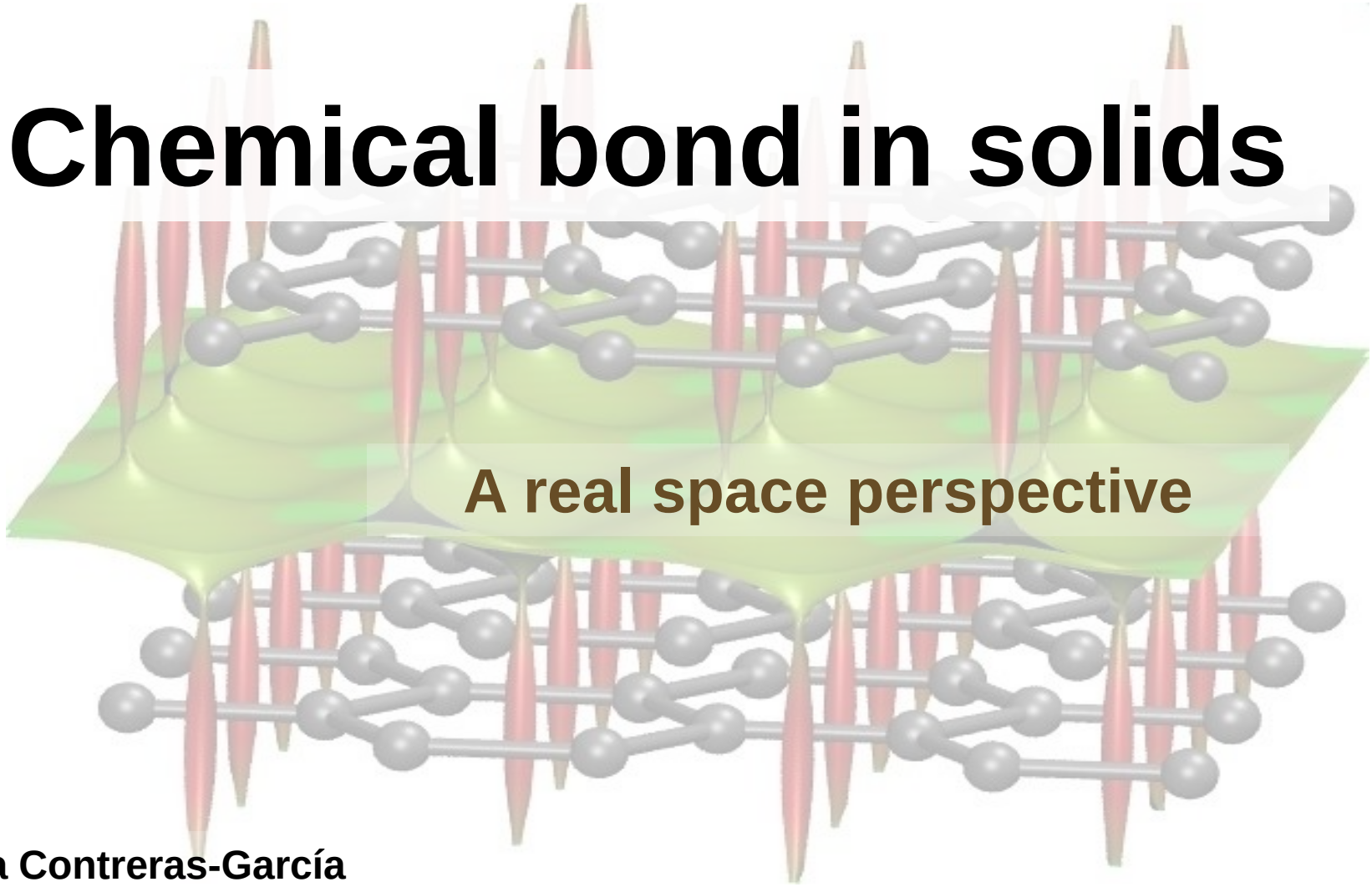
UPMC
SORBONNE UNIVERSITÉS

Chemical bond in solids



A real space perspective

Julia Contreras-García

Outline

1. Why studying chemical bonds?

2. Quantum Chemical topology

3. Chemical functions

    a) electron density

    b) ELF

    c) NCI

    1. The function
    2. The topology
    3. Old concepts
    4. New insight

4. Summary

Outline

5. Applications to high pressure

    a) ELF: Predicting compressibility and transitions

    b) NCI: He bonds

    c) Electron density: the borate family

6. The codes

7. Summary

Outline

1. Why studying chemical bonds?
2. Quantum Chemical topology
3. Chemical functions
   - a) electron density
   - b) ELF
   - c) NCI

   1. The function
   2. The topology
   3. Old concepts
   4. New insight
4. Summary

Motivation

« It's nice to know that the computer understands the problem. But I would like to understand it too. »

E.P. Wigner in Physics Today

The chemical bond is a divide-and-conquer approach

Motivation

Motivation

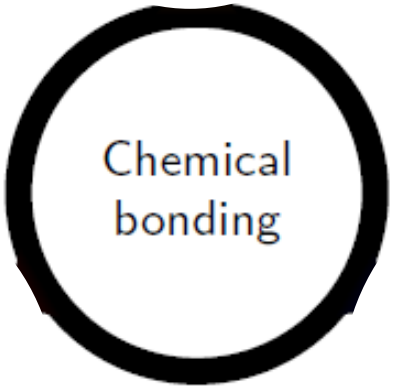

Materials by Inverse Design
Conventional Approach
Desired Properties
Materials

Quantum chemical topology

How do we divide and conquer in chemical bonds?

- Quantum chemistry gives us a quantitative description of chemical systems. It is predictive
- Bonds are objects from Classical Chemistry
- We need extra tools to extract quantitative information from Quantum Chemistry

(and reduce the dimensionality)



Quantum chemical topology

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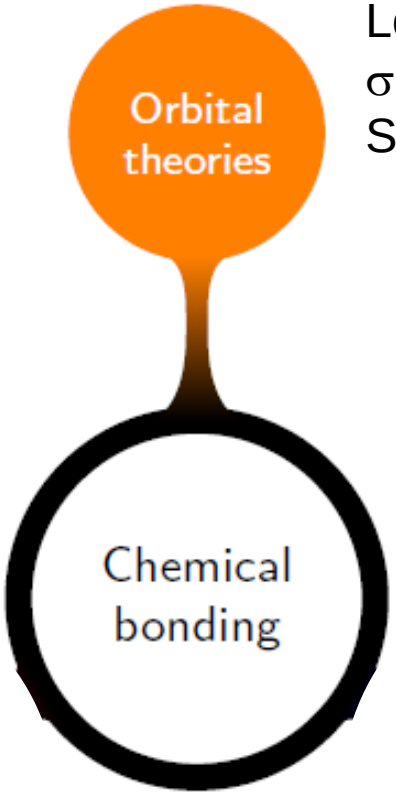

Localized orbitals

σ *vs* π

Symmetry

Quantum chemical topology

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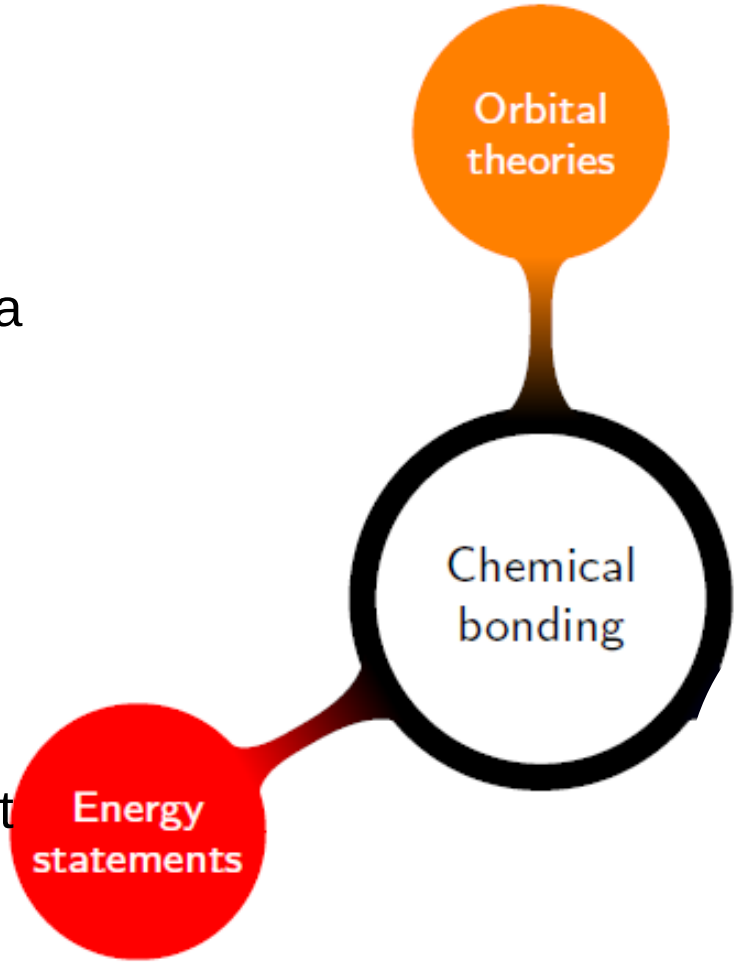

Dispersion
Charge transfer

Quantum chemical topology

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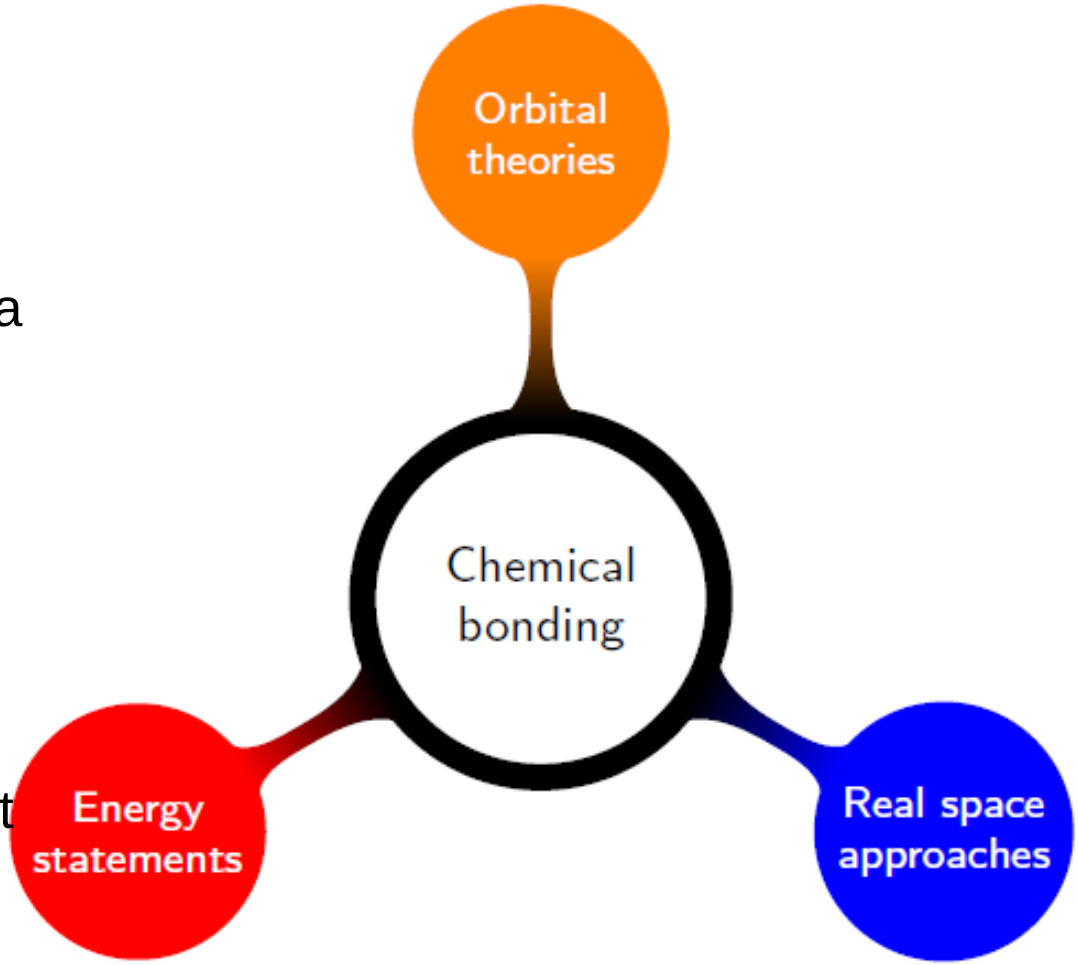
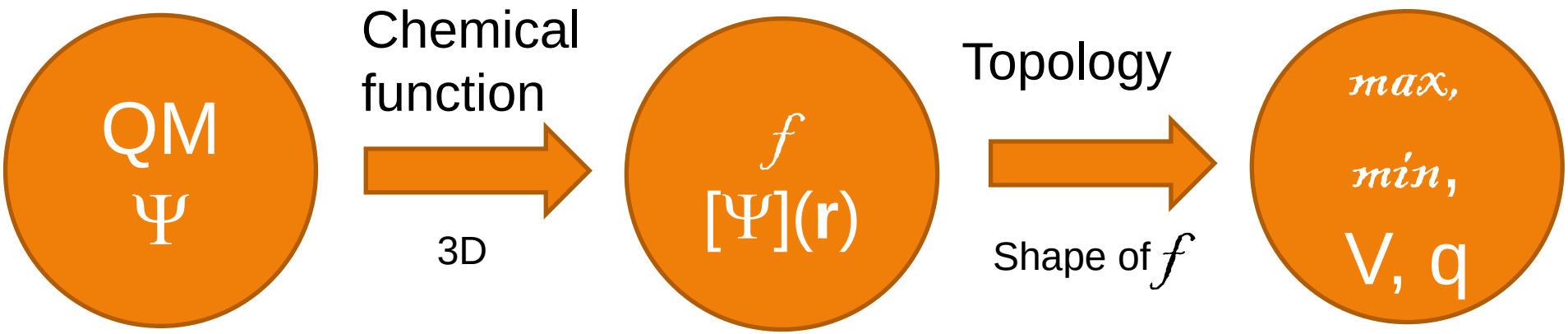
(and reduce the dimensionality)



QCT in a nutshell

Quantum topology

Classical Chemistry ⟷ 3D ⟷ **Quantum chemistry**



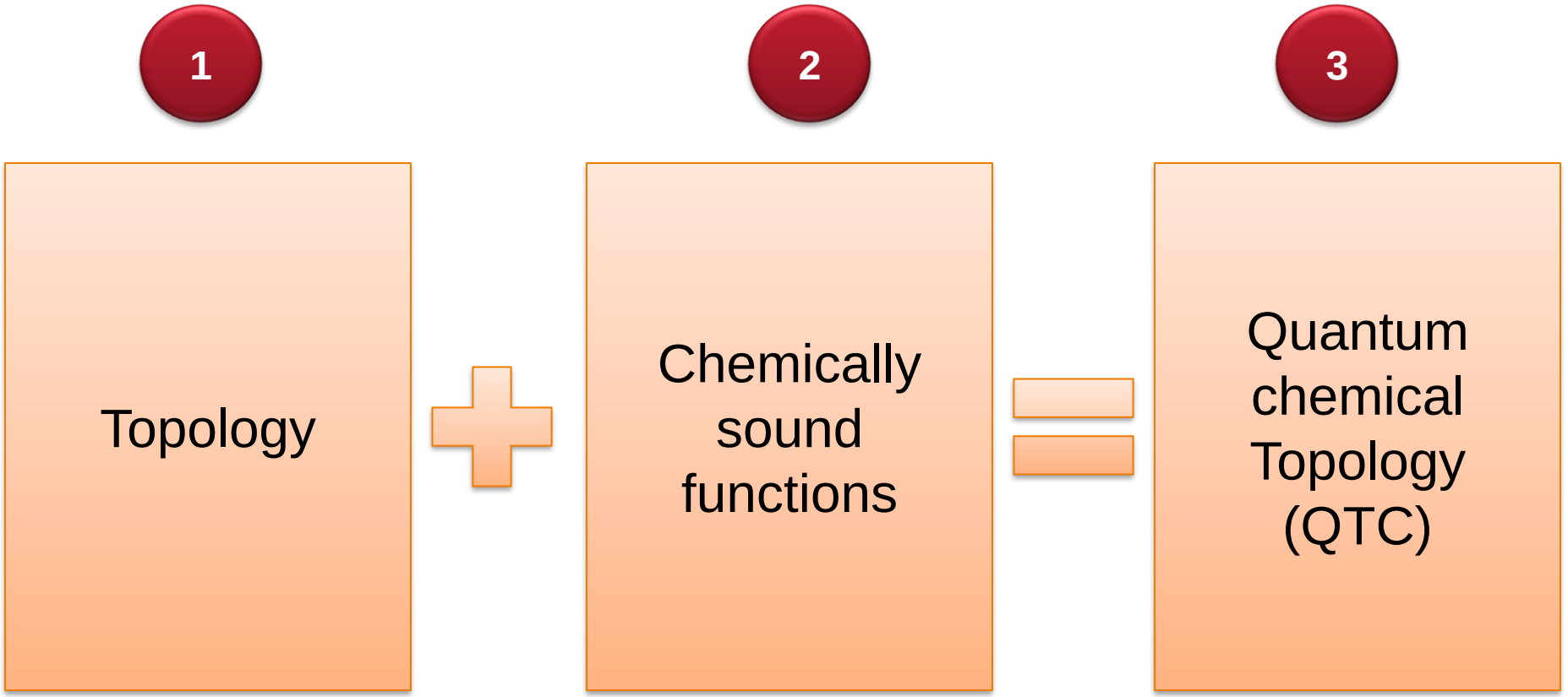
QTC in a nutshell

Real space approaches

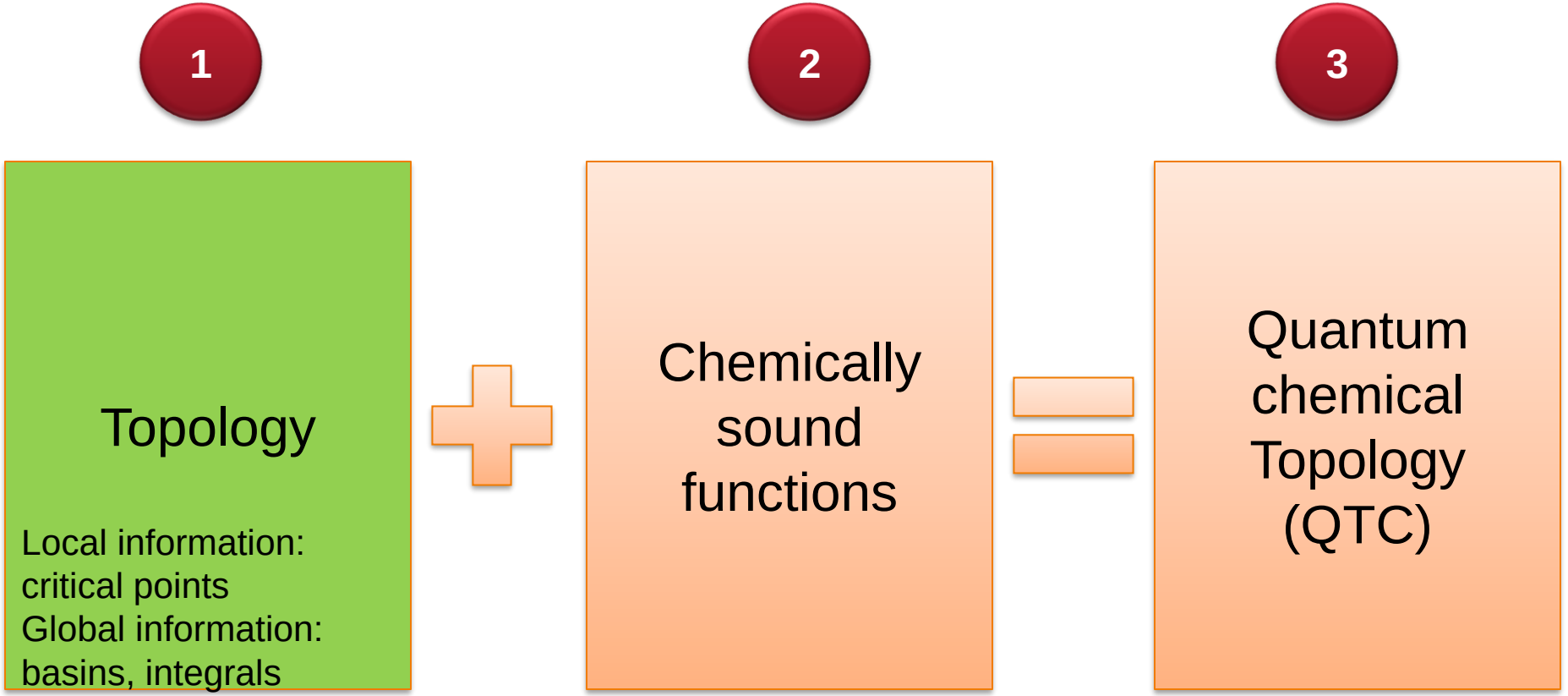
- Orbital invariant (summation over orbitals)
- Inherently defined in 3D (comprehensible dimensionality)
- Do not depend on the method (applicable to all approximations)
- Usually related to experimental data

- BUT no direct connexion to energetics (lack of the exact functional)

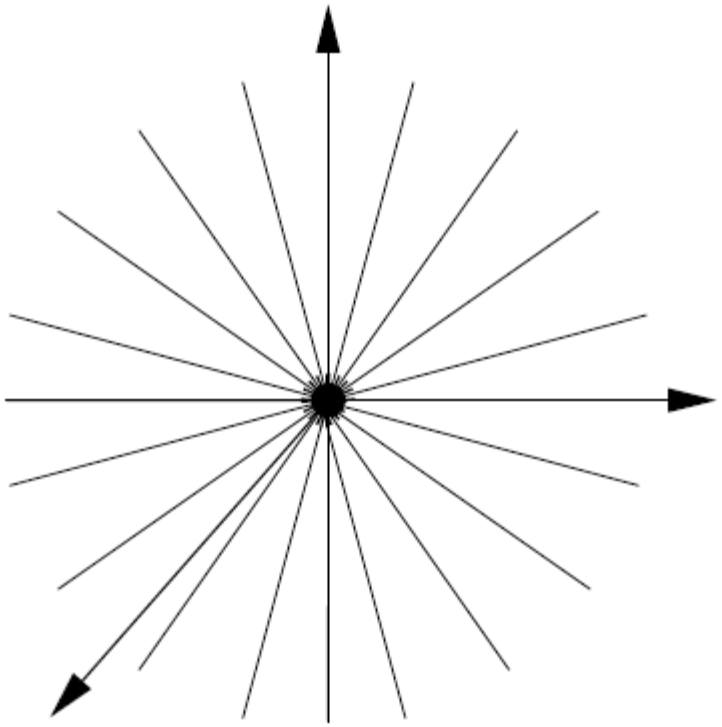
QCT in a nutshell



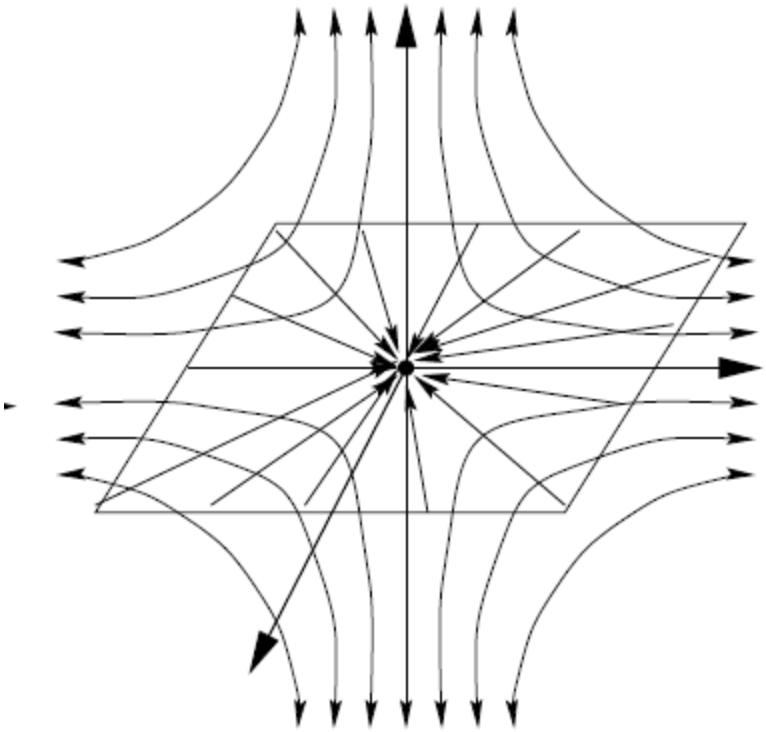
QCT in a nutshell



Types of CPs in 3D

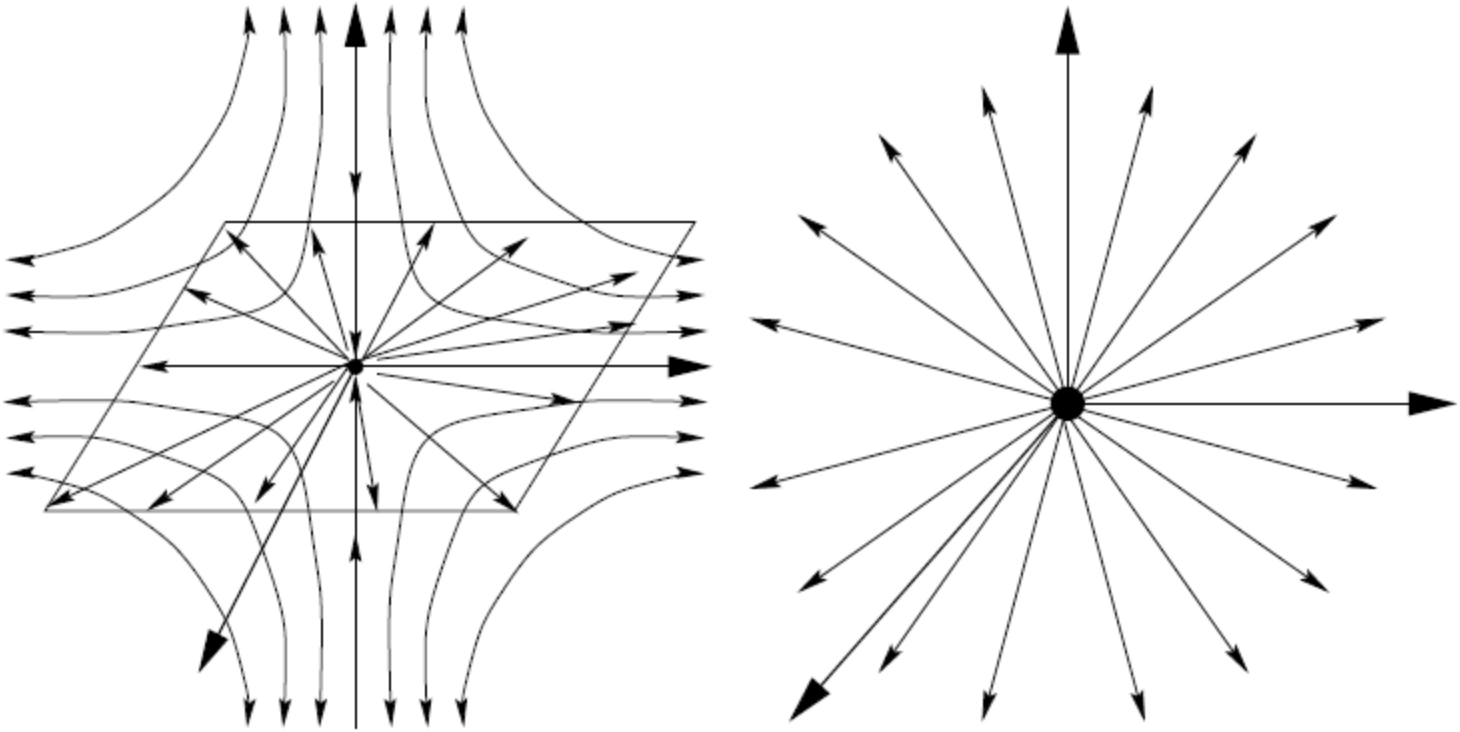


Maximum



Saddle point of order 1

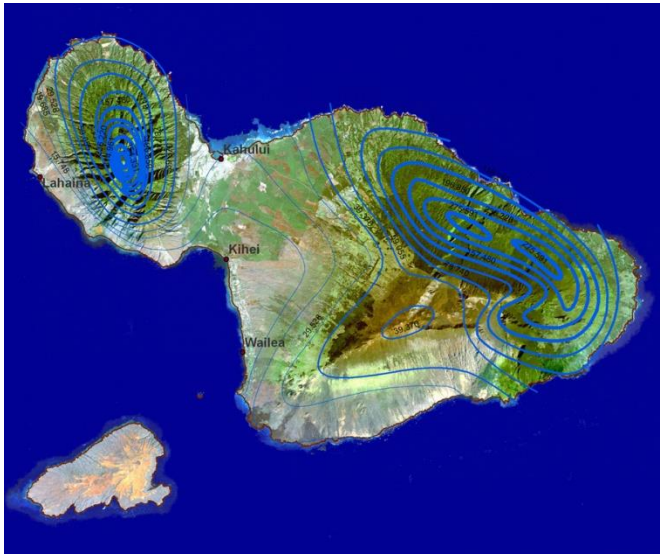
Types of CPs in 3D



Saddle point of order 2

Minimum

Topological partitions are intuitive



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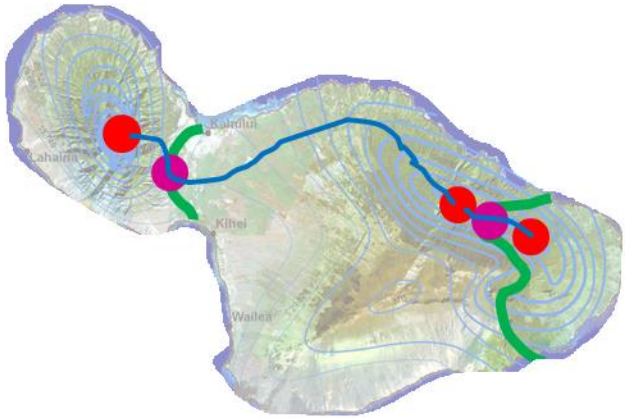
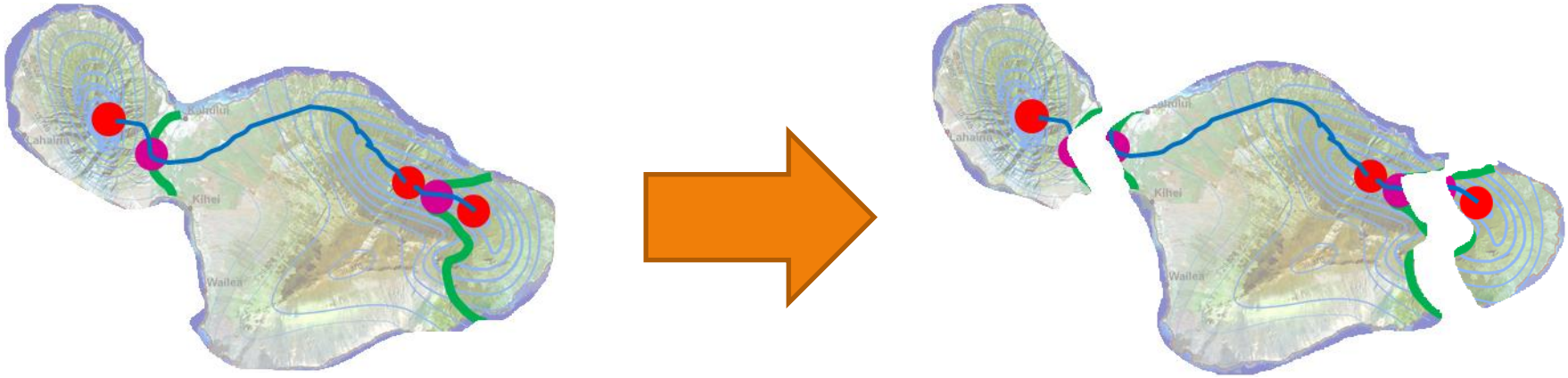


We automatically

- Identify cusps
- Divide through the valleys
- Identify the lowest point in the valley

Topological partitions are intuitive



We automatically

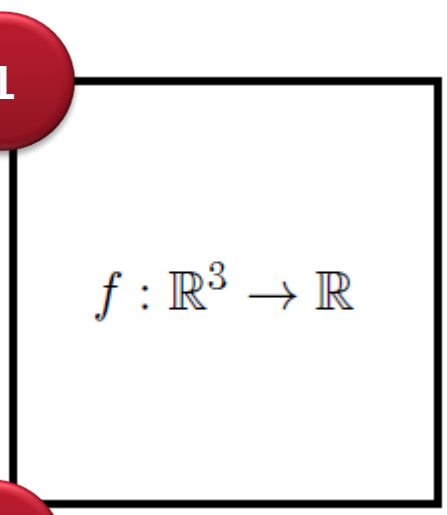
- Identify cusps
- Divide through the valleys
- Identify the lowest point in the valley

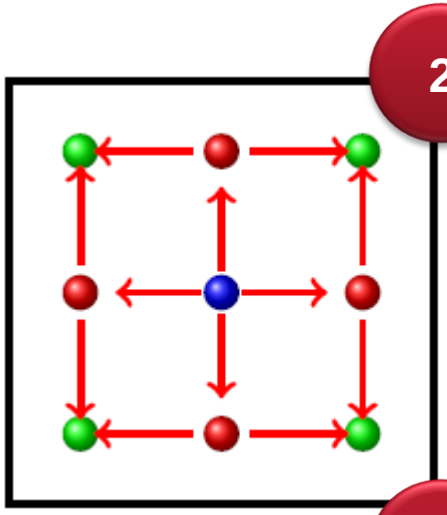
- Use this information to see three regions
- These regions contain orography information

Meaning is inherited

QCT in a nutshell

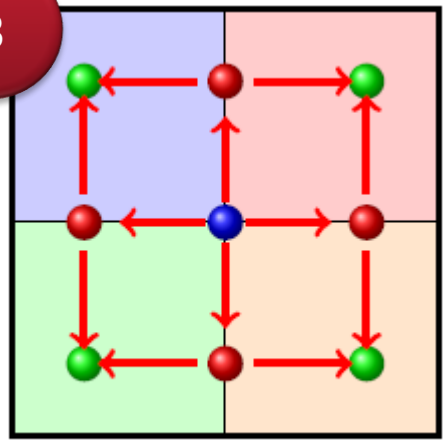
Compute scalar in the molecular /crystal space

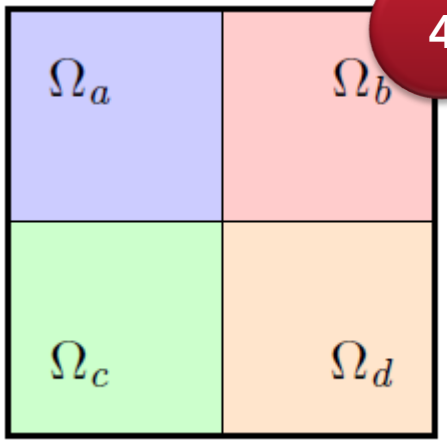




Find critical points (gradient=0)

