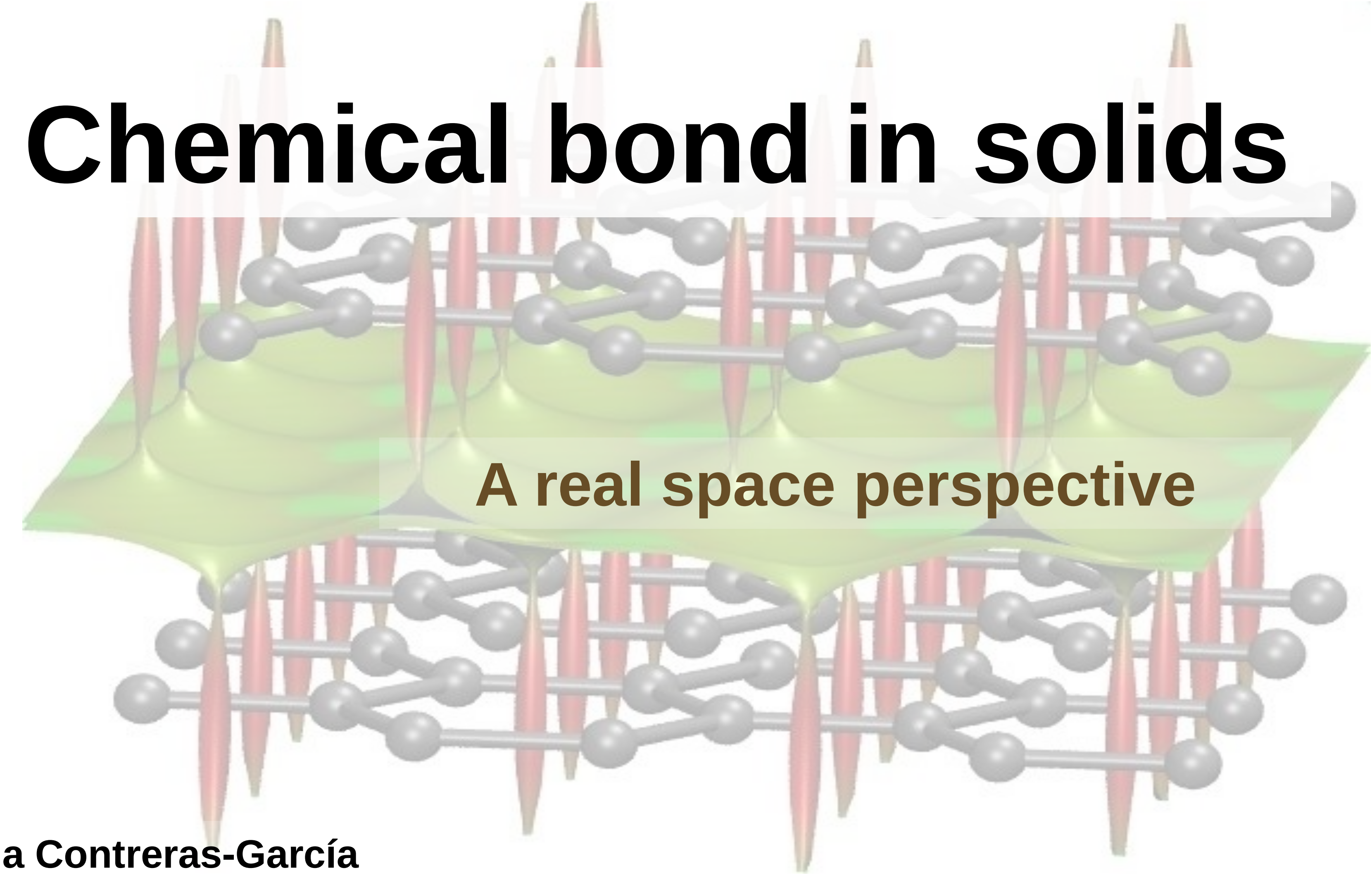


Chemical bond in solids

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

4. Summary

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

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

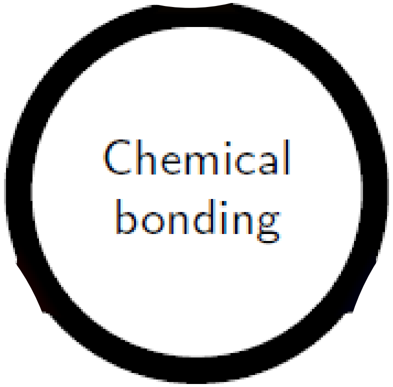

Materials by Inverse Design
Conventional Approach
Desired Properties
Materials

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)



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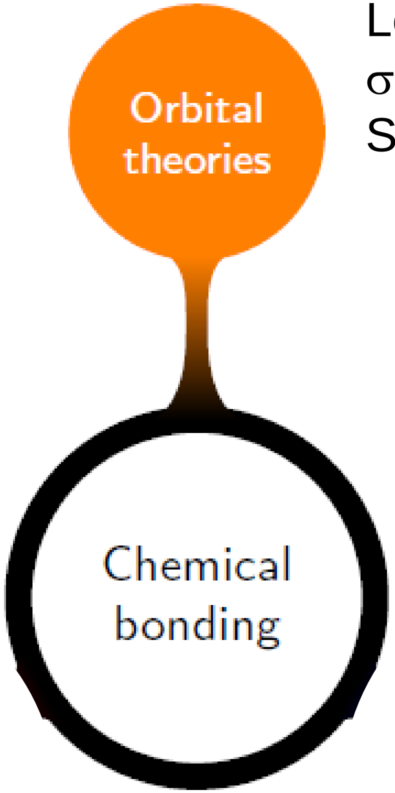

Localized orbitals
σ *vs* π
Symmetry

Quantum chemical topology

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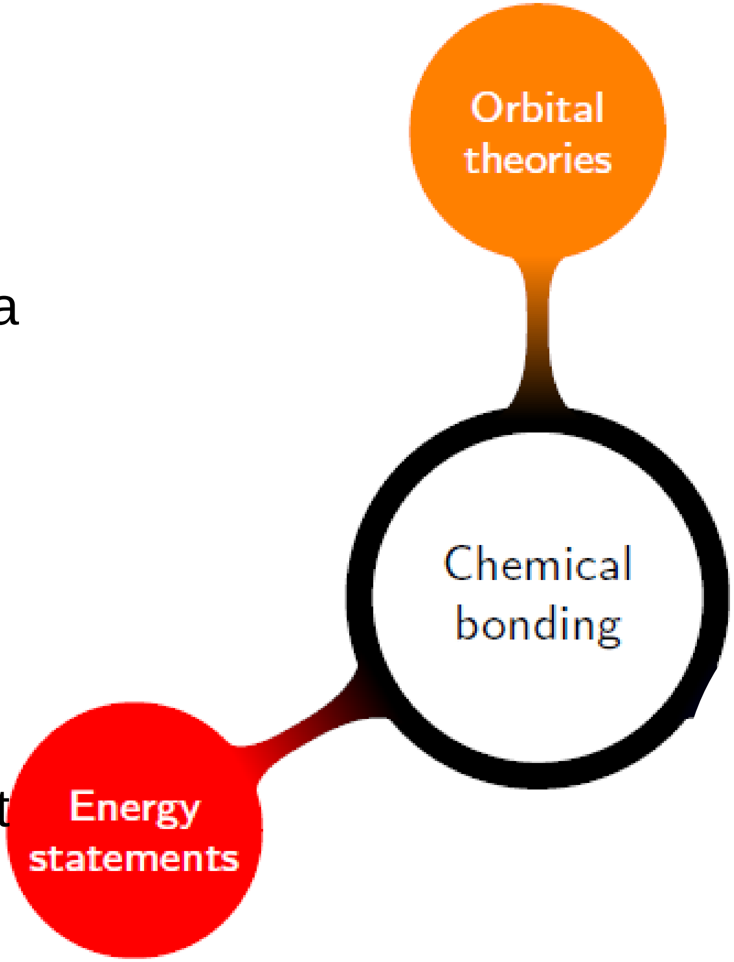
(and reduce the dimensionality)



Dispersion
Charge transfer

Quantum chemical topology

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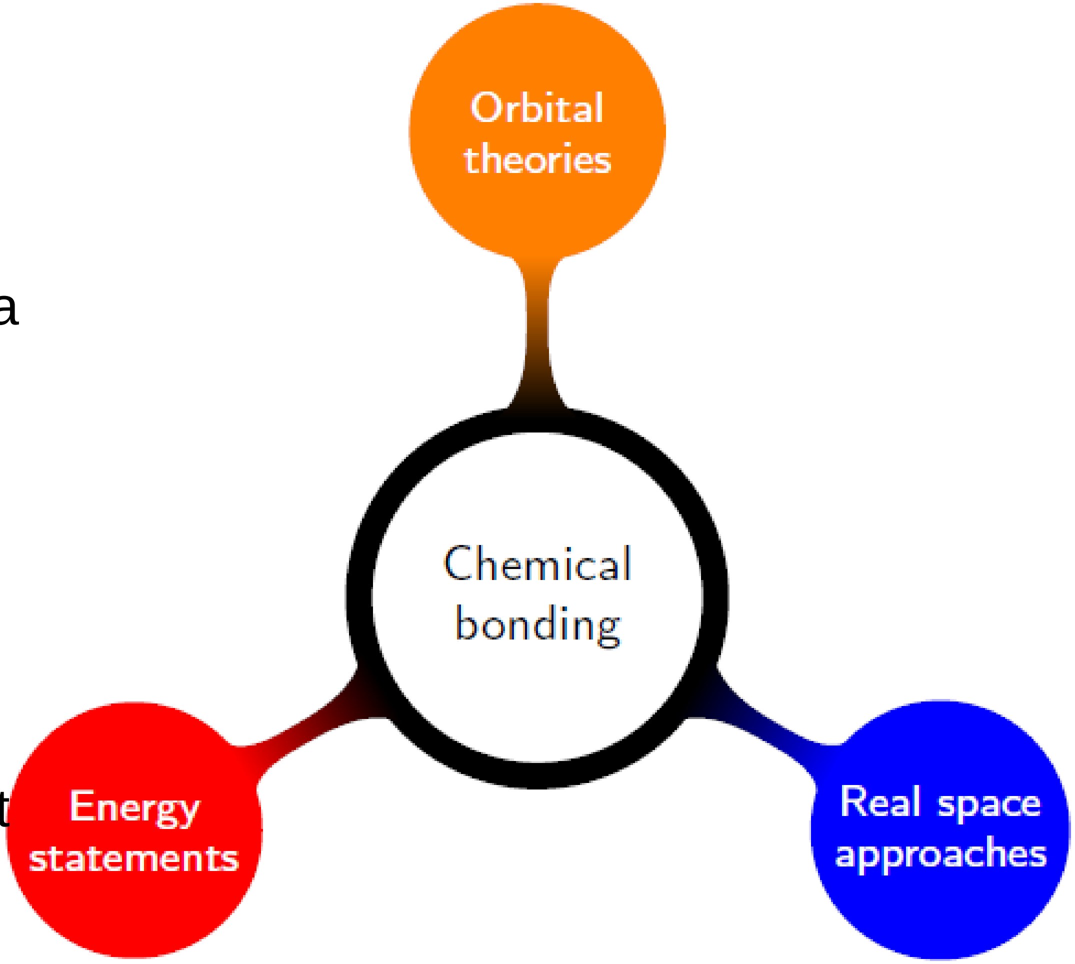
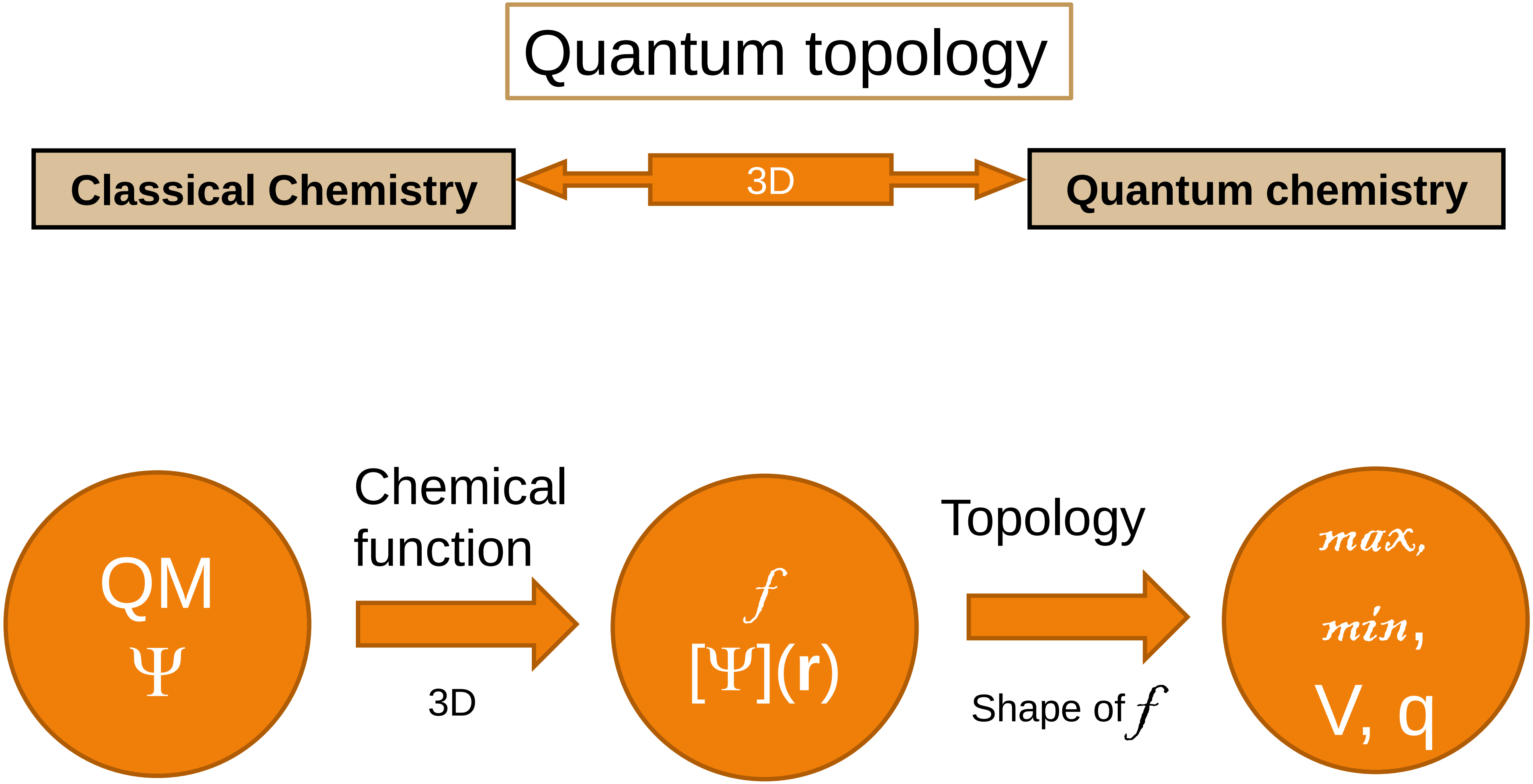
(and reduce the dimensionality)



QCT in a nutshell



Quantum topology

Classical Chemistry

3D

Quantum chemistry

QM

Ψ

Chemical function

3D

f

$[\Psi](\mathbf{r})$

Topology

Shape of f

max,

min,

V, q

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

1

Topology

+

2

Chemically sound functions

=

3

Quantum chemical Topology (QTC)

QCT in a nutshell

1

Topology

Local information:
critical points
Global information:
basins, integrals

+

2

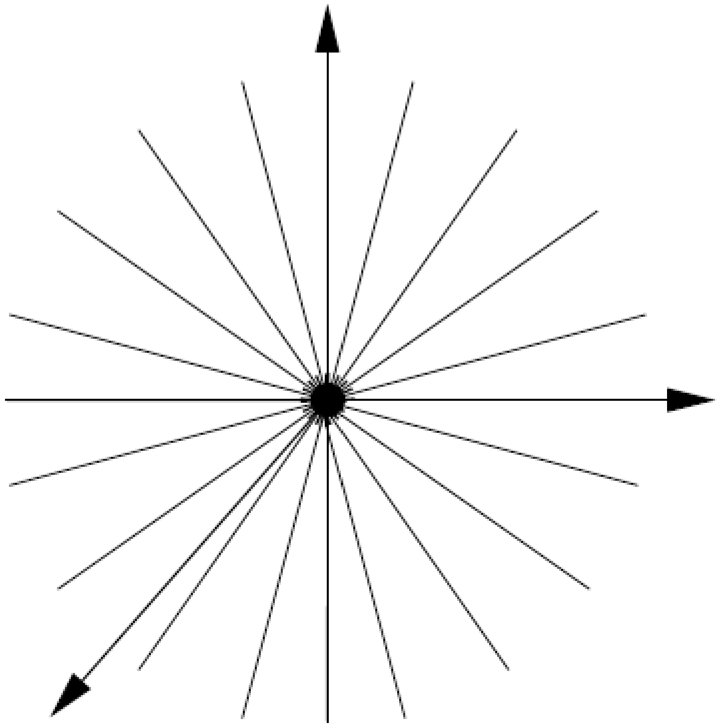
Chemically sound functions

=

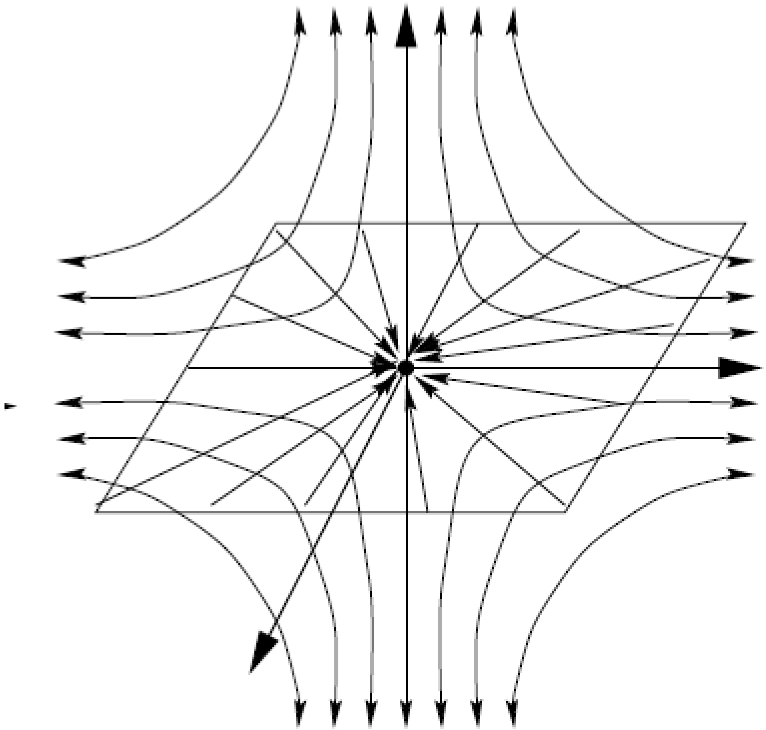
3

Quantum chemical Topology (QTC)

Types of CPs in 3D

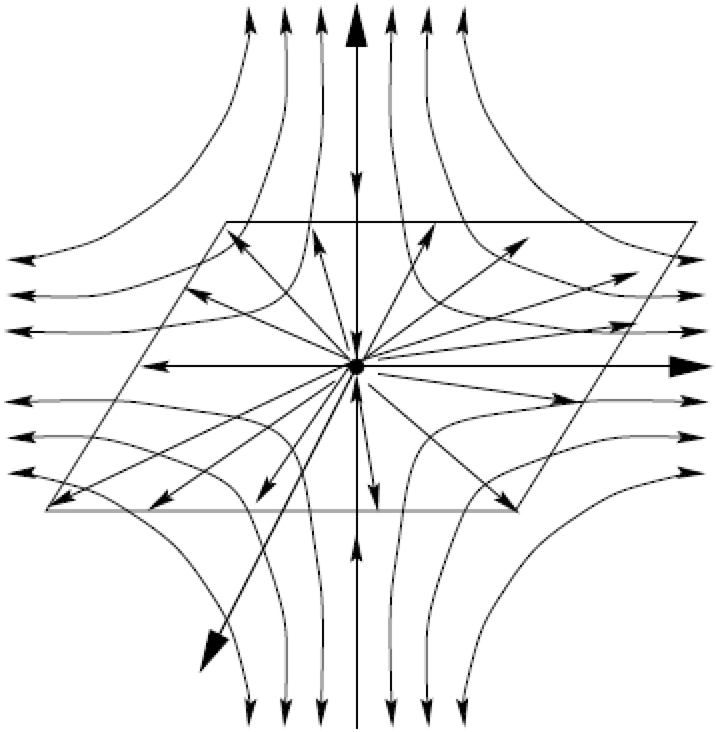


Maximum

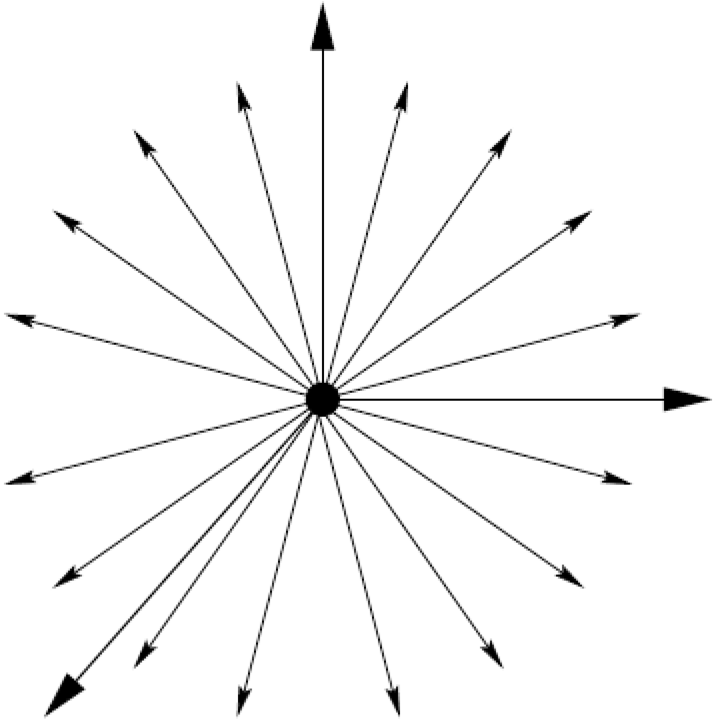


Saddle point of order 1

Types of CPs in 3D

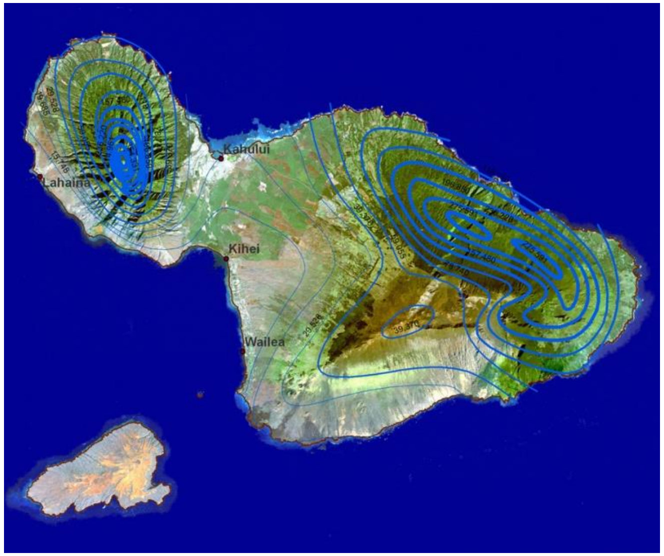


Saddle point of order 2

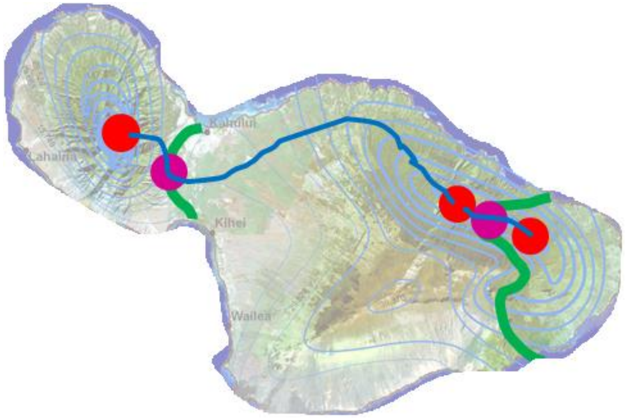


Minimum

Topological partitions are intuitive



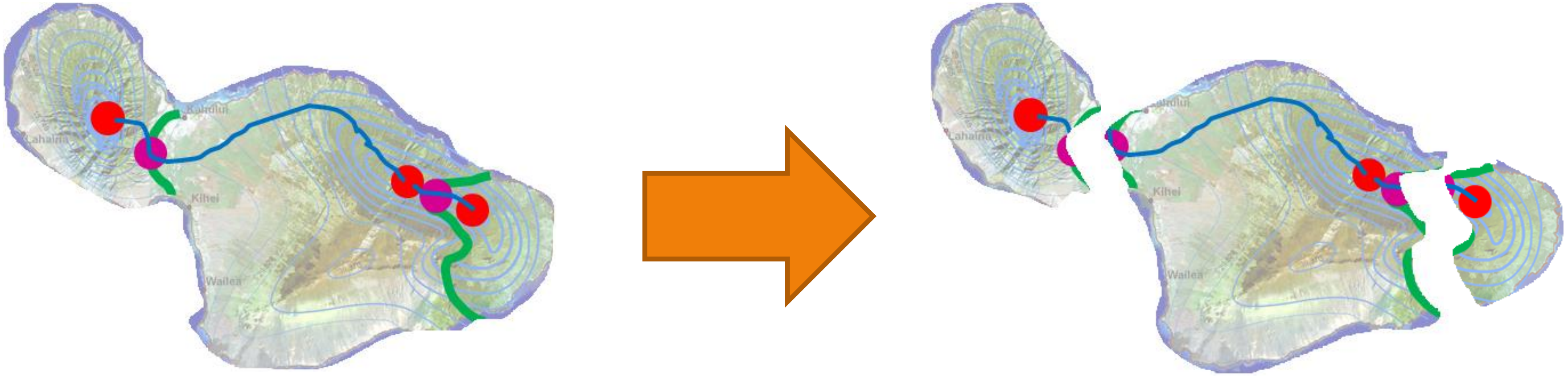
Topological partitions are intuitive



We automatically

- Identify cusps 🔴
- Divide through the valleys ▬
- Identify the lowest point in the valley 🟣

Topological partitions are intuitive



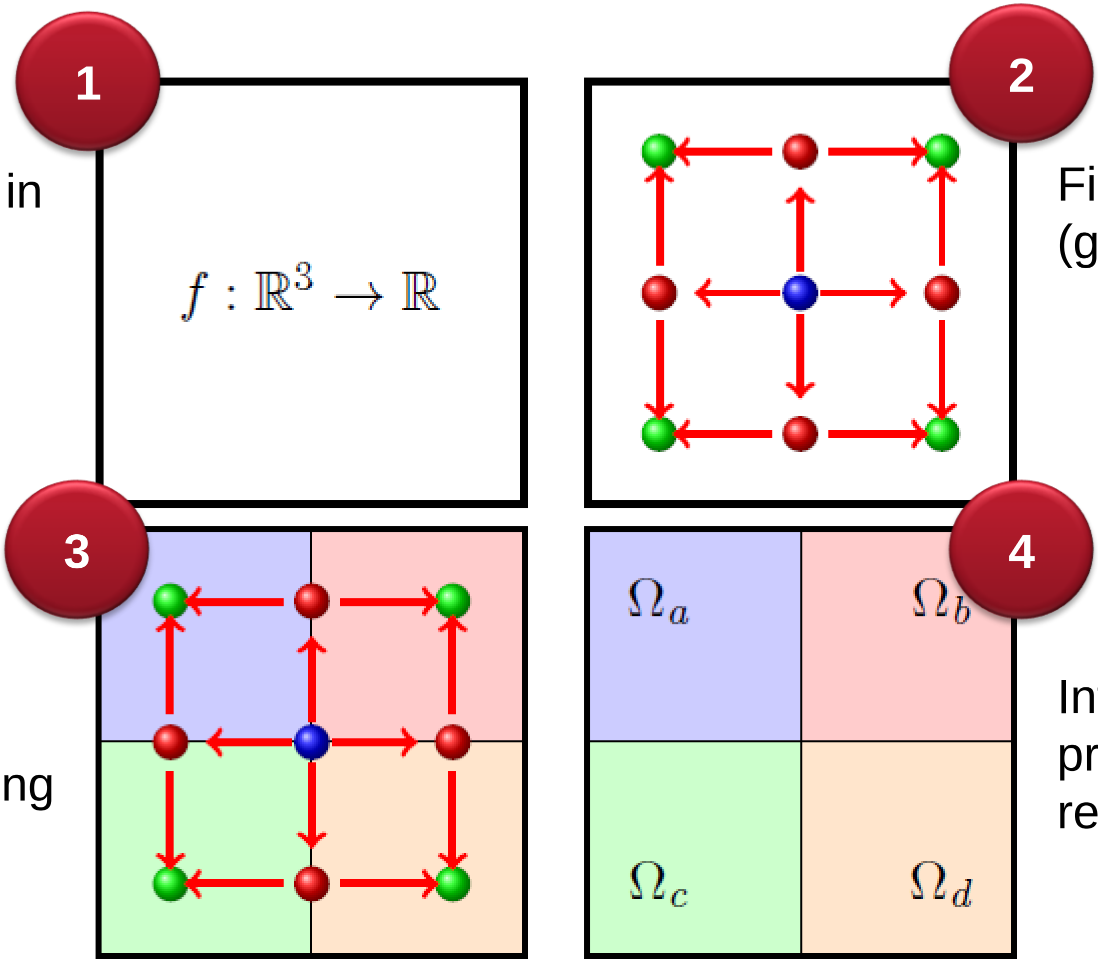
We automatically

- 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



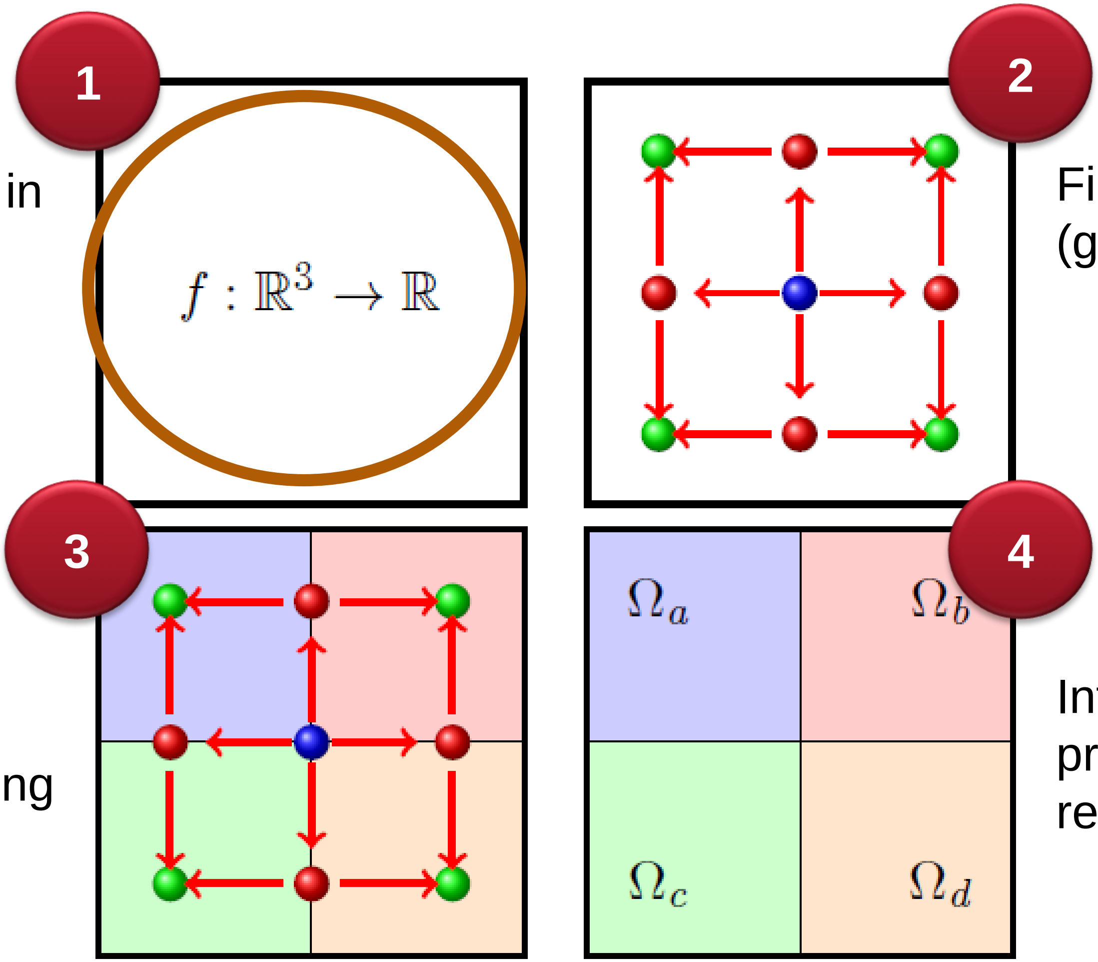
Compute scalar in the molecular /crystal space

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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Outline

1. Why studying chemical bonds?

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    b) ELF

    c) NCI

4. Summary

The electron density

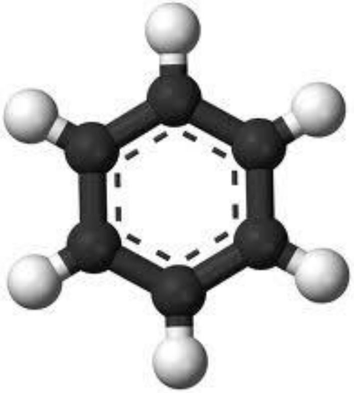
- ρ(r) is a fundamental property of any electronic system

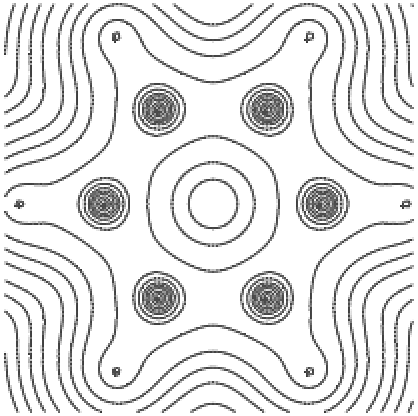
$$\rho(\vec{r}) = N \int \ldots \int \left|\Psi(\vec{x}_1, \vec{x}_2, \ldots, \vec{x}_N)\right|^2 ds\, d\vec{x}_2 \ldots \vec{x}_N$$

- ➢ 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

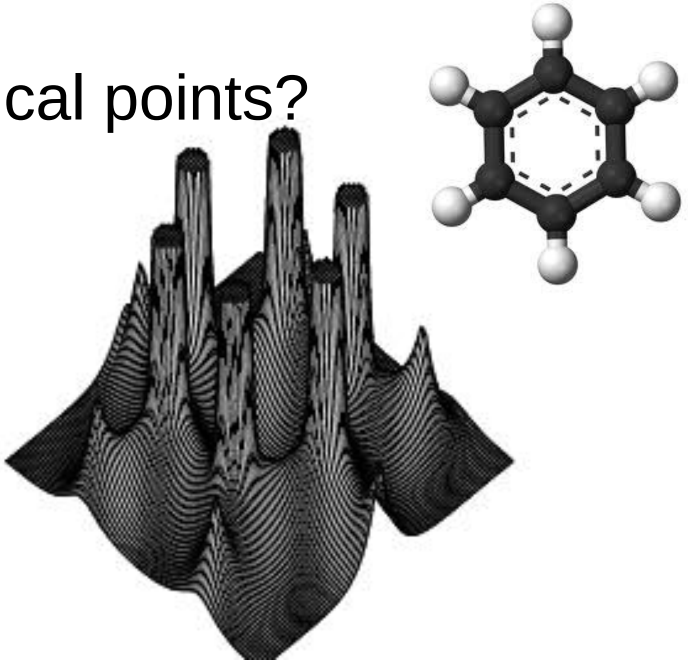


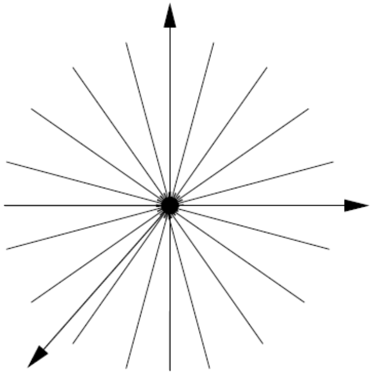


Example: the electron density

Where are the critical points?

