Adsorption, clustering and reactions of H atoms on graphene

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Elementary Reactive Processes at Surfaces
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Outline

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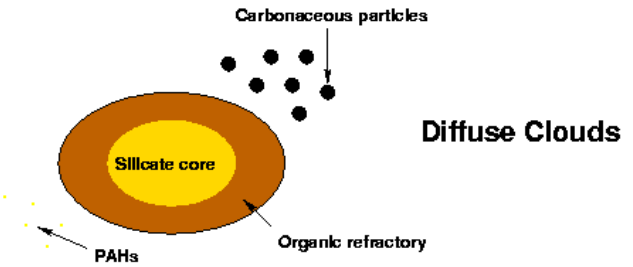
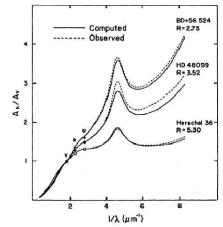
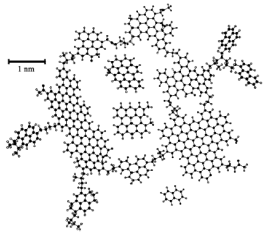
H_2 in ISM

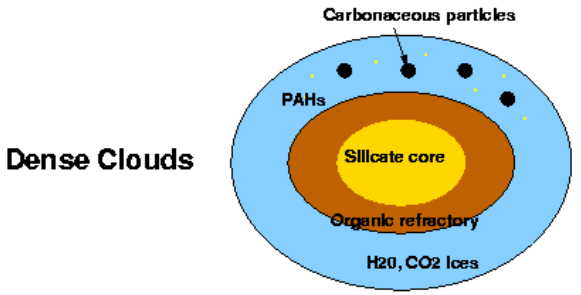
- Hydrogen is the most abundant element of the Universe
- H_2 is formed on the surface of *dust* grain

$f_{grain}=n_{grain}/n_H \sim 10^{-12}$ i.e. $\sim$1% of ISM mass





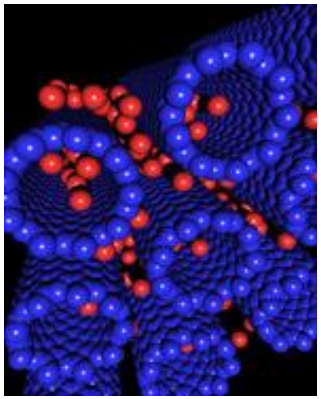


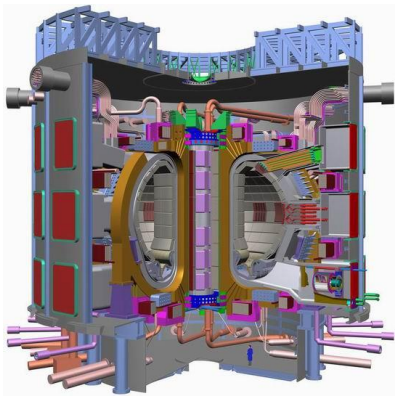


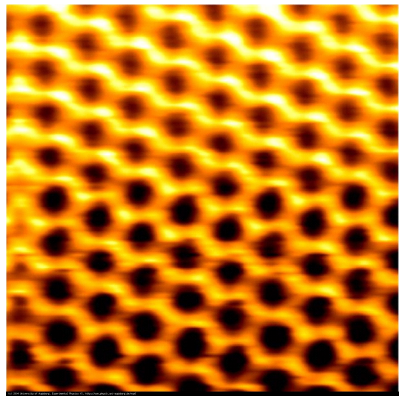
Hydrogen-graphite is an important model for understanding H_2 formation in ISM

Technology

- Hydrogen storage
- Nuclear fusion
- Nanoelectronics, spintronics, nanomagnetism







The need for understanding adsorption

H on Graphite (Graphene) *vs* metal substrates

- Chemisorption is thermally activated[1,2]
- Substantial lattice reconstruction upon sticking[1,2]
- Diffusion of chemisorbed H atoms does not occur[3]
- Preferential sticking[3]
- Clustering of H atoms[3,4,5]
- Dimer recombination[6]

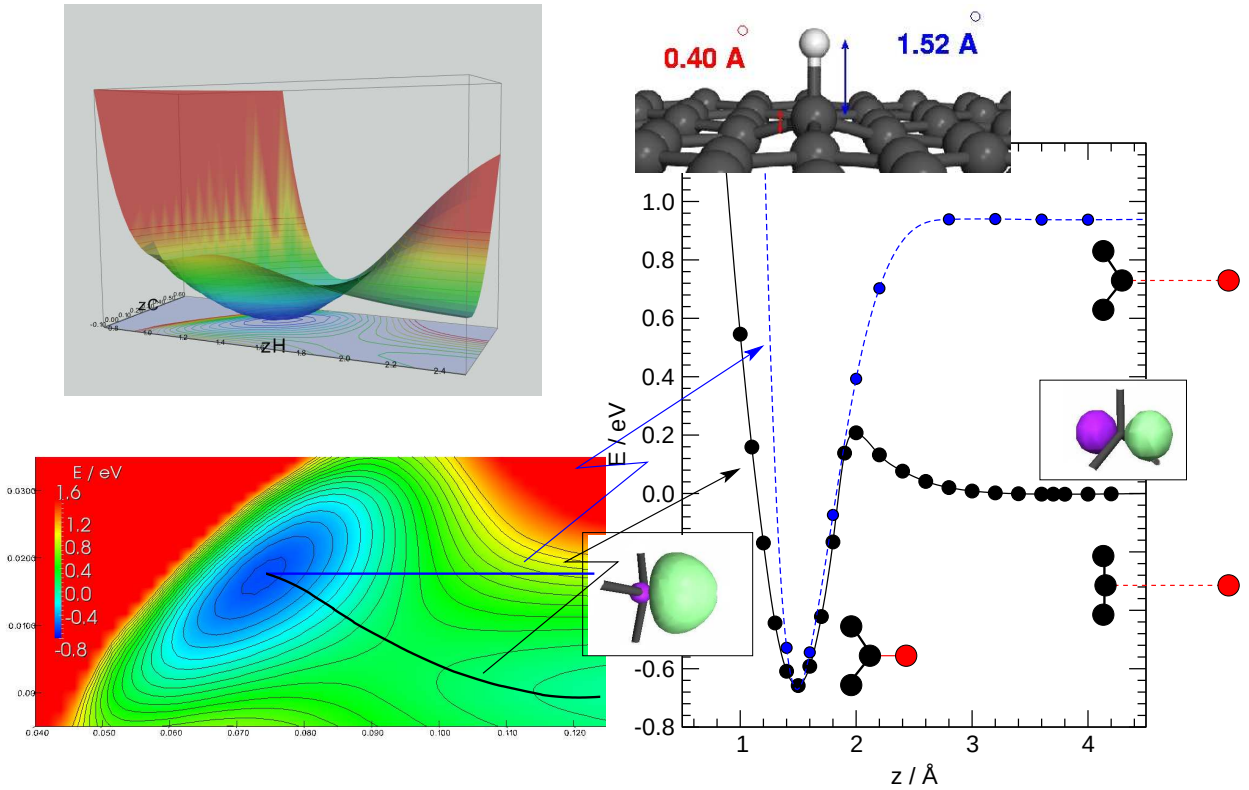
[1] L. Jeloaica and V. Sidis, *Chem. Phys. Lett.* **300**, 157 (1999) [2] X. Sha and B. Jackson, *Surf. Sci.* **496**, 318 (2002)

[3] L. Hornekaer *et al.*, *Phys. Rev. Lett.* **97**, 186102 (2006) [4] A. Andree *et al.*, *Chem. Phys. Lett.* **425**, 99 (2006) [5]

L. Hornekaer *et al.*, *Chem. Phys. Lett.* **446**, 237 (2007) [6] L. Hornekaer *et al.*, *Phys. Rev. Lett.* **96**, 156104 (2006)

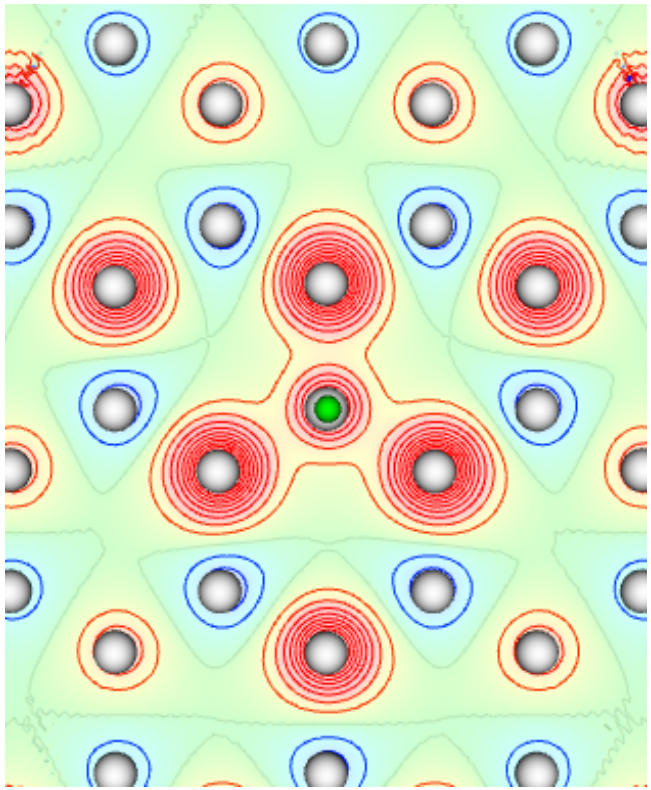
Outline

Single-H adsorption

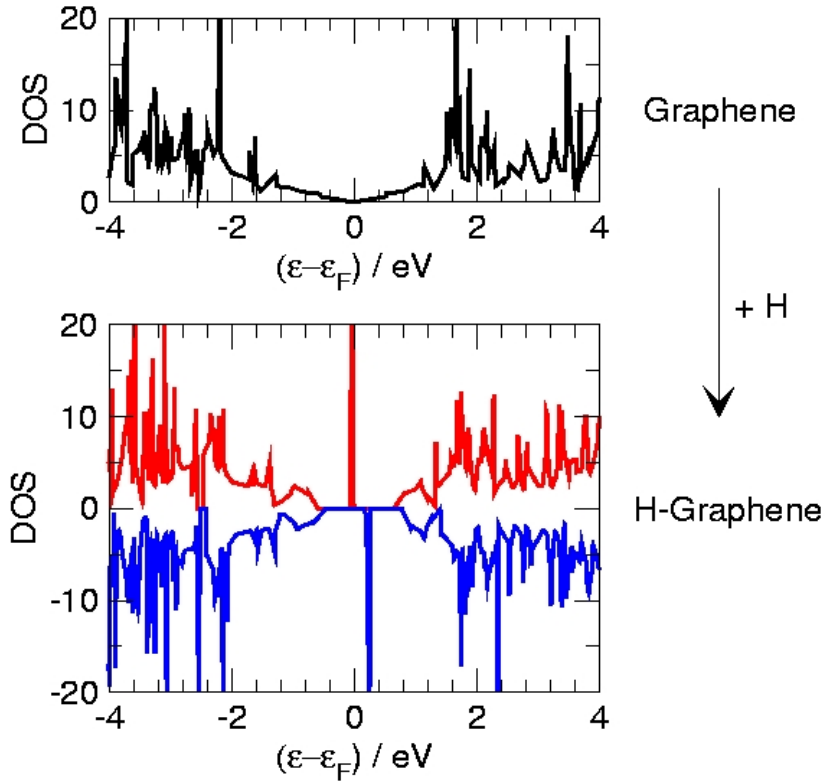


L. Jeloaica and V. Sidis, *Chem. Phys. Lett.* **300**, 157 (1999)
X. Sha and B. Jackson, *Surf. Sci.* **496**, 318 (2002)