Find separatrix (flux=0) separating the regions

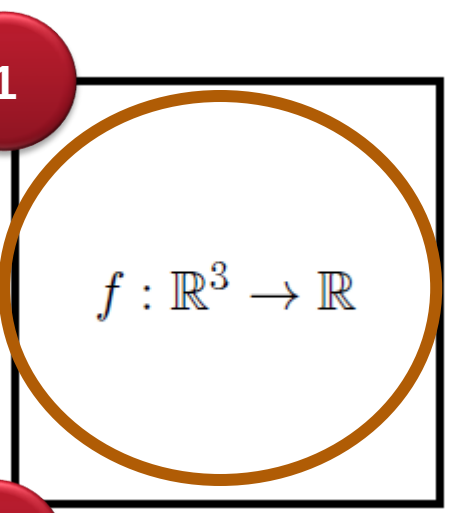


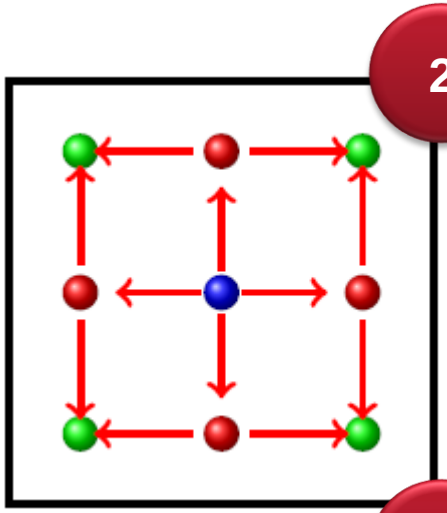


Integrate properties over regions

QCT in a nutshell

Compute scalar in the molecular /crystal space





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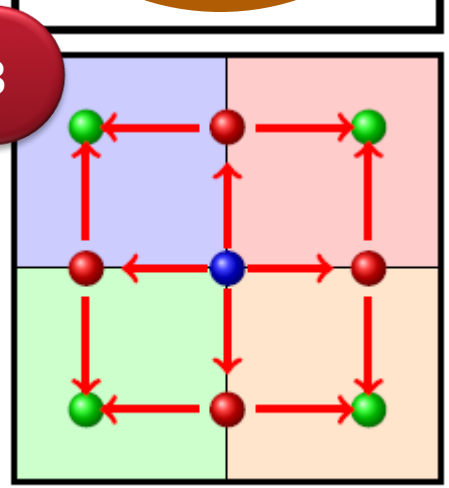

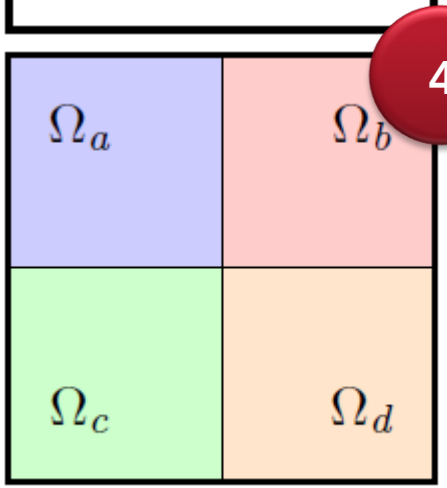

Integrate properties over regions

Outline

1. Why studying chemical bonds?

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3. Chemical functions

    a) electron density

    b) ELF

    c) NCI

4. Summary

The electron density

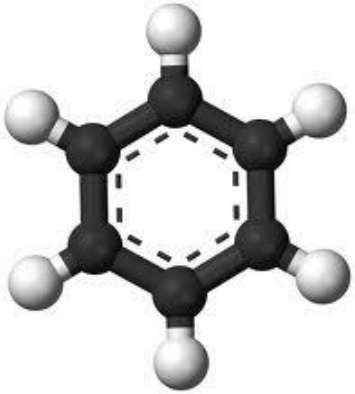
• ρ(r) is a fundamental property of any electronic system

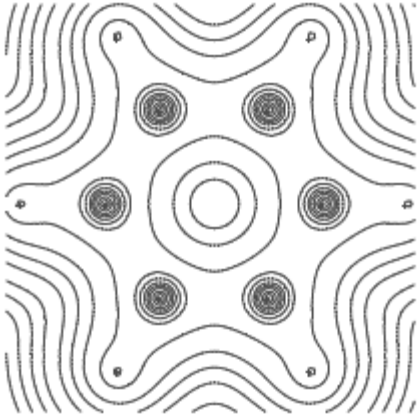
$$\rho(\vec{r}) = N \int \ldots \int \left|\Psi(\vec{x}_1, \vec{x}_2, \ldots, \vec{x}_N)\right|^2 ds\, d\vec{x}_2 \ldots \vec{x}_N$$

- is experimentally accessible
- is defined within the exact many-body theory,
- is supported by the Hohenberg−Kohn theorem

Example: the electron density

Approxiamately, sum of exponentials over the atoms

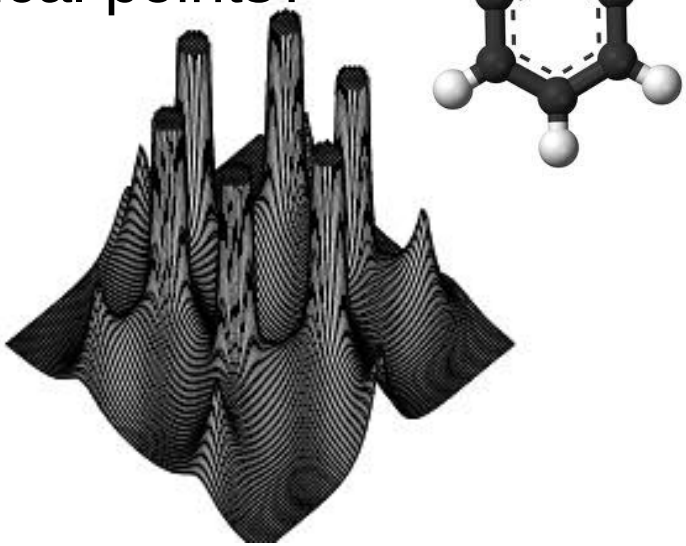


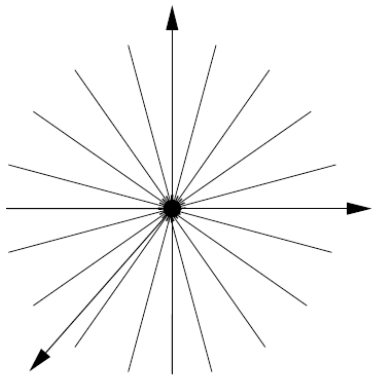


Example: the electron density

Where are the critical points?

- Maxima = nuclei

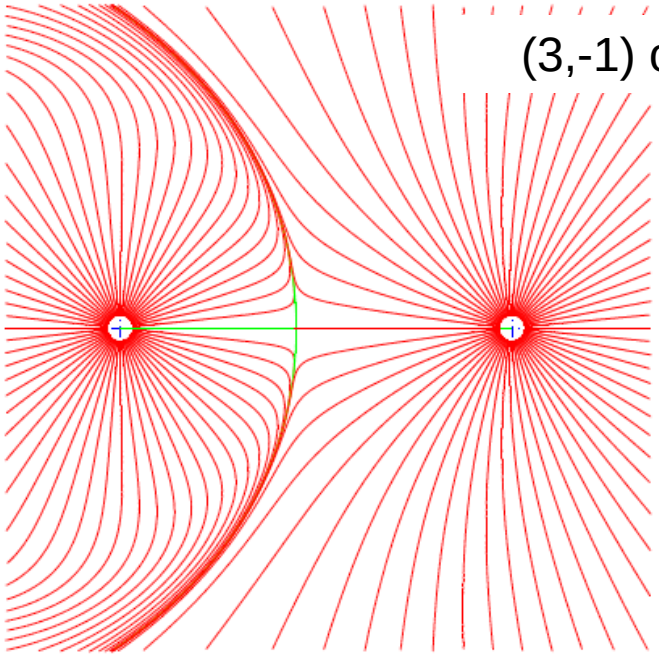


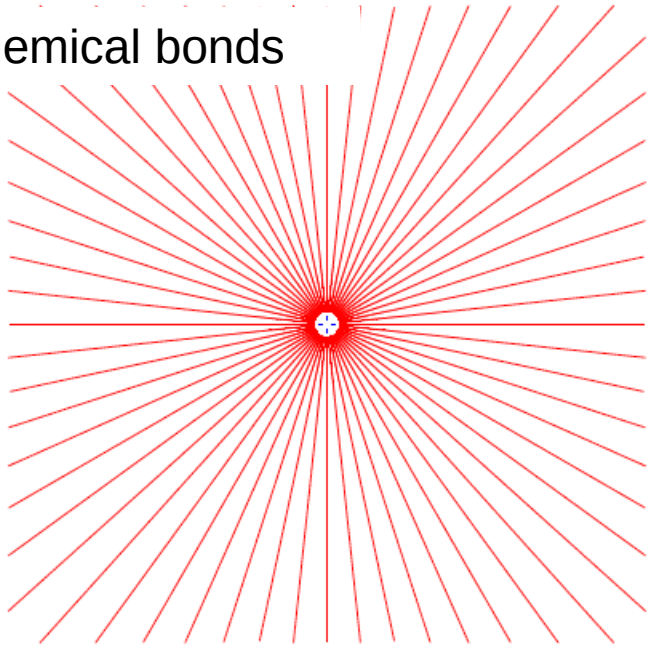


(a) Sumidero de líneas de campo.

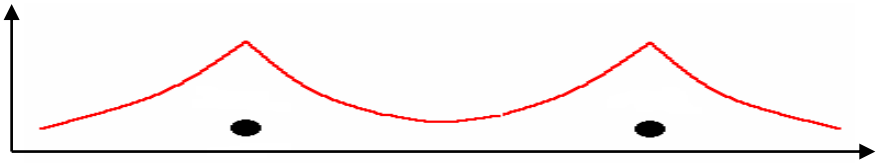
The electron density

(3,-1) occur at chemical bonds

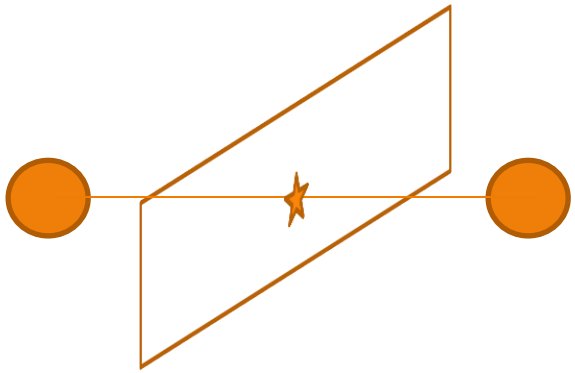




Plane that contains the nuclei

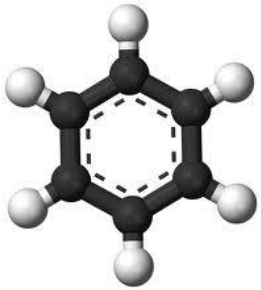


Plane perpendicular to the internuclear line at the critical point that contains the nuclei

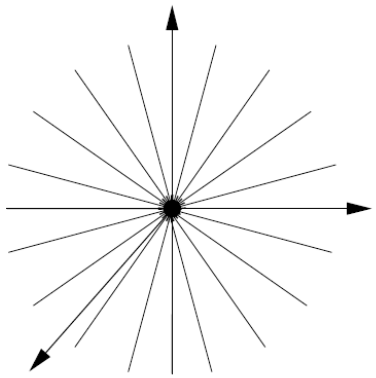


Example: the electron density

Where are the critical points?

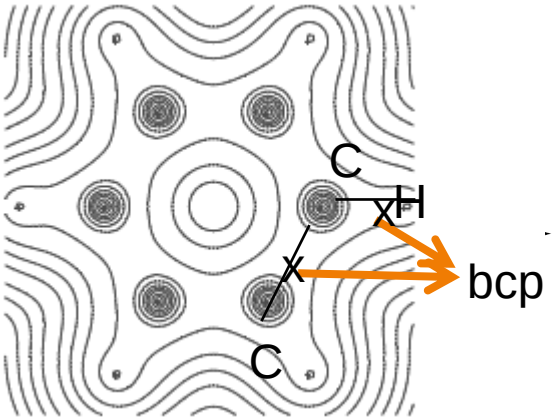


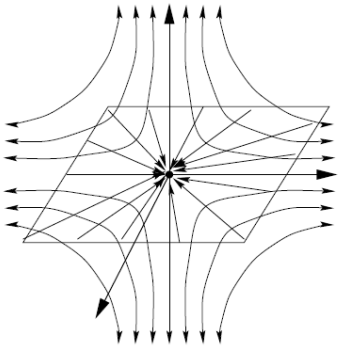
- Maxima = nuclei



(a) Sumidero de líneas de campo.

- 1st order saddle points=bonds

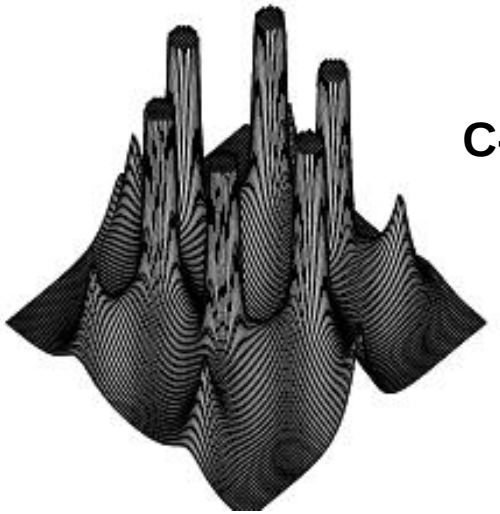




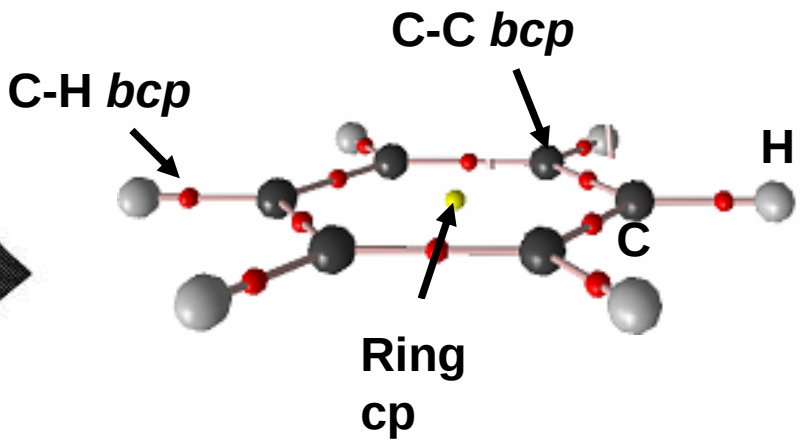
(b) Silla tipo 1.

The electron density

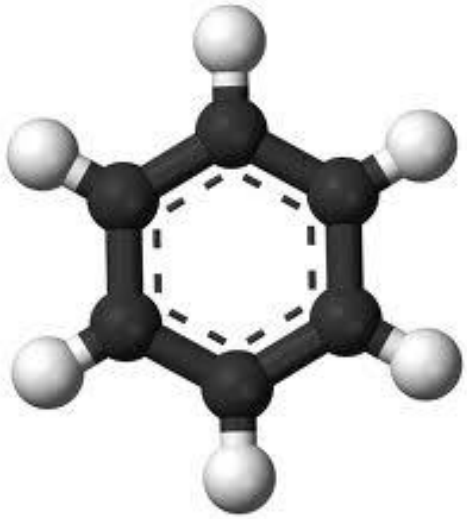
We can know from ab initio methods the chemical structure i.e. Where do we draw lines between atoms?



Density



ρ topology



Chemical structure

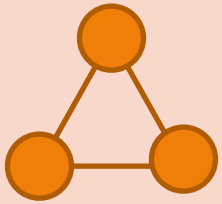
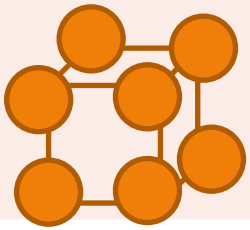
- Maxima = nuclei
- Bond = 1st order saddle point (*bcp*)

QCT in a nutshell

Directions along which the field grows

Directions along which the field decreases

Sum of signs of eigenvalues

CP	λ>0	λ<0	Signature (s)	(r,s)	name	acronym	Figure
Maximum	0	3	-3	(3,-3)	maximum		
1st order saddle point	1	2	-1	(3,-1)	Bond critical point	bcp	
2nd order saddle point	2	1	+1	(3,+1)	Ring critical point	rcp	
Minimum	3	0	+3	(3,+3)	Cage critical point	ccp	

Local information: CPs

- In a periodic system, you will always have the 4 types of non-degenerated critical points
- Morse relationship MUST hold:

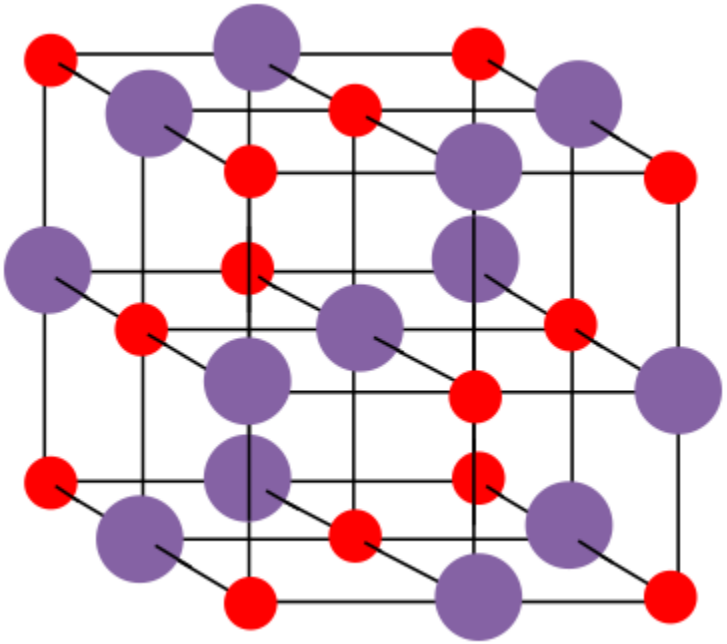
$$n_{(3,-3)}-n_{(3,-1)}+n_{(3,+1)}-n_{(3,+3)}=0$$

$$\begin{cases} n_{(3,-3)} \geq 1 \\ n_{(3,-1)} \geq 3 \\ n_{(3,+1)} \geq 3 \\ n_{(3,+3)} \geq 1 \end{cases}$$

- If $\lambda_i=0$, these are degenerated critical « points » (we will see an example later).

  E.g. (2,-2)

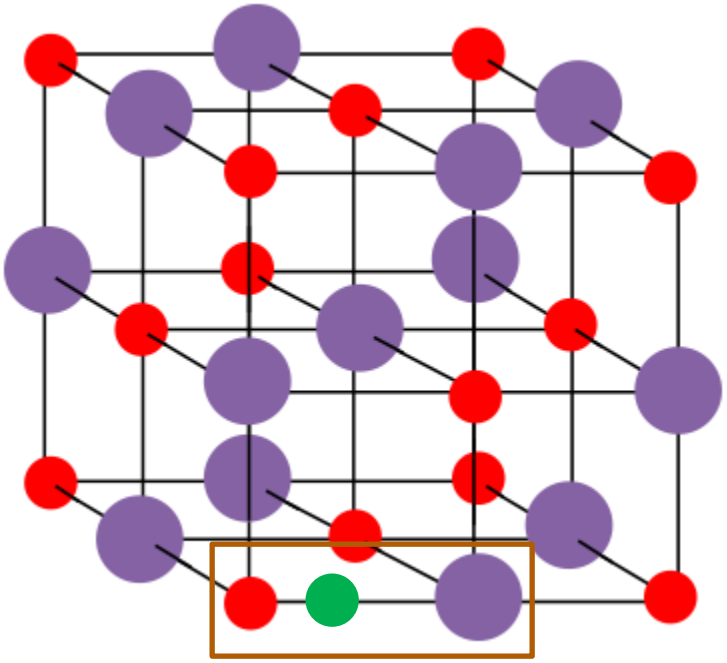
Local information: CPs



- Attractors are at the nuclei positions

Simet.	Clase	Tipo	x	y	z
Oh	(3,-3)	Nucl. Na	0.00000	0.00000	0.00000
Oh	(3,-3)	Nucl. Cl	0.50000	0.50000	0.50000

Local information: CPs

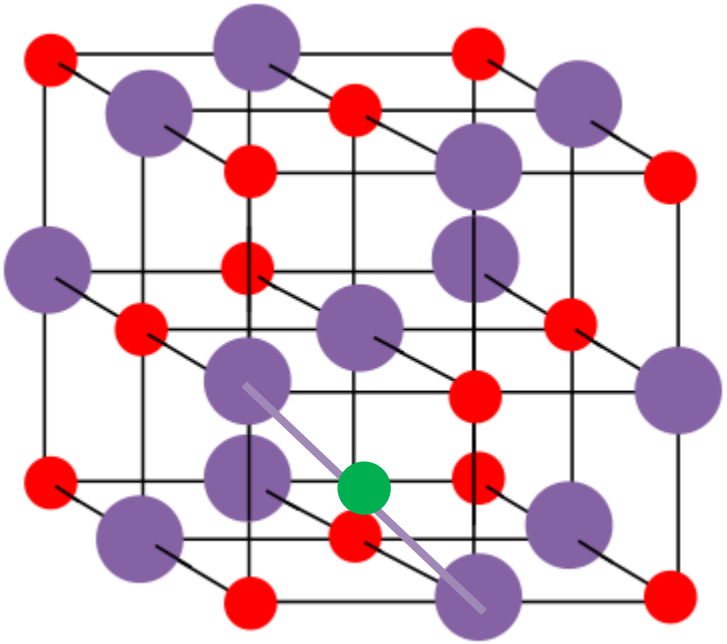


- Attractors are at the nuclei positions
- (3,-1) signal interactions

Simet.	Clase	Tipo	x	y	z
Oh	(3,-3)	Nucl. Na	0.00000	0.00000	0.00000
Oh	(3,-3)	Nucl. Cl	0.50000	0.50000	0.50000
C3v	(3,-1)	Enlace	0.20618	0.20618	0.20618

Cation-anion

Local information: CPs

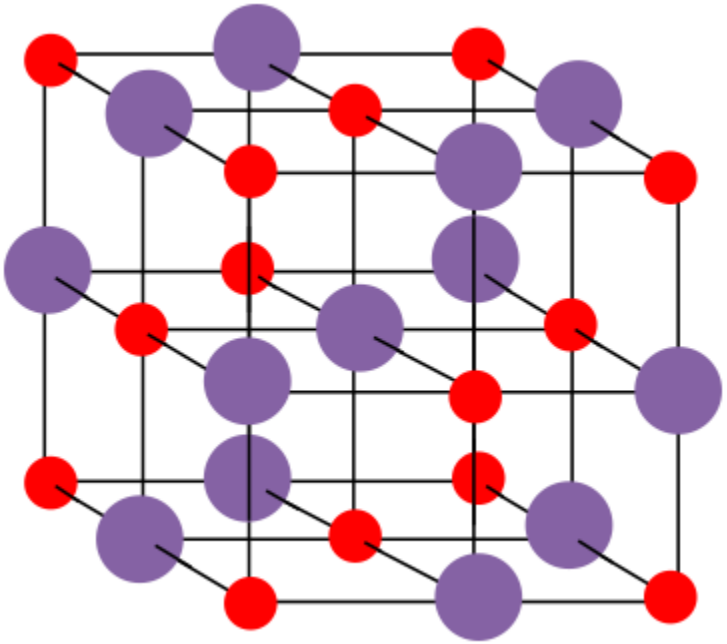


- Attractors are at the nuclei positions
- (3,-1) signal interactions

Anion-anion interactions are quite common in crystals

Simet.	Clase	Tipo	x	y	z	
Oh	(3,-3)	Nucl. Na	0.00000	0.00000	0.00000	
Oh	(3,-3)	Nucl. Cl	0.50000	0.50000	0.50000	
C3v	(3,-1)	Enlace	0.20618	0.20618	0.20618	Cation-anion
D4h	(3,-1)	Enlace	0.00000	0.50000	0.50000	Anion-anion

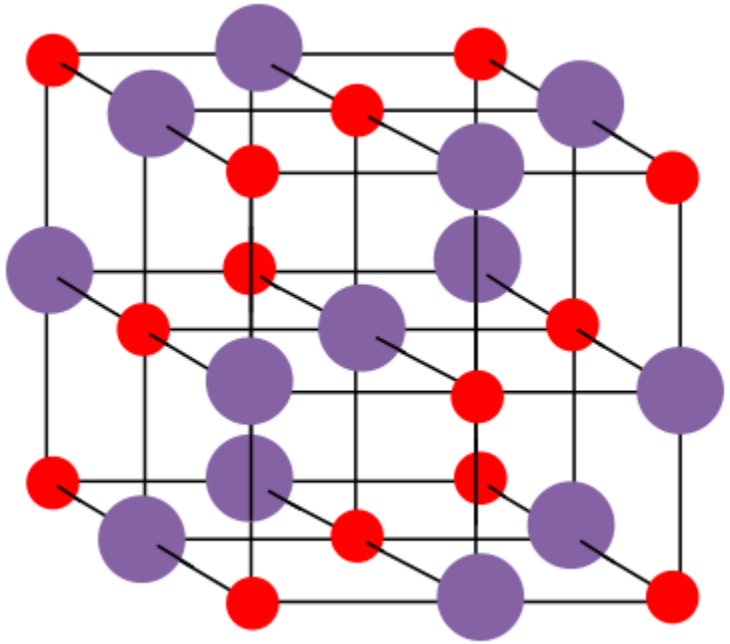
Local information: CPs



- We have all types of critical points

Simet.	Clase	Tipo	x	y	z
Oh	(3,-3)	Nucl. Na	0.00000	0.00000	0.00000
Oh	(3,-3)	Nucl. Cl	0.50000	0.50000	0.50000
C3v	(3,-1)	Enlace	0.20618	0.20618	0.20618
D4h	(3,-1)	Enlace	0.00000	0.50000	0.50000
C2v	(3, 1)	Anillo	0.00000	0.28136	0.28136
D4h	(3, 3)	Caja	0.00000	0.00000	0.50000

Local information: CPs

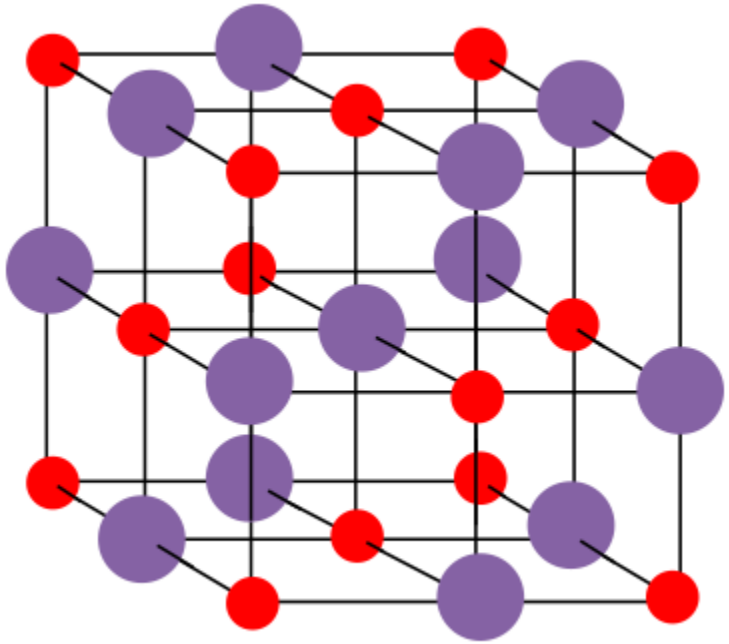


- We have all types of critical points
- Morse sum is working

2-11+12-3=0

Simet.	Clase	Tipo	x	y	z	Mult.
Oh	(3,-3)	Nucl. Na	0.00000	0.00000	0.00000	+ 1
Oh	(3,-3)	Nucl. Cl	0.50000	0.50000	0.50000	+ 1
C3v	(3,-1)	Enlace	0.20618	0.20618	0.20618	- 8
D4h	(3,-1)	Enlace	0.00000	0.50000	0.50000	- 3
C2v	(3, 1)	Anillo	0.00000	0.28136	0.28136	+ 12
D4h	(3, 3)	Caja	0.00000	0.00000	0.50000	- 3

Local information: CPs



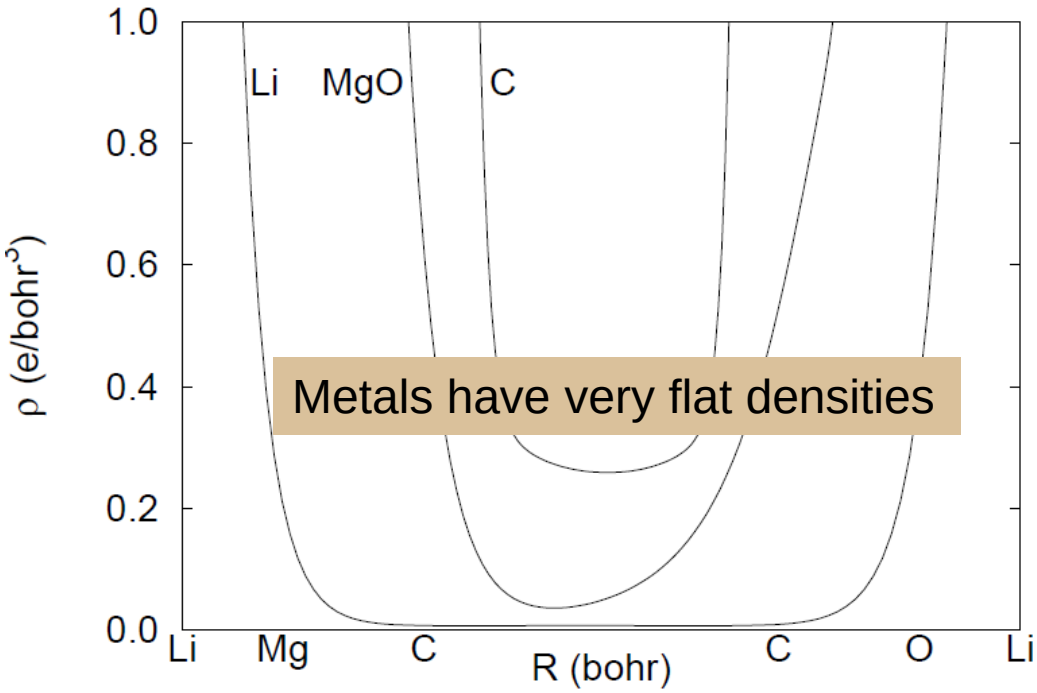
- We have all types of critical points
- Morse sum is working

  2-11+12-3=0

- We only have (3,-3) at the nuclei?

Simet.	Clase	Tipo	x	y	z		Mult.
Oh	(3,-3)	Nucl. Na	0.00000	0.00000	0.00000	+	1
Oh	(3,-3)	Nucl. Cl	0.50000	0.50000	0.50000	+	1
C3v	(3,-1)	Enlace	0.20618	0.20618	0.20618	-	8
D4h	(3,-1)	Enlace	0.00000	0.50000	0.50000	-	3
C2v	(3, 1)	Anillo	0.00000	0.28136	0.28136	+	12
D4h	(3, 3)	Caja	0.00000	0.00000	0.50000	-	3

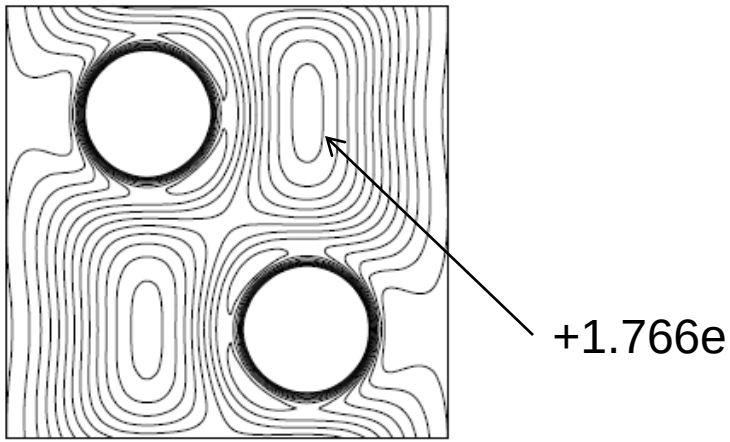
Local information: CPs

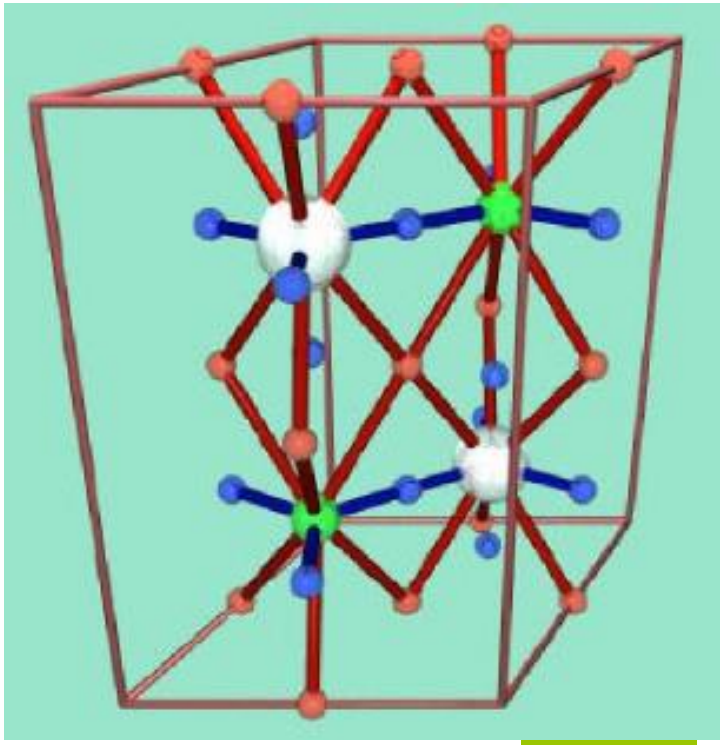


Metals have very flat densities

Beriullium HCP

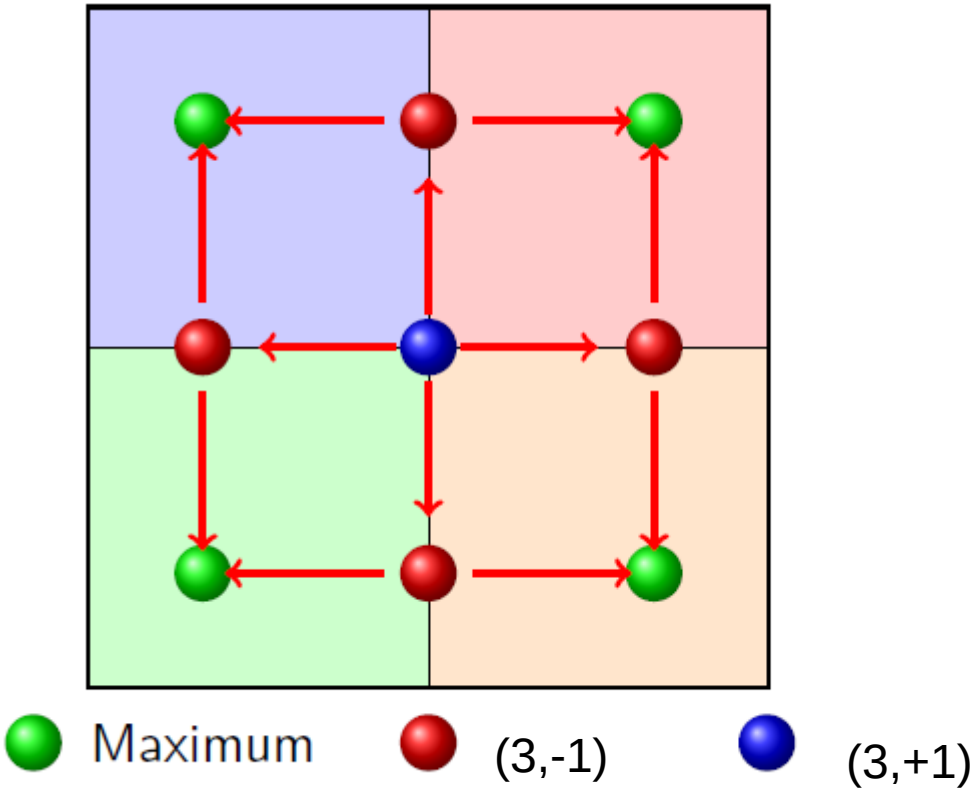
PC	x	y	z	ρ(PC)
n(Be)	0.3333	0.6667	0.2500	32.6222
n(MNN)	0.3333	0.6667	0.7500	0.0488





