Properties of graphene in-plane hybrid embracing hexagonal shaped hexagonal-Boron Nitride (h-BN) islands and vacancy induced magnetism

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Introduction & Aim

- h-BN islands in hexagonal shape with defect.
- Pristine hybrids (GBN) are all non-magnetic and semiconducting.
- Defective hybrids might be metallic and posses magnetic moment.
- Outline:
  - Graphene & h-BN
  - GBN hybrids
  - Graphene and h-BN sheets with mono vacancy
  - GBN hybrids with mono vacancy

Methods & Formulae I

- Method: Density Functional Theory
- Exchange-correlation: GGA (PW91)
- Basis set: Plane waves, PAW Pseudopotential
- Code: VASP
- **Magnetization energy**; difference between the non spin polarized (NSP) and spin polarized (SP) total energies

$$\Delta E_M = E_{\mathrm{NSP}} - E_{\mathrm{SP}} \, . \tag{1}$$

Methods & Formulae II

- Solid state reaction,

$$\mathbf{G}_{162} + \mathbf{B}_Y + \mathbf{N}_Z \longrightarrow \textbf{h-BN@G} + \mathbf{C}_{Y+Z}. \qquad (2)$$

- **Energetics of island implantation: Formation energy** $\mathcal{E}_{\mathrm{f}}$ (at zero temperature and pressure)

$$\begin{aligned} \mathcal{E}_{\mathrm{f}} = \quad & (E_{\textbf{h-BN@G}} + (Y+Z) \times \mu[\mathbf{C}]) - \\ & (E_{\mathbf{G}_{162}} + Y \times \mu[\mathbf{B}] + Z \times \mu[\mathbf{N}])\,. \end{aligned} \qquad (3)$$

- μ (chemical potential): either atomic or asymptotic bulk limits

Methods & Formulae III

- Minimum and maximum formation energies of the hybrid embracing an h-BN island

$$\begin{aligned}\mathcal{E}_{\mathrm{f}_{\mathrm{min}}} = \quad & (E_{\textbf{h-BN@G}} + (Y+Z)\times\mu[\textbf{C}_{\textbf{bulk}}]) - \\ & (E_{\textbf{G}_{162}} + Y\times\mu[\textbf{B}_{\textbf{atom}}] + Z\times\mu[\textbf{N}_{\textbf{atom}}) \\ \mathcal{E}_{\mathrm{f}_{\mathrm{max}}} = \quad & (E_{\textbf{h-BN@G}} + (Y+Z)\times\mu[\textbf{C}_{\textbf{atom}}]) - \\ & (E_{\textbf{G}_{162}} + Y\times\mu[\textbf{B}_{\textbf{bulk}}] + Z\times\mu[\textbf{N}_{\textbf{bulk}})) \end{aligned} \quad (4)$$

- **Energetics of defect formation: Defect formation energy**

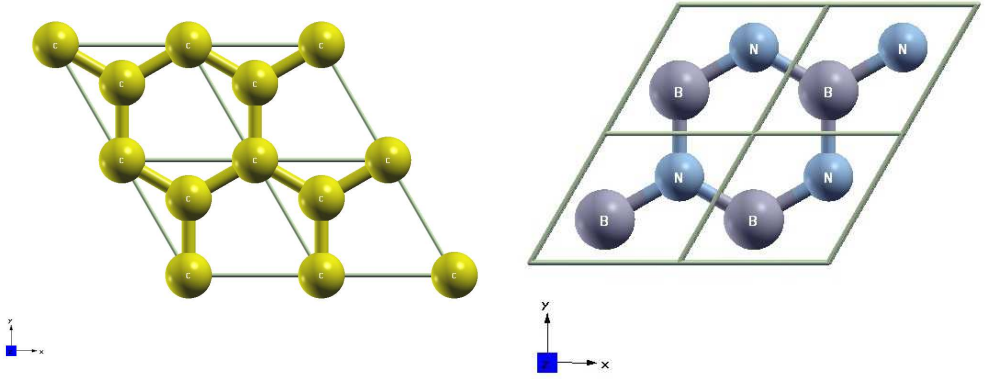
$$\begin{aligned}E_{form}[D(i,q)] = \quad & E_{total}[D(i,q)] - E_{total}[D(0,q)] \\ & + \sum[n(i) * \mu(i)]\end{aligned} \quad (5)$$

Pristine Graphene & h-BN

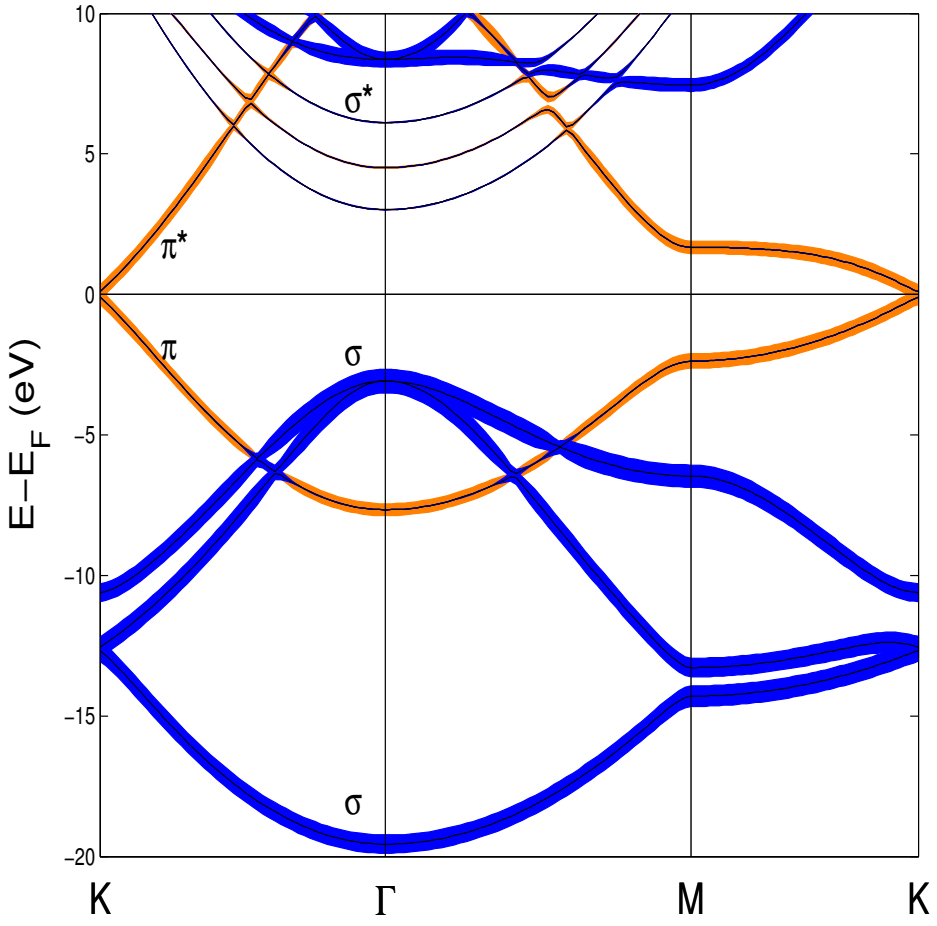
- Crystalline lattice of graphene and h-BN. Hexagonal. Ideal 2D systems.

Pristine Structures Unit Cell

Graphene h-BN

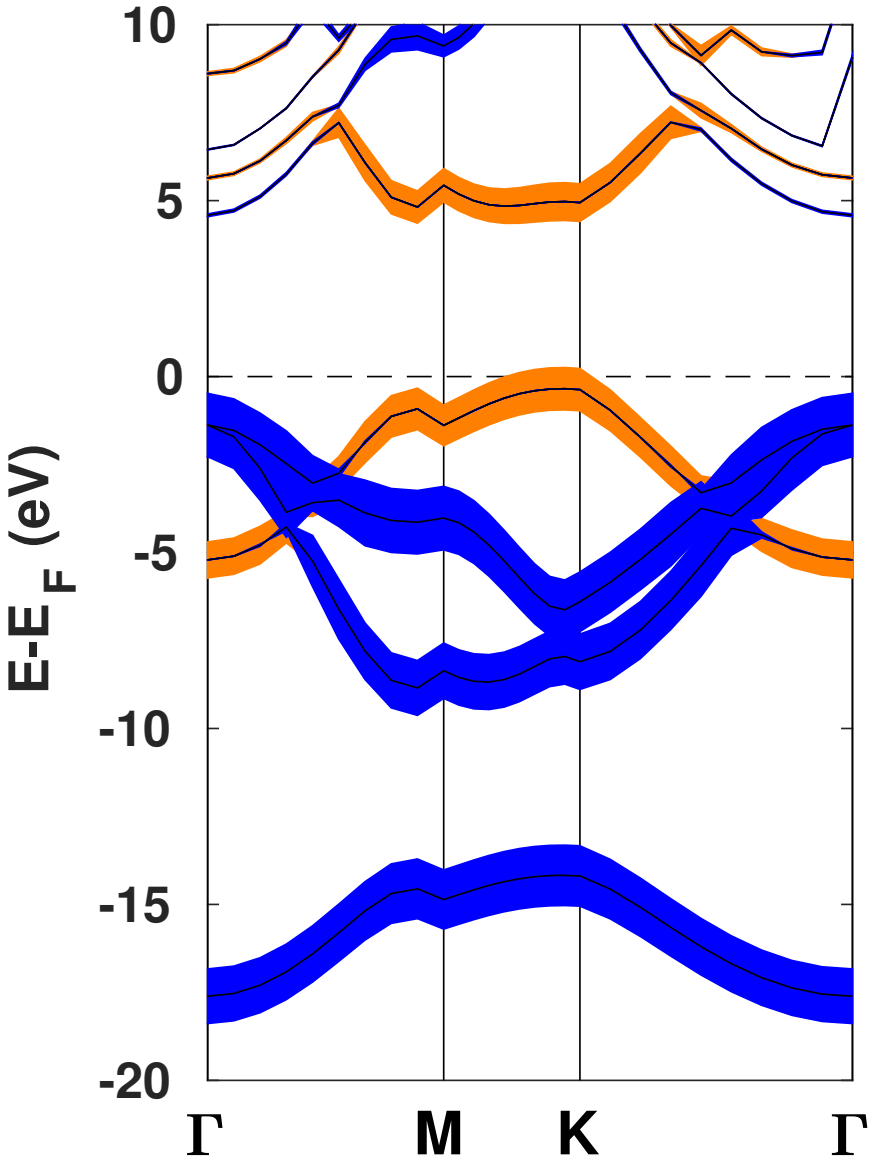


Pristine Graphene & h-BN



- Crystalline lattice of graphene and h-BN. Hexagonal. Ideal 2D systems.
- Band structure of graphene unit cell. 2 atoms. sp^2 hybdrization. σ states (in-) and π states (out of plane).

