The effect of atomic-scale defects and dopants on Graphene electronic structure

Rocco Martinazzo

Dip. di Chimica-Fisica e Elettrochimica
Universita' degli Studi di Milano, Milan, Italy

GraphITA
GSNL, Assergi (L'Aquila), May 15^{th} - 18^{rd} 2011

Outline

1. Introduction

2. Hydrogen adsorption

3. Bandgap engineering

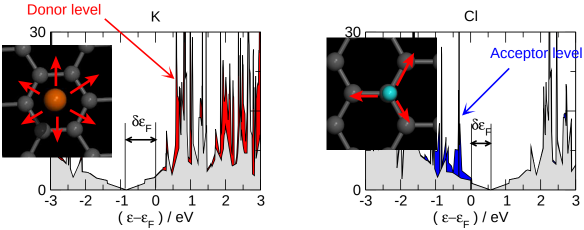
Outline

1. Introduction
2. Hydrogen adsorption
3. Bandgap engineering

Outline

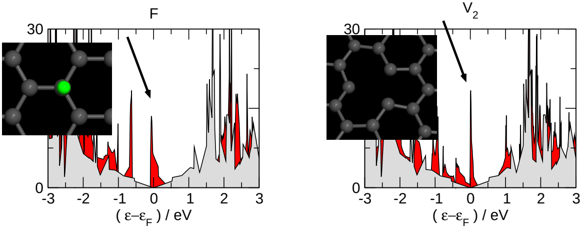
Outline

Ionic binding



- DOSs are unchaged except for donor/acceptor levels
- electron / hole doping
- Atomic species are mobile
- Li, Na, K, Cs.. vs Cl,Br,I,..

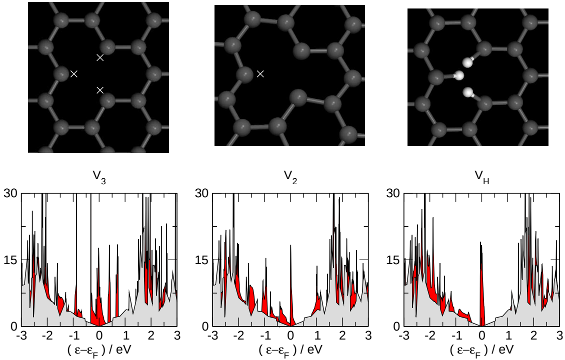
Covalent binding



- Midgap states show up in the DOSs
- Atomic species are immobile
- H, F, OH, CH_3, etc. behave similarly to vacancies

See e.g., T. O. Wehling, M. I. Katsnelson and A. I. Lichtenstein, *Phys. Rev. B* **80**, 085428 (2008)

Vacancies *vs* adatoms

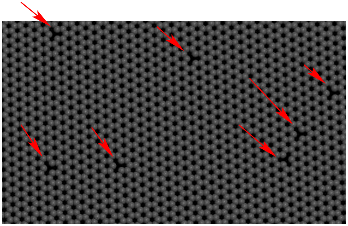


Unrelaxed Relaxed Saturated

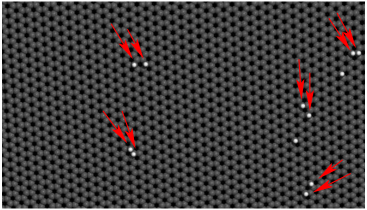
See e.g., F. Banhart, J. Kotakoski, A. V. Krasheninnikov, *ACS Nano* **5**, 26 (2011)

Vacancies *vs* adatoms

High-energy e^{-}/ion beams
$\Rightarrow$ **Random** arrangement



Low-energy beams (kinetic control)
$\Rightarrow$ **Clustering** due to preferential sticking



Outline

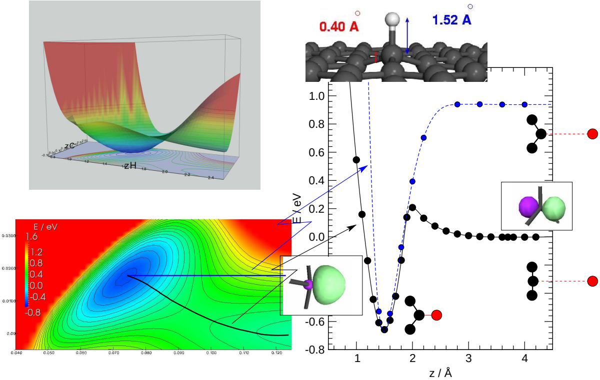
1. Introduction
2. Hydrogen adsorption
3. Bandgap engineering

