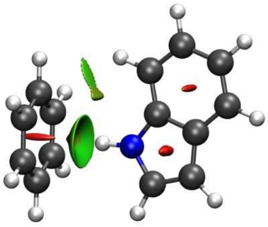
The chemical bond

The topological approach



Julia Contreras-García

1. Why and how studying chemical bonds?

2. Topology
   a) critical points
   b) topological partitions

3. Chemical functions
   a) electron density
   b) ELF
   c) NCI

4. Applications

Why studying chemical bonds?

Motivation

Why studying the chemical bond in solids?

"Many solid chemists have isolated themselves from their organic or even inorganic colleagues by choosing not to see bonds in their materials.
One is unlikely to **understand new materials** with novel properties if one is wearing purely chemical or physical blinkers. We should aim at a coupled approach – a chemical understanding of bonding merged with a deep physical description."

Nobel Prize Winner Prof. Roald Hoffmann

How studying chemical bonds?

Is reconciliation between classical and quantum chemistry possible?

Quantum Chem
System:Global
Concepts: rigurous, QUANTITATIVE

Classical Chem
System: Atoms, Bonds
Concepts: empirical, QUALITATIVE

We will see one of these way-outs: the topological approach

6

The topological approach reconciles quantum and classical chemistry through a real space description of the system and its partition into chemically meaninful (*a la* classical) parts

Quantum Chem
System:Global
Concepts: rigurous, QUANTITATIVE

Real space

Classical Chem
System: Atoms, Bonds
Concepts: empirical, QUALITATIVE

It provides a mathematical definition of atoms in a molecule, bonds, etc.