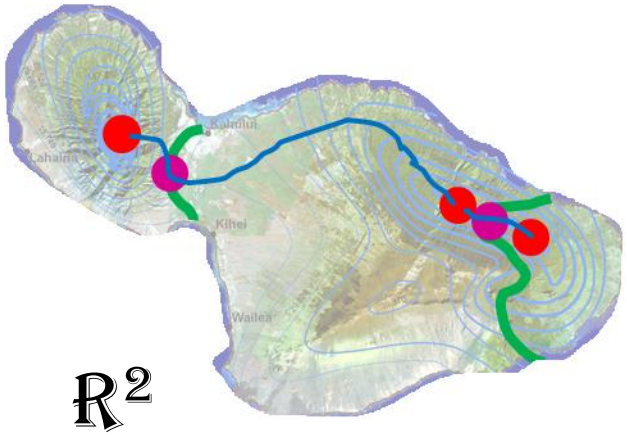
QCT in a nutshell

3 Computing the Morse complex of f

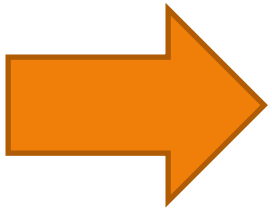


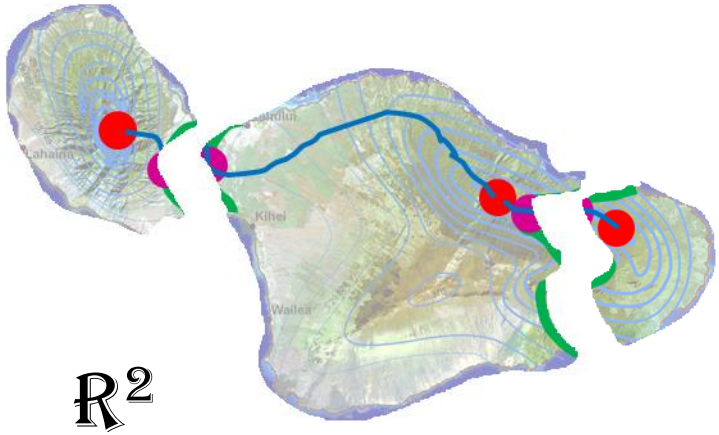
Each maximum has an associated region of space (basin)

Example: the electron density

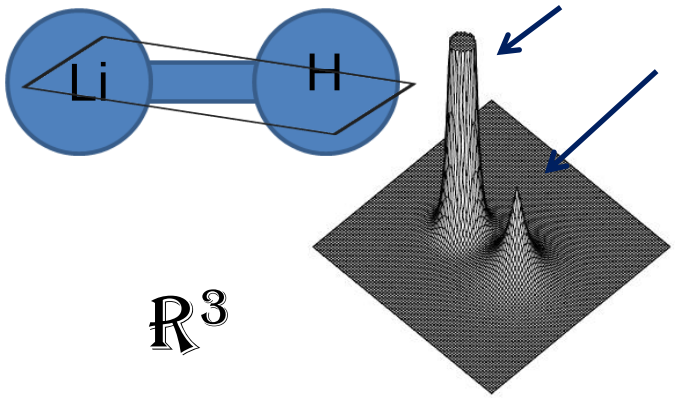


$\mathbb{R}^2$

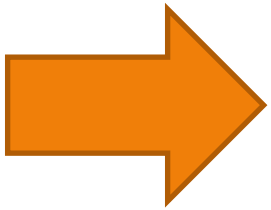


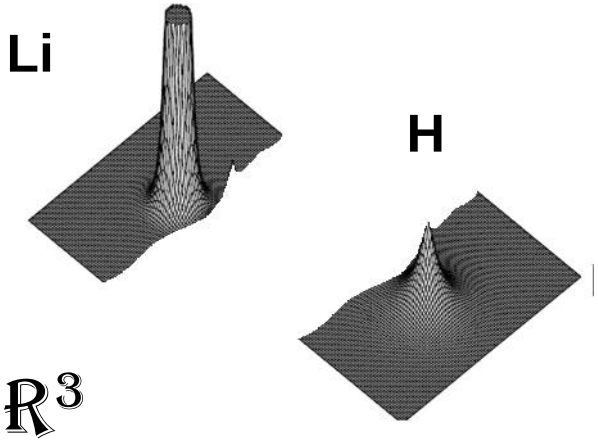


$\mathbb{R}^2$



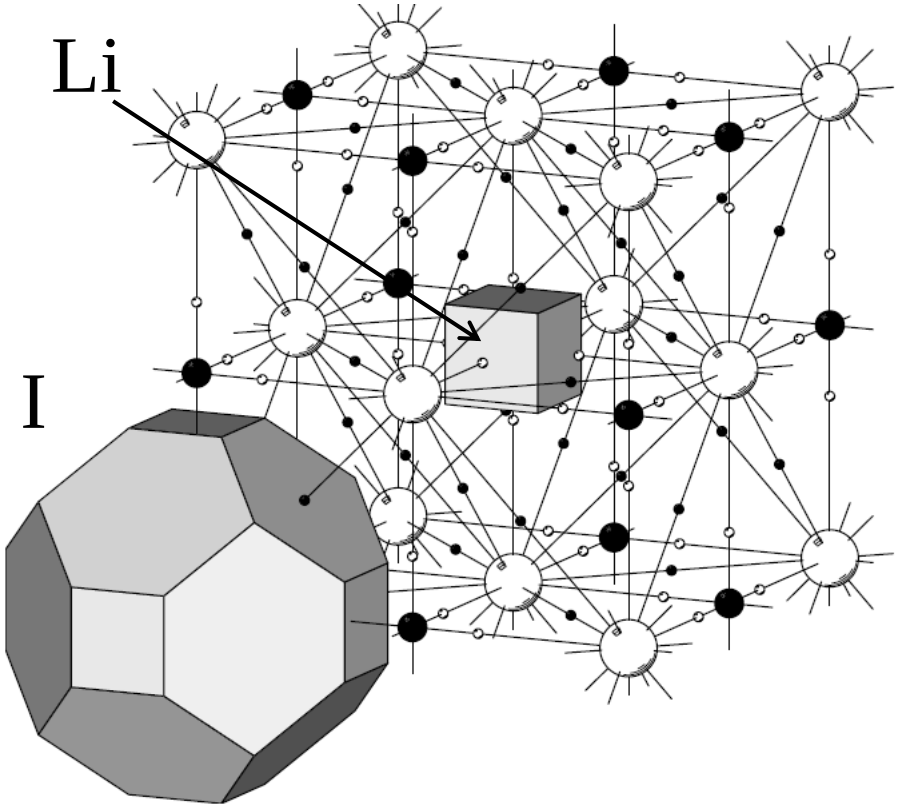
$\mathbb{R}^3$





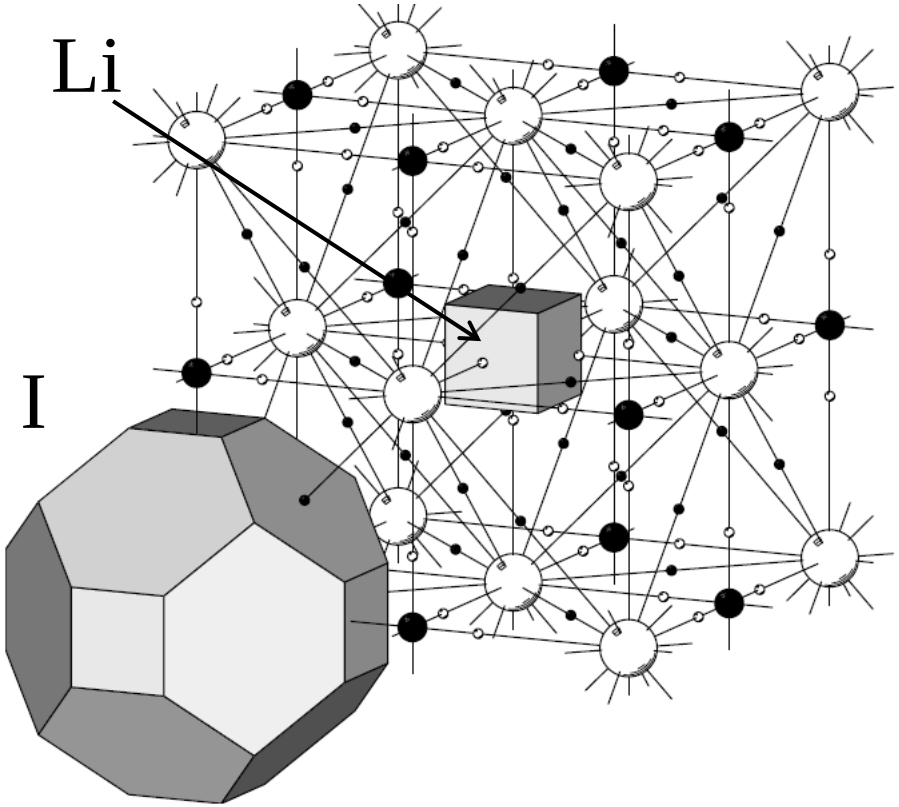
$\mathbb{R}^3$

Old concepts

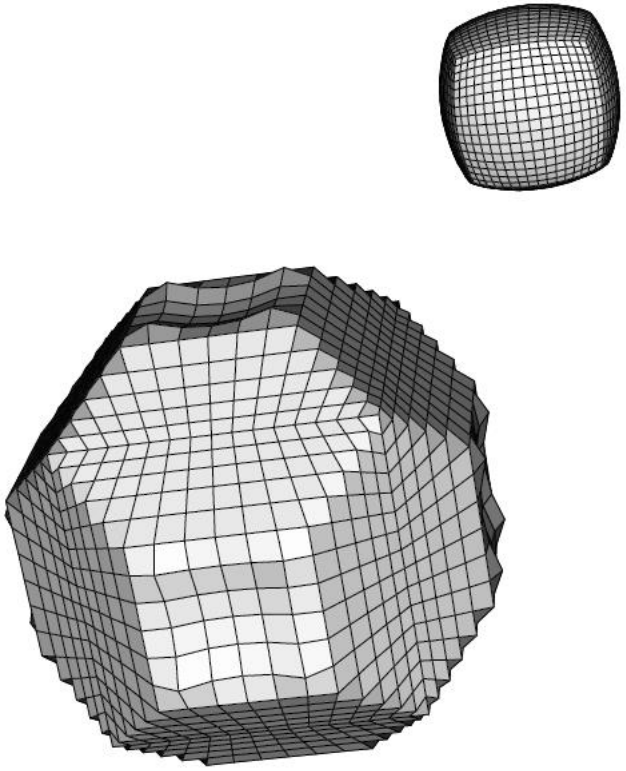


Contact Polyhedra

Old concepts



Contact Polyhedra



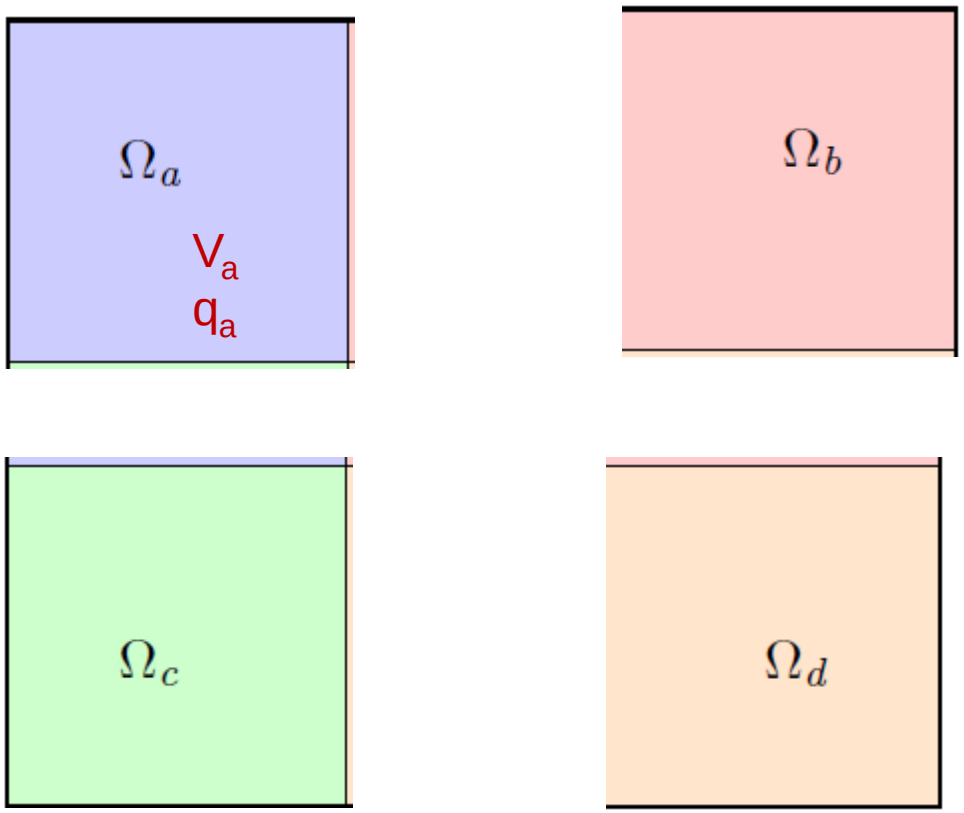
Electron density basins

QCT in a nutshell

4

Calculate properties within the basins of $f(\Omega)$

$$q_A = \int_{\Omega_A} \rho dV$$



QCT in a nutshell

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Calculate properties within the basins of $f(\Omega)$

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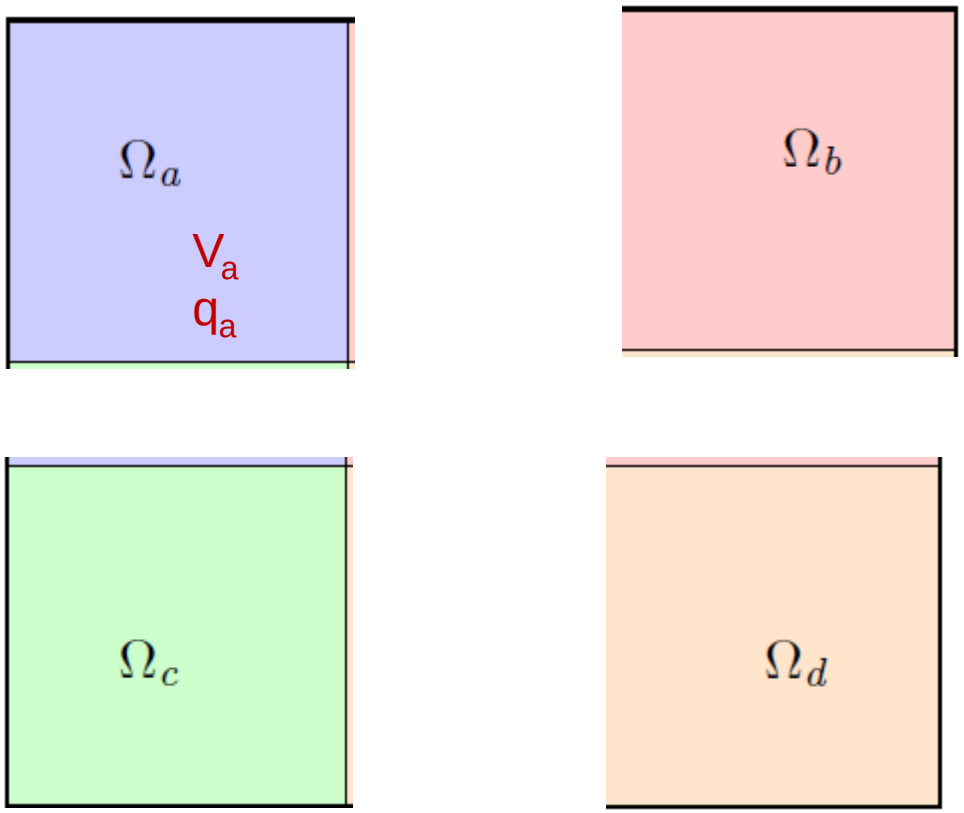
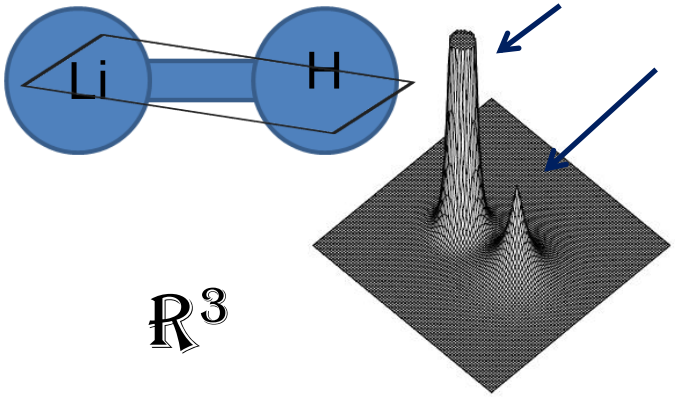


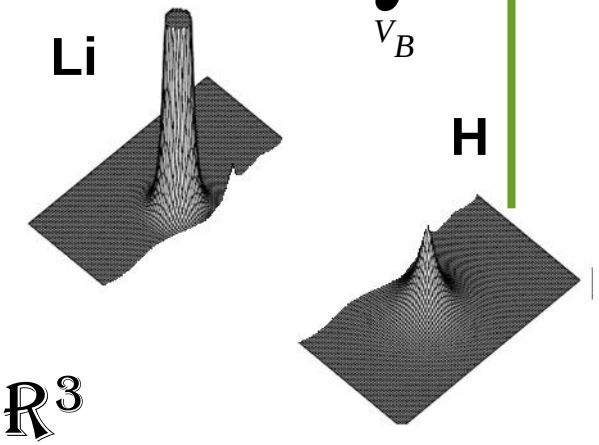
$$N = \sum_A q_A$$

Properties are additive



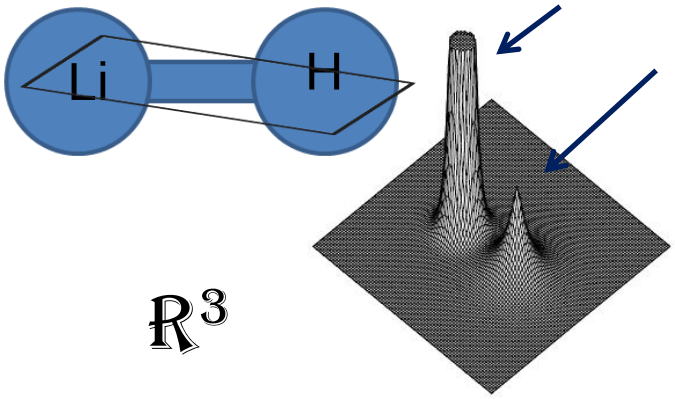
$\mathbb{R}^3$

$$q_B = \int_{V_B} \rho(\vec{r})d\vec{r} \approx 2e$$



$\mathbb{R}^3$

$$q_{Li} + q_H = Q_{tot}$$



$\mathbb{R}^3$

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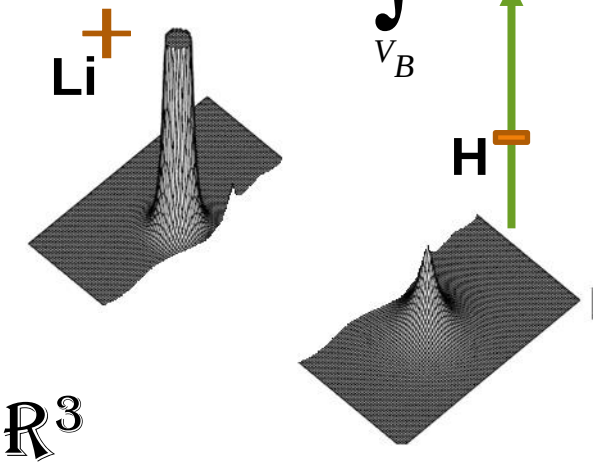
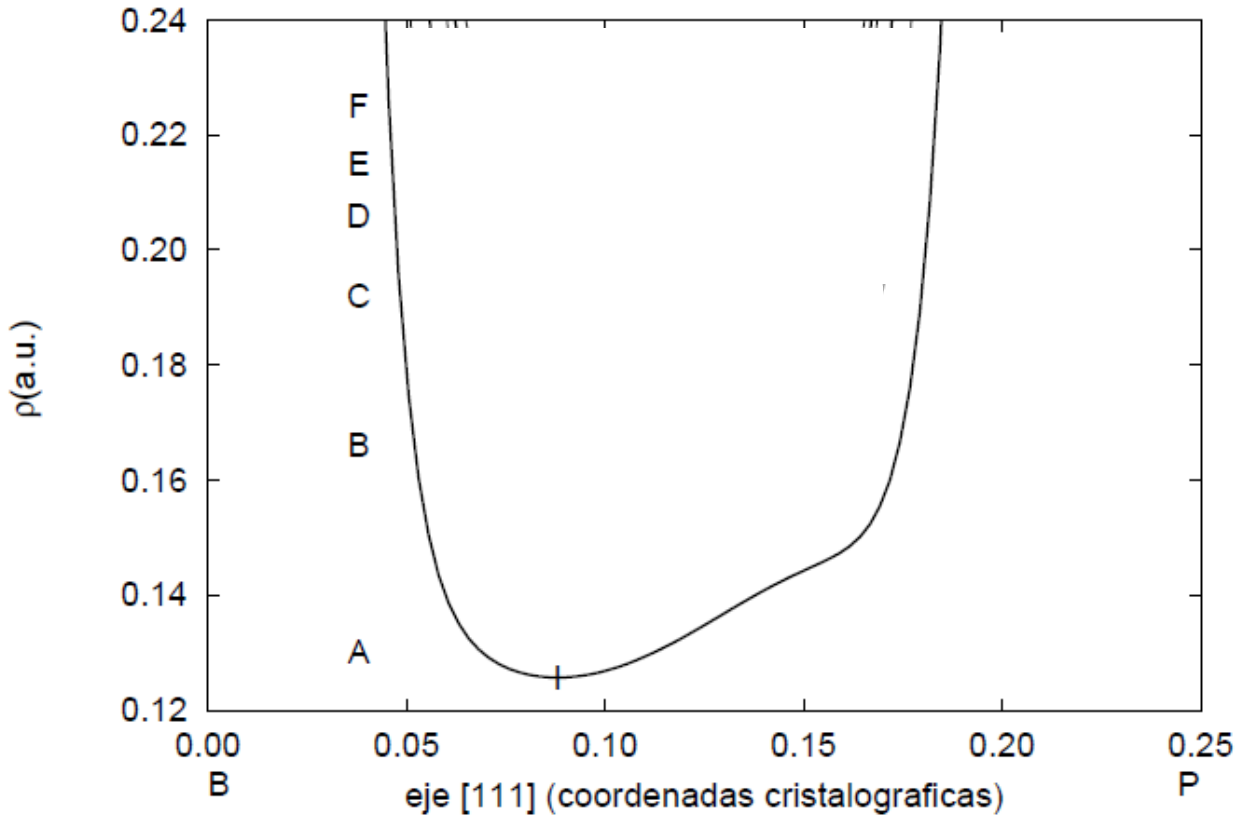


$\mathbb{R}^3$

$$q_{Li} + q_H = Q_{tot}$$

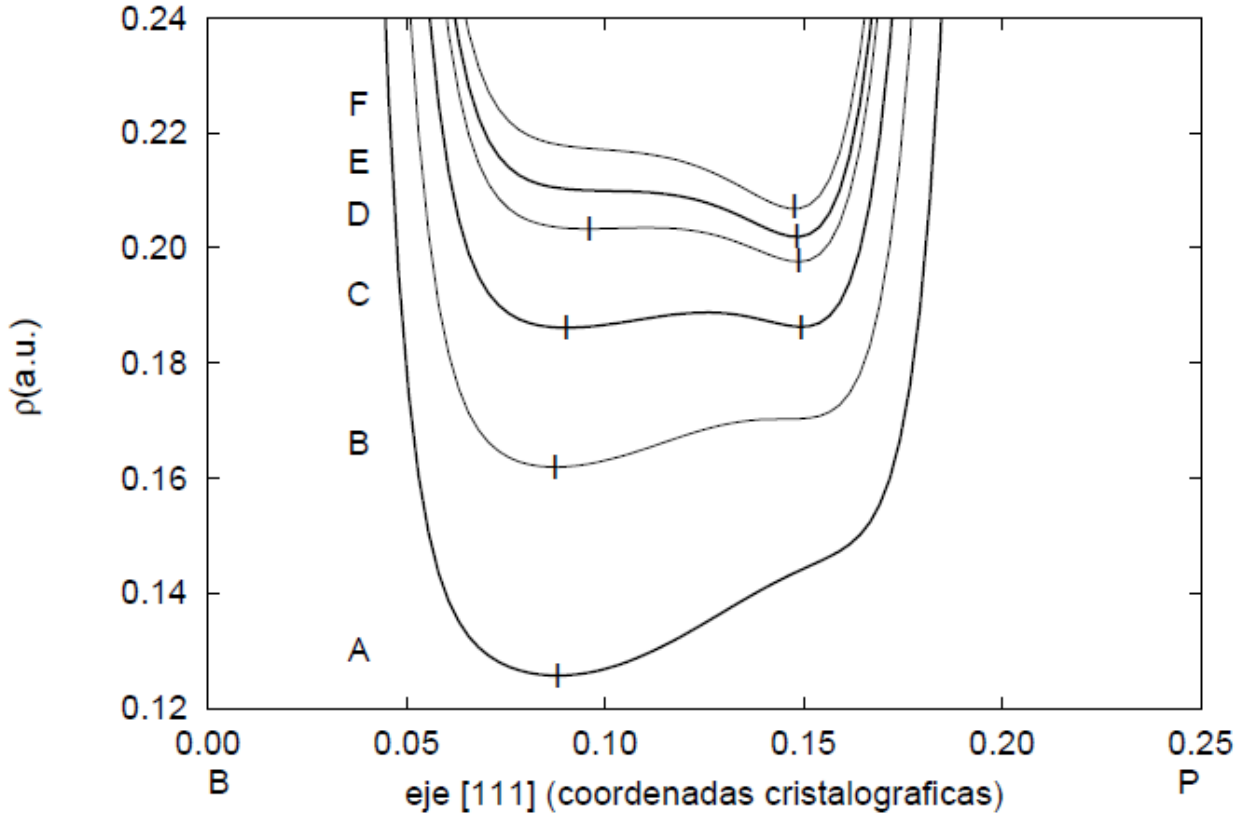
Properties

- BP



Properties

- BP



When the crystal is compressed, the electron density is displaced, leading to a change in polarity from $B^{\delta+}P^{\delta-}$ at V_0 to $B^{\delta-}P^{\delta+}$ at $V=0.57V_0$

Outline

1. Why studying chemical bonds?

2. Quantum Chemical topology

3. Chemical functions

   a) electron density

   b) ELF

   c) NCI

   1. The function
   2. The topology
   3. Old insight
   4. New insight

4. Summary

The electron localization function

Fermionic information

- ELF can be interpreted as an excess of local kinetic energy density due to Pauli repulsion.

$$t_P(\vec{r}) = t(\vec{r}) - \frac{1}{8}\frac{\left|\nabla\rho(\vec{r})\right|^2}{\rho(\vec{r})}$$

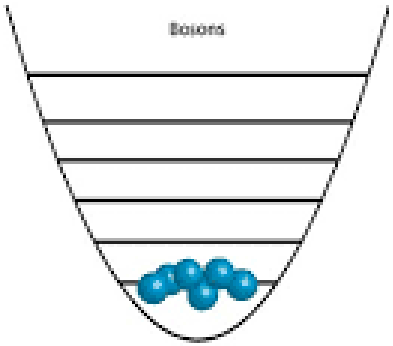
The electron localization function

Bosonic system (iso-orbital)

If we are in a region that can be described by a solely orbital j:

$$\rho = \sum_i |\varphi_i|^2 = |\varphi_j|^2$$

$$\begin{cases} \varphi_j = \sqrt{\rho} \\ \nabla\varphi_j = \dfrac{\nabla\rho}{2\sqrt{\rho}} \end{cases}$$



Kinetic energy densities

$$t = \frac{1}{2}\sum_i \nabla\varphi_i^*\nabla\varphi_i \Rightarrow t_w = \frac{1}{2}\frac{\nabla\rho}{2\sqrt{\rho}}\frac{\nabla\rho}{2\sqrt{\rho}} = \frac{1}{8}\frac{(\nabla\rho)^2}{\rho}$$

$$t_{bose}(\mathbf{r}) = \frac{\tau_w(\mathbf{r})}{\tau_{TF}(\mathbf{r})}$$

Its a scaled reference

- with the same density
- Pauli principle has been turned off

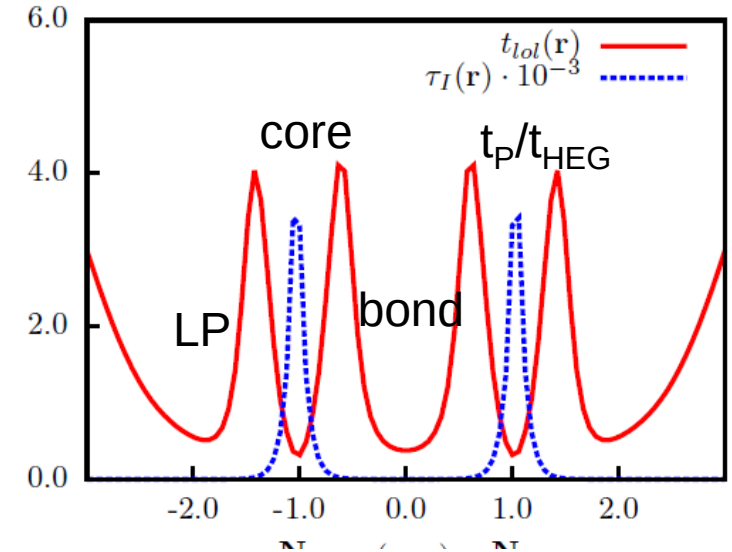
The electron localization function

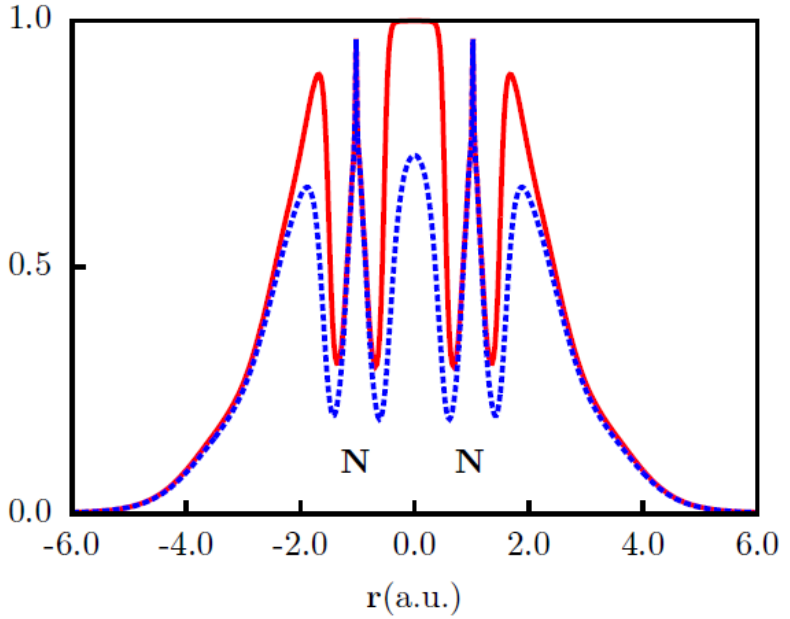
Fermionic information

- It is divided by TF to get rid of electro density dependence
- Re-scaled to go from 0 to 1

$$t_P(\vec{r}) = t(\vec{r}) - \frac{1}{8}\frac{|\nabla\rho(\vec{r})|^2}{\rho(\vec{r})}$$

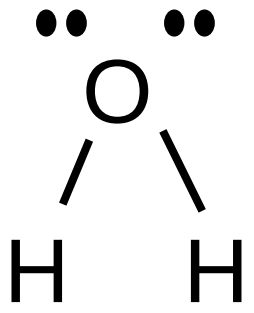
$$\chi(\vec{r}) = \frac{t_P(\vec{r})}{c_F\rho(\vec{r})^{5/3}} \qquad ELF = \frac{1}{(1+\chi^2(\vec{r}))}$$





The electron localization function

- It recovers the Lewis picture of a system
- ELF is close to one in:
  - Lone pairs



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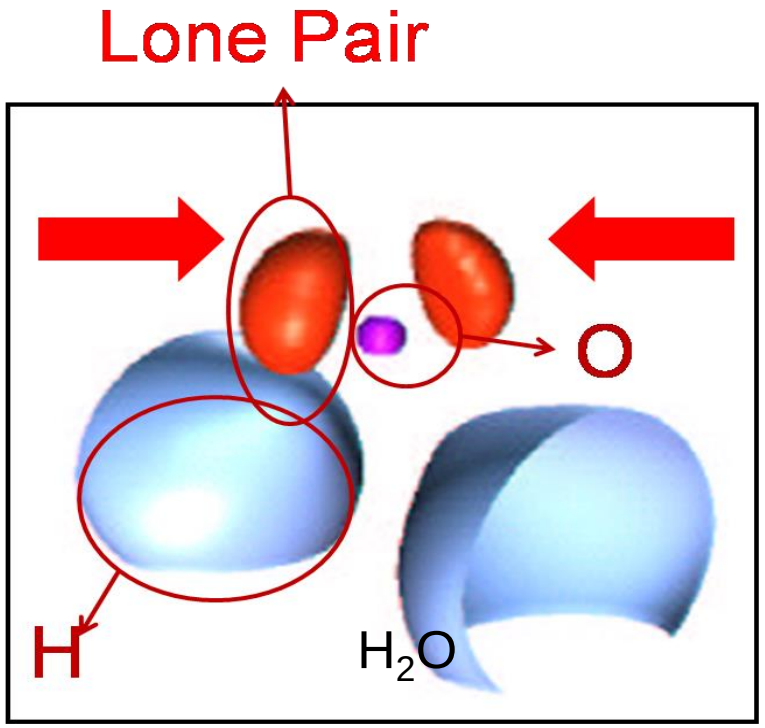

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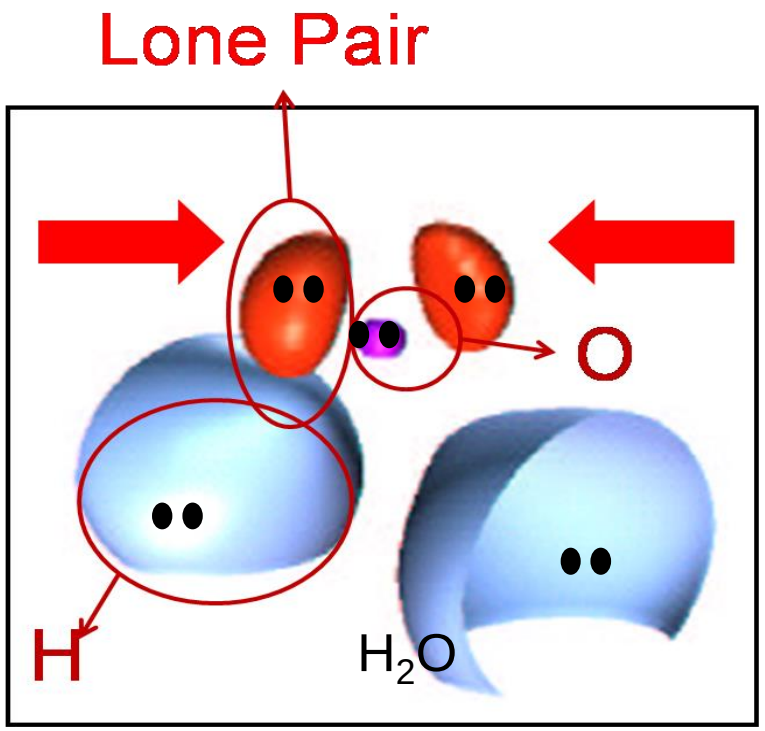

