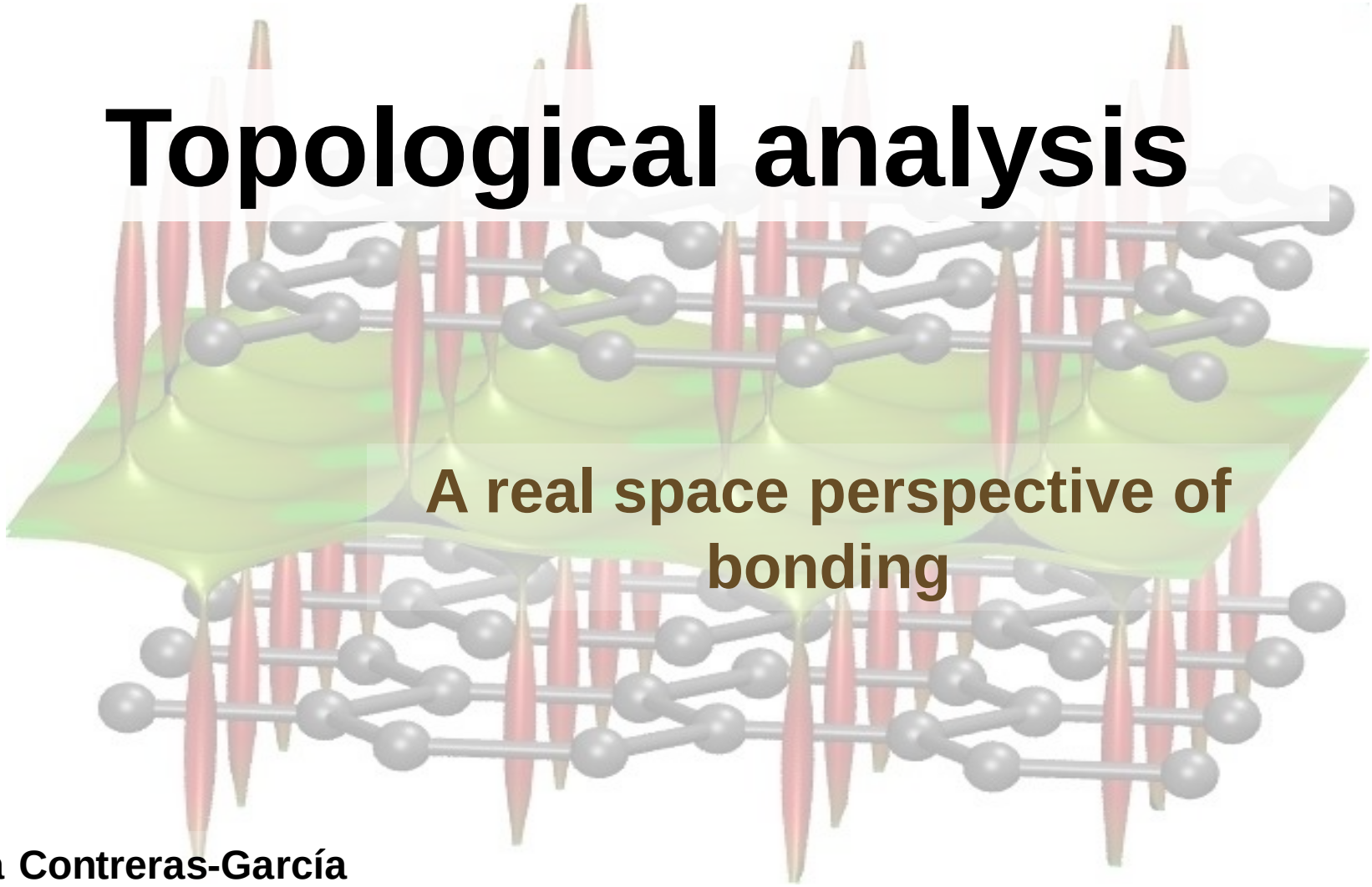
UPMC
SORBONNE UNIVERSITÉS

Topological analysis



A real space perspective of bonding

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. Applications

4. Workout example
5. Summary

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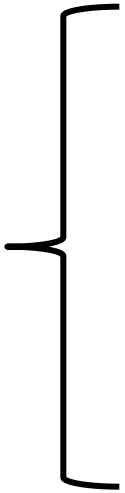


1. The function
2. The topology
3. Applications

4. Workout example
5. 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

QCT in a nutshell

Quantum topology

QCT in a nutshell

- Bonds are objects from **Classical** Chemistry, they are **qualitative** but provide **local** information

QCT in a nutshell

Quantum topology

- Bonds are objects from **Classical** Chemistry, they are **qualitative** but provide **local** information

- **Quantum** chemistry gives us a quantitative description of chemical systems. It is **quantitative** but **global**

QCT in a nutshell

Quantum topology

- Bonds are objects from **Classical** Chemistry, they are **qualitative** but provide **local** information
- **Quantum** chemistry gives us a quantitative description of chemical systems. It is **quantitative** but **global**

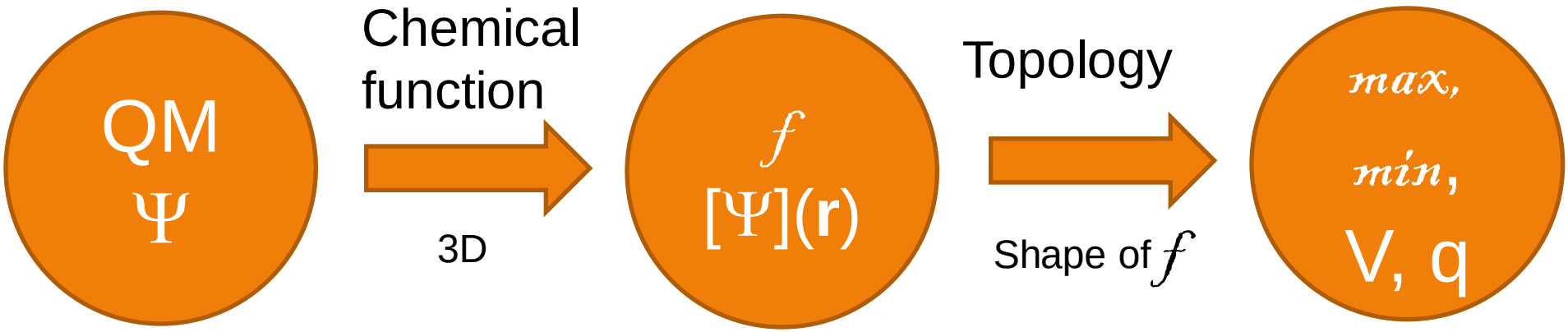
We need extra tools to extract local information from Quantum Chemistry

(and reduce the dimensionality)

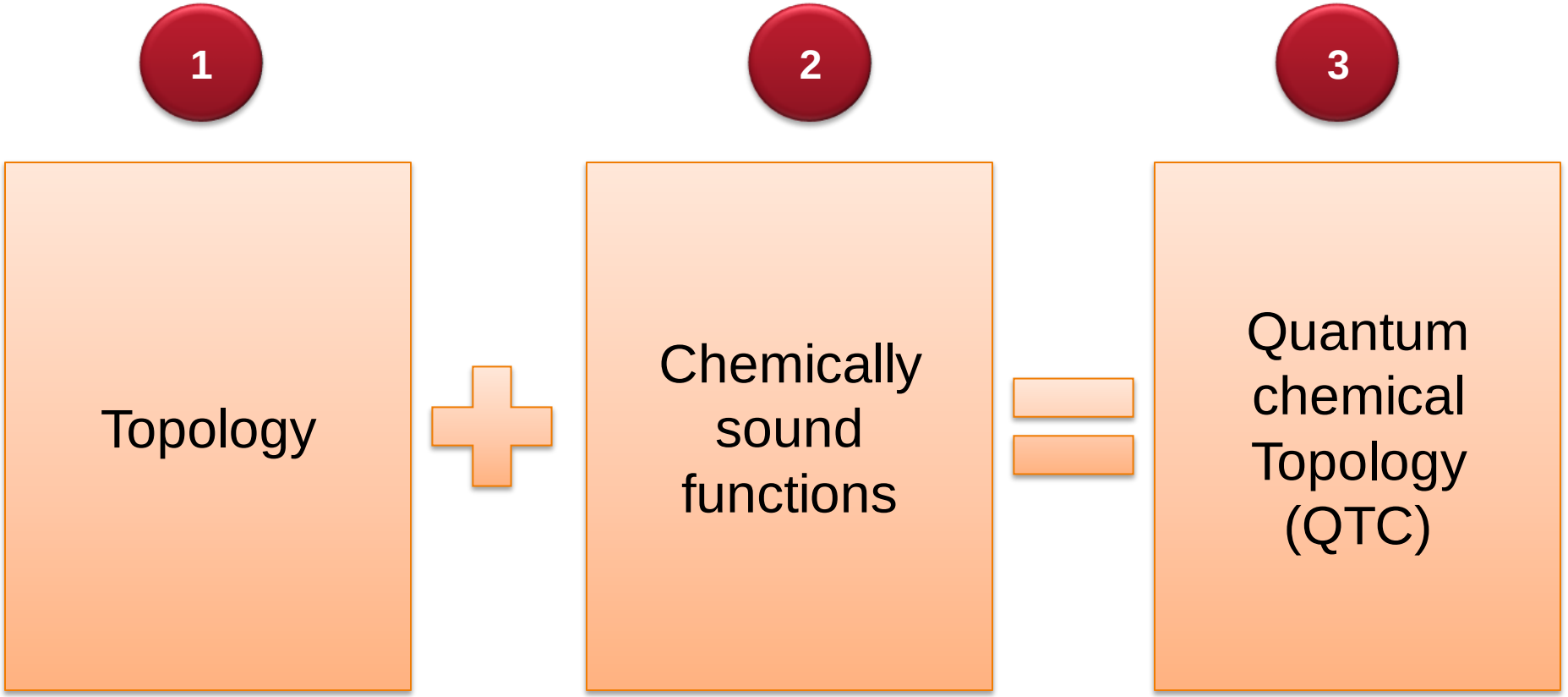
QCT in a nutshell

Quantum topology

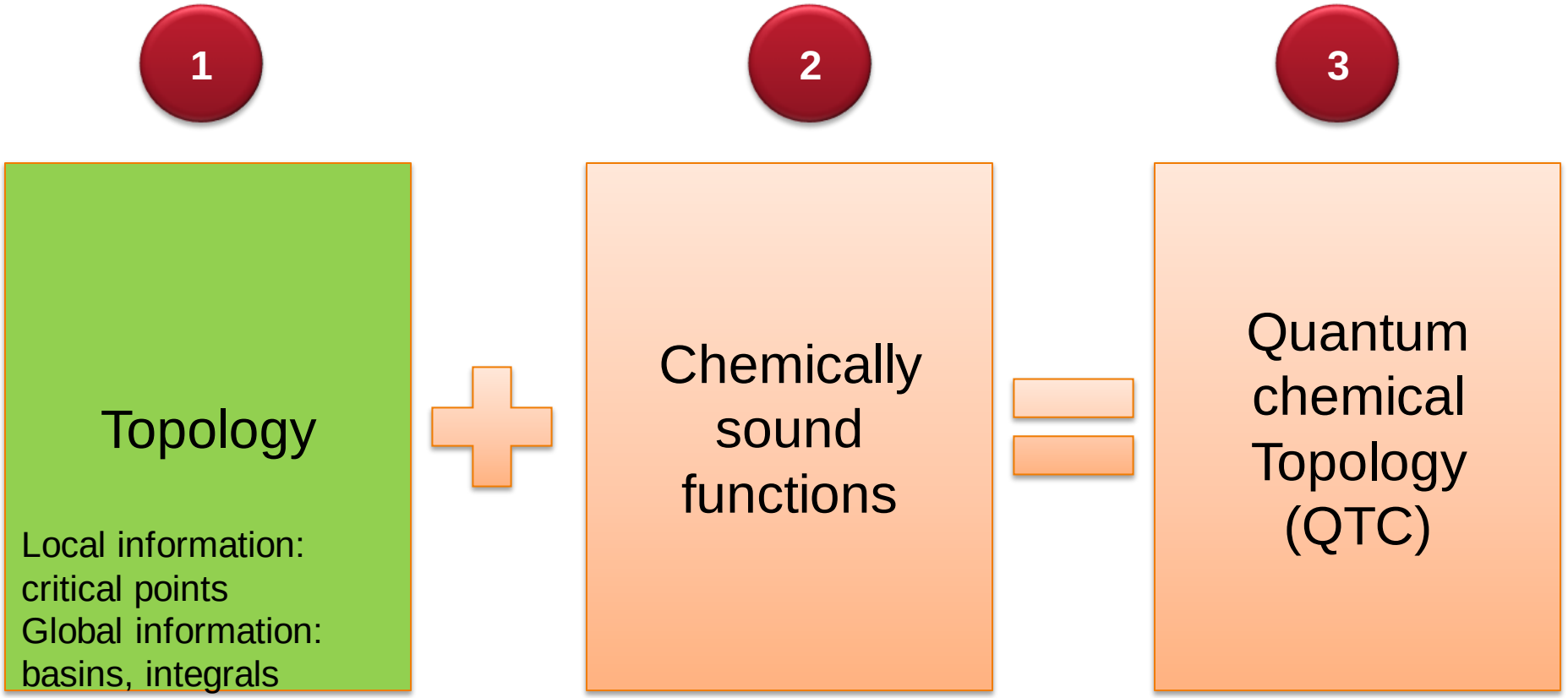
Classical Chemistry ⟷ 3D ⟶ **Quantum chemistry**



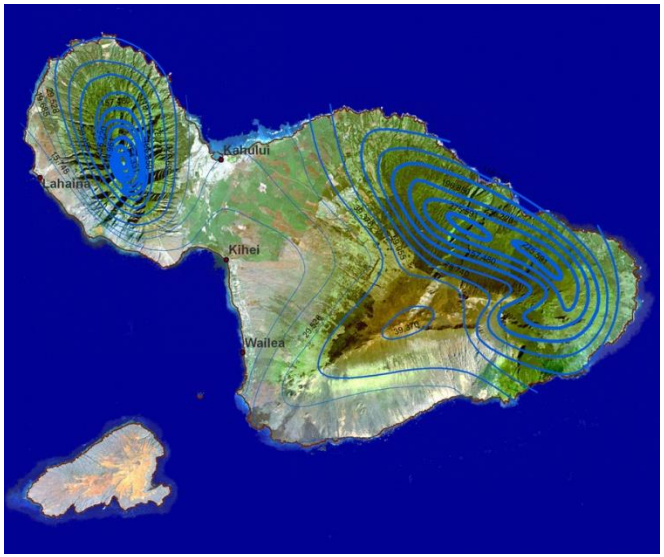
QCT in a nutshell



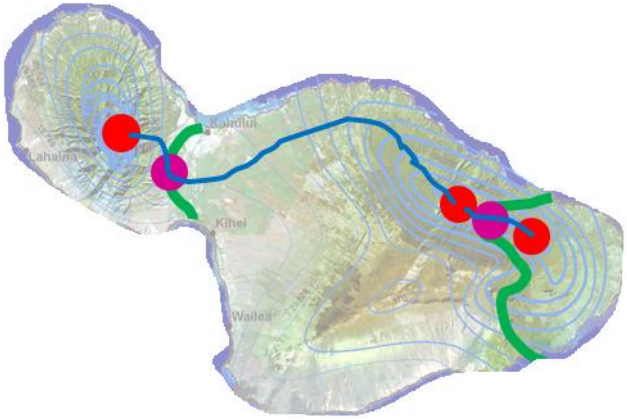
QCT in a nutshell



Topological partitions are intuitive



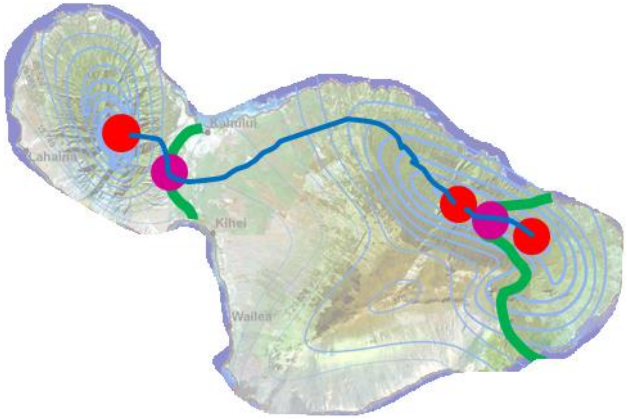
Topological partitions are intuitive



We automatically

- Identify cusps

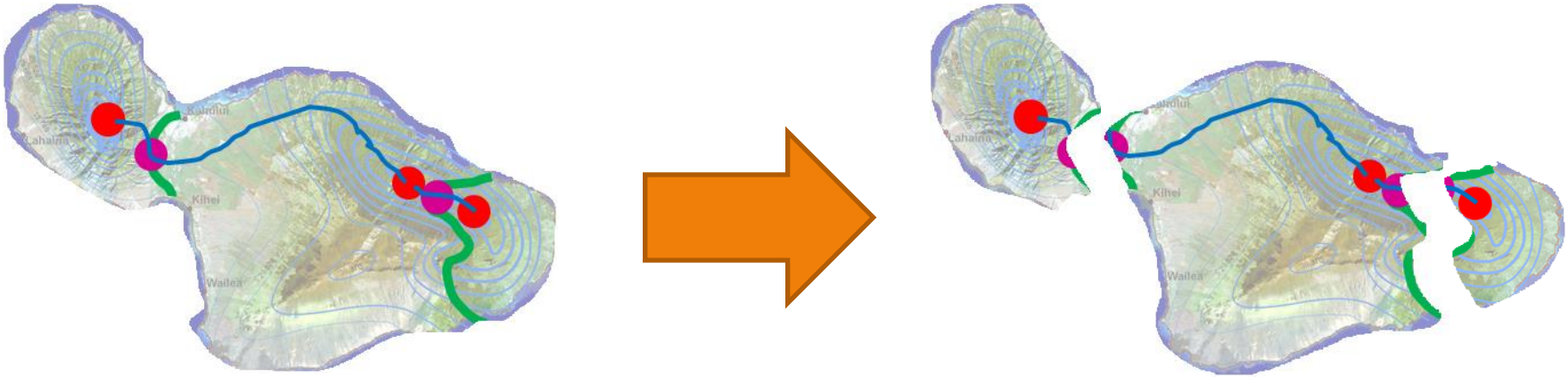
Topological partitions are intuitive



We automatically

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

Topological partitions are intuitive



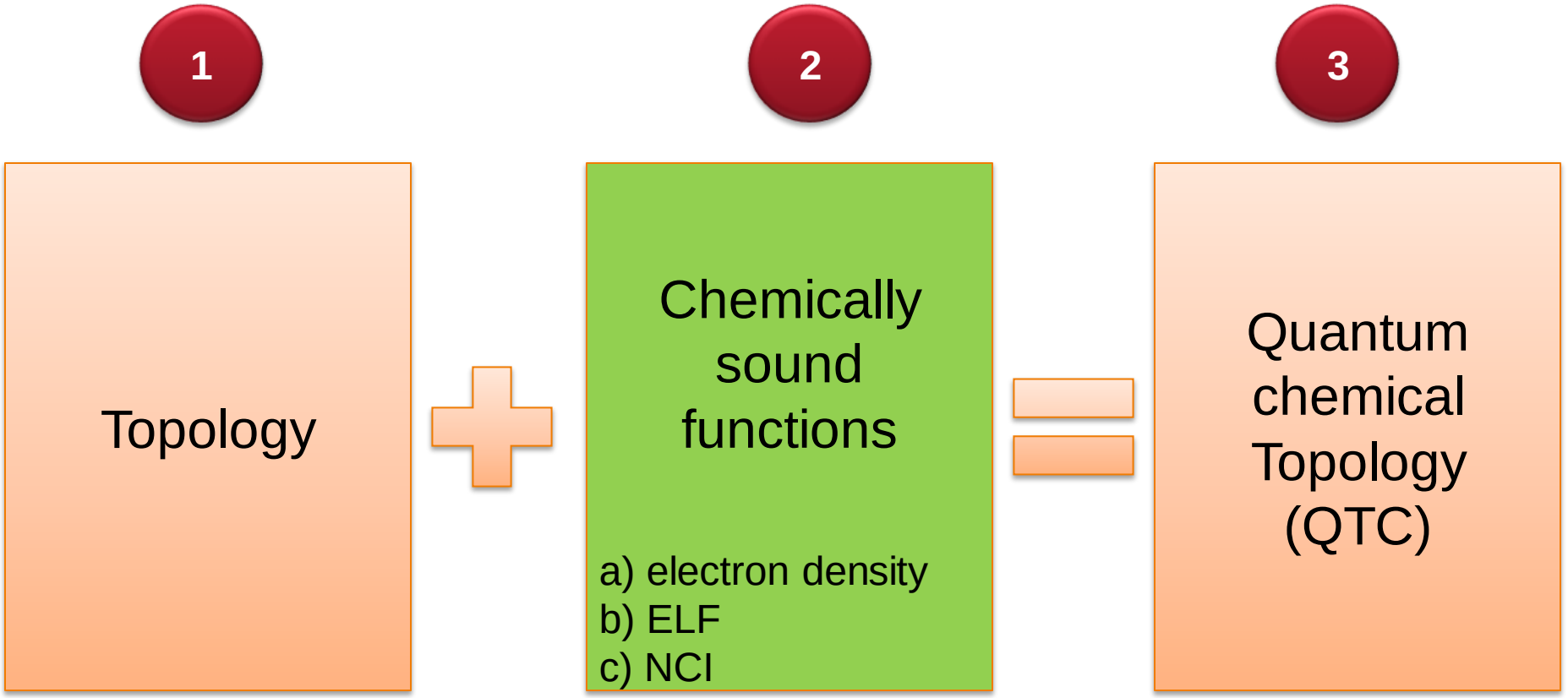
We automatically

- 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



Outline

1. Why studying chemical bonds?

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The electron density

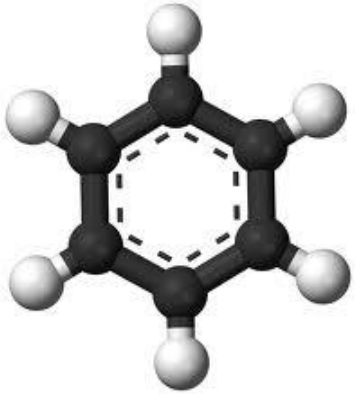
• ρ(r) is a fundamental property of any electronic system

