A New Wide-BandGap Form Of Hydrogenated Graphene

Simone Casolo,
Rocco Martinazzo, Gian Franco Tantardini

Department of Physical Chemistry and Electrochemistry
Universitá degli Studi di Milano, Italy

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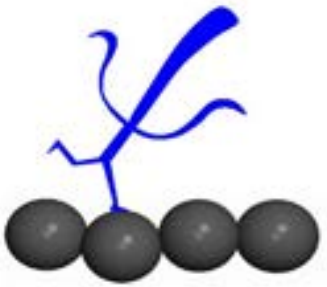
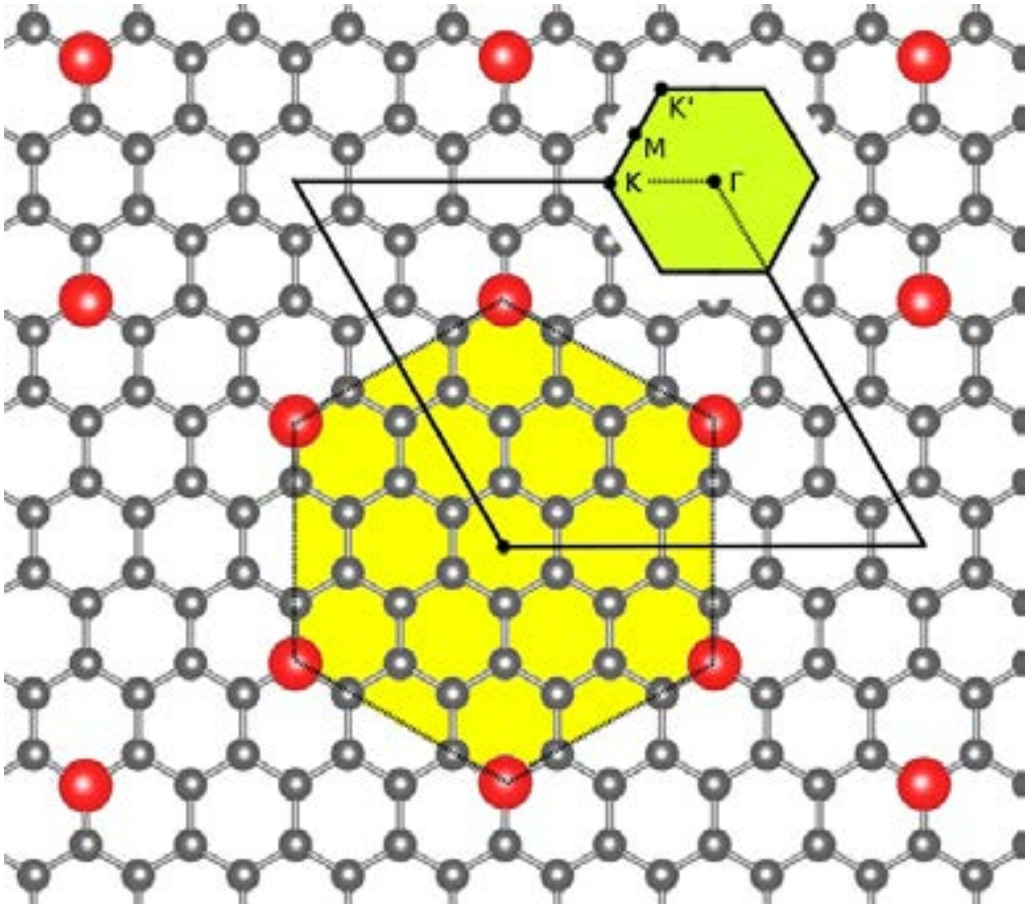


Honeycomb Superlattices
of vacancy, adsorbates, dopants, ...



Symmetrical arrangements of π defects open a large bandgap in graphene because of symmetry.

Phys. Rev. B **81** 245420 (2010), *J. Phys. Chem. C* **115** 3250 (2011)

Honeycomb Superlattices
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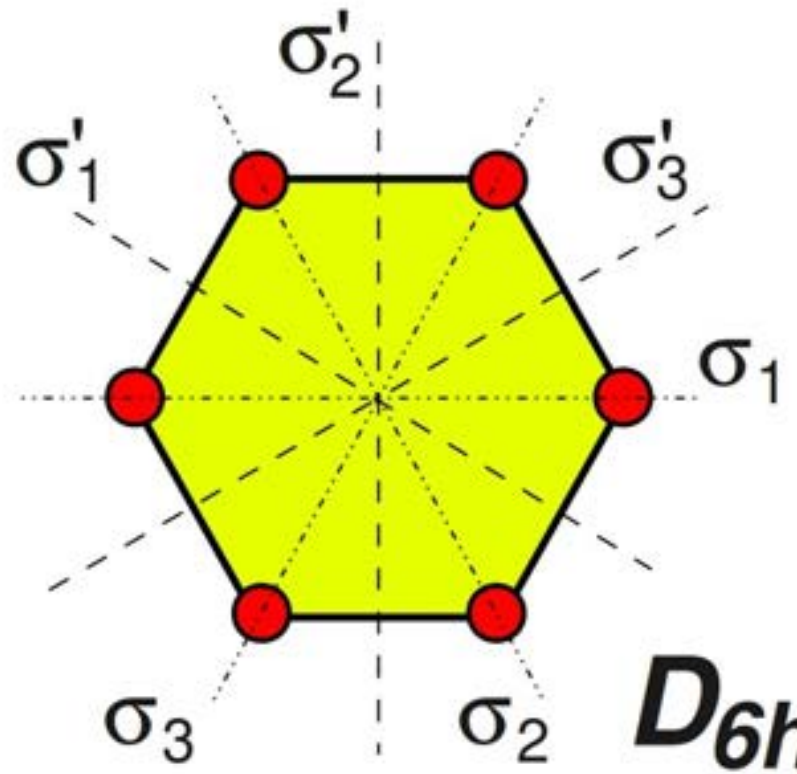
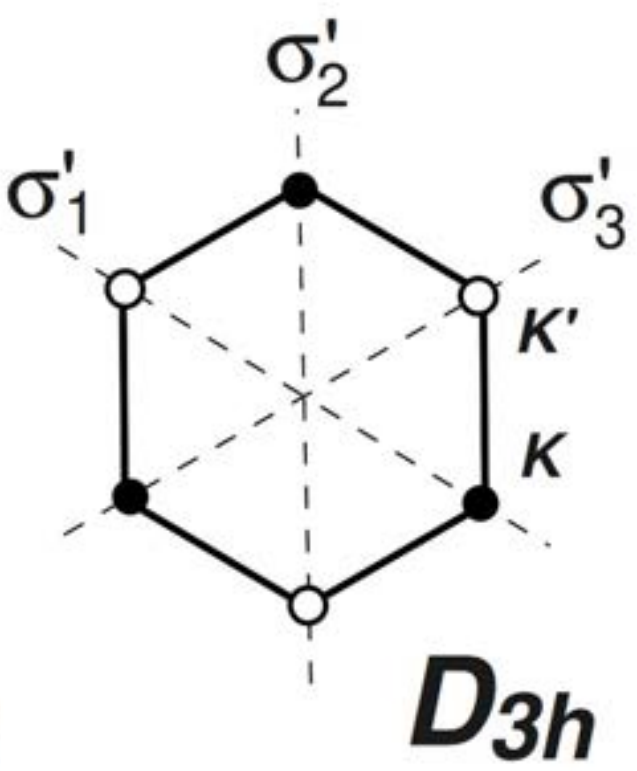




