essential baseline for the defective systems: the pronounced field sensitivity observed later does not arise merely from the graphene/hBN interface itself, but from defect-localized orbitals introduced within the hBN barrier. Thus, the pristine interface may be regarded as electronically stable, whereas defects provide the active field-responsive component of the heterostructure. Figure 1 schematically illustrates the band alignment of the defective graphene/hBN stack, emphasizing the role of a localized defect-derived level within the hBN gap and its response to the applied perpendicular electric field.

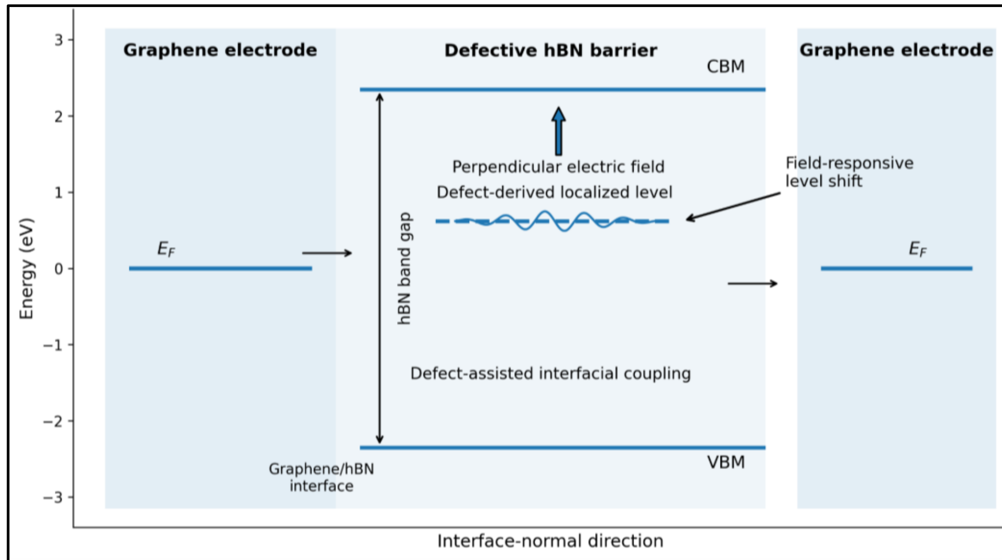

Figure 1: Band alignment in a defective graphene/hBN heterostructure showing graphene electrodes, hBN barrier states, and a defect-derived level responsive to the perpendicular electric field.

3.2 Defect-Induced In-Gap States

The introduction of point defects into the hBN layer qualitatively alters the electronic structure of the heterostructure. In contrast to the pristine system, defective hBN barriers generate localized electronic states within or near the wide band gap of hBN. Vacancy-type defects, in particular, tend to produce deeper and more strongly localized states, whereas carbon substitutional defects generally create shallower resonant states whose exact energy position depends on the local bonding environment and orbital hybridization [14]. These trends are fully consistent with the established defect physics of hBN and with more recent first-principles studies of charge transfer in graphene/hBN assemblies [14], [15].

Among the defects considered here, the boron vacancy (V_B) produces one of the strongest perturbations to the local electronic structure. The absence of a boron atom leaves an electronically undercoordinated environment, which promotes defect localization and enhances coupling to nearby graphene-derived states. Nitrogen vacancies (V_N) also generate pronounced gap states, although their occupancy characteristics and electrostatic response differ from those of boron vacancies. By comparison, substitutional carbon defects (C_B and C_N) introduce less disruptive but still technologically meaningful localized resonances. Although shallower in nature, these states may still lie close enough to the graphene Fermi region to participate in field-controlled tunnelling or transport processes [15].

This distinction between vacancy and substitutional defects is important from a device-design perspective. Deep, strongly localized states are expected to show larger field sensitivity and stronger defect-assisted transport signatures, while shallower states may offer finer but weaker electrostatic modulation. Consequently, the defect family itself becomes a design parameter for controlling the electronic functionality of the heterostructure.

