Adsorption and reaction of hydrogen atoms on graphitic surfaces

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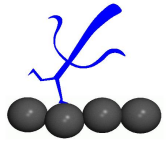
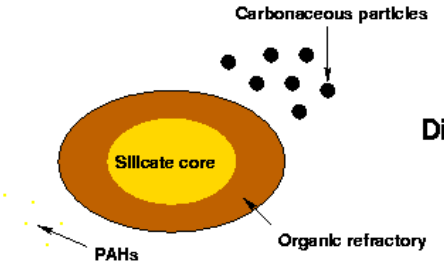
Exploring mechanisms for H_2 formation on very small carbonaceous grains and PAHs of astrophysical interest
Toulouse, April 25, 2013

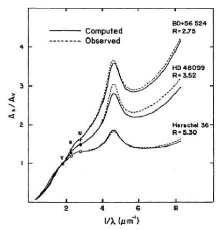


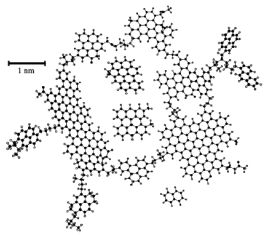
H_2 in the ISM

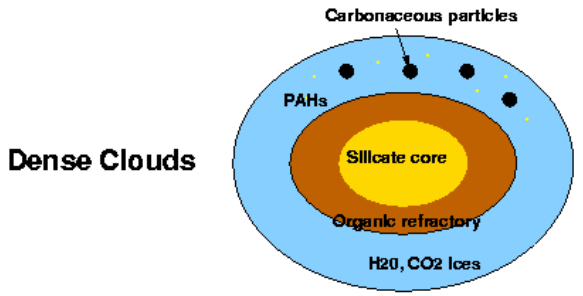
- Hydrogen is the most abundant element of the Universe
- H_2 is formed on the surface of *dust* grain

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

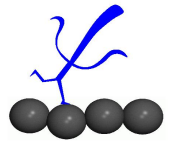




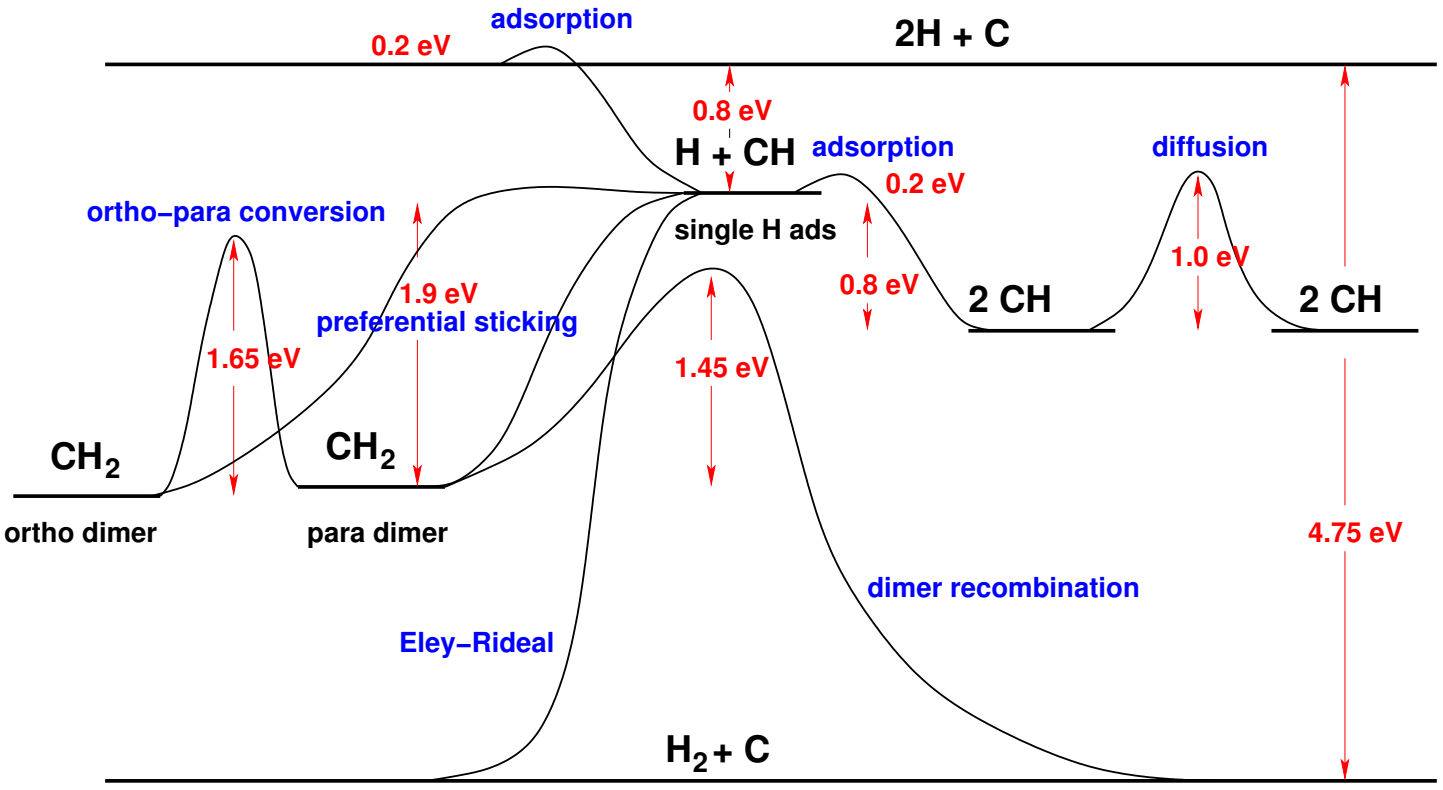




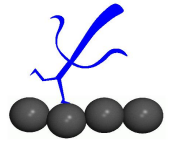
Hydrogen-graphite is an important model for understanding H_2 formation in ISM



Chemisorption and reaction



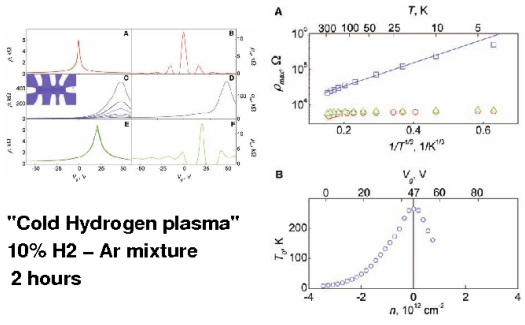
R. Martinazzo, S. Casolo and L. Horneaker
in *Dynamics of Gas-Surface Interactions*, Ed.s R. D. Muino and H. F. Busnengo, Springer (2013)

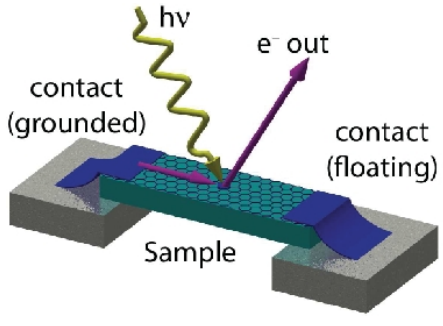


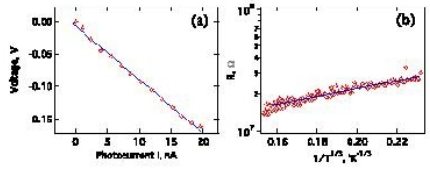
Technology: graphene physics and devices

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

MIT occurs when hydrogenating graphene





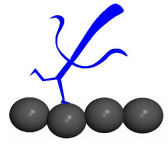


UHV (p ~ 10^{-9} torr)
T(H_2) ~ 2000 C

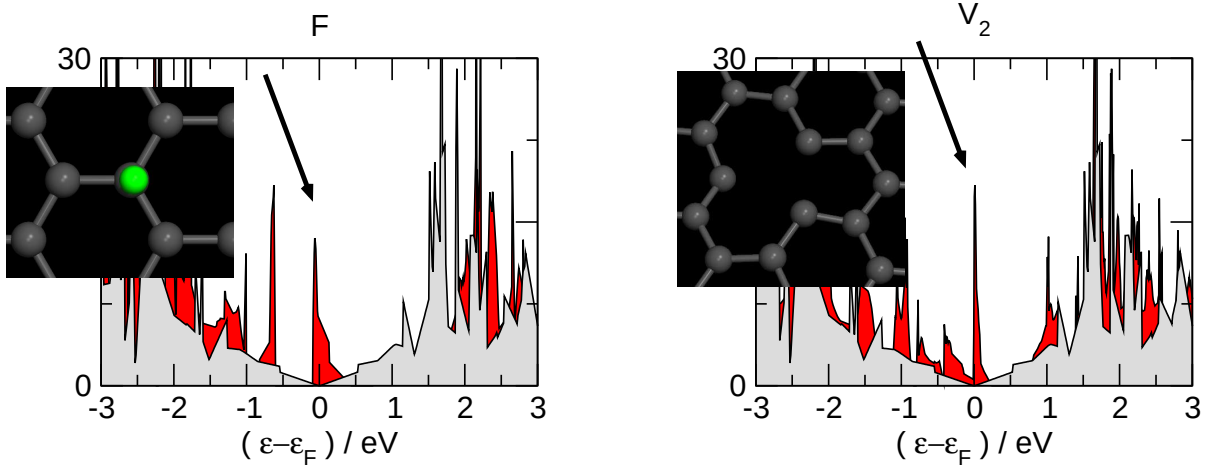
..σ *vs* T agrees well with VRH in two dimensions

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)

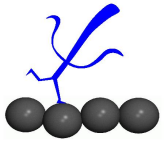


p_z vacancies



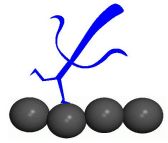
- Midgap states show up in the DOSs
- H, F, OH, CH_3, etc. behave similarly to vacancies

Outline



Outline

1. Point defects in graphene
   - H adsorption and clustering
   - Edge effects
   - Vacancies
2. Eley-Rideal reaction
   - Quantum Dynamics at high E_{coll}
   - Quantum Dynamics at cold E_{coll}
   - Ab initio molecular dynamics



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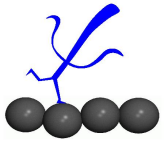
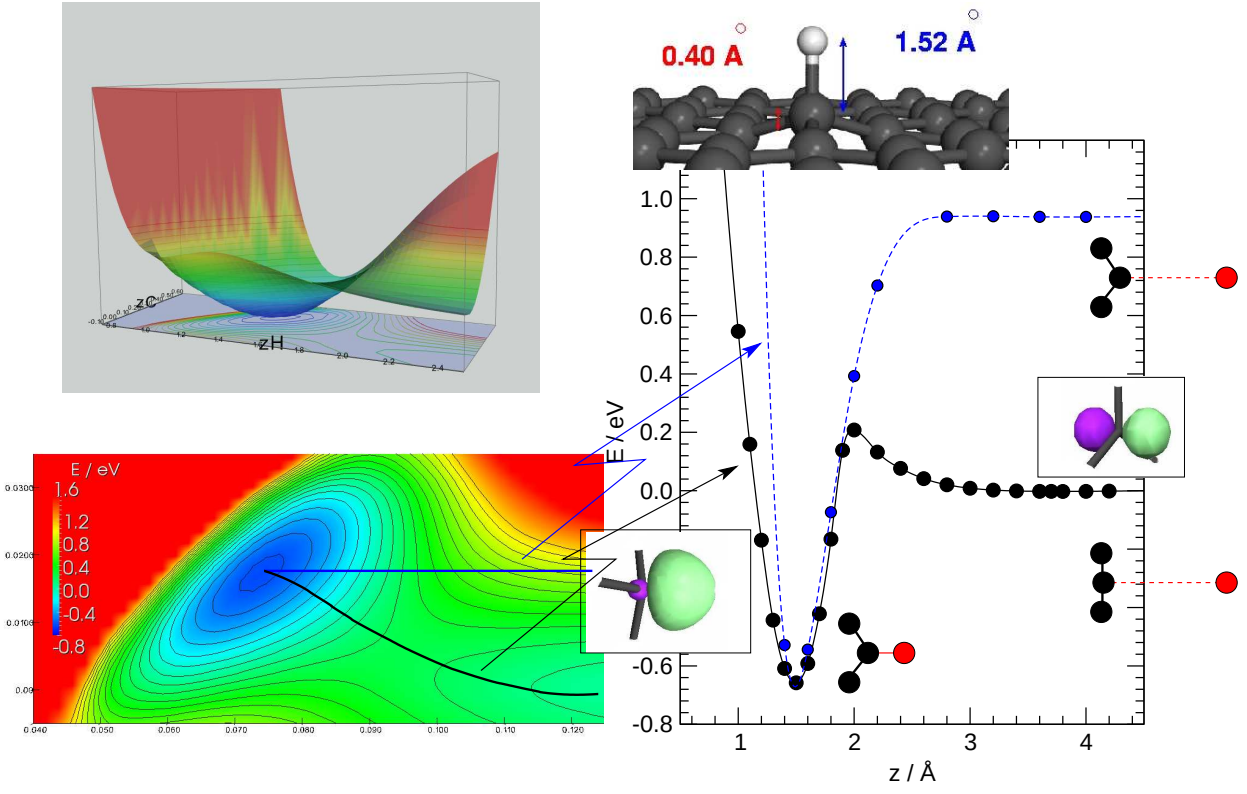


Single-H chemisorption



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

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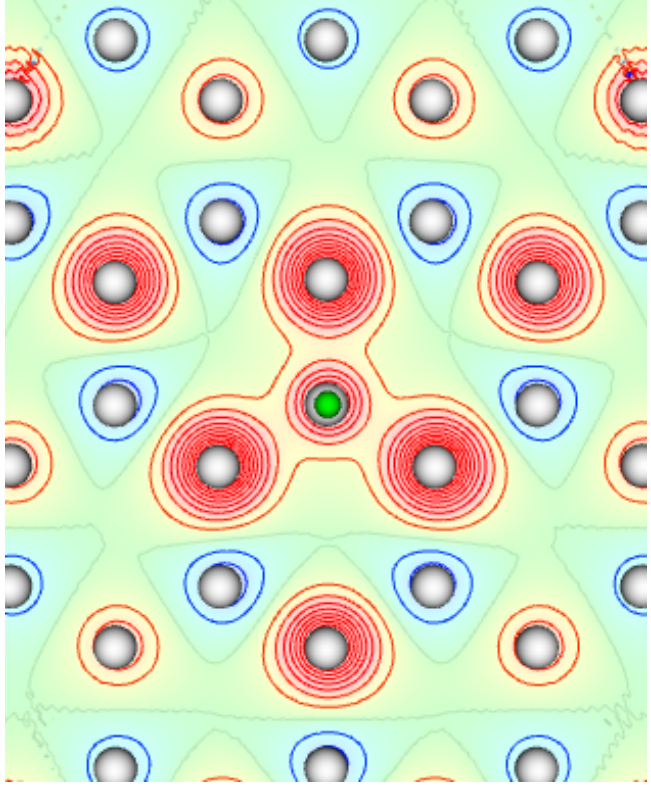
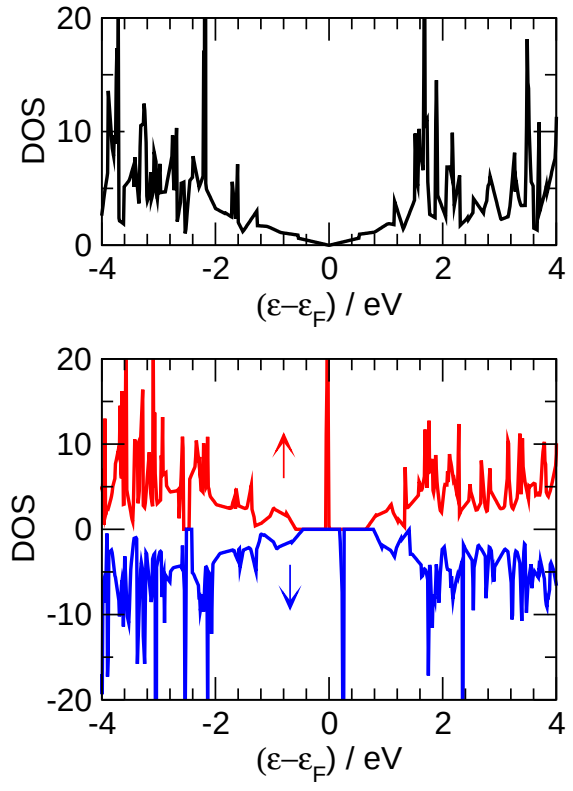
Midgap states

