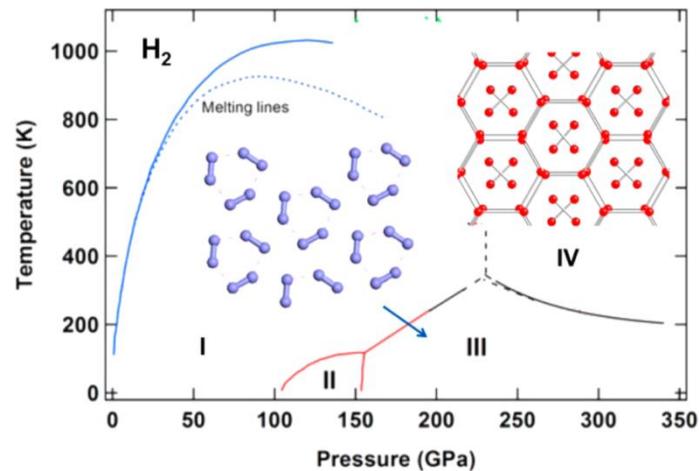


# Chemical Bonding Forces and Metallization of Hydrogen

Ivan I. Naumov

Geophysical Laboratory,  
Carnegie Institution of Washington



Naumov & Hemley, *Accts. Chem. Res.*, 47(12), 3551 (2014)

# Importance of Fundamental Studies of Hydrogen and Hydrogen-rich Materials

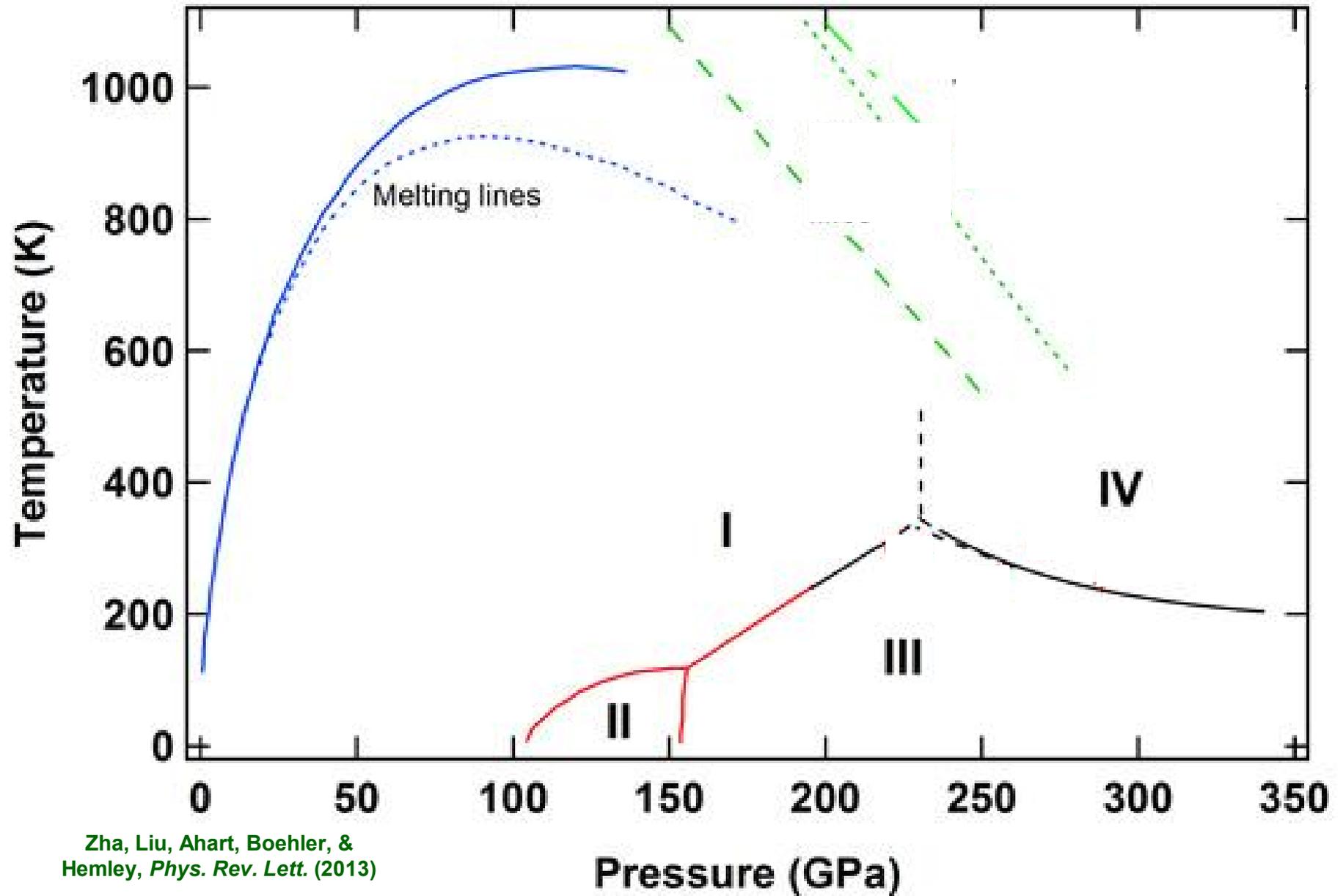
- “ H in a metallic state is expected to exhibit high  $T_c$  (Neil Ashcroft, 1968)
- “ Evidence for  $T_c$  near 200K in hydrogen-rich sulfur compound (Eremets et al.)
- “ Hydrogen-dominant materials could be important for
  - (i) hydrogen storage
  - (ii) general energy storage (as high density materials)
  - (iii) for solving structural problems in nuclear industry (hydrogen embrittlement)

Understanding pure hydrogen over the broadest range of P-T is an important starting point

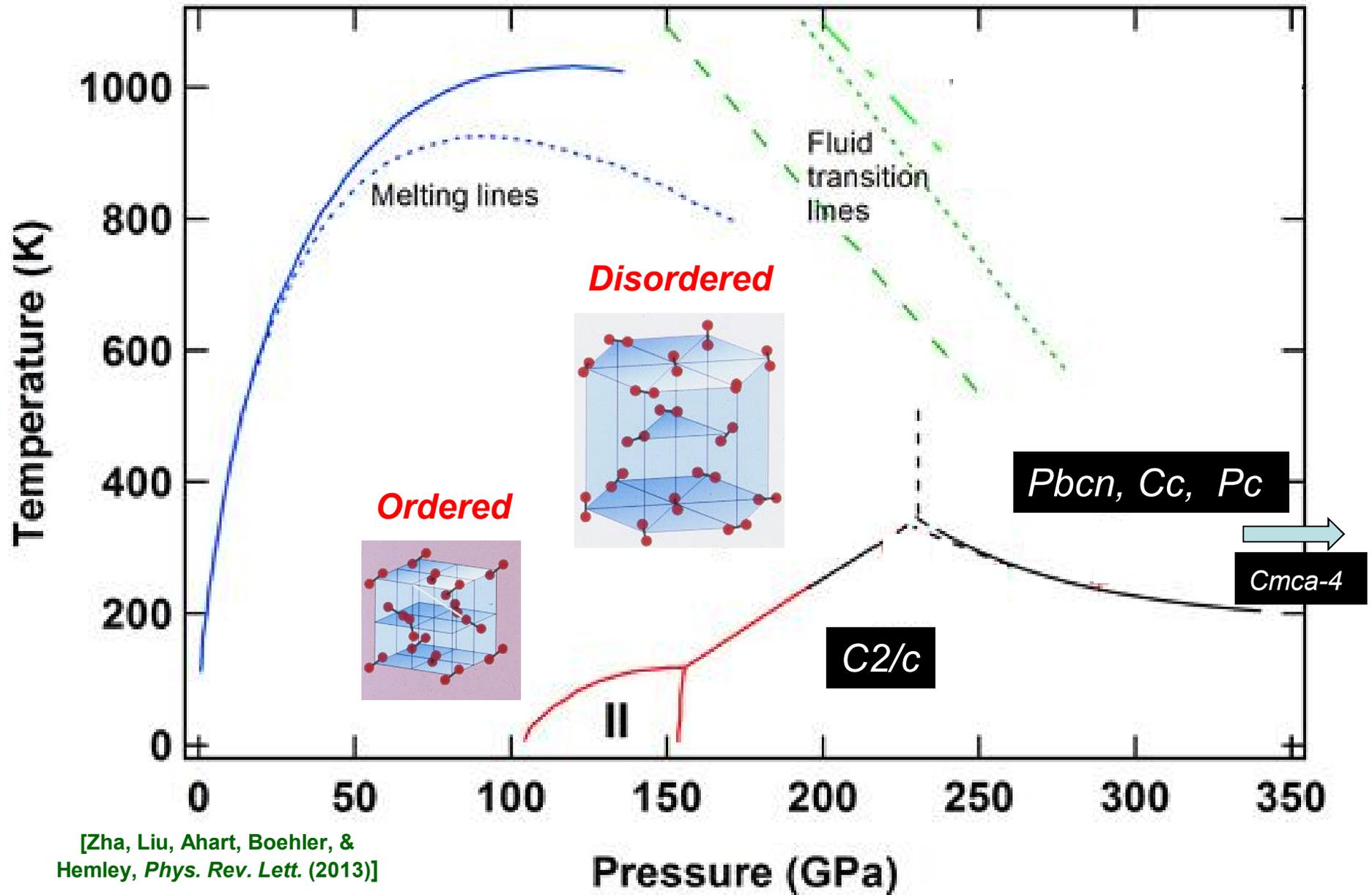
# Goals

- É To discuss the properties of dense hydrogen from the chemical point of view
- É To argue that they are controlled by closed shell effects over a wide range of pressures
- É To touch the question why hydrogen behaves so differently from simple alkali metals

