Hydrogen and Carbon-based Nanoscience

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Nanoscale Modeling of New Molecular Experiments
March, 6th 2009

Outline

Outline

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Acknowledgements

University of Milan

Gian Franco Tantardini

Simone Casolo

Matteo Bonfanti

Chemical Dynamics Theory Group

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Ole Martin Lovvik

ISTM

Alessandro Ponti

+-x:

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

Notur

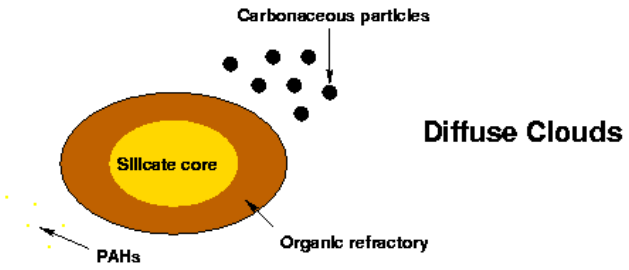
I.S.T.M.

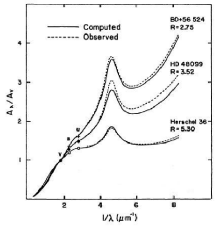
Outline

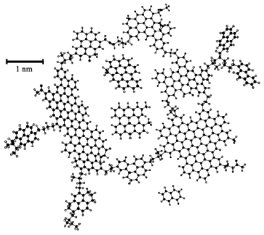
H_2 in ISM

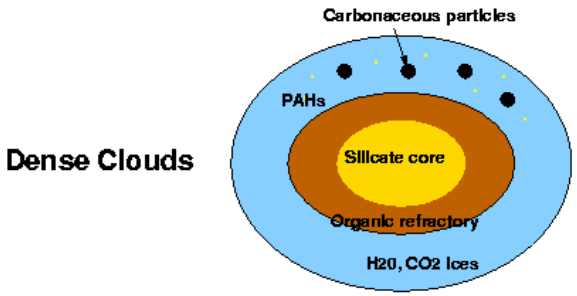
- Hydrogen is the most abundant element of the Universe
- H_2 is formed on the surface of *dust* grain

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





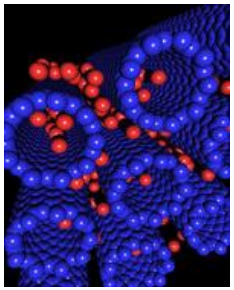


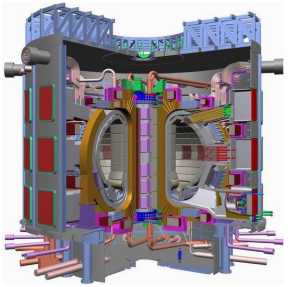


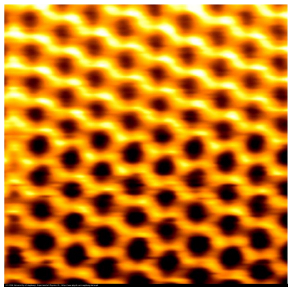
Hydrogen-graphite is an important model for understanding H_2 formation in ISM

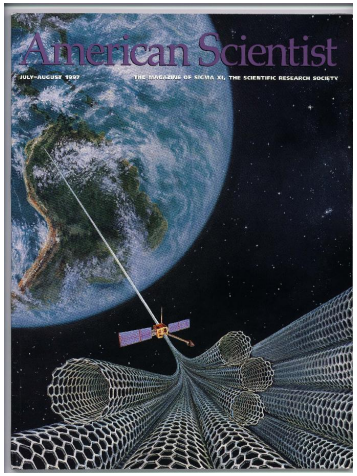
Technology

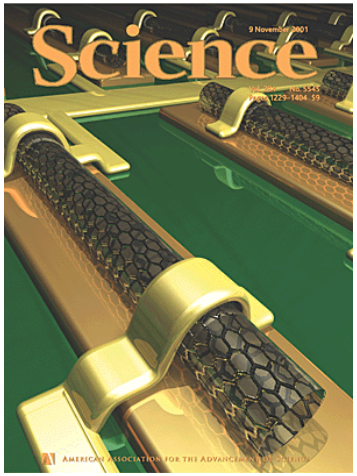
- Hydrogen storage
- Nuclear fusion
- Nanoelectronics, spintronics, nanomagnetism











Technology

Electric Field Effect in Atomically Thin Carbon Films

K. S. Novoselov,[1] A. K. Geim,[1*] S. V. Morozov,[2] D. Jiang,[1] Y. Zhang,[1] S. V. Dubonos,[2] I. V. Grigorieva,[1] A. A. Firsov[2]

We describe monocrystalline graphitic films, which are a few atoms thick but are nonetheless stable under ambient conditions, metallic, and of remarkably high quality. The films are found to be a two-dimensional semimetal with a tiny overlap between valence and conductance bands, and they exhibit a strong ambipolar electric field effect such that electrons and holes in concentrations up to 10^{13} per square centimeter and with room-temperature mobilities of ~10,000 square centimeters per volt-second can be induced by applying gate voltage.

The ability to control electronic properties of a material by externally applied voltage is at the heart of modern electronics. In many cases, it is the electric field effect that allows one to vary the carrier concentration in a semiconductor device and, consequently, change an electric current through it. As the semiconductor industry is nearing the limits of performance improvements for the current technologies dominated by silicon, there is a constant search for new, nontraditional materials whose properties can be controlled by the electric field. The most notable recent examples of such materials are organic conductors (*1*) and carbon nanotubes (*2*). It has long been tempting to extend the use of the field effect to metals [e.g., to develop all-metallic transistors that could be scaled down to much smaller sizes and would consume less energy and operate at higher frequencies

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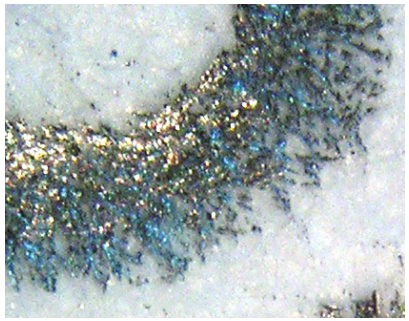
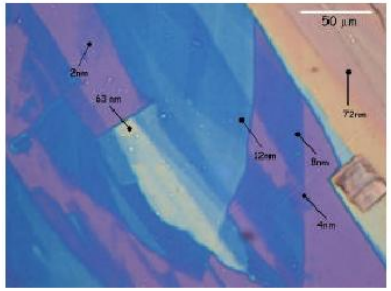
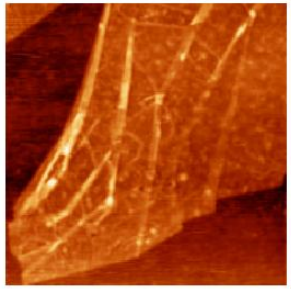
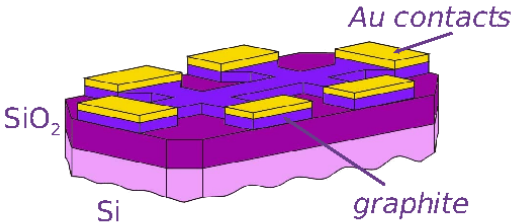


than tradi
However,
metal fil
screened
and bulk
large com
be induce
tend to b
coming d
eral nanometers; so far, this has proved to be
an insurmountable obstacle to metallic elec-





graphene sheets rolled up into nanometer-sized
cylinders) (*5–7*). Planar
been presumed not to exi
being unstable with respect
curved structures such as
nanotubes (*5–14*).



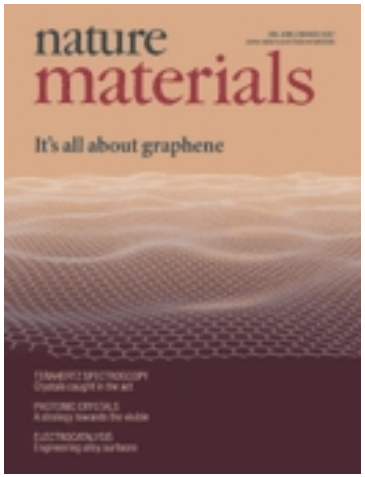
Technology

Two-dimensional gas of massless Dirac fermions in graphene

K. S. Novoselov[1], A. K. Geim[1], S. V. Morozov[2], D. Jiang[1], M. I. Katsnelson[3], I. V. Grigorieva[1], S. V. Dubonos[2] & A. A. Firsov[2]

Experimental observation of the quantum Hall effect and Berry's phase in graphene

Yuanbo Zhang[1], Yan-Wen Tan[1], Horst L. Stormer[1,2] & Philip Kim[1]



The rise of graphene

Science AAAS

Electric Field Effect in Atomically Thin Carbon Films
K. S. Novoselov, *et al.*
Science **306**, 666 (2004);
DOI: 10.1126/science.1102896

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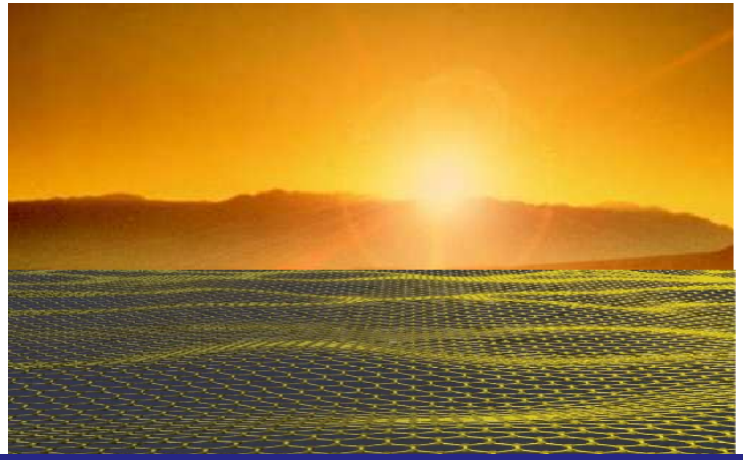
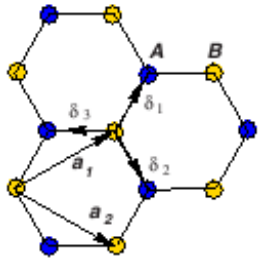
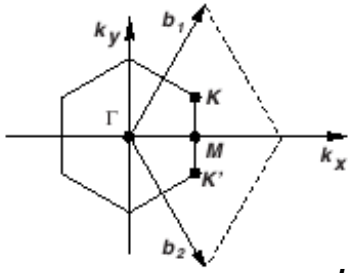


Technology

$$H \approx -t \sum_{i,\tau} \sum_j a_\tau^\dagger(\mathbf{R}_i) b_\tau(\mathbf{R}_i + \delta_j) + c.c.$$

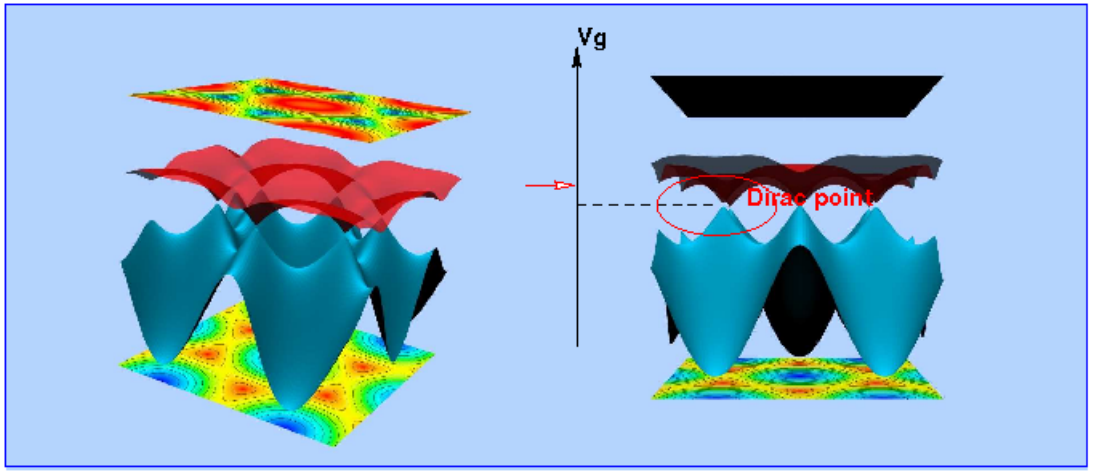


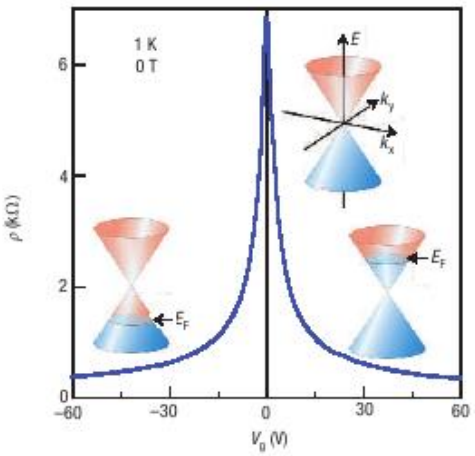


$$a_{\tau;i} = \frac{1}{N} \sum_{\mathbf{k}} e^{-i\mathbf{k}\mathbf{R}_i} a_\tau(\mathbf{k})$$

$$H = -t \sum_{\mathbf{k},\tau} f(\mathbf{k}) a_\tau^\dagger(\mathbf{k}) b_\tau(\mathbf{k}) + c.c.$$

$$H = -t \sum_{\mathbf{k},\tau} \left[a_\tau^\dagger(\mathbf{k}), b_\tau^\dagger(\mathbf{k}) \right] \begin{bmatrix} 0 & f(\mathbf{k}) \\ f^*(\mathbf{k}) & 0 \end{bmatrix} \begin{bmatrix} a_\tau(\mathbf{k}) \\ b_\tau(\mathbf{k}) \end{bmatrix}$$





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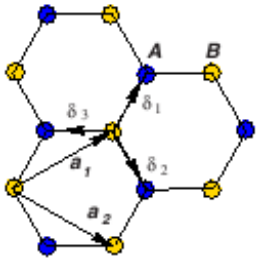
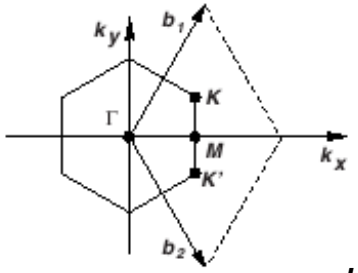
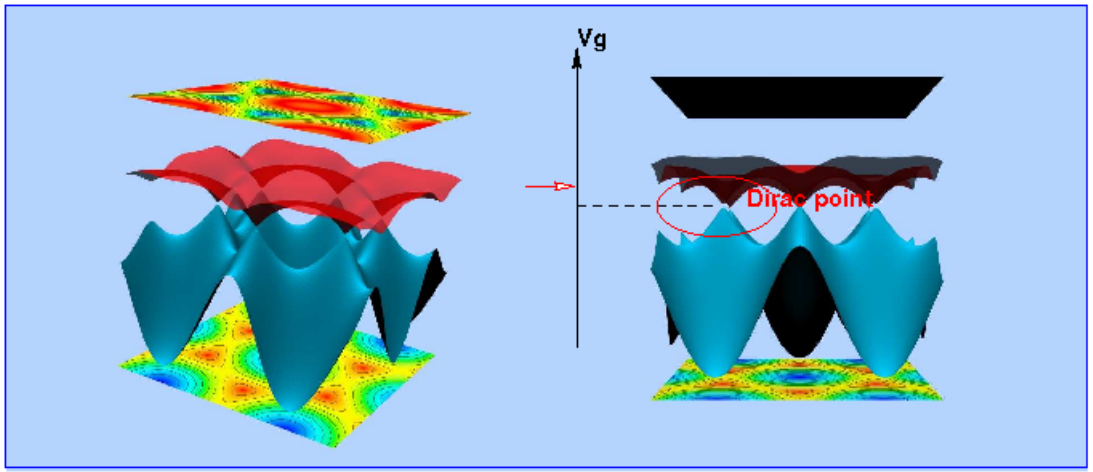


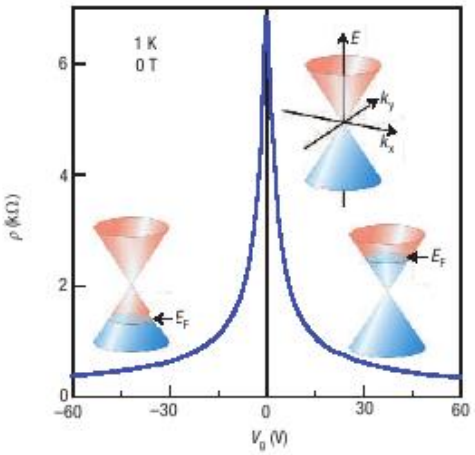


$$t\, f(\mathbf{K}_\pm + \mathbf{k}) \approx \mp v_F (k_y \pm i k_x) \text{ with } v_F = \tfrac{3}{2} d_{CC} t$$

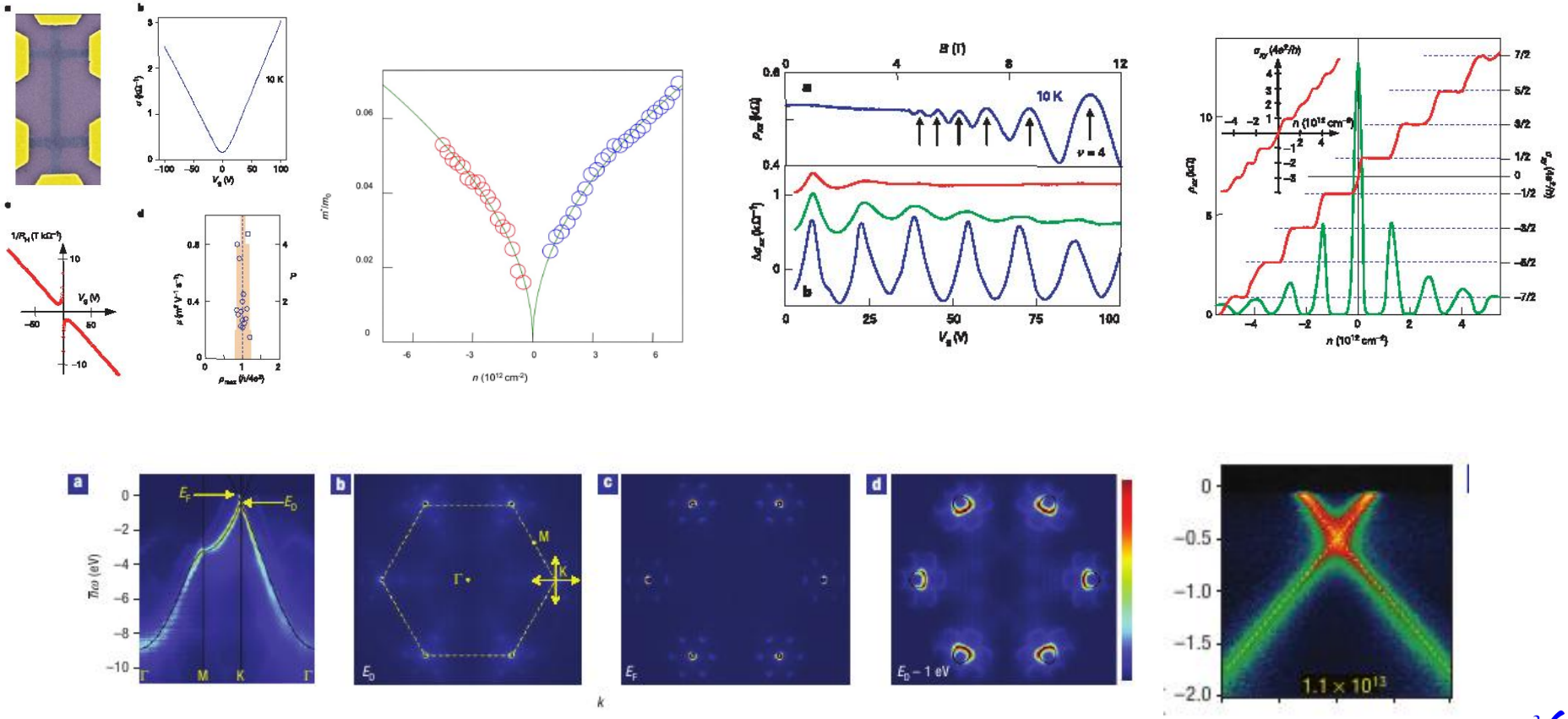
$$v_F \approx 1 * 10^6 m/s \approx c/300$$

$$H_{\mathbf{K}_+} \approx v_F \sum_{\mathbf{k},\tau} \hat{\Psi}_\tau^\dagger(\mathbf{k}) \mathbf{k} \sigma \hat{\Psi}_\tau(\mathbf{k}) \text{ with } \hat{\Psi}_\tau^\dagger = [a_\tau^\dagger(\mathbf{k}), b_\tau^\dagger(\mathbf{k})]$$





Technology


10 K
V_g (V)
n (10^{12} cm^{-2})
m^*/m_0
B (T)
$\nu = 4$
σ_{xy} ($4e^2/h$)
ρ_{xx} (kΩ)
$\Delta\sigma_{xx}$ (kΩ^{-1})
E_F
E_D
M
K
Γ
$E_D - 1$ eV
1.1 × 10^{13}

Technology

Graphene is a true 2D-electron gas (2DEG) system with pseudo-relativistic conduction electrons!