Hydrogen chemisorption on graphene

- Sticking is thermally activated[1,2]
- Midgap states are generated upon sticking
- Diffusion of chemisorbed species does not occur[3,4]
- Preferential sticking and clustering[3,5,6]

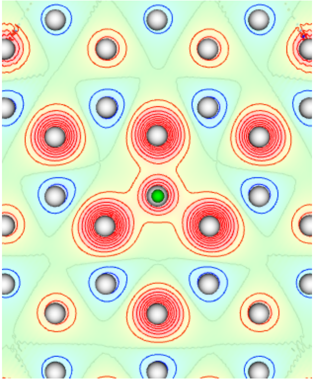
[1] L. Jeloaica and V. Sidis, *Chem. Phys. Lett.* **300**, 157 (1999)
[2] X. Sha and B. Jackson, *Surf. Sci.* **496**, 318 (2002)
[3] L. Hornekaer *et al.*, *Phys. Rev. Lett.* **97**, 186102 (2006)
[4] J. C. Meyer *et al.*, *Nature* **454**, 319 (2008)
[5] A. Andree *et al.*, *Chem. Phys. Lett.* **425**, 99 (2006)
[6] L. Hornekaer *et al.*, *Chem. Phys. Lett.* **446**, 237 (2007)

Sticking

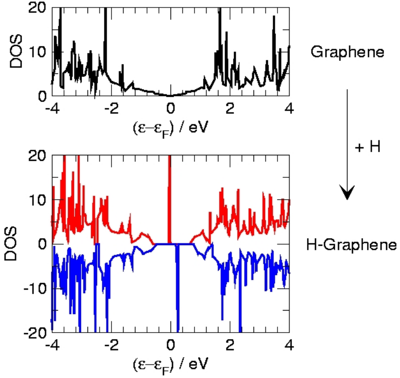


L. Jeloaica and V. Sidis, *Chem. Phys. Lett.* **300**, 157 (1999)
X. Sha and B. Jackson, *Surf. Sci.* **496**, 318 (2002)

Midgap states



..*patterned* spin-density



Midgap states

$$H^{TB} = \sum_{\sigma,ij}(t_{ij}a^\dagger_{i,\sigma}b_{j,\sigma} + t_{ji}b^\dagger_{j,\sigma}a_{i,\sigma})$$

Electron-hole symmetry

$$b_i \rightarrow -b_i \Longrightarrow \mathbf{h} \rightarrow -\mathbf{h}$$

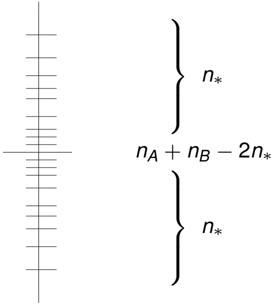
if ϵ_i is eigenvalue and

$c_i^\dagger = \sum_i \alpha_i a_i^\dagger + \sum_j \beta_j b_j^\dagger$ eigenvector

$$\Downarrow$$

$-\epsilon_i$ is also eigenvalue and

$c_i^{\prime\dagger} = \sum_i \alpha_i a_i^\dagger - \sum_j \beta_j b_j^\dagger$ is eigenvector



Midgap states

$$H^{TB} = \sum_{\tau,ij}(t_{ij}a^{\dagger}_{i,\tau}b_{j,\tau} + t_{ji}b^{\dagger}_{j,\tau}a_{i,\tau})$$

Theorem

If $n_A > n_B$ there exist (at least) $n_I = n_A - n_B$ "midgap states" with vanishing components on B sites

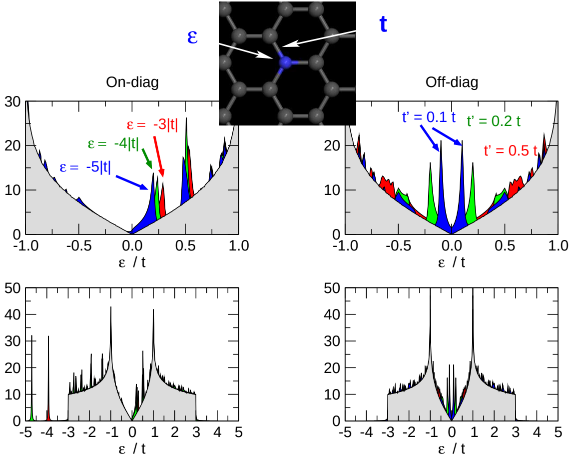
Proof.

