

Band structure studies for graphene and modified graphene structures

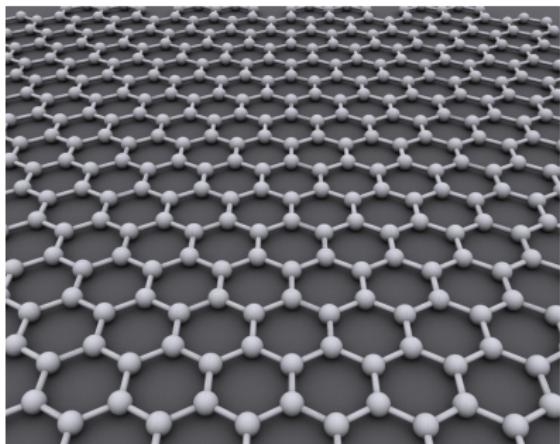
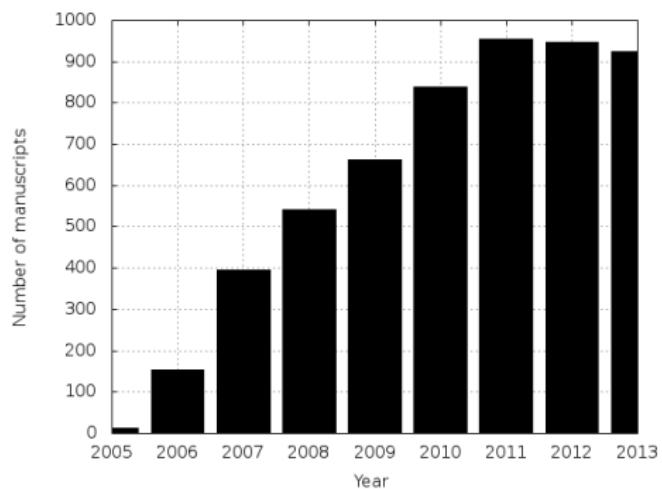
Dirk Hornung

09.03.2014

Structure

- Introduction
- Carbon materials
- Tight binding fit
- DFT results

Introduction



Left Data from '<http://www.arxiv.org>'

Right Image from article '<http://de.wikipedia.org/wiki/Graphen>'

Introduction

- thickness of one atom
- transparent
- strongest material
- best heat conductivity
- electric conductivity equal to copper
- electrons show relativistic behavior