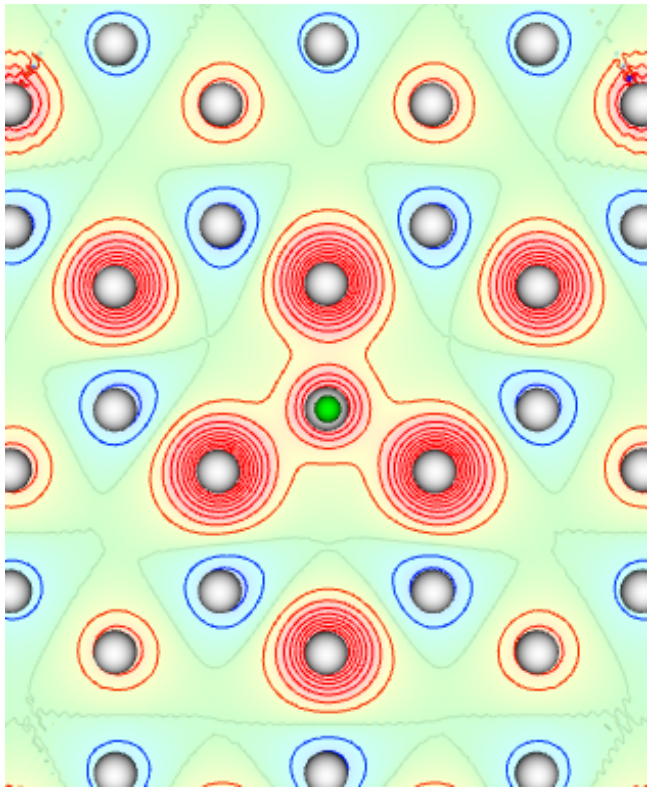
Substrate electronic structure



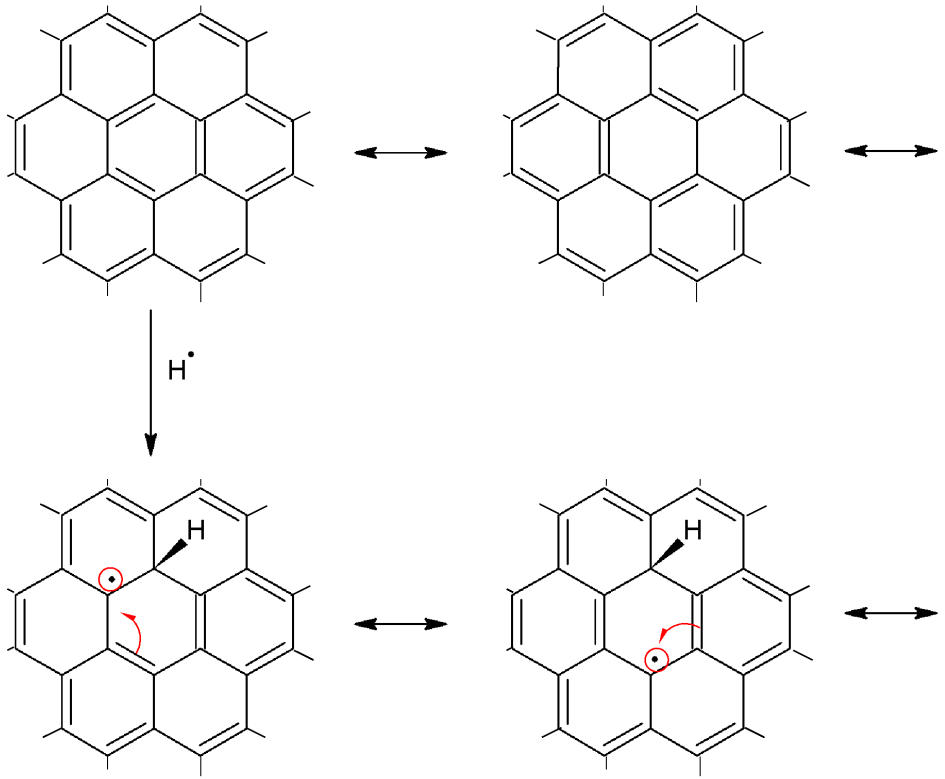
..*patterned* spin-density



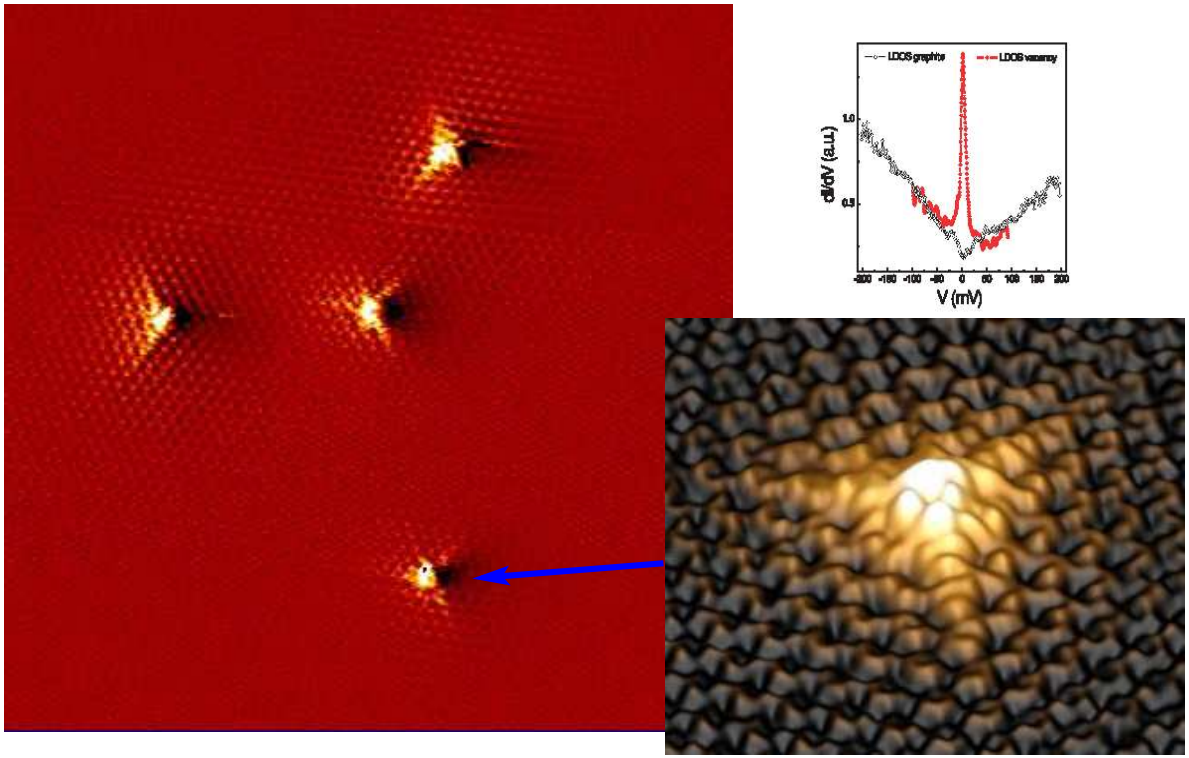
Substrate electronic structure



..*patterned* spin-density



Substrate electronic structure



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

Properties of *bipartite* lattices

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

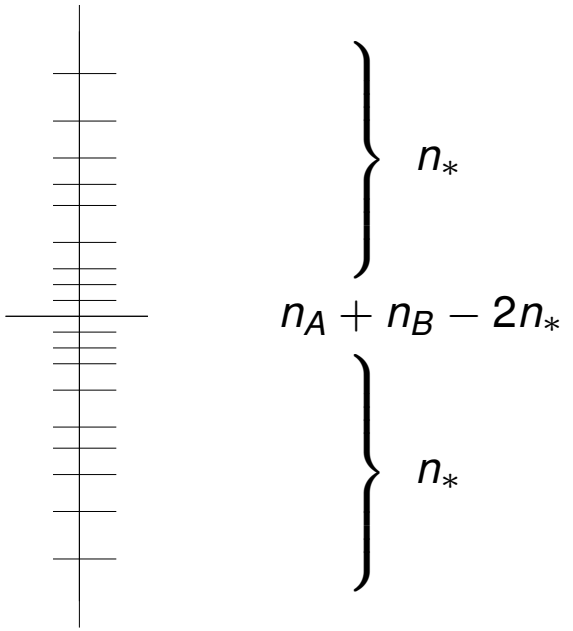
Electron-hole symmetry

$$b_i \longrightarrow -b_i \Longrightarrow \mathbf{H} \longrightarrow -\mathbf{H}$$

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



Properties of *bipartite* lattices

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

Theorem

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

Proof.

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

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

□

Properties of *bipartite* lattices

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

Theorem

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

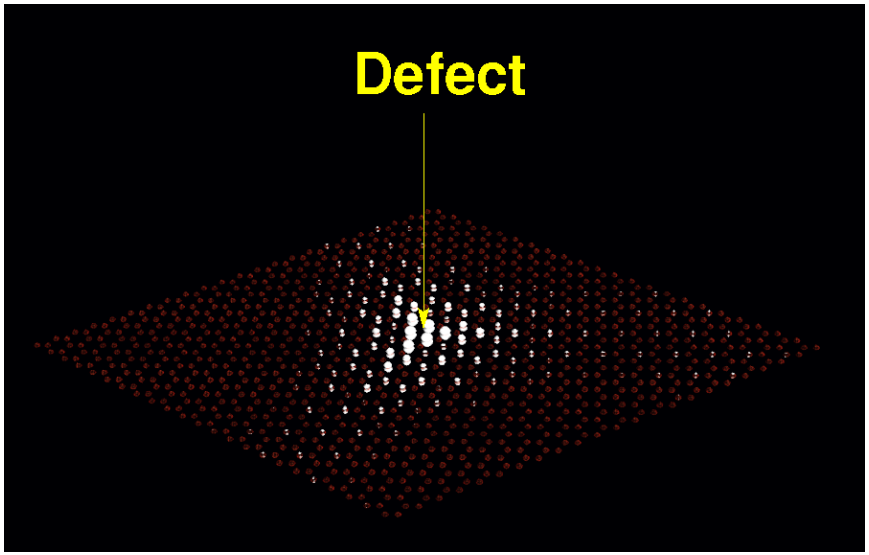
$$S = |n_A - n_B|/2 = n_I/2$$

Proof.

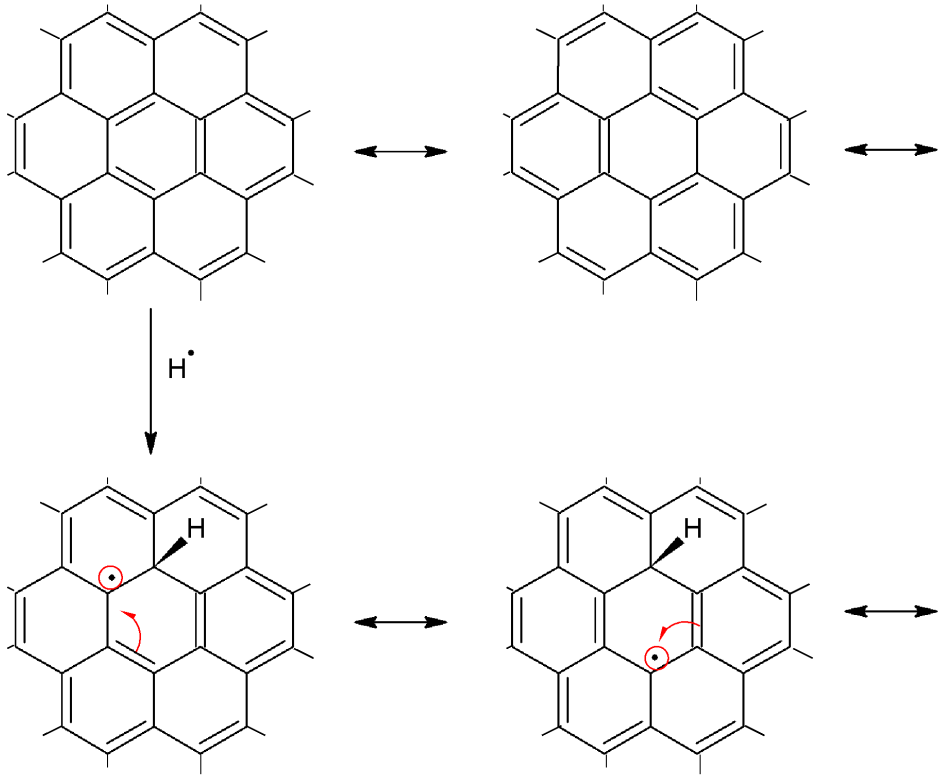
E.H. Lieb, *Phys. Rev. Lett.* **62** (1989) 1201 □

