

# Supplementary material for “Unique Raman fingerprint of Boron Nitride Substitution Patterns in Graphene.”

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# Computational details

We utilize the periodic ab-initio code CRYSTAL14<sup>1</sup> and an all-electron Gaussian-type basis set, allowing us for the efficient use of the hybrid DFT-functional B3LYP, shown to outperform semilocal functionals like PBE in the prediction of band gaps and structures (Figure 1 shows that PBE-D2 catches on average 56% of B3LYP-D\*) as well as vibrational properties<sup>2-7</sup>. Additionally, we include electron correlation effects by means of Grimme’s empirical dispersion correction D2/D\*<sup>8,9</sup>.

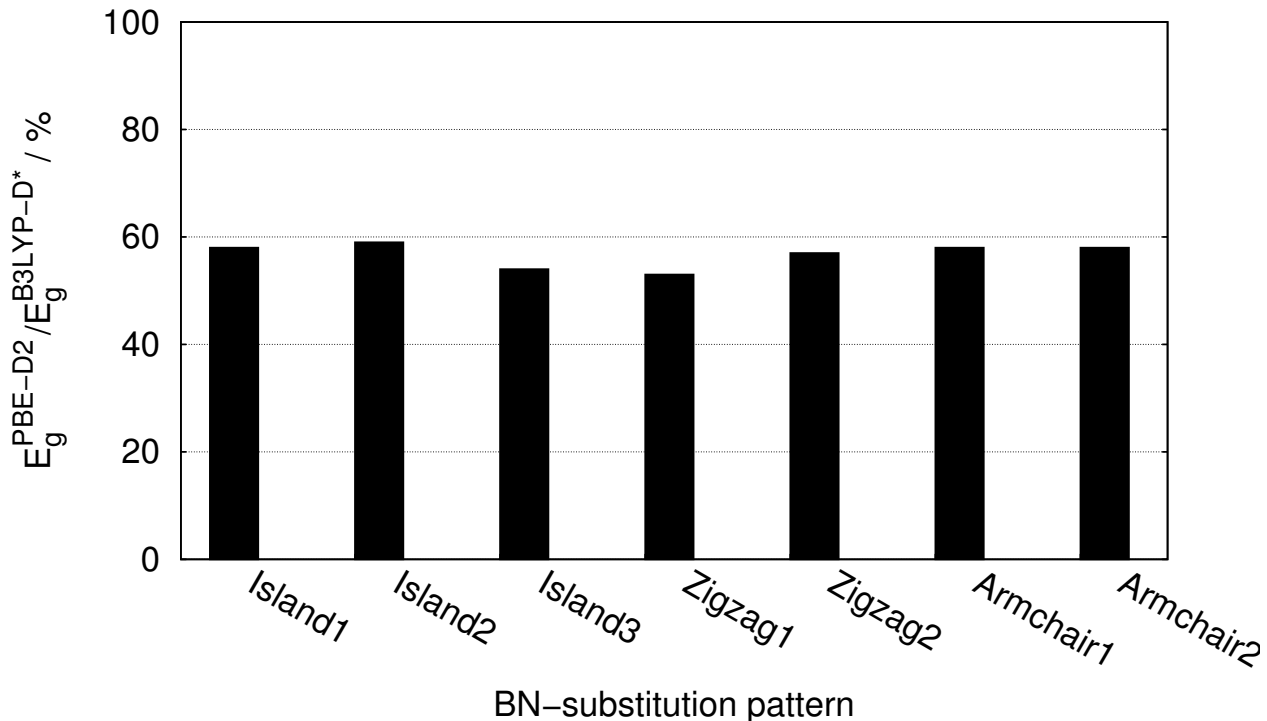
In Figure 3 we show the computed band structures and density of states (DOS) for the Armchair1 structure at 33% and 25% BN-substitutions. In the former, the bands on the path from  $\Gamma$  to  $M$  point and  $K$  to  $\Gamma$  drop down and close the gap while, for the latter, the topology of the pattern and the amount of BN lead to a band gap opening. The DOS around the Fermi level is in both cases dominated by carbon contributions.

