Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Energetics, barriers and vibrational spectra of partially and fully hydrogenated hexagonal boron-nitride : **supplementary information**

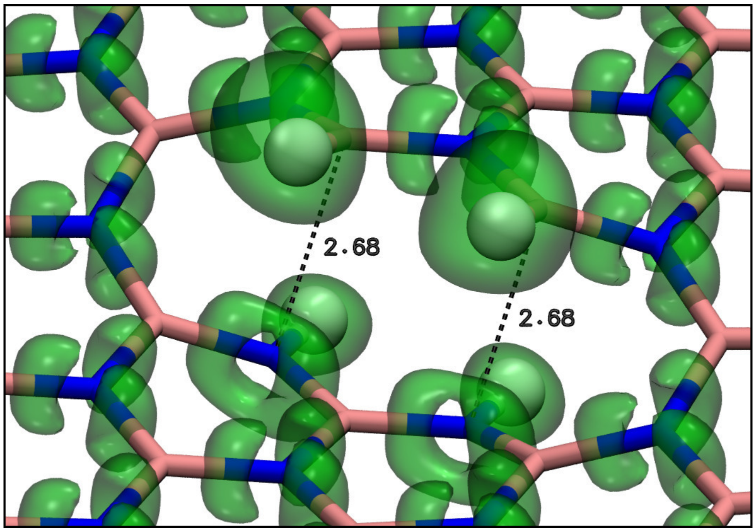
J.M.H. Kroes*, A. Fasolino, and M.I. Katsnelson

Radboud University, Institute for Molecules and Materials, Heijendaalseweg 135, 6525 AJ Nijmegen, The Netherlands.

Contents

S1 Configuration 4δ

Figure S1: The electron localization function (green) for the optimized structure of 4δ at an isovalue of 0.8. Notice the lack of density between BN atoms a distance of 2.68 Å, illustrative of the broken bonds



S2 Structural properties computed with CP2K and QE

Table S1: Comparison of structural properties and the electronic band gap for fully hydrogenated samples as calculated with CP2K or Quantum Espresso (QE)

pristine	CP2K	QE
#[B/N atoms per cell]	2	2
r_{BN}/Å	1.457	1.444
a / Å	2.524	2.502

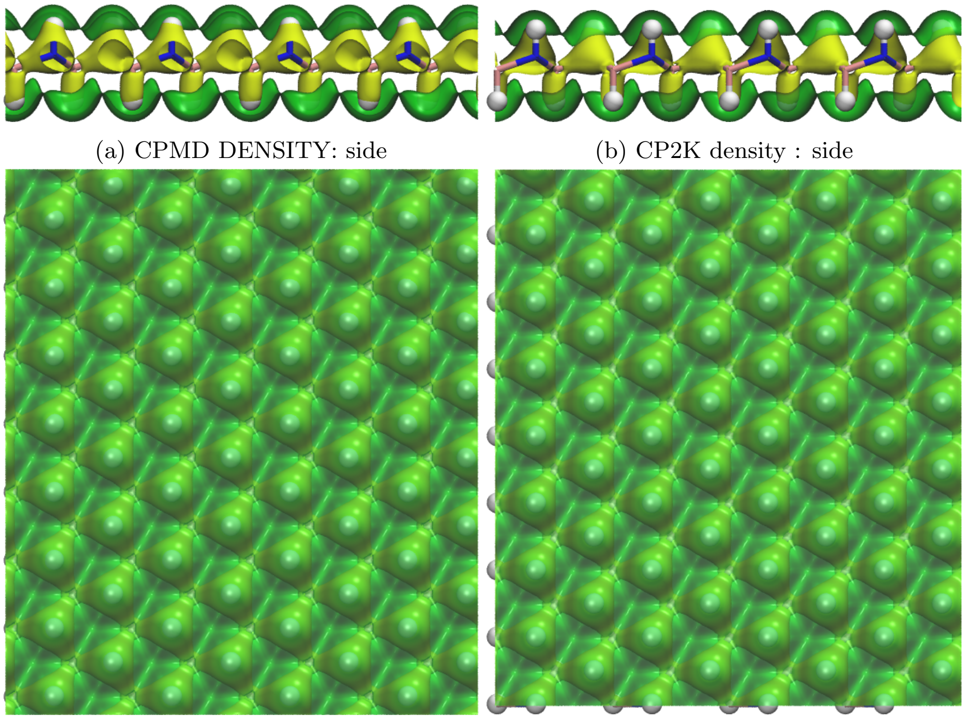
stirrup	CP2K	QE
#[B/N atoms per cell]	4	4
r_{BN}/Å	1.585, 1.575	1.575, 1.564
r_{BH}/Å	1.230	1.218
r_{NH}/Å	1.034	1.021
a / Å	5.197	5.168
b / Å	2.599	2.584
γ/°	124.1	124.1