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

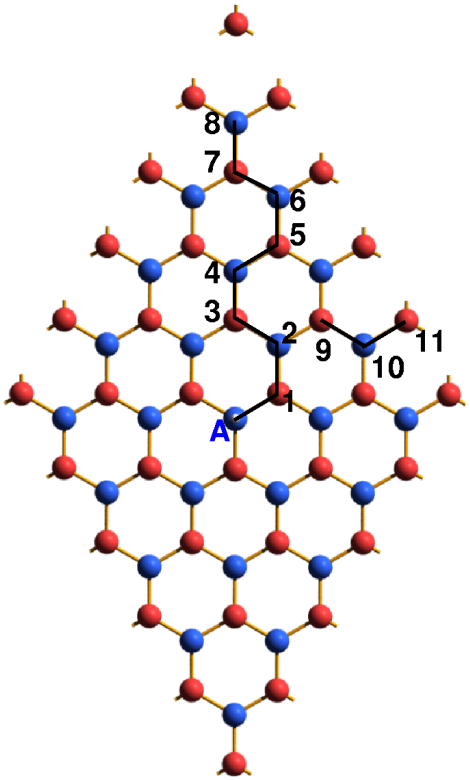
Midgap states for isolated “defects”

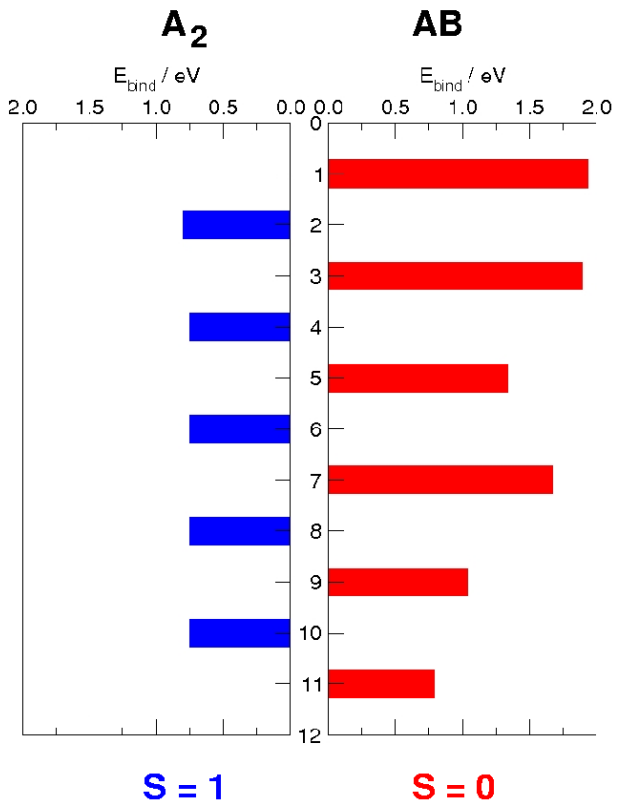


$\psi(x, y, z) \sim 1/r$

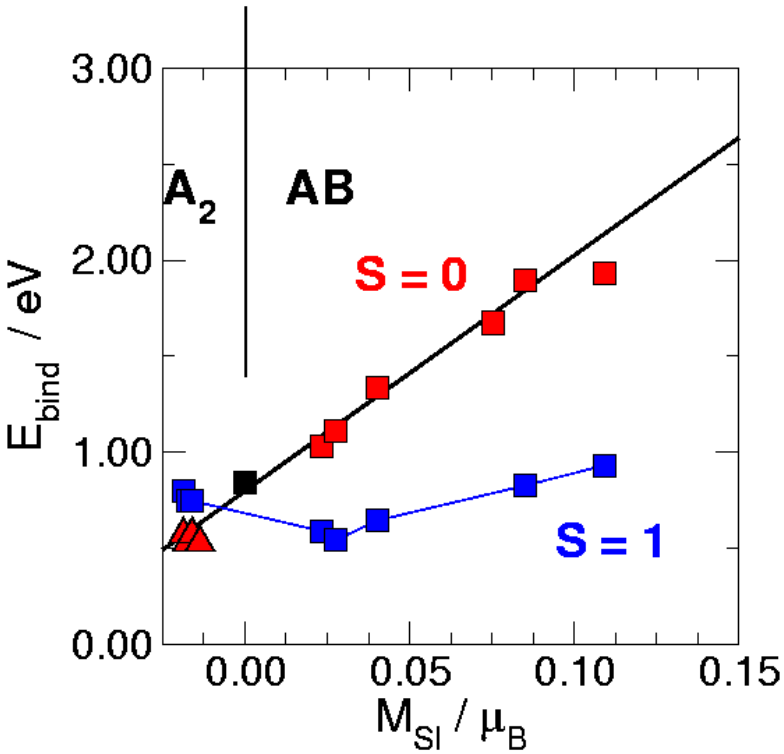


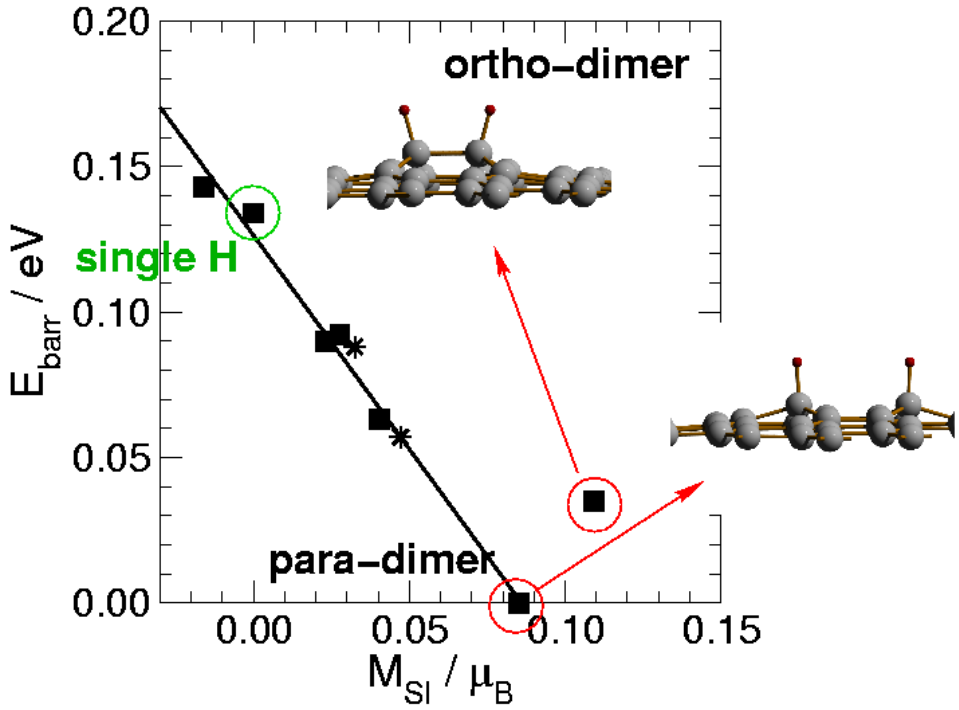
Dimers


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


A2
AB
Ebind / eV
Ebind / 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

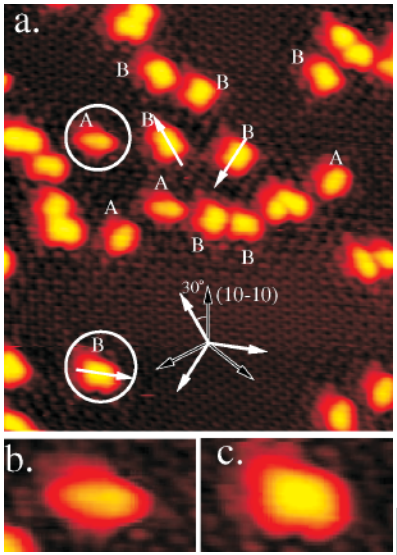
Dimers





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

Dimers



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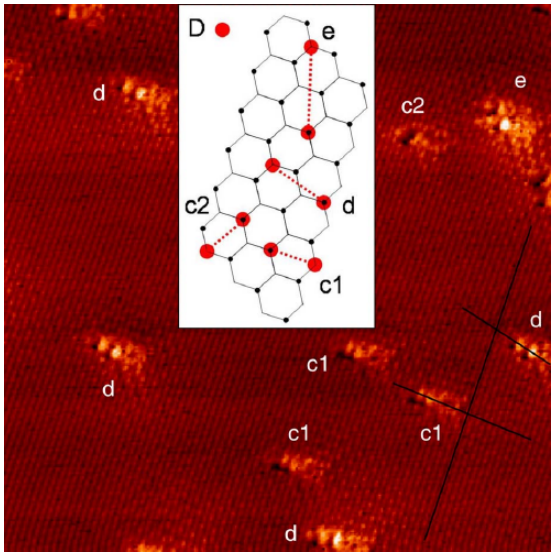
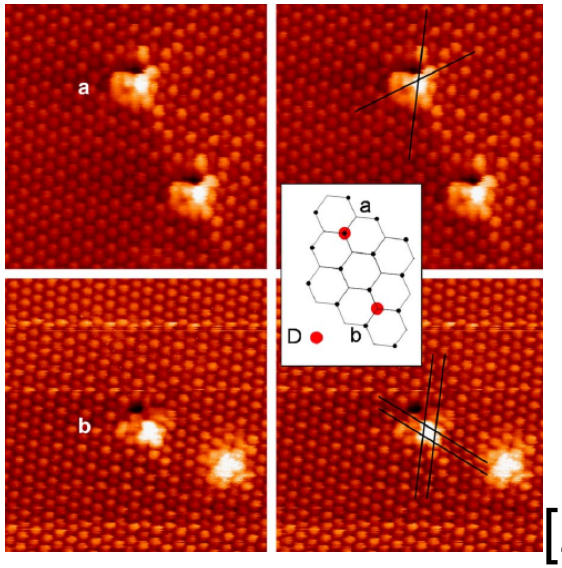


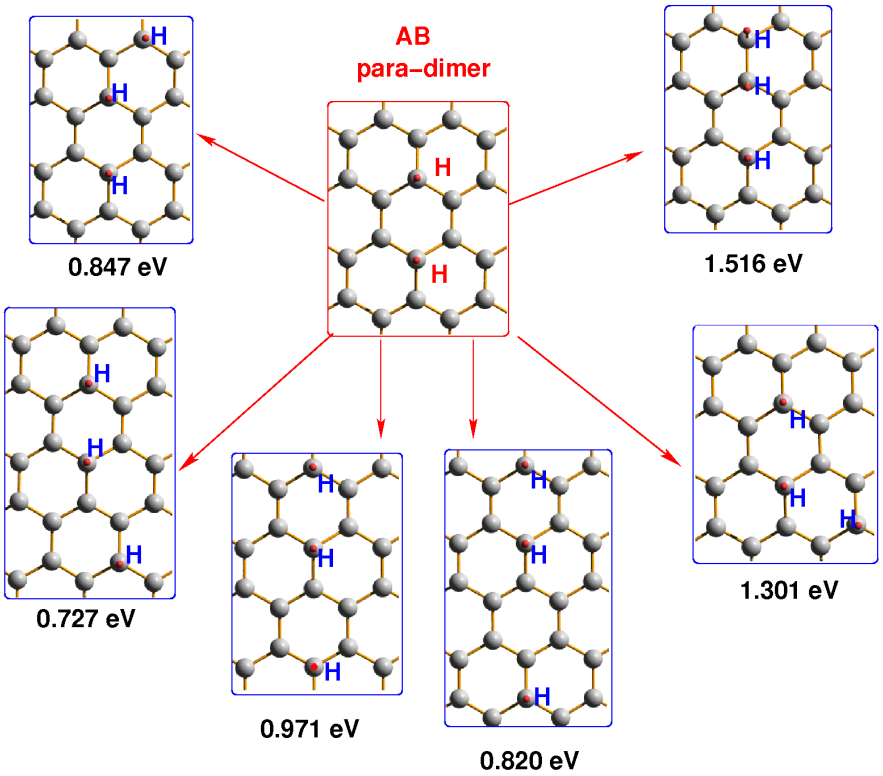


[2]