- Maxima = nuclei

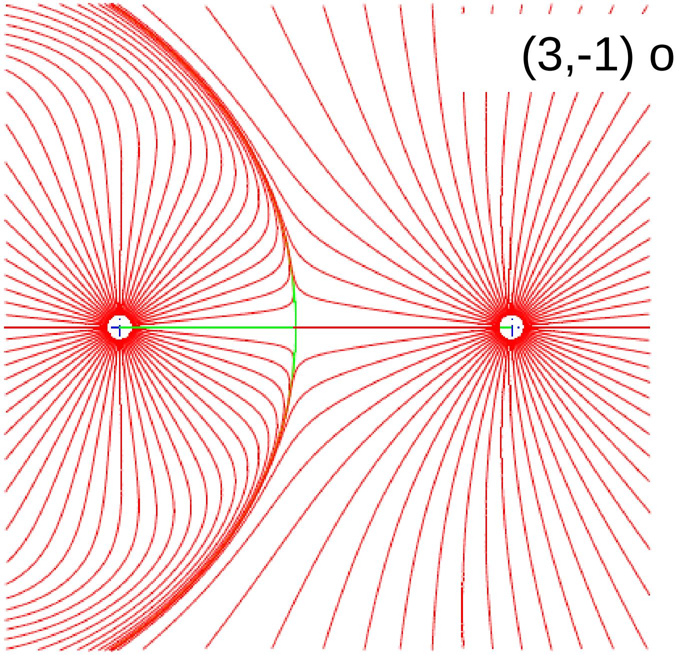




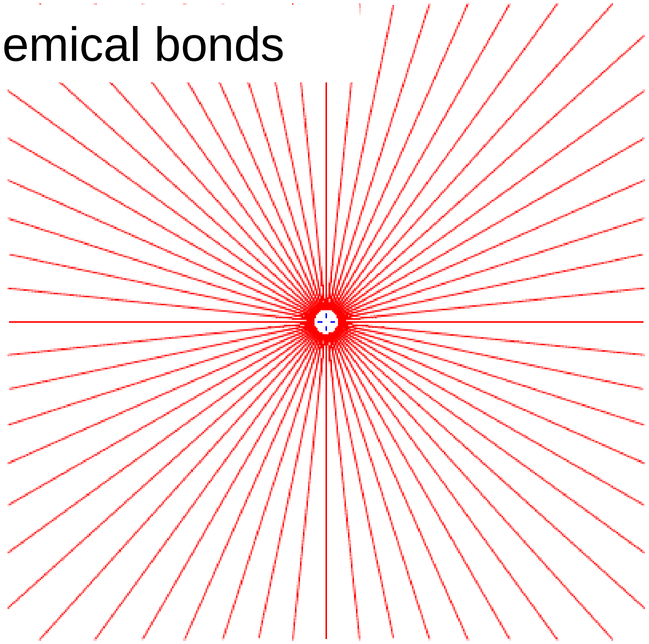
(a) Sumidero de líneas de campo.

The electron density

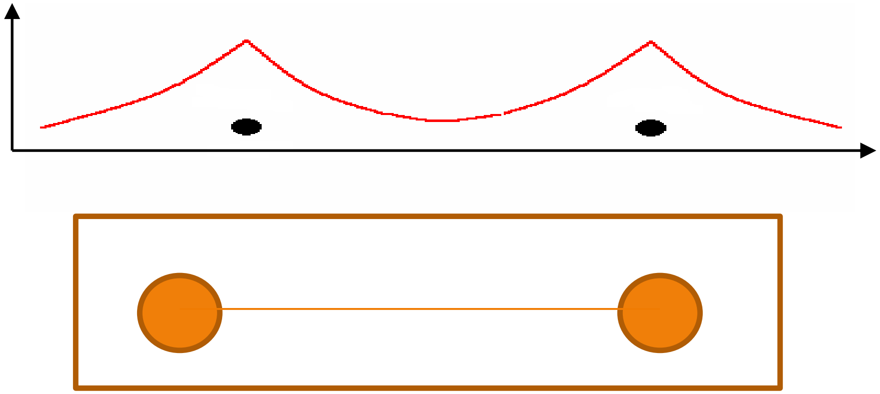
(3,-1) occur at chemical bonds

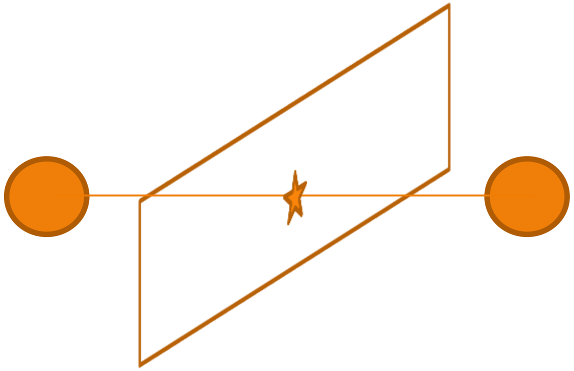


Plane that contains the nuclei



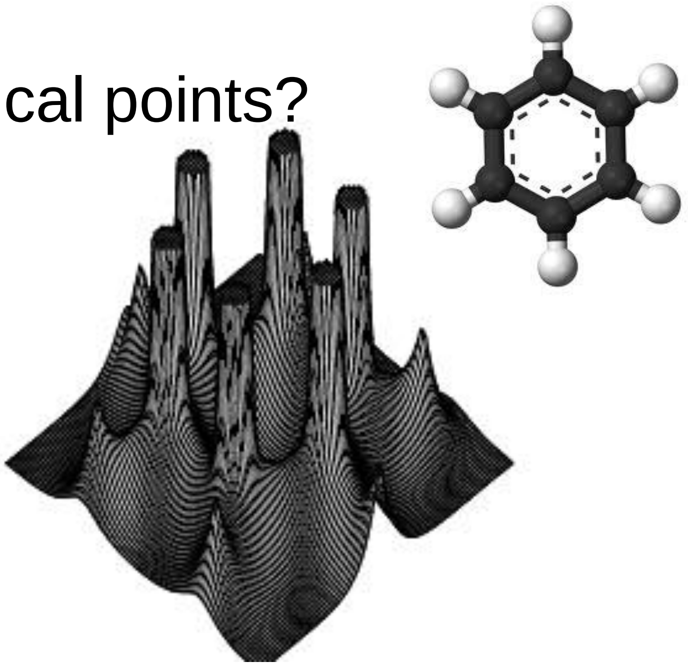
Plane perpendicular to the internuclear line at the critical point that contains the nuclei



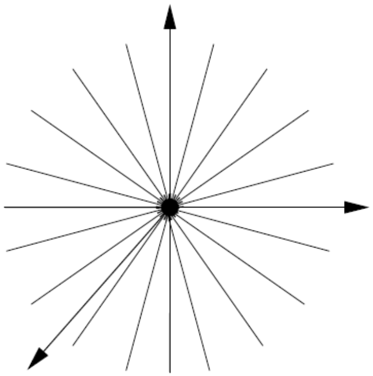


Example: the electron density

Where are the critical points?

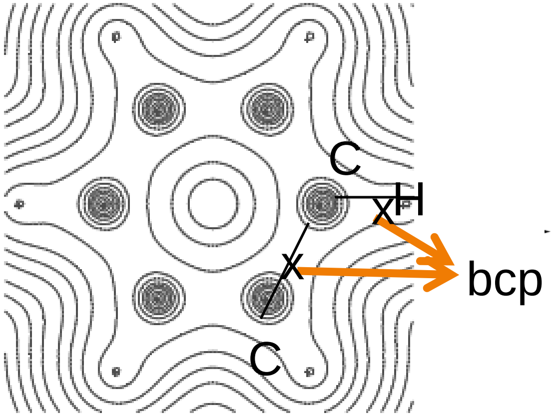


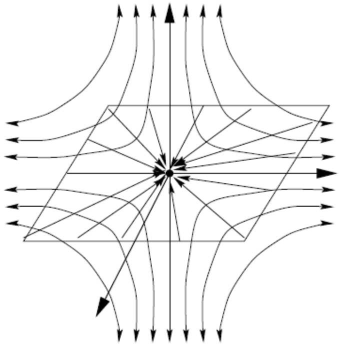
- Maxima = nuclei



(a) Sumidero de líneas de campo.

- 1st order saddle points=bonds

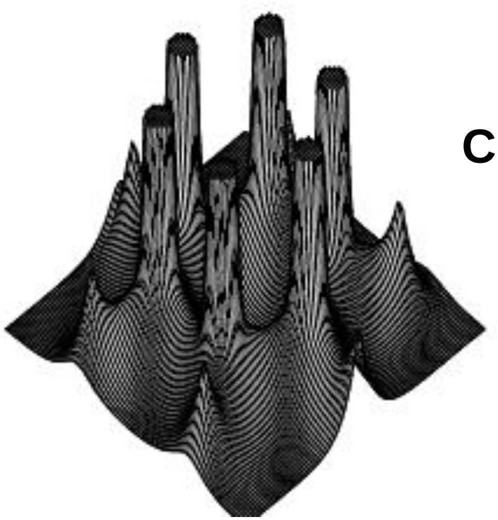


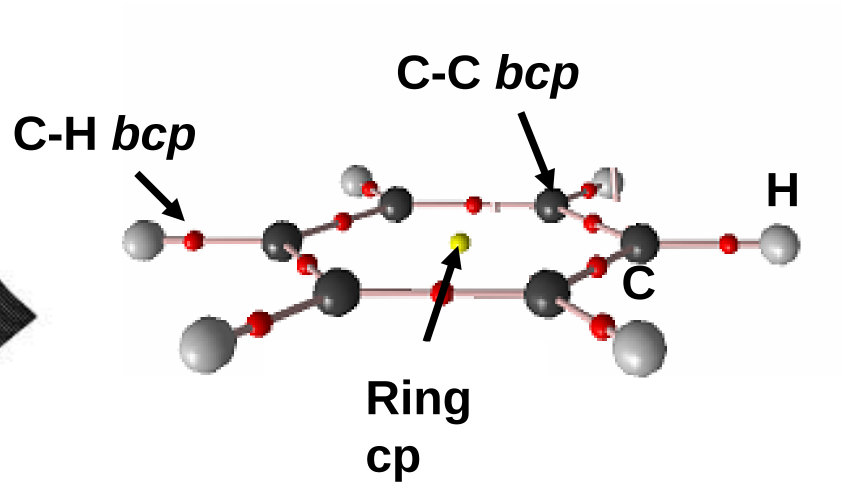


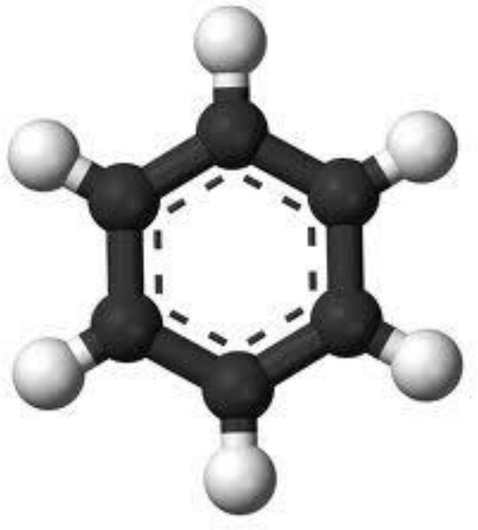
(b) Silla tipo 1.

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**

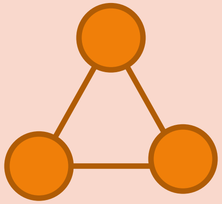
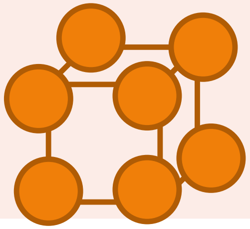
- Maxima = nuclei
- Bond = 1st order saddle point (*bcp*)

QCT in a nutshell

Directions along which the field grows

Directions along which the field decreases

Sum of signs of eigenvalues

CP	$\lambda>0$	$\lambda<0$	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

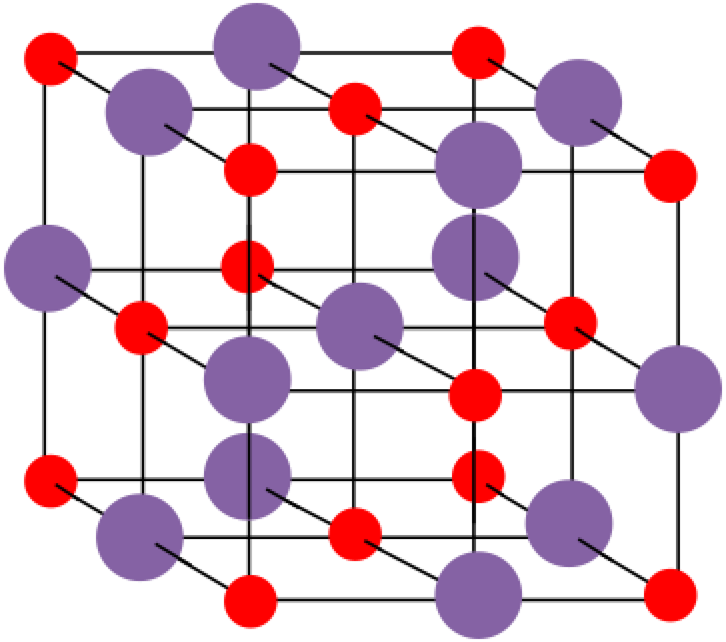
- In a periodic system, you will always have the 4 types of non-degenerated critical points
- Morse relationship MUST hold:

$$n_{(3,-3)}-n_{(3,-1)}+n_{(3,+1)}-n_{(3,+3)}=0 \qquad \left\{\begin{array}{l} n_{(3,-3)} \geq 1 \\ n_{(3,-1)} \geq 3 \\ n_{(3,+1)} \geq 3 \\ n_{(3,+3)} \geq 1 \end{array}\right.$$

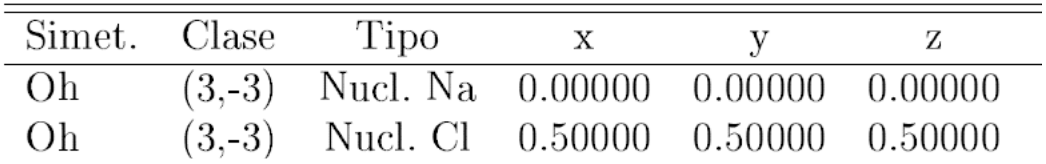
- If $\lambda_i=0$, these are degenerated critical « points » (we will see an example later).

  E.g. (2,-2)

Local information: CPs

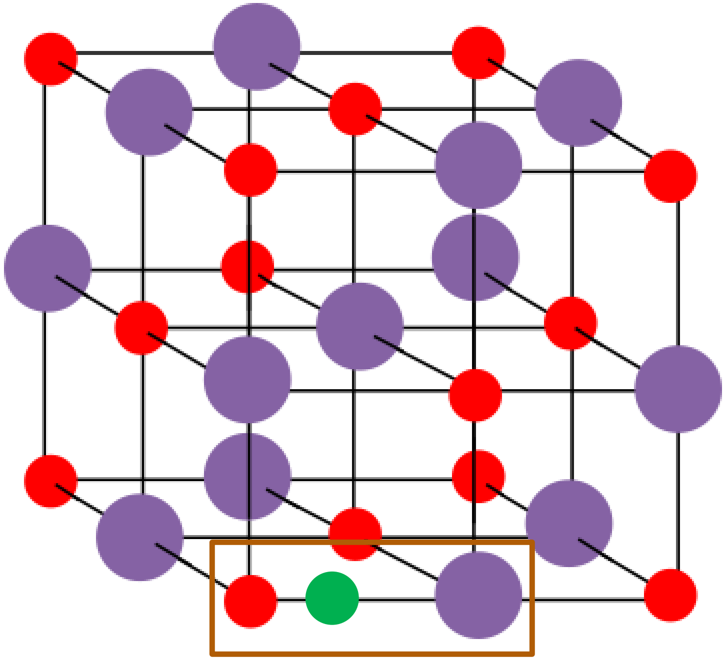


- Attractors are at the nuclei positions



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

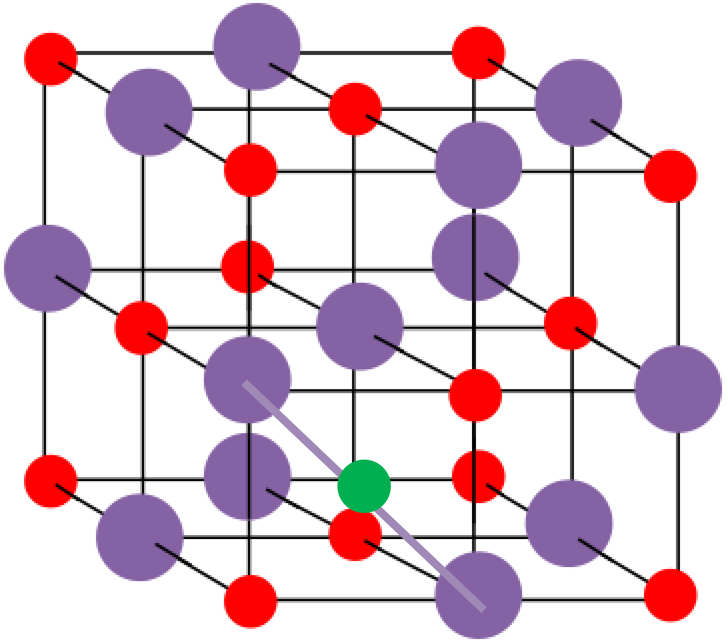
Local information: CPs



- 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

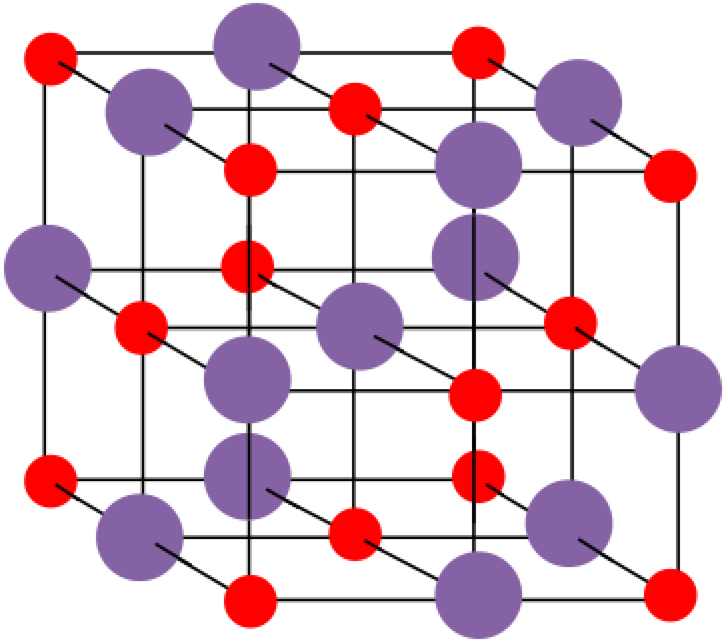


- Attractors are at the nuclei positions
- (3,-1) signal interactions

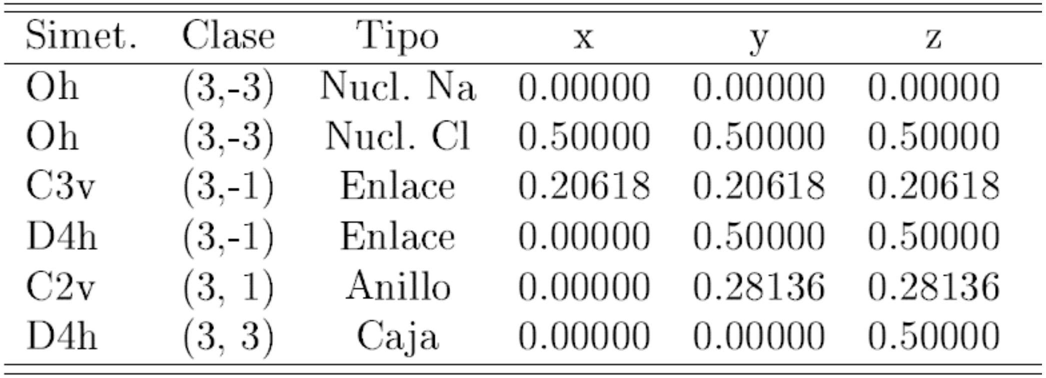
Anion-anion interactions are quite common in crystals

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

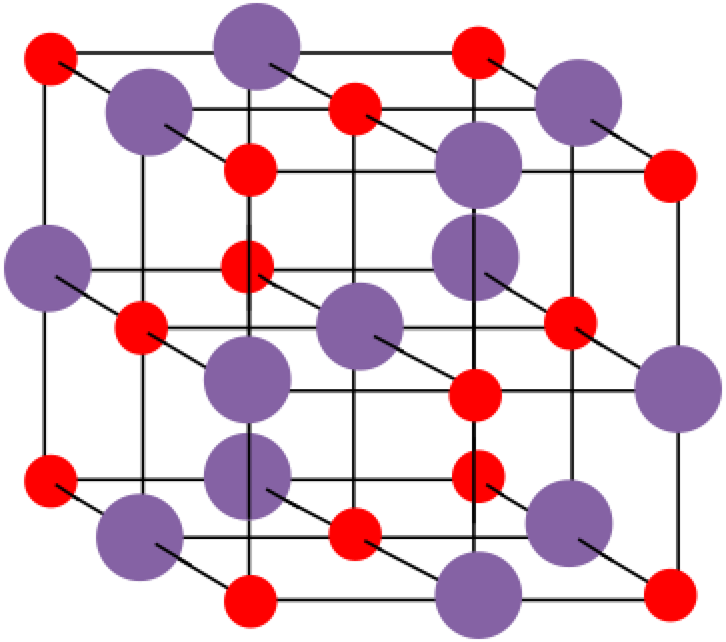


- We have all types of critical points



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

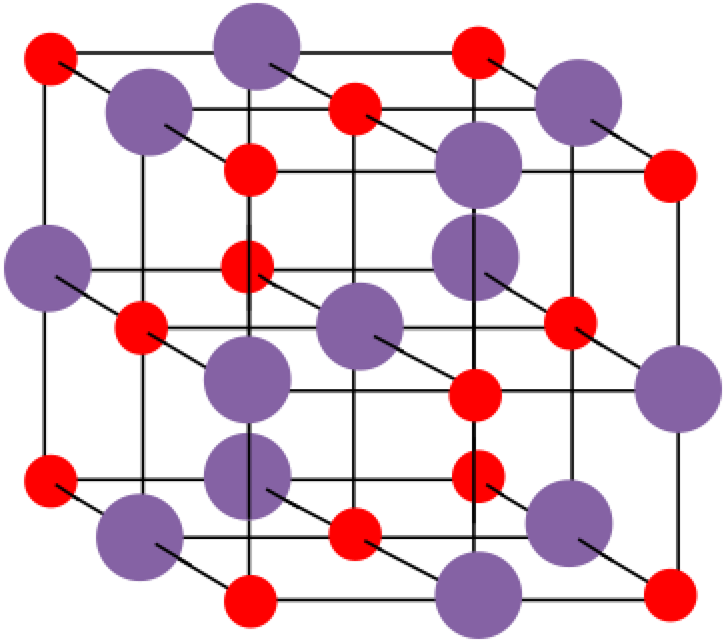


- We have all types of critical points
- Morse sum is working

2-11+12-3=0

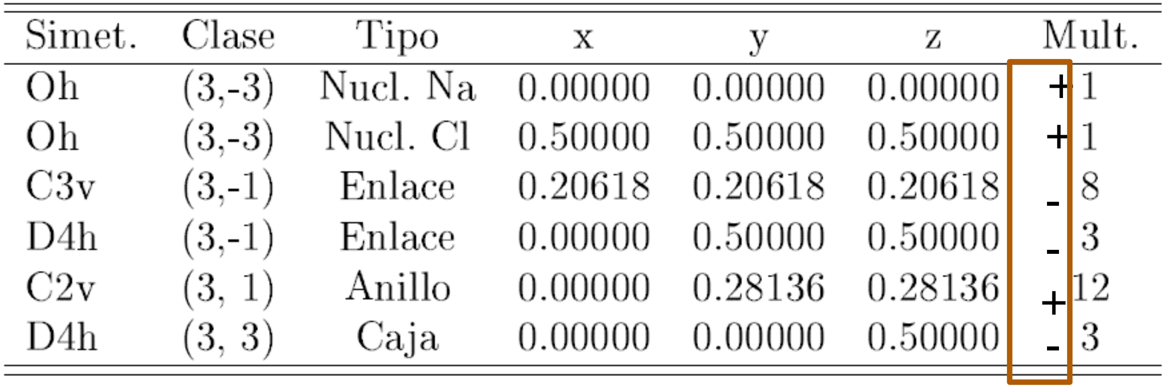
Simet.	Clase	Tipo	x	y	z	Mult.
Oh	(3,-3)	Nucl. Na	0.00000	0.00000	0.00000	+ 1
Oh	(3,-3)	Nucl. Cl	0.50000	0.50000	0.50000	+ 1
C3v	(3,-1)	Enlace	0.20618	0.20618	0.20618	- 8
D4h	(3,-1)	Enlace	0.00000	0.50000	0.50000	- 3
C2v	(3, 1)	Anillo	0.00000	0.28136	0.28136	+ 12
D4h	(3, 3)	Caja	0.00000	0.00000	0.50000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

Local information: CPs



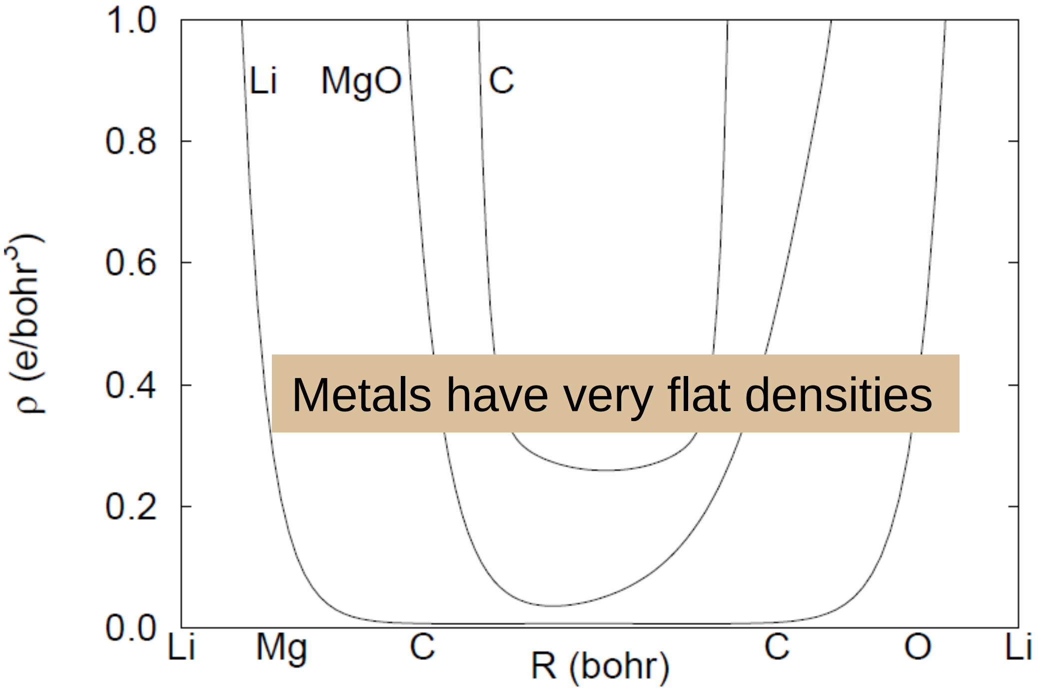
- We have all types of critical points
- Morse sum is working

  2-11+12-3=0 ☺
- We only have (3,-3) at the nuclei?

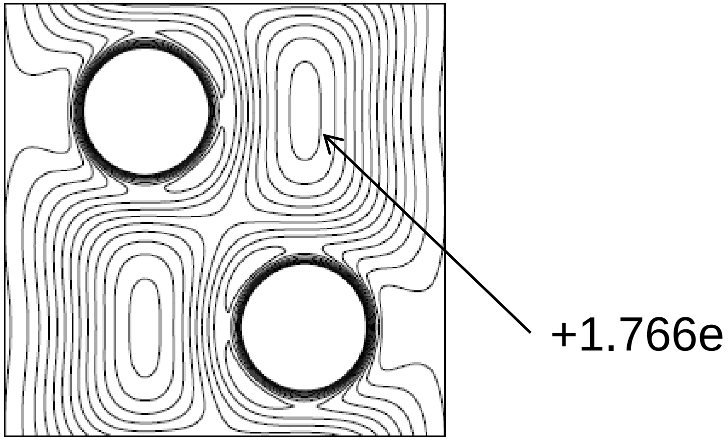


Simet.	Clase	Tipo	x	y	z		Mult.
Oh	(3,-3)	Nucl. Na	0.00000	0.00000	0.00000	+	1
Oh	(3,-3)	Nucl. Cl	0.50000	0.50000	0.50000	+	1
C3v	(3,-1)	Enlace	0.20618	0.20618	0.20618	-	8
D4h	(3,-1)	Enlace	0.00000	0.50000	0.50000	-	3
C2v	(3, 1)	Anillo	0.00000	0.28136	0.28136	+	12
D4h	(3, 3)	Caja	0.00000	0.00000	0.50000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

Local information: CPs

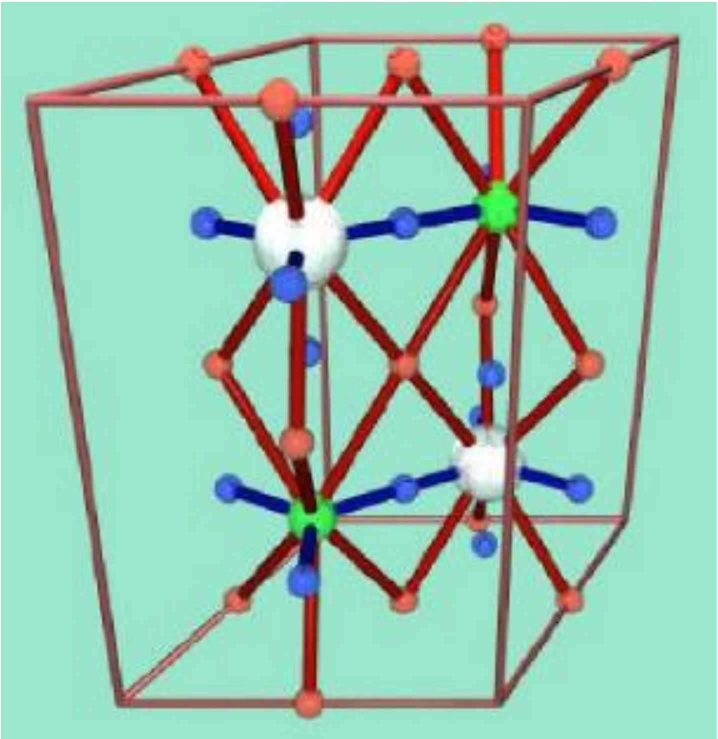


Metals have very flat densities



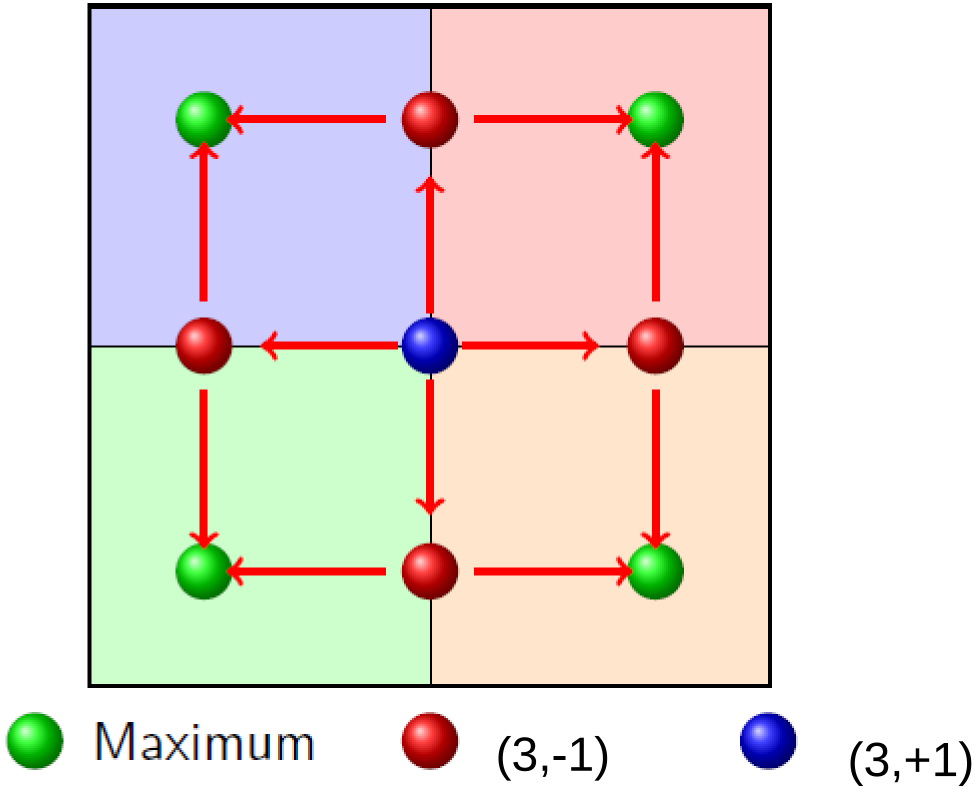
Beriullium HCP

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



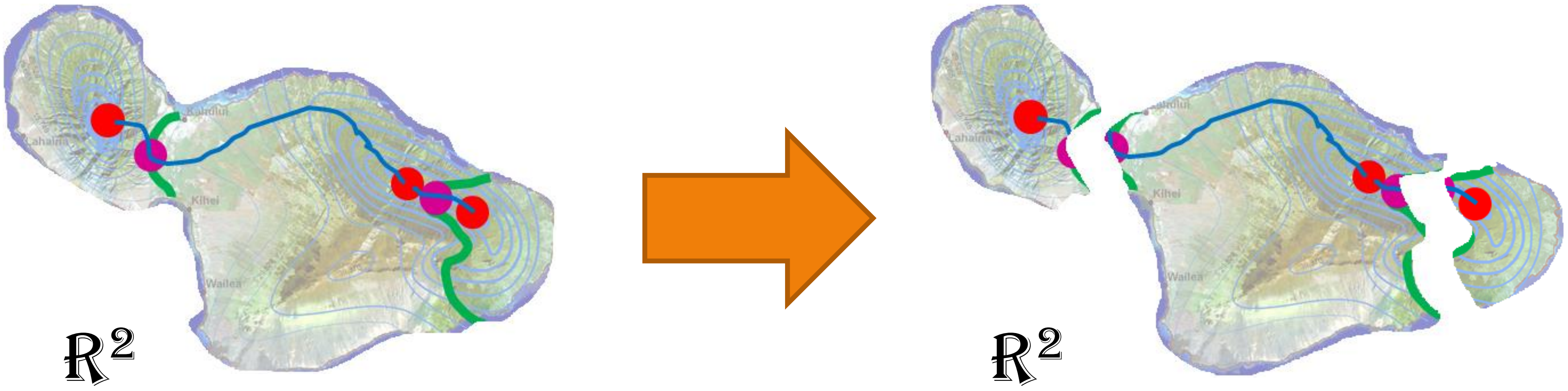
QCT in a nutshell

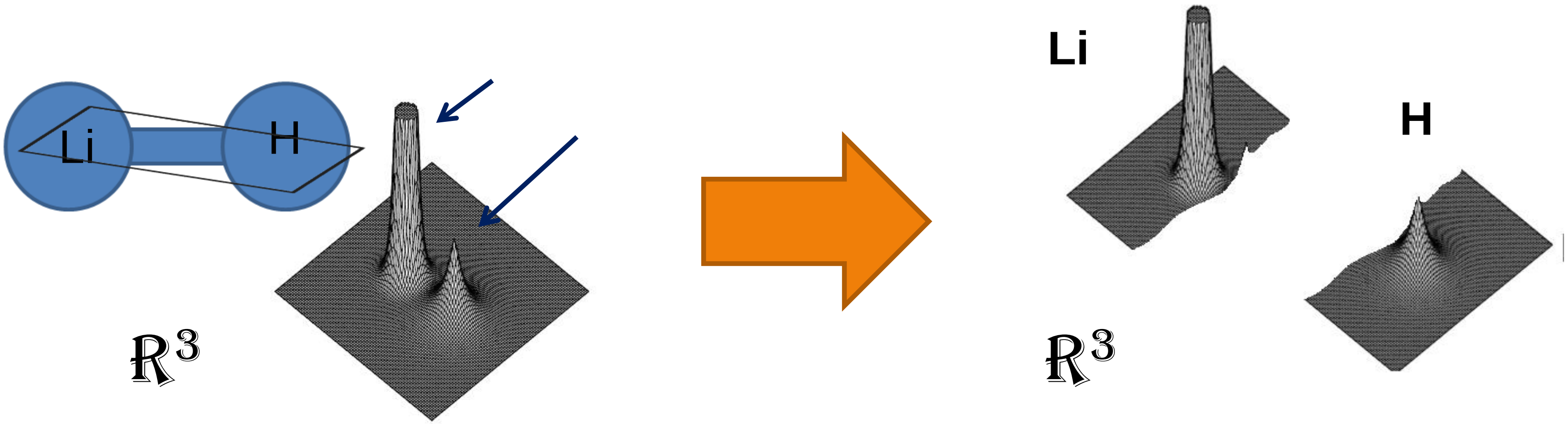
3 Computing the Morse complex of f



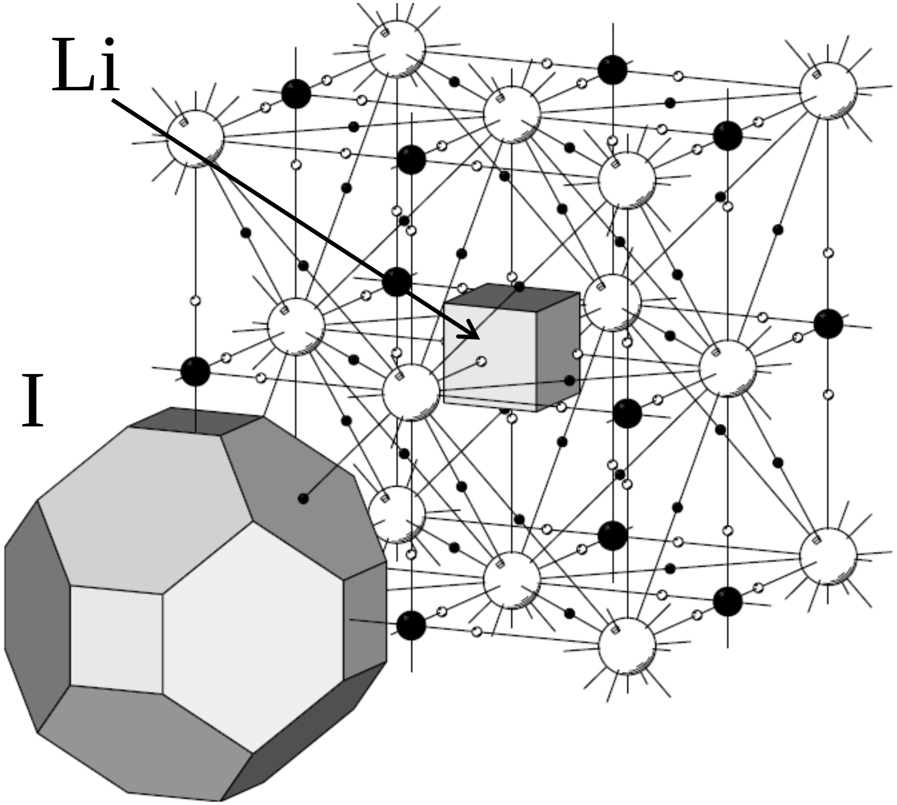
Each maximum has an associated region of space (basin)

