Interaction of hydrogen atoms with carbon-sp^2 structures

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Domaine du Mas Blanc, Alénya (Pyrénées Orientales)
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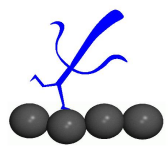
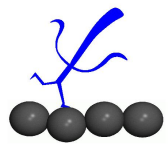


Outline



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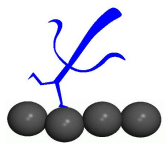

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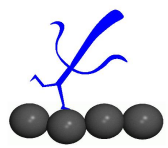

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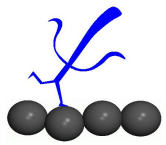
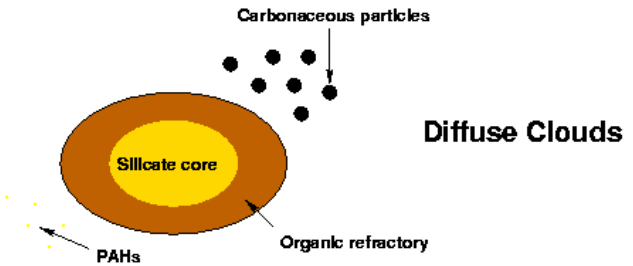
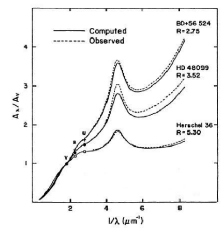


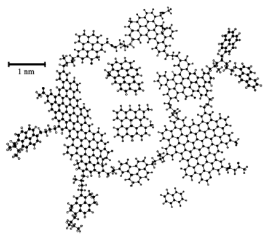
H_2 in the ISM

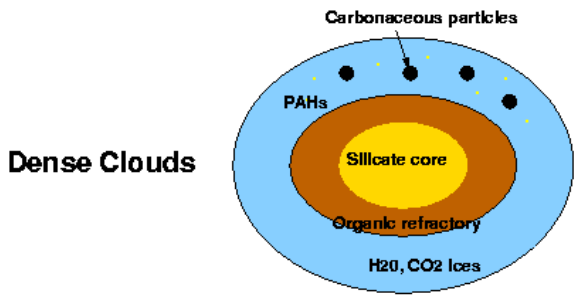
- Hydrogen is the most abundant element of the Universe
- H_2 is formed on the surface of *dust* grain

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

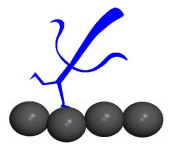






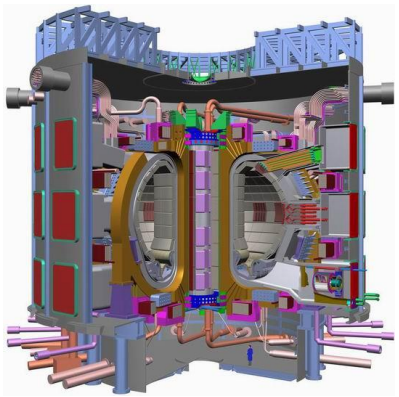


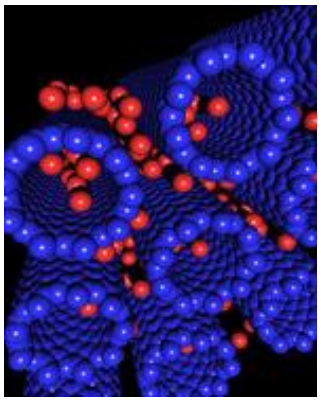
Hydrogen-graphite is an important model for understanding H_2 formation in ISM

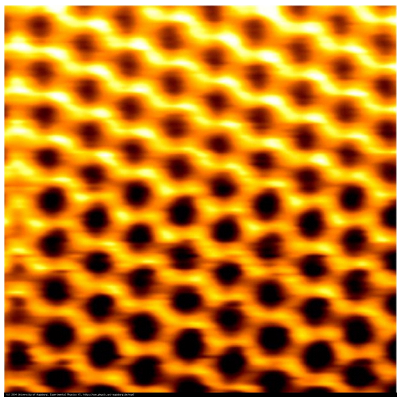


Technology

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



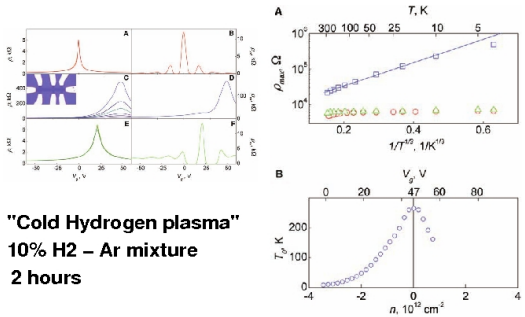


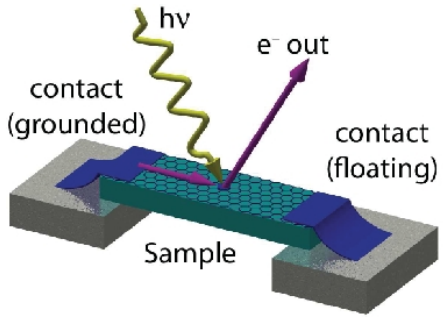


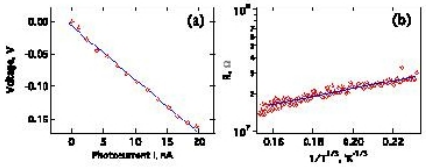
Technology: graphene physics and devices

Graphene is a true 2D-electron gas (2DEG) system with pseudo-relativistic charge-carriers

MIT occurs when hydrogenating graphene



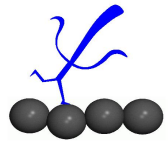




..σ *vs* T agrees well with VRH in two dimensions

High n_H : D. C. Elias *et al.*, *Science* **323**, 610 (2009)

Low n_H : A. Bostwick *et al.*, *Phys. Rev. Lett.* **103**, 056404 (2009)



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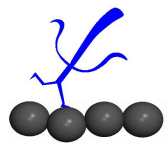
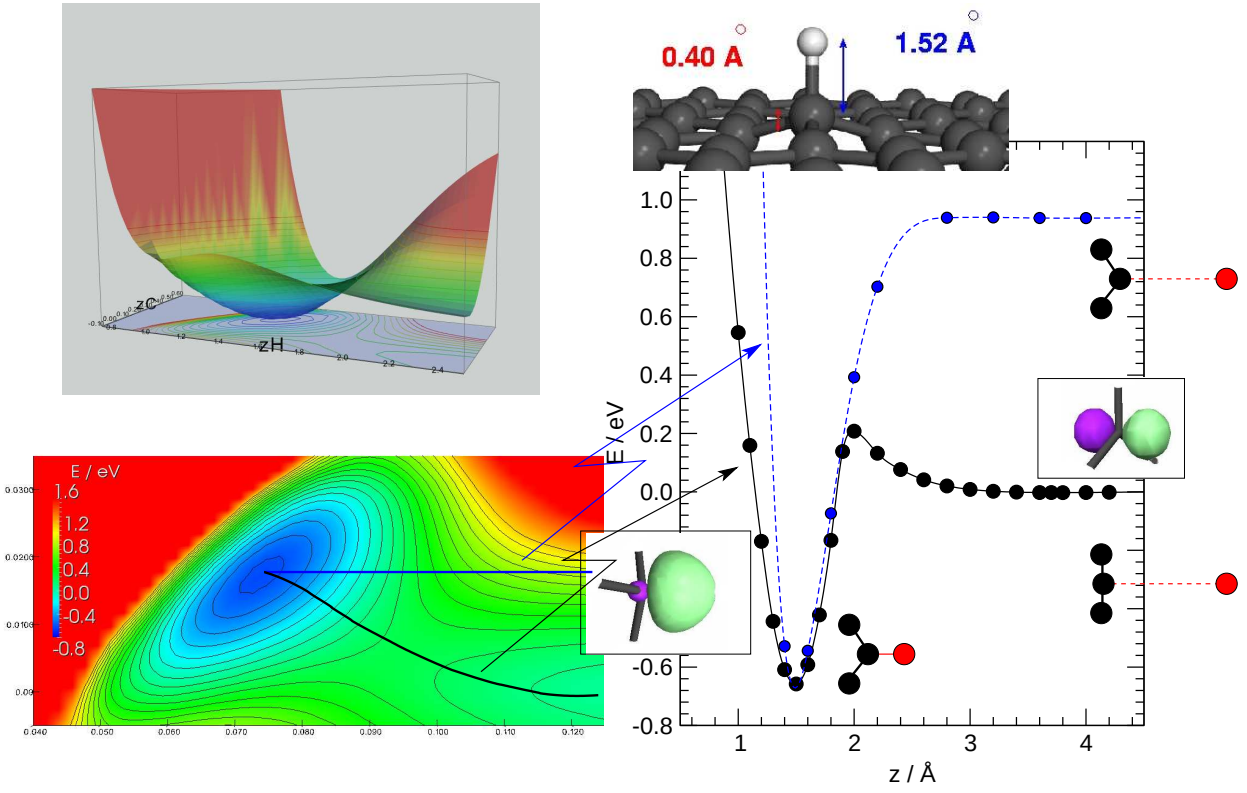
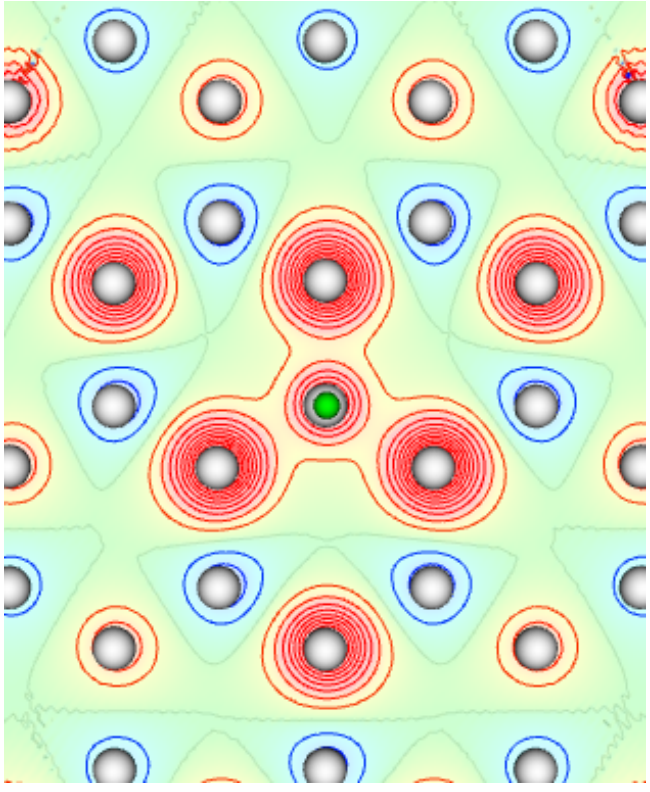


Single-H

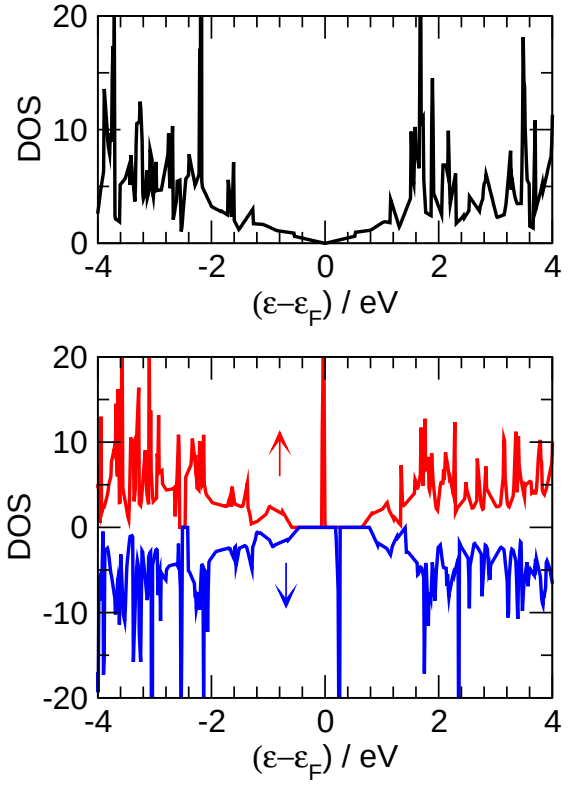


L. Jeloaica and V. Sidis, *Chem. Phys. Lett.* **300**, 157 (1999)
X. Sha and B. Jackson, *Surf. Sci.* **496**, 318 (2002)