Since the in-line patterns exhibit a dipole moment in the unit cell in periodic directions, we also investigated its influence on the band gap. At 25% BN-substitutions Zigzag1 and Armchair1 show a band gap of 1.30 and 1.85 eV, respectively. Zigzag3 (see Fig. ??) is a variation of Zigzag1, having a zero dipole moment. The band gap nearly vanishes (0.15 eV). Also the Armchair3 pattern has a zero dipole moment, and the band gap drops to 0.08 eV. The Armchair1 pattern also allows for different ways to zero the dipole moment, exploited in Armchair4 and Armchair5 patterns. They show a band gap of 0.75 and 1.53 eV, respectively, so that the dipole moment may play a role in increasing the band gap, but not a primary one. A conclusive dependency on the point group symmetry operators in direct space can also not be found: e.g. Zigzag1 and Zigzag3 both have the same single point symmetry operator in direct space but the band gap is completely different. The band structures and DOS of the Armchair patterns Armchair1, Armchair3, Armchair4 and Armchair5 show only slight differences. While in the first three systems the states around the band gap have mainly contributions from carbons, and the contributions from boron and nitrogen are close to zero, in Armchair5 there are substantial contributions from nitrogen to the HOMO and

from boron to the LUMO. In this case, the band gap is also slightly indirect.

When adding an underlying h-BN layer as a support to graphene, as shown in Figure ?? (b), the picture does not change much for small to intermediate amount of BN-substitutions. The band gaps are slightly increased from 2 to 10%. At 75% substitutions, the Island2 pattern does not show a decrease in the band gap with respect to 33% and 47% substitutions. At 50%, the Armchair1 pattern opens a band gap of 3.34 eV, only 0.02 eV higher than without a supporting h-BN layer. The effect of the h-BN support to band structure and DOS of Zigzag1 pattern is also tiny. There are virtually no states of h-BN mixing in the vicinity of the band gap. The band gap is slightly increased from 1.30 to 1.35 eV.

Figure 1: Average deviations of the band gaps obtained with semilocal PBE-D2 with respect to the hybrid B3LYP-D\* for different patterns.