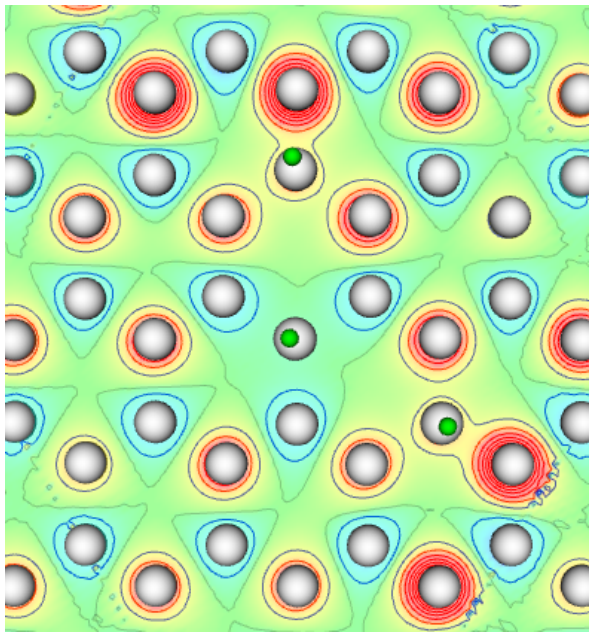
[1] L. Hornekaer, Z. Sljivancanin, W. Xu, R. Otero, E. Rauls, I. Stensgaard, E. Laegsgaard, B. Hammer and F. Besenbacher. *Phys. Rev. Lett.* **96** 156104 (2006)

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

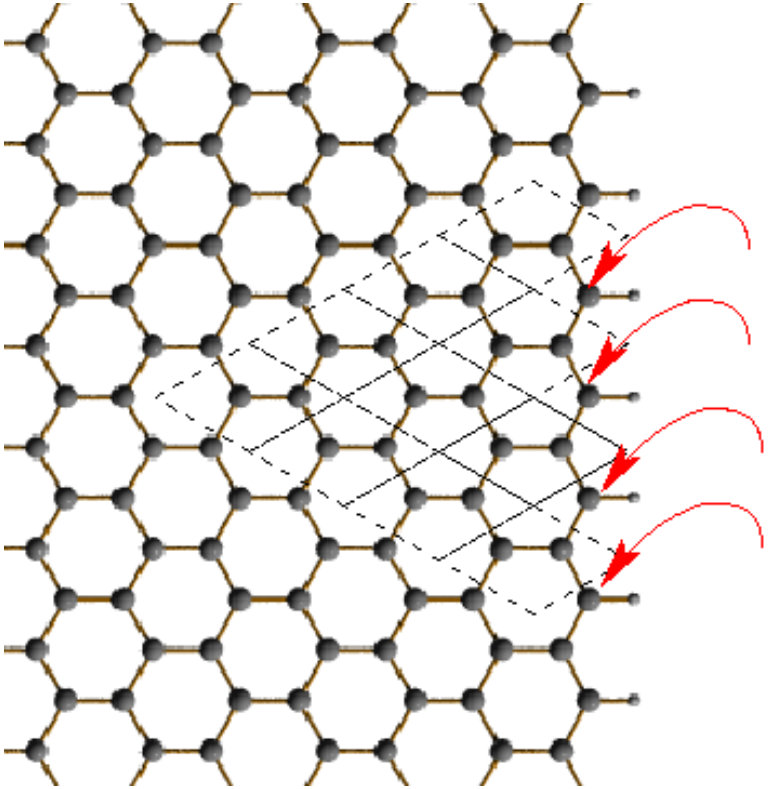
3-atom clusters, etc.



A_2B



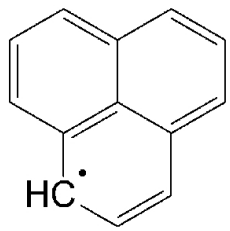
Role of edges



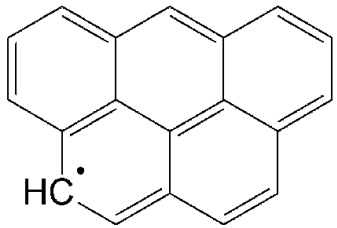
- *zig-zag* edges have enhanced hydrogen affinity
- geometric effects can be investigated in small graphenes

$\Rightarrow$ DFT and Multi-Reference Quasi-Degenerate PT on CASSCF wavefunctions

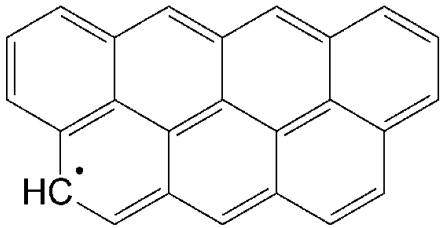
Systems



perinaftenile / fenalene

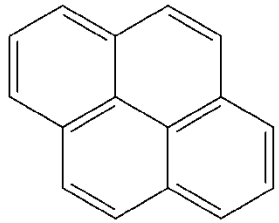


benzo[cd]pirenile

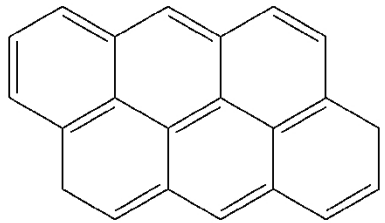


7 - PAH

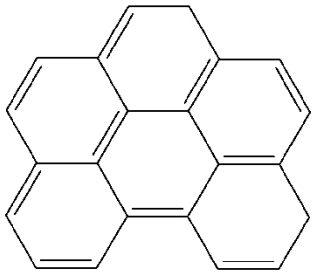
imbalanced ‘PAHs’



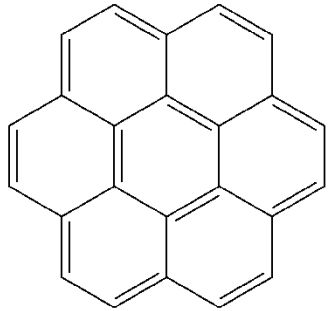
pirene



dibenzo[def,mno]crisene / antrantrene



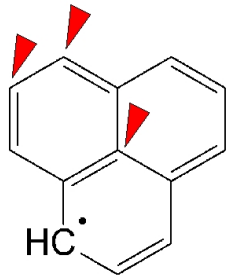
benzo[ghi]perilene



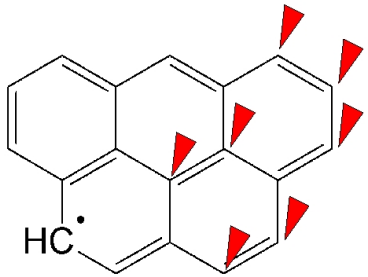
coronene

balanced PAHs

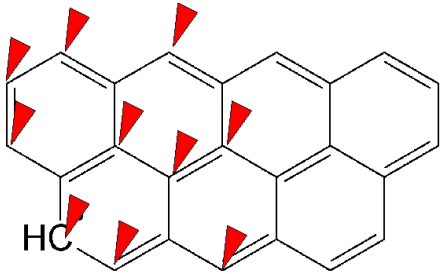
Systems



perinaftenile / fenalene



benzo[cd]pirenile



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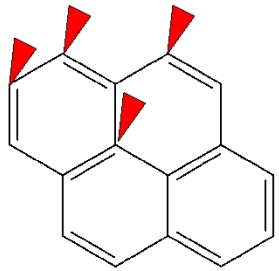
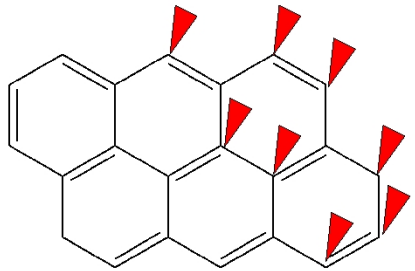
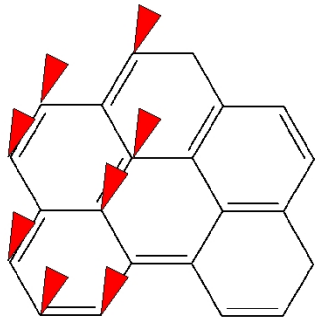
imbalanced ‘PAHs’