The electron localization function

- It recovers the Lewis picture of a system
- ELF is close to one in:
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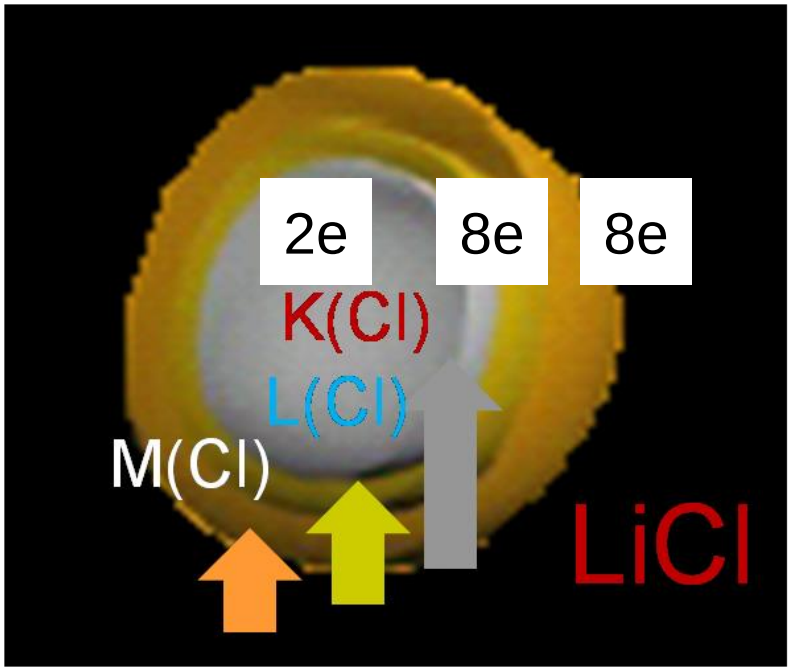
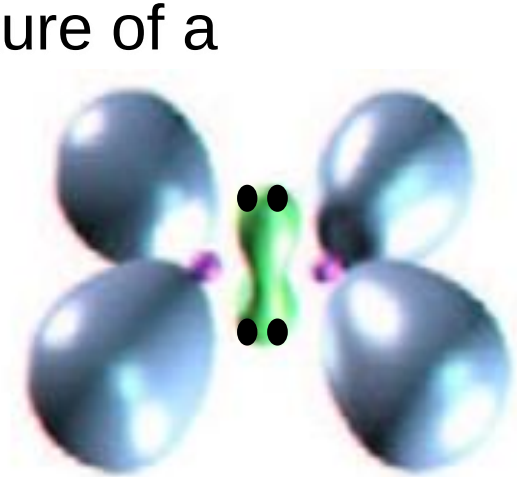
  - Atomic shells



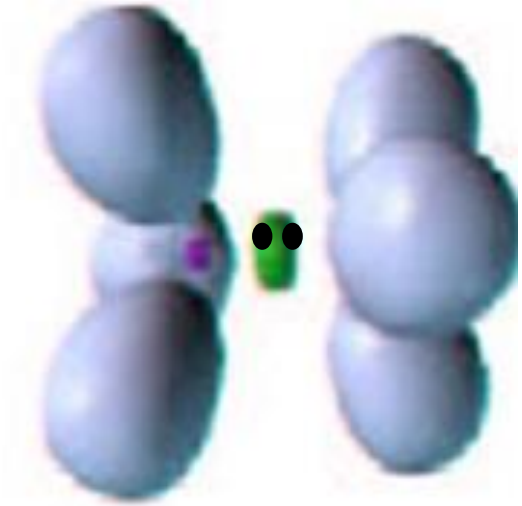
Electron numbers and charge transfer

The electron localization function

- It recovers the Lewis picture of a system
- ELF is close to one in:
  - Lone pairs
  - Atomic shells
  - Bonds



$H_2C=CH_2$

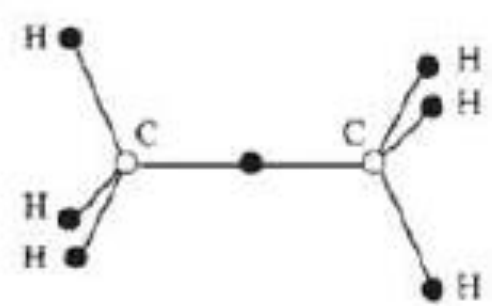


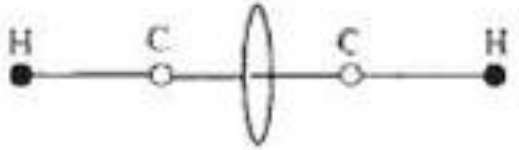
$H_3C\text{-}CH_3$

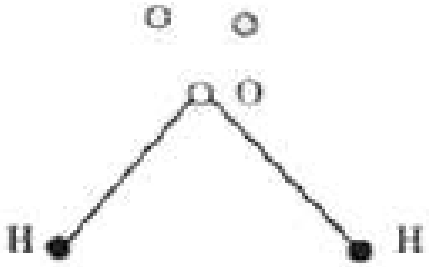
Bond order

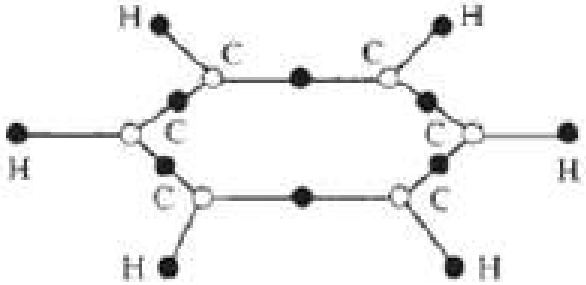
The electron localization function

Critical points



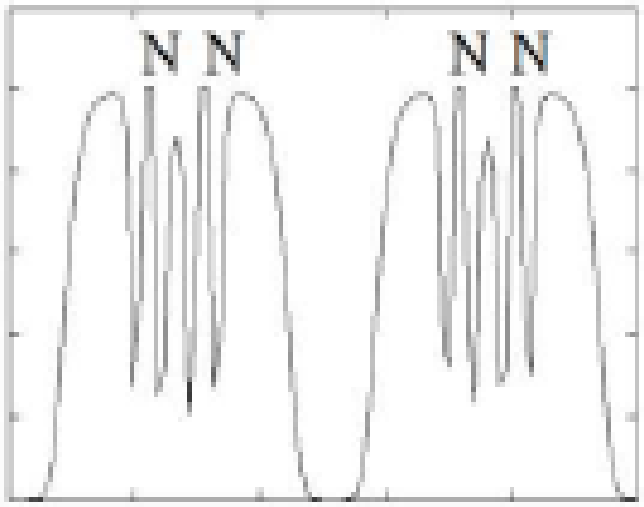


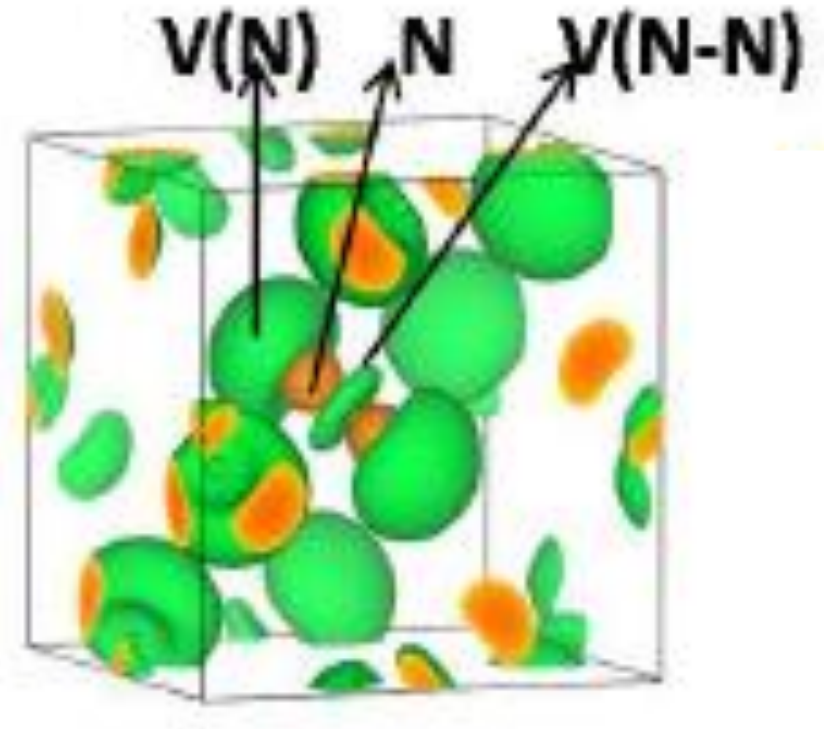




ELF in solids

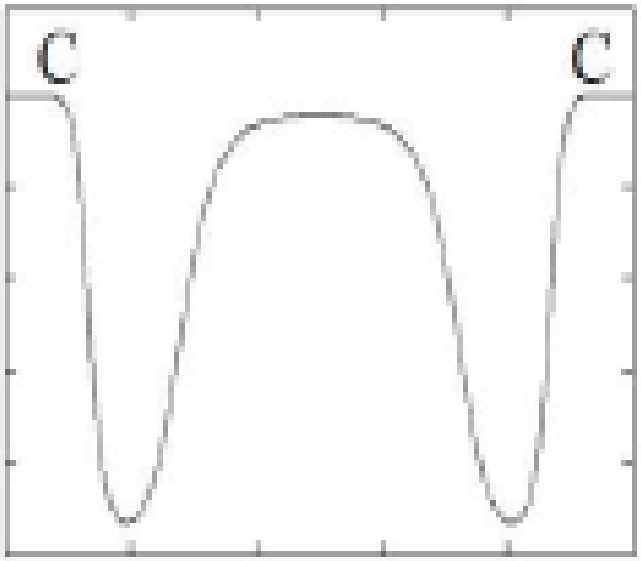
Molecular solids

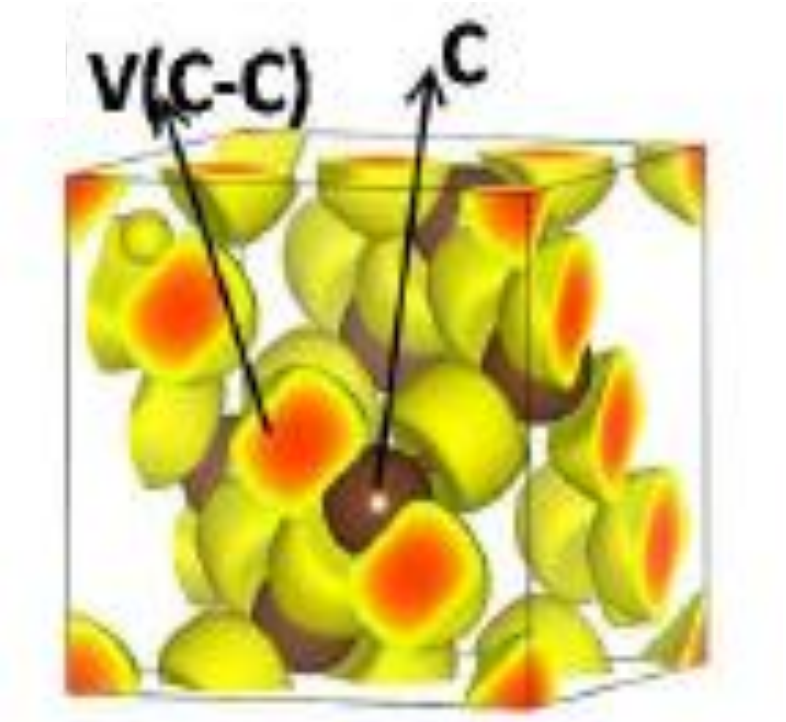




ELF in solids

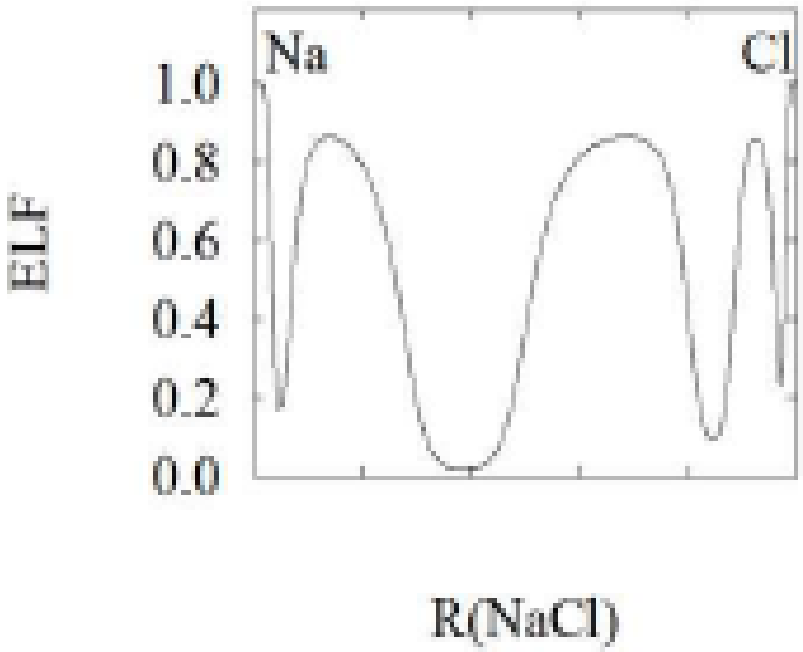
Covalent solids

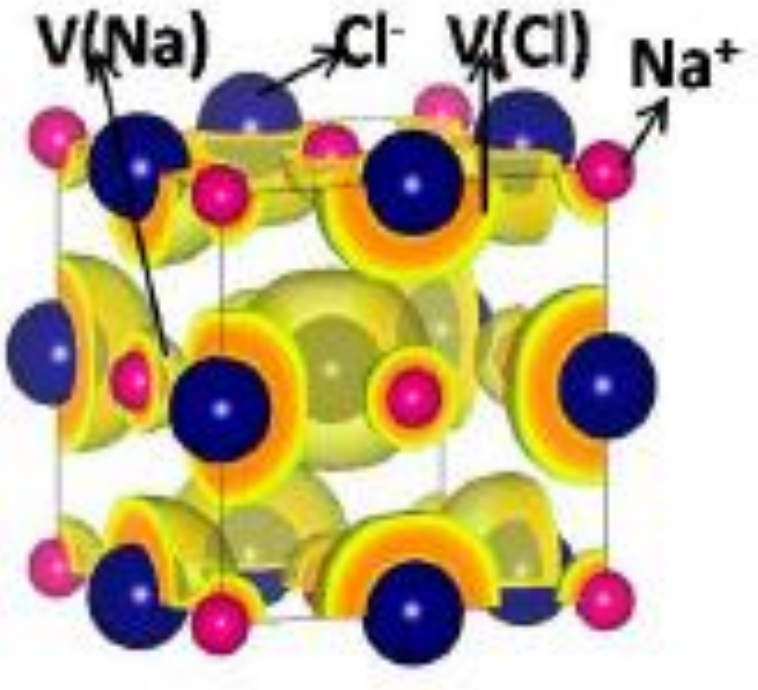




ELF in solids

Ionic solids

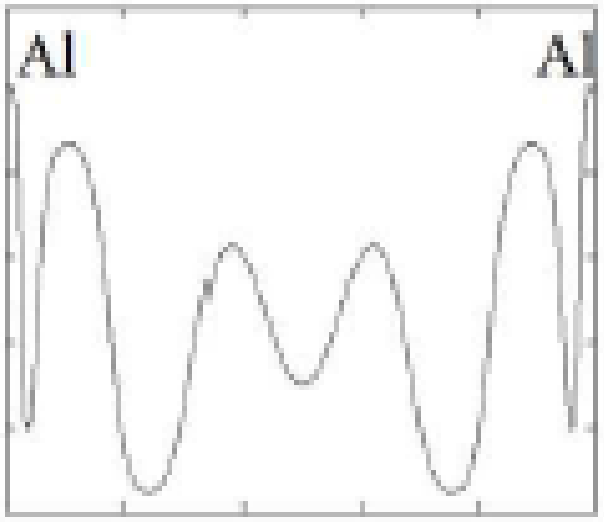




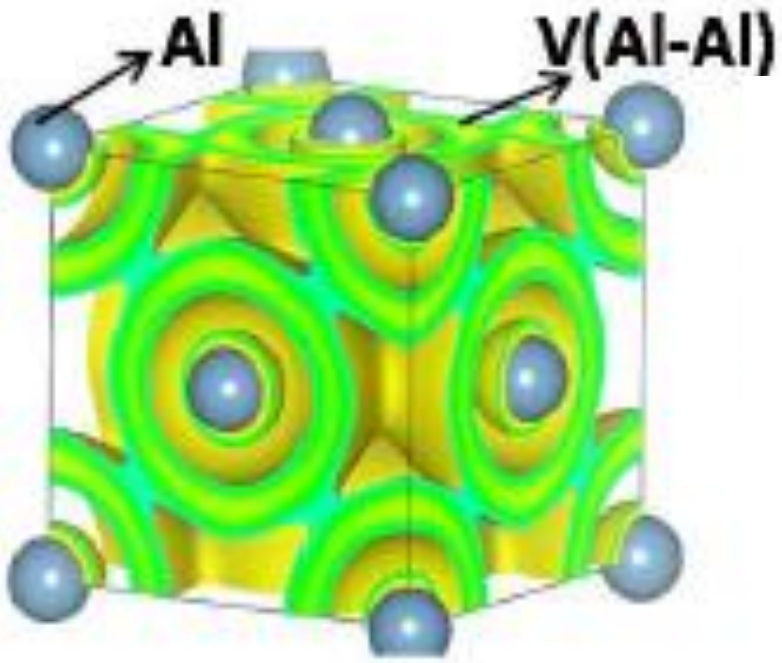
Charge transfer is verified
Na=10 e
Cl=18 e

ELF in solids

Metals

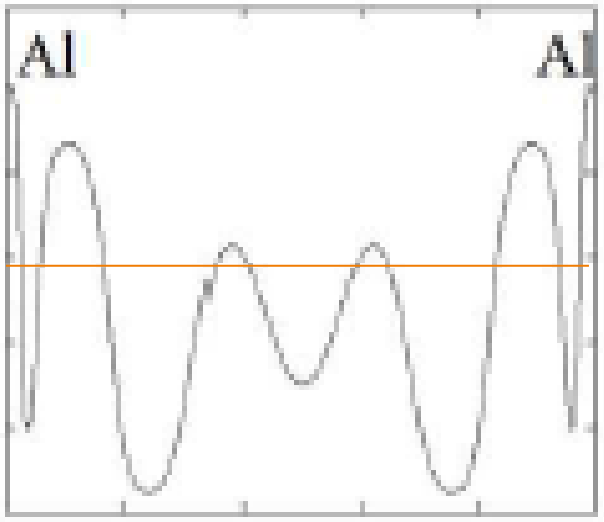


R(Al)



ELF in solids

Metals



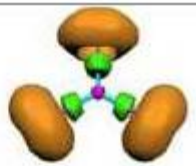
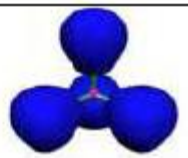
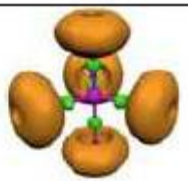
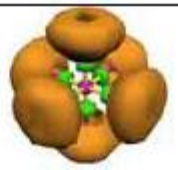
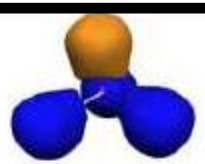
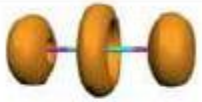
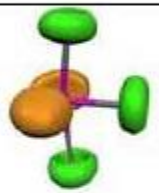
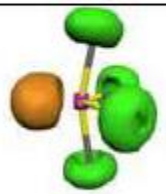
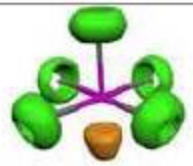
R(Al)

$$\chi(\vec{r}) = \frac{t_P(\vec{r})}{c_F \rho(\vec{r})^{5/3}} \qquad ELF = \frac{1}{\left(1+\chi^2(\vec{r})\right)}$$

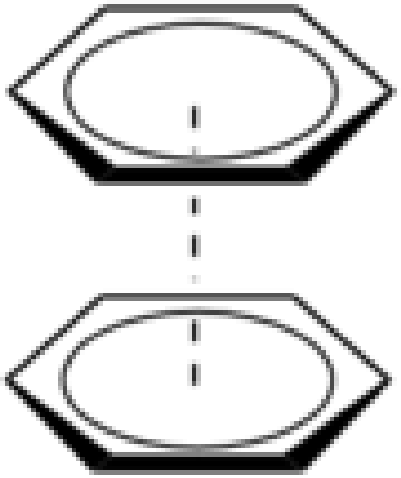
$$t_P(\vec{r}) = t_{HEG}(\vec{r}) \qquad ELF = 0.5$$

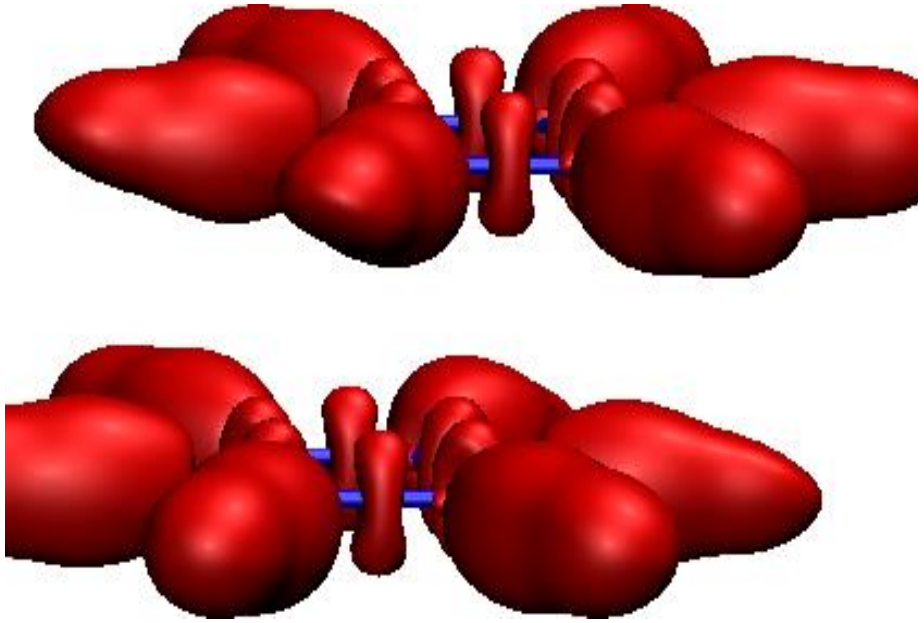
Metallic valence close to HEG

ELF pictures recover VSEPR

ab_2	$BeCl_2$		
ab_3	BCl_3		
ab_4	CH_4		
ab_5	PCl_5		
ab_6	SCl_6		
ab_3e	NH_3		
ab_2e_3	$XeCl_2$		
ab3e2	ClF_3		
ab4e	SF_4		
ab5e	BrF5		

Still missing something…





Outline

1. Why studying chemical bonds?

2. Quantum Chemical topology

3. Chemical functions

   a) electron density

   b) ELF

   c) NCI

   1. The function
   2. The topology
   3. Old insight
   4. New insight

4. Applications

NCI

Critical point : $\nabla\rho = 0$

Let's look at the region $\nabla\rho \to 0$

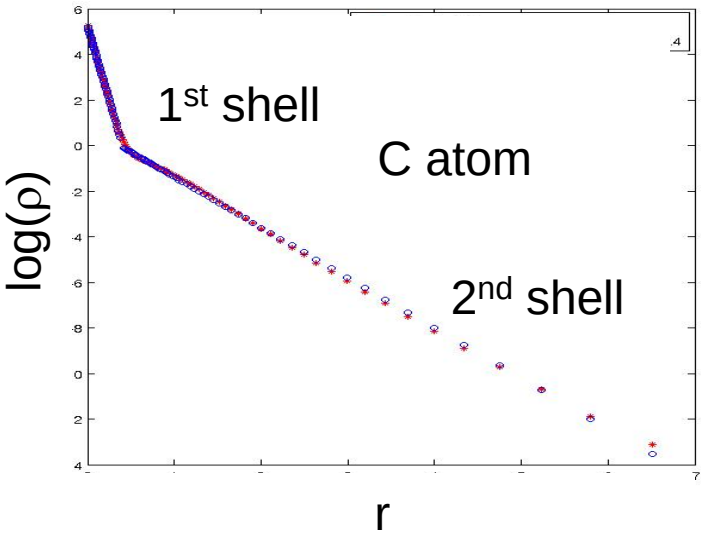
NCI:

analysis of the reduced density gradient at low densities

$$s = \frac{1}{c_s}\frac{|\nabla\rho|}{\rho^{4/3}} \quad \text{with } c_s = 2(3\pi^2)^{1/3}$$

•How does it work?

Model densities



Atoms

- Atomic densities can be mimicked like a sum of $Nshells$ exponentials

$$\rho^{at}(r) = \sum_{i}^{Nshells} c_i e^{-\zeta_i r}$$

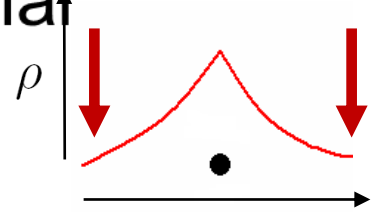
- 1st shell can be approximated by a 1s orbital

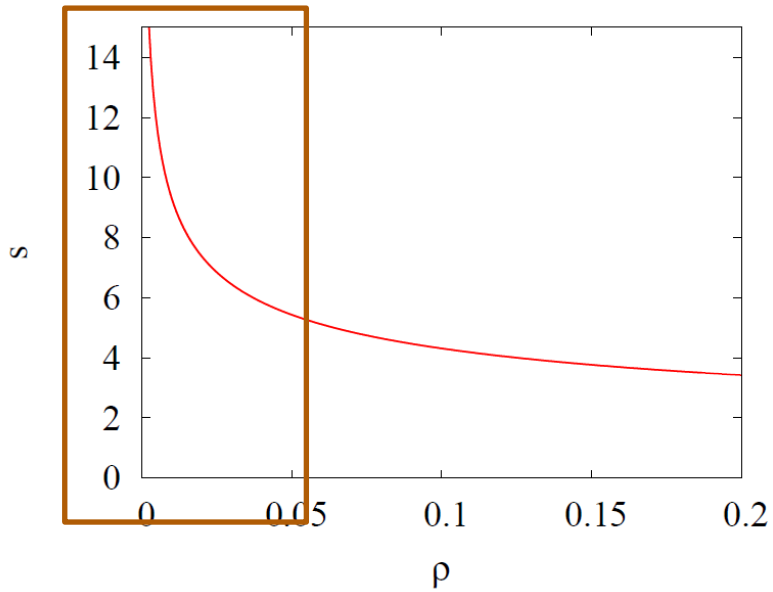
$$\rho_{1s} = \frac{n_{1s}}{\pi}\left(\frac{Z}{a_0}\right)^3 e^{-2Zr/a_0}$$

Atoms

At ∞ taking the outermost exponential

- $\rho(r) = ce^{-\zeta r}$
- $|\nabla\rho(r)| = c\zeta e^{-\zeta r}$
- $s = \frac{1}{c_s}\frac{|\nabla\rho|}{\rho^{4/3}} = \frac{1}{c_s}\frac{\zeta}{(ce^{-\zeta r})^{1/3}} = \frac{\zeta}{c_s}\rho^{-1/3}$





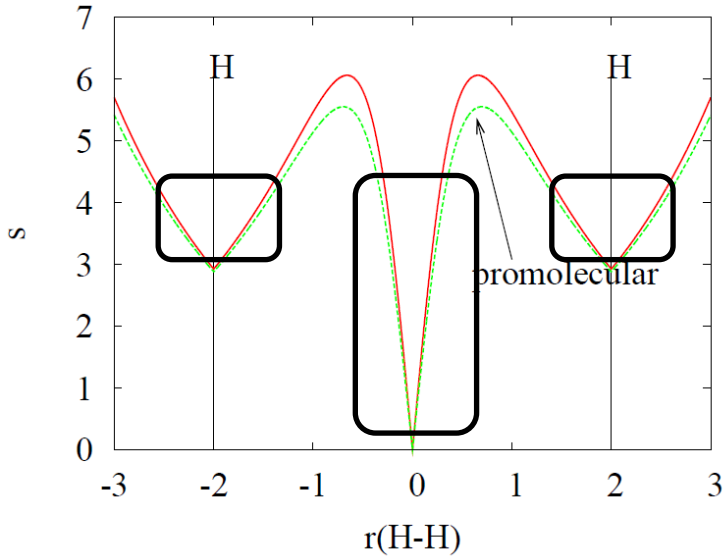
- $\lim_{r\to\infty} s(r) = \infty$ (i.e. when $\rho \to 0$)

Model densities

Molecules

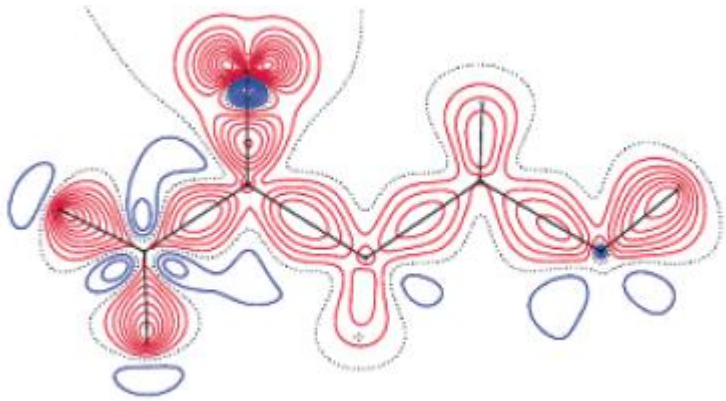
- Promolecular densities: no interference (SCF cycle 0)

$$\rho_{molec}(r) = \sum_{j}^{Natoms} \rho_j^{at}(r) = \sum_{j}^{Natoms} \sum_{i}^{Nshells} c_{i,j} e^{-\zeta_{i,j} r}$$



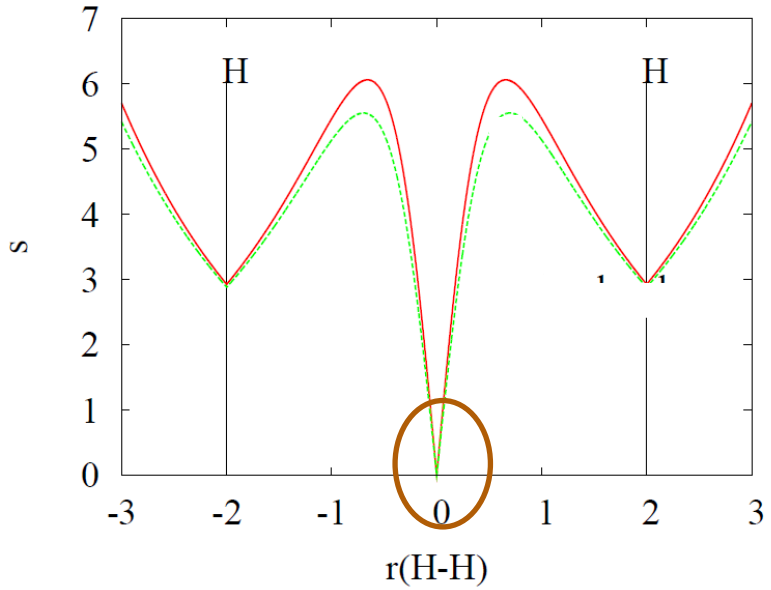
- Works specially well at low densities ($s \to 0$) at atomic positions (1s orbital)

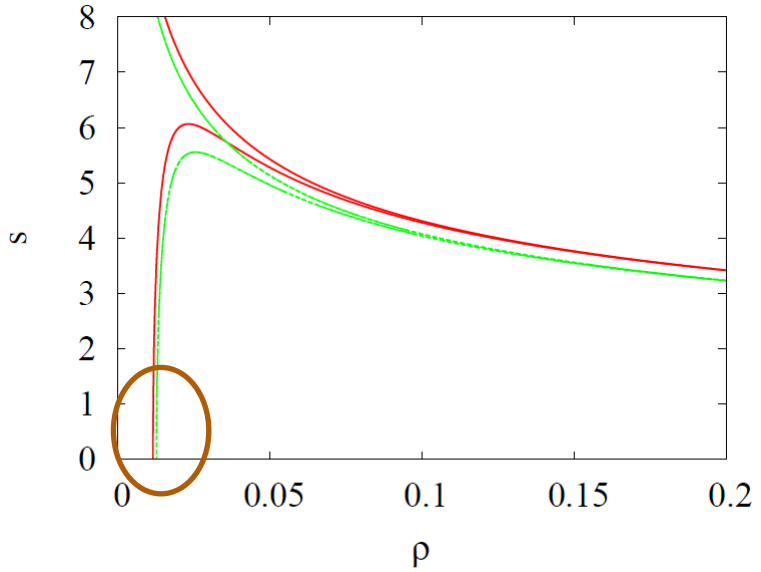
Promolecular densities



Crystallography: promolecular densities are used in refinement of high-resolution X-Ray data of large systems

Interactions





- Promolecular approach

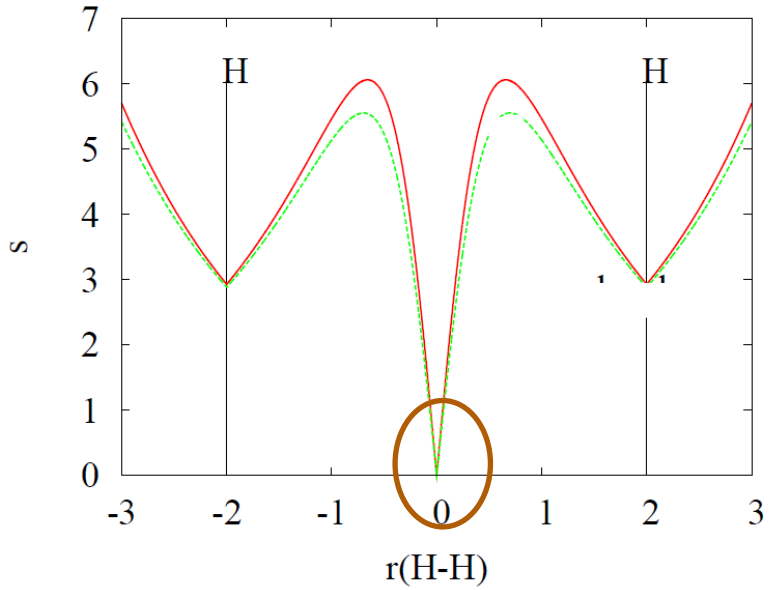
$$\rho(x,y,z) = \rho_{1s}^{A} + \rho_{1s}^{B} = \left(ce^{-\zeta\sqrt{x^2+y^2+(z-R/2)^2}}\right)^2 + \left(ce^{-\zeta\sqrt{x^2+y^2+(z+R/2)^2}}\right)^2$$

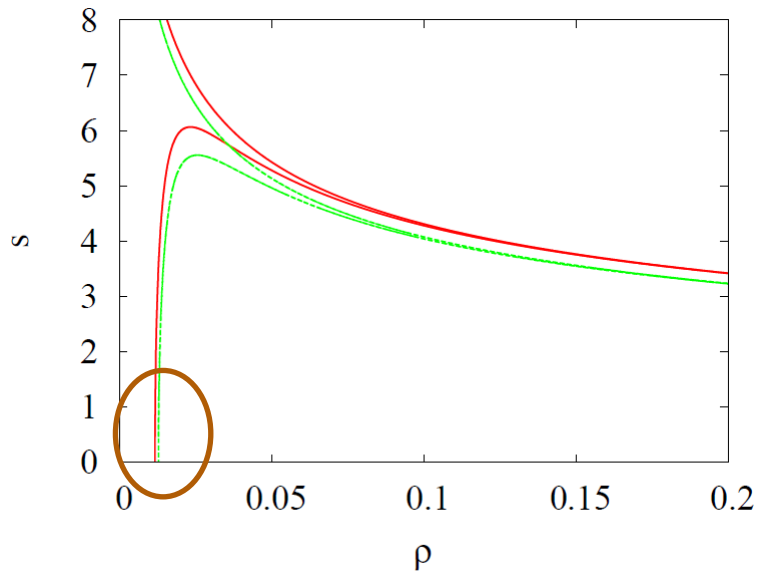
- s goes to 0 in the interactions

$$\lim_{z\to 0} s(\rho) = \lim_{z\to 0}(e^{R/3}r + O(r^3)) = 0$$

- When we plot $s(\rho)$ at low densities, the behavior is very characteristic

Interactions





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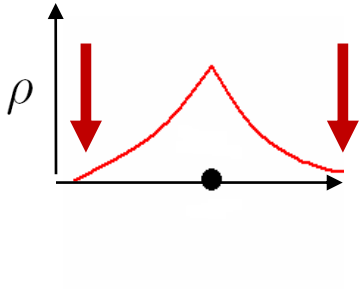
- When we plot $s(\rho)$ at low densities, the behavior is very characteristic

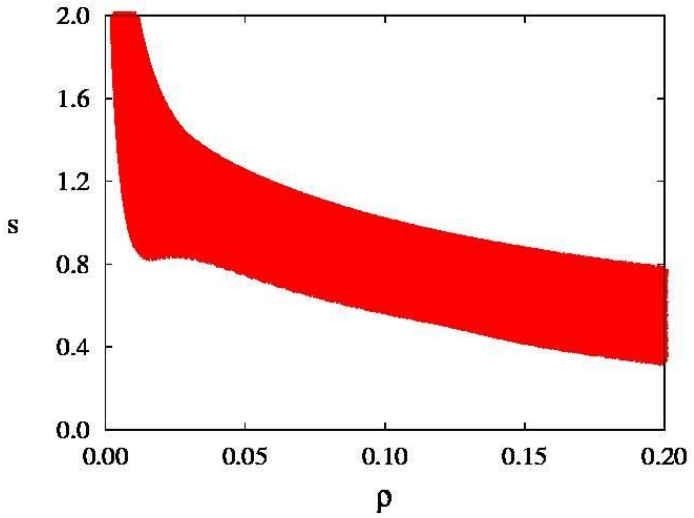
Let's see an example!