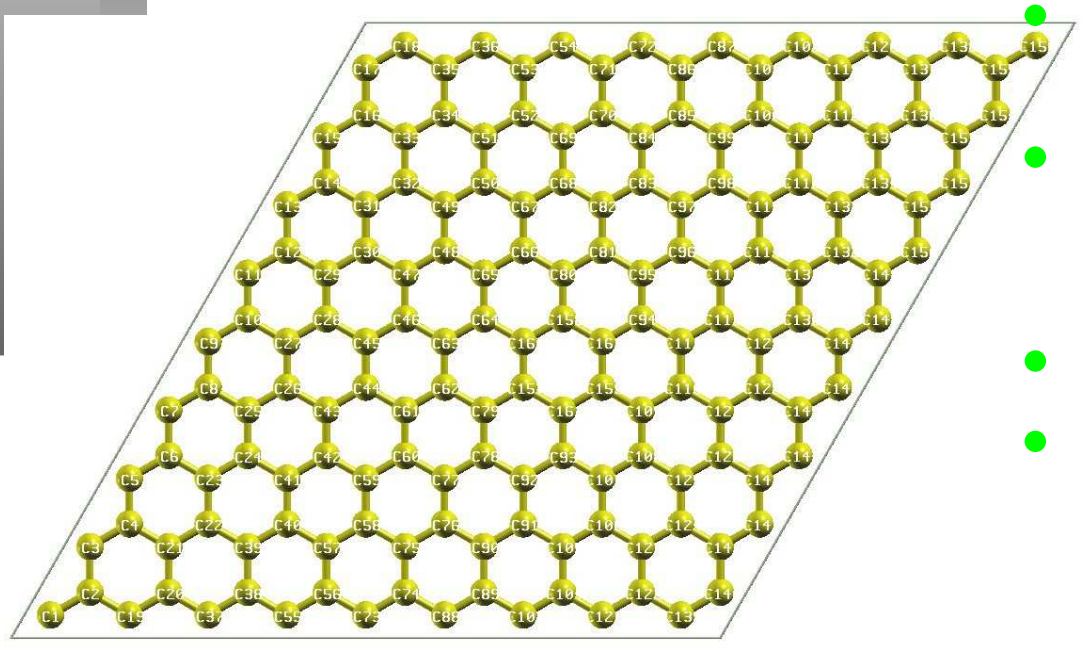
Pristine Graphene & h-BN



- Crystalline lattice of graphene and h-BN. Hexagonal. Ideal 2D systems.
- Band structure of graphene unit cell. 2 atoms. sp^2 hybdrization. σ states (in-) and π states (out of plane).
- Band structure of h-BN. 2 atoms.

Pristine Graphene & h-BN

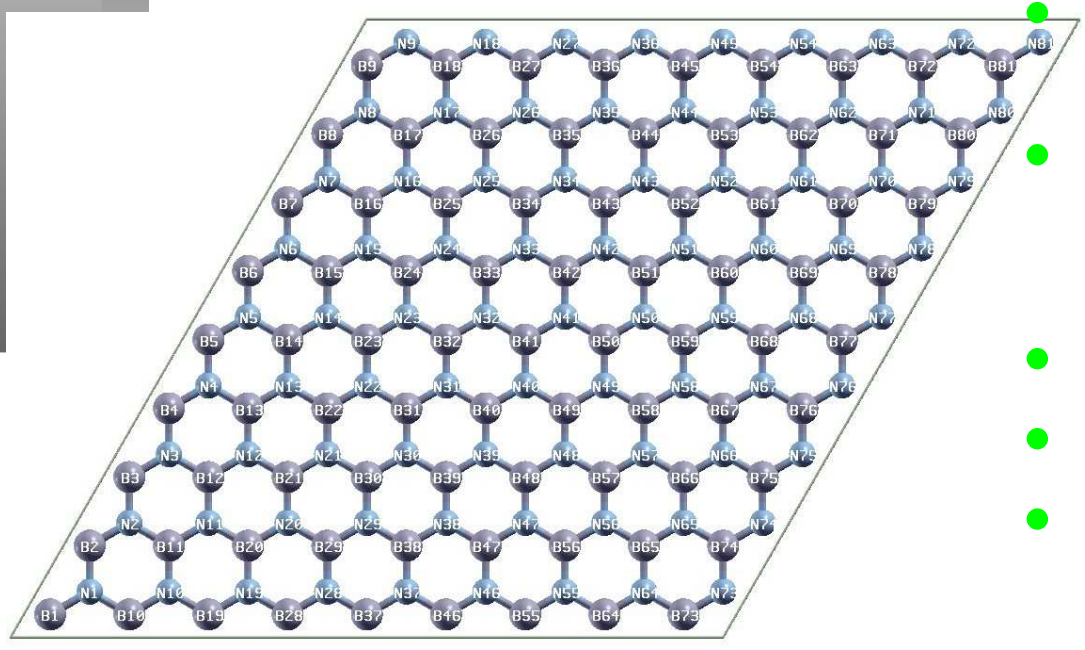
Pristine Structures Working Cell



- Crystalline lattice of graphene and h-BN. Hexagonal. Ideal 2D systems.
- Band structure of graphene unit cell. 2 atoms. sp^2 hybdrization. σ states (in-) and π states (out of plane).
- Band structure of h-BN. 2 atoms.
- Graphene super cell. 162 atoms.

Pristine Graphene & h-BN

Pristine Structures Working Cell

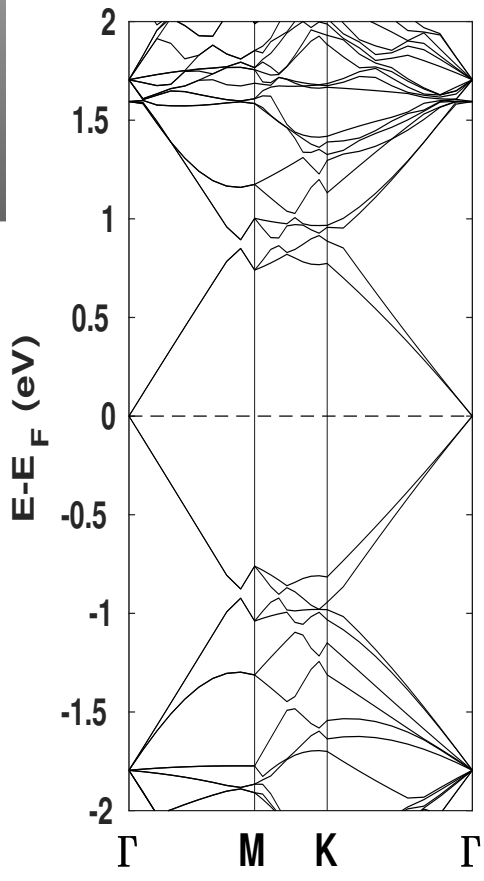


- Crystalline lattice of graphene and h-BN. Hexagonal. Ideal 2D systems.
- Band structure of graphene unit cell. 2 atoms. sp^2 hybdrization. σ states (in-) and π states (out of plane).
- Band structure of h-BN. 2 atoms.
- Graphene super cell. 162 atoms.
- h-BN super cell. 162 atoms.