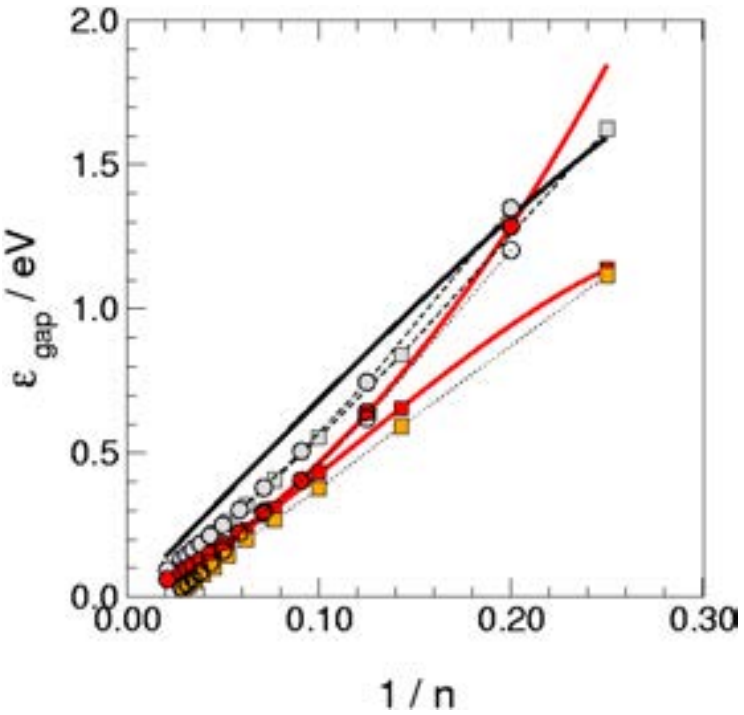
Wigner-Seitz

Brillouin zone

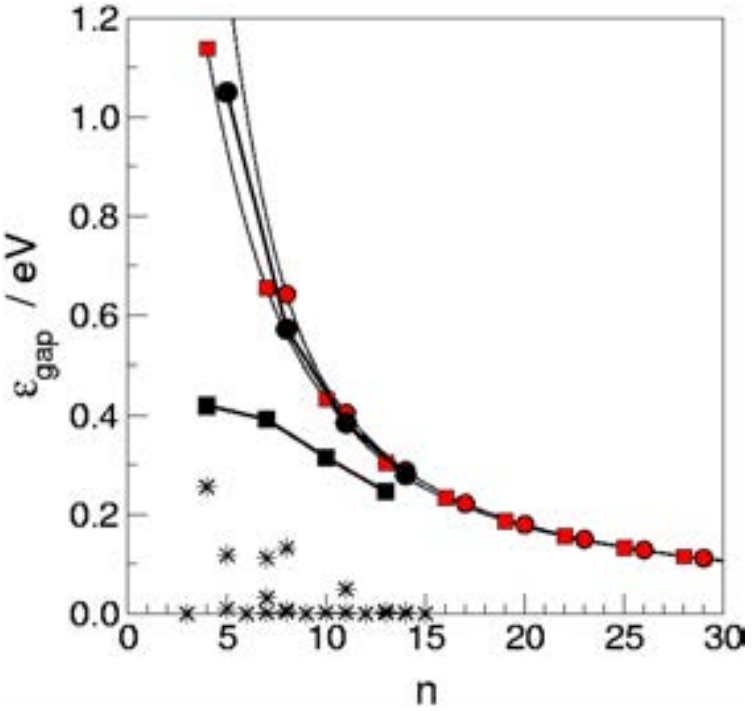
graphene symmetry holds

Honeycomb Superlattices
of vacancy, adsorbates, dopants, ...

Tight-binding

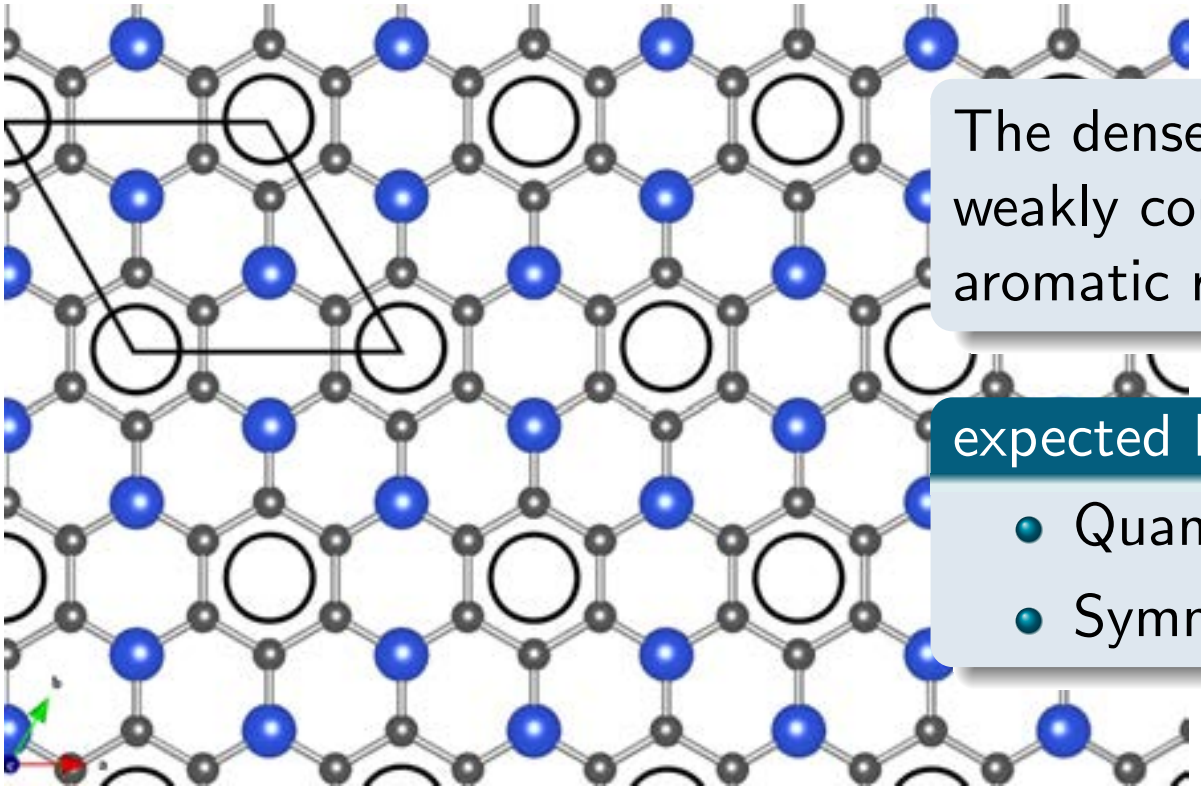


DFT



$$\epsilon_{gap}(K) \propto 1/n$$

Honeycomb Superlattices
of vacancy, adsorbates, dopants, ...