Example: the electron density



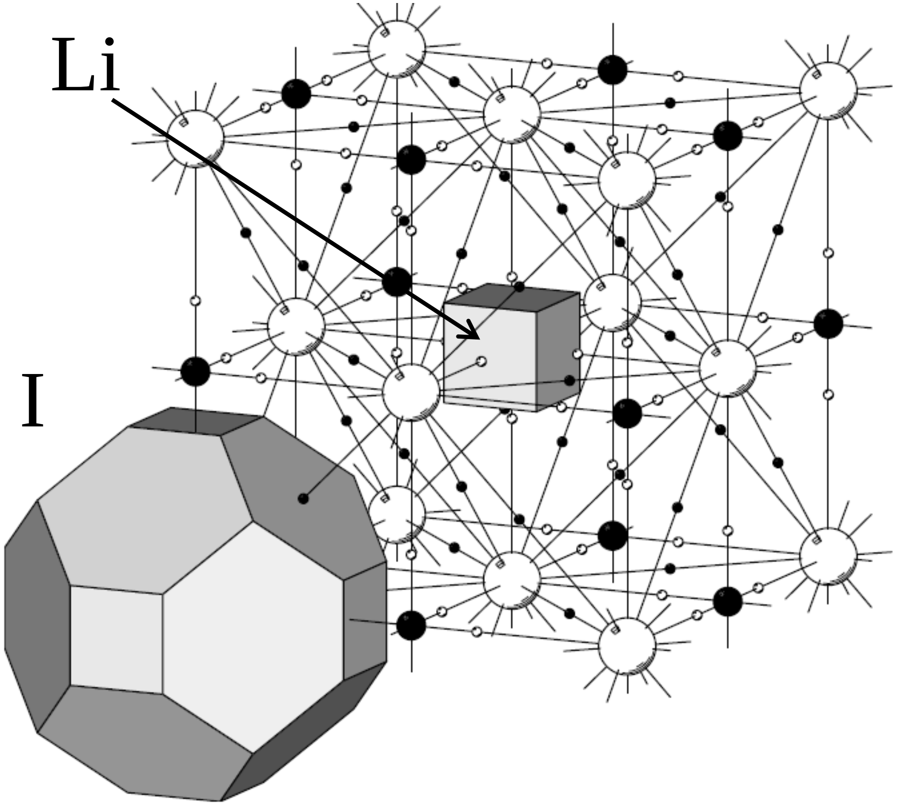


Old concepts

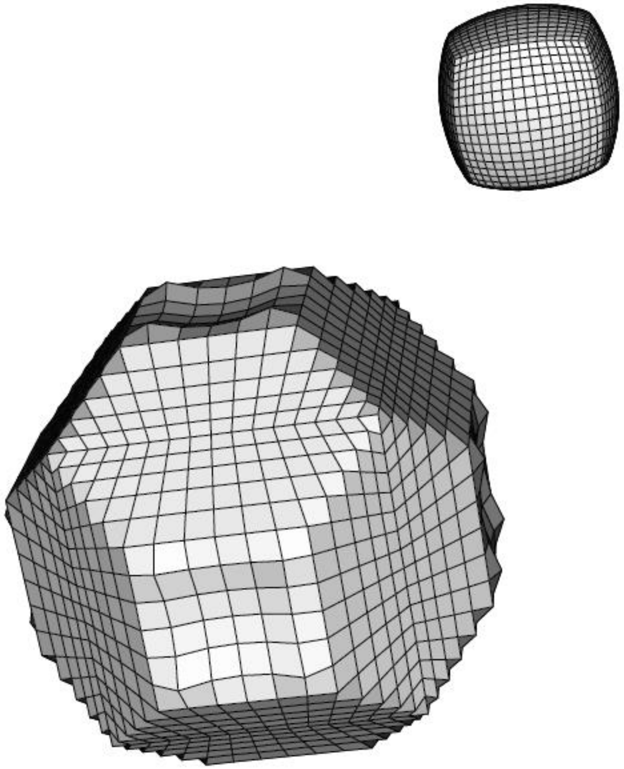


Contact polyhedra

Old concepts



Contact Polyhedra

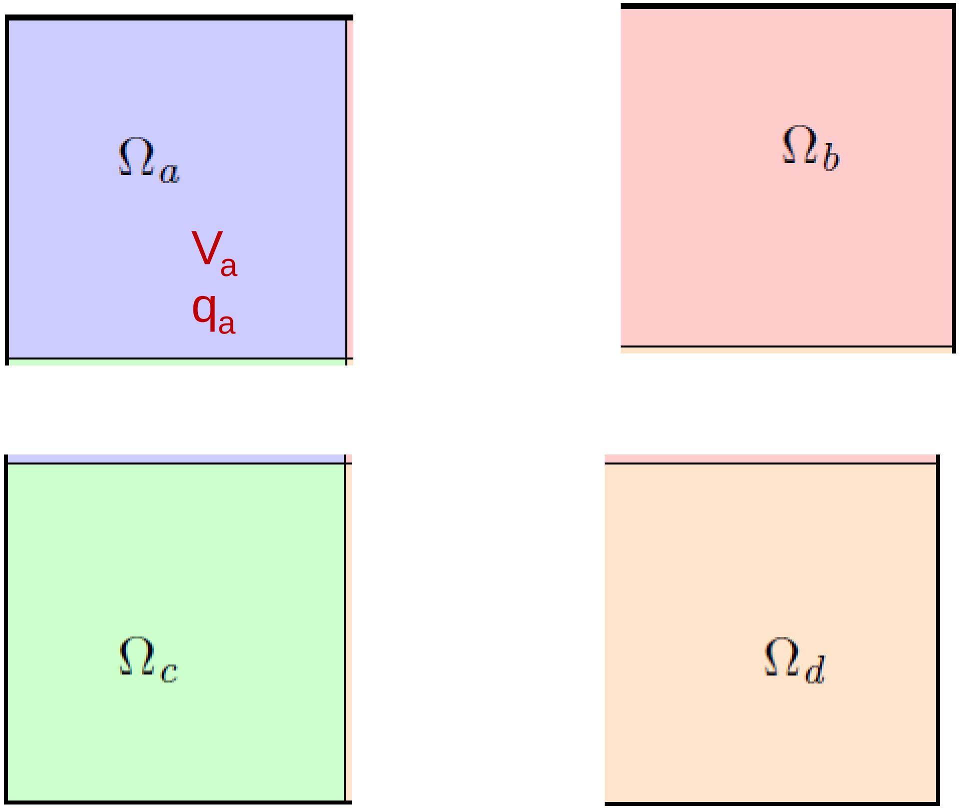


Electron density basins

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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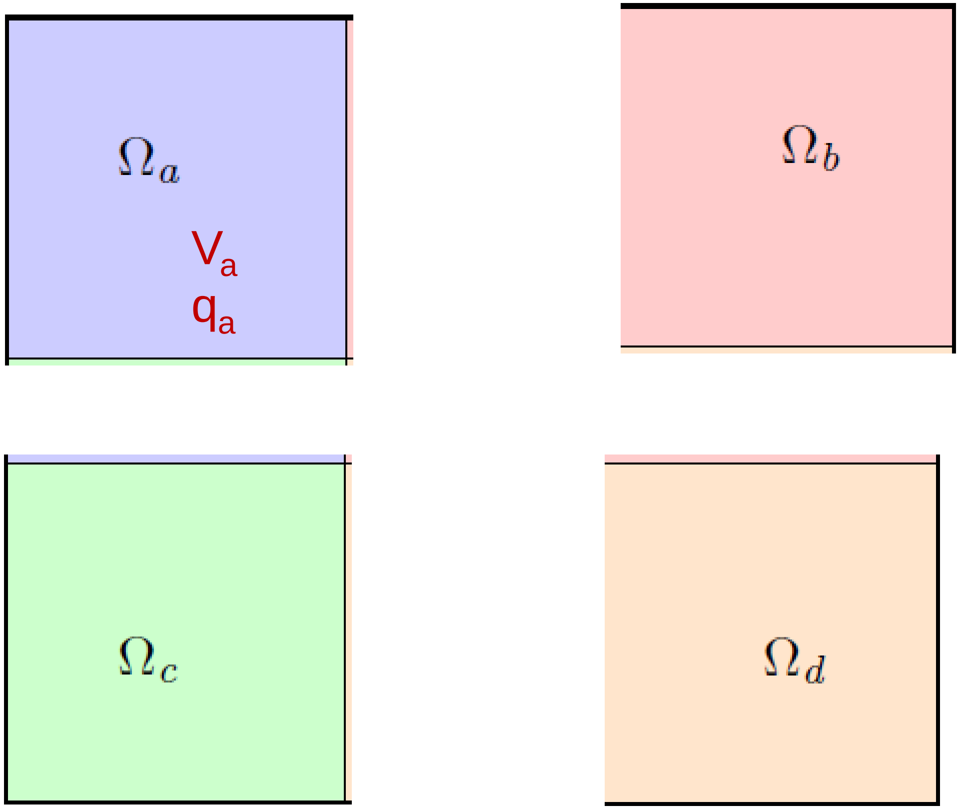
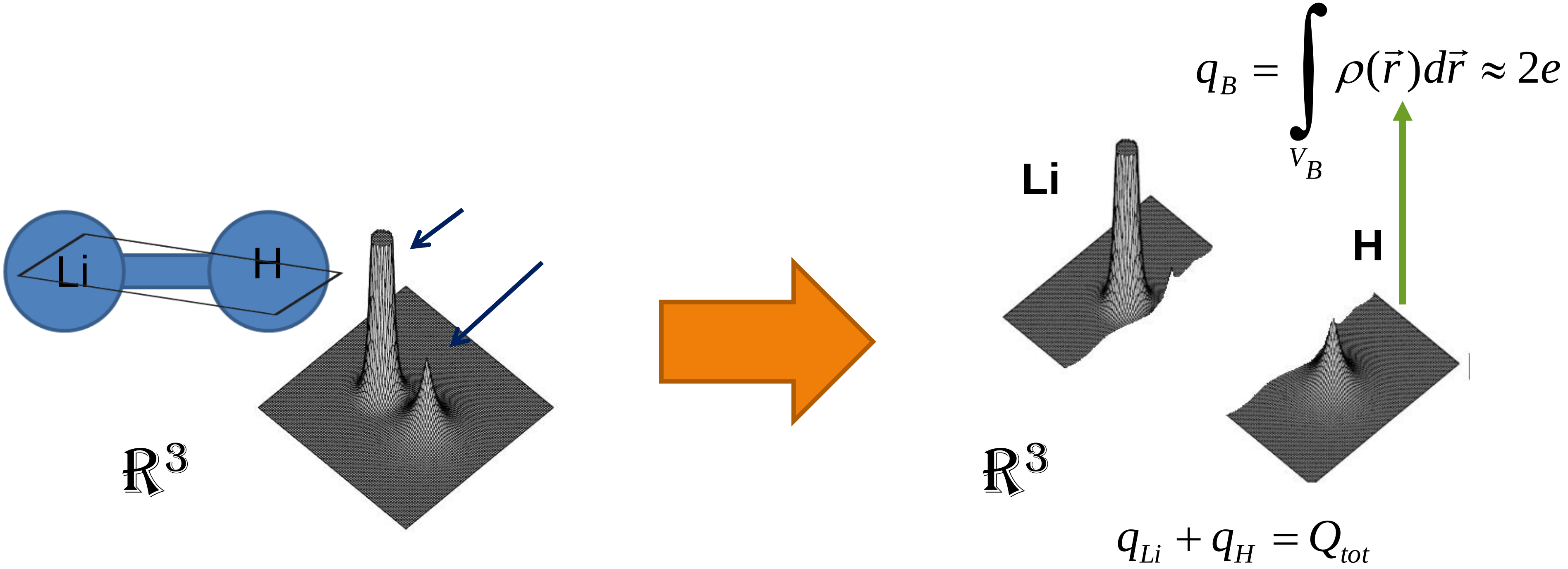


$$N = \sum_A q_A$$

Properties are additive

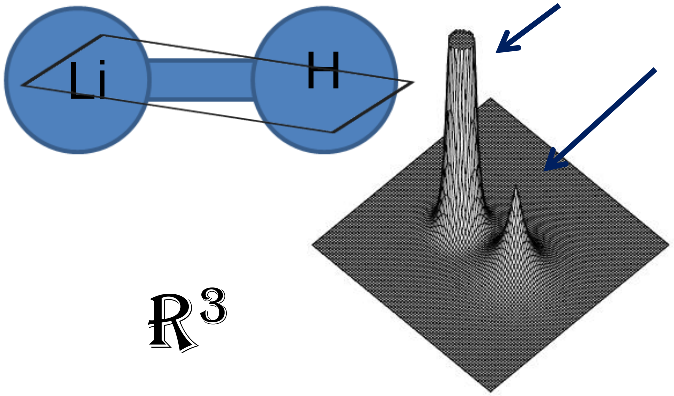


$\mathbb{R}^3$

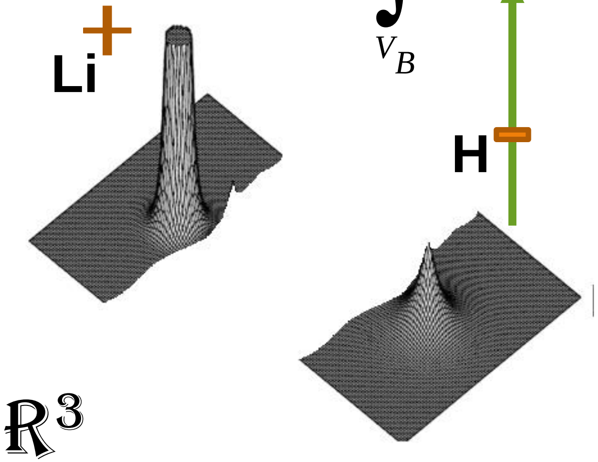
$\mathbb{R}^3$

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

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



$\mathbb{R}^3$



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$\mathbb{R}^3$

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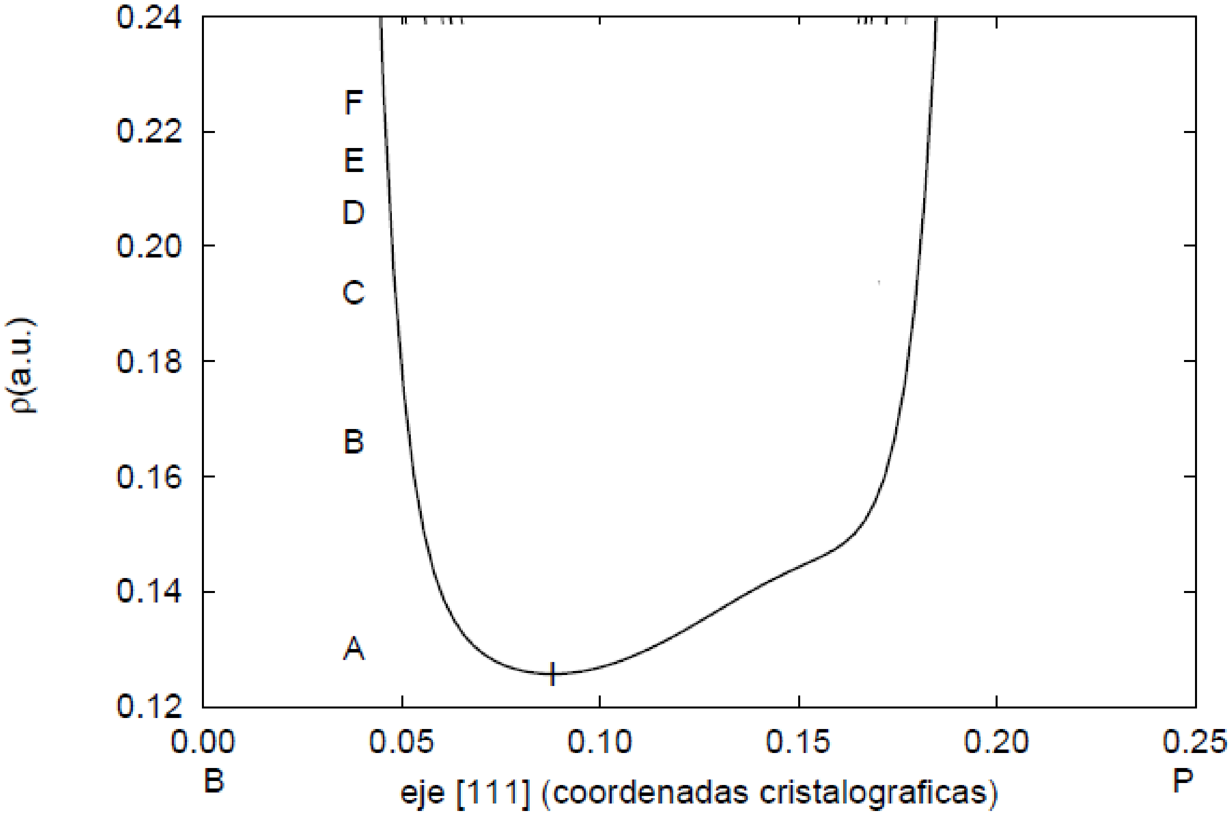
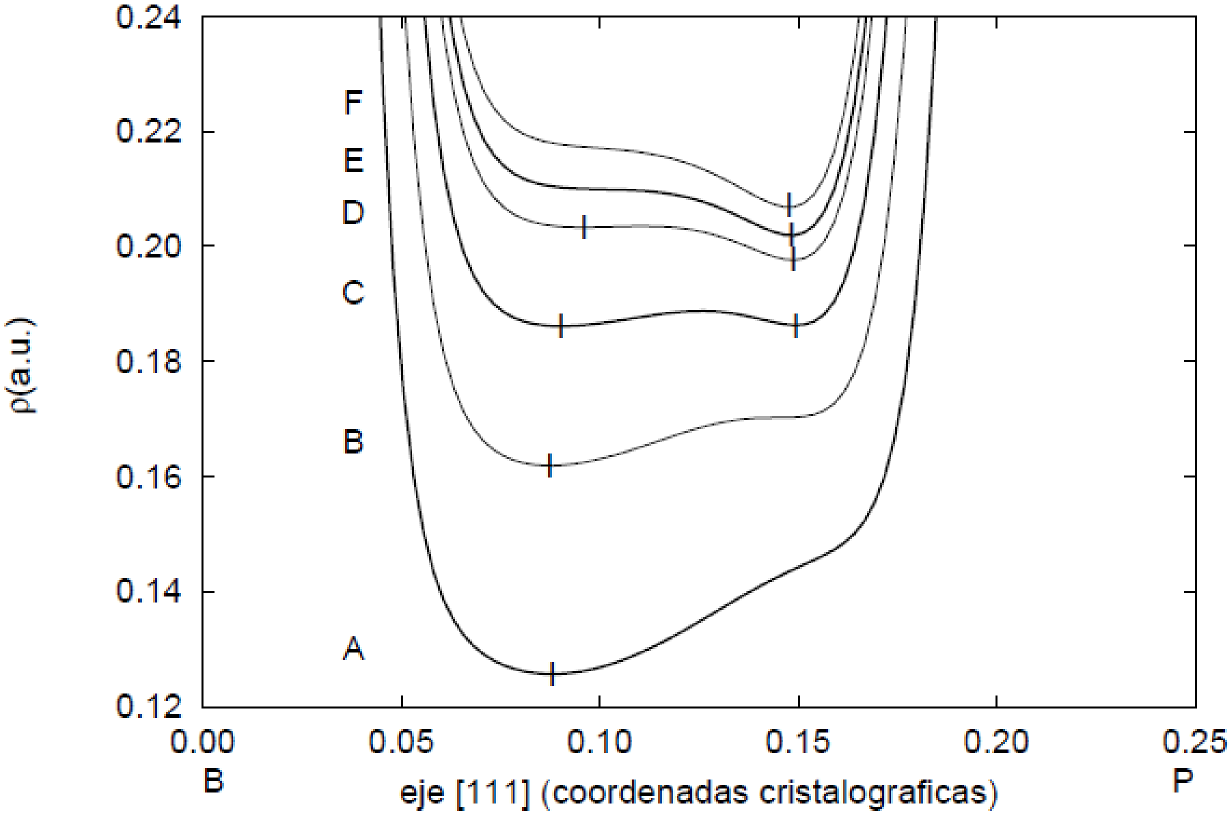
Properties

- 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

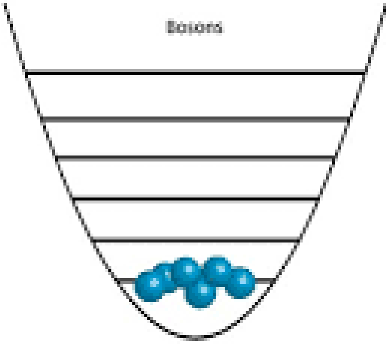
- ELF can be interpreted as an excess of local kinetic energy density due to Pauli repulsion.

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

The electron localization function

Bosonic system (iso-orbital)

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



$$\rho = \sum_i \, |\varphi_i|^2 = |\varphi_j|^2 \qquad \left\{ \begin{aligned} \varphi_j &= \sqrt{\rho} \\ \nabla\varphi_j &= \frac{\nabla\rho}{2\sqrt{\rho}} \end{aligned} \right.$$

Kinetic energy densities

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

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

Its a scaled reference

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

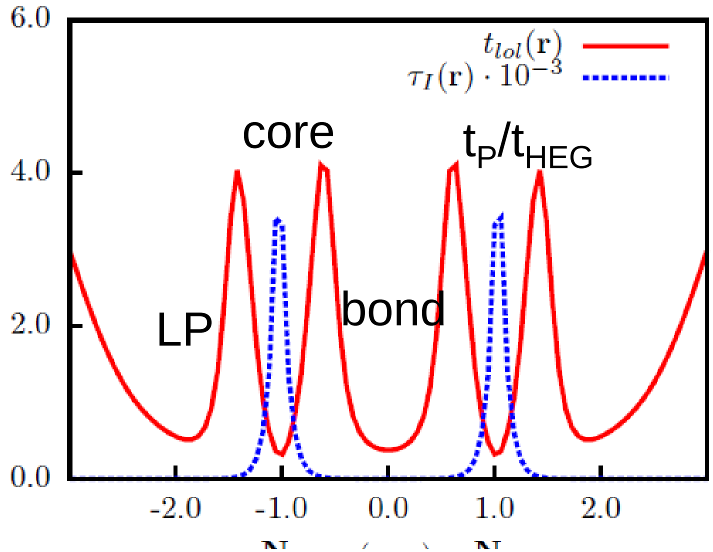
The electron localization function

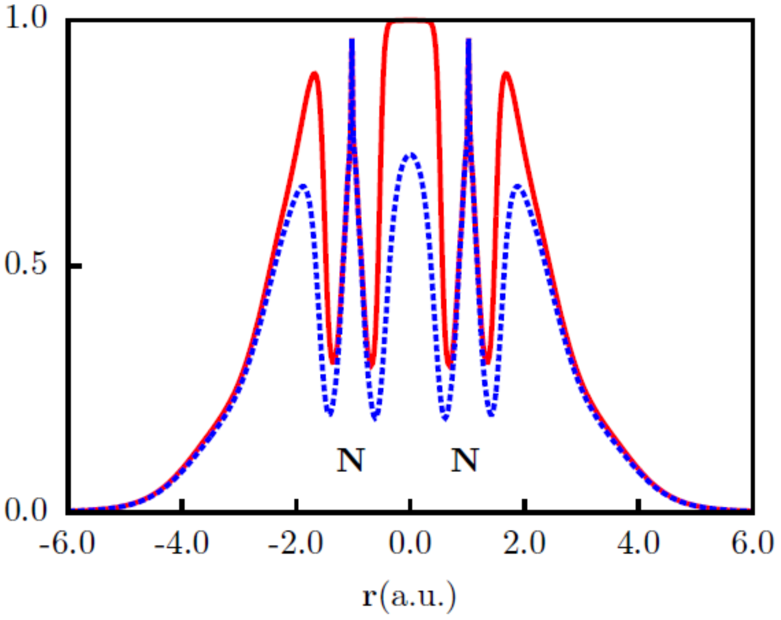
Fermionic information

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

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

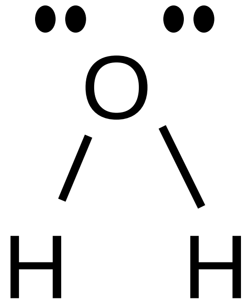
$$\chi(\vec{r}) = \frac{t_P(\vec{r})}{c_F\,\rho(\vec{r})^{5/3}} \qquad ELF = \frac{1}{\left(1+\chi^2(\vec{r})\right)}$$





The electron localization function

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



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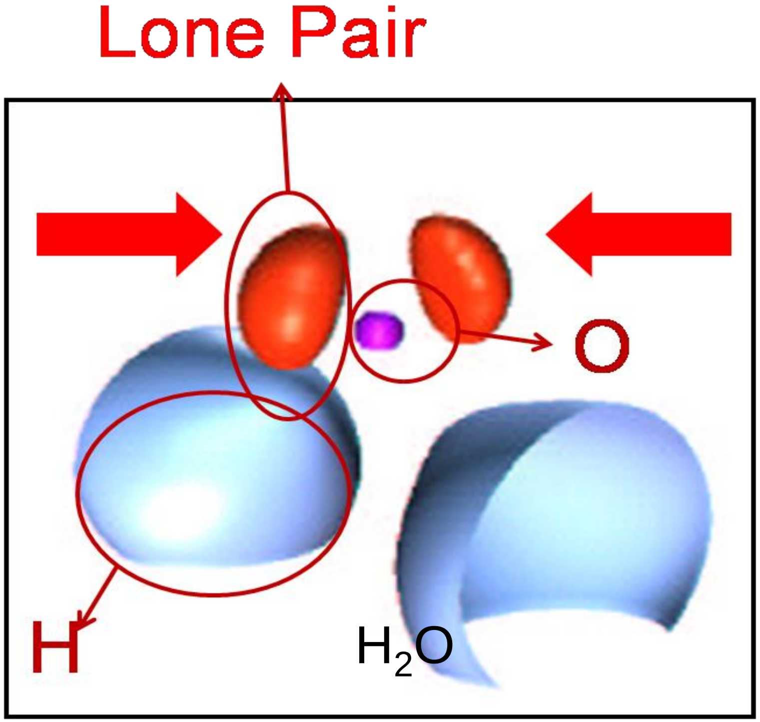

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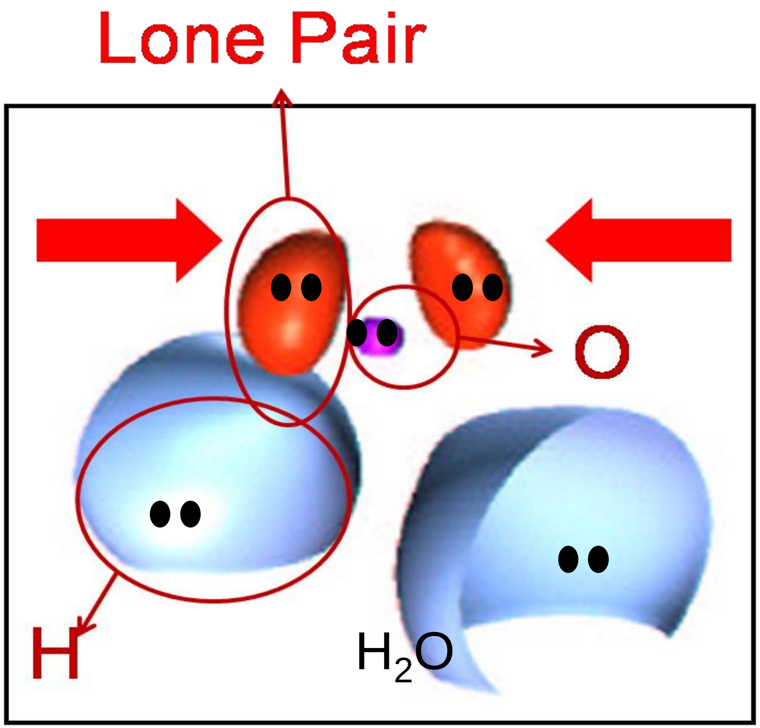
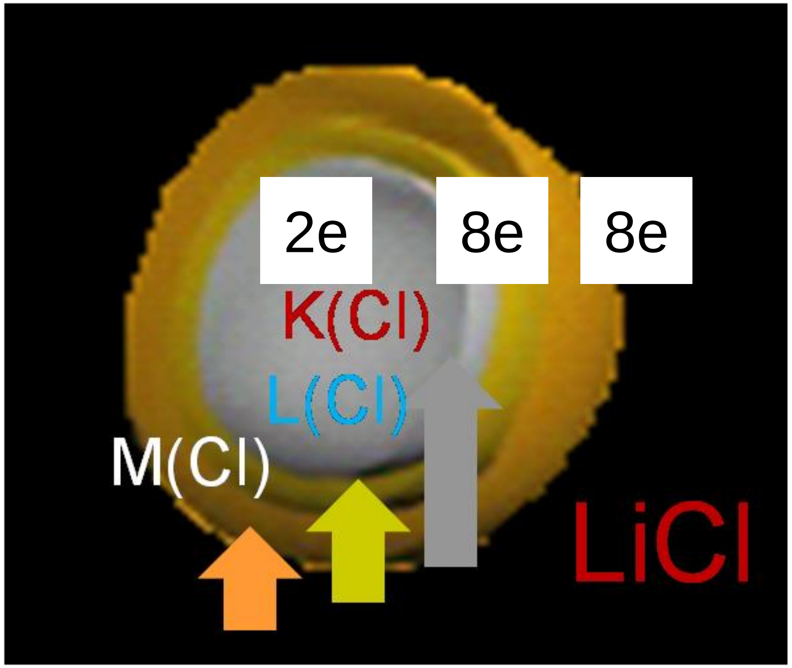


The electron localization function

- It recovers the Lewis picture of a system

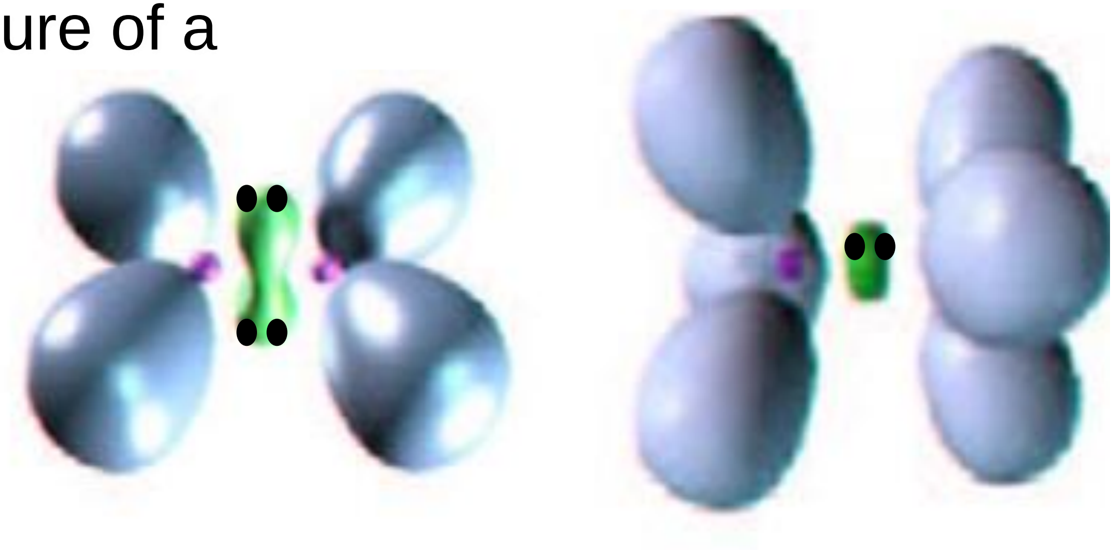
- ELF is close to one in:
  - Lone pairs
  - Atomic shells



