

# Interaction of hydrogen atoms with carbon- $sp^2$ structures

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*ARCHEs plenary meeting*  
Domaine du Mas Blanc, Alénya (Pyrénées Orientales)  
Oct 3-6, 2011



# Outline

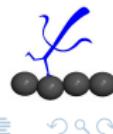
## 1 Introduction

## 2 Adsorption energetics

- ‘Bulk’ adsorption and clustering
- Edge effects

## 3 Eley-Rideal reaction

- Dynamics at cold  $E_{coll}$
- Energy barrier



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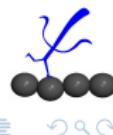
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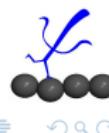
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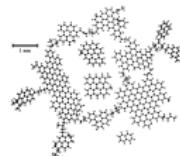
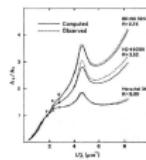
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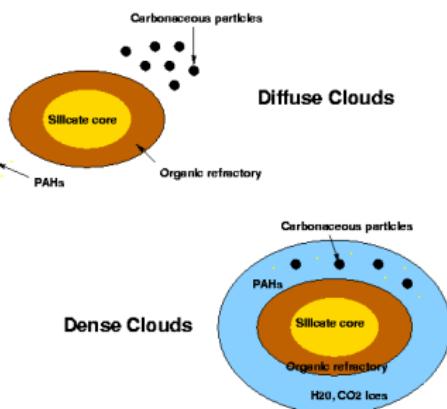


# H<sub>2</sub> in the ISM

- Hydrogen is the most abundant element of the Universe
- H<sub>2</sub> is formed on the surface of *dust grain*



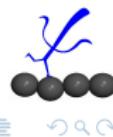
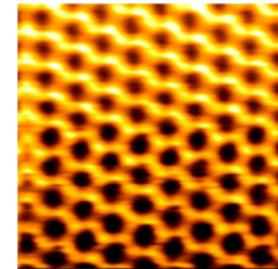
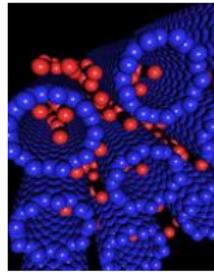
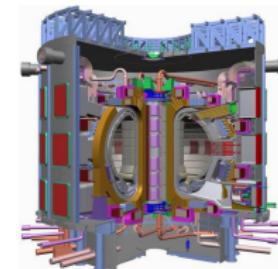
$$f_{\text{grain}} = n_{\text{grain}} / n_H \sim 10^{-12} \text{ i.e. } \sim 1\% \text{ of ISM mass}$$



Hydrogen-graphite is an important model for understanding H<sub>2</sub> formation in ISM

# Technology

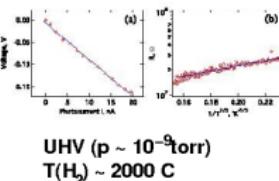
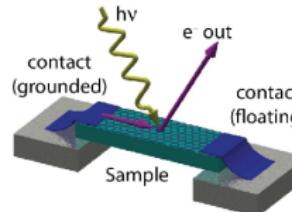
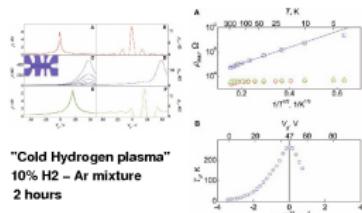
- Hydrogen storage
- Nuclear fusion
- Nanoelectronics, spintronics, nanomagnetism



# Technology: graphene physics and devices

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

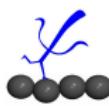
MIT occurs when **hydrogenating** graphene



.. $\sigma$  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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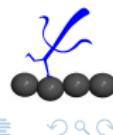
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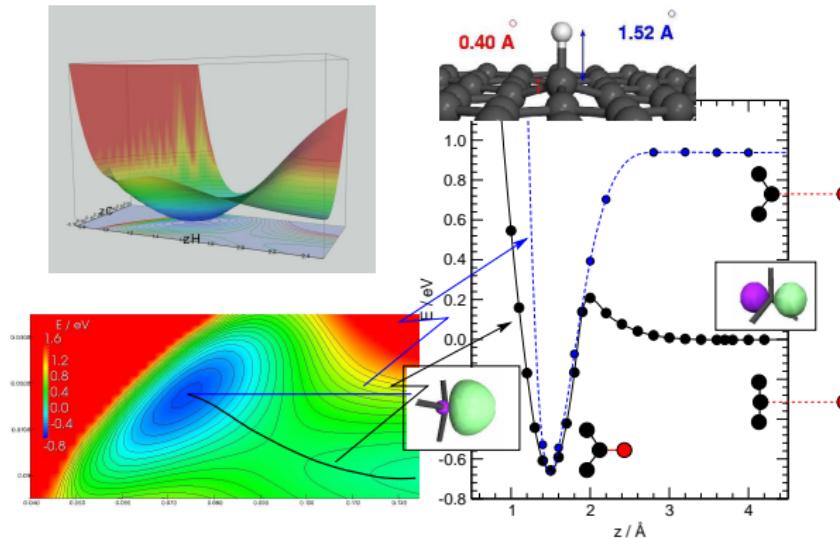
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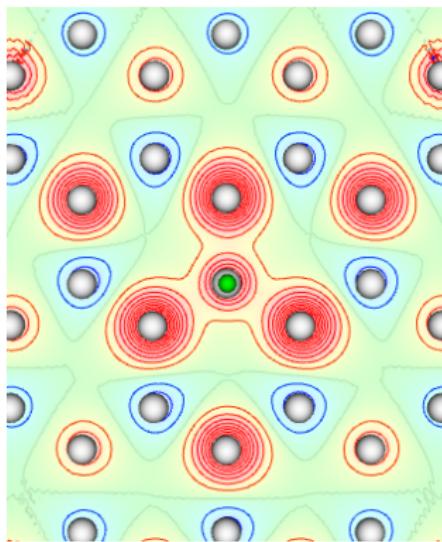


# Single-H

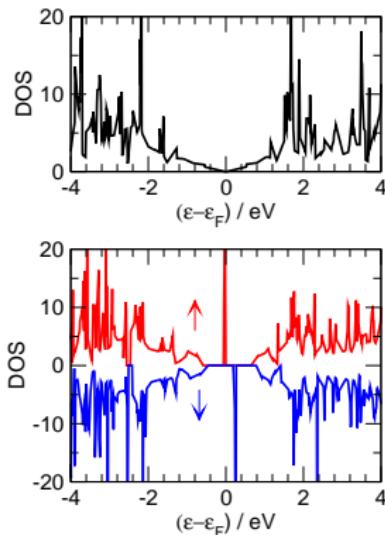


L. Jeloaica and V. Sidis, *Chem. Phys. Lett.* **300**, 157 (1999)  
X. Sha and B. Jackson, *Surf. Sci.* **496**, 318 (2002)

# Midgap states



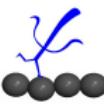
*..patterned spin-density*



Graphene

+ H

H-Graphene

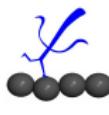
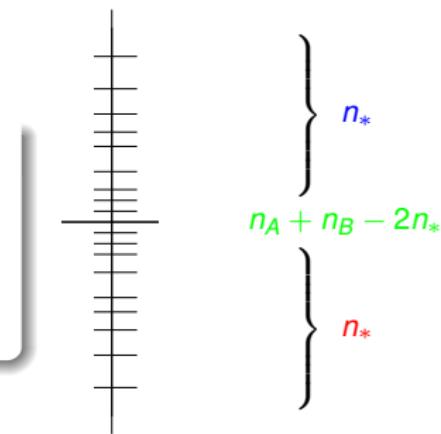