# New Hydrogen Phase Diagram



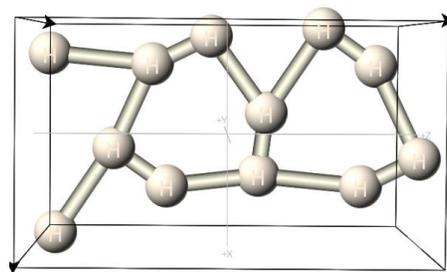
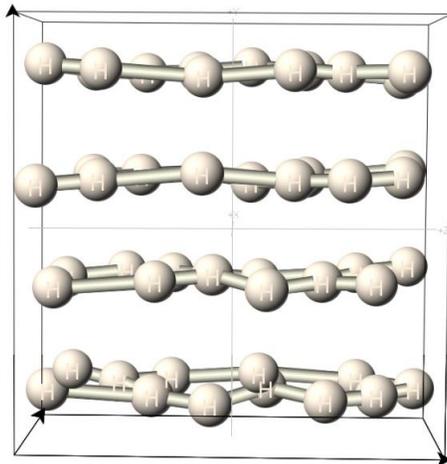
# New Hydrogen Phase Diagram



[Zha, Liu, Ahart, Boehler, & Hemley, *Phys. Rev. Lett.* (2013)]

# $C2/c$ and $Pbcn$ structures

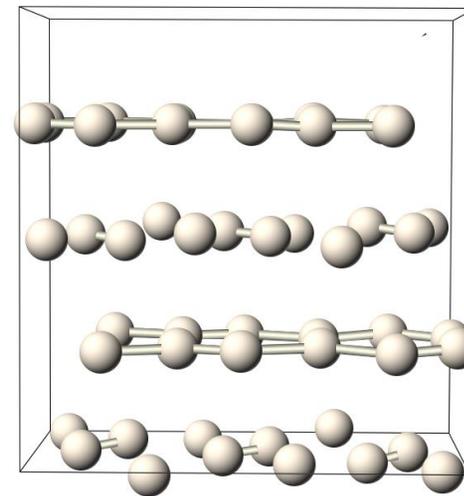
$C2/c$  (III)



D

$Pbcn$  (IV)

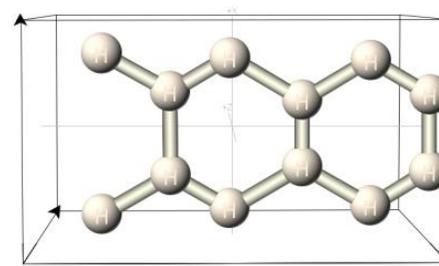
A



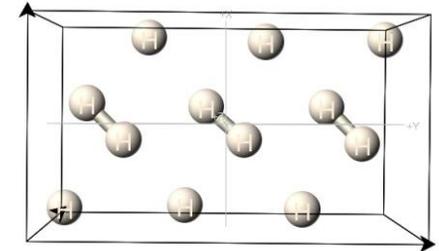
B

C

D



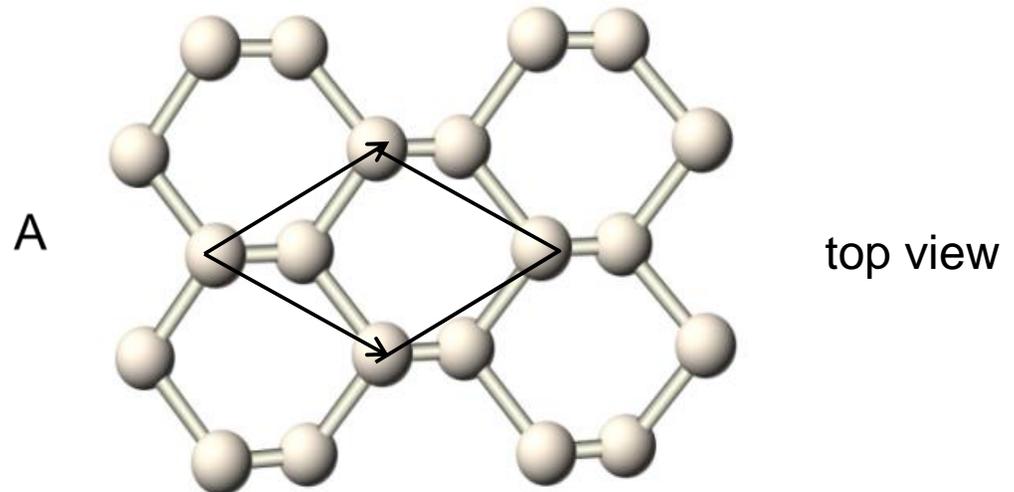
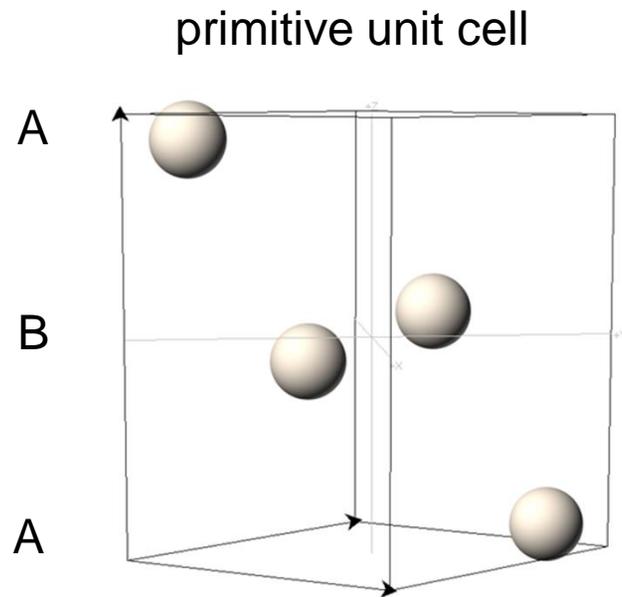
C



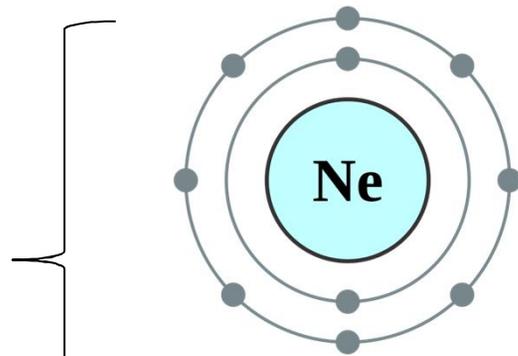
D

# $Cmca-4$ : graphite-like structure

---

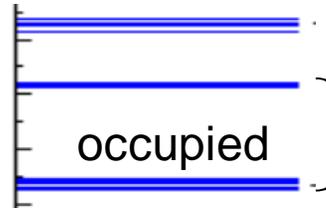


# Closed Shell Effect



Noble atoms have a closed valence shell

Molecules



Metallic clusters

→ W. D. Knight *et al.*, Phys. Rev. Lett. **52**, 2141 (1984).



1D nanowires

→ A. I. Yanson *et al.*, Nature, **400**, 144 (1999).



2D thin films

→ D.-A. Luh *et al.*, Science, **292**, 1131 (2001).