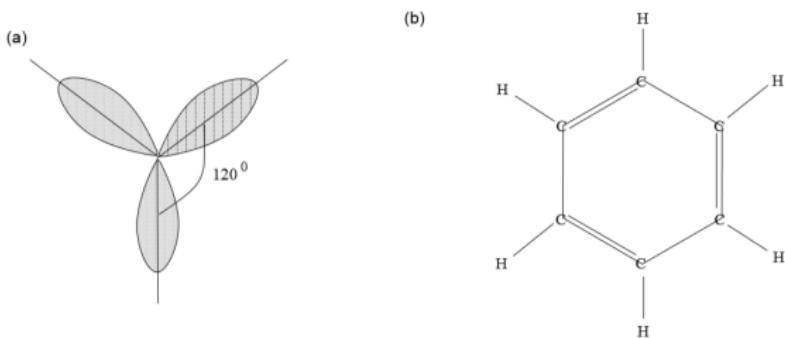
The carbon atom

H	Wasserstoff	1	1,008	Normalpotential 0,0000 V bei 25 °C in der Elektrolyse	Ordnungszahl	1	1,008	Relative Atommasse u -1,0001	Elektronegativität 0,73 bei 25 °C in der Elektrolyse	Elektronenaffinität -289 / -253	Schmelz- / Schmelztemperatur in °C -259	Name Wasserstoff	Nichtmetalle	Alkalimetalle	Erdsalkalimetalle	Übergangsmetalle	Lanthaniden	Actinide	Andere Metalle	Halogene	Edelmetale	He	Helium
Li	Li	3	6,94	0,0123									B	10,81	4,00	12,011	9	14,307	16,995	9	18,998	10	20,188
Be	Be	4	9,370	0,0123									C	11,99	4,00	12,011	10	14,307	16,995	10	18,998	11	20,188
Na	Na	11	22,990	0,0123									D	12,011	4,00	12,011	11	14,307	16,995	11	18,998	12	20,188
Mg	Mg	12	24,318	0,0123									E	12,011	4,00	12,011	12	14,307	16,995	12	18,998	13	20,188
K	K	19	39,070	0,0123									F	12,011	4,00	12,011	13	14,307	16,995	13	18,998	14	20,188
Ca	Ca	20	40,070	0,0123									G	12,011	4,00	12,011	14	14,307	16,995	14	18,998	15	20,188
Sc	Sc	21	44,955	0,0123									H	12,011	4,00	12,011	15	14,307	16,995	15	18,998	16	20,188
Ti	Ti	22	47,907	0,0123									I	12,011	4,00	12,011	16	14,307	16,995	16	18,998	17	20,188
V	V	23	50,742	0,0123									J	12,011	4,00	12,011	17	14,307	16,995	17	18,998	18	20,188
Cr	Cr	24	51,976	0,0123									K	12,011	4,00	12,011	18	14,307	16,995	18	18,998	19	20,188
Mn	Mn	25	54,933	0,0123									L	12,011	4,00	12,011	19	14,307	16,995	19	18,998	20	20,188
Fe	Fe	26	55,845	0,0123									M	12,011	4,00	12,011	20	14,307	16,995	20	18,998	21	20,188
Co	Co	27	56,755	0,0123									N	12,011	4,00	12,011	21	14,307	16,995	21	18,998	22	20,188
Ni	Ni	28	58,934	0,0123									O	12,011	4,00	12,011	22	14,307	16,995	22	18,998	23	20,188
Cu	Cu	29	61,964	0,0123									P	12,011	4,00	12,011	23	14,307	16,995	23	18,998	24	20,188
Zn	Zn	30	63,921	0,0123									Q	12,011	4,00	12,011	24	14,307	16,995	24	18,998	25	20,188
Nb	Nb	31	64,955	0,0123									R	12,011	4,00	12,011	25	14,307	16,995	25	18,998	26	20,188
Mo	Mo	32	65,930	0,0123									S	12,011	4,00	12,011	26	14,307	16,995	26	18,998	27	20,188
Tc	Tc	33	66,934	0,0123									T	12,011	4,00	12,011	27	14,307	16,995	27	18,998	28	20,188
Ru	Ru	34	67,930	0,0123									U	12,011	4,00	12,011	28	14,307	16,995	28	18,998	29	20,188
Rh	Rh	35	68,934	0,0123									V	12,011	4,00	12,011	29	14,307	16,995	29	18,998	30	20,188
Pd	Pd	36	69,934	0,0123									W	12,011	4,00	12,011	30	14,307	16,995	30	18,998	31	20,188
Ag	Ag	37	70,934	0,0123									X	12,011	4,00	12,011	31	14,307	16,995	31	18,998	32	20,188
Cd	Cd	38	71,934	0,0123									Y	12,011	4,00	12,011	32	14,307	16,995	32	18,998	33	20,188
In	In	39	72,934	0,0123									Zn	12,011	4,00	12,011	33	14,307	16,995	33	18,998	34	20,188
Sb	Sb	40	73,934	0,0123									Ga	12,011	4,00	12,011	34	14,307	16,995	34	18,998	35	20,188
Tl	Tl	41	74,934	0,0123									Ge	12,011	4,00	12,011	35	14,307	16,995	35	18,998	36	20,188
Pt	Pt	42	75,934	0,0123									As	12,011	4,00	12,011	36	14,307	16,995	36	18,998	37	20,188
Au	Au	43	76,934	0,0123									Se	12,011	4,00	12,011	37	14,307	16,995	37	18,998	38	20,188
Hg	Hg	44	77,934	0,0123									Br	12,011	4,00	12,011	38	14,307	16,995	38	18,998	39	20,188
Tl	Tl	45	78,934	0,0123									Kr	12,011	4,00	12,011	39	14,307	16,995	39	18,998	40	20,188
Pt	Pt	46	79,934	0,0123									Br	12,011	4,00	12,011	40	14,307	16,995	40	18,998	41	20,188
Bi	Bi	47	80,934	0,0123									Br	12,011	4,00	12,011	41	14,307	16,995	41	18,998	42	20,188
Os	Os	48	81,934	0,0123									Br	12,011	4,00	12,011	42	14,307	16,995	42	18,998	43	20,188
Ir	Ir	49	82,934	0,0123									Br	12,011	4,00	12,011	43	14,307	16,995	43	18,998	44	20,188
Pt	Pt	50	83,934	0,0123									Br	12,011	4,00	12,011	44	14,307	16,995	44	18,998	45	20,188
Ir	Ir	51	84,934	0,0123									Br	12,011	4,00	12,011	45	14,307	16,995	45	18,998	46	20,188
Os	Os	52	85,934	0,0123									Br	12,011	4,00	12,011	46	14,307	16,995	46	18,998	47	20,188
Ir	Ir	53	86,934	0,0123									Br	12,011	4,00	12,011	47	14,307	16,995	47	18,998	48	20,188
Ir	Ir	54	87,934	0,0123									Br	12,011	4,00	12,011	48	14,307	16,995	48	18,998	49	20,188
Ir	Ir	55	88,934	0,0123									Br	12,011	4,00	12,011	49	14,307	16,995	49	18,998	50	20,188
Fr	Fr	56	89,934	0,0123									Br	12,011	4,00	12,011	50	16,995	50	51			
Ra	Ra	57	90,934	0,0123									Br	12,011	4,00	12,011	51	16,995	51	52			
Ac	Ac	58	91,934	0,0123									Br	12,011	4,00	12,011	52	16,995	52	53			
Th	Th	59	92,934	0,0123									Br	12,011	4,00	12,011	53	16,995	53	54			
Pa	Pa	60	93,934	0,0123									Br	12,011	4,00	12,011	54	16,995	54	55			
U	U	61	94,934	0,0123									Br	12,011	4,00	12,011	55	16,995	55	56			
Np	Np	62</b																					

ground state: $1s^2 2s^2 2p^2$

Image from '<http://www.wolfenthal.de/drucken>'.

sp²-hybridization



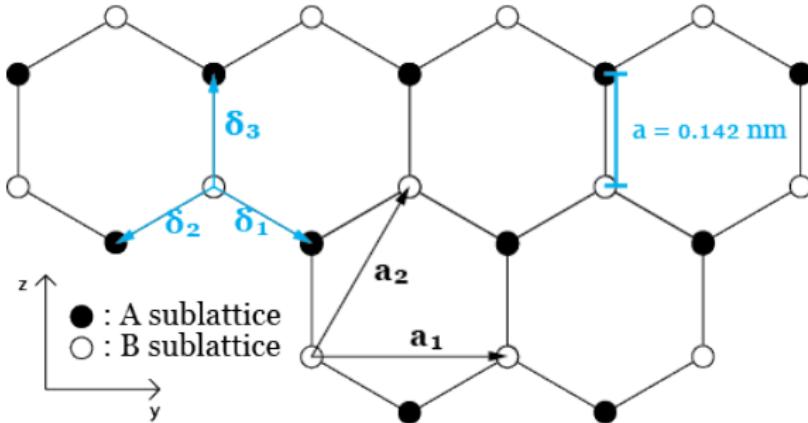
$$|sp_1^2\rangle = \frac{1}{\sqrt{3}}|2s\rangle - \sqrt{\frac{2}{3}}|2p_y\rangle, \quad (2)$$

$$|sp_2^2\rangle = \frac{1}{\sqrt{3}}|2s\rangle + \sqrt{\frac{2}{3}}\left(\frac{\sqrt{3}}{2}|2p_x\rangle + \frac{1}{2}|2p_y\rangle\right), \quad (3)$$

$$|sp_3^2\rangle = -\frac{1}{\sqrt{3}}|2s\rangle + \sqrt{\frac{2}{3}}\left(-\frac{\sqrt{3}}{2}|2p_x\rangle + \frac{1}{2}|2p_y\rangle\right) \quad (4)$$

