Ab initio study of graphene/hBN Van der Waals heterostructures: from bilayer to four layers coincidence lattices

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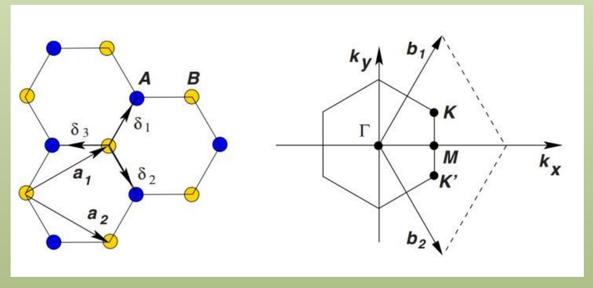
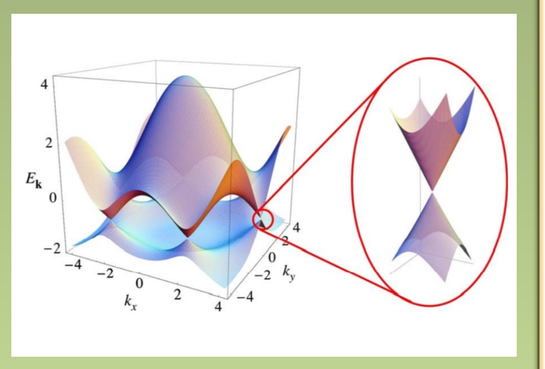
The aim of this work is to study, via DFT calculations performed with the Quantum ESPRESSO suite, VdW-heterostructures based on graphene and hexagonal boron nitride (hBN), two systems with a very similar crystal structure (they have almost the same lattice parameter), but with totally different electronic properties. The goal is to modify the optoelectronic properties of graphene. Starting from the monolayers, several VdW-heterostructures have been designed changing both the number of layers and their relative rotation angle in the structure. In particular, the attention has been focused on the bilayer phase (CBN-AB), the quadrilayer (CBNBNC), and the coincidence lattice achieved by twisting graphene on hBN by 21.8°. For all these systems stability analysis, structural relaxation and band structure calculation have been performed. We explore the changes induced by both the structural design and by the external environment, investigating the response to an external electric field. The calculations show a small but significant modification [1] of the optoelectronic properties of graphene and hBN when they are paired in a VdW-heterostructure, that results in particular in the opening of a tunable [2] band gap at the Dirac cones of graphene, even if the linearity of the bands still survives in a wide energy range.

Why graphene/hBN heterostructures



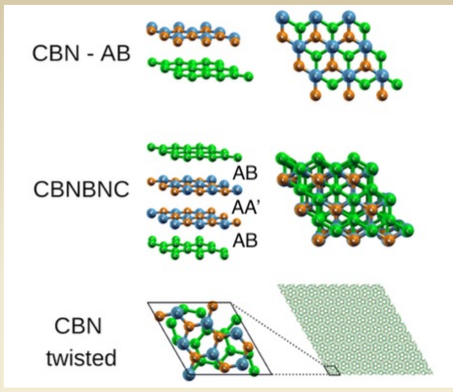
Stacking several layers in a VdW heterostructure allows to get new materials with structural and optoelectronic on-demand features. This possibility has been exploited to find a way to use graphene in photonics and nanoelectronics applications

Graphene shows fascinating thermal, mechanical and electronical properties. Nevertheless, due to the crystal honeycomb structure and the equivalence of the carbon sublattices, it is a zero-gap semiconductor with Dirac Cones at the K,K' points of the first Brillouin zone, preventing its application in semiconductor logic nanodevices. Involving graphene in VdW heterostructure is a powerful way to manipulate its electronic properties. The choice of hBN is based on the strong structural analogy with graphene.