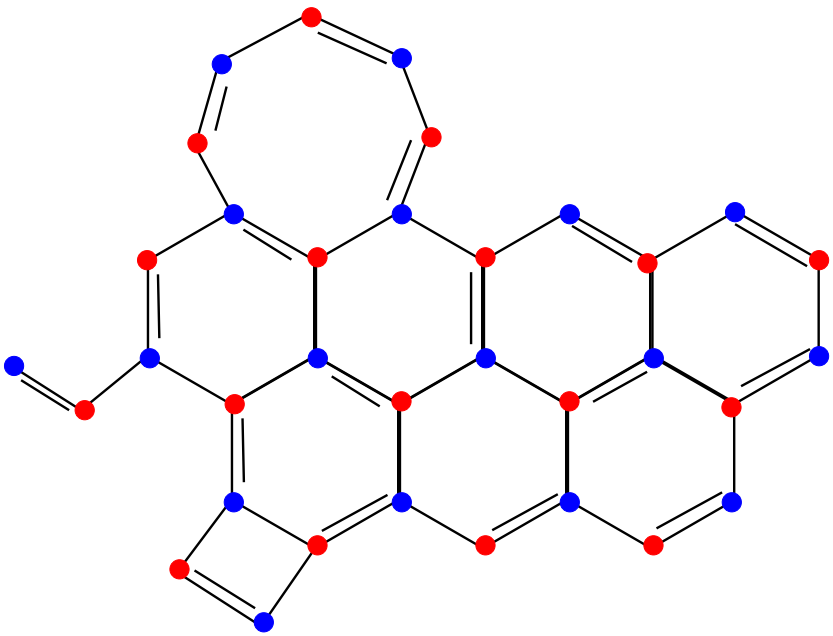


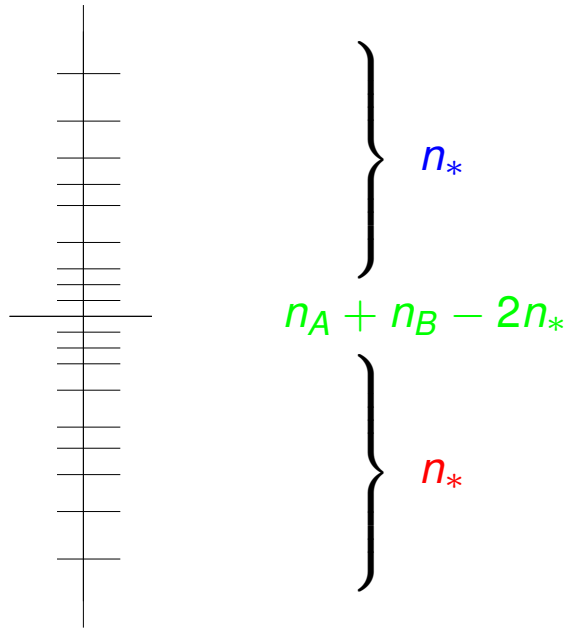
..*patterned* spin-density



Midgap states

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





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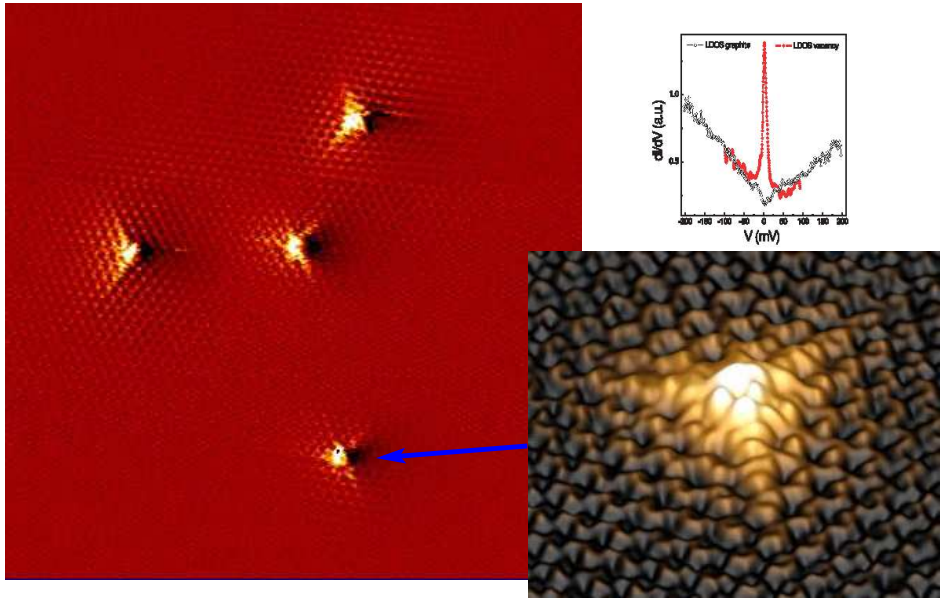
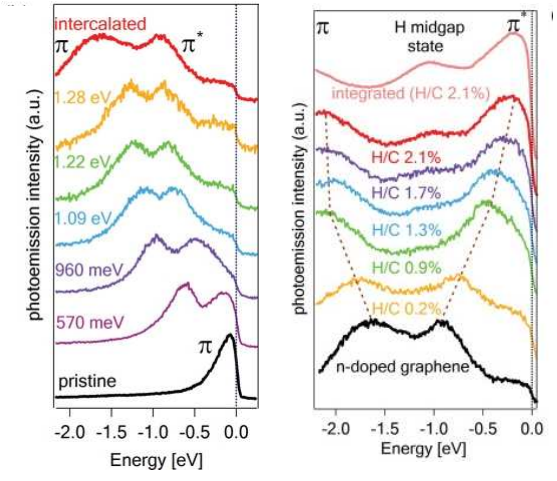
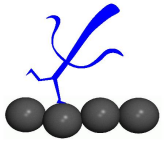
Midgap states

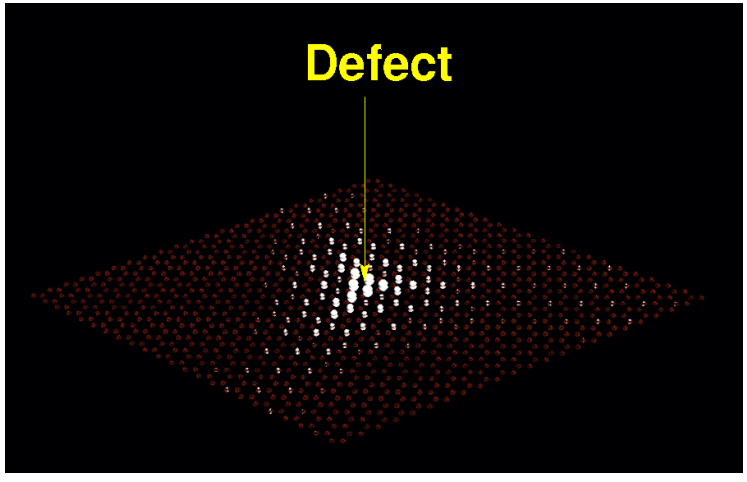




M.M. Ugeda, I. Brihuega, F. Guinea and J.M. Gomez-Rodriguez, *Phys. Rev. Lett.* **104**, 096804 (2010)
D. Haberer *et al.*, *Phys. Rev. B* **83**, 165433 (2011)

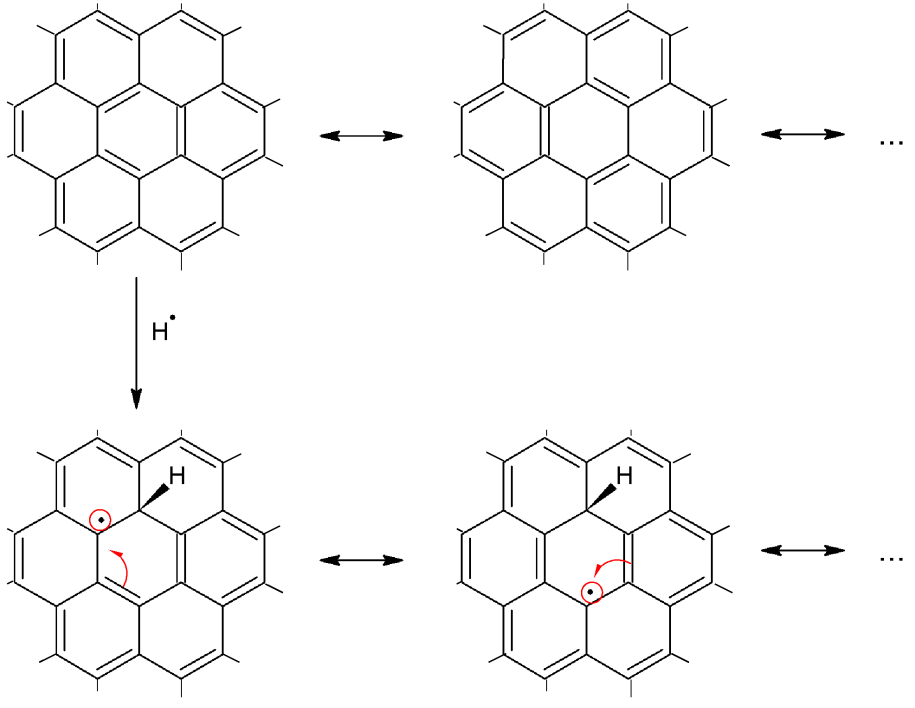


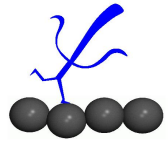
Midgap states



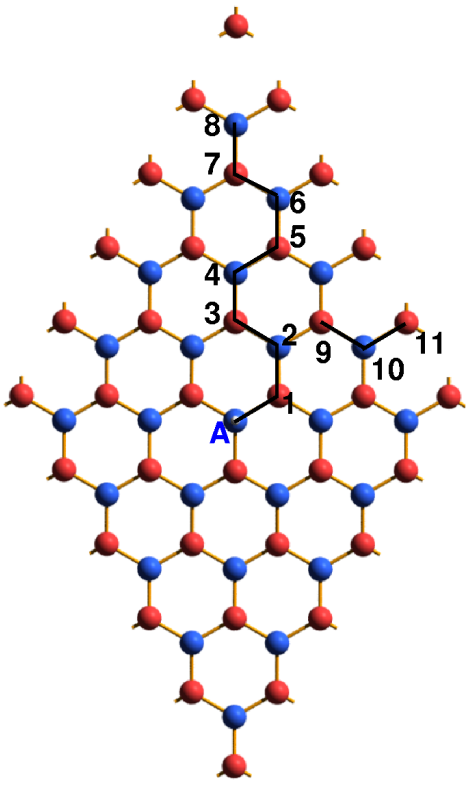
$$\psi(x, y, z) \sim 1/r$$

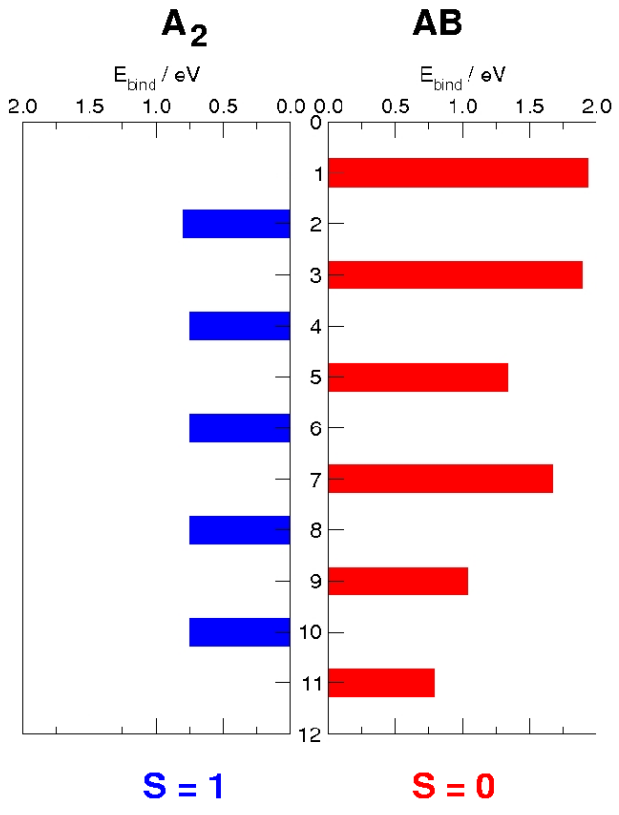
V. M. Pereira *et al.*, *Phys. Rev. Lett.* **96**, 036801 (2006);
Phys. Rev. B **77**, 115109 (2008)



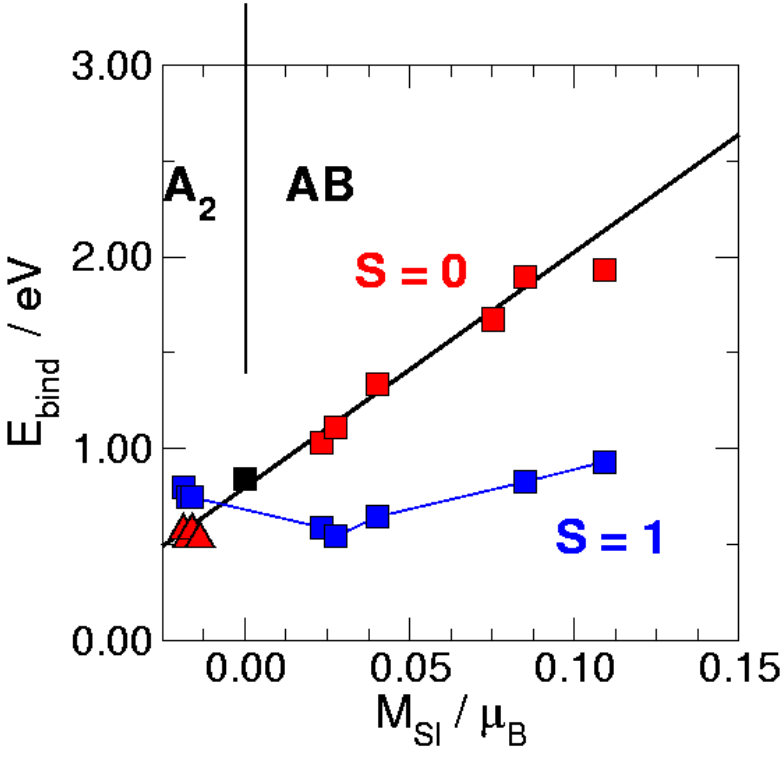


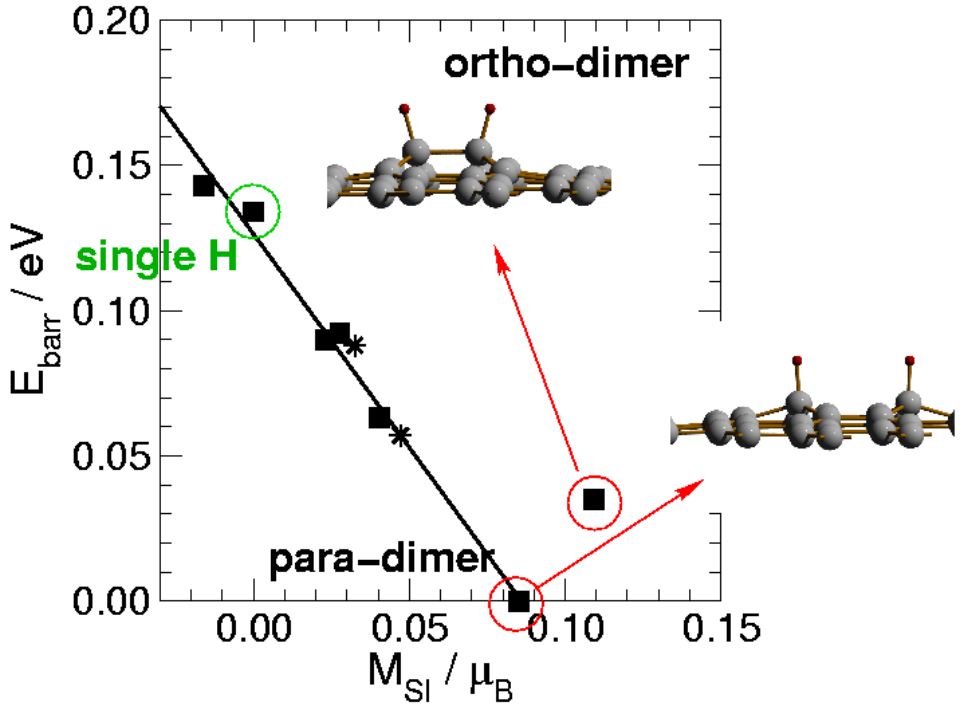
Dimers


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


A2
AB
Ebind / eV
2.0 1.5 1.0 0.5 0.0
Ebind / eV
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

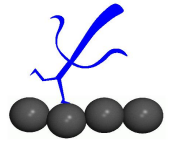
Dimers





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

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



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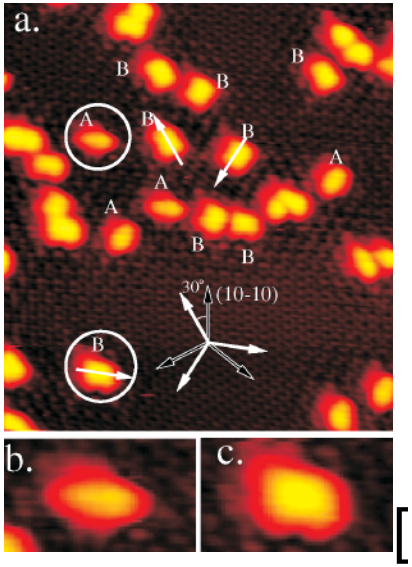

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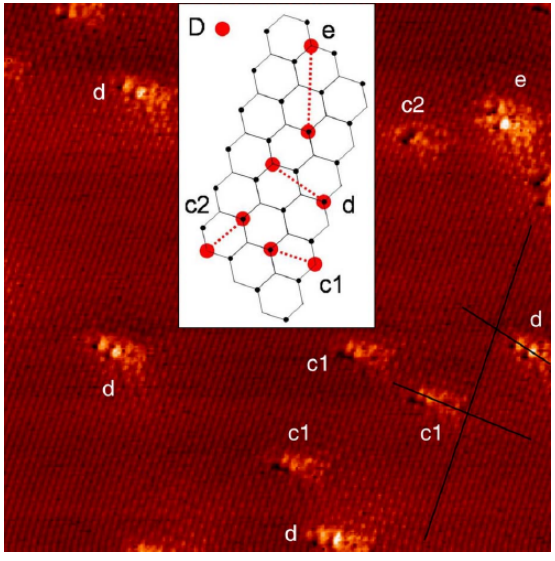

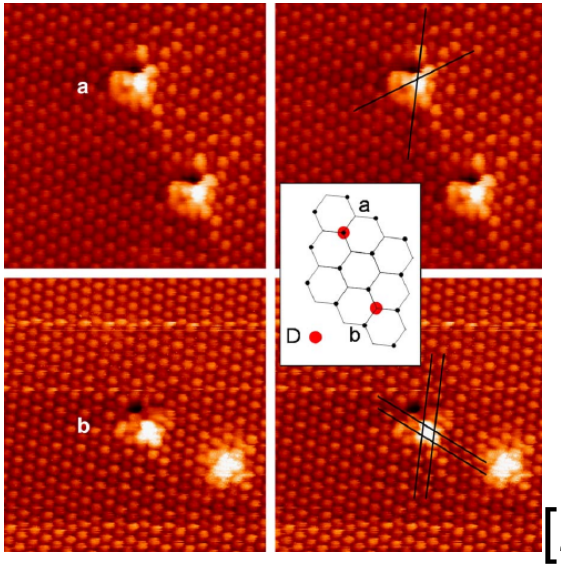

[2]

[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)