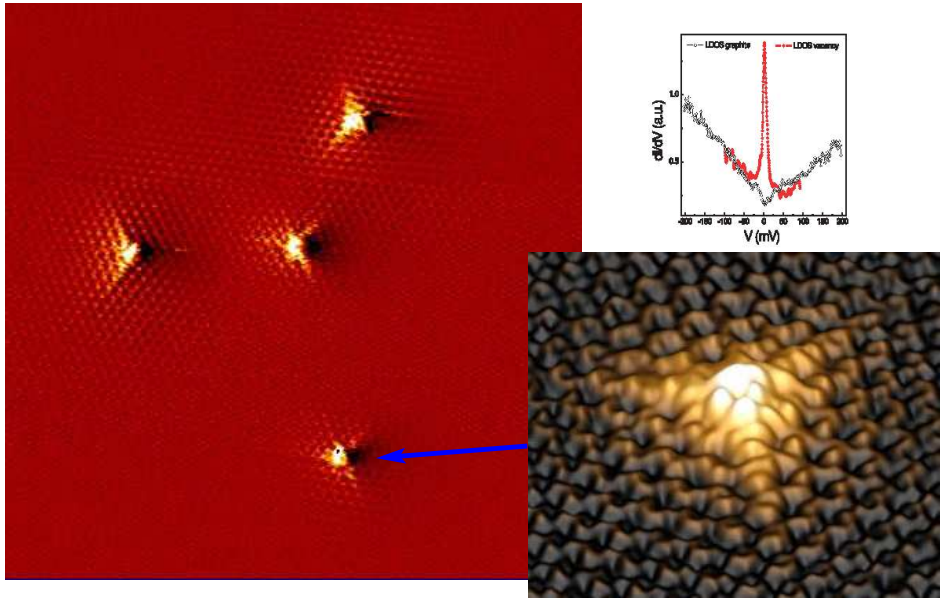
Midgap states

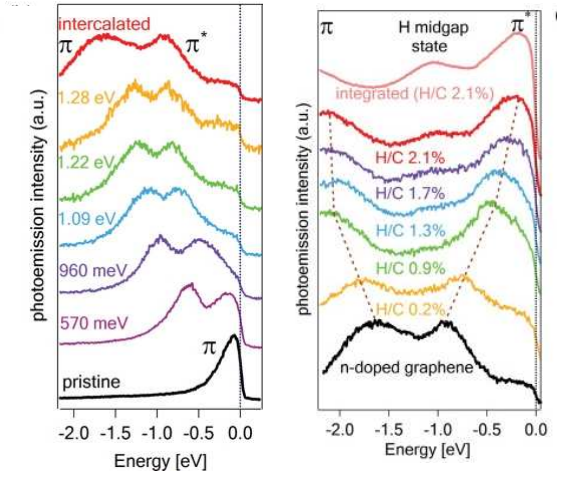


..*patterned* spin-density

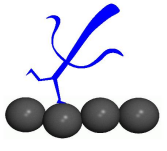


Midgap states





M.M. Ugeda, I. Brihuega, F. Guinea and J.M. Gomez-Rodriguez, *Phys. Rev. Lett.* **104**, 096804 (2010)
D. Haberer *et al.*, *Phys. Rev. B* **83**, 165433 (2011)

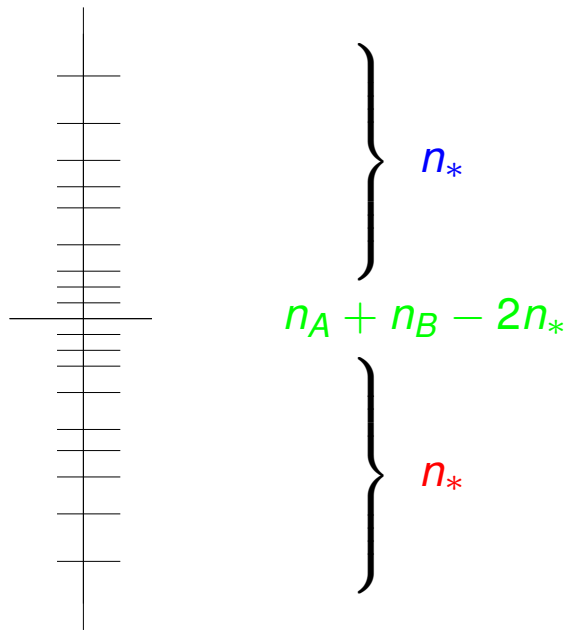


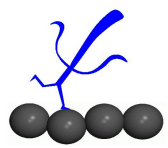
Midgap states

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

Basic results

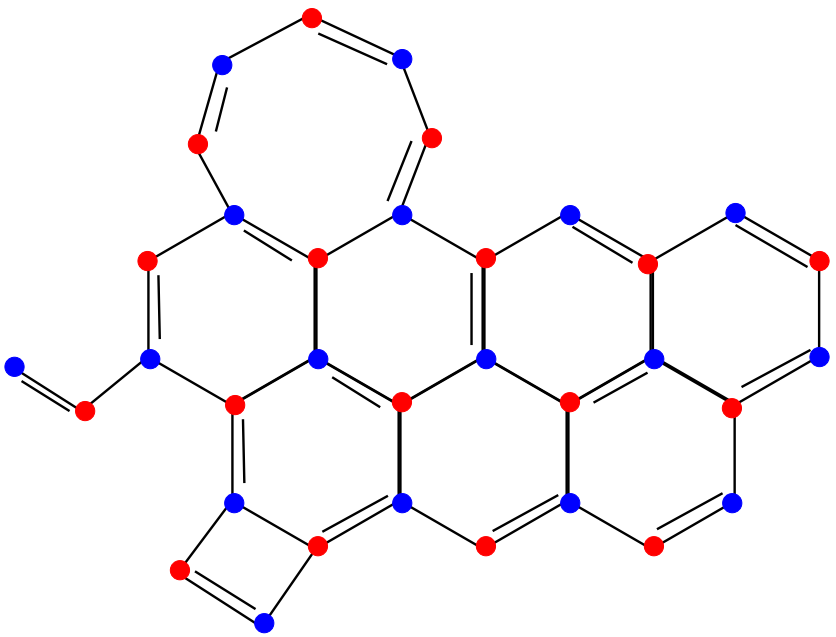
- Electron-hole symmetry: $\epsilon_i \rightarrow -\epsilon_i$
- Imbalance rule: $\nu \geqslant \eta = |n_A - n_B|$
- Spin alignment: $S = |n_A - n_B|/2$





Midgap states

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



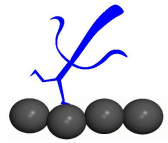
Electron-hole symmetry

$$b_i \rightarrow -b_i \Longrightarrow H^{\pi} \rightarrow -H^{\pi}$$

$$\epsilon_i, |\psi_i^{(+)}\rangle = \sum_k \alpha_k |a_k\rangle + \sum_j \beta_i |b_j\rangle$$

$$\Downarrow$$

$$-\epsilon_i, |\psi_i^{(-)}\rangle = \sum_k \alpha_k |a_k\rangle - \sum_j \beta_i |b_j\rangle$$



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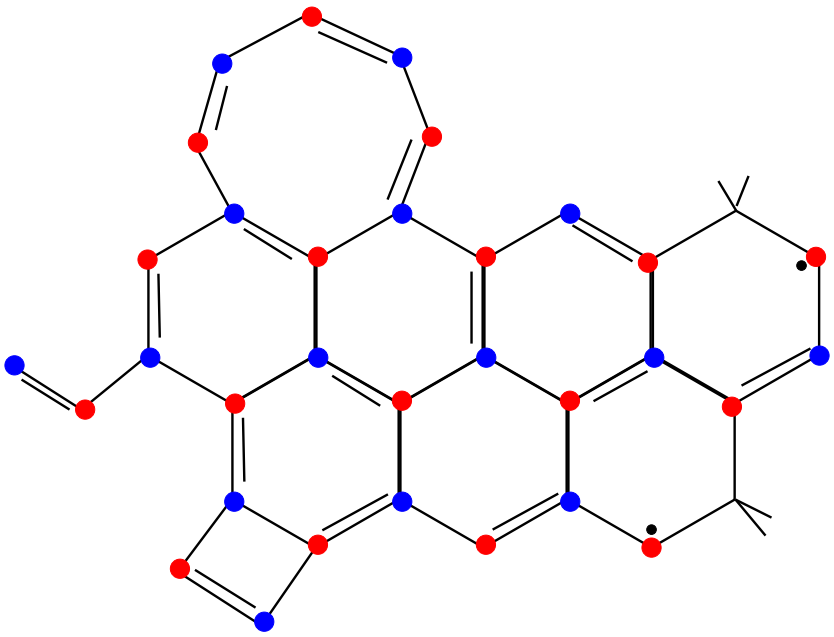


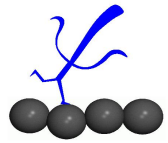
Imbalance rule

Let $n_A > n_B$, $\mathbf{T}(n_B x n_A)$

$$\begin{bmatrix} \mathbf{0} & \mathbf{T}^{\dagger} \\ \mathbf{T} & \mathbf{0} \end{bmatrix} \begin{bmatrix} \boldsymbol{\alpha} \\ \boldsymbol{\beta} \end{bmatrix} = \begin{bmatrix} \mathbf{0} \\ \mathbf{0} \end{bmatrix}$$

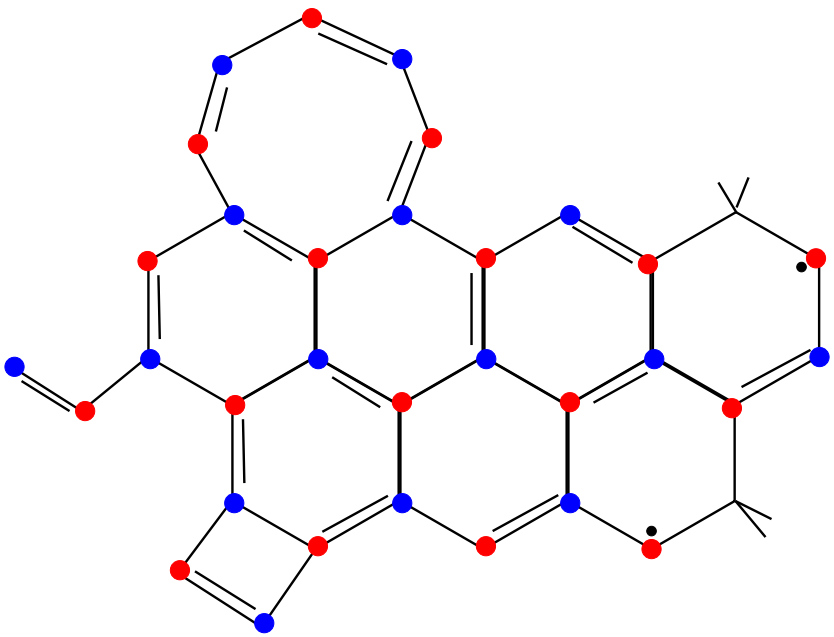
$\Longrightarrow \mathbf{T}\boldsymbol{\alpha} = \mathbf{0}$ has (at least) $n_A - n_B$ solutions

$\Longrightarrow \psi_{E=0}$ have vanishing components on B sites



Midgap states

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

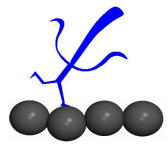


Spin alignment

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

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

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



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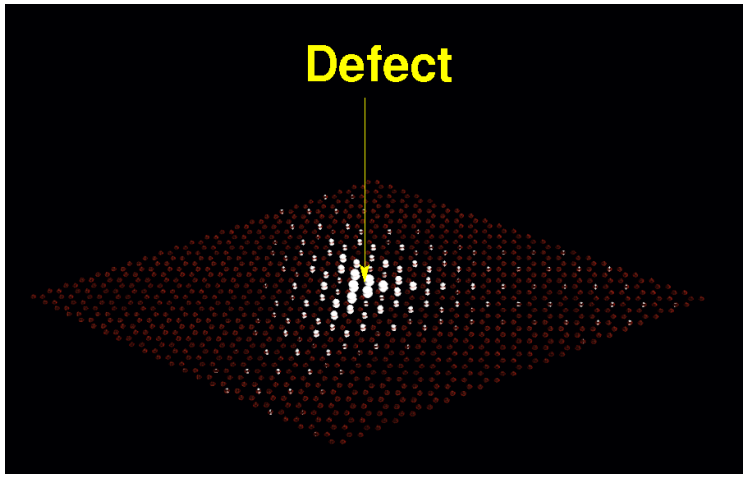
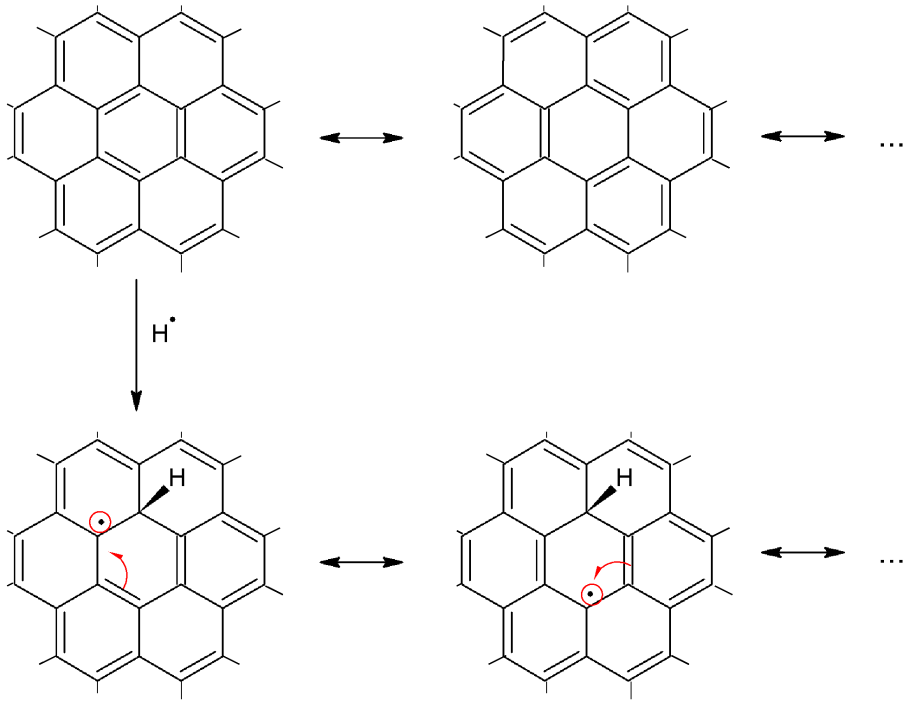
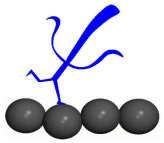


$$\psi(x, y, z) \sim 1/r$$

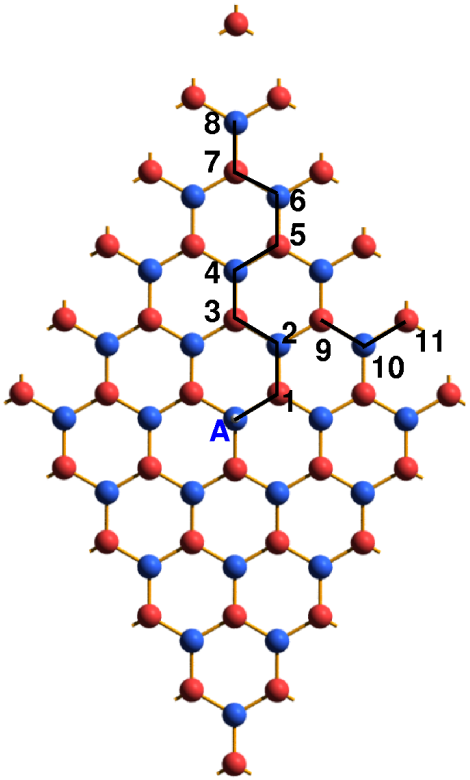
V. M. Pereira *et al.*, *Phys. Rev. Lett.* **96**, 036801 (2006); *Phys. Rev. B* **77**, 115109 (2008)