Structure optimization

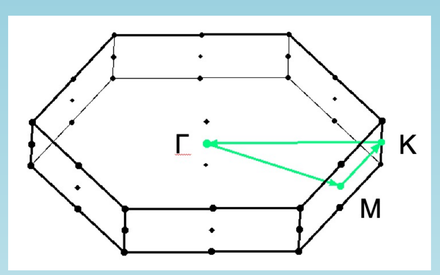
System	a(Å)	c(Å)	E_{st} (meV/atom)
Graphene	2.46		
hBN-ML	2.51		
2BN-AA'	2.52	3.55	-25.75
CBN-AB	2.49	3.25	-22.71
CBN-AB tw21.8	3.47	3.44	-20.20
CBNBNC	2.49	C-BN 3.28 BN-BN 3.26 BN-C 3.28	-38.03
CBNBNC tw21.8	3.47	C-BN 3.41 BN-BN 3.26 BN-C 3.37	-34.26

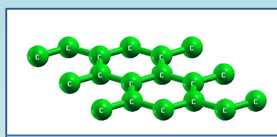
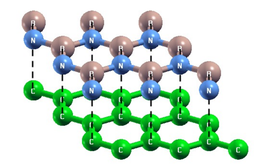


Using density functional theory (DFT) the crystal structures of several 2D graphene/hBN VdW heterostructure have been optimized. Starting from the monolayer we optimized the structure of the bilayer hBN-AA', CBN-AB and CBNBNC quadrilayer, calculating the minimum energy value of the lattice parameter *a(Å),* the interplanar distance *c(Å)* and the stacking energy of the structures. CBN and CBNBNC have been also studied in one of their twisted configuration (CBN-tw21.8 and CBNBNC-tw21.8) achieved rotating by a 21.8° angle the graphene layer on the BN layer. The negative sign of E_s for all the systems shows that these structures are experimentally achievable. The calculations have been performed using the QUANTUM ESPRESSO code [3] with the VdW-DF2-b86r [4] functional to take into account the Van der Waals interaction between the layers.

Brillouin zone and symmetry breaking

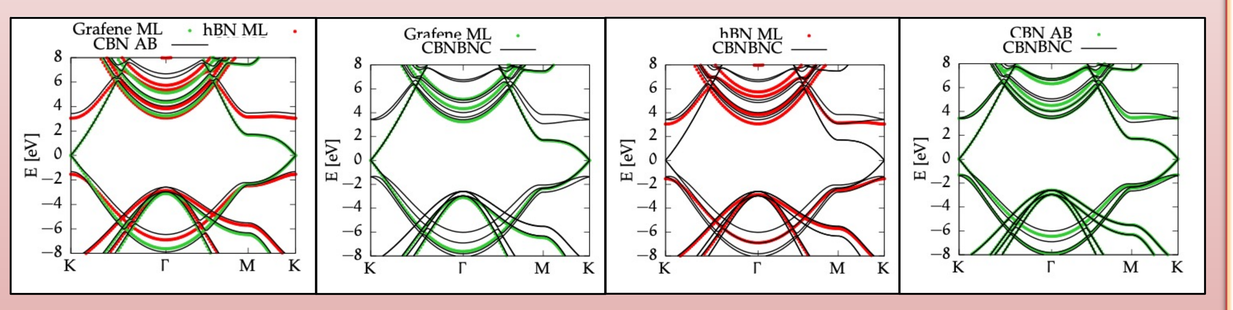
Brillouin zone of graphene and graphene/hBN VdW heterostructures. The green lines show the path K – Γ – M – K chosen for the band structure calculations. The attention is focused on the K point, where in graphene the Dirac cones are located.



	Graphene
	CBN-AB

The slightly different interaction between the C atoms in the graphene and the B and N atoms in the hBN layer breaks the equivalence of the two carbon sublattices, reducing the D6h symmetry of the isolated graphene to the C3v symmetry of che CBN bilayer. As a results a small gap opens at the K point of the 1BZ.