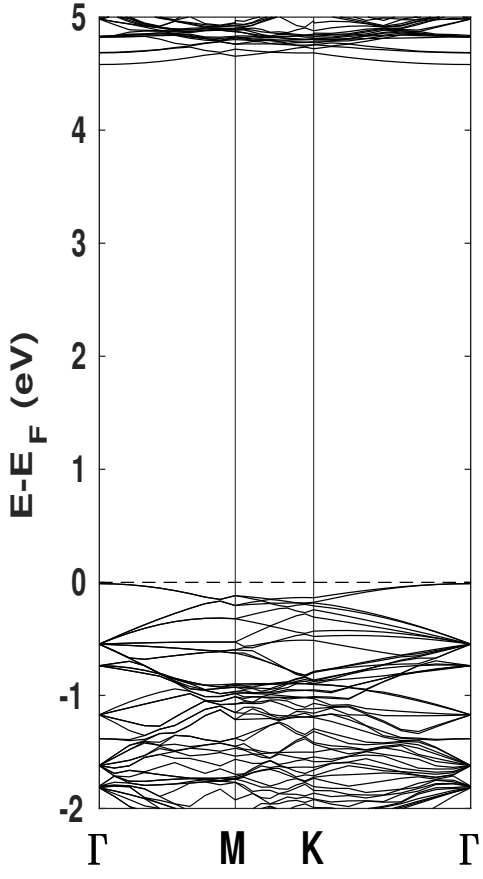
Pristine Graphene & h-BN

Pristine Structures Electronic Bands

Graphene



h-BN



- Crystalline lattice of graphene and h-BN. Hexagonal. Ideal 2D systems.
- Band structure of graphene unit cell. 2 atoms. sp^2 hybdrization. σ states (in-) and π states (out of plane).
- Band structure of h-BN. 2 atoms.
- Graphene super cell. 162 atoms.
- h-BN super cell. 162 atoms.
- Band structures of pristine systems.
  - Graphene: Semimetal
  - h-BN: Direct band gap of 4.6 eV

h-BN hexagonal island in graphene layout

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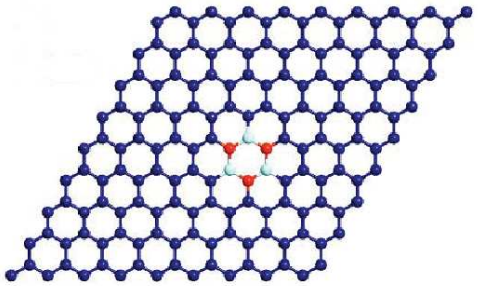
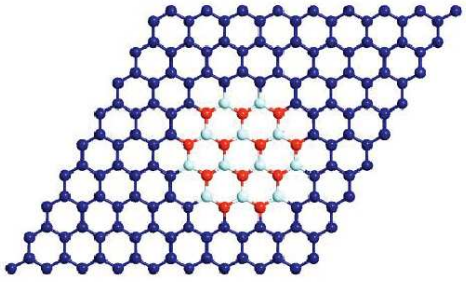
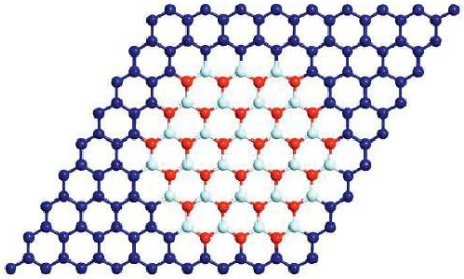
Xh-BN(H)@G; Increasing Island Size X=1,7,19



$C_{156}B_3N_3$



$C_{138}B_{12}N_{12}$



$C_{108}B_{27}N_{27}$

Table 1: Formation energies (Eqn. 4). Electronic and magnetic properties.

Hybrid	Name	$\mathcal{E}_{\mathrm{f}_{\min}}$ (eV)	$\mathcal{E}_{\mathrm{f}_{\max}}$ (eV)	ΔE_M (meV)	E_g (eV)	μ (μ_B)
$C_{156}B_3N_3$	1h-BN(H)@G	-6.65	7.27	-18.0	0.17	NM
$C_{138}B_{12}N_{12}$	7h-BN(H)@G	-6.92	7.01	-19.0	0.47	NM
$C_{108}B_{27}N_{27}$	19h-BN(H)@G	-7.01	6.92	0.4	0.82	NM

Formation energies could be even exothermic. Nonmagnetic. Increasing E_g.

Graphene and h-BN sheets with mono vacancy I

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Pristine Working Cell Structures with Mono Vacancy

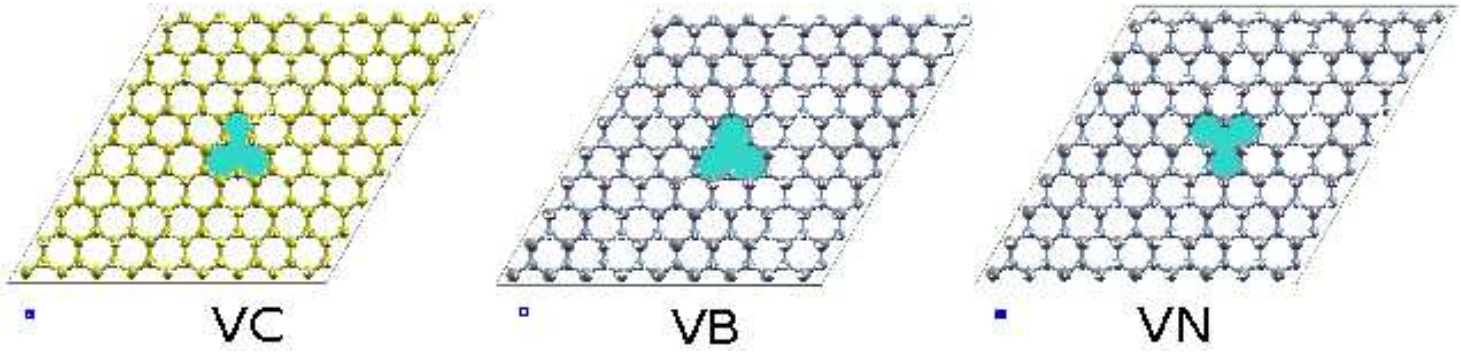


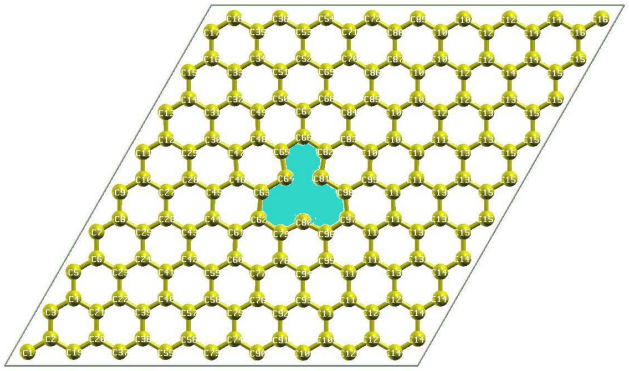
Table 2: Defect formation energies (Eqn. 5). Electronic and magnetic properties.

System	Name	E_{total} (eV)	E_{form} (eV)	ΔE_M (meV)	E_g (eV)	μ (μ_B)
C_{162}	pristine	-1496.12	-	-3.2	semi-metal	NM
C_{161}	VC	-1479.28	7.60	77.5	metallic	0.4
$B_{81}N_{81}$	pristine	-1431.56	-	0.4	4.59	NM
$B_{80}N_{81}$	VB	-1414.72	10.16	381.4	0.30	1
$B_{81}N_{80}$	VN	-1415.51	7.72	128.9	1.79	1

Induced magnetism.

Graphene and h-BN sheets with mono vacancy II

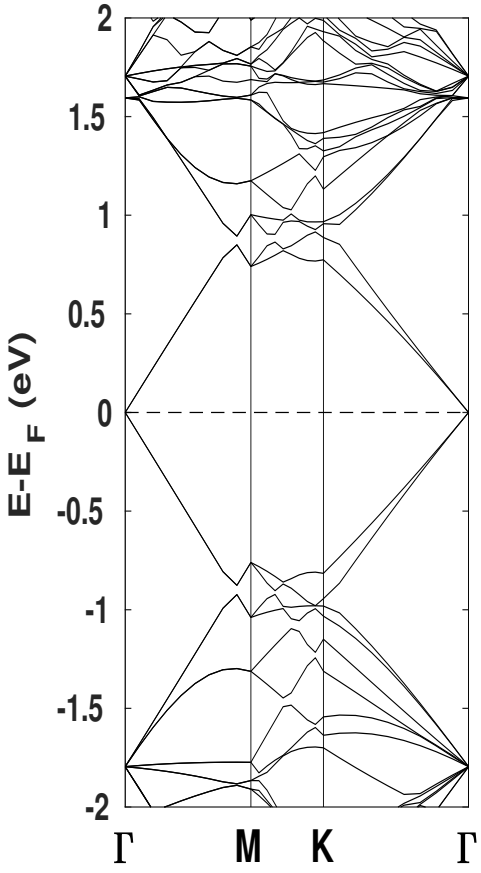
Carbon vacancy graphene



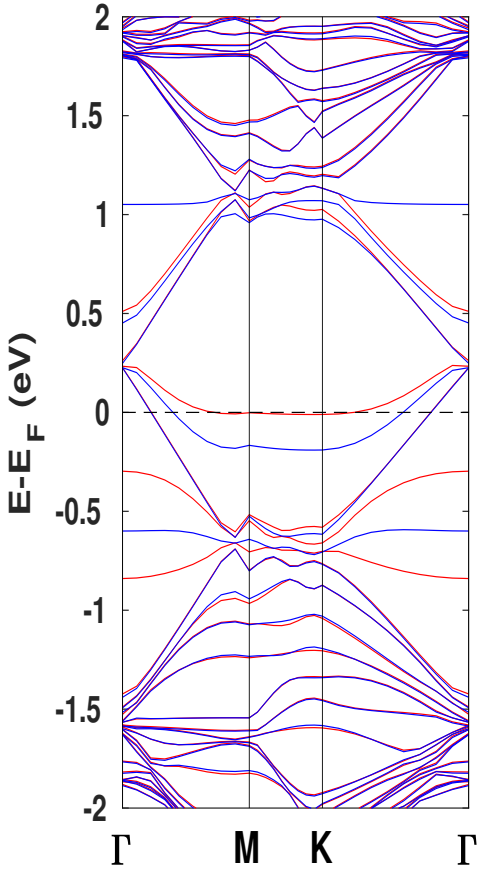
Decrease in Fermi energy, E_F level. Spin splitting. Small ΔE_M. Metallic.