...what about us?

- **Chemistry**: graphene is a large polycylic aromatic hydrocarbon
- **Surface Science**: adsorption of atoms/molecules may tremendously affect transport properties

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Outline

Understanding adsorption

H on Graphite *vs* metal substrates

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

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

[3] L. Hornekaer *et al.*, Phys. Rev. Lett. 97, 186102 (2006) [4] A. Andree *et al.*, Chem. Phys. Lett. 425, 99 (2006) [5] L. Hornekaer *et al.*, Chem. Phys. Lett. 446, 237 (2007) [6] L. Hornekaer *et al.*, Phys. Rev. Lett. 96, 156104 (2006)

Bipartite lattices

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

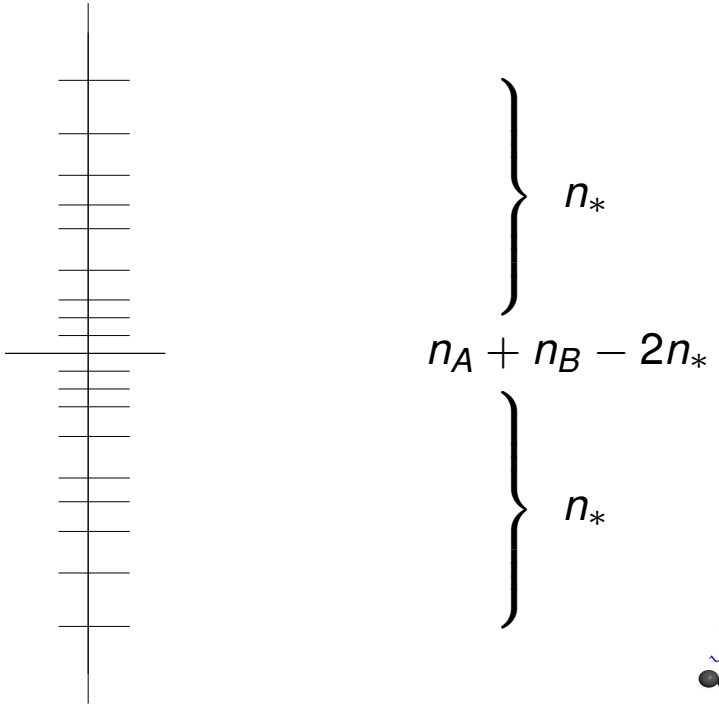
Electron-hole symmetry

$b_i \to -b_i \Longrightarrow t_{ij} \to -t_{ij}$, i.e. $\mathbf{h} \to -\mathbf{h}$

if ϵ_i is an eigenvalue and $c_i^\dagger = \sum_i \alpha_i a_i^\dagger + \sum_j \beta_j b_j^\dagger$ the corresponding eigenvector

$\Downarrow$

$-\epsilon_i$ is also eigenvalue and $c_i'^\dagger = \sum_i \alpha_i a_i^\dagger - \sum_j \beta_j b_j^\dagger$ is eigenvector



Bipartite lattices: the “alternating" theorem

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

Theorem

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

Proof.

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

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

□

Bipartite lattices: Lieb's theorem

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

Theorem

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

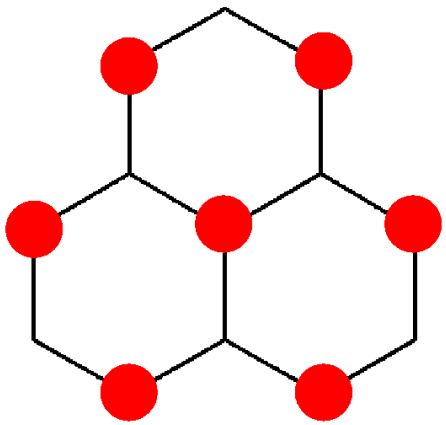
$$S = |n_A - n_B|/2 = n_I/2$$

Proof.

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

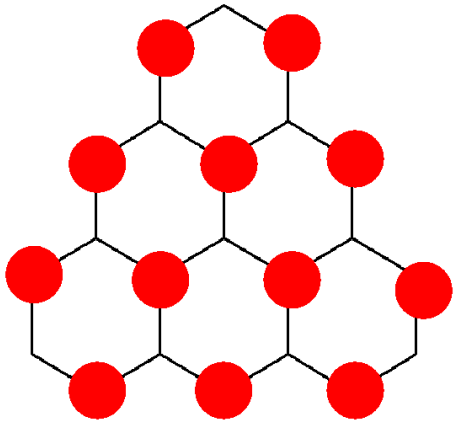
...basically, we can apply Hund's rule to previous result

Bipartite lattices: theorems at work



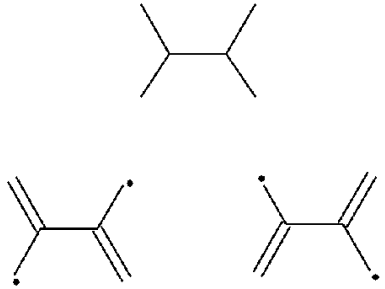
$n_A = n_B + 1$

$S = 1/2$



$n_A = n_B + 2$

$S = 1$



$n_A = n_B$

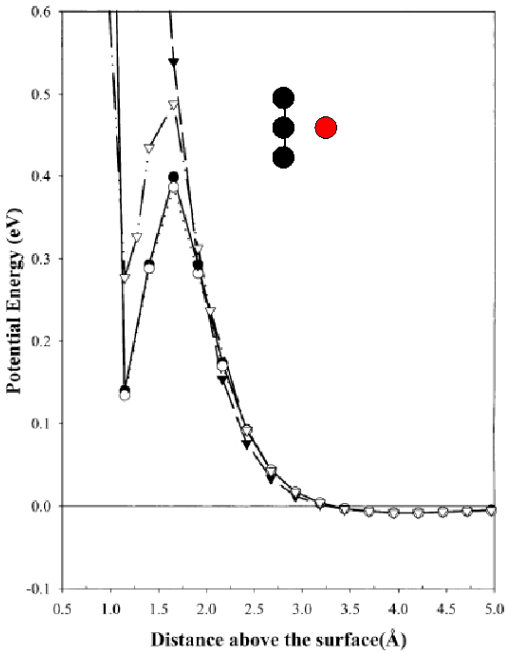
$S = 0$

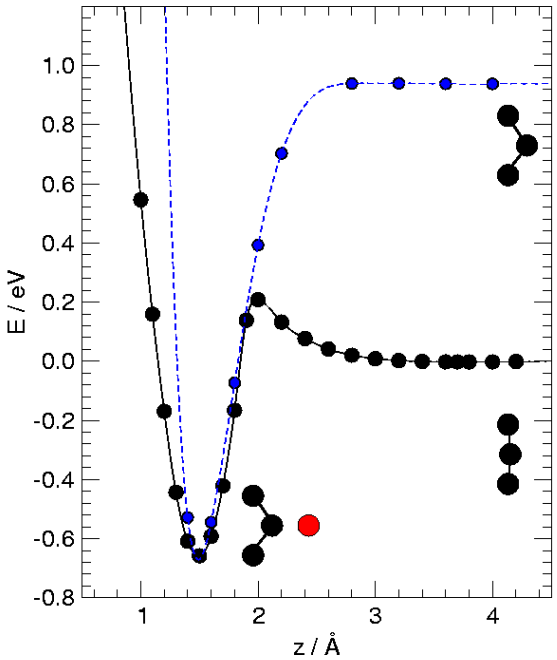
Technicalities

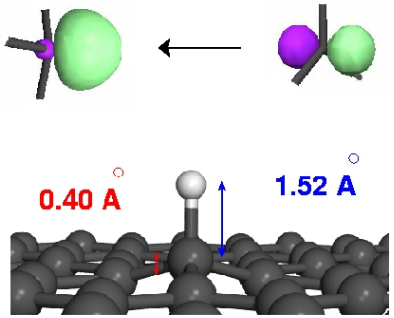
DFT calculations

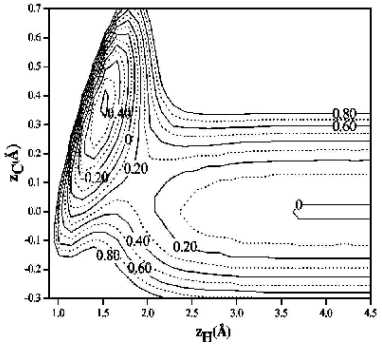
- Periodic, plane wave based calculations with VASP
- PAW method within the frozen *core* approximation
- Perdew-Burke-Ernzerhof (PBE) functional
- 5x5x1 unit cell with a 20 Å vacuum layer along *c*
- 6x6x1 Γ-centered *k* mesh, E_{cut} = 500 eV
- Spin polarization

Adsorption PES



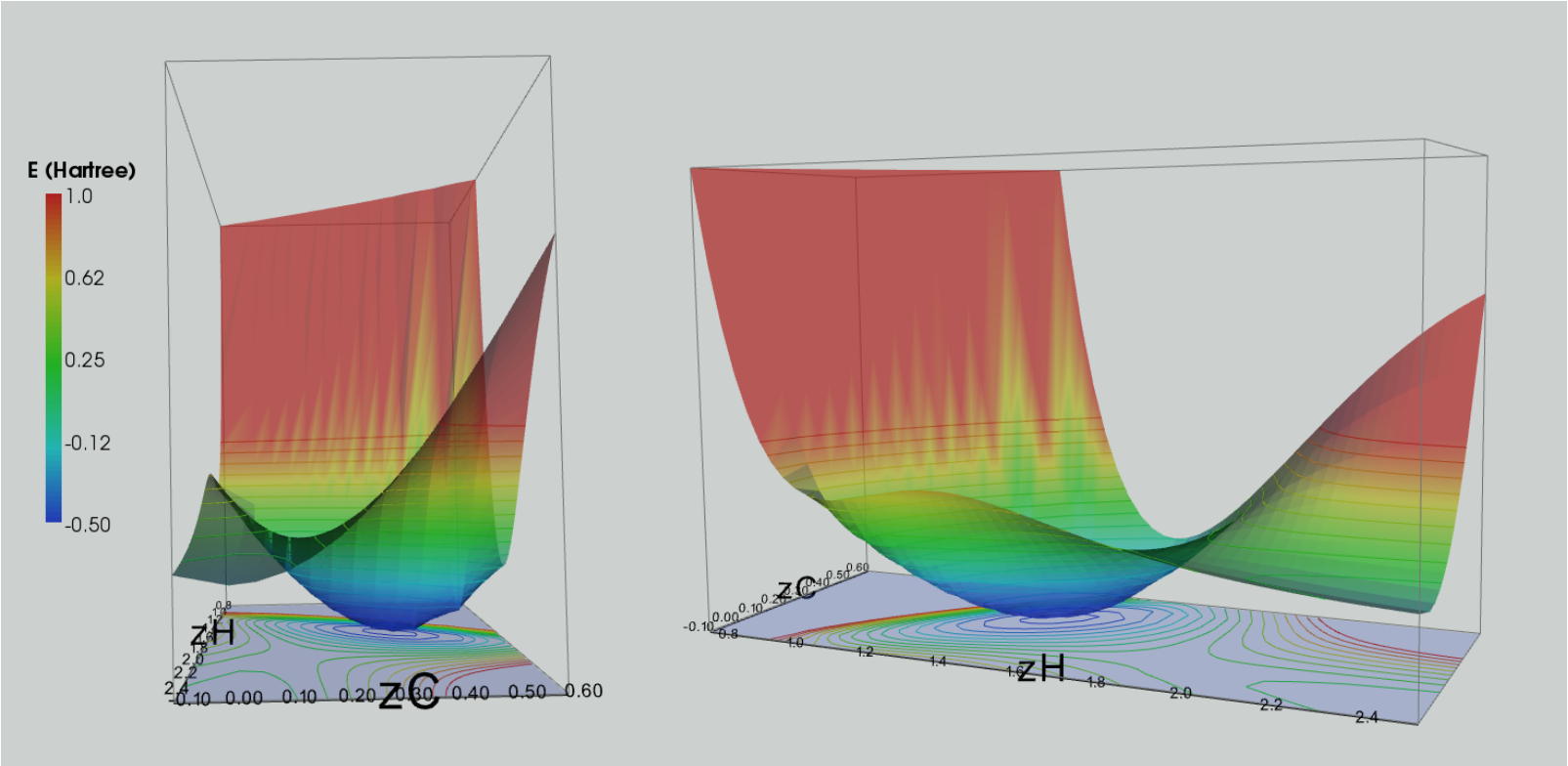




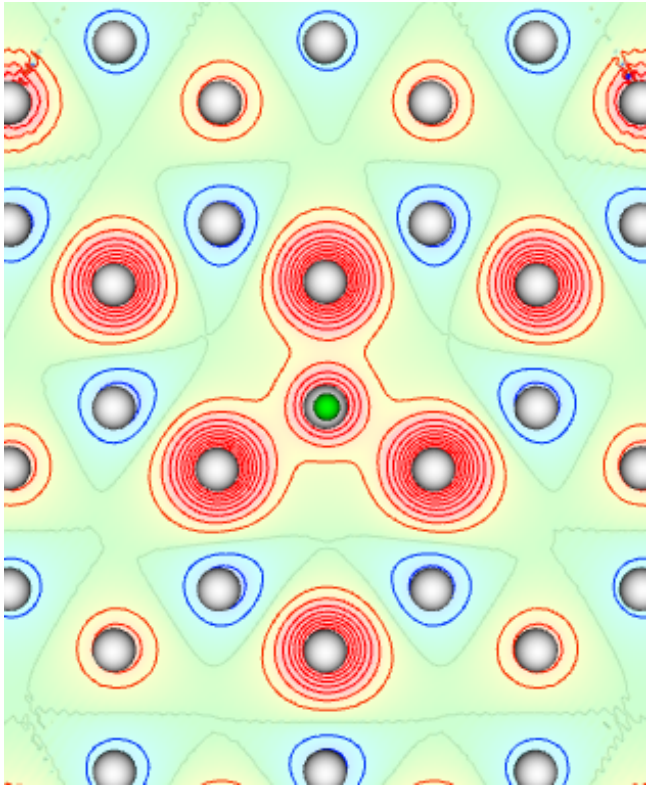


[1] X. Sha and B. Jackson, Surf. Sci. 496, 318 (2002)

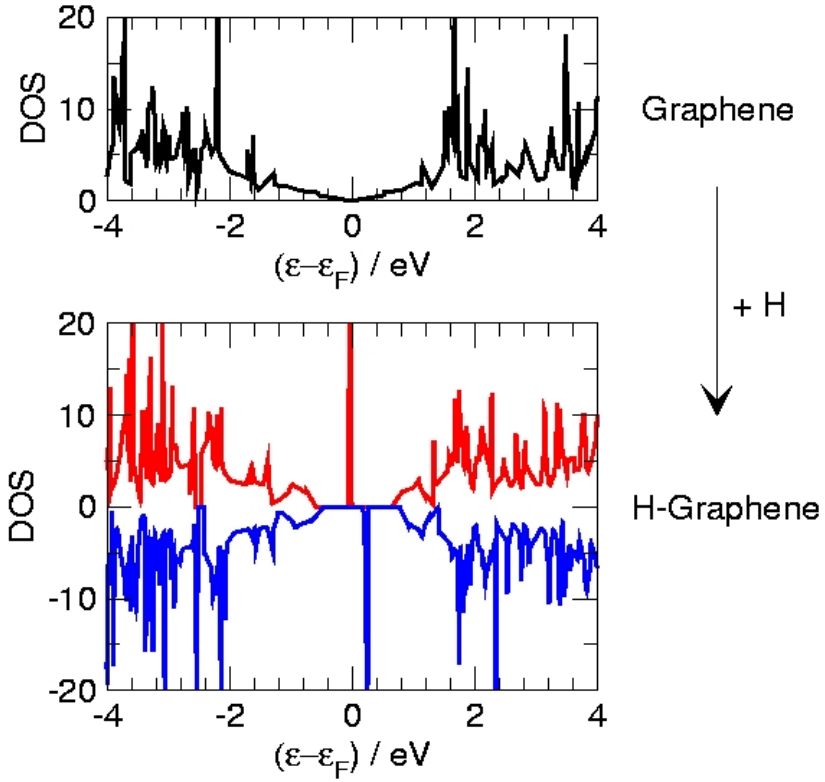
Adsorption PES



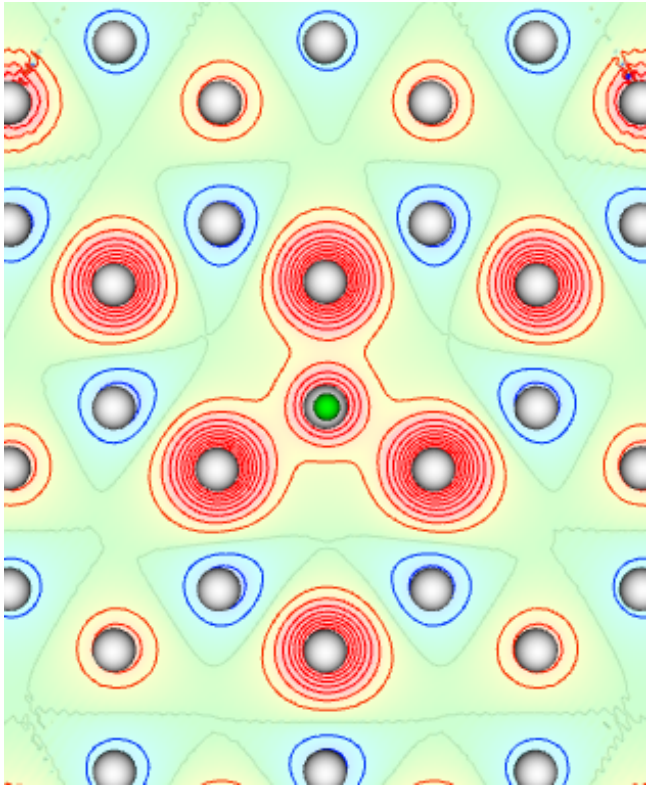
Substrate electronic structure



For adsorption on an A site spin-density localizes on B sites



Substrate electronic structure



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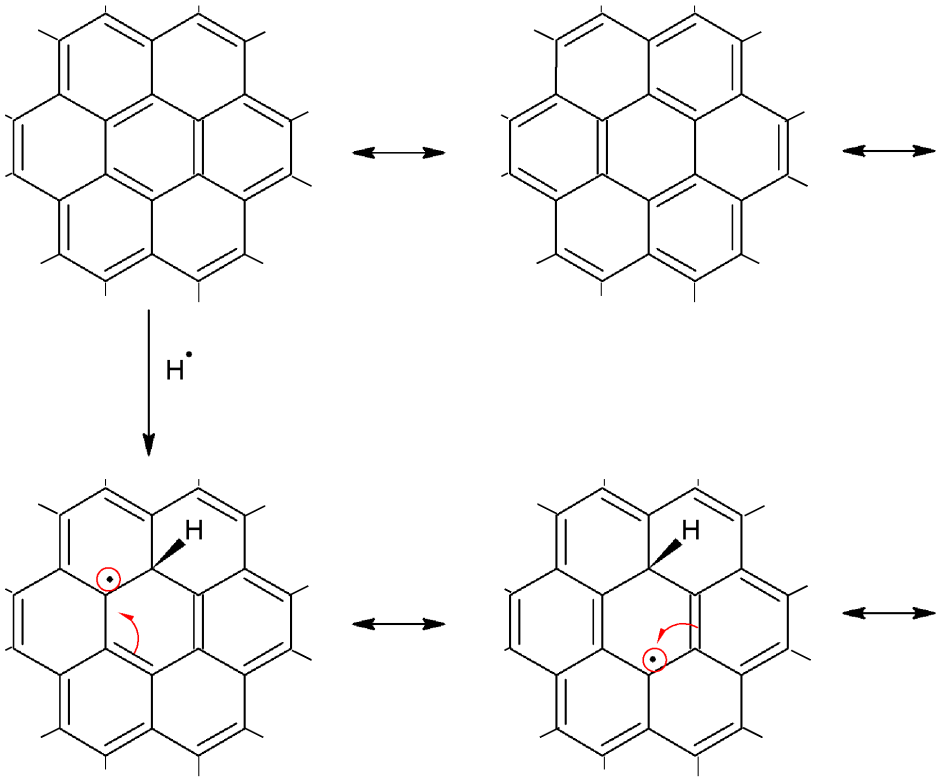