$$\begin{bmatrix} \mathbf{0} & \mathbf{T}^{\dagger} \\ \mathbf{T} & \mathbf{0} \end{bmatrix} \begin{bmatrix} \boldsymbol{\alpha} \\ \boldsymbol{\beta} \end{bmatrix} = \begin{bmatrix} \mathbf{0} \\ \mathbf{0} \end{bmatrix} \text{ with } \mathbf{T}\ n_B x n_A(\ > n_B)$$

$$\Longrightarrow \mathbf{T}\boldsymbol{\alpha} = \mathbf{0} \text{ has } n_A - n_B \text{ solutions}$$

$\square$

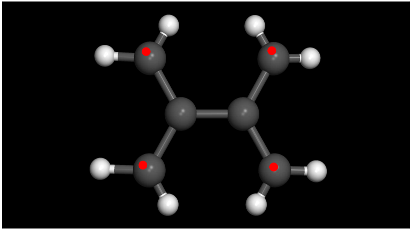
Midgap states



Midgap states

Counting the midgap states

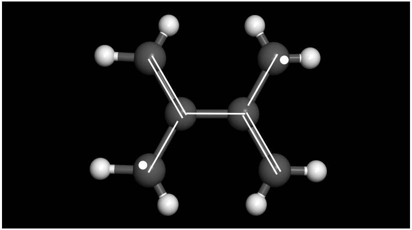
- Maximal set(s) of non-adjacent sites, $\mathcal{A}$
- $\eta_{\mathcal{A}} = \text{card}\{\mathcal{A}\}$, $n_I = 2\eta_{\mathcal{A}} - N$
- $\eta_{\mathcal{A}} \geq n_A \Rightarrow n_I \geq n_A - n_B$



Midgap states

Counting the midgap states

- Maximal set(s) of non-adjacent sites, $\mathcal{A}$
- $\eta_{\mathcal{A}} = \text{card}\{\mathcal{A}\}$, $n_I = 2\eta_{\mathcal{A}} - N$
- $\eta_{\mathcal{A}} \geq n_A \Rightarrow n_I \geq n_A - n_B$



Midgap states

$$H^{Hb} = \sum_{\tau,ij}(t_{ij}a^{\dagger}_{i,\tau}b_{j,\tau} + t_{ji}b^{\dagger}_{j,\tau}a_{i,\tau}) + U\sum_i n_{i,\tau}n_{i,-\tau}$$

Theorem

If $U > 0$, the ground-state at half-filling has

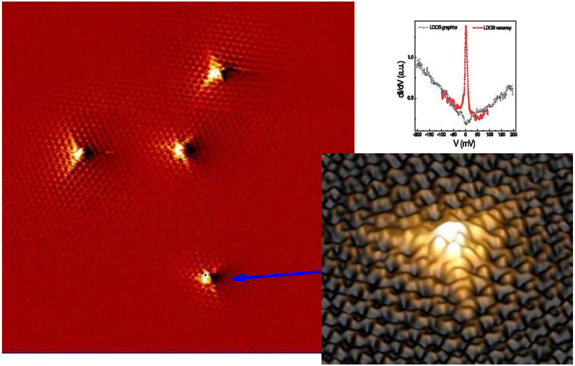
$$S = |n_A - n_B|/2 = n_I/2$$

Proof.

E.H. Lieb, *Phys. Rev. Lett.* **62**, 1201 (1989) □

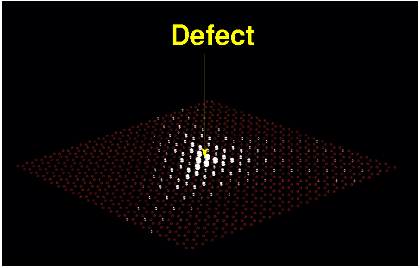
...basically, we can apply Hund's rule to previous result

Midgap states for isolated "defects"



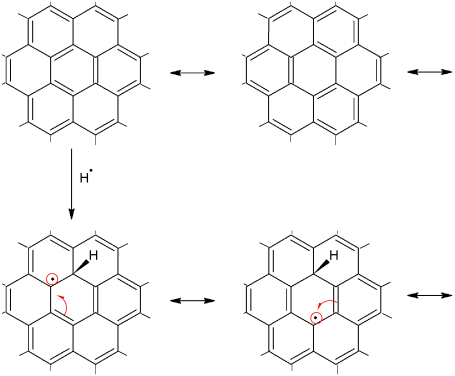
M.M. Ugeda, I. Brihuega, F. Guinea and J.M. Gomez-Rodriguez, *Phys. Rev. Lett.* **104**, 096804 (2010)

Midgap states for isolated “defects”