The reduced density gradient

Non-interacting densities

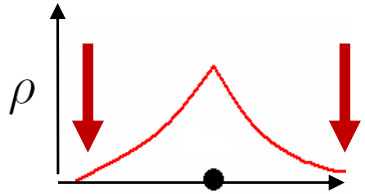


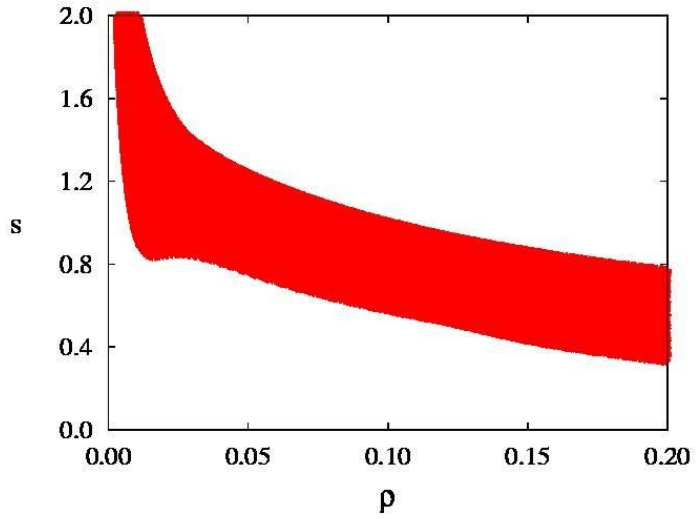
$$s(\rho) \propto \rho^{-1/3} \xrightarrow{\rho \to 0} \infty$$



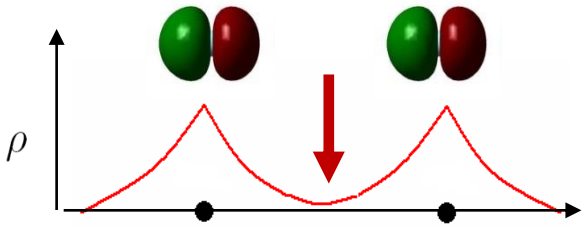
The reduced density gradient

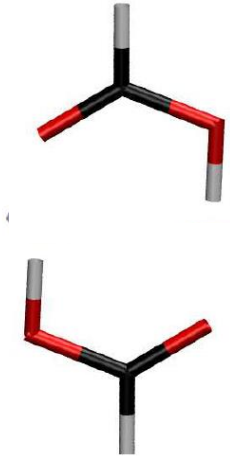
Non-interacting densities

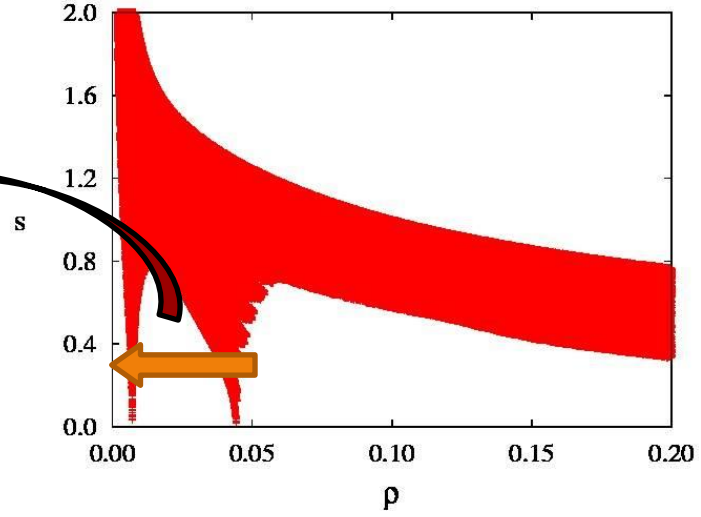




Interacting densities



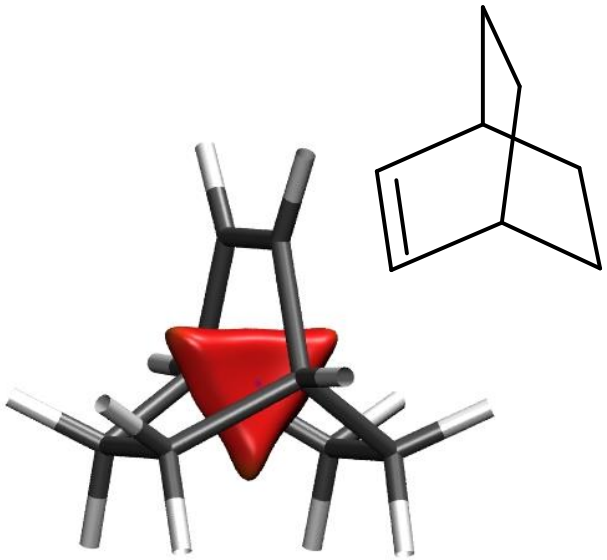


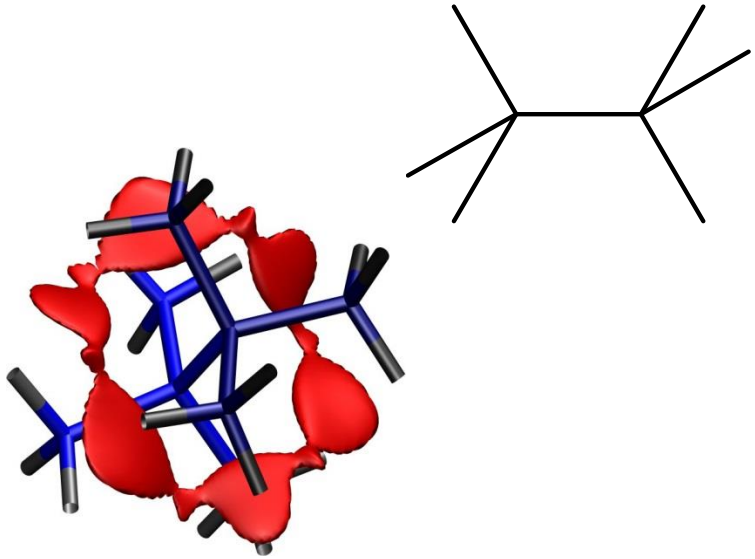


The reduced density gradient

Repulsive interactions

- Steric clashes

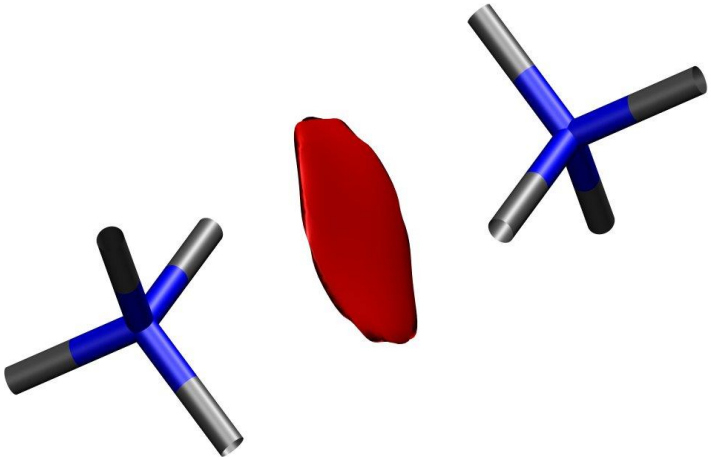




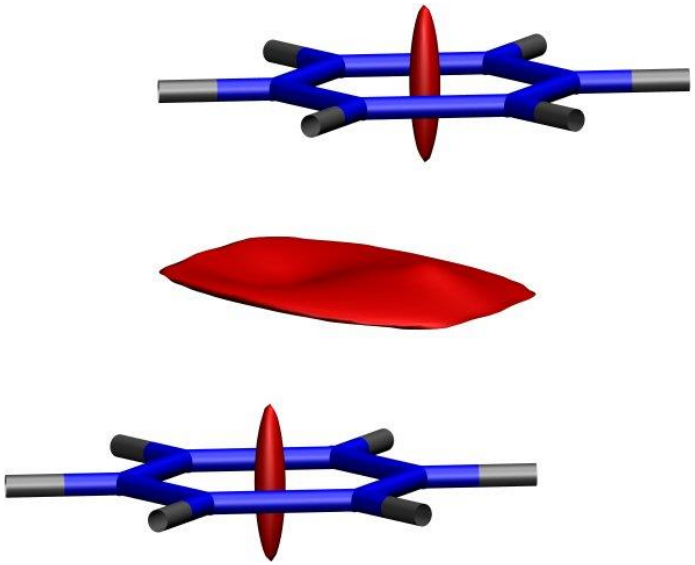
The reduced density gradient

Weak interactions

- Van der Waals



Methane dimer

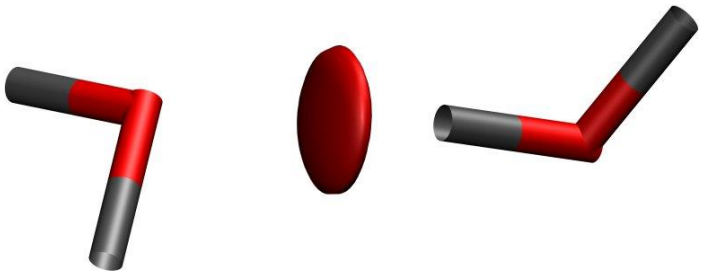


Benzene dimer

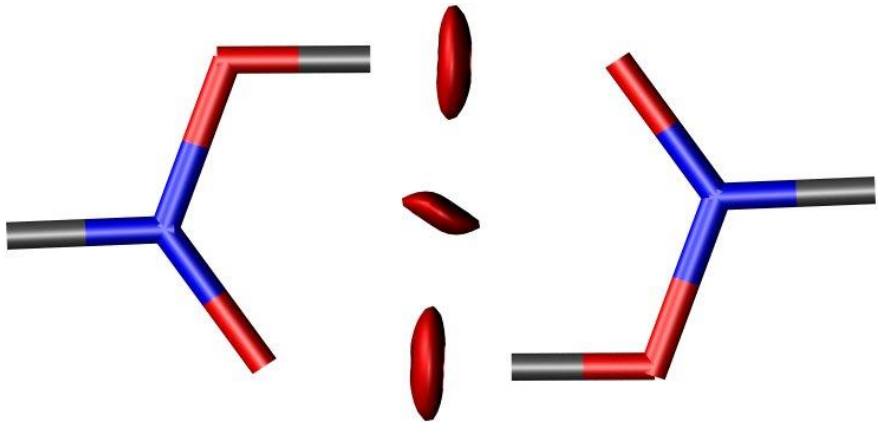
The reduced density gradient

Strongly attractive interactions

- Hydrogen bonds



Water dimer



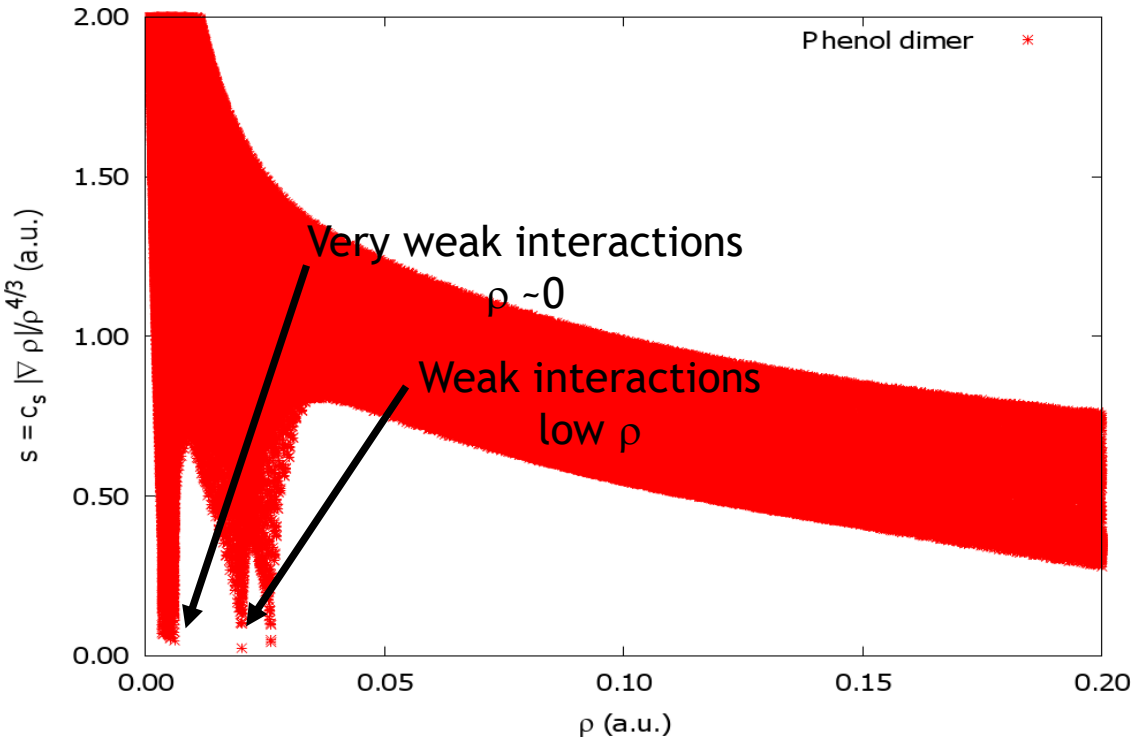
Formic acid dimer

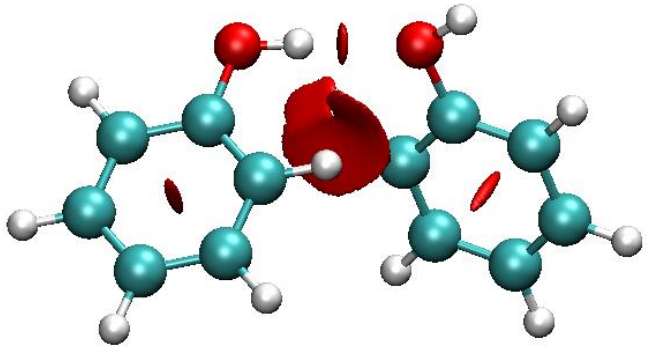
The reduced density gradient

Differentiating interaction types

1

•Density is proportional to the strength of the interaction



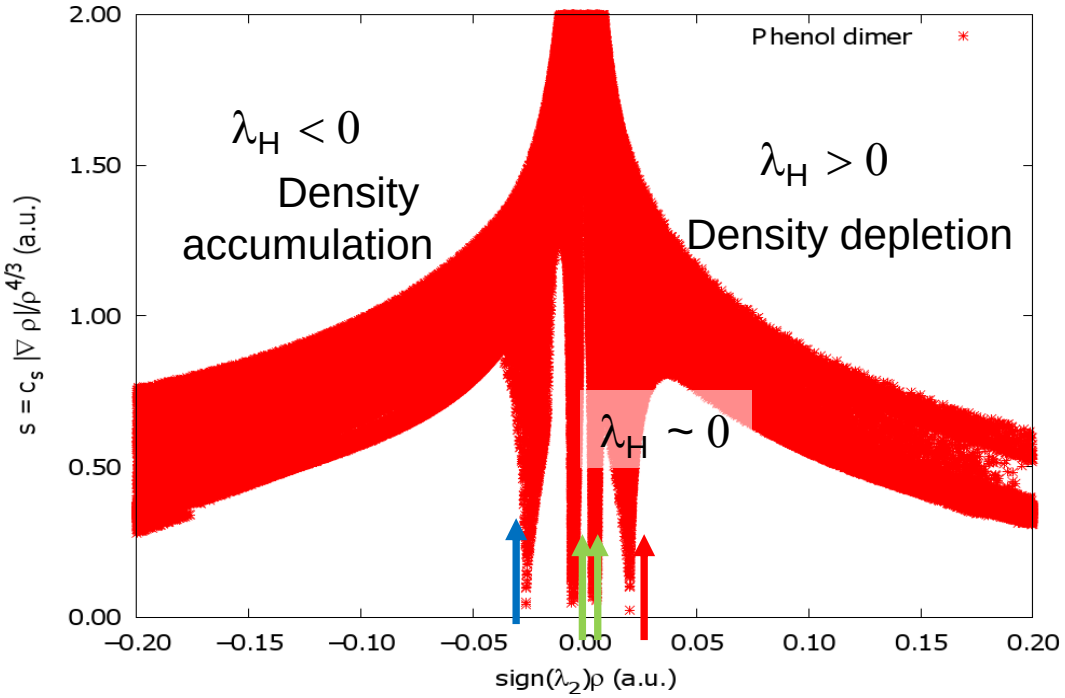


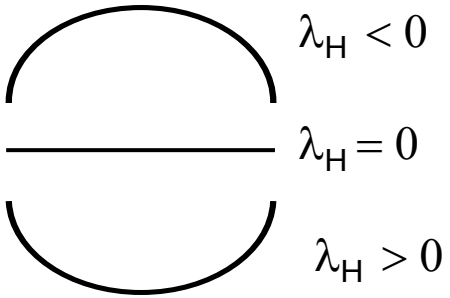
The reduced density gradient

Differentiating interaction types

2

- Bonding interactions →charge accumulation ($\lambda_H < 0$)
- Antibonding interactions → charge depletion ($\lambda_H > 0$)

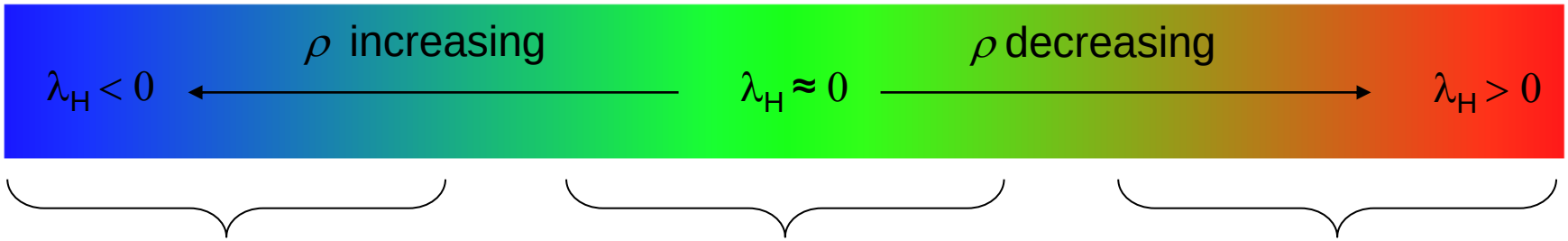




The reduced density gradient

1) Represent s isosurfaces in real space

2) Colour them in terms of sign(λ_H) x ρ



Strong and attractive:

Hydrogen bonds

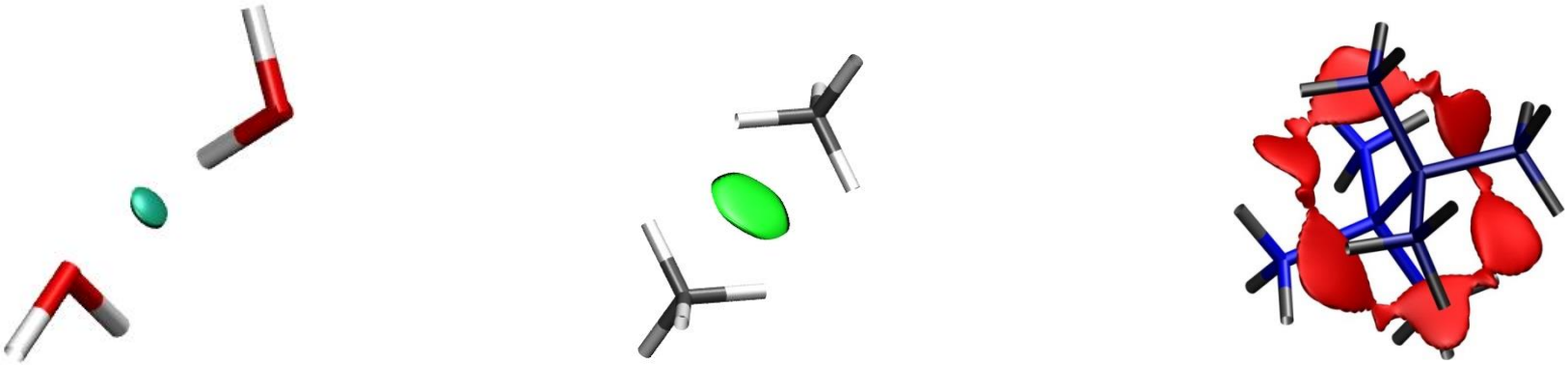
Very weak:

van der Waals

Strong and repulsive:

Steric clashes

The reduced density gradient



ρ increasing

$\lambda_H < 0$ ← $\lambda_H \approx 0$ → ρ decreasing $\lambda_H > 0$

Strong and attractive:

Hydrogen bonds

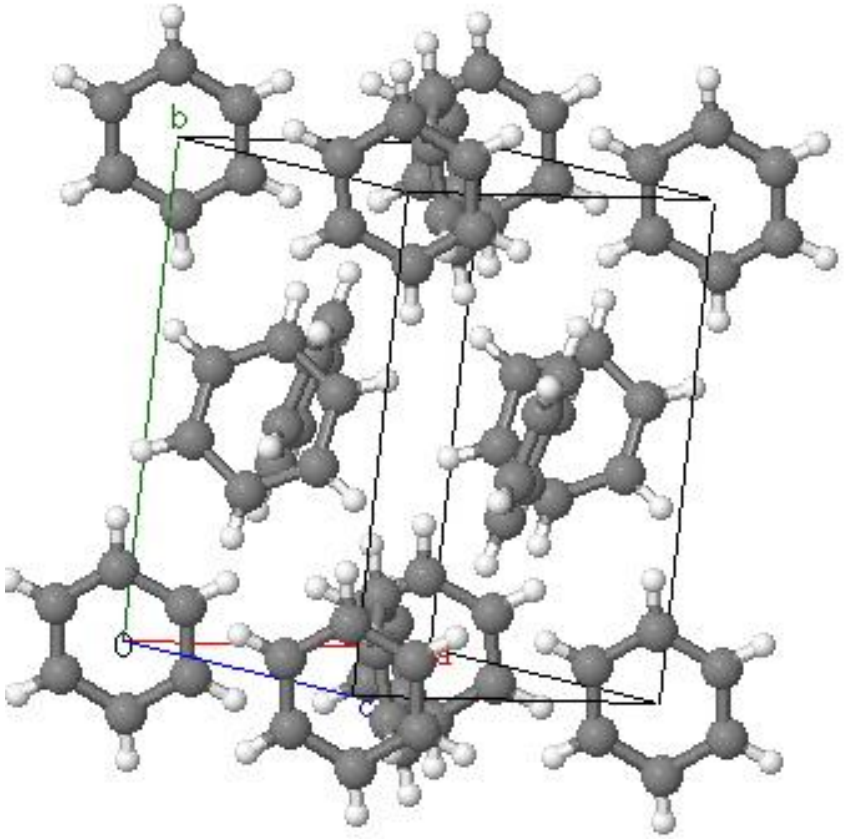
Very weak:

van der Waals

Strong and repulsive:

Steric clashes

Delocalized interactions



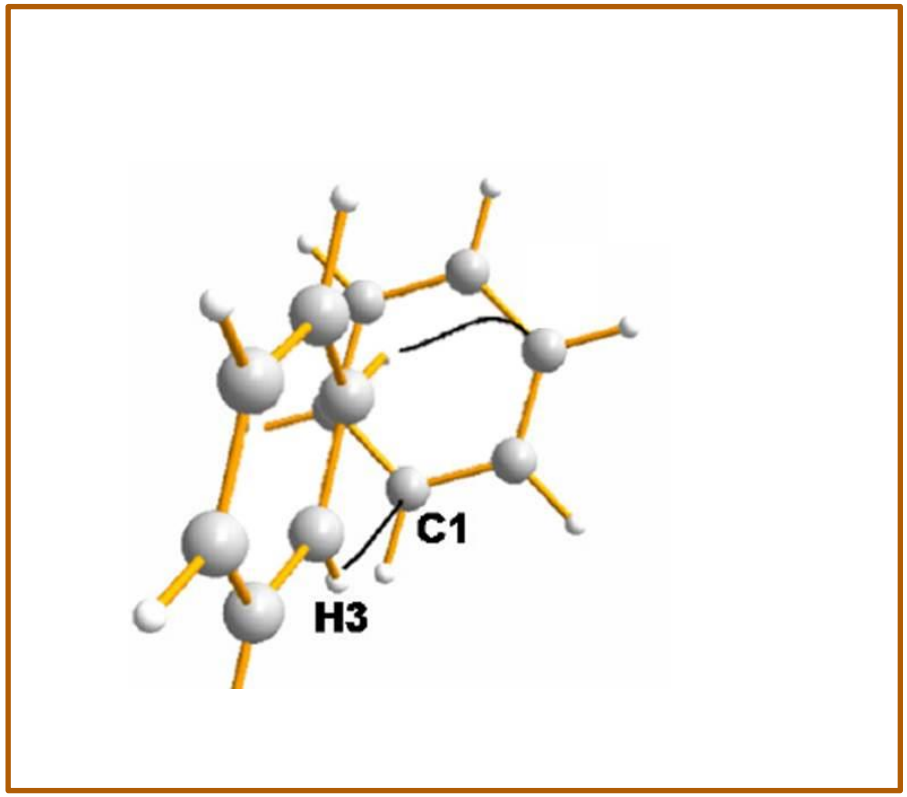
Benzene packing maximizes the number of C-H···π and C-H···C contacts.

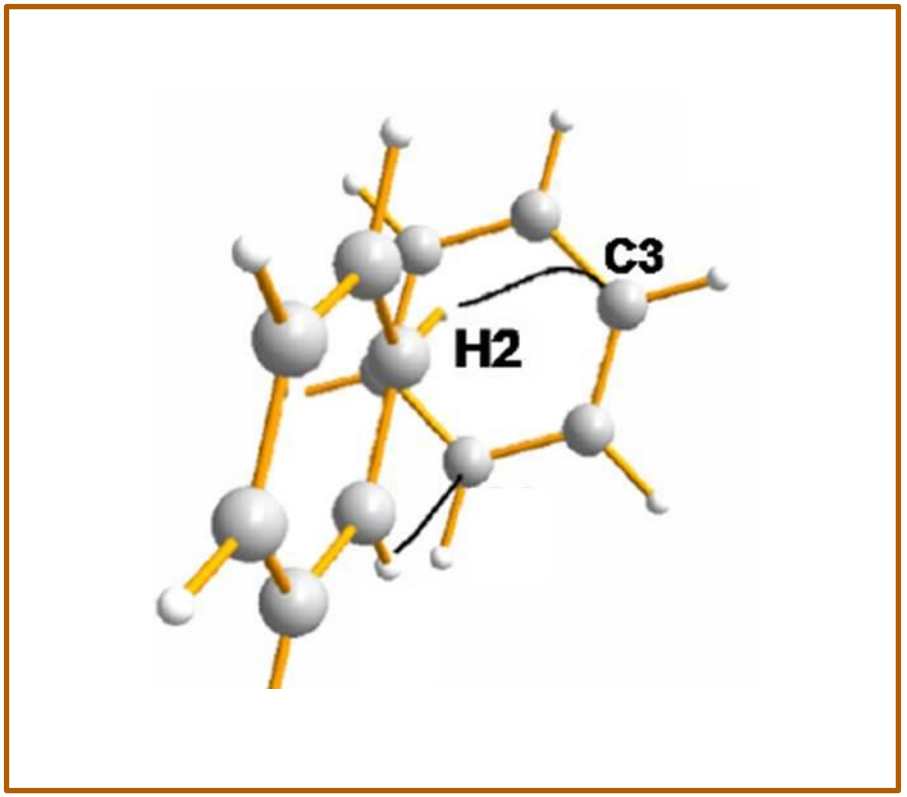
Delocalized interactions

AIM

CH-C
Straight bond path

CH-π
H roughly equidistant to the whole ring
Bond path significantly bent



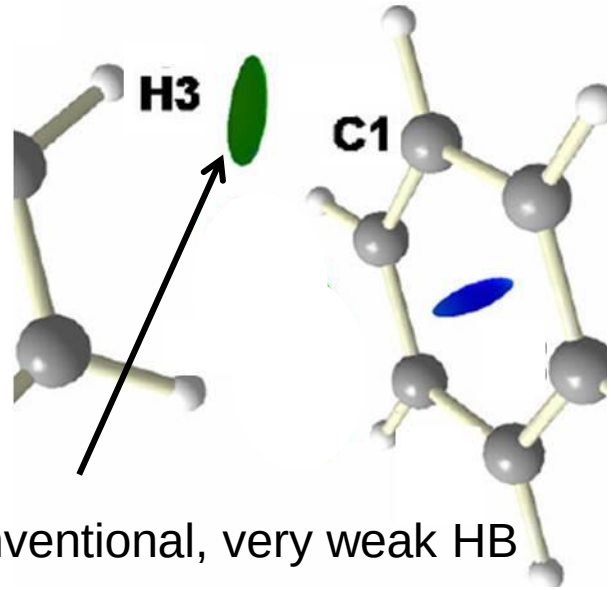


Delocalized interactions

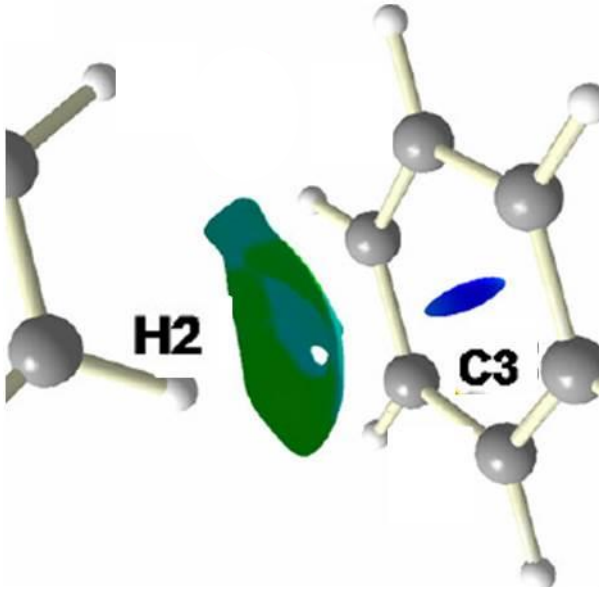
NCI

CH-C
Disc-shaped and localized

CH-π
Large isosurface involving the whole π electron cloud



conventional, very weak HB



nonclassical hydrogen bond

Big systems

- One of the major areas of application of weak interactions are biomolecules
- HOWEVER, wavefunctions are not available
- In the non covalent region, there is very little density reconstruction, so we can use and independent atom model (non relaxed or promolecular densities)

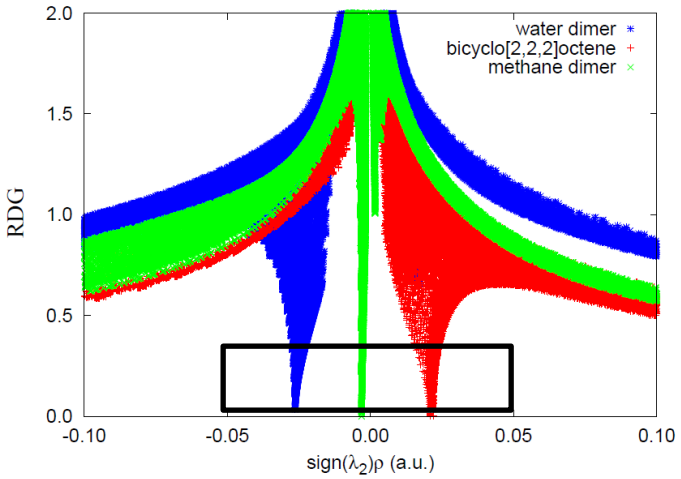
Big systems

How can we apply NCI to such big systems ?

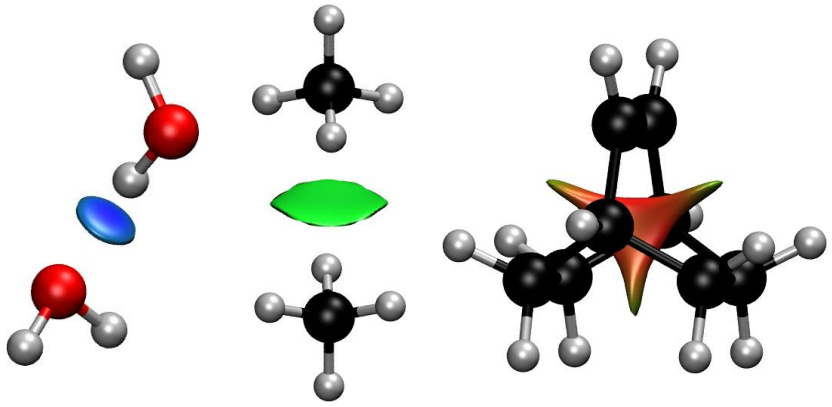
- Since promolecular works well for small densities, we use the promolecular approximation
- Parameters ζ_i and c_i for each atom are internally stored in the code
- No need for wavefunction
- Sum on a grid (very fast)

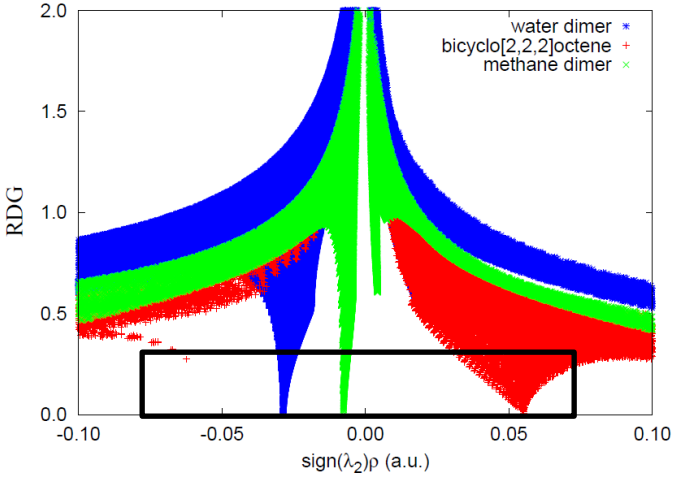
Big systems

Are characteristics really preserved?