boat	CP2K	QE
#[B/N atoms per cell]	4	4
r_{BN}/Å	1.597, 1.581	1.589, 1.570
r_{BH}/Å	1.226	1.214
r_{NH}/Å	1.034	1.020
a / Å	5.197	5.036
b / Å	2.586	2.570
γ/°	120.7	120.7

chair	CP2K	QE
#[B/N atoms per cell]	2	2
r_{BN}/Å	1.588	1.578
r_{BH}/Å	1.208	1.194
r_{NH}/Å	1.042	1.028
a / Å	2.599	2.584

S3 Band gap of the chair configuration

The hydrogenated configurations show a strong dependence of the electronic properties as function of the method. Here we look in detail at the chair configuration. For pristine h-BN we consistently find a DFT-PBE gap of 4.7 eV, indepdendent of the methods (CP2K with mixed Gaussians and plane waves, CPMD [1] or QE using a pure plane-wave basis, or by increasing the vacuum spacing in a calculation). However for the chair configuration we find a gap which depends strongly on the underlying assumptions of basis set of vacuum separation. This can be understood as originating from a dipole-coupling between periodic images. While this is destructive for the DFT predictions of the electronic band gap of fully hydrogenated h-BN the occupied part of the electronic spectrum appears unmodified and independent of the method up to a constant shift of the ionization potential (see for example the band structures in Fig. S3 and tables S2 and S3). As such, ground state properties such as vibrational spectra, binding energies and strucural parameters are expected to be unaffected.



(a) CPMD DENSITY: side

(b) CP2K density : side

(c) CPMD DENSITY: top

(d) CP2K density : top

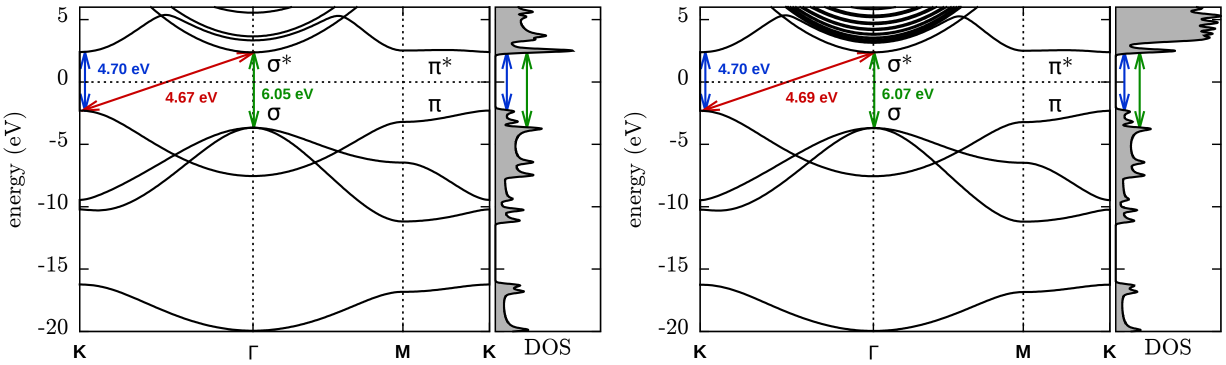
Figure S2: Total electronic density as computed with CP2K (DZVP-MOLOPT basis), and CPMD (MT pseudopotential, 70 Ry cutoff), with $L_z = 60$ Å. Isosurfaces at 0.1 (solid yellow) and 0.01 (transparent green) states/bohr^3.