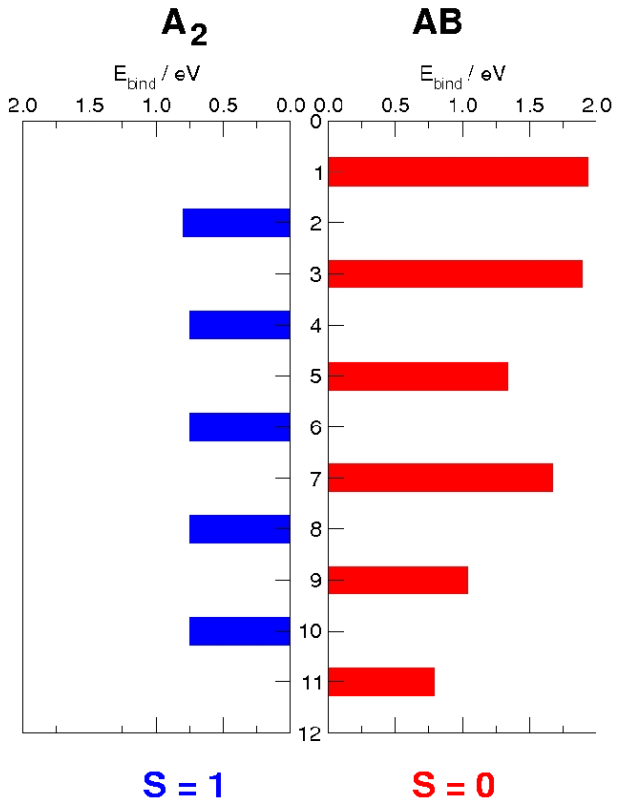


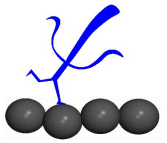
See also, e.g., Y. Ferro *et al.*, *Phys. Rev. B* **78**, 085417 (2008)



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



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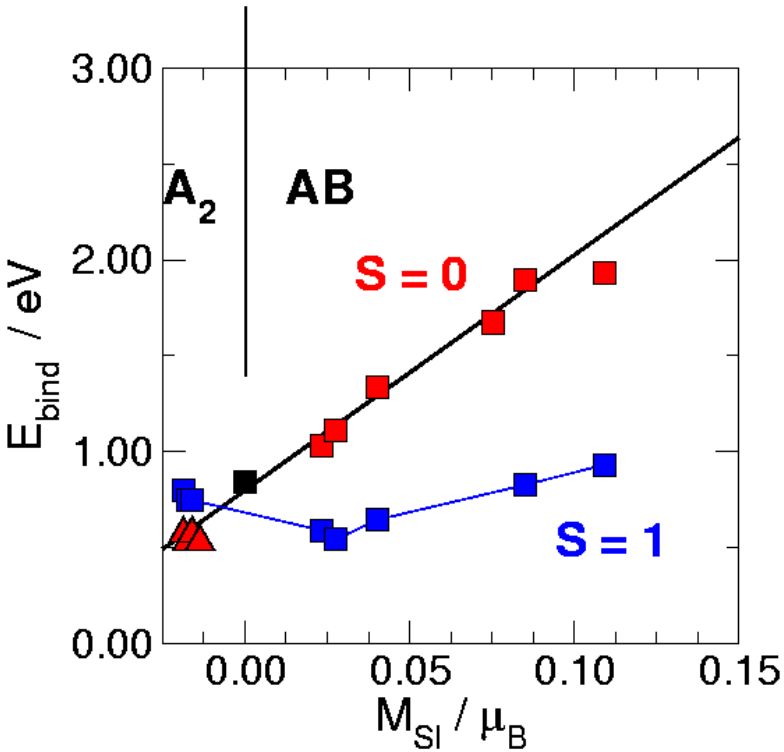
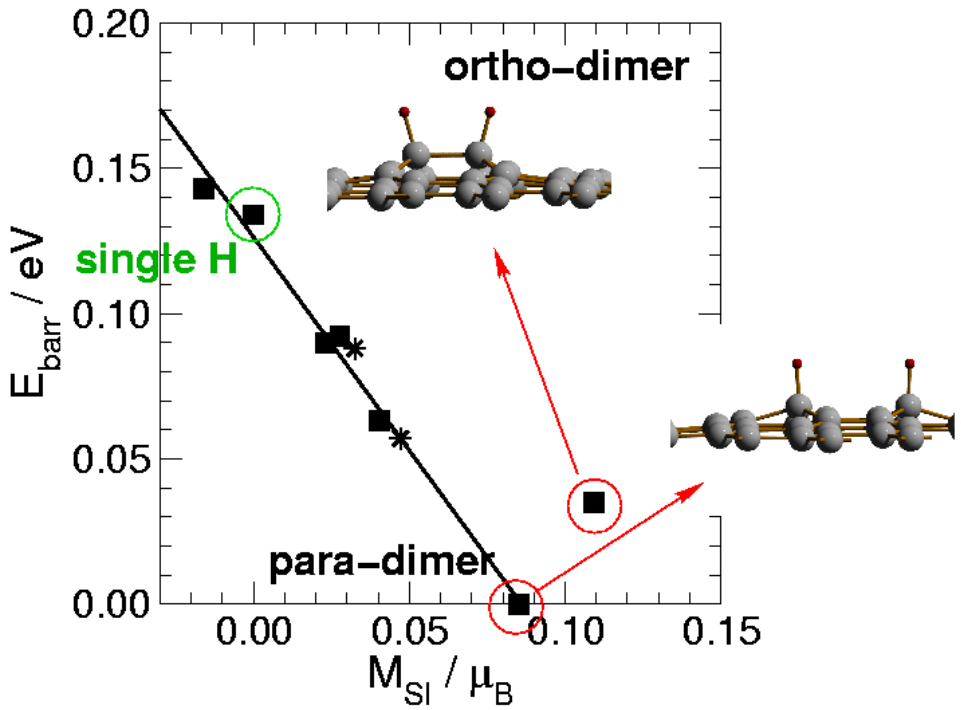
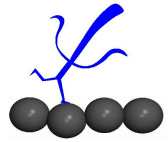




S. Casolo, O.M. Lovvik, R. Martinazzo and G.F. Tantardini, *J. Chem. Phys.* **130** 054704 (2009)
arXiv:0808.1312 (2008)

Preferential sticking: L. Hornekaer *et al.*, *Phys. Rev. Lett.* **96** 156104 (2006)



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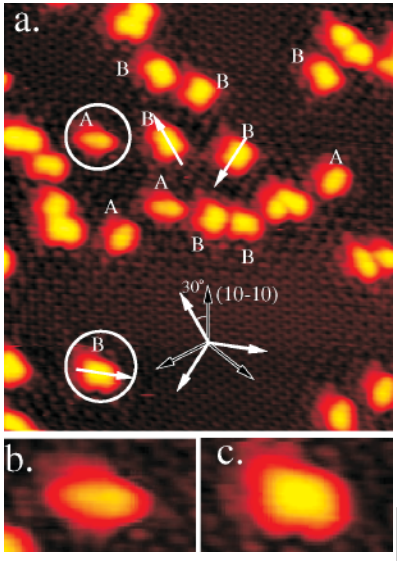

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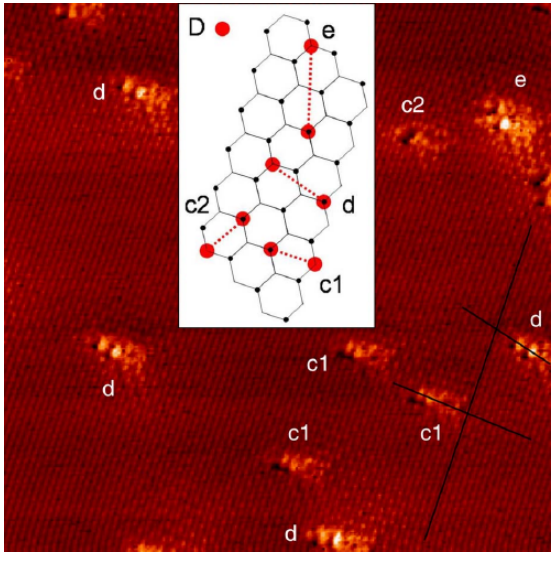
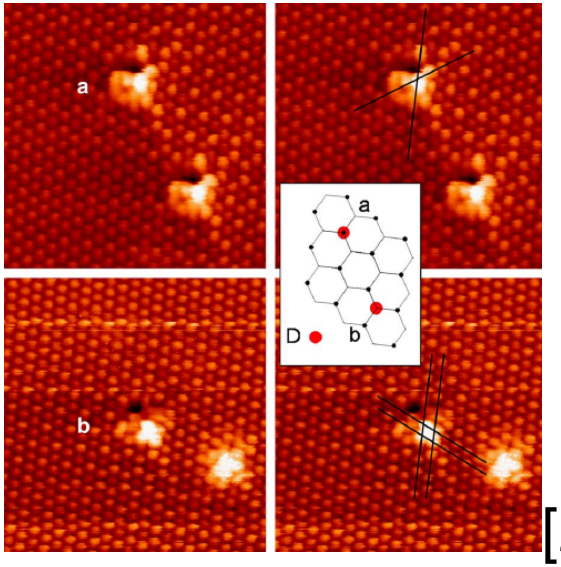
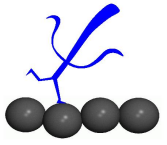




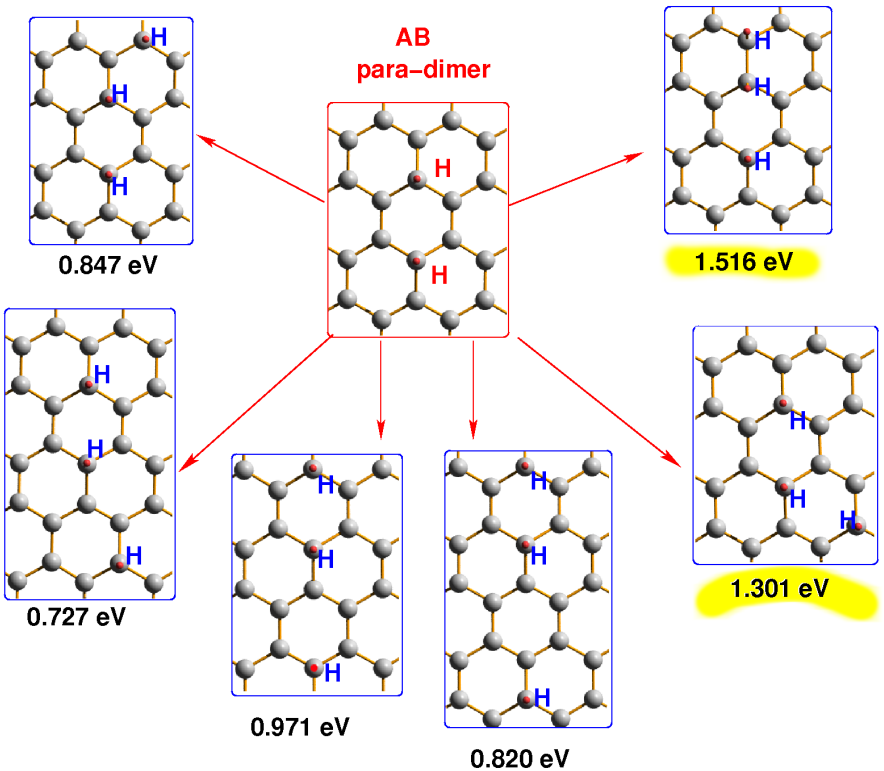
[2]

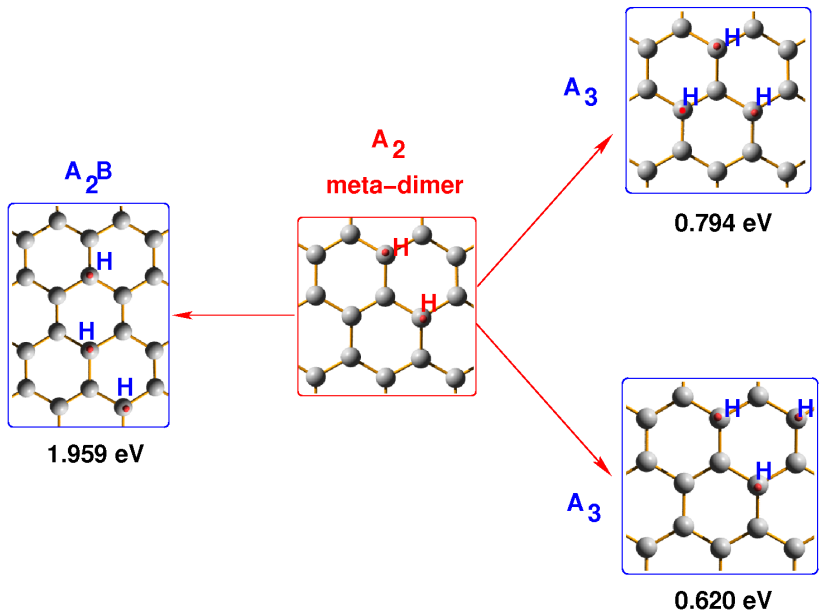
[1] L. Hornekaer, Z. Sljivancanin, W. Xu, R. Otero, E. Rauls, I. Stensgaard, E. Laegsgaard, B. Hammer and F. Besenbacher. *Phys. Rev. Lett.* **96** 156104 (2006)