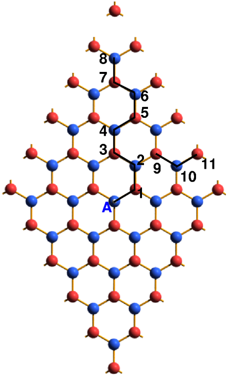


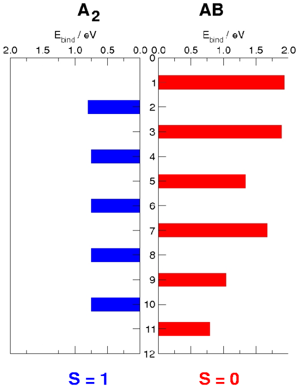
$\psi(x, y, z) \sim 1/r$

V. M. Pereira *et al.*, *Phys. Rev. Lett.* **96**, 036801 (2006);
Phys. Rev. B **77**, 115109 (2008)

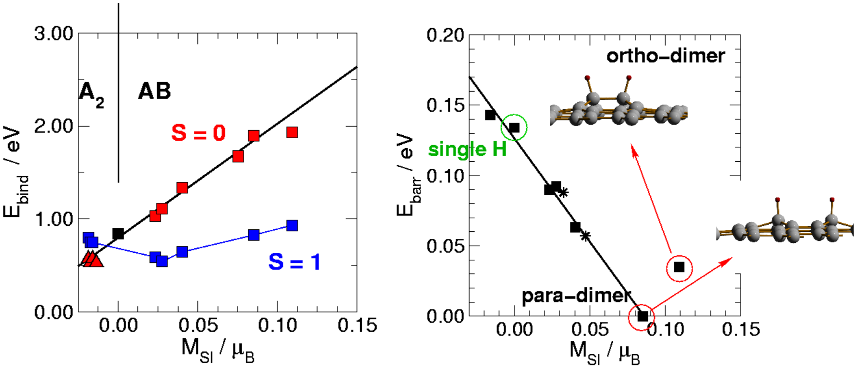


Dimers


8
7
6
5
4
3
2
9
11
10
1
A

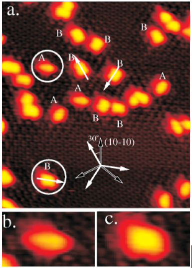

A2
AB
E_bind / eV
E_bind / eV
2.0 1.5 1.0 0.5 0.0
0.0 0.5 1.0 1.5 2.0
0
1
2
3
4
5
6
7
8
9
10
11
12
S = 1
S = 0

Dimers

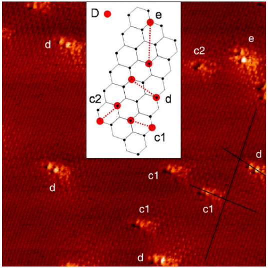


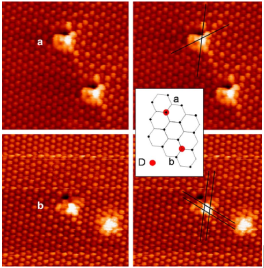
S. Casolo, O.M. Lovvik, R. Martinazzo and G.F. Tantardini, *J. Chem. Phys.* **130** 054704 (2009)

Dimers



[1]



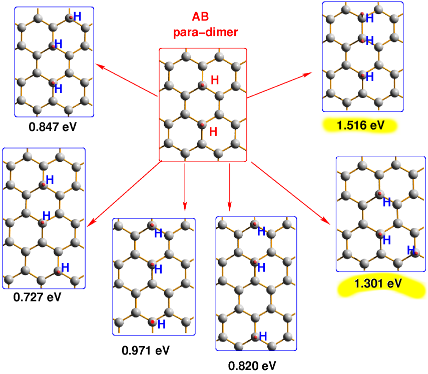


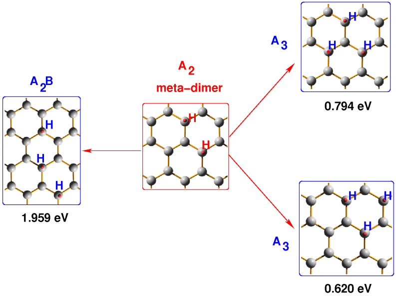
[2]

[1] L. Hornekaer, Z. Sljivancanin, W. Xu, R. Otero, E. Rauls, I. Stensgaard, E. Laegsgaard, B. Hammer and F. Besenbacher. *Phys. Rev. Lett.* **96** 156104 (2006)

[2] A. Andree, M. Le Lay, T. Zecho and J. Kupper, *Chem. Phys. Lett.* **425** 99 (2006)