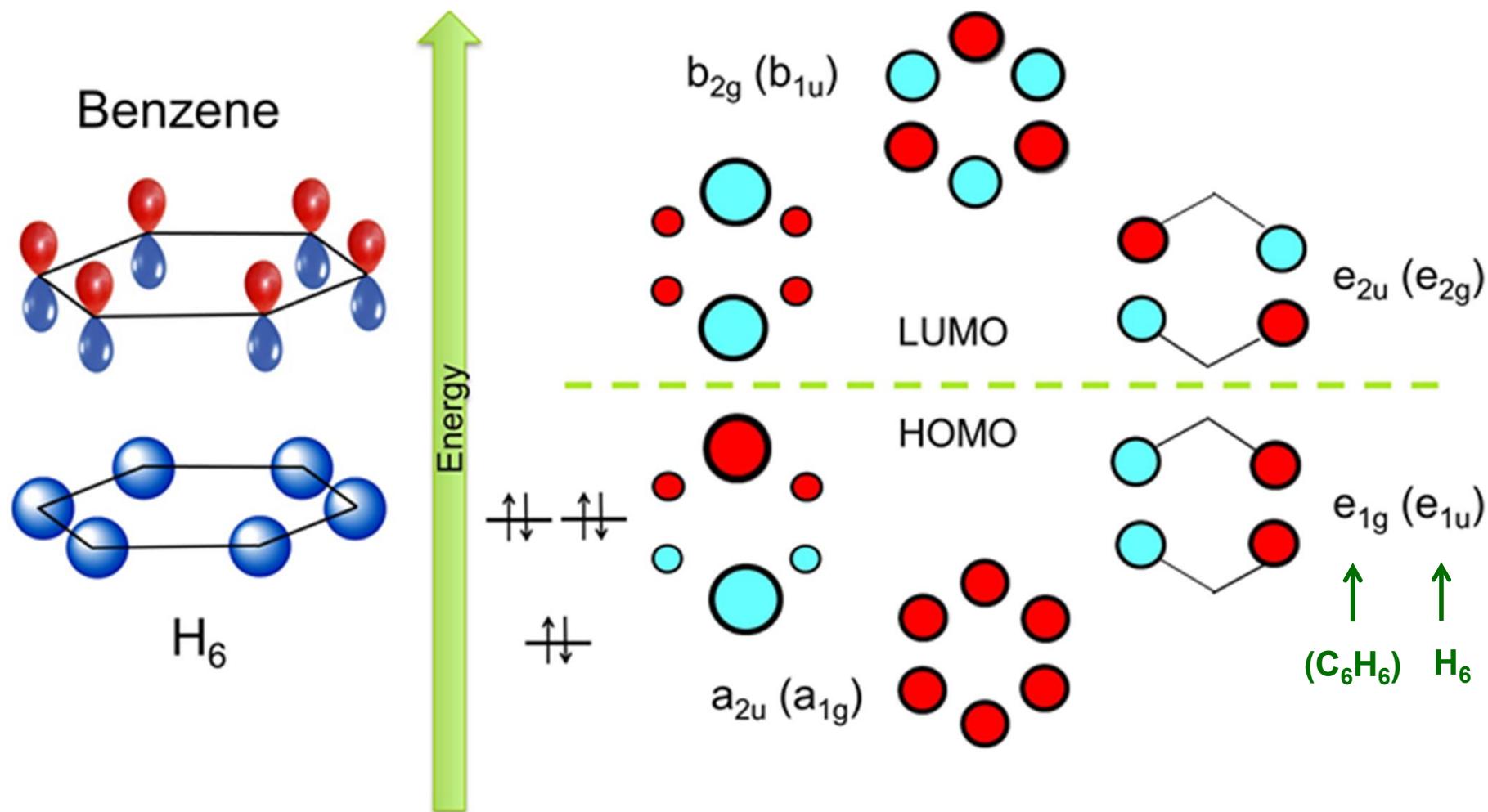
Ag: N=1,2,5



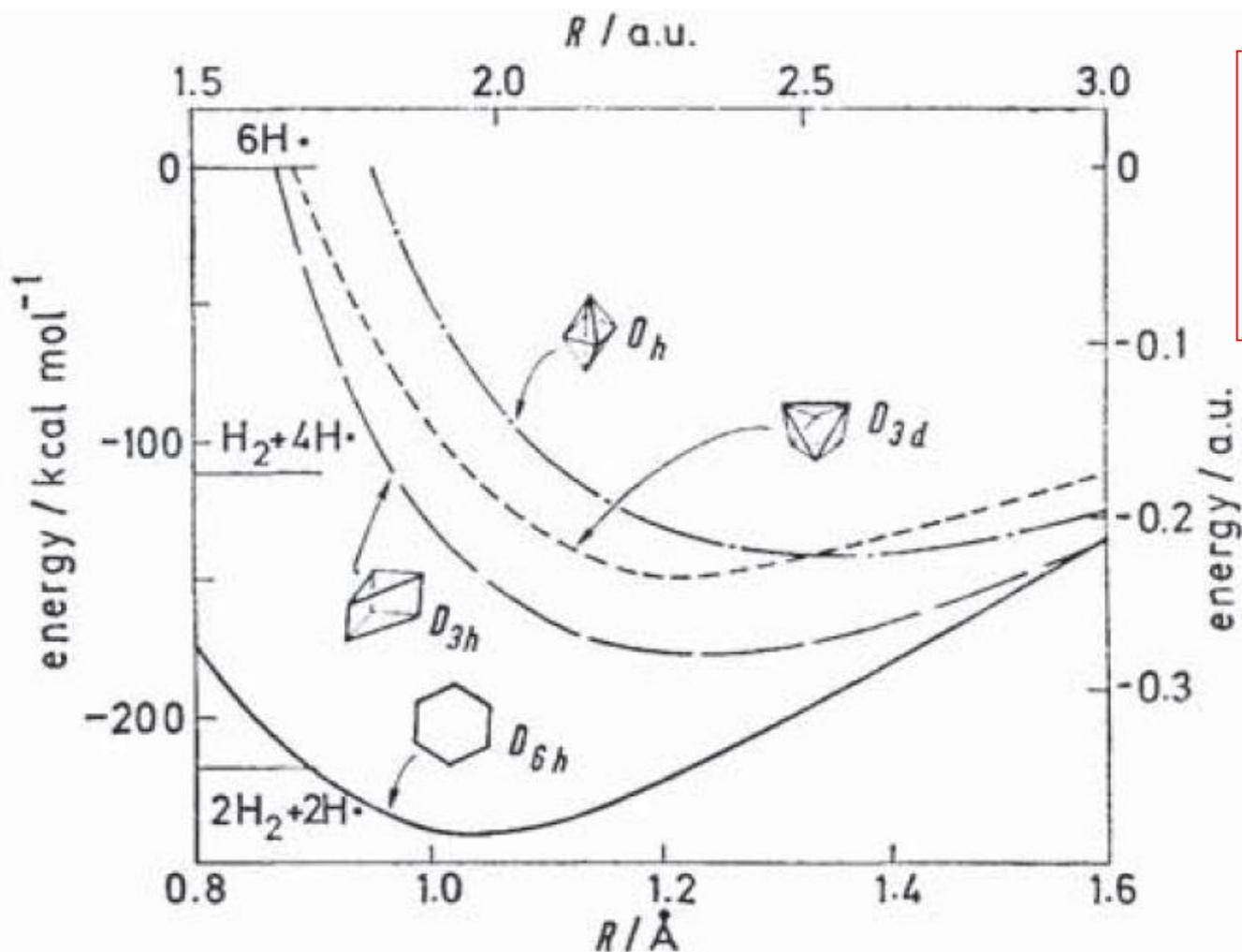
3D solids

→ Insulators, Quasicrystals, Hume-Rothery phases

# Analogy between 1s electrons in hydrogen and electrons in carbon



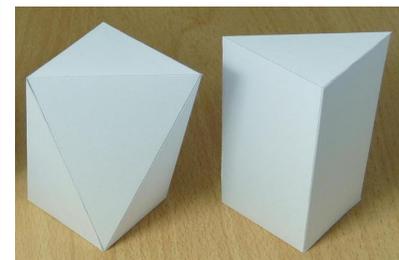
# H<sub>6</sub> ring vs nonplanar isomers



O<sub>h</sub> - octahedron  
D<sub>3d</sub> - staggered trigonal prism  
D<sub>3h</sub> - trigonal prism

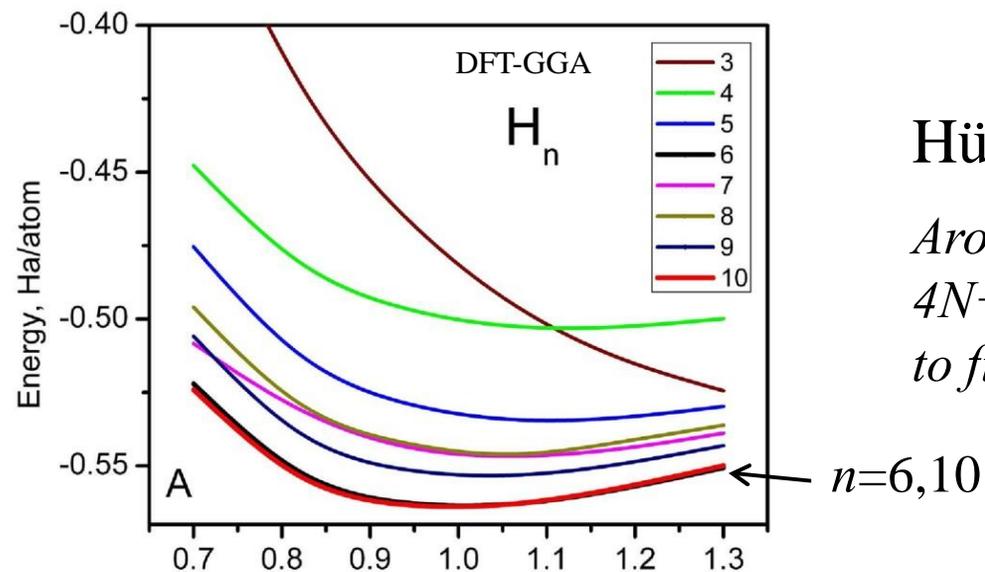
D<sub>3d</sub>

D<sub>3h</sub>



D. A. Dixon et al. *Faraday Discuss. Chem. Soc.*, **62**, 110 (1977).

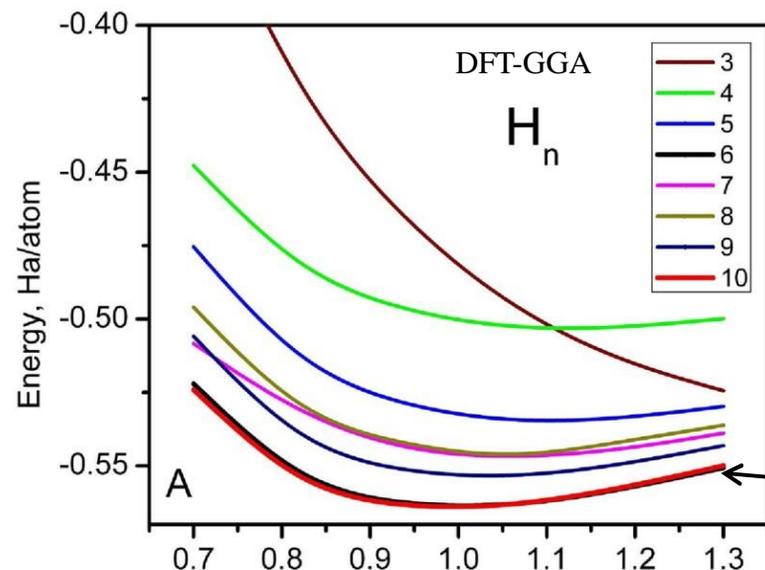
# Total energies per atom for $H_n$ rings ( $n = 3 - 10$ )



Hückel's rule:

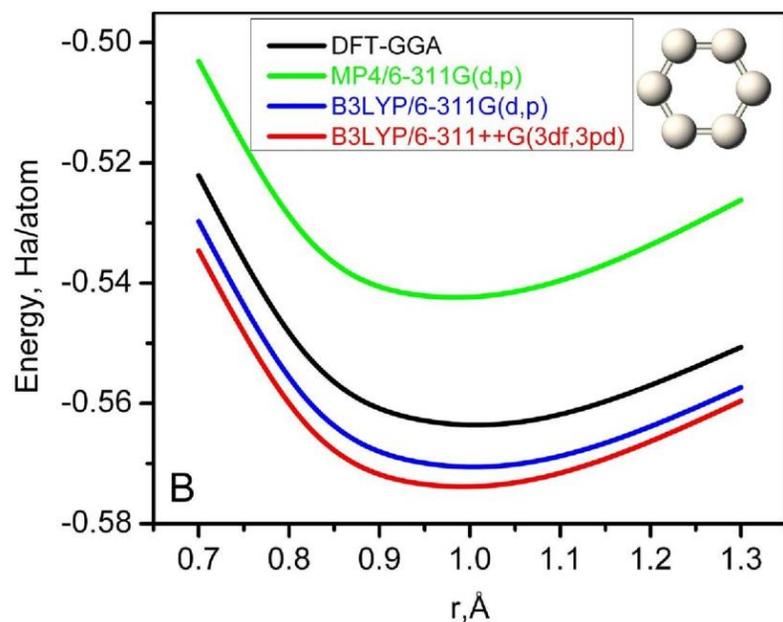
*Aromatic compounds must have  $4N+2$   $\pi$  electrons,  $N=0, 1, 2, 3, \dots$ , to fill a  $\pi$  shell*

# Total energies per atom for $H_n$ rings ( $n = 3 - 10$ )



Hückel's rule:

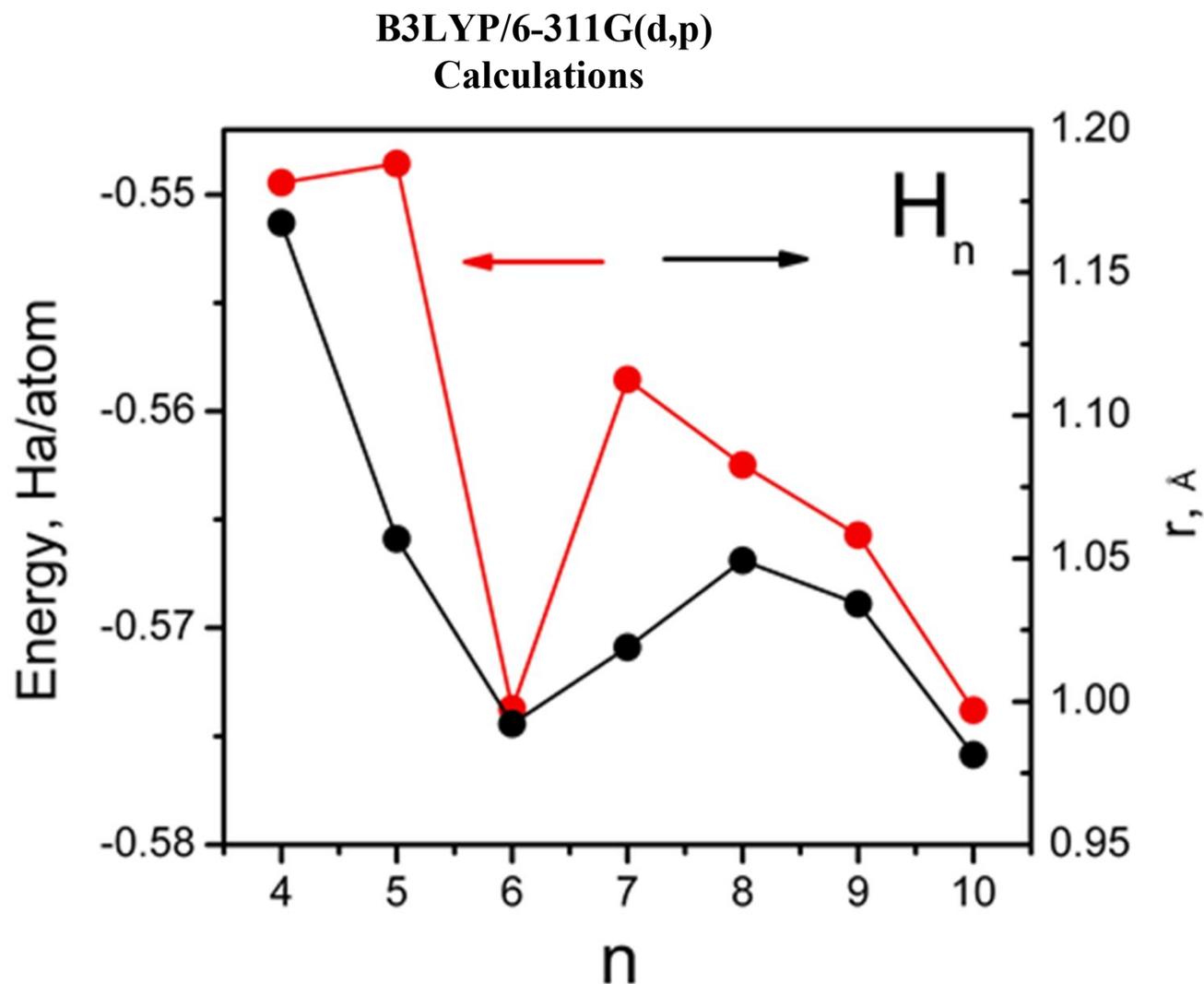
*Aromatic compounds must have  $4N+2$   $\pi$  electrons,  $N=0, 1, 2, 3, \dots$ , to fill a  $\pi$  shell*



Correlation corrections:

*Lower the total energy but have only little effect on energy differences*

# Total energies and interatomic distances in $H_n$ rings

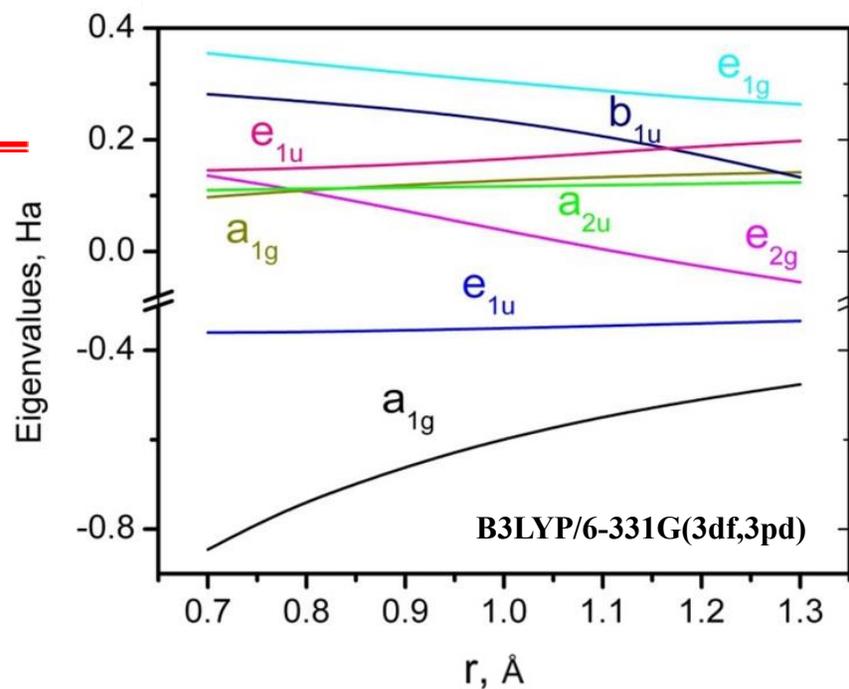


# H<sub>6</sub> molecular energy levels and vibrational frequencies

---

É Bonding  $a_{1g}$ ,  $e_{1u}$ , and  $a_{2u}$  orbitals go down in energy with pressure

É  $a_{2u}$  stems from the  $2p_z$  atomic orbitals



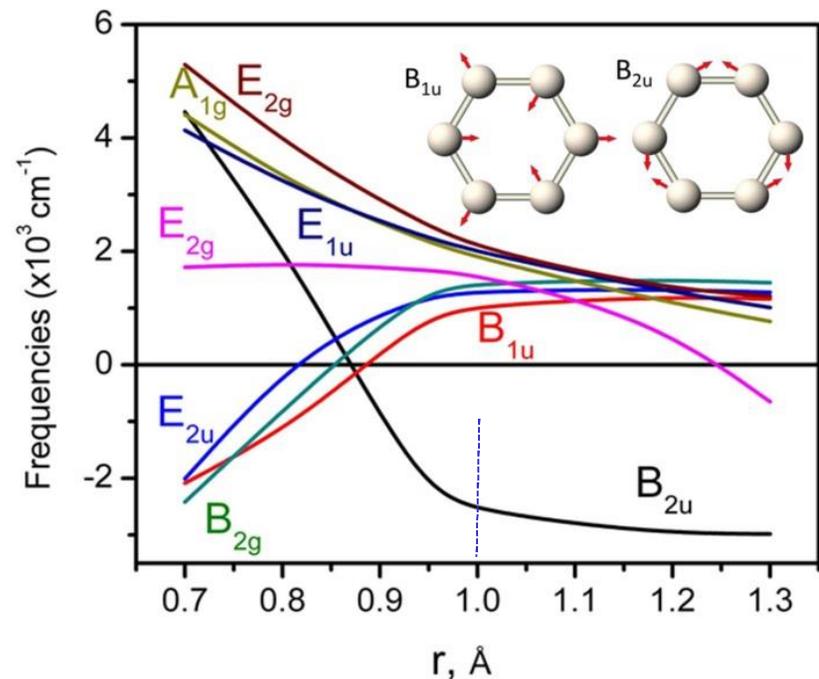
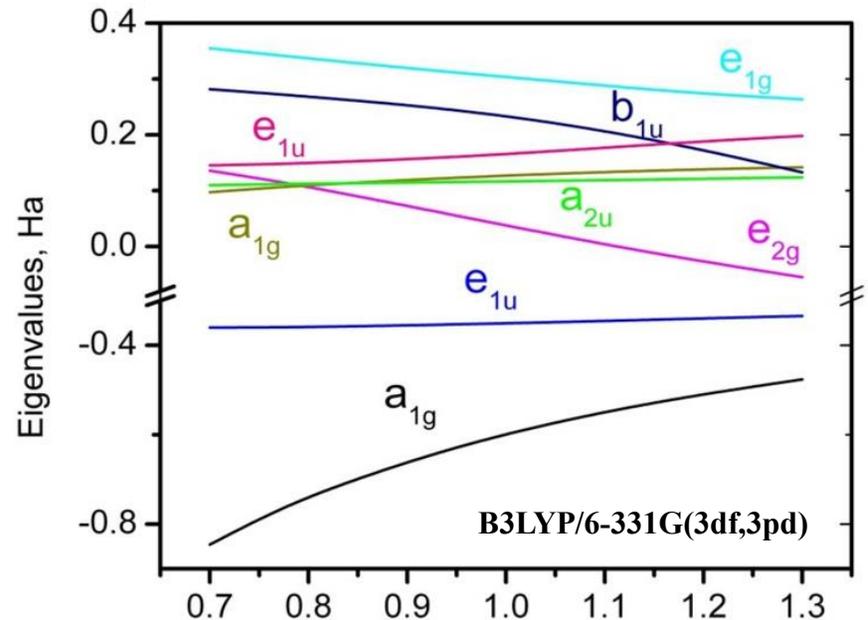
# H<sub>6</sub> molecular energy levels and vibrational frequencies

É Bonding  $a_{1g}$ ,  $e_{1u}$ , and  $a_{2u}$  orbitals go down in energy with pressure