# Midgap states

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

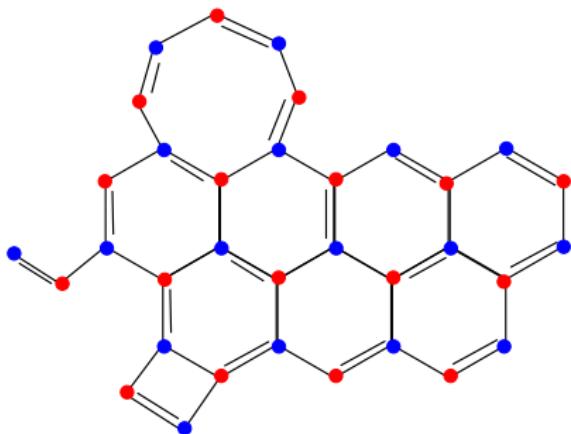
## Basic results

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



# Midgap states

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



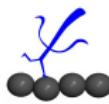
## Electron-hole symmetry

$$b_i \rightarrow -b_i \implies H_e^\pi \rightarrow -H_e^\pi$$

$$\epsilon_i, |\psi_i^{(+)}\rangle = \sum_k \alpha_k |\mathbf{a}_k\rangle + \sum_j \beta_i |\mathbf{b}_j\rangle$$

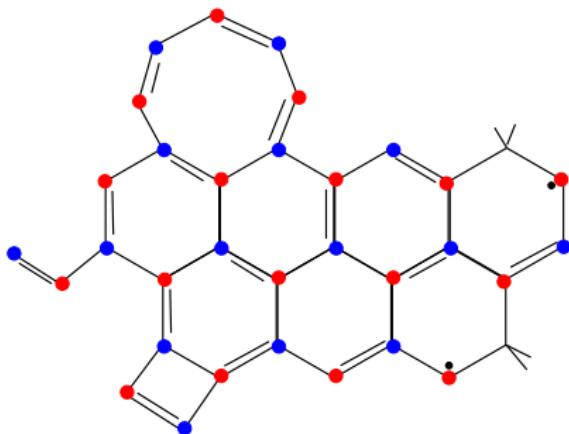
↓

$$-\epsilon_i, |\psi_i^{(-)}\rangle = \sum_k \alpha_k |\mathbf{a}_k\rangle - \sum_j \beta_i |\mathbf{b}_j\rangle$$



# Midgap states

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



## Imbalance rule

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

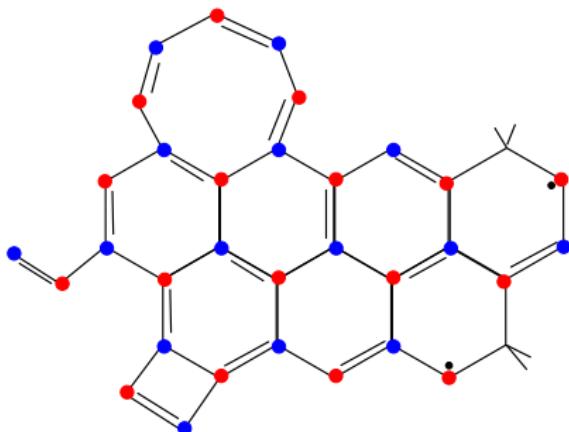
$$\begin{bmatrix} \mathbf{0} & \mathbf{T}^\dagger \\ \mathbf{T} & \mathbf{0} \end{bmatrix} \begin{bmatrix} \alpha \\ \beta \end{bmatrix} = \begin{bmatrix} \mathbf{0} \\ \mathbf{0} \end{bmatrix}$$

$\Rightarrow \mathbf{T}\alpha = \mathbf{0}$  has  $n_A - n_B$  solutions



# Midgap states

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

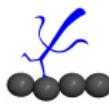


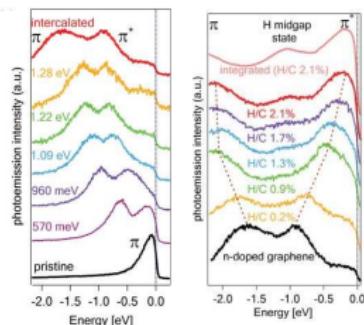
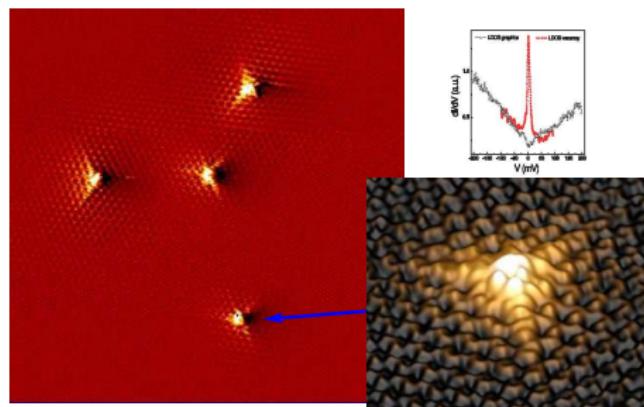
## Spin alignment

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

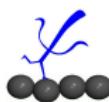
$$S = |n_A - n_B|/2 = n_I/2$$

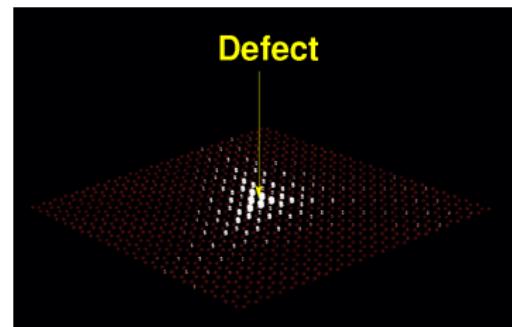
E.H. Lieb, *Phys. Rev. Lett.* **62**, 1201 (1989)





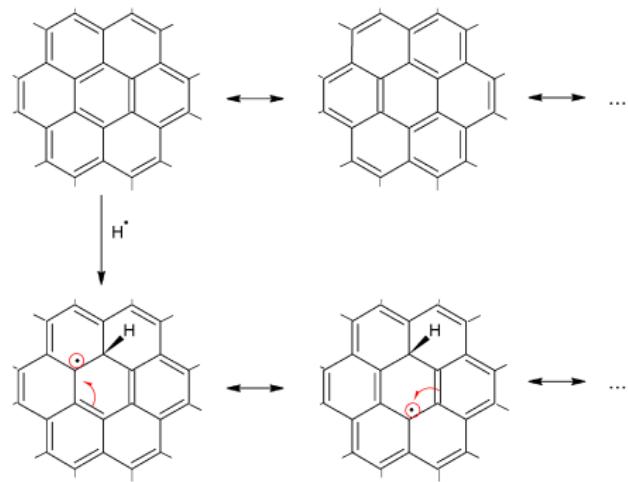
M.M. Ugeda, I. Brihuega, F. Guinea and J.M. Gomez-Rodriguez, *Phys. Rev. Lett.* **104**, 096804 (2010)  
 D. Haberer *et al.*, *Phys. Rev. B* **83**, 165433 (2011)