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



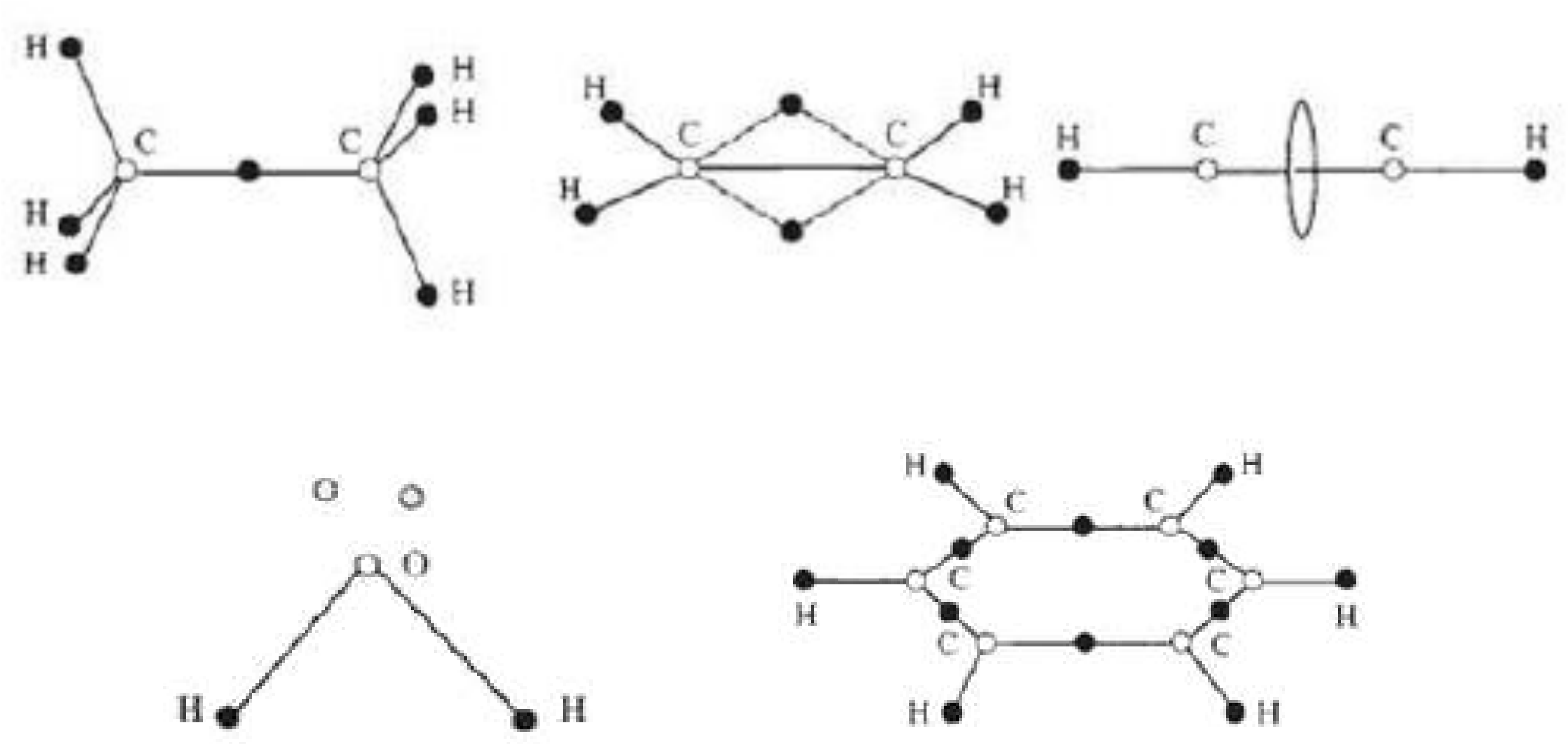
$H_2C=CH_2$

$H_3C\text{-}CH_3$

Bond order

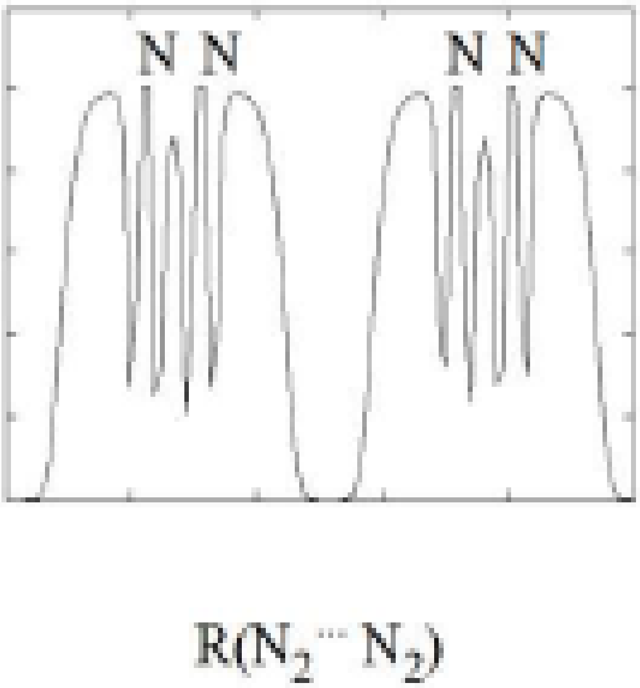
The electron localization function

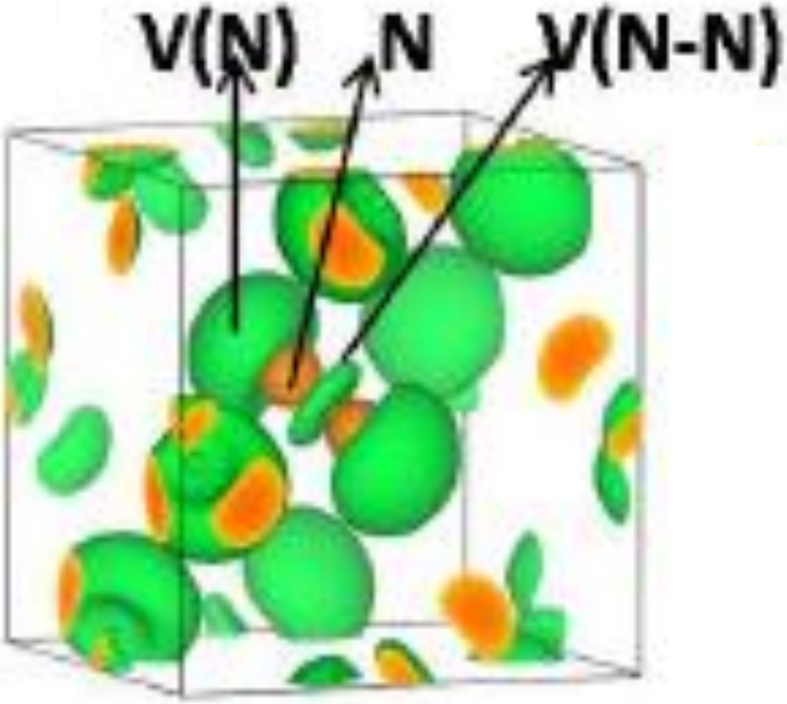
Critical points



ELF in solids

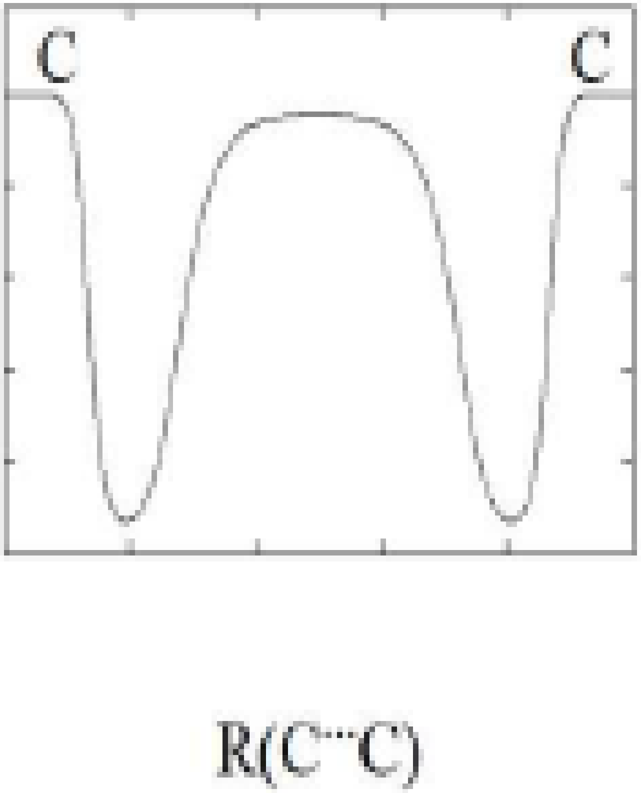
Molecular solids

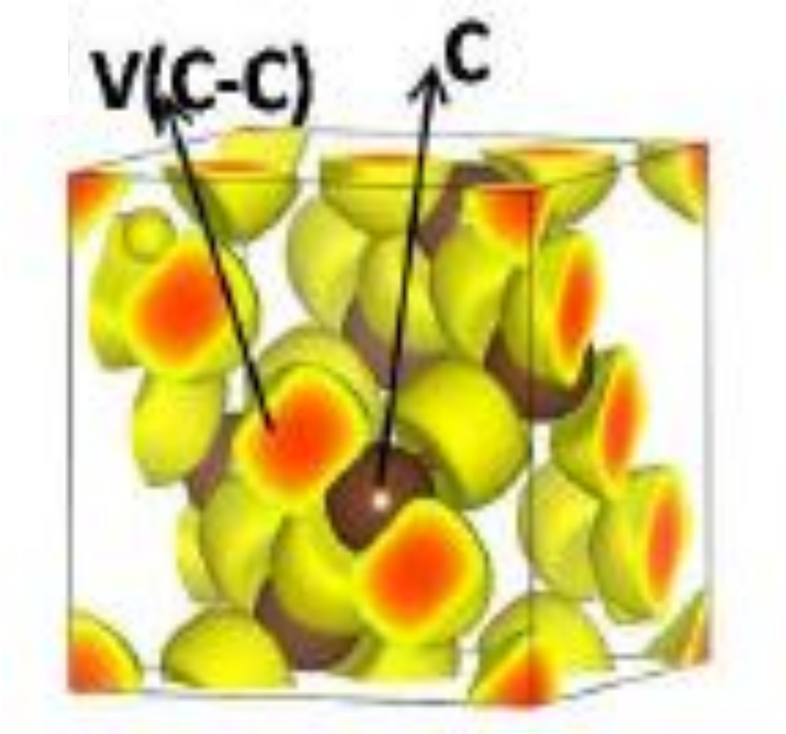




ELF in solids

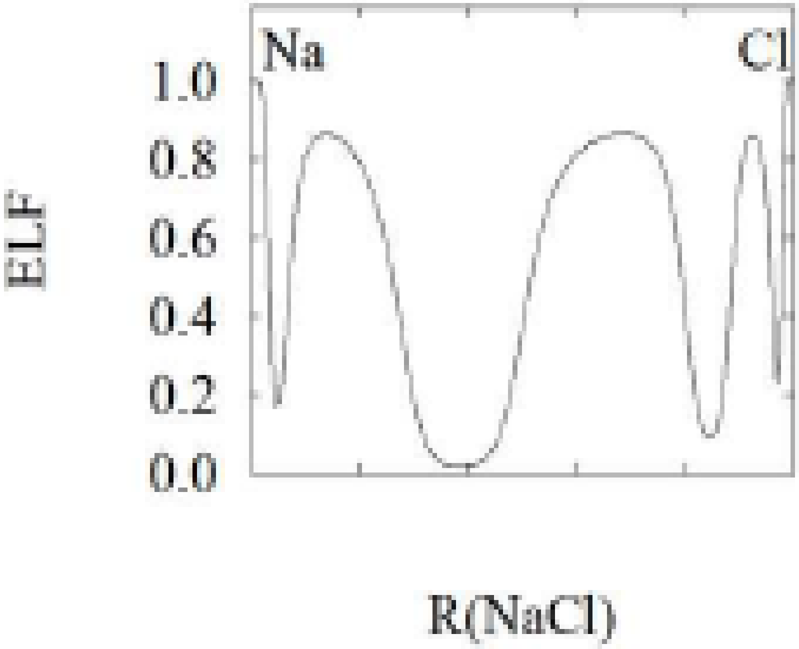
Covalent solids

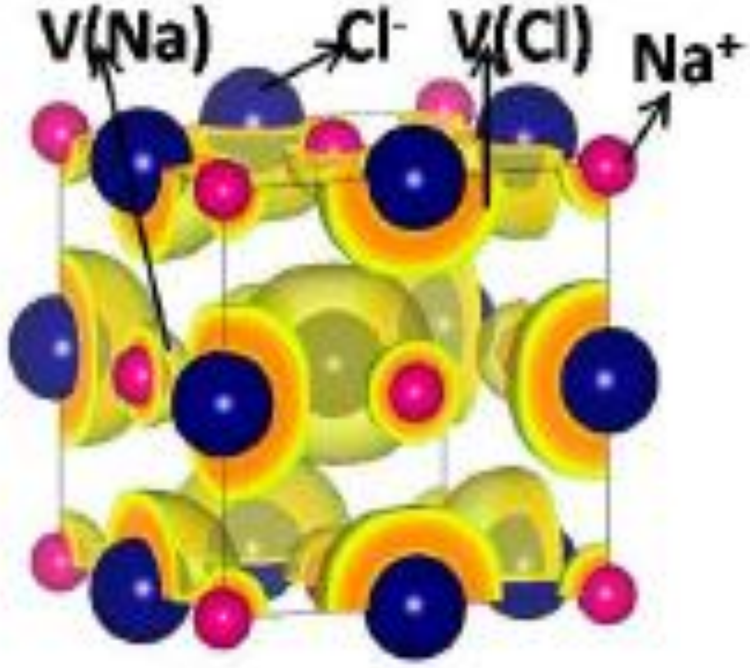




ELF in solids

Ionic solids

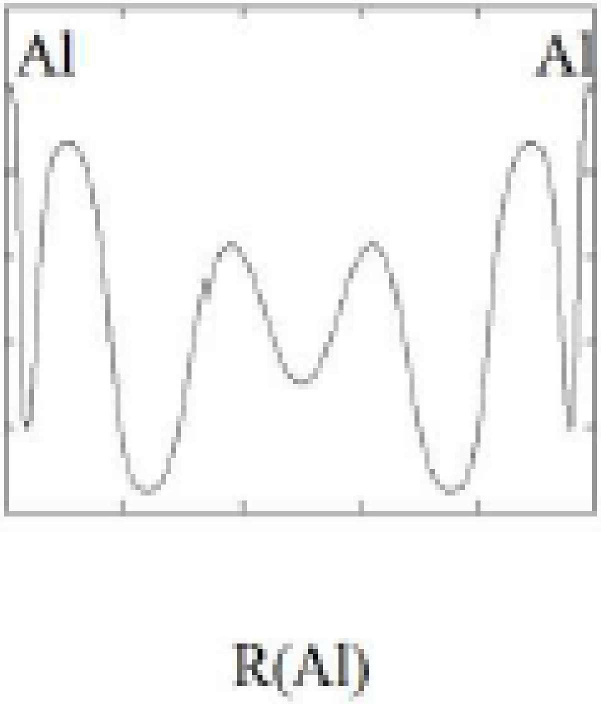


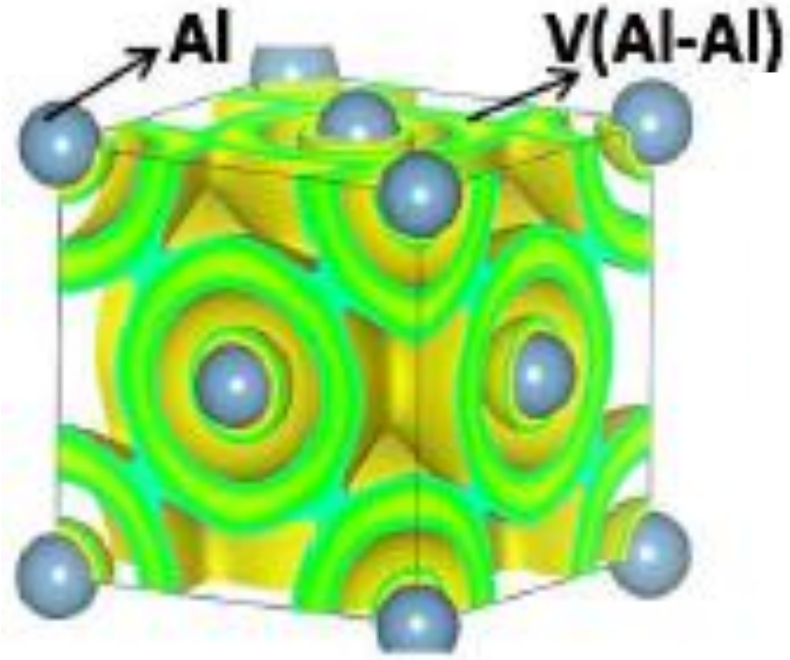


Charge transfer is verified
Na=10 e
Cl=18 e

ELF in solids

Metals



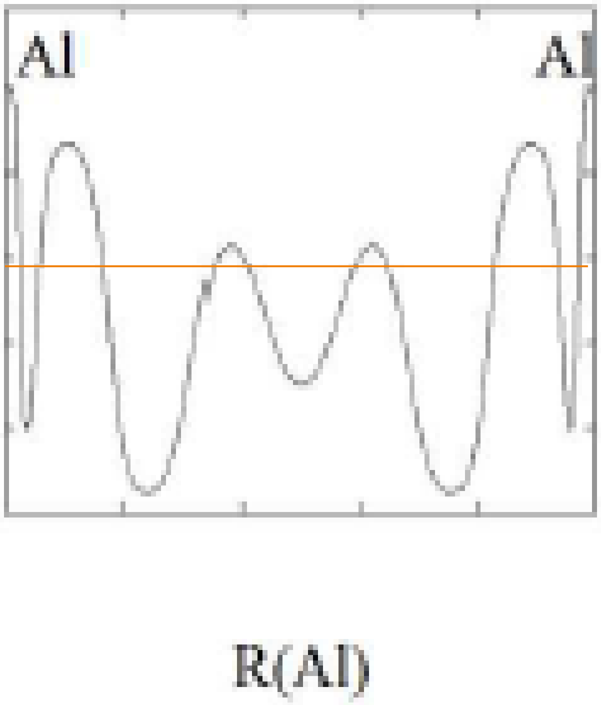


ELF in solids

Metals

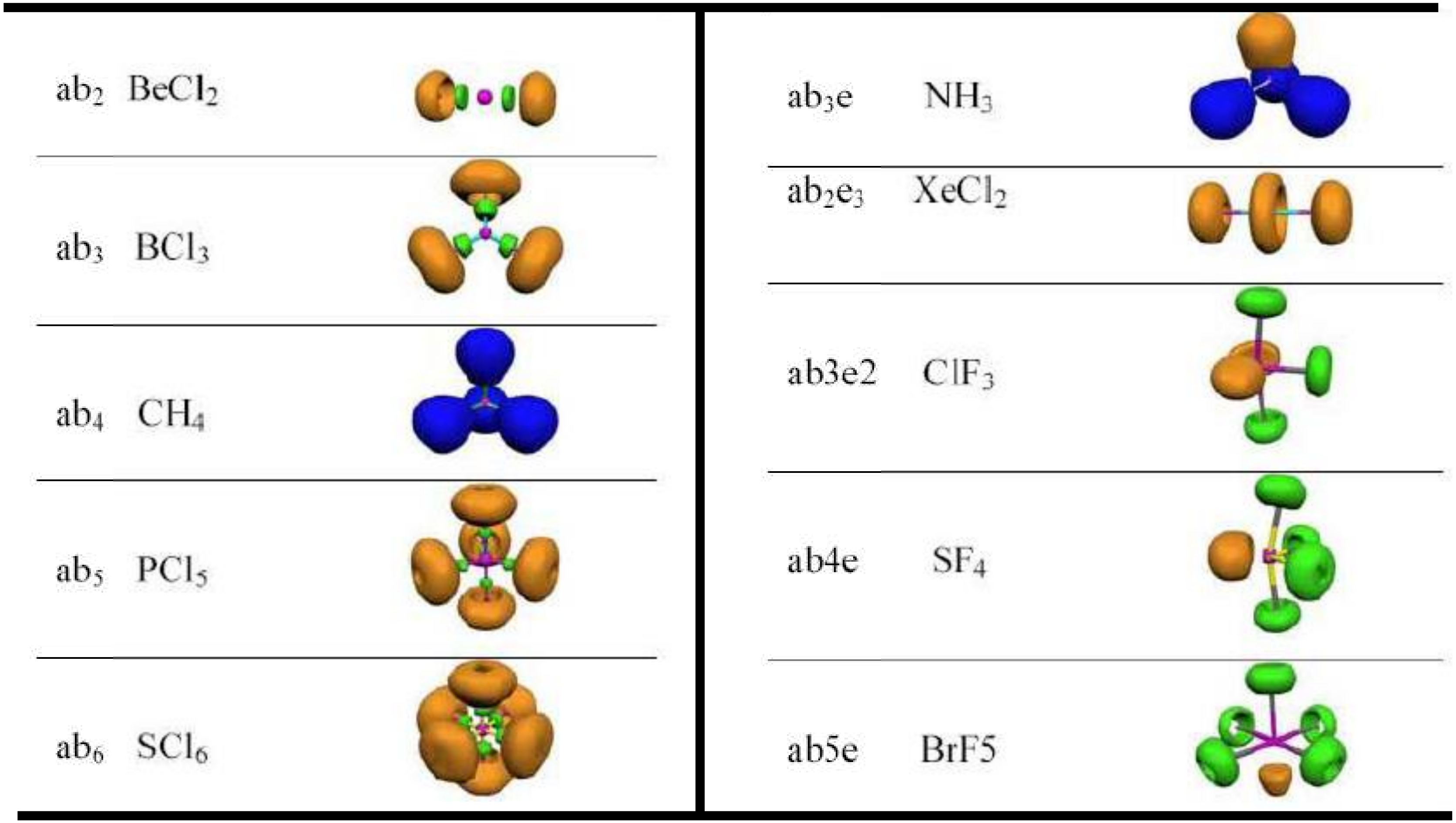
$$\chi(\vec{r}) = \frac{t_P(\vec{r})}{c_F\,\rho(\vec{r})^{5/3}} \qquad ELF = \frac{1}{\left(1+\chi^2(\vec{r})\right)}$$

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



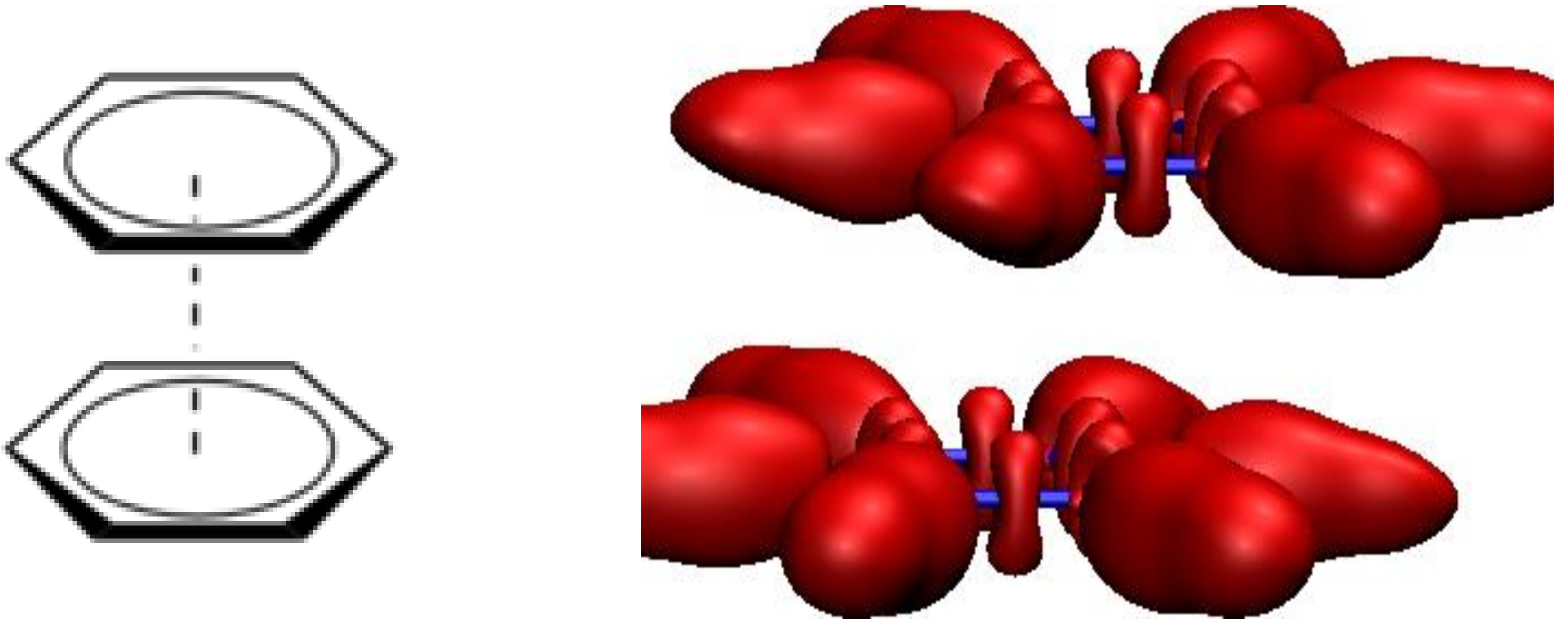
Metallic valence close to HEG

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?

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   a) electron density

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- The function
- The topology
- Old insight
- New insight

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 $\nabla\rho \to 0$

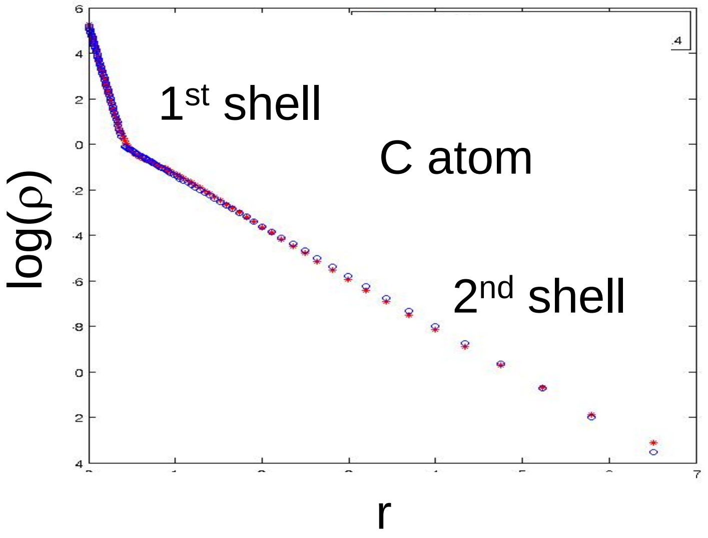
NCI:

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

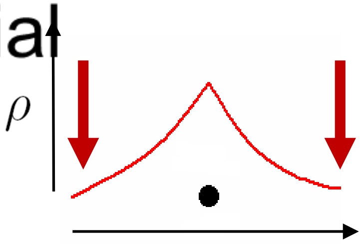
$$\rho^{at}(r) = \sum_{i}^{Nshells} c_i e^{-\zeta_i r}$$

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

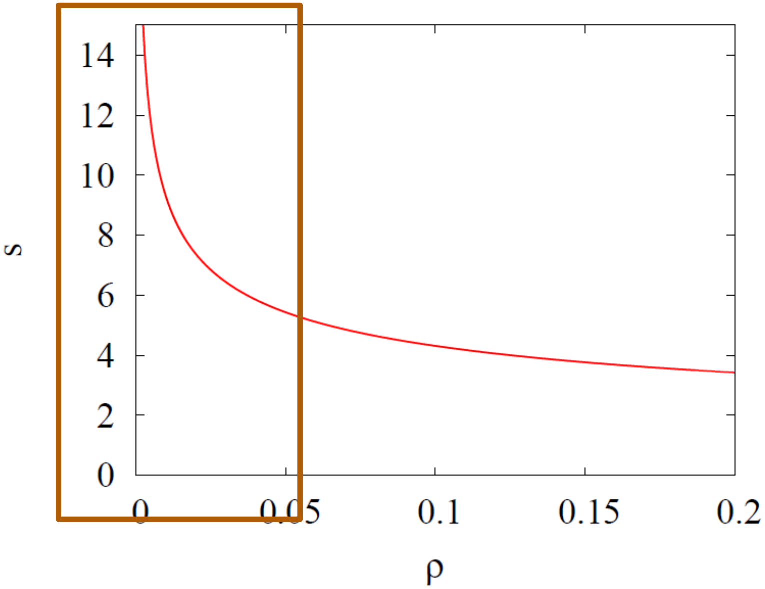
$$\rho_{1s} = \frac{n_{1s}}{\pi}\left(\frac{Z}{a_0}\right)^3 e^{-2Zr/a_0}$$

Atoms

At ∞ Taking the outermost exponential



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



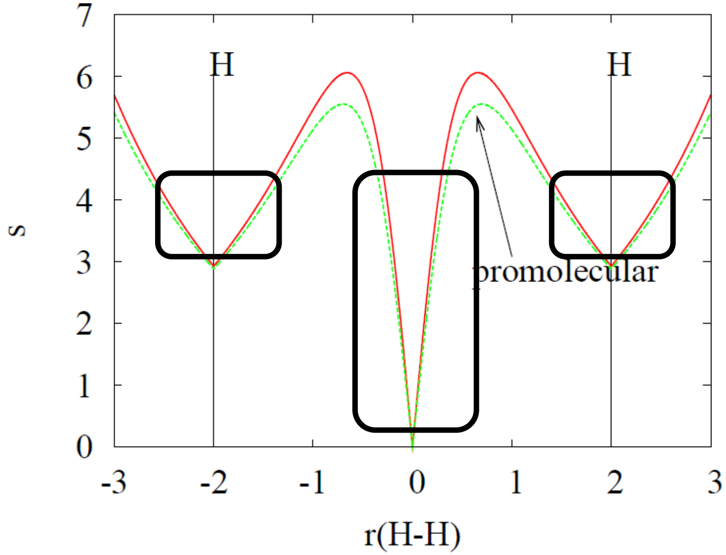
- $\lim_{r\to\infty} s(r) = \infty$ (i.e. when $\rho \to 0$)

Model densities

Molecules

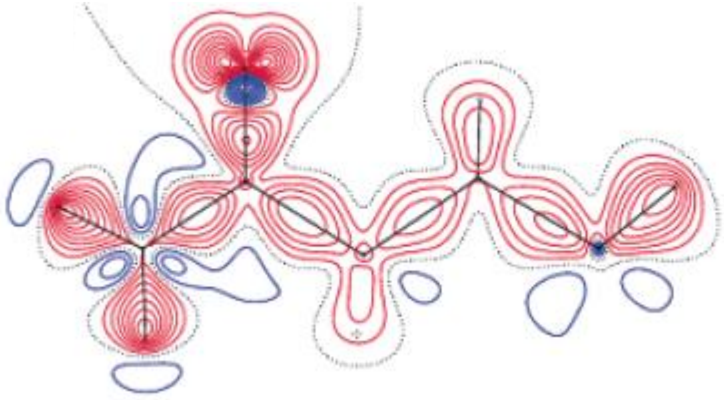
- Promolecular densities: no interference (SCF cycle 0)

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



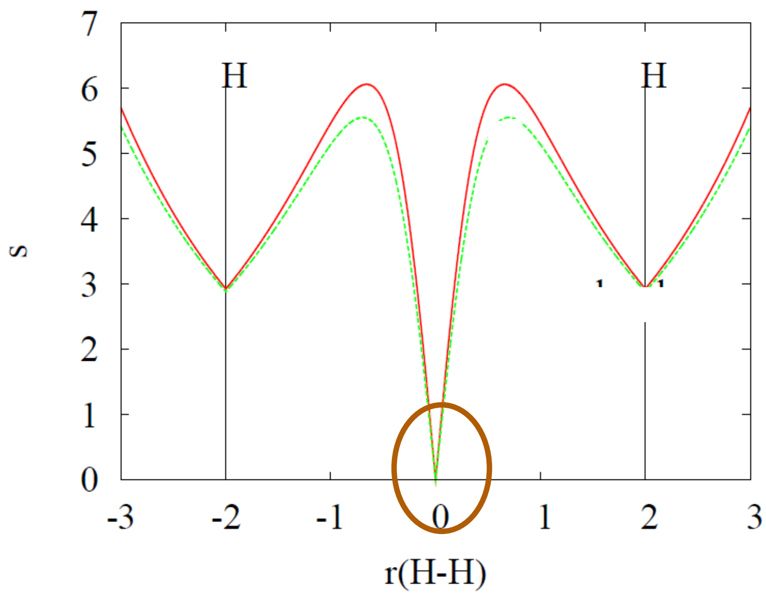
- Works specially well at low densities ($s \to 0$) at atomic positions (1s orbital)

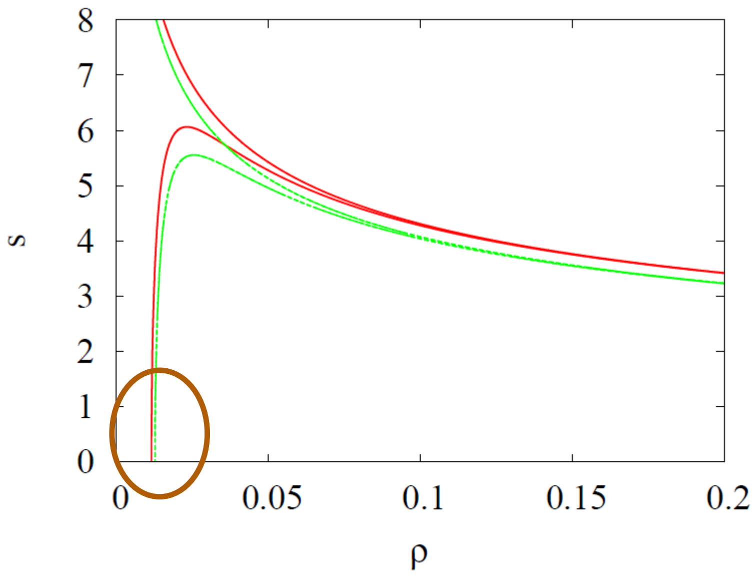
Promolecular densities



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

Interactions





- Promolecular approach

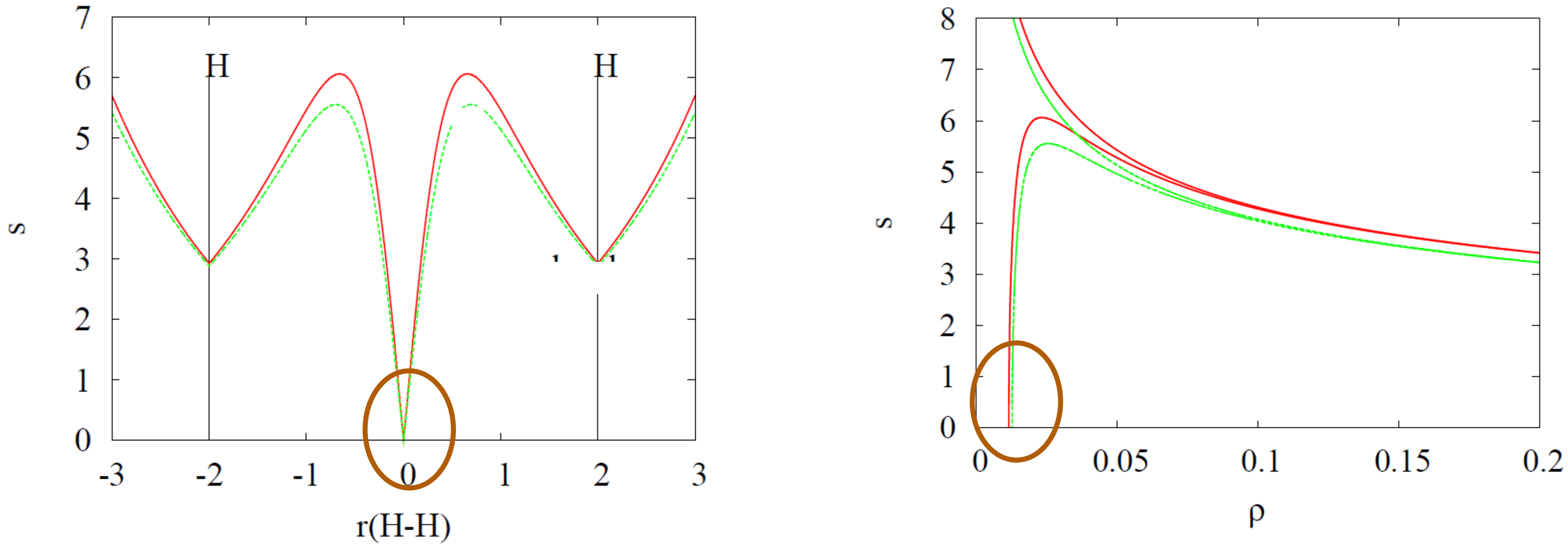
$$\rho(x,y,z) = \rho_{1s}^{A} + \rho_{1s}^{B} = \left(ce^{-\zeta\sqrt{x^2+y^2+(z-R/2)^2}}\right)^2 + \left(ce^{-\zeta\sqrt{x^2+y^2+(z+R/2)^2}}\right)^2$$

- s goes to 0 in the interactions

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

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

Interactions



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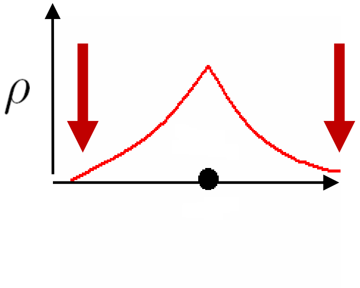
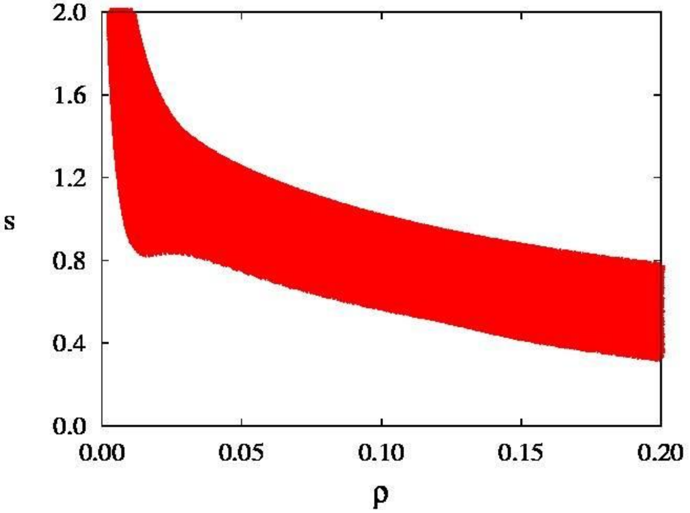
Let's see an example!