Electronic Band Structures

Graphene

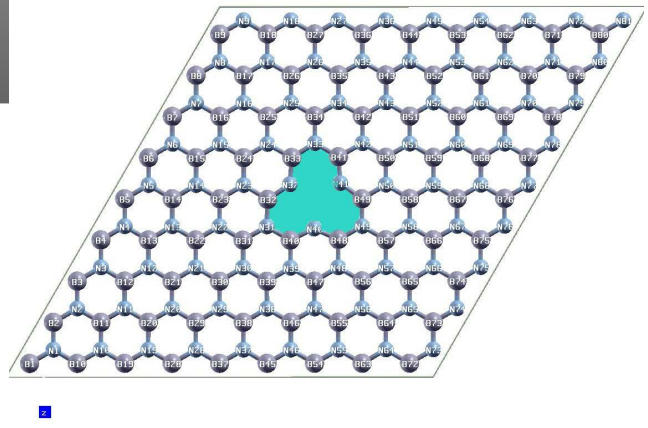


Carbon Vacancy



Graphene and h-BN sheets with mono vacancy III

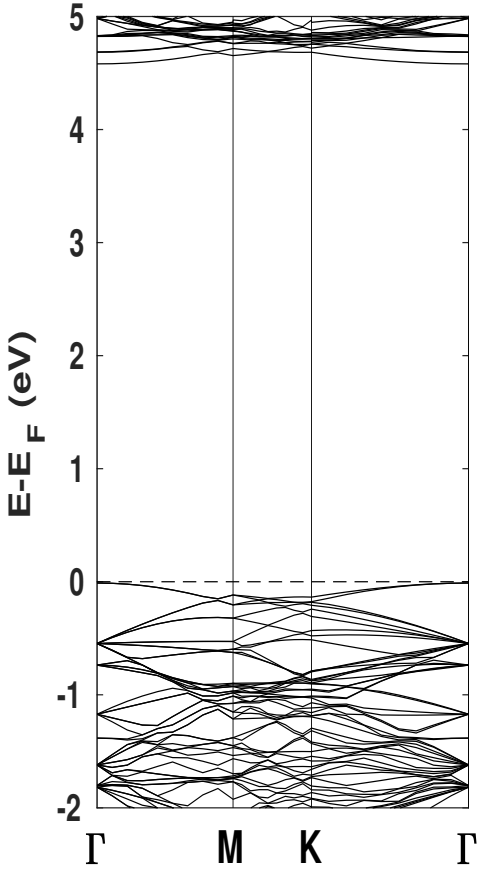
Boron vacancy h-BN



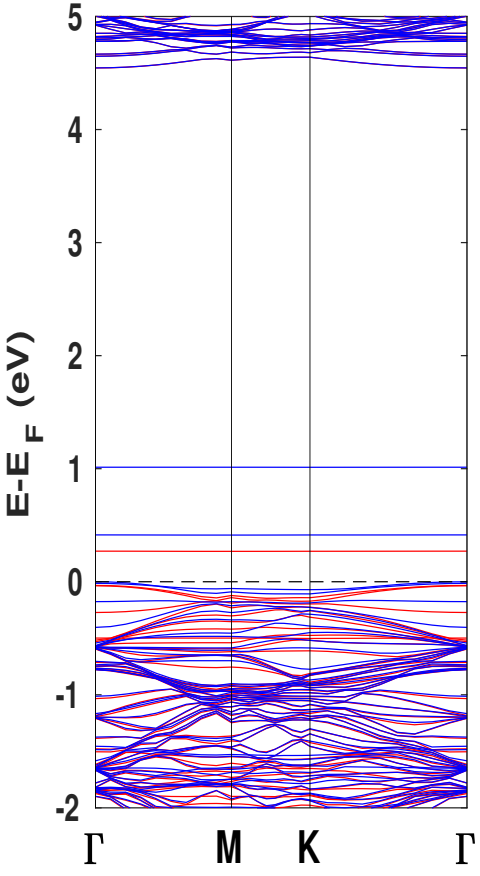
Decrease E_F level. Spin splitting. Large ΔE_M. Stable Magnetism. E_g=0.30 eV.

Electronic Band Structures

h-BN



Boron Vacancy



Graphene and h-BN sheets with mono vacancy IV

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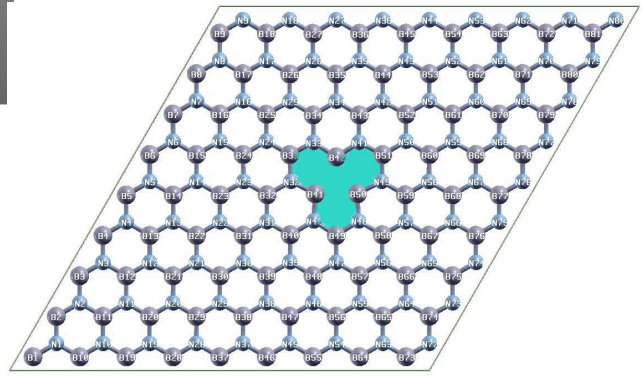
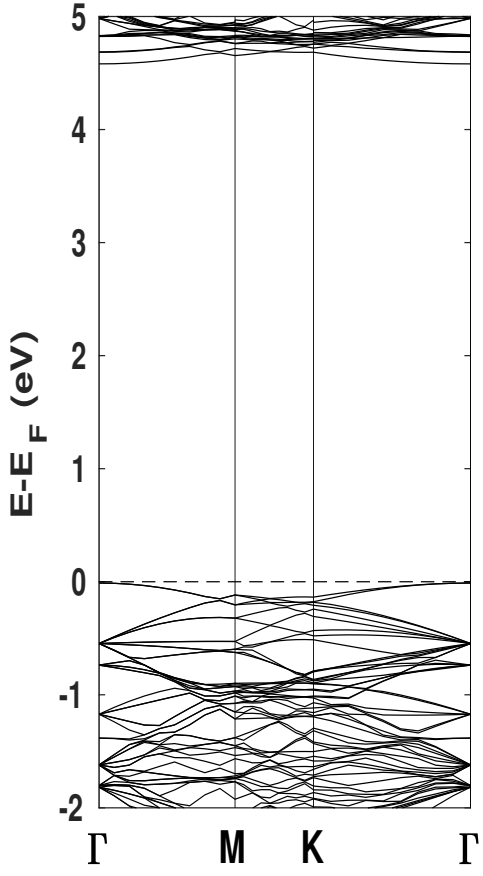
Nitrogen vacancy h-BN



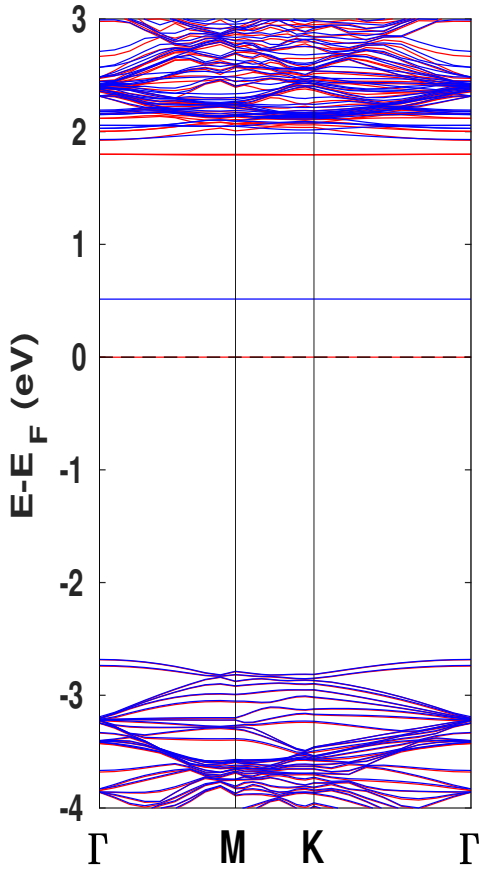
Increase E_F level. Spin splitting. Moderate ΔE_M. Magnetism. E_g=1.79 eV.

Electronic Band Structures

h-BN



Nitrogen Vacancy



h-BN hexagonal island in graphene layout with mono vacancy I

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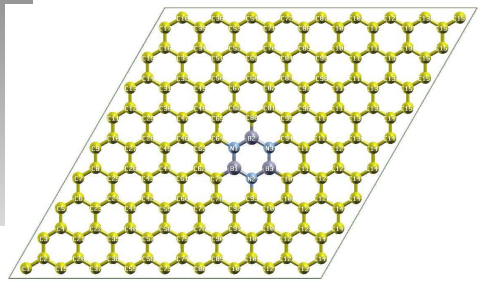
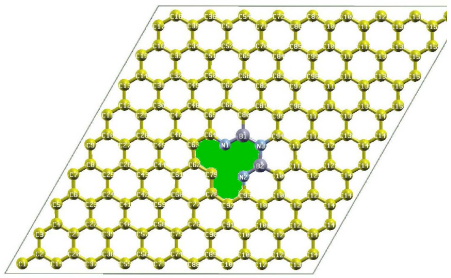
- "Interface, Layout and Island". Ten possibilities.
  - VB_I: Boron mono vacancy at the interface
  - VB_L: Boron mono vacancy in the layout
  - VB_i: Boron mono vacancy in the island
  - VC_{I1}: Removed a carbon bonding with B at the interface
  - VC_{I2}: Removed a carbon bonding with N at the interface
  - VC_L: Carbon mono vacancy in the layout
  - VC_i: Carbon mono vacancy in the island
  - VN_I: Nitrogen mono vacancy at the interface
  - VN_L: Nitrogen mono vacancy in the layout
  - VN_i: Nitrogen mono vacancy in the island