7

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

8

1. Why studying chemical bonds?

2. Topology
   a) critical points
   b) topological partitions

3. Chemical functions
   a) electron density
   b) ELF
   c) NCI

4. Application to solid state

Study of a function: 1D

Example: f is a cubic function given by

$f(x) = x^3$

Analyse f

10

Study of a function: 1D

Example: f is a cubic function given by

$f'(x) = 3x^2$

$f'(x) = 0 \rightarrow x=0$

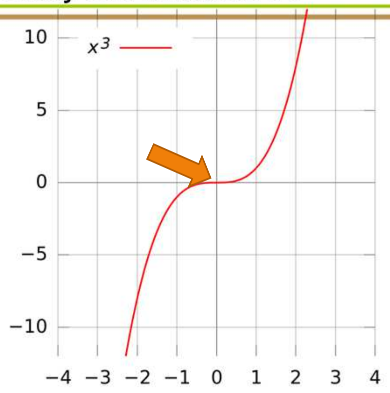
There is a critical point at x=0

$f''(x) = 6x$

$f''(0)=0 \rightarrow$ saddle point

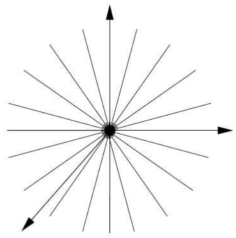
11

Study of a function: 1D

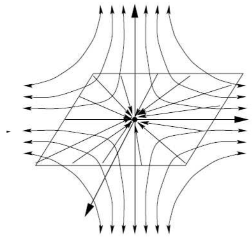


12

There are 4 types of CPs in 3D



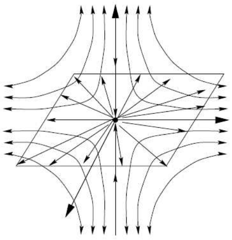
Maximum



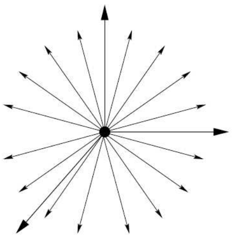
Saddle point of order 1

13

There are 4 types of CPs in 3D



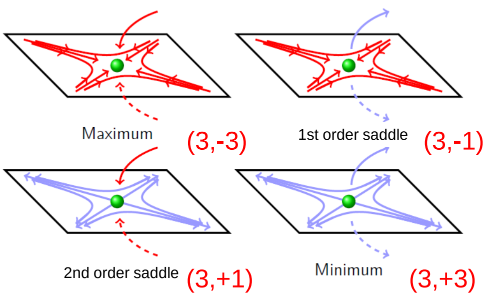
Saddle point of order 2



Minimum

14

There are 4 types of CPs in 3D



15

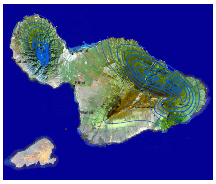
Topology

Critical points

Topological partition

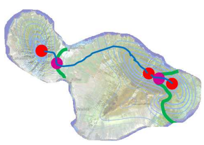
16

Topological partitions are intuitive



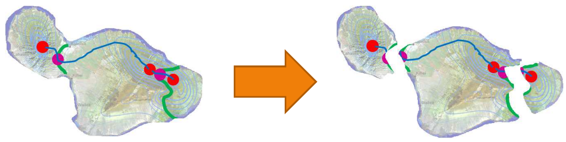
17

Topological partitions are intuitive



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

Topological partitions are intuitive



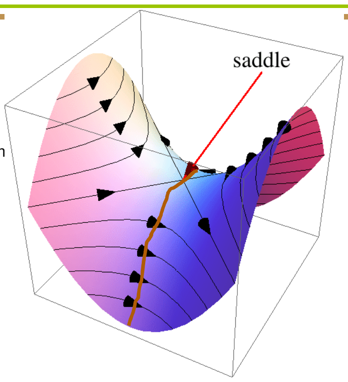
We automatically
- Identify cusps
- Divide through the valleys
- Identify the lowest point in the valley

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

Meaning is inherited

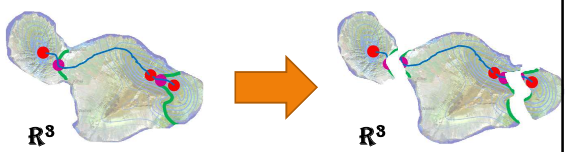
How is it done mathematically?

We follow the zero gradient path



20

IMPORTANT PROPERTIES
- Each maximum has an associated region of space (basin)
  - Non overlapping
  - They fill up the volume



QCT in a nutshell

1 Topology + 2 Chemically sound functions = 3 Quantum chemical Topology (QTC)

Chemical functions

Electron density

ELF

NCI

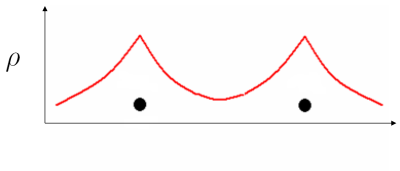
23

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

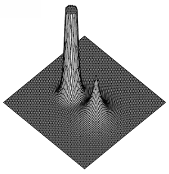
$$\rho(\vec{r}) = N \int \ldots \int \left| \Psi(\vec{x}_1, \vec{x}_2, \ldots, \vec{x}_N) \right|^2 ds \, d\vec{x}_2 \ldots \vec{x}_N$$

  - It condenses all the information of the system (Hohenberg-Kohn theorem)

24



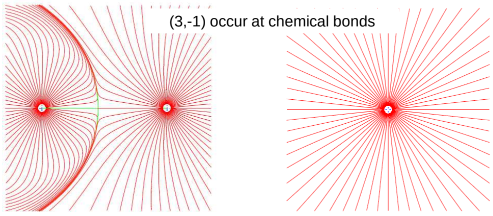
Electron density is maximal at the nuclei



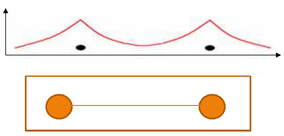
25

The electron density

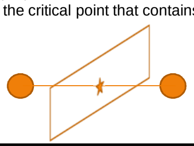
(3,-1) occur at chemical bonds



Plane that contains the nuclei

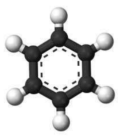


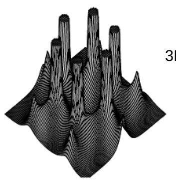
Plane perpendicular to the internuclear line at the critical point that contains the nuclei