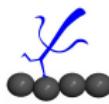


$$\psi(x, y, z) \sim 1/r$$

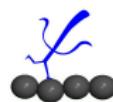
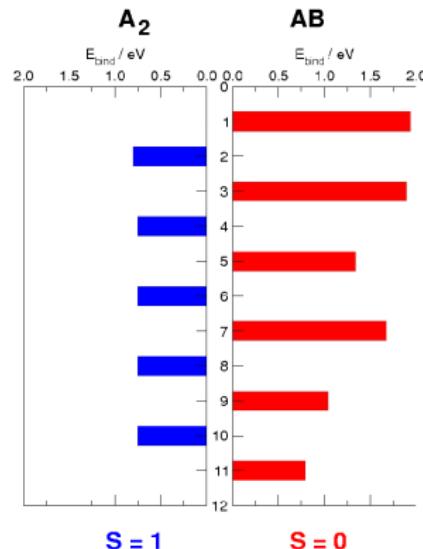
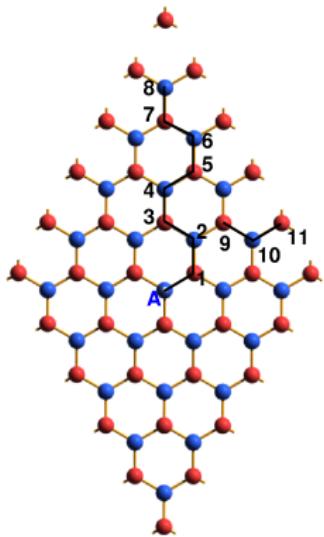
V. M. Pereira et al., *Phys. Rev. Lett.* **96**, 036801 (2006);  
*Phys. Rev. B* **77**, 115109 (2008)



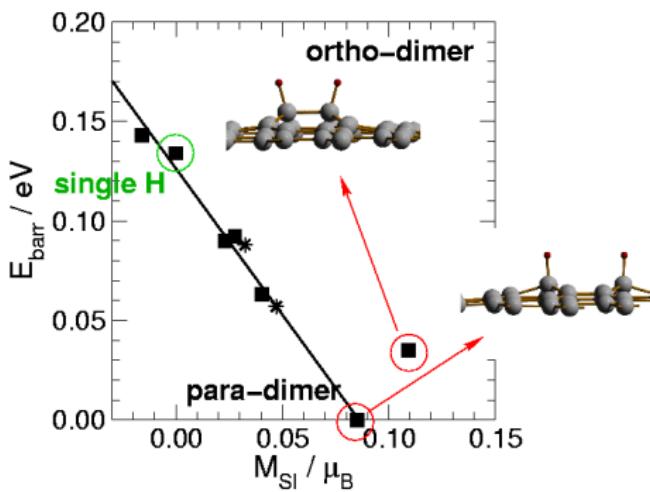
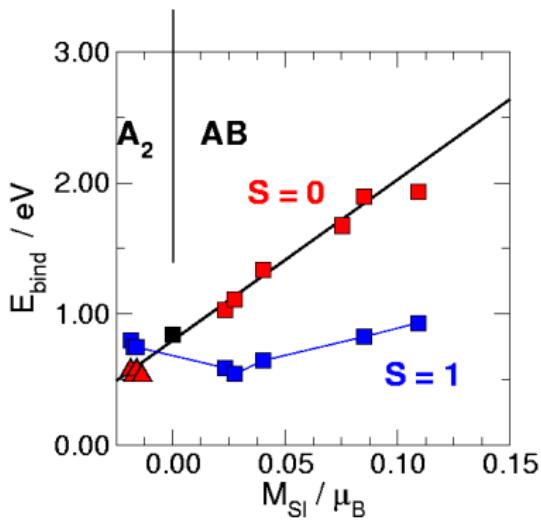
See e.g. Y. Ferro et al., *Phys. Rev. B* **78**, 085417 (2008)



# Dimers

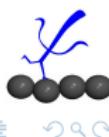


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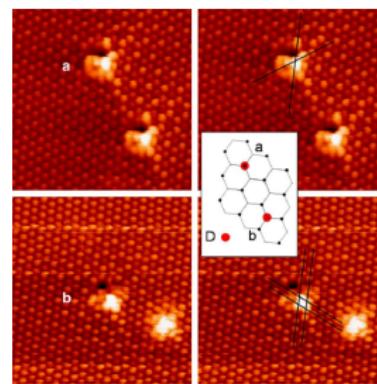
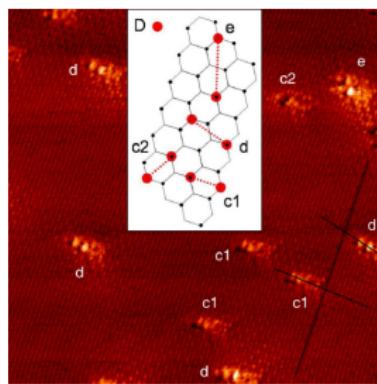
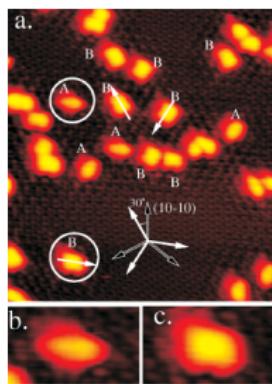


S. Casolo, O.M. Lovvik, R. Martinazzo and G.F. Tantardini, *J. Chem. Phys.* **130** 054704 (2009)  
arXiv:0808.1312 (2008)

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



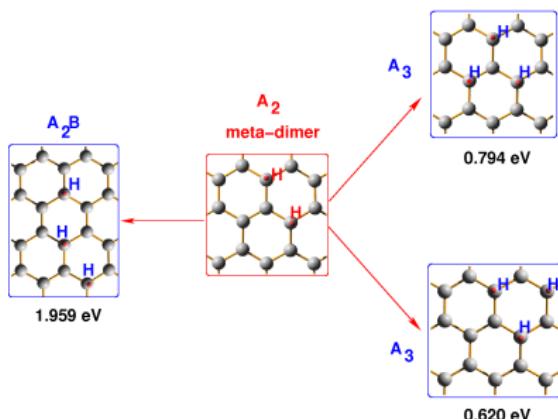
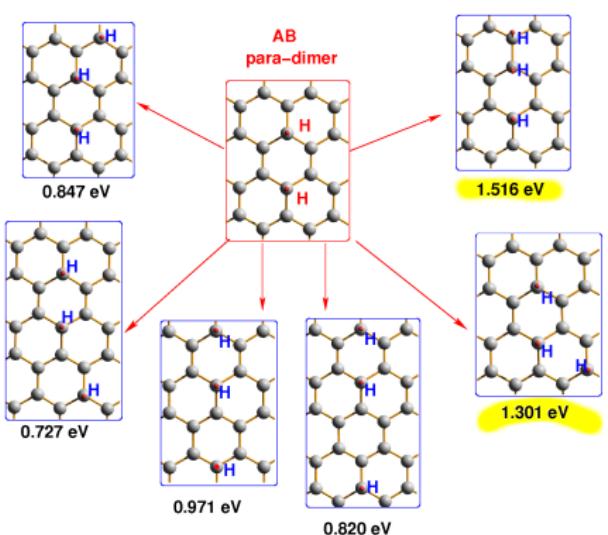
# Dimers



[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)

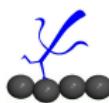
[2] A. Andree, M. Le Lay, T. Zecho and J. Kupper, *Chem. Phys. Lett.* **425** 99 (2006)