Valence Bond picture

Basics

(Simple) VB *ansatz*

$$\Psi = \mathcal{A}\{\phi_1\phi_2\phi_3...\phi_N\Theta^N_{S,M}\}$$

$$\Theta^N_{S,M} = \sum_k^{f_s^N} c_k \Theta^N_{S,M;k}$$

- orbitals ϕ_i are (or turn out to be) localized on atoms
- spin-function is the best coupling for the given S

Advantages

- simple, accurate 0th order picture of chemical bond
- route to Heisenberg/Hubbard models (frozen/polarizable VB orbitals)

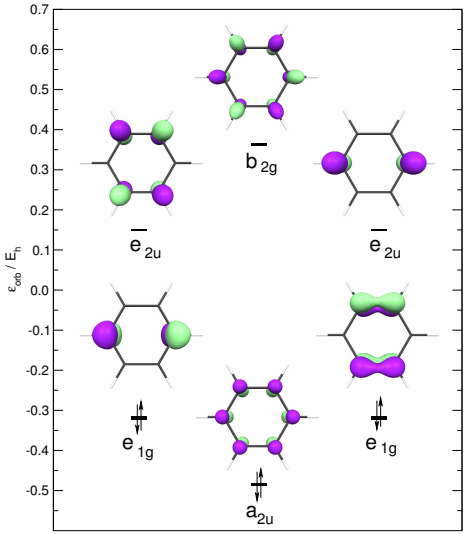
Disadvantages

- non-orthogonal many-electron basis

Valence Bond picture

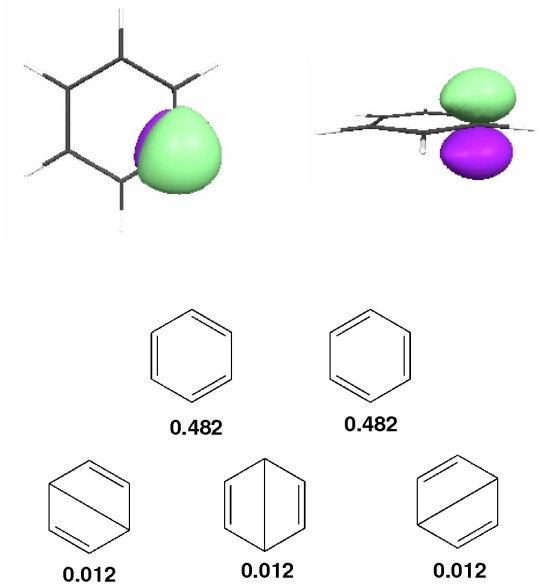
Benzene

Molecular Orbital theory



$$\Psi = \mathcal{A}\{\phi_1\phi_1\phi_2\phi_2\phi_3\phi_3\Theta^6_{0,0;1}\}$$

Valence Bond theory

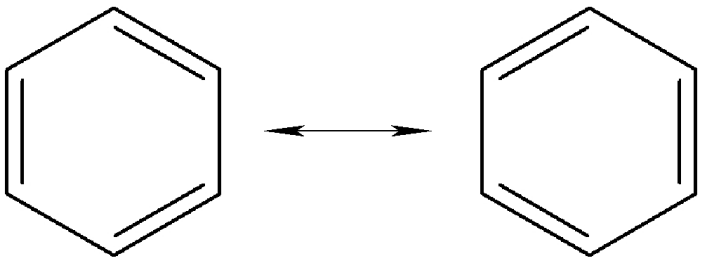


$$\Psi = \sum_{k=1}^{6} c_k \mathcal{A}\{\phi_1\phi_2\phi_3\phi_4\phi_5\phi_6\Theta^6_{0,0;k}\}$$

Valence Bond picture

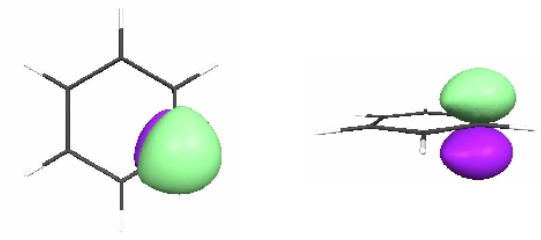
Benzene

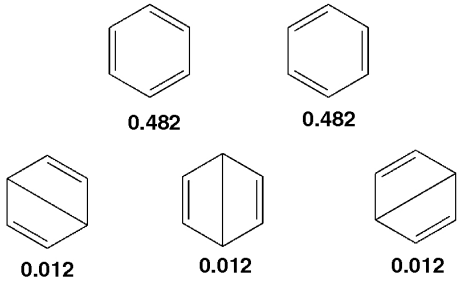
Kekule (1865)



$$\Psi \simeq \Psi_1^{kek} + \Psi_2^{kek}$$

Valence Bond theory

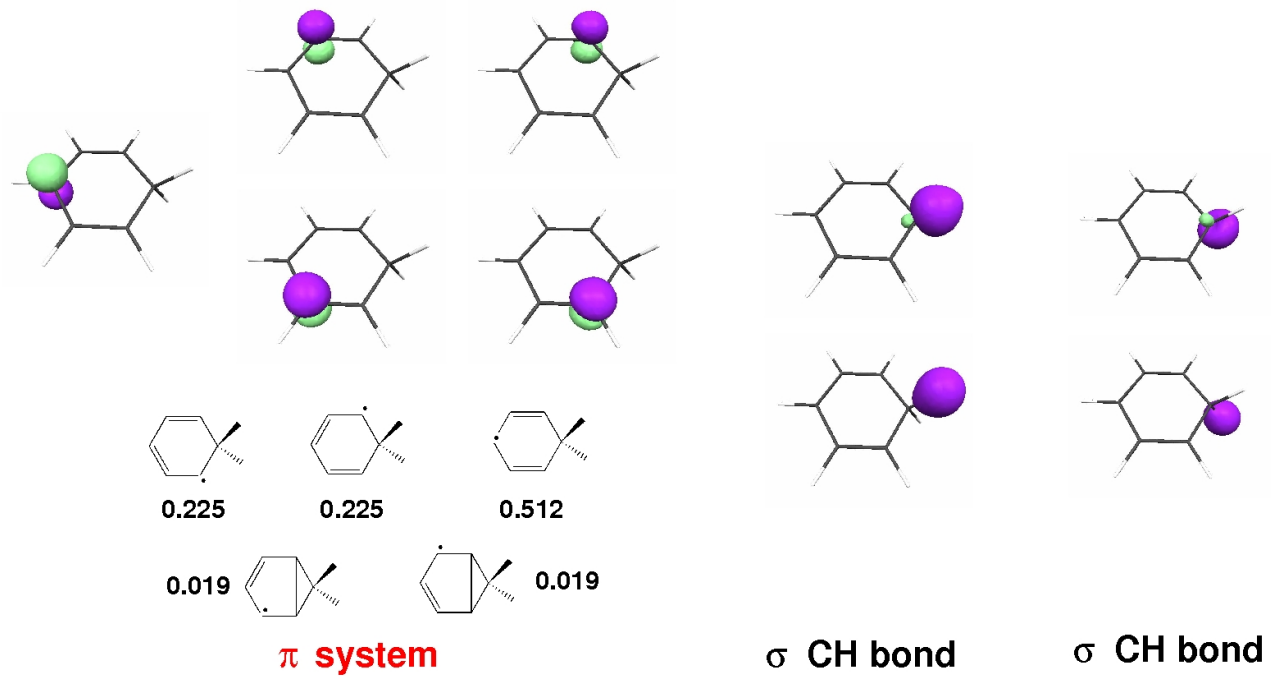




$$\Psi = \sum_{k=1}^{6} c_k \mathcal{A}\{\phi_1\phi_2\phi_3\phi_4\phi_5\phi_6\Theta^6_{0,0;k}\}$$

Valence Bond picture

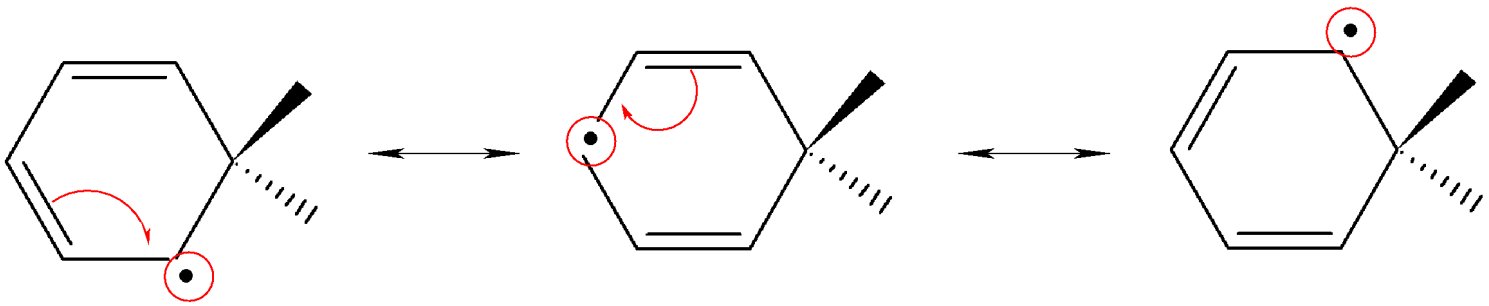
Benzene-H



$$\Psi = \sum_{k=1}^{5} c_k \mathcal{A}\{\phi_1\phi_2\phi_3\phi_4\phi_5\Theta^5_{0,0;k}\phi_6\phi_7\Theta^2_{0,0}\phi_8\phi_9\Theta^2_{0,0}\}$$