Image from Noel, Jean and Oliver, Mark : 'Introduction of the Physical Properties of Graphen'

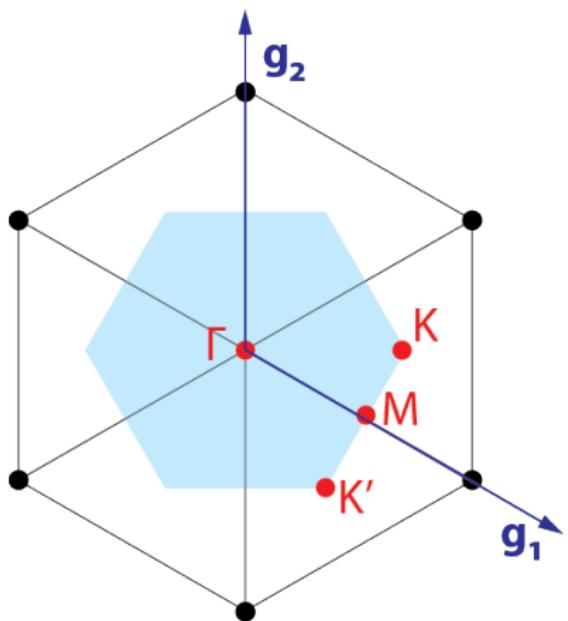
Graphene lattice



$$\delta_1 = \frac{a}{2}(\sqrt{3}\vec{e}_y - \vec{e}_z) \quad \delta_2 = -\frac{a}{2}(\sqrt{3}\vec{e}_y + \vec{e}_z) \quad \delta_3 = a\vec{e}_z. \quad (5)$$

$$\vec{a}_1 = \sqrt{3}a\vec{e}_y \quad \vec{a}_2 = \frac{\sqrt{3}a}{2}(\vec{e}_y + \sqrt{3}\vec{e}_z). \quad (6)$$

Graphene Lattice



$$\vec{g}_1 = \frac{2\pi}{\sqrt{3}a} \left(\vec{e}_y - \frac{\vec{e}_z}{\sqrt{3}} \right) \quad (7)$$

$$\vec{g}_2 = \frac{4\pi}{3a} \vec{e}_z \quad (8)$$

$$\pm \vec{K} = \pm \frac{4\pi}{3\sqrt{3}a} \vec{e}_y \quad (9)$$

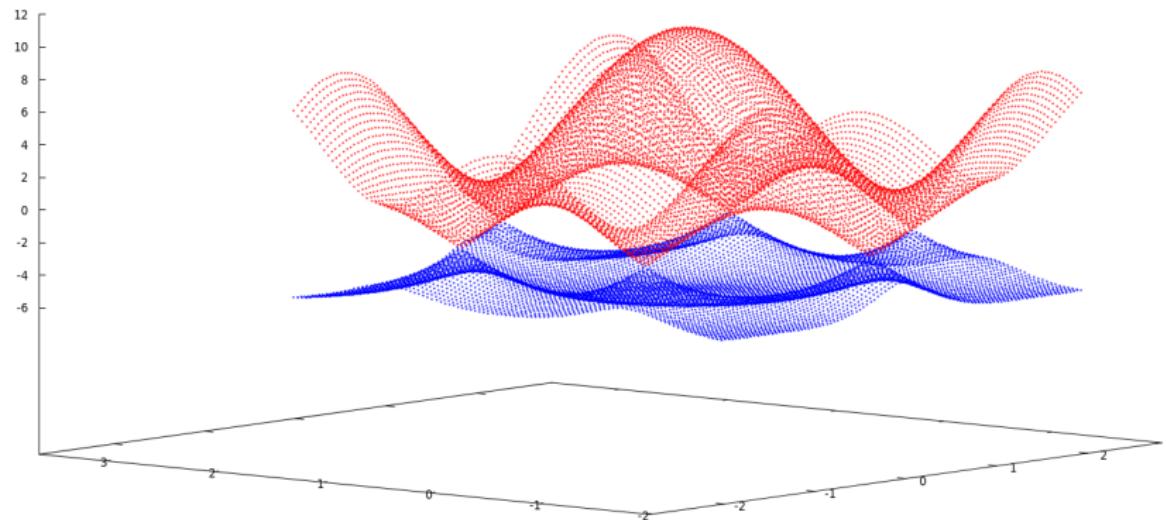
Nearest neighbor analytical solution

$$\epsilon_k^{\pm\pi} = t' f_{nnn}(\vec{k}) \pm t \sqrt{3 + f_{nnn}(\vec{k})} \quad (10)$$

with

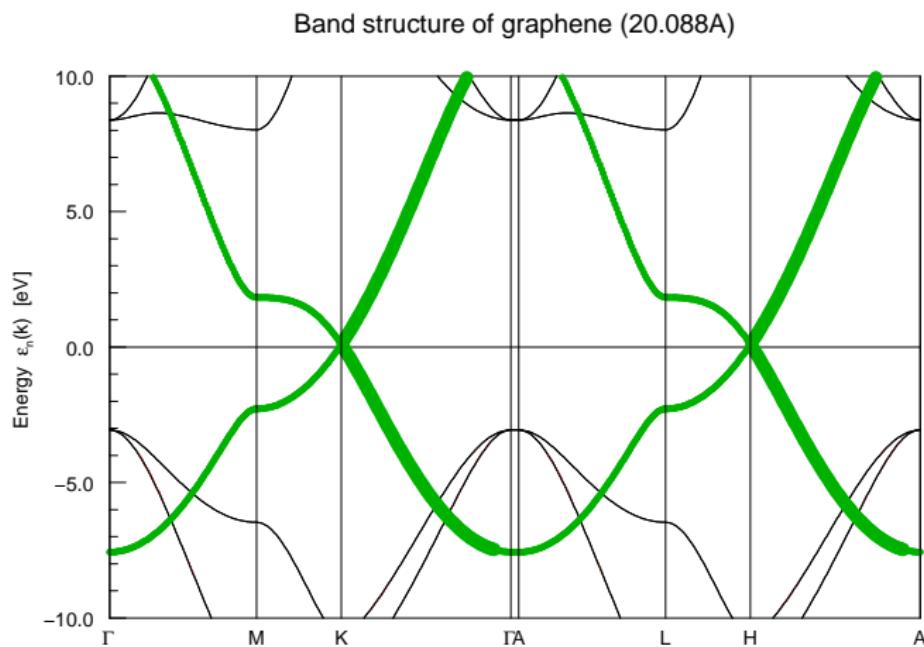
$$f_{nnn}(\vec{k}) = 2 \cos(\sqrt{3}k_x a) + 4 \cos\left(\frac{3}{2}k_y a\right) \cos\left(\frac{\sqrt{3}}{2}k_x a\right). \quad (11)$$