# 3-atom clusters



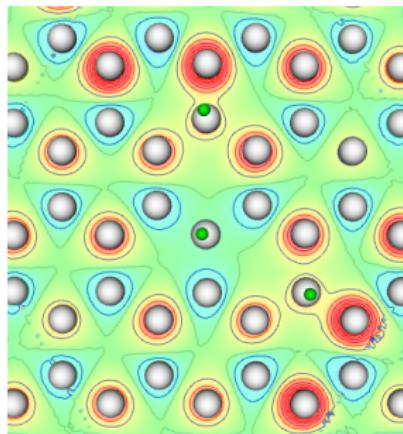
$$\mu = 1\mu_B \Rightarrow \mu = 2\mu_B \Rightarrow \mu = 3\mu_B$$

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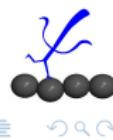
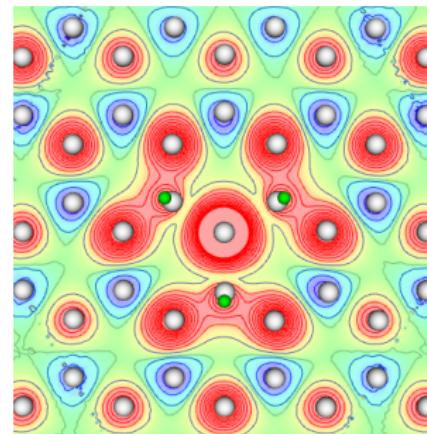


## 3-atom clusters

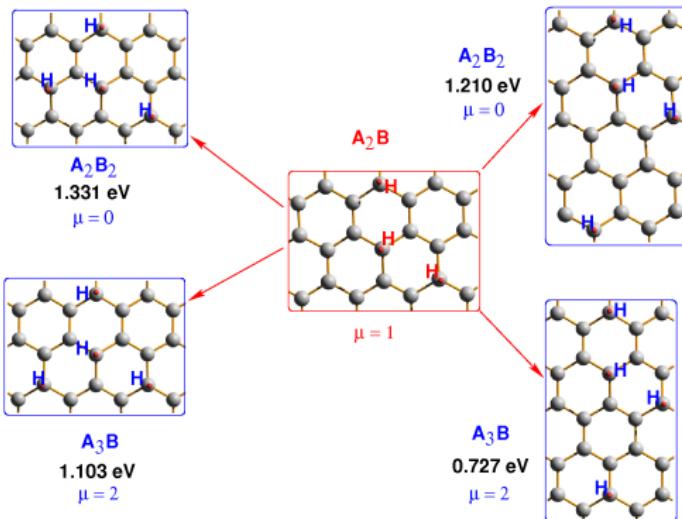
$A_2B$



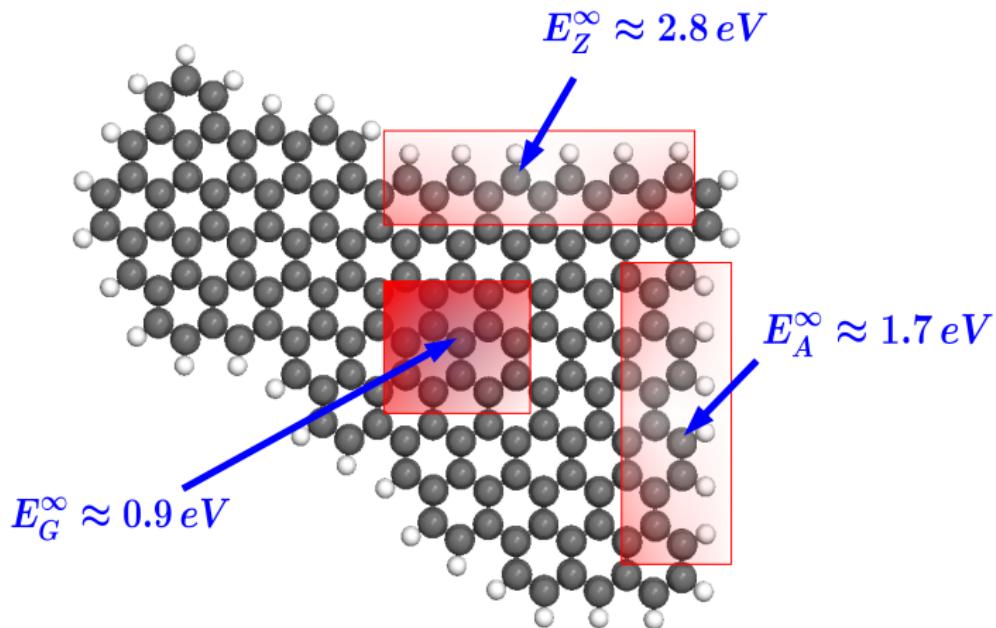
$A_3$



## 4-atom clusters



# Role of edges



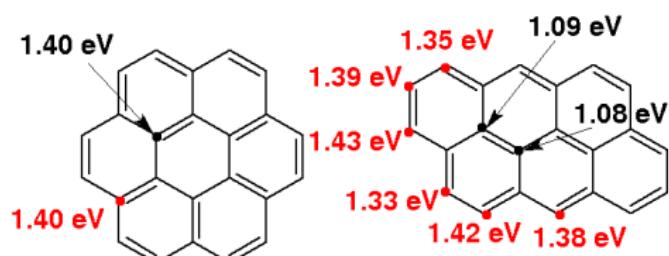
# 'Geometric' effect?

'Reorganization' energy  
upon binding

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

**E sites:**  $\delta E \sim 1.4 \pm 0.1 \text{ eV}$

**G sites:**  $\delta E \sim 1.0 \pm 0.1 \text{ eV}$



...purely electronic effect

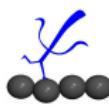
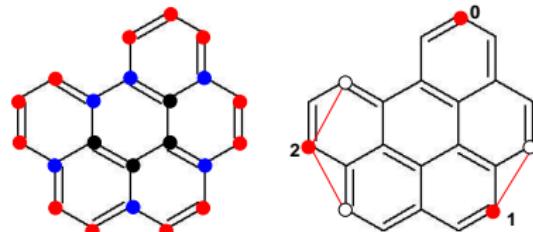
# Hints from the tight-binding Hamiltonian $H^\pi$

Shape of low-energy orbitals  
..from a 'lattice renormalization'

- Coordination ( $Z$ )
- Hypercoordination ( $\xi$ )
- sublattice imbalance ( $\eta$ )

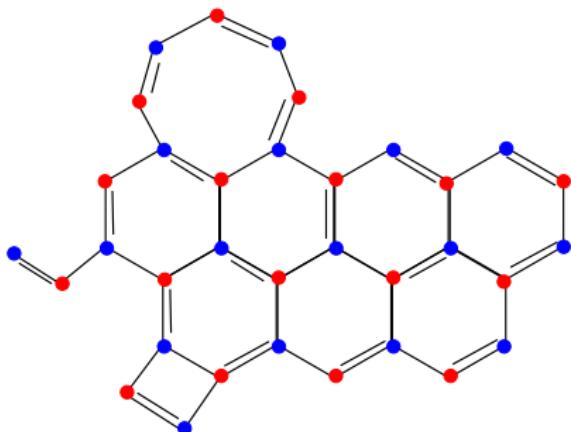
$Z = 2 \Rightarrow \mathbf{E}$

$Z = 3 \Rightarrow \mathbf{F}, \mathbf{G}$



# Hints from the tight-binding Hamiltonian $H^\pi$

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



## ‘Lattice renormalization’

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

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

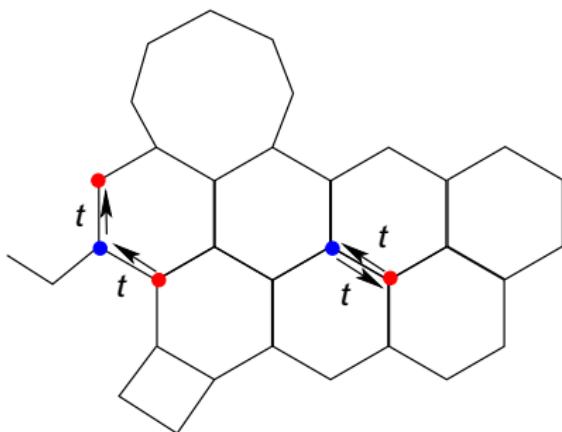
1

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

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

# Hints from the tight-binding Hamiltonian $H^\pi$

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



'Lattice renormalization'