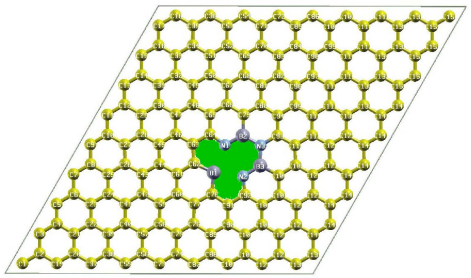
h-BN hexagonal island in graphene layout with mono vacancy II



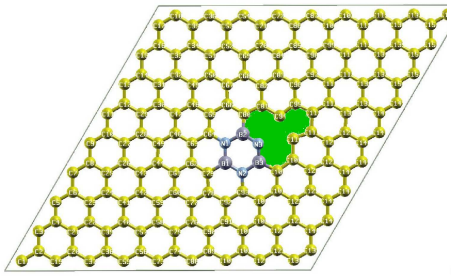
1h-BN(H)@G



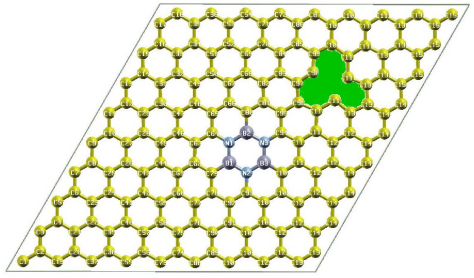
VB_I



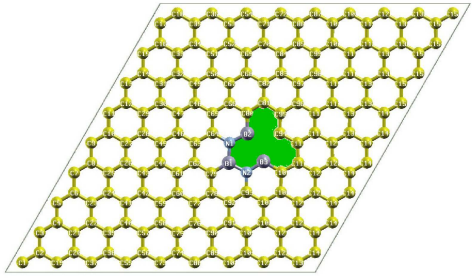
VC_{I1}



VC_{I2}



VC_L



VN_I

h-BN hexagonal island in graphene layout with mono vacancy II

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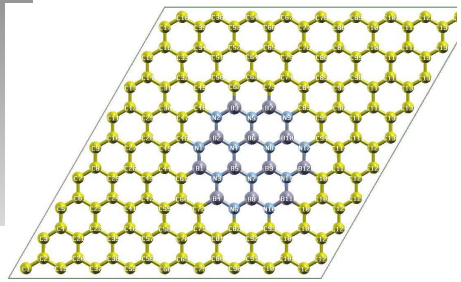
1h-BN(H)@G

Table 3: Defect formation energies (Eqn. 5). Electronic and magnetic properties.

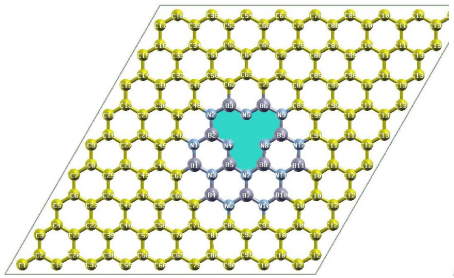
System	Name	E_{total} (eV)	E_{form} (eV)	ΔE_M (meV)	E_g (eV)	μ (μ_B)
$C_{156}B_3N_3$	1h-BN(H)@G	-1490.39	-	-17.5	0.17	NM
$C_{156}B_2N_3$	1h-BN(H-VB_I)@G	-1476.97	6.73	13.6	metallic	NM
$C_{155}B_3N_3$	1h-BN(H-VC_{I1})@G	-1476.00	5.15	28.4	metallic	NM
$C_{155}B_3N_3$	1h-BN(H-VC_{I2})@G	-1474.43	6.72	111.2	metallic	0.06
$C_{155}B_3N_3$	1h-BN(H-VC_L)@G	-1473.48	7.67	77.1	metallic	0.5
$C_{156}B_3N_2$	1h-BN(H-VN_I)@G	-1475.02	7.03	13.1	metallic	1

Metallic and Nonmagnetic.

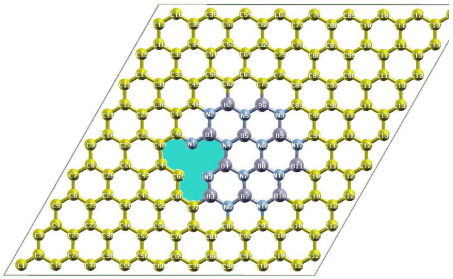
h-BN hexagonal island in graphene layout with mono vacancy III



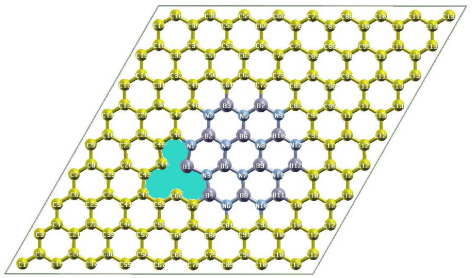
7h-BN(H)@G



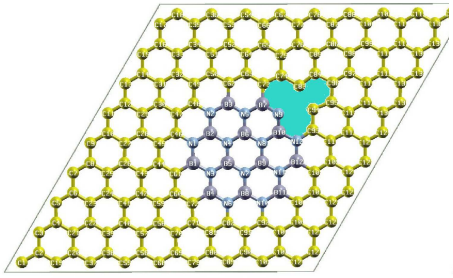
VB_i



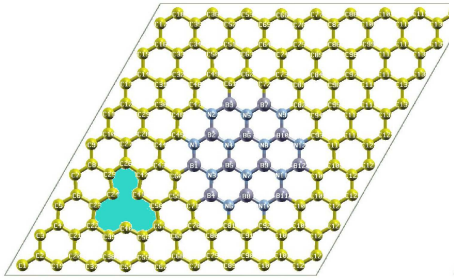
VB_I



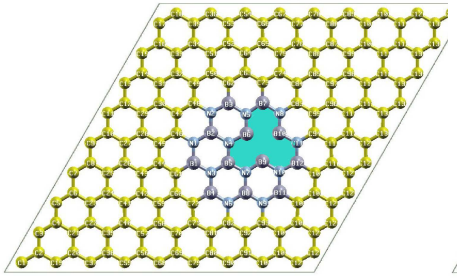
VC_{I1}



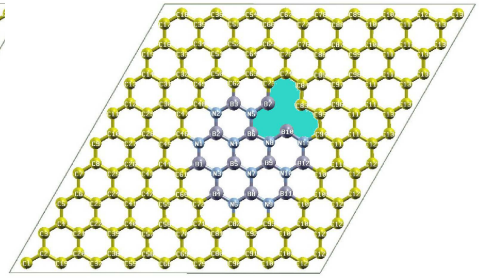
VC_{I2}



VC_L



VN_i



VN_I

h-BN hexagonal island in graphene layout with mono vacancy III

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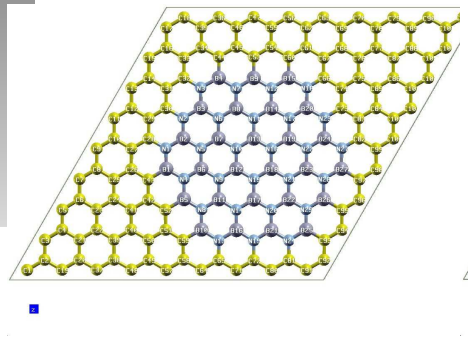
7h-BN(H)@G

Table 4: Defect formation energies (Eqn. 5). Electronic and magnetic properties.

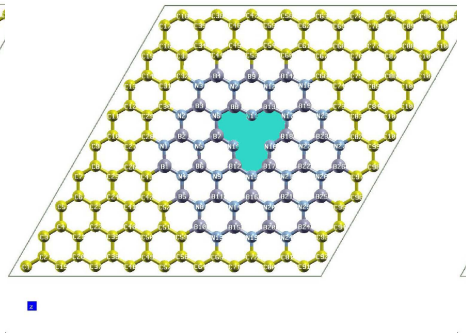
System	Name	E_{total} (eV)	E_{form} (eV)	ΔE_M (meV)	E_g (eV)	μ (μ_B)
$C_{138}B_{12}N_{12}$	7h-BN(H)@G	-1479.53	-	-19.4	0.47	NM
$C_{138}B_{11}N_{12}$	7h-BN(H-VB_i)@G	-1464.25	8.59	288.7	metallic	2
$C_{138}B_{11}N_{12}$	7h-BN(H-VB_I)@G	-1465.53	7.31	-4.5	metallic	NM
$C_{137}B_{12}N_{12}$	7h-BN(H-VC_{I1})@G	-1464.68	5.61	67.4	0.31	NM
$C_{137}B_{12}N_{12}$	7h-BN(H-VC_{I2})@G	-1463.40	6.89	426.9	metallic	NM
$C_{137}B_{12}N_{12}$	7h-BN(H-VC_L)@G	-1463.00	7.30	136.6	metallic	1.4
$C_{138}B_{12}N_{11}$	7h-BN(H-VN_i)@G	-1463.76	7.43	24.3	metallic	1
$C_{138}B_{12}N_{11}$	7h-BN(H-VN_I)@G	-1464.28	6.92	-3.3	metallic	0.8

Mostly Metallic and Nonmagnetic.