Clusters

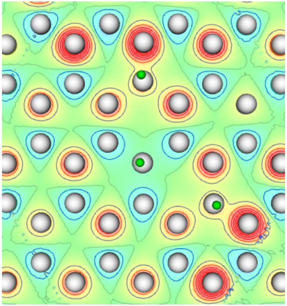




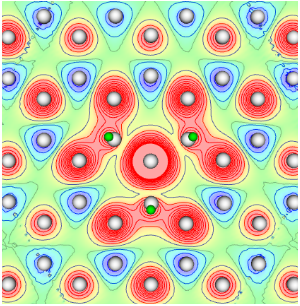
$$\mu = 1\mu_B \Rightarrow \mu = 2\mu_B \Rightarrow \mu = 3\mu_B$$

Clusters

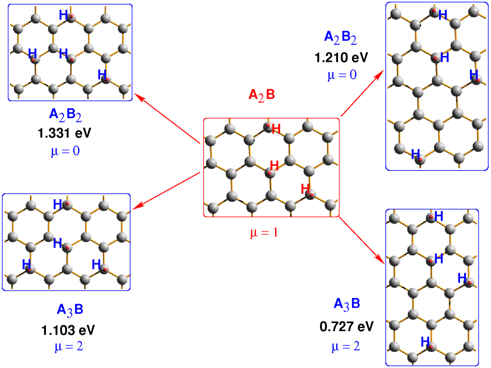
A_2B



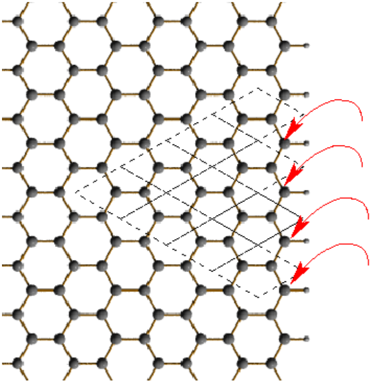
A_3



Clusters

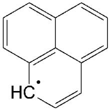

A2B2
1.331 eV
μ = 0
A3B
1.103 eV
μ = 2
A2B
μ = 1
A2B2
1.210 eV
μ = 0
A3B
0.727 eV
μ = 2

Role of edges

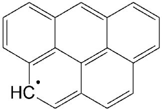


- *zig-zag* edge sites have enhanced hydrogen affinity
- geometric effects can be investigated in small graphenes

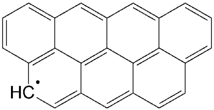
Role of edges



perinaftenile / fenalene

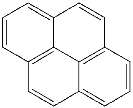


benzo[cd]pirenile

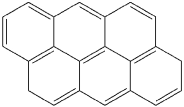


7 - PAH

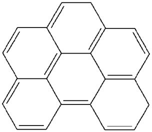
imbalanced ‘PAHs’



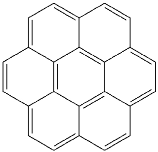
pirene



dibenzo[def,mno]crisene / antrantrene



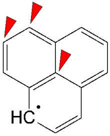
benzo[ghi]perilene



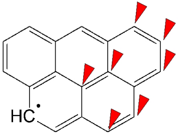
coronene

balanced PAHs

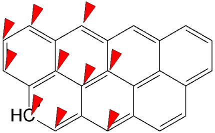
Role of edges



perinaftenile / fenalene

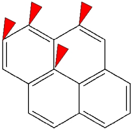


benzo[cd]pirenile

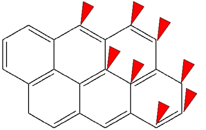


7 - PAH

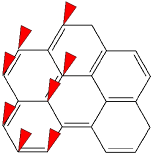
imbalanced 'PAHs'