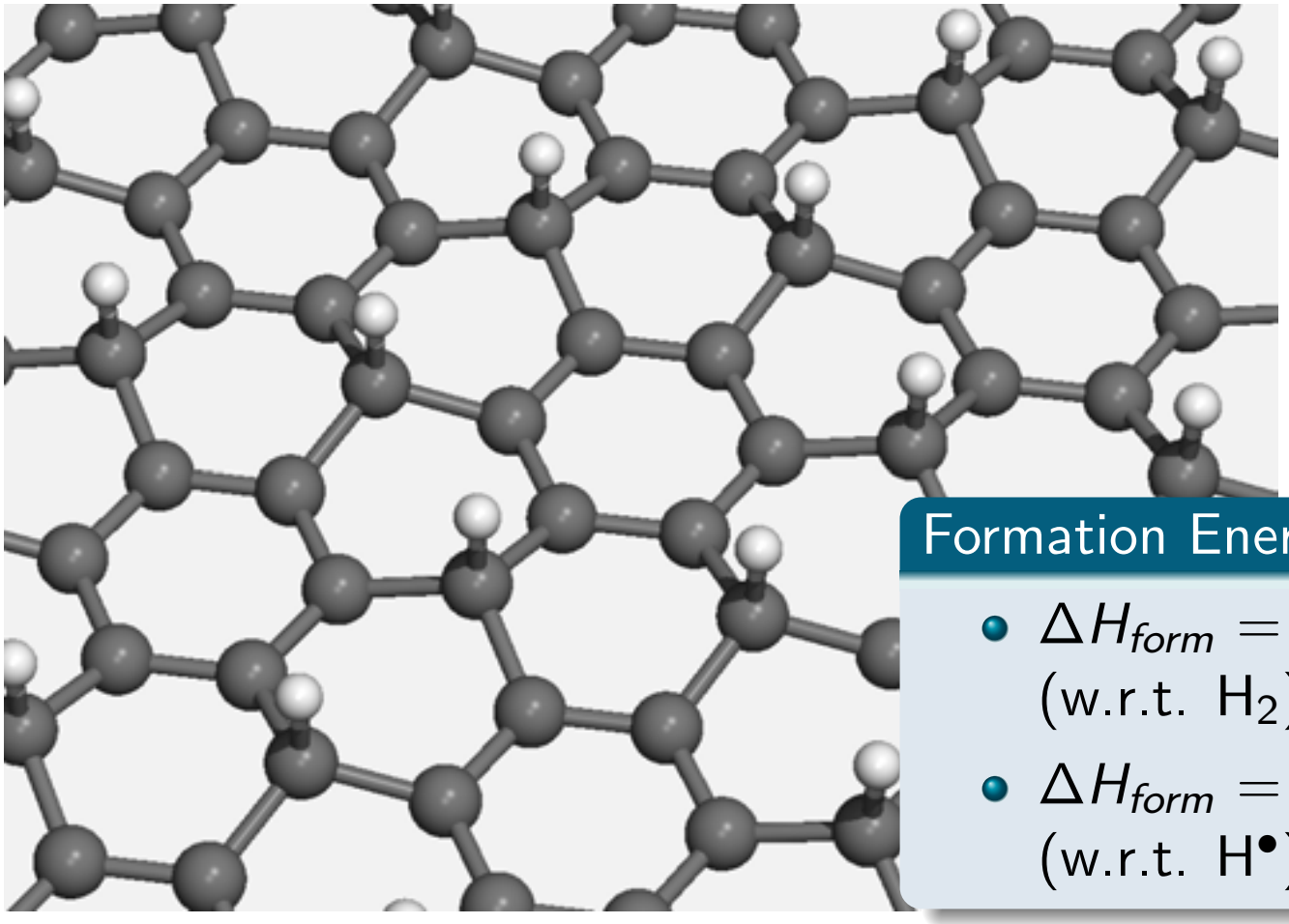
The dense limit would localize weakly coupled benzene-like aromatic regions.

expected band gap

- Quantum Confinement
- Symmetry Induced

this can be realized by selective hydrogenation of graphene

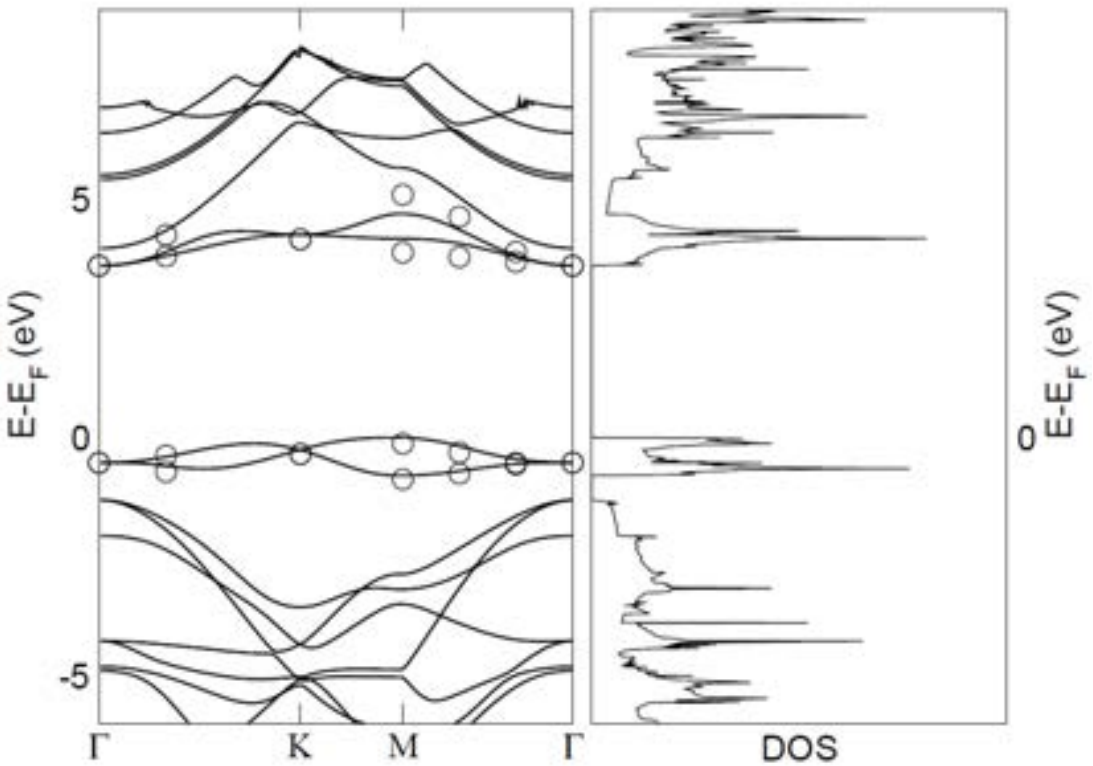
Honeycomb Hydrogenated Graphene
structure



Formation Energy

- $\Delta H_{form} = +118$ eV/atom (w.r.t. H_2)
- $\Delta H_{form} =$ -336 eV/atom (w.r.t. $H^{\bullet}$)

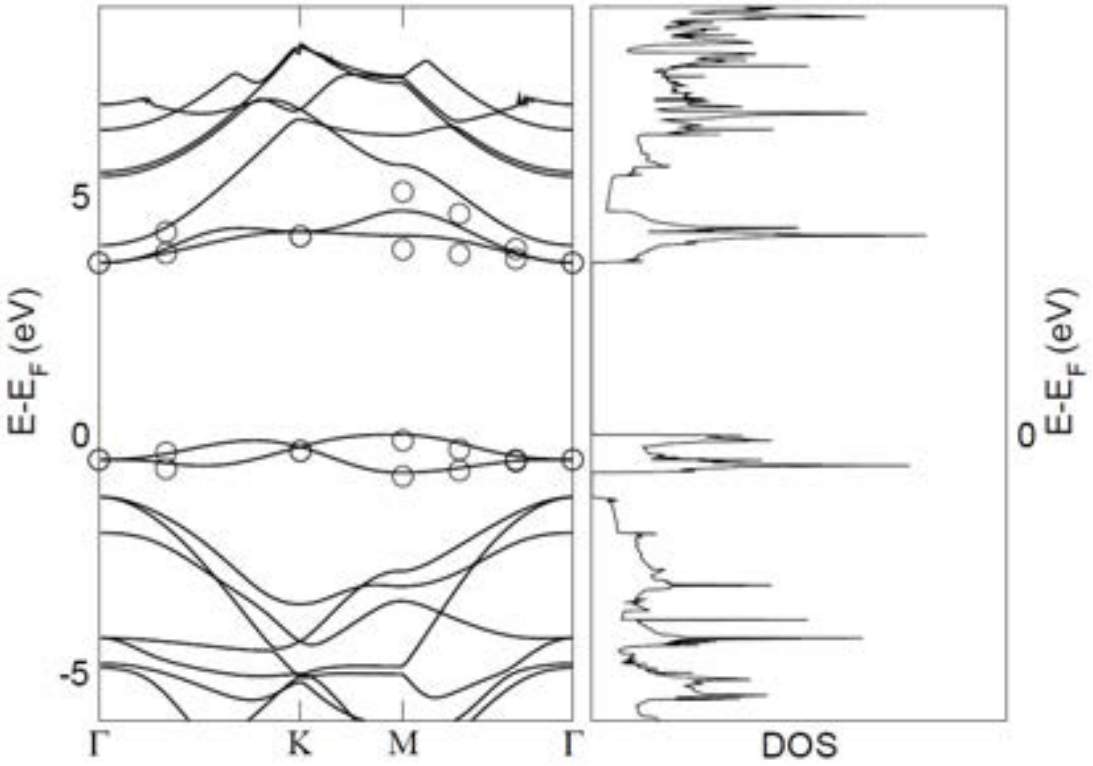
Honeycomb Hydrogenated Graphene
band structure