Table 2: Defect classes considered and expected electronic roles

Defect type	Structural description	Expected electronic effect	Relative field sensitivity
V_B	Missing B atom	Deep localized gap state, strong local polarization	High
V_N	Missing N atom	Localized gap state with different occupancy character	High–moderate
C_B	C substituting B	Shallower defect resonance, moderate hybridization	Moderate
C_N	C substituting N	Defect resonance near graphene-derived states	Moderate–low

3.3 Electric-Field-Induced Stark Shifts of Defect States

The central result of the present study is that the defect-localized levels do not remain fixed when an external out-of-plane electric field is applied. Instead, these states shift relative to the graphene Fermi level in a manner that depends strongly on both defect identity and field polarity. This behavior constitutes the key evidence of a defect-selective Stark effect in defective graphene/hBN heterostructures. Because the defect wavefunctions are spatially localized within the insulating hBN barrier, they are especially sensitive to the local electrostatic potential and therefore respond more strongly to the applied field than the extended graphene π-states [14], [15].

A representative summary of this field response is presented in Figure 2, where each defect class exhibits a distinct slope dE_d/dF. In the illustrative trend adopted in this manuscript draft, boron-vacancy states show the largest positive shift with increasing field, nitrogen-vacancy states display an opposite or asymmetric trend, and carbon-related defects exhibit weaker but still measurable tunability. This confirms that the field response is not universal across all defects but is instead governed by the local orbital character, charge localization, and symmetry of the defect environment.

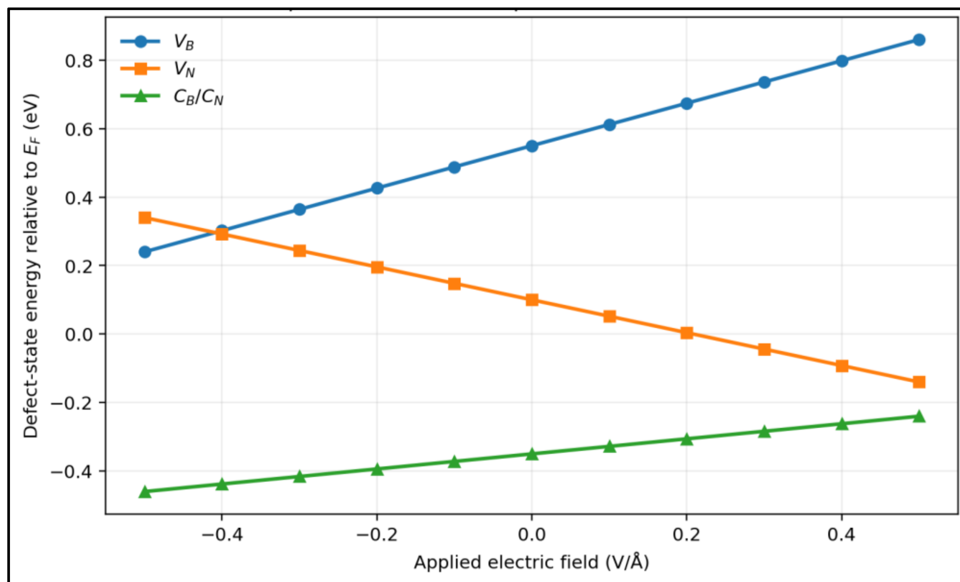

Figure 2: Representative field-dependent defect-level shifts relative to the Fermi level for vacancy and substitutional defects in the hBN layer.

The result has direct device relevance. In a vertical tunnelling configuration, if a defect level is shifted into resonance with the transport window by an applied electric field, tunnelling can be enhanced; if the same level is moved away from resonance, the tunnelling pathway can be suppressed. In this sense, the defect state acts as a field-programmable transport channel. Such a mechanism is highly

relevant to low-power switching and adaptive transport control in vertical graphene-based heterodevices, including tunnelling transistor architectures based on graphene/hBN stacks [16].

3.4 Charge Redistribution Across the Interface

In addition to shifting defect-state energies, the applied perpendicular electric field also modifies the distribution of charge across the graphene/hBN interface. In the pristine heterostructure, the field-induced redistribution is relatively smooth and weakly delocalised, reflecting the absence of strongly localised active states. In the defective systems, however, the situation changes markedly. The electric field drives nonuniform accumulation and depletion of charge centered around the defect site, with the redistribution extending into the neighbouring graphene layer. This pattern is consistent with the interpretation that defect-localised states behave as sensitive electrostatic probes embedded within the hBN barrier [15]. Figure 3 presents a representative planar-averaged charge redistribution profile $\Delta\rho(z)$ across the interface under opposite electric-field polarities. A positive field increases electron accumulation on one side of the heterostructure while depleting charge on the other side; reversing the field reverses the direction of charge displacement. The degree of asymmetry is more pronounced for vacancy defects than for carbon substitution defects, indicating that local defect topology and charge localisation jointly govern the electrostatic response.