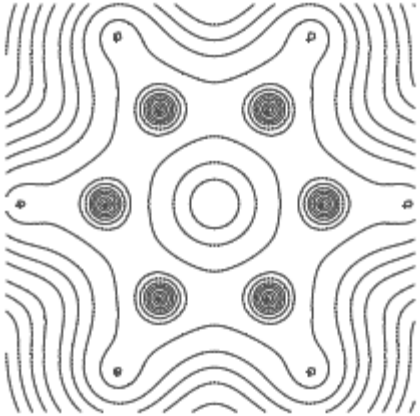
$$\rho(\vec{r}) = N \int \ldots \int \left|\Psi(\vec{x}_1, \vec{x}_2, \ldots, \vec{x}_N)\right|^2 ds\, d\vec{x}_2 \ldots \vec{x}_N$$

- 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

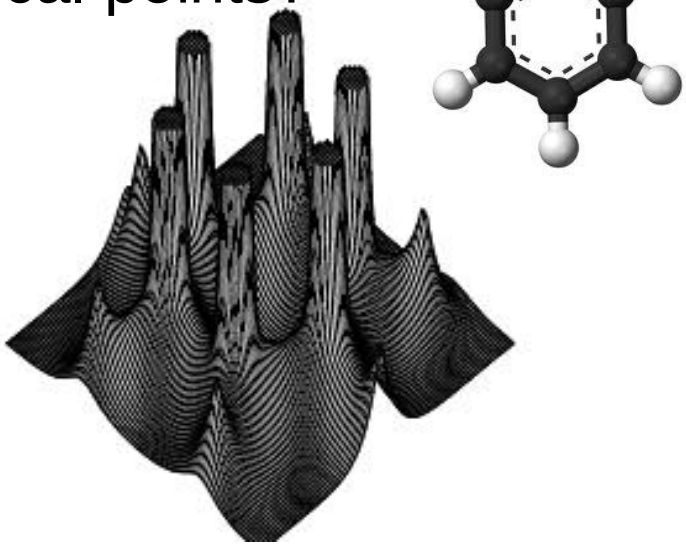


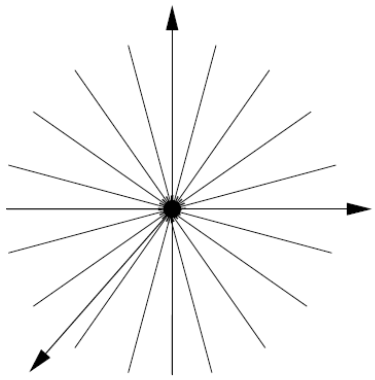


Example: the electron density

Where are the critical points?

- Maxima = nuclei

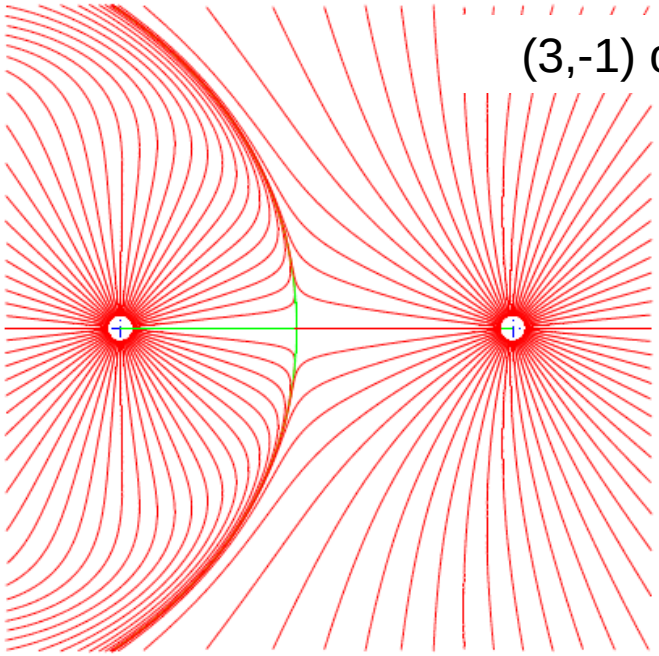


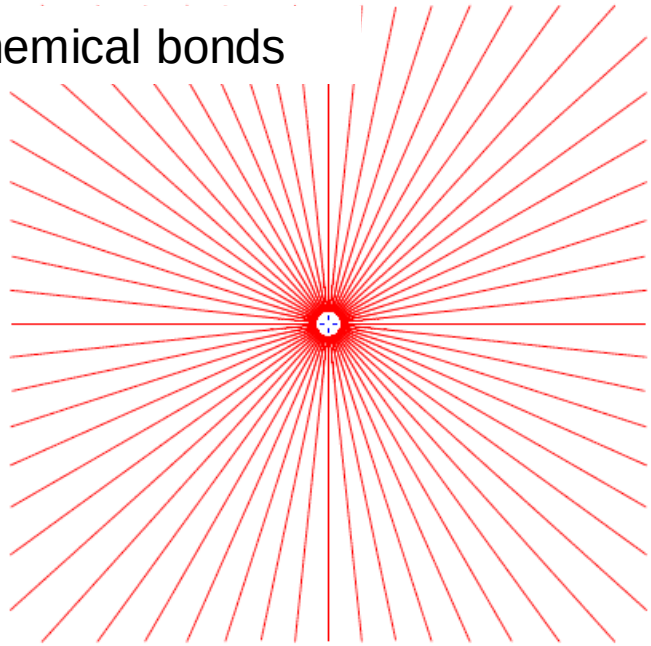


(a) Sumidero de líneas de campo.

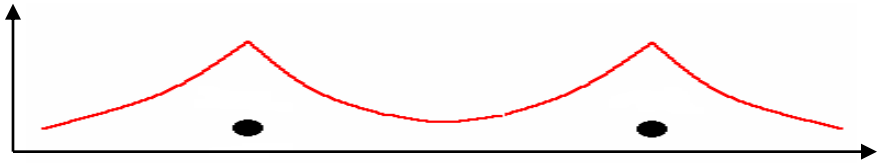
The electron density

(3,-1) occur at chemical bonds

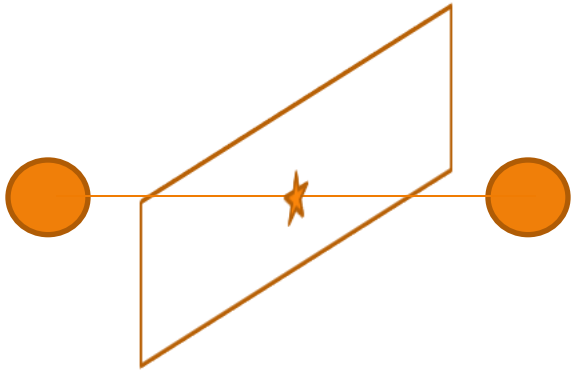




Plane that contains the nuclei

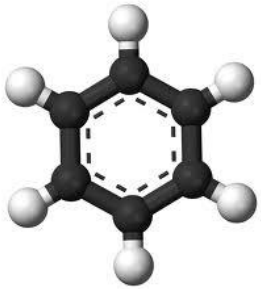


Plane perpendicular to the internuclear line at the critical point that contains the nuclei

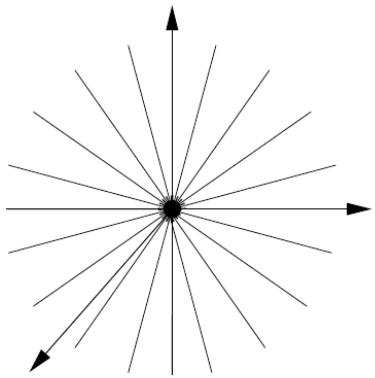


Example: the electron density

Where are the critical points?

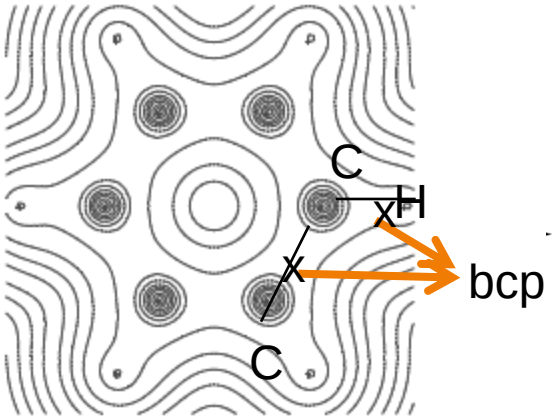


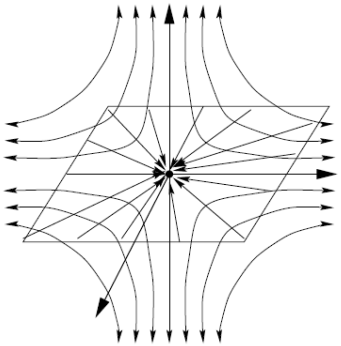
- Maxima = nuclei



(a) Sumidero de líneas de campo.

- 1st order saddle points=bonds





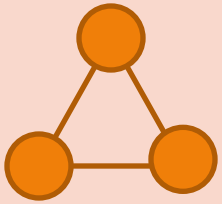
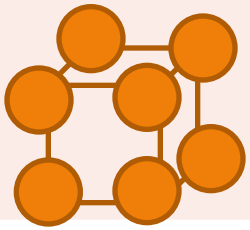
(b) Silla tipo 1.

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:

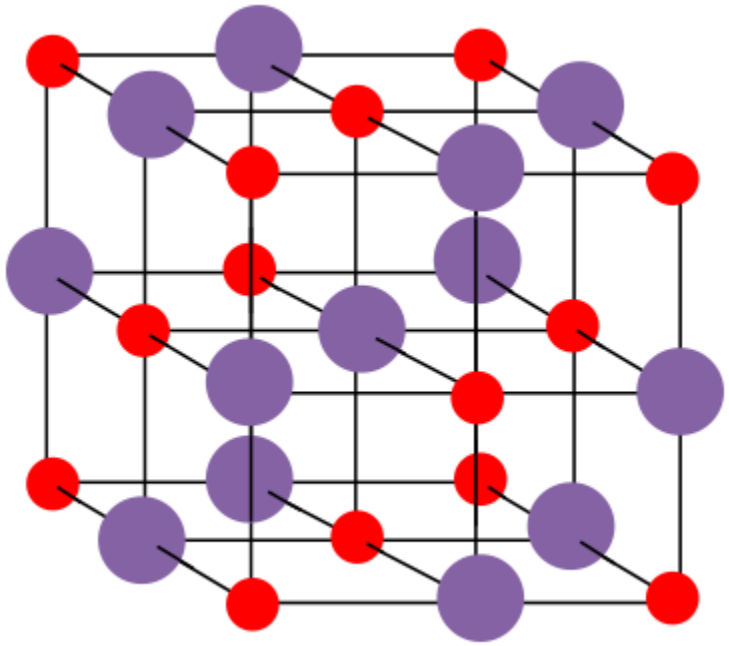
$$n_{(3,-3)}-n_{(3,-1)}+n_{(3,+1)}-n_{(3,+3)}=0$$

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

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

  E.g. (2,-2)