Valence Bond picture

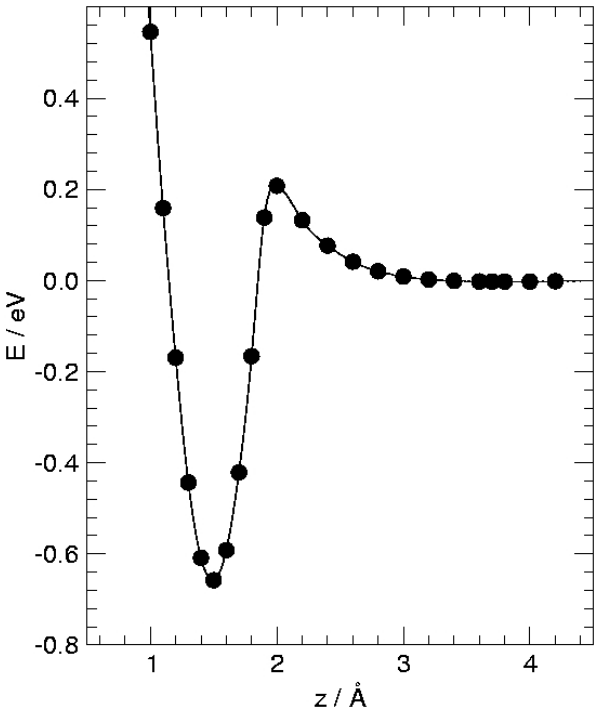
Benzene-H

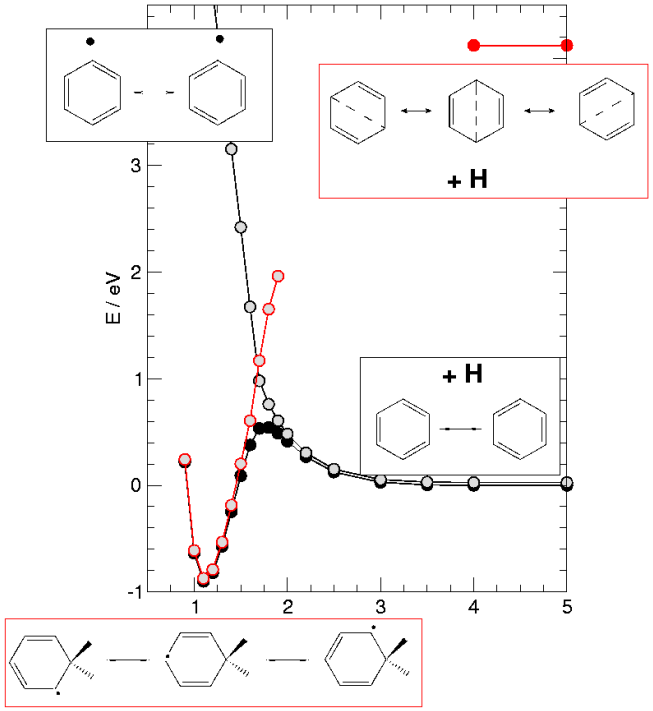


$$\Psi \simeq c_0 \Psi_1^{kek} + c_1 \Psi_2^{kek} + c_0 \Psi_3^{kek}$$

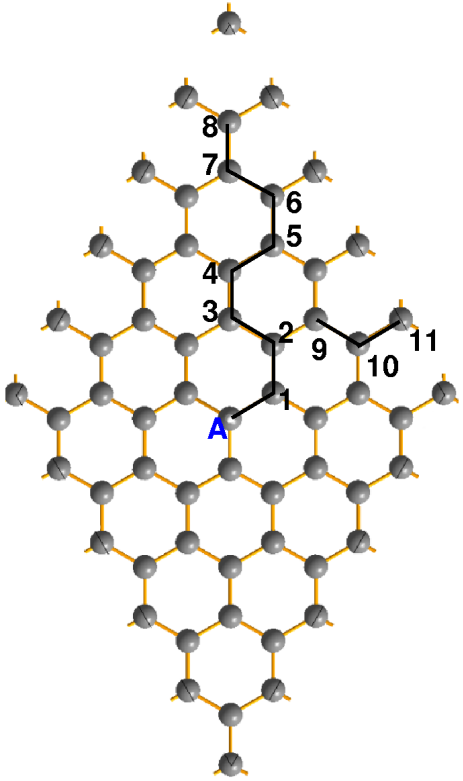
Valence Bond picture

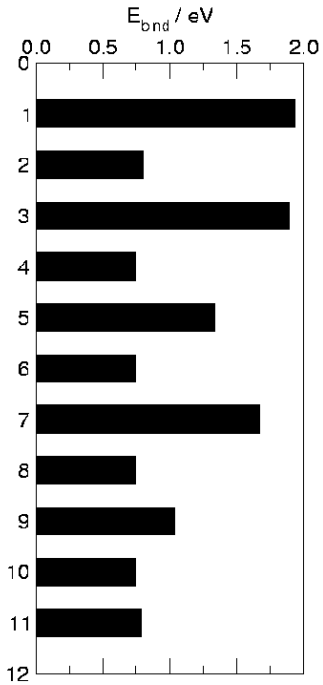
Example: Adsorption barrier



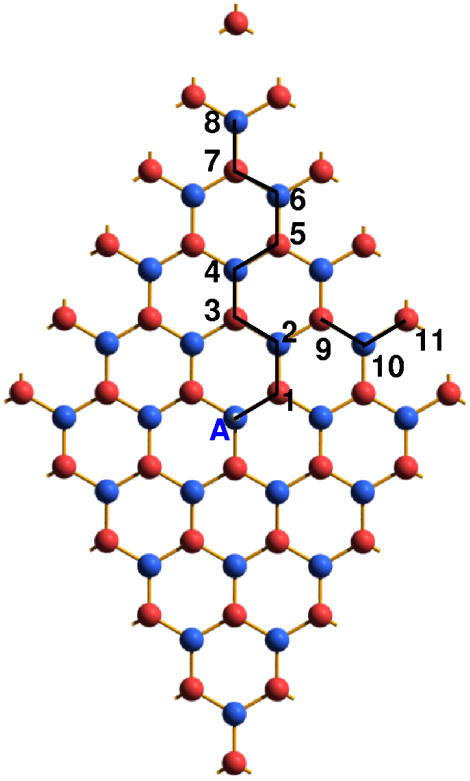


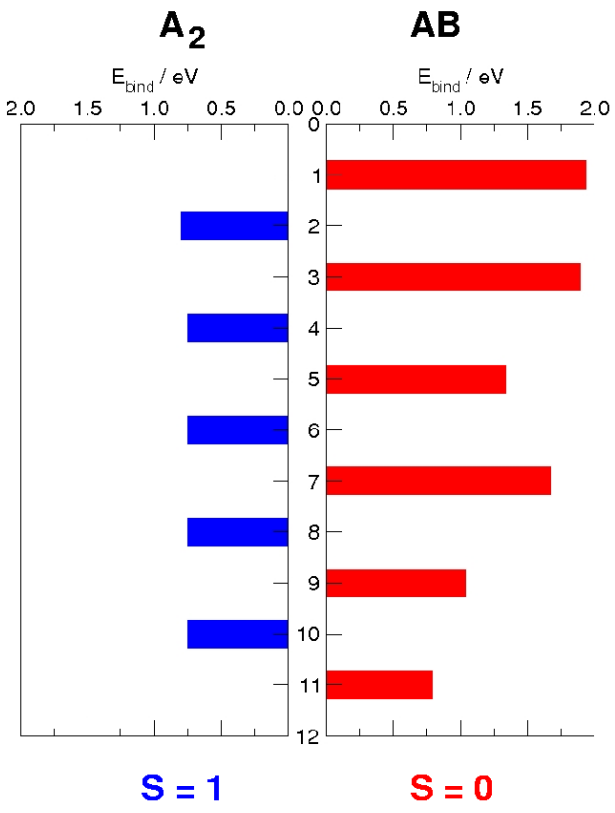
Dimers



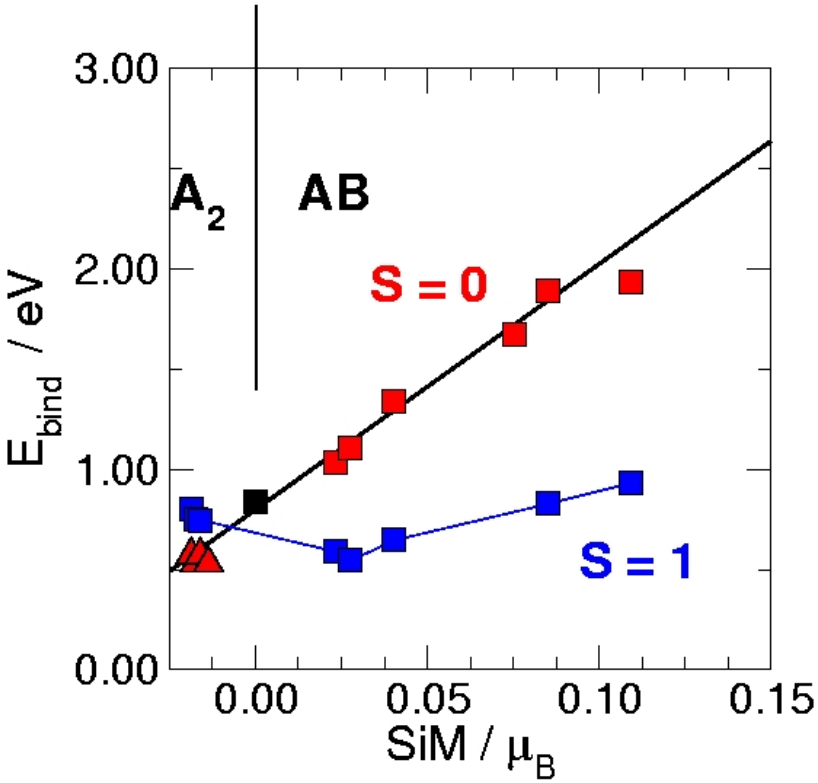


Dimers


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

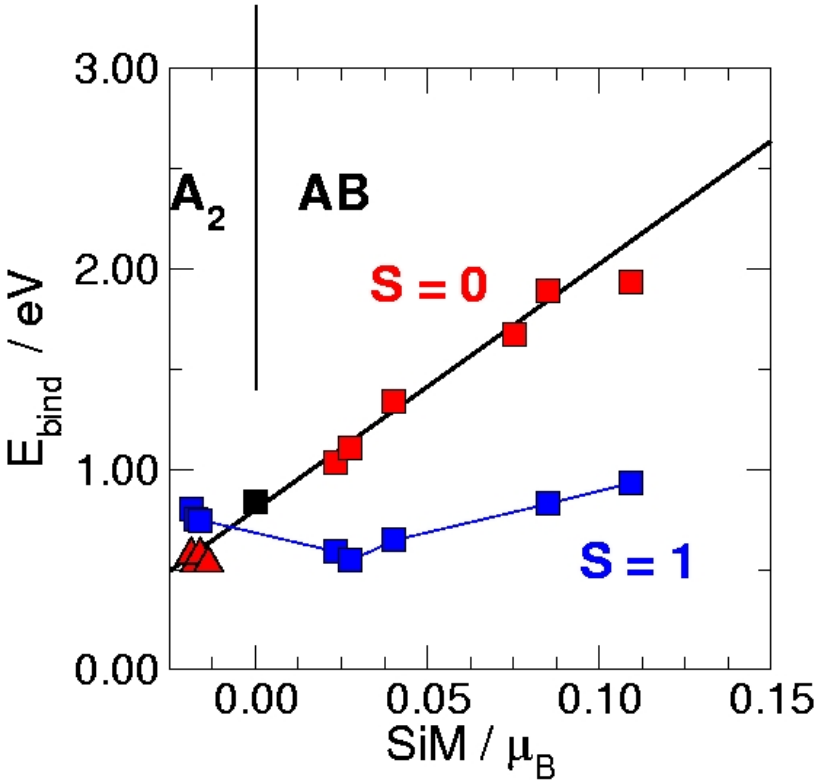

A2
AB
Ebind / eV
Ebind / eV
2.0 1.5 1.0 0.5 0.0
0.0 0.5 1.0 1.5 2.0
0 1 2 3 4 5 6 7 8 9 10 11 12
S = 1
S = 0

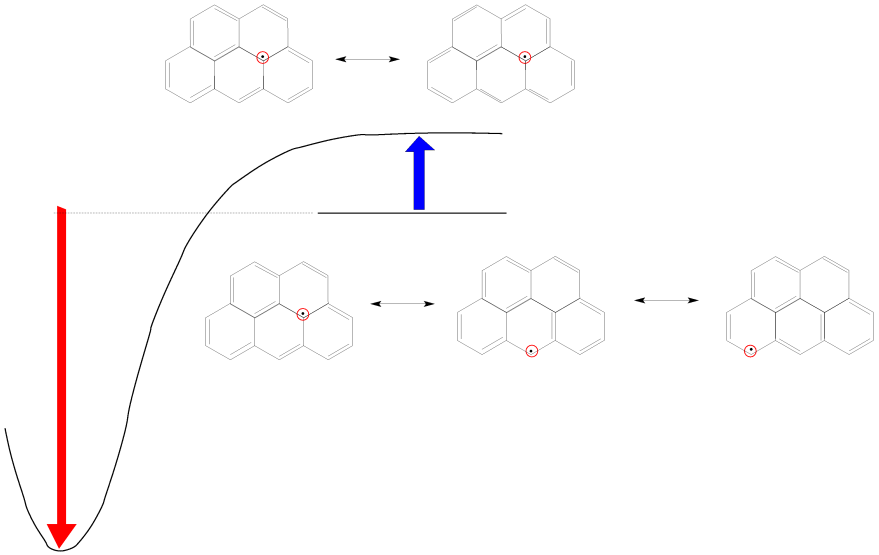
Dimers



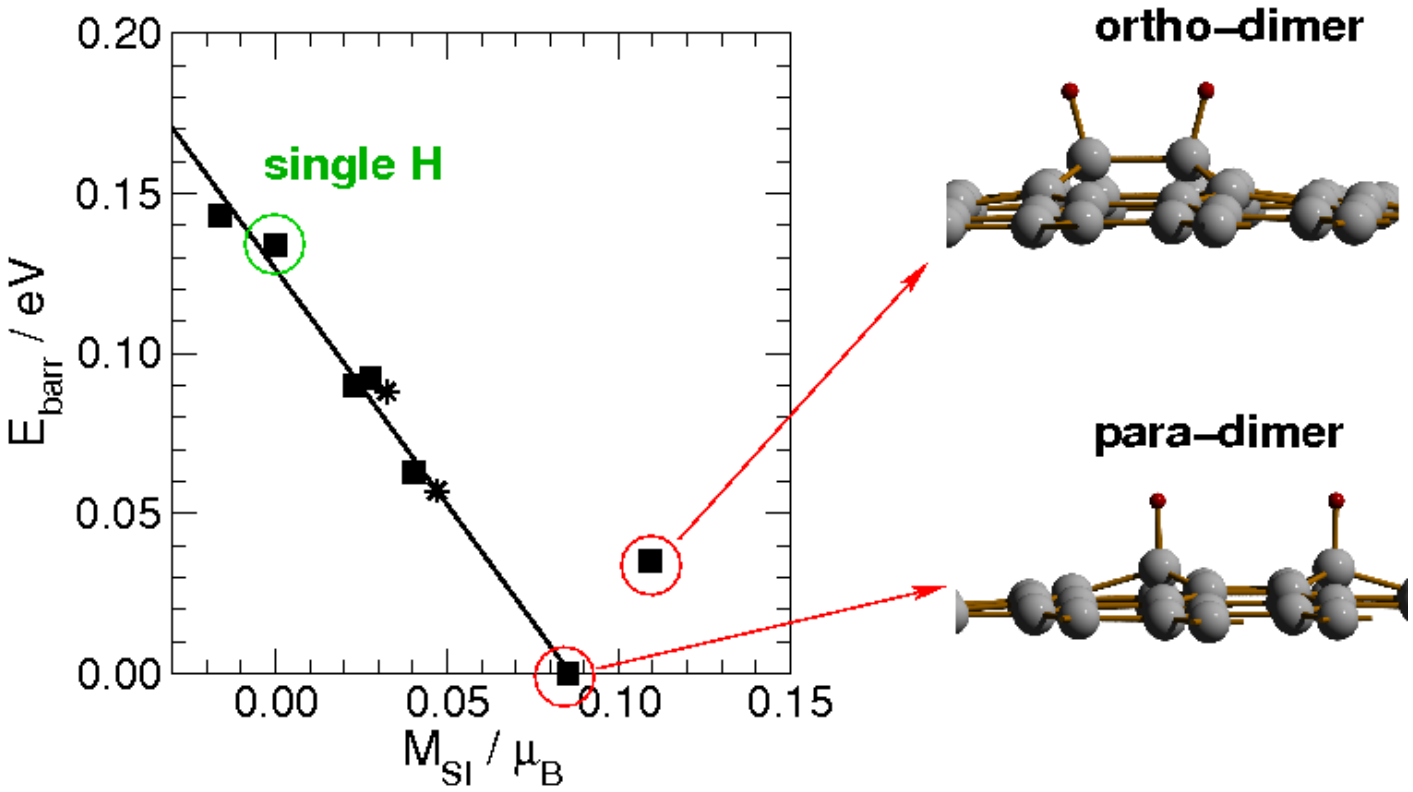
Binding energies depend ∼ linearly on the site integrated magnetization (SiM)

Dimers

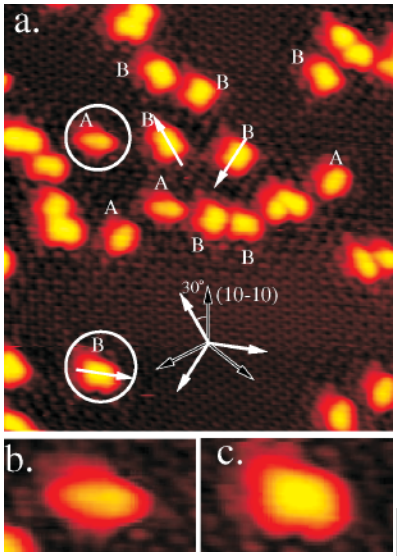




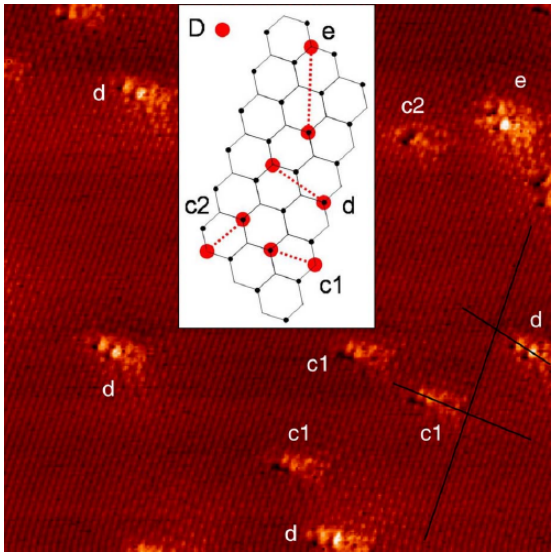
Dimers

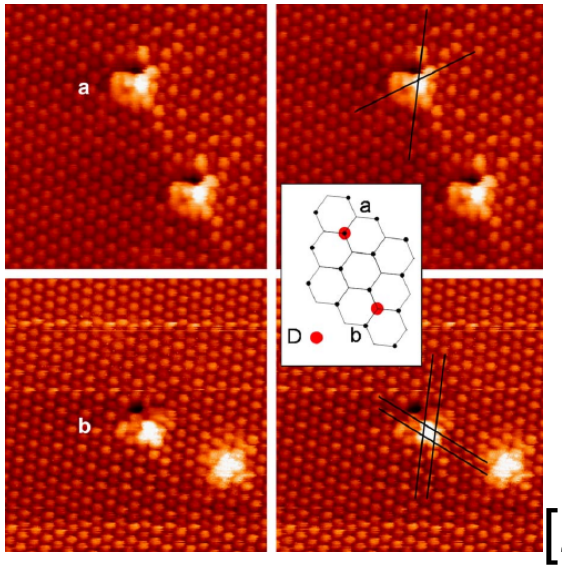

0.20
0.15
0.10
0.05
0.00
0.00
0.05
0.10
0.15
single H
E_{barr} / eV
M_{SI} / μ_B
ortho–dimer
para–dimer

Dimers



[1]



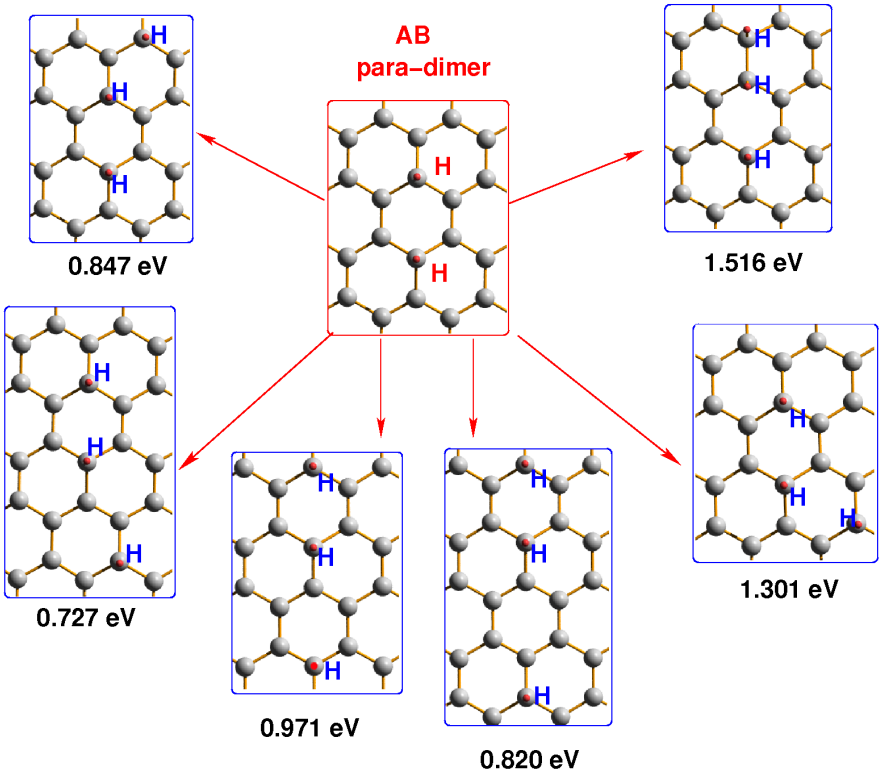


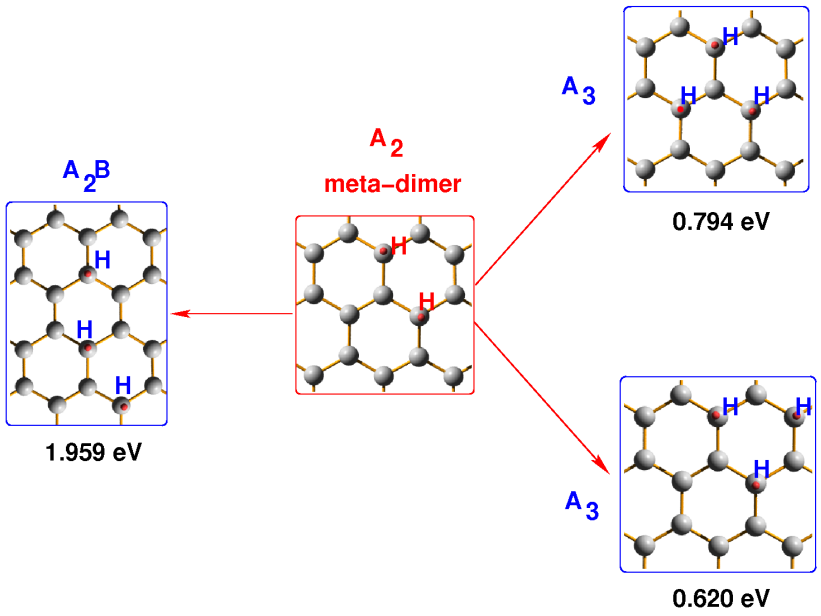
[2]

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

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

3-atom clusters

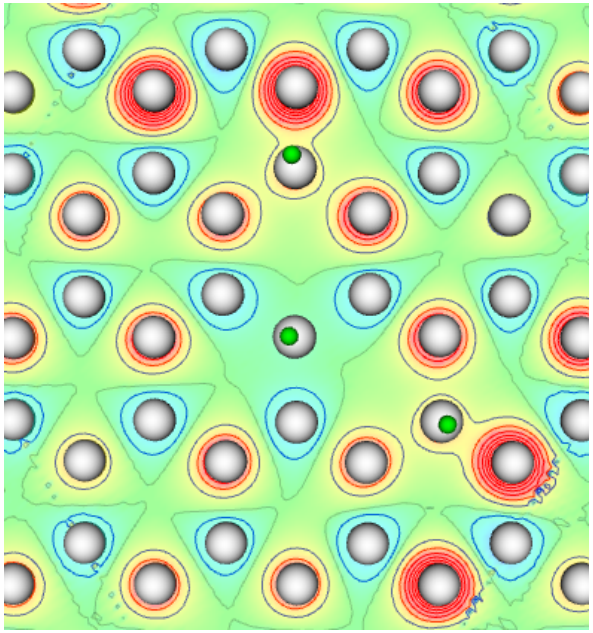




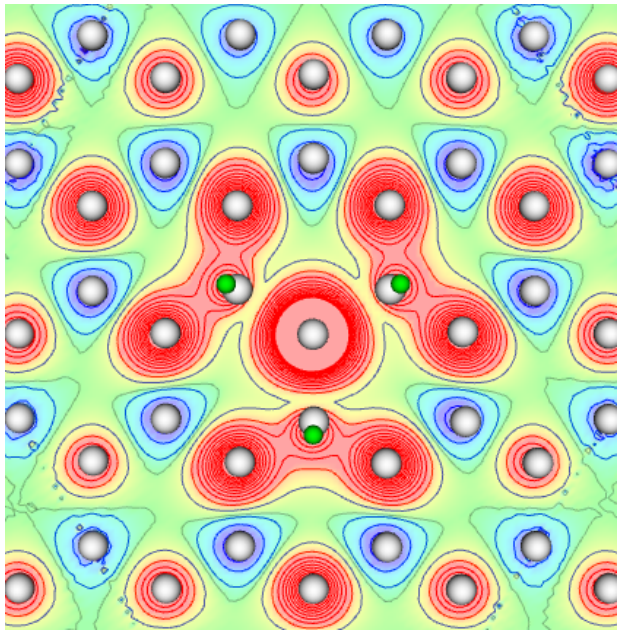
$$\mu = 1\mu_B \Rightarrow \mu = 2\mu_B \Rightarrow \mu = 3\mu_B$$