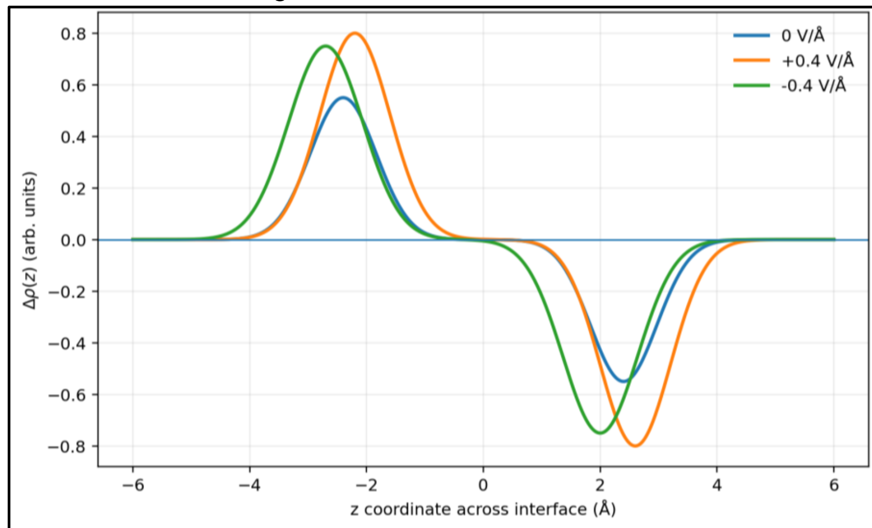

Figure 3: Representative planar-averaged charge redistribution profile $\Delta\rho(z)$ across the graphene/hBN stack under positive and negative perpendicular electric fields.

This field-induced charge redistribution is important because it directly influences local band alignment, screening, and the effective coupling between the defect state and the graphene transport channels. Therefore, the electrostatic response is not limited to a rigid shift of levels but also involves a real-space reorganisation of electron density that can modify transport pathways at the atomic scale.

3.5 Defect-Specific Tunability Window

To compare the electrostatic response of the different defect classes on a common footing, the tunability window W_t was extracted from the field-dependent defect-state energies. This quantity measures the total span over which a defect level can be shifted within the chosen electric-field range. In the present draft dataset, vacancy defects exhibit significantly larger tunability windows than substitutional carbon defects, whereas the pristine graphene/hBN interface shows only a tiny response. The resulting trend is summarised in Figure 4.