E_{gap}/eV	$L_z = 15$ Å	$L_z = 30$ Å	$L_z = 60$ Å
DZVP-GTH	4.72		
DZVP-GTH (2x2 supercell, 1024 atoms)	4.72		
DZVP-MOLOPT	4.82	4.73	4.69
TZVP-MOLOPT	4.30	4.20	
TZV2PX-MOLOPT]	3.75	3.53	
CPMD (MT)	3.40	3.11	2.99
CPMD (Go)	3.40		
QE (MT)	3.38		2.93

Table S2: Shifting of the gap with vacuum spacing and basis set size (CP2K). The TZVP and TZV2PX basis sets are generated by taking several molecules with B in different chemical environments (BH_2, BH_3, H_4BN and H_6BN), and using the GTH-def2-QZVP all-electron basis as reference basis (for B). The first step of the fitting is against a calculation for atomic B. The TZV2PX has the same exponents as the TZVP basis. The CPMD and Quantum Espresso (QE) calculations use a plane-wave basis set with Martins-Troullier (MT) or Goedecker (Go) pseudopotentials.

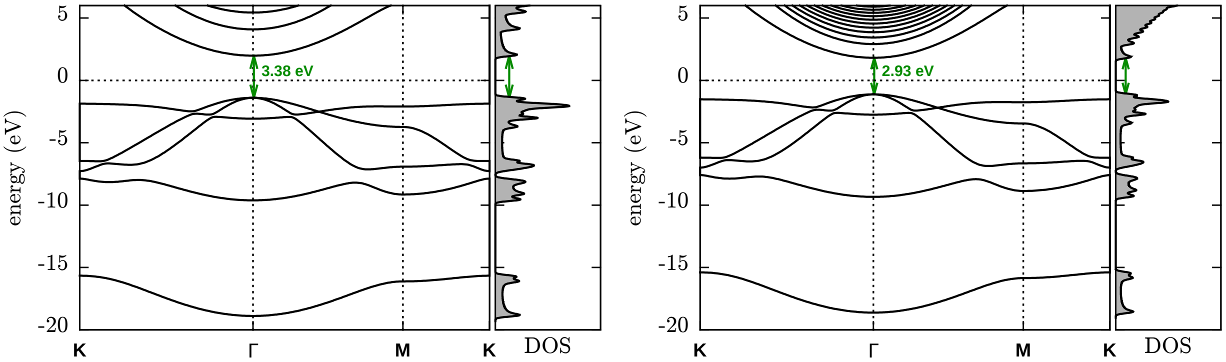
IP /eV	$L_z = 15$ Å	$L_z = 30$ Å	$L_z = 60$ Å
DZVP-GTH	3.48 eV		
DZVP-GTH (2x2 supercell, 1024 atoms)	3.48 eV		
DZVP-MOLOPT	3.67 eV	4.76 eV	5.31 eV
TZVP-MOLOPT	4.30 eV	4.20 eV	
TZV2PX-MOLOPT	3.75 eV	3.53 eV	
CPMD (MT)	3.47 eV	4.72 eV	5.36 eV
CPMD (Goedecker)	3.44 eV		
QE (MT)	3.48		5.40

Table S3: Shifting of the ionization potential (IP) with vacuum spacing and basis set size. The IP equals minus the eigenvalue of the highest occupied orbital. Same symbols as table S2.