DFT Settings

- VASP code
- GGA-PBE 500 eV cutoff
- 15x15x1 k-points
- self-consistent GW
- 3x3x1 k-points

Honeycomb Hydrogenated Graphene
band structure



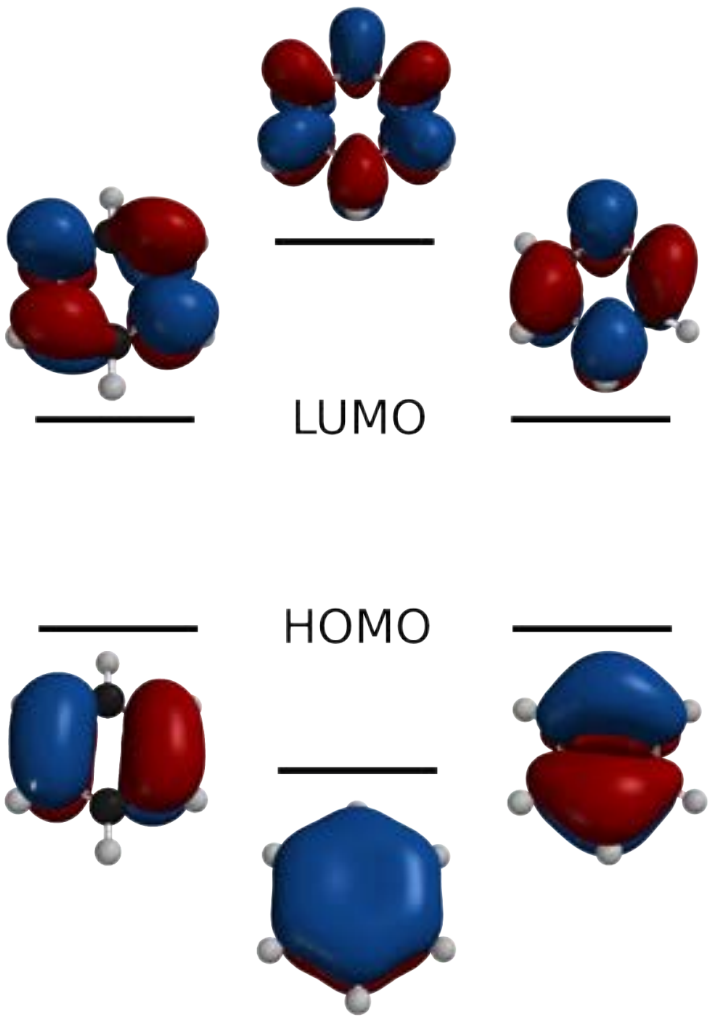
Band Gap

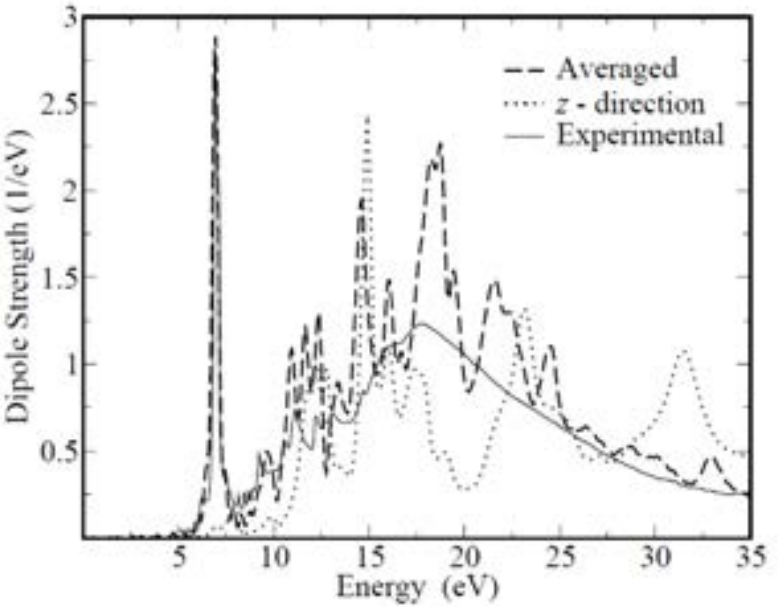
- PBE: 3.17 eV
- G_0W_0: 5.28 eV
- GW: 5.90 eV
- GW Graphane[1]: 5.4 eV
- GW Graphane[2]: 6.1 eV

[1] S. Lebégue, M. Klintenberg, O. Eriksson and M. I. Katsnelson, Phys. Rev. B. **79** 245117 (2009)

[2] M. Marsili and O. Pulci, J. Phys. D Appl. Phys. **43** 374016 (2010)