3-atom clusters

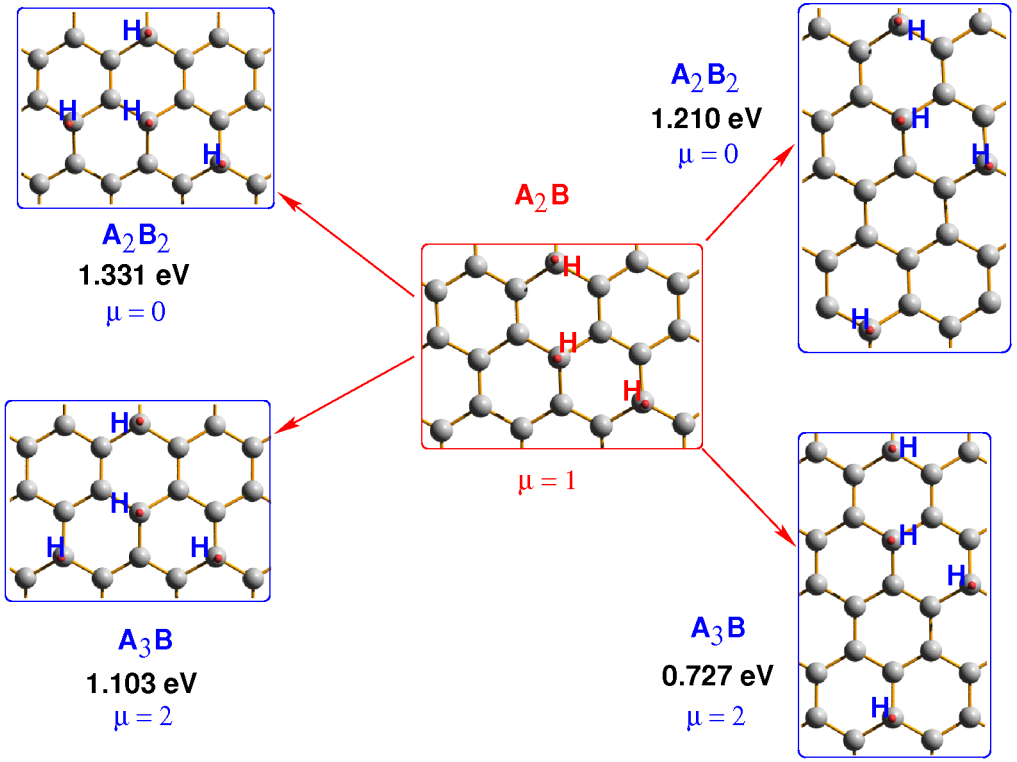
A_2B



A_3



4-atom clusters



Clustering of H atoms

Understanding adsorption of hydrogen atoms on graphene
S. Casolo, O.M. Lovvik, R. Martinazzo and G.F. Tantardini
J. Chem. Phys. **130** (2009) 054704

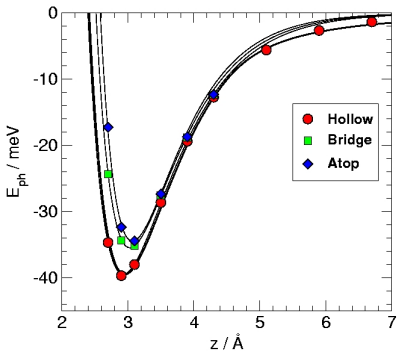
Technicalities

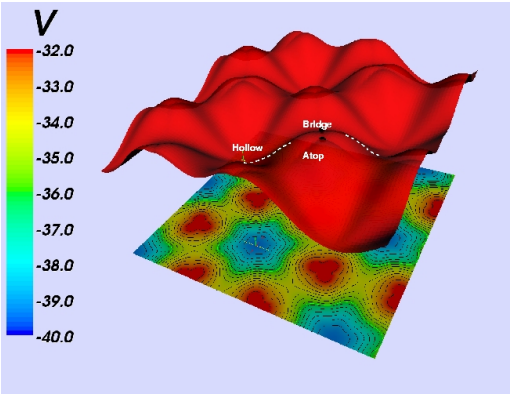
Many-body wf calculations

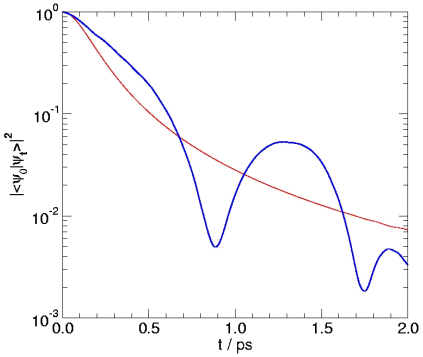
- Calculations with GAMESS and GAUSSIAN codes
- Atom centered cc-pVDZ basis-set
- Geometry optimizations at the DFT-(U)B3LYP level
- Complete Active Space (CASSCF) reference wavefunctions
- MultiReference QuasiDegenerate Perturbation Theory (MRQDPT) as implemented in GAMESS

Physisorption

Coronene-H [1]



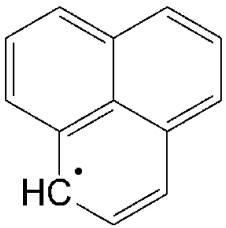




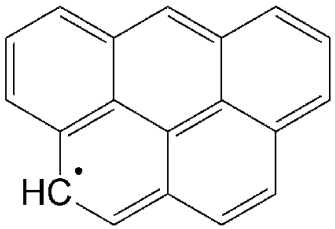
- HF-MP2 / aug-cc-pVDZ + BFs / CP-BSSE
- D_e = 39.5 meV *vs* D_e(exp)=39.2±0.5 meV
- E_{barr} = 4.0 meV, $D_{T=0K}$ = 1.7 10^{-4} cm^2s^{-1}

[1] M. Bonfanti, R. Martinazzo, G.F. Tantardini and A. Ponti, J. Phys. Chem. C 111, 5825 (2007)
[2] E. Ghio *et al.*, J. Chem. Phys. 73, 596 (1980)

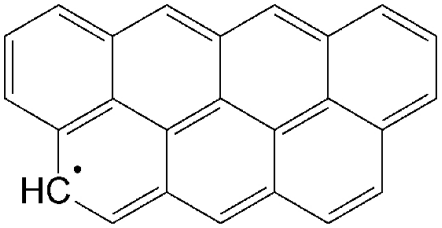
Systems



perinaftenile / fenalene

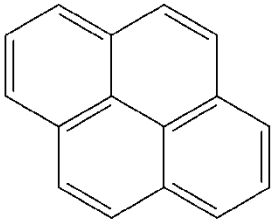


benzo[cd]pirenile

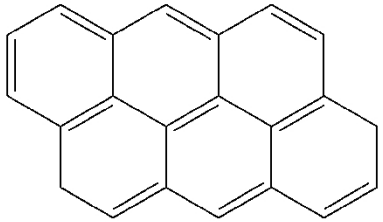


7 - PAH

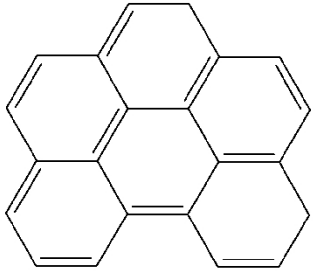
open-shell ‘PAHs’



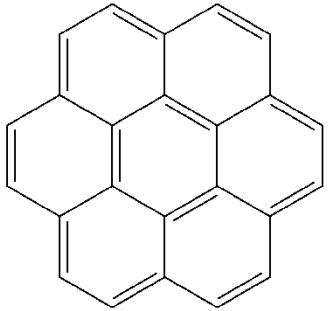
pirene



dibenzo[def,mno]crisene / antrantrene



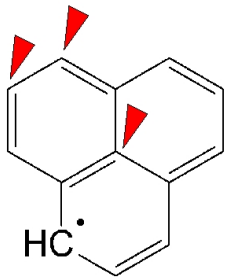
benzo[ghi]perilene



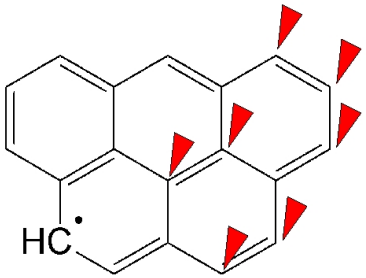
coronene

closed-shell PAHs

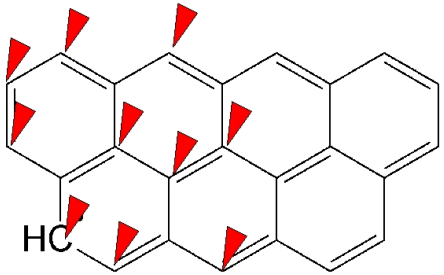
Systems



perinaftenile / fenalene

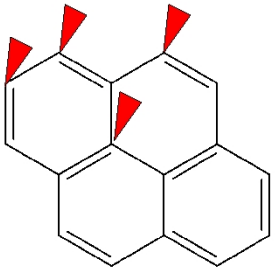


benzo[cd]pirenile

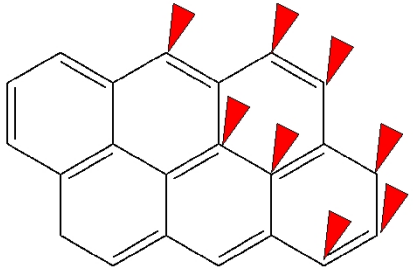


7 - PAH

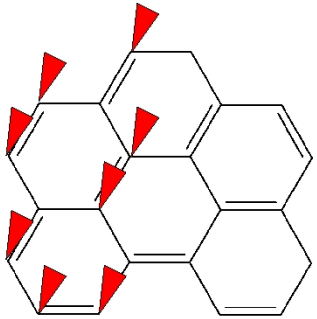
open-shell ‘PAHs’