The reduced density gradient

Non-interacting densities

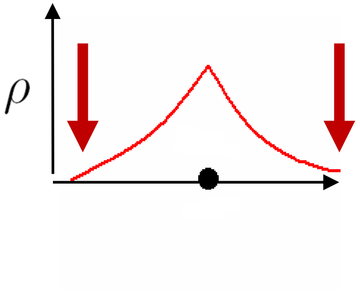


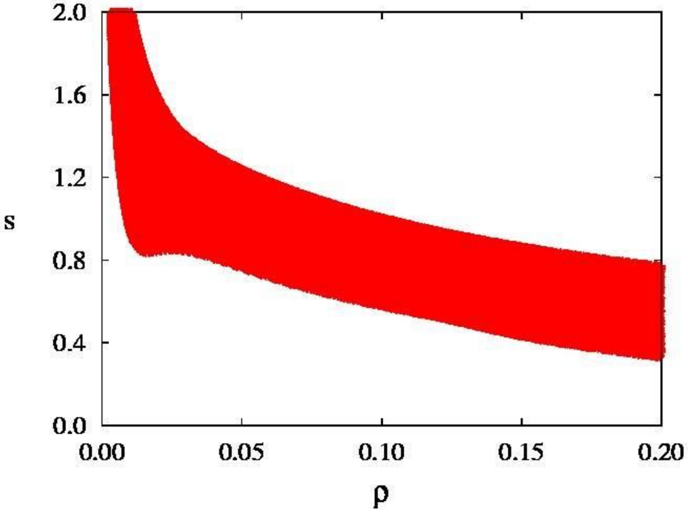
$$s(\rho) \propto \rho^{-1/3} \xrightarrow{\rho\to 0} \infty$$



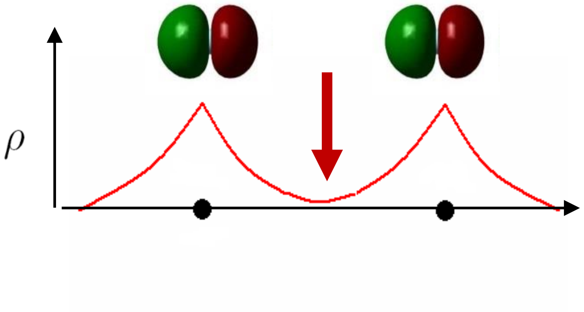
The reduced density gradient

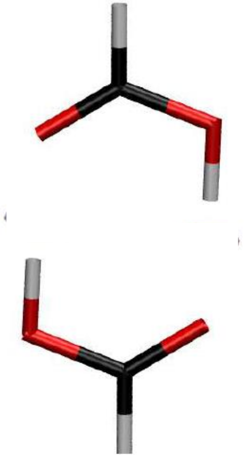
Non-interacting densities

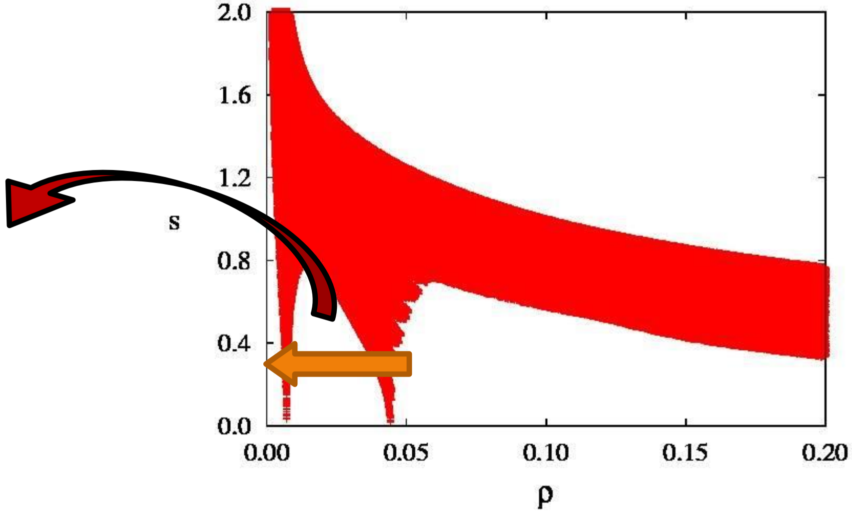




Interacting densities



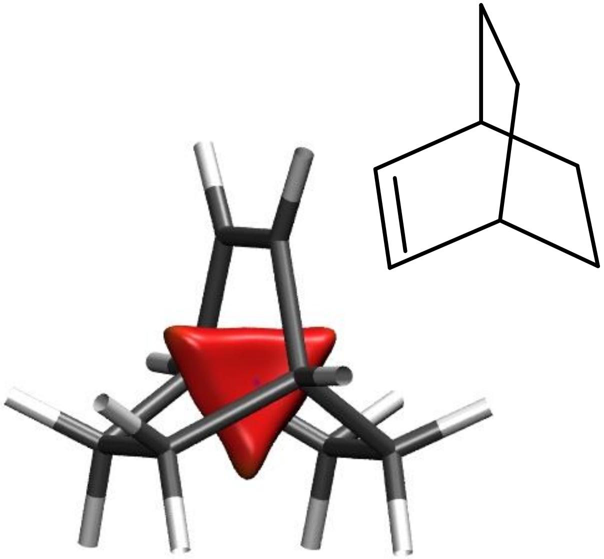


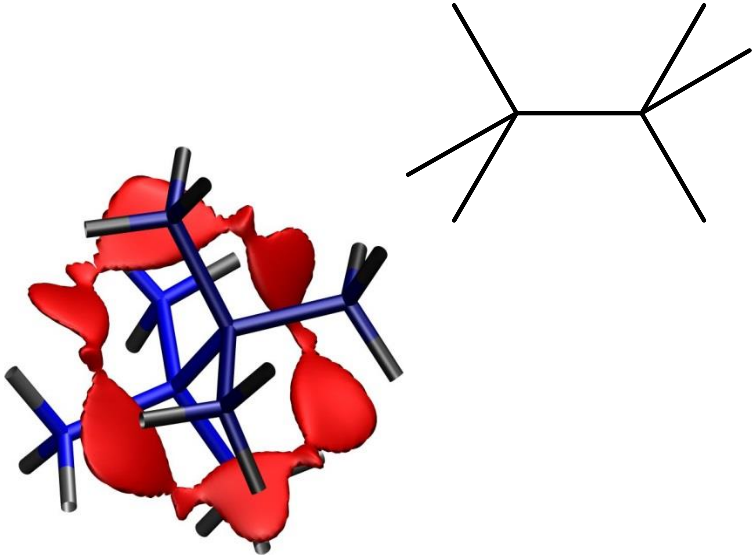


The reduced density gradient

Repulsive interactions

- Steric clashes

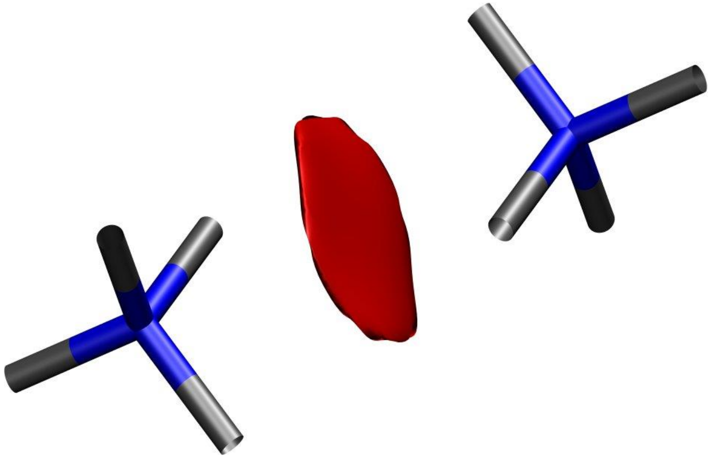




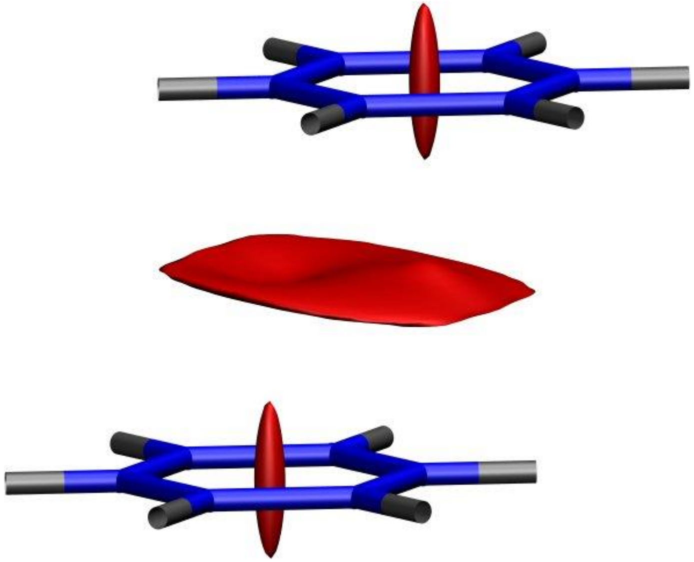
The reduced density gradient

Weak interactions

- Van der Waals



Methane dimer

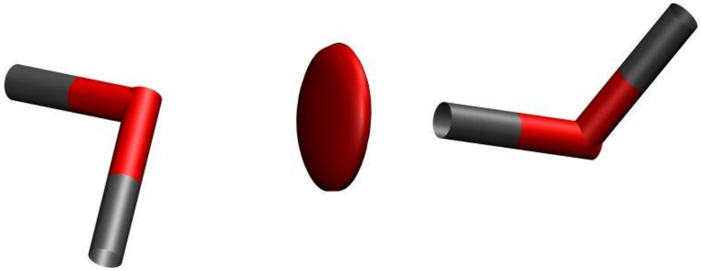


Benzene dimer

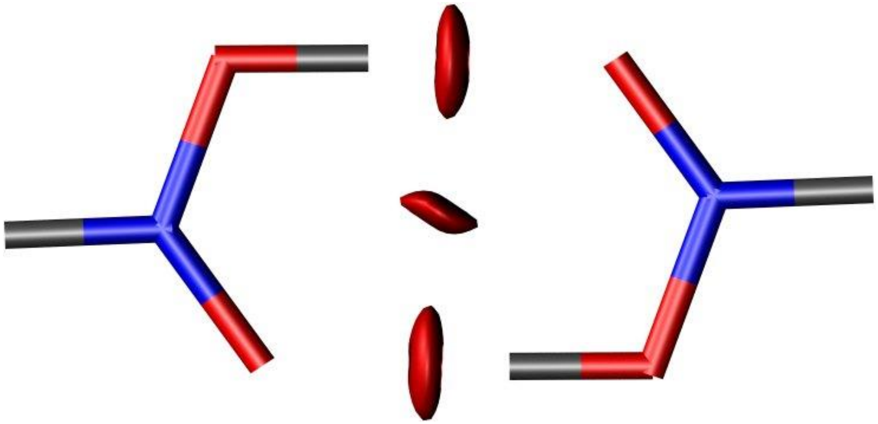
The reduced density gradient

Strongly attractive interactions

- Hydrogen bonds



Water dimer

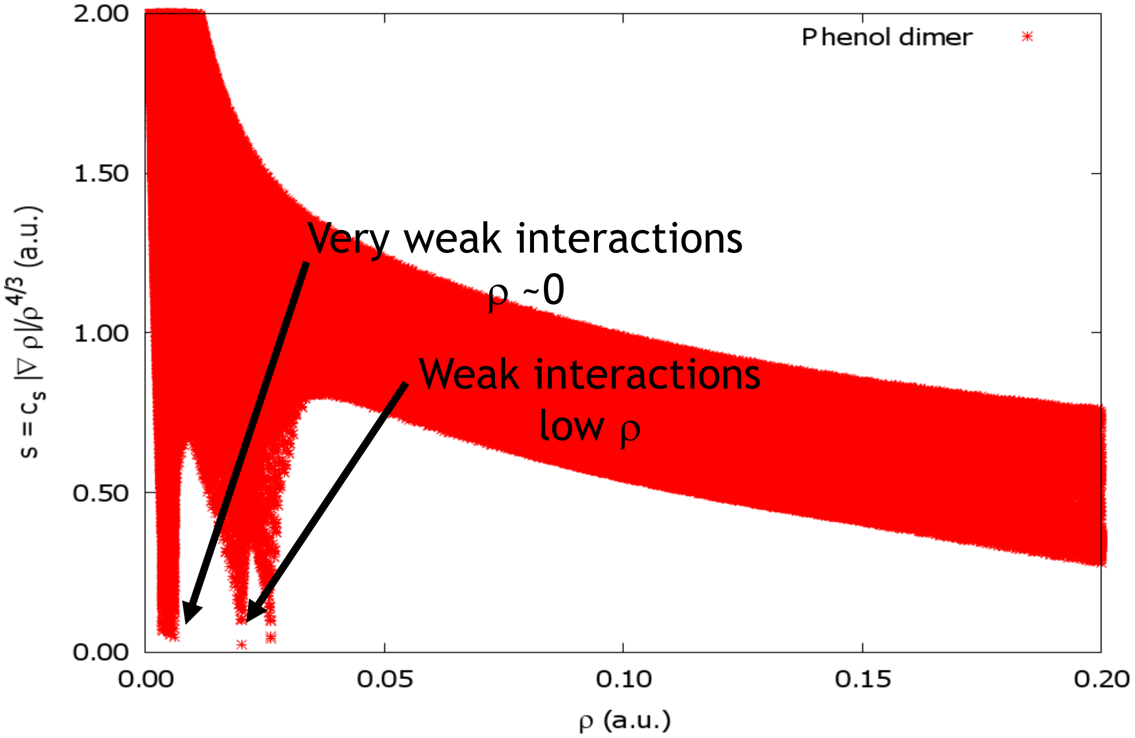


Formic acid dimer

The reduced density gradient

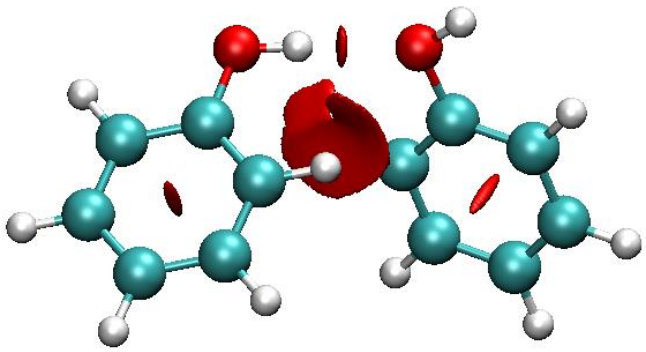
Differentiating interaction types

① •Density is proportional to the strength of the interaction



Very weak interactions
ρ ~0

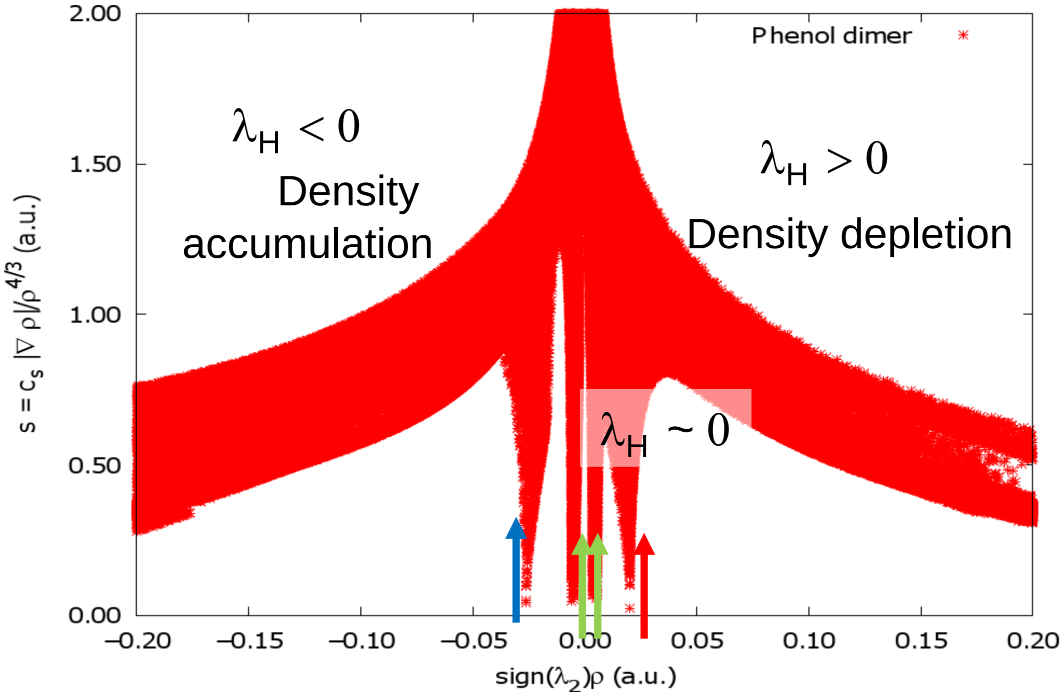
Weak interactions
low ρ

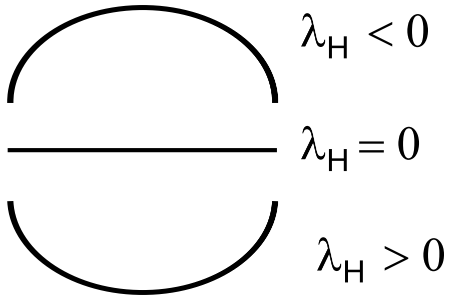


The reduced density gradient

Differentiating interaction types

②
- •Bonding interactions →charge accumulation ($\lambda_H < 0$)
- •Antibonding interactions → charge depletion ($\lambda_H > 0$)

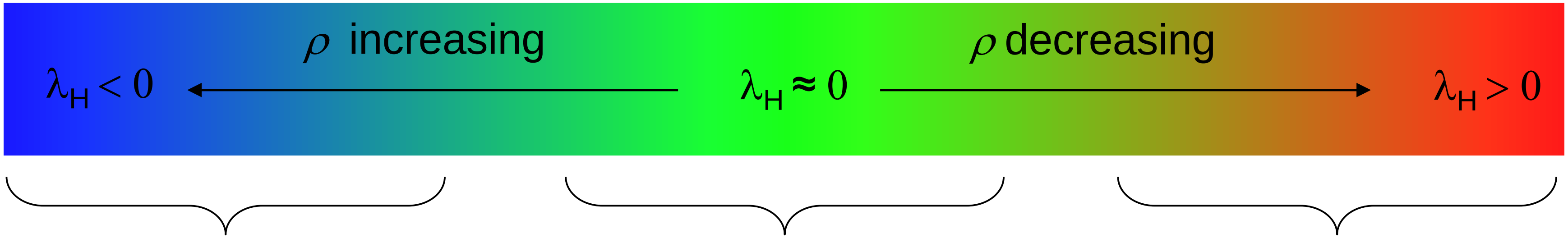




The reduced density gradient

1) Represent s isosurfaces in real space

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



ρ increasing

ρ decreasing

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

Strong and attractive:

Hydrogen bonds

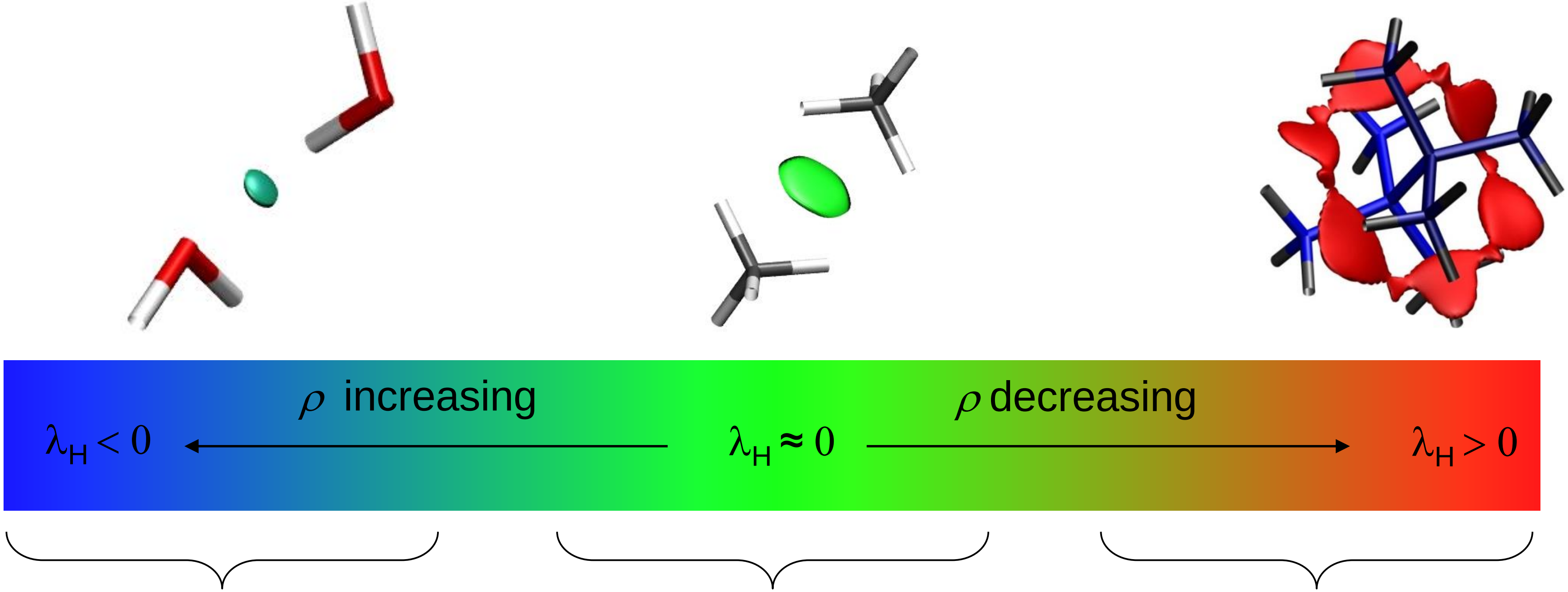
Very weak:

van der Waals

Strong and repulsive:

Steric clashes

The reduced density gradient



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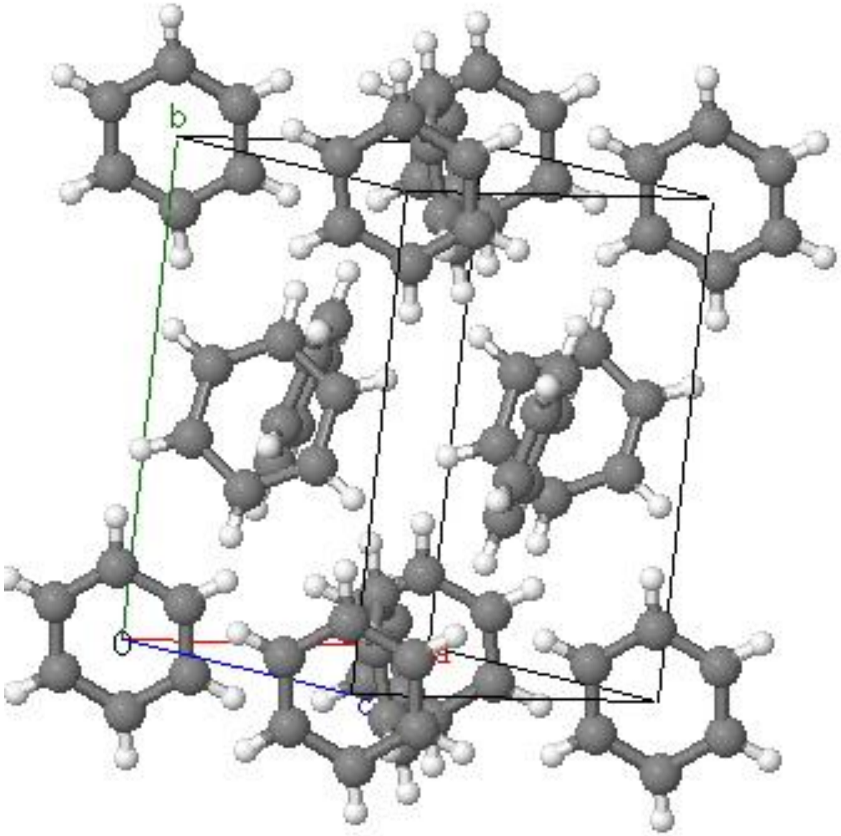
Steric clashes

Delocalized interactions



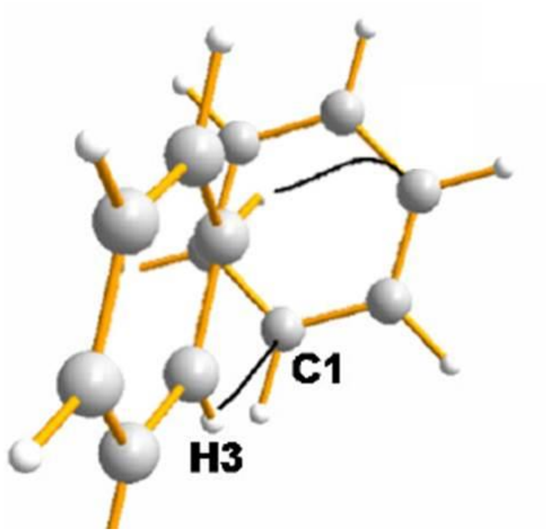
Benzene packing maximizes the number of C-H···π and C-H···C contacts.

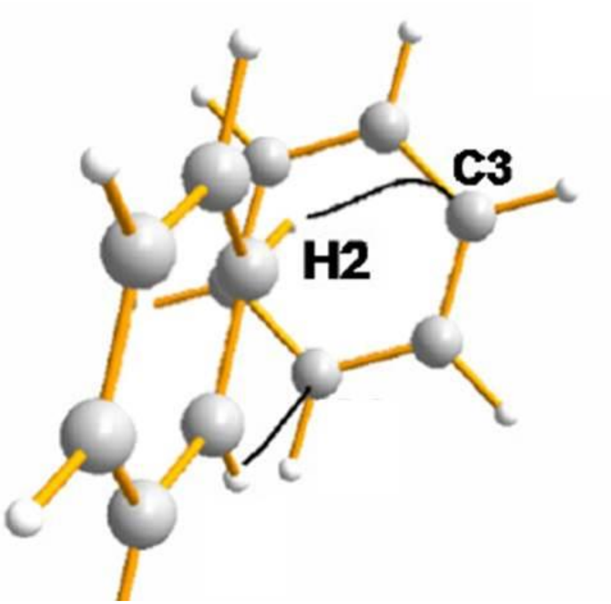
Delocalized interactions

AIM

CH-C
Straight bond path

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



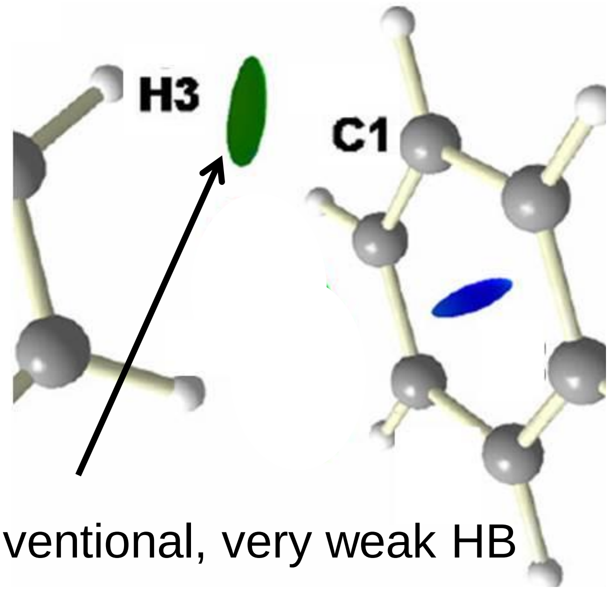


Delocalized interactions

NCI

CH-C

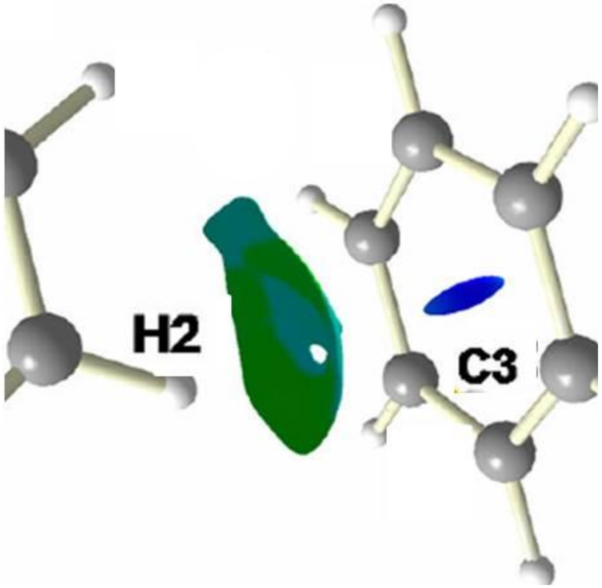
Disc-shaped and localized



conventional, very weak HB

CH-π

Large isosurface involving the whole π electron cloud



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)

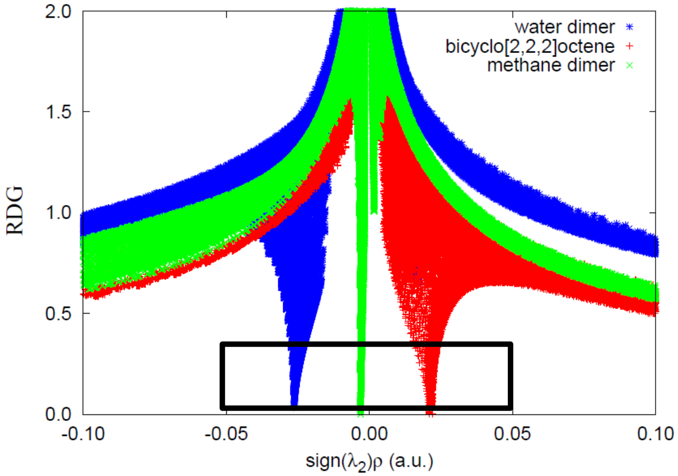
Big systems

How can we apply NCI to such big systems ?

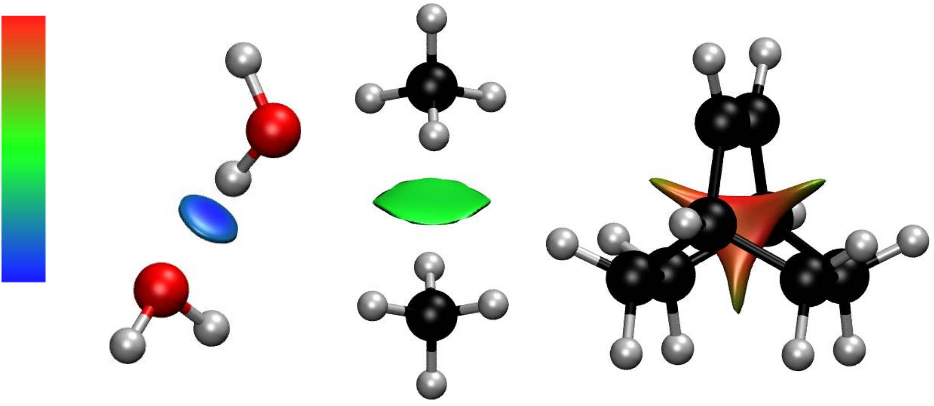
- Since promolecular works well for small densities, we use the promolecular approximation
- Parameters ζ_i and c_i for each atom are internally stored in the code
- No need for wavefunction
- Sum on a grid (very fast)

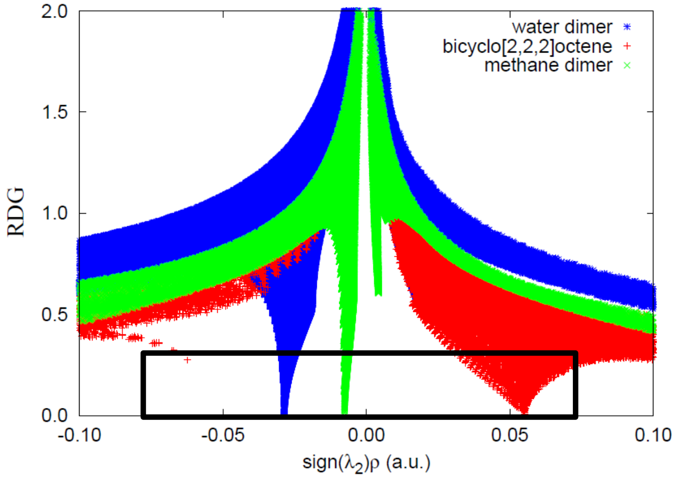
Big systems

Are characteristics really preserved?

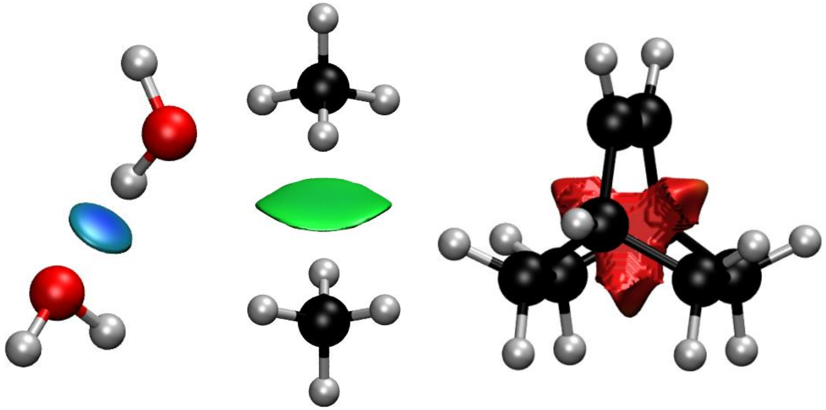


SCF



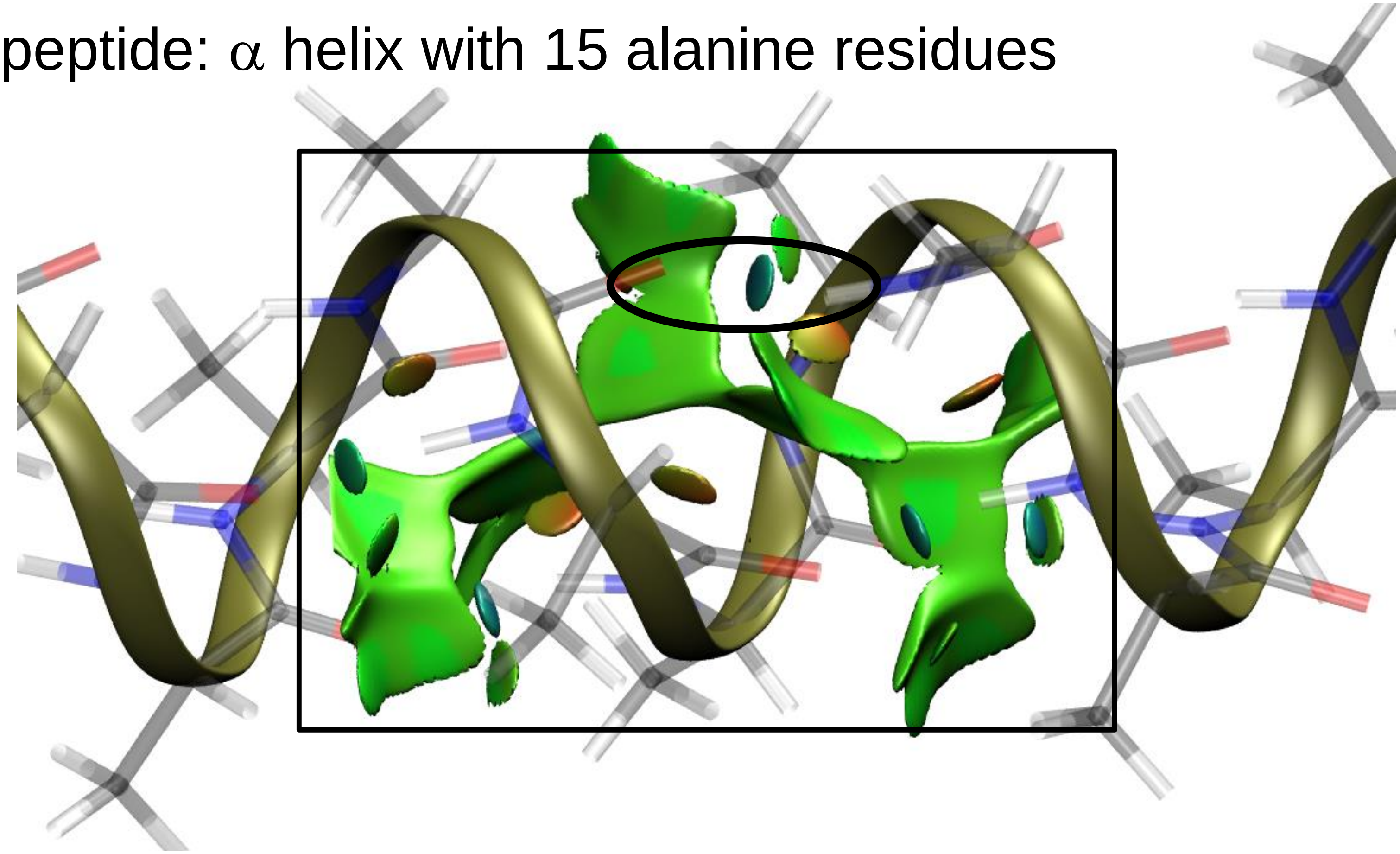


PROMOLECULAR



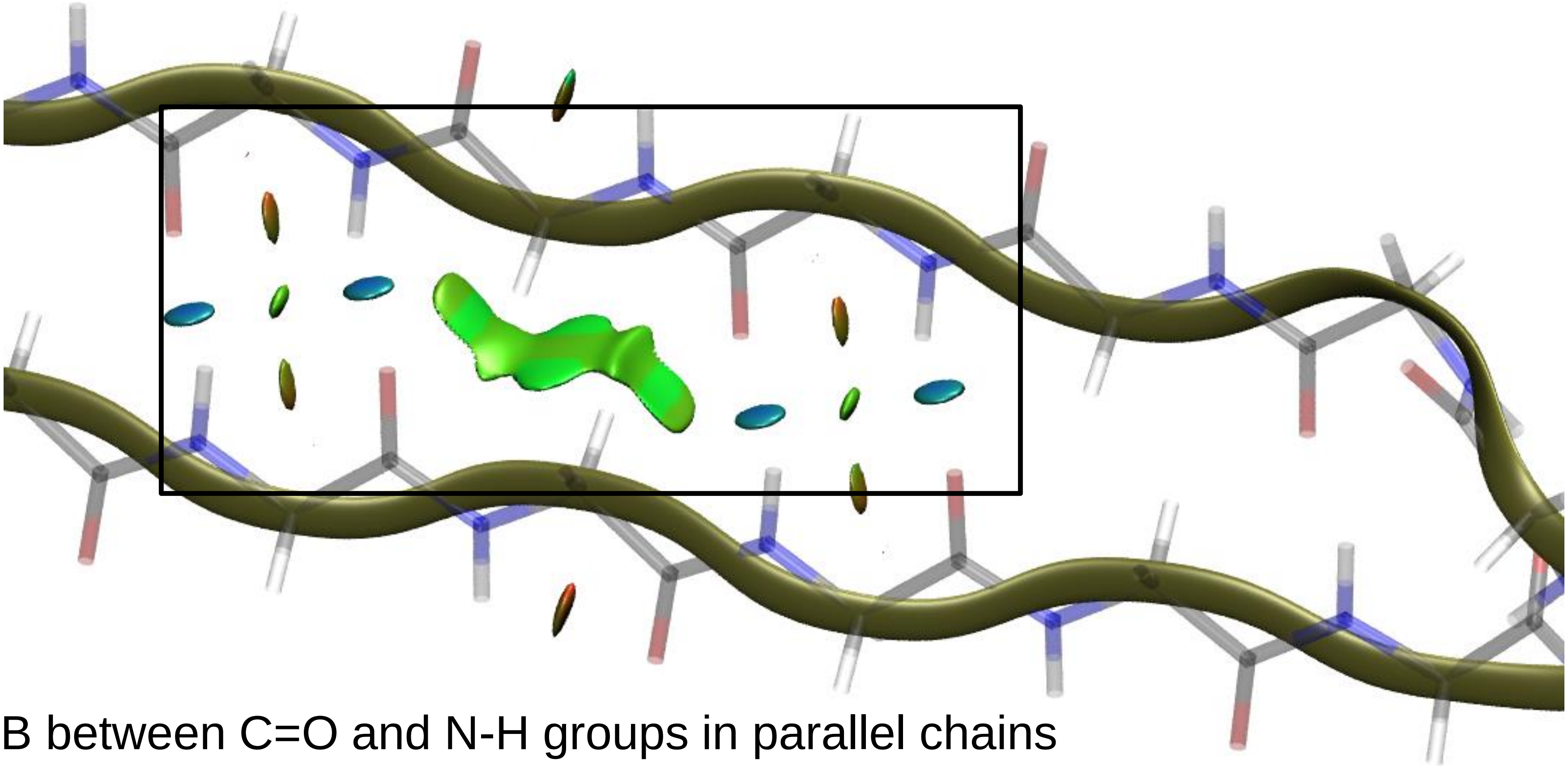
Proteins

Polipeptide: α helix with 15 alanine residues



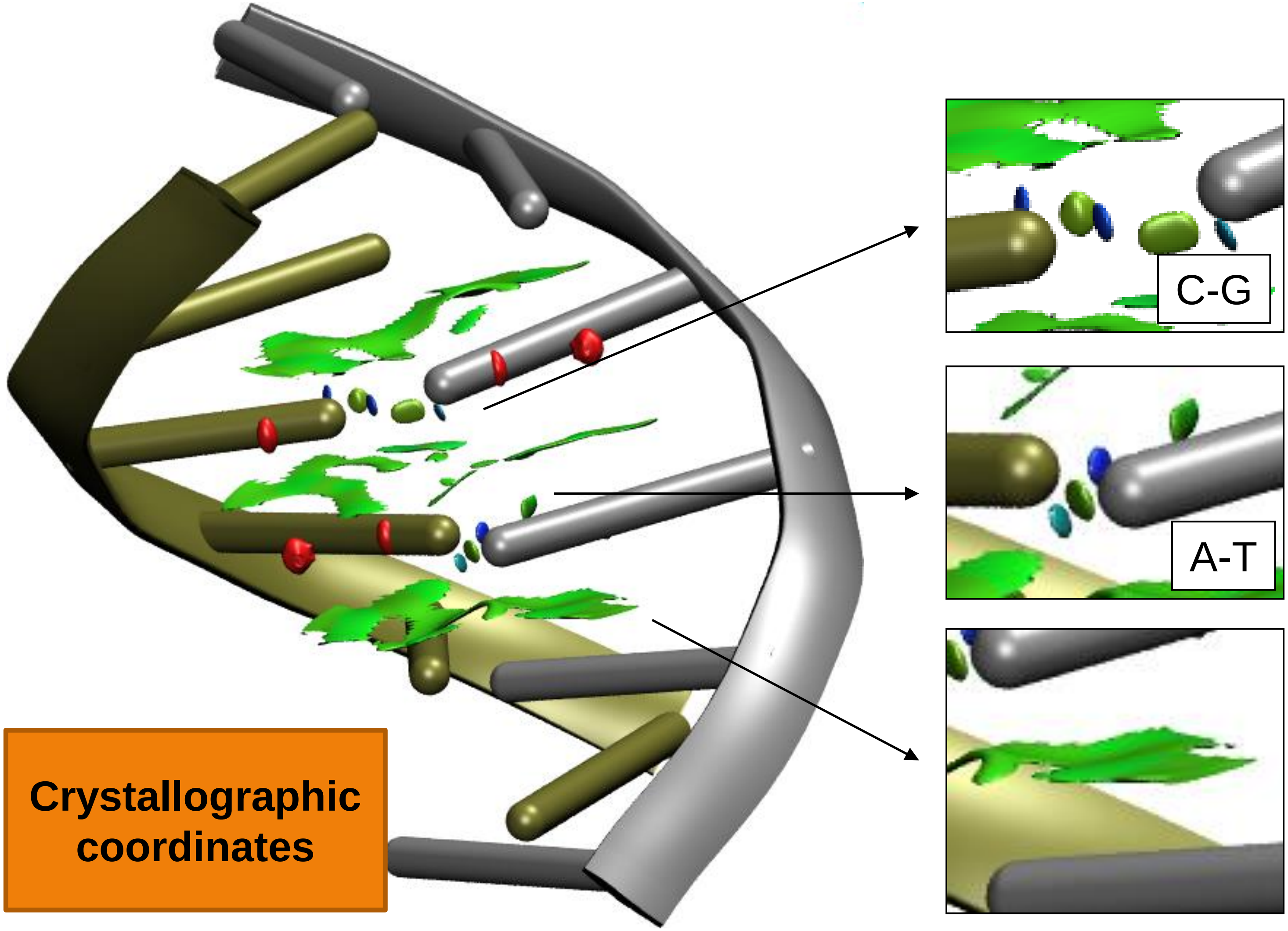
- Hydrogen bonds stabilize the helix
- Big region of van der Waals interaction inside the helix and between methyle lateral chains one step away