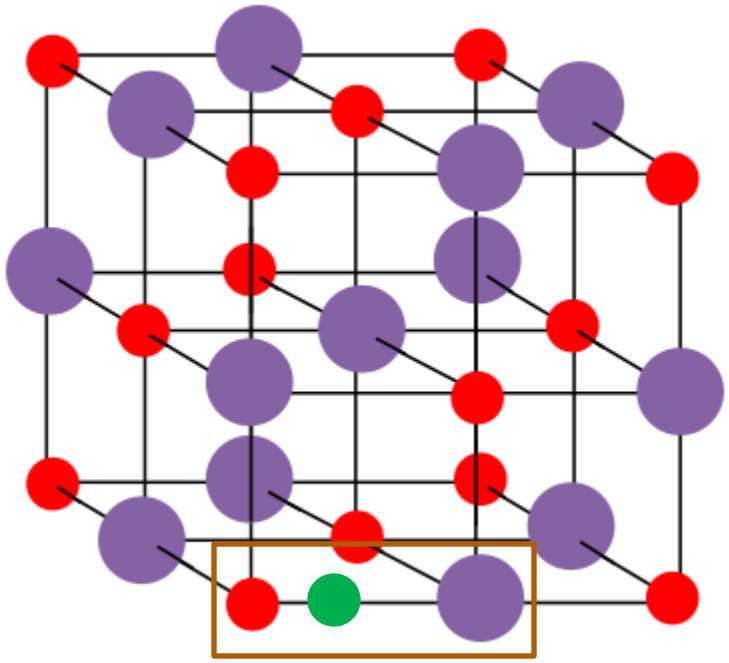
Local information: CPs



- 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

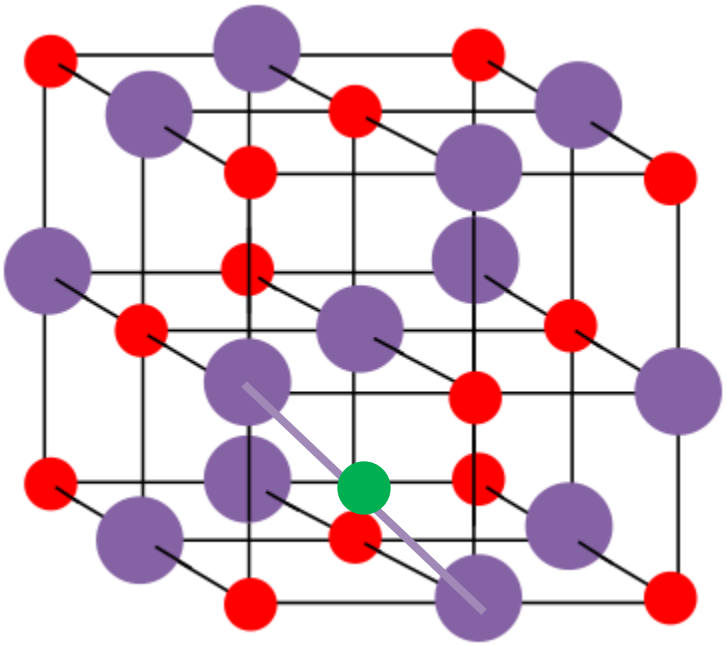
Local information: CPs



- 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

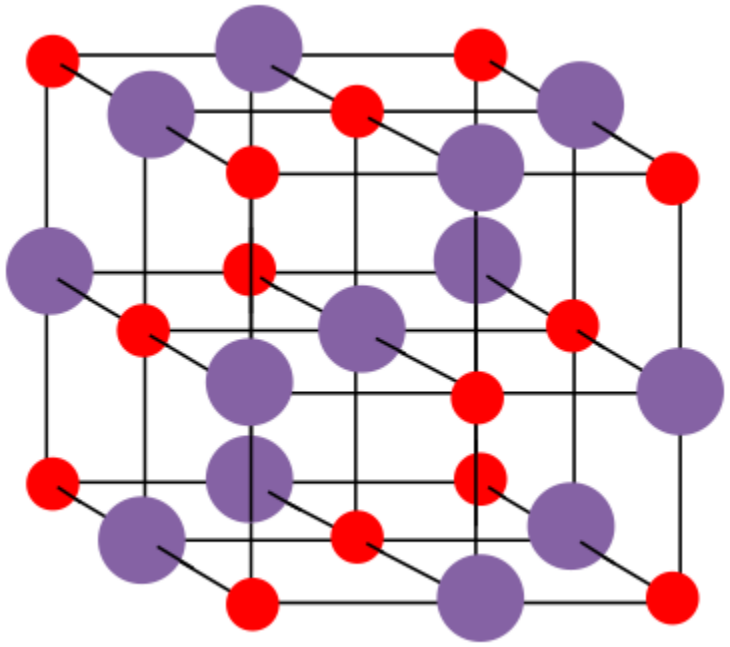


- Attractors are at the nuclei positions
- (3,-1) signal interactions

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

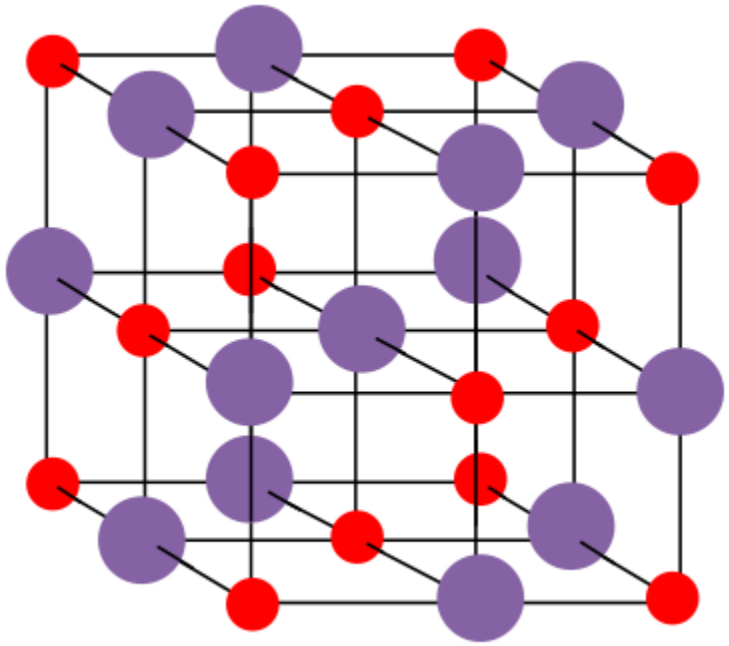
Local information: CPs



- 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

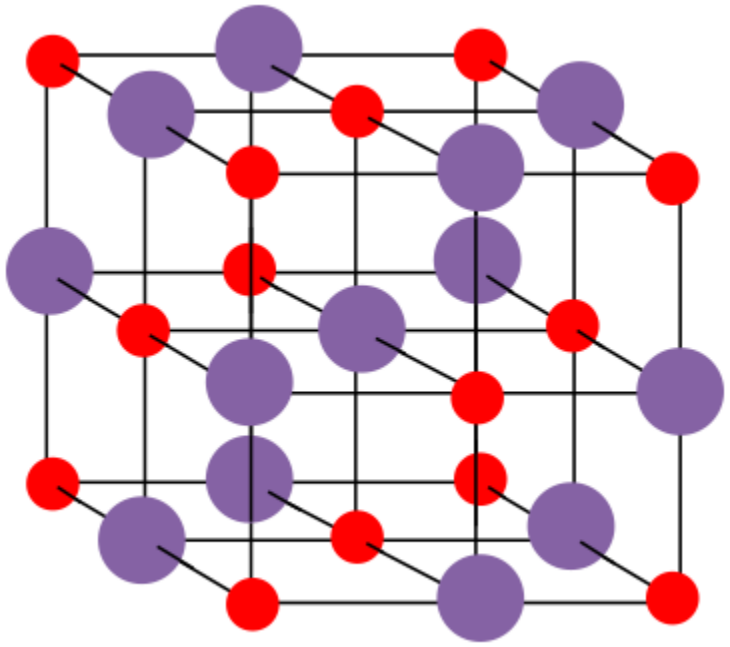


- We have all types of critical points
- Morse sum is working

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



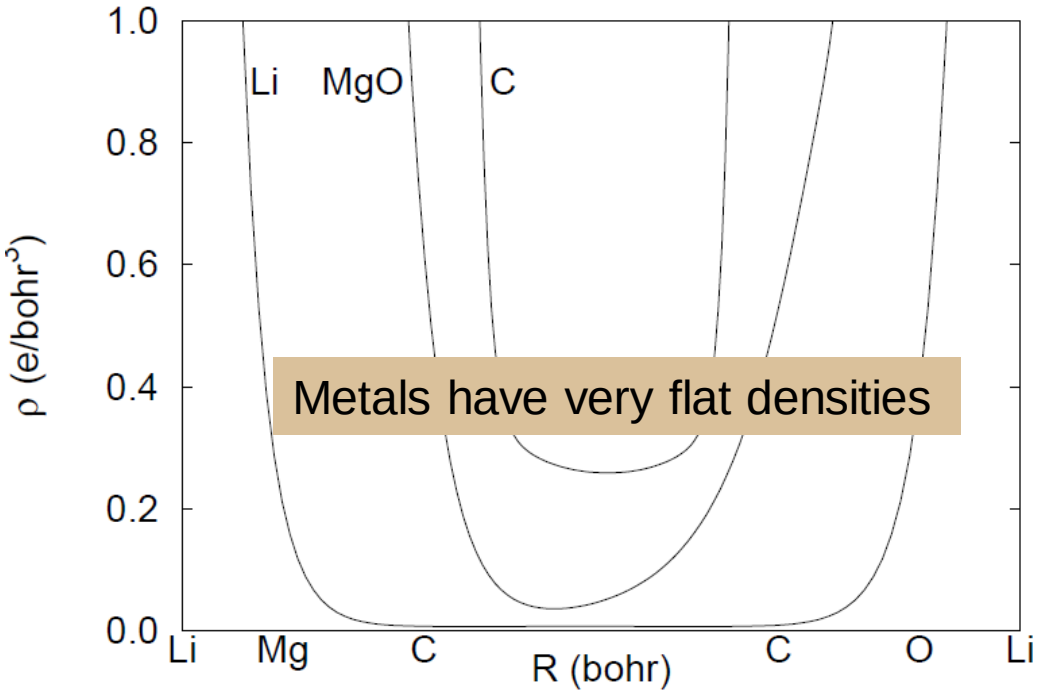
- We have all types of critical points
- Morse sum is working

  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

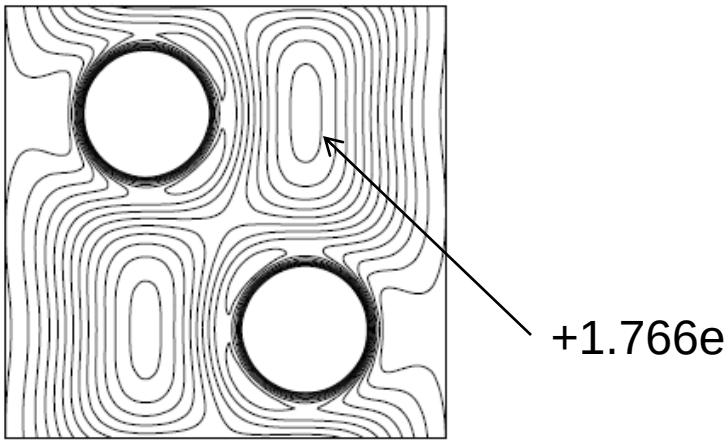
Local information: CPs

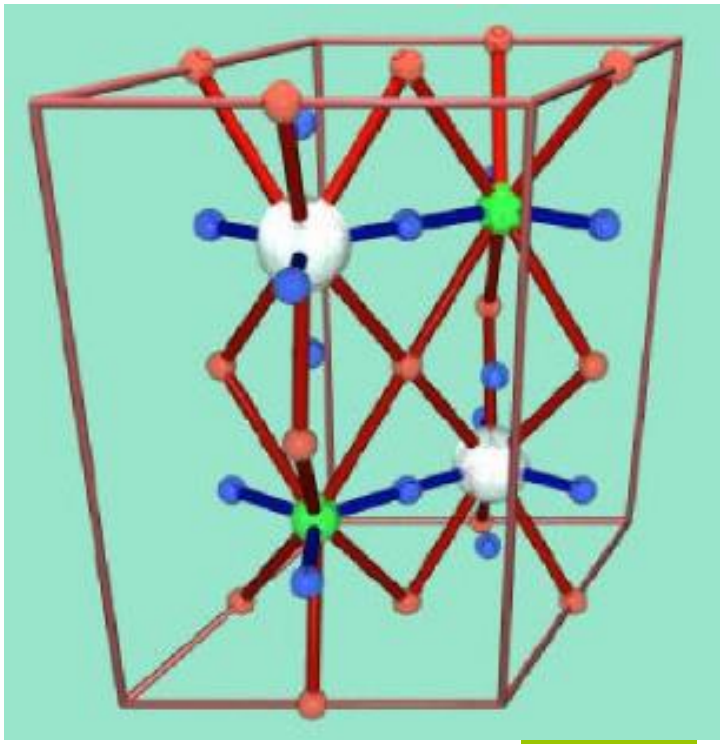


Metals have very flat densities

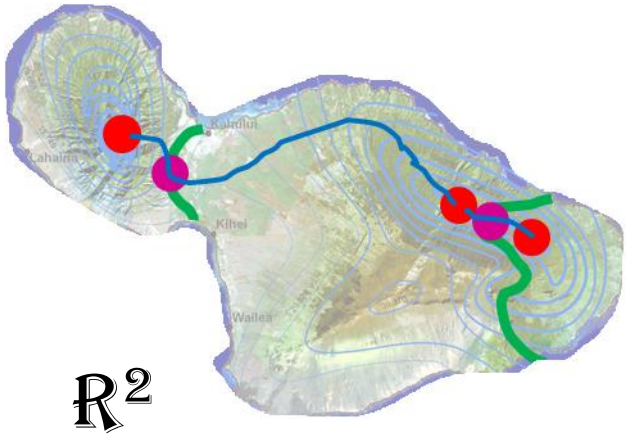
Beriullium HCP

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

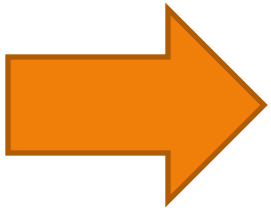


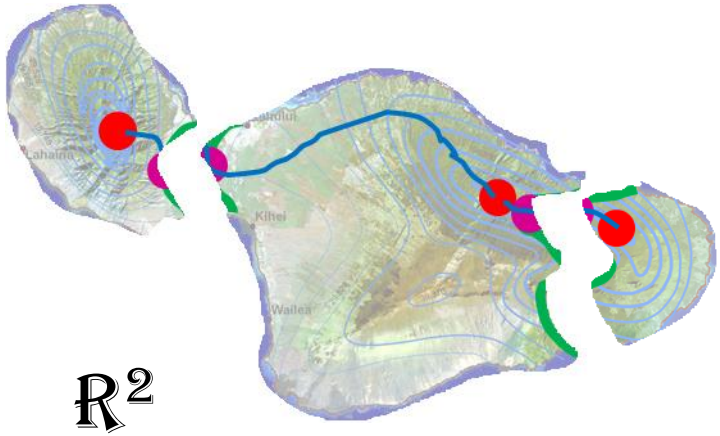


Example: the electron density

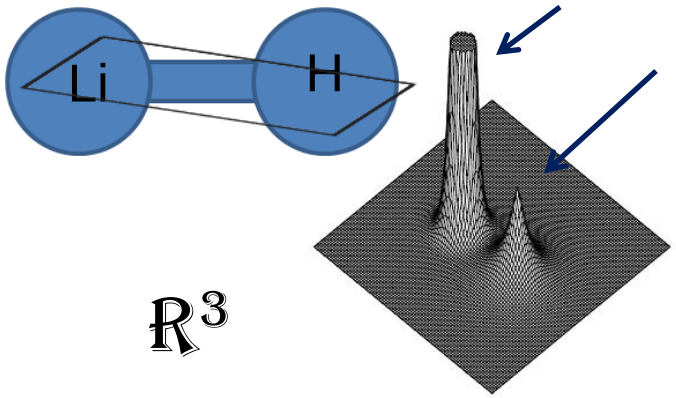


$\mathbb{R}^2$

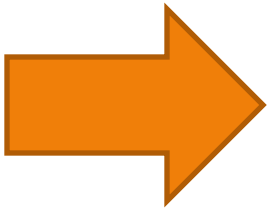


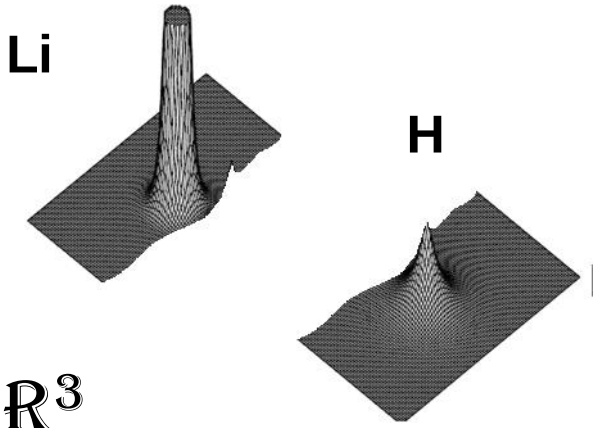


$\mathbb{R}^2$



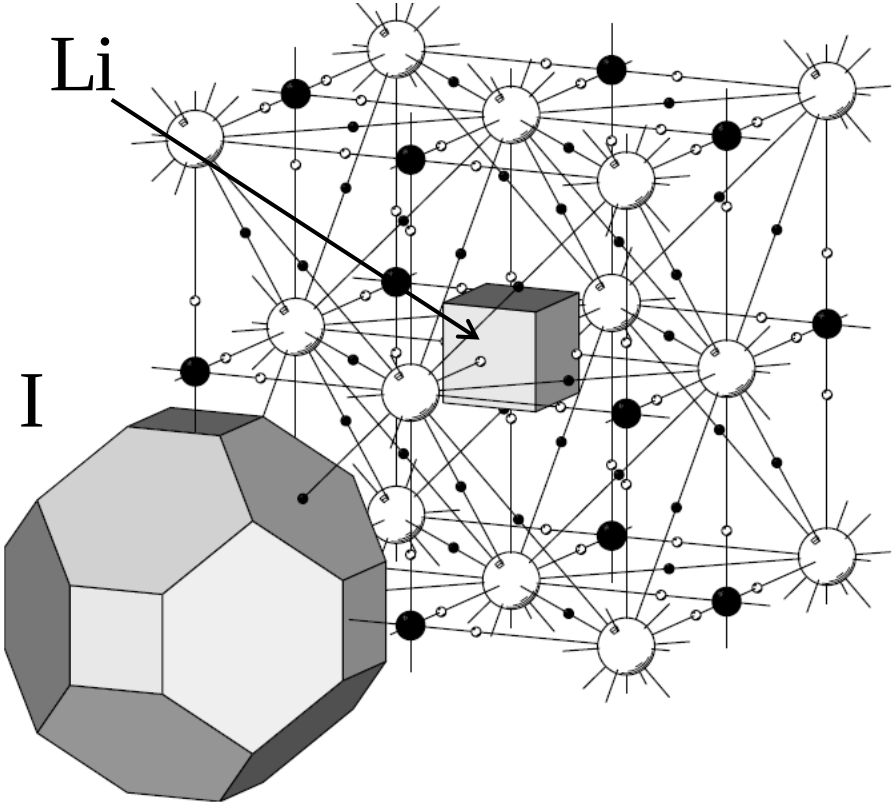
$\mathbb{R}^3$





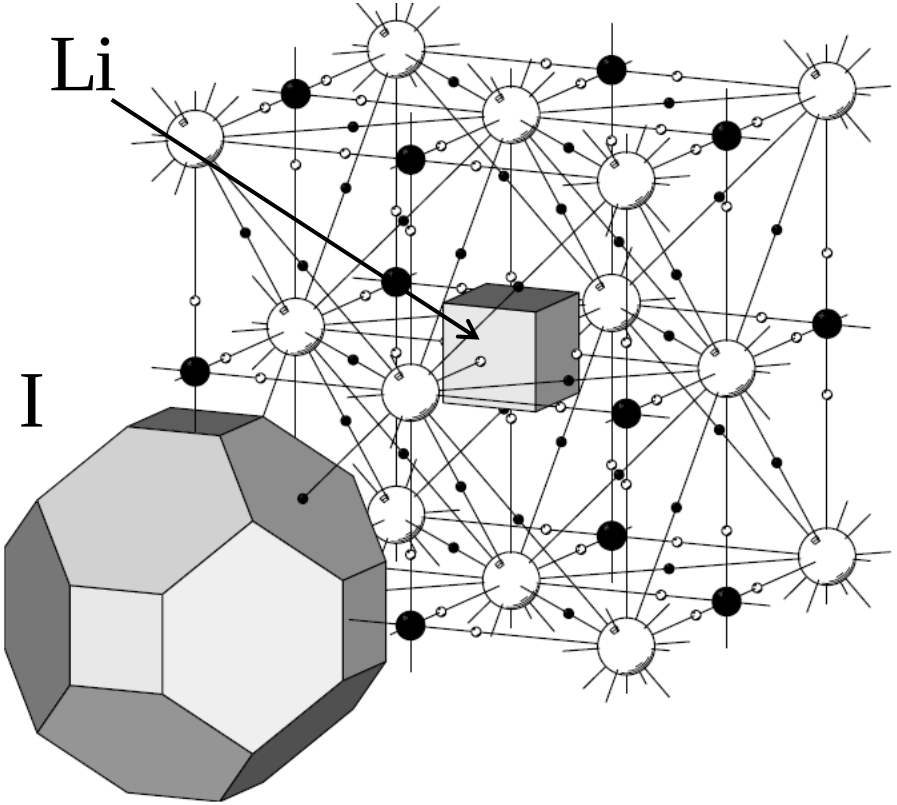
$\mathbb{R}^3$

Old concepts



Contact Polyhedra

Old concepts



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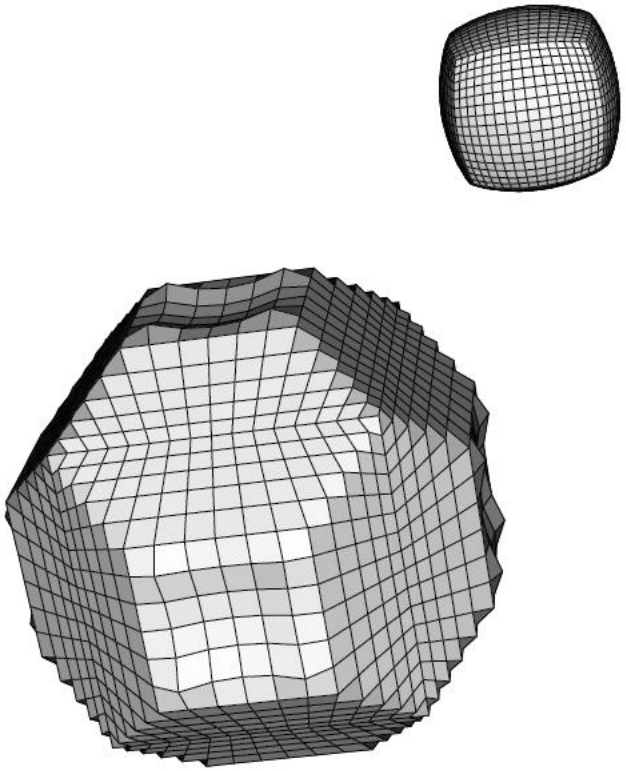
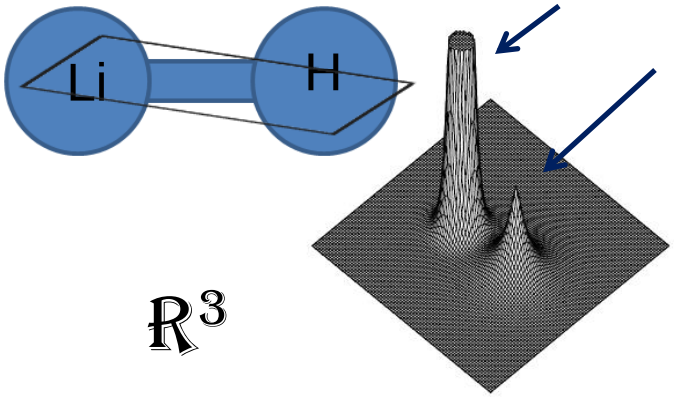
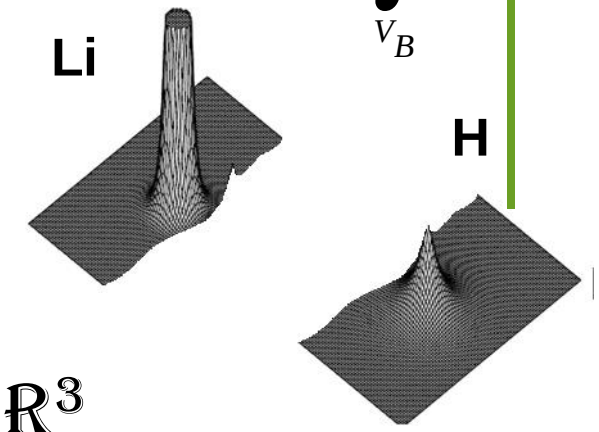