Band structure comparison

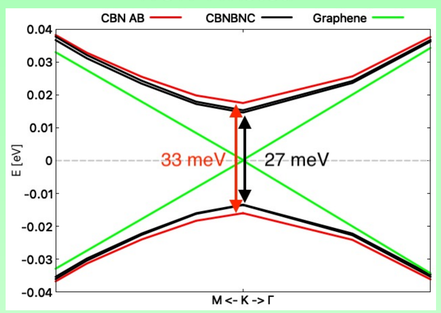


The plots show the overlay of the band structure of the bilayer CBN, the quadrilayer CBNBNC (black line), graphene (green dots) and hBN (red dots). There are clear analogies between the band structure of the multilayer and those of the starting monolayers. It is possible, in fact, to distinguish the different contributions of graphene and hBN in the energy states of CBN and CBNBNC. From this general view one can conclude that in a VdW heterostructure the band structure is qualitatively given by the overlap of the band structures of the starting monolayers

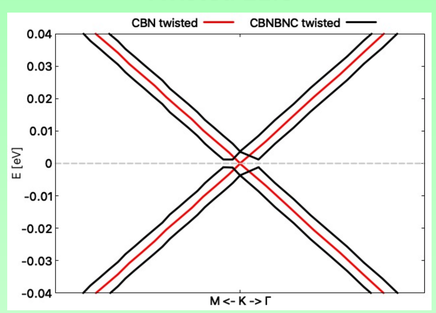
Gap opening in the multilayer band structures

Twist angle effect

NON Twisted



Twisted 21.8°

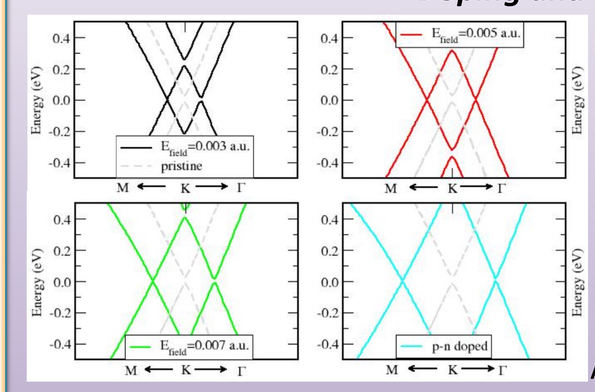


The different interaction between the C atoms and the B,N atoms in the hBN layers results in the opening of a small band gap in both the twisted and non twisted cases.

System	Twist angle	Band gap (meV)	C-BN dist c(Å)
CBN	no	33	3.25
CBN	21.8°	0.1	3.44
CBNBNC	no	27	3.28
CBNBNC	21.8°	2.4	3.37

In the non-twisted systems the band gap is larger than that of the twisted multilayer. This is a consequence of the different interplanar C-BN distance in all the structures. Non-twisted systems have smaller C-BN distance, resulting in a better overlap of the the p_z orbitals and hence a stronger C-BN VdW interaction. The bigger interplanar distances in the twisted systems make the C-BN interaction weaker, making the band structure of the multilayer very close to that of the isolated graphene.

Doping and Electric Field effect



CBNBNC	$E_{gap}^{(K)}$ [eV]	E_{gap}^{dir} [meV]	v_F [10^5 m/s]	
			M → K	K → Γ
Pristine	0.043	27	7.54	7.54
$\vec{E}$ 0.003	0.430	6.6	7.61	7.97
$\vec{E}$ 0.005	0.639	4.0	7.39	8.10
$\vec{E}$ 0.007	0.819	5.8	7.21	8.00
doped	1.245	7.3	6.69	7.81

A perpendicular electric field or a p-n doping on the carbon layers imply a compenetration of the Dirac cones of graphene in the band structure of the CBNBNC, with a small band gap opening close to the K point of the 1BZ. For three different value of the electric field and the p-n doped case the band gap and the Fermi velocity around the K point have been calculated.

Conclusions

- Coupling two or more graphene and hBN layers in a VdW heterostructure allows to manipulate the electronic properties of graphene
- The stacking sequence of the layers, twisting angles electric field and doping affect significantly the electronic properties of the multilayer

Future works

- Exploring different stacking sequences and twisting angles
- Study of the optical properties with polarizability and dielectric function calculations
- Study of the influence of excitonic effect

Bibliography

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