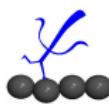
$$\tilde{H}_{AA} = H_{AB} H_{BA}$$

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⇓

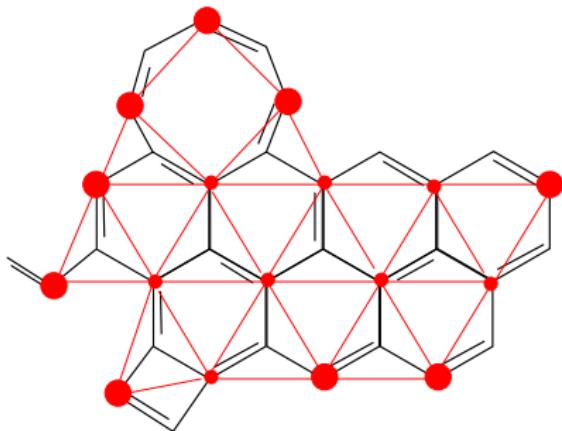
$$\epsilon_i^\pm = \pm \sqrt{\tilde{\epsilon}_i}, |\psi_i^{(\pm)}\rangle = |\psi_{A,i}\rangle \pm |\psi_{B,i}\rangle$$

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



# Hints from the tight-binding Hamiltonian $\tilde{H}^\pi$

$$\tilde{H}^\pi \approx \sum_i Z_i t^2 \mathbf{a}_i^\dagger \mathbf{a}_i + \sum_{ij} t^2 \mathbf{a}_i^\dagger \mathbf{a}_j$$



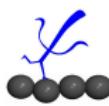
'Lattice renormalization'

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

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

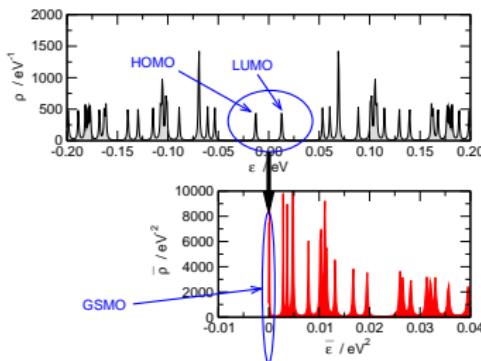
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$$\begin{aligned} \epsilon_i^\pm &= \pm\sqrt{\tilde{\epsilon}_i}, |\psi_i^{(\pm)}\rangle = |\psi_{A,i}\rangle \pm |\psi_{B,i}\rangle \\ |\psi_{B,i}\rangle &= \tilde{\epsilon}_i^{-1/2} H_{BA} |\psi_{A,i}\rangle \end{aligned}$$



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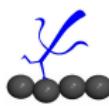
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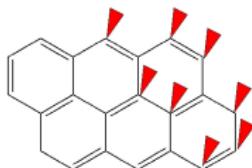
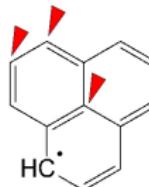
$$\begin{aligned} \epsilon_i^\pm &= \pm\sqrt{\tilde{\epsilon}_i}, |\psi_i^{(\pm)}\rangle = |\psi_{A,i}\rangle \pm |\psi_{B,i}\rangle \\ |\psi_{B,i}\rangle &= \tilde{\epsilon}_i^{-1/2} H_{BA} |\psi_{A,i}\rangle \end{aligned}$$



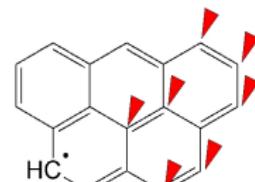
# Systems



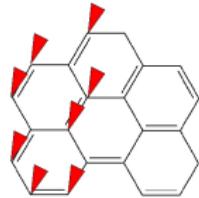
pirene

dibenzo[def,mno]crisene /  
antrantrene

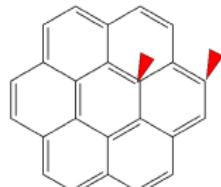
perinaftenile / fenalene



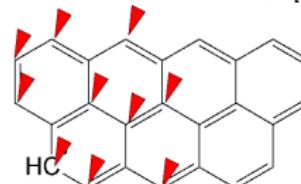
benzo[cd]pirenile



benzo[ghi]perilene



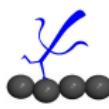
coronene



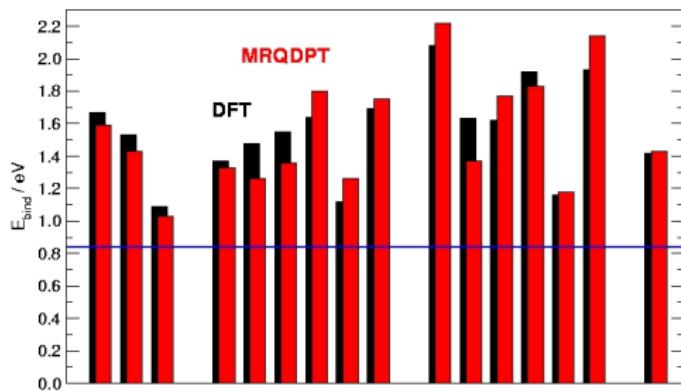
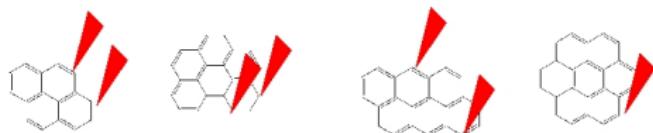
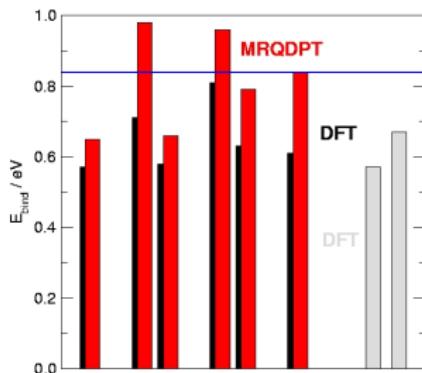
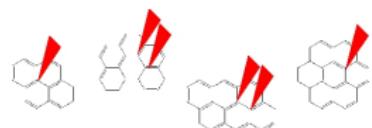
7 - PAH