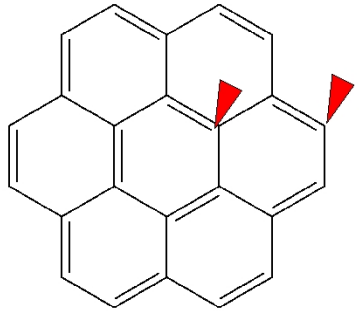
pirene



dibenzo[def,mno]crisene / antrantrene



benzo[ghi]perilene

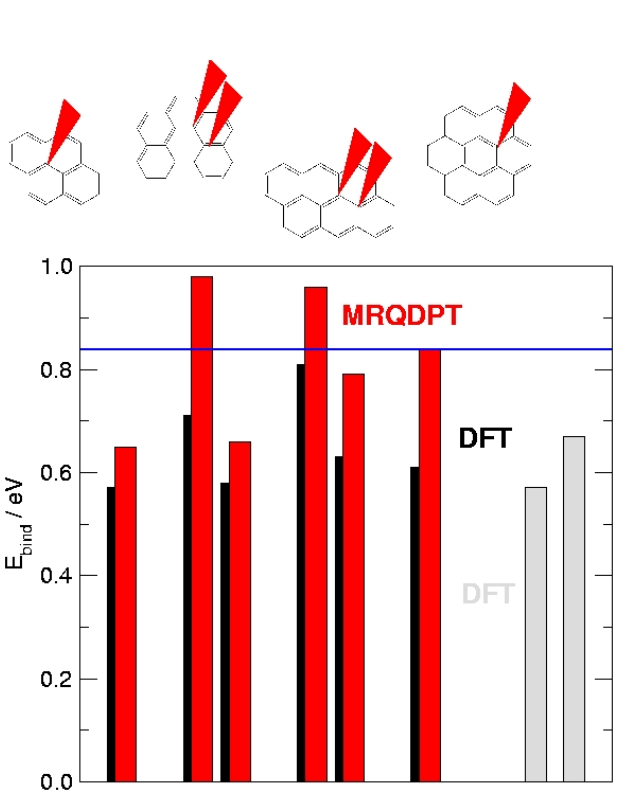


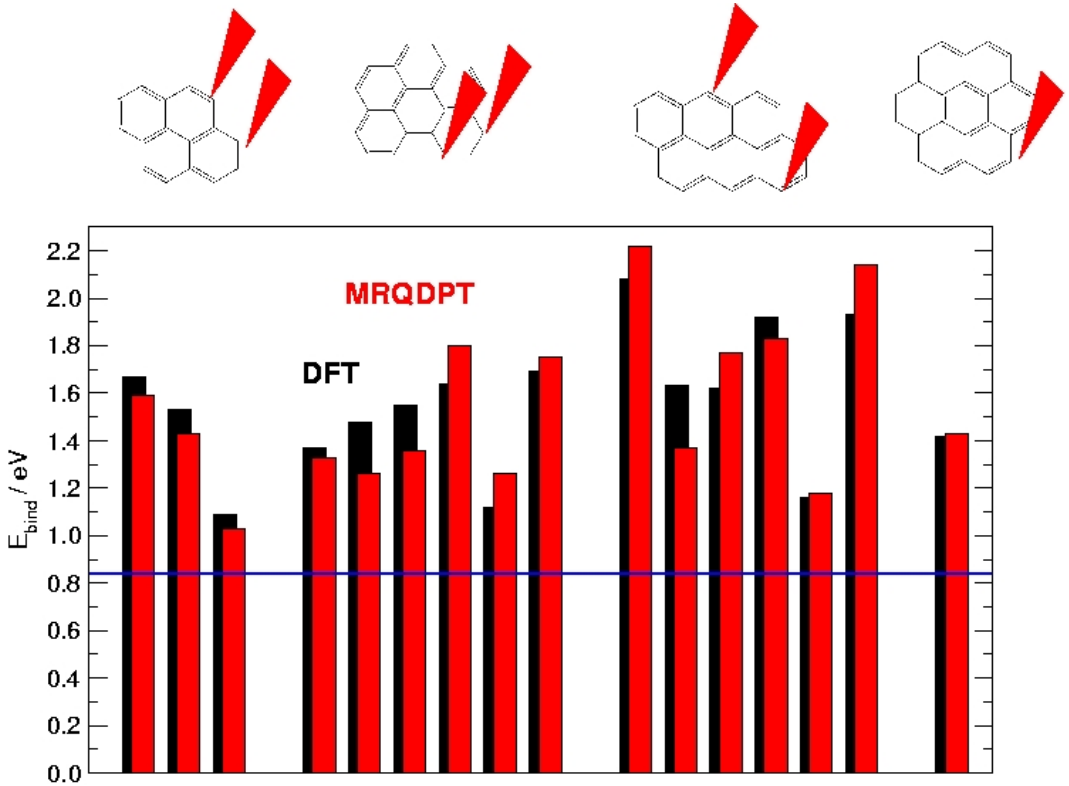
coronene

balanced PAHs

Balanced PAHs

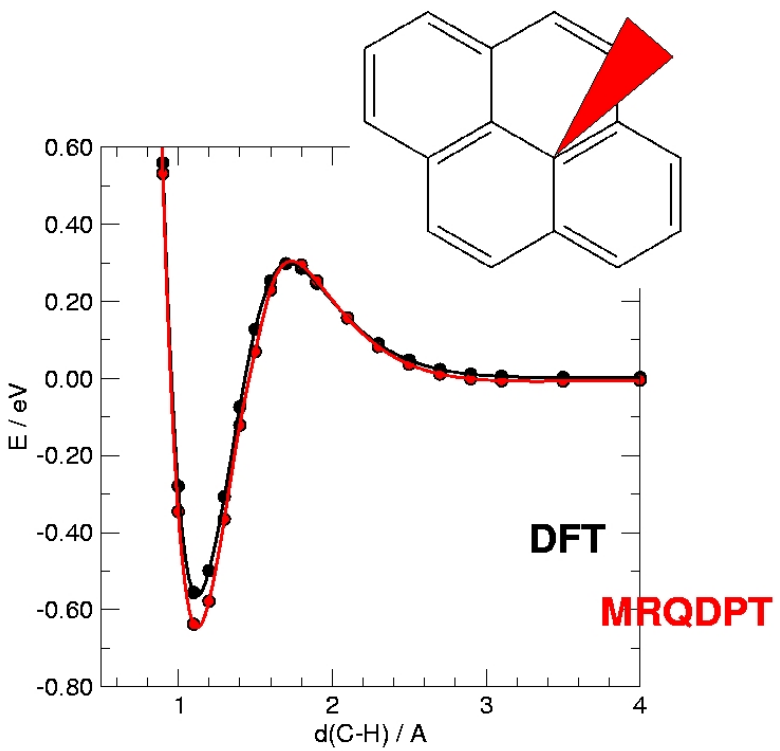
Graphitic *vs* edge carbons

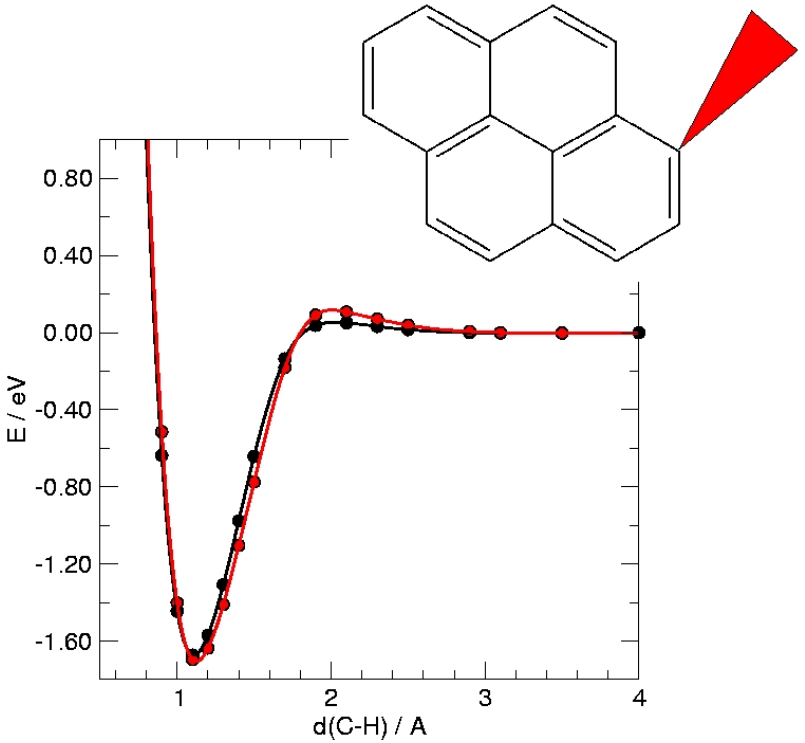




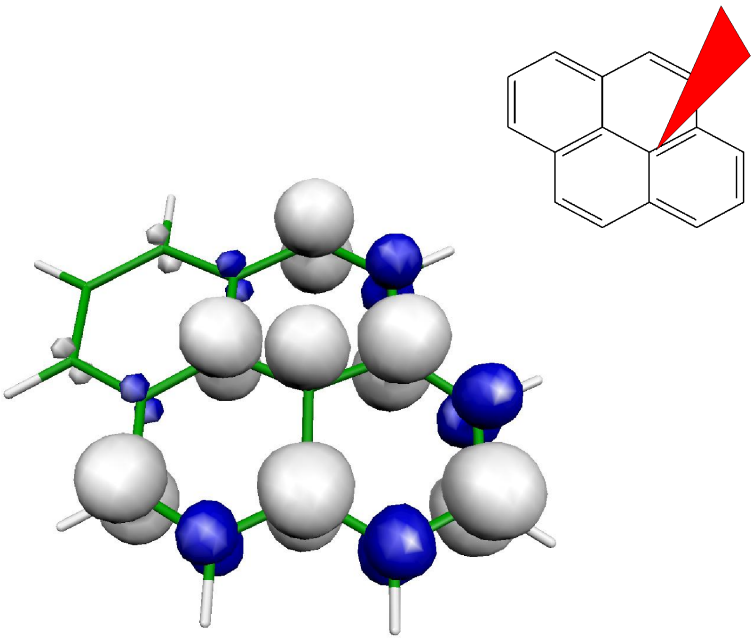
M. Bonfanti, S. Casolo, G.T. Tantardini, R. Martinazzo, *to be submitted*

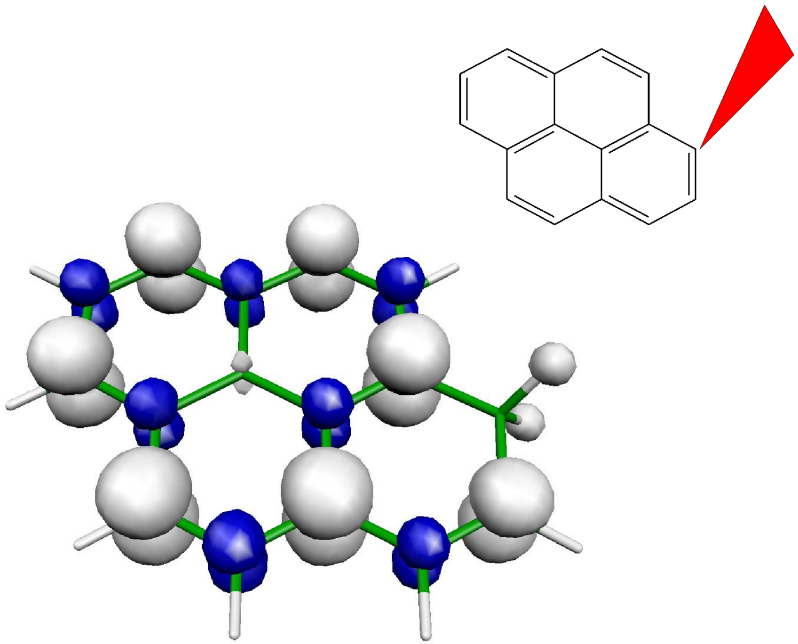
Adsorption paths
Balanced PAH





Spin-density
H + Balanced PAH





Outline

H_2 formation

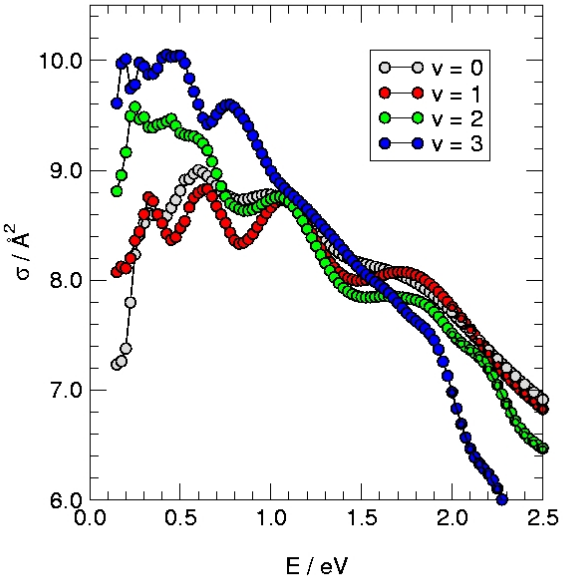
- Chemisorbed H atoms are stable up to high-temperatures
- Chemisorbed H atoms are immobile on the surface: barrier to diffusion matches desorption energy

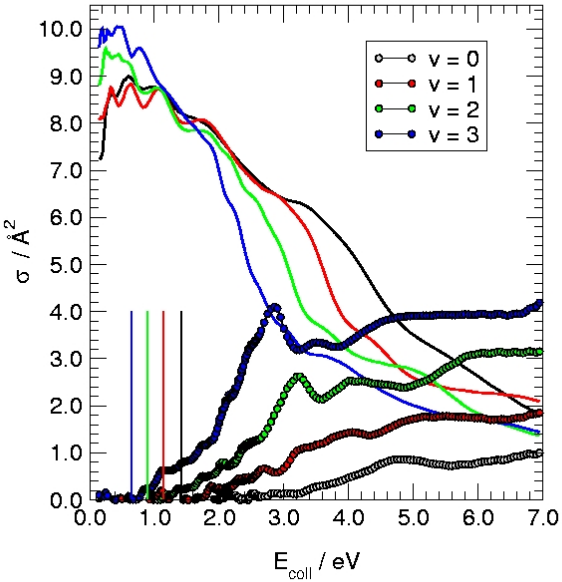
Eley-Rideal is the only possible mechanism at low-coverage..

- Physisorbed species are stable up to $T_S \sim 40K$ only
- Physisorbed species are highly mobile on the surface