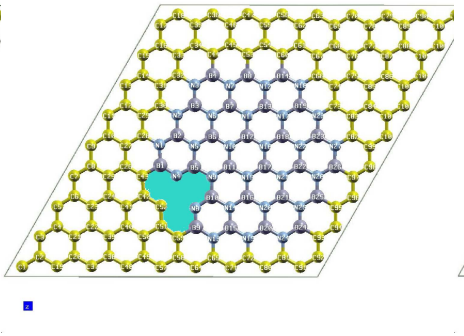
h-BN hexagonal island in graphene layout with mono vacancy IV



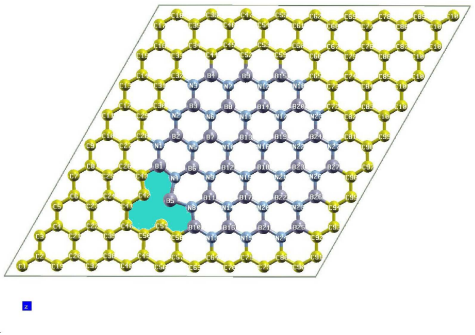
19h-BN(H)@G



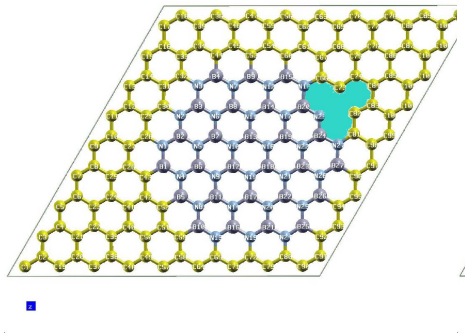
VB_i



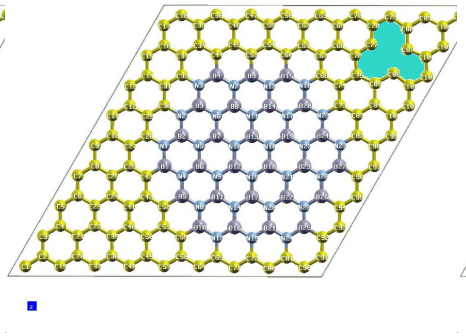
VB_I



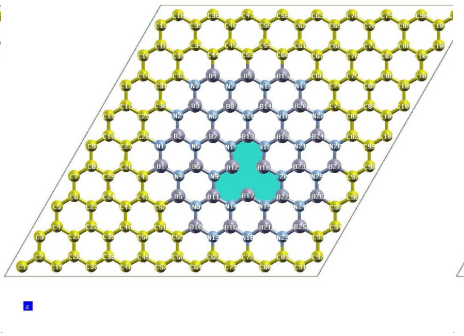
VC_{I1}



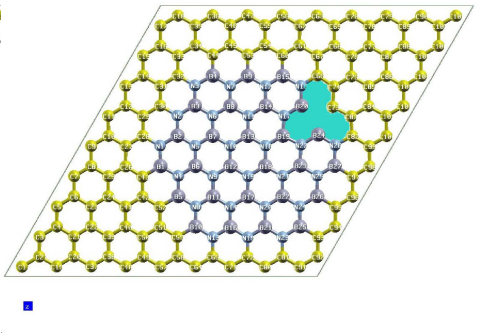
VC_{I2}



VC_L



VN_i



VN_I

h-BN hexagonal island in graphene layout with mono vacancy IV

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19h-BN(H)@G

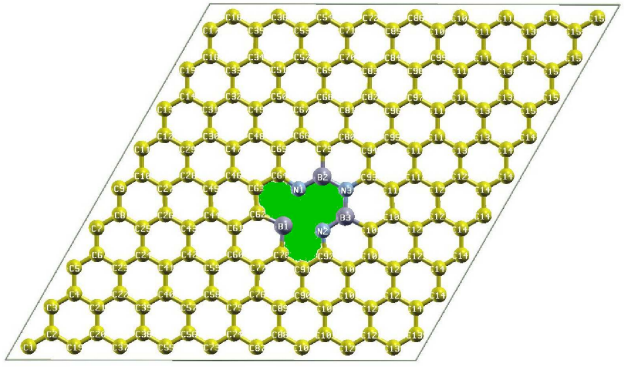
Table 5: Defect formation energies (Eqn. 5). Electronic and magnetic properties.

System	Name	E_{total} (eV)	E_{form} (eV)	ΔE_M (meV)	E_g (eV)	μ (μ_B)
$C_{108}B_{27}N_{27}$	19h-BN(H)@G	-1463.57	-	0.4	0.82	NM
$C_{108}B_{26}N_{27}$	19h-BN(H-VB_i)@G	-1447.83	9.06	537.8	metallic	2
$C_{108}B_{26}N_{27}$	19h-BN(H-VB_I)@G	-1448.65	8.23	8.2	0.79	0.7
$C_{107}B_{27}N_{27}$	19h-BN(H-VC_{I1})@G	-1448.37	5.96	63.5	0.55	NM
$C_{107}B_{27}N_{27}$	19h-BN(H-VC_{I2})@G	-1447.31	7.03	35	metallic	1
$C_{107}B_{27}N_{27}$	19h-BN(H-VC_L)@G	-1446.54	7.80	439.4	metallic	2
$C_{108}B_{27}N_{26}$	19h-BN(H-VN_i)@G	-1447.66	7.57	54.8	metallic	1
$C_{108}B_{27}N_{26}$	19h-BN(H-VN_I)@G	-1448.31	6.92	3.4	metallic	NM

Mostly Metallic and Induced Magnetism.

h-BN hexagonal island in graphene layout with mono vacancy V

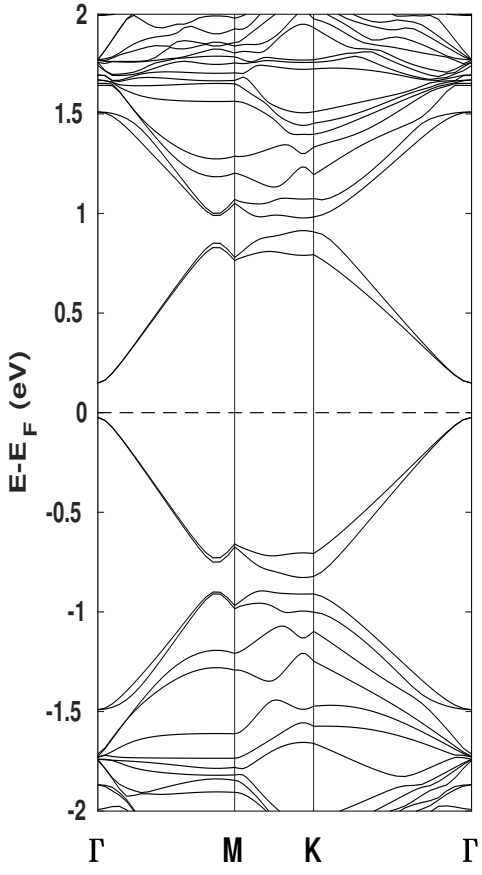
1h-BN(H-VC$_{I1}$)@G



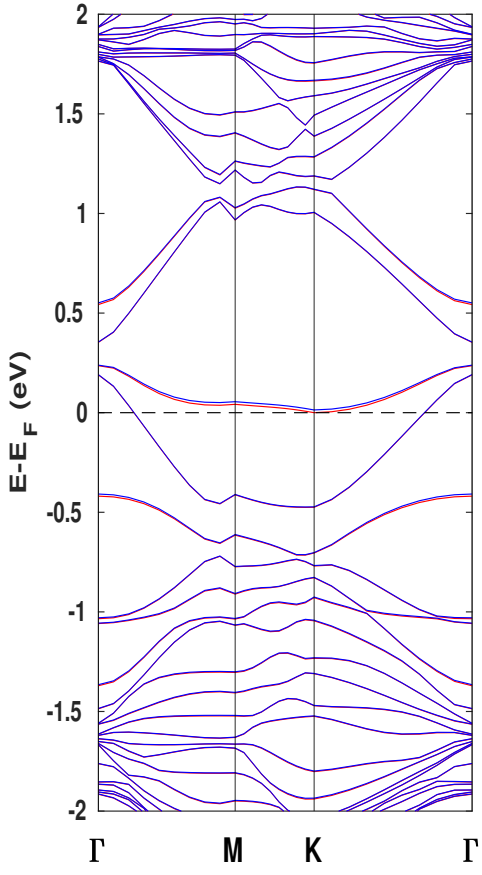
Decrease E_F level. No spin splitting. Small ΔE_M. No magnetic moment. Metallic.