(a) pristine h-BN, $L_z = 15$ Å

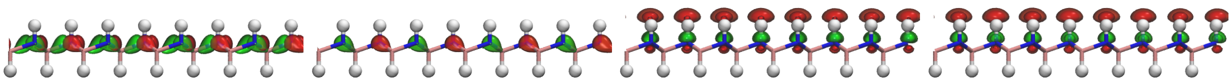
(b) pristine h-BN, $L_z = 60$ Å



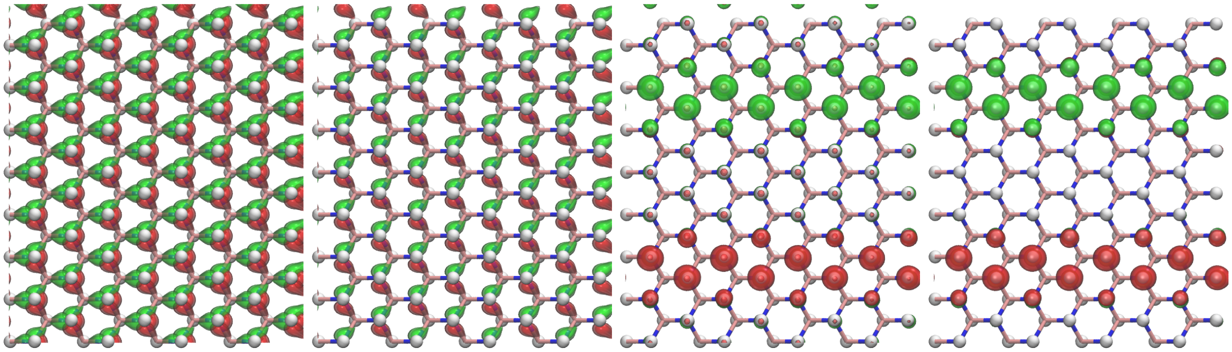
(c) chair hydrogenated h-BN, $L_z = 15$ Å

(d) chair hydrogenated h-BN, $L_z = 60$ Å

Figure S3: Quantum Espresso, Martins-Troullier pseudopotentials (100 Ry cutoff). Electronic band structure of pristine and chair hydrogenated hexagonal boron nitride (h-BN) with $L_z = 15$ Å. And chair hydrogenated h-BN with $L_z = 60$ Å

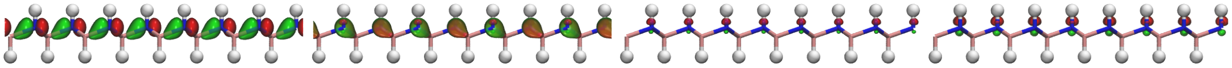


(a) 319: side (b) 320: side (c) 321: side (d) 322: side

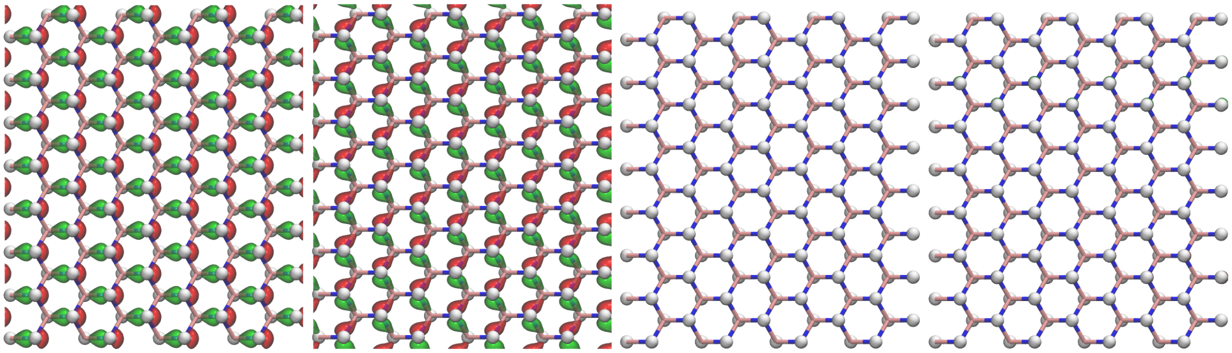


(e) 319: top (f) 320: top (g) 321: top (h) 322: top

Figure S4: CP2K, DZVP-MOLOPT basis, $L_z = 60$ Å. Wavefunctions of the Kohn-Sham states 319 (-5.32 eV) and 320 (-5.31 eV) are occupied while 321 (-0.62 eV) and 322 (-0.37 eV) are unoccupied. The gap from this calculation is 4.70 eV. Isosurfaces are plotted with an isovalue of 0.2 states/bohr^3. Boron (nitrogen) is blue (pink).