Eley-Rideal, Langmuir-Hinshelwood & Hot-atom

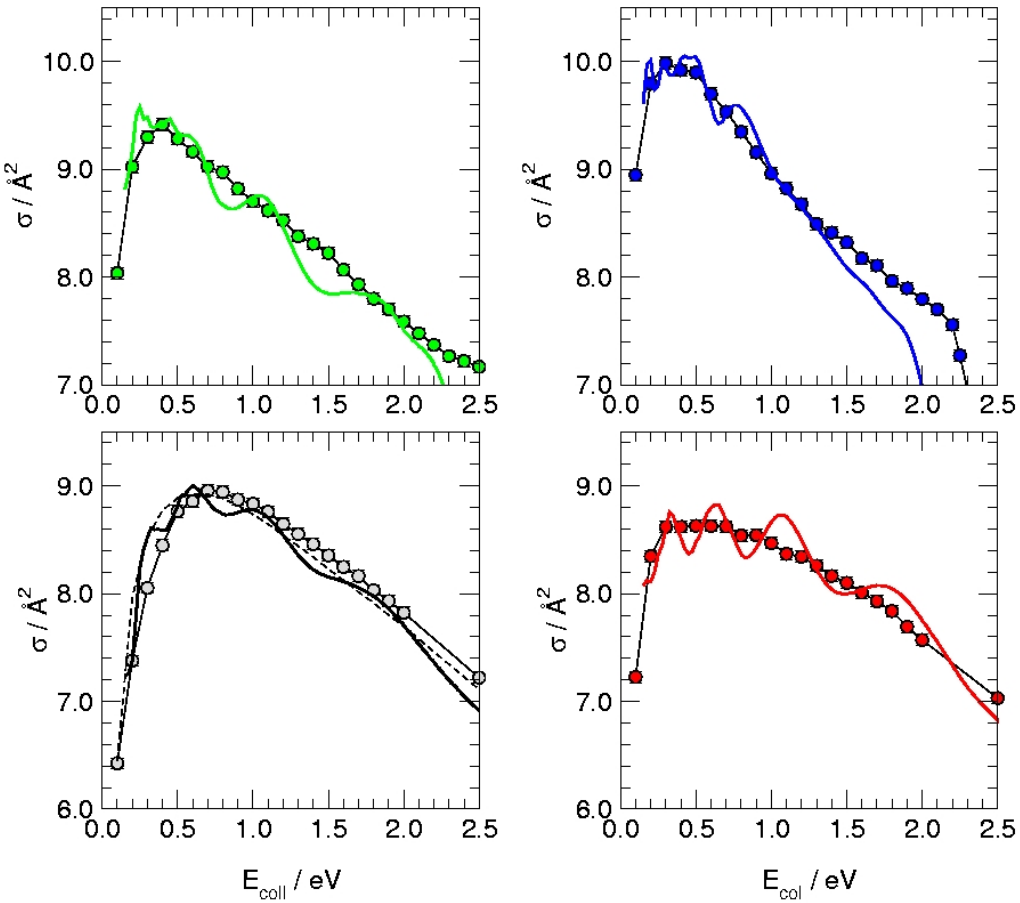
I. H-chemisorbed case





We find oscillations in both ER and CID xsections

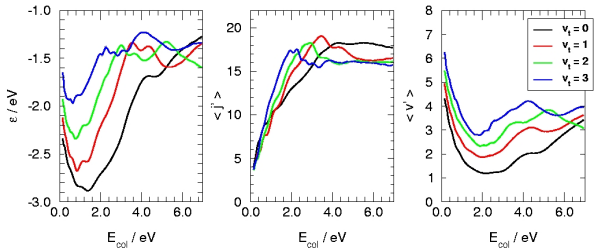
I. H-chemisorbed case



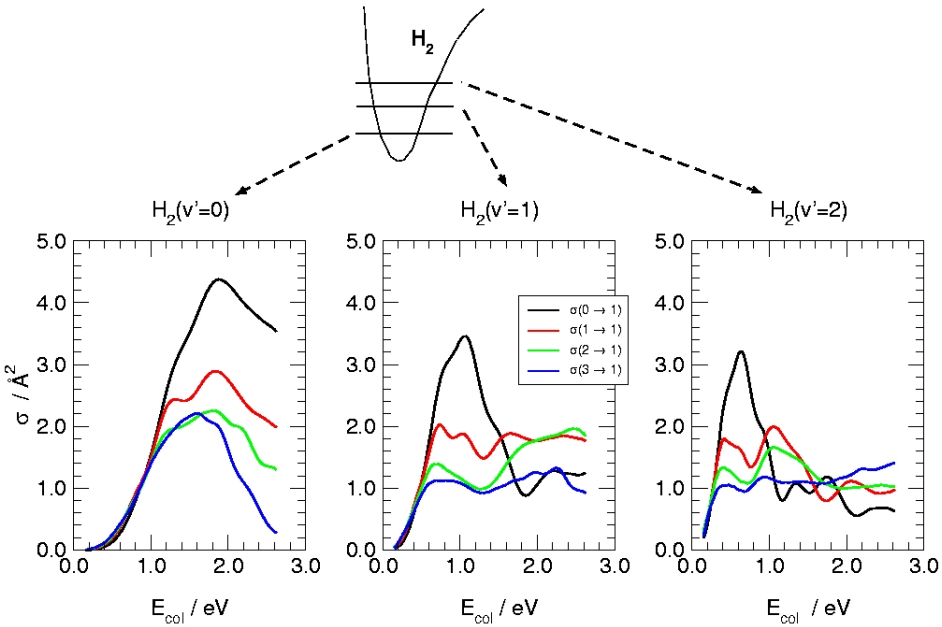
Quantum vs (quasi) classical dynamics: quantum effects

R. Martinazzo and G.F. Tantardini, *J. Phys. Chem. A*, **109**, 9379; *J. Chem. Phys.* **124** 124272 (2006)

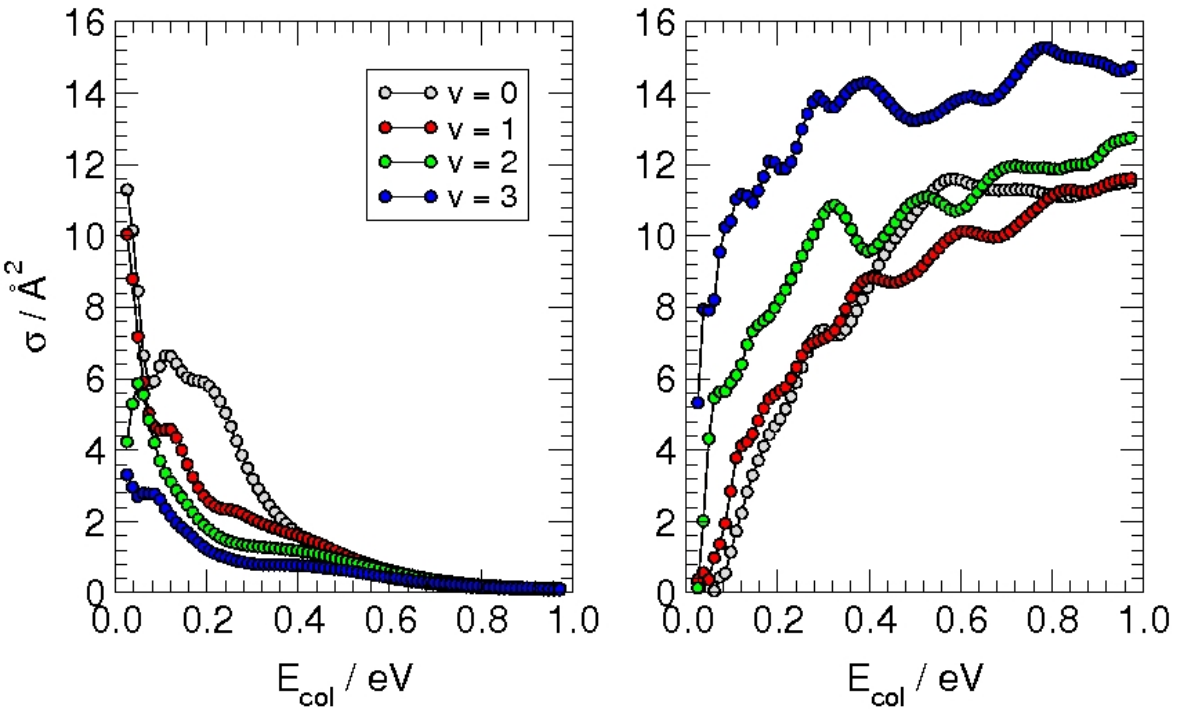
I. H-chemisorbed case



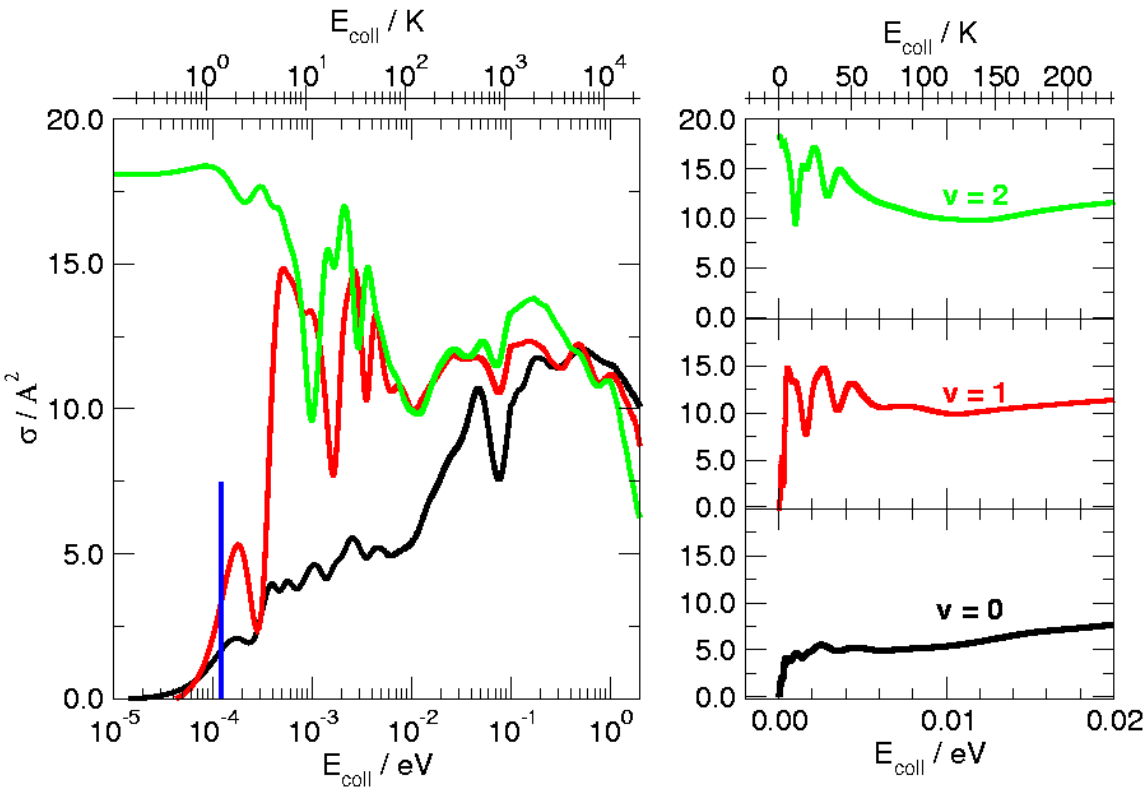
- Product molecules are internally hot
- Internal excitation is a steep decreasing function of E_{coll}