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



3-atom clusters





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

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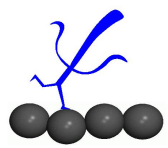
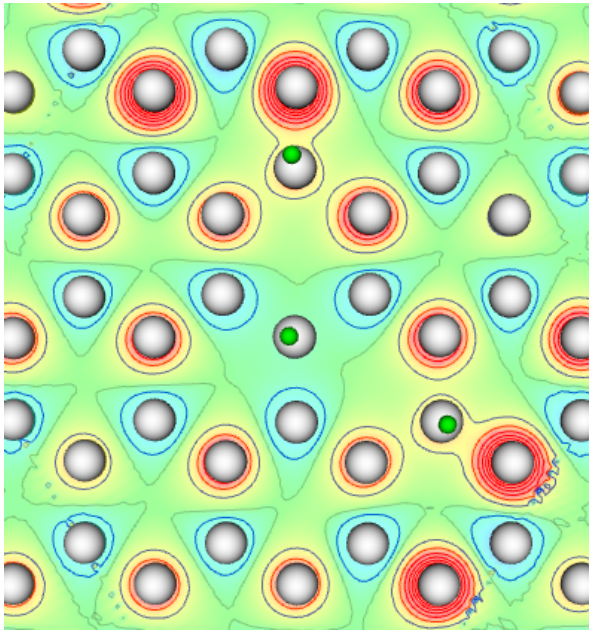
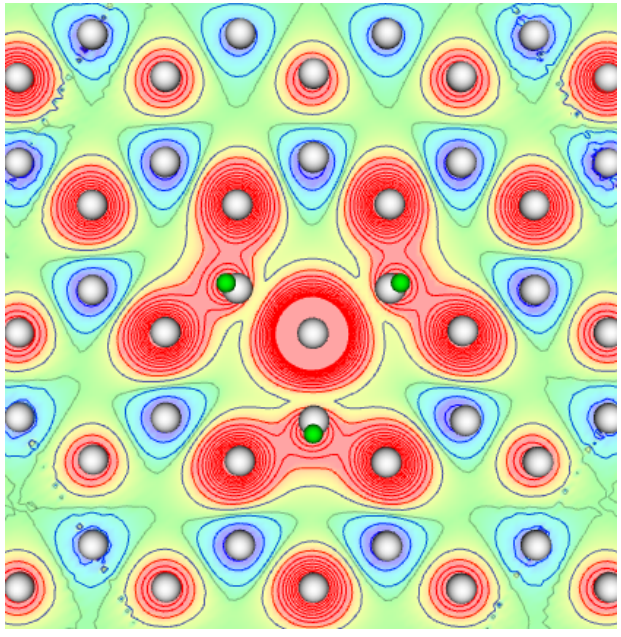


3-atom clusters

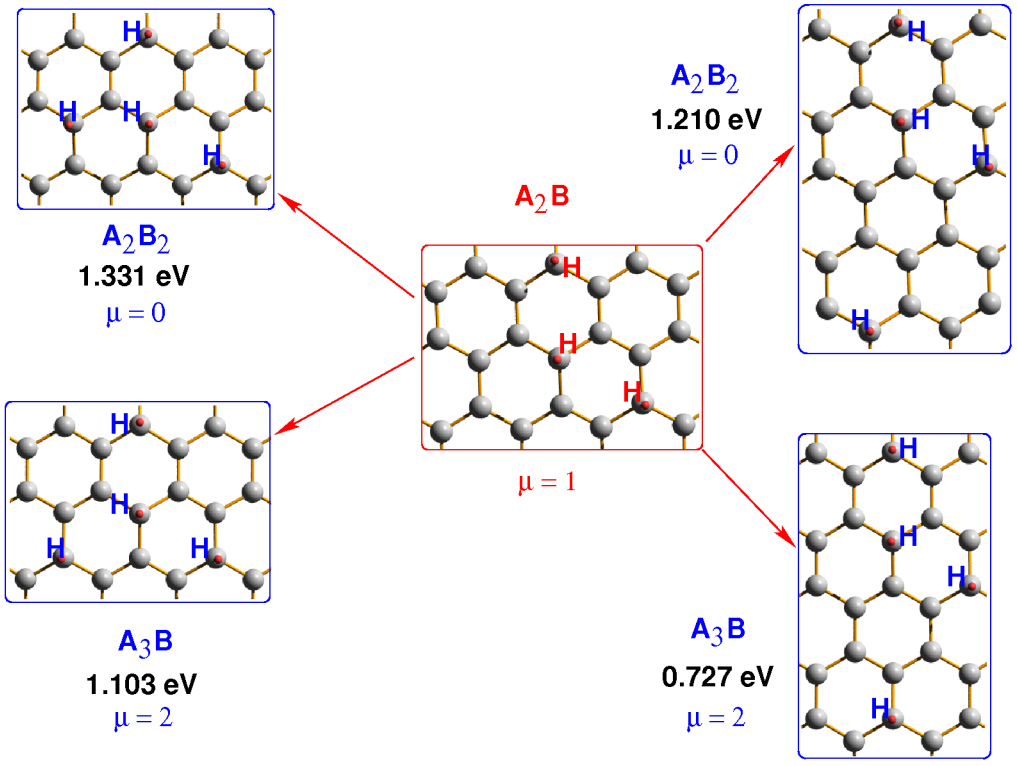
A_2B



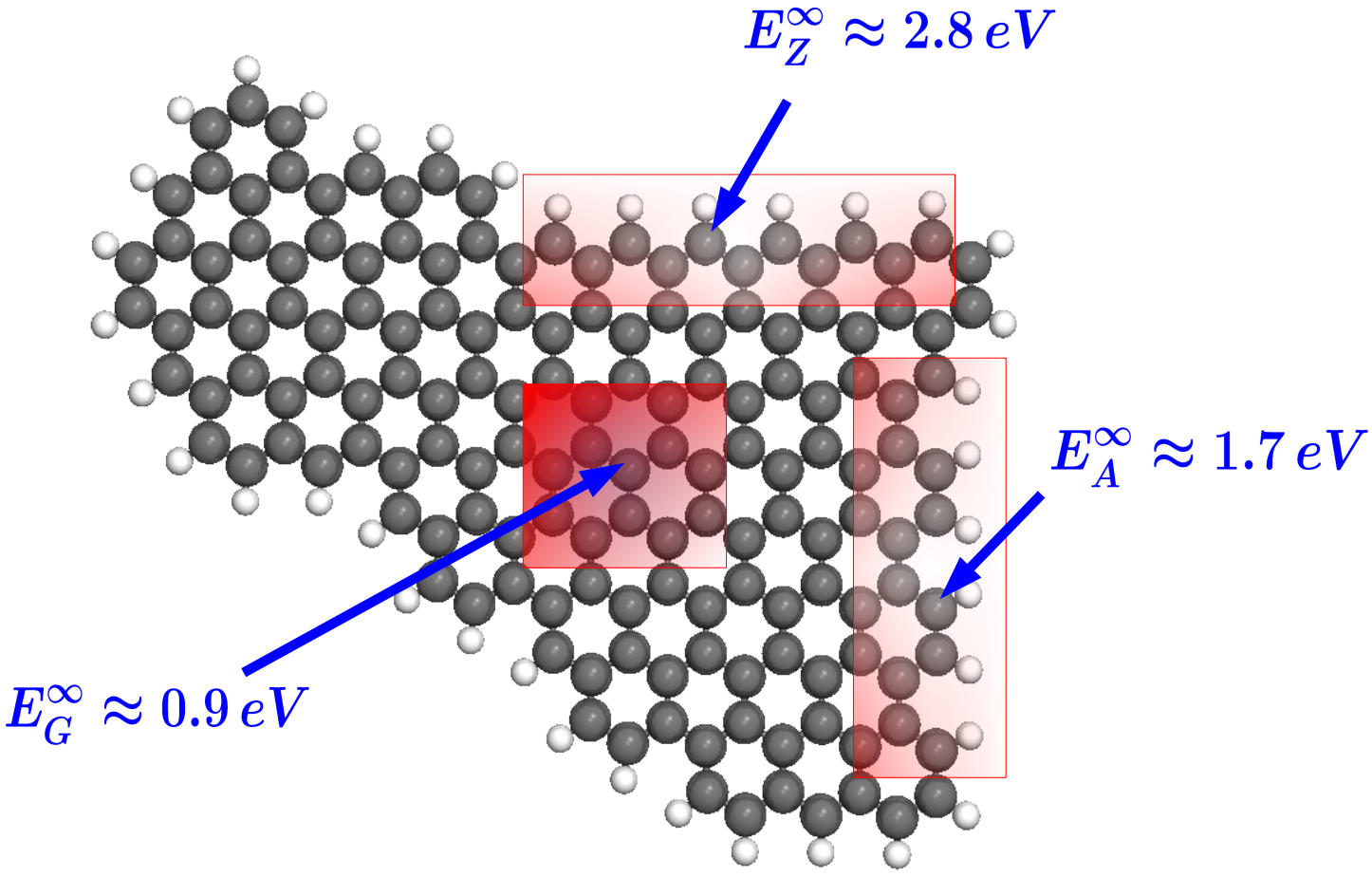
A_3



4-atom clusters



Role of edges



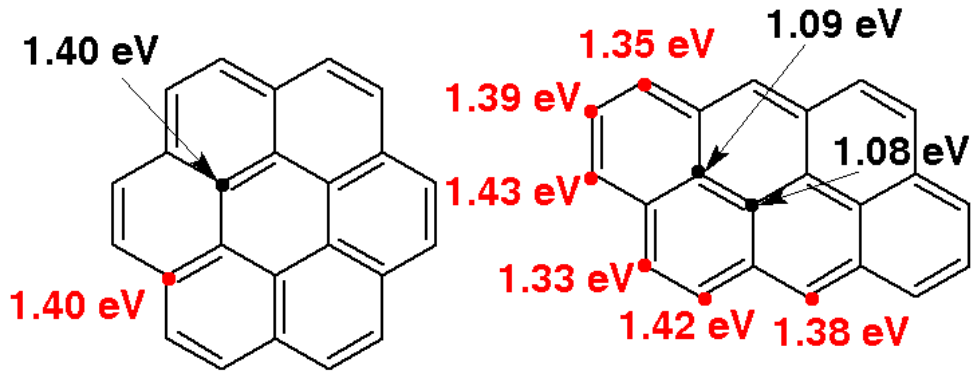
'Geometric' effect?

'Reorganization' energy upon binding

$$\delta E = E(PAH^*) - E(PAH^{eq})$$

E sites: $\delta E \sim 1.4 \pm 0.1 eV$

G sites: $\delta E \sim 1.0 \pm 0.1 eV$



...purely electronic effect

Hints from the tight-binding Hamiltonian H^{π}

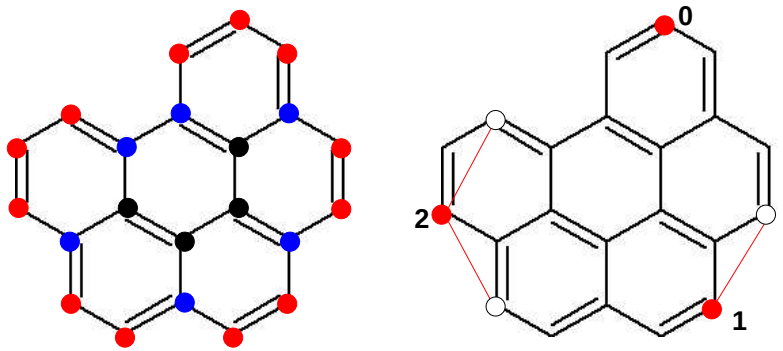
Shape of low-energy orbitals

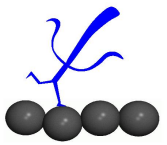
..from a 'lattice renormalization'

- Coordination (Z)
- Hypercoordination (ξ)
- sublattice imbalance (η)

$Z = 2 \Rightarrow$ **E**

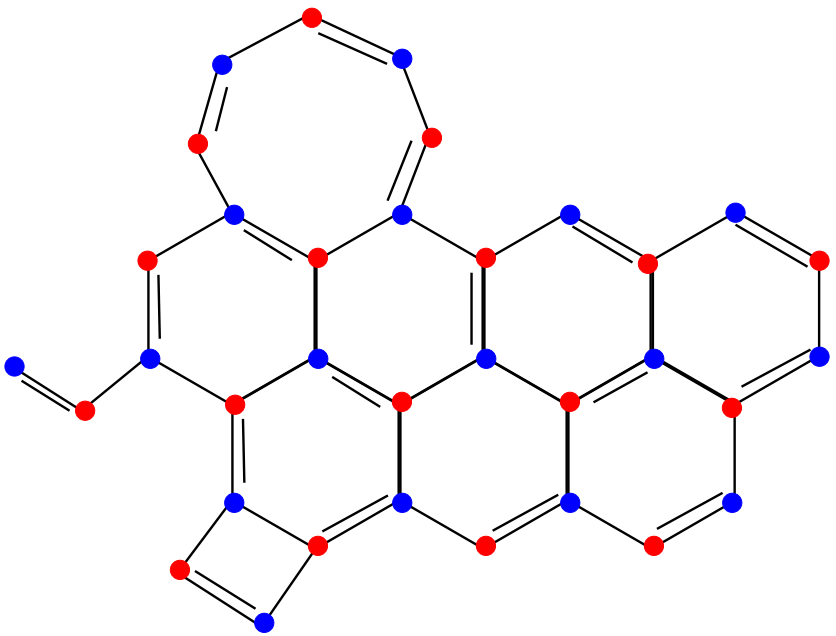
$Z = 3 \Rightarrow$ **F**,**G**





Hints from the tight-binding Hamiltonian H^π

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



'Lattice renormalization'

$$\tilde{H}_{AA} = H_{AB}H_{BA}$$

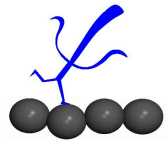
$$\tilde{\epsilon}_i, |\psi_{A,i}\rangle$$

$$\Downarrow$$

$$\epsilon_i^\pm = \pm\sqrt{\tilde{\epsilon}_i}, |\psi_i^{(\pm)}\rangle = |\psi_{A,i}\rangle \pm |\psi_{B,i}\rangle$$

$$|\psi_{B,i}\rangle = \tilde{\epsilon}_i^{-1/2} H_{BA} |\psi_{A,i}\rangle$$

G. Naumis, *Phys. Rev. B* **76** 153403 (2007)
R. Martinazzo, S. Casolo and G.F. Tantardini, *Phys. Rev. B* **81** 245420 (2010)