Electronic dispersion in the honeycomb lattice



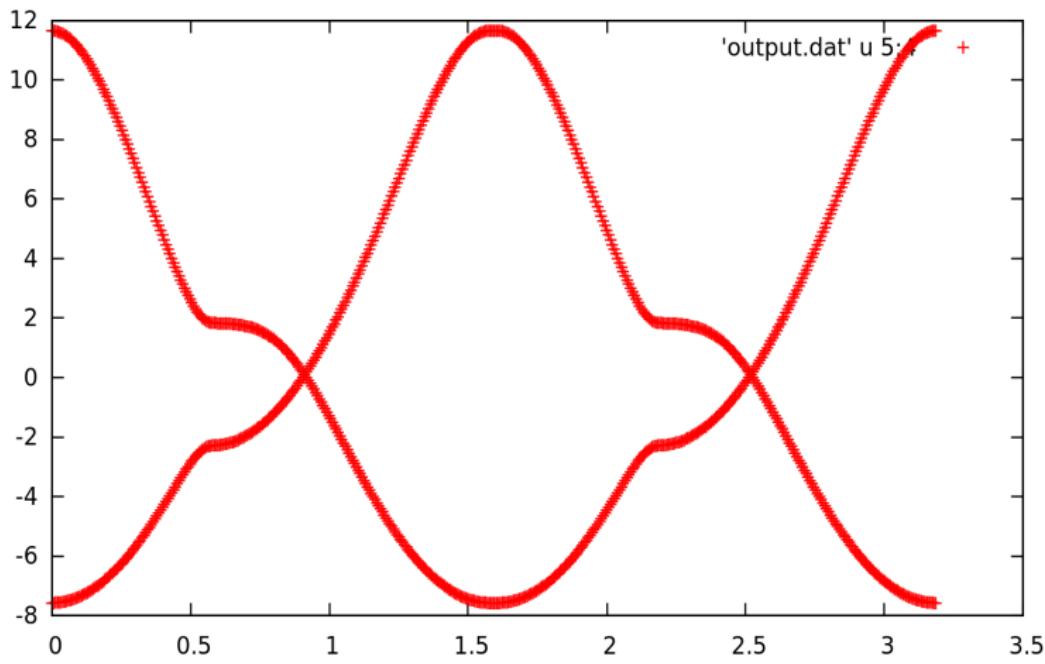
Pi bands

Band structure of graphene



Pi bands

Separation



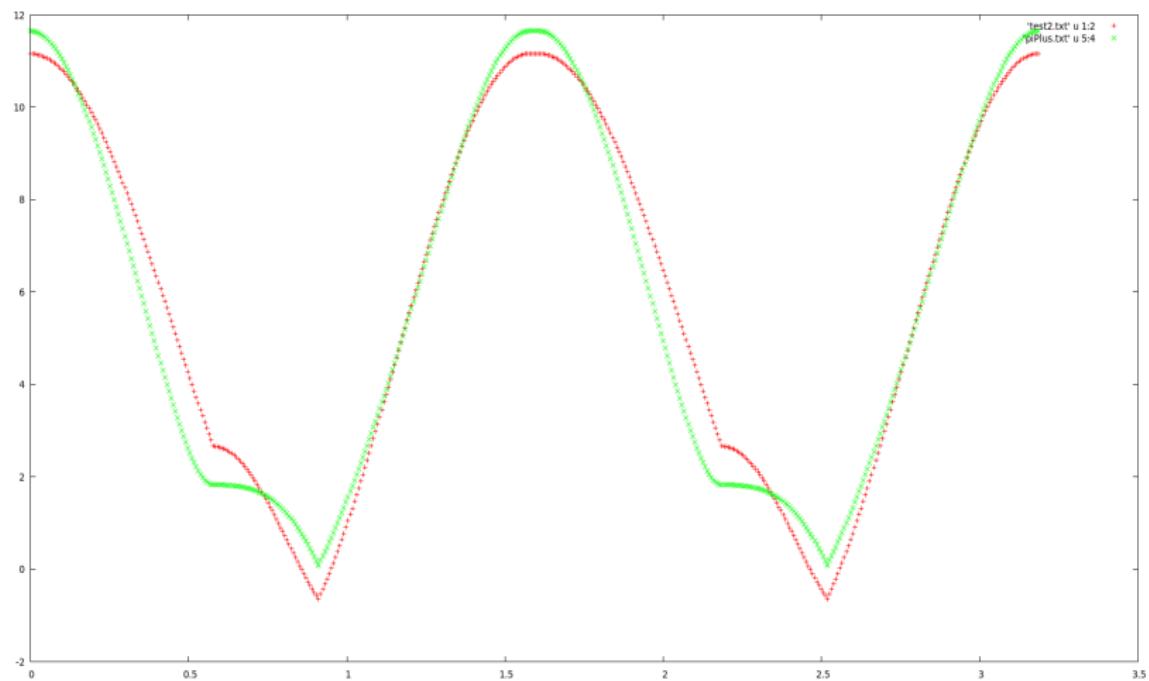
Calculated parameters

$$\sigma = \sqrt{(\epsilon_k^{\pm\pi} - \epsilon_{FPL0})^2}, \quad (12)$$