II. H-physisorbed case



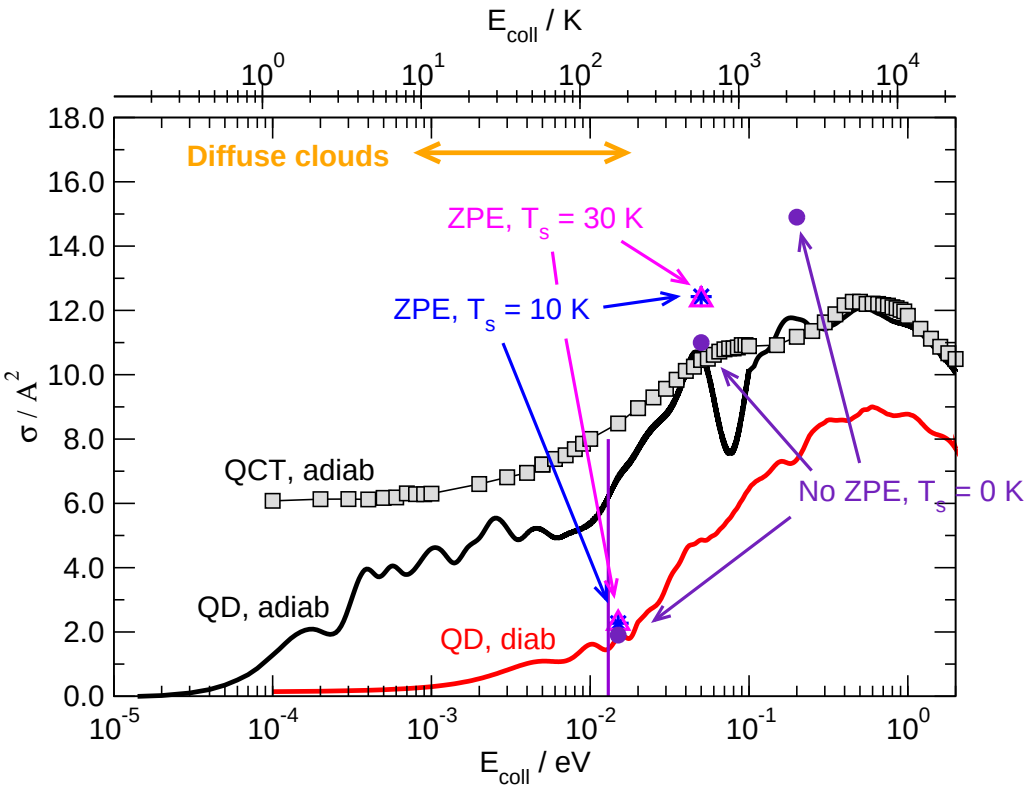
I. H-chemisorbed case



S. Casolo, M. Bonfanti, R. Martinazzo and G.F. Tantardini, *J. Phys. Chem. A*, **113** 14545 (2009)

I. H-chemisorbed case

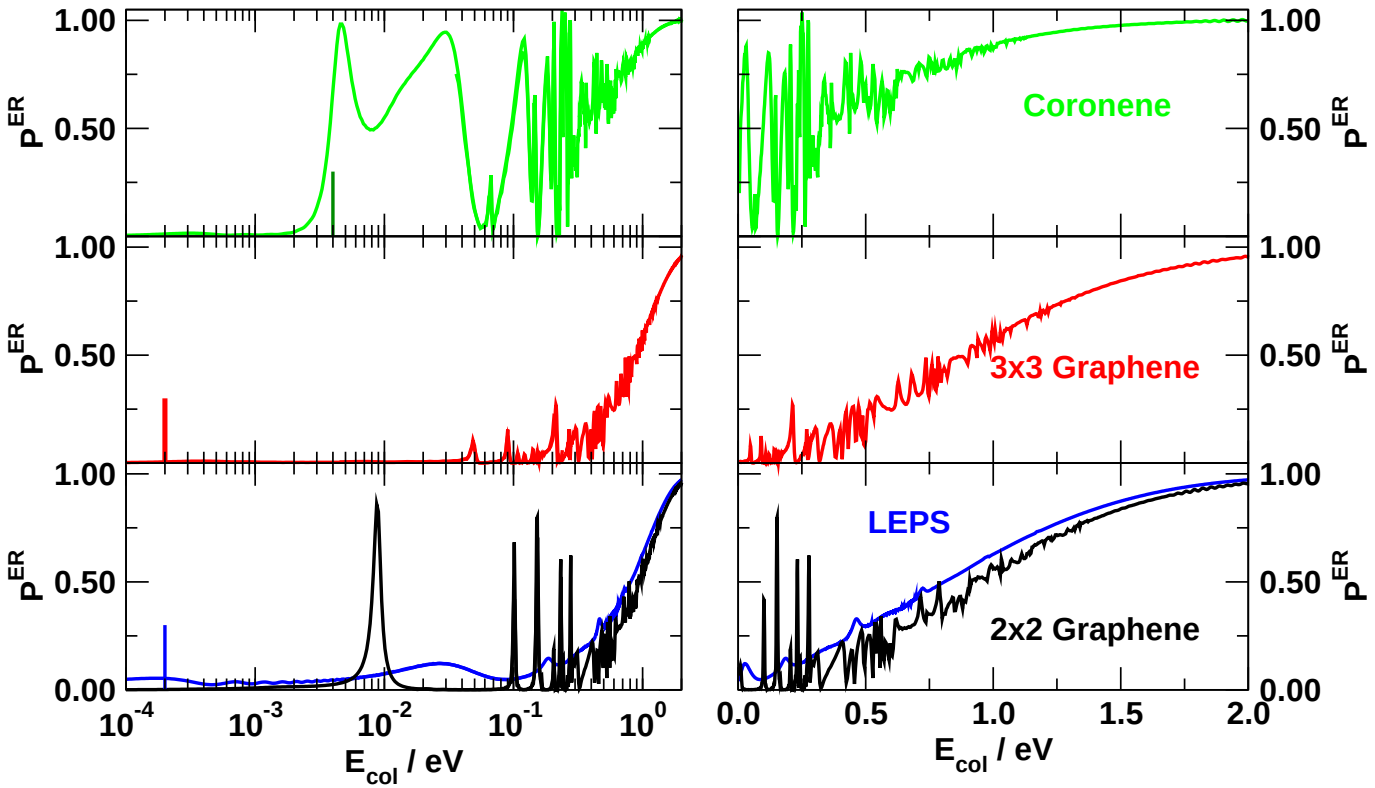
QCT comparison, $v = 0$



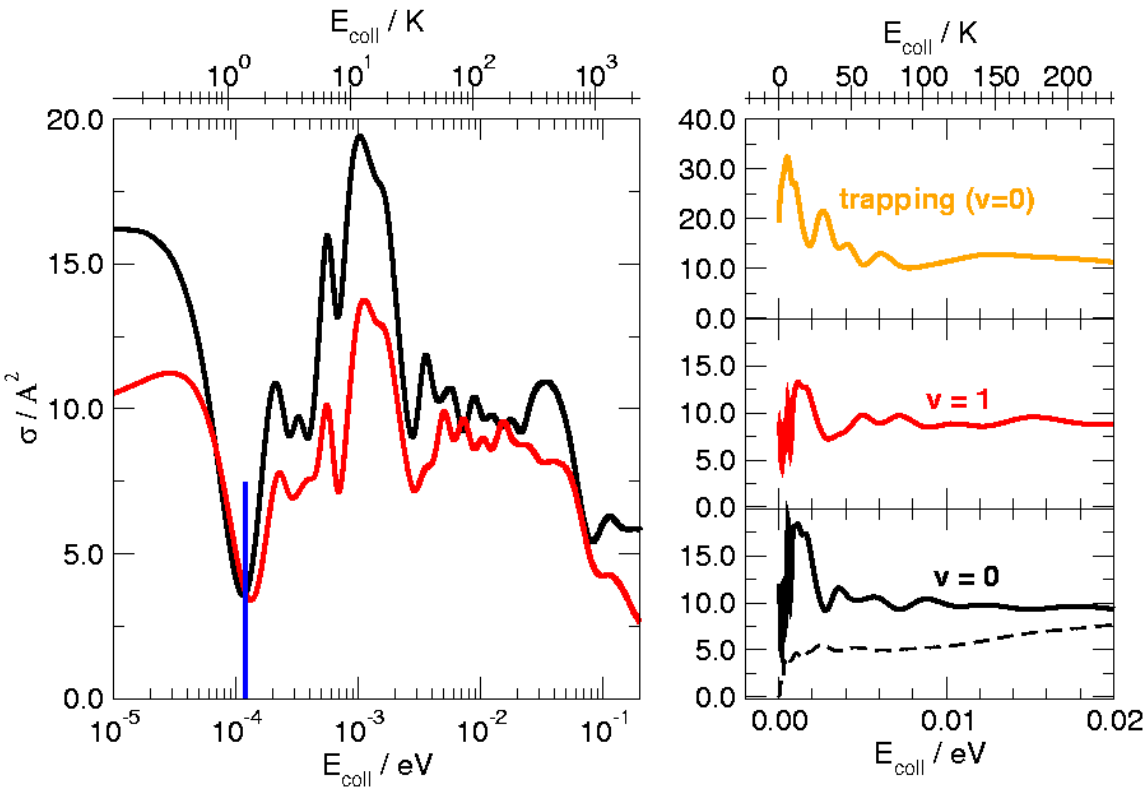
M. Sizun, D. Bachellerie, F. Anguillon, V. Sidis *Chem. Phys. Lett.* 32 **498** 2010
D. Bachellerie, M. Sizun, F. Anguillon, D. Teillet-Billy, N. Rougeau, *Phys. Chem. Chem. Phys.* 2715 **11** 2009

I. H-chemisorbed case

Effect of the substrate model

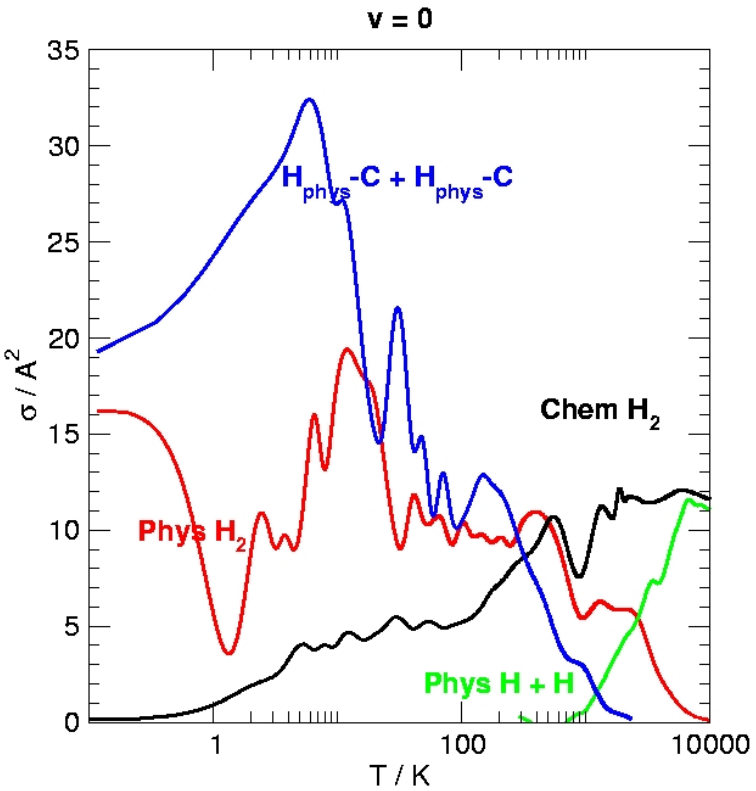


II. H-physisorbed case

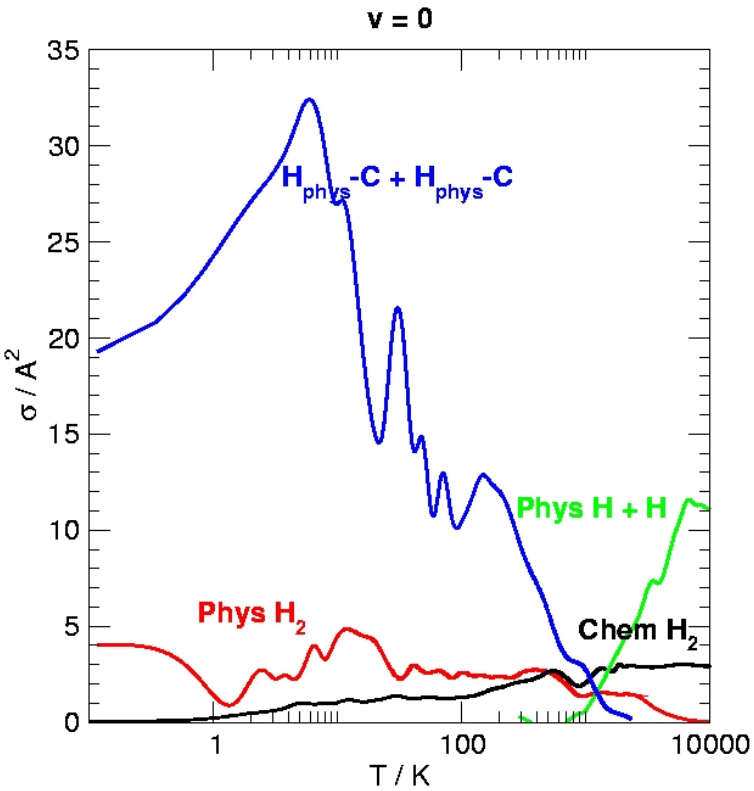


S. Casolo, M. Bonfanti, R. Martinazzo and G.F. Tantardini, *J. Phys. Chem. A*, **113** 14545 (2009)

H-chem vs H-phys



H-chem vs H-phys



Cross-sections have to be corrected for the spin-factor (1/4)

Outline

Device related properties

- **Thickness**: thinnest gate-controlled regions in transistors
- **Mobility**: high-mobility carriers
- **High-field transport**: high saturation velocities
- **Band-gap**: high on-off ratios are not achievable without a bandgap