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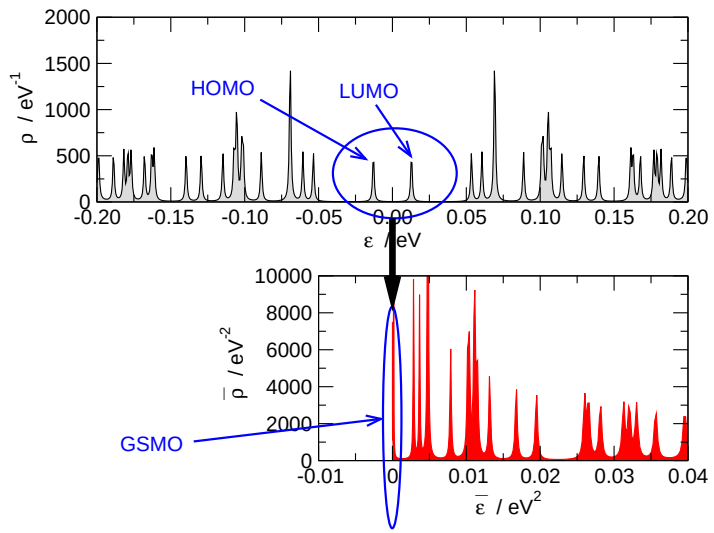

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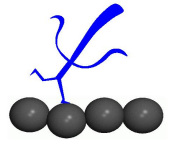

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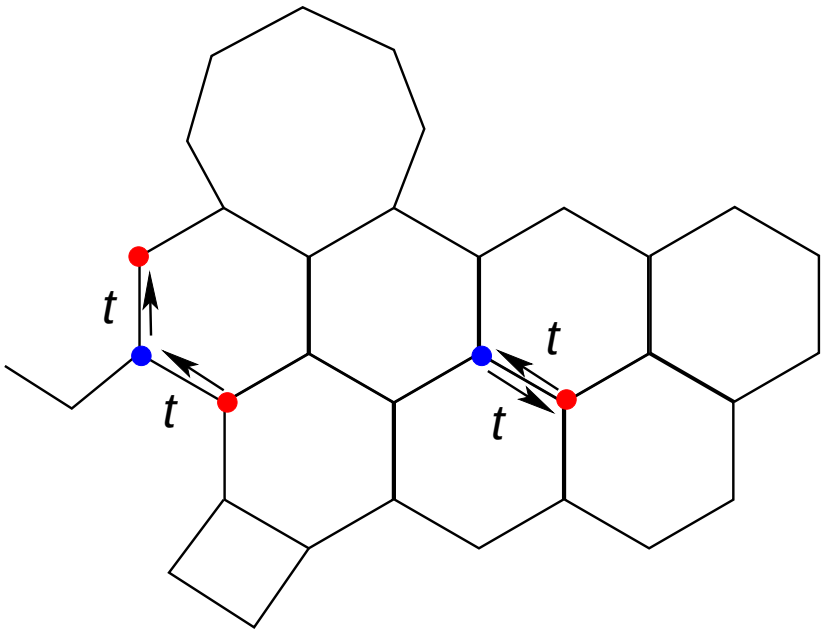

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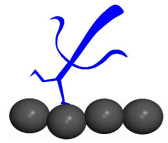
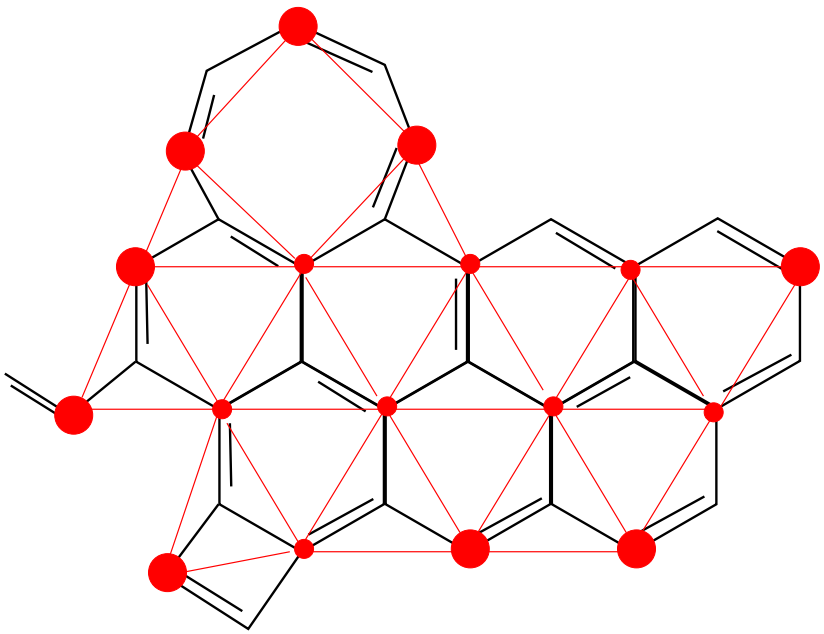


Hints from the tight-binding Hamiltonian H^π

$$\tilde{H}^\pi \approx \sum_i Z_i t^2 a_i^\dagger a_i + \sum_{ij} t^2 a_i^\dagger a_j$$



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G. Naumis, *Phys. Rev. B* **76** 153403 (2007)
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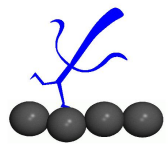
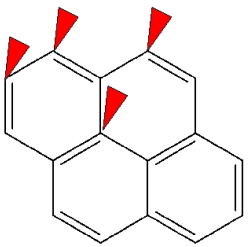
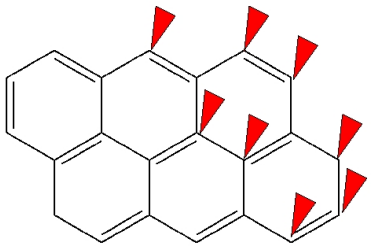