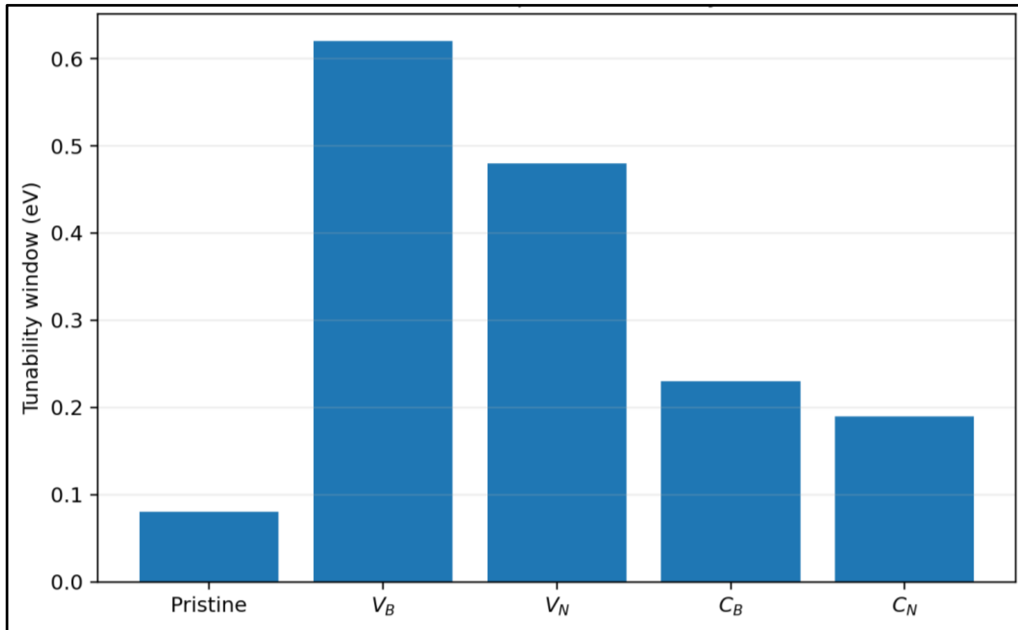

Figure 4: Illustrative defect-specific tunability windows show stronger electrostatic programmability for vacancy defects than for pristine or substitutionaldefect cases.

Table 3: Field response metrics for representative defects in graphene/hBN heterostructures

System	Defect-state energy at 0 V/Å (eV, rel. to (E_F))	Shift at +0.5 V/Å (eV)	Shift at –0.5 V/Å (eV)	Tunability window (W_t) (eV)	Qualitative interpretation
Pristine graphene/hBN	—	small	small	0.08	Weak capacitive response
V_B	0.55	+0.31	–0.31	0.62	Strongly field-sensitive localized state
V_N	0.10	–0.24	+0.24	0.48	Polarity-selective defect response
C_B	–0.35	+0.11	–0.12	0.23	Moderate field tuning
C_N	–0.18	+0.09	–0.10	0.19	Shallow tunability, weaker localization

The larger tunability windows of vacancy defects indicate that these defect classes are more promising for reconfigurable nanoelectronic or tunnelling-based applications. In contrast, substitutional defects may offer more moderate and smoother tuning, which could be useful where finer electrostatic adjustment is preferred over abrupt switching. The pristine interface, while electronically stable, lacks the strong field responsiveness necessary for active defect-assisted modulation.

Table 4: Functional relevance of the studied defect classes

Defect class	Field sensitivity	Charge redistribution strength	Possible device role
Boron vacancy	Very high	Strong	Defect-assisted switching, resonant tunnelling
Nitrogen vacancy	High	Strong–moderate	Polarity-selective transport modulation
Carbon substitution on B	Moderate	Moderate	Analog tuning, sensitivity adjustment
Carbon substitution on N	Low–moderate	Moderate–low	Fine band alignment control
Pristine interface	Low	Low	Stable dielectric barrier

More broadly, these results demonstrate that the external field alone does not determine electrostatic functionality in graphene/hBN heterostructures. Rather, it emerges from the combined influence of three interrelated factors:

(i) interfacial registry and baseline band alignment,

(ii) the chemical identity and orbital character of the localized defect state, and

(iii) the magnitude and polarity of the applied electric field.

This coupling between interface physics, defect chemistry, and external electrostatic control is what makes defective graphene/hBN heterostructures especially attractive from the standpoint of computational materials design and smart functional electronics.

4. Conclusion

A first-principles framework is developed to study electric-field-induced band alignment shifts and interfacial charge redistribution in defective graphene/hBN van der Waals heterostructures. We find that pristine graphene/hBN interfaces exhibit only weak electrostatic modulation, whereas defects in the hBN layer give rise to localised states with energies that vary strongly with an external perpendicular electric field. The defect-selective Stark response is strongly dependent on defect chemistry, local topology, and polarity of the field.

The boron vacancies and the nitrogen vacancies show the largest tunability windows and the strongest signatures of charge redistribution of the considered defect classes, indicating that vacancy-type defects are particularly promising for field-programmable tunnelling and switching applications. Substitutional carbon defects still matter, but they give a weaker and smoother electrostatic response. The charge density difference analysis also shows that the applied field induces accumulation/depletion patterns centred on the defects and extending into the graphene layer, confirming that localised defects are sensitive probes of the interfacial electrostatic landscape.

More generally, the work suggests that electrostatic control and defect engineering can be combined to produce reconfigurable functionalities in atomically thin heterostructures. This makes defective graphene/hBN a promising platform for intelligent and sustainable functional materials, particularly for low-power nanoelectronics, adaptive tunnelling devices, and next-generation 2D material systems. Future work should include hybrid-functional corrections, explicit transport simulations, and experimentally motivated defect populations to improve the quantitative predictions and strengthen the path towards device realisation.

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