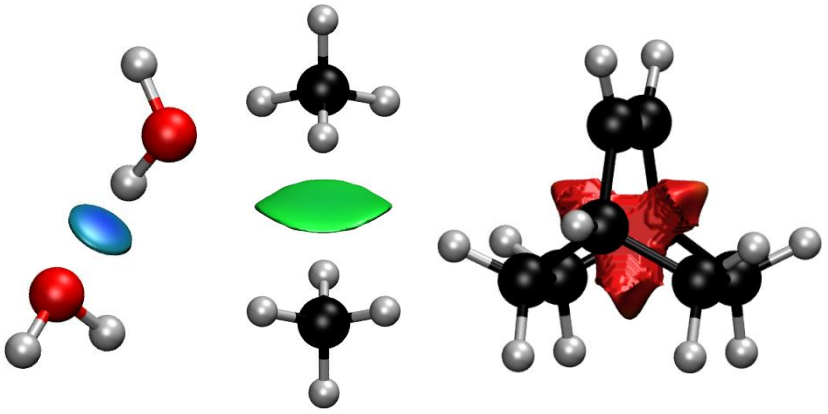


SCF



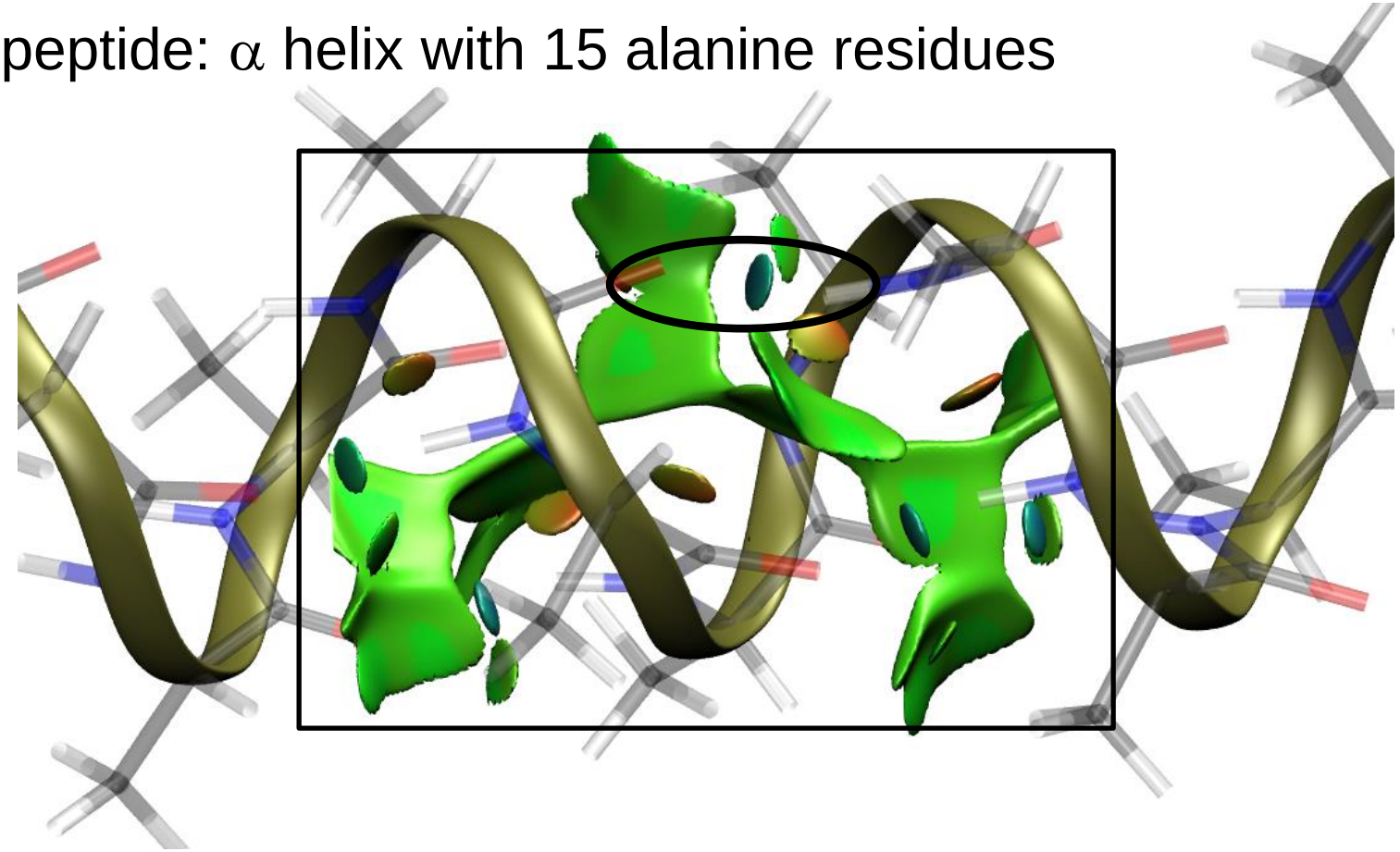


PROMOLECULAR



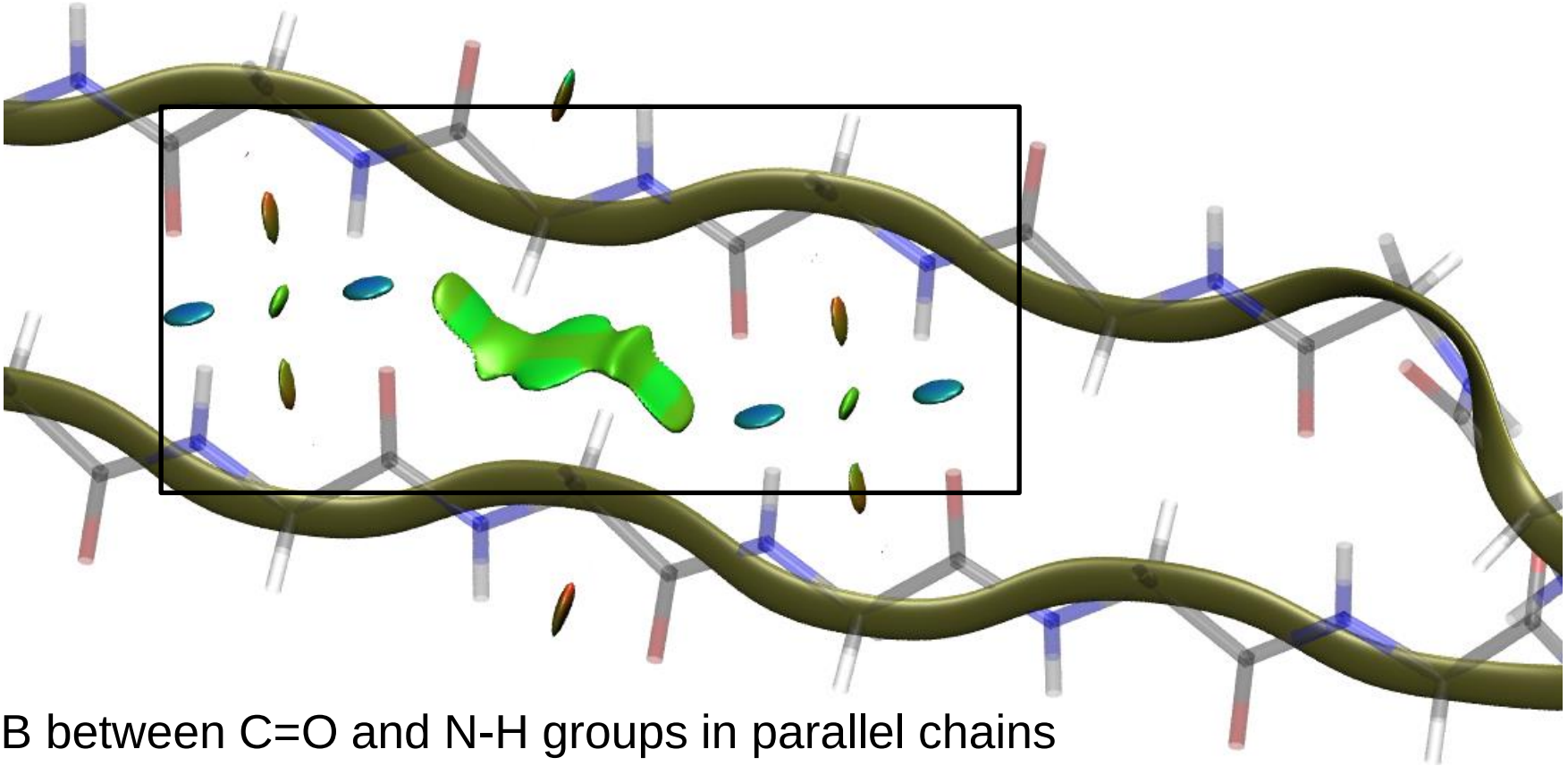
Proteins

Polipeptide: α helix with 15 alanine residues



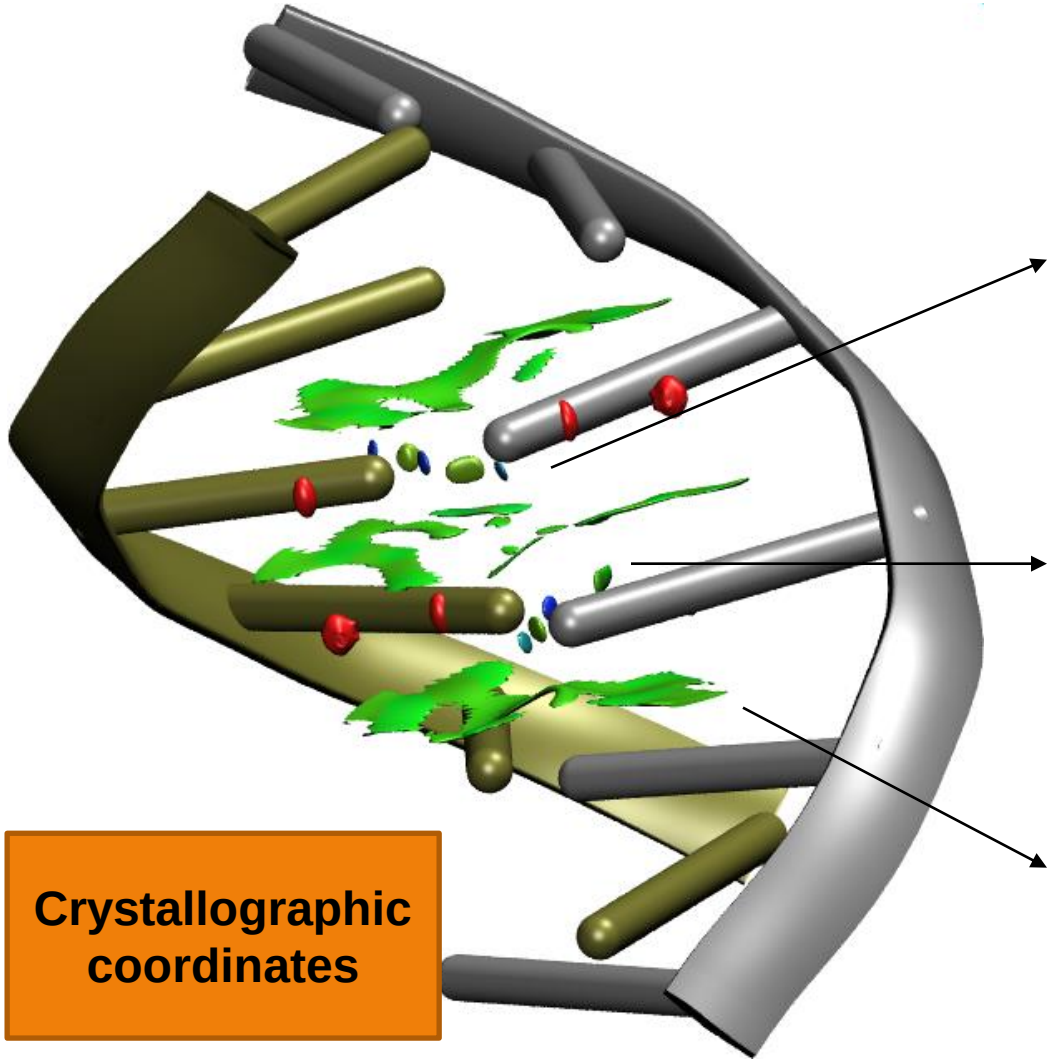
- Hydrogen bonds stabilize the helix
- Big region of van der Waals interaction inside the helix and between methyle lateral chains one step away

Proteins

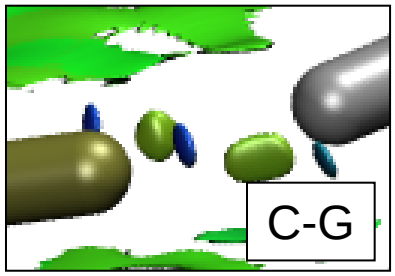


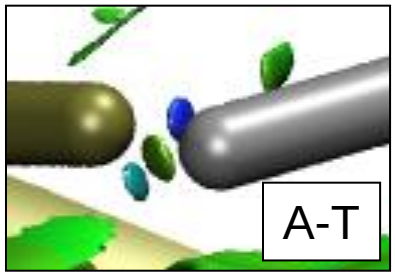
- HB between C=O and N-H groups in parallel chains
- Van der Waals interactions between CH_2 groups

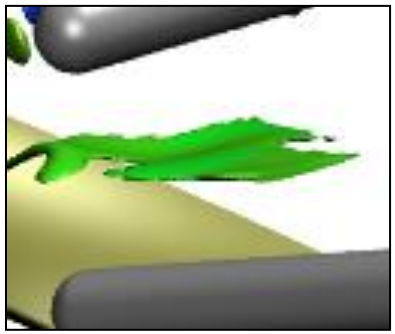
DNA



Crystallographic coordinates



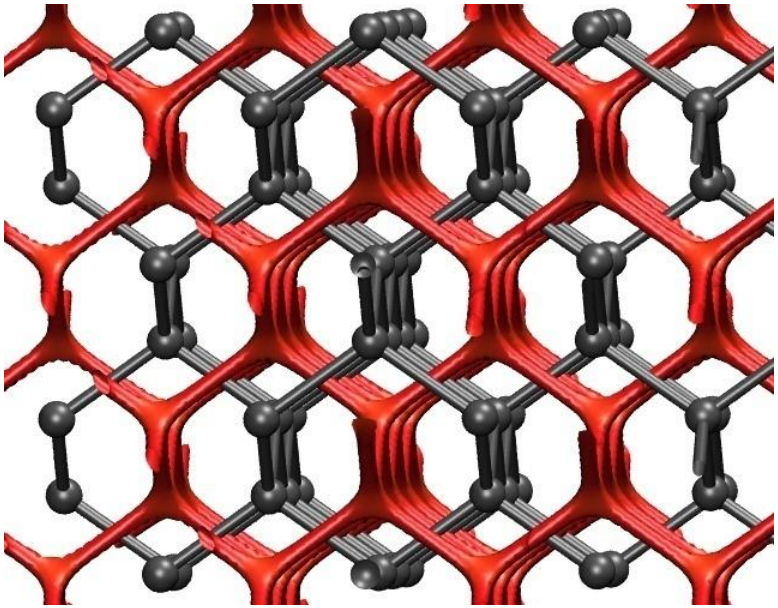




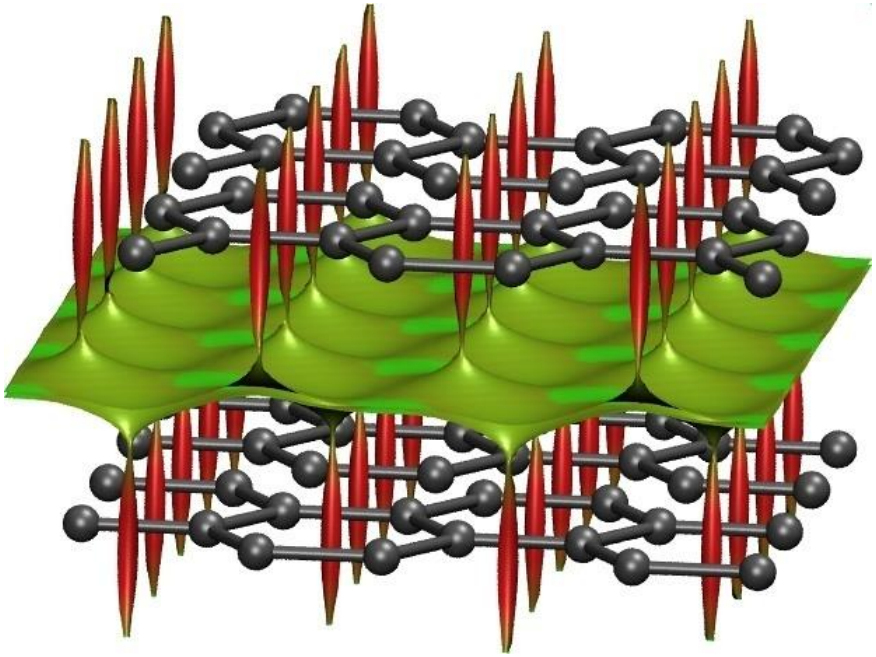
H-bonds between bases

π-stacking

2. QM classification of solids

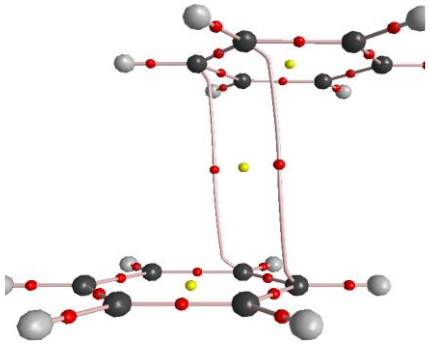
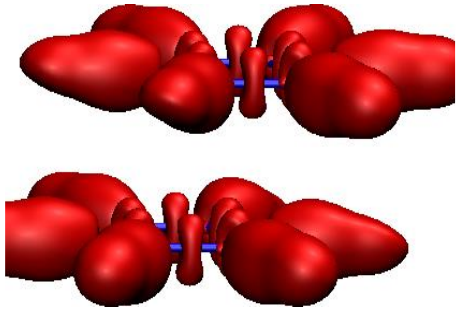
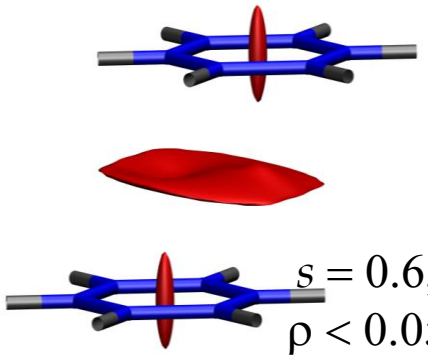


Diamond



Graphite

Summary

What are you looking for	**Atoms and bonds Atomic charges**	**Bonds, lone pairs Charges and volumes in Lewis entities**	**Non covalent interactions (even in big systems)**
You should use…	Electron density	ELF	NCI
Example		 ELF = 0.9	 $s = 0.6$, $\rho < 0.05$

Summary

- It is important to choose the correct tool
- …or even to mix them all: for example, in chemical transformations, where we usually go from non covalent to covalent interactions

Outline

5. Applications to high pressure
   a) ELF: high pressure metals
   b) NCI: He bonds
6. The codes
7. Summary

Metals under pressure

New materials : Electronic structure of high pressure metals

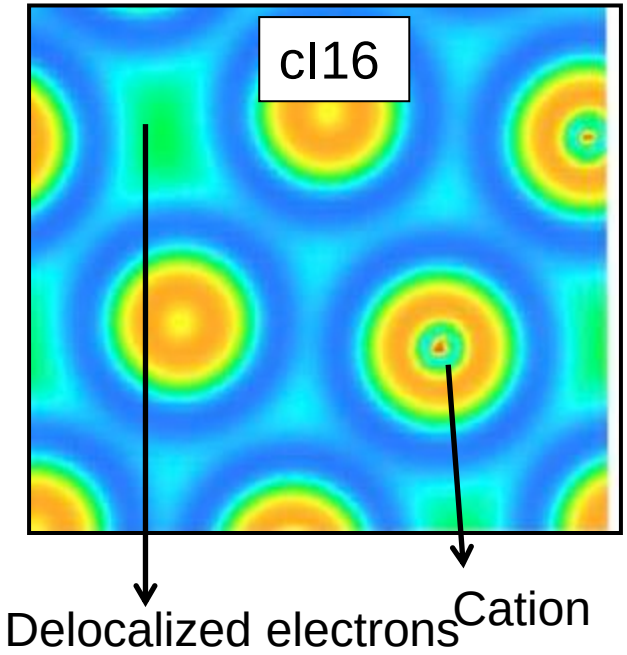
- Under pressure, solids exhibit increasingly shorter interatomic distances. Intuitively, this response is expected to be accompanied by an increase in the widths of the valence and conduction bands and hence a more pronounced free-electron-like behavior.

- However, recent experiments have shown a pressure-induced transformation of Na into an optically transparent and insulating phase at 200 GPa (5.0-fold compression)

- What is the electronic structure behind this new state of matter?

New bonding patterns: new properties

Na



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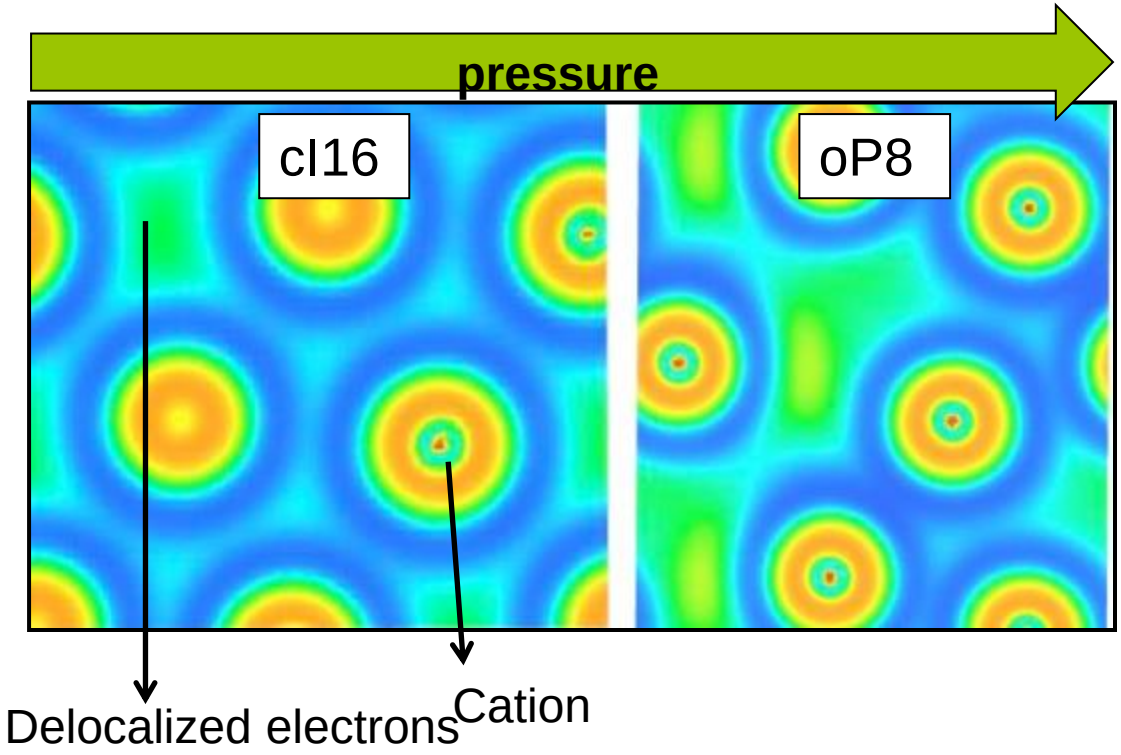
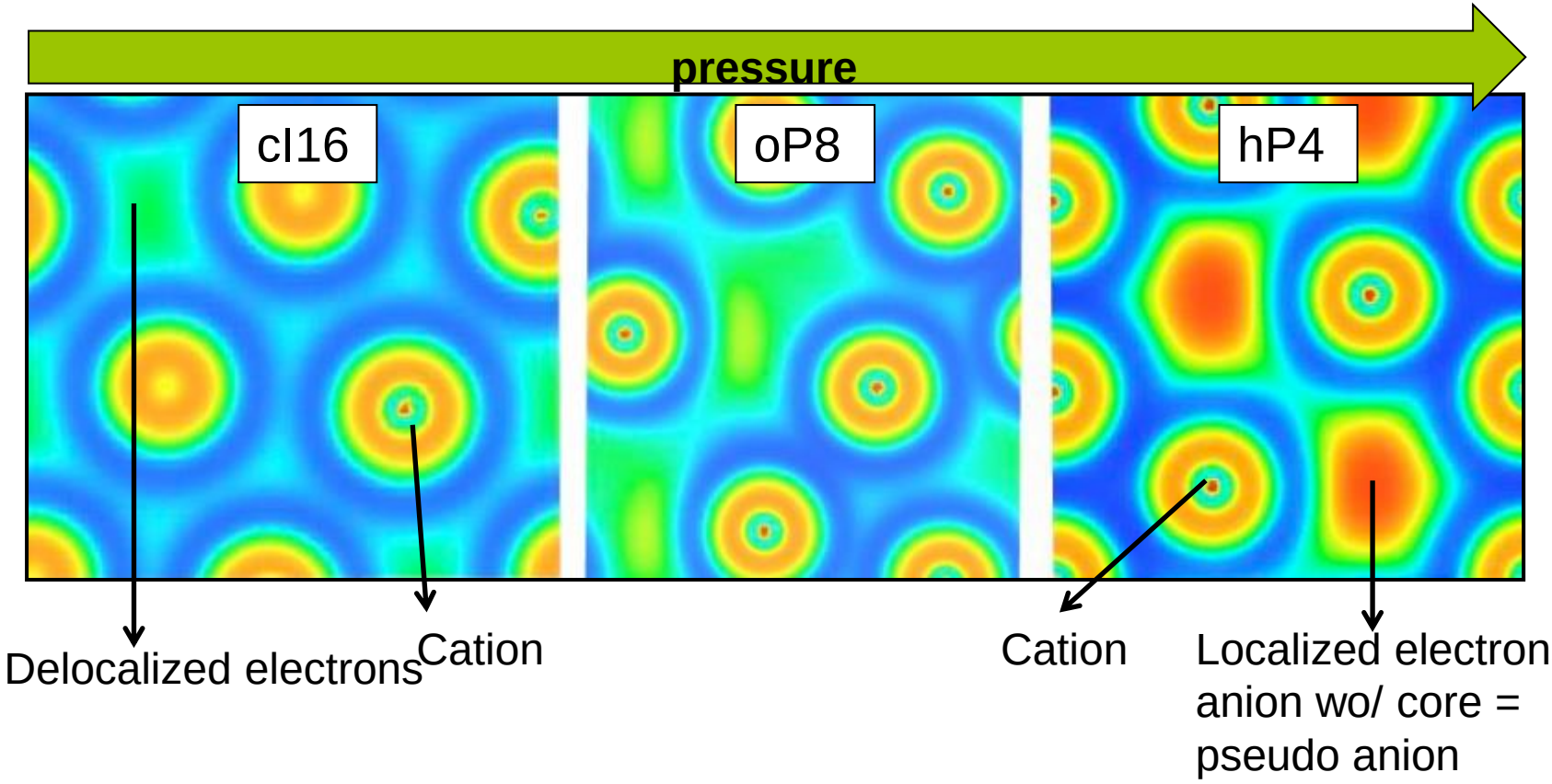


New bonding patterns: new properties

Na

Localization of valence electrons is again observed under pressure



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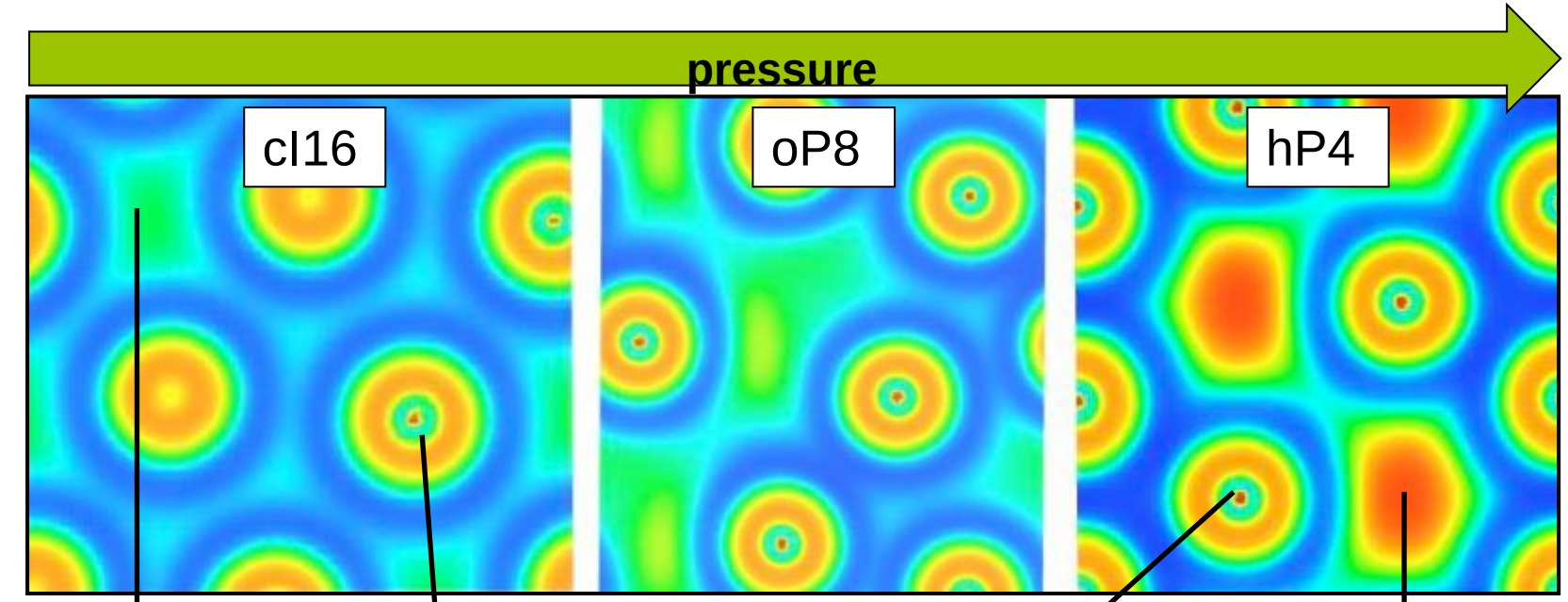


Metallic, conducting → *Insulating, pseudo-ionic !*

New bonding patterns: new properties

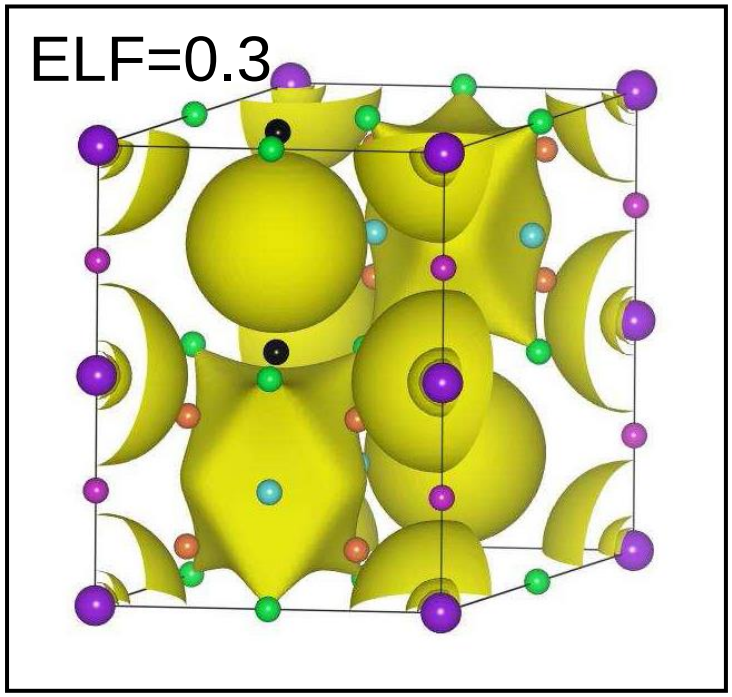
K

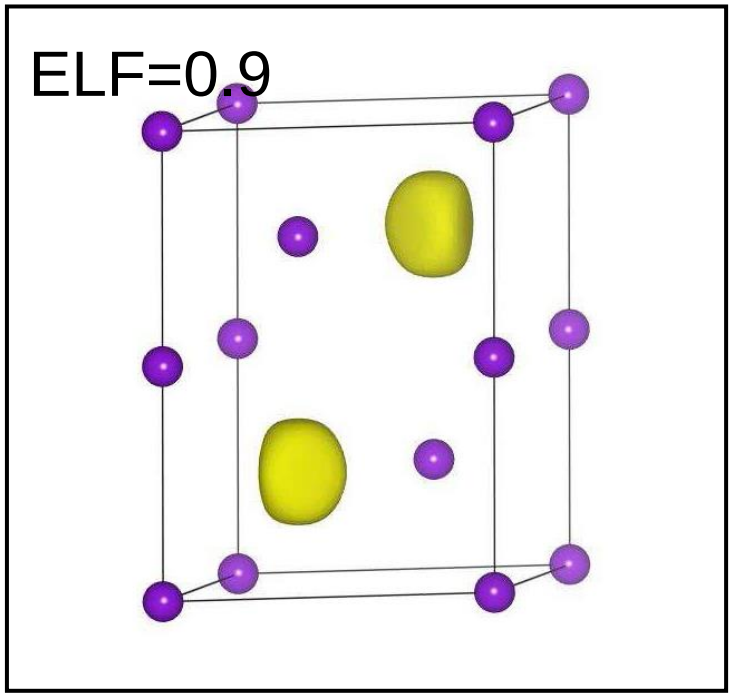
Same structure as A_2X and AX_2 compounds!
Electrons in same position as anions!

Equivalency external and chemical pressure

COUMPOUND→IONIC-LIKE

ELECTRONS→PSEUDOANIONS





27 GPa

Outline

5. Applications to high pressure

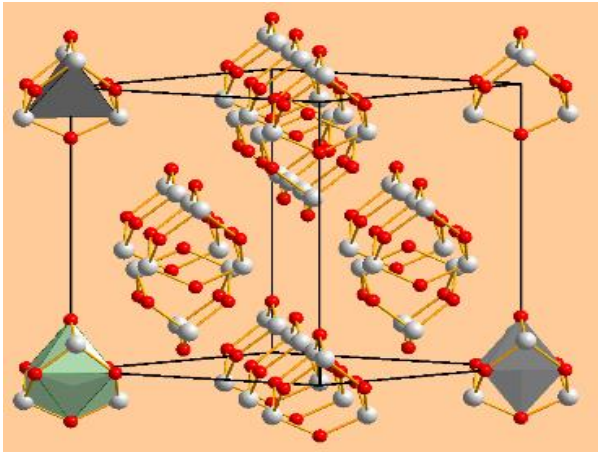
   a) ELF: predicting compressibility & transformations

   b) NCI: He bonds

   c) Electron density: the borate family

6. The codes
7. Summary

He is noble?