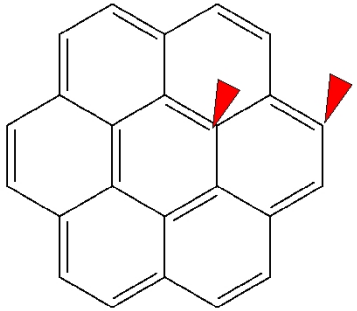
pirene



dibenzo[def,mno]crisene / antrantrene



benzo[ghi]perilene

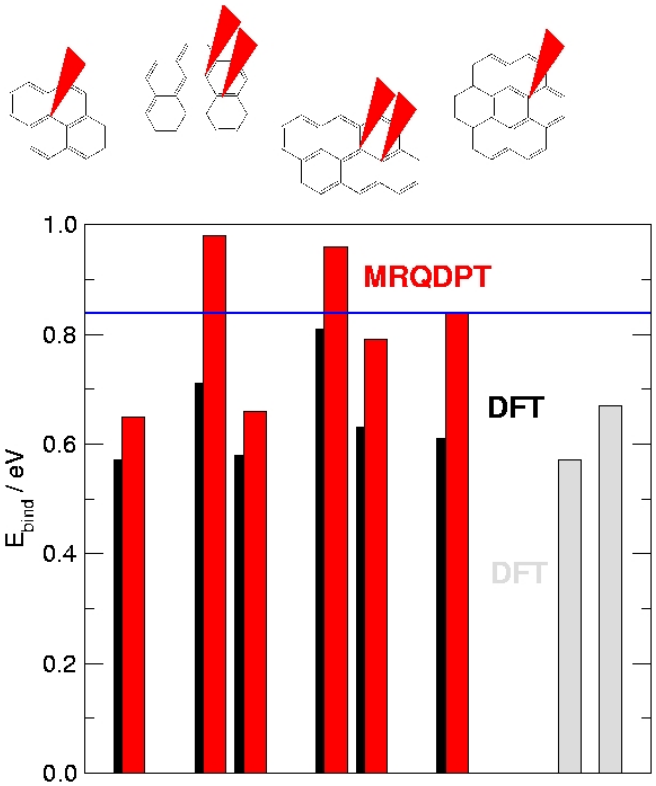


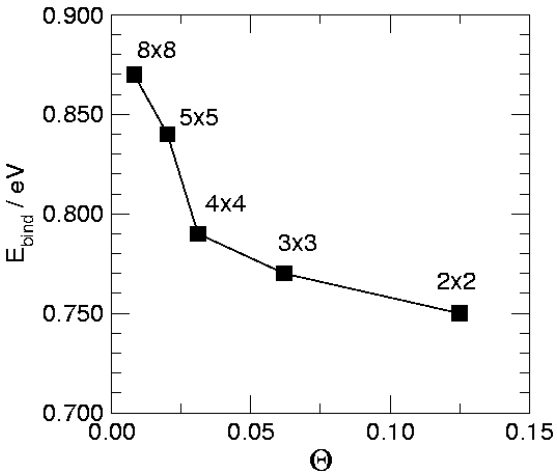
coronene

closed-shell PAHs

Closed-shell PAHs

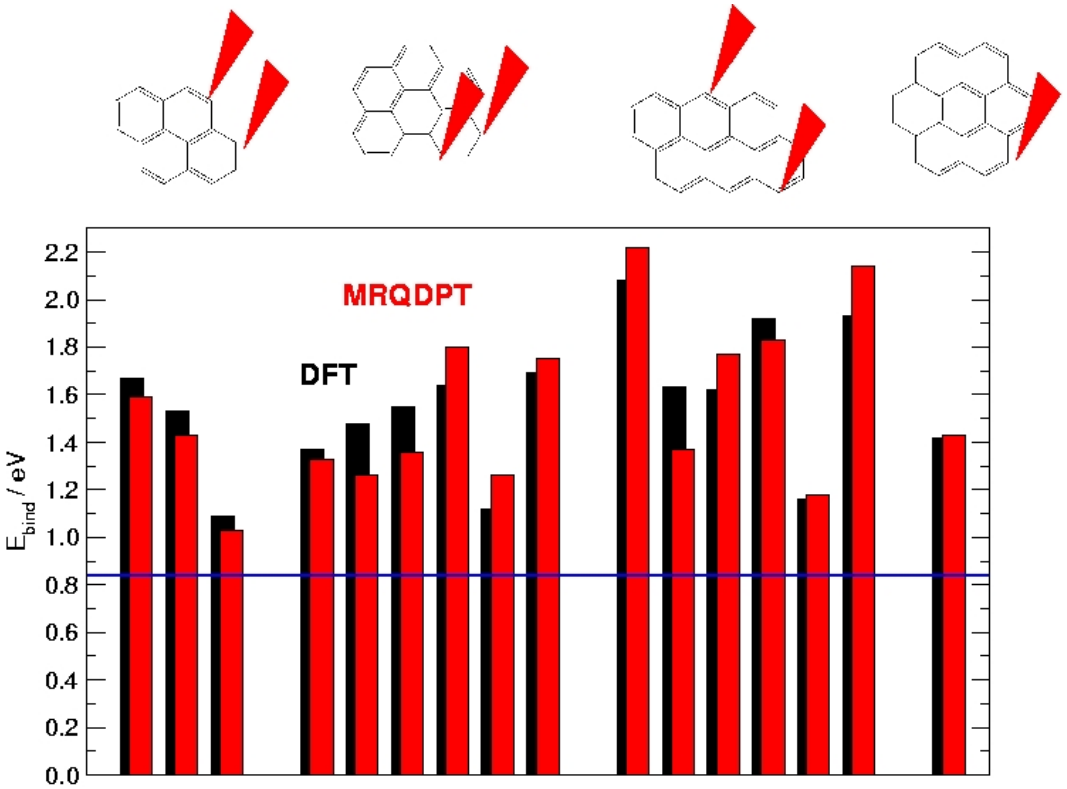
Graphitic carbons





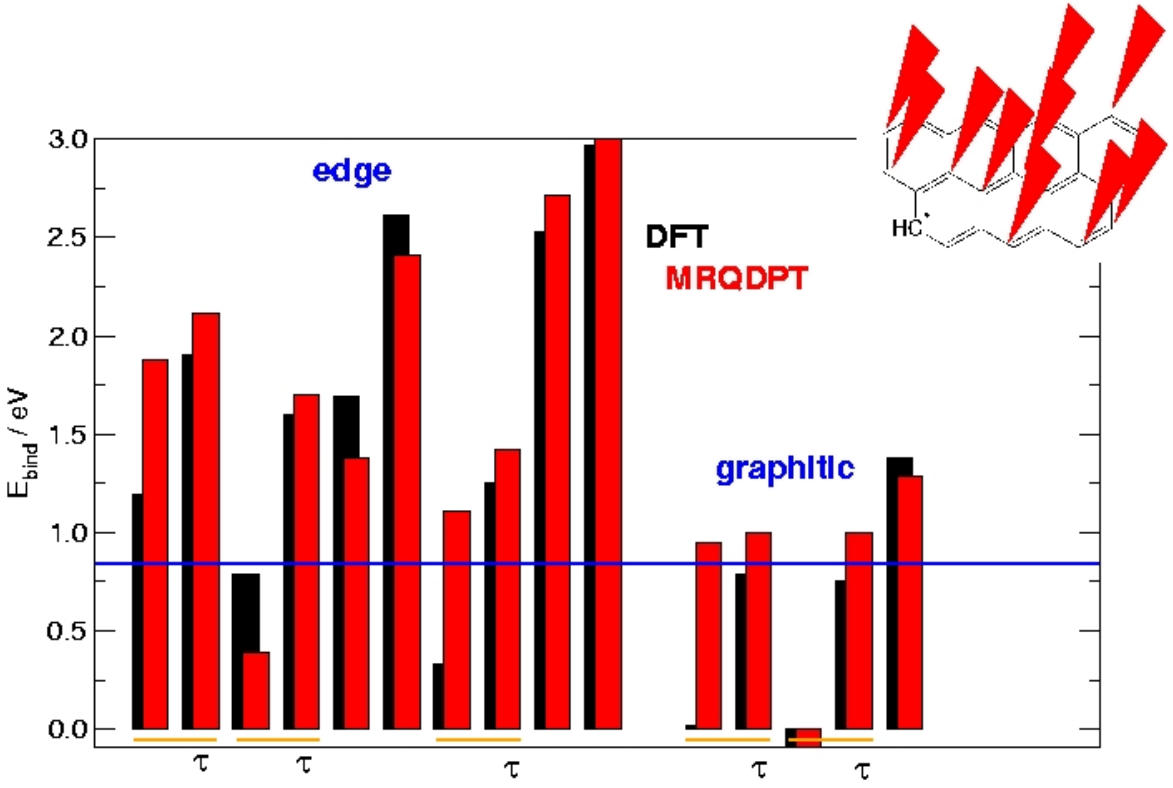
Closed-shell PAHs

Edge carbons



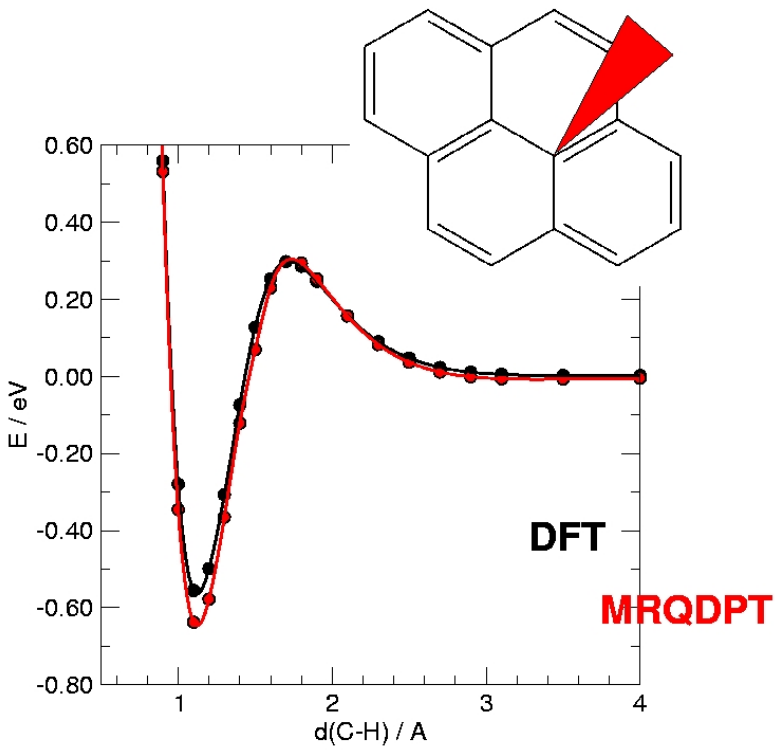
Open-shell PAHs

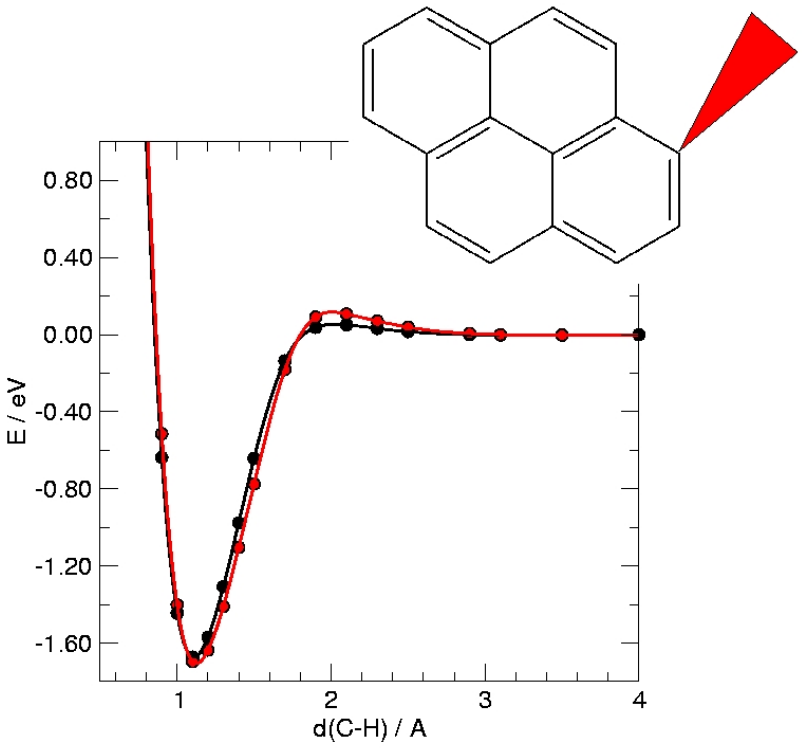
Example: PAH{7:2}



Adsorption paths

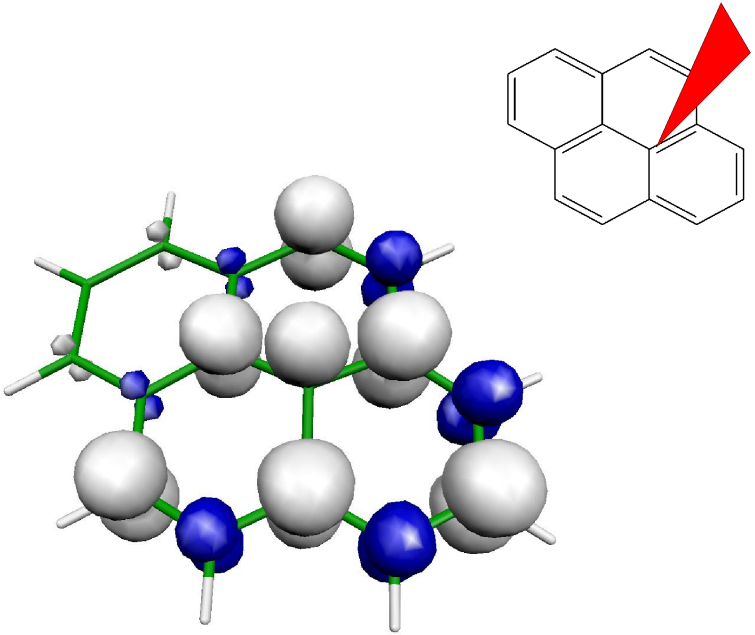
Closed-shell

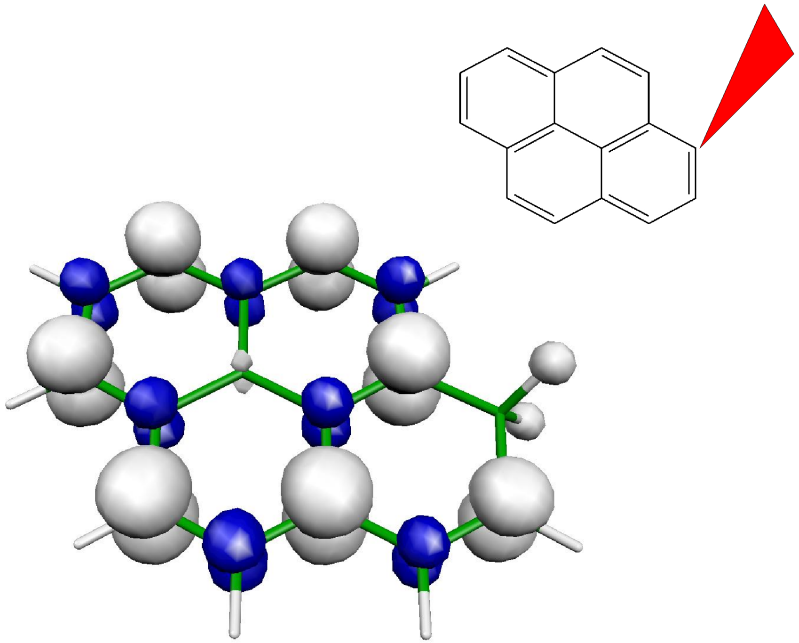




Spin-density

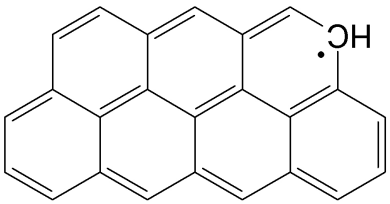
H + Closed-shell PAH

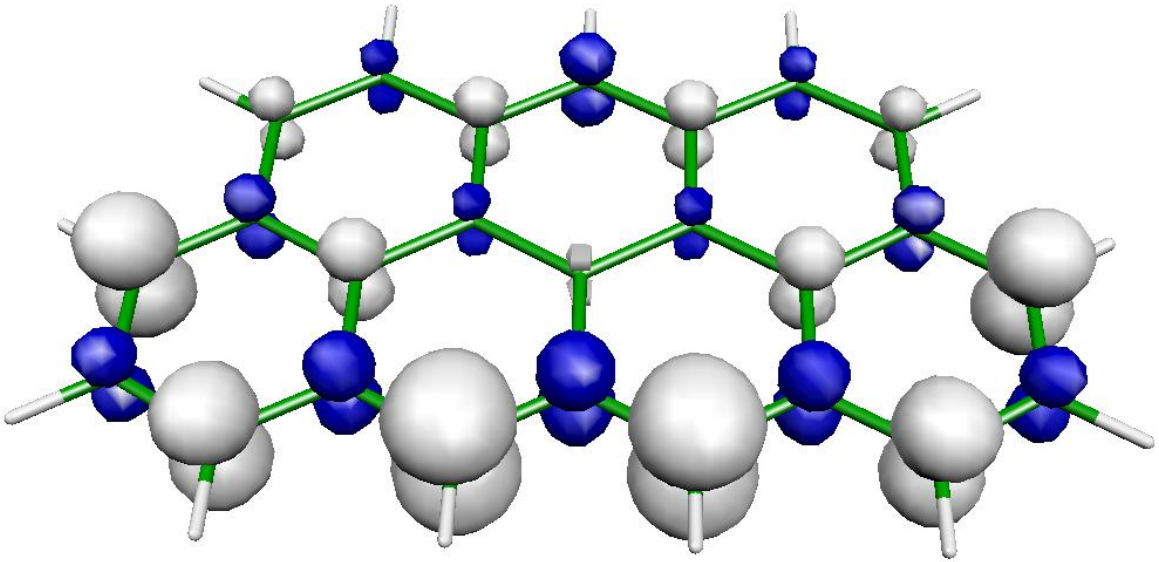




Spin-density

Open-shell PAH





Clustering of H atoms

Hydrogen affinity and magnetic properties of sub-nanographenes
M. Bonfanti, R. Martinazzo, A. Ponti and G.F. Tantardini
In preparation

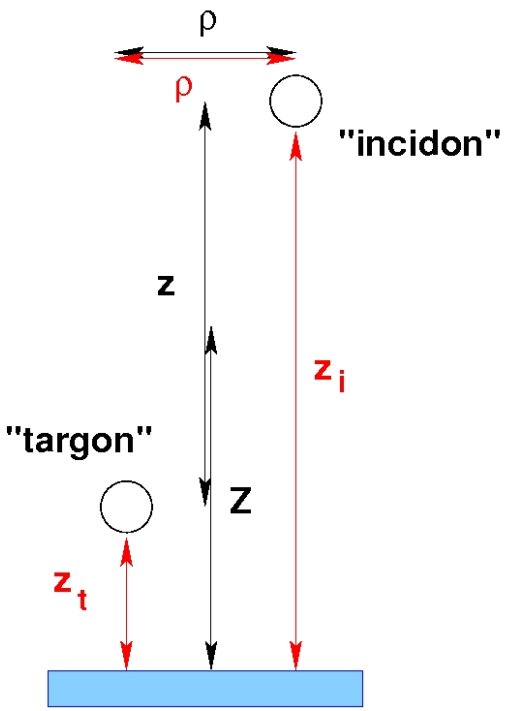
Outline

Technicalities

Time-Dependent Wavepacket calculations

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

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



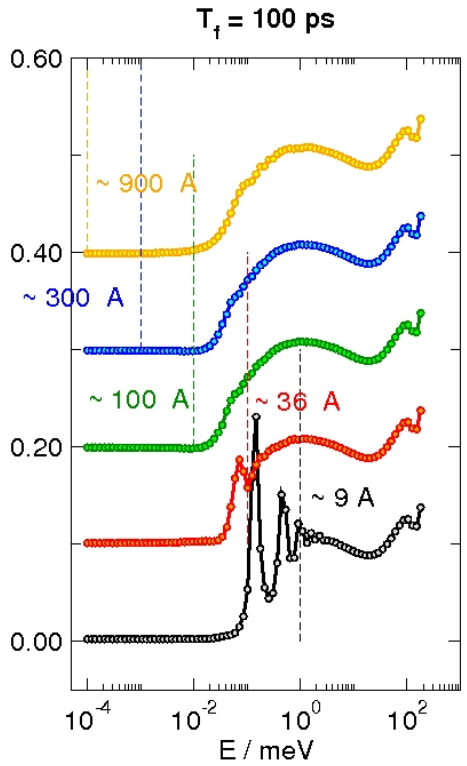
[1] M. Persson and B. Jackson, J. Chem. Phys. 102, 1078 (1995); D. Lemoine and B. Jackson, Comput. Phys. Commun. 137, 415 (2001)
[2] R. Martinazzo and G.F. Tantardini, J. Phys. Chem. A, 109 (2005) 9379; J. Chem. Phys. 124, 124703 (2006); J. Chem. Phys. 124, 124704 (2006)

Technicalities

TDWP calculations at low E_{col}

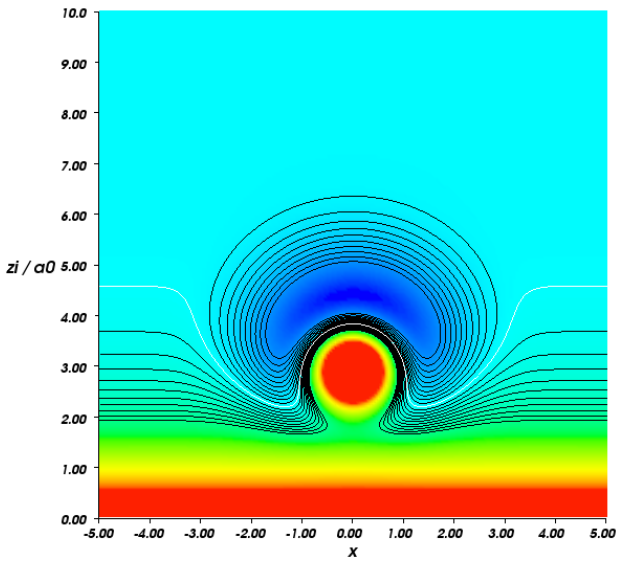
- Two-wavepacket approach[1]
- Transmission-free[2] absorbing potentials and Fourier mapping[3] in reagent coordinates

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

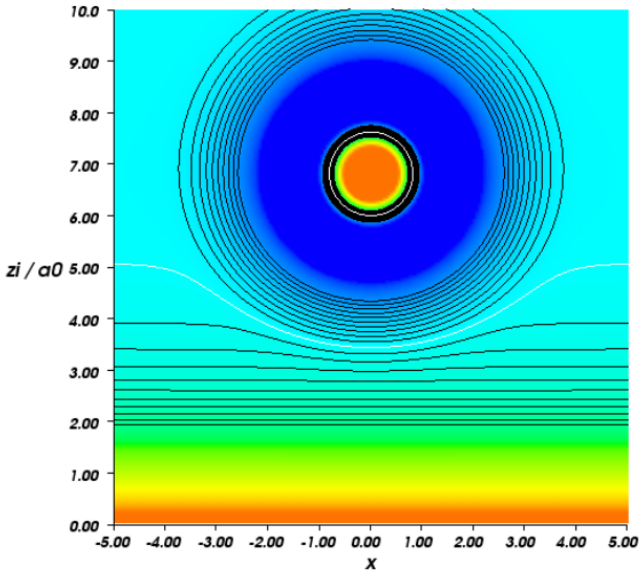


[1] R. Martinazzo and G.F. Tantardini, J. Chem. Phys. 122, 094109 (2005)
[2] D. Manolopoulos, J. Chem. Phys. 117, 9552 (2002)
[3] A.G. Borisov, J. Chem. Phys. 114, 7770 (2001)

Potential Energy Surfaces[1]



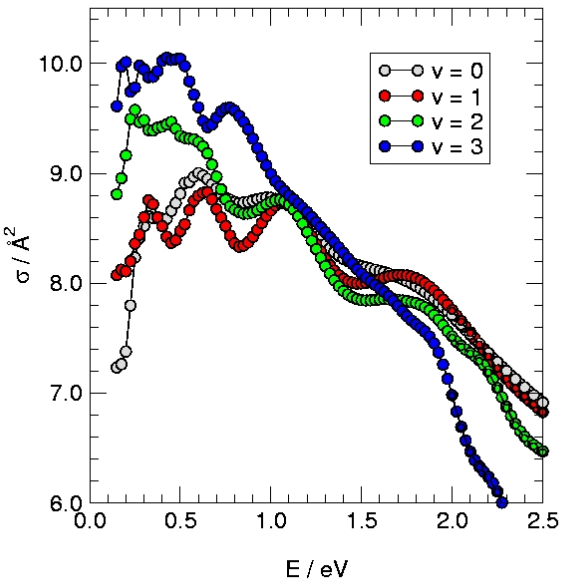
Chemisorbed target H (z_{eq})

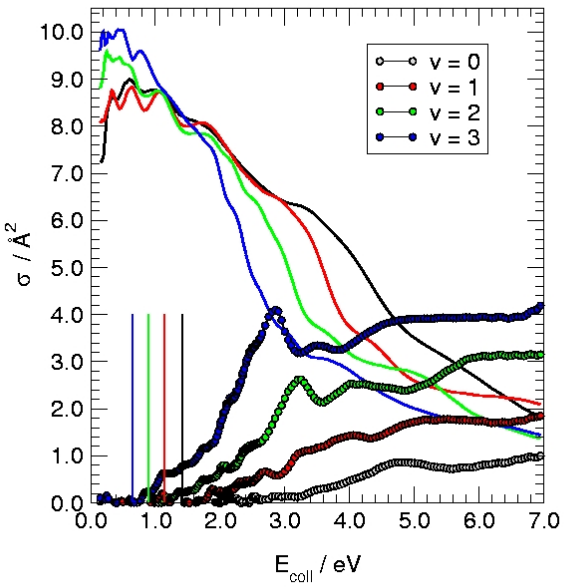


Physisorbed target H (z_{eq})