Honeycomb Hydrogenated Graphene
band edges

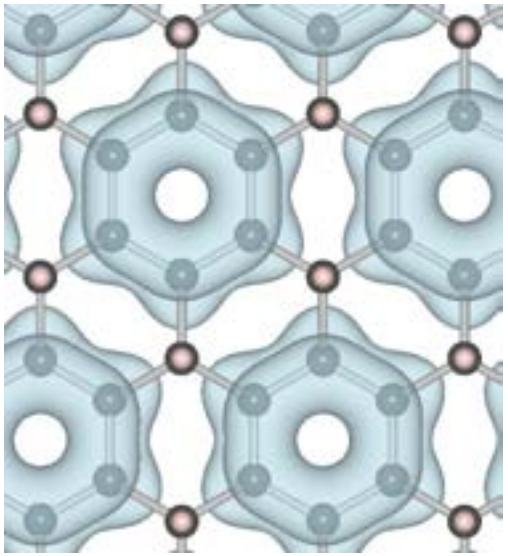


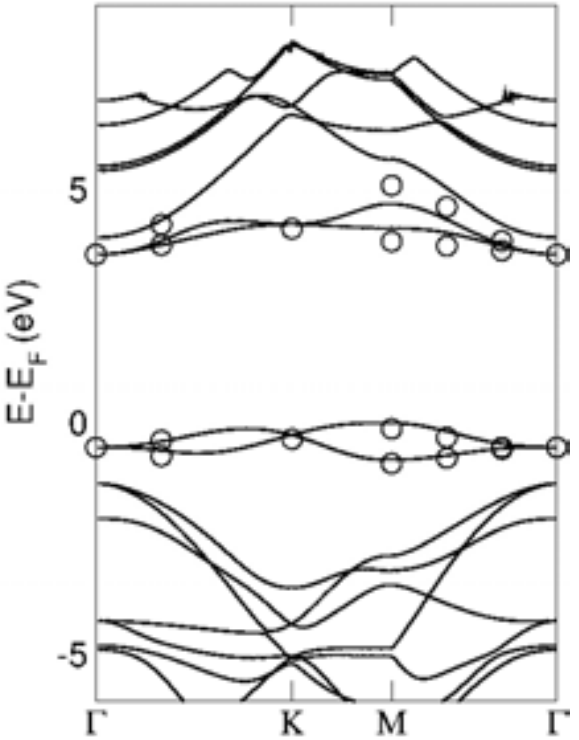


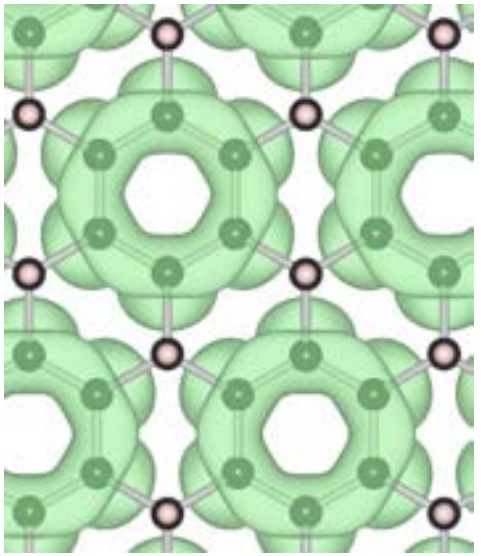
HOMO-LUMO Benzene

$\pi - \pi*$ transition at $\sim$ 7 eV in gas phase

Honeycomb Hydrogenated Graphene
band edges

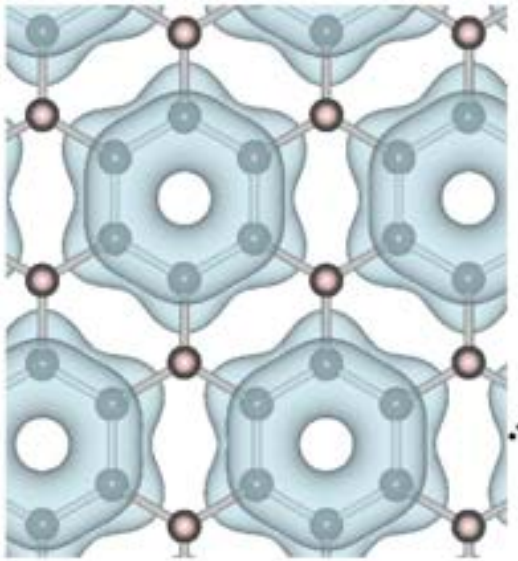


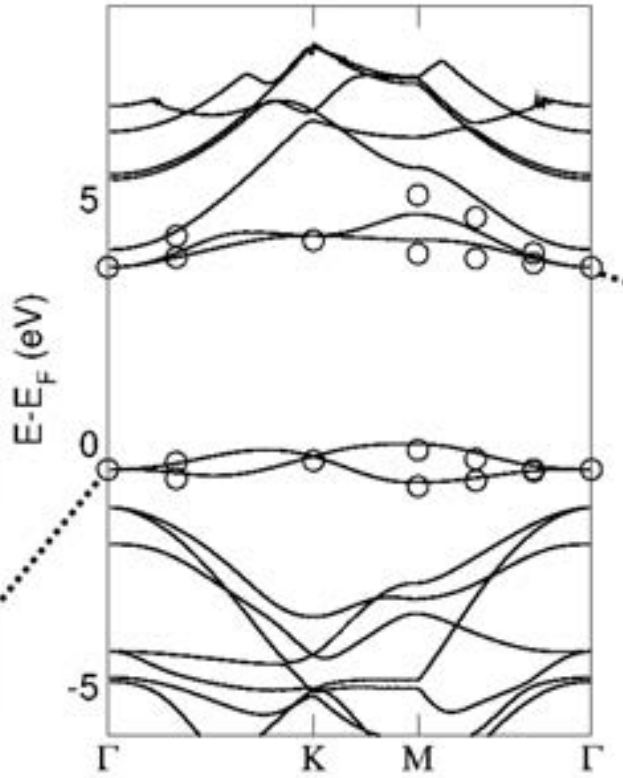


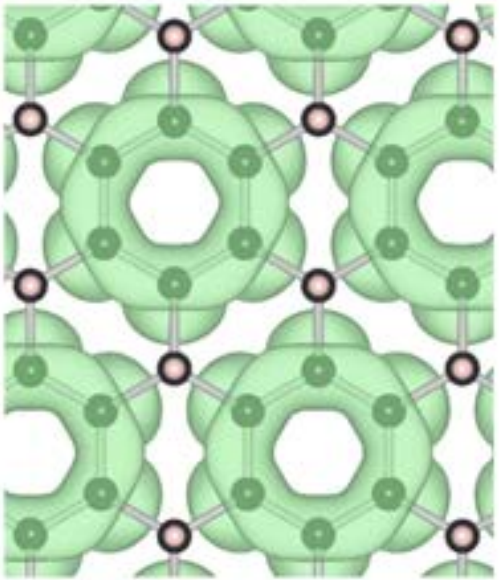


Honeycomb Hydrogenated Graphene
band edges

GW valence band top

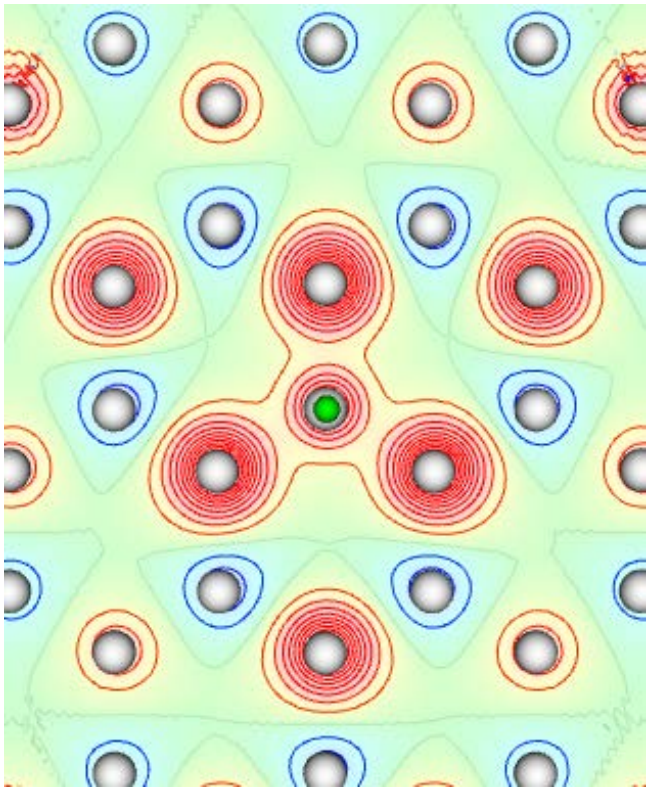


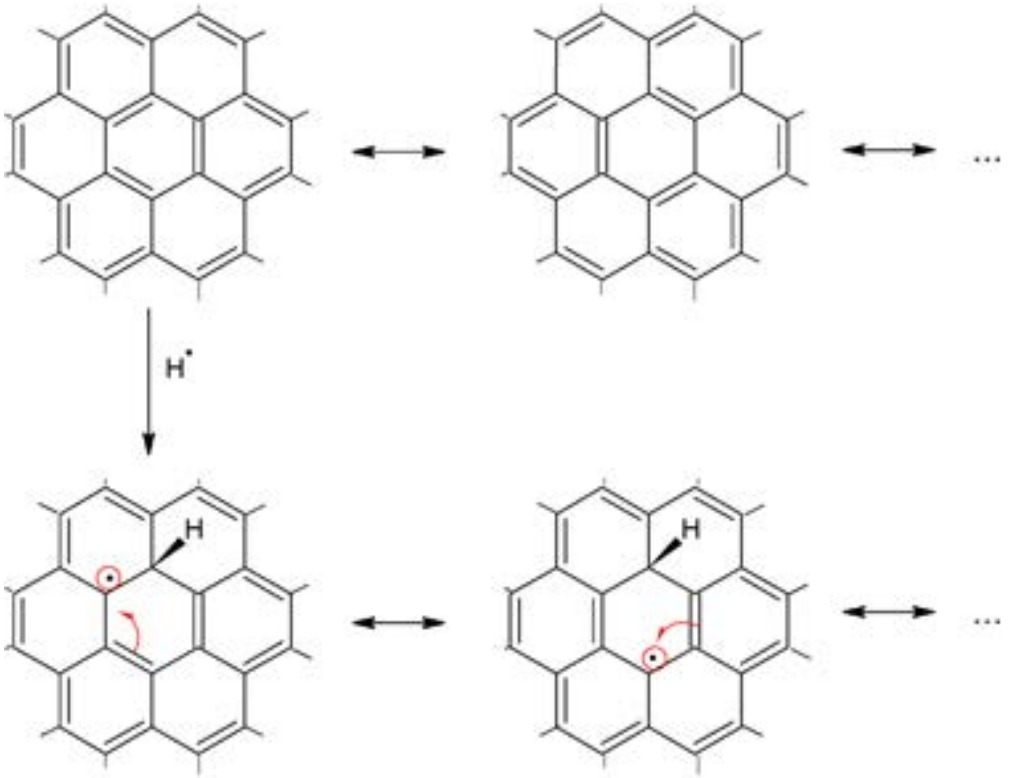




GW conduction band bottom