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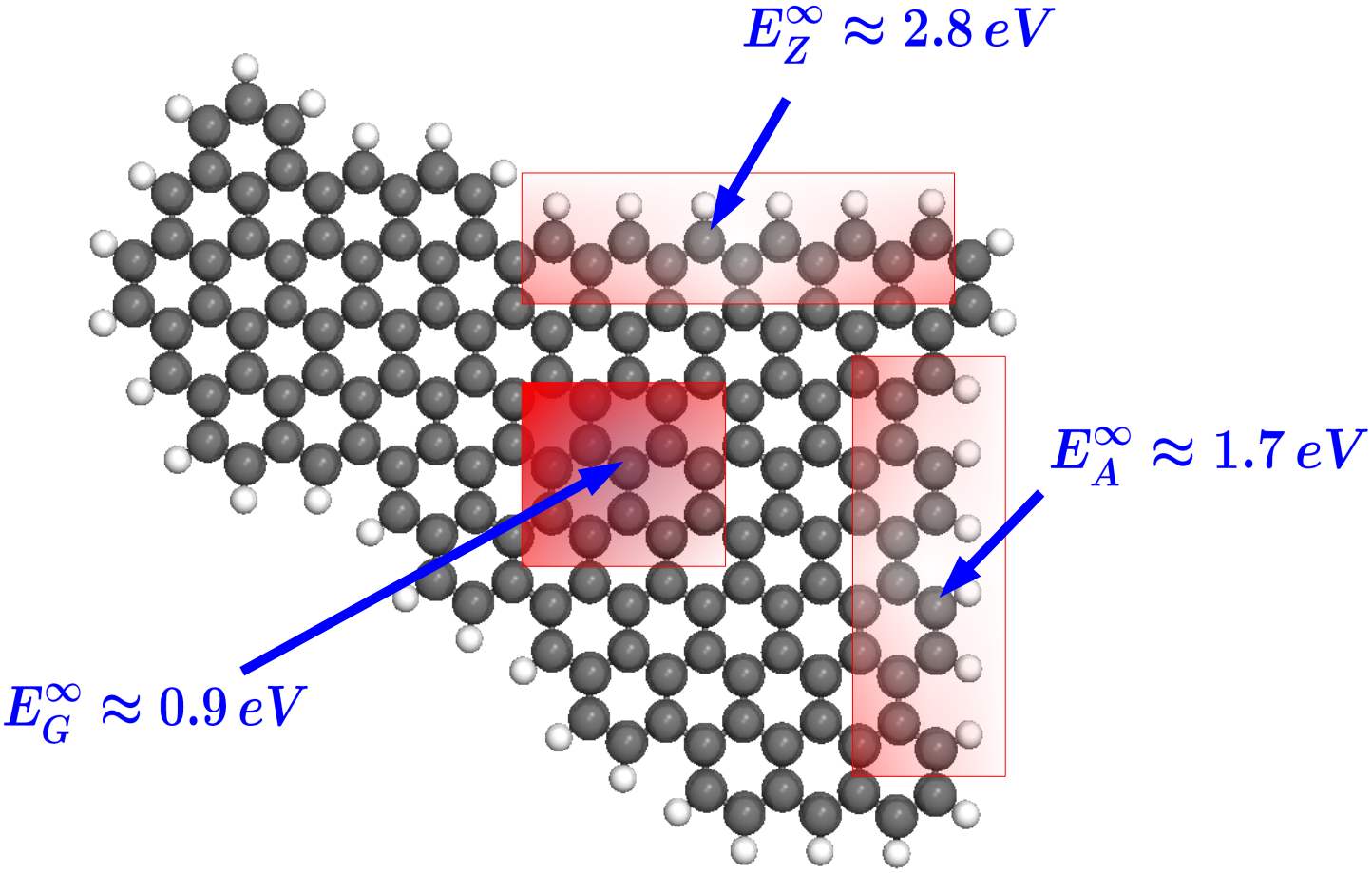
Role of edges



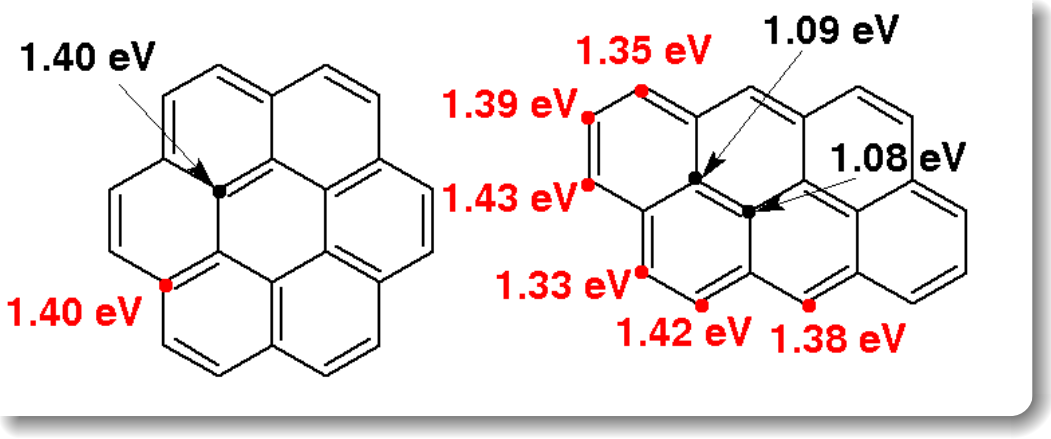
‘Geometric’ effect?

‘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}

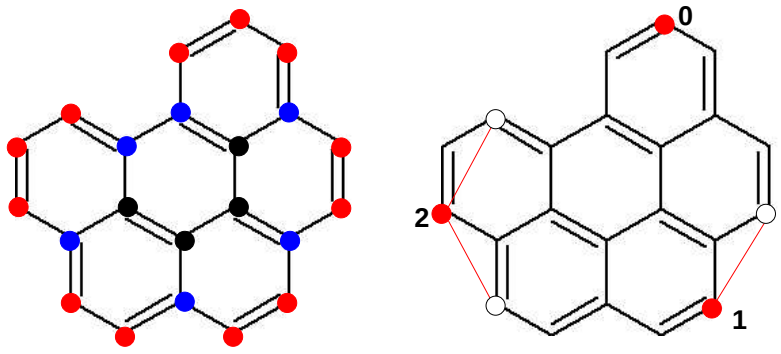
Shape of low-energy orbitals

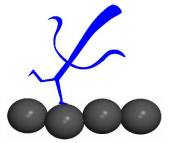
..from a 'lattice renormalization'

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

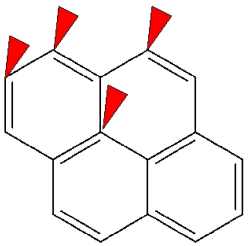
$Z = 2 \Rightarrow$ **E**

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

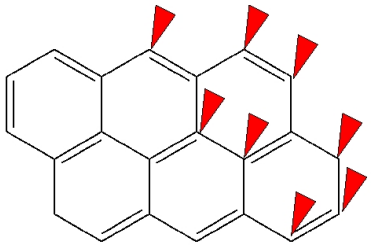




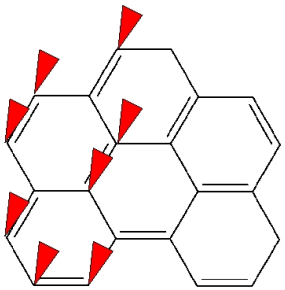
Systems



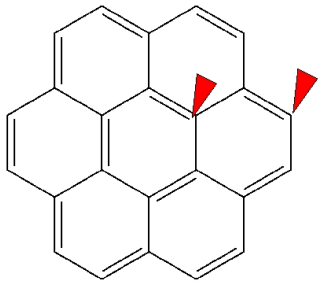
pirene



dibenzo[def,mno]crisene / antrantrene

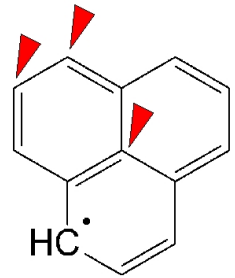


benzo[ghi]perilene

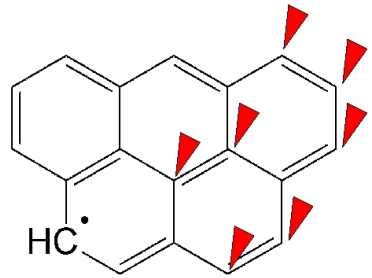


coronene

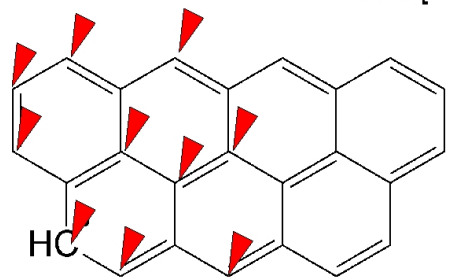
$\eta = 0$



perinaftenile / fenalene

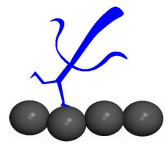


benzo[cd]pirenile

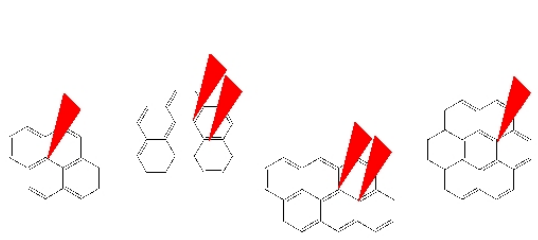


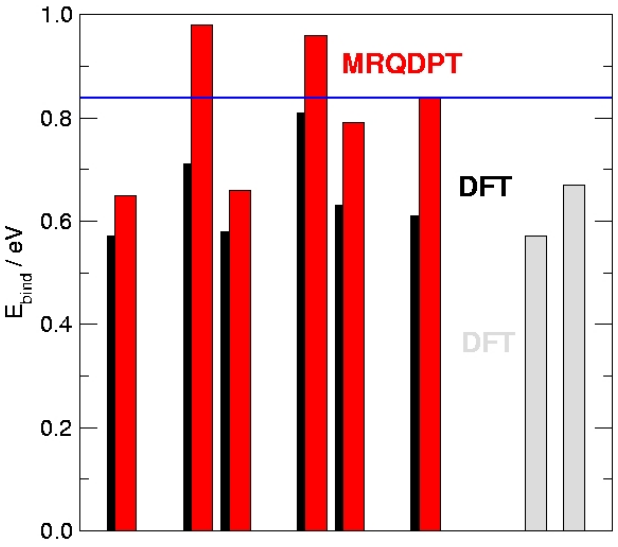
7 - PAH

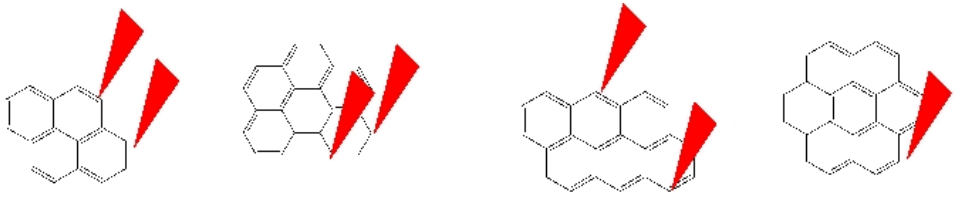
$\eta \neq 0$

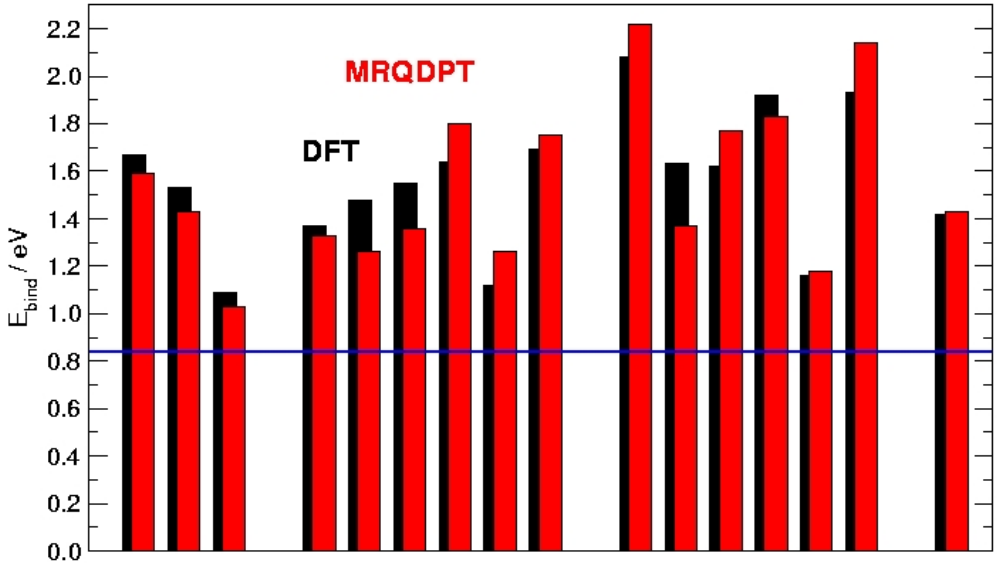


Graphitic *vs* edge carbons

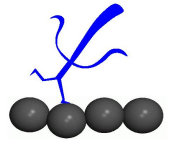




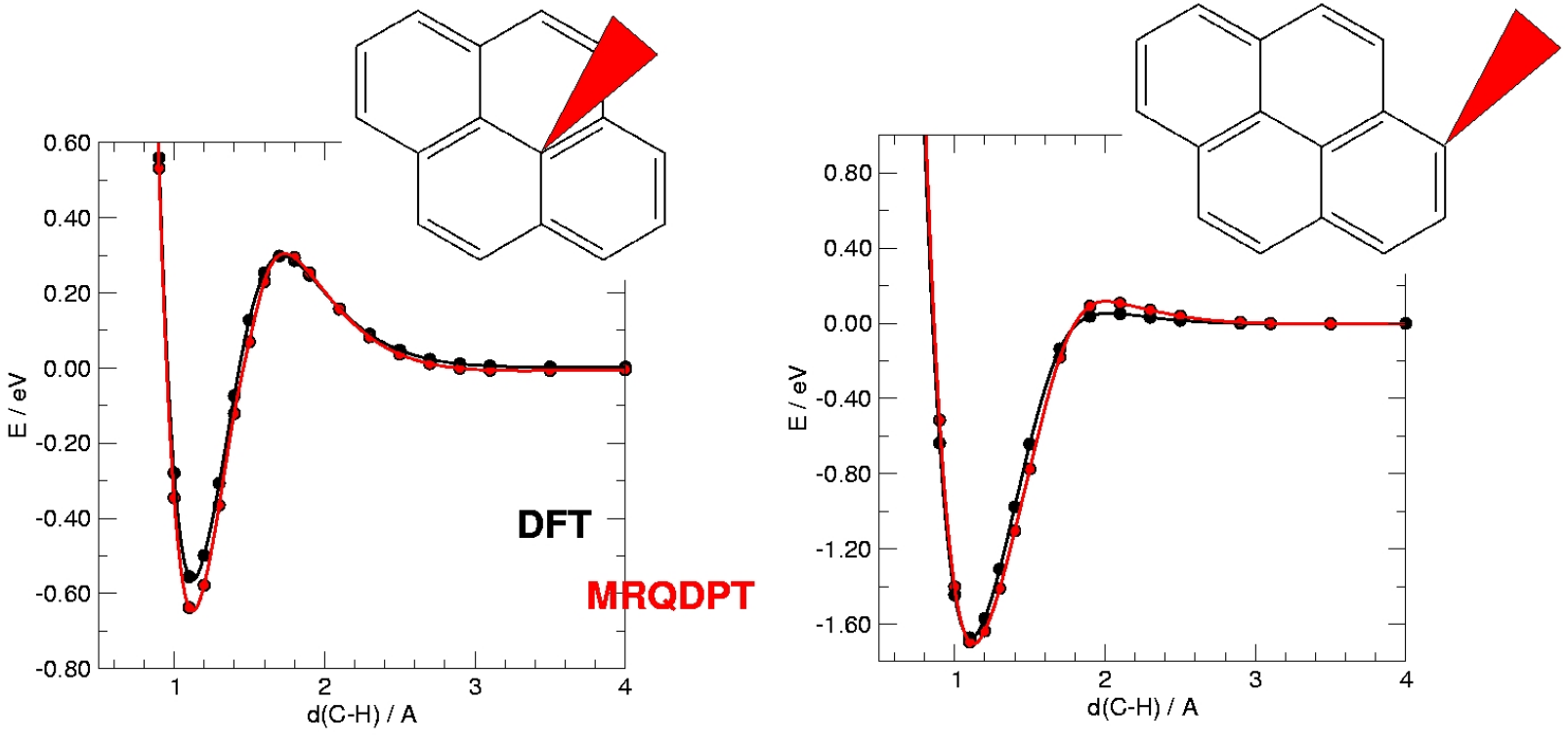




M. Bonfanti, S. Casolo, G. F. Tantardini, A. Ponti and R. Martinazzo, *J. Chem. Phys.*, **135** 164701 (2011)



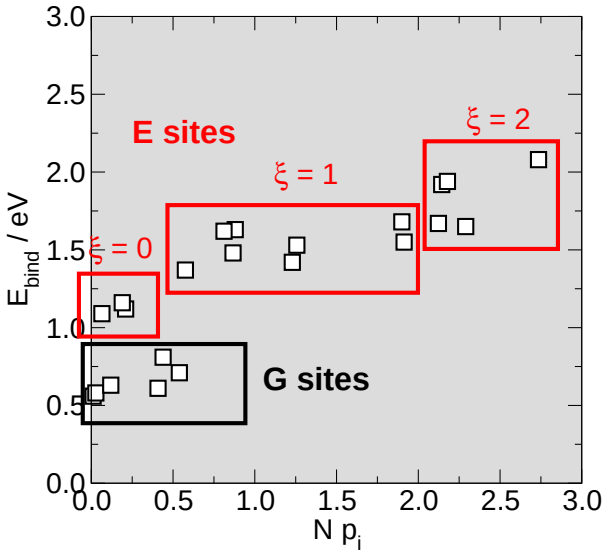
Adsorption paths



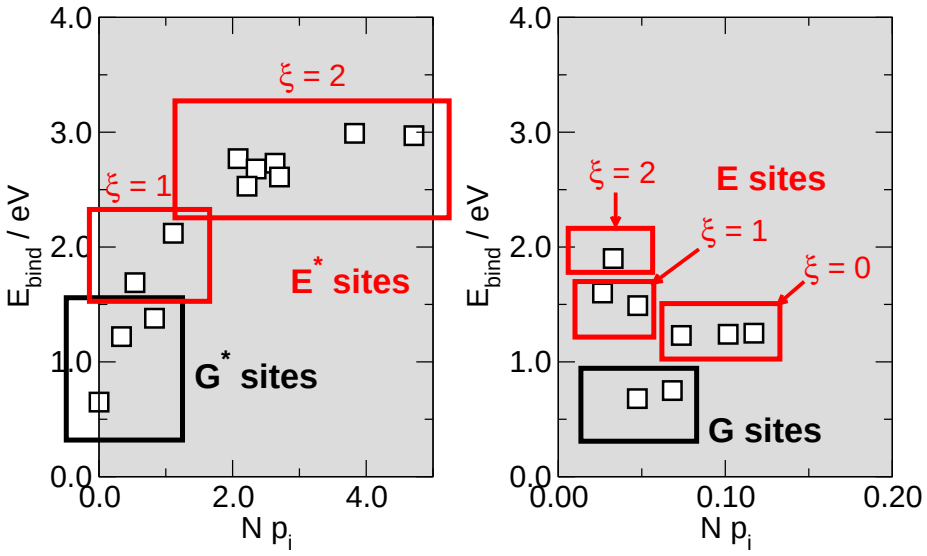
M. Bonfanti, S. Casolo, G. F. Tantardini, A. Ponti and R. Martinazzo, *J. Chem. Phys.*, **135** 164701 (2011)