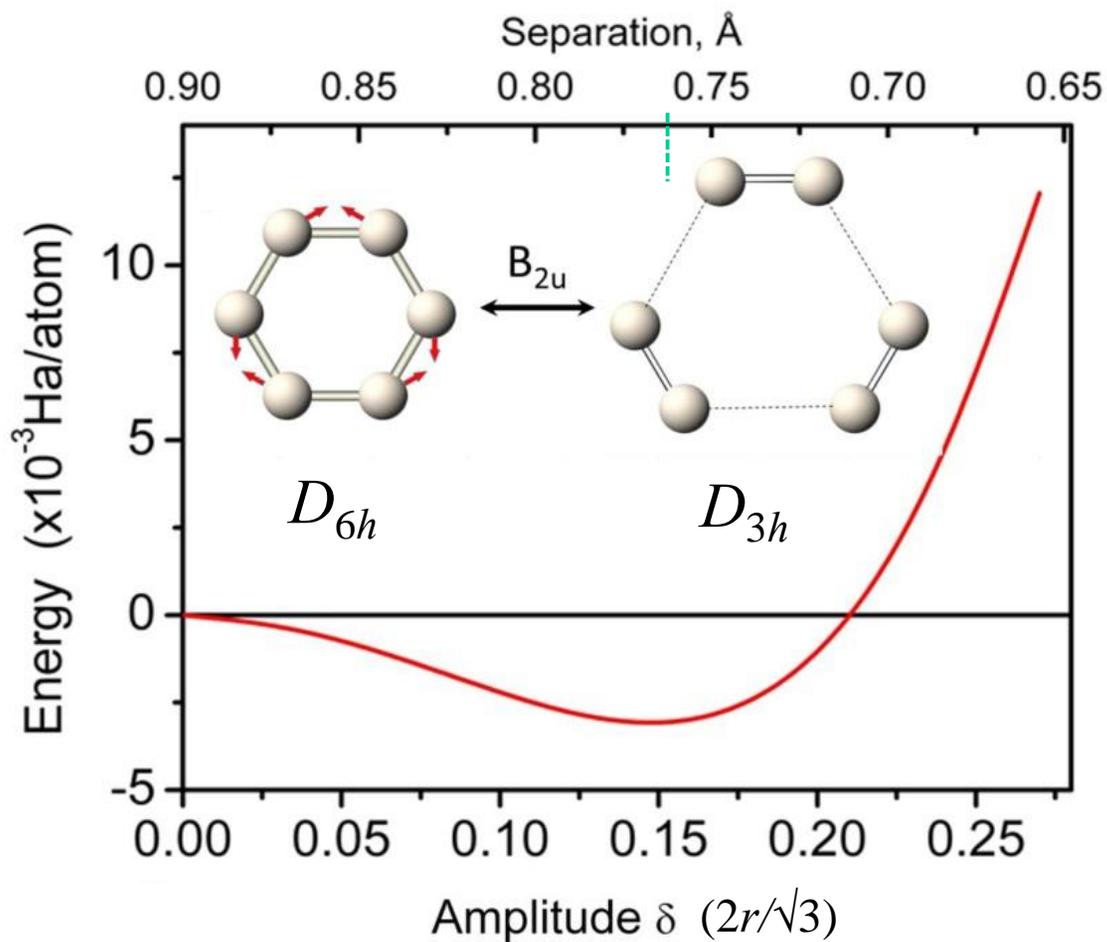
É  $a_{2u}$  stems from the  $2p_z$  atomic orbitals

É Kekulean  $B_{2u}$  vibrational mode becomes stable for  $r < 0.86$

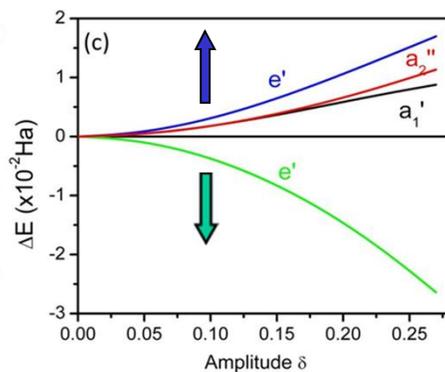
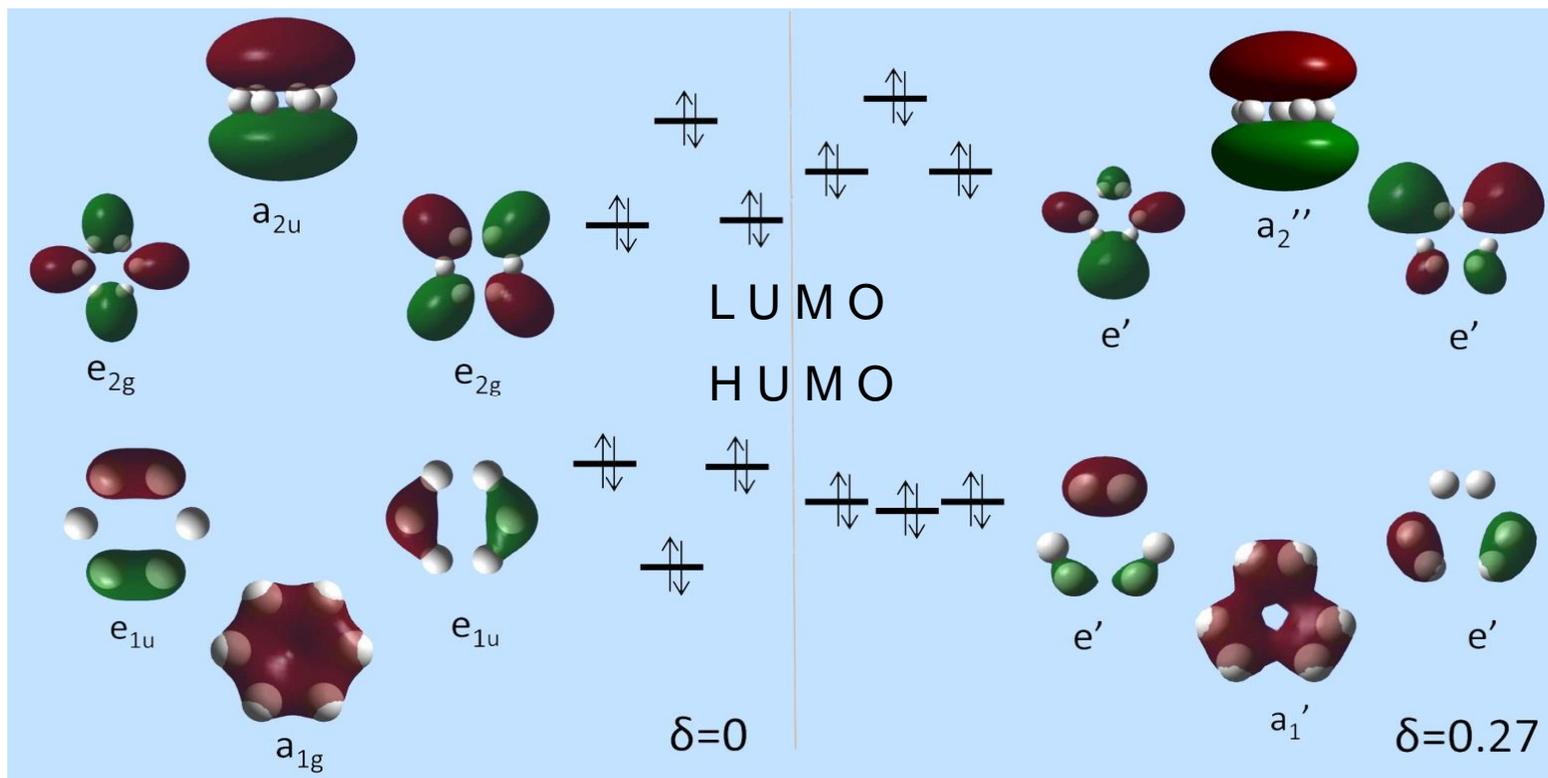
0.86 ~ 500 GPa



# H<sub>6</sub> ring energetics with respect to the B<sub>2u</sub> mode



# Correlation between the molecular orbitals for $D_{6h}$ and $D_{3h}$ structures:

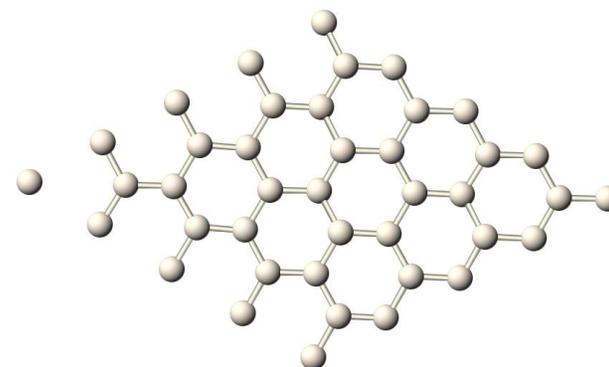
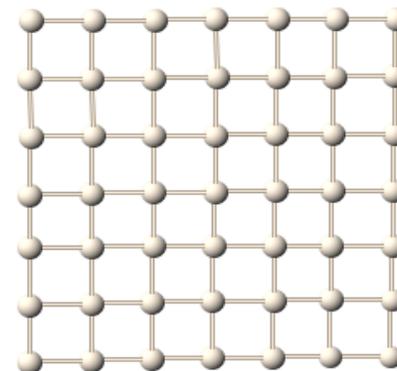
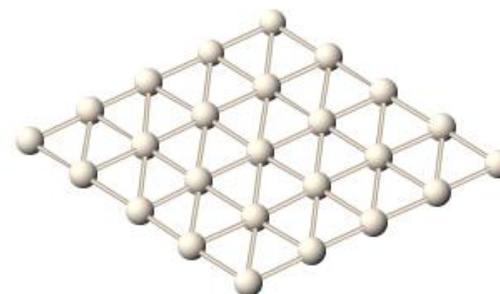


The 3rd lowest unoccupied MOs  $a_{2u}$  and  $a_2''$  are bonding states stem from the atomic  $2p_z$  electrons