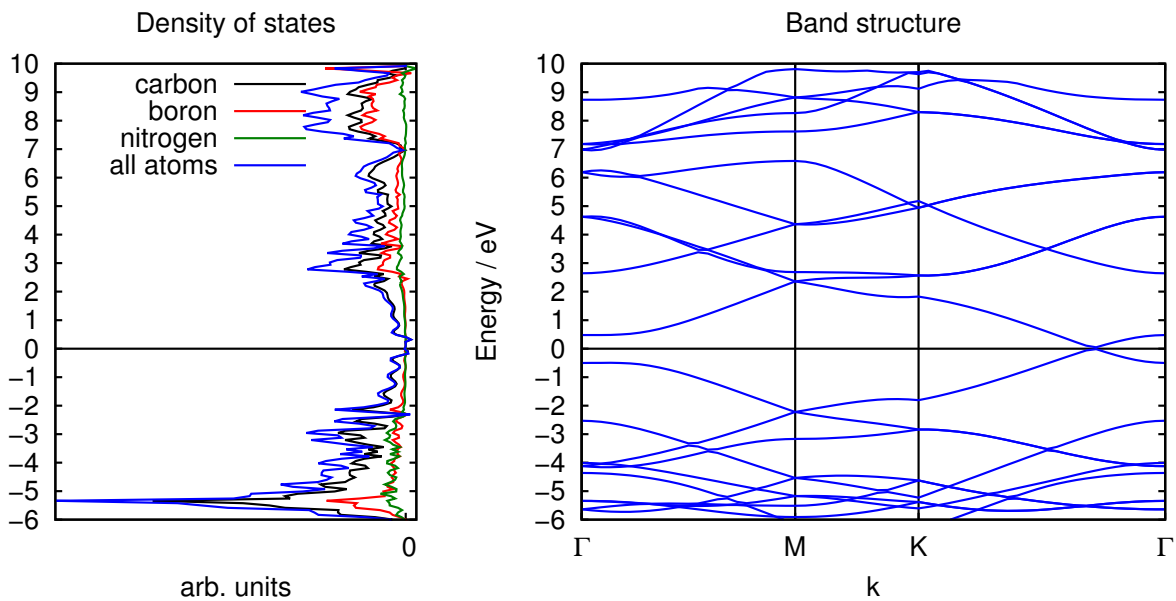
# Density of States and band structures

Density of States (DOSS) and band structures for different armchair and zigzag patterns as well as the Zigzag1 pattern supported by a layer of hexagonal BN (h-BN) are depicted in Figure 3.

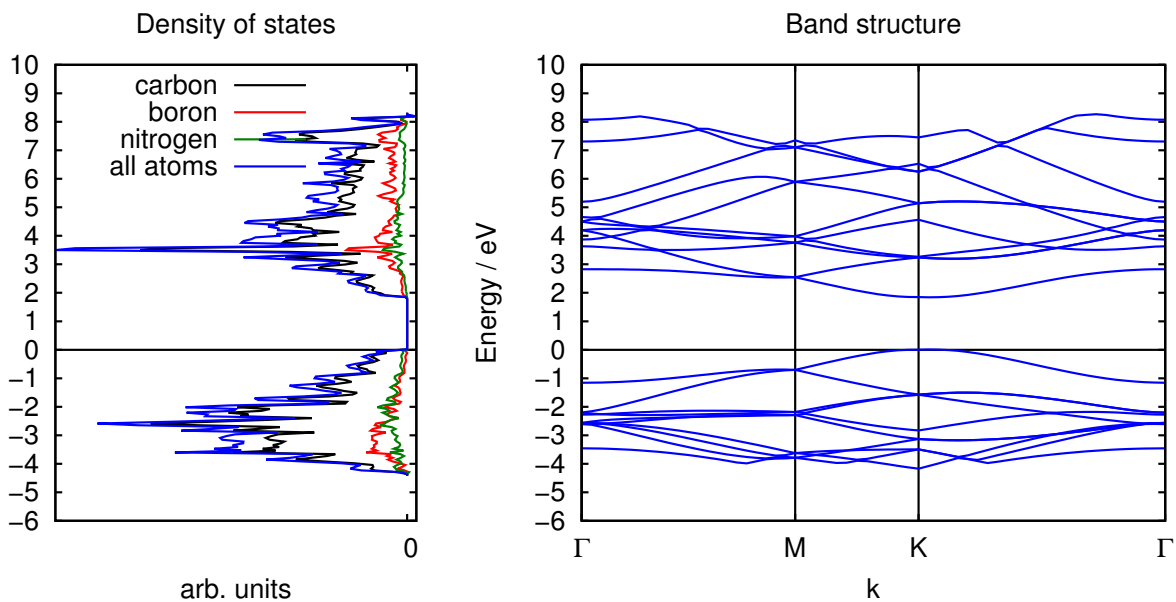
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Figure 2: Density of States (DOS) and band structures (21 bands) of Armchair1 BNsG at different amounts of BN substitutions.