Predicting reactivity

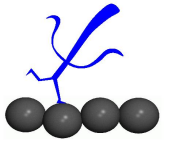
$\eta = 0$



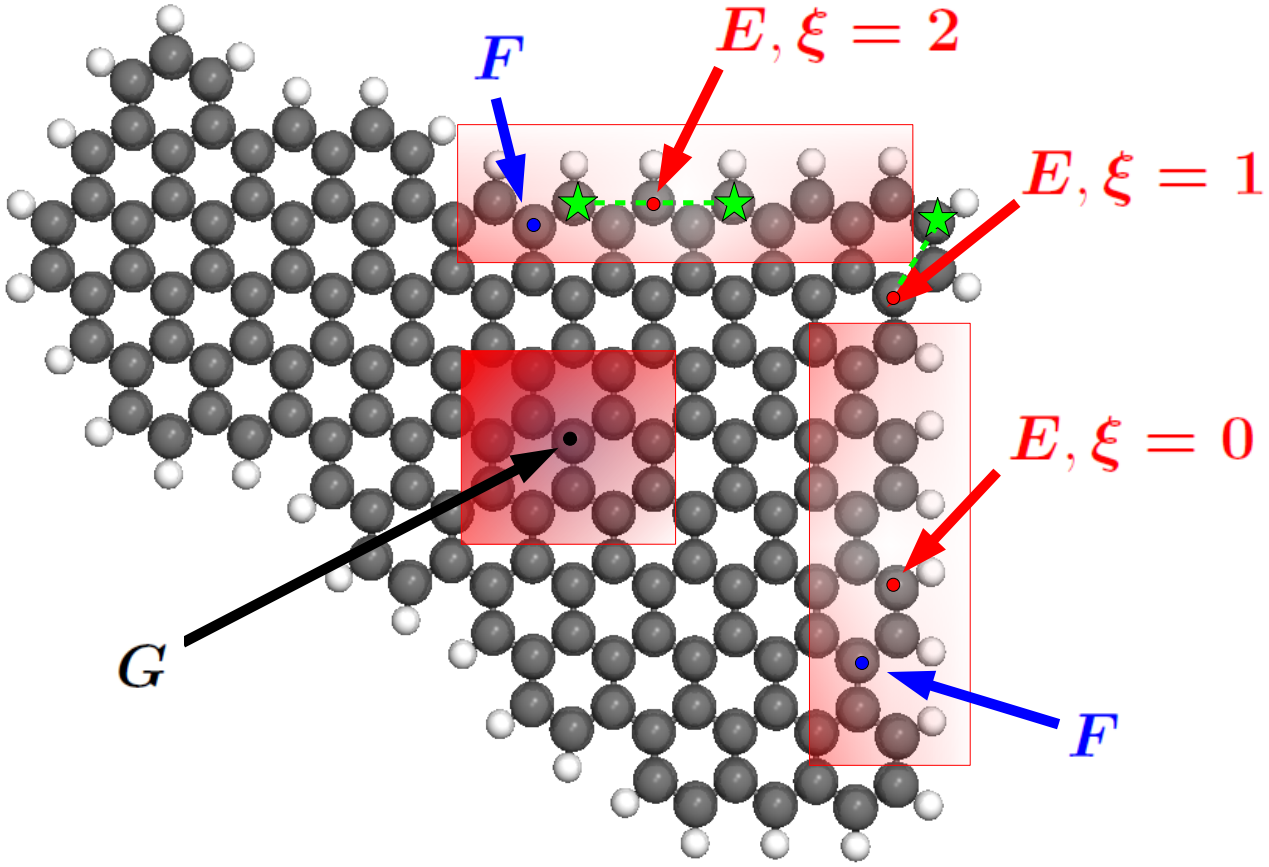
$\eta \neq 0$



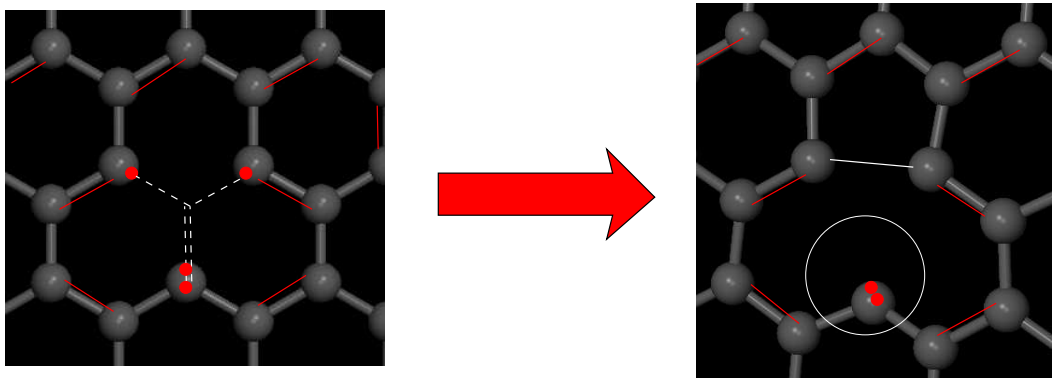
M. Bonfanti, S. Casolo, G. F. Tantardini, A. Ponti and R. Martinazzo, *J. Chem. Phys.*, **135** 164701 (2011)



Predicting reactivity



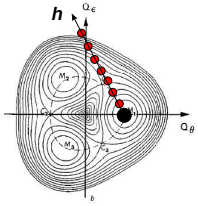
Spin-coupling around a carbon atom vacancy

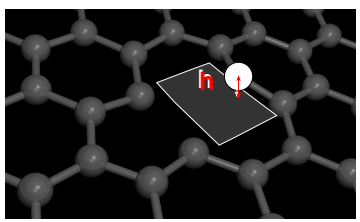


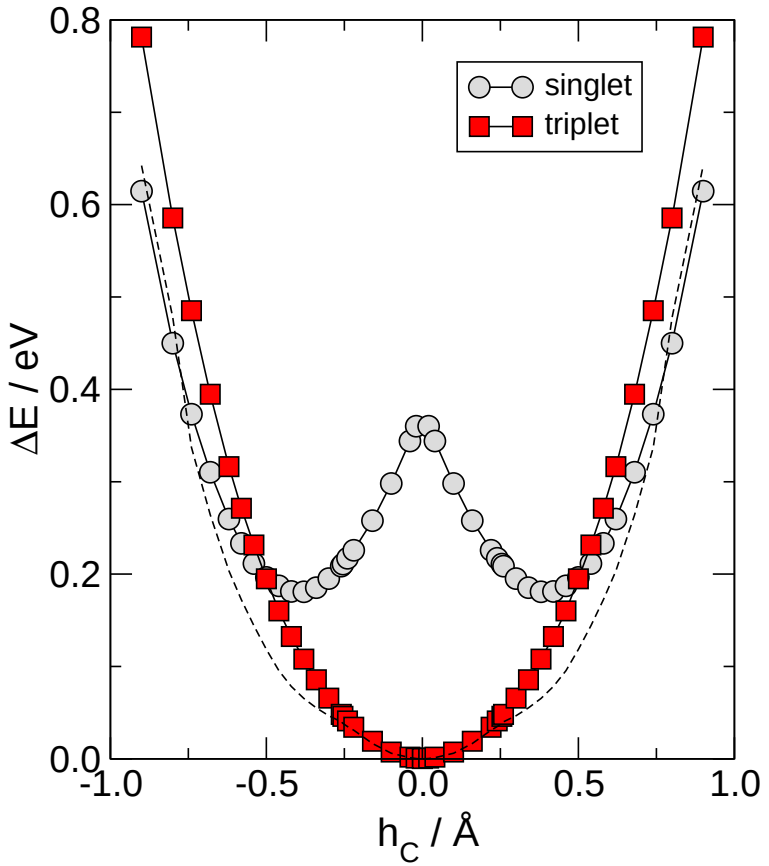
How the two *e* spins couple at a vacancy?
How large is the splitting?
Can that be used in applications? *

Magnetization constrained results

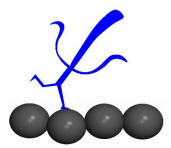
Partial geometrical relaxation,
$M_S = 0, 1$ constrained



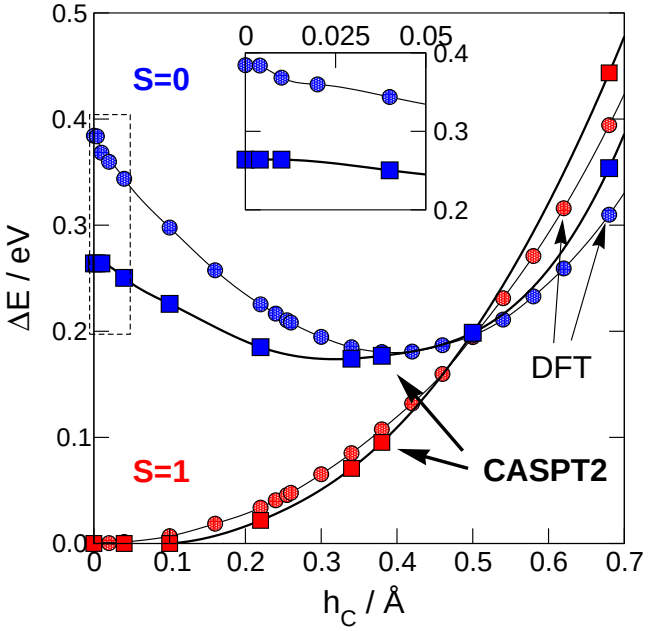


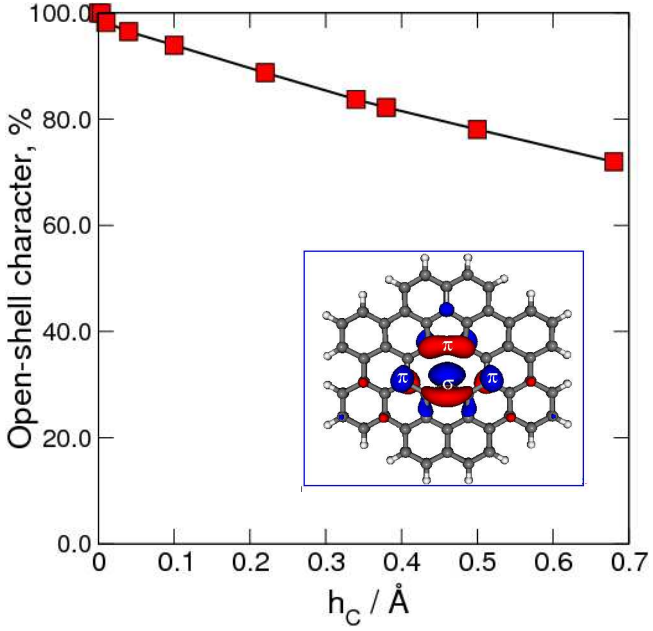


- triplet is stable, $\omega_\perp \sim 200 cm^{-1}$
- singlet is bistable, $\omega_\perp \sim 263 cm^{-1}$
- $S = 1$ is the ground-state up to $h \sim 0.5$ Å



CASPT2 results

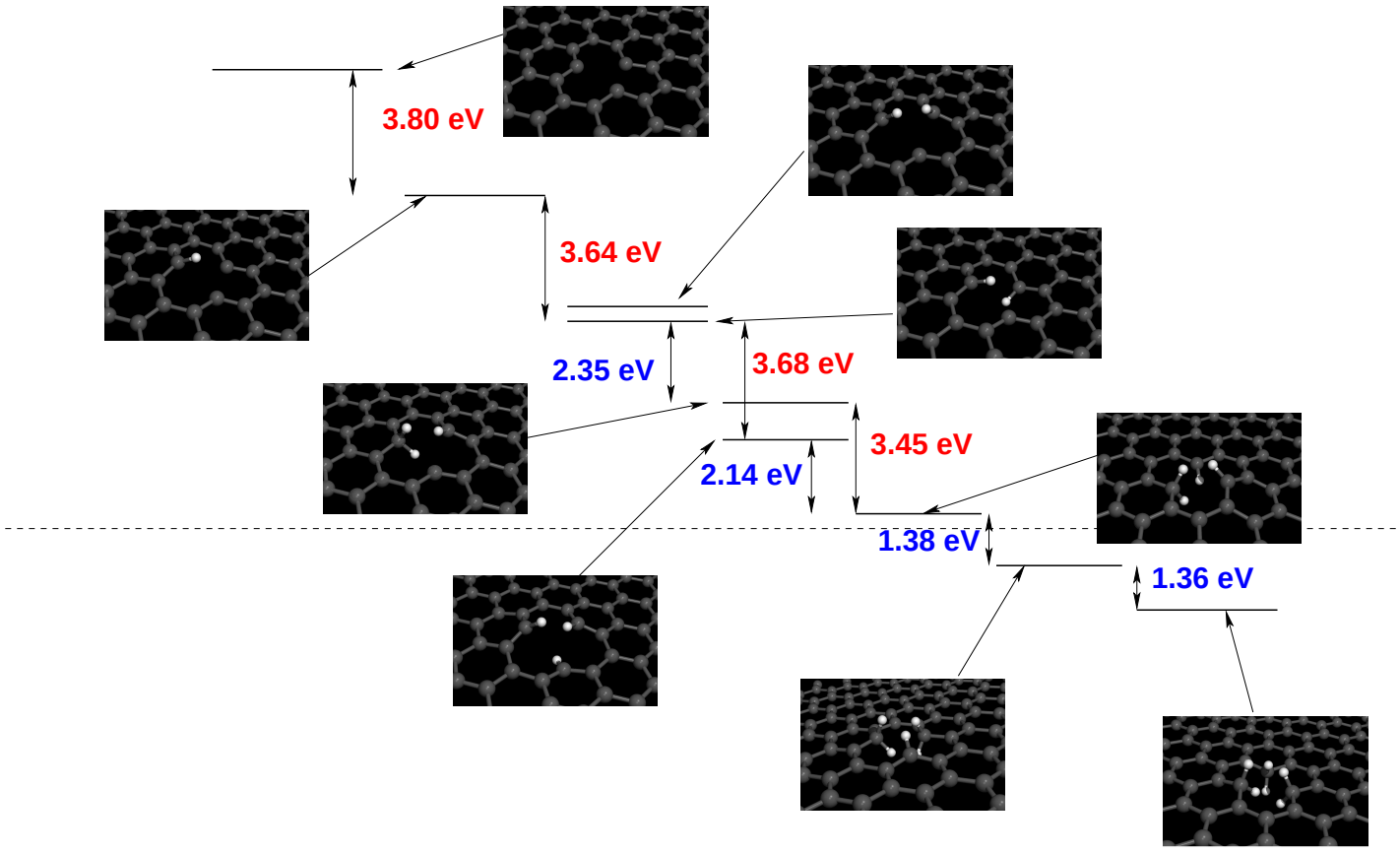




- Magnetization constrained DFT results are reliable
- Accurate energies from CASPT2
- Singlet-state has a dominant open-shell character, $\Psi \propto (\sigma\pi + \pi\sigma)(\alpha\beta - \beta\alpha)$

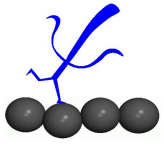
M. Casartelli, S. Casolo, G.F. Tantardini and R. Martinazzo, *submitted*

Hydrogenation



Mono-, **Three-** and **Penta-** hydrogenated vacancies are all **spin-**$1/2$ species

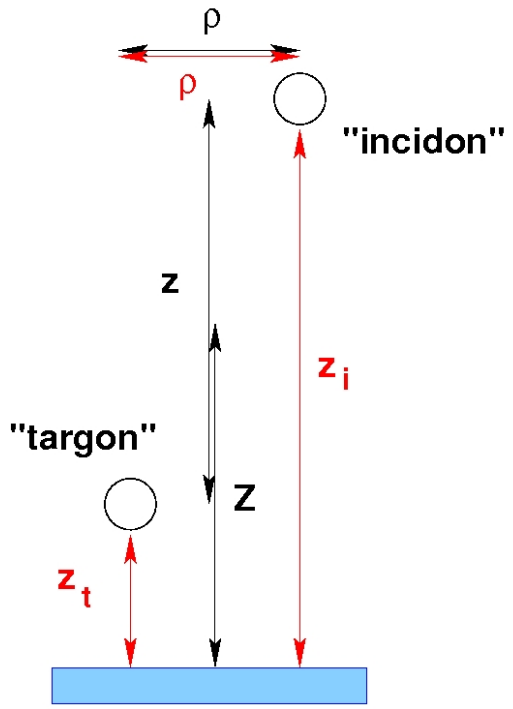
Outline



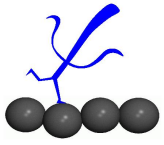
Reaction: technicalities

- 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]

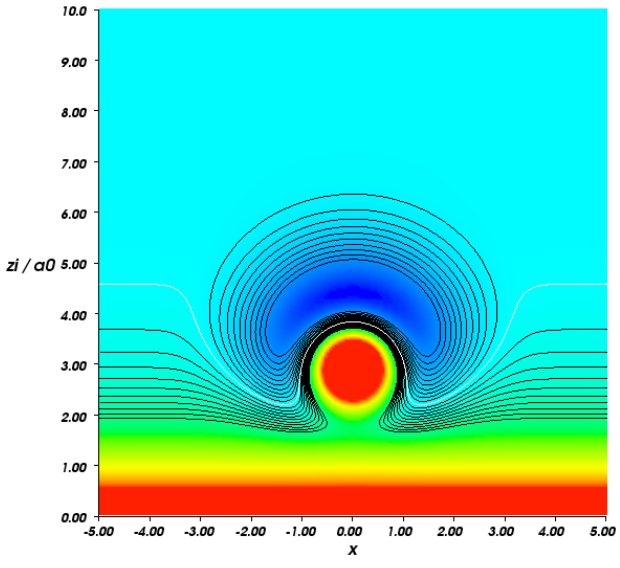
$\Rightarrow$ state-to-state, energy-resolved cross sections for all possible processes



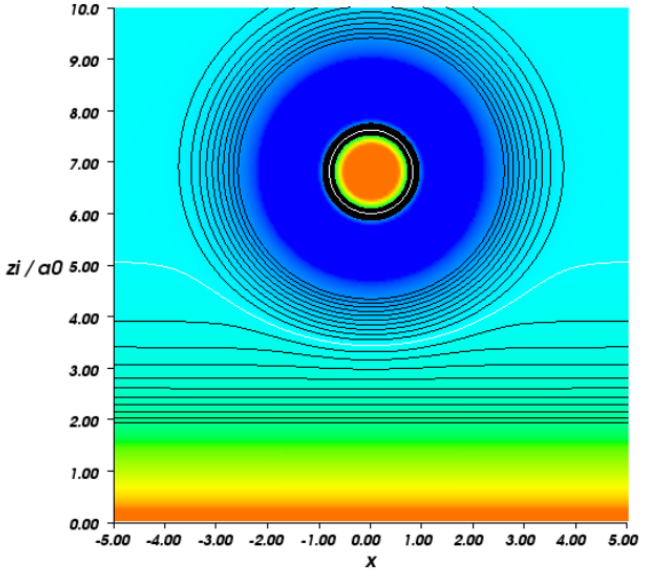
[1] M. Persson and B. Jackson, J. Chem. Phys. 102, 1078 (1995); D. Lemoine and B. Jackson, Comput. Phys. Commun. 137, 415 (2001)
[2] R. Martinazzo and G.F. Tantardini, J. Phys. Chem. A, 109 (2005) 9379; J. Chem. Phys. 124, 124703 (2006); J. Chem. Phys. 124, 124704 (2006)



Reaction: Potential Energy Surfaces

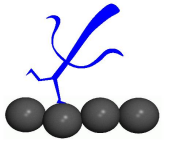


Chemisorbed target H (z_{eq})