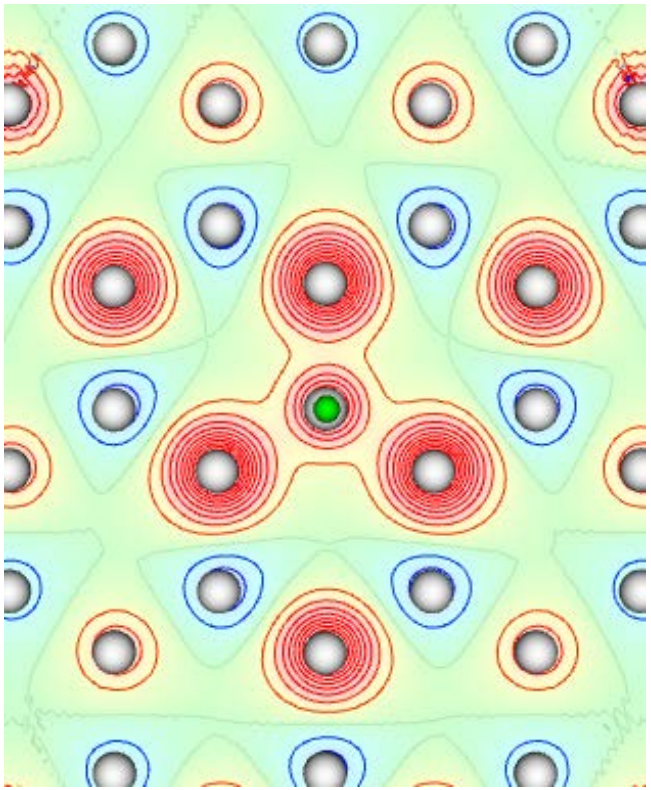
Hydrogenated Graphene
the first H chemisorption



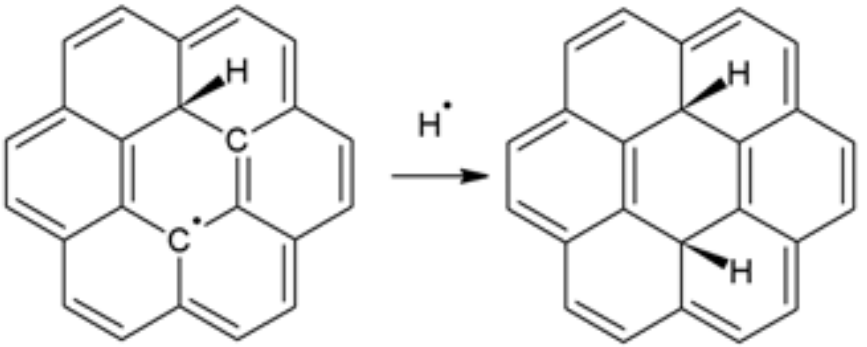


For adsorption on an A site spin-density localizes on B sites

Hydrogenated Graphene
the first H chemisorption



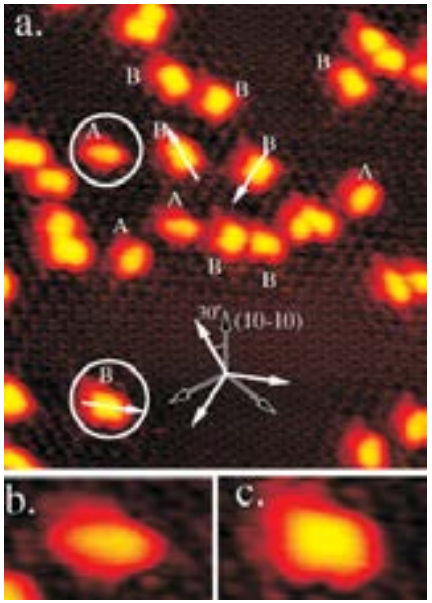
For adsorption on an A site spin-density localizes on B sites



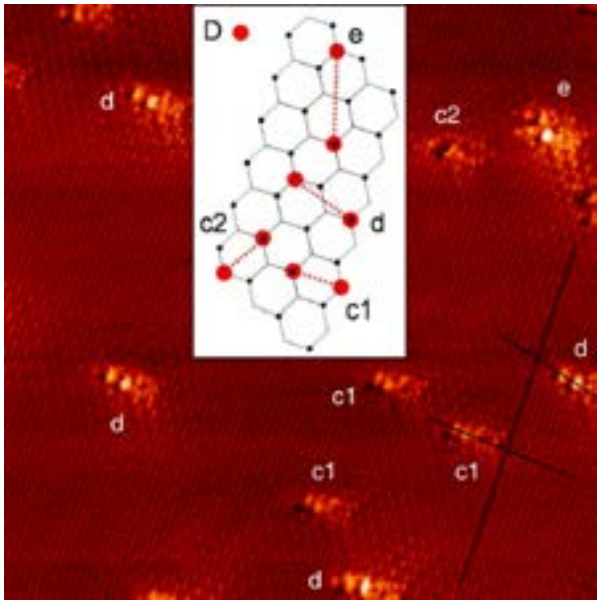
Electronic effects drive every *second* H chemisorption.

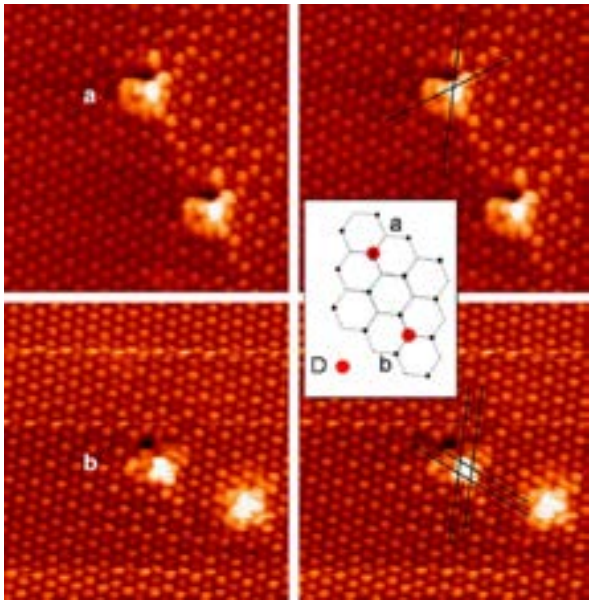
J. Chem. Phys. **130** 054704 (2009)

Hydrogenated Graphene
STM experiments



Ortho and Para [1]