Proteins



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

DNA



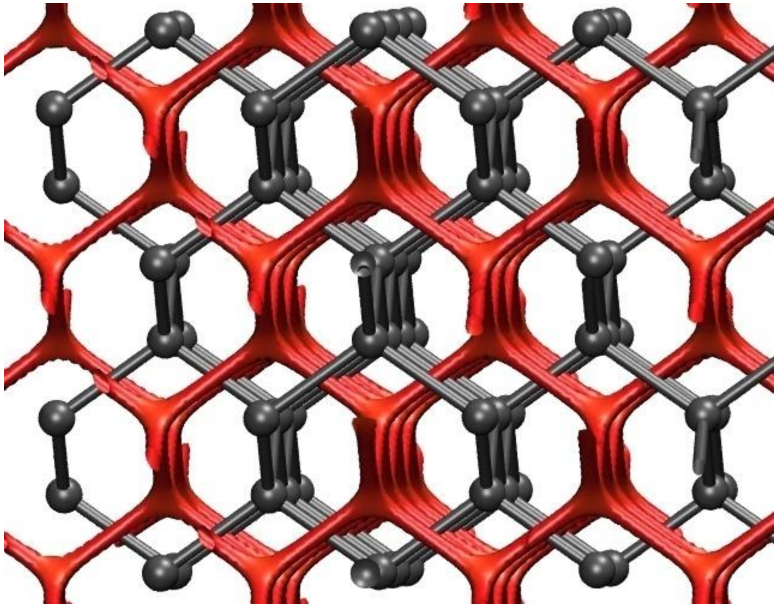
H-bonds between bases

π-stacking

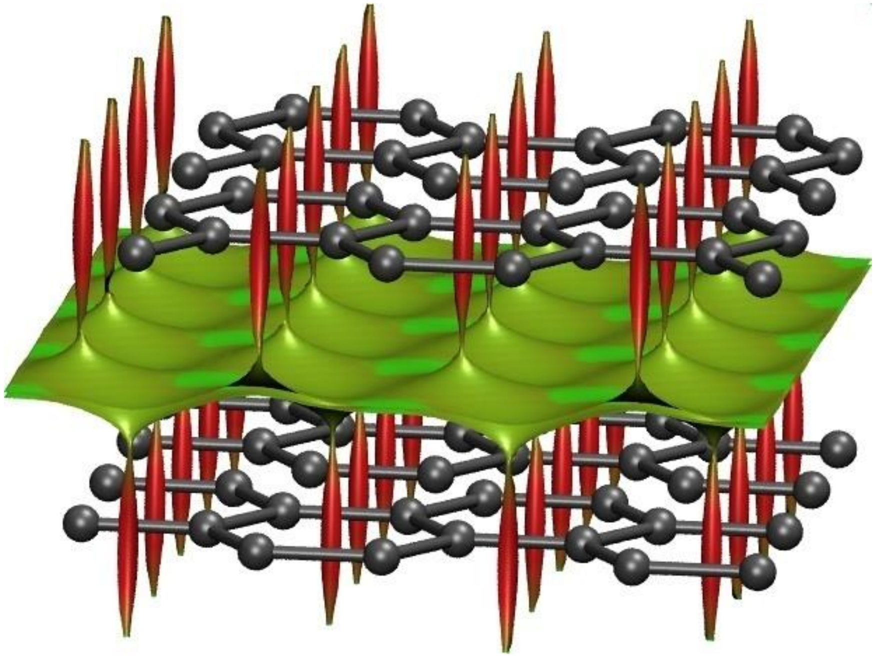
Crystallographic coordinates

J. Chem. Theor. Comp. 7, 625 (2011)

2. QM classification of solids

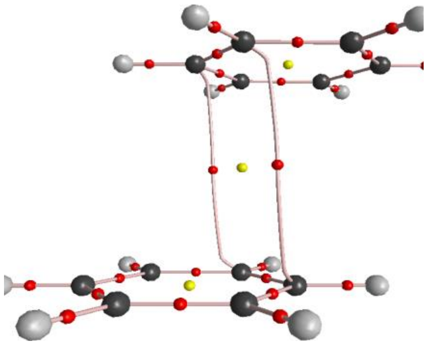
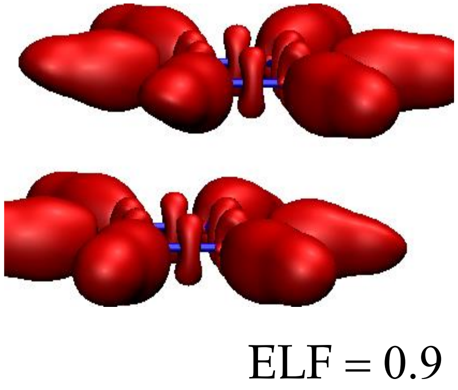
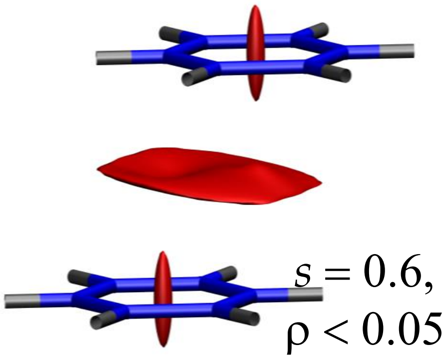


Diamond



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			

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

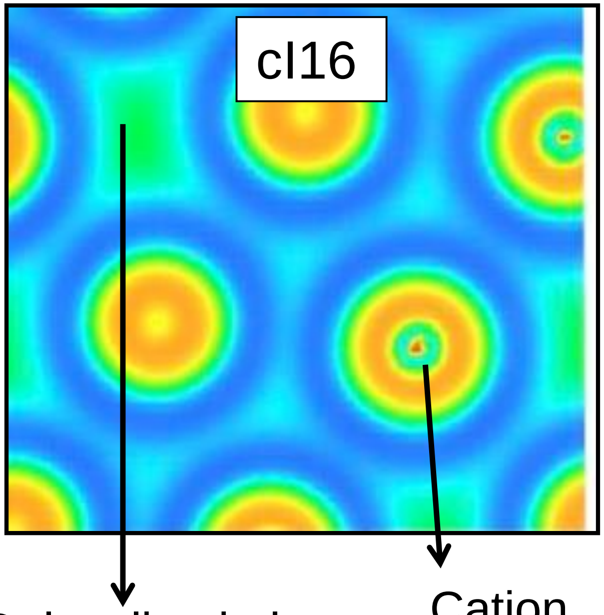
- Under pressure, solids exhibit increasingly shorter interatomic distances. Intuitively, this response is expected to be accompanied by an increase in the widths of the valence and conduction bands and hence a more pronounced free-electron-like behavior.

- 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

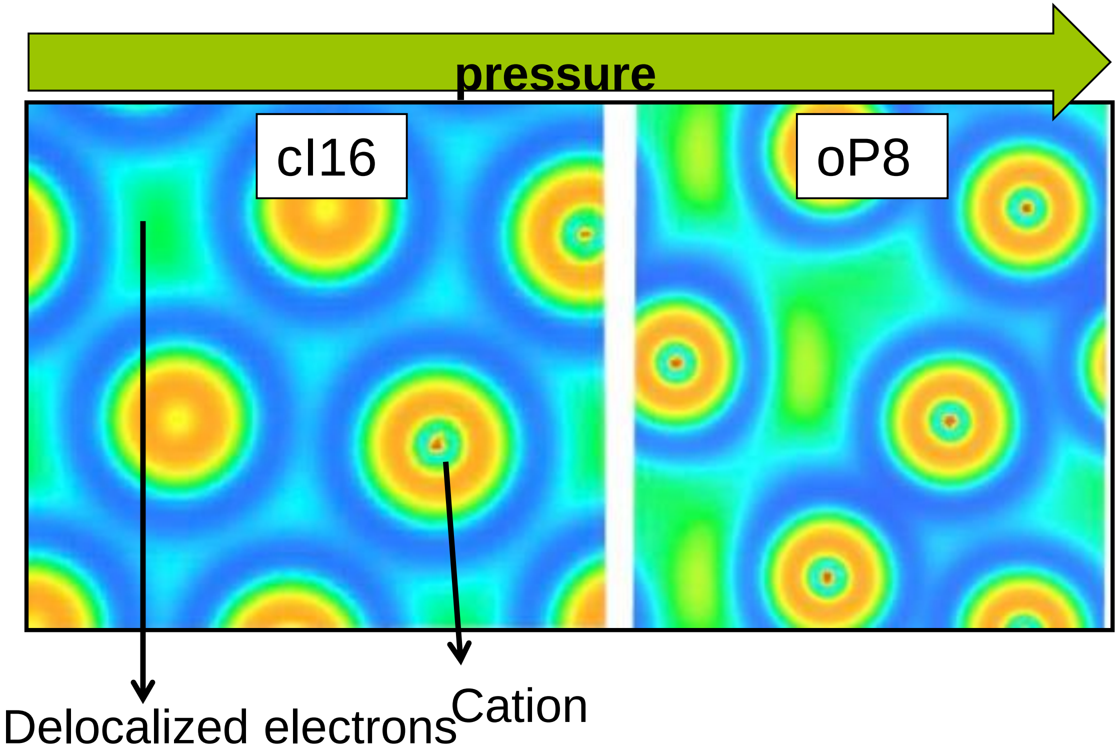


Delocalized electrons

Phys. Rev. B 83, 184106 (2011)

New bonding patterns: new properties

Na

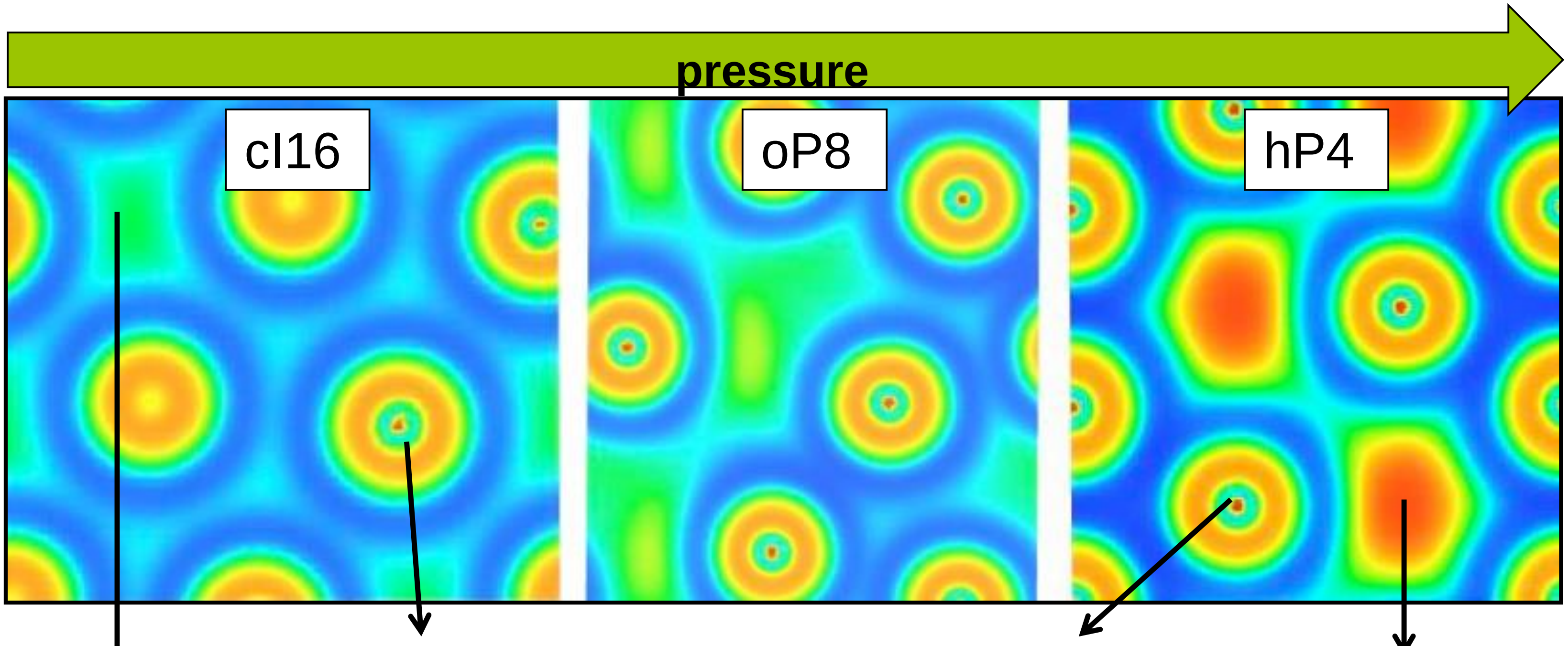


Phys. Rev. B 83, 184106 (2011)

New bonding patterns: new properties

Na

Localization of valence electrons is again observed under pressure



Delocalized electrons

Cation

Cation

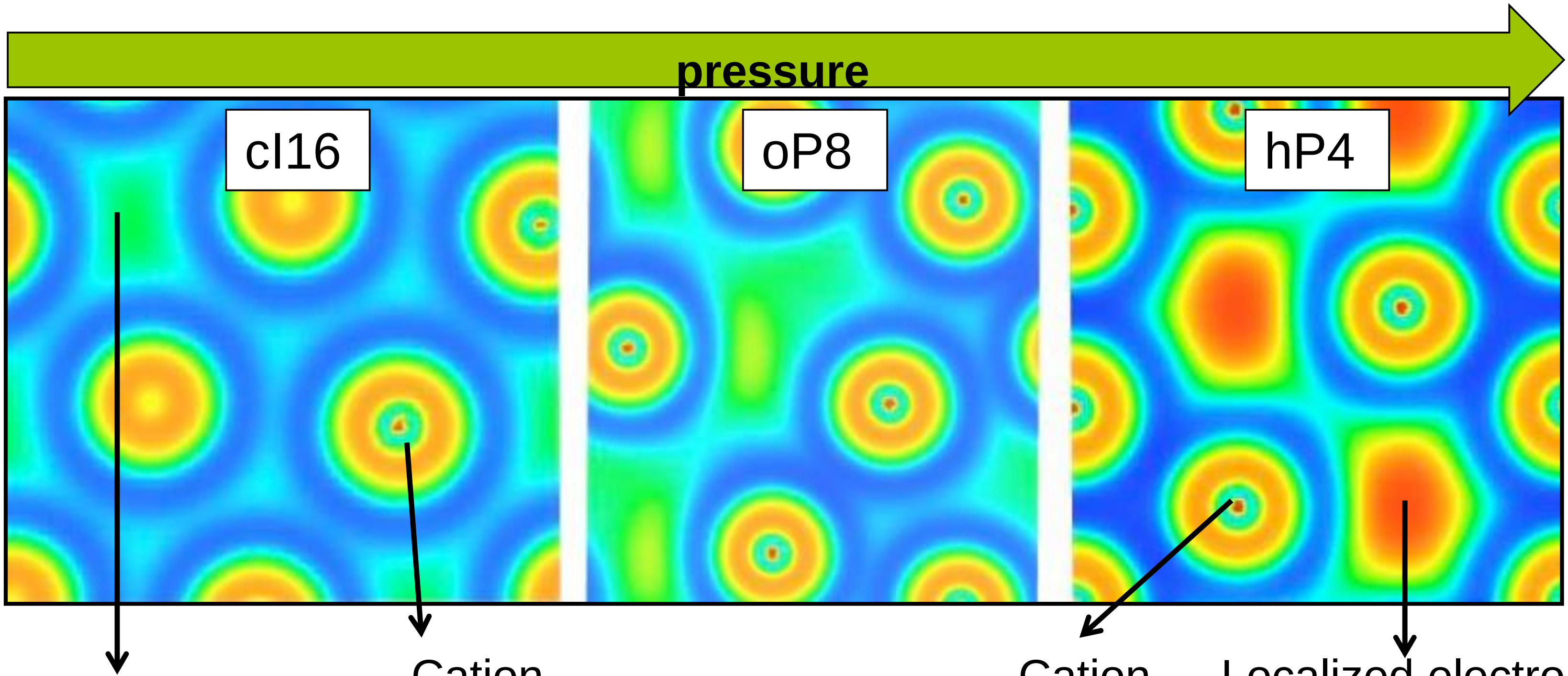
Localized electrons= anion wo/ core = pseudo anion

Phys. Rev. B 83, 184106 (2011)

New bonding patterns: new properties

Na

Localization of valence electrons is again observed under pressure



Delocalized electrons

Cation

Cation

Localized electrons=
anion wo/ core =
pseudo anion

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

Phys. Rev. B 83, 184106 (2011)

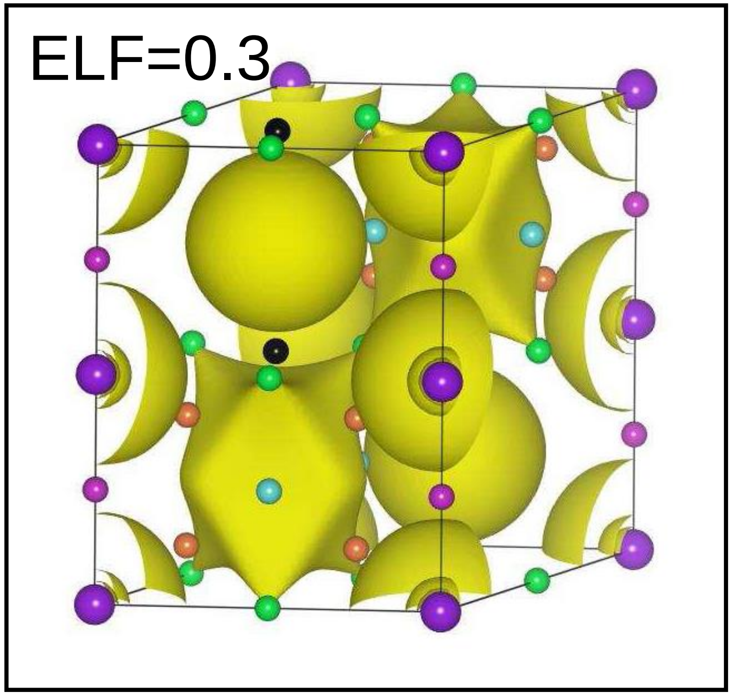
New bonding patterns: new properties

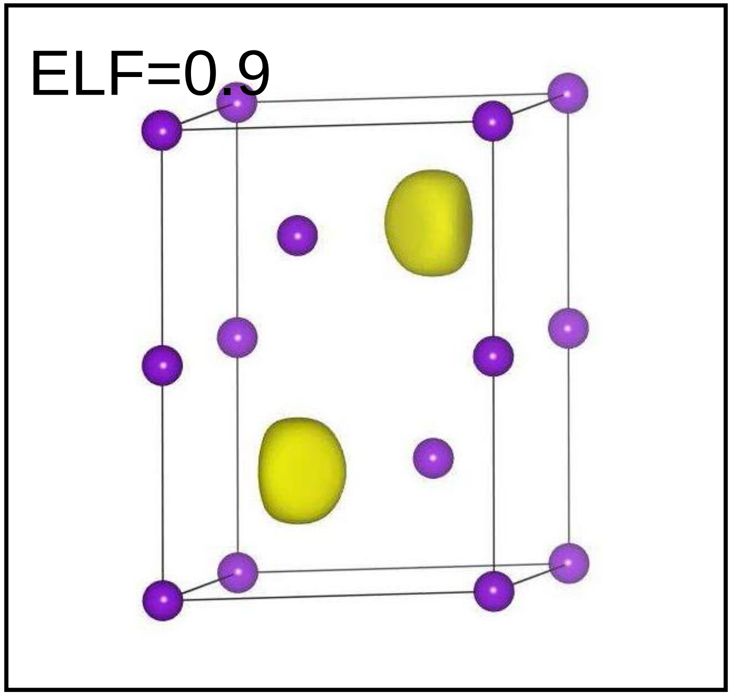
K

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

COUMPOUND→IONIC-LIKE

ELECTRONS→PSEUDOANIONS


ELF=0.3


ELF=0.9

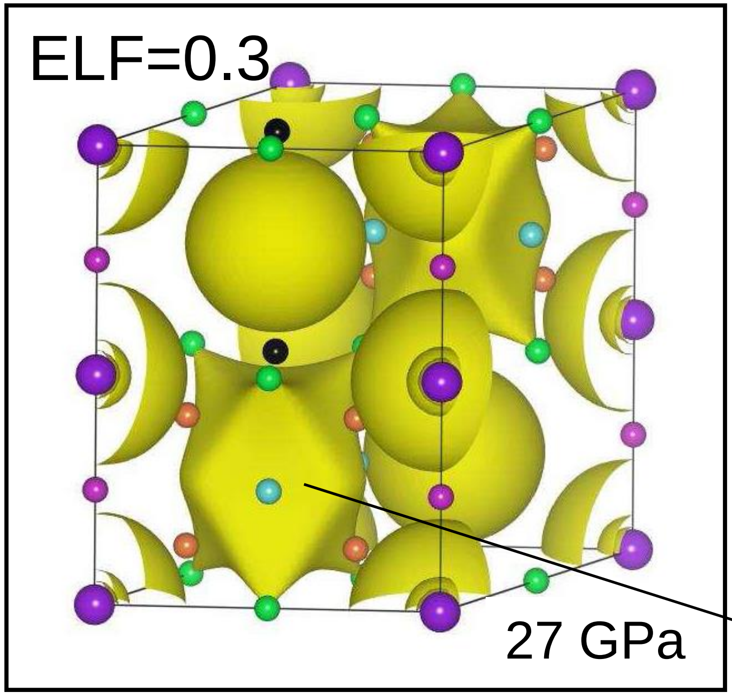
27 GPa

New bonding patterns: new properties

K

Same structure! Ni2In, P=0GPa K2*X*, P=27GPa

Electrons in same position as anions!



1.76e

- Localized electrons behave optically and structurally like anions
- Structures appear at lower volumes:

Equivalency external and chemical pressure

Phys. Rev. Lett. 103, 115501 (2009)

Outline

5. Applications to high pressure

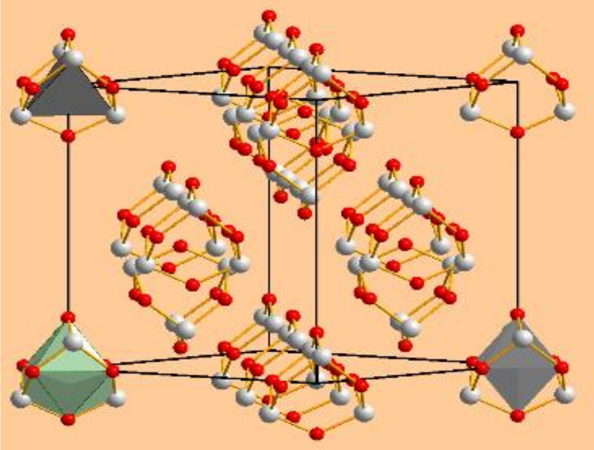
   a) ELF: predicting compressibility & transformations

   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.

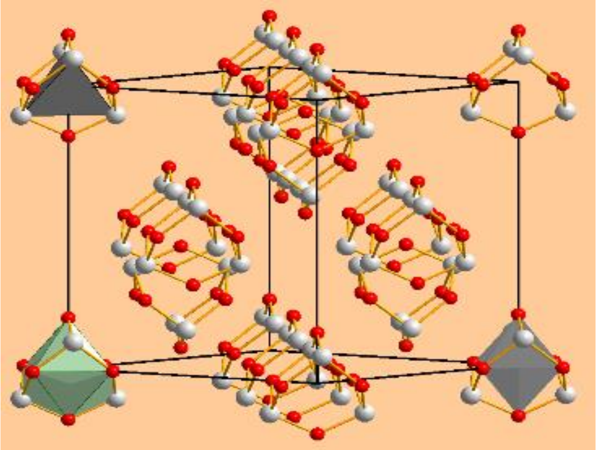
WHY??

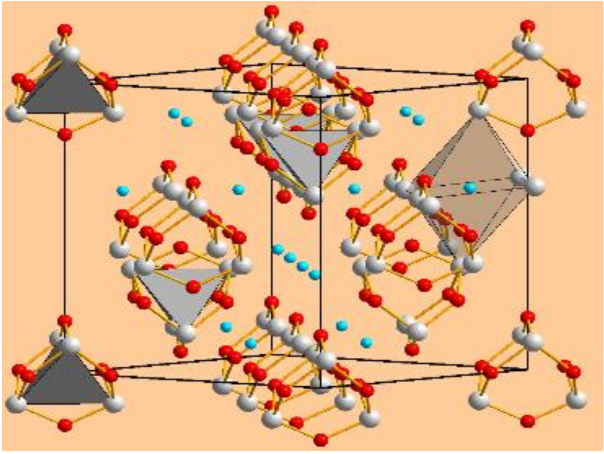
As_4O_6

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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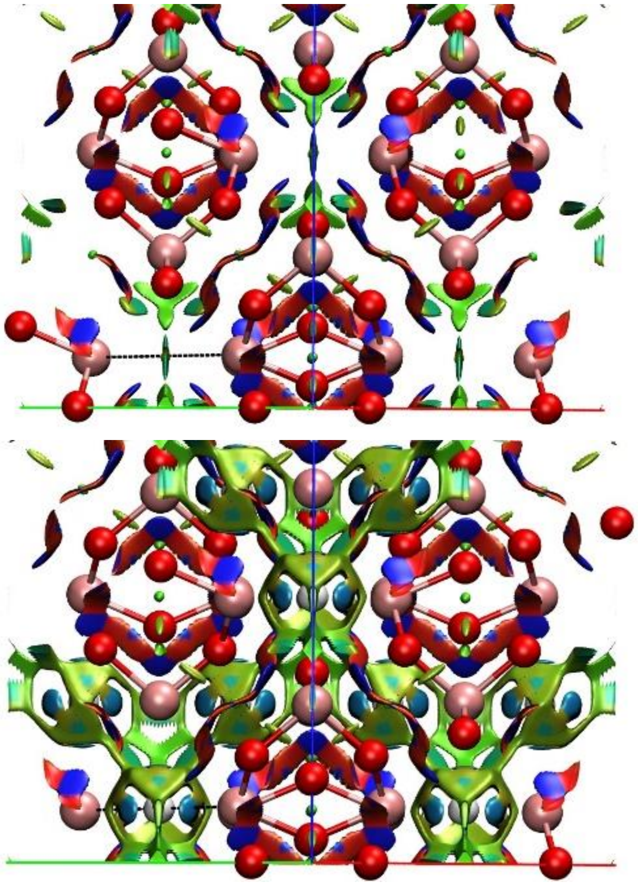
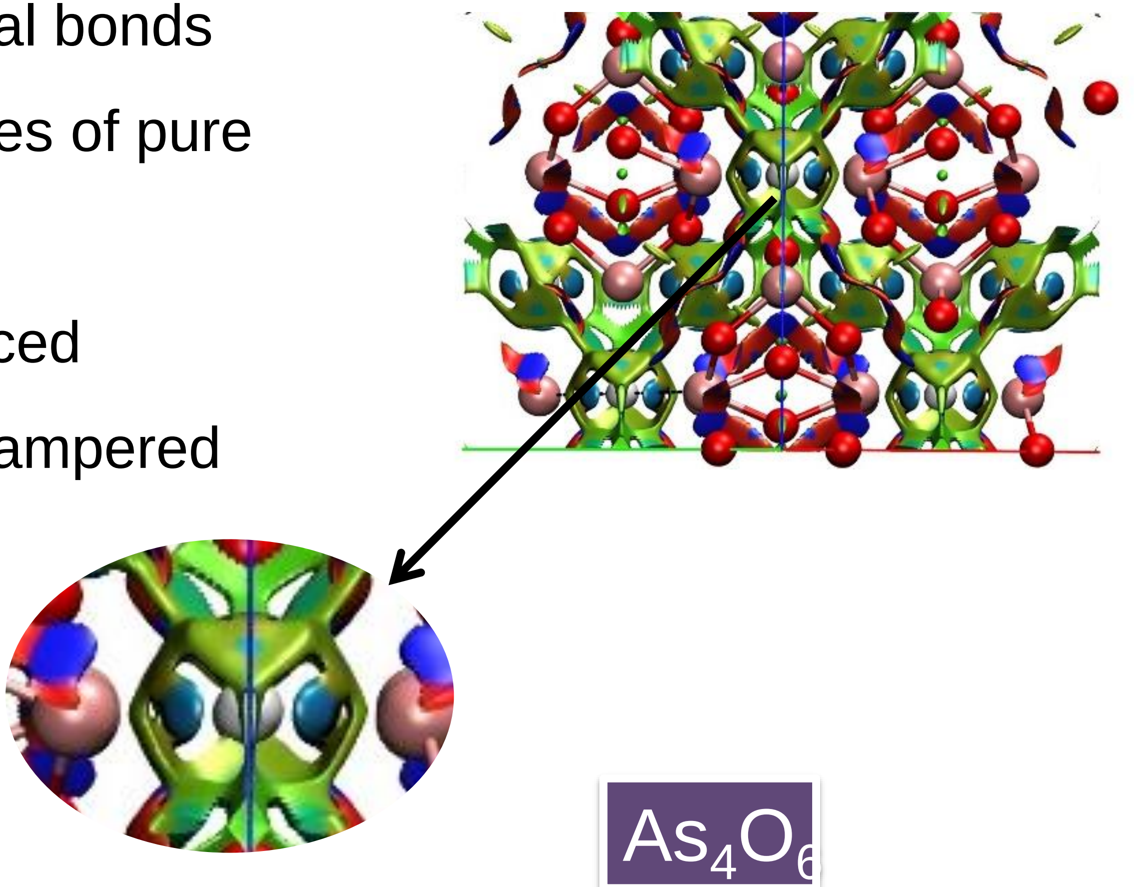


As_4O_6

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



As_4O_6

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

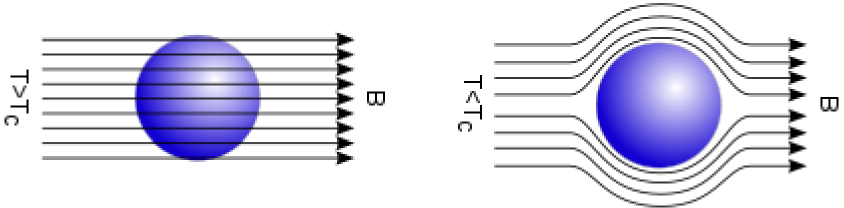
   c) ELF: superconductivity

8. The codes
9. Summary

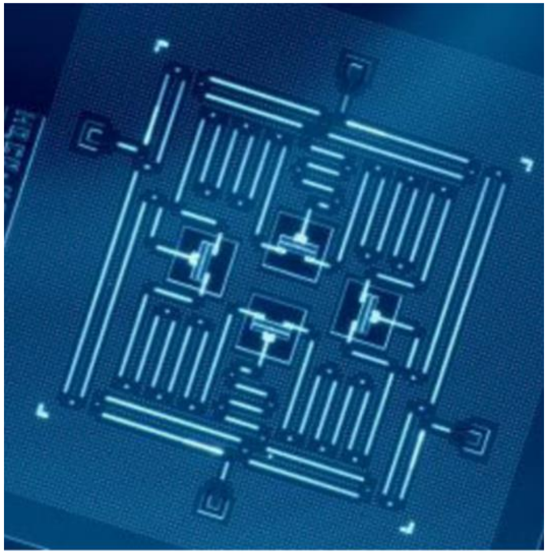
Superconducting materials

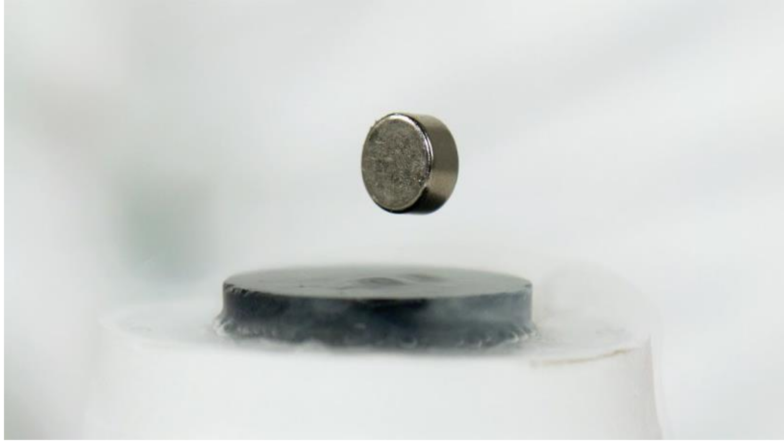
Superconductivity is technologically very interesting…

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



- Interesting applications: electronics, levitation





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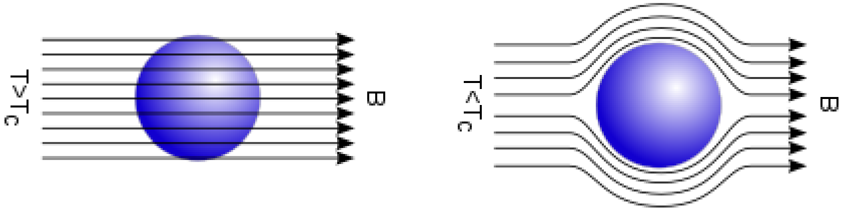

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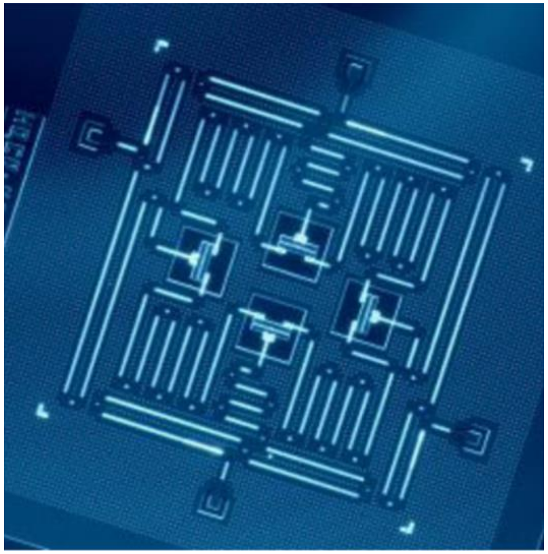
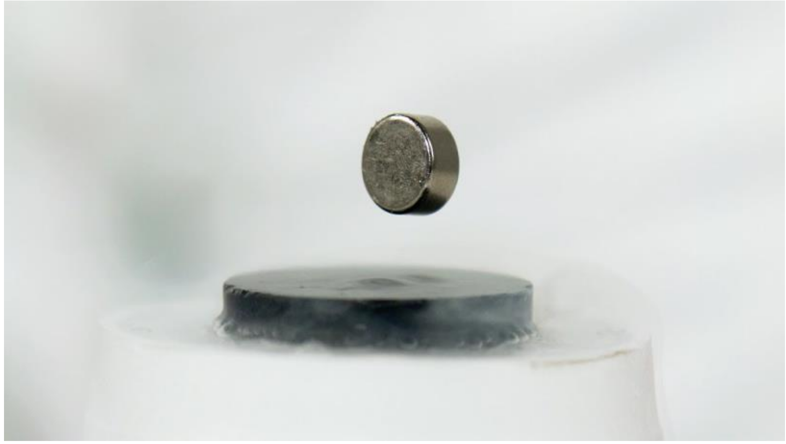
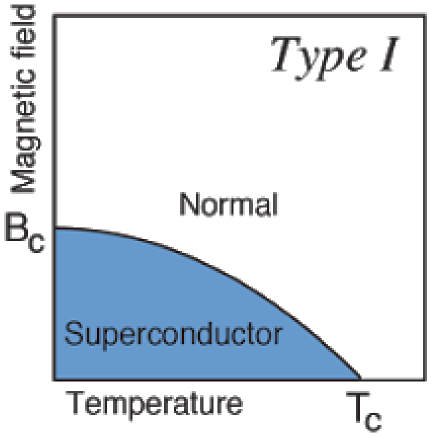




However…

Superconducting materials

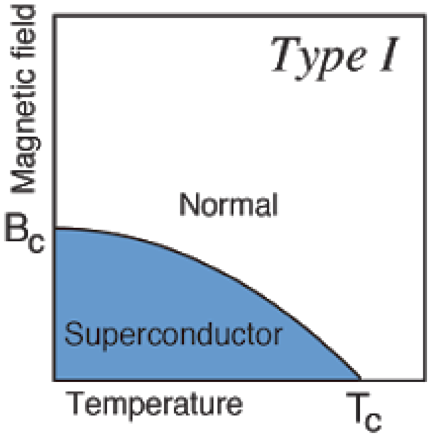
- Superconductivity appears at very low temperatures



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

Superconducting materials

- Superconductivity appears at very low temperatures



- The problem: very low is VERY low: Al (1.2K), Zn (0.88 K)
- Calculations are extremely expensive, and not always work

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

Superconducting materials

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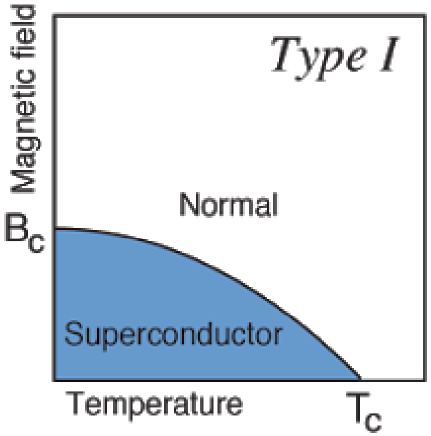

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Superconducting materials

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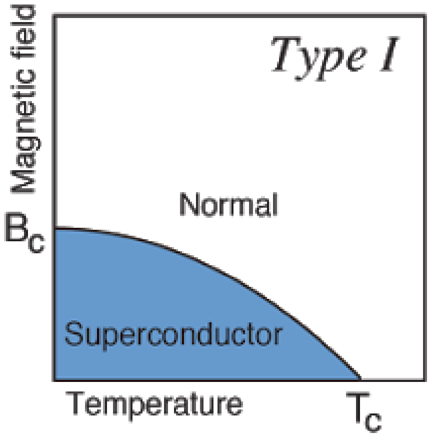

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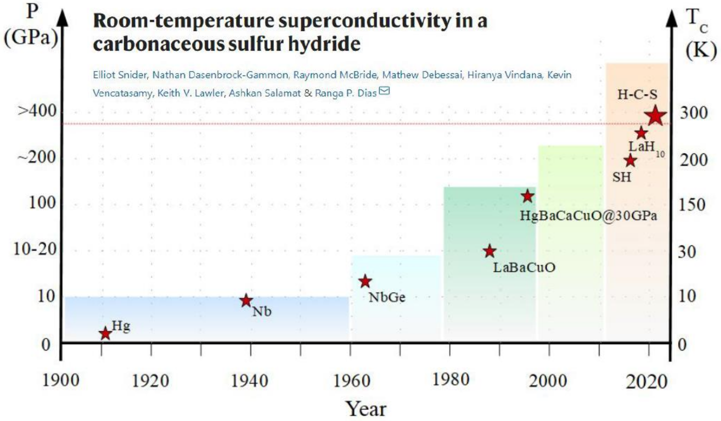
Let’s start from a reasonable starting point…H-based systems!