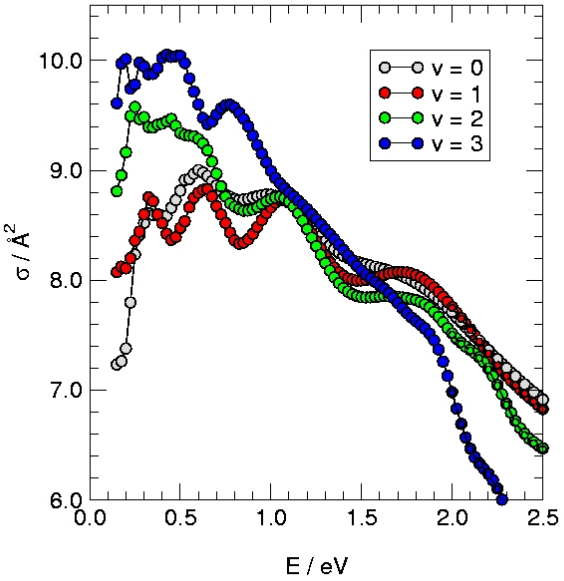


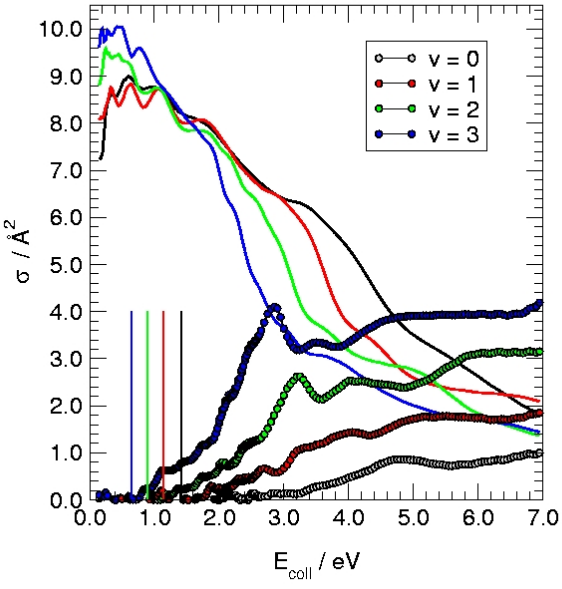
Physisorbed target H (z_{eq})

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

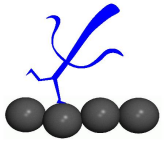


I. H-chemisorbed case

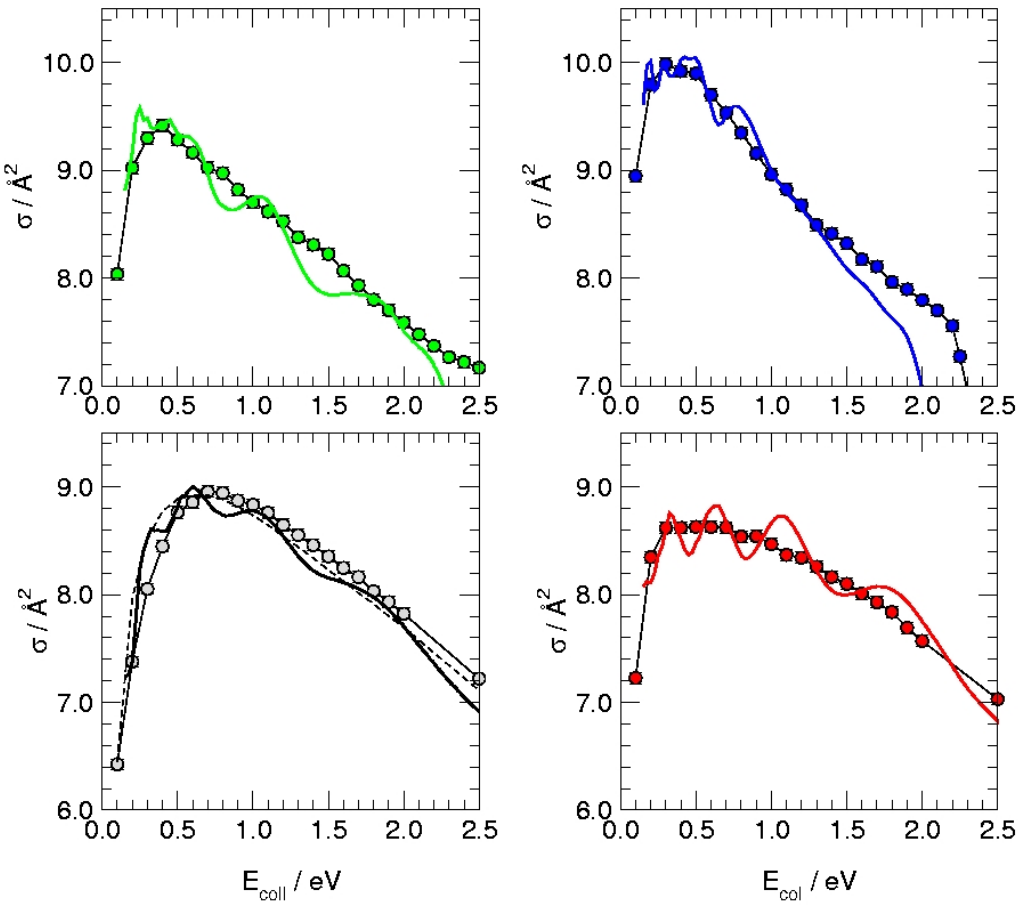




Oscillations in both ER and CID xsections

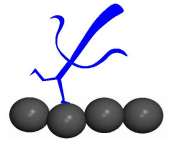


I. H-chemisorbed case

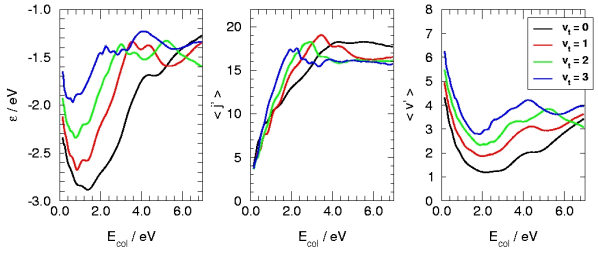


Quantum vs (quasi) classical dynamics:
quantum effects

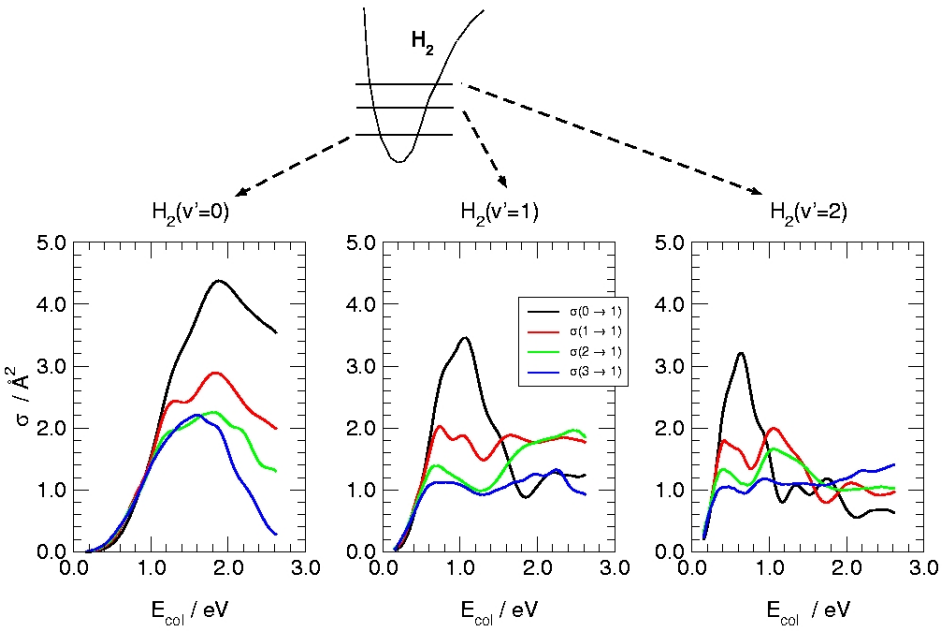
R. Martinazzo and G.F. Tantardini, *J. Phys. Chem. A* **109**, 9379; *J. Chem. Phys.* **124** 124272 (2006)

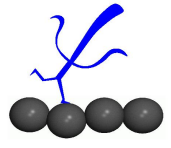


I. H-chemisorbed case

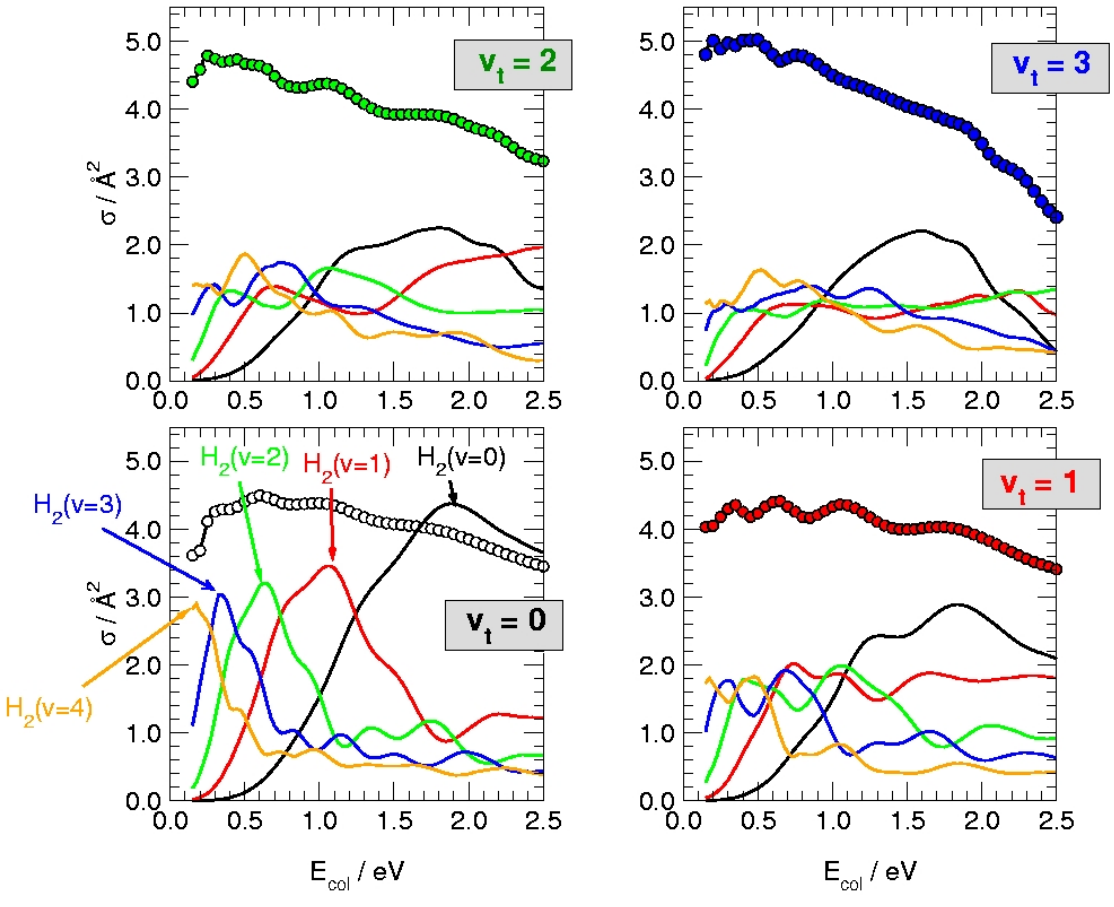


- Product molecules are internally hot
- Internal excitation is a steep decreasing function of E_{coll}

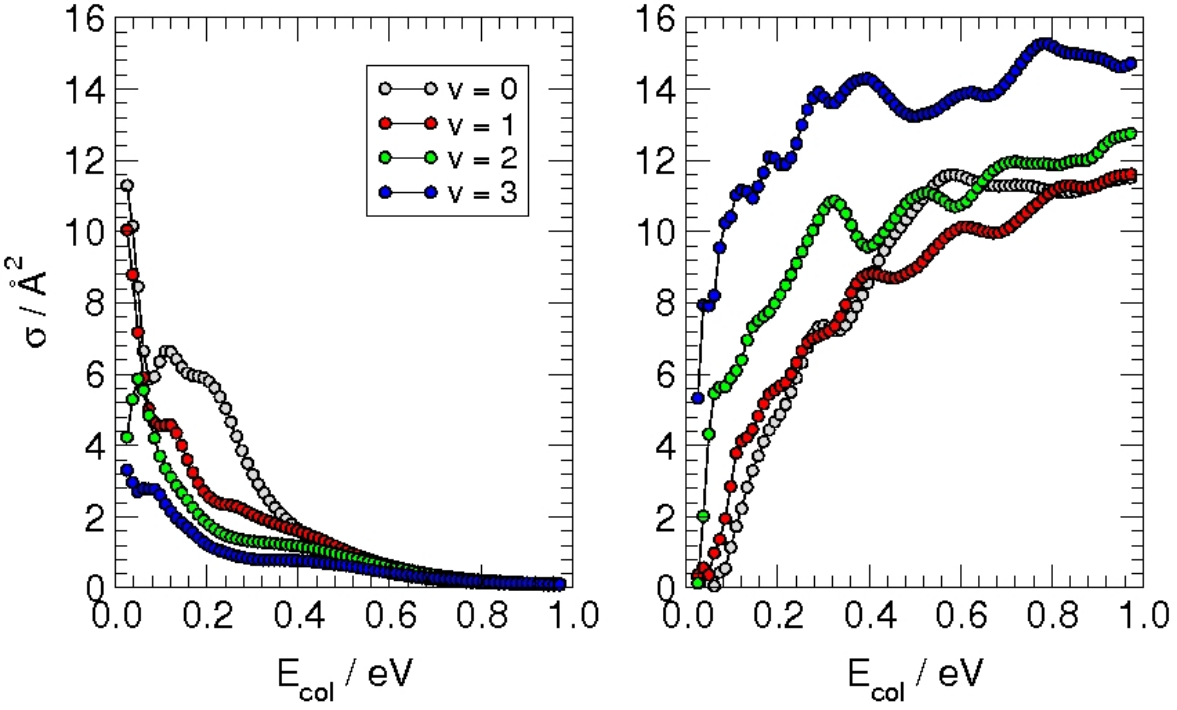




I. H-chemisorbed case



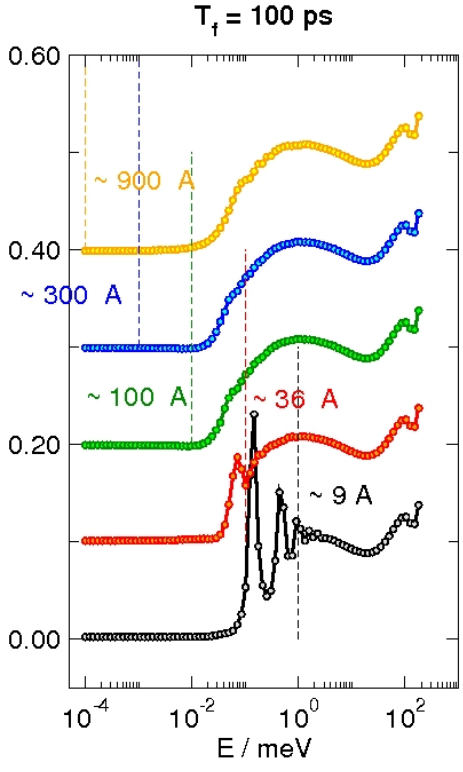
II. H-physisorbed case



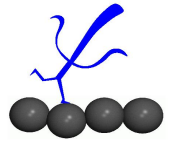
Reaction: technicalities (low E_{col})

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

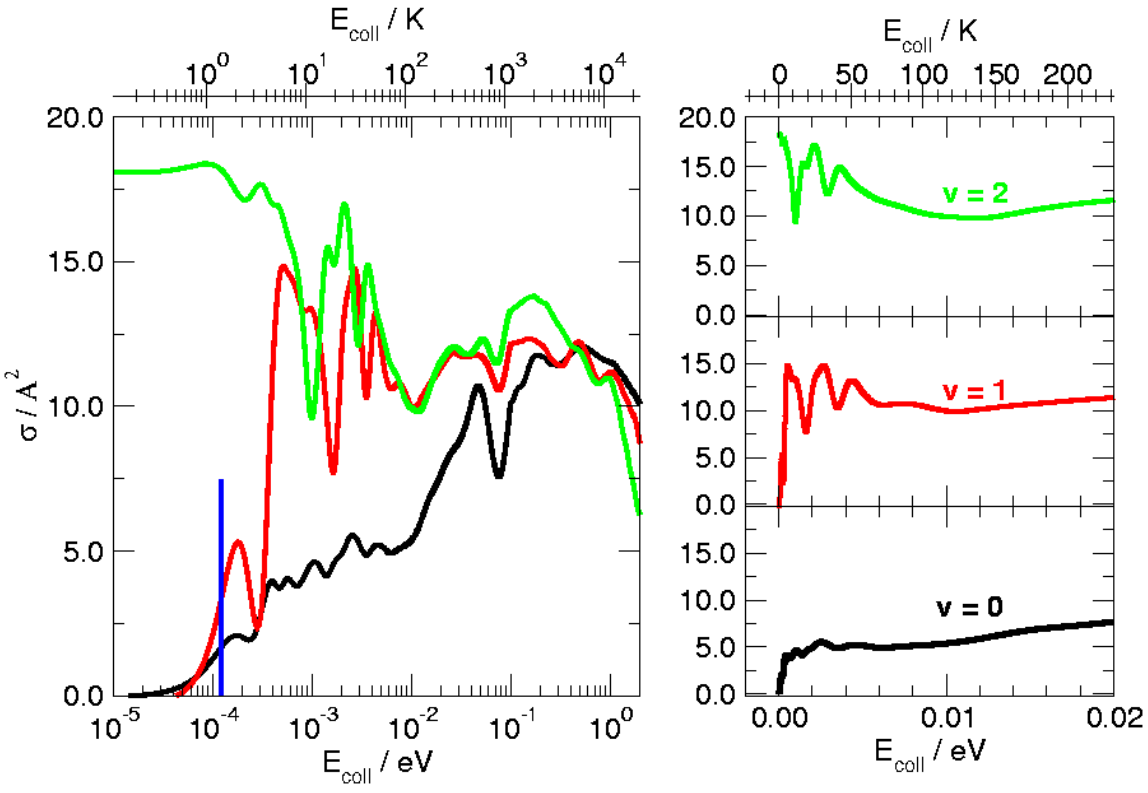
In 3D T_f=25-30 ps and AP lengths $\sim$ 50Å in order to get converged xsections down to $\sim 10^{-5}$ eV, i.e. $\sim$ 0.1 K



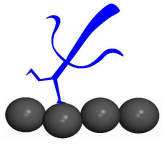
[1] R. Martinazzo and G.F. Tantardini, J. Chem. Phys. 122, 094109 (2005)
[2] D. Manolopoulos, J. Chem. Phys. 117, 9552 (2002)
[3] A.G. Borisov, J. Chem. Phys. 114, 7770 (2001)