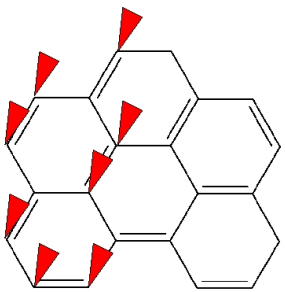
Systems



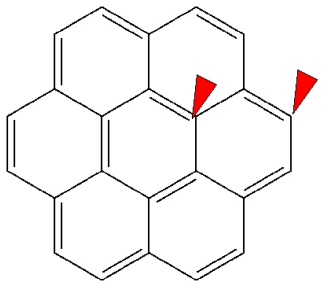
pirene



dibenzo[def,mno]crisene / antrantrene

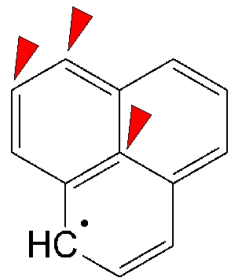


benzo[ghi]perilene

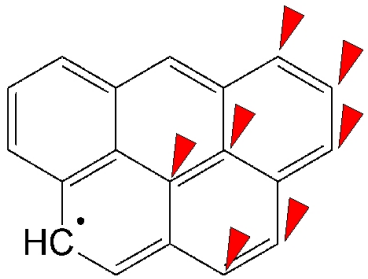


coronene

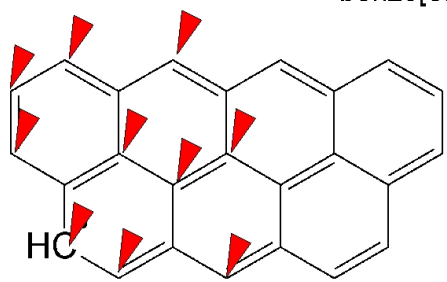
$\eta = 0$



perinaftenile / fenalene

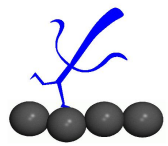


benzo[cd]pirenile

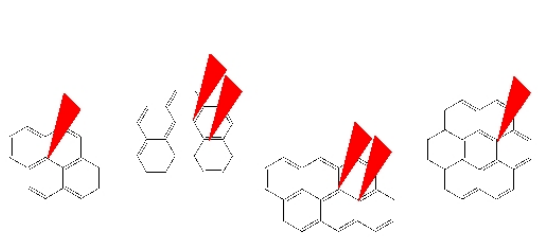


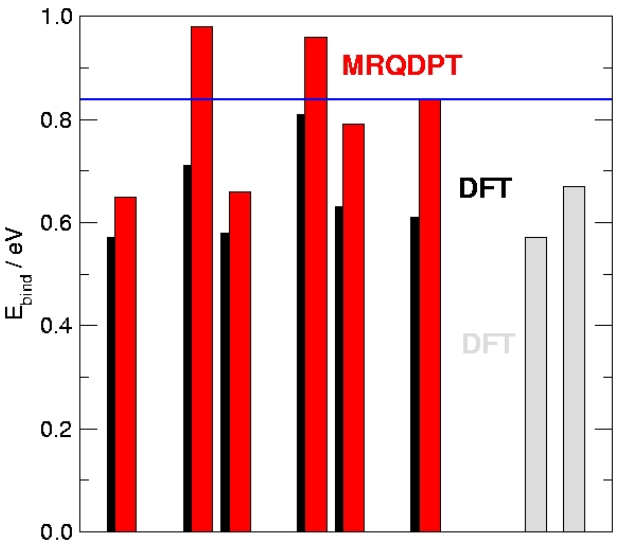
7 - PAH

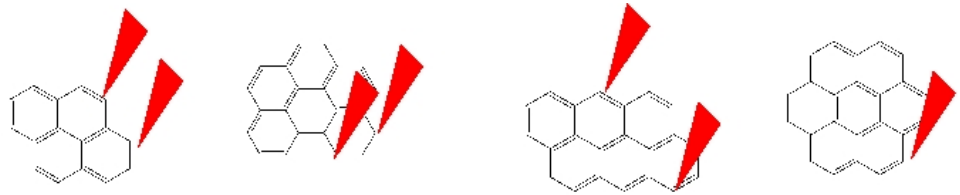
$\eta \neq 0$

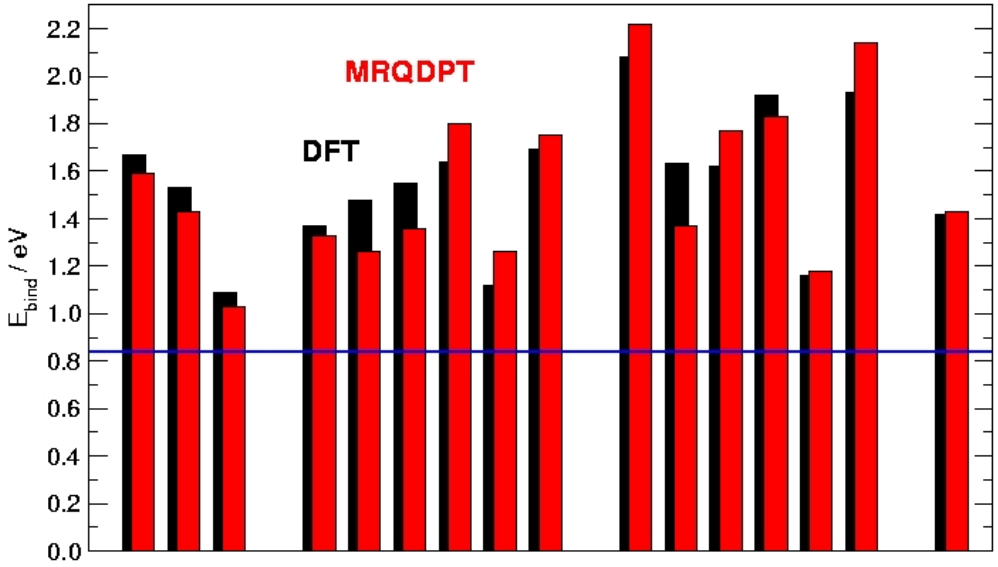


Graphitic *vs* edge carbons

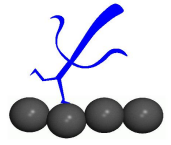




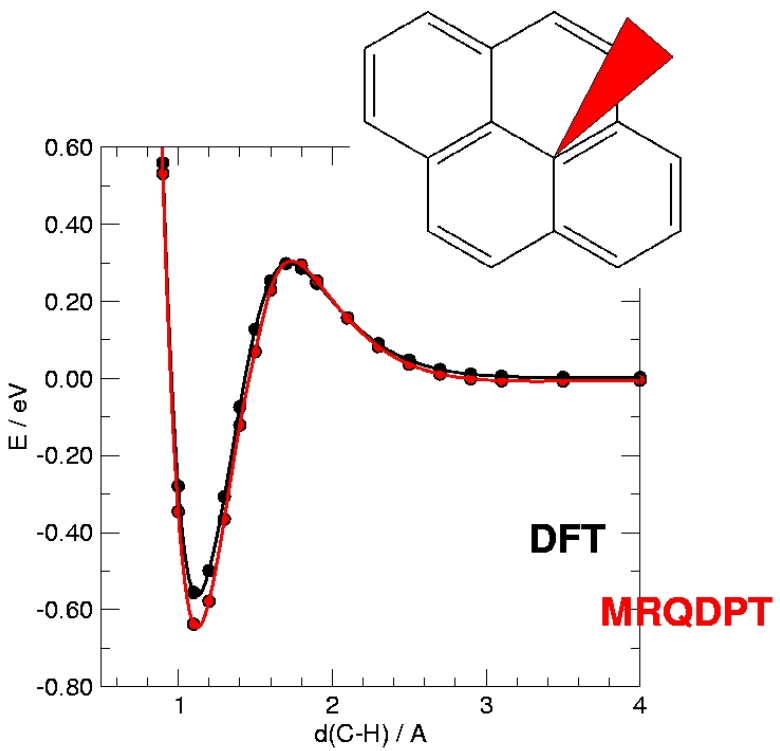


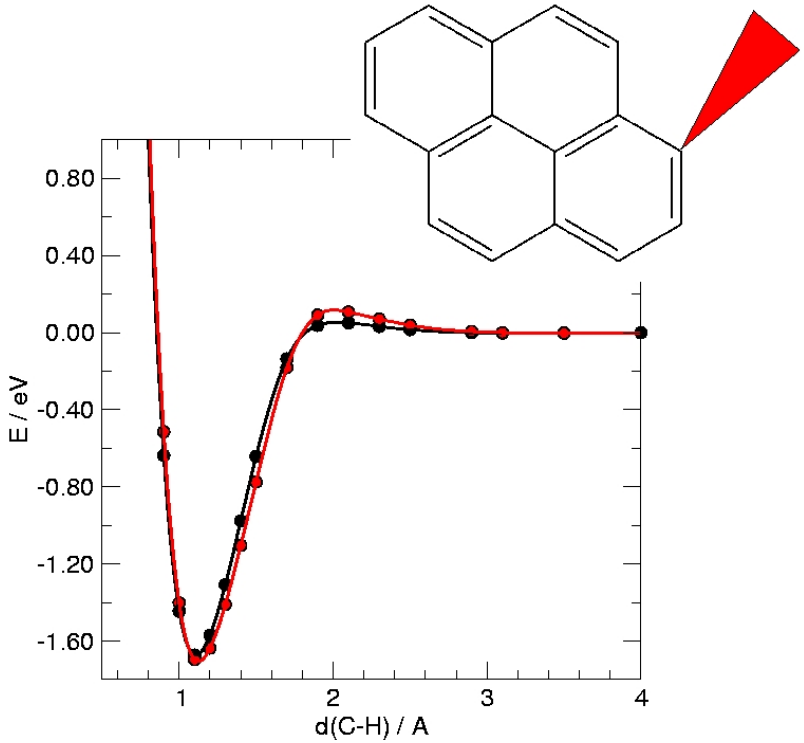


M. Bonfanti, S. Casolo, G. F. Tantardini, A. Ponti and R. Martinazzo, *JCP, in press*; arXiv:1107.4324 (2011)



Adsorption paths





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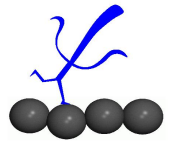
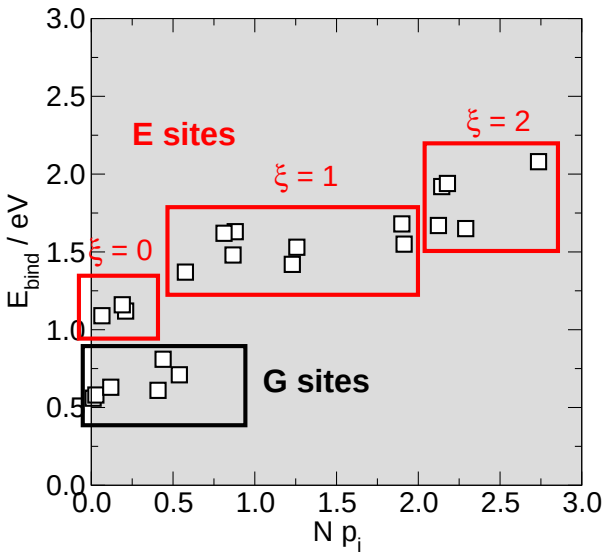
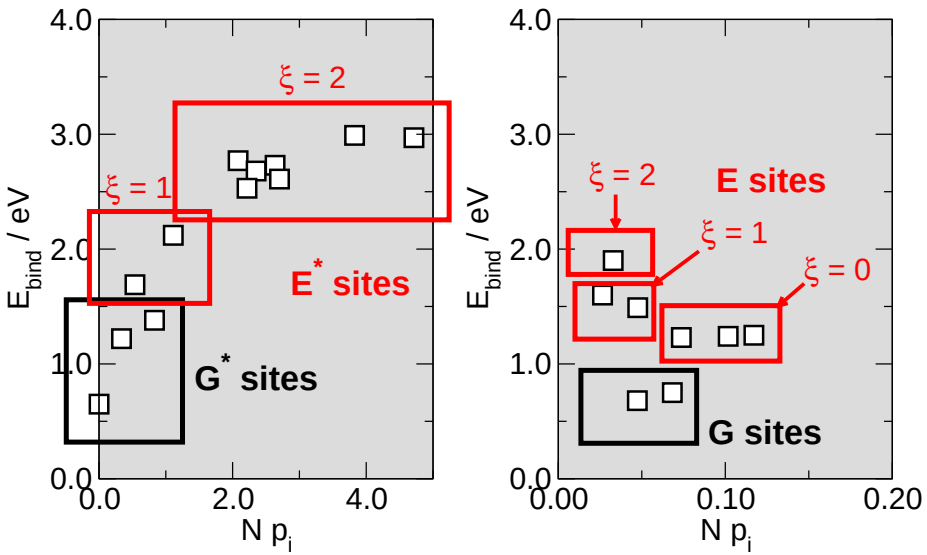


Predicting reactivity

$\eta = 0$



$\eta \neq 0$



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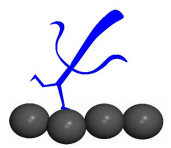

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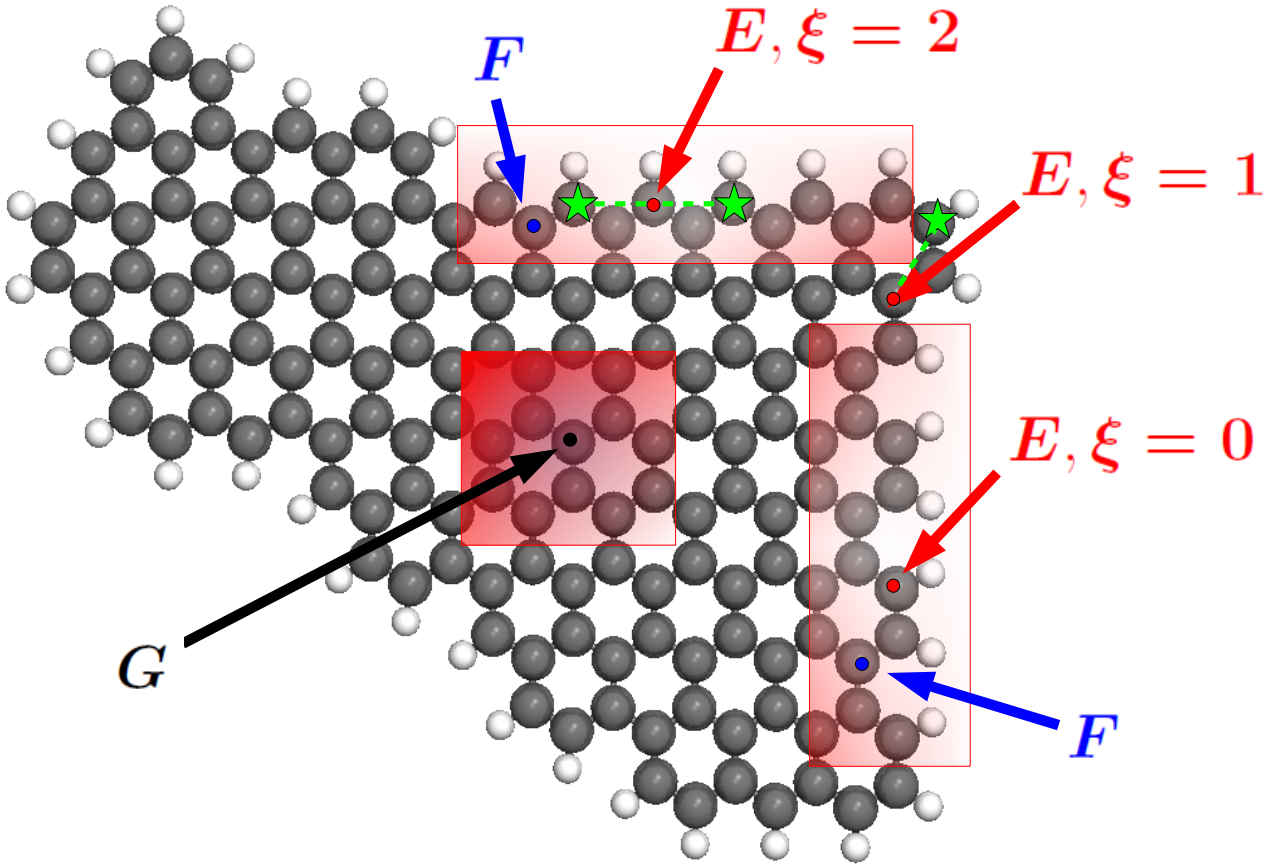
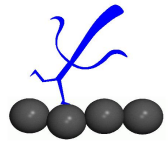


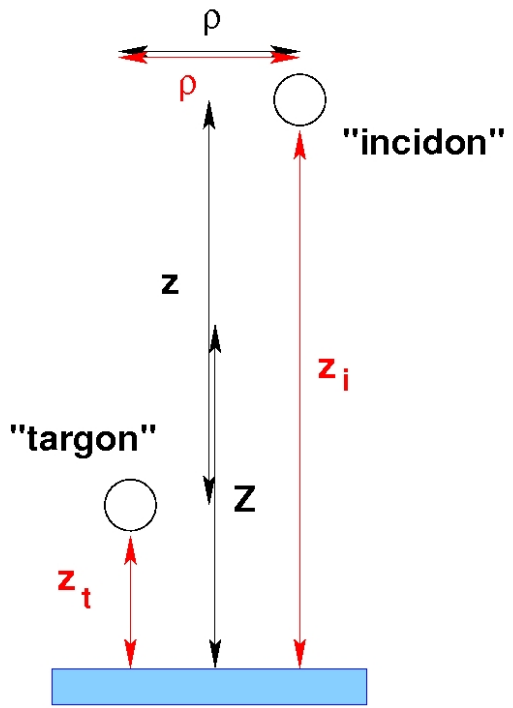
Outline



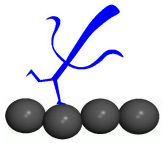
Reaction: technicalities

- Rigid, flat surface approximation[1]
- Split-Operator with FFT along cartesian coordinates and DBT along ρ [1]
- propagation in both product and reagent coordinate sets[2]

$\Rightarrow$ state-to-state, energy-resolved cross sections for all possible processes



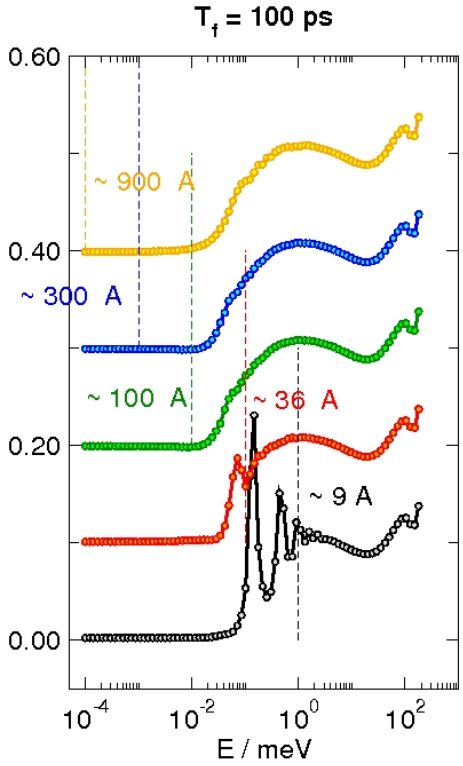
[1] M. Persson and B. Jackson, J. Chem. Phys. 102, 1078 (1995); D. Lemoine and B. Jackson, Comput. Phys. Commun. 137, 415 (2001)
[2] R. Martinazzo and G.F. Tantardini, J. Phys. Chem. A, 109 (2005) 9379; J. Chem. Phys. 124, 124703 (2006); J. Chem. Phys. 124, 124704 (2006)



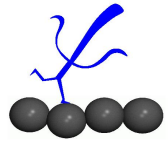
Reaction: technicalities (low E_{col})

- Two-wavepacket approach[1]
- Transmission-free[2] absorbing potentials and Fourier mapping[3] in reagent coordinates

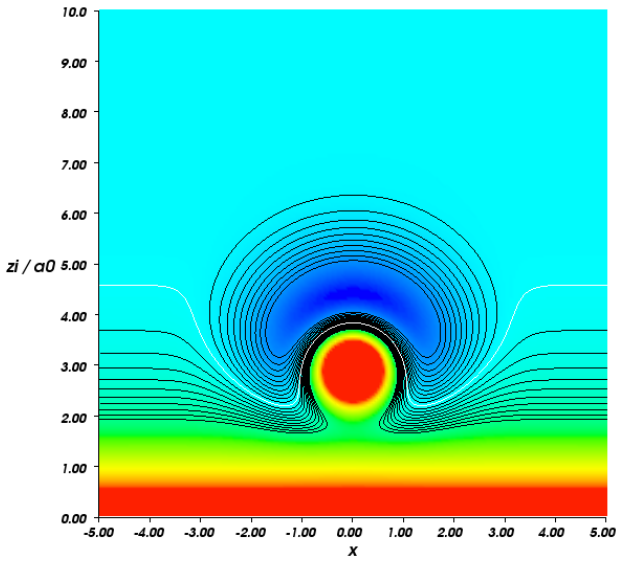
In 3D T_f=25-30 ps and AP lengths $\sim$ 50Å in order to get converged xsections down to $\sim 10^{-5}$ eV, i.e. $\sim$ 0.1 K