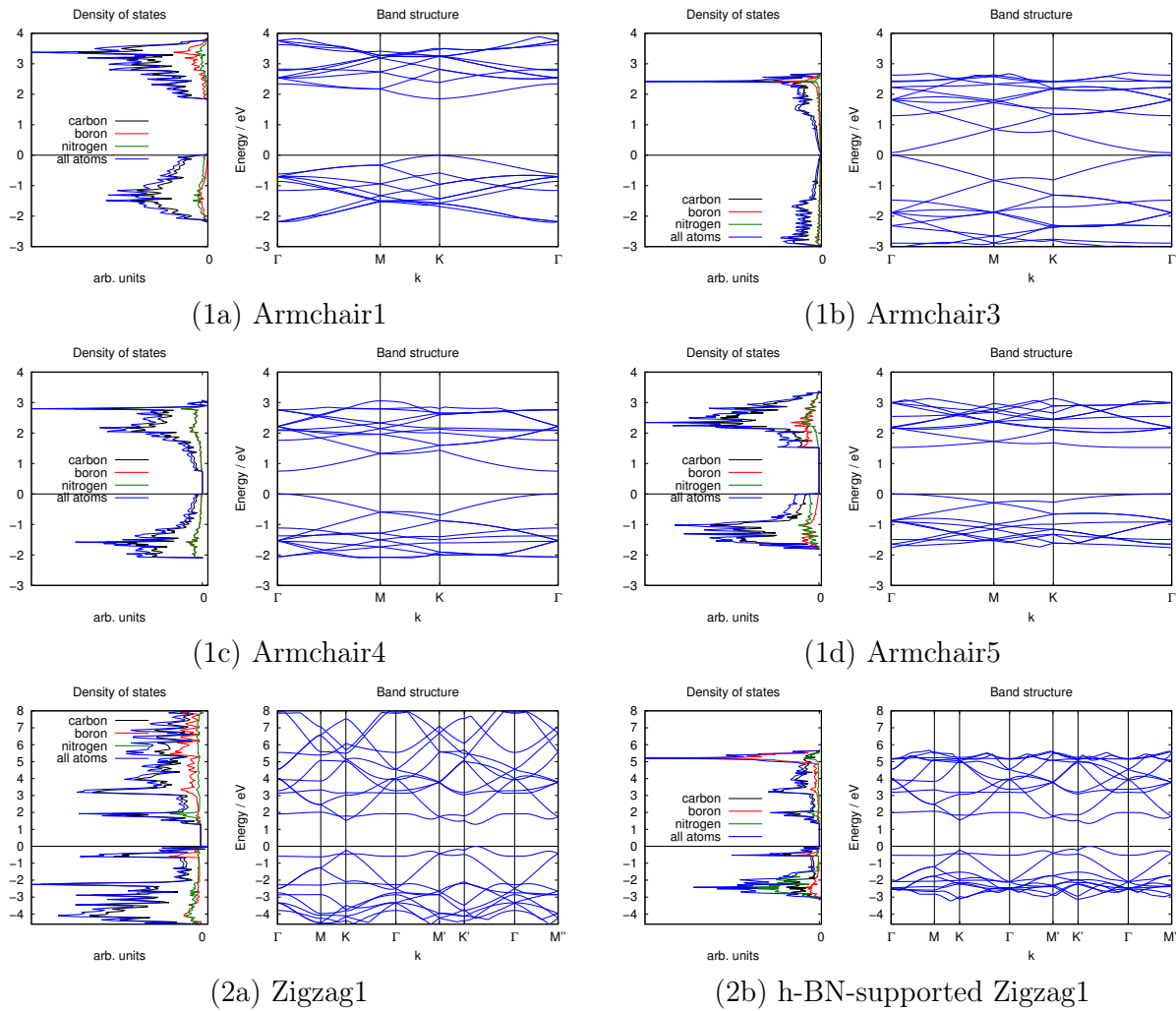


(a) Armchair1 at 33% BN-substitutions



(b) Armchair1 at 25% BN-substitutions

Figure 3: Density of States (DOSS) and band structures (21 bands) of different armchair (1a-1d) (using a 8x8 supercell) and zigzag patterns (2a, 2b) (using at 4x4 supercell) at 25% BN-substitutions without and with a supporting layer of h-BN.



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