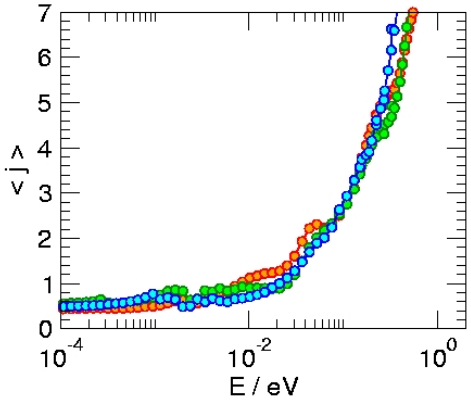
I. H-chemisorbed case

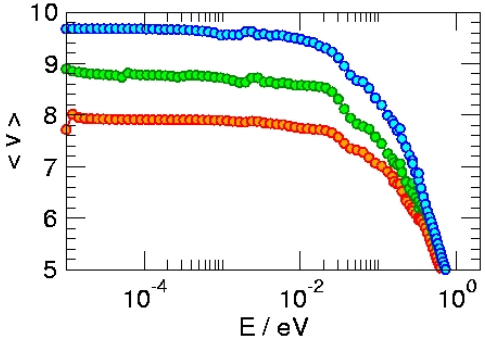


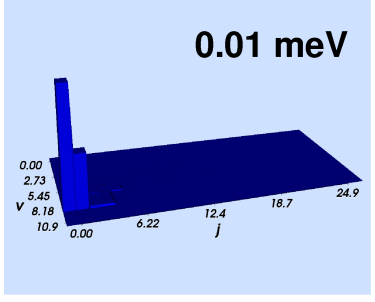
S. Casolo, M. Bonfanti, R. Martinazzo and G.F. Tantardini, *J. Phys. Chem. A*, **113** 14545 (2009)

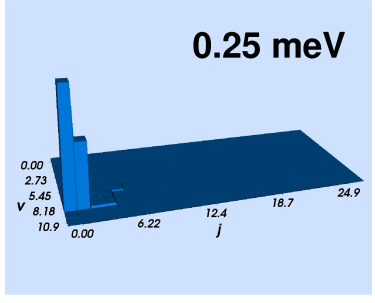


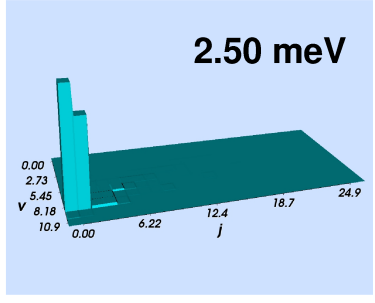
I. H-chemisorbed case

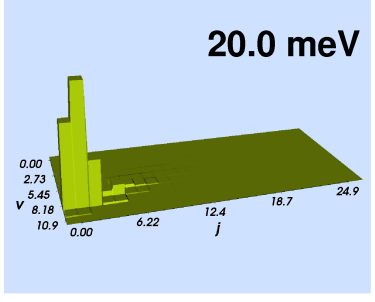


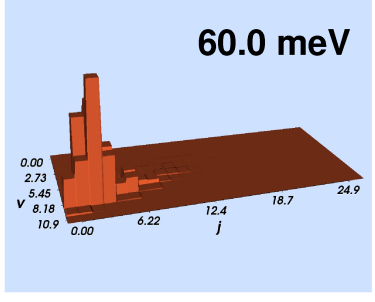


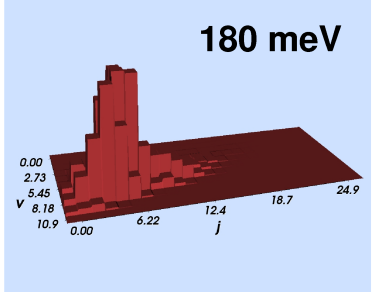


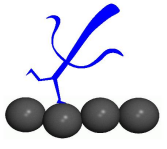






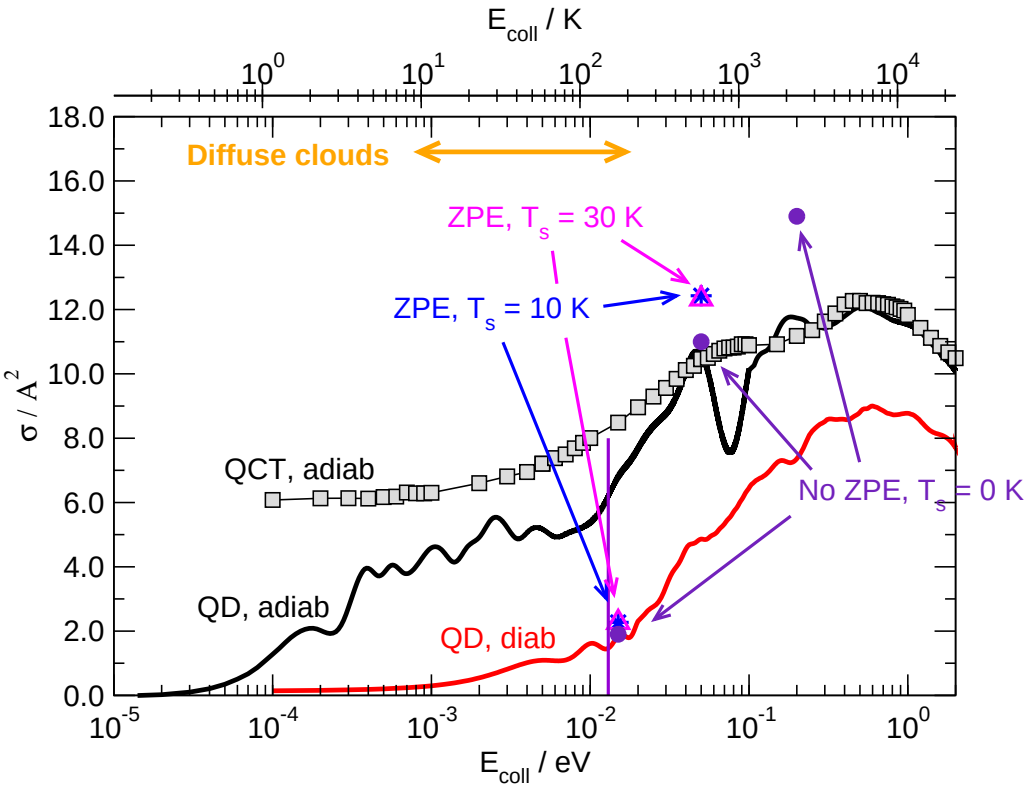




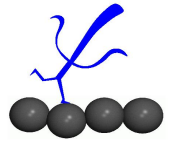


I. H-chemisorbed case

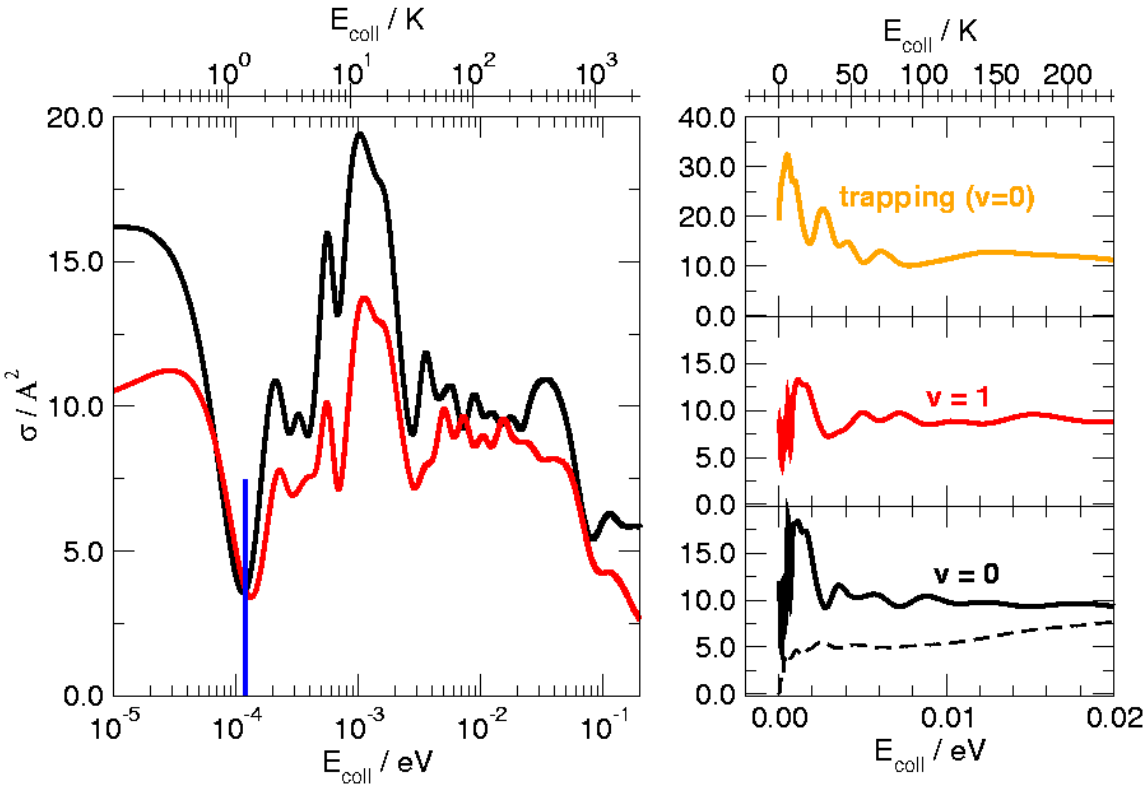
QCT comparison, $v = 0$



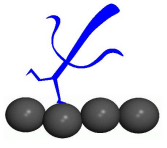
M. Sizun, D. Bachellerie, F. Anguillon, V. Sidis *Chem. Phys. Lett.* 32 **498** 2010
D. Bachellerie, M. Sizun, F. Anguillon, D. Teillet-Billy, N. Rougeau, *Phys. Chem. Chem. Phys.* 2715 **11** 2009



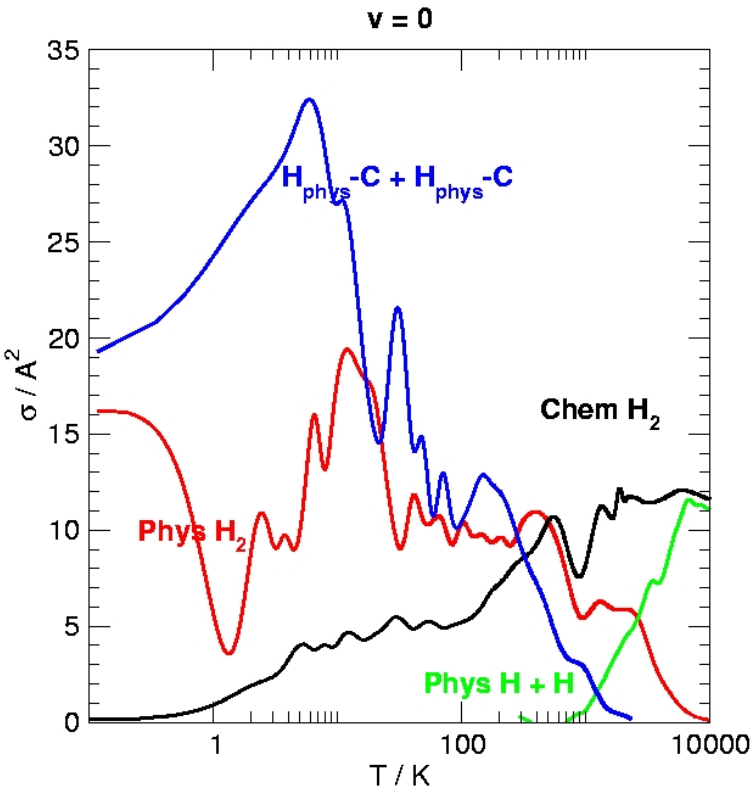
II. H-physisorbed case



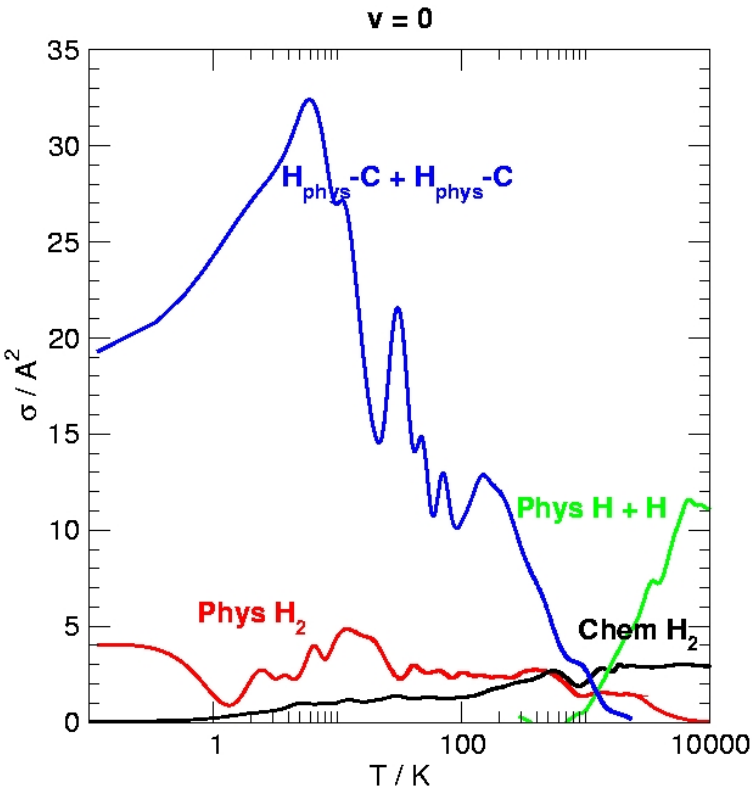
S. Casolo, M. Bonfanti, R. Martinazzo and G.F. Tantardini, *J. Phys. Chem. A*, **113** 14545 (2009)



H-chem vs H-phys



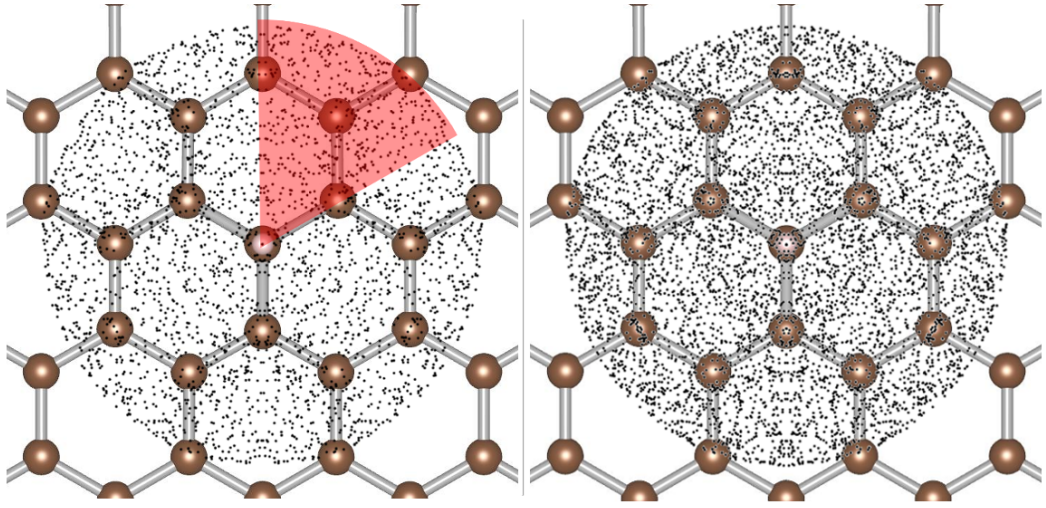
H-chem vs H-phys



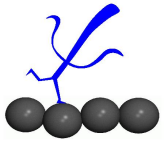
Cross-sections have to be corrected for the spin statistics (1/4)

Ab initio molecular dynamics

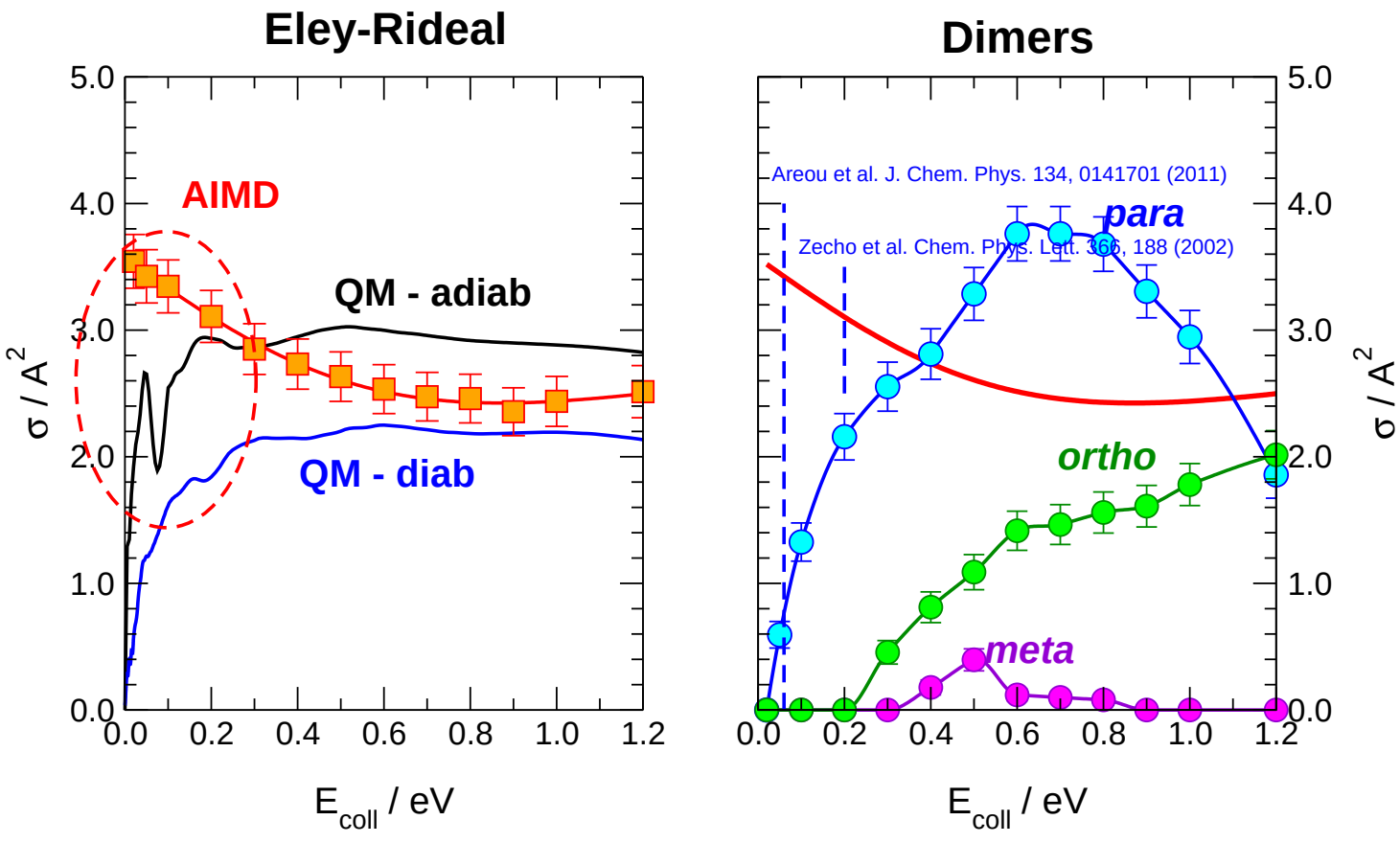
- lattice corrugation
- lattice dynamics
- dimer formation