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

I. H-chemisorbed case

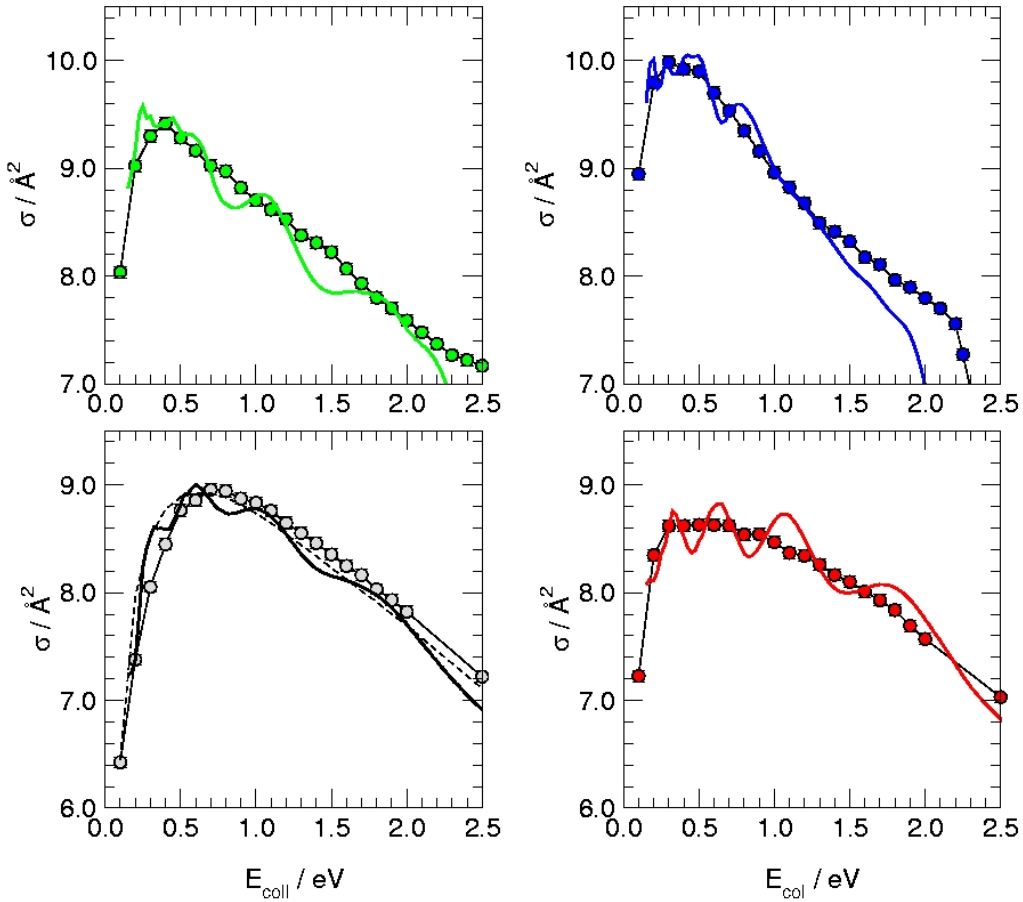




We find oscillations in both ER and CID xsections

I. H-chemisorbed case

Eley-Rideal



Quantum vs (quasi) classical dynamics: quantum effects

I. H-chemisorbed case

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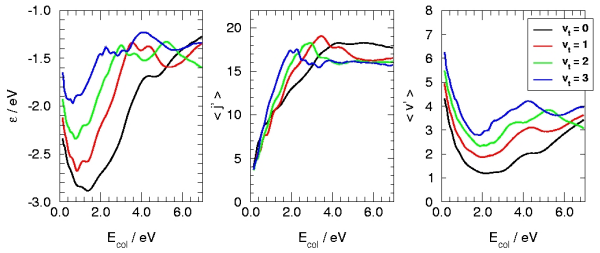
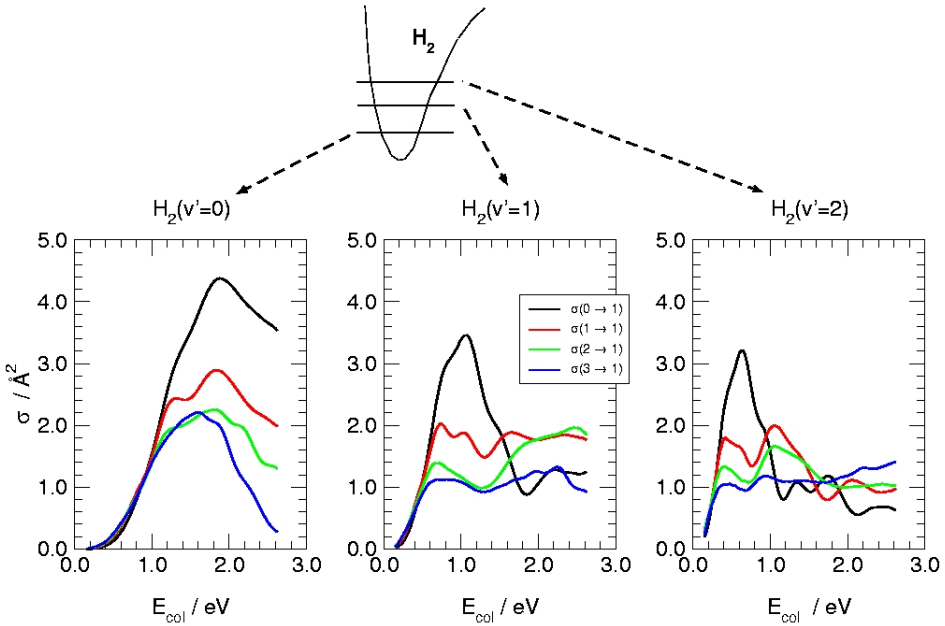
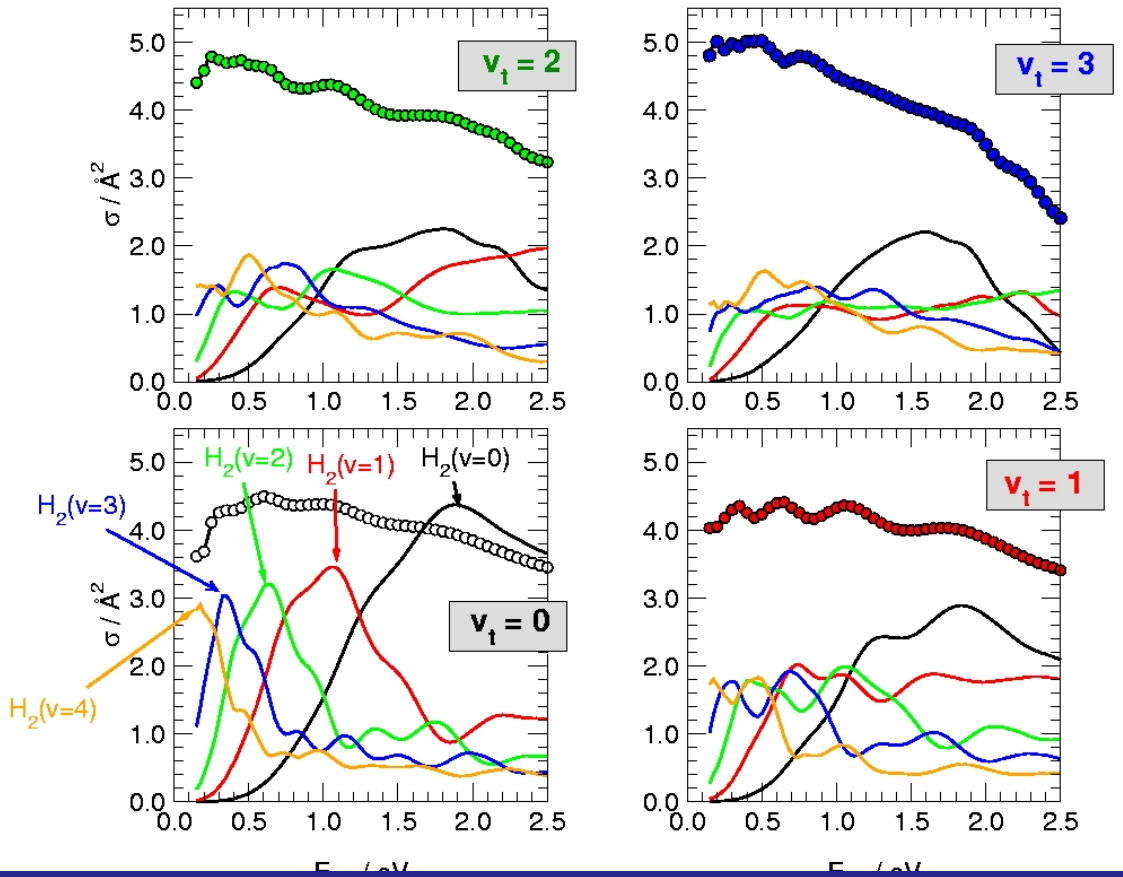




- Product molecules are internally hot
- Internal excitation is a steep decreasing function of E_{coll}

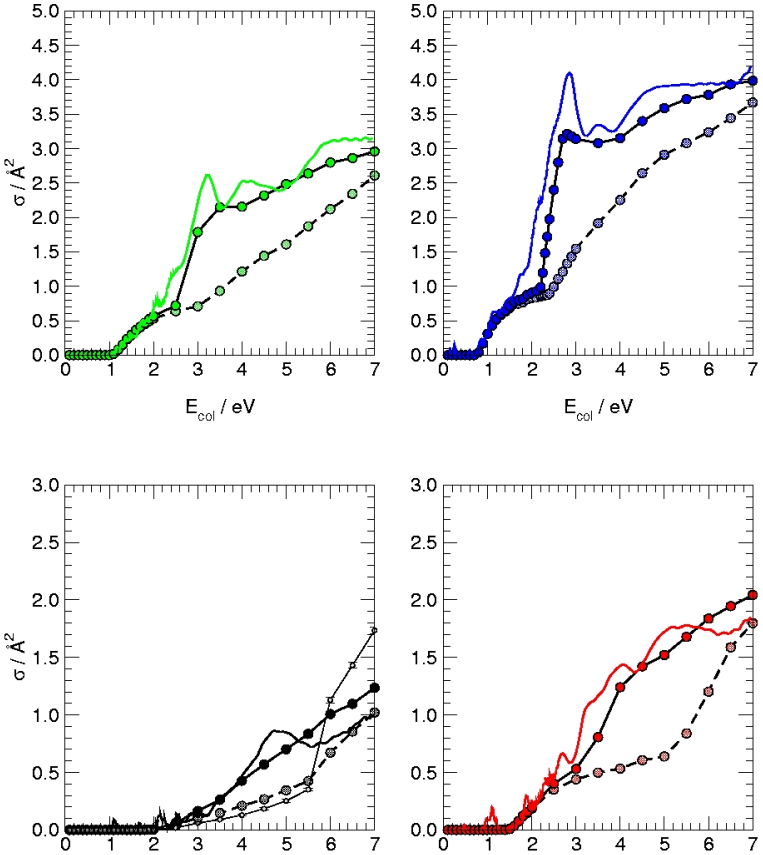
I. H-chemisorbed case

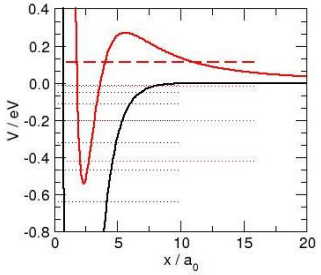
Eley-Rideal



I. H-chemisorbed case

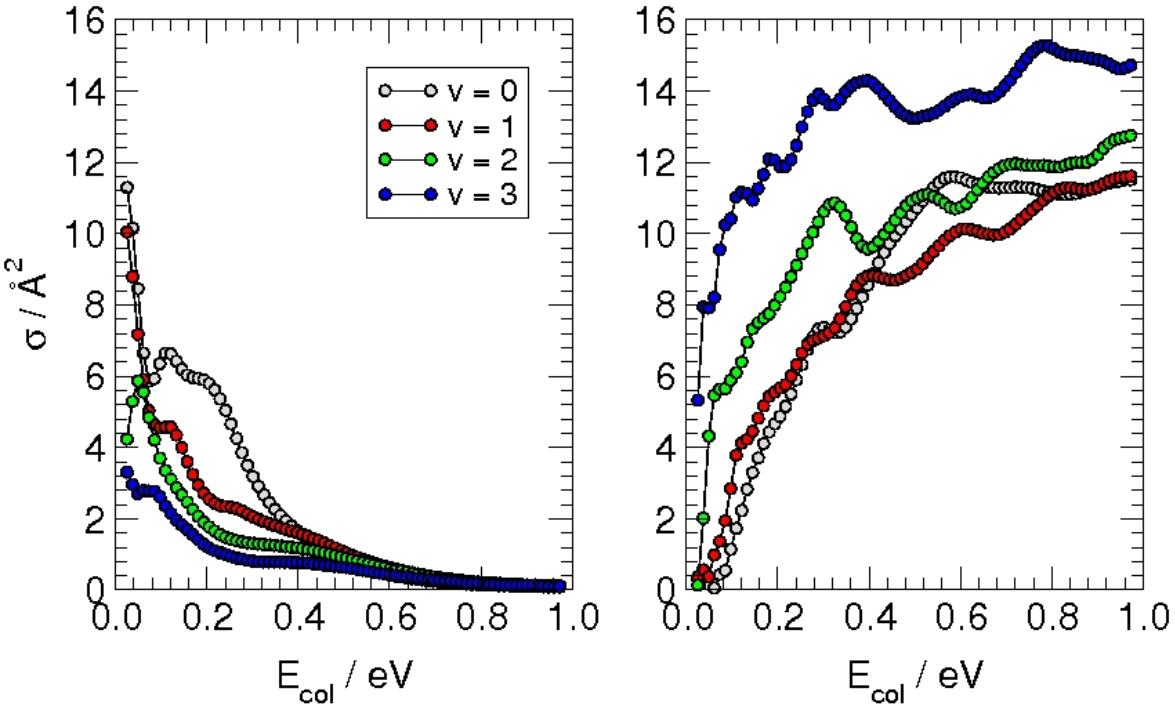
CID





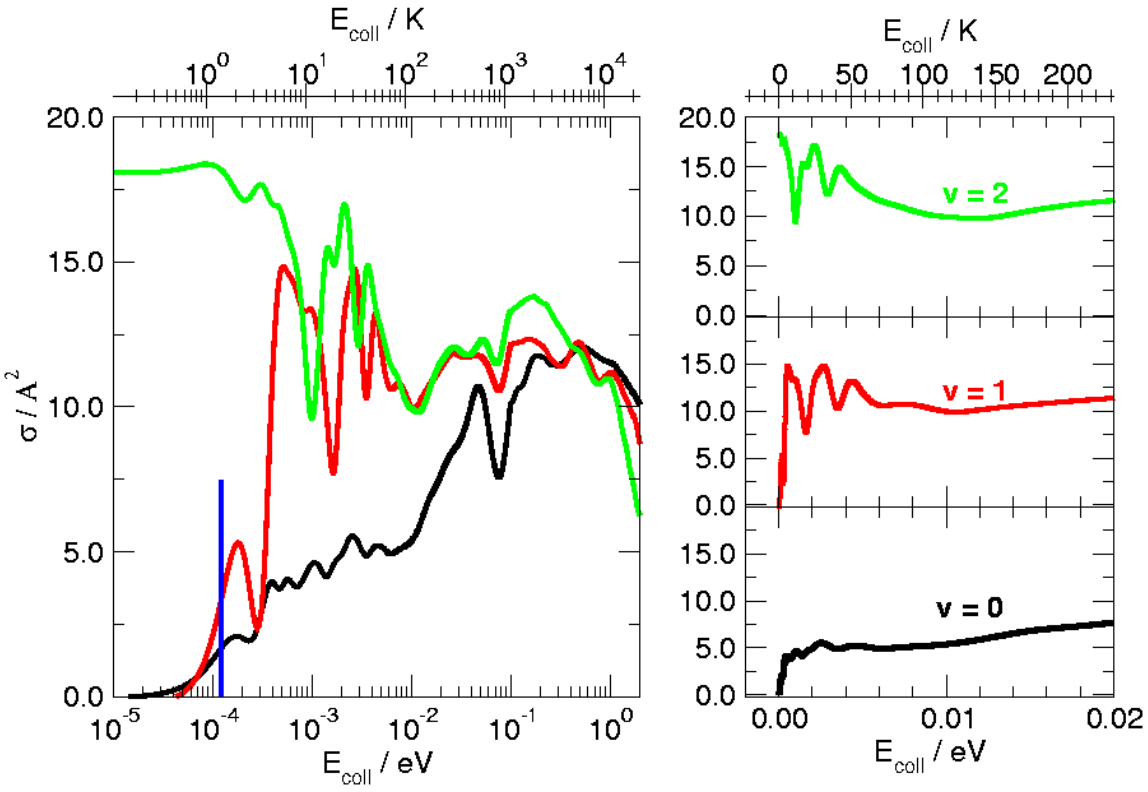
Quantum vs (quasi) classical dynamics: indirect CID

II. H-physisorbed case



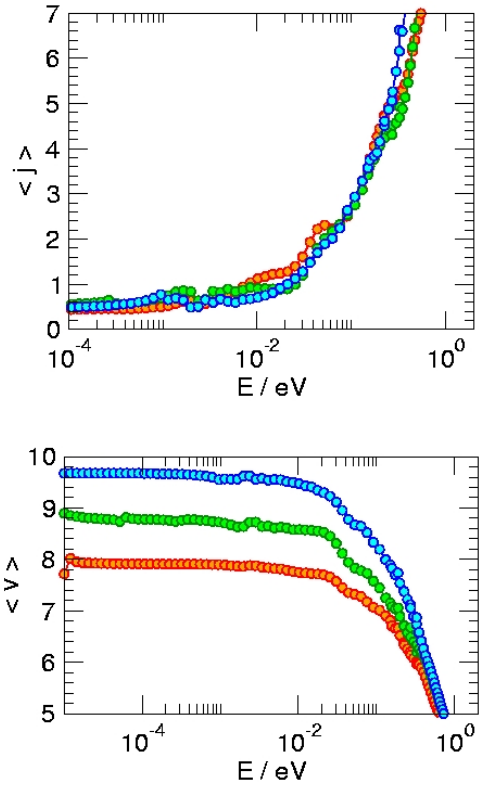
I. H-chemisorbed case

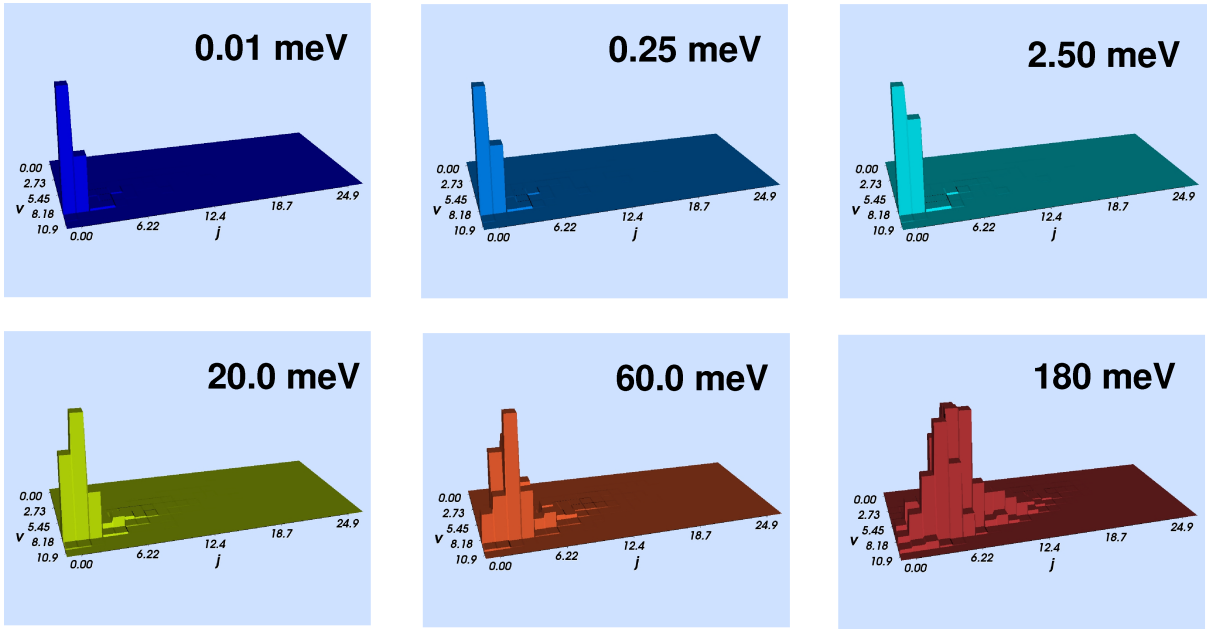
Eley-Rideal



I. H-chemisorbed case

H_2 rovibrational excitation





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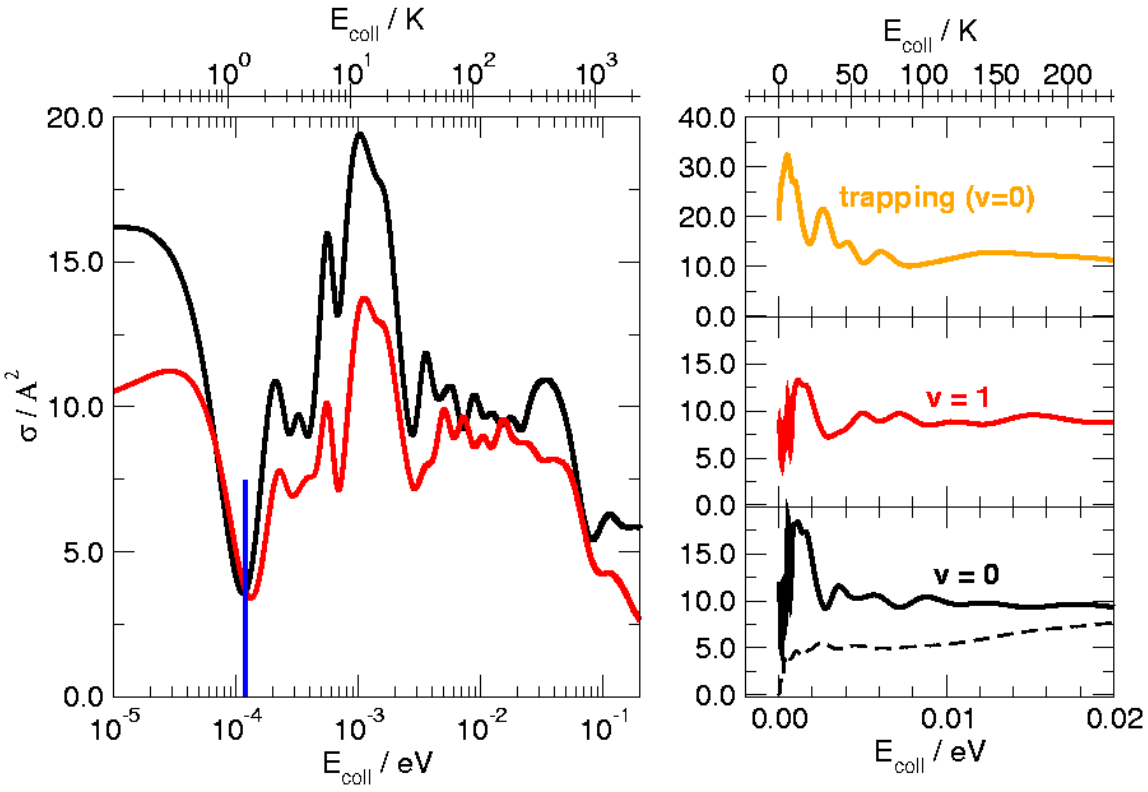
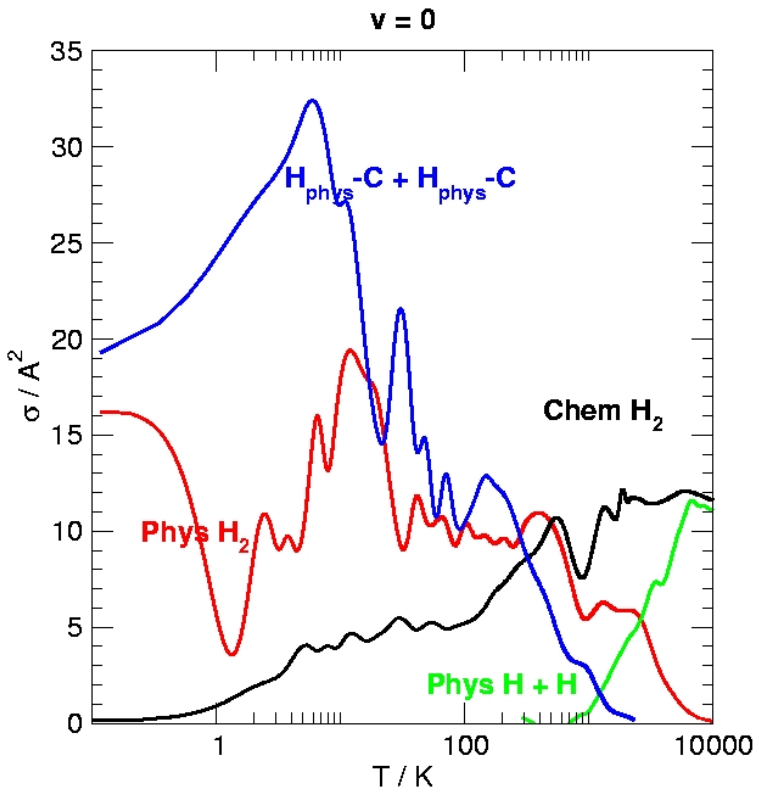