- Arsenolite has a closed-compact As_4O_6 cages
- It amorphizes at 15 GPa when compressed alone
- It does not amorphize when He is used as pressure transmiting medium.

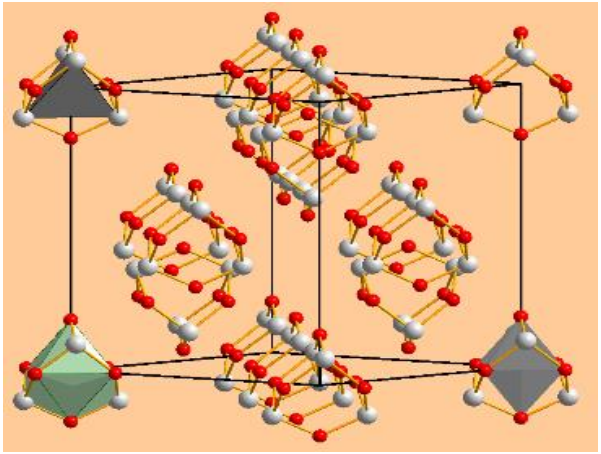
WHY??

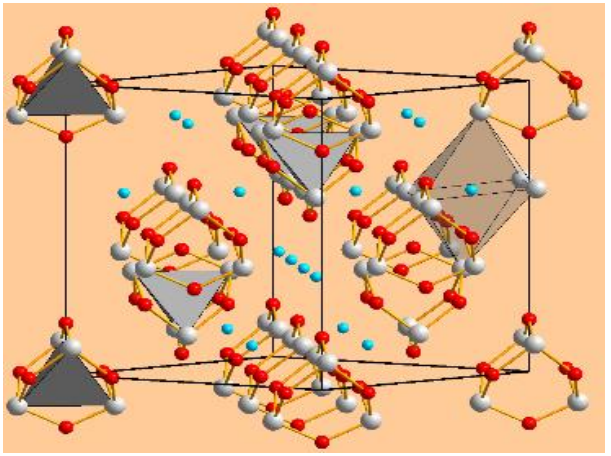
As_4O_6

Phys. Rev. B 93, 054102 (2016)

He is noble?

- It gives ordered helium trapping in the voids when compressed in He





As_4O_6

Phys. Rev. B 93, 054102 (2016)

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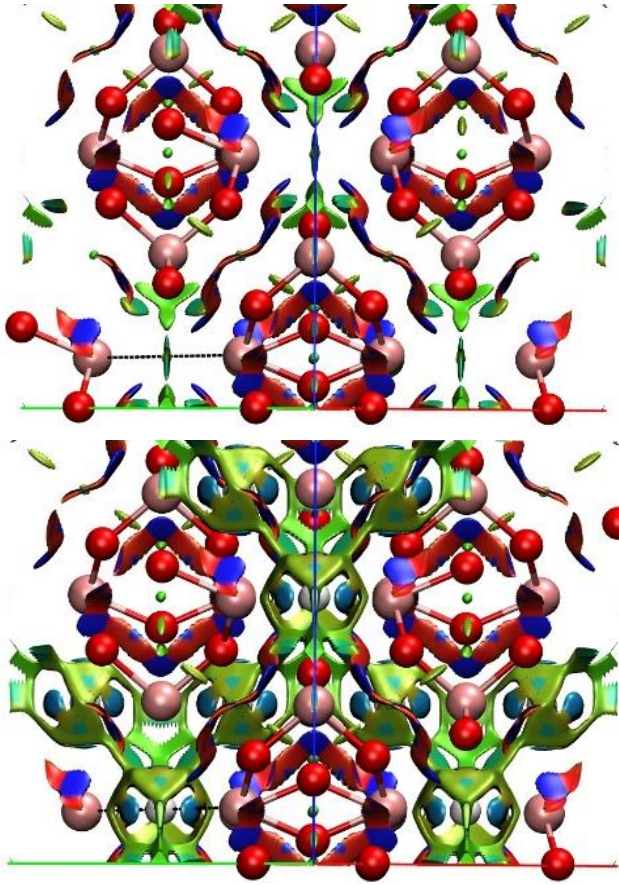
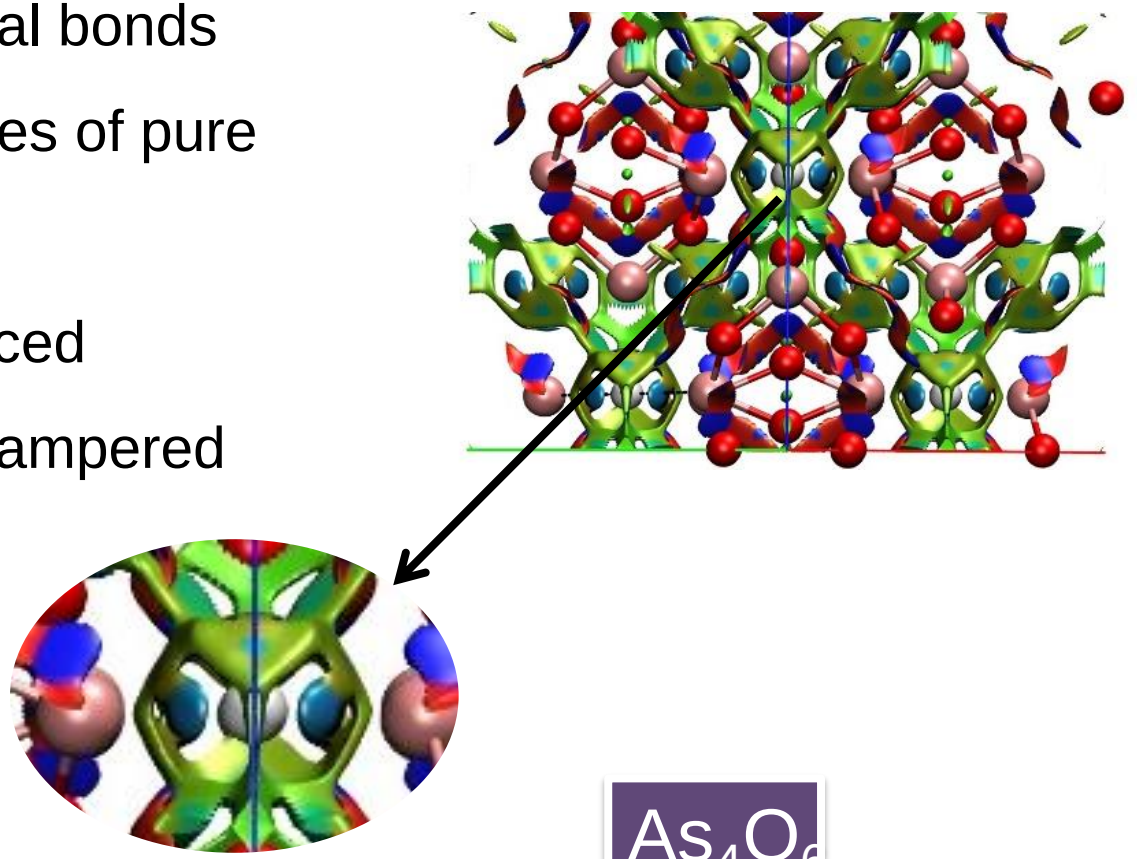


Phys. Rev. B 93, 054102 (2016)

He is noble?

- Very localized structural bonds
- They alter the properties of pure As_4O_6,
  - e.g. pressure-induced amorphization is hampered



Phys. Rev. B 93, 054102 (2016)

Outline

5. Applications to high pressure

   a) ELF

      Polarity of ionic compounds
      Predicting compressibility
      Rationalizing phase transitions

   b) NCI: He bonds

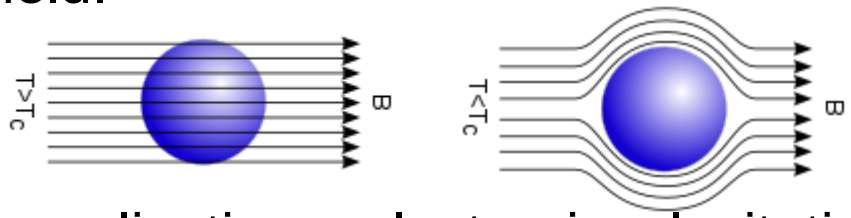
   c) ELF: superconductivity

8. The codes
9. Summary

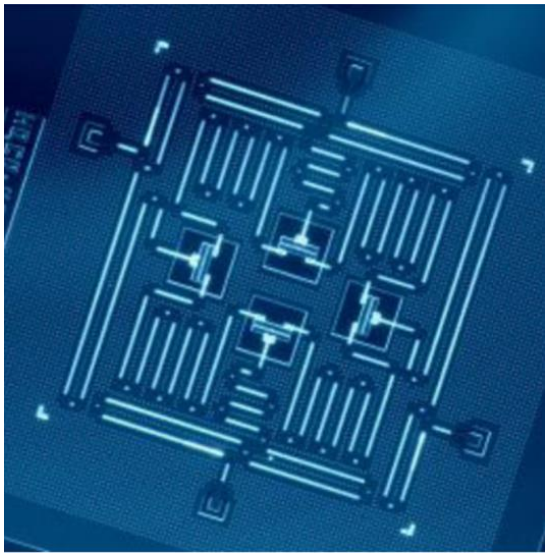
Superconducting materials

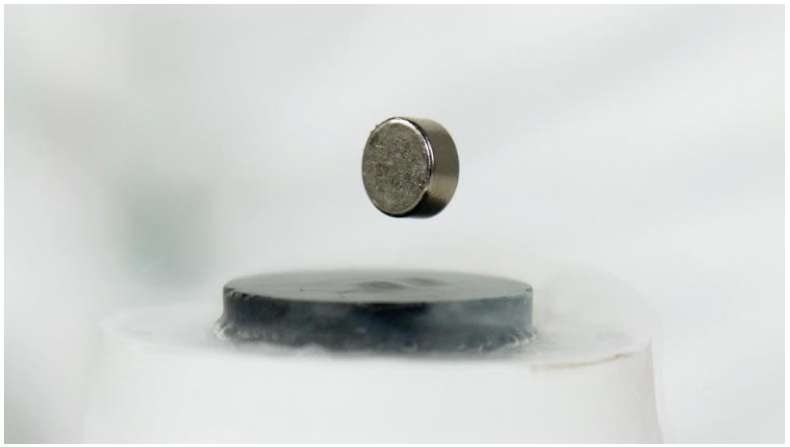
Superconductivity is technologically very interesting…

- Two key features: null resistivity and perfect repulsion of magnetic field.



- Interesting applications: electronics, levitation





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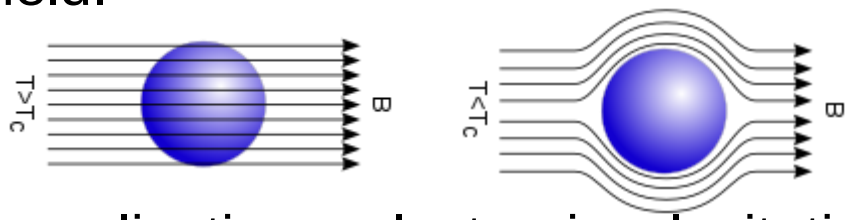

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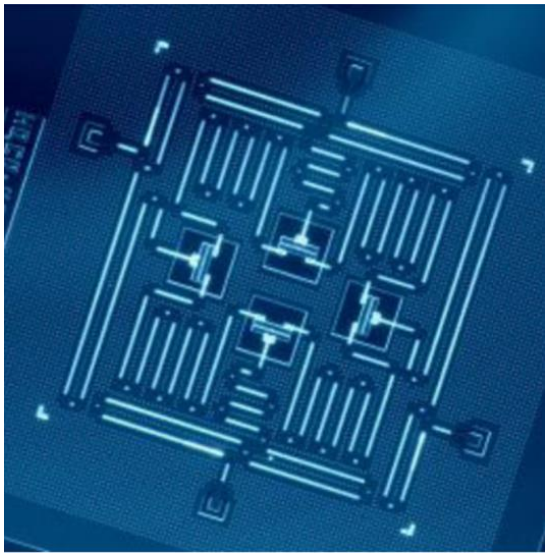
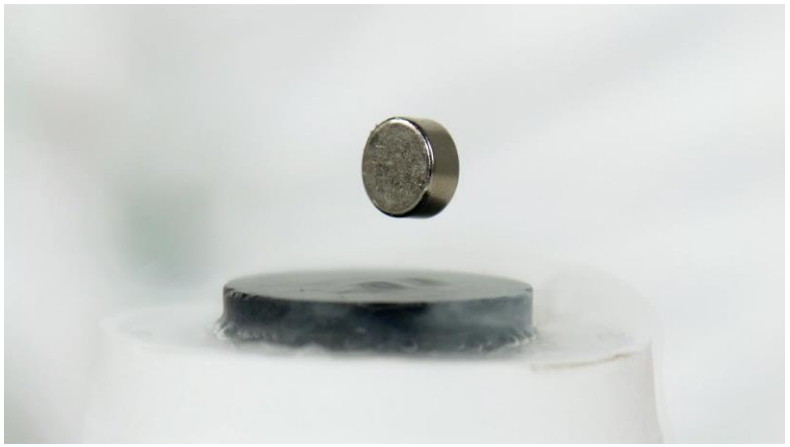
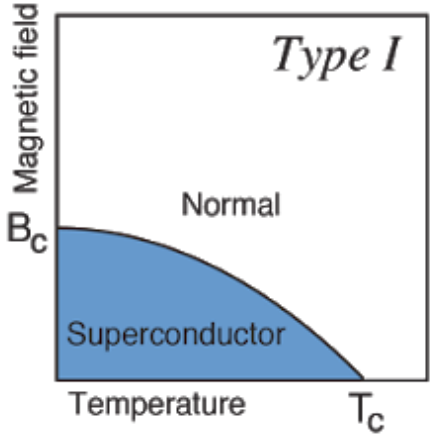




However….

Superconducting materials

- Superconductivity appears at very low temperatures



- The problem: very low is VERY low: Al (1.2K), Zn (0.88 K)

Superconducting materials

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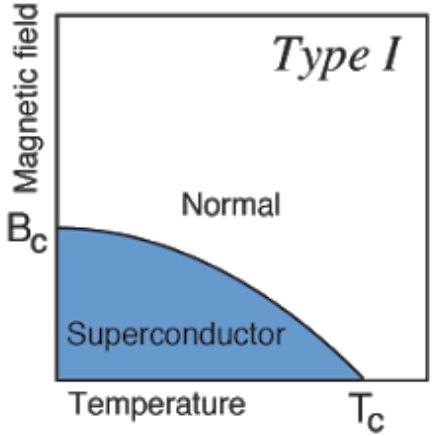

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- Calculations are extremely expensive, and not always work

AlH_3 : Tc theo= 132-146 K … Tc exp=4 K! (250GPa)

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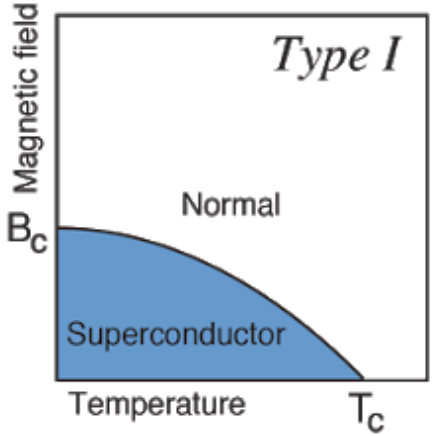

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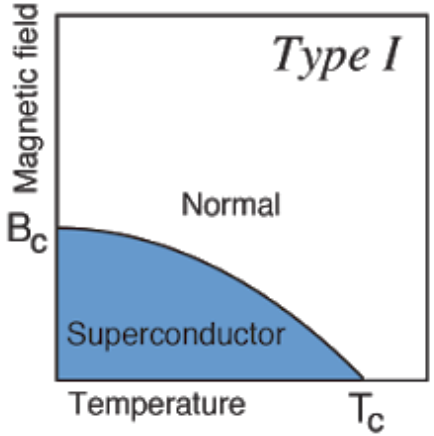

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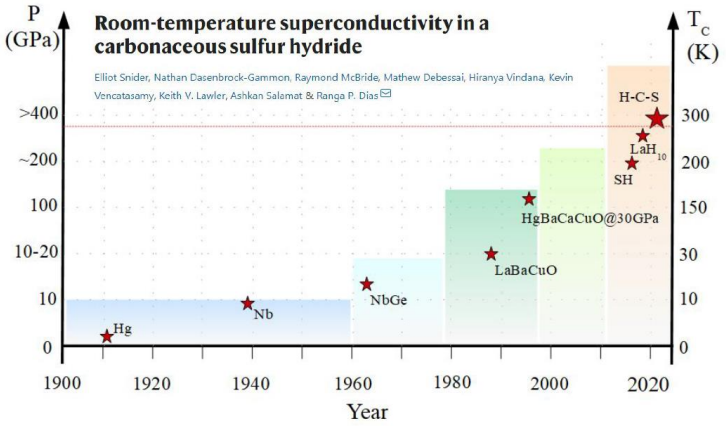
Let's start from a reasonable starting point…H-based systems!

Hydrogen based superconductors

- A new family of high-temperature superconductors: H_3S (203K), LaH_{10} (260K). **Room temperature SC of C-S-H system!**



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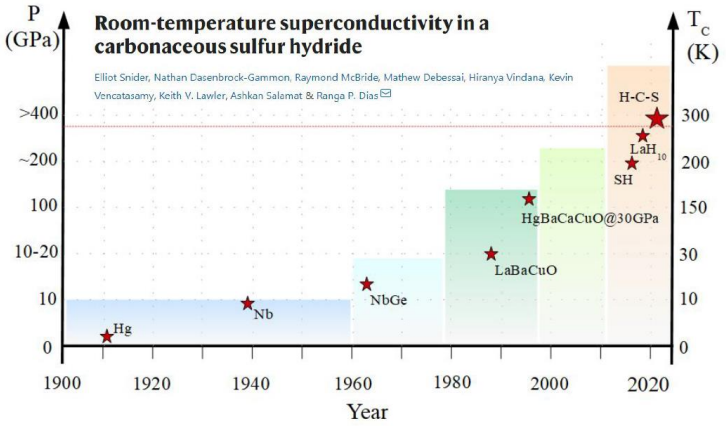

- Something to keep in mind:
  - High pressures are needed:

    H_3S at 203K **and 150GPa**, LaH_{10} at 260K and **190GPa**.
  - Hopefully replaced by chemical pressure! (next step)

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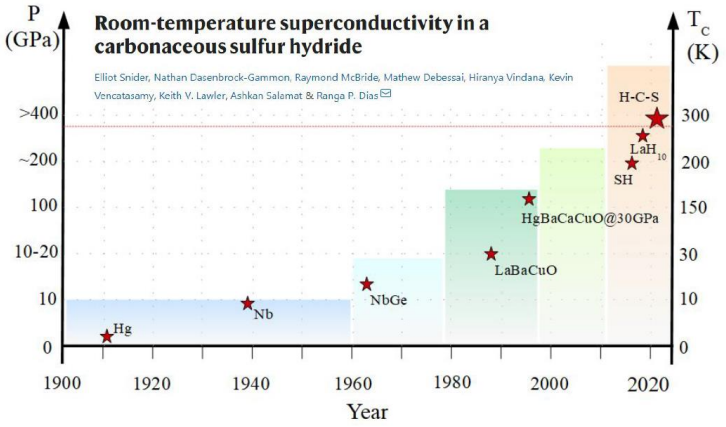

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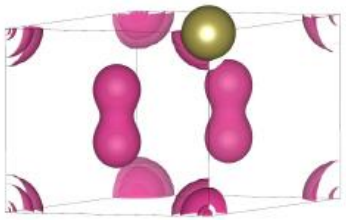
Let's start!

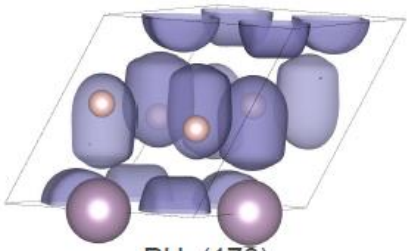
- 178 systems with available Tc values (pure and binary compounds)

Molecular



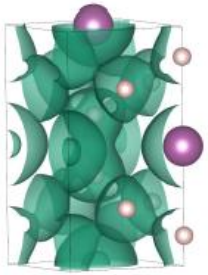
TeH_4 (150)
ELF = 0.9

Covalent



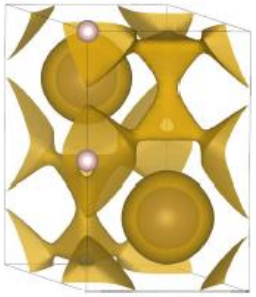
PH_2 (173)
ELF = 0.65

Weak H Interactions



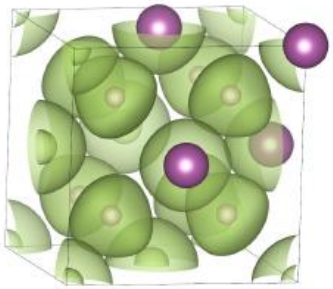
ScH_4 (17)
ELF = 0.45

Electride



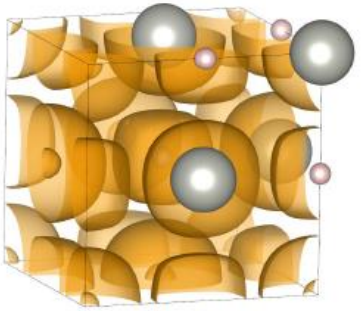
CrH (53)
ELF = 0.39

Ionic

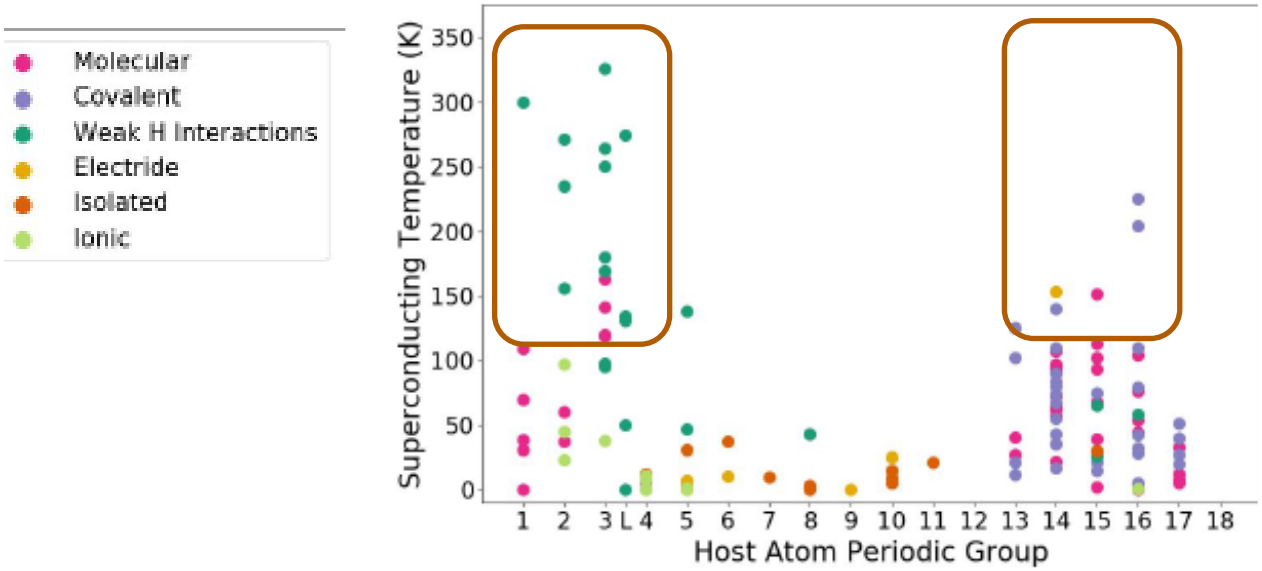


ScH_2 (14)
ELF = 0.52

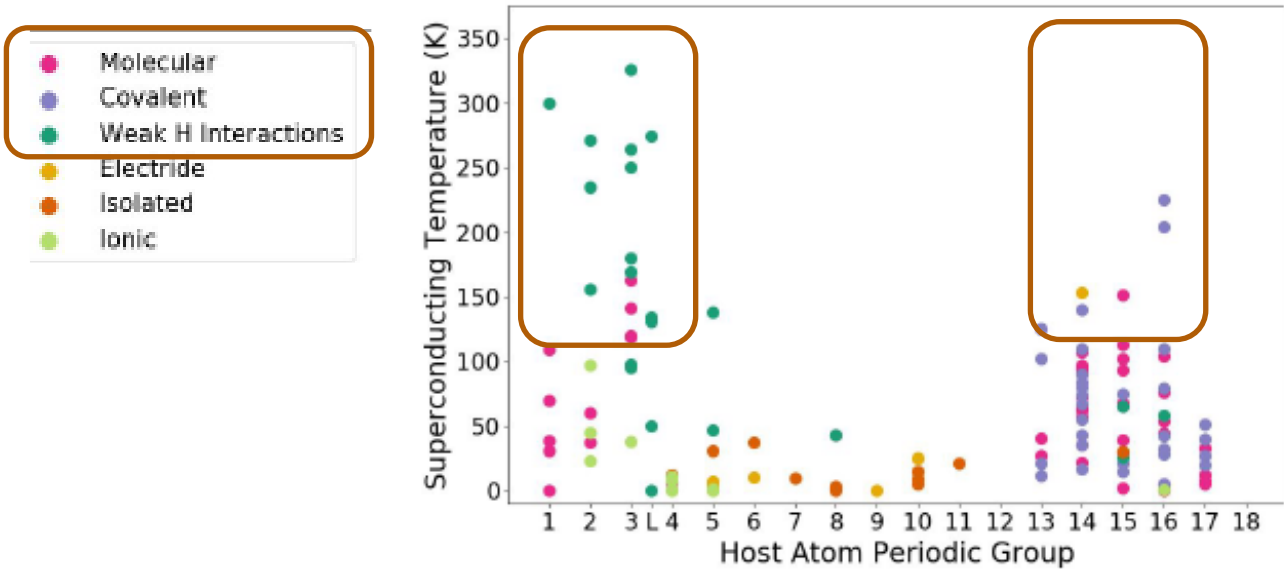
Isolated



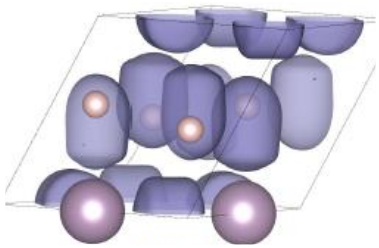
PdH (70)
ELF = 0.25

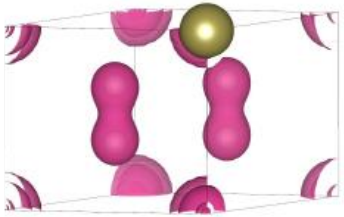


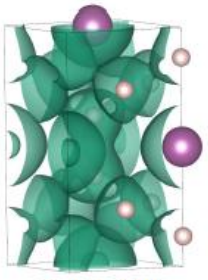
- Characteristics:
  - s, p atoms

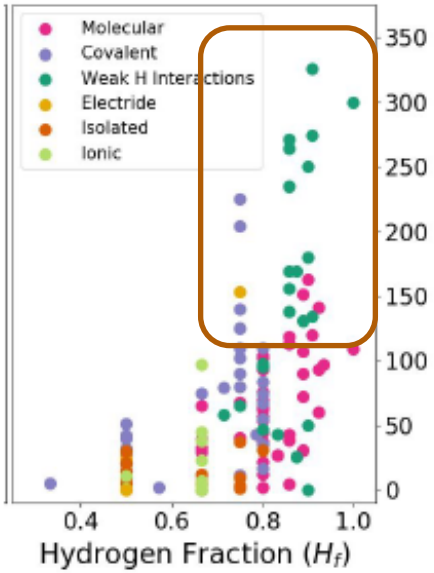


- Characteristics:
  - s, p atoms
  - Non charged (covalent, molecular or weak H interactions)

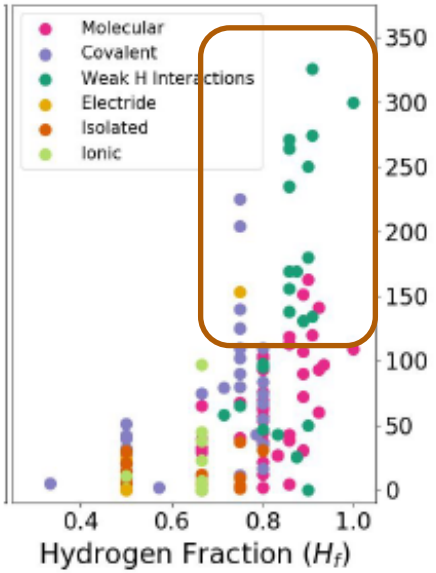


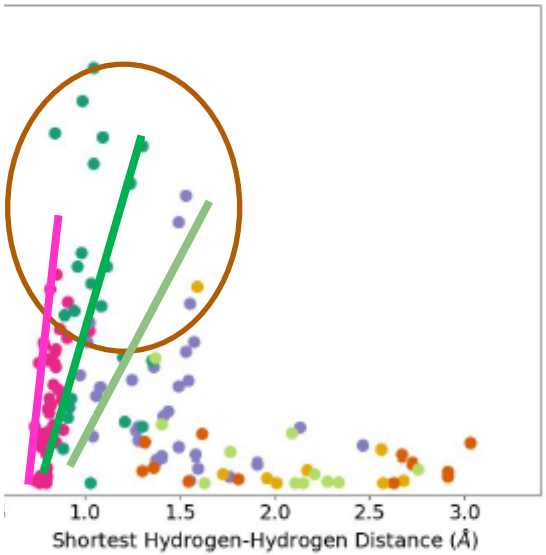




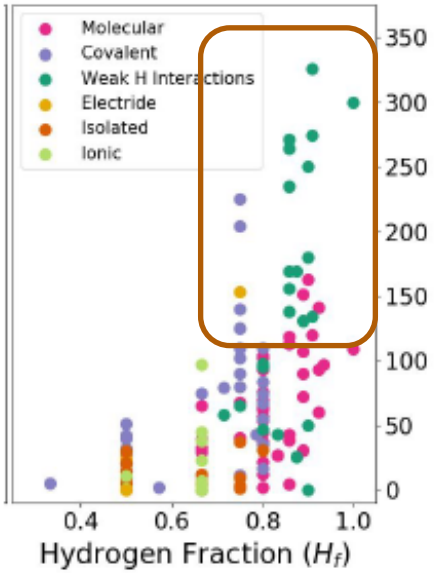


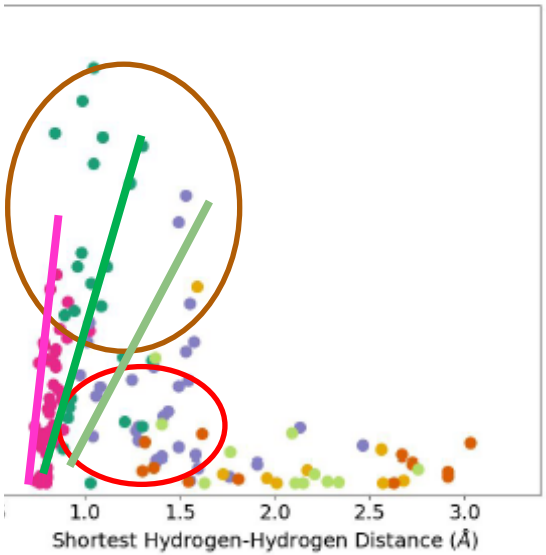
- Characteristics:
  - Hydrogen rich systems



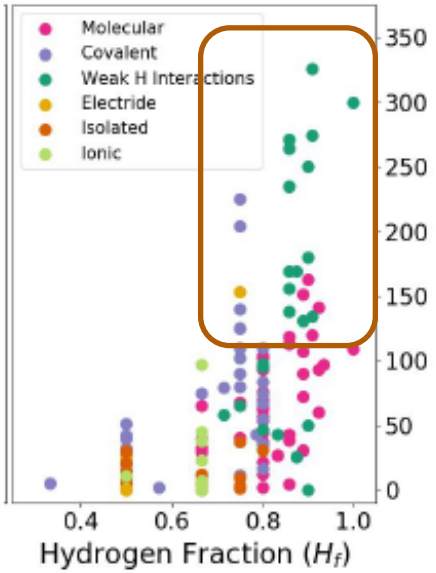


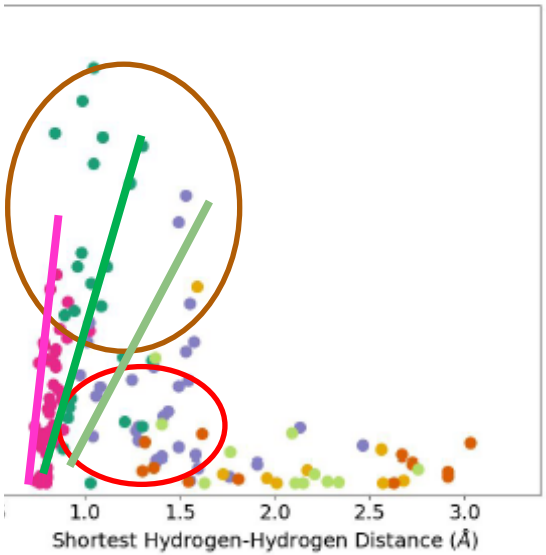
- Characteristics:
  - Hydrogen rich systems
  - Stretched H-H bonds





- Characteristics:
  - Hydrogen rich systems
  - Stretched H-H bonds
- Necessary but not sufficient conditions!

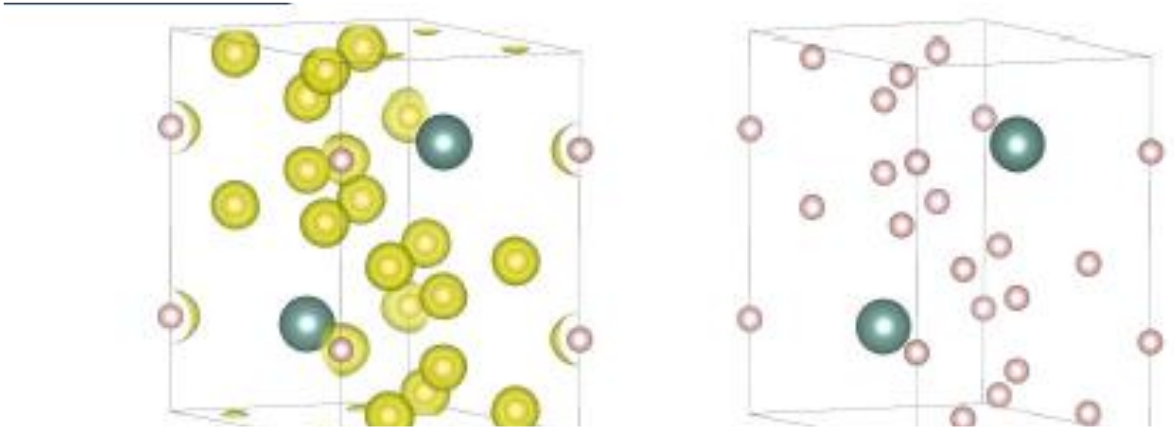




- Characteristics:
  - Hydrogen rich systems
  - Stretched H-H bonds
- Necessary but not sufficient conditions!