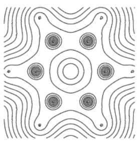
26

•The density





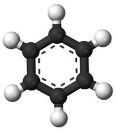
3D Density

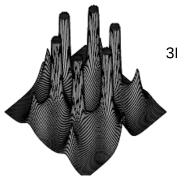


Density isosurfaces

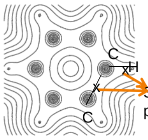
27

•The density



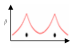


3D Density



Density isosurfaces

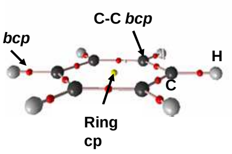
Saddle point=Bond

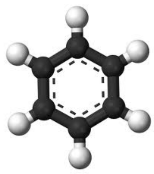


28

We can predict the presence of strong bonds thanks to the topology of the density

QTAIM



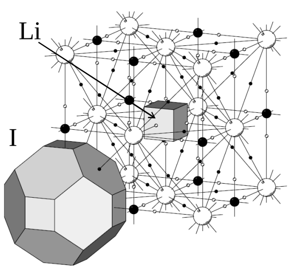


Density → ρ topology → Chemical structure

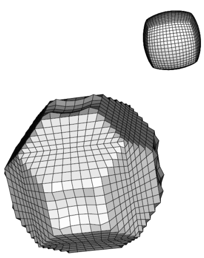
- Maxima = nuclei
- Bond = 1st order saddle point (*bcp*)

29

Old concepts



Contact Polyhedra

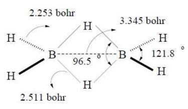


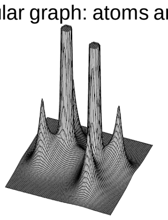
Electron density basins

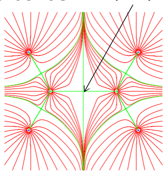
30

Controversial cases

- It recovers the molecular graph: atoms and bonds







31

Quantification

- Each region has its own properties, which can be obtained by integration of density properties within each region

  E.g. if we integrate the density within a volume defined by ELF as a bond, we will know the bond charge

$$q_{bond} = \int_{\Omega_{bond}} \rho dV$$

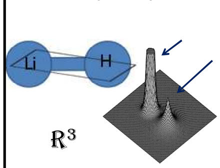
- These properties
  - are additive
  - recover the molecular value

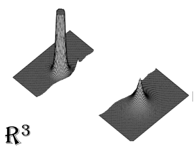
$$N = \int_{allspace} \rho dV = \sum_i \int_{\Omega_i} \rho dV$$

32

•Electron density

- Each maximum has an associated region of space (basin)
  - Non overlapping
  - They fill up the volume

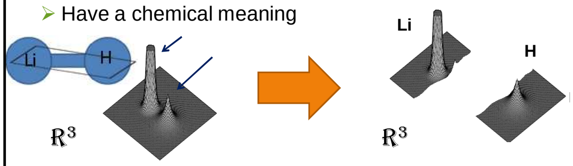




33

•Electron density

- Each maximum has an associated region of space (basin)
  - Non overlapping
  - They fill up the volume
  - Have a chemical meaning

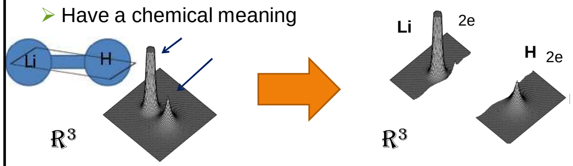


34

•Electron density

- Each maximum has an associated region of space (basin)
  - Non overlapping
  - They fill up the volume
  - Have a chemical meaning

We can integrate properties!



35

Chemical functions

Electron density

ELF

NCI

36

•The Electron Localization Function (ELF)

- Defined by Becke and Edgecombe, 1990
- It can be interpreted as an excess of local kinetic energy density due to Pauli repulsion.