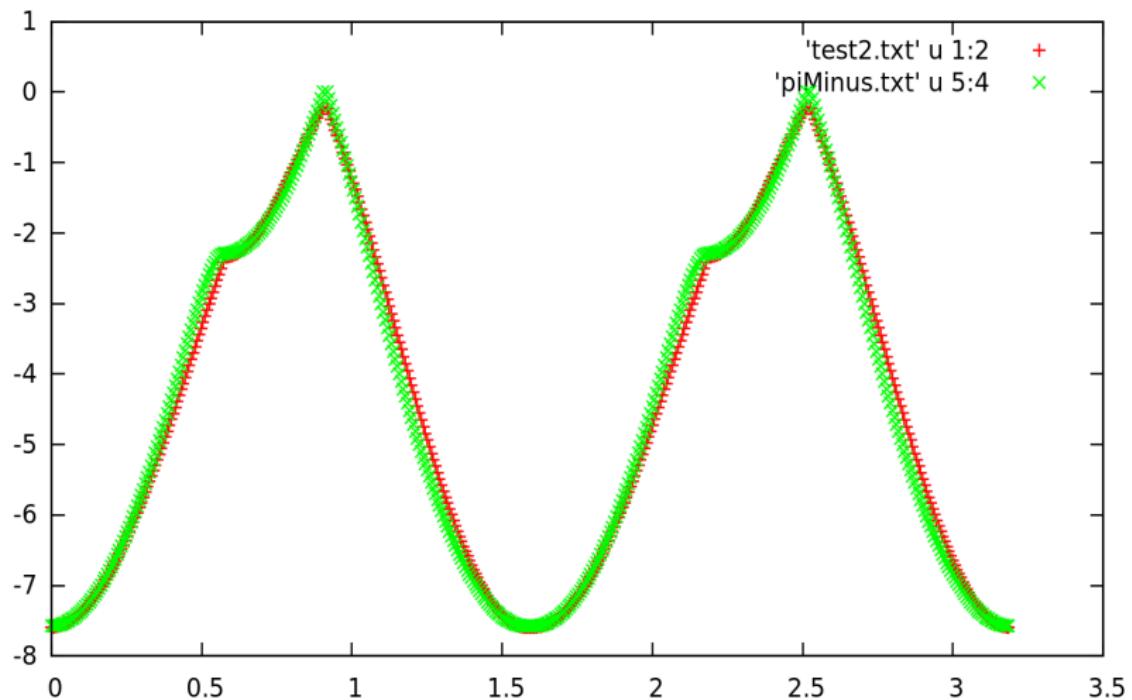
	t	t'	σ
π_+	1.54	-1.09	272.89
π_-	1.35	0.59	80.52

Table: The tight binding parameters t, t' and the plot variance σ .

Pi plus fit

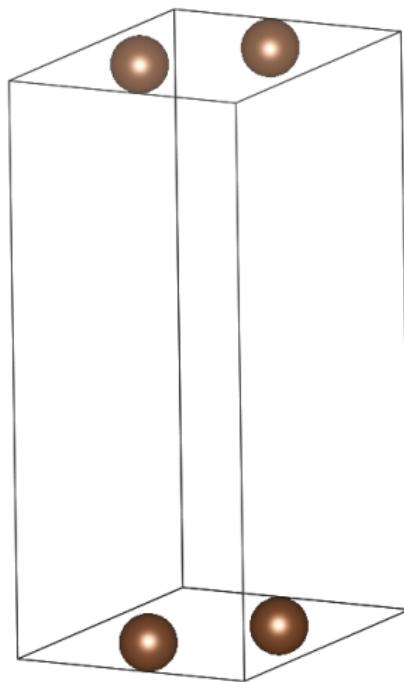
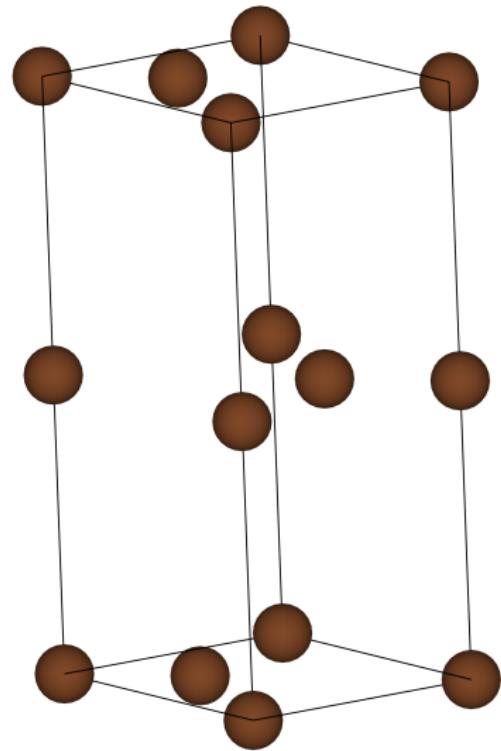