Electron density basins



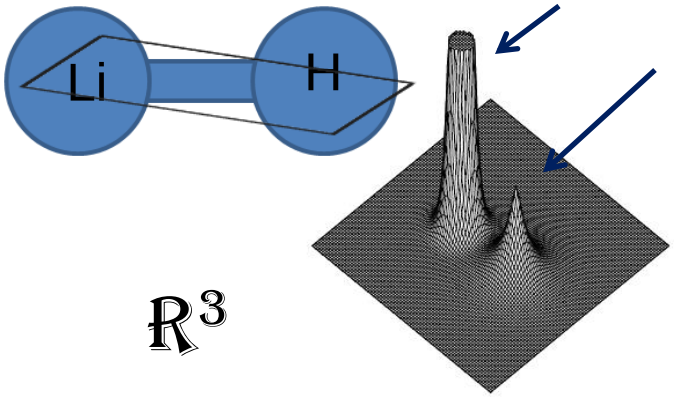
$\mathbb{R}^3$

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



$\mathbb{R}^3$

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



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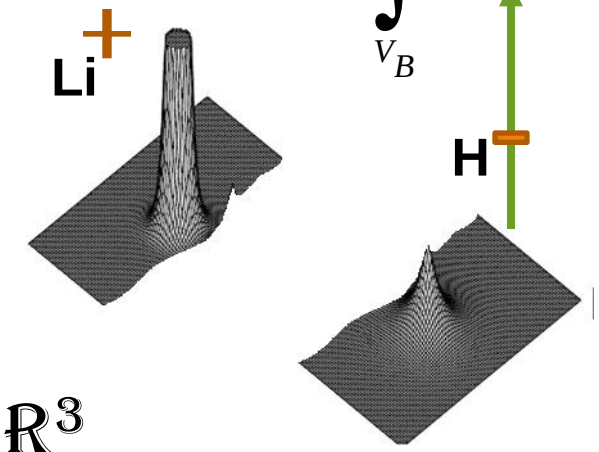
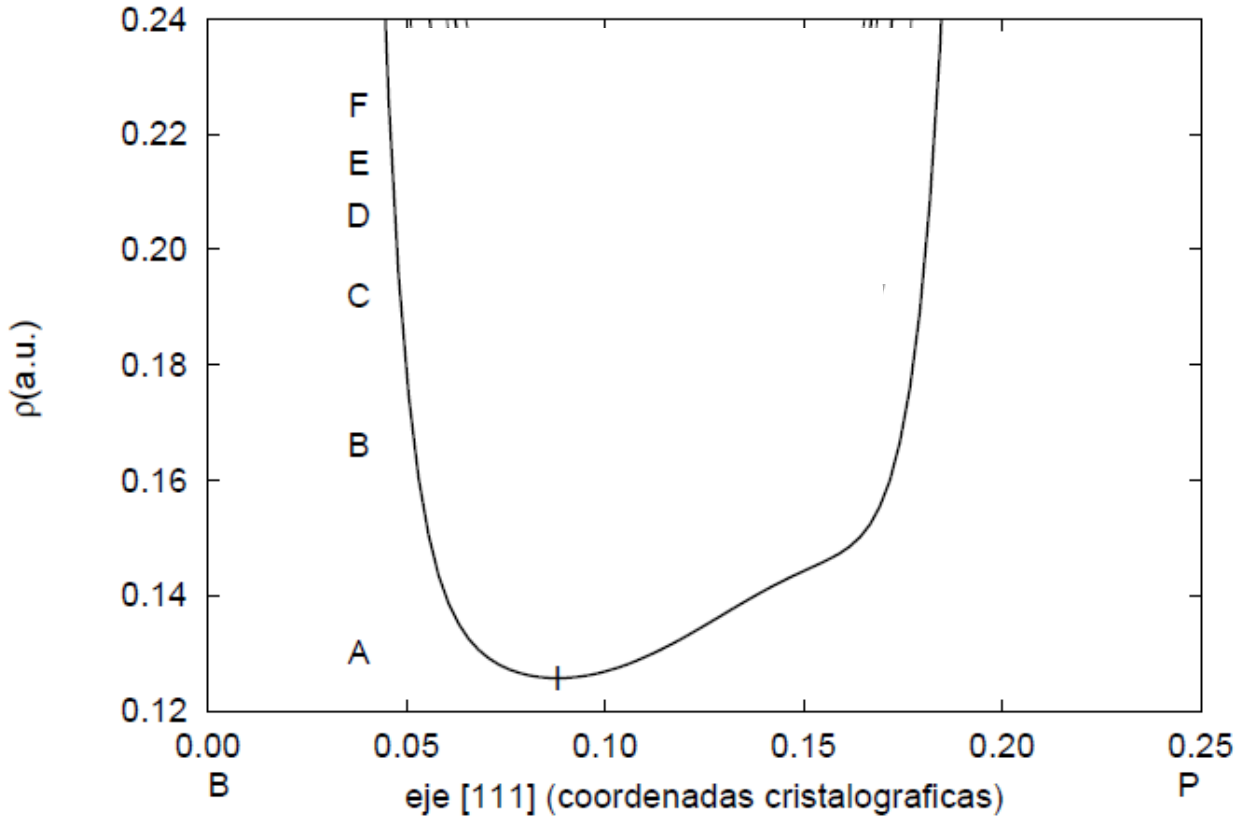


$\mathbb{R}^3$

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

Properties

- BP



Properties

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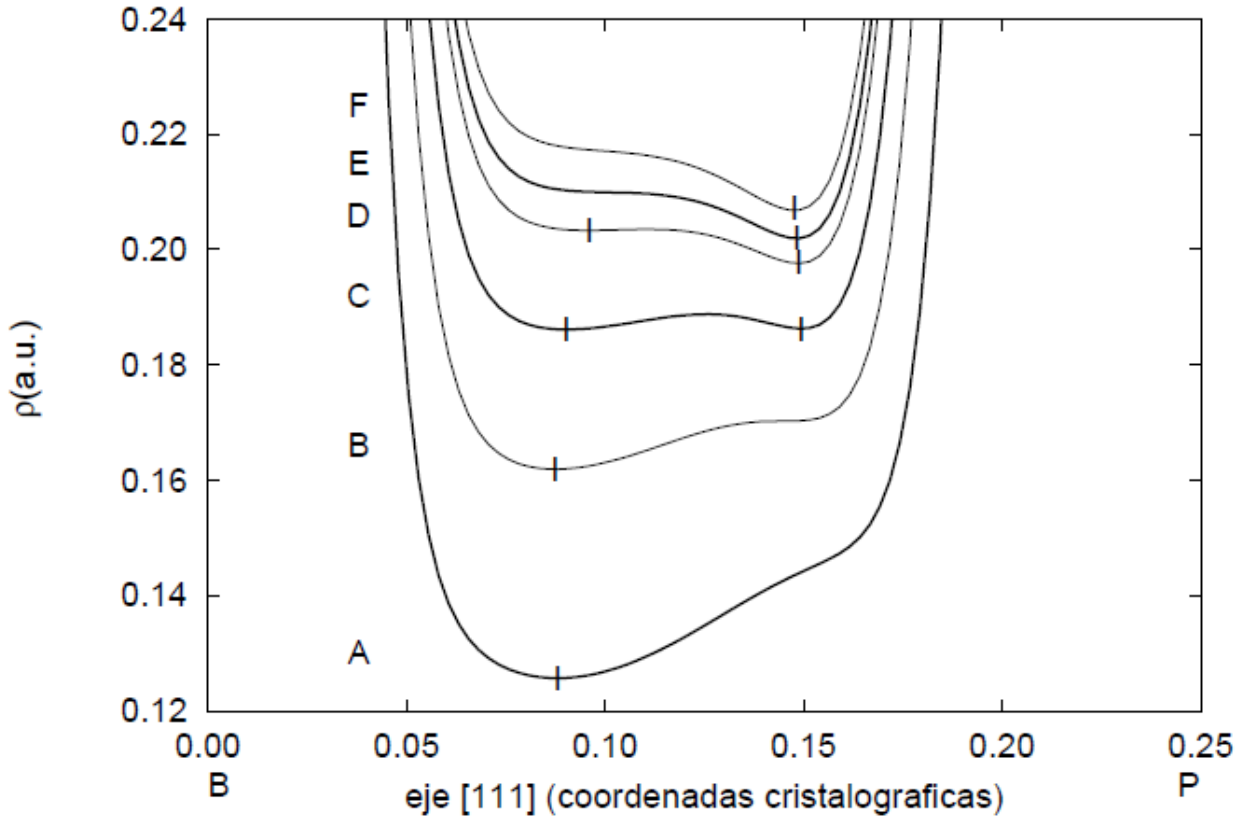

When the crystal is compressed, the electron density is displaced, leading to a change in polarity from $B^{\delta+}P^{\delta-}$ at V_0 to $B^{\delta-}P^{\delta+}$ at $V=0.57V_0$

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. Applications
4. Workout example
5. Summary

The electron localization function

Fermionic information

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

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

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

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

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

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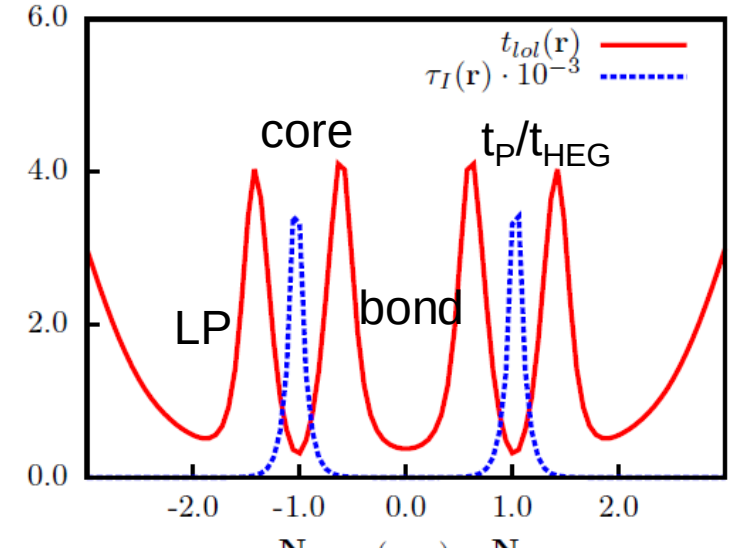
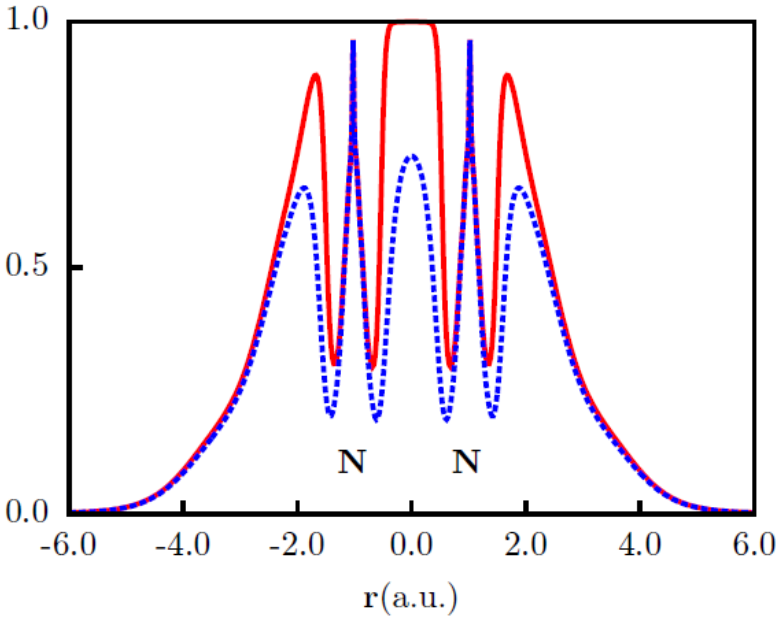
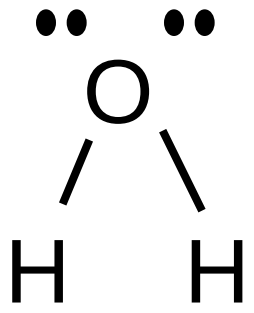




The electron localization function

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



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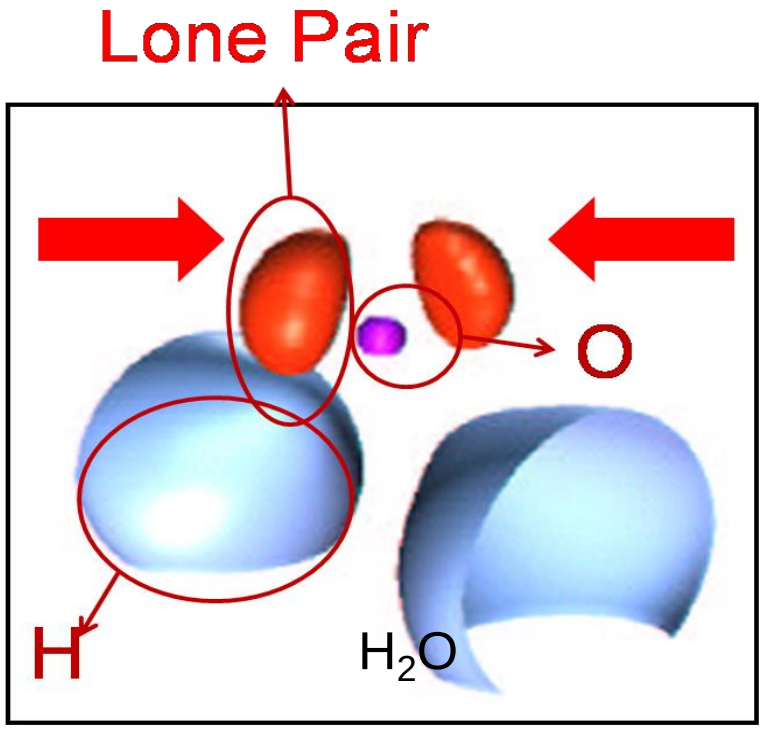

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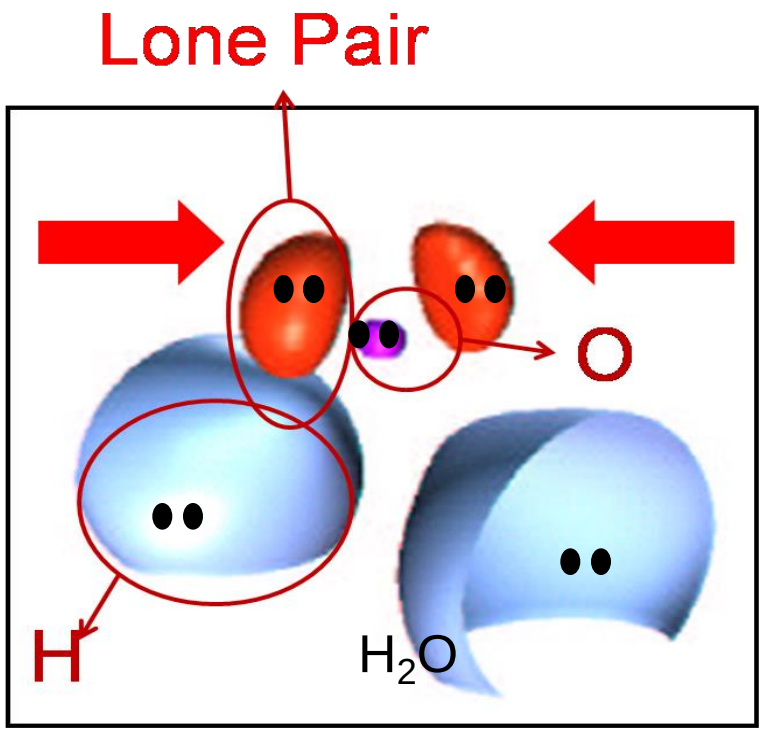

The electron localization function

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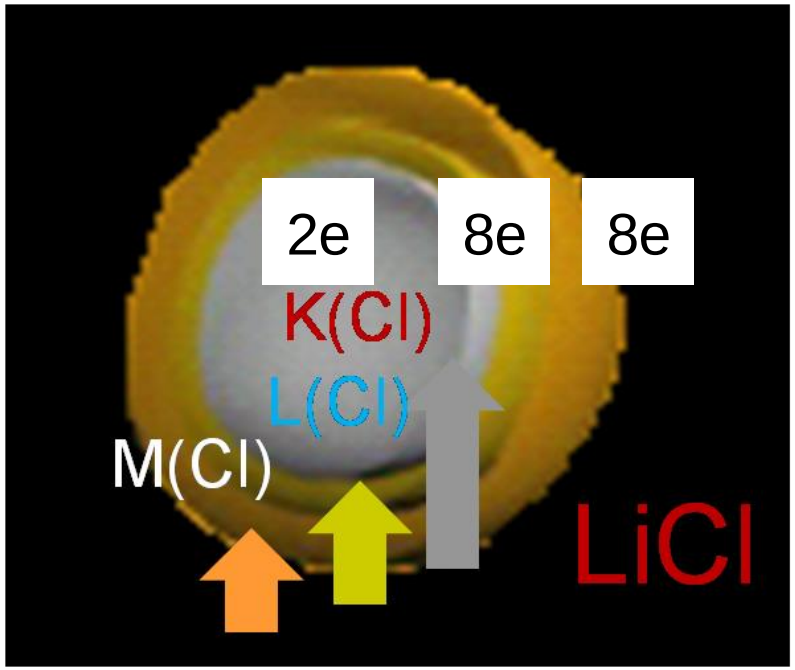
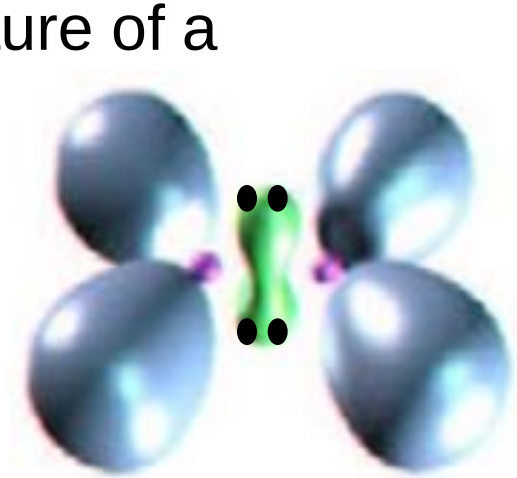
  - Atomic shells