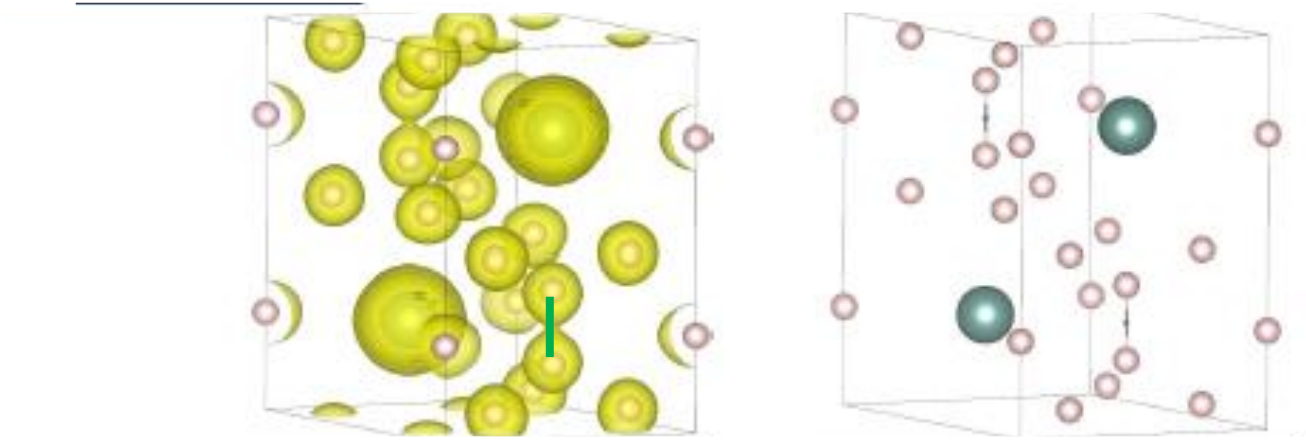
How about the electron localization?

YH_9



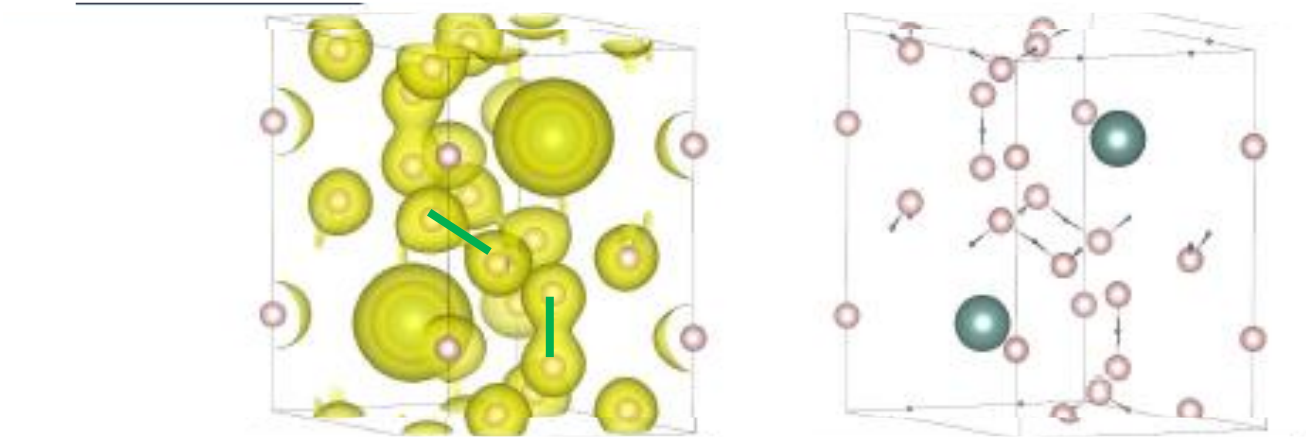
ELF=0.9

YH_9



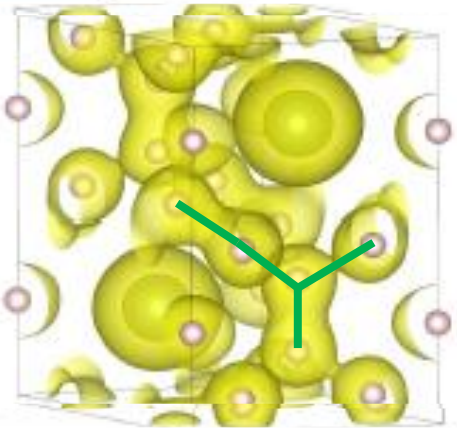
ELF=0.78

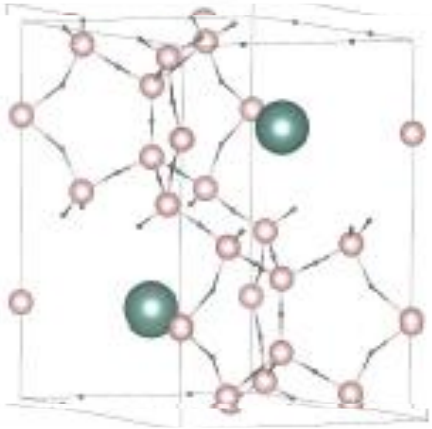
YH_9



ELF=0.72

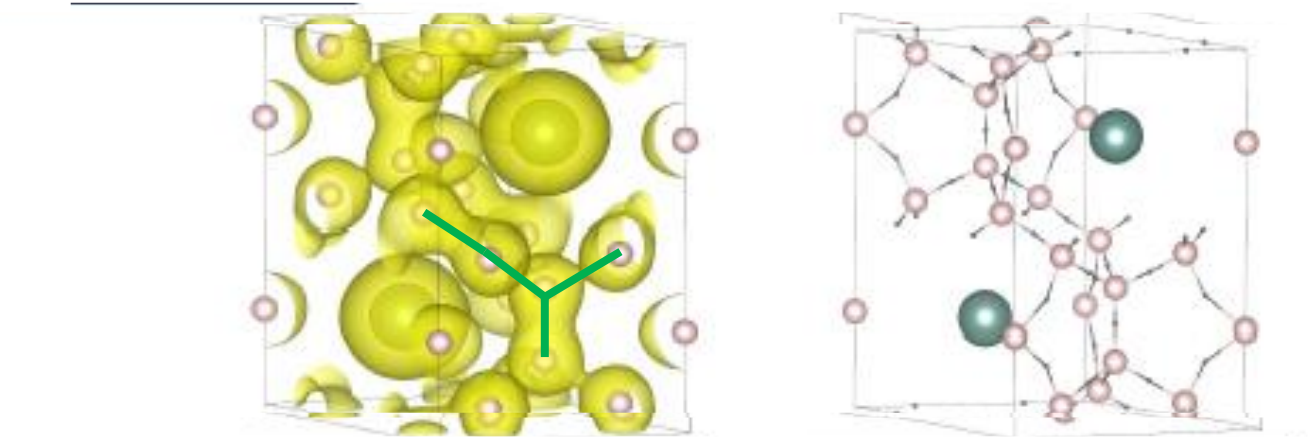
YH_9





ELF=0.57

YH_9



ELF=0.57

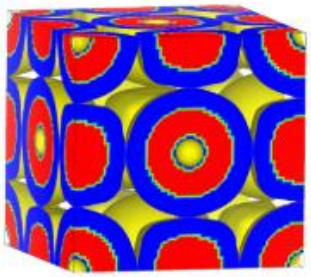
- At ELF=0.57 the hydrogen network is connected
- We call this ELF value the networking value, ϕ

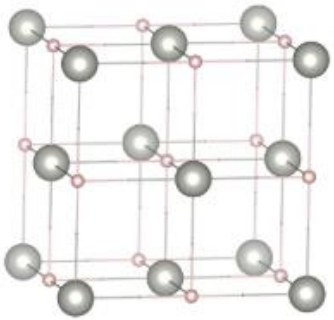
Networking value ϕ

- We determined it in the 178 crystalline structures

PdH(70)

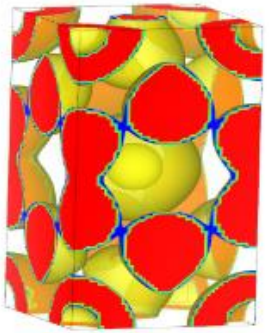
ELF = 0.19

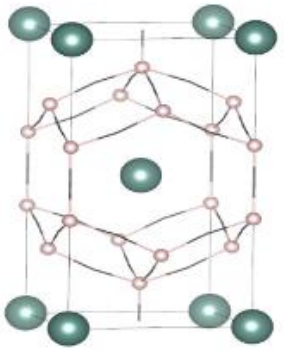




YH4(15)

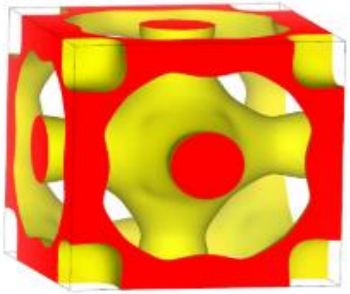
ELF = 0.43

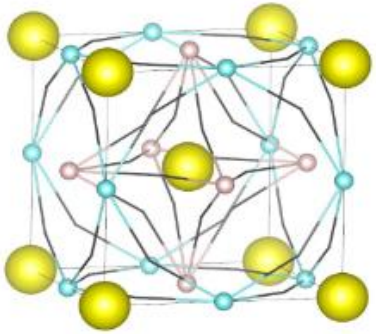




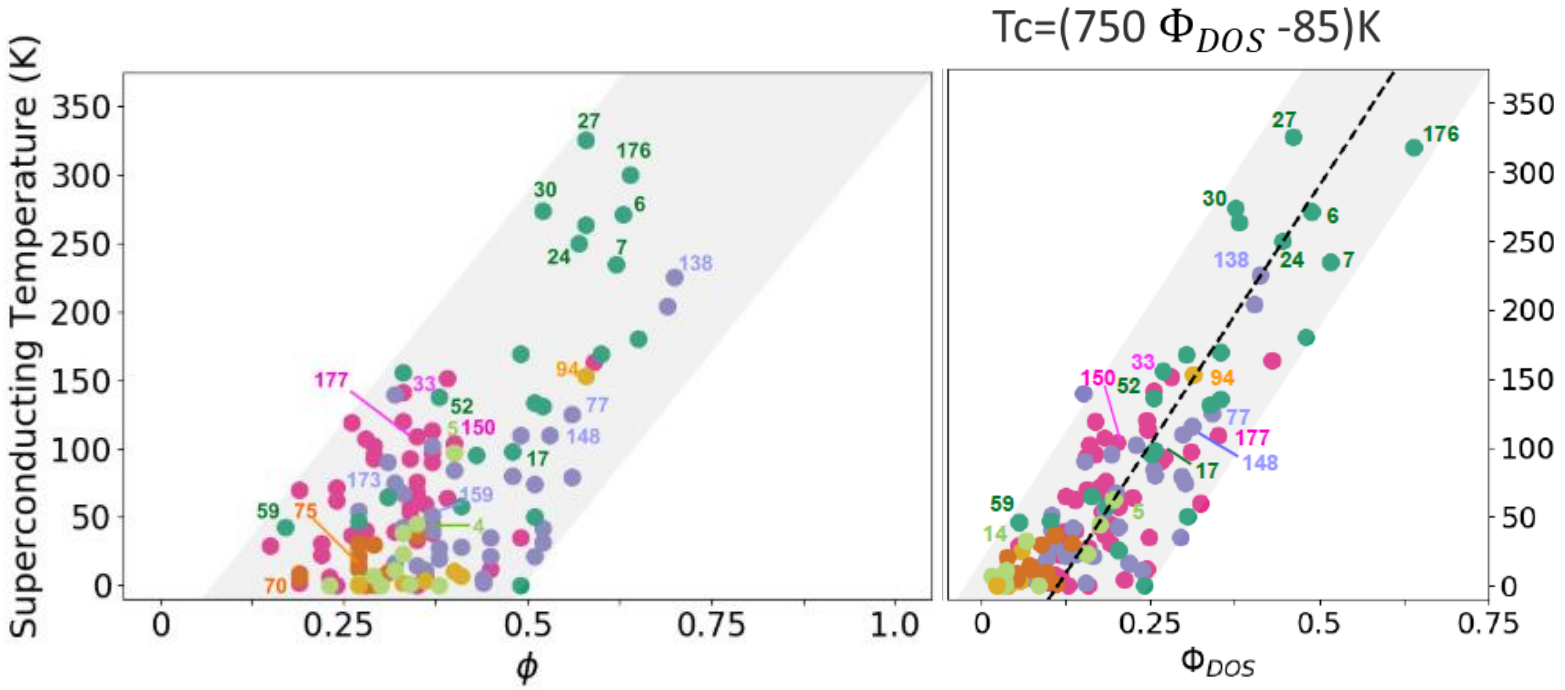
H3S(138)

ELF = 0.68





Correlation between T_c and ϕ



- ϕ provides a first estimate of the superconducting critical temperature
- Including chemical and electronic structure features reduces the dispersion within 60K
- Sufficient condition, avoids very expensive calculations!

Nat Comm 12, 5381 (2021)

Summary

- We can derive macroscopic properties from the electronic structure/bonding
- It improves all other structural or electronic indexes previously proposed
- It only requires DFT ground state+ELF calculations

- It offers a simple way of screening new superconductors
- Points the way to inverse engineering new hydrogen-based superconductors

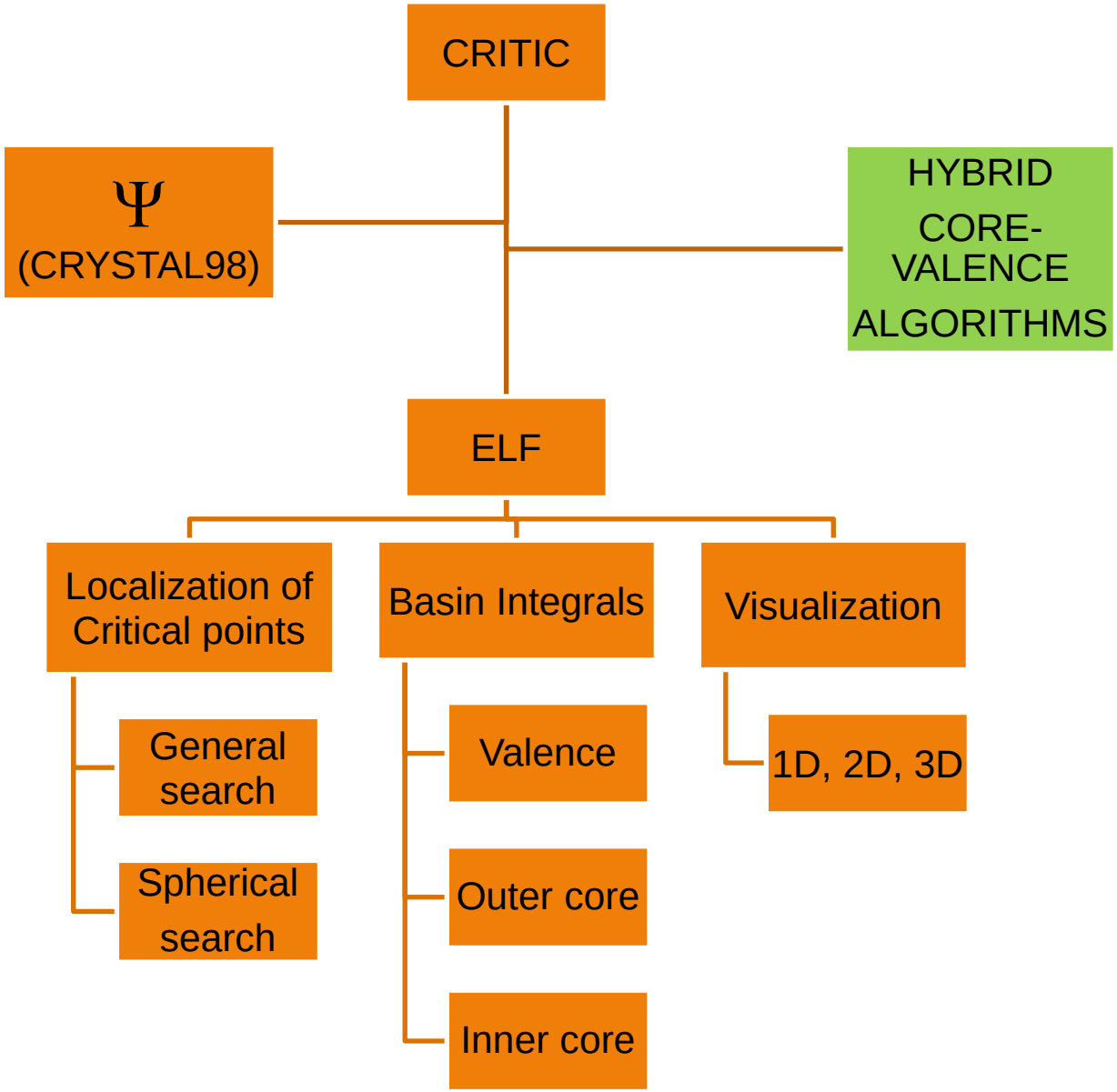
Programs

- ELF and NCI from periodic calculations: CRITIC

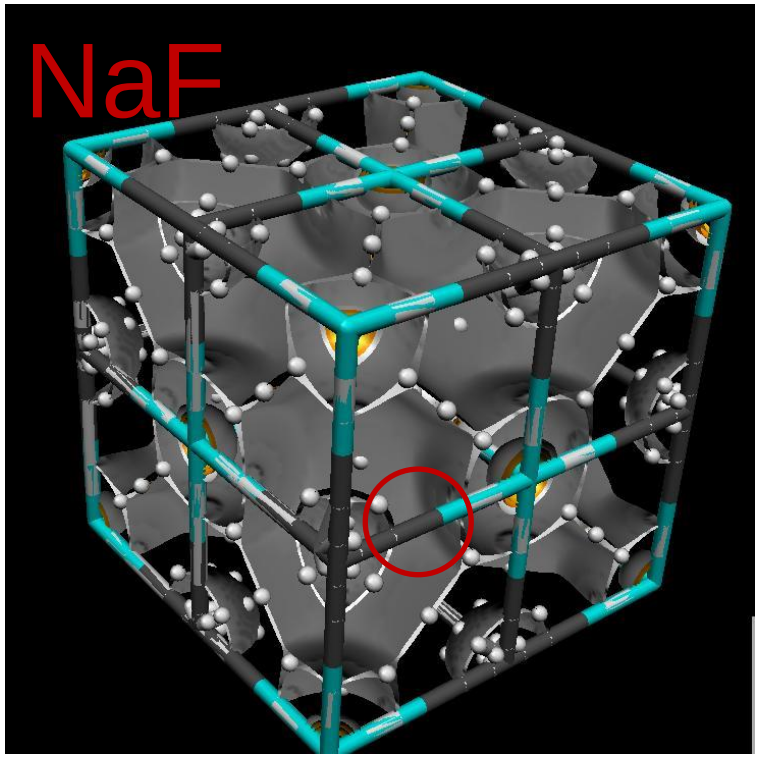
- NCI from molecular calculations, PDBs and crystallographic data

- NCI from PDB with PDB treatment: NCIWeb now also available at:

https://nciweb.dsi.upmc.fr/index.php


CRITIC
Ψ
(CRYSTAL98)
HYBRID
CORE-
VALENCE
ALGORITHMS
ELF
Localization of
Critical points
Basin Integrals
Visualization
General
search
Spherical
search
Valence
Outer core
Inner core
1D, 2D, 3D

CRITIC

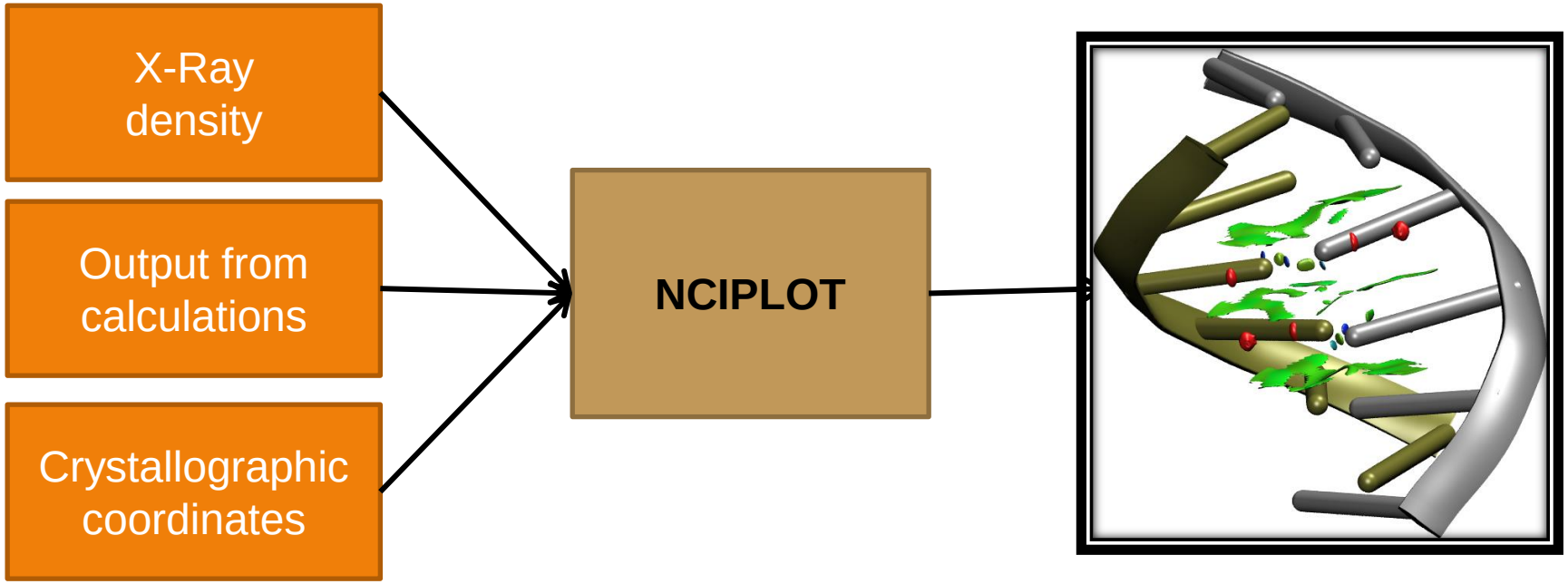


Total	Generic	Hybrid
Maximum number	64	64
Bond number	176	200
Ring number	200	200
Cage number	64	64
Morse sum equals	24	0

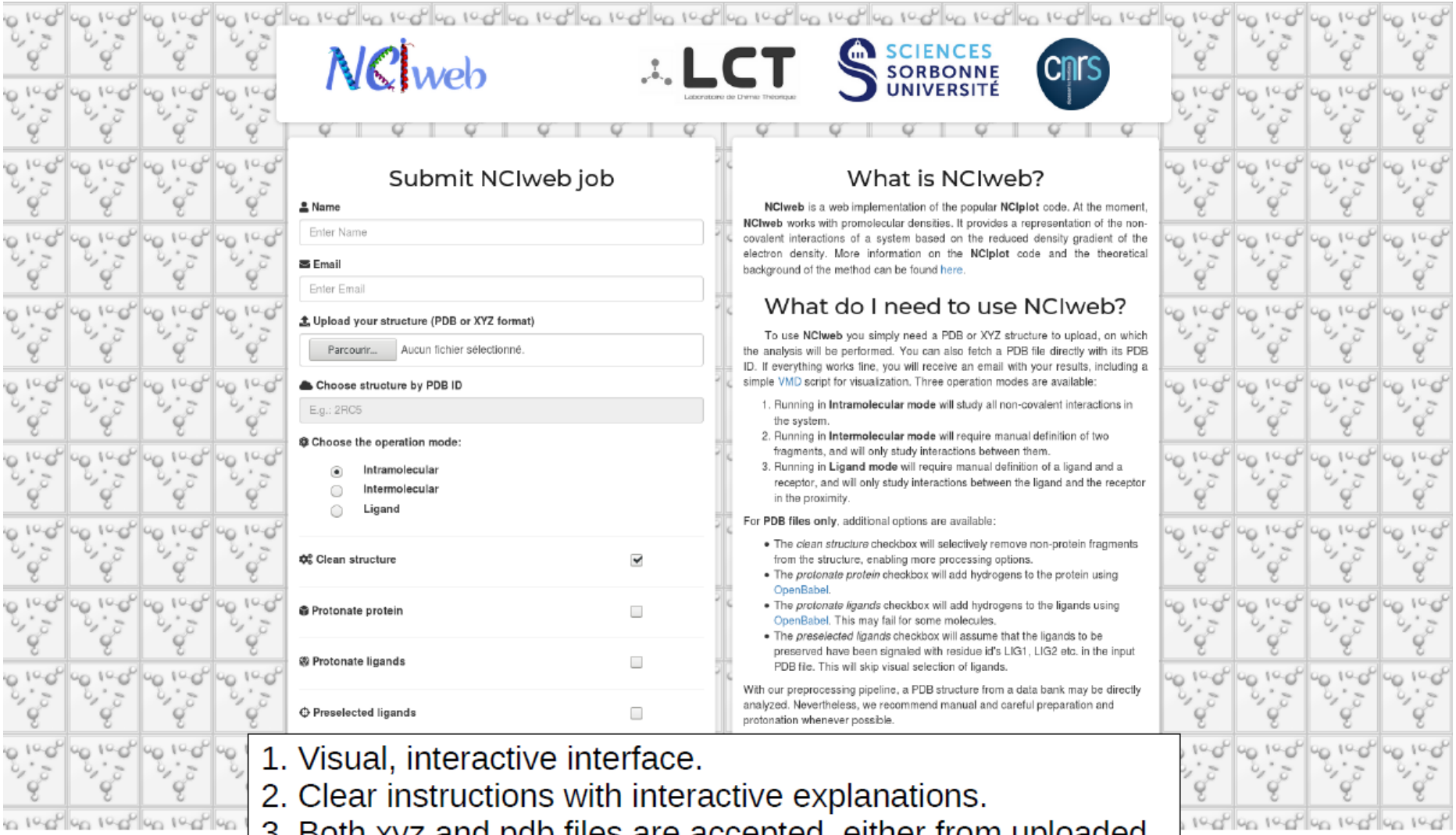
N	SYM	CP	TYPE	X	Y	Z	M
1	Oh	(3,-3)	Nucleus	0.000	0.000	0.000	4
2	Oh	(3,-3)	Nucleus	0.000	0.000	0.500	4
3	C3v	(3,-3)	Maximum	0.038	0.462	0.462	32
4	C4v	(3,-3)	Maximum	0.000	0.084	0.500	24
5	D2h	(3,-1)	Bond	0.250	0.500	0.250	24
6	C4v	(3,-1)	Bond	0.790	0.500	0.500	24
7	C2v	(3,-1)	Bond	0.059	0.500	0.941	48
8	C2v	(3,-1)	Bond	0.000	0.453	0.453	48
9	C3v	(3,-1)	Bond	0.487	0.487	0.013	32
10	C4v	(3,-1)	Bond	0.000	0.000	0.530	24
11	C2v	(3,+1)	Ring	0.000	0.320	0.320	48
12	C3v	(3,+1)	Ring	0.048	0.048	0.452	32
13	C4v	(3,+1)	Ring	0.000	0.000	0.934	24
14	C2v	(3,+1)	Ring	0.521	0.021	0.000	48
15	C2v	(3,+1)	Ring	0.516	0.016	0.500	48
16	Td	(3,+3)	Cage	0.250	0.250	0.250	8
17	C3v	(3,+3)	Cage	0.982	0.518	0.018	32
18	C4v	(3,+3)	Cage	0.500	0.500	0.023	24

Morse sum must is zero

NCIPLOT

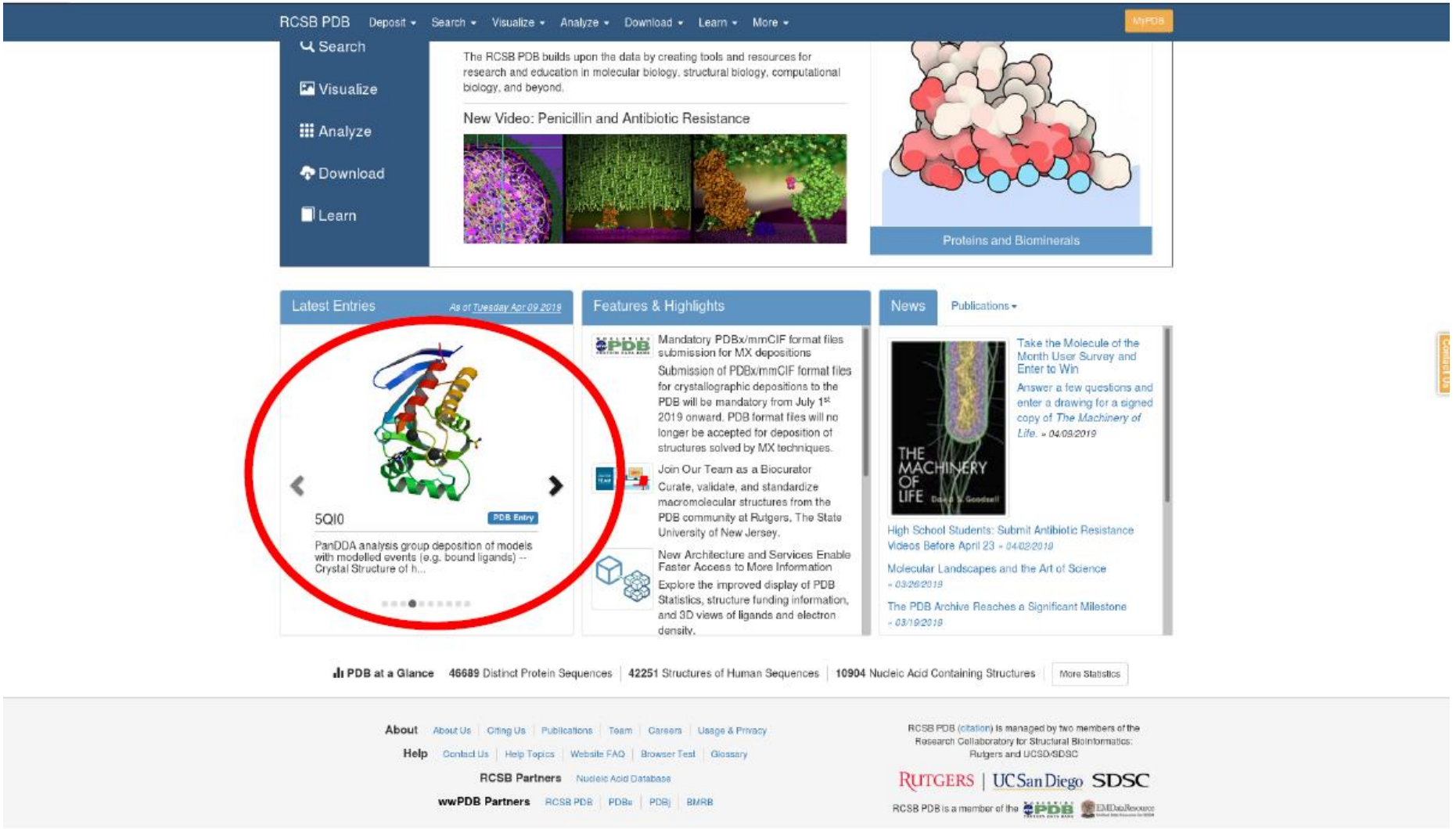

X-Ray density
Output from calculations
Crystallographic coordinates
NCIPLOT

NCIWEB



1. Visual, interactive interface.
2. Clear instructions with interactive explanations.
3. Both xyz and pdb files are accepted, either from uploaded or from a PDB record.

NCIWEB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Proteins and Biominerals
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As of Tuesday Apr 09 2019
5QI0
PDB Entry
PanDDA analysis group deposition of models with modelled events (e.g. bound ligands) -- Crystal Structure of h...
Features & Highlights
Mandatory PDBx/mmCIF format files submission for MX depositions
Submission of PDBx/mmCIF format files for crystallographic depositions to the PDB will be mandatory from July 1st 2019 onward. PDB format files will no longer be accepted for deposition of structures solved by MX techniques.
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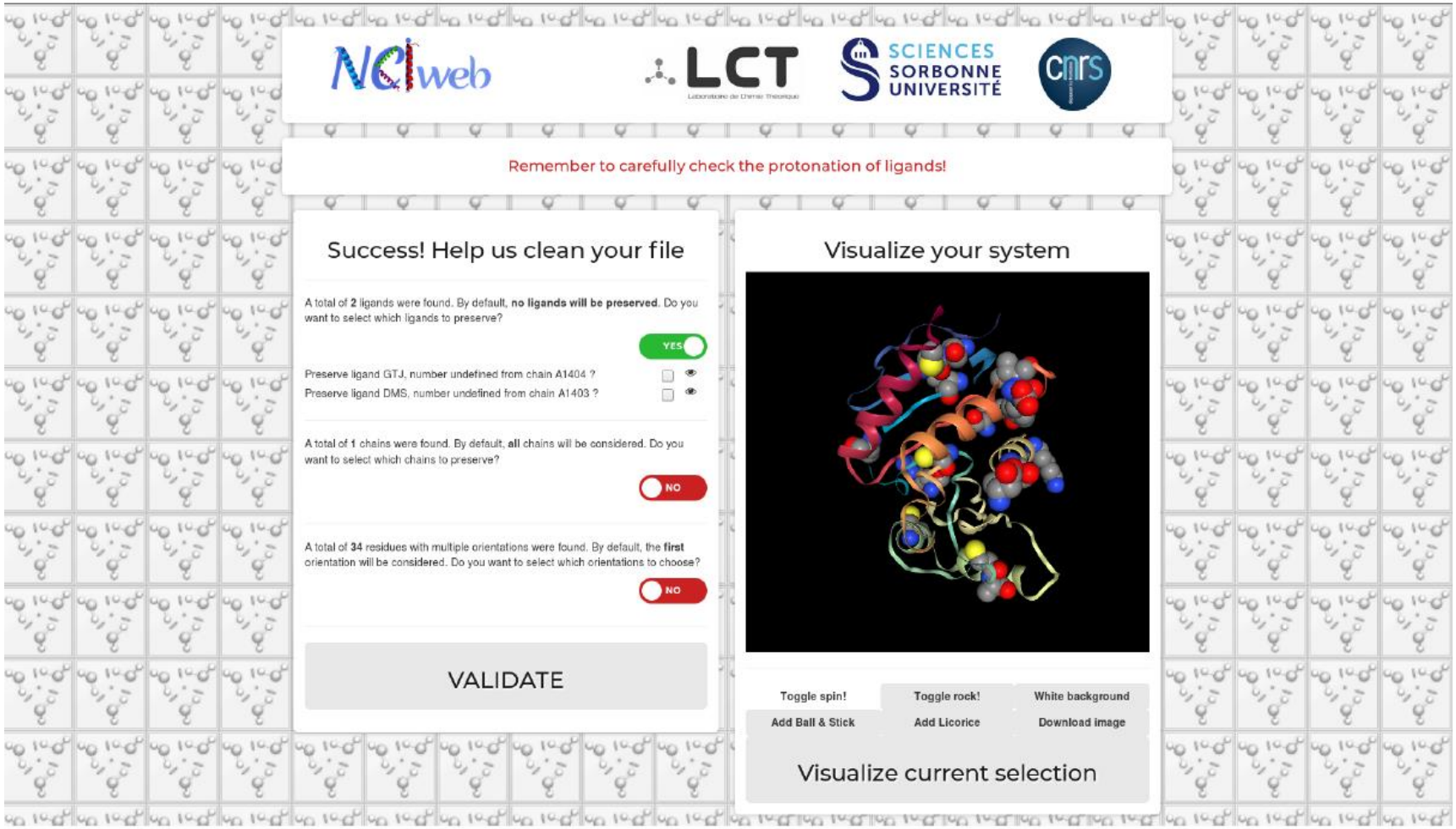
NCIWEB



1. All crystallographic molecules and salts have been removed automatically.
2. An **interactive visualization** page lets us select chains, ligands and orientations to properly prepare our structure.

Summary

- Quantum chemistry and topology can be coupled to provide a quantitative picture of bonding
- This picture is very helpful in understanding high pressure behavior

Keep all this in mind for this afternoon lab work!!!