Pi minus fit



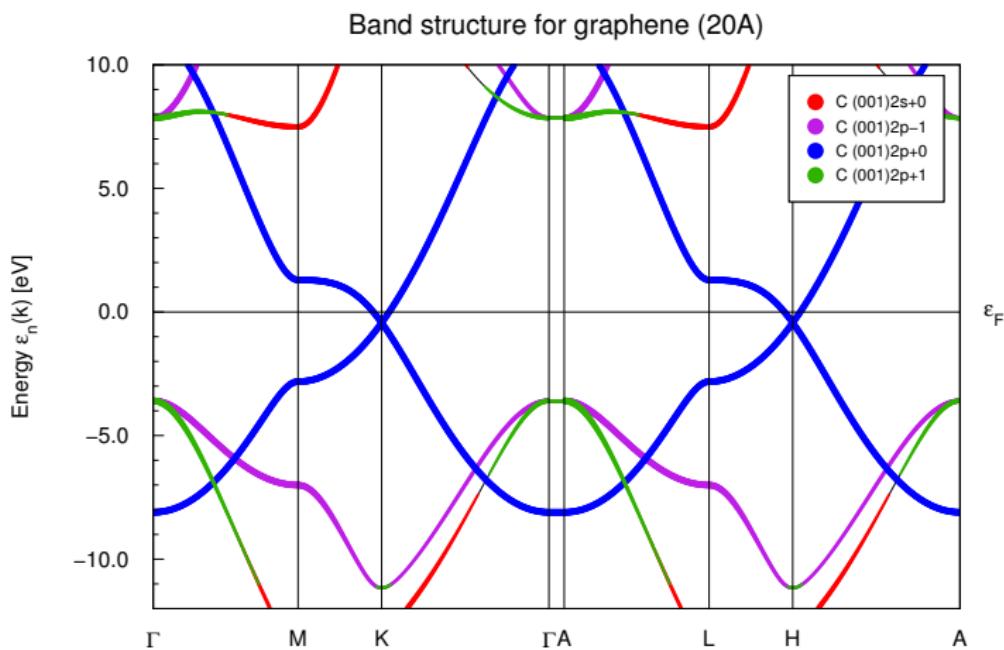
Graphene

Vesta structure



Graphene

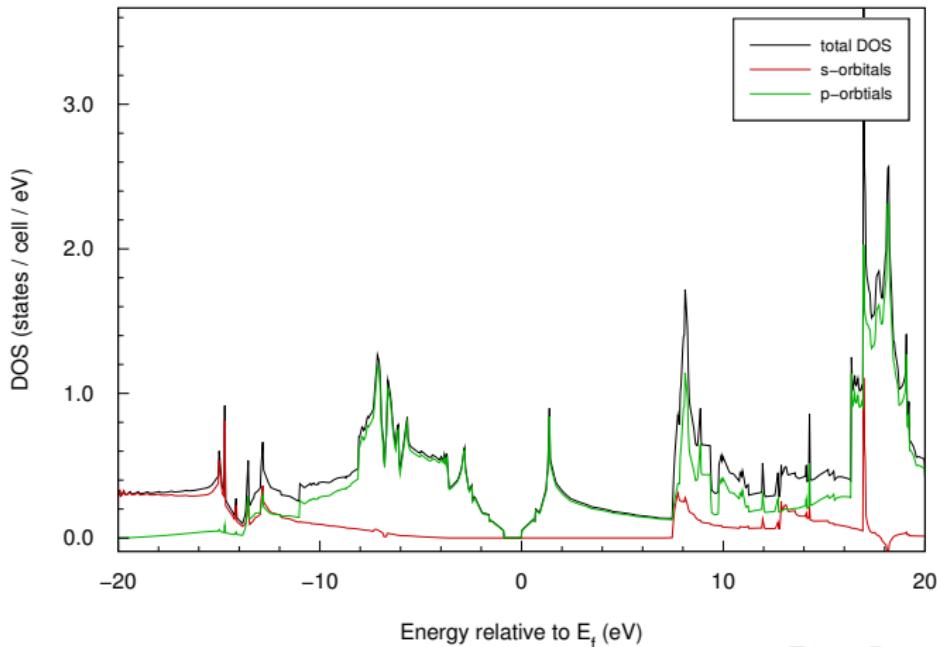
Weighted band structure



Graphene

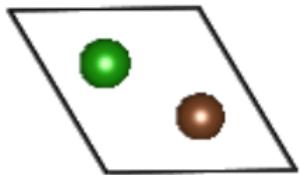
DOS

DOS for graphene (20A)