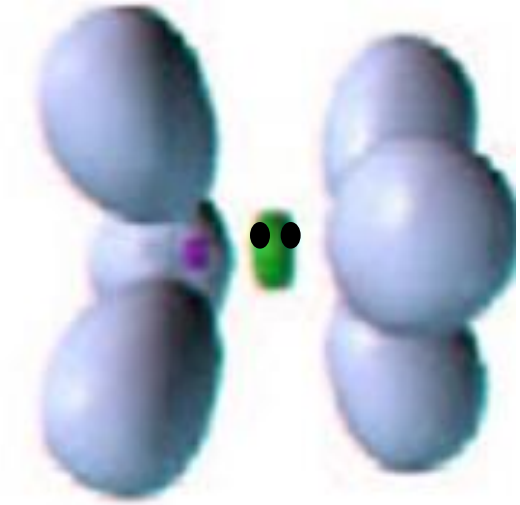
Electron numbers and charge transfer

The electron localization function

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



$H_2C=CH_2$

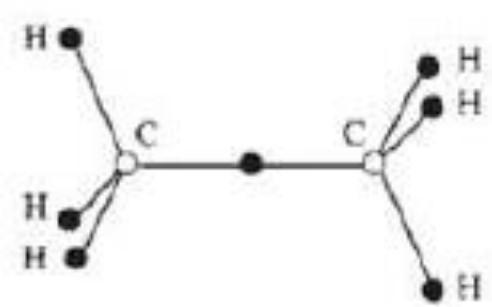


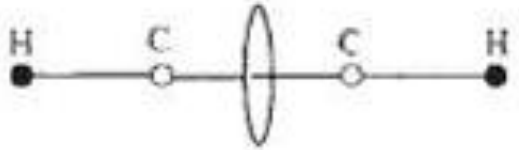
$H_3C\text{-}CH_3$

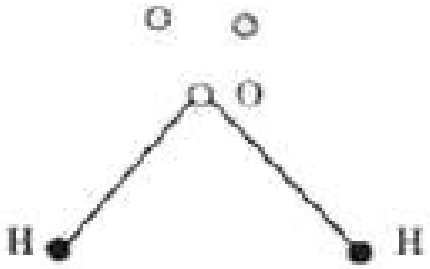
Bond order

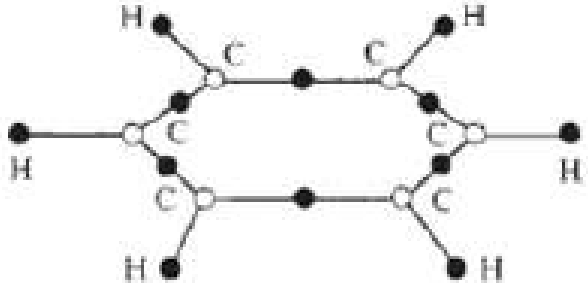
The electron localization function

Critical points



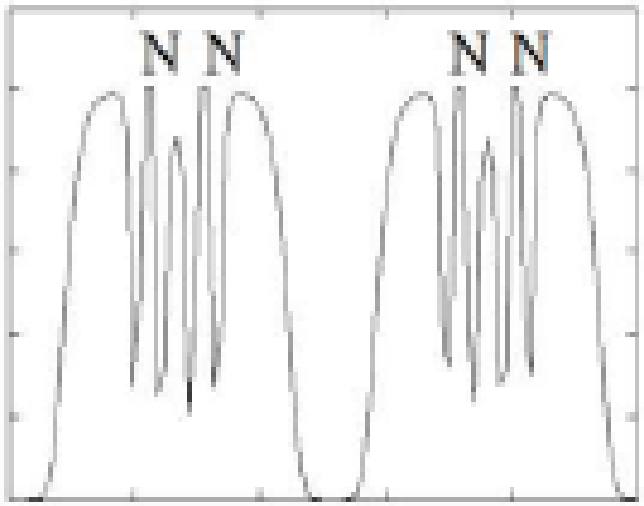


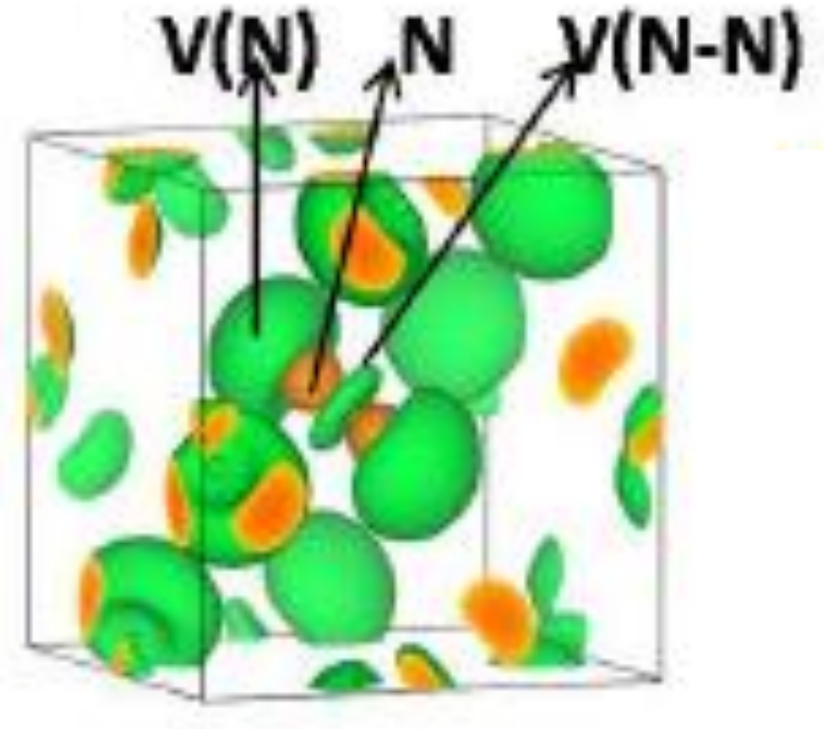




ELF in solids

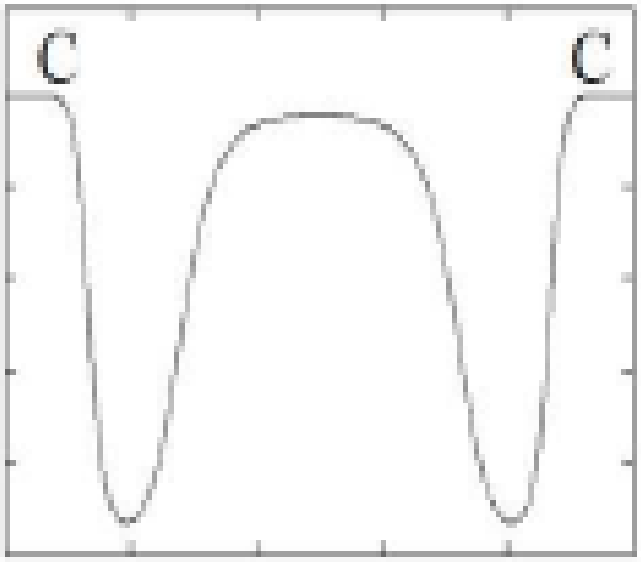
Molecular solids

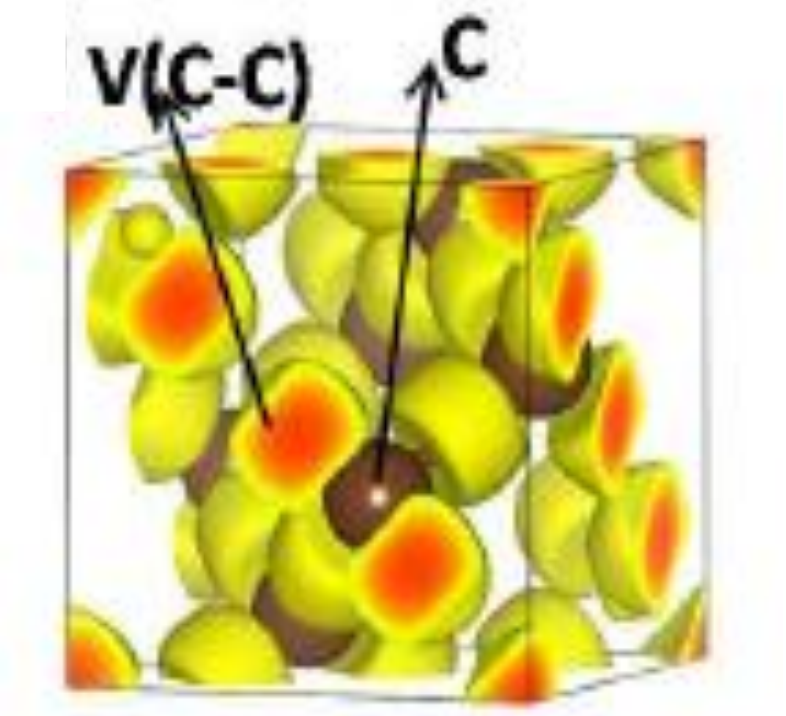




ELF in solids

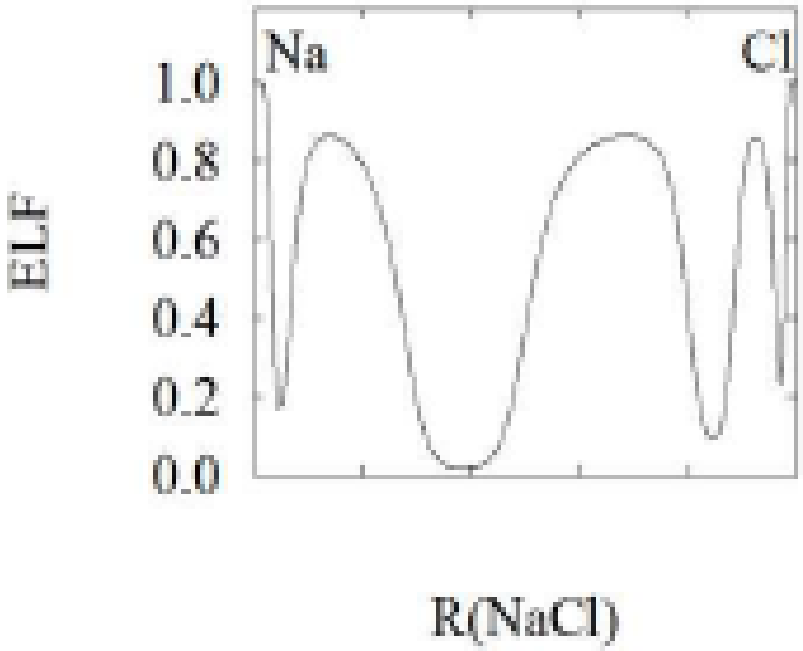
Covalent solids

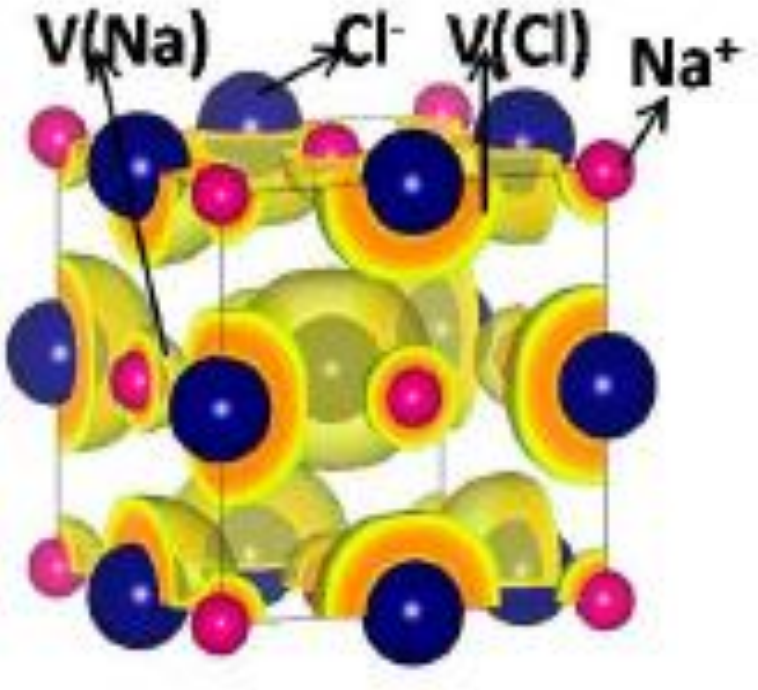




ELF in solids

Ionic solids

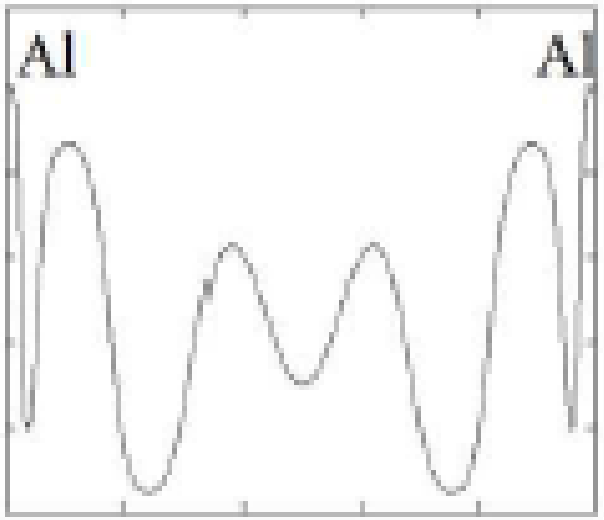




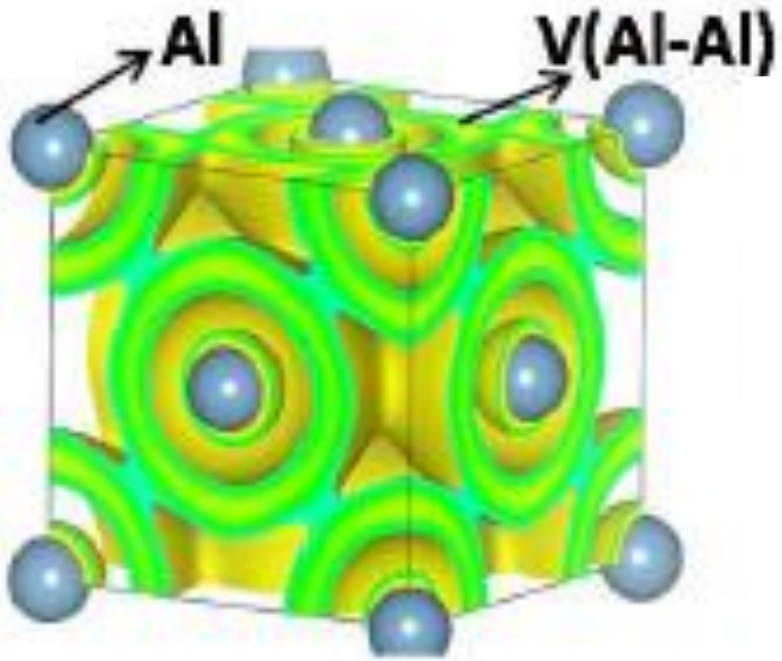
Charge transfer is verified
Na=10 e
Cl=18 e

ELF in solids

Metals

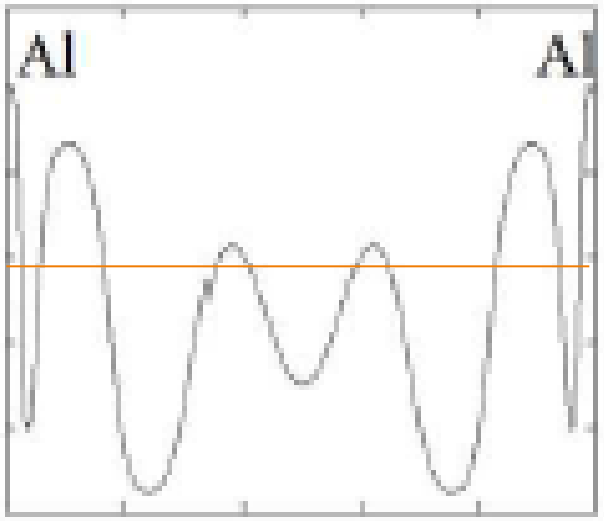


R(Al)



ELF in solids

Metals



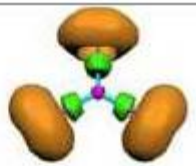
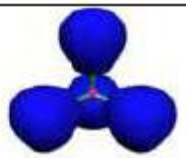
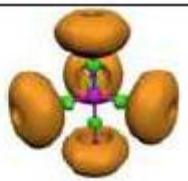
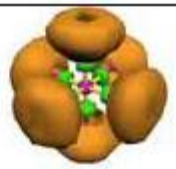
R(Al)

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

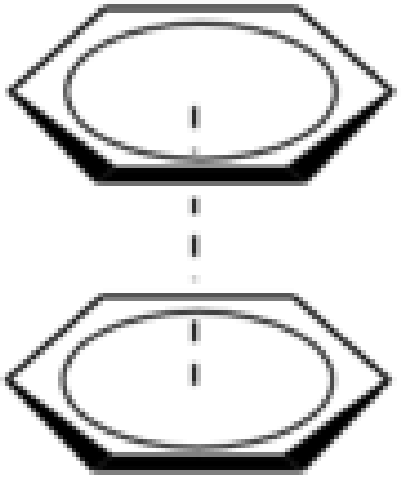
$$t_P(\vec{r}) = t_{HEG}(\vec{r}) \qquad ELF = 0.5$$

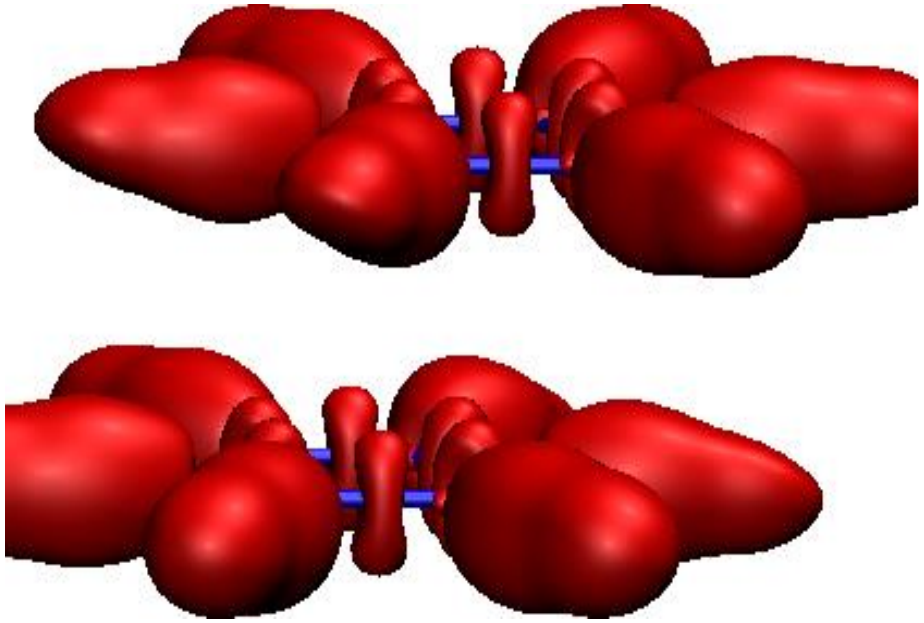
Metallic valence close to HEG

ELF pictures recover VSEPR

ab_2	$BeCl_2$		ab_3e	NH_3
ab_3	BCl_3		ab_2e_3	$XeCl_2$
ab_4	CH_4		ab3e2	ClF_3
ab_5	PCl_5		ab4e	SF_4
ab_6	SCl_6		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
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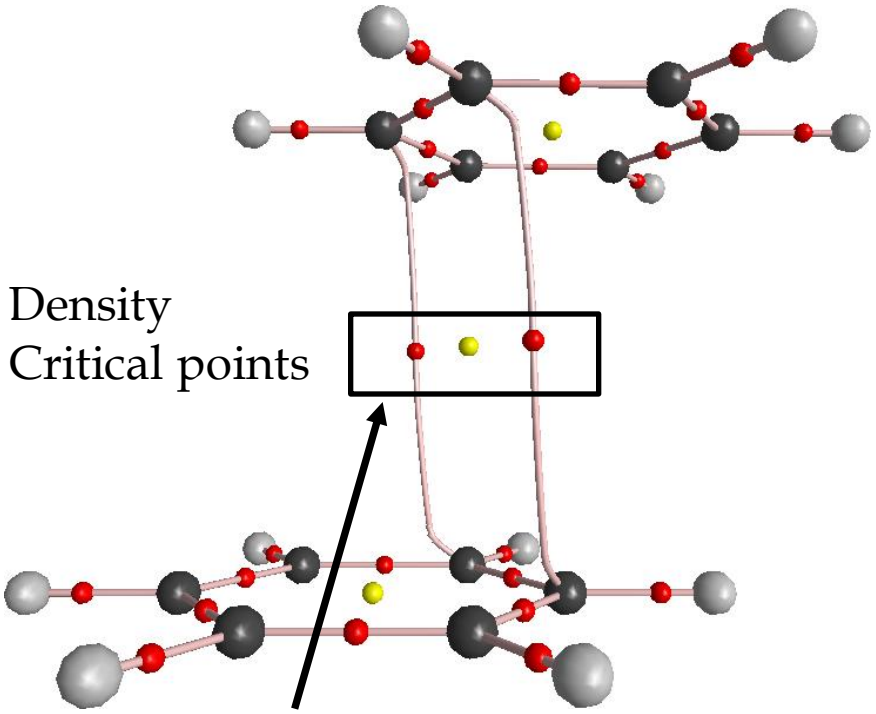
5. Summary

Electron density

The topology of the density alone is not able to provide a satisfactory picture of **weak bonds**

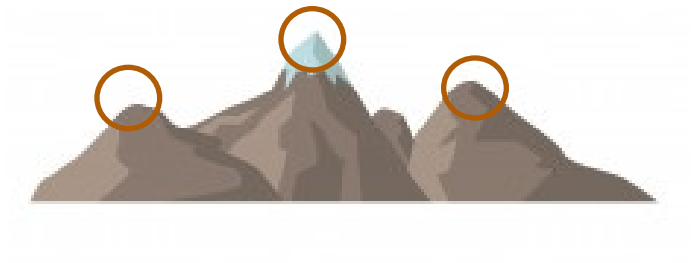


Non-Pair interactions are not well described by critical points

Mathematical description of interactions

Identifying a general shape

Critical point : $\nabla\rho = 0$



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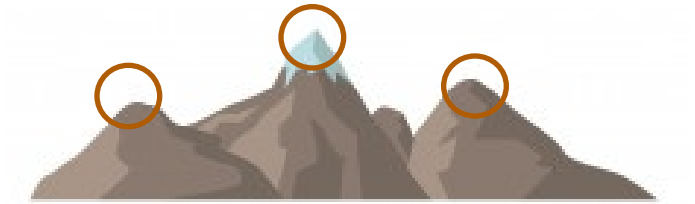
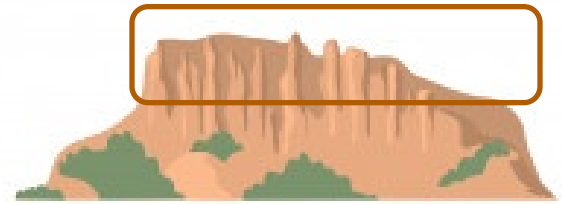