Electronic Band Structures

Graphene

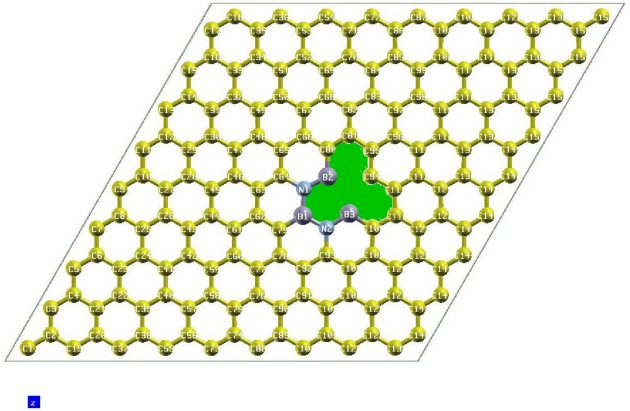


h-BN



h-BN hexagonal island in graphene layout with mono vacancy V

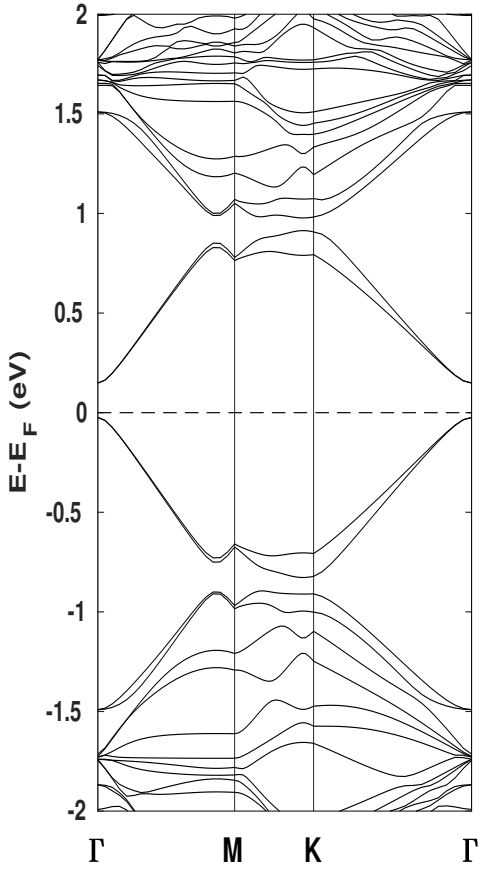
1h-BN(H-VN$_I$)@G



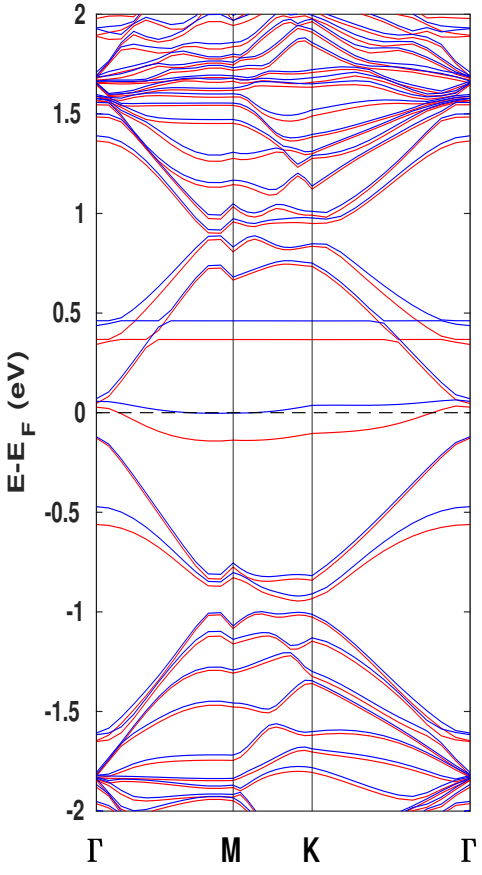
Increase E_F level. Spin splitting. Nearly flat bands. Small ΔE_M. Unlikely magnetism. Metallic.

Electronic Band Structures

Graphene



h-BN



h-BN hexagonal island in graphene layout with mono vacancy V

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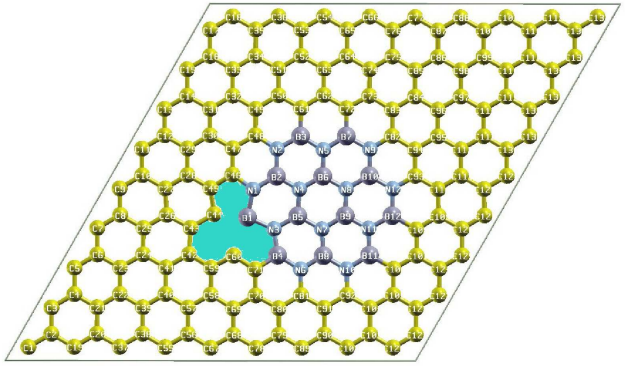
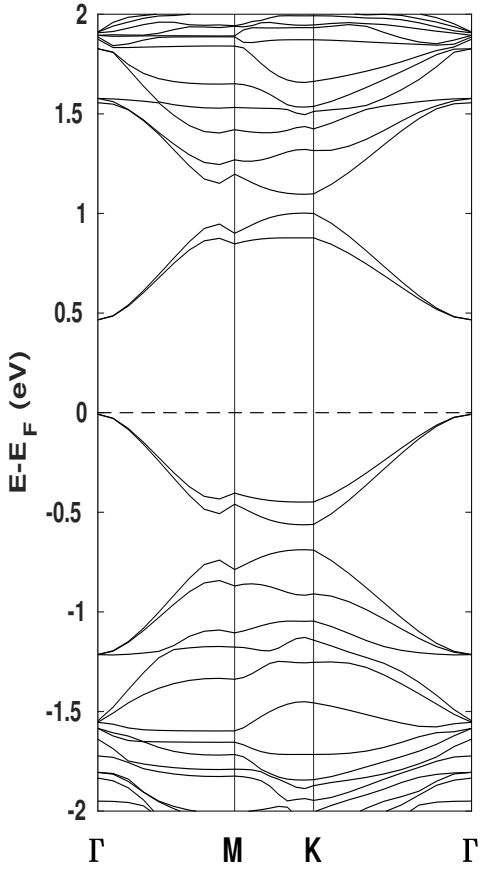
7h-BN(H-VC$_{I1}$)@G



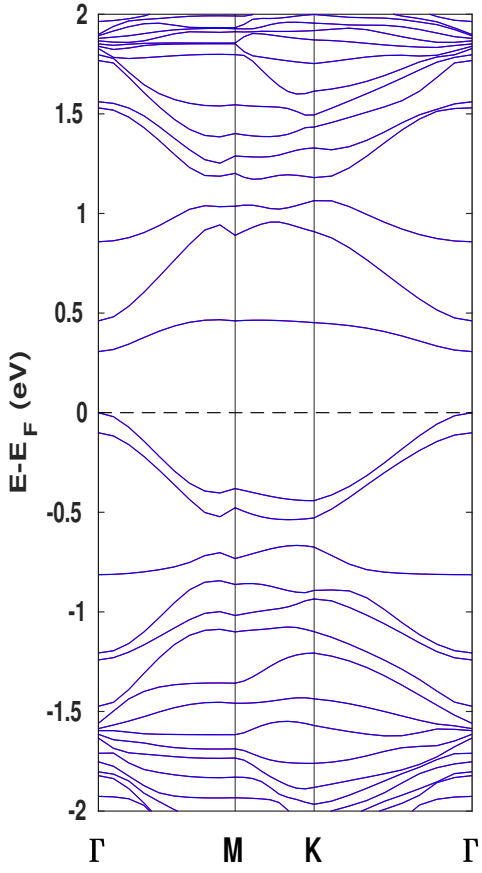
Not affecting E_F level. No spin splitting. Small ΔE_M. No magnetic moment. E_g=0.31 eV.

Electronic Band Structures

Graphene



h-BN



h-BN hexagonal island in graphene layout with mono vacancy V

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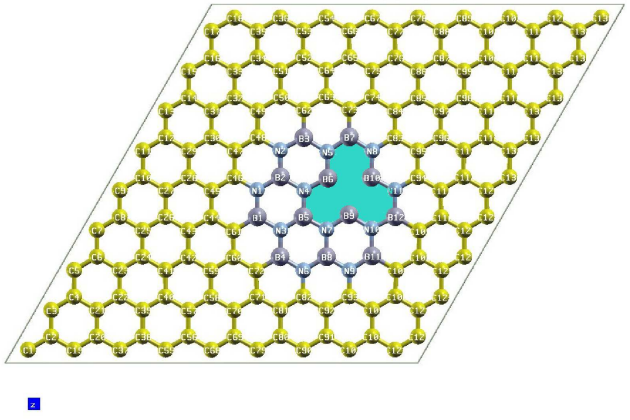
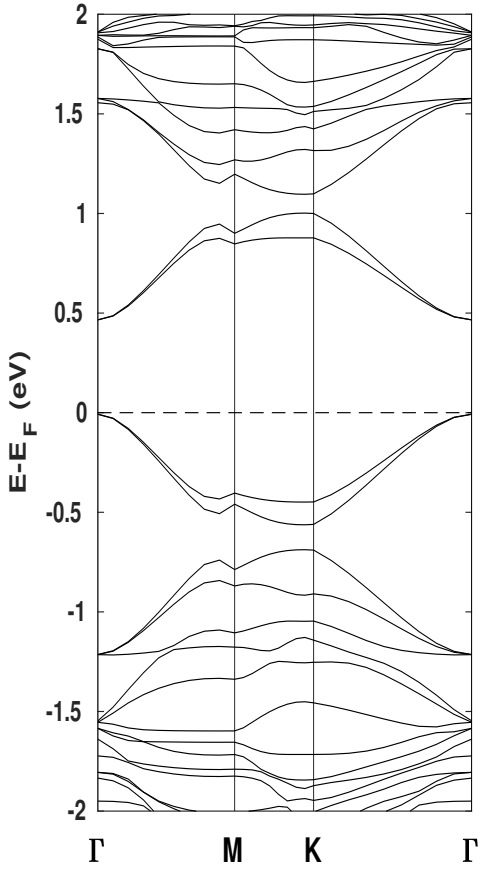
7h-BN(H-VN$_i$)@G



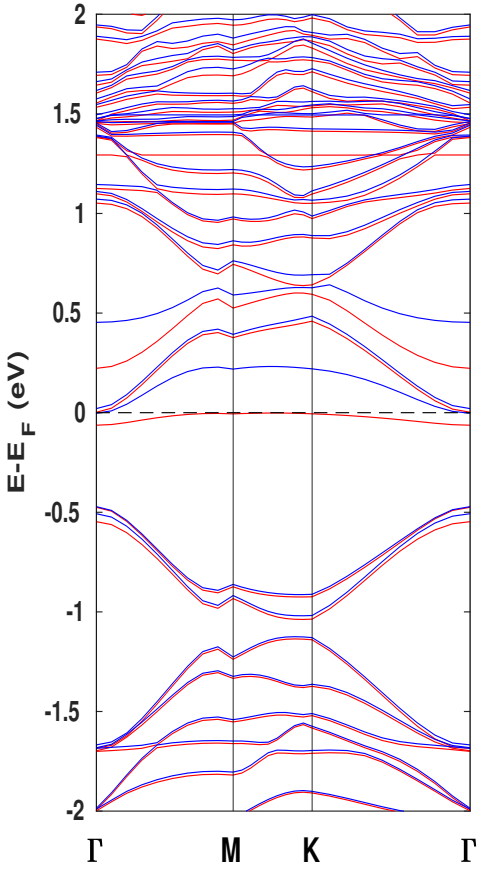
Increase E_F level. Spin splitting. Nearly flat band. Small ΔE_M. Unlikely magnetism. Metallic.