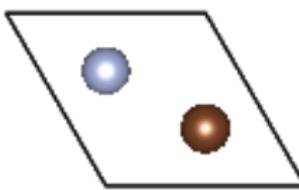


Modifying graphene

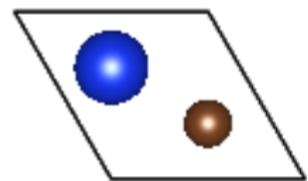
Vesta structures



Unit cell length :
2.687 Å



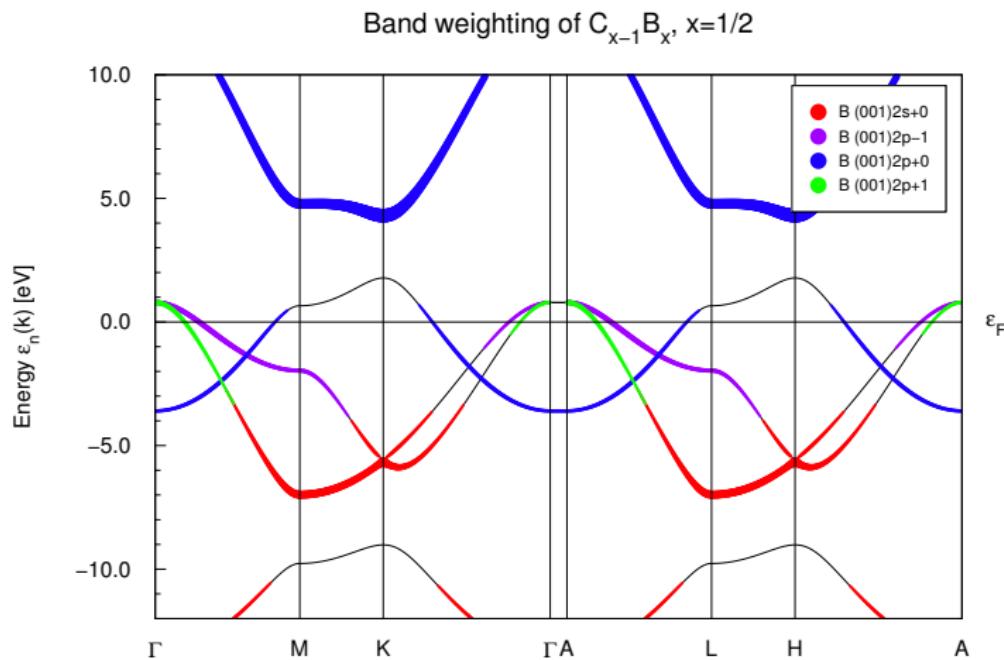
Unit cell length :
2.477 Å



Unit cell length :
3.112 Å

Boron modified graphene

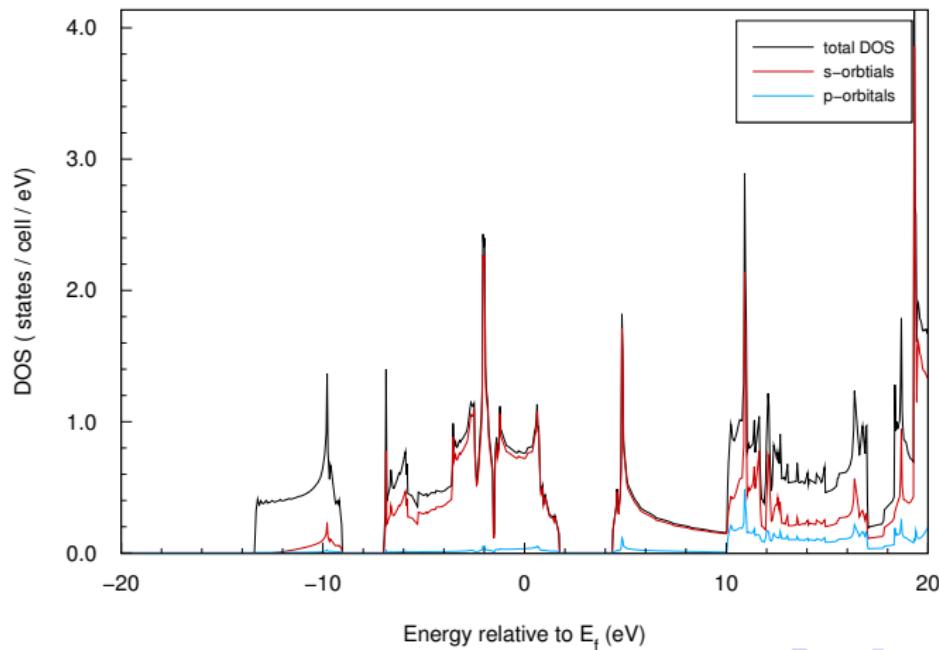
Weighted band structure



Boron modified graphene

DOS

DOS for $C_{x-1}B_x$, $x=1/2$



Boron modified graphene

Stability

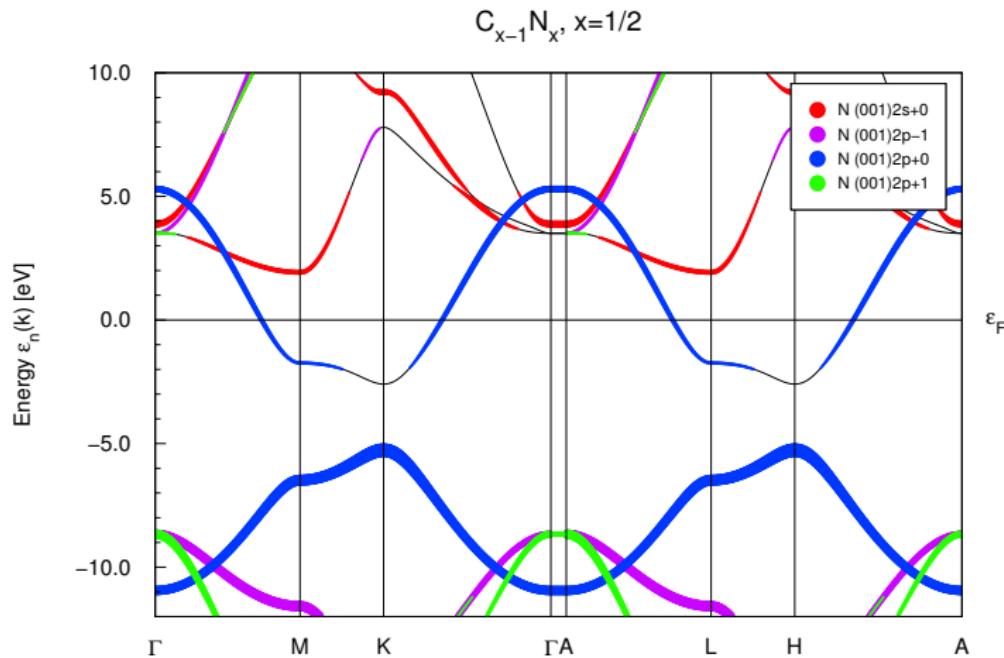
Total energy of **-62.881 eV**



$$\Delta E = -13.287 \text{ eV}$$

Nitrogen modified graphene

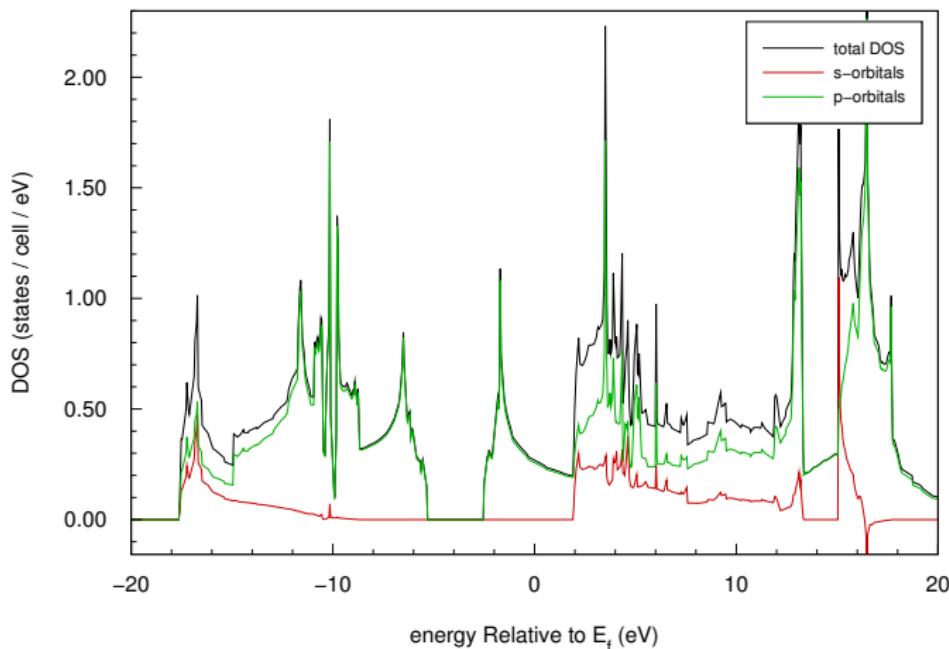