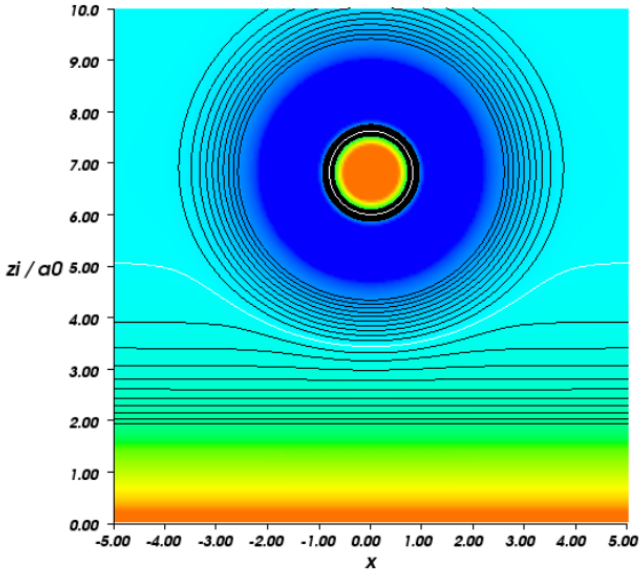
[1] R. Martinazzo and G.F. Tantardini, J. Chem. Phys. 122, 094109 (2005)
[2] D. Manolopoulos, J. Chem. Phys. 117, 9552 (2002)
[3] A.G. Borisov, J. Chem. Phys. 114, 7770 (2001)



Reaction: Potential Energy Surfaces

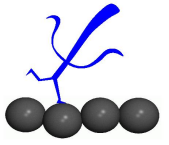


Chemisorbed target H (z_{eq})

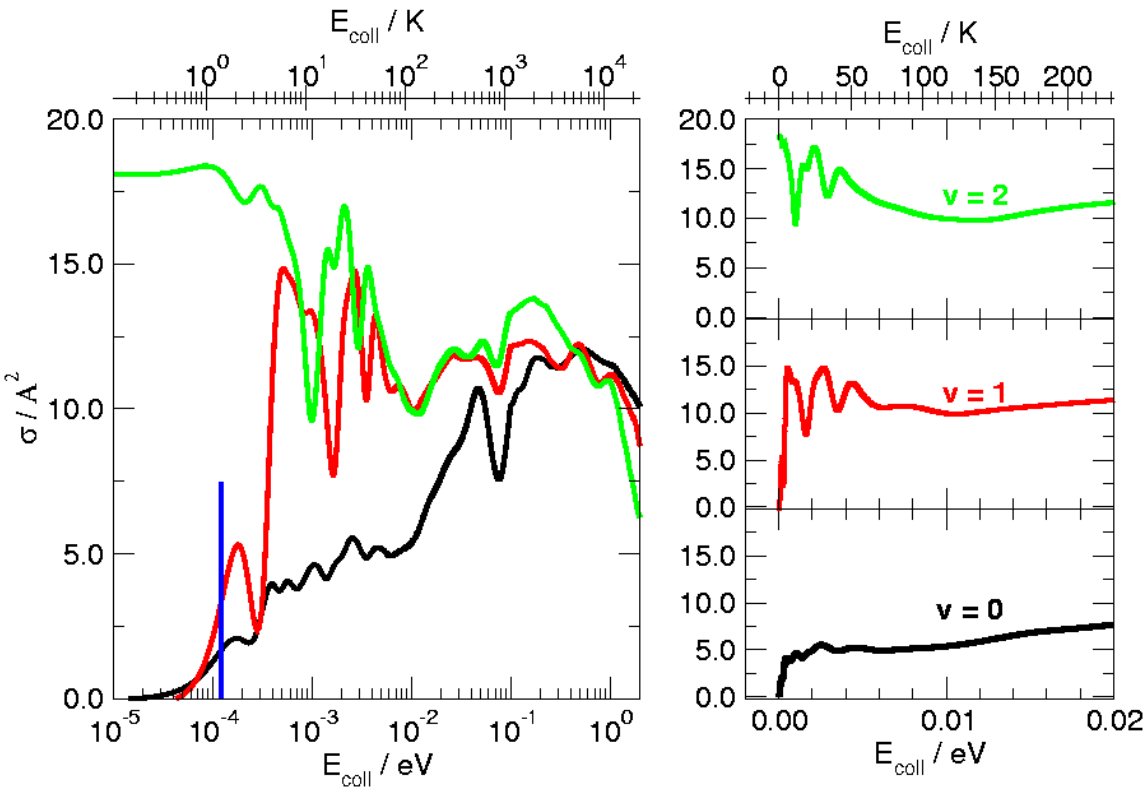


Physisorbed target H (z_{eq})

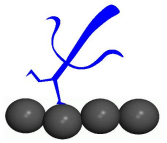
X. Sha, B. Jackson and D. Lemoine, J. Chem. Phys. 116, 7158 (2002)



I. H-chemisorbed case

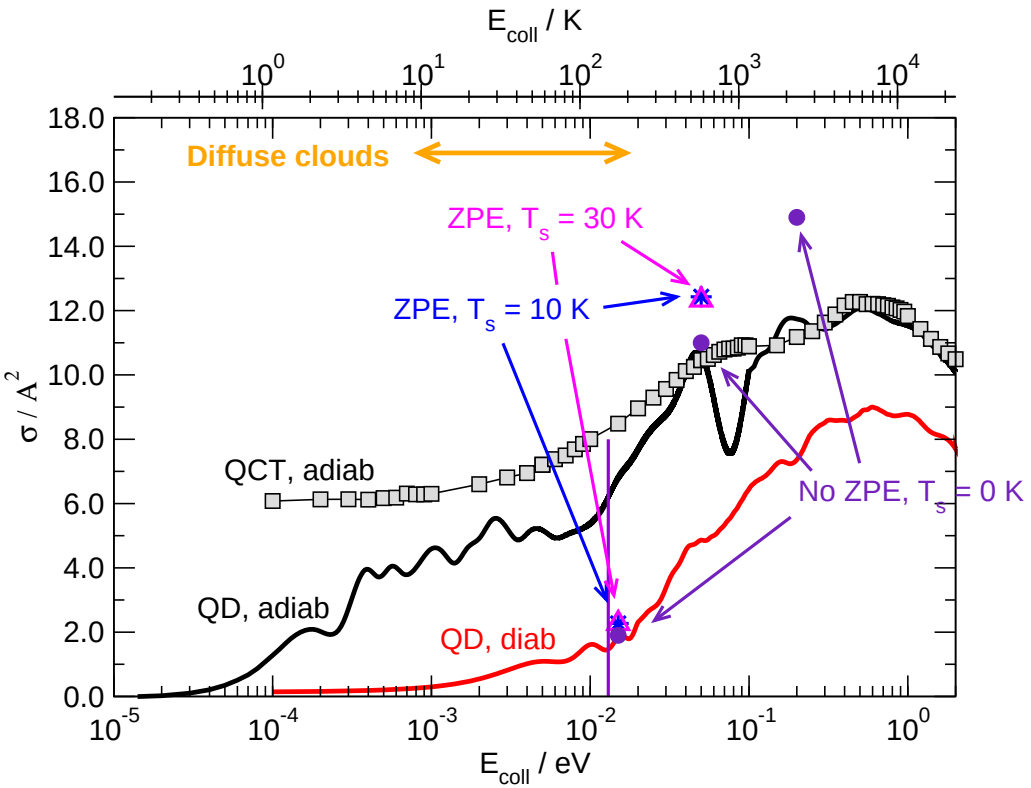


S. Casolo, M. Bonfanti, R. Martinazzo and G.F. Tantardini, *J. Phys. Chem. A*, **113** 14545 (2009)

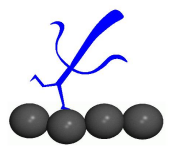


I. H-chemisorbed case

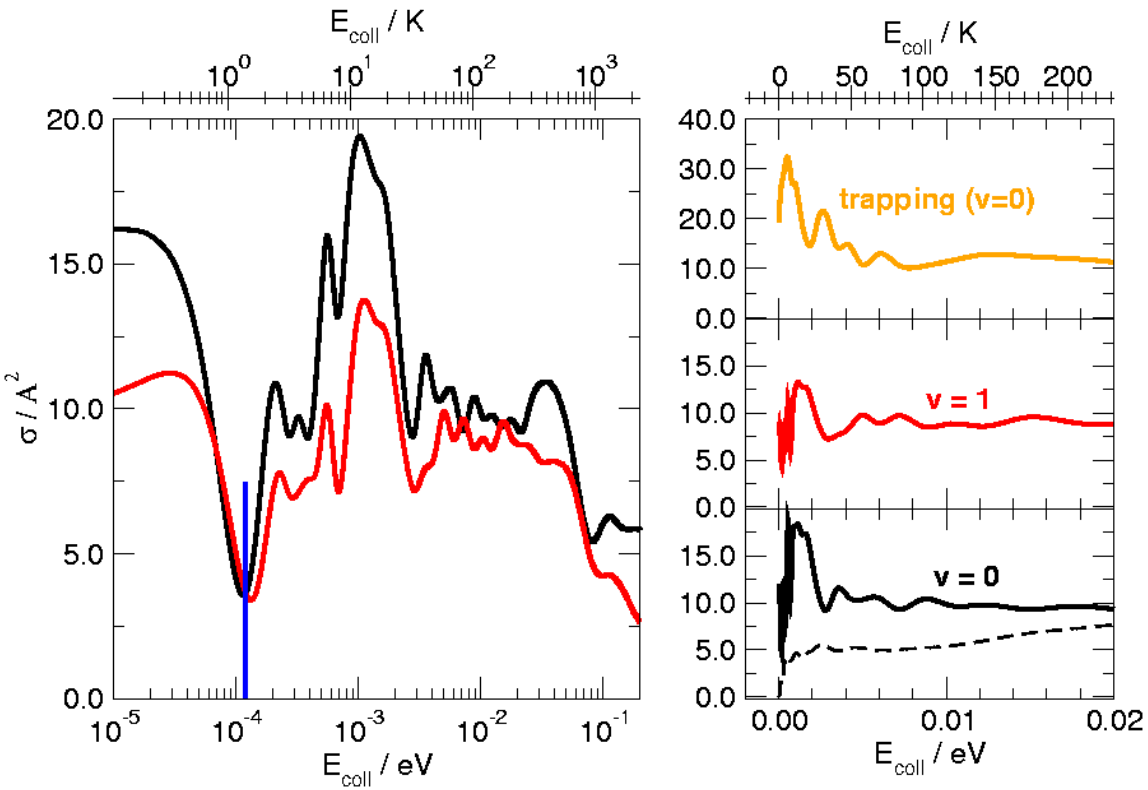
QCT comparison, $v = 0$



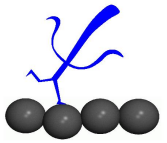
M. Sizun, D. Bachellerie, F. Anguillon, V. Sidis *Chem. Phys. Lett.* 32 **498** 2010
D. Bachellerie, M. Sizun, F. Anguillon, D. Teillet-Billy, N. Rougeau, *Phys. Chem. Chem. Phys.* 2715 **11** 2009



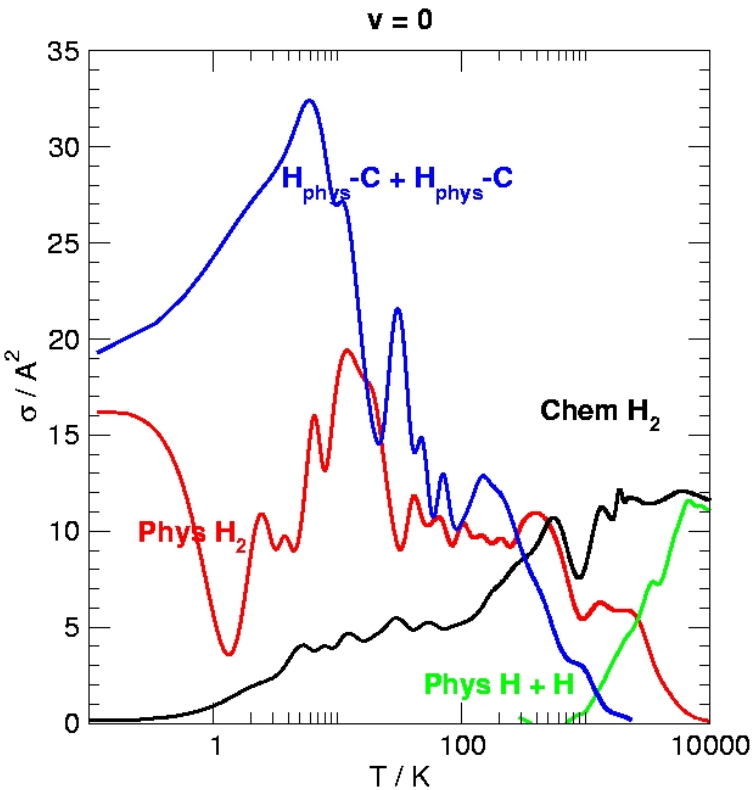
II. H-physisorbed case

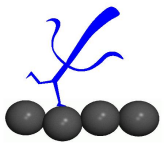


S. Casolo, M. Bonfanti, R. Martinazzo and G.F. Tantardini, *J. Phys. Chem. A*, **113** 14545 (2009)



H-chem vs H-phys





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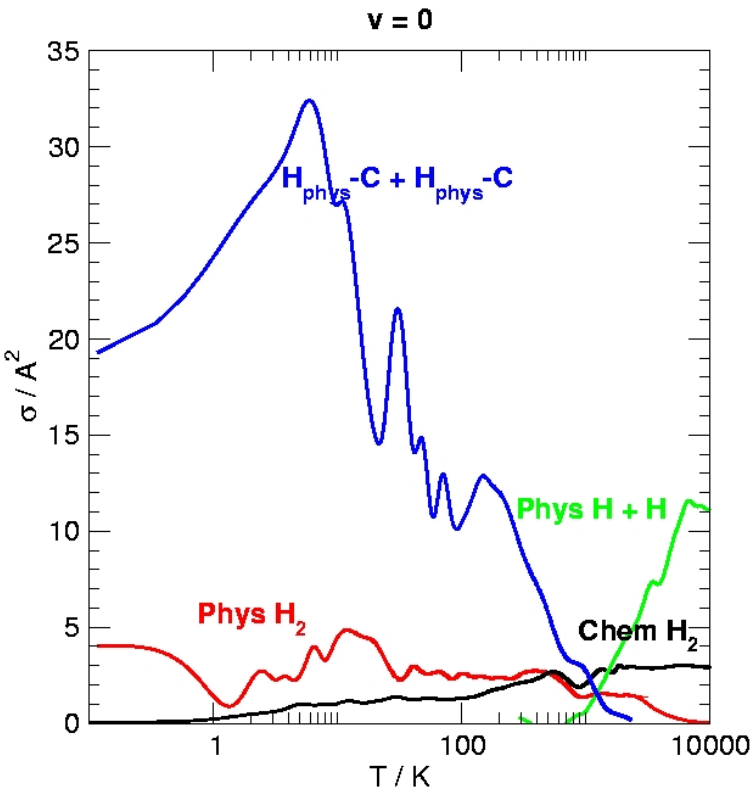
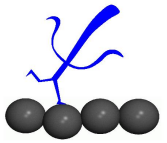
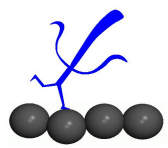