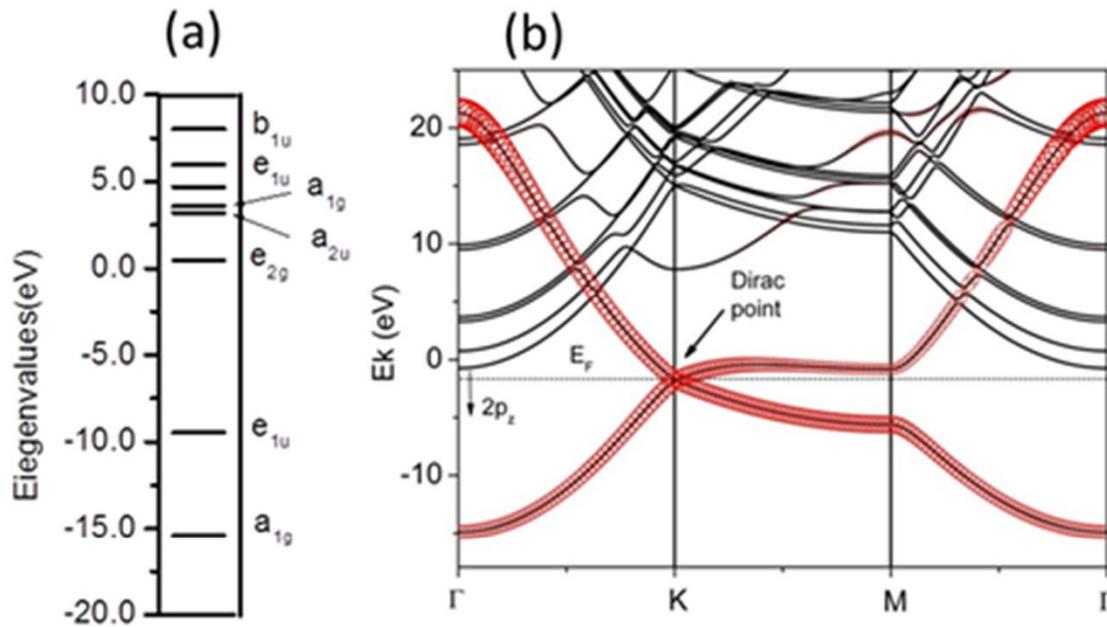
# From isolated rings to 2D lattices

	Optimized distance ↓ <b>r (Å)</b>	Energy ↓ <b>E (Ha)</b>	Relative to ring ↓ <b>ΔE (Ha)</b>
<b>triangle</b>	4.23	-0.451	0.075
<b>square</b>	4.35	-0.451	0.052
<b>graphene-like</b>	1.18	-0.555	0.009

The graphene structure is far more stable than the other two



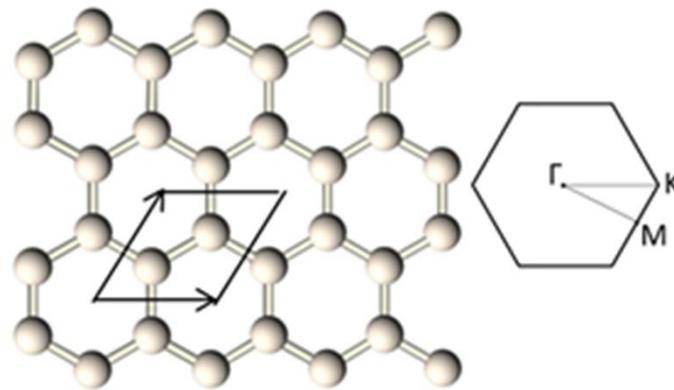
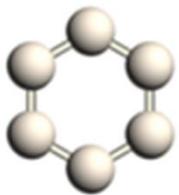
# From H<sub>6</sub> to H-graphene



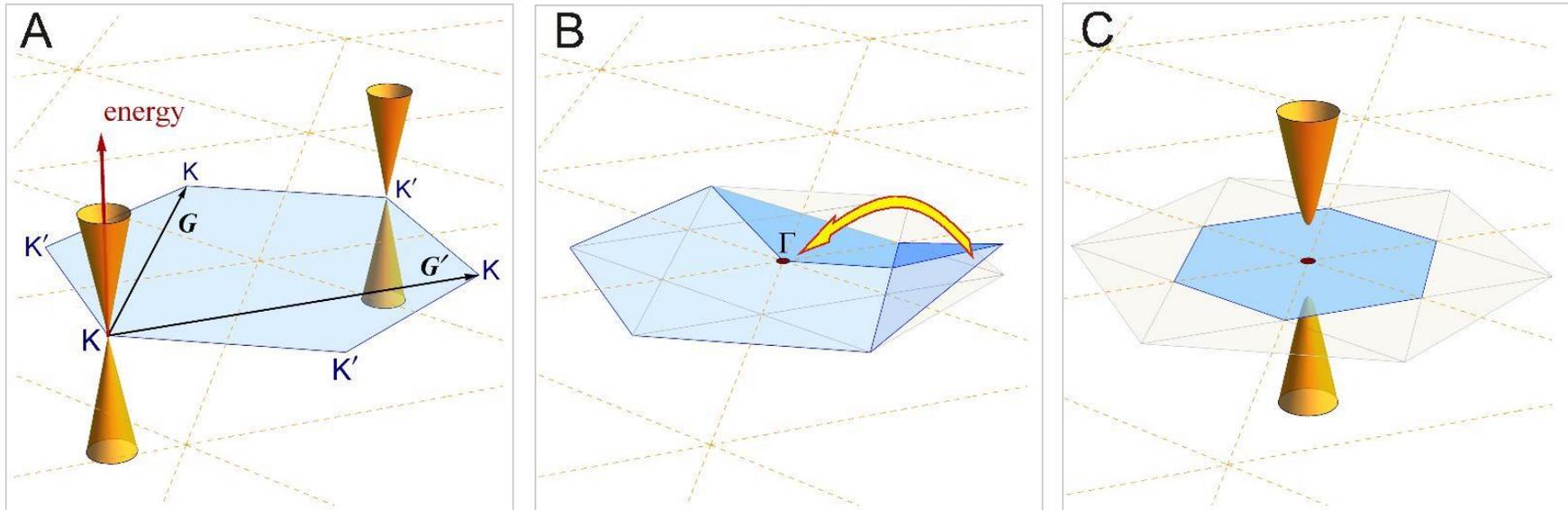
Semimetal

Exhibits two inequivalent Dirac levels  $\mathbf{K}$  and  $\mathbf{K}'$ ; 1s derived

But the second level at  $\mathbf{K}'$  is of 2p<sub>z</sub> nature



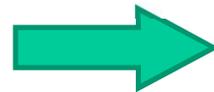
# Gap opening: Peierls distortions



Nestings between the valence and conduction bands:

$$\begin{cases} -\varepsilon_i(\mathbf{k}) = \varepsilon_j(\mathbf{k}), \\ -\varepsilon_i(\mathbf{k}) = \varepsilon_j(\mathbf{k} + \mathbf{K} - \mathbf{K}') \end{cases}$$

Kohn anomaly:



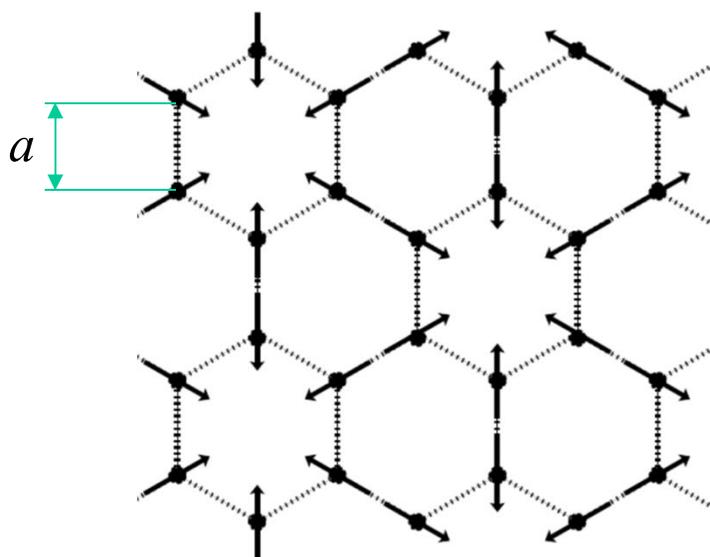
$$\omega_\lambda(q): q = \Gamma, q = \mathbf{K}$$

↓  
TO, LA

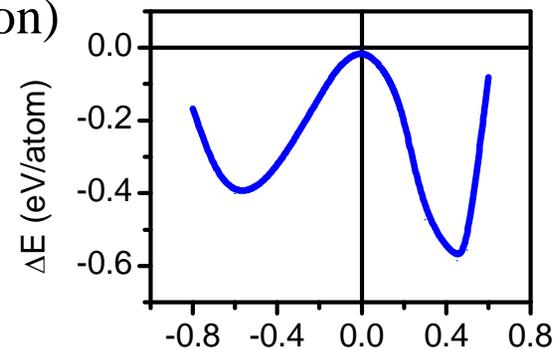
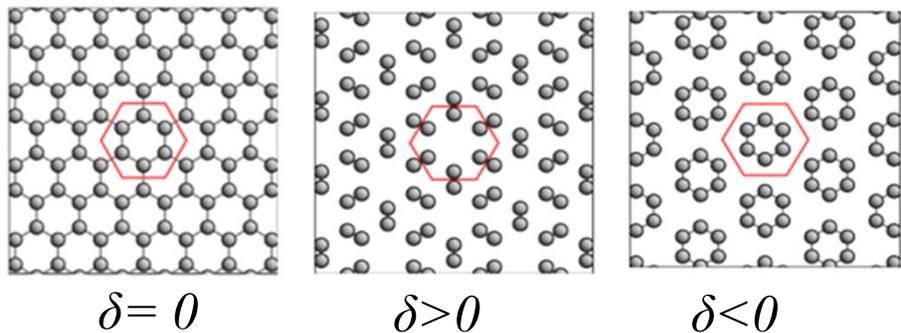
Naumov, Cohen & Hemley, *Phys. Rev. B*, 88, 045125 (2013)

# TO-mode

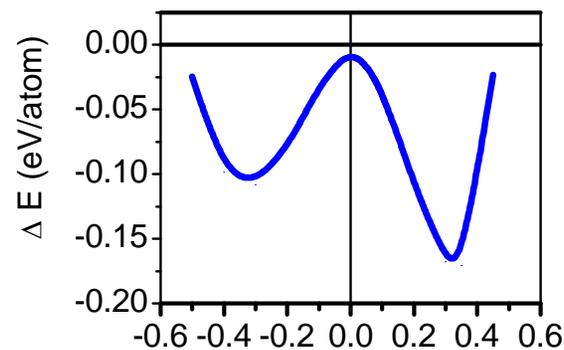
TO-mode at  $\mathbf{k}=\mathbf{K}$  (Kekulean distortion)