Weighted band structure



Nitrogen modified graphene

DOS

DOS for $C_{x-1}N_x, x=1/2$



Nitrogen modified graphene

Stability

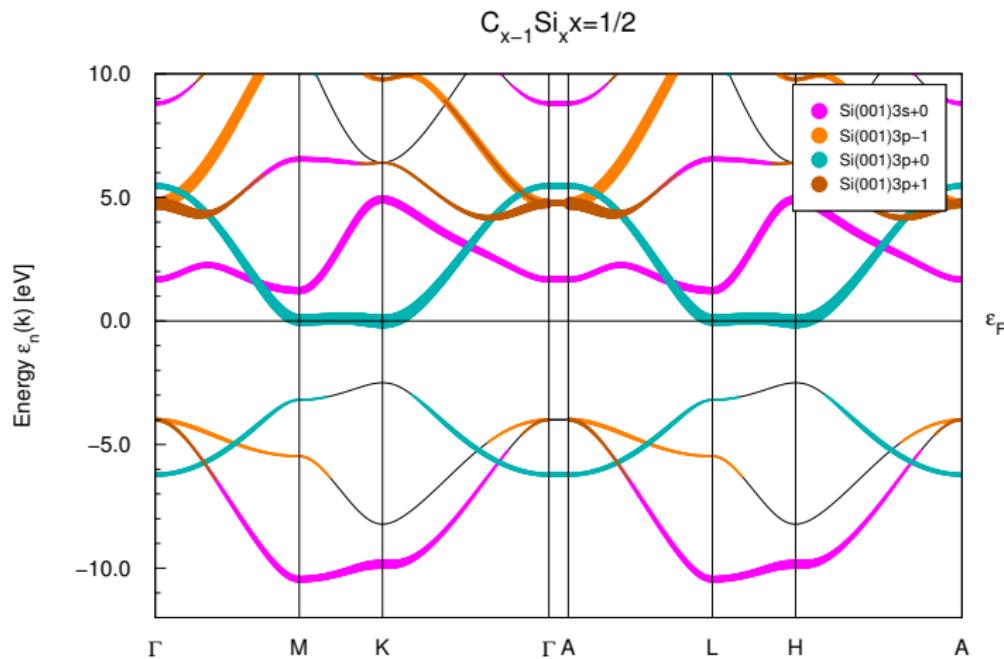
Total energy of **-92.743 eV**



$$\Delta E = 16.575 \text{ eV}$$

Silicon modified graphene

Weighted band structure



Silicon modified graphene

Stability

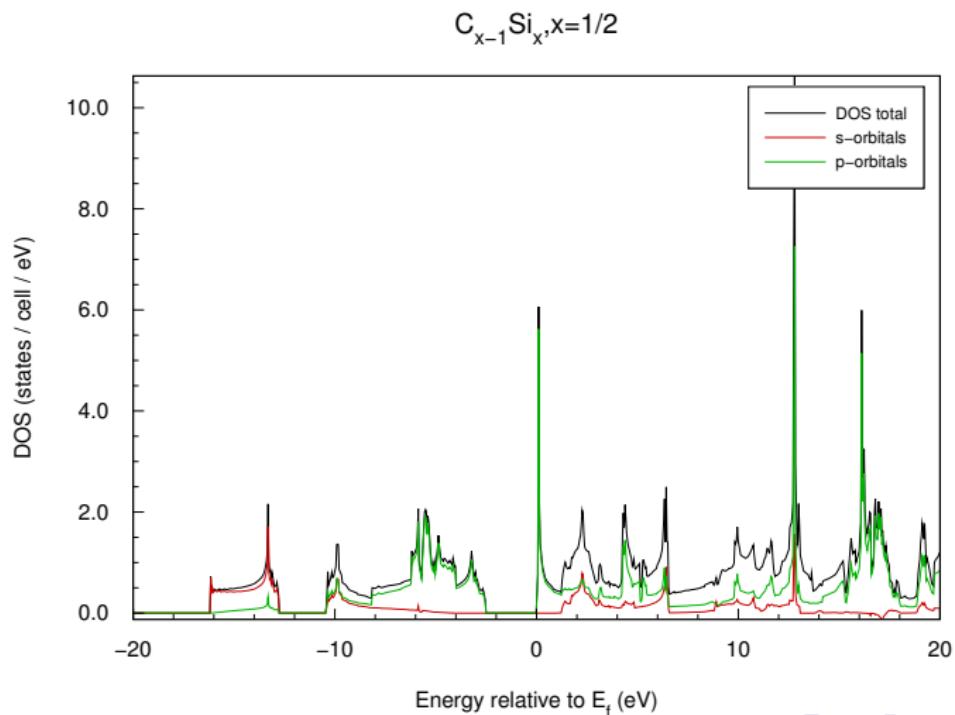
Total energy of **-327.459 eV**



$$\Delta E = 251.291 \text{ eV}$$

Silicon modified graphene

DOS



Structure
o

Introduction
oo

Carbon materials
oooo

Tight binding fit
oooooooo

DFT results
oooooooooooo●

Thank you