$$\eta = 0$$

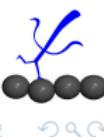
$$\eta \neq 0$$



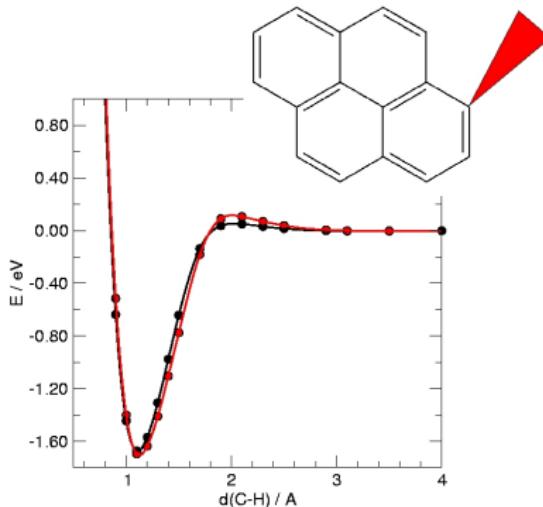
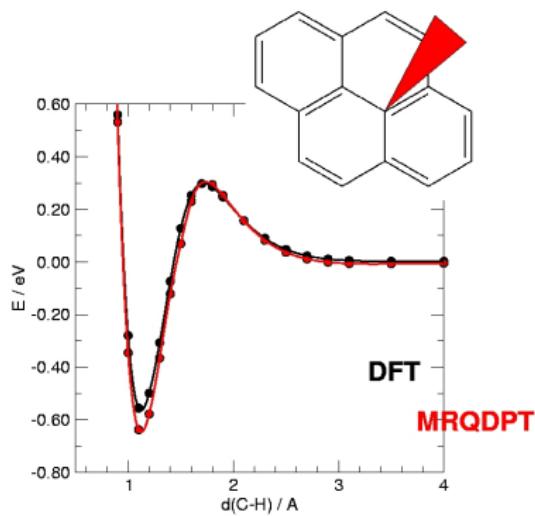
# Graphitic vs edge carbons



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



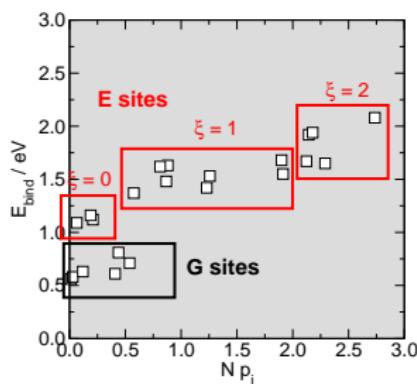
# Adsorption paths



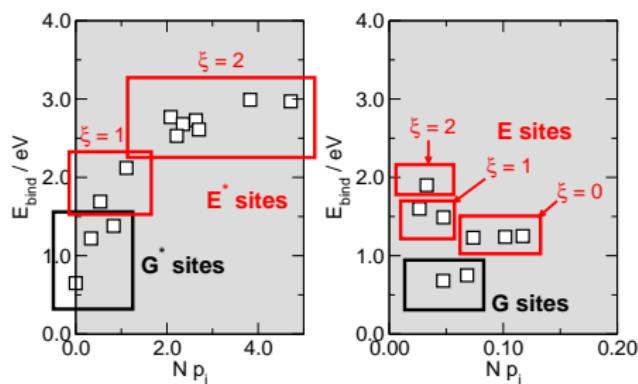
M. Bonfanti, S. Casolo, G. F. Tantardini, A. Ponti and R. Martinazzo, *JCP*, *in press*; arXiv:1107.4324 (2011)

# Predicting reactivity

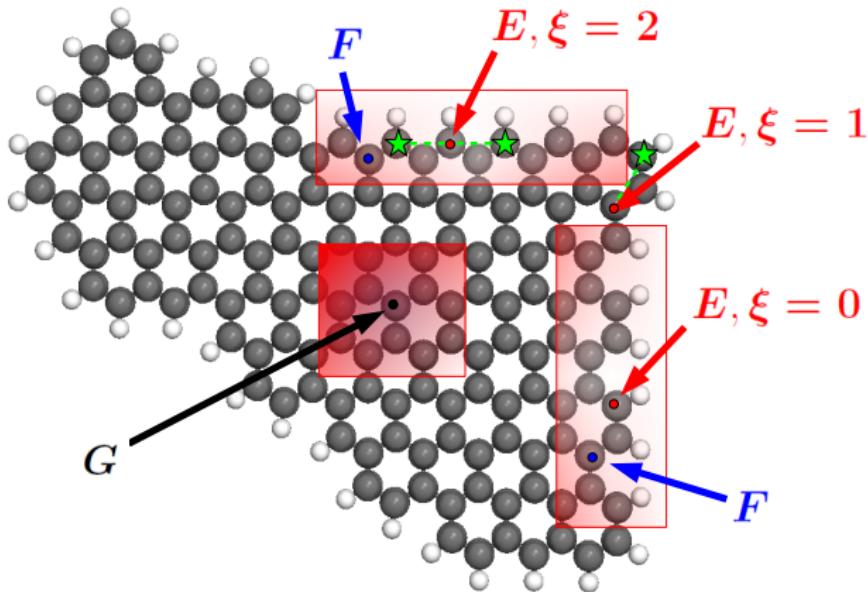
$$\eta = 0$$



$$\eta \neq 0$$



# Predicting reactivity



# Outline

## 1 Introduction

## 2 Adsorption energetics

- ‘Bulk’ adsorption and clustering
- Edge effects

## 3 Eley-Rideal reaction

- Dynamics at cold  $E_{coll}$
- Energy barrier



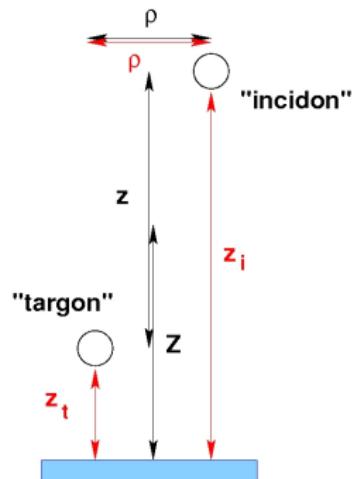
# Reaction: technicalities

- Rigid, flat surface approximation<sup>1</sup>
- Split-Operator with FFT along cartesian coordinates and DBT along  $\rho$ <sup>1</sup>
- propagation in both product and reagent coordinate sets<sup>2</sup>

⇒ 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)

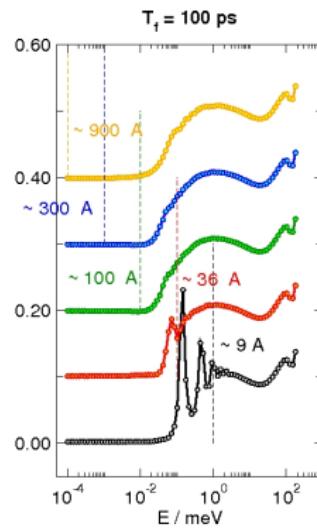
[2] R. Martinazzo and G.F. Tantardini, J. Phys. Chem. A, 109 (2005) 9379; J. Chem. Phys. 124, 124703 (2006); J. Chem. Phys. 124, 124704 (2006)



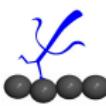
## Reaction: technicalities (low $E_{col}$ )

- Two-wavepacket approach<sup>1</sup>
  - Transmission-free<sup>2</sup> absorbing potentials and Fourier mapping<sup>3</sup> in reagent coordinates