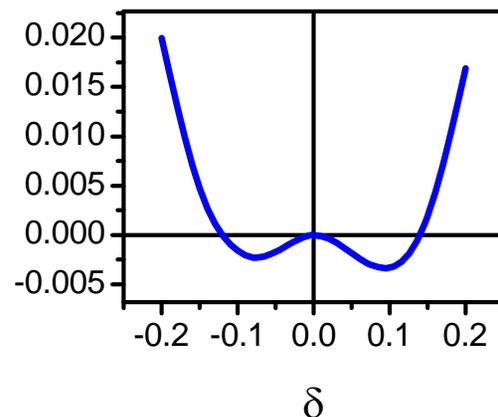
$\zeta 3 \times \zeta 3$  superstructure  
(can be recognized in C2/c)



$a=1.40$



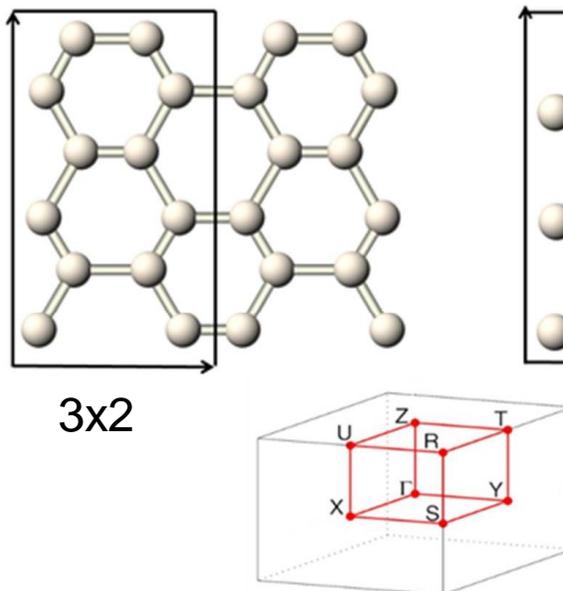
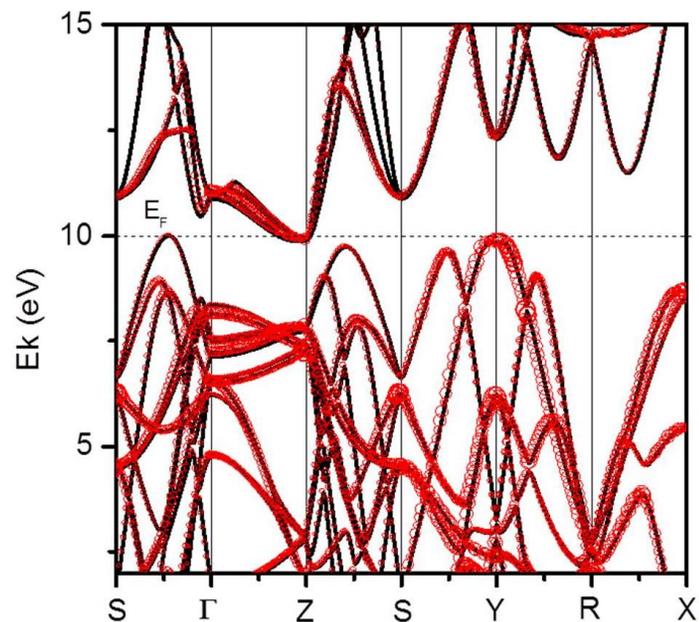
$a=1.18$



$a=1.00$

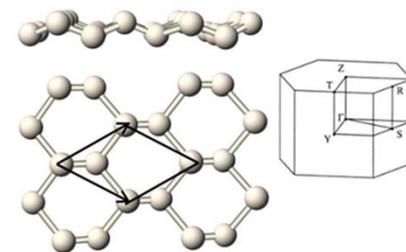
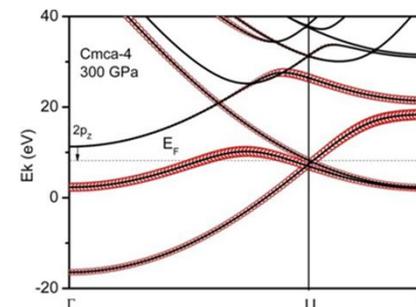
# 3D Candidate Structures

*Pbcn*



Insulator due to a  $3 \times 2$  superlattice stabilized by Peierls-like distortions

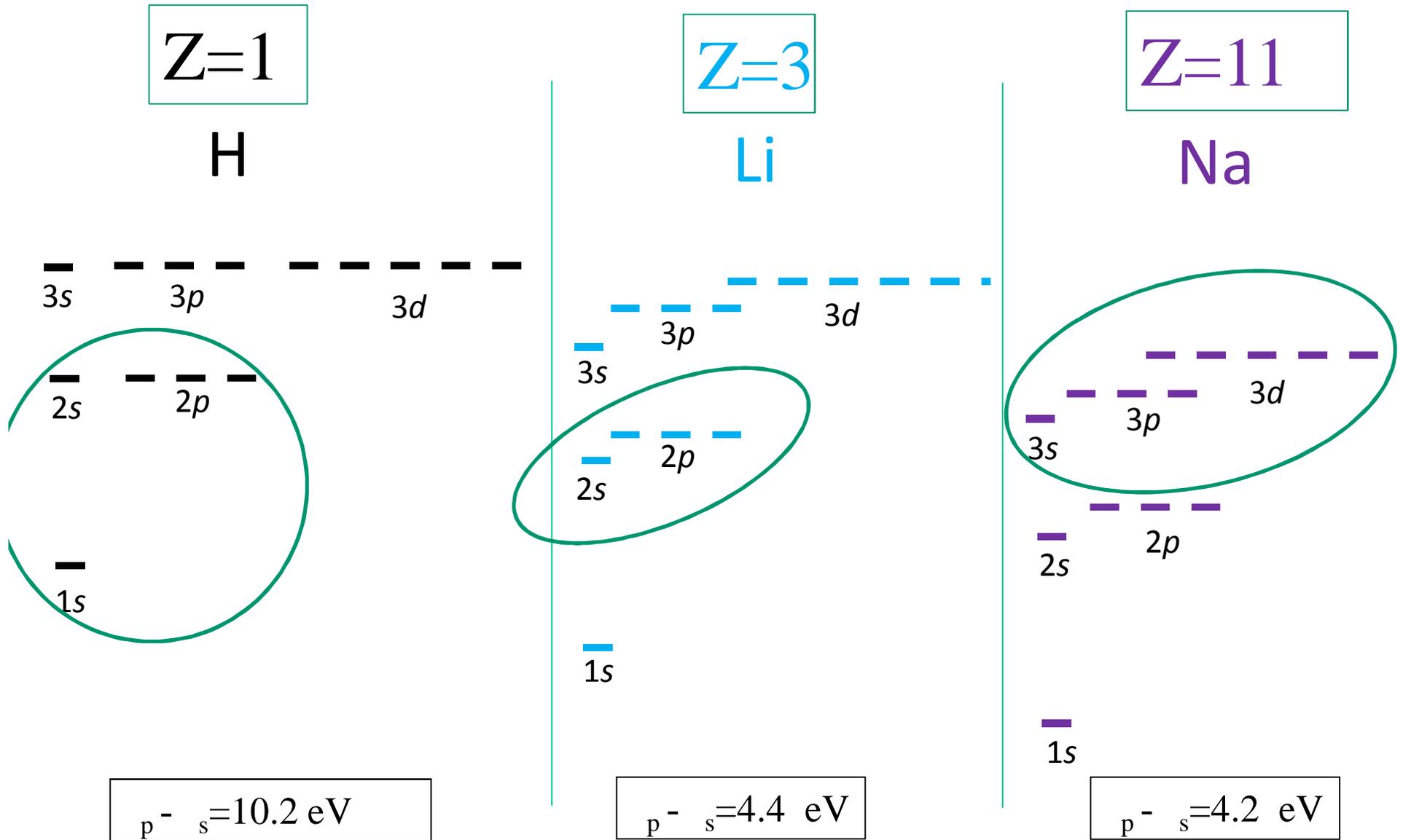
*Cmca-4*



Semimetal

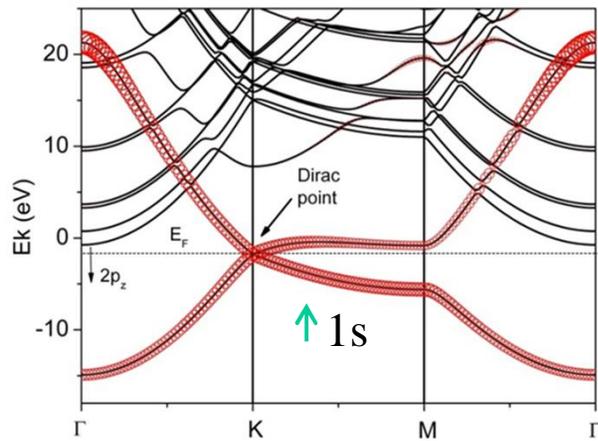
Naumov, Cohen & Hemley, *Phys. Rev. B*, **88**, 045125 (2013)  
 Naumov & Hemley, *Accts. Chem. Res.*, **47**(12), 3551 (2014)