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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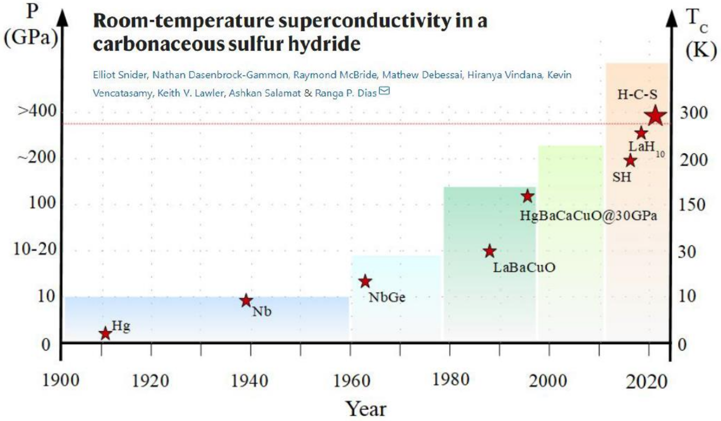

- Something to keep in mind:
  - High pressures are needed:

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

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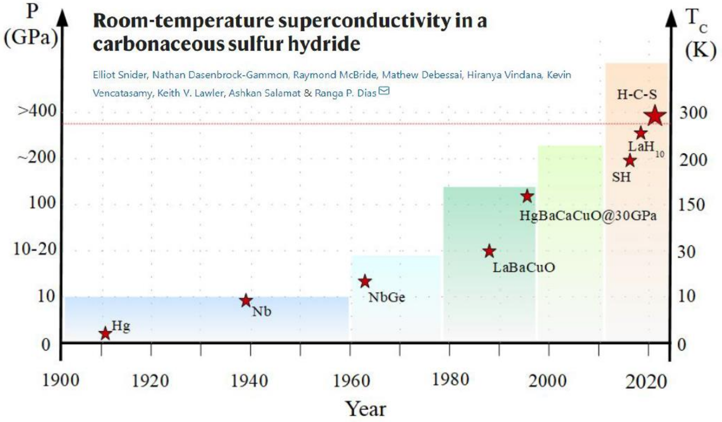
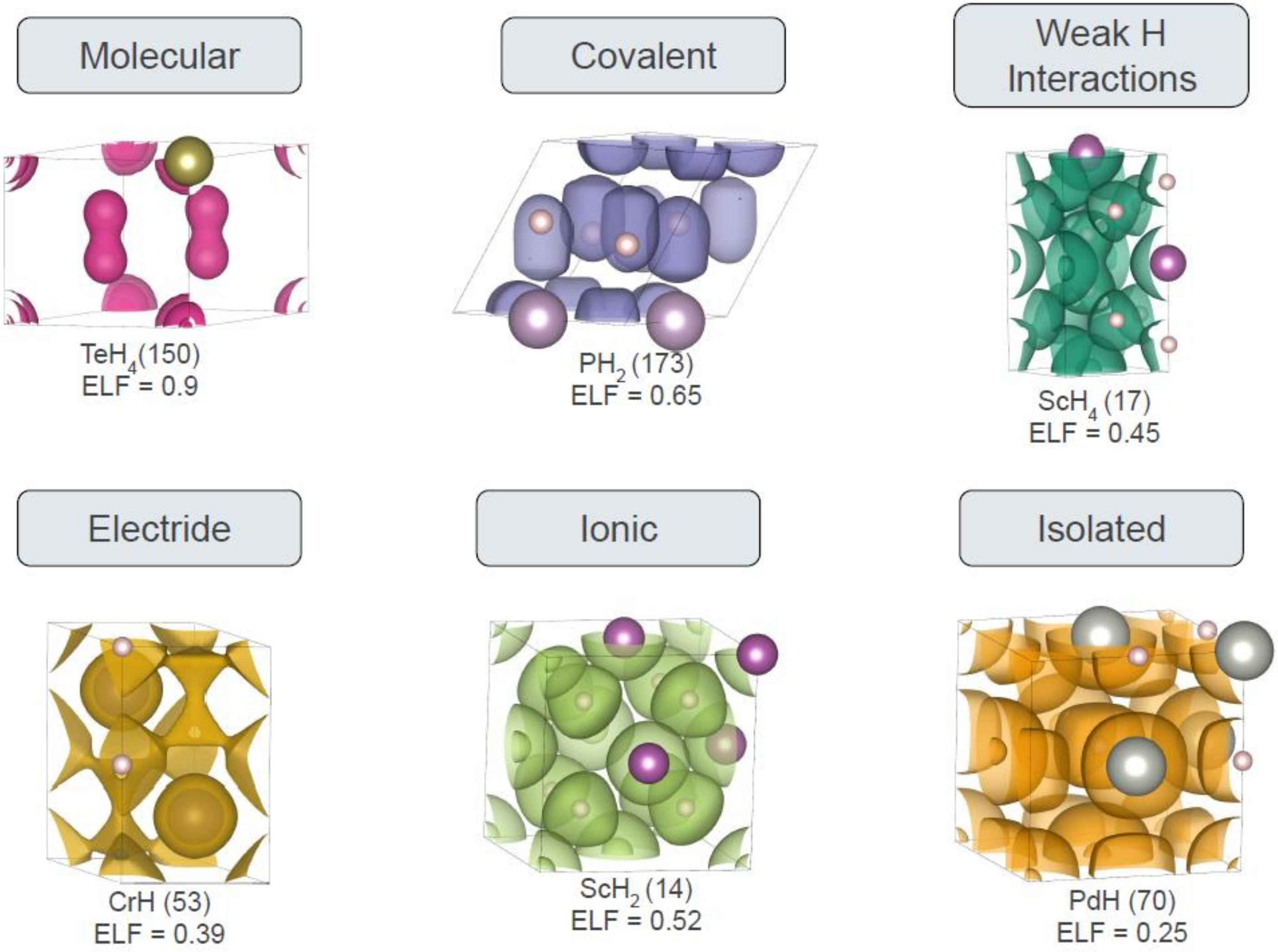
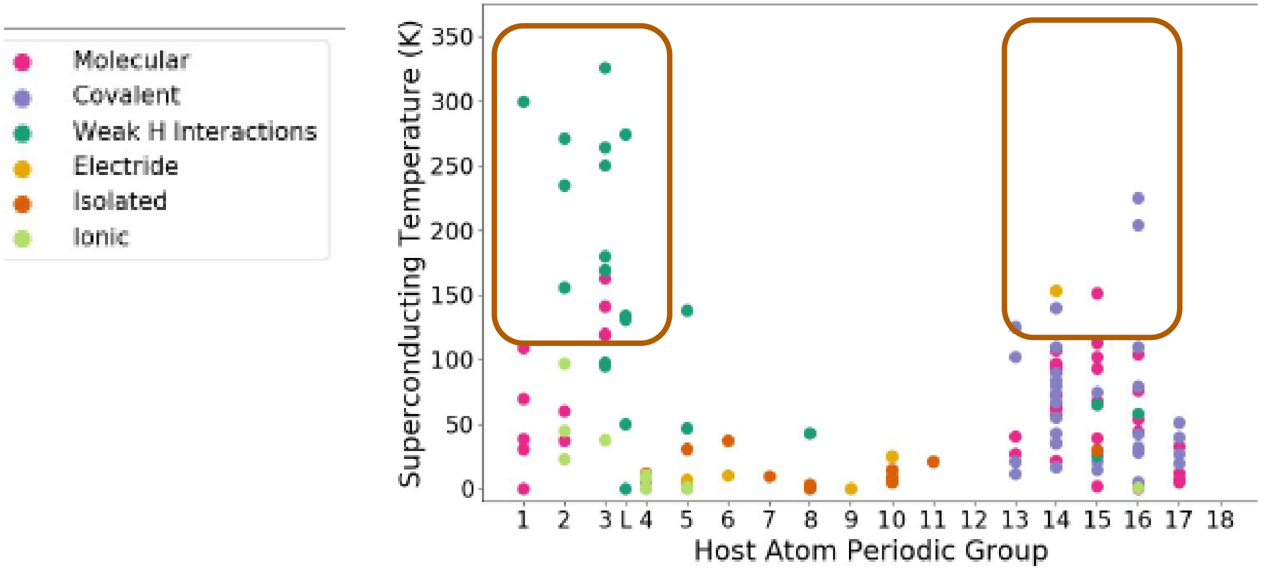


- Something to keep in mind:
  - High pressures are needed:
    H_3S at 203K **and 150GPa**, LaH_{10} at 260K and **190GPa**.
  - Hopefully replaced by chemical pressure! (next step)

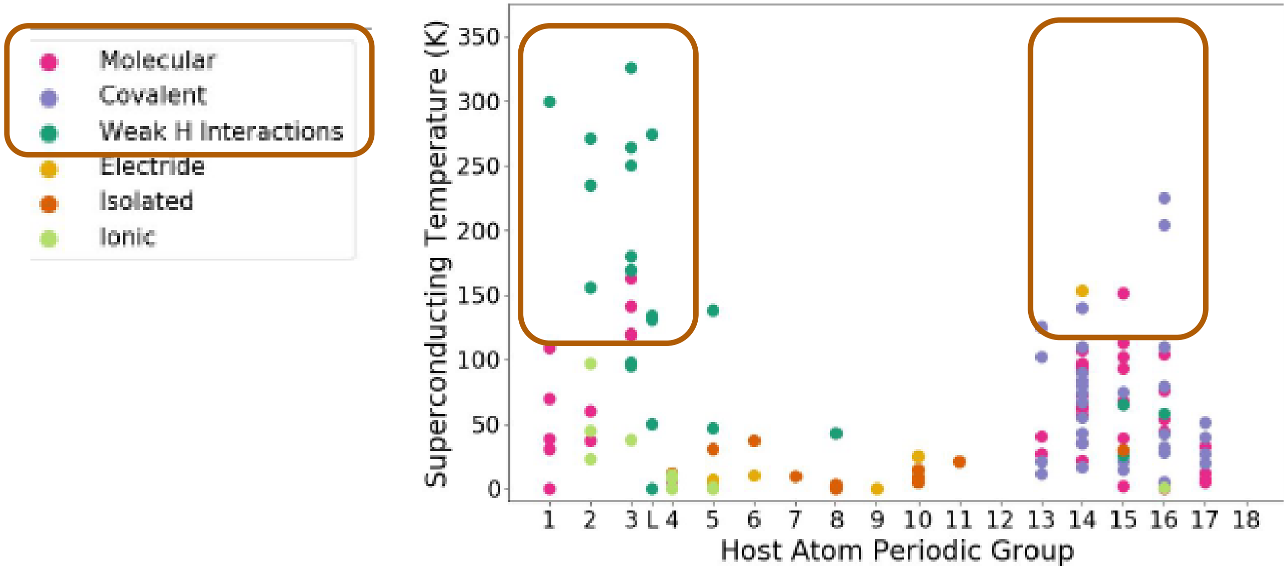
Let's start!

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

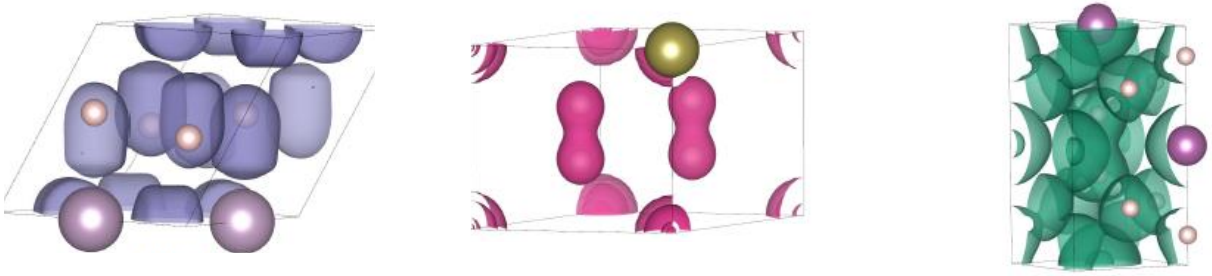


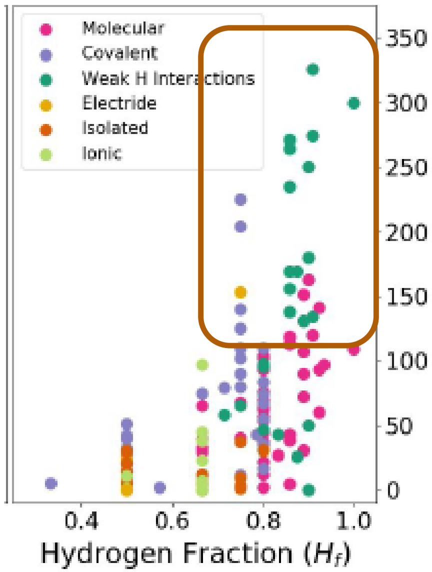


- Characteristics:
  - s, p atoms

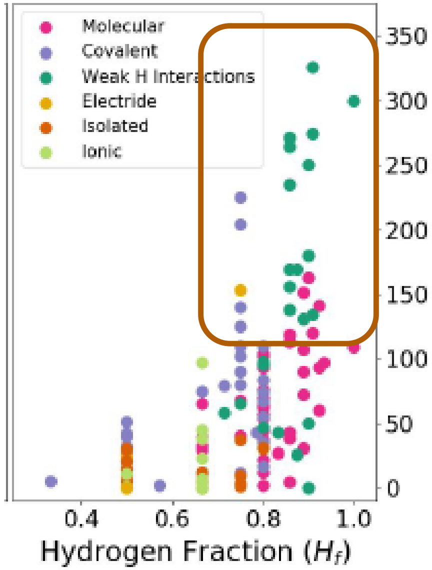


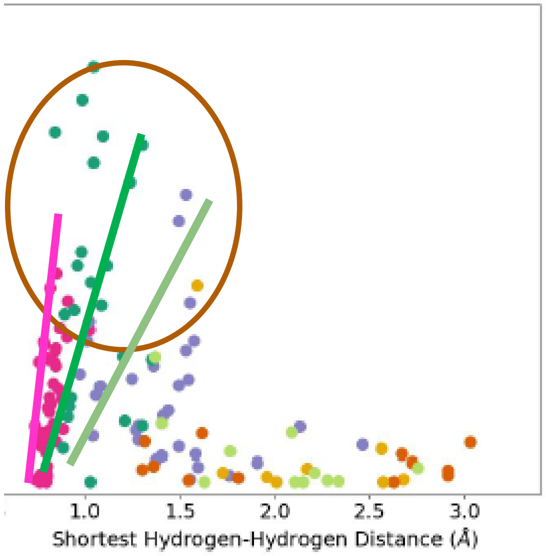
- Characteristics:
  - s, p atoms
  - Non charged (covalent, molecular or weak H interactions)





- Characteristics:
  - Hydrogen rich systems





- Characteristics:
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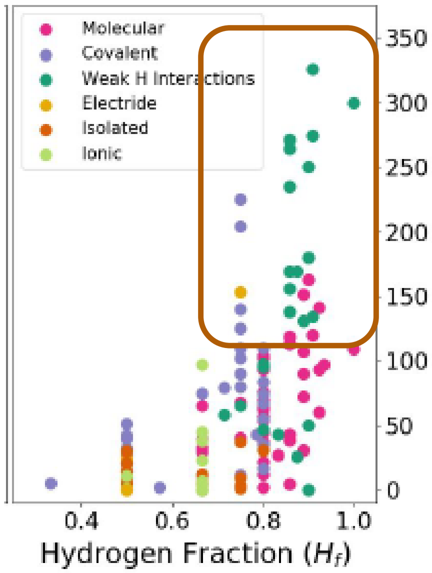

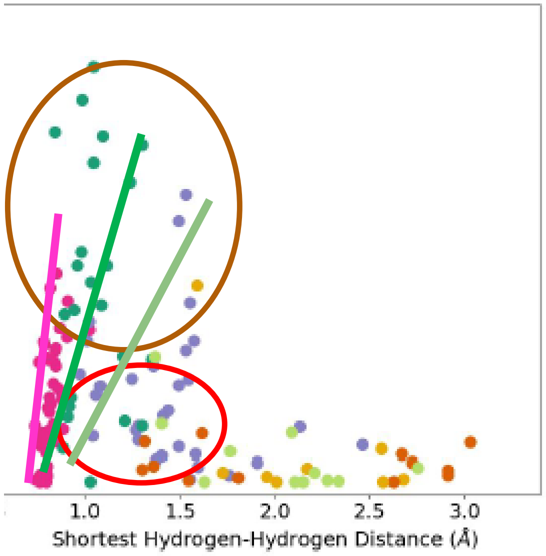

- Characteristics:
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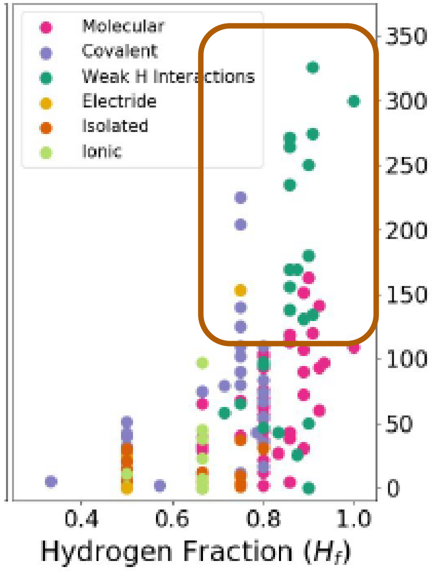
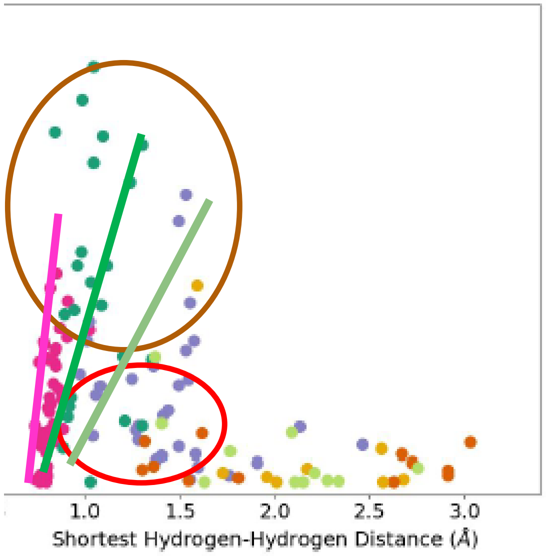
- Necessary but not sufficient conditions!





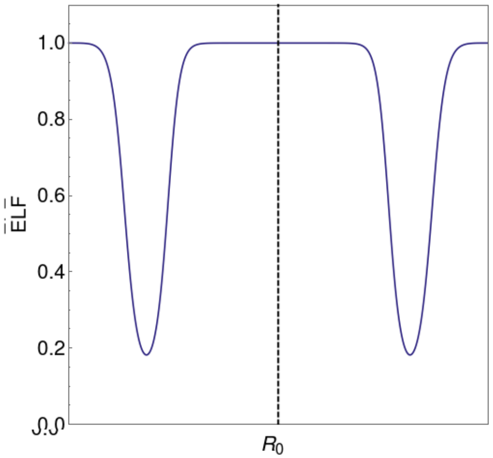
- Characteristics:
  - Hydrogen rich systems
  - Stretched H-H bonds
- Necessary but not sufficient conditions!

How about the electron localization?

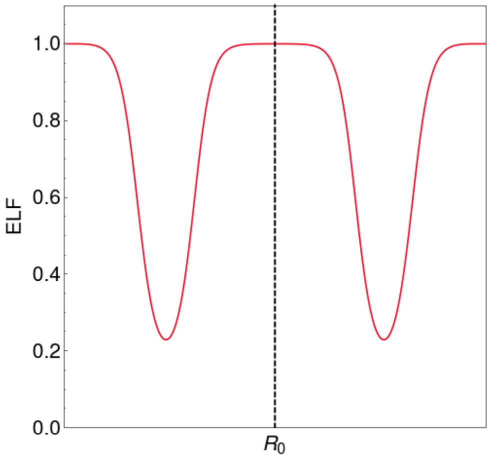
- We have made a two atom model with two electrons in a metallic state or forming a Cooper pair

$$\Psi(R) \equiv \Psi(\xi_0(R),R) \propto \cos\left(\frac{(9\pi\rho(R)^2)^{1/3}}{\Delta}\right) K_o\left(\frac{1}{\pi}\right)$$

- Radial wavefunction
- r_1-r_2= coherence length
- LDA approximation



R_0=3 au



R_0=2 au

- We have made a two atom model with two electrons in a metallic state or forming a Cooper pair

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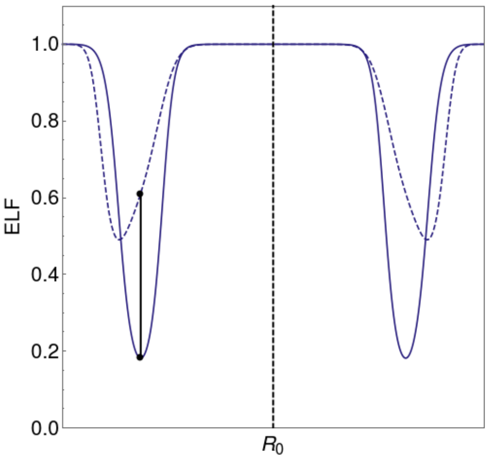
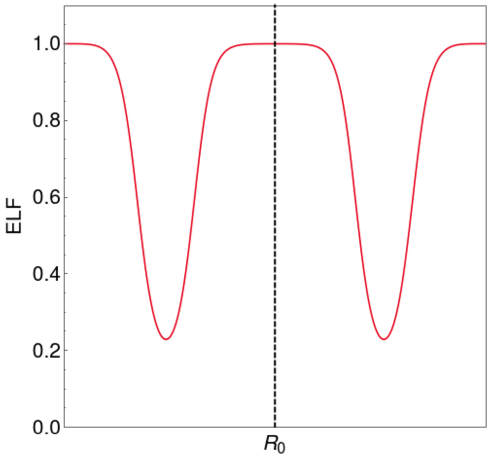


R_0=3 au



R_0=2 au

Increasing the networking value in the metal also increases it for the Cooper pair

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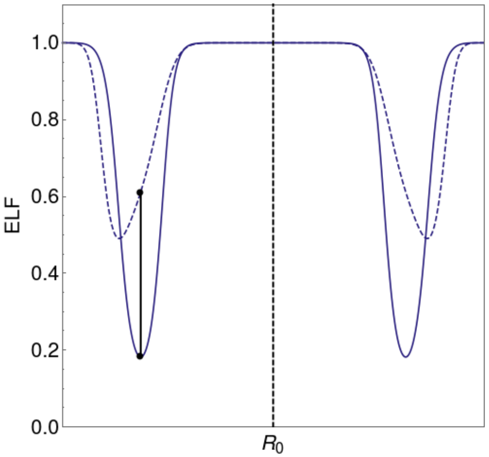
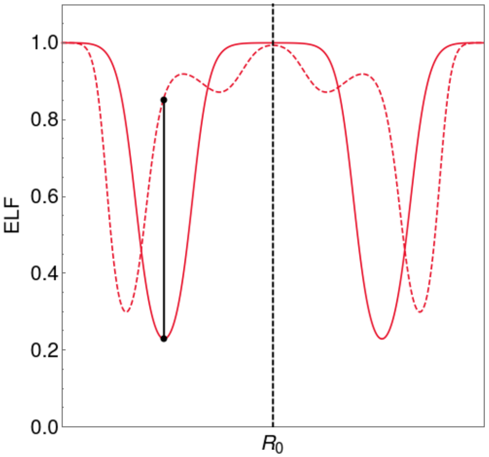


R_0=3 au



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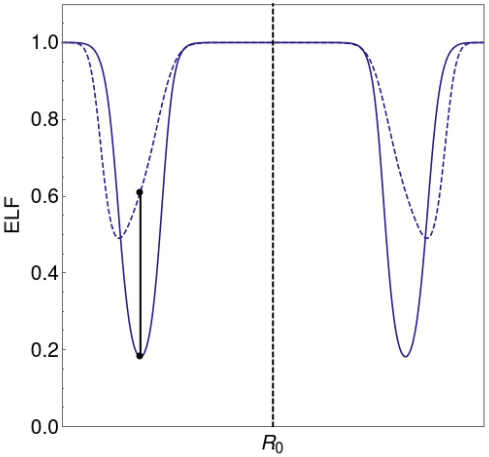

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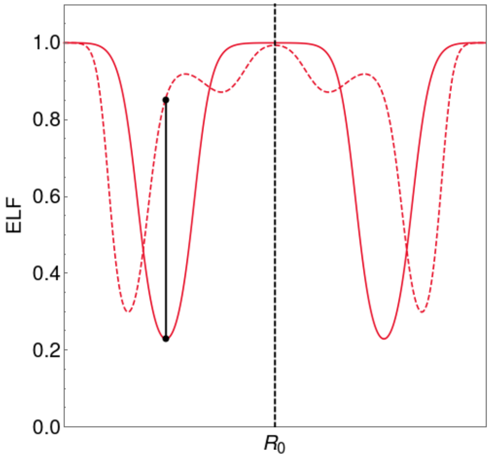
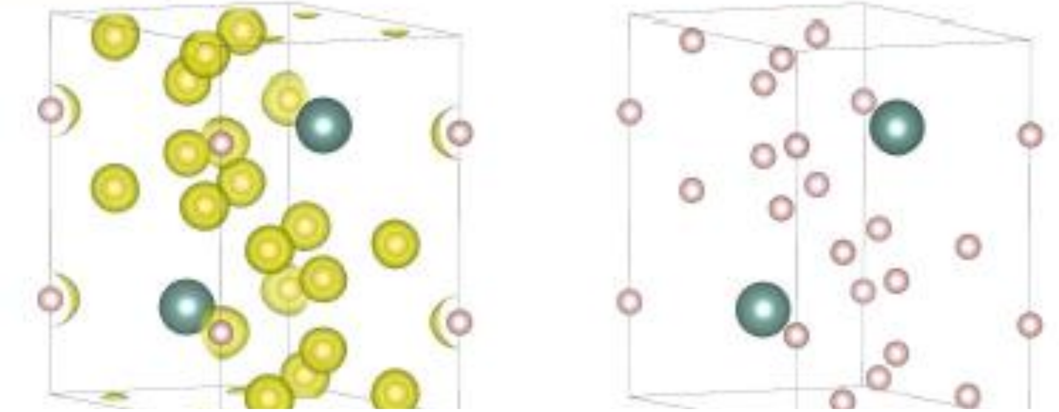


R_0=2 au

Increasing the networking value in the metal also increases it for the Cooper pair

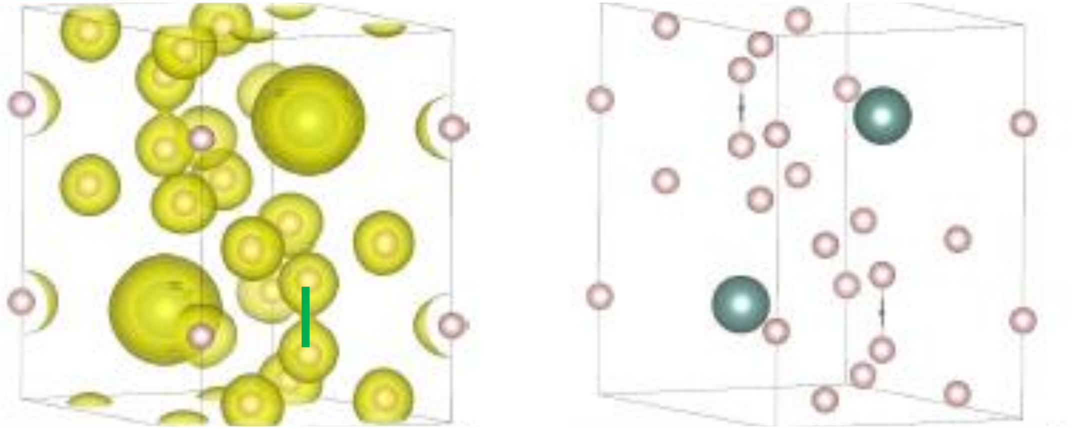
3D delocalization values in the normal calculation can be used to glimpse superconducting connectivity