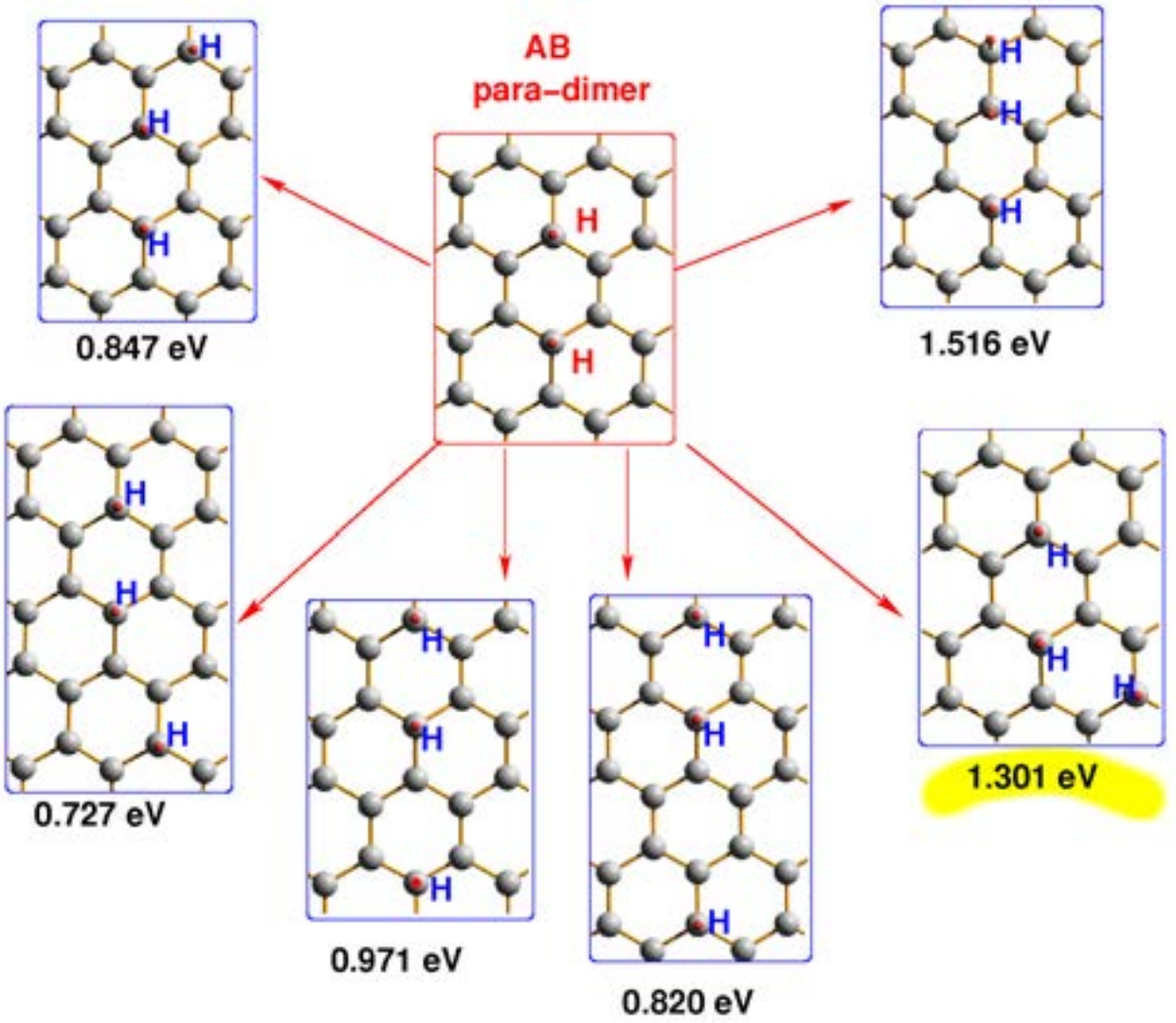


AB pairs [2]

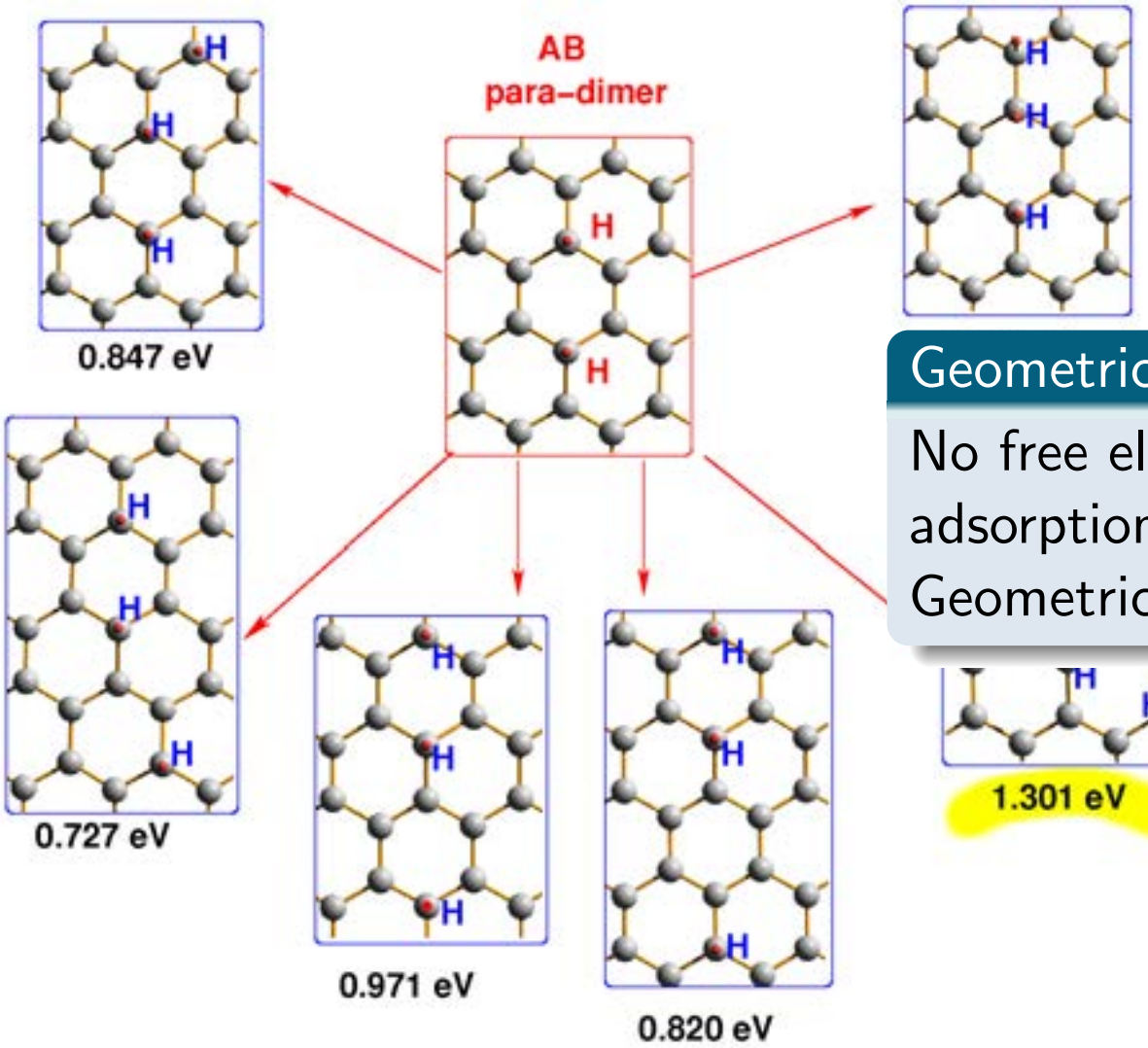
[1] L. Hornekaer, Z. Sljivancanin, W. Xu, R. Otero, E. Rauls, I. Stensgaard, E. Laegsgaard, B. Hammer and F. Besenbacher. Phys. Rev. Lett. 96 156104 (2006)