If the profile is flat…

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



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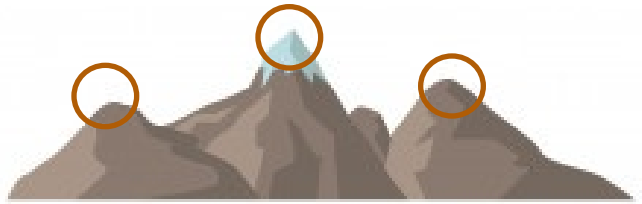

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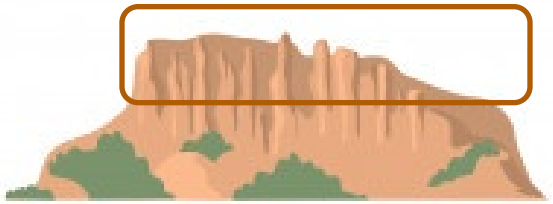
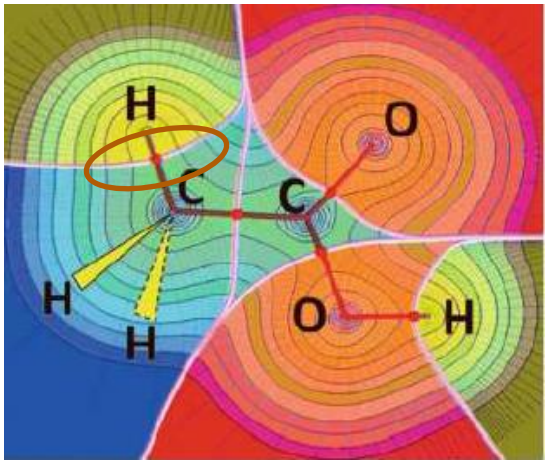


NCI:

analysis of the reduced density gradient at low densities

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



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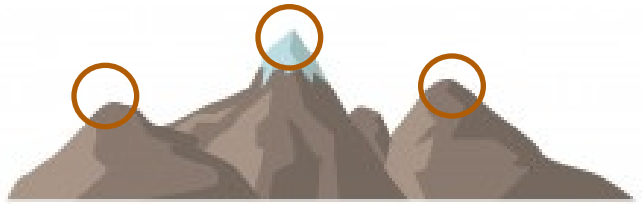

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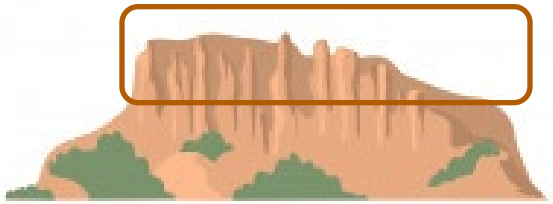

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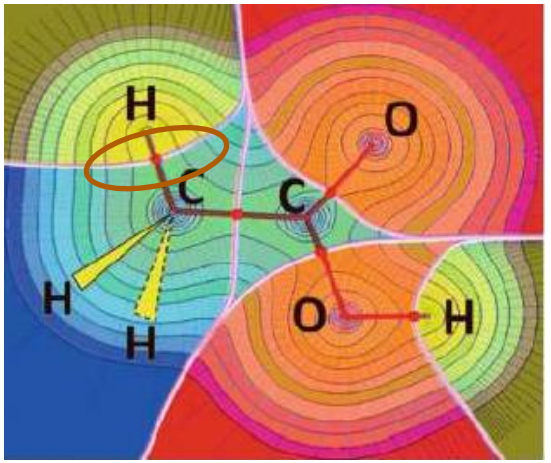
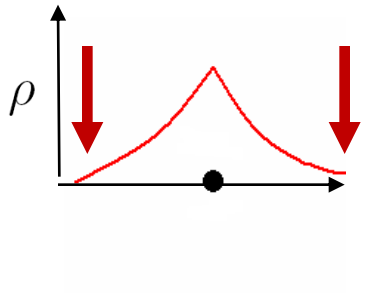


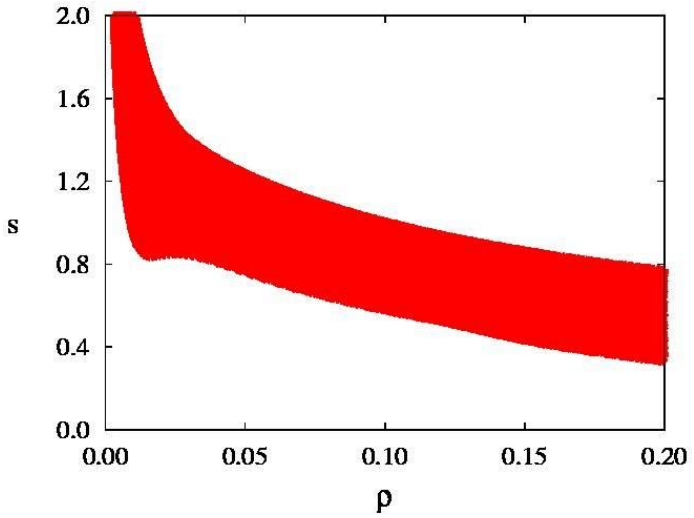
How does it work?

The reduced density gradient

Non-interacting densities

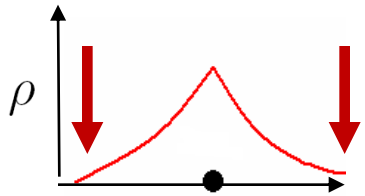


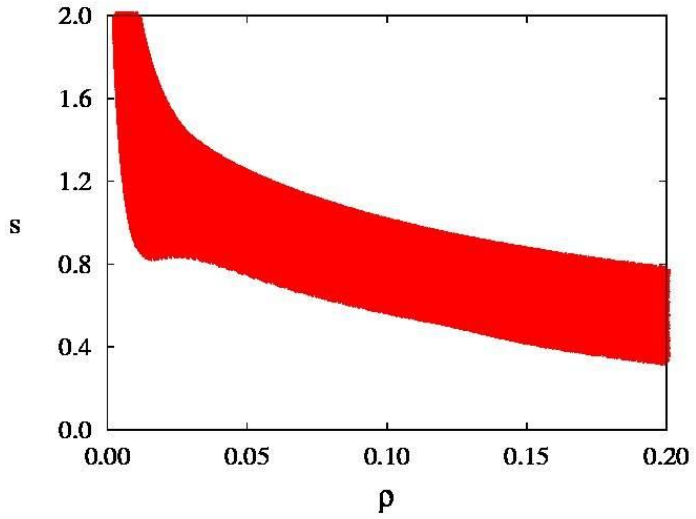
$$s(\rho) \propto \rho^{-1/3} \xrightarrow{\rho \to 0} \infty$$



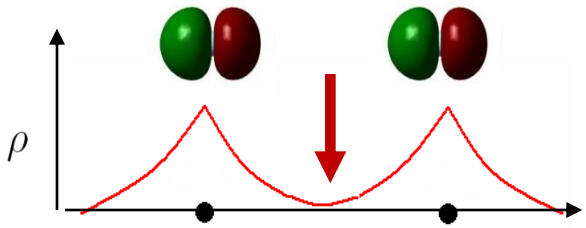
The reduced density gradient

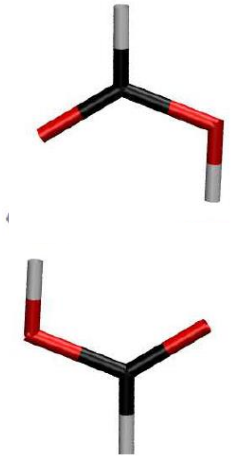
Non-interacting densities

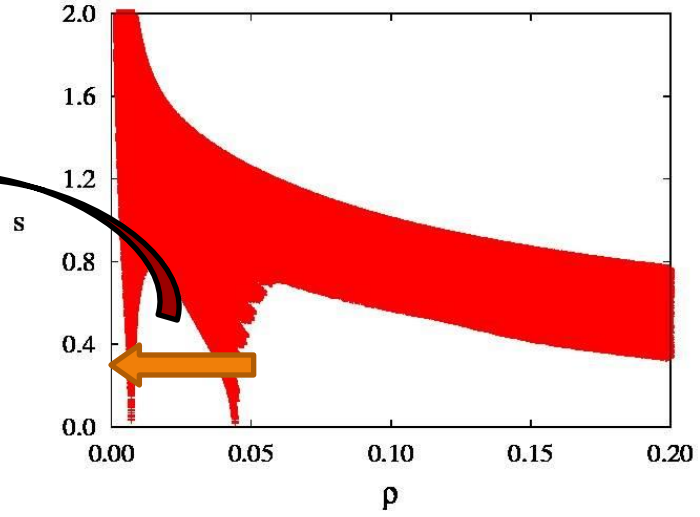




Interacting densities



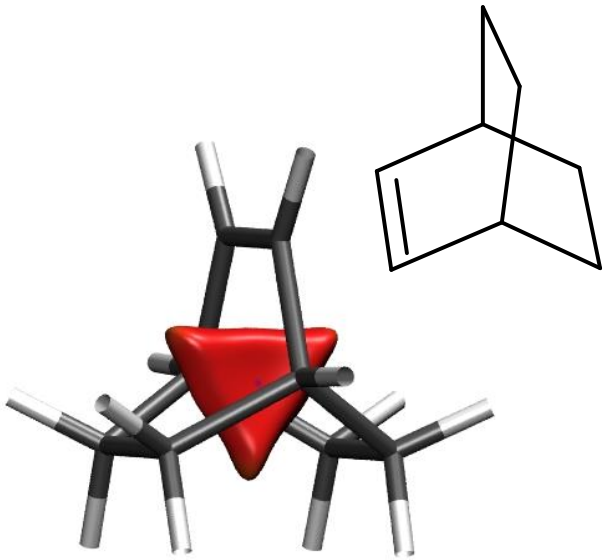


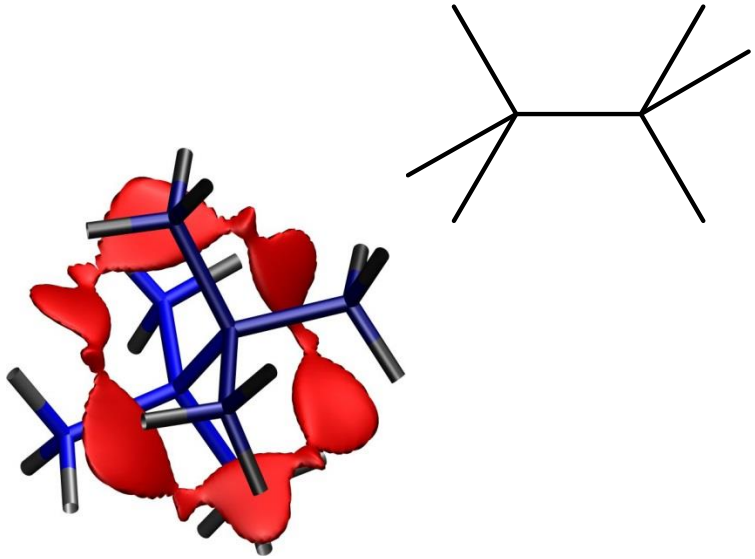


The reduced density gradient

Repulsive interactions

- Steric clashes

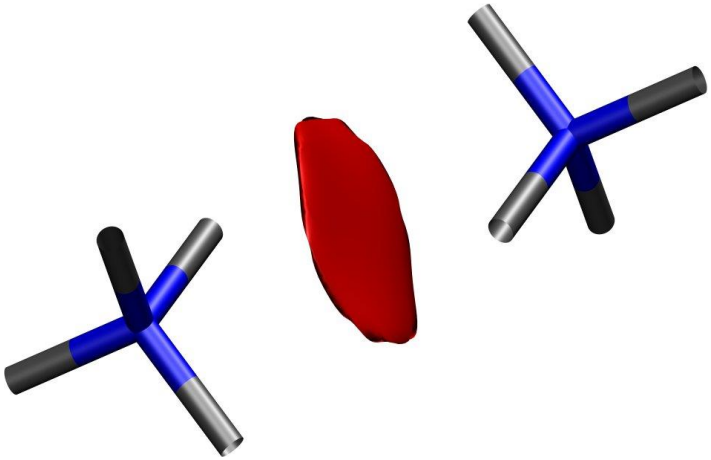




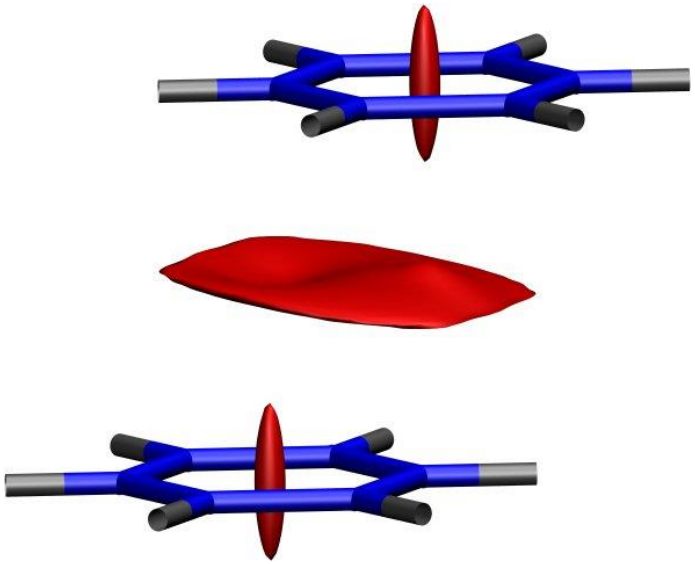
The reduced density gradient

Weak interactions

- Van der Waals



Methane dimer

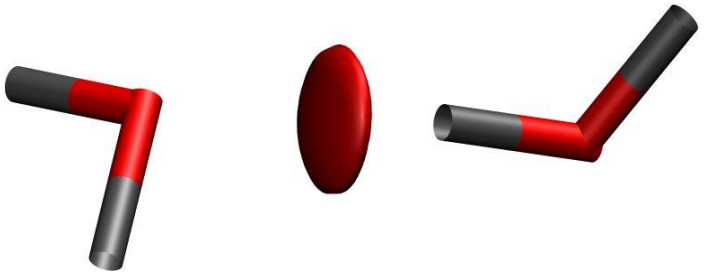


Benzene dimer

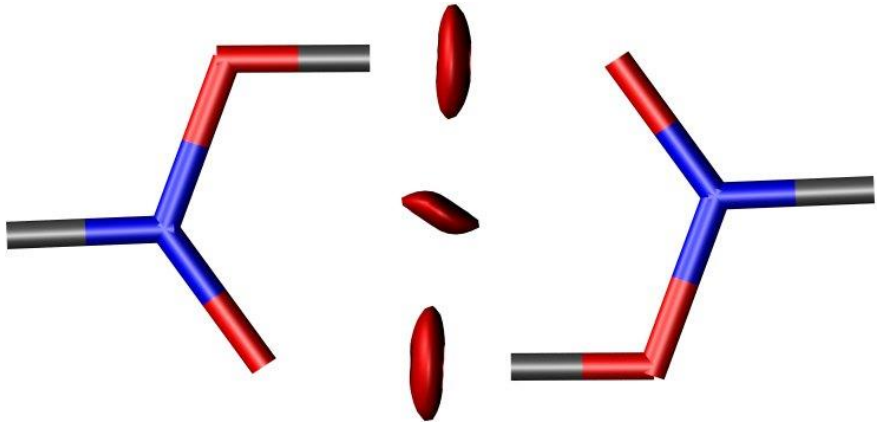
The reduced density gradient

Strongly attractive interactions

- Hydrogen bonds

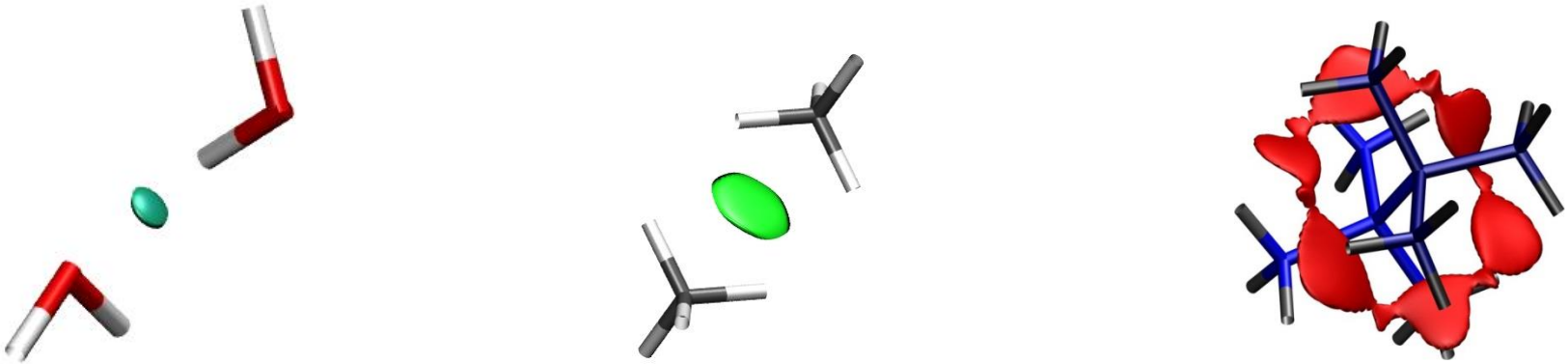


Water dimer



Formic acid dimer

The reduced density gradient



Strong and attractive:

Hydrogen bonds

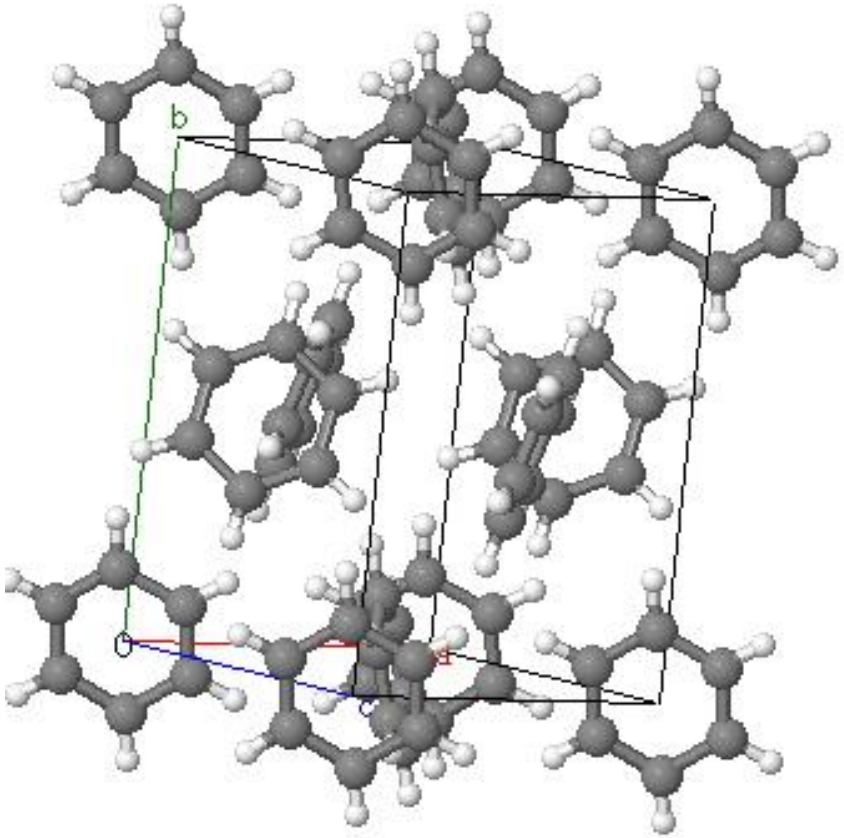
Very weak:

van der Waals

Strong and repulsive:

Steric clashes

Delocalized interactions



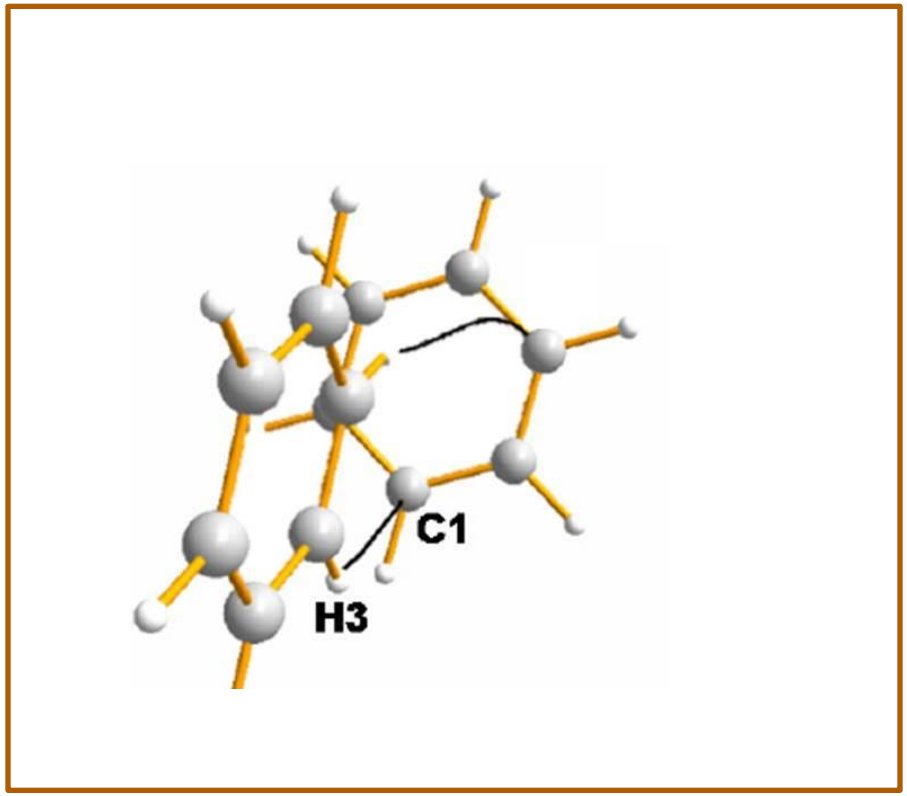
Benzene packing maximizes the number of C-H···π and C-H···C contacts.