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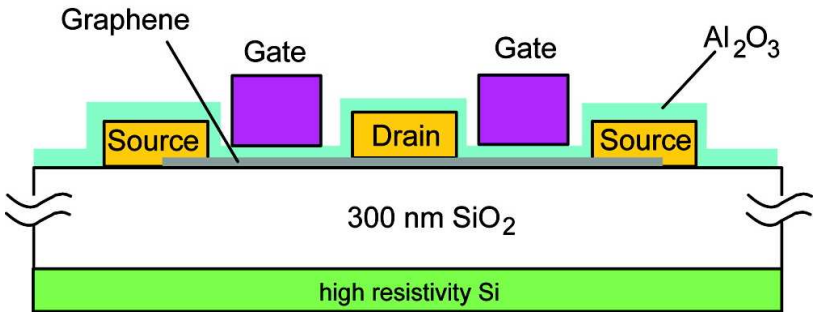
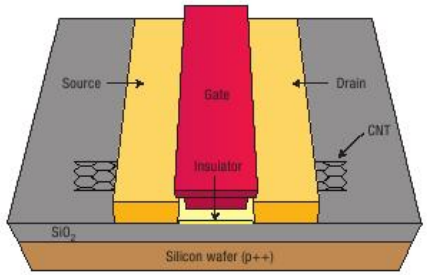
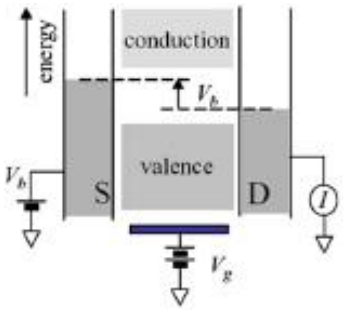
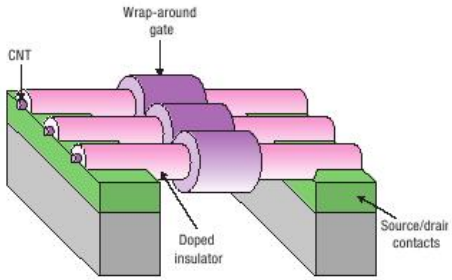
Logic applications





$$n_S = \epsilon_0 \epsilon \frac{V_g}{t\,e}$$





CNT-FET with ordinary and wrapped around gates

P. Avouris *et al.*, *Nat. Mat.*, 605, 2, (2007)

F. Schwiertz, *Nat. Nanotech.* **5**, 487 (2010)

Band-gap opening

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

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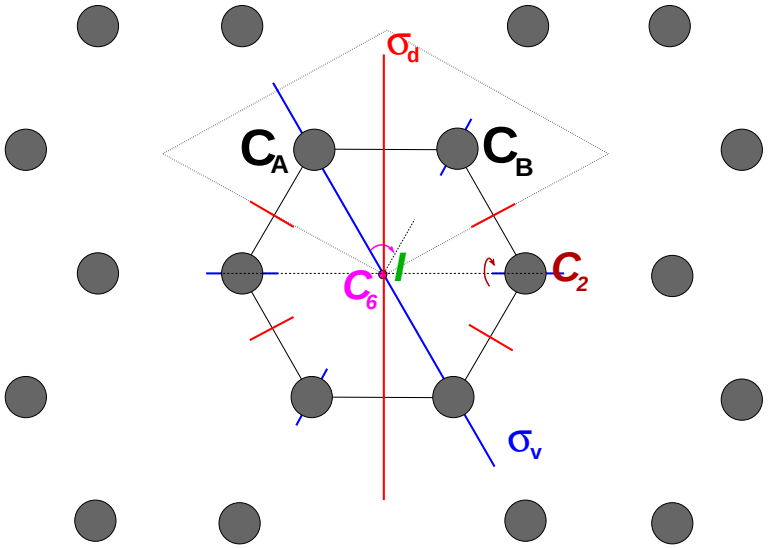
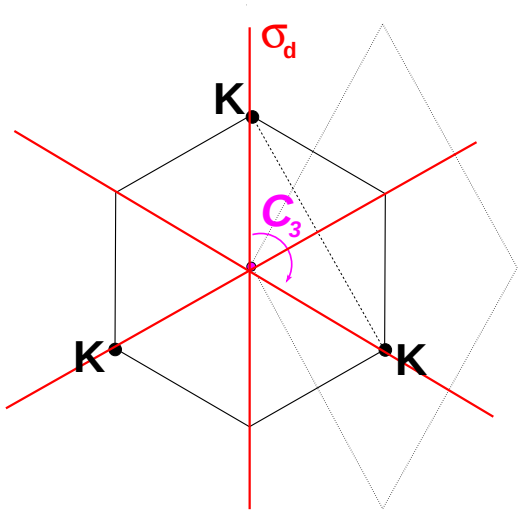
Spatial symmetry

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 and *e-h* symmetry

Lemma

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

Theorem

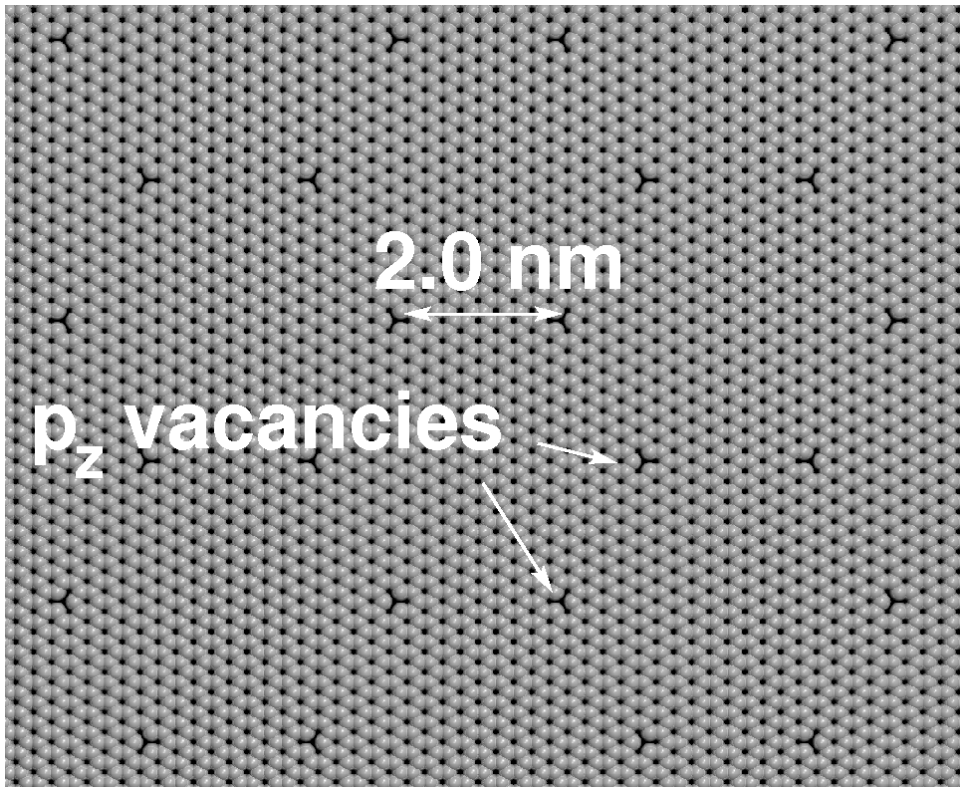
For any bipartite lattice at half-filling, if the number of E irreps is odd at a special point, there is a degeneracy at the Fermi level, i.e. $E_{gap} = 0$

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

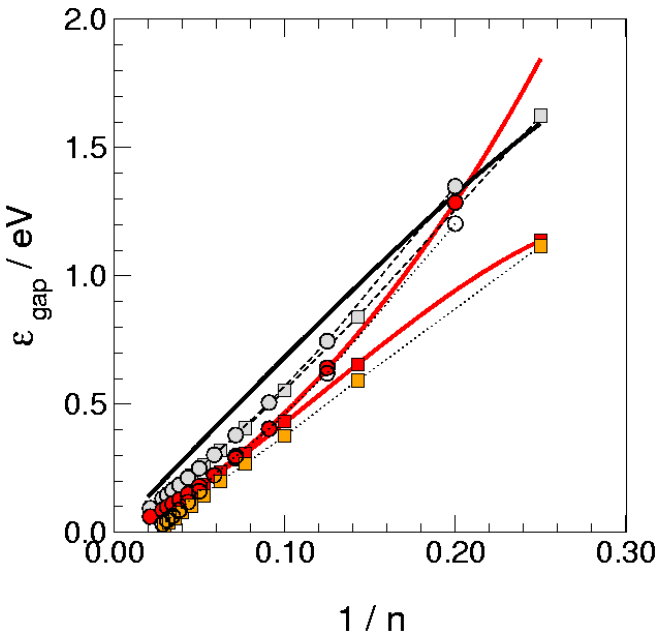
An example

$(14, 0)$-honeycomb



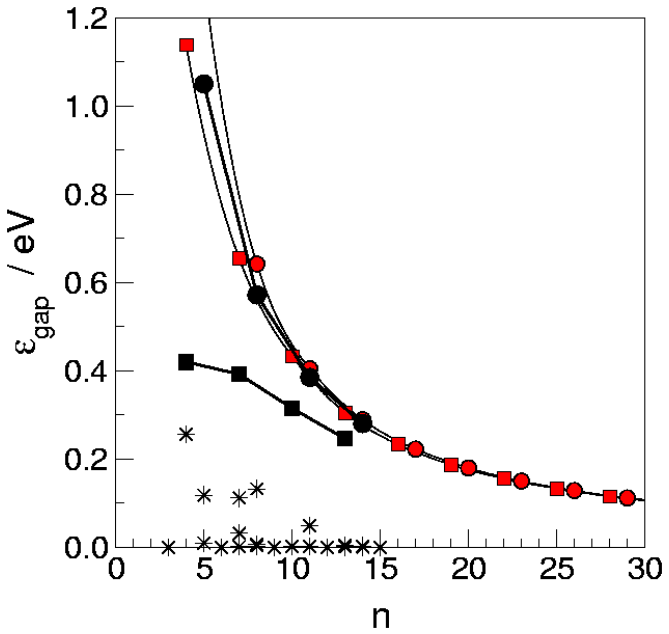
Band-gap opening..

Tight-binding



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

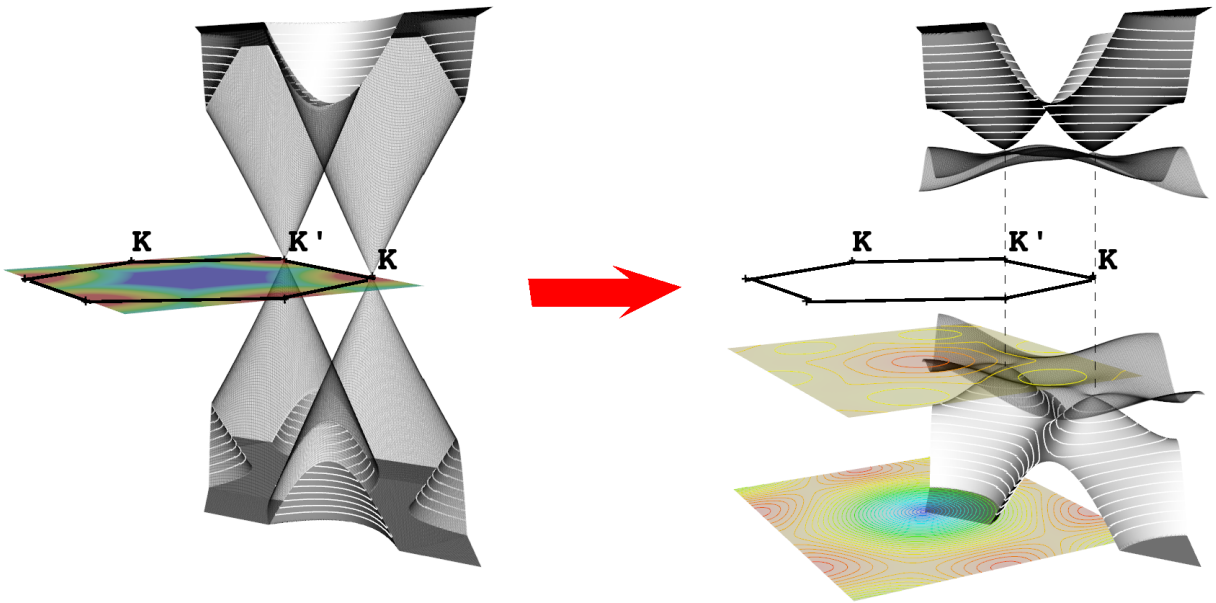
DFT



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

Summary

- Thermodynamically and kinetically favoured H clusters minimize sublattice imbalance
- Chemisorbed H atoms are immobile and have small ER xsections at low energy
- Physisorbed H atoms are highly mobile and have larger ER xsections at low energy
- Symmetry *breaking* is not necessary to open a gap

Acknowledgements

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http://users.unimi.it/cdtg

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ISTM

Alessandro Ponti

+-x:

C.I.L.E.A. Supercomputing Center

Notur

I.S.T.M.

Acknowledgements

Thank you for your attention!