YH_9



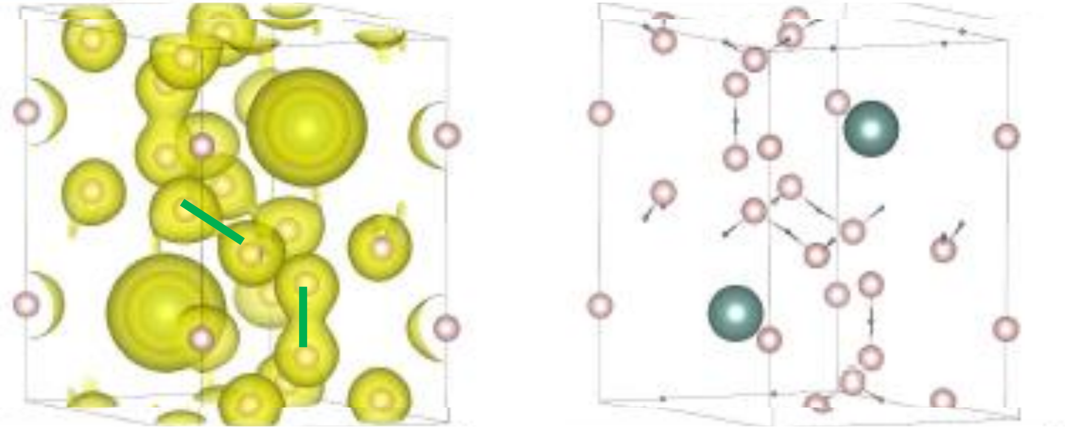
ELF=0.9

YH_9



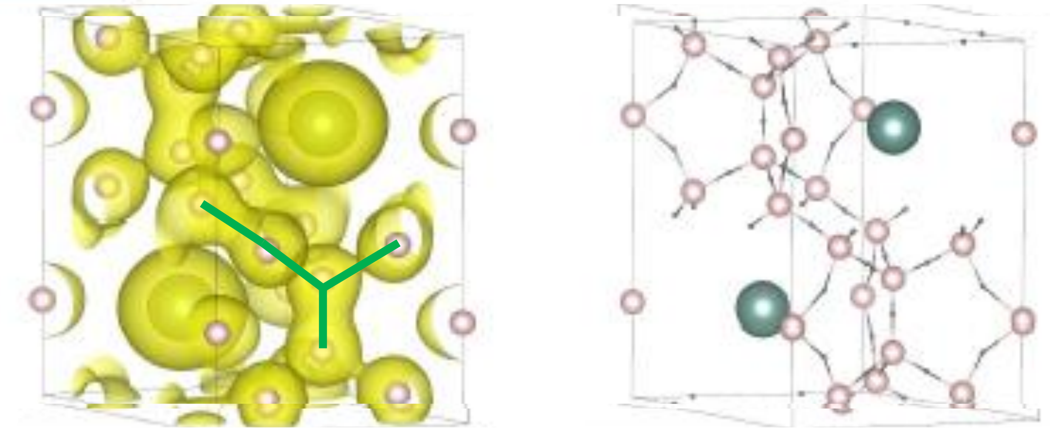
ELF=0.78

YH_9



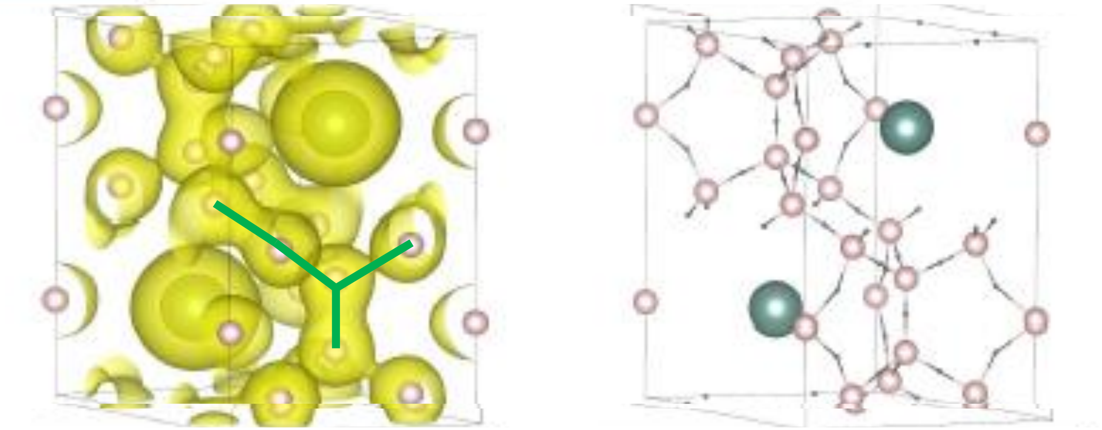
ELF=0.72

YH_9



ELF=0.57

YH$_9$

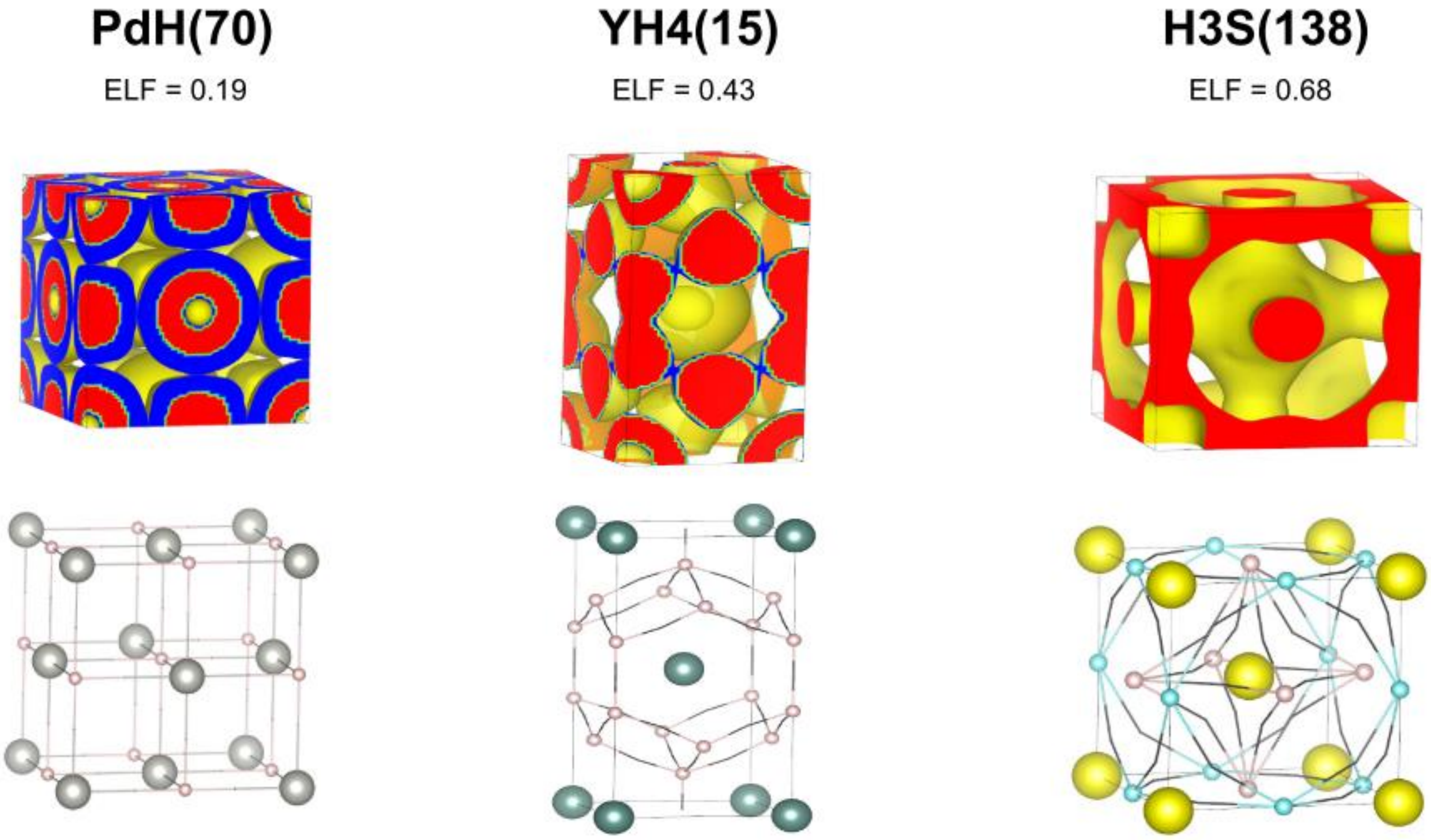


ELF=0.57

- 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

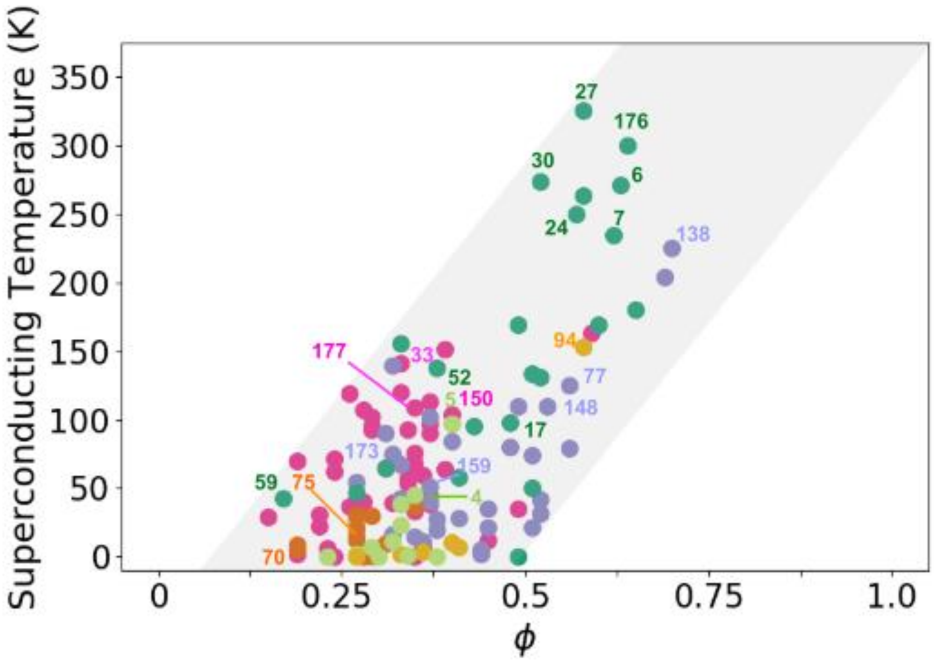
YH4(15)

ELF = 0.43

H3S(138)

ELF = 0.68

Correlation between T_c and φ

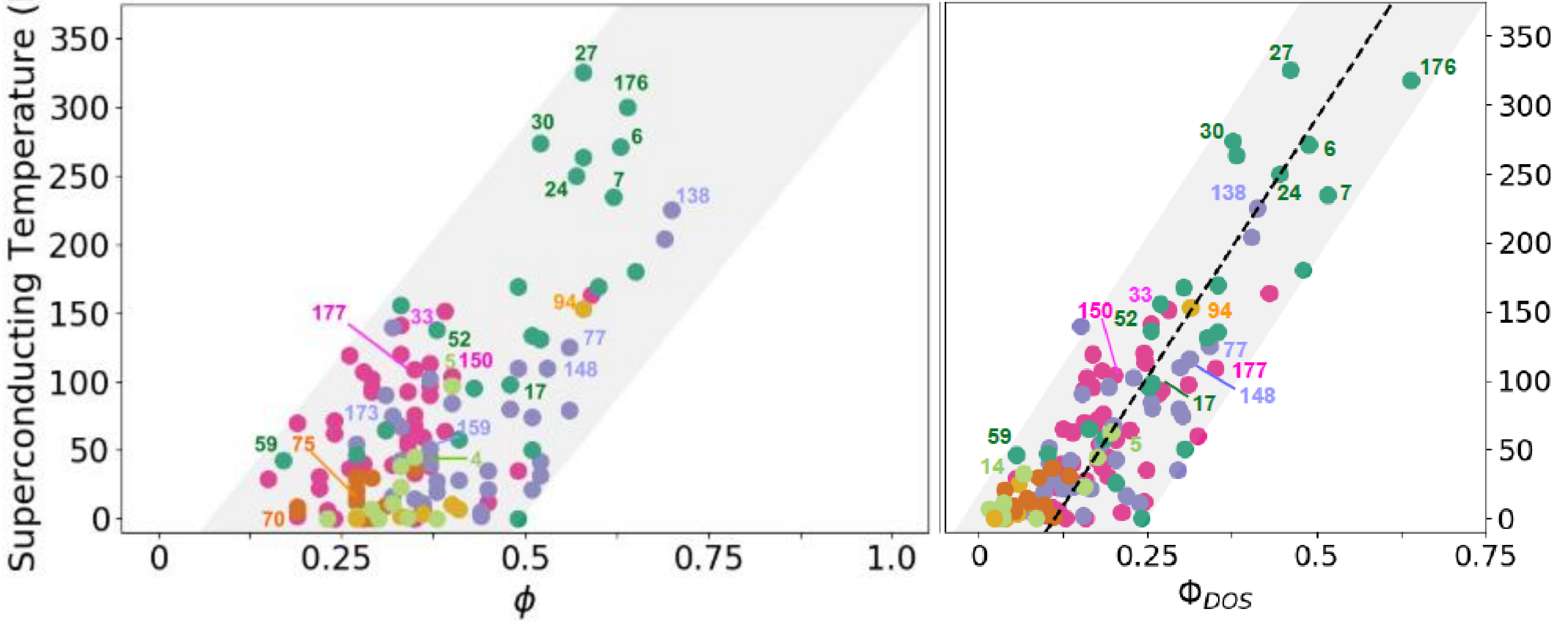


- ϕ provides a first estimate of the superconducting critical temperature

Nat Comm 12, 5381 (2021)

Correlation between T_c and φ

$T_c = (750\,\Phi_{DOS} - 85)\,K$



- ϕ provides a first estimate of the superconducting critical temperature
- Including chemical and electronic structure features reduces the dispersion within 60K

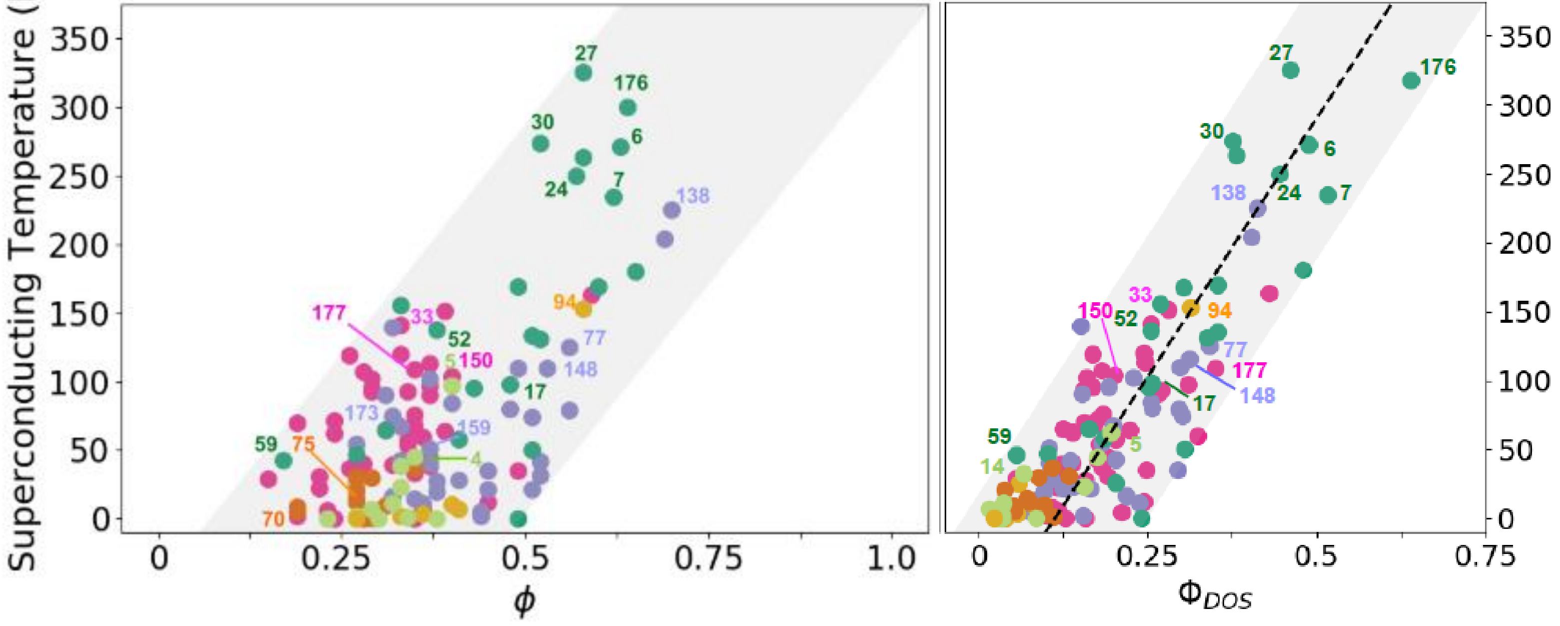
$$\Phi_{DOS} = H_f \sqrt[3]{H_{DOS}}$$

H_{DOS}=DOS at the Fermi level projected on H
H_f=Hydrogen fraction

Nat Comm 12, 5381 (2021)

Correlation between T_c and φ

Tc=(750 Φ_{DOS} -85)K



- ϕ provides a first estimate of the superconducting critical temperature
- Including chemical and electronic structure features reduces the dispersion within 60K

$$\Phi_{DOS} = H_f \sqrt[3]{H_{DOS}}$$

H_{DOS}=DOS at the Fermi level projected on H
H_f=Hydrogen fraction

- Sufficient condition, avoids very expensive calculations!

Nat Comm 12, 5381 (2021)

Summary

- The networking value is able to capture effectively how sensitive the electronic cloud is to lattice vibrations, hence correlating with Tc
- It improves all other structural or electronic indexes previously proposed
- It only requires DFT ground state+ELF calculations

Summary

- The networking value is able to capture effectively how sensitive the electronic cloud is to lattice vibrations, hence correlating with Tc
- It improves all other structural or electronic indexes previously proposed
- It only requires DFT ground state+ELF calculations

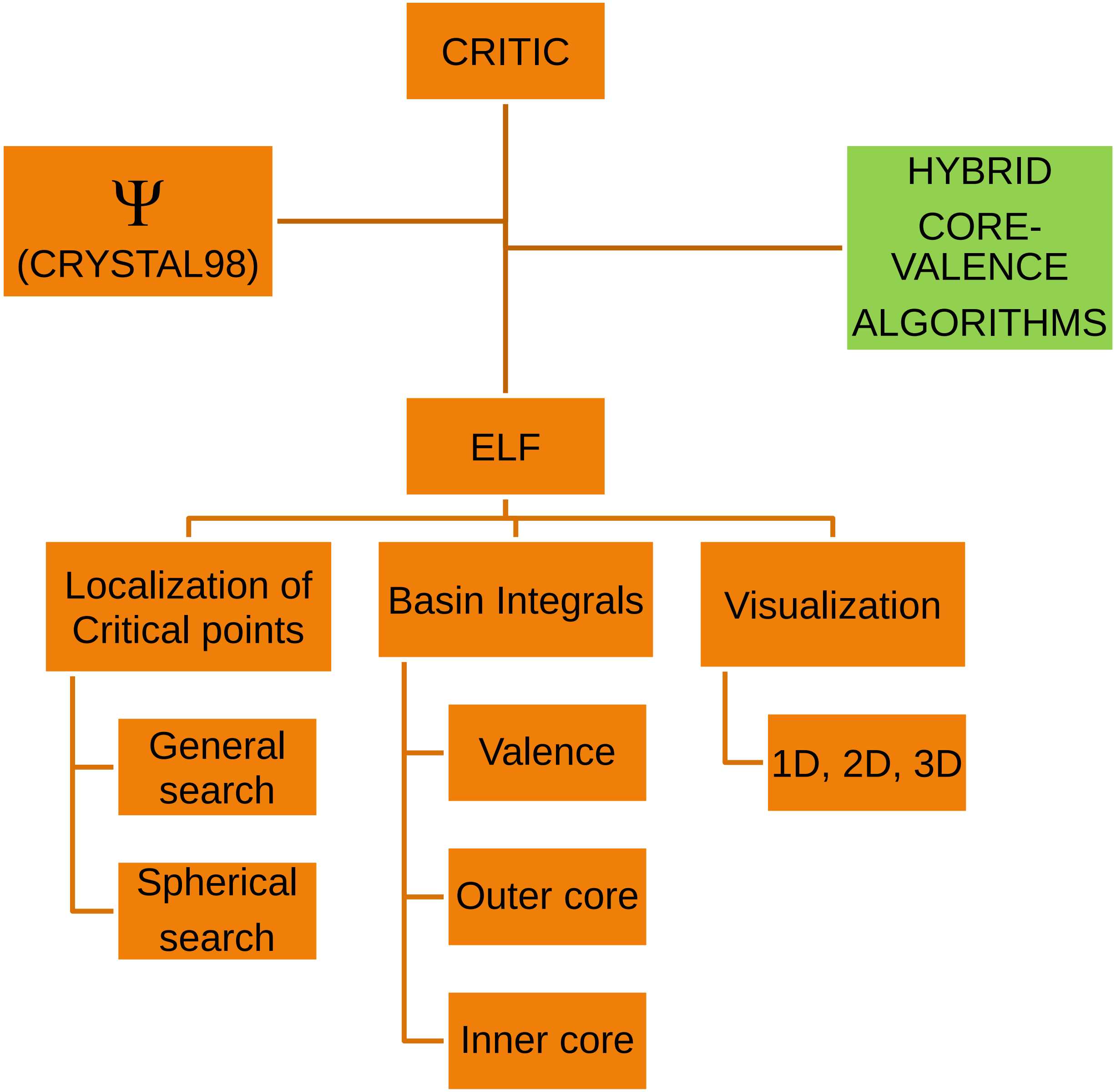
- It offers a simple way of screening new superconductors
- Points the way to inverse engineering new hydrogen-based superconductors

Programs

- ELF and NCI from periodic calculations: CRITIC

- NCI from molecular calculations, PDBs and crystallographic data

- NCI from PDB with PDB treatment: NCIWeb coming soon!



CRITIC

Ψ

(CRYSTAL98)

HYBRID

CORE-VALENCE

ALGORITHMS

ELF

Localization of Critical points

- General search
- Spherical search

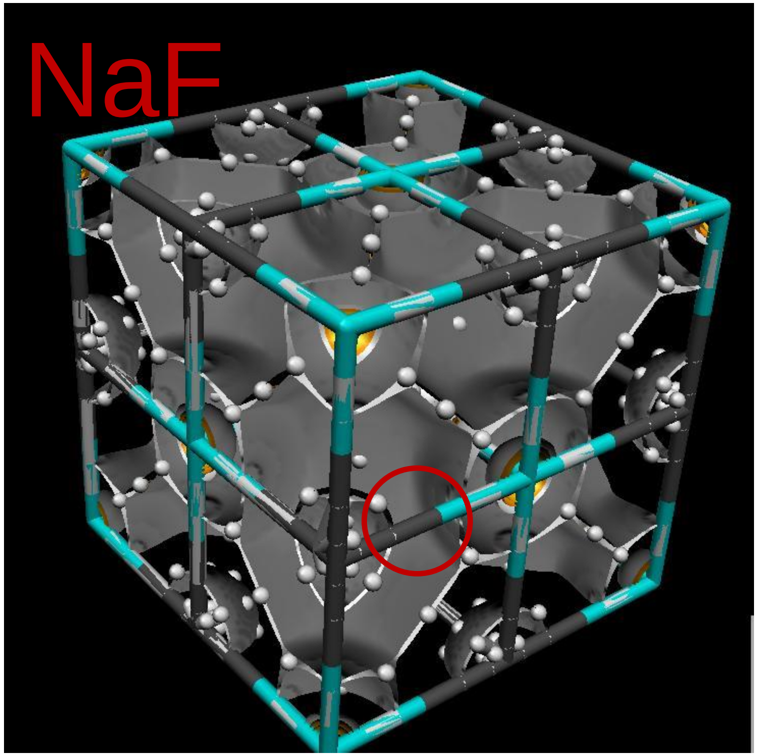
Basin Integrals

- Valence
- Outer core
- Inner core

Visualization

- 1D, 2D, 3D

CRITIC

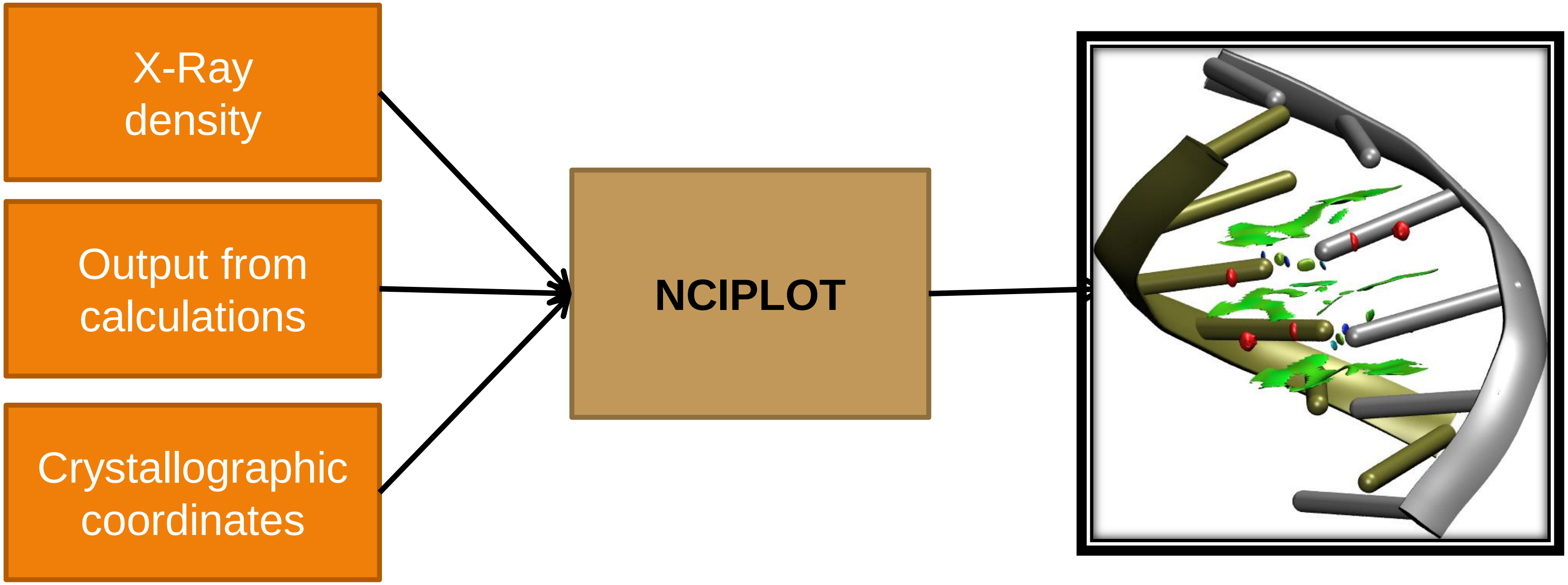


Total	Generic	Hybrid
Maximum number	64	64
Bond number	176	200
Ring number	200	200
Cage number	64	64
Morse sum equals	24	0

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



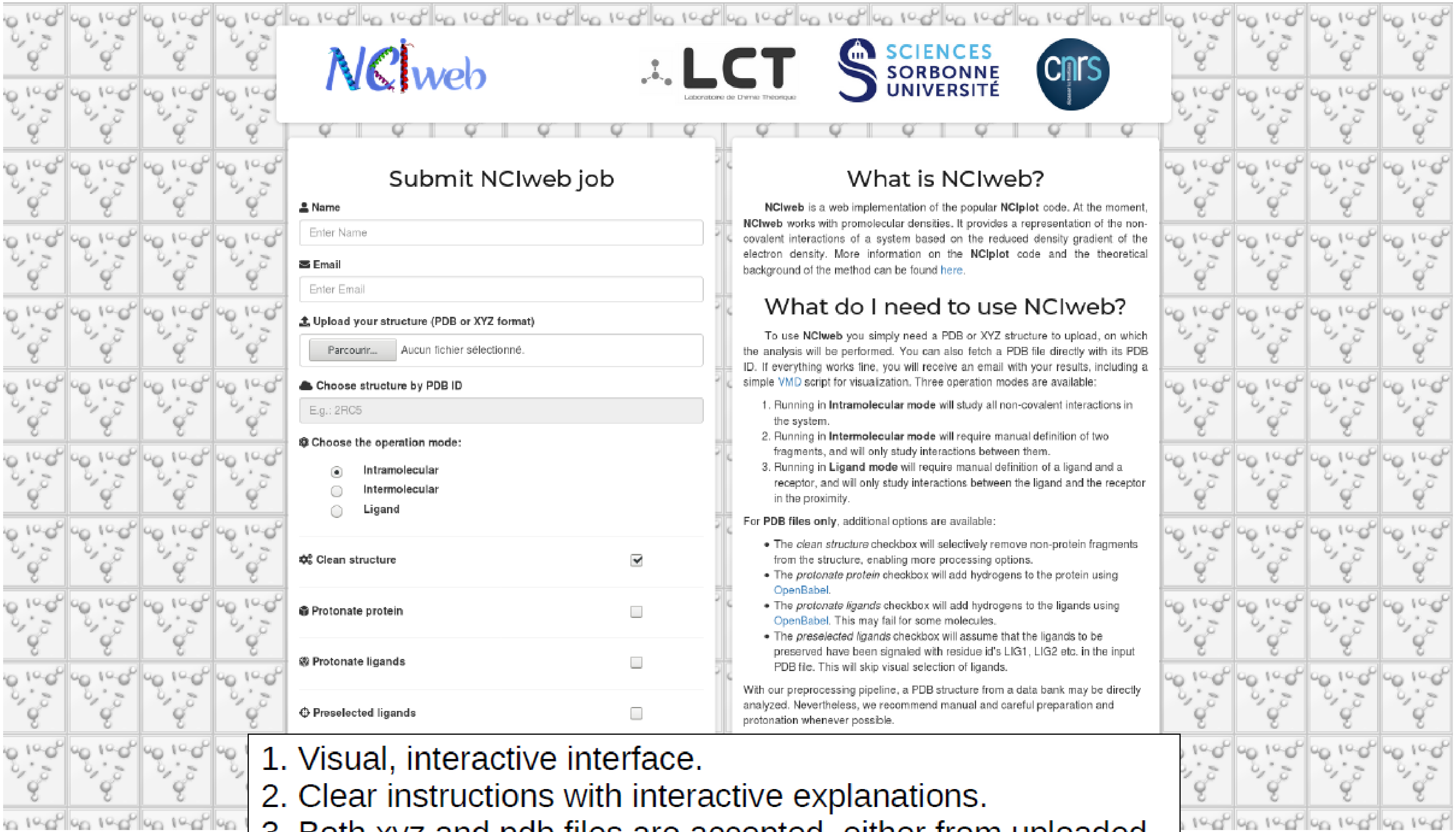
X-Ray density

Output from calculations

Crystallographic coordinates

NCIPLOT

NCIWEB



Submit NCIweb job

Name

Enter Name

Email

Enter Email

Upload your structure (PDB or XYZ format)

Aucun fichier sélectionné.

Choose structure by PDB ID

E.g.: 2RC5

Choose the operation mode:

● Intramolecular
○ Intermolecular
○ Ligand

Clean structure ☑

Protonate protein ☐

Protonate ligands ☐

Preselected ligands ☐

What is NCIweb?

NCIweb is a web implementation of the popular **NCIplot** code. At the moment, **NCIweb** works with promolecular densities. It provides a representation of the non-covalent interactions of a system based on the reduced density gradient of the electron density. More information on the **NCIplot** code and the theoretical background of the method can be found here.

What do I need to use NCIweb?

To use **NCIweb** you simply need a PDB or XYZ structure to upload, on which the analysis will be performed. You can also fetch a PDB file directly with its PDB ID. If everything works fine, you will receive an email with your results, including a simple VMD script for visualization. Three operation modes are available:

1. Running in **Intramolecular mode** will study all non-covalent interactions in the system.
2. Running in **Intermolecular mode** will require manual definition of two fragments, and will only study interactions between them.
3. Running in **Ligand mode** will require manual definition of a ligand and a receptor, and will only study interactions between the ligand and the receptor in the proximity.

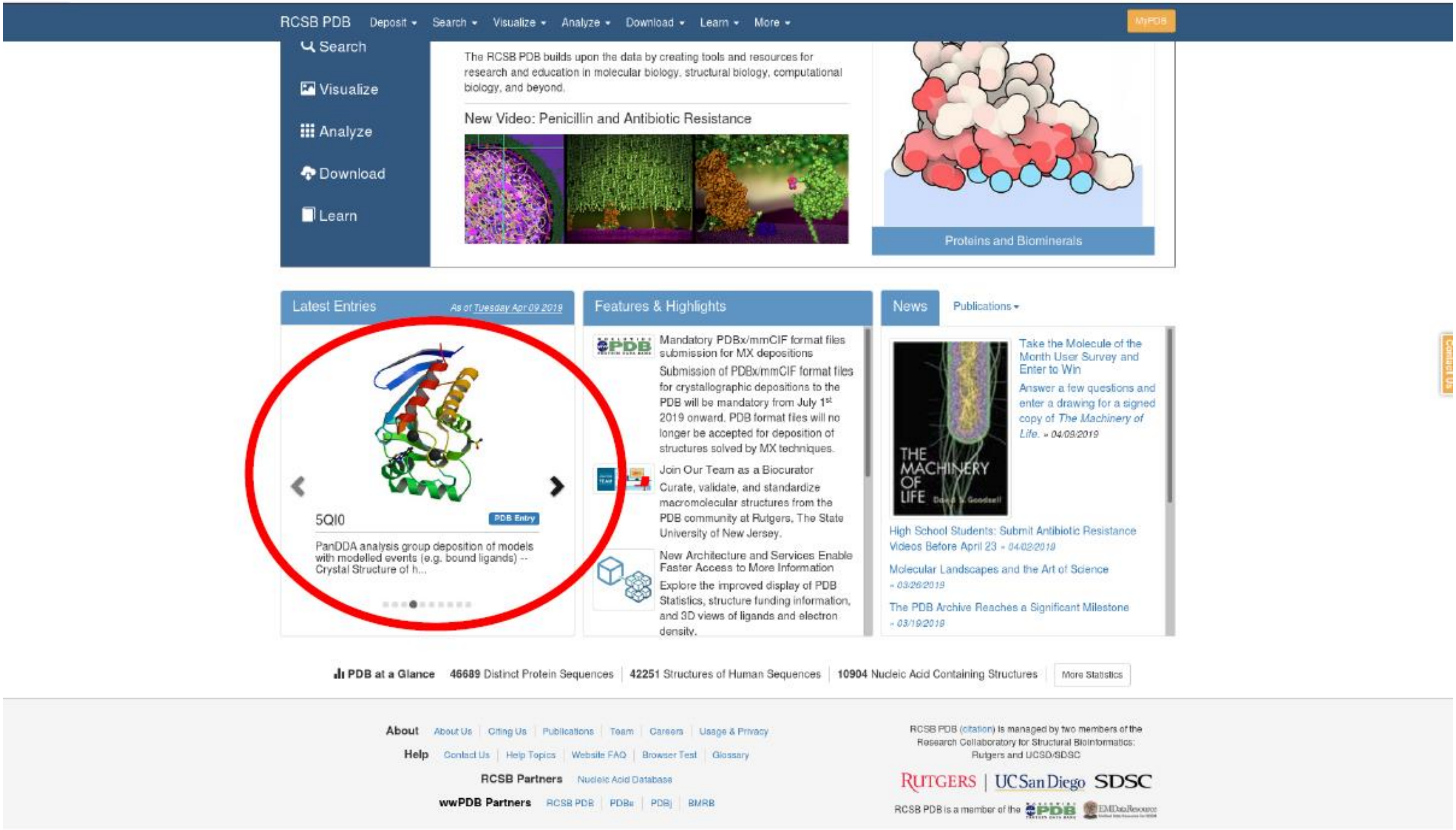
For **PDB files only**, additional options are available:

- The *clean structure* checkbox will selectively remove non-protein fragments from the structure, enabling more processing options.
- The *protonate protein* checkbox will add hydrogens to the protein using OpenBabel.
- The *protonate ligands* checkbox will add hydrogens to the ligands using OpenBabel. This may fail for some molecules.
- The *preselected ligands* checkbox will assume that the ligands to be preserved have been signaled with residue id's LIG1, LIG2 etc. in the input PDB file. This will skip visual selection of ligands.

With our preprocessing pipeline, a PDB structure from a data bank may be directly analyzed. Nevertheless, we recommend manual and careful preparation and protonation whenever possible.

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



The RCSB PDB builds upon the data by creating tools and resources for research and education in molecular biology, structural biology, computational biology, and beyond.

New Video: Penicillin and Antibiotic Resistance

Latest Entries *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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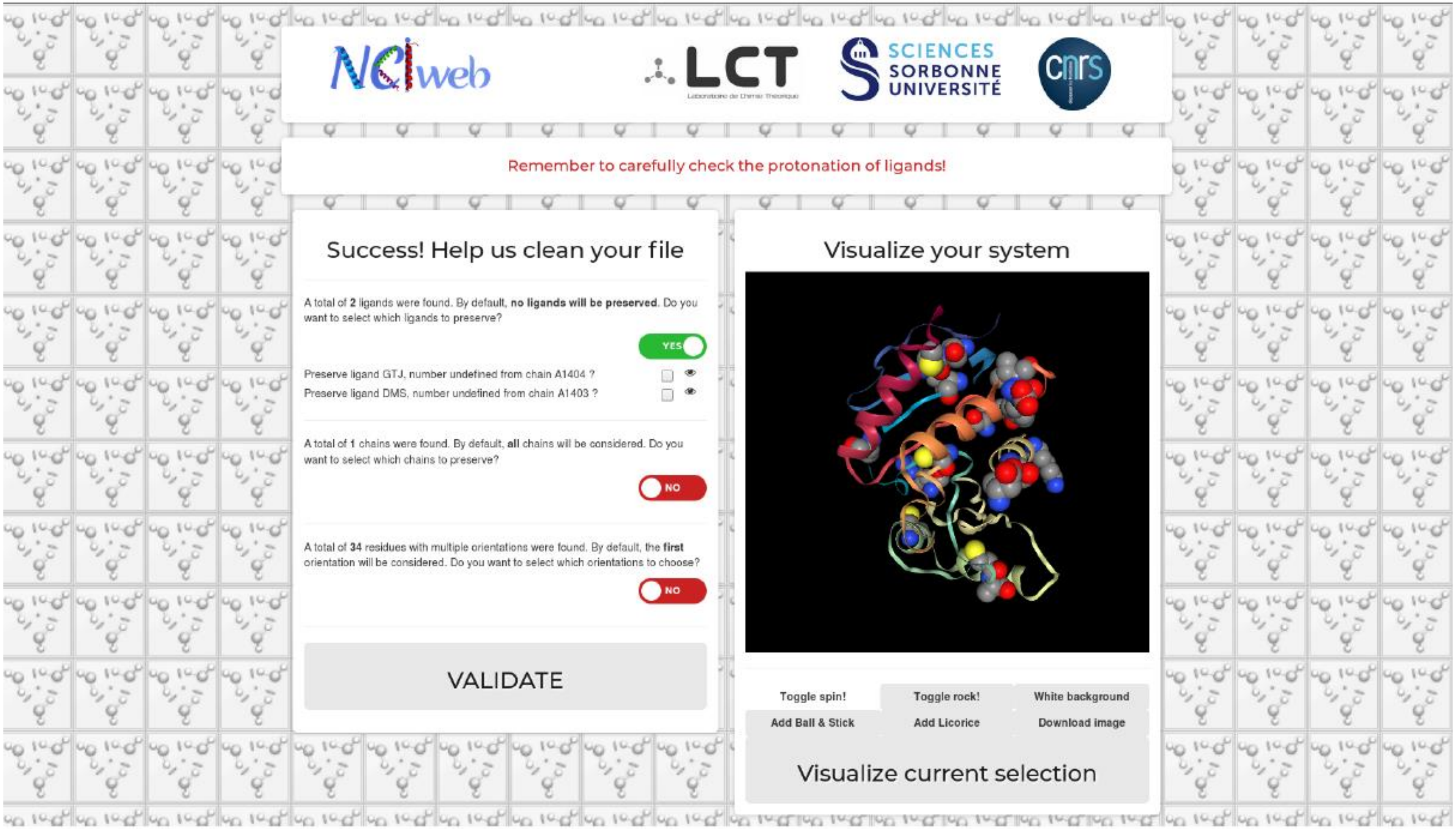
RCSB Partners Nucleic Acid Database

wwPDB Partners RCSB PDB | PDBe | PDBj | BMRB

RCSB PDB (citation) is managed by two members of the Research Collaboratory for Structural Bioinformatics: Rutgers and UCSD/SDSC

RCSB PDB is a member of the

NCIWEB



Remember to carefully check the protonation of ligands!

Success! Help us clean your file

A total of **2** ligands were found. By default, **no ligands will be preserved**. Do you want to select which ligands to preserve?

Preserve ligand GTJ, number undefined from chain A1404 ? ☐

Preserve ligand DMS, number undefined from chain A1403 ? ☐

A total of **1** chains were found. By default, **all** chains will be considered. Do you want to select which chains to preserve?

A total of **34** residues with multiple orientations were found. By default, the **first** orientation will be considered. Do you want to select which orientations to choose?

Visualize your system

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

Thank you for your attention!!!