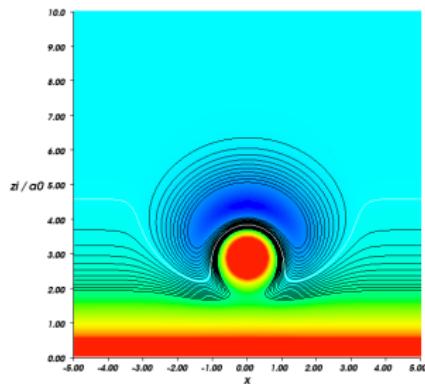
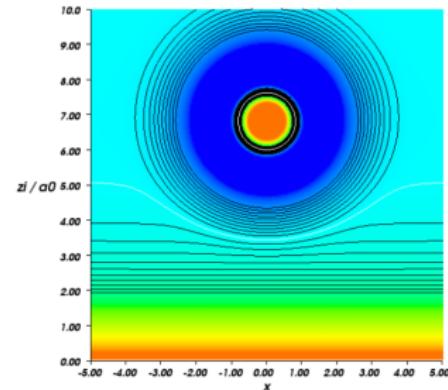
In 3D  $T_f=25\text{-}30 \text{ ps}$  and AP lengths  $\sim 50\text{\AA}$  in order to get converged xsections down to  $\sim 10^{-5} \text{ eV}$ , i.e.  $\sim 0.1 \text{ K}$



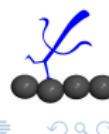
- [1] R. Martinazzo and G.F. Tantardini, J. Chem. Phys. 122, 094109 (2005)  
 [2] D. Manolopoulos, J. Chem. Phys. 117, 9552 (2002)  
 [3] A.G. Borisov, J. Chem. Phys. 114, 7770 (2001)



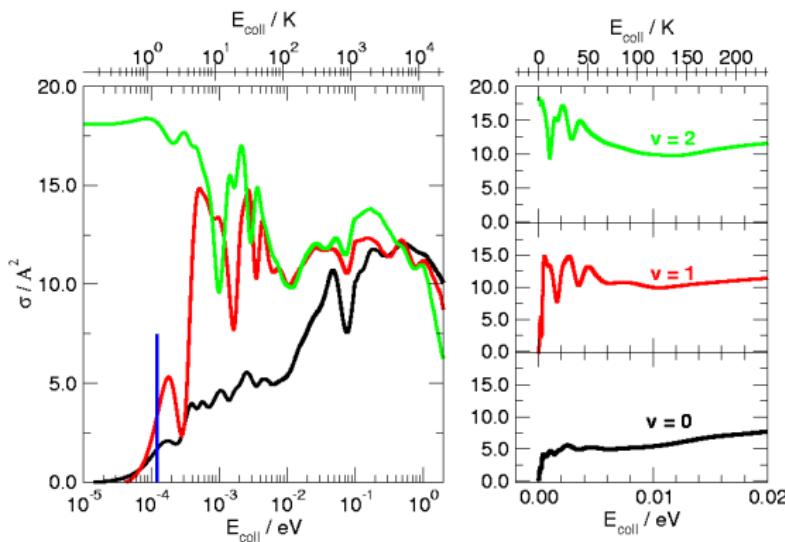
# Reaction: Potential Energy Surfaces

Chemisorbed target H ( $z_{eq}$ )Physisorbed target H ( $z_{eq}$ )

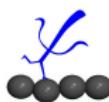
X. Sha, B. Jackson and D. Lemoine, J. Chem. Phys. 116, 7158 (2002)



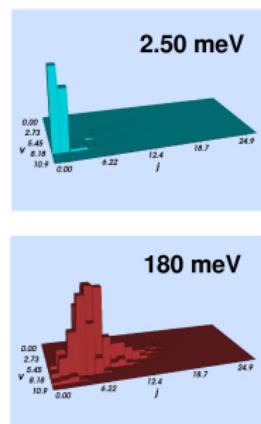
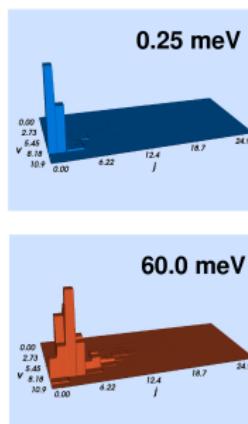
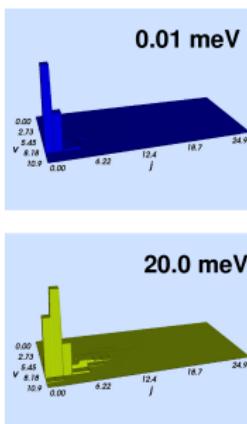
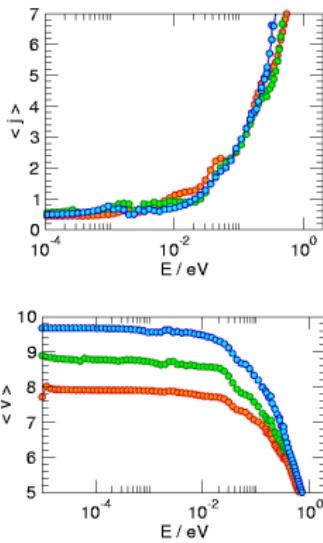
# I. H-chemisorbed case



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

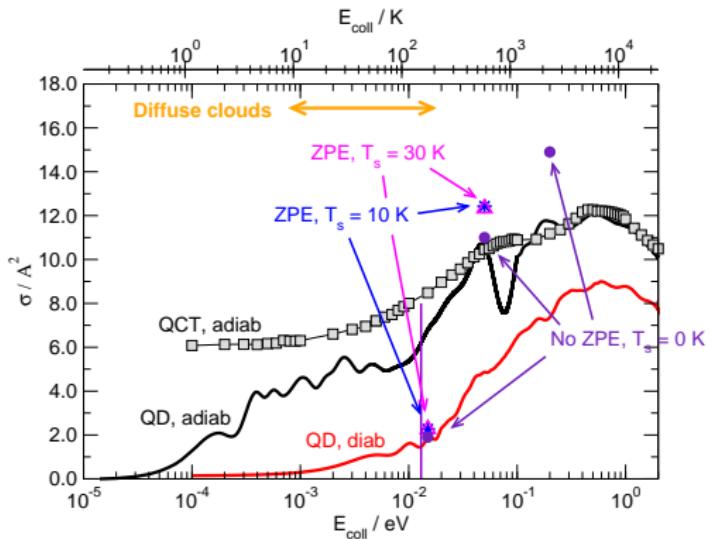


## I. H-chemisorbed case

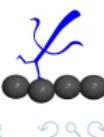


# I. H-chemisorbed case

QCT comparison,  $v = 0$



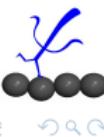
M. Sizun, D. Bachellerie, F. Anguillon, V. Sidis *Chem. Phys. Lett.* 32 498 2010  
D. Bachellerie, M. Sizun, F. Anguillon, D. Teillet-Billy, N. Rougeau, *Phys. Chem. Chem. Phys.* 2715 11 2009



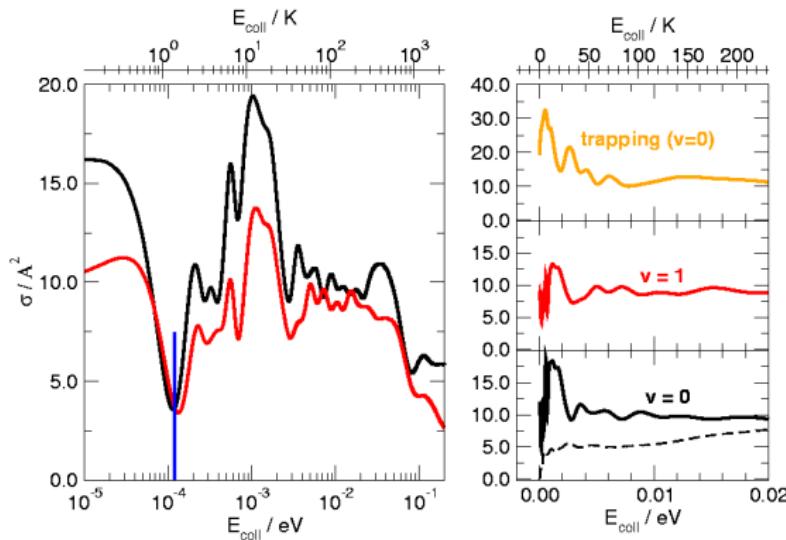
## I. H-chemisorbed case

### Challenges

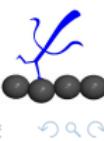
- Quantum dynamics is needed at ISM conditions
- C<sub>puck</sub> atom plays an active role in the dynamics
- Energy transfer might be important
- Accurate Potential Energy Surfaces