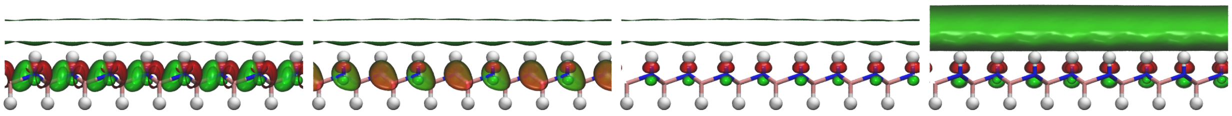


(a) 319: side (b) 320: side (c) 321: side (d) 322: side



(e) 319: top (f) 320: top (g) 321: top (h) 322: top

Figure S5: CPMD, MT pseudopotential (70 Ry cutoff), $L_z = 60$ Å. Wavefunctions of the Kohn-Sham states 319 (-5.36 eV) and 320 (-5.36 eV) are occupied while 321 (-2.36 eV) and 322 (-2.09 eV) are unoccupied. The gap from this calculation is 2.99 eV. Isosurfaces are plotted with an isovalue of 0.2 states/bohr^3.



(a) 319: side (b) 320: side (c) 321: side (d) 322: side

Figure S6: Same as Fig. S5 but with an isovalue of 0.1 states/bohr^3.

S4 Electronic gaps for N=1–6

Table S4: Comparison of the electronic band gap for partially hydrogenated samples as calculated with CP2K or CPMD. For spin-polarized calculations (odd N), the smallest electronic gap without spin flip is given in brackets.

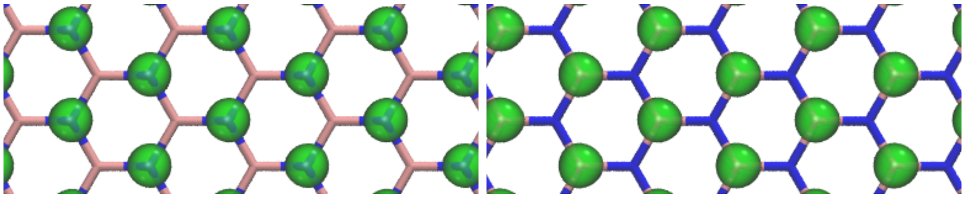
	CP2K	CPMD
1α	0.88 (1.24)	0.61 (1.06)
1β	0.70 (1.26)	0.72 (1.37)
2α	3.76	3.82
2β	3.55	3.56
2γ	3.08	3.11
2δ	3.01	2.99
2ϵ	3.56	3.57
3α	0.44 (0.87)	0.45 (0.88)
3β	0.12 (0.12)	0.14 (0.14)
3γ	0.35 (0.35)	0.25 (0.25)
3δ	0.88 (1.11)	0.92 (1.18)
3ϵ	0.42 (0.42)	0.43 (0.43)
4α	3.94	4.00
4β	3.67	3.67
4γ	3.66	3.67
4δ	3.93	3.99
4ϵ	3.59	3.60
5α	1.26 (1.26)	1.30 (1.30)
5β	1.39 (1.64)	1.36 (1.77)
5γ	1.24 (1.24)	1.26 (1.26)
5δ	1.46 (1.61)	1.44 (1.66)
5ϵ	1.21 (1.29)	1.12 (1.32)
6α	4.25	4.27
6β	4.13	4.11
6γ	4.18	4.27
6δ	4.21	4.16
6ϵ	4.10	4.07

S5 Comparison of PBE and PBE0 electronic properties

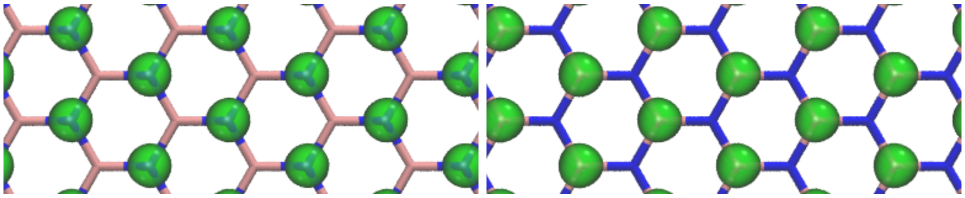
To check the effect of the exchange-correlation functional we performed several calculations using the hybrid PBE0 functional [2] (at fixed PBE structure). For these calculations we used the CPMD code [1]. As shown in table S4 the CPMD calculated PBE gaps are in good agreement with CP2K results. The quantitive positions of the levels change significantly (see table S5) with PBE0 mainly opening the gap with respect to PBE. However, the nature of the states and the relative position of the impurity levels are nearly identical for both functionals (see figures S7 and S8).