H-chem vs H-phys



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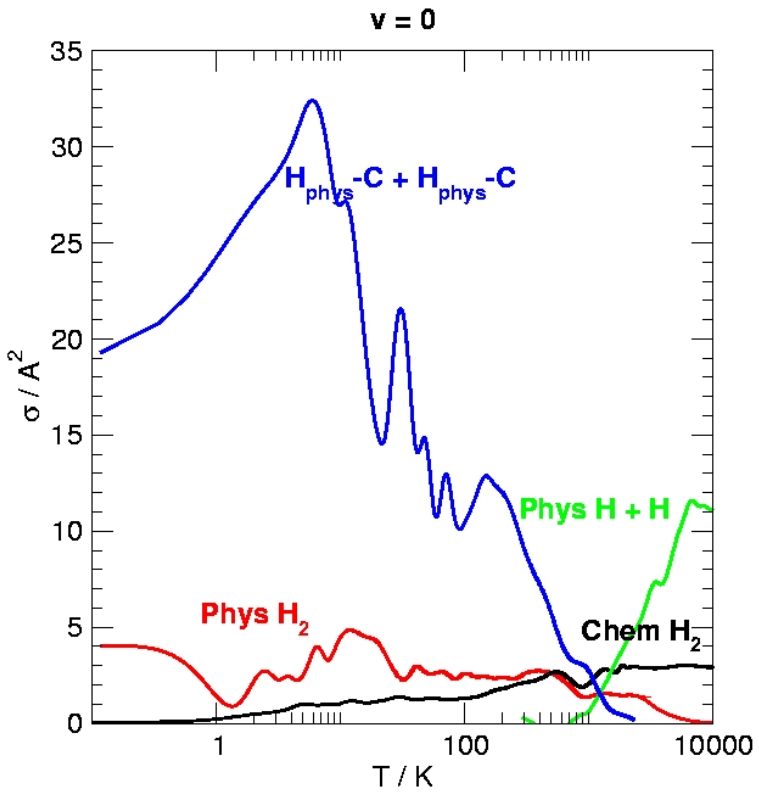


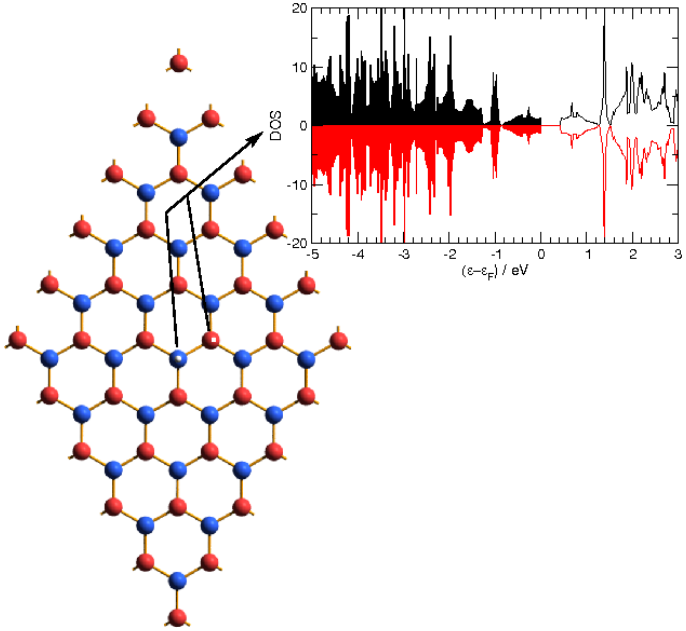
Cross-sections have to be corrected for the spin-factor (1/4)

Summary

- Thermodynamically and kinetically favoured H clusters minimize sublattice inbalance
- Adsorption on magnetic C-substrates is roughly governed by spin density only
- Adsorption on edges is favoured (even for small systems)
- Eley-Rideal recombination is efficient but limited by quantum reflection at low energy
- Adsorbate-induced trapping in the physisorbed regime may be important

Outlook

- Opening band gaps in graphene *via* surface chemistry



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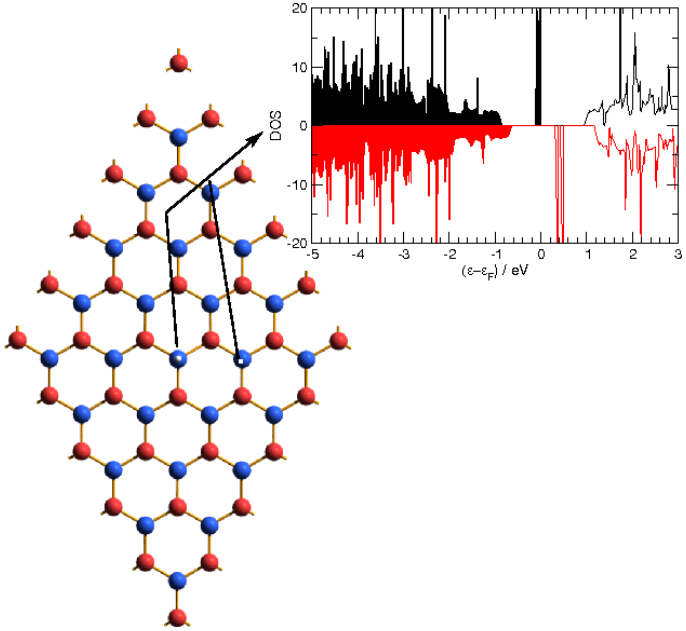

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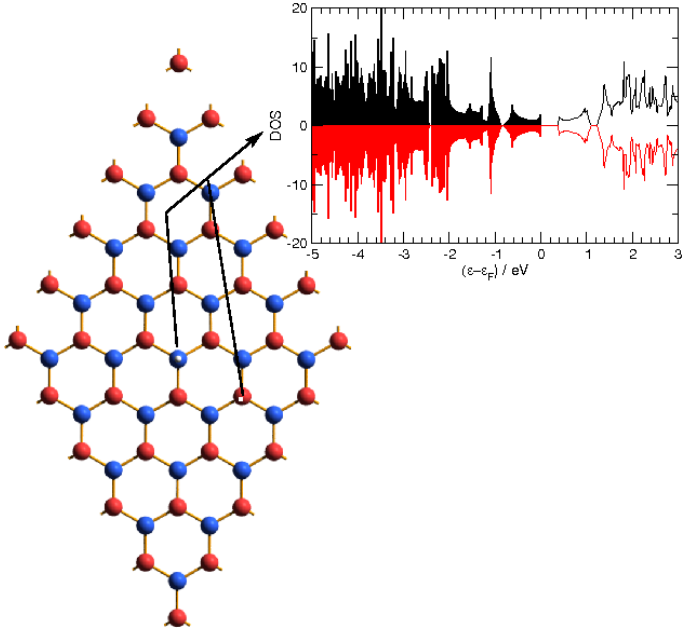

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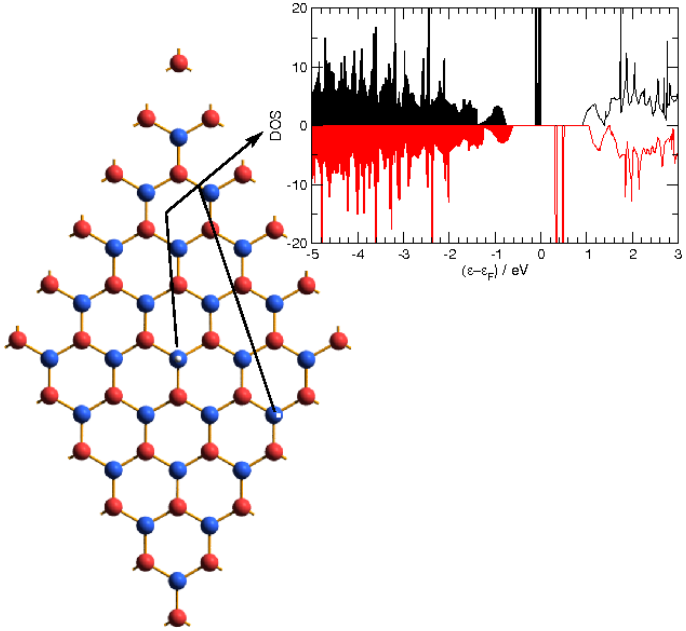

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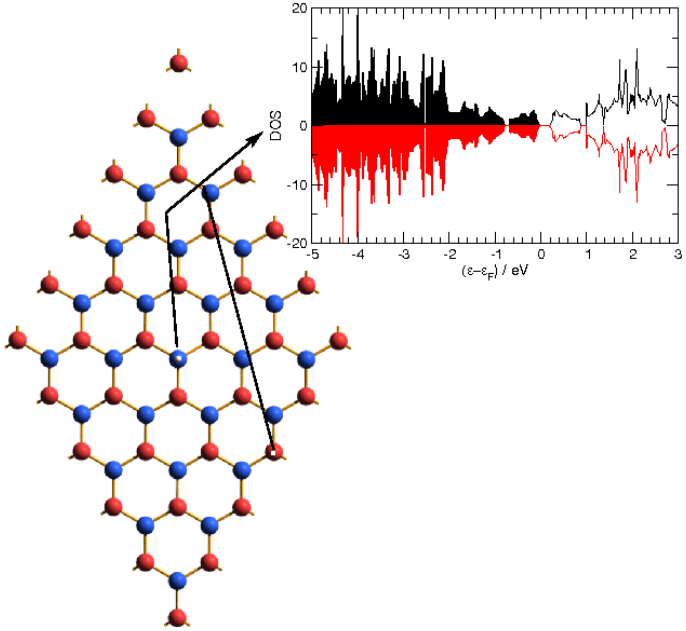
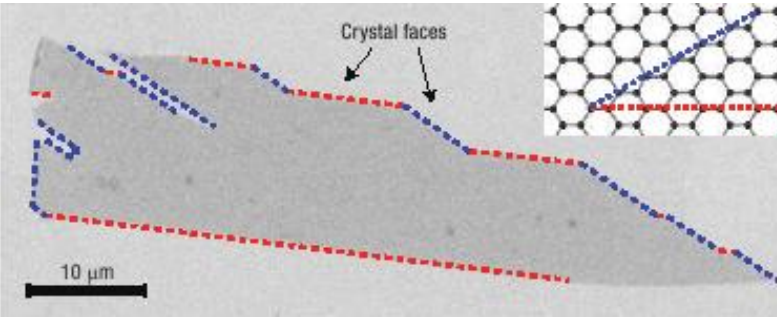
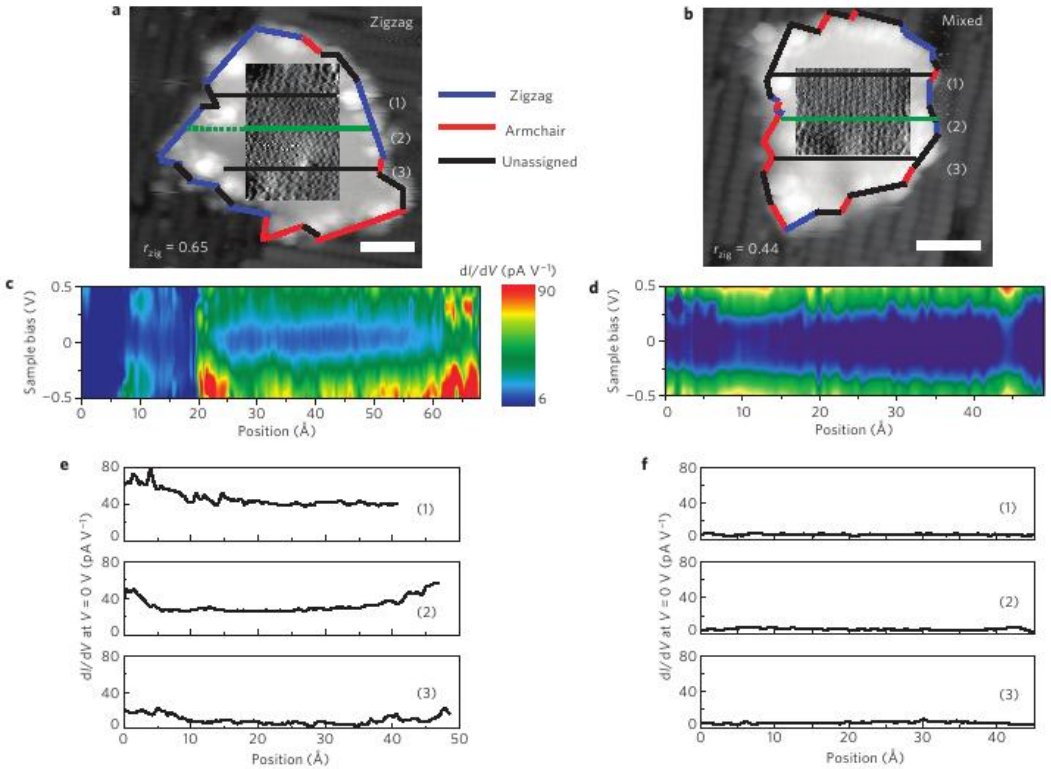


Outlook

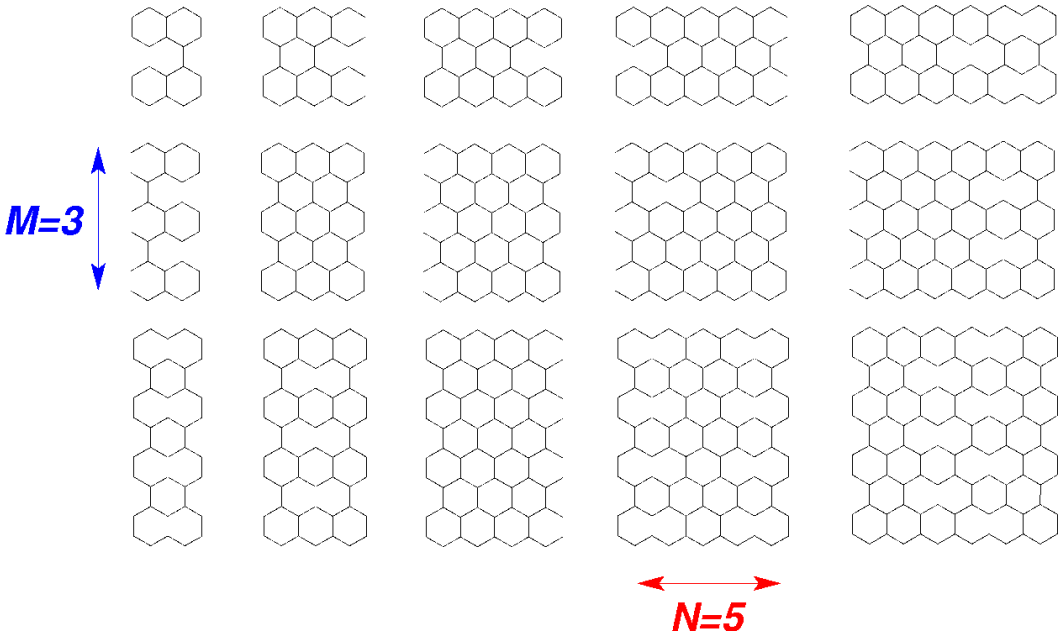
- Edges properties are extremely intriguing..





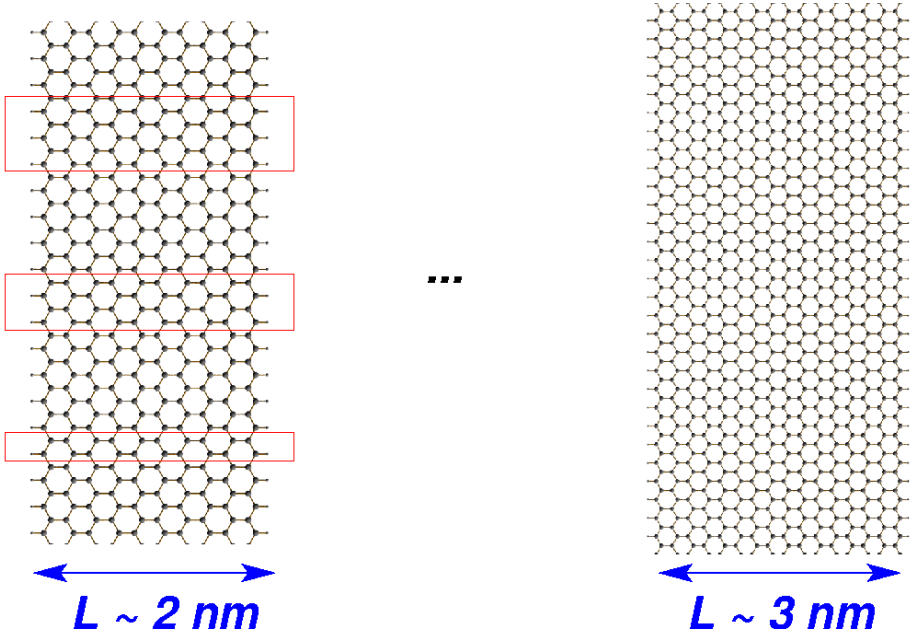
Outlook

..CASSCF calculations



Outlook

..and periodic DFT



Outlook

- dissociative chemisorption of hydrogen molecules at edges
- first principles study of sticking dynamics
- diffusion energetics and dynamics of chemisorbed hydrogen atoms
- ...

Thank you for your attention!

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