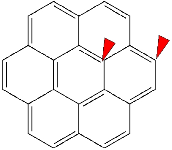
pirene



dibenzo[def,mno]crisene / antrantrene



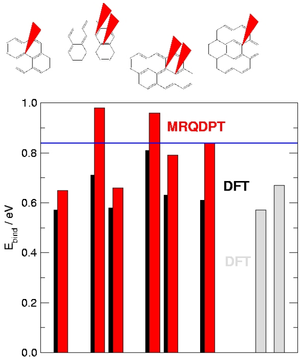
benzo[ghi]perilene

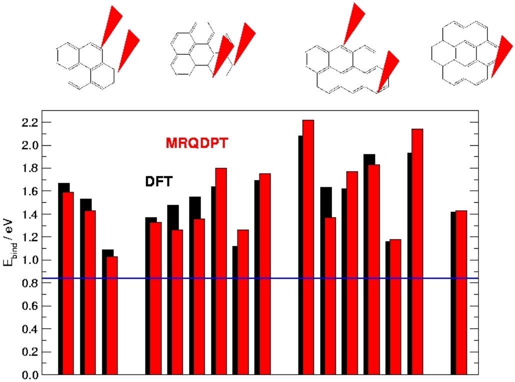


coronene

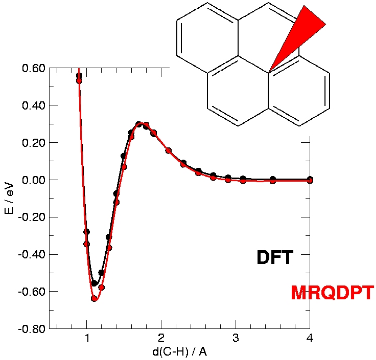
balanced PAHs

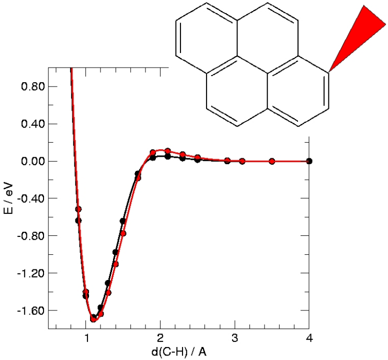
Role of edges: graphenic *vs* edge sites





Role of edges: graphenic *vs* edge sites





Outline

1. Introduction

2. Hydrogen adsorption

3. Bandgap engineering

Band-gap opening

- **Electron confinement**: nanoribbons, (nanotubes),etc.
- **Symmetry breaking**: epitaxial growth, deposition, etc.
- **Symmetry preserving**: “supergraphenes”

Band-gap opening

- **Electron confinement**: nanoribbons, (nanotubes),etc.
- **Symmetry breaking**: epitaxial growth, deposition, etc.
- **Symmetry preserving**: “supergraphenes”

Band-gap opening

- **Electron confinement**: nanoribbons, (nanotubes),etc.
- **Symmetry breaking**: epitaxial growth, deposition, etc.
- **Symmetry preserving**: “supergraphenes”

e-*h* symmetry

$$H^{TB} = \sum_{\sigma,ij}(t_{ij} a^{\dagger}_{i,\sigma} b_{j,\sigma} + t_{ji} b^{\dagger}_{j,\sigma} a_{i,\sigma})$$

Electron-hole symmetry

$$b_i \rightarrow -b_i \Longrightarrow \mathbf{h} \rightarrow -\mathbf{h}$$

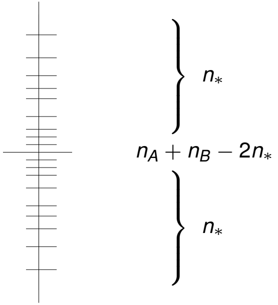
if ϵ_i is eigenvalue and

$c^{\dagger}_i = \sum_i \alpha_i a^{\dagger}_i + \sum_j \beta_j b^{\dagger}_j$ eigenvector

$$\Downarrow$$

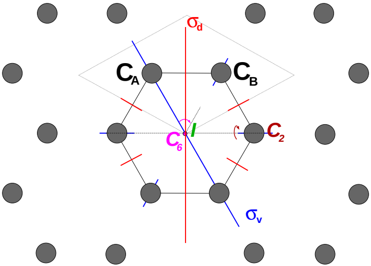
$-\epsilon_i$ is also eigenvalue and

$c'^{\dagger}_i = \sum_i \alpha_i a^{\dagger}_i - \sum_j \beta_j b^{\dagger}_j$ is eigenvector



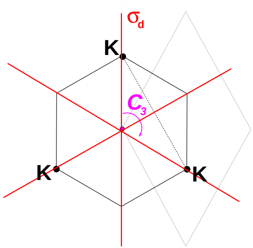
Spatial symmetry

r-space



$$G_0 = D_{6h}$$

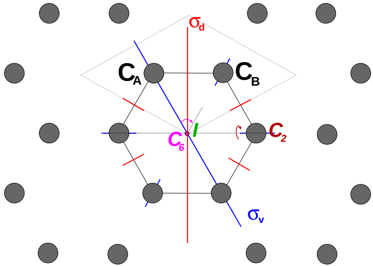
k-space



$$G(\mathbf{k}) = \{g \in G_0 | g\mathbf{k} = \mathbf{k} + \mathbf{G}\}$$
$$\Rightarrow G(\mathbf{K}) = D_{3h}$$