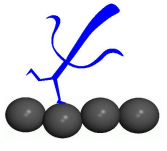
..expensive, but solves the problem of computing and fitting a model potential



Ab initio molecular dynamics



S. Casolo, G.F. Tantardini and R. Martinazzo, PNAS *in press*



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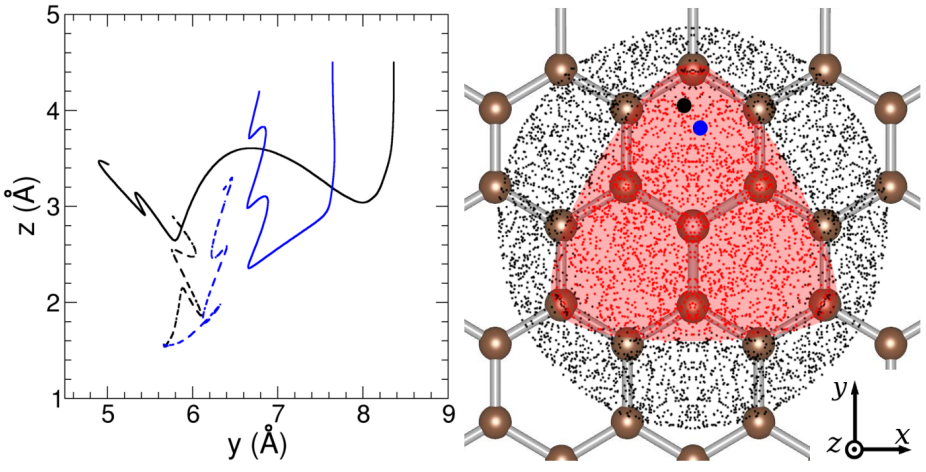
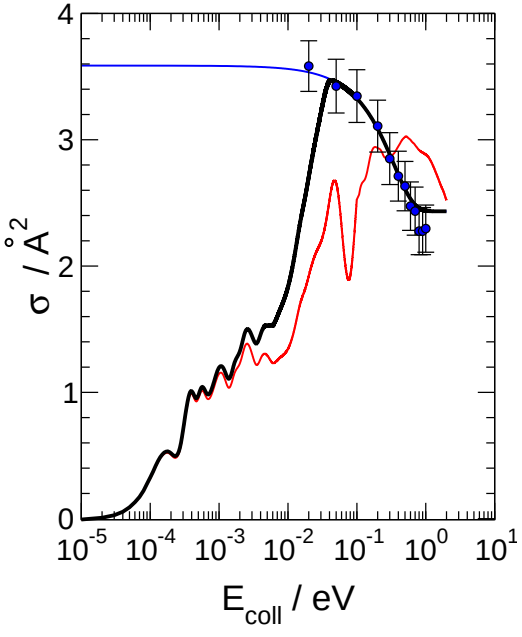
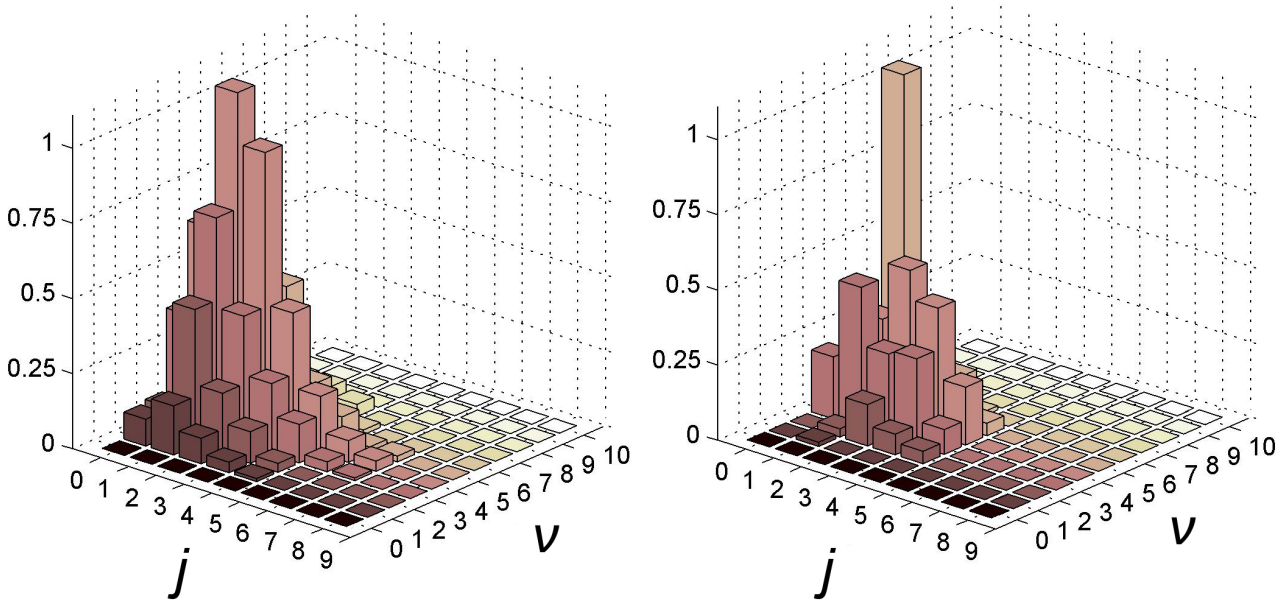




S. Casolo, G.F. Tantardini and R. Martinazzo, PNAS *in press*

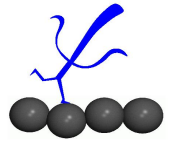
Ab initio molecular dynamics



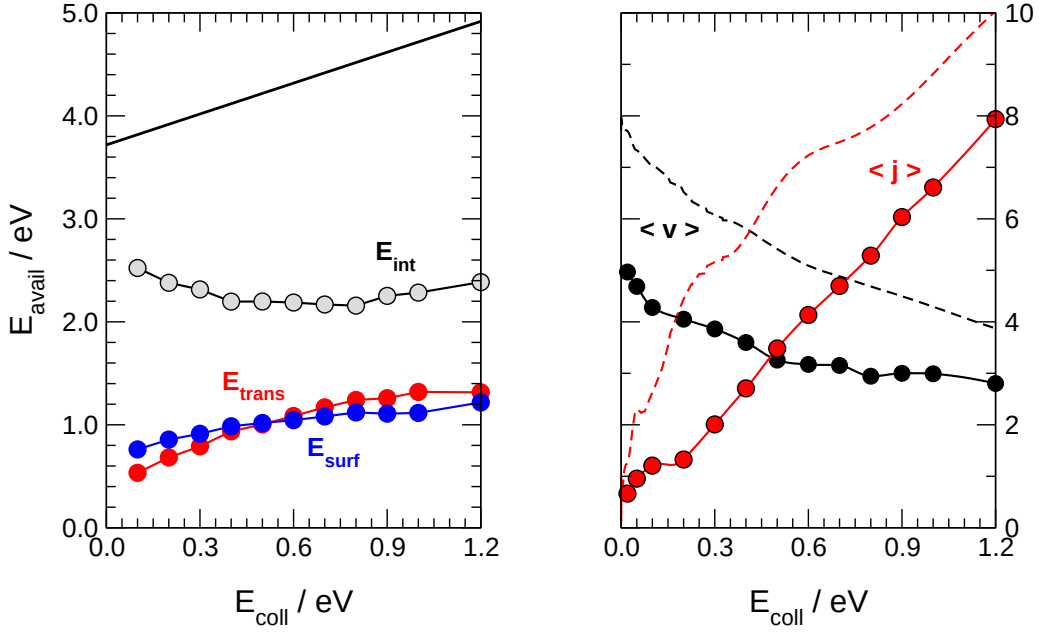
$T_g = 300K$, $T_s = 15K$

Latimer et al. Chem. Phys. Lett. 455, 174 (2008)

AIMD for H/D @ 0.025 eV



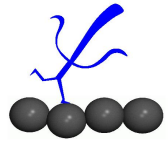
Ab initio molecular dynamics



..most of energy is internal, but energy transfer to the surface is considerable

Summary

- H dimers (clusters) which minimize sublattice imbalance form easily in the bulk
- Edges and vacancies are chemically active and facile sticking is possible at these sites
- Eley-Rideal reaction out of chemisorbed species is reasonably efficient
- and dominates over dimer formation
- Product molecules are hot, but up to $\sim 1eV$ can be left on the surface



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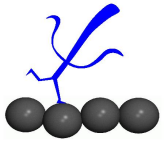
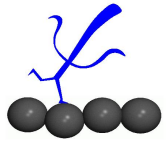
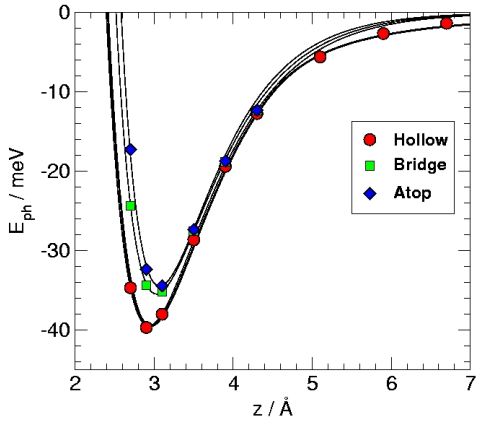


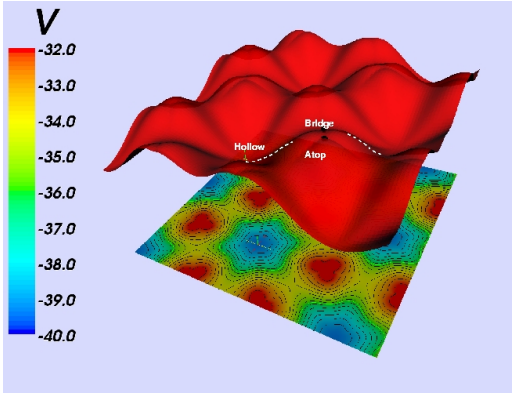
Acknowledgements

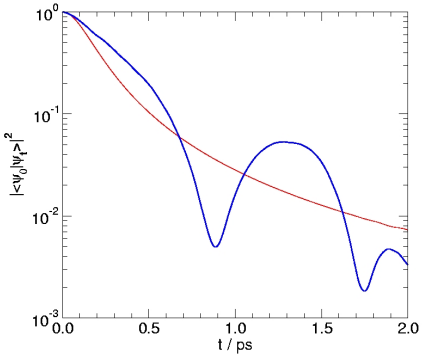
Thank you for your attention!



Physisorption







- HF-MP2 / aug-cc-pVDZ + BFs / CP-BSSE
- D_e = 39.5 meV *vs* D_e(exp)=39.2$\pm$0.5 meV
- E_{barr} = 4.0 meV, $D_{T=0K}$ = 1.7 10^{-4} $cm^2 s^{-1}$

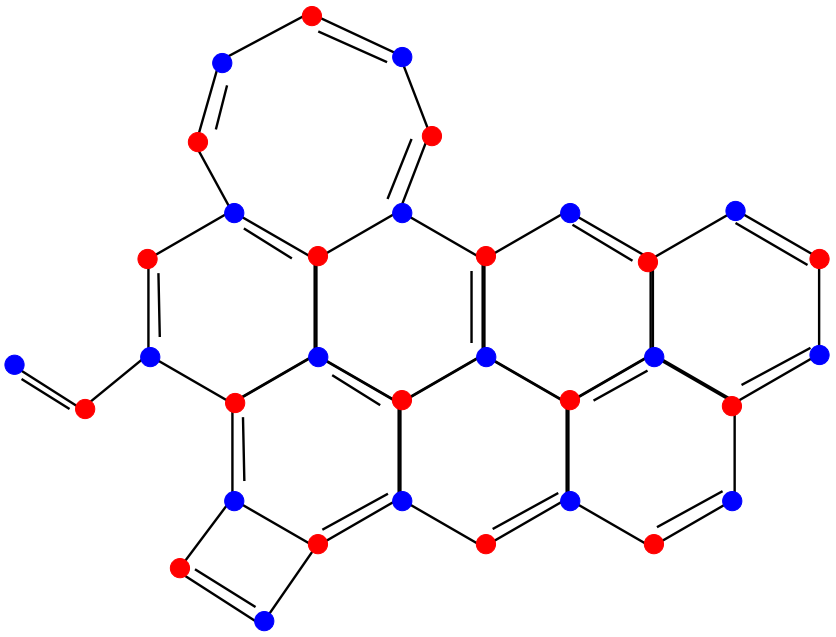
M. Bonfanti, R. Martinazzo, G.F. Tantardini and A. Ponti, *J. Phys. Chem. C*,**111**, 5825 (2007)

Exp: E. Ghio *et al.*, *J. Chem. Phys.*, **73**, 596 (1980)

*

Midgap states

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



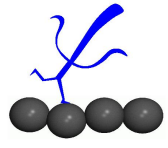
Electron-hole symmetry

$$b_i \to -b_i \Longrightarrow H_e^{\pi} \to -H_e^{\pi}$$

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

$$\Downarrow$$

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



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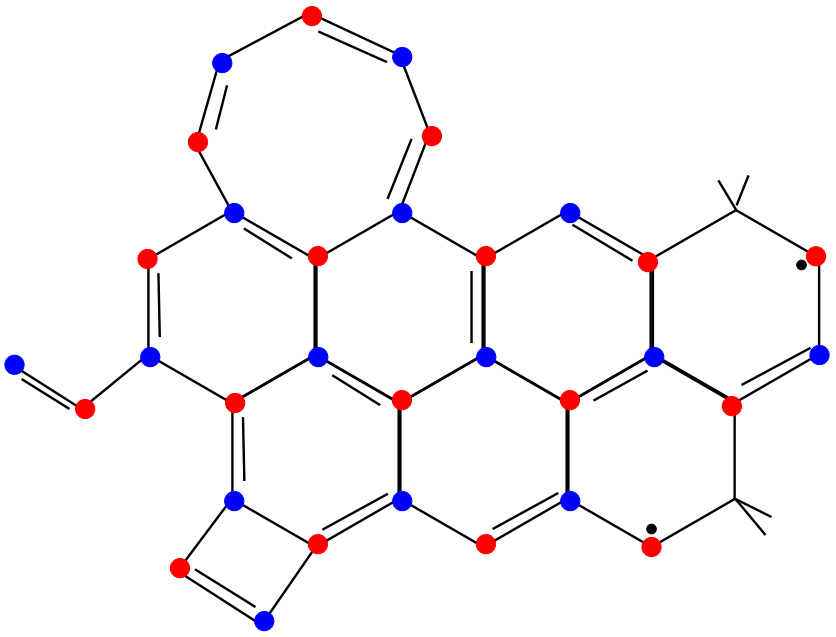
$$H^{\pi} \approx \sum_{\sigma,ij} (t_{ij} a^{\dagger}_{i,\sigma} b_{j,\sigma} + t_{ji} b^{\dagger}_{j,\sigma} a_{i,\sigma})$$

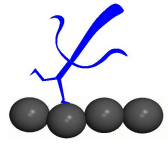


Imbalance rule

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

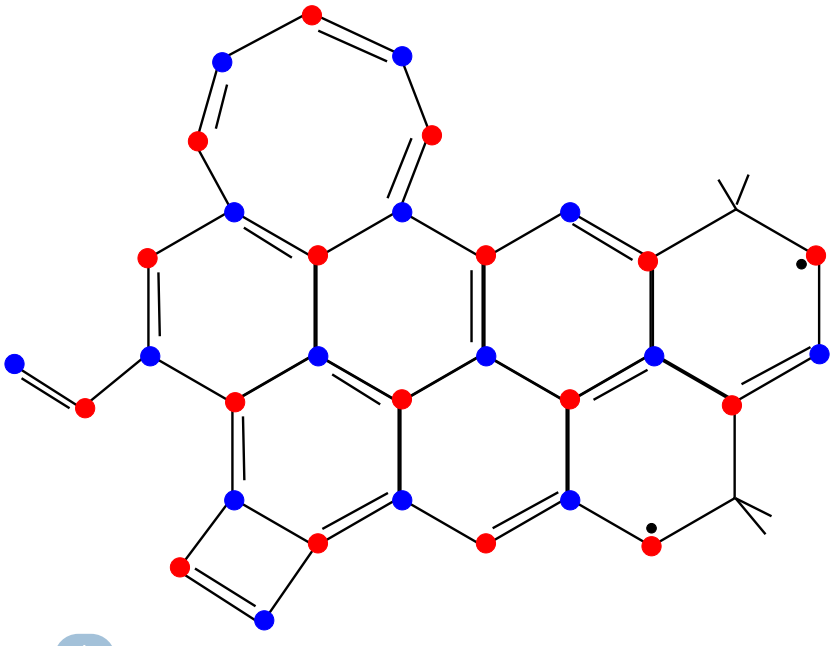
$$\begin{bmatrix} \mathbf{0} & \mathbf{T}^{\dagger} \\ \mathbf{T} & \mathbf{0} \end{bmatrix} \begin{bmatrix} \alpha \\ \beta \end{bmatrix} = \begin{bmatrix} \mathbf{0} \\ \mathbf{0} \end{bmatrix}$$