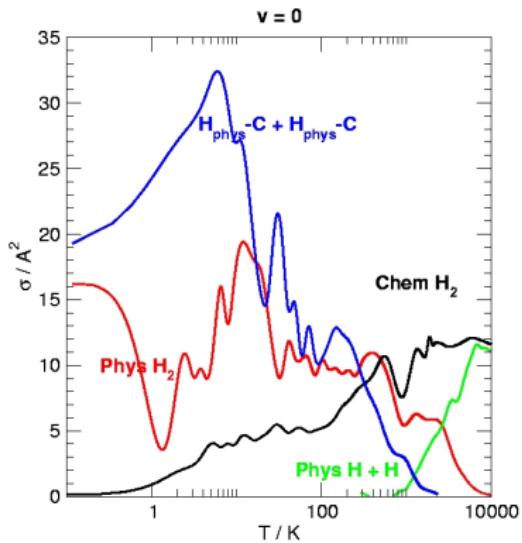
## II. H-physisorbed case



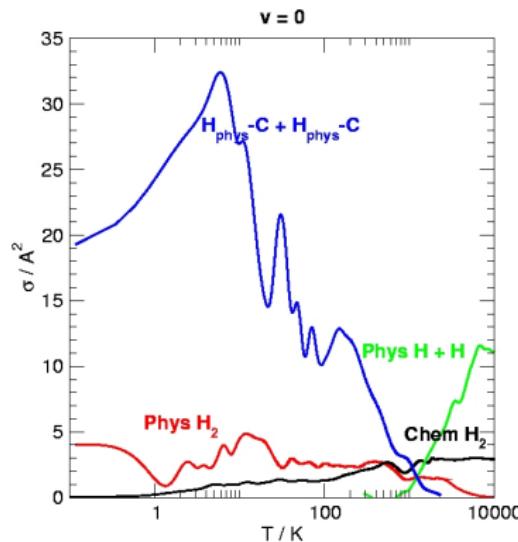
S. Casolo, M. Bonfanti, R. Martinazzo and G.F. Tantardini, *J. Phys. Chem. A*, 113 14545 (2009)



# H-chem vs H-phys



# H-chem vs H-phys

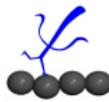
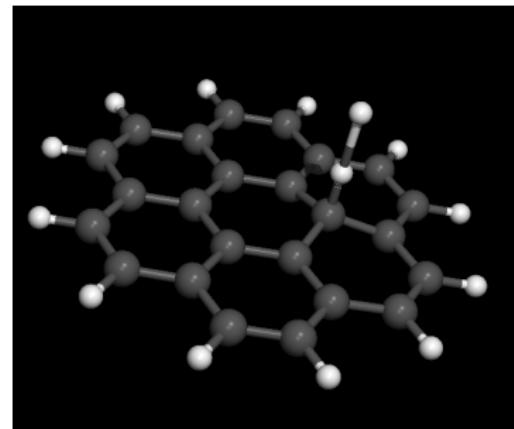


Cross-sections have to be corrected for the **spin** statistics (1/4)

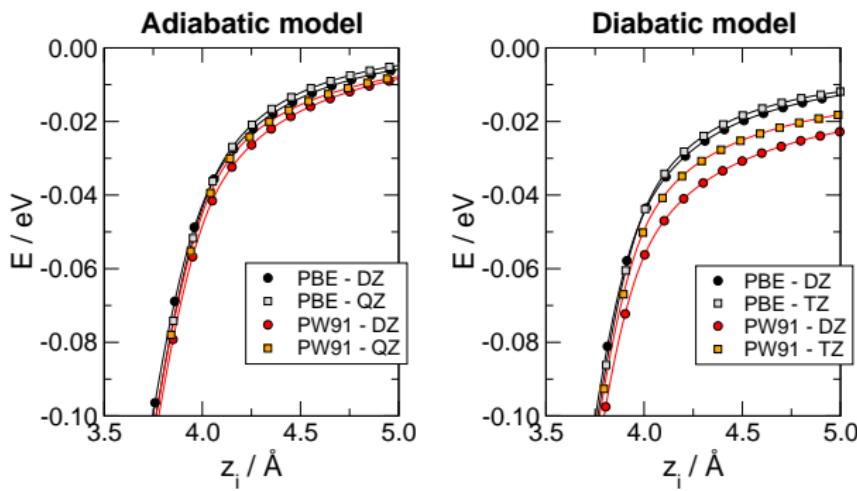


# Checking the models

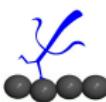
- **Coronene** and 2x2, 3x3 **periodic** models
- **Diabatic** and **Adiabatic** cases
- PBE (PW91)
- cc-pVDZ, (cc-pVTZ, cc-pvQZ) /  
 $15 \times 15 \times 1, E_{cut}=500 \text{ eV}$



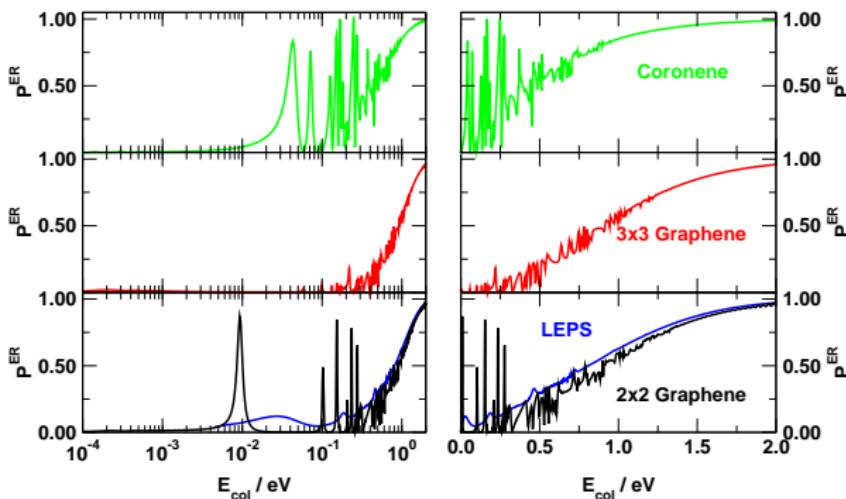
# Energy barrier?



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



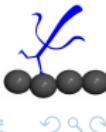
# Influence on the (collinear) dynamics



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

# 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
- Eley-Rideal dynamics is challenging at typical interstellar cloud conditions



# Acknowledgements

## University of Milan

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Matteo Bonfanti

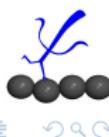


+x:

C.I.L.E.A. Supercomputing  
Center  
Notur  
I.S.T.M.

Chemical Dynamics Theory Group

<http://users.unimi.it/cdtg>



# Acknowledgements

Thank you for your attention!