Electronic Band Structures

Graphene



h-BN



h-BN hexagonal island in graphene layout with mono vacancy V

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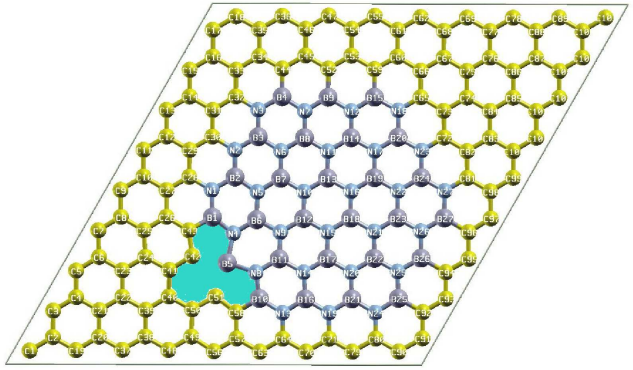
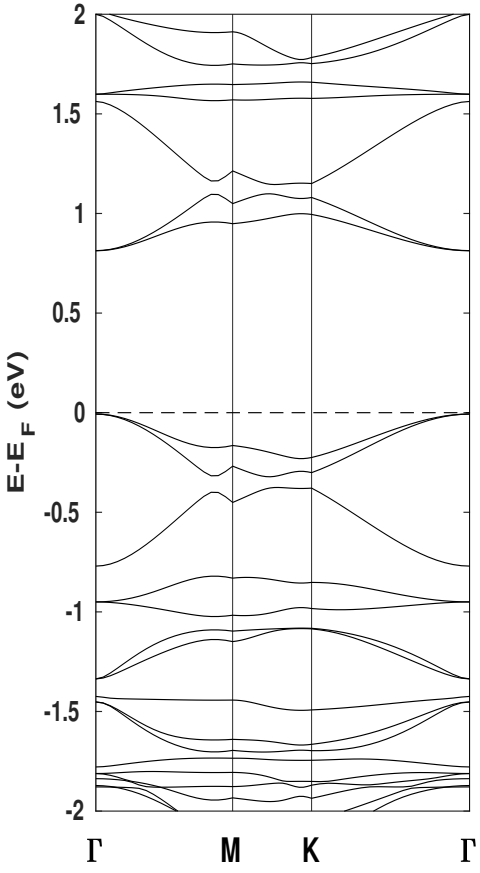
19h-BN(H-VC$_{I1}$)@G



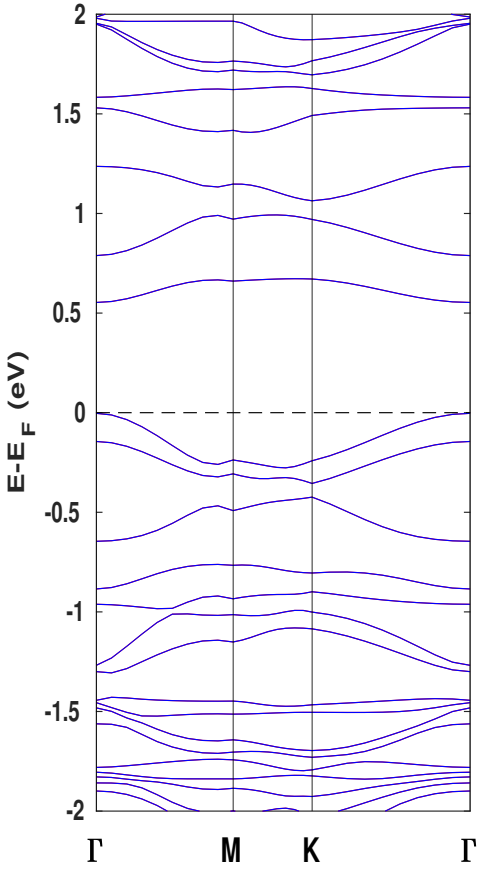
Not affecting E_F level. No spin splitting. Small ΔE_M. No magnetic moment. E_g=0.55 eV.

Electronic Band Structures

Graphene



h-BN



h-BN hexagonal island in graphene layout with mono vacancy V

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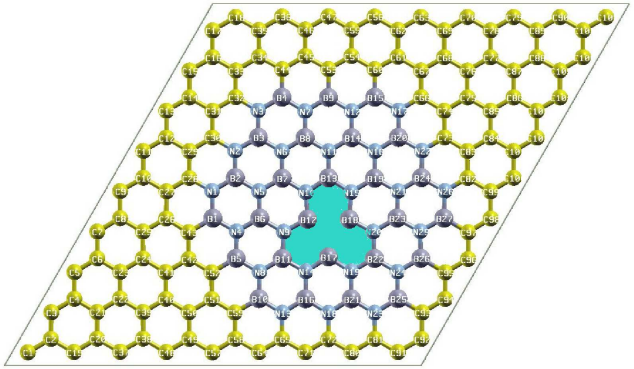
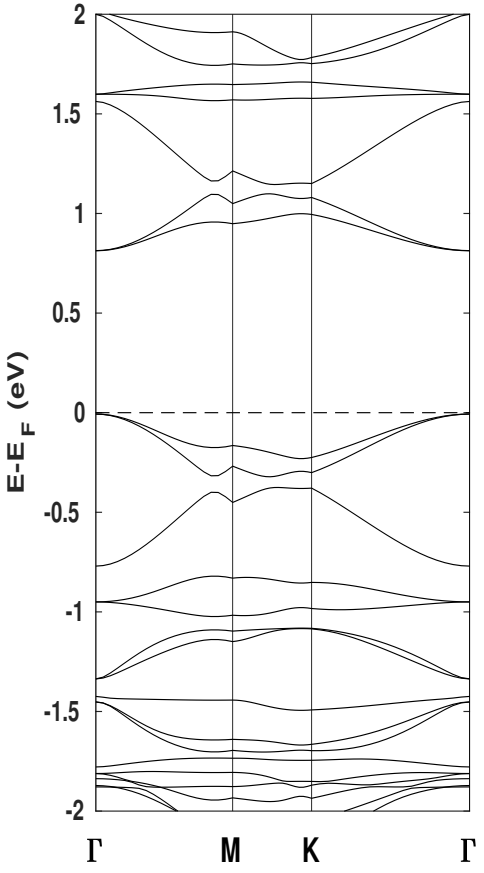
19h-BN(H-VN$_i$)@G



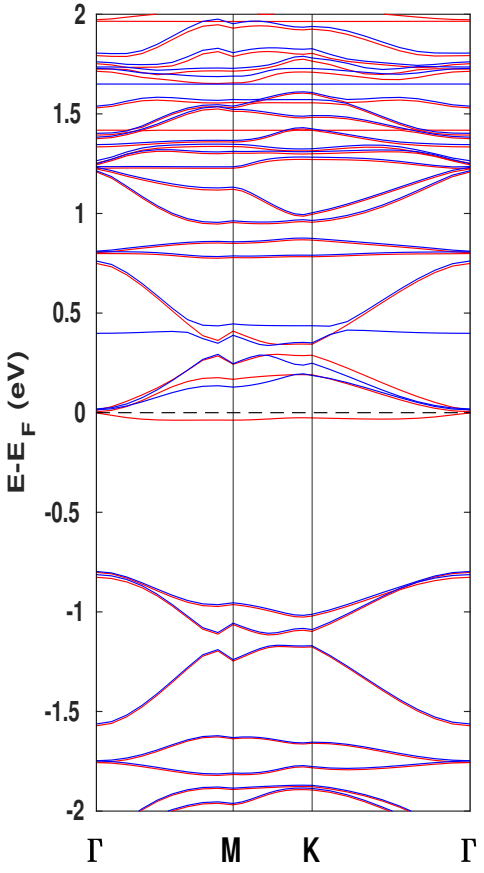
Increase E_F level. Spin splitting. Nearly flat band. Small ΔE_M. Unlikely magnetism. Metallic.

Electronic Band Structures

Graphene



h-BN



Summary I

- Energetics of implantation, defect formation, electronic, and magnetic properties of graphene-h-BN (GBN) 2D planar hybrids is analyzed through the DFT method.
- All relaxed GBN hybrids we studied here preserve their 2D planar geometry.
- Nonmagnetic ground states of hybrids including a hexagonal island display semiconducting properties.
- Their energy gaps E_g increase with increasing island size in the graphene layout.

Summary II

- We suggest that increasing the stability mainly depends on the number of atoms at the interface rather than the size of island.
- It seems to be possible that the nonmagnetic GBN hybrid can attain a stable magnetism when it includes a C, B or an N mono vacancy.

Akman, N., Özdoğan, C., Journal of Physics and Chemistry of Solids, **115**, 187 - 198 (2018).

Akman, N., Özdoğan, C., Journal of Magnetism and Magnetic Materials,(to be submitted).

Thanks

Thanks for your attention

Available at

http://boron.physics.metu.edu.tr/ozdogan/sunum/imstec2018.pdf