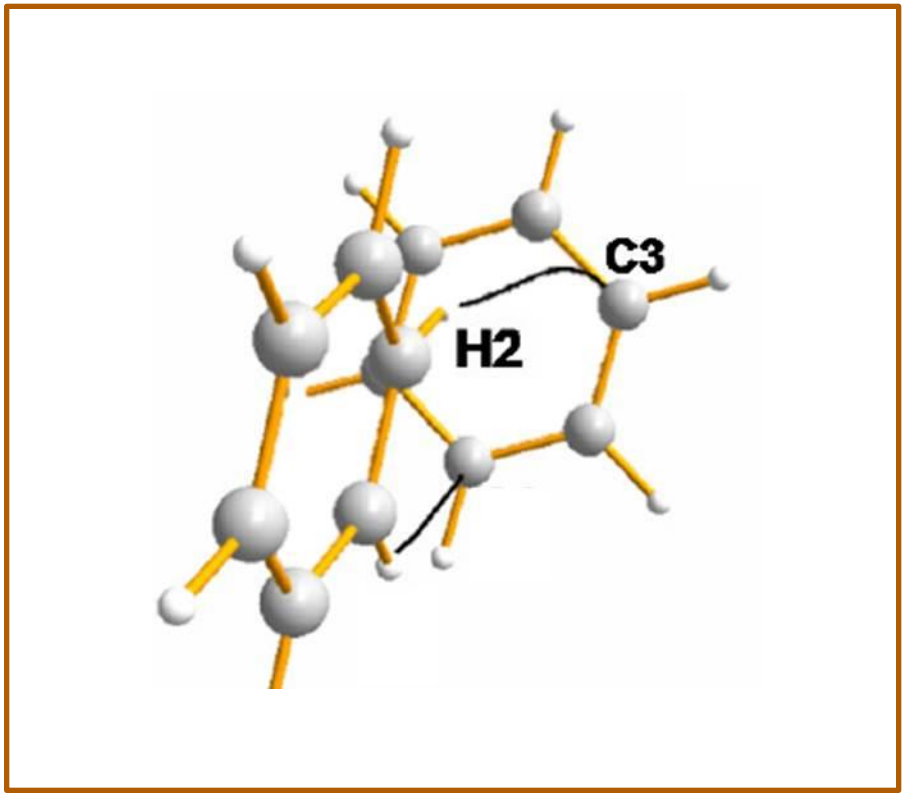
Delocalized interactions

AIM

CH-C
Straight bond path

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



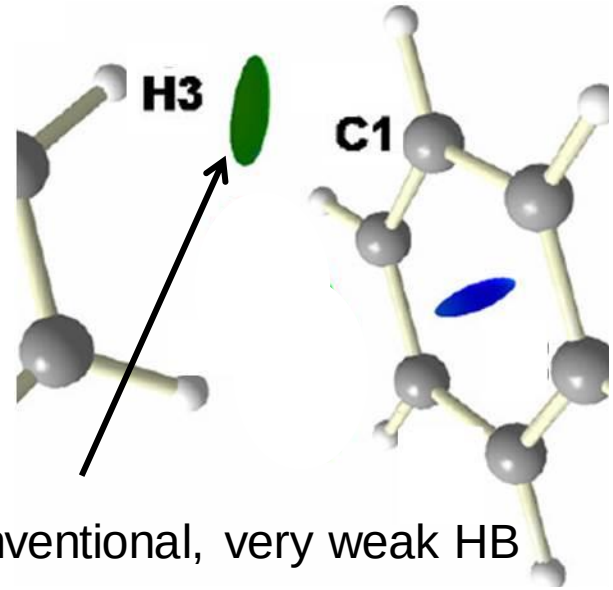


Delocalized interactions

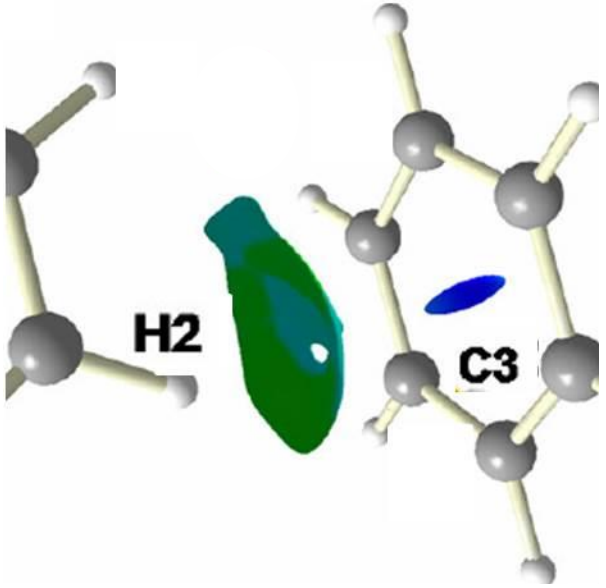
NCI

CH-C
Disc-shaped and localized

CH-π
Large isosurface involving the whole π electron cloud



conventional, very weak HB



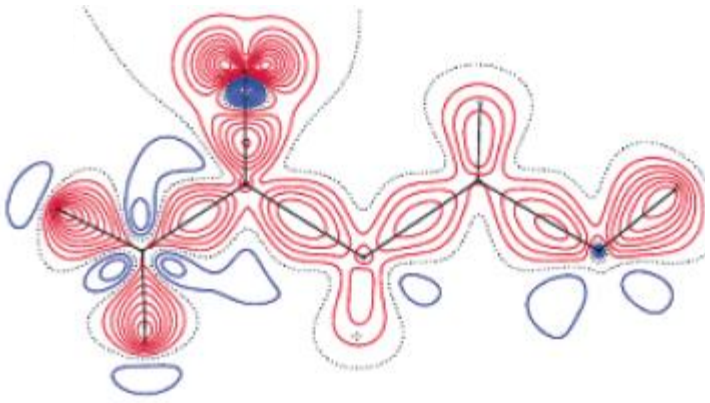
nonclassical hydrogen bond

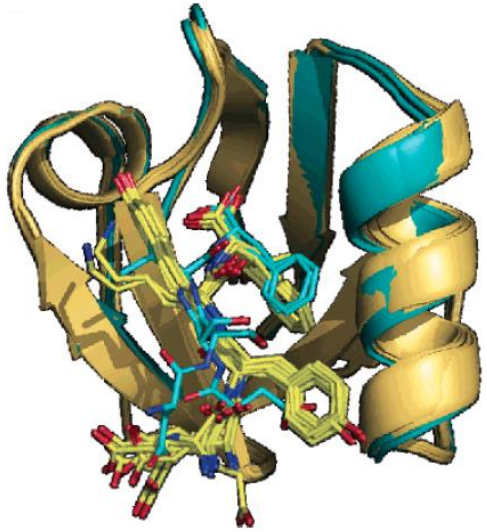
Big systems

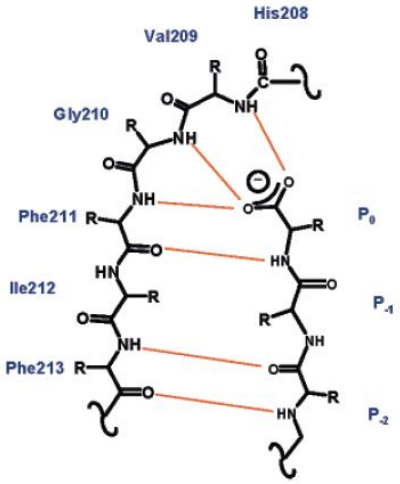
- One of the major areas of application of weak interactions are biomolecules
- HOWEVER, wavefunctions are not available
- In the non covalent region, there is very little density reconstruction, so we can use and independent atom model (non relaxed or promolecular densities)

What do we want promolecular for??

- Used in crystallography







Promolecular densities are used in the refinement of high-resolution X-Ray data of large systems

1
1
1

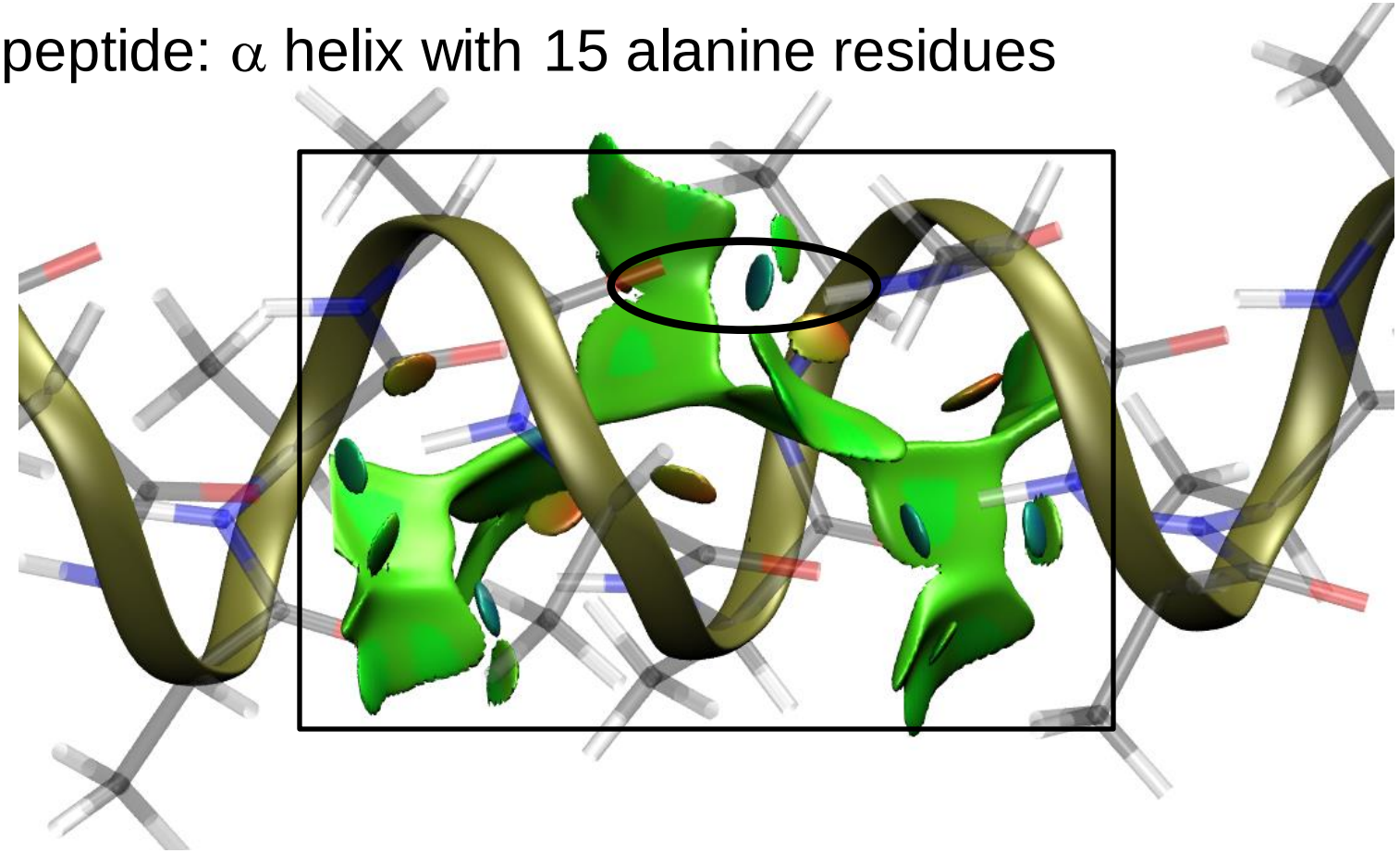
Big systems

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)

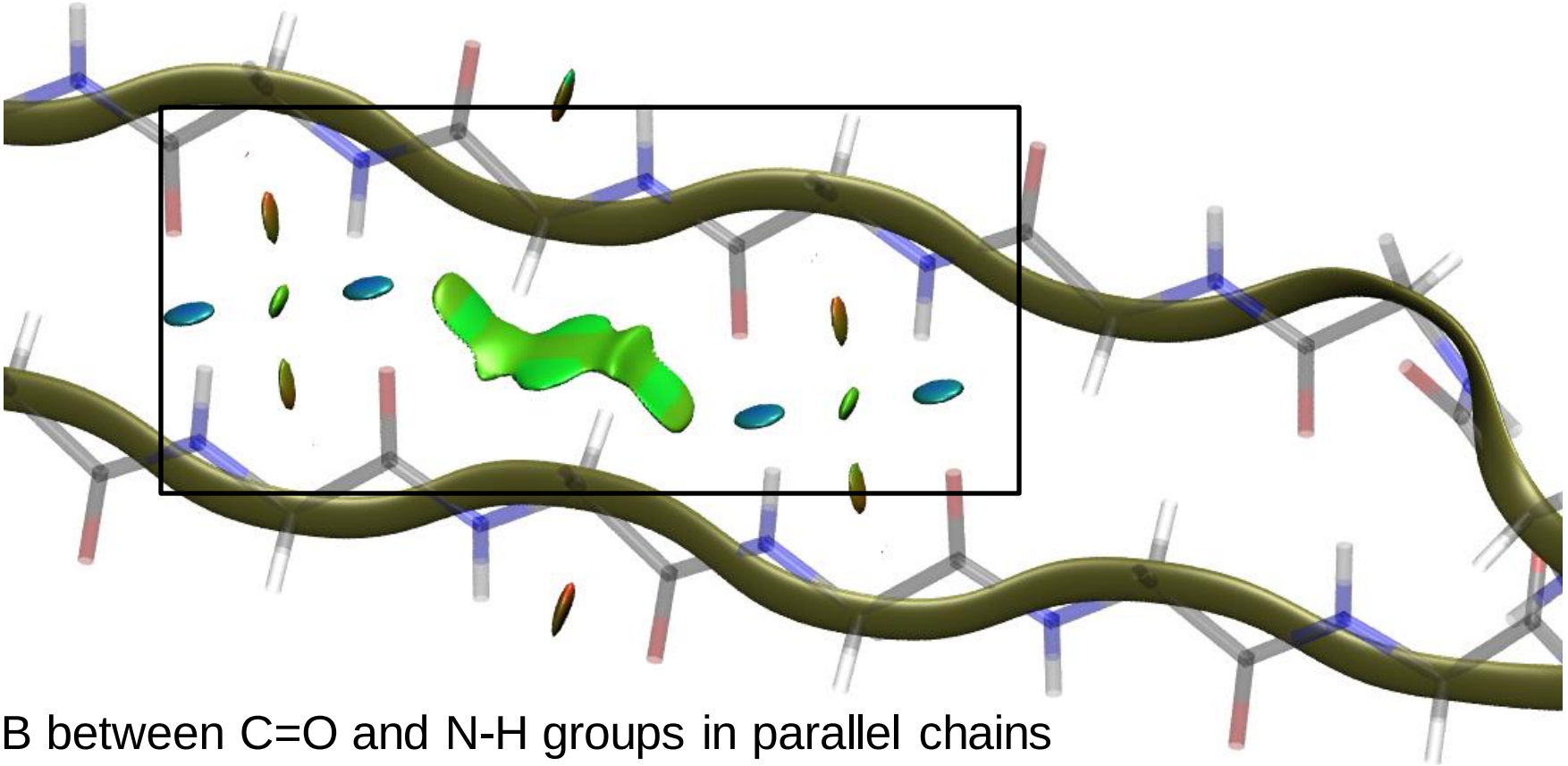
Proteins

Polipeptide: α helix with 15 alanine residues



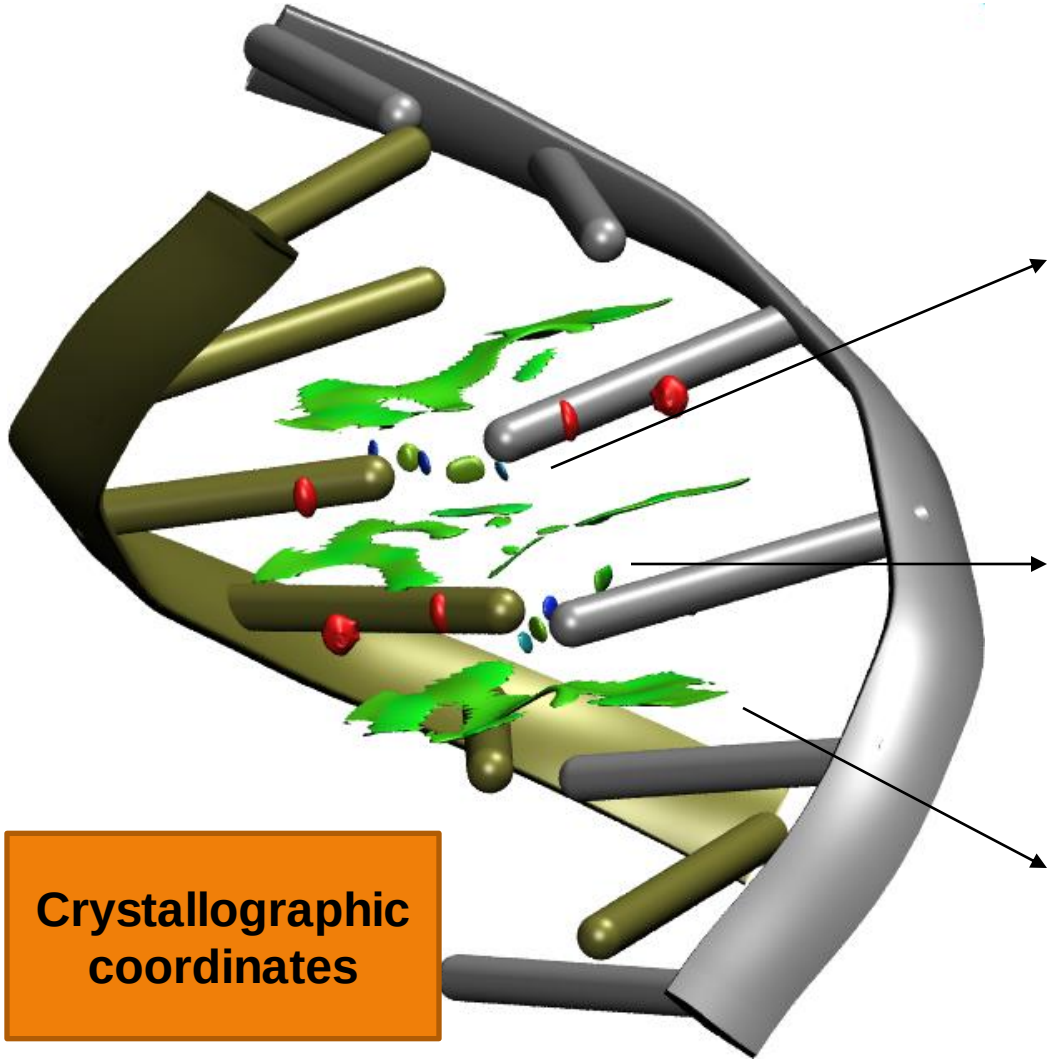
- Hydrogen bonds stabilize the helix
- Big region of van der Waals interaction inside the helix and between methyle lateral chains one step away