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

Hydrogenated Graphene
third H chemisorption



Hydrogenated Graphene
third H chemisorption

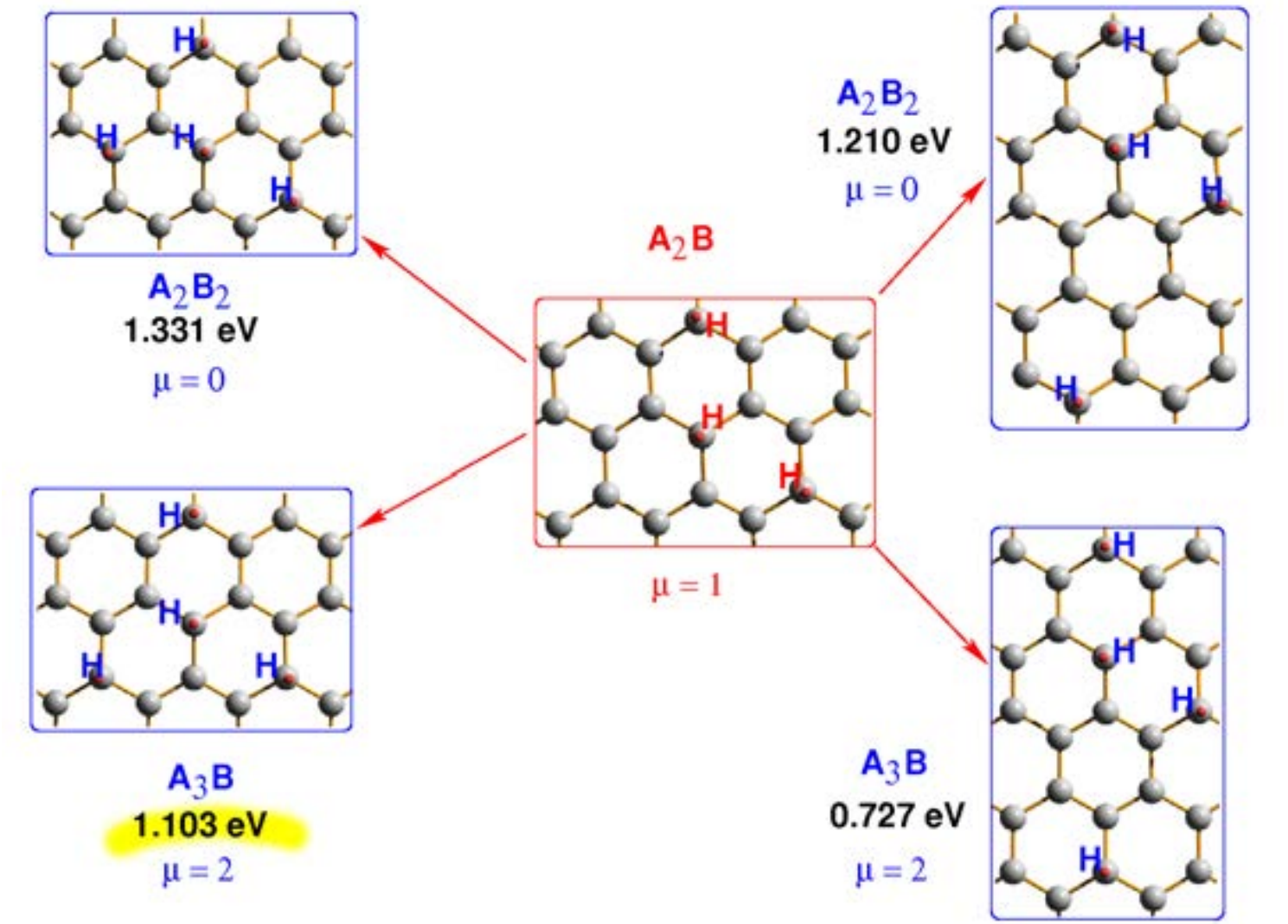


Geometric Effect

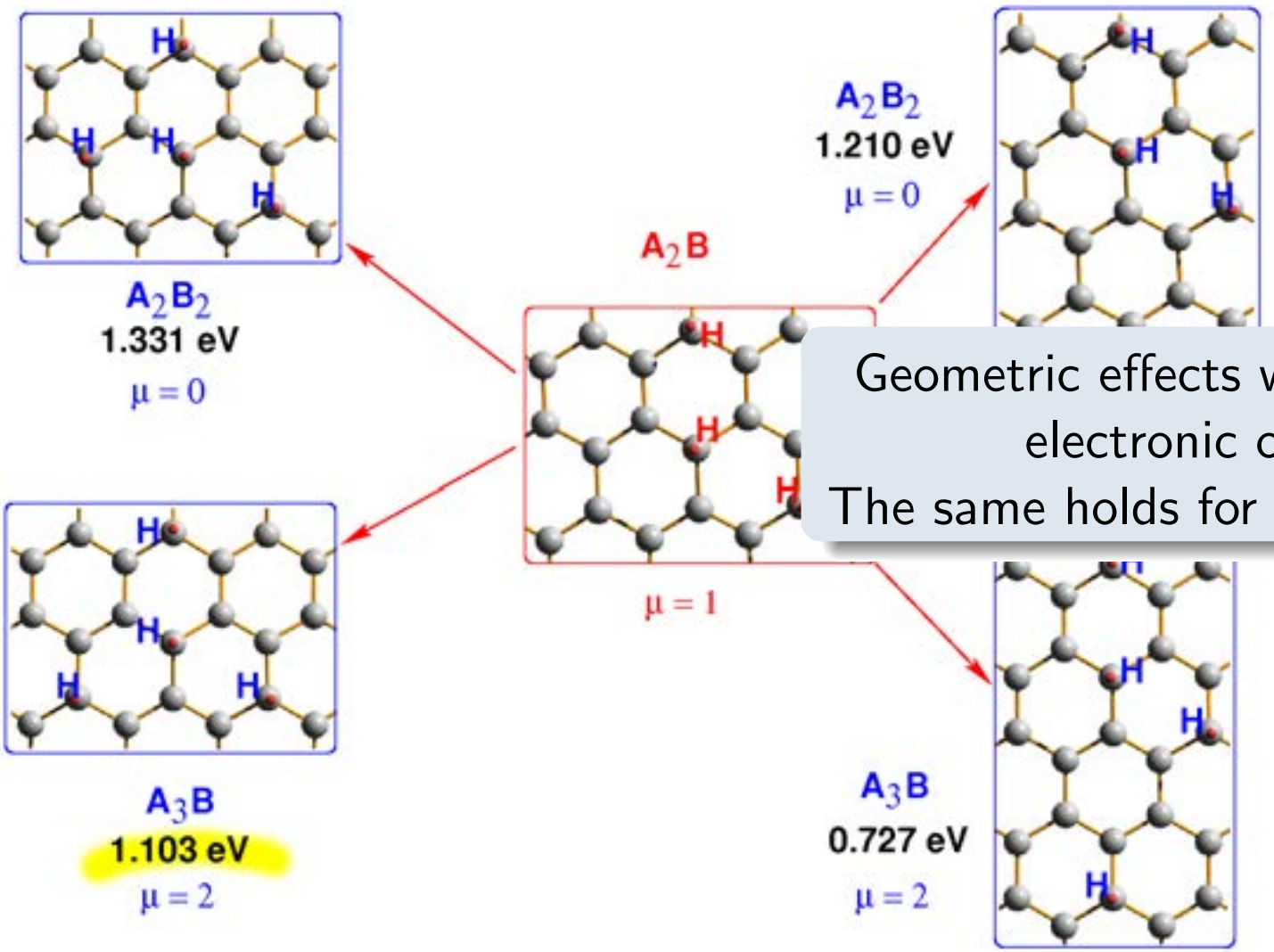
No free electrons for 3rd H adsorption

Geometric effects only!

Hydrogenated Graphene
Fourth H chemisorption



Hydrogenated Graphene
Fourth H chemisorption



Geometric effects work against electronic ones.
The same holds for ads. barriers.

Summary + Conclusions

- A honeycomb shaped superlattice of H atoms give rise to a thermodynamically stable new form of hydrogenated graphene.
- This material has a wide band gap comparable with graphane due to its symmetry and to confinement effects.
- Localized states at band edges suggest applications as q-bits.
- Its synthetic pathway might be favoured (w.r.t. disordered H clusters) by geometric (strain) and electronic effects induced by other adsorbates.

For Further Reading

R. Martinazzo, S. Casolo, G. F. Tantardini
Symmetry-induced band gap opening in graphene defects superlattices
Phys. Rev. B **81** 245420 (2010)

S. Casolo, R. Martinazzo, G. F. Tantardini
Band engineering in graphene with substitutional defects superlattices
J. Phys Chem. C **115** 3250 (2011)

S. Casolo, O. M. Løvvik, R. Martinazzo, G. F. Tantardini
Understanding H atoms adsorption on graphene
J. Chem. Phys. **130** 074504 (2009)

Thank you for your attention!