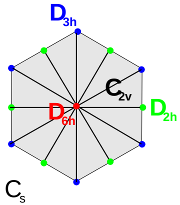
Spatial symmetry

r-space



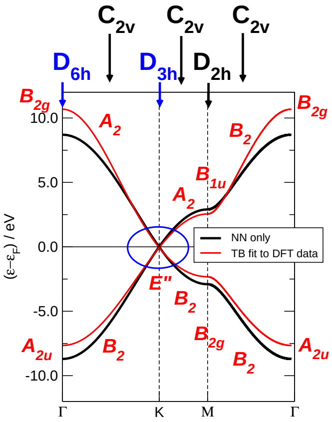
$$G_0 = D_{6h}$$

k-space



$$G(\mathbf{k}) = \{g \in G_0 | g\mathbf{k} = \mathbf{k} + \mathbf{G}\}$$
$$\Rightarrow G(\mathbf{K}) = D_{3h}$$

Spatial symmetry



$$|A_{\mathbf{k}}\rangle = \frac{1}{\sqrt{N_{BK}}} \sum_{\mathbf{R}\in BK} e^{-i\mathbf{kR}} |A_{\mathbf{R}}\rangle$$

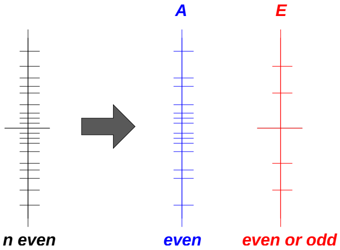
$$|B_{\mathbf{k}}\rangle = \frac{1}{\sqrt{N_{BK}}} \sum_{\mathbf{R}\in BK} e^{-i\mathbf{kR}} |B_{\mathbf{R}}\rangle$$

$$\langle r|A_{\mathbf{R}}\rangle = \phi_{p_Z}(\mathbf{r} - \mathbf{R})$$

For $\mathbf{k} = \mathbf{K}$ (or $\mathbf{K}'$)

- $\{|A_{\mathbf{k}}\rangle, |B_{\mathbf{k}}\rangle\}$ span the E'' irrep of D_{3h}
- Degeneracy is lifted at first order (no i symmetry in D_{3h})

Spatial and *e-h* symmetry



Lemma

e-h symmetry holds within each kind of symmetry species (A, E, ..)

Theorem

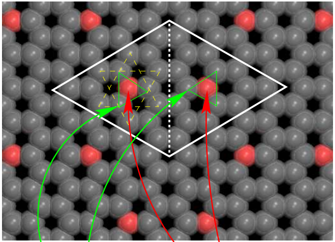
For any bipartite lattice at half-filling, if the number of E irreps is odd at a special point, there is a degeneracy at the Fermi level, i.e. $E_{gap} = 0$

A simple recipe

- Consider *nxn* graphene superlattices (i.e. $G = D_{6h}$): degeneracy is expected at Γ, K
- Introduce p_z vacancies while preserving point symmetry
- Check whether it is possible to turn the number of E irreps to be even both at Γ and at K

Counting the number of E irreps

$$n = 4$$



Γ: 2A + 2E
K: 2A + 2E

Γ: 2A
K: E

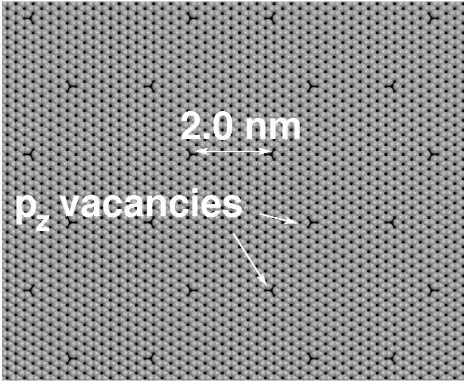
Γ	A	E
$\bar{0}_3$	$2m^2$	$2m^2$
$\bar{1}_3$	$2(3m^2+2m+1)$	$2(3m^2+2m)$
$\bar{2}_3$	$2(3m^2+4m+2)$	$2(3m^2+4m+1)$

K_n	A	E
$\bar{0}_3$	$2m^2$	$2m^2$
$\bar{1}_3$	$2m(3m+2)$	$2m(3m+2)+1$
$\bar{2}_3$	$2(3m^2+4m+1)$	$2(3m^2+4m+1)+1$

$$\Rightarrow n = 3m+1, 3m+2,\ m \in \mathbb{N}$$

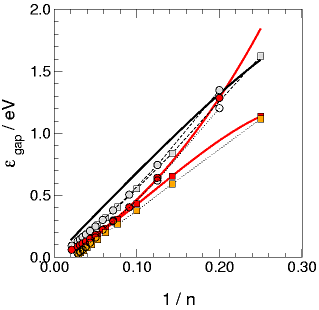
An example

$(14, 0)$-honeycomb



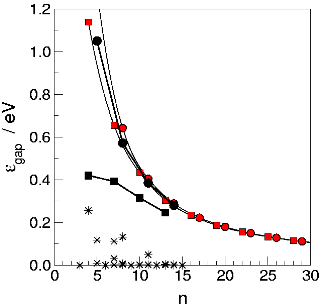
Band-gap opening..