Table S5: Comparison of the electronic band gap for partially hydrogenated samples as calculated with CPMD for the PBE and PBE0 functionals

energy gap (eV)	PBE	PBE0
pristine	4.64	6.76
2α	3.82	5.87
occupied energy levels (eV)		
pristine	-3.54 (2x)	-4.71 (2x)
2α	-3.58, -3.48, -3.12	-4.75, -4.64, -4.28
unoccupied energy levels (eV)		
pristine	1.10 (2x)	2.06 (2x)
2α	0.69, 1.01, 1.10, 1.12	1.58, 1.67, 1.90, 1.95

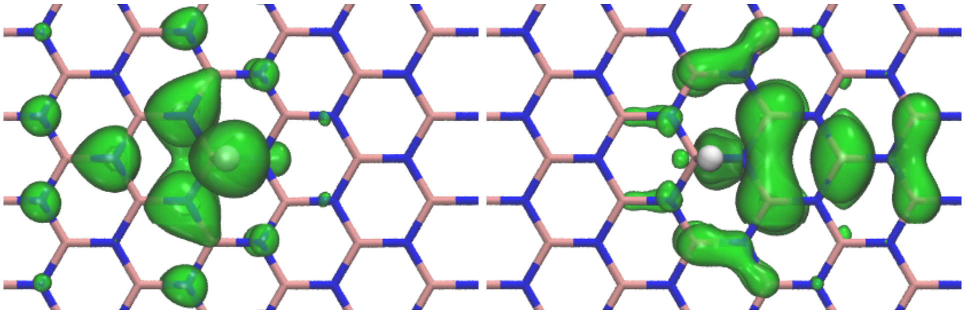


(a) PBE : pristine HOMO (-3.54 eV) (b) PBE : pristine LUMO (1.10 eV)

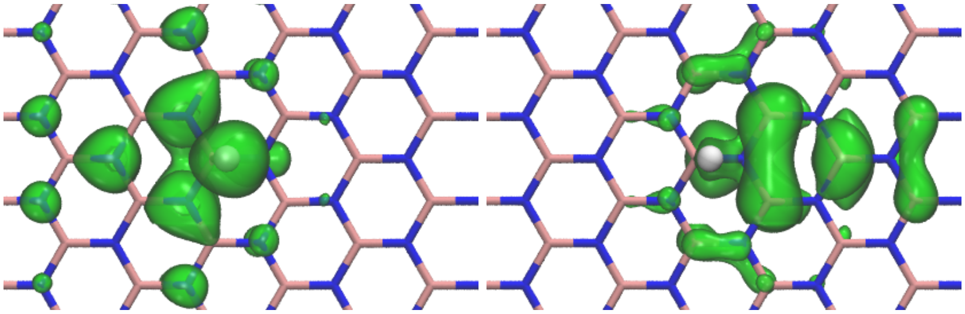


(c) PBE0 : pristine HOMO (-4.71 eV) (d) PBE0 : pristine LUMO (2.06 eV)

Figure S7: Electronic density of the highest occupied and lowest unoccupied orbitals of pristine h-BN. HOMO and LUMO levels are the sum of degerate eigenstates. Isosurfaces are at 0.001 states/bohr^3.



(a) PBE : 2α HOMO (-3.12 eV) (b) PBE : 2α LUMO (0.69 eV)



(c) PBE0 : 2α HOMO (-4.28 eV) (d) PBE0 : 2α LUMO (1.58 eV)

Figure S8: Electronic density of the HOMO and LUMO impurity level pair in the partially hydrogenated case 2α. Isosurfaces are at 0.001 states/bohr^3.

References

[1] CPMD http://www.cpmd.org, copyright IBM corp 1990-2016, copyright IBM corp 1990-2016, copyright MPI für festkörperforschung stuttgart 1997-2001, 2016.

[2] Carlo Adamo and Vincenzo Barone. Toward reliable density functional methods without adjustable parameters: The PBE0 model. *J. Phys. Chem.*, 110(13):6158–6170, April 1999.