# Energy Level Diagram

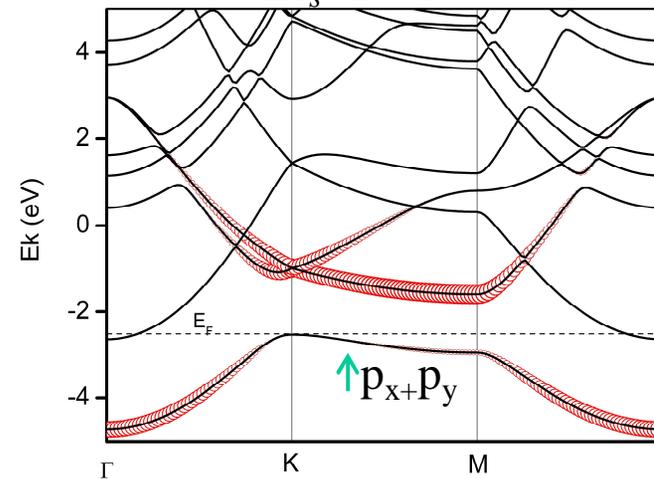


# Comparison between H and Li

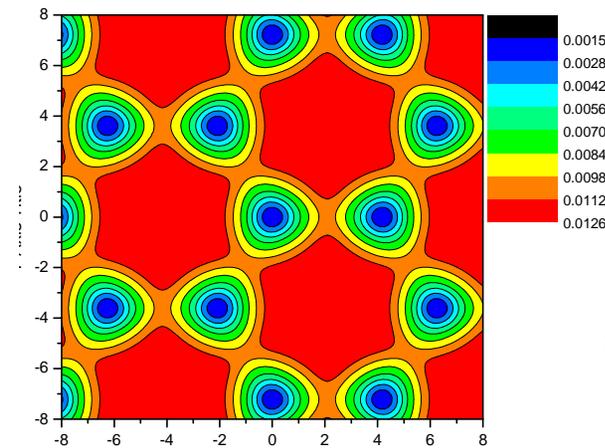
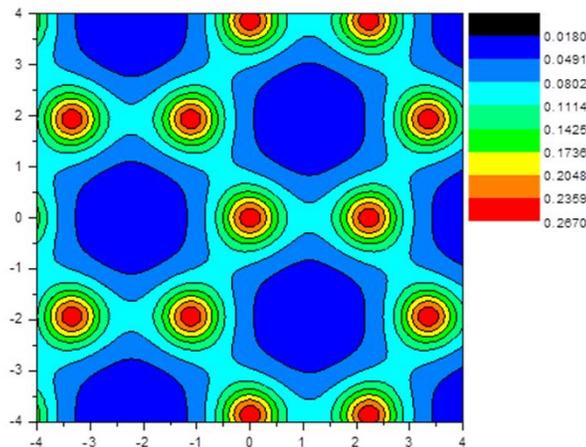
H graphene,  
 $r_s = 1.43$



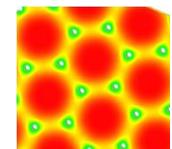
Li graphene,  
 $r_s = 2.68$



● -s character  
of WF's



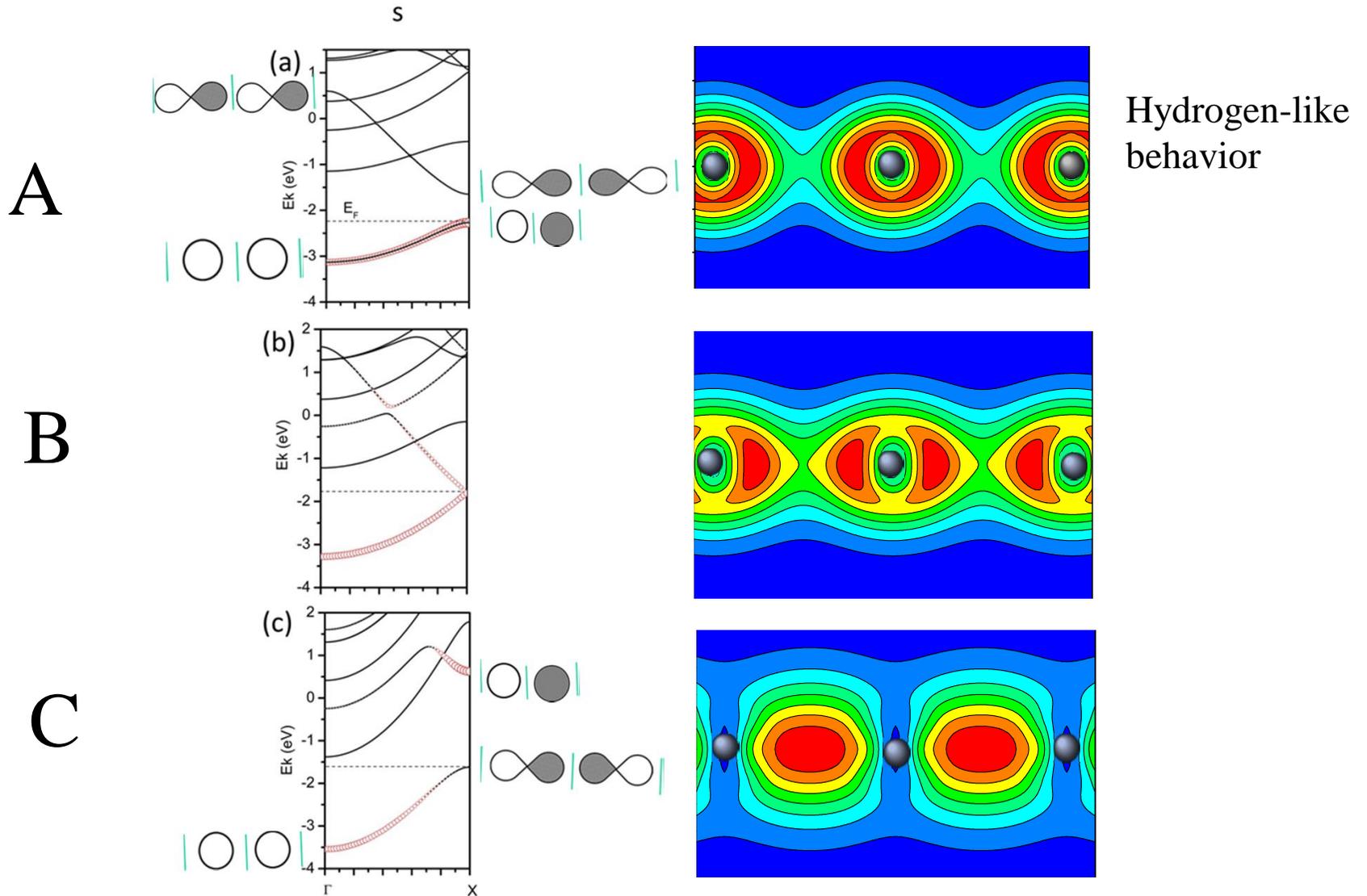
WF at K



s-p hybridization

Li: direct band gap and interstitial valence charge!

# Li: interstitial localization in 1D

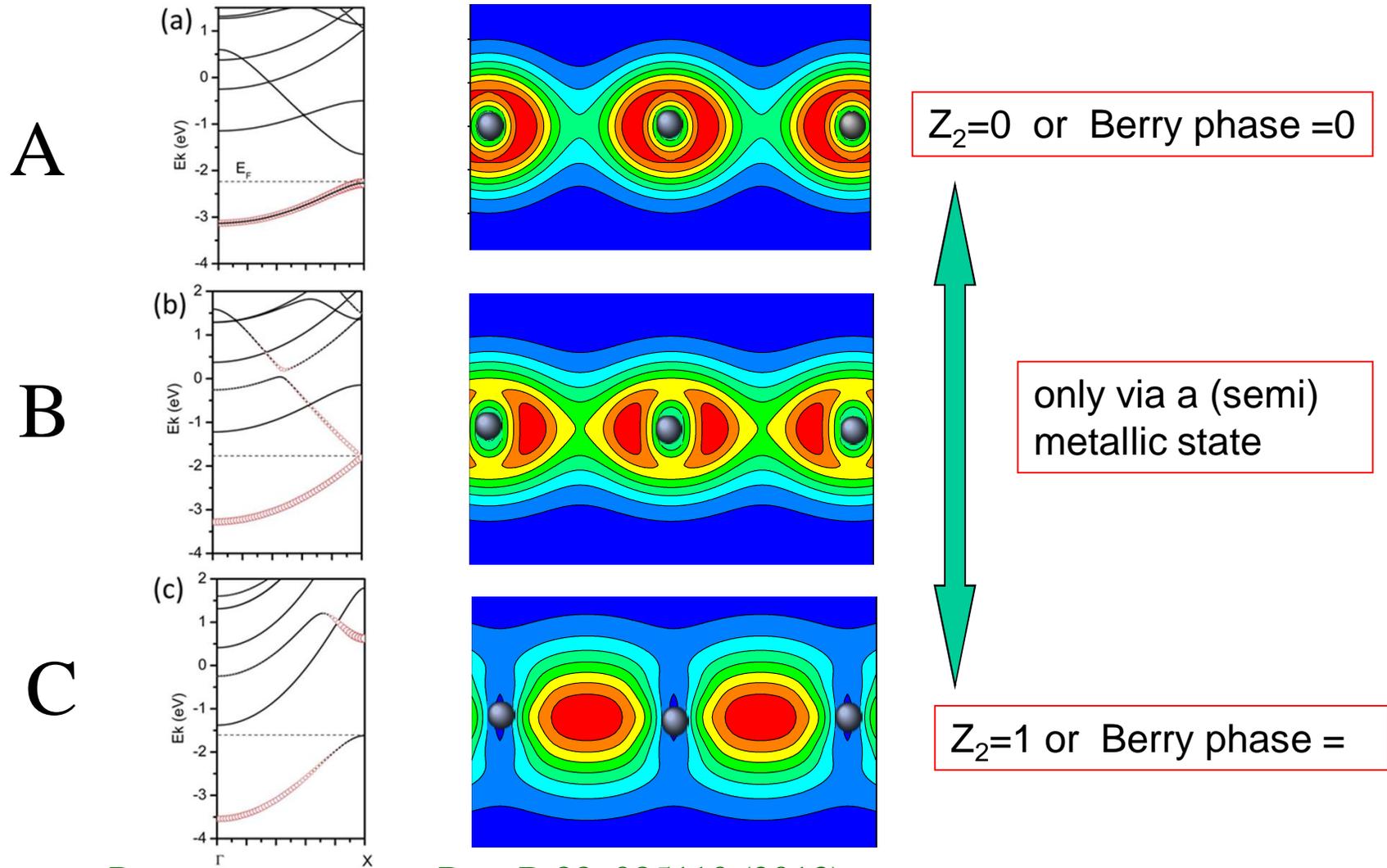


$A, B, C \rightarrow a = 9.0, 8.7$  and  $6.0$  Bohr

Li treated as having valence=2

# Topology and interstitial localization in 1D

$Z_2 =$  additive group of the integers mod 2 or two-valued invariant



P.Jadaun, *et al.* Phys. Rev. B 88, 085110 (2013)

# Summary

- É H<sub>6</sub> rings and hydrogenic graphene-like layers are especially stable due to aromatic and closed shell effects.
- É This stability is inherited by 3D structures of dense H.
- É Metallization of compressed H should occur by destroying the closed shell electronic structure, *f.e.* by lowering the bonding states associated with 2s and 2p orbitals.