Proteins

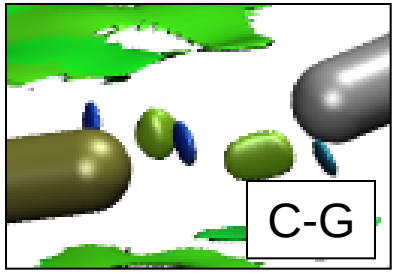


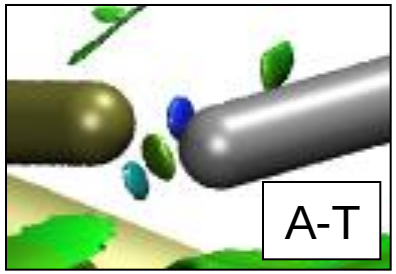
- HB between C=O and N-H groups in parallel chains
- Van der Waals interactions between CH_2 groups

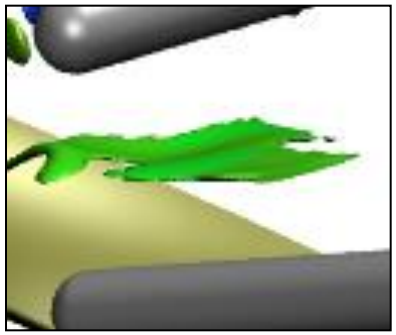
DNA



Crystallographic coordinates



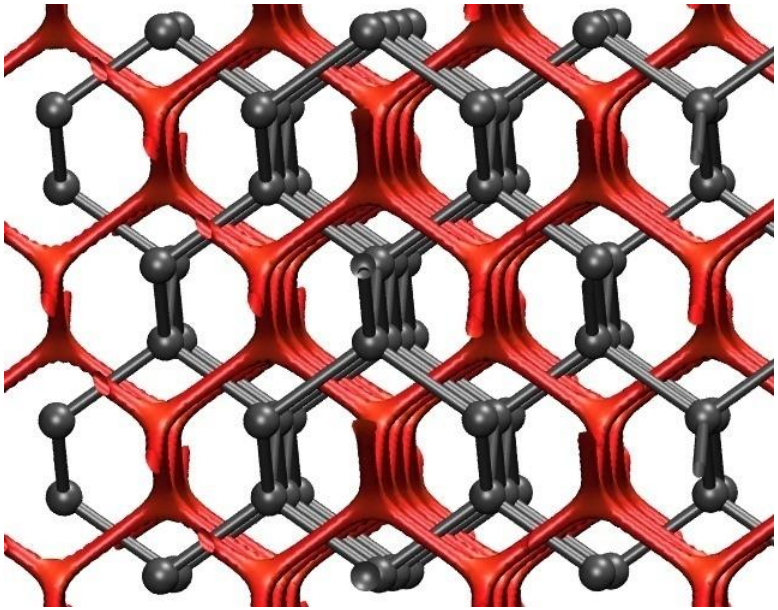




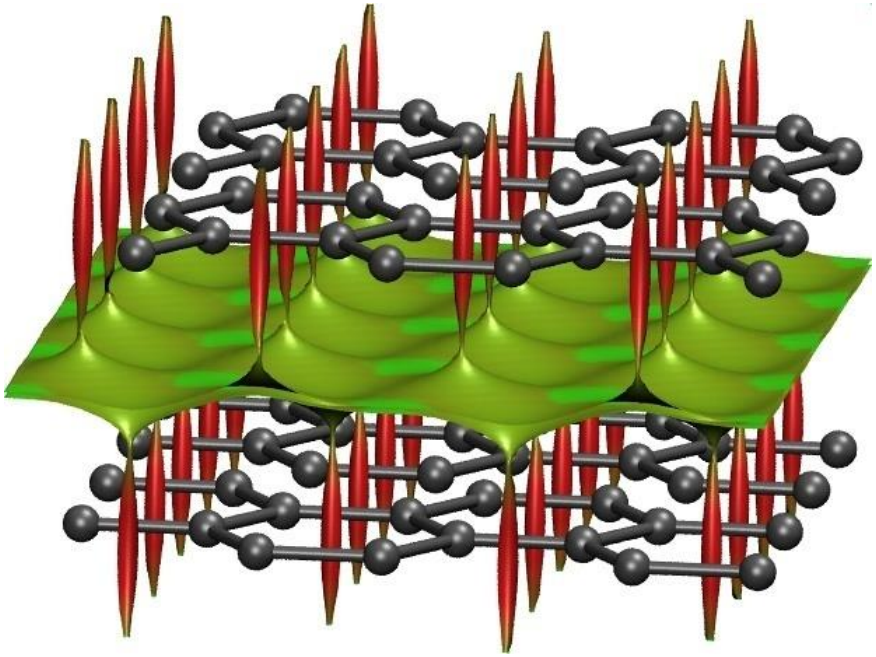
H-bonds between bases

π-stacking

2. QM classification of solids



Diamond



Graphite

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. Applications

4. Workout example

5. Summary

Metals under pressure

New materials : Electronic structure of high pressure metals

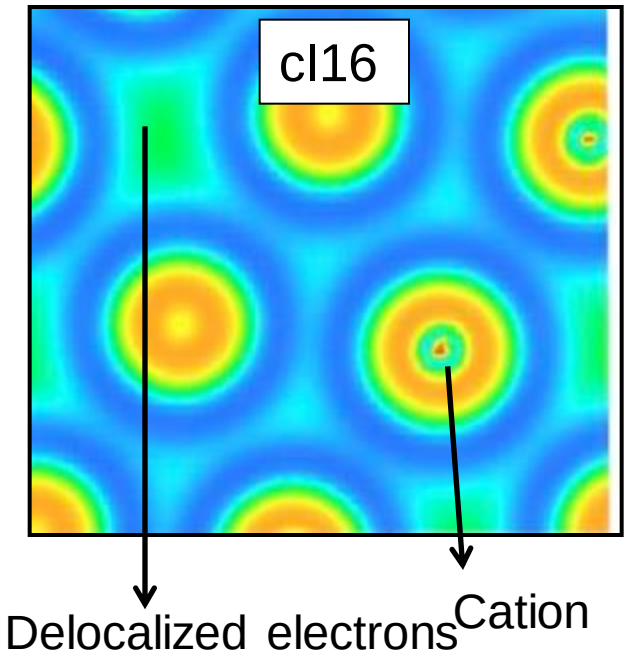
- Under pressure, solids exhibit increasingly shorter interatomic distances. Intuitively, this response is expected to be accompanied by an increase in the widths of the valence and conduction bands and hence a more pronounced free-electron-like behavior.

- However, 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?

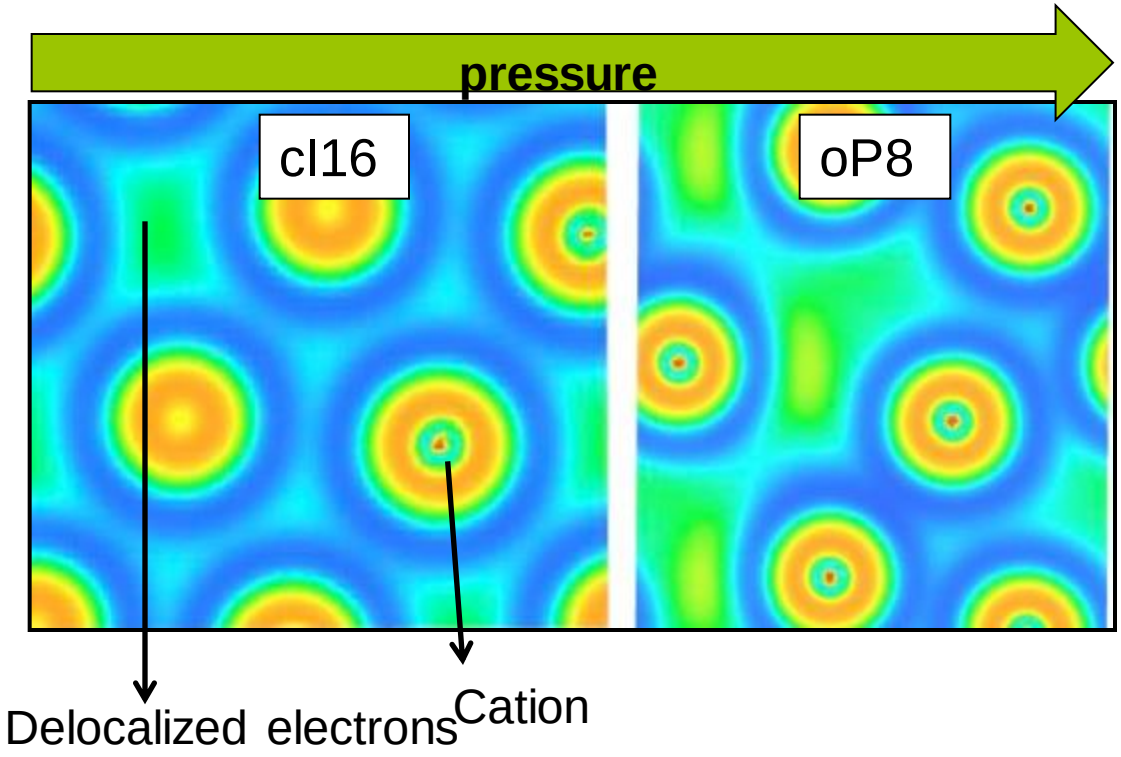
New bonding patterns: new properties

Na



New bonding patterns: new properties

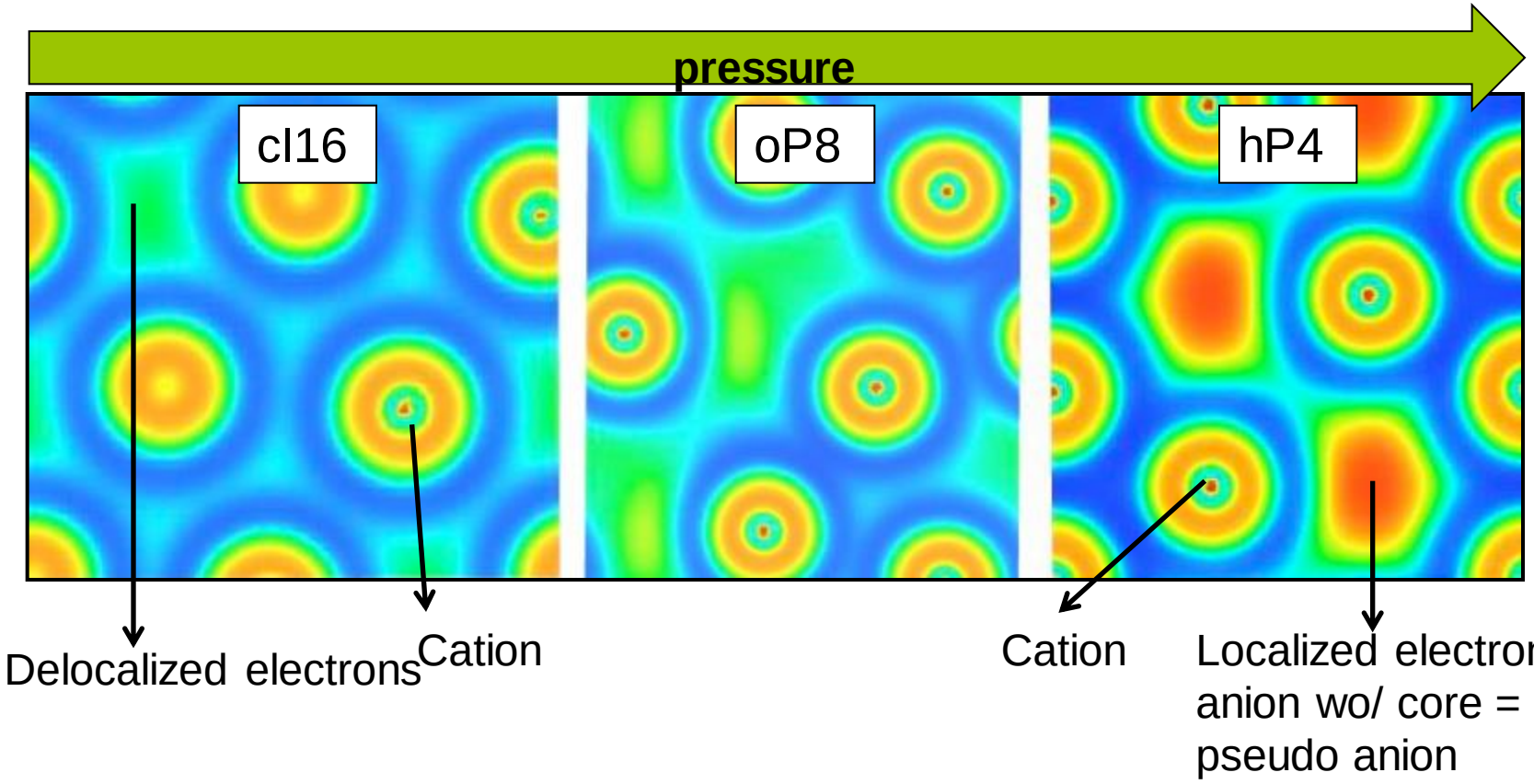
Na



New bonding patterns: new properties

Na

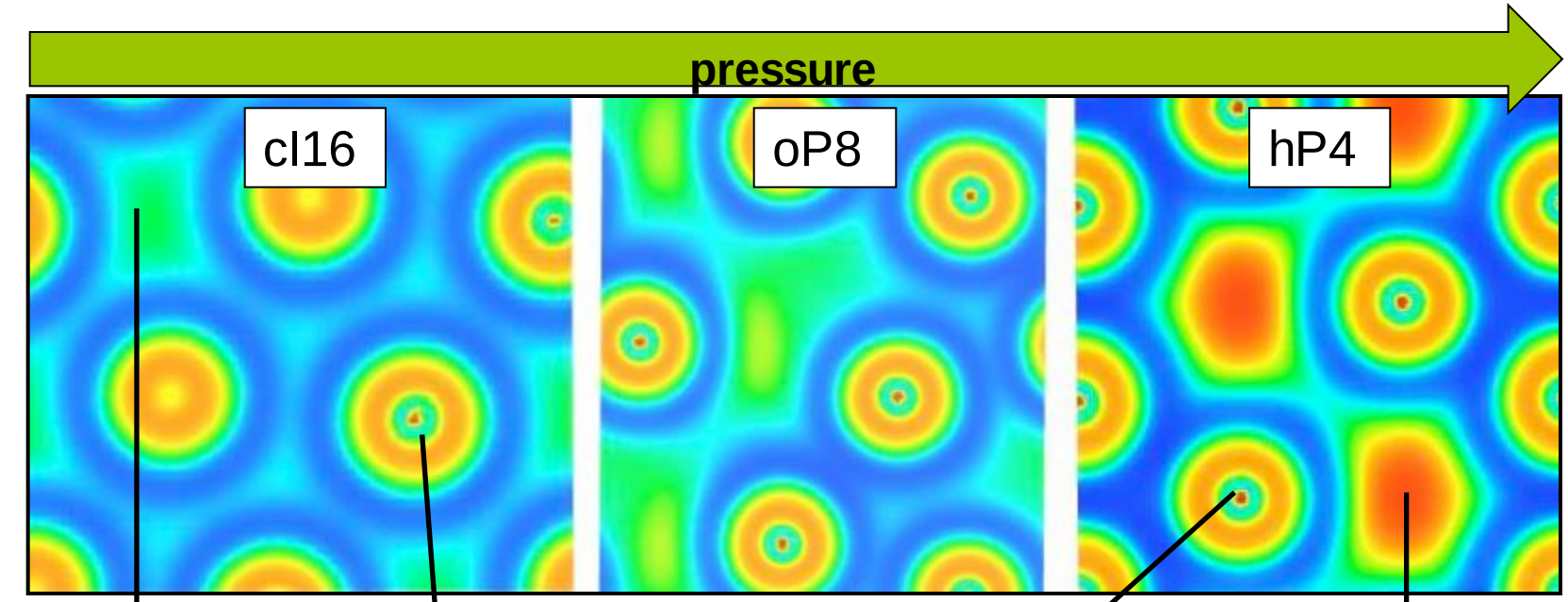
Localization of valence electrons is again observed under pressure



New bonding patterns: new properties

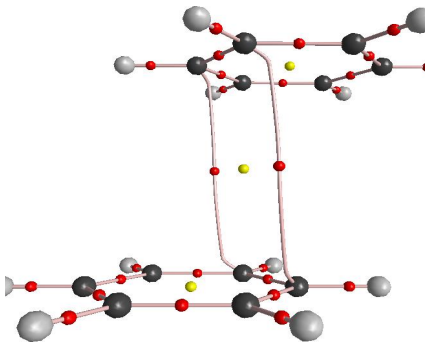
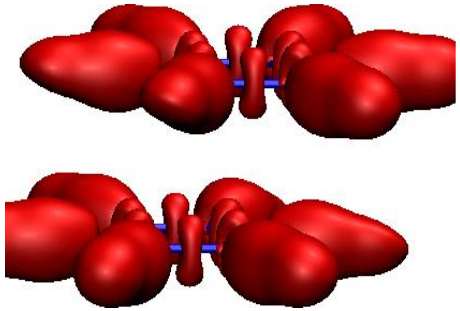
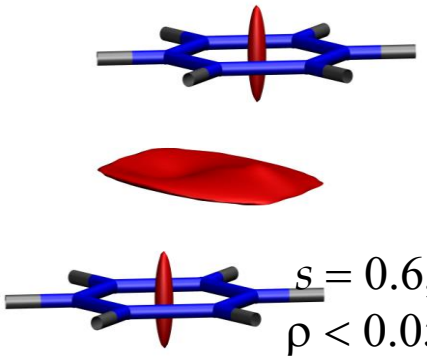
Na

Localization of valence electrons is again observed under pressure



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

Summary

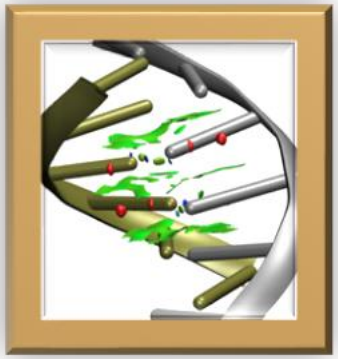
What are you looking for	**Atoms and bonds Atomic charges**	**Bonds, lone pairs Charges and volumes in Lewis entities**	**Non covalent interactions (even in big systems)**
You should use…	Electron density	ELF	NCI
Example		 ELF = 0.9	 $s = 0.6$, $\rho < 0.05$

The programs

NCIPLOT

NCI for molecules and biomolecules

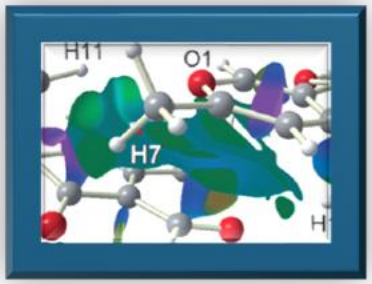
JCTC 7, 625 (2011)



NCIMILANO

NCI for experimental densities

Chem. Eur. J. 18, 15523 (2012)



CRITIC

NCI for solid calculations

PCCP 14, 12165 (2012)

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