Tight-binding



$$\epsilon_{gap}(K) \sim 2t\sqrt{1.683}/n$$

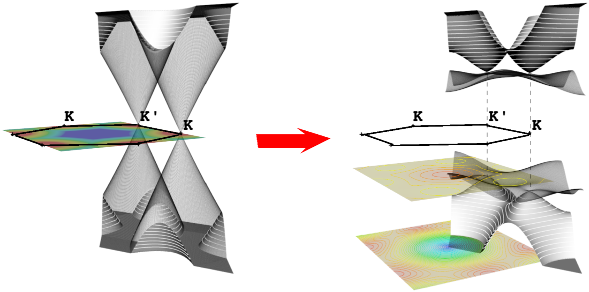
DFT



R. Martinazzo, S. Casolo and G.F. Tantardini, *Phys. Rev. B*, **81** 245420 (2010)

..and Dirac cones

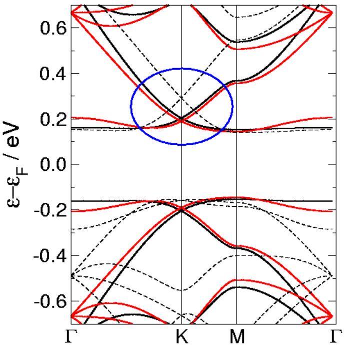
..not only: as degeneracy may still occur at $\epsilon \neq \epsilon_F$
new Dirac points are expected

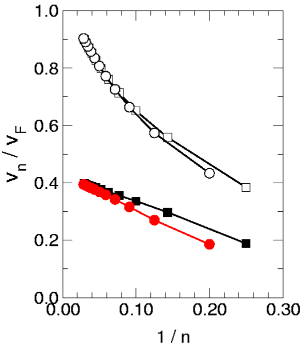


graphene (4x4) (4,0)–honeycomb

..and Dirac cones

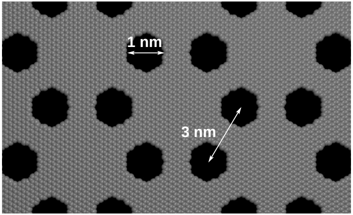
..not only: as degeneracy may still occur at $\epsilon \neq \epsilon_F$
new Dirac points are expected

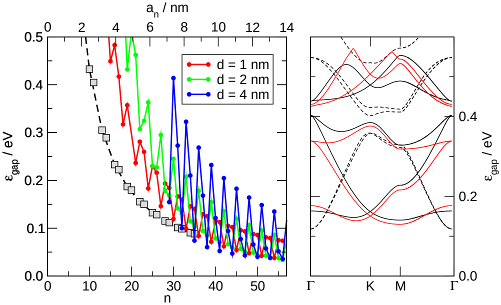




Antidot superlattices

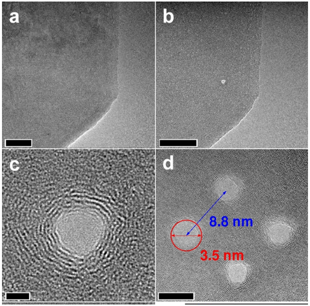
...the same holds for honeycomb antidots



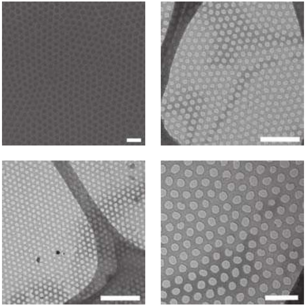


Antidot superlattices

...the same holds for honeycomb antidots



M. D. Fishbein and M. Drndic, *Appl. Phys. Lett.* **93**, 113107 (2008)
T. Shen *et al. Appl. Phys. Lett.* **93**, 122102 (2008)



J. Bai *et al. Nature Nantotech.* **5**, 190 (2010)

Summary

- Covalently bound species generate midgap species upon bond formation
- Midgap states affect chemical reactivity
- Thermodynamically and kinetically favoured configurations minimize sublattice imbalance
- Symmetry *breaking* is not necessary to open a gap

Acknowledgements

University of Milan

Gian Franco Tantardini 

Simone Casolo 

Matteo Bonfanti 

Chemical Dynamics Theory Group

http://users.unimi.it/cdtg

+-x:
C.I.L.E.A. Supercomputing Center
Notur
I.S.T.M.

Acknowledgements

Thank you for your attention!