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



Midgap states

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



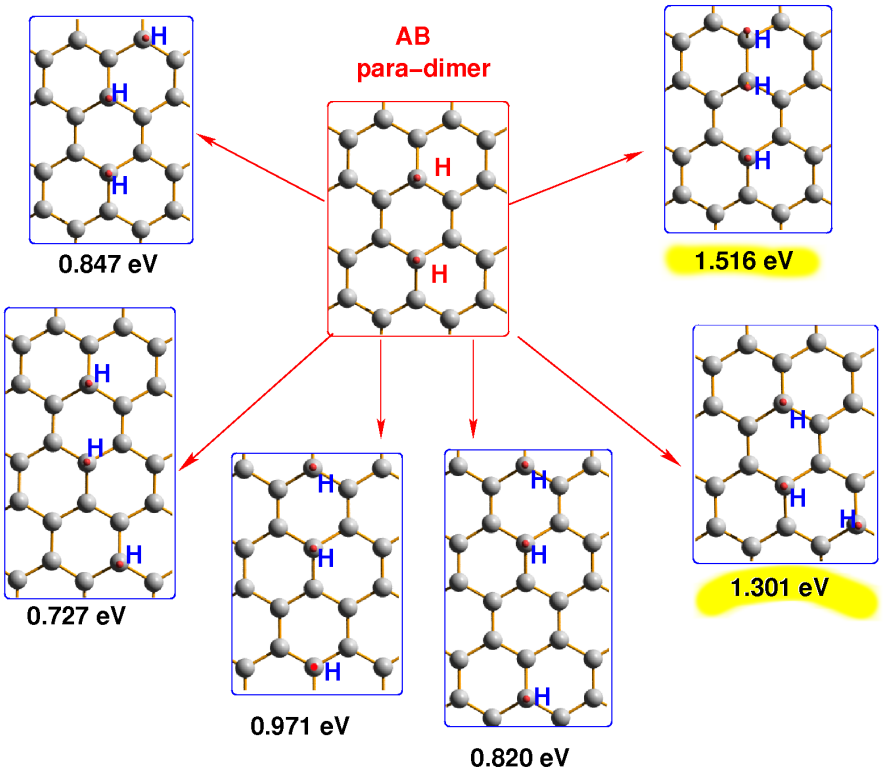
Spin alignment

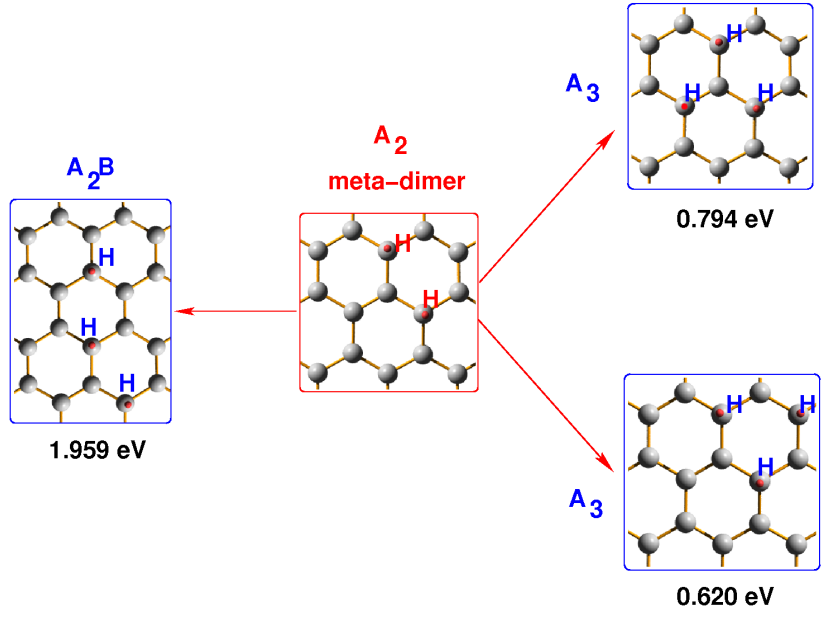
If $U > 0$, the ground-state at *half-filling* has

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

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

3-atom clusters





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

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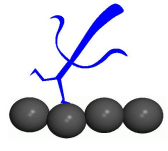
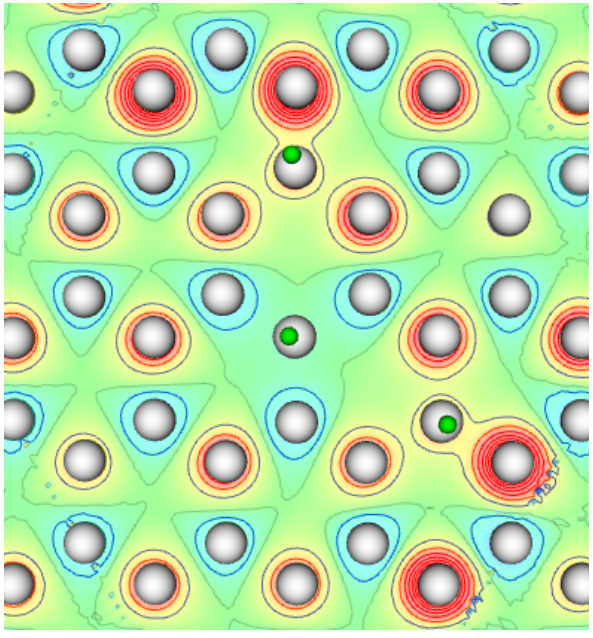
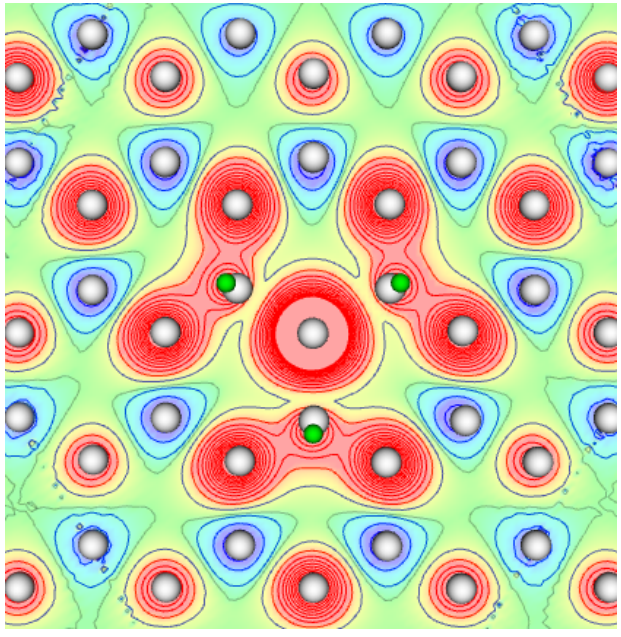


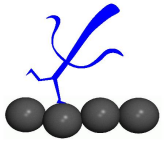
3-atom clusters

A_2B

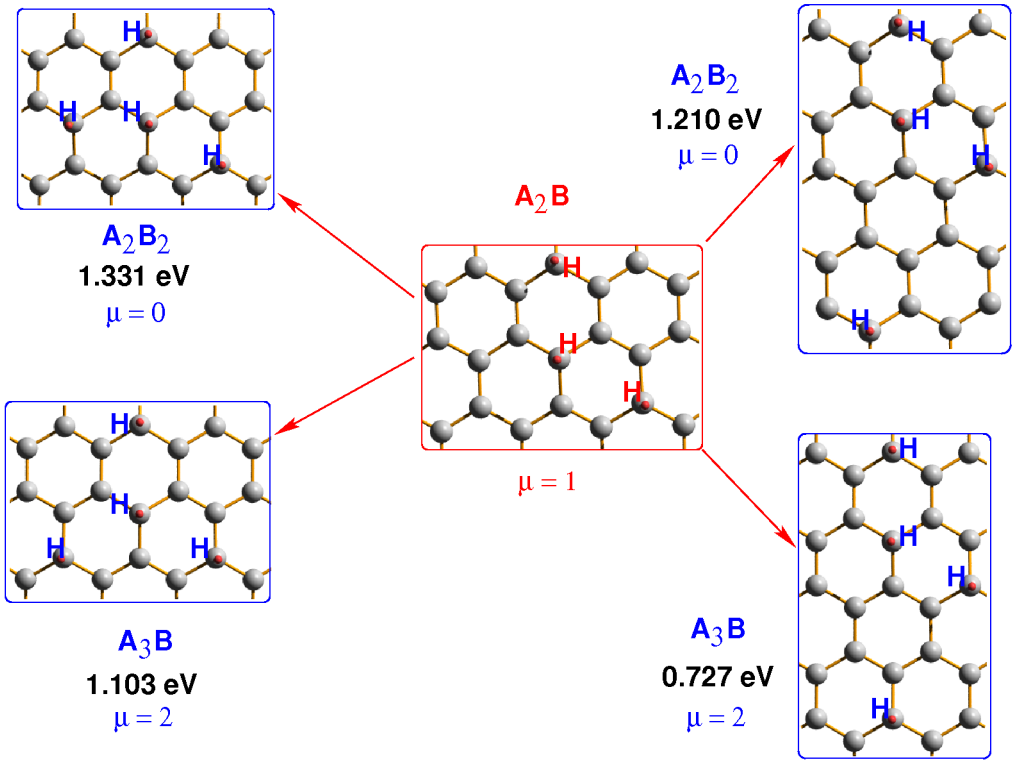


A_3



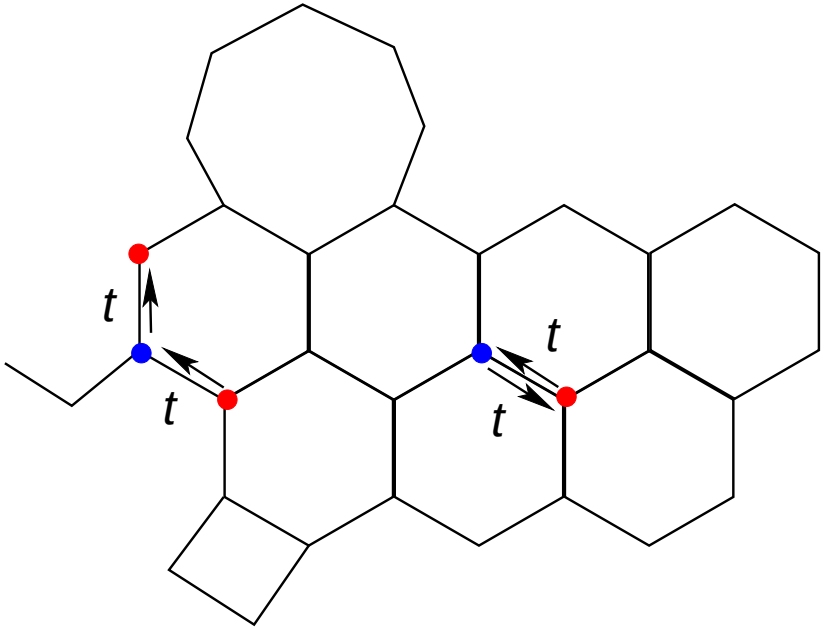


4-atom clusters



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'

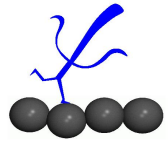
$$\tilde{H}_{AA} = H_{AB} H_{BA}$$

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

$$\Downarrow$$

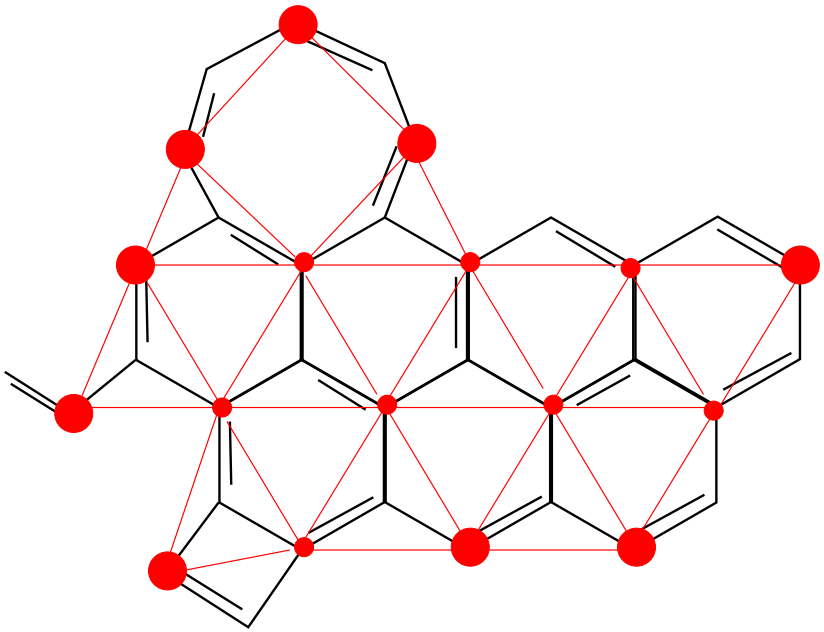
$$\epsilon_i^\pm = \pm\sqrt{\tilde{\epsilon}_i}, |\psi_i^{(\pm)}\rangle = |\psi_{A,i}\rangle \pm |\psi_{B,i}\rangle$$

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



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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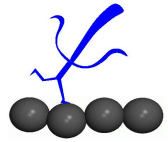

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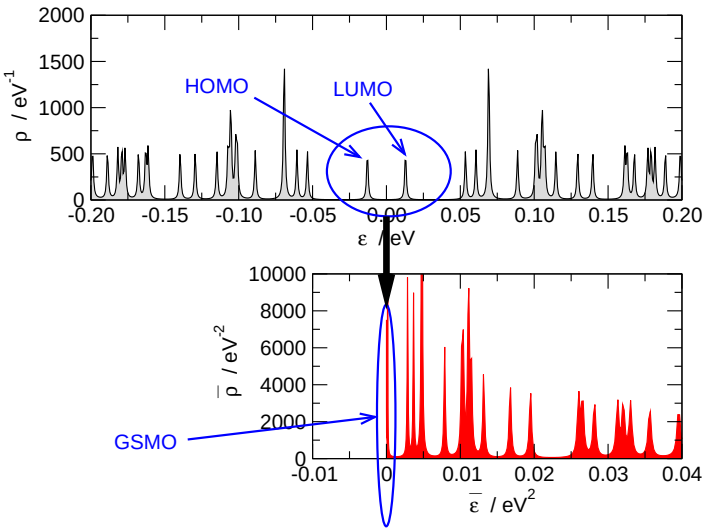

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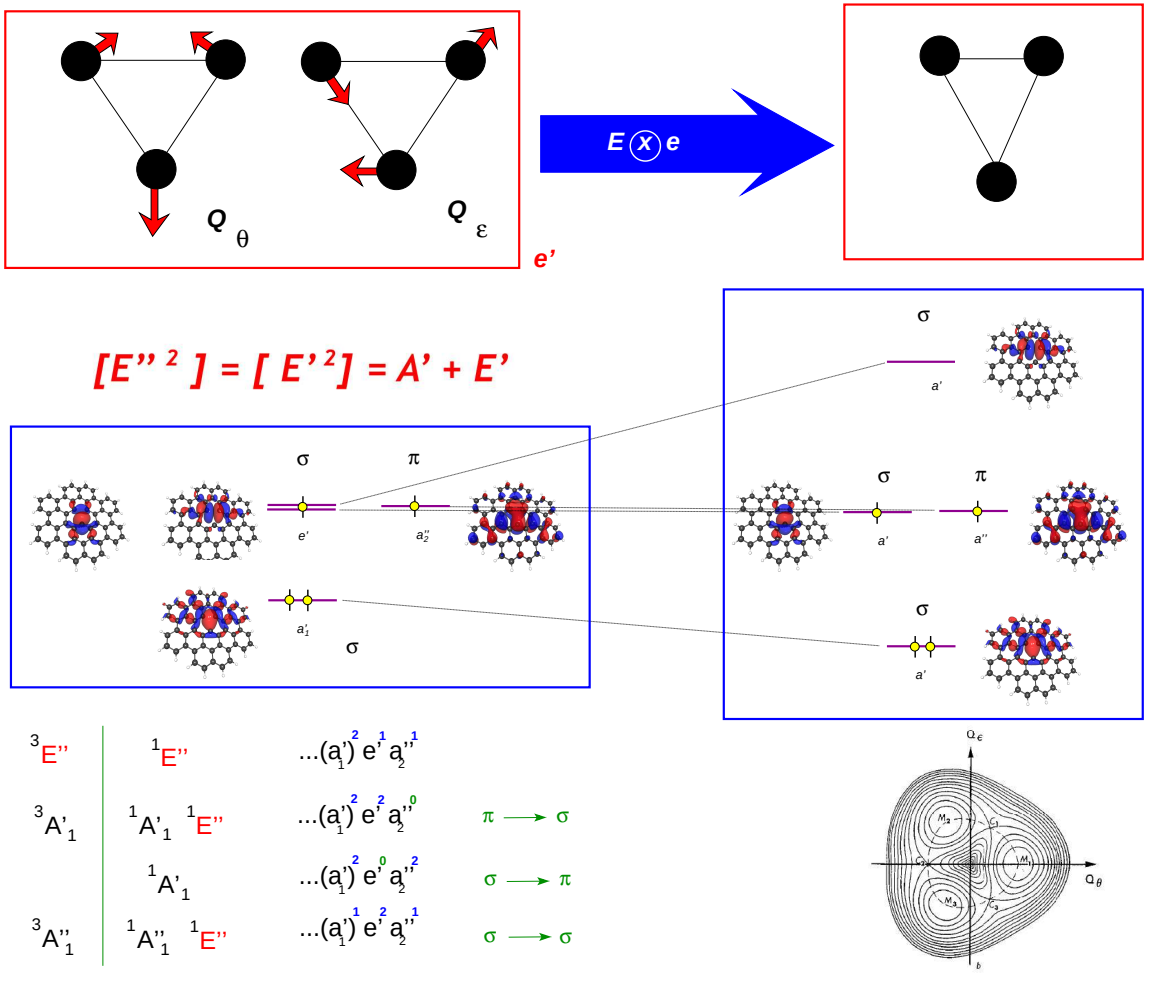
$$|\psi_{B,i}\rangle = \tilde{\epsilon}_i^{-1/2} H_{BA} |\psi_{A,i}\rangle$$

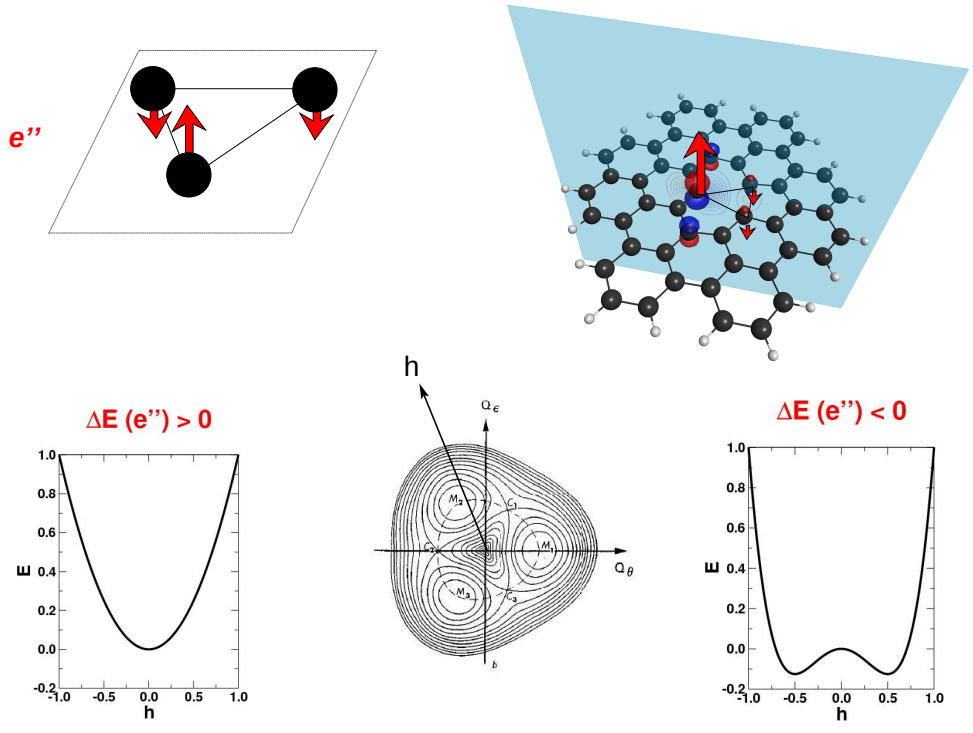
*

$E \otimes e$ JT problem



..with interacting higher-energy states

Out-of-plane, *E″* vibrations do not lift degeneracy at first order..



..but give corrections to second order, either positive or negative *

Zecho's kinetic experiments