Cross-sections have to be corrected for the spin statistics (1/4)



Summary

- Thermodynamically and kinetically favoured H clusters in the bulk minimize sublattice imbalance
- Edges are chemically active, adsorption may be barrierless
- At low energies, physisorbed H atoms are more reactive than chemisorbed species



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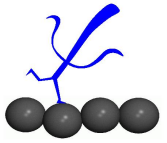
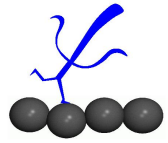
Chemical Dynamics Theory Group

http://users.unimi.it/cdtg

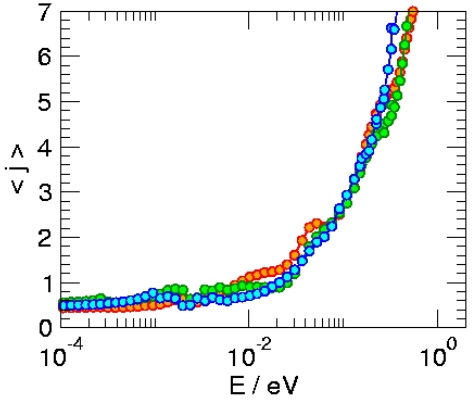


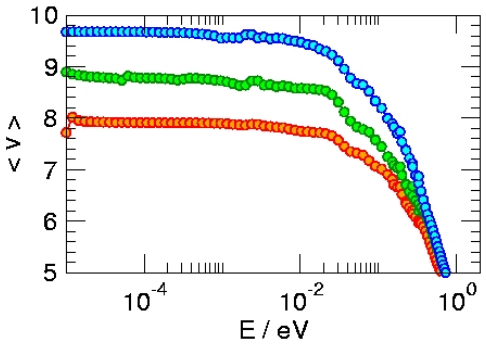
Acknowledgements

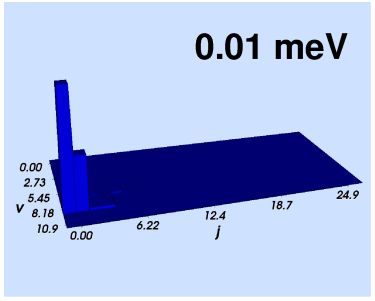
Thank you for your attention!

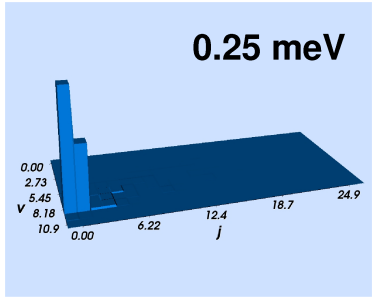


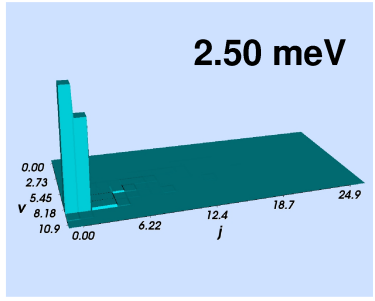
I. H-chemisorbed case

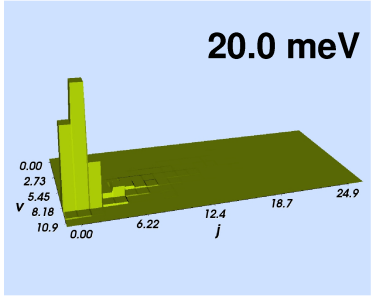


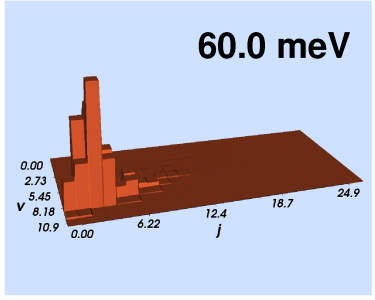


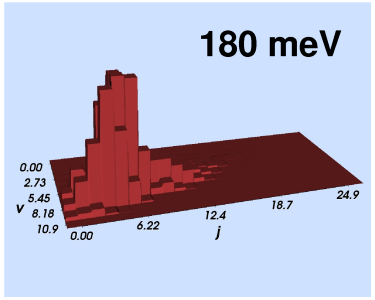


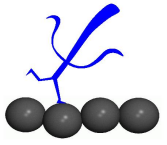








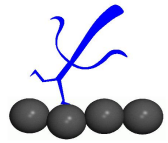




I. H-chemisorbed case

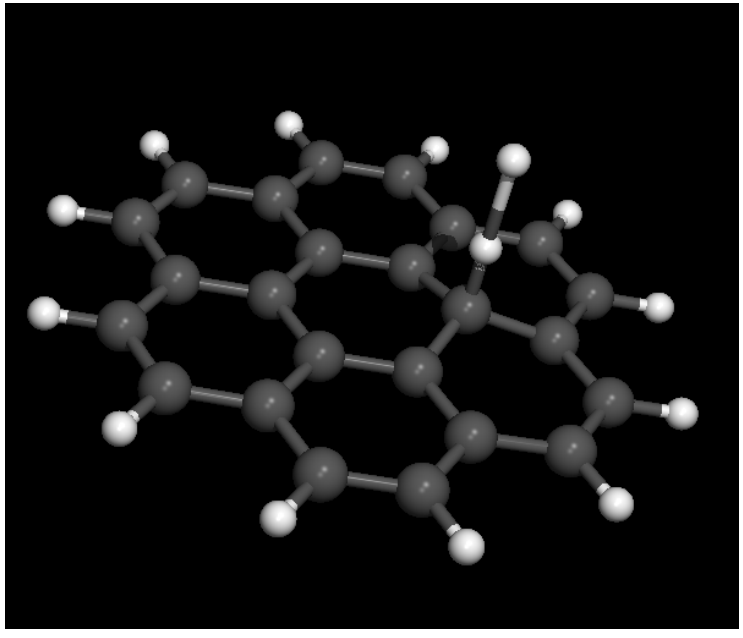
Challenges

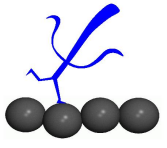
- Quantum dynamics is needed at ISM conditions
- C_{puck} atom plays an active role in the dynamics
- Energy transfer might be important
- Accurate Potential Energy Surfaces



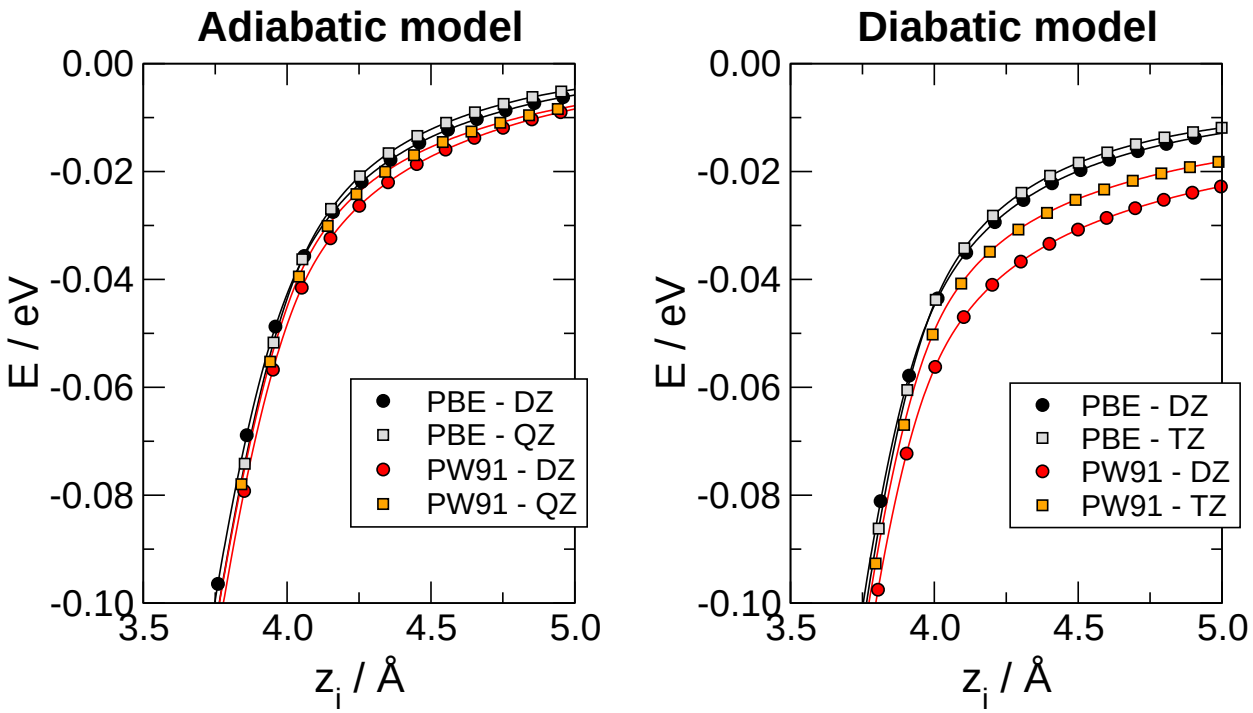
Checking the models

- **Coronene** and 2x2, 3x3 **periodic** models
- Diabatic and Adiabatic cases
- PBE (PW91)
- cc-pVDZ, (cc-pVTZ, cc-pvQZ) / 15x15x1, E_{cut}=500 eV

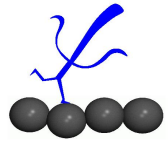




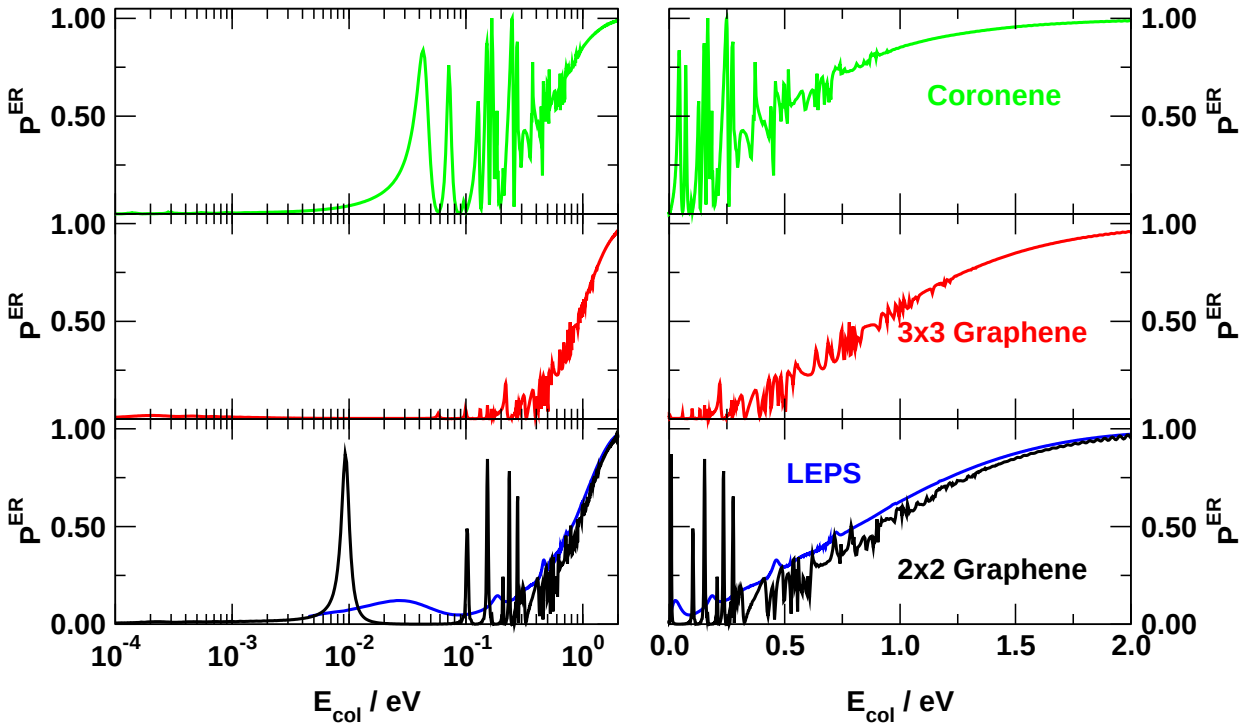
Energy barrier?



M. Bonfanti, S. Casolo, G. F. Tantardini and R. Martinazzo, *Phys. Chem. Chem. Phys.*, **13** 16680 (2011)



Influence on the (collinear) dynamics



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