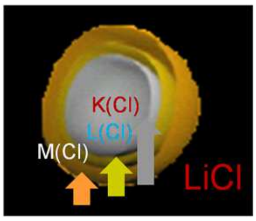
$$t_p(\vec{r}) = t(\vec{r}) - \frac{1}{8}\frac{|\nabla\rho(\vec{r})|^2}{\rho(\vec{r})}$$

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

37

•The Electron Localization Function (ELF)

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

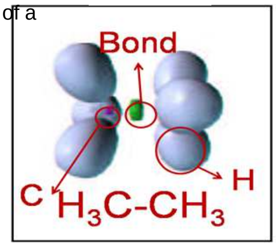


38

•The Electron Localization Function (ELF)

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

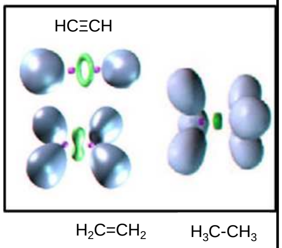
H_3C-CH_3



39

•The Electron Localization Function (ELF)

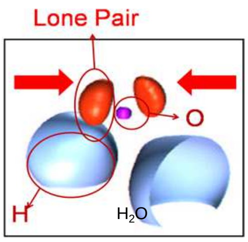
- It recovers the Lewis picture of a system
- ELF is close to one in:
  - Atomic shells
  - Bonds



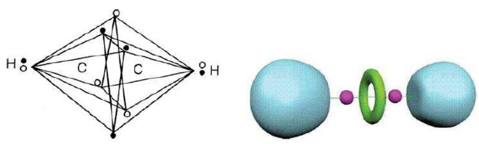
40

•The Electron Localization Function (ELF)

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

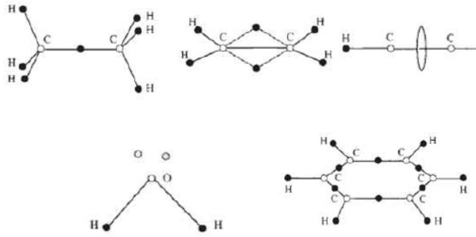


41



42

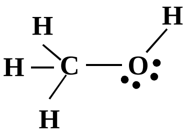
ELF critical points



43

ELF and Lewis

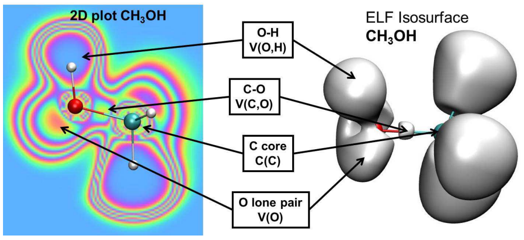
Example CH_3OH



Lewis structure

44

ELF and Lewis



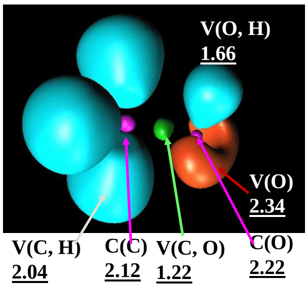
45

ELF and Lewis

Basin population

$$\bar{N}_i = \int_{\Omega ELF} \rho(r)dr$$

	N
C core	2.12
O core	2.22
Bond C-H	2.04
Bond O-H	1.66
LP O	2.34
Bond C-O	1.22



46

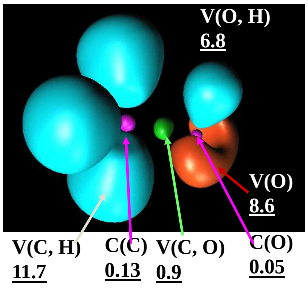
ELF and VSEPR

Basin size

$$V_i = \int_{\Omega ELF} dr$$

Core < Bond < Lone pair

	V
C core	0.13
O core	0.05
Bond C-H	11.7-12.8
Bond O-H	6.8
LP O	8.6
Bond C-O	0.9



47

Chemical functions

Electron density

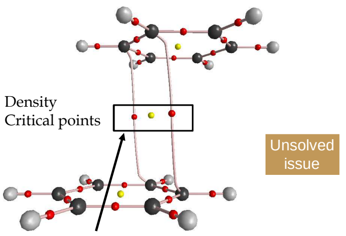
ELF

NCI

48

NCI

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



Pair interactions are not well described by critical points

49

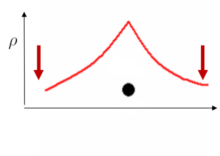
NCI

$$s = c_F \frac{|\nabla \rho|}{\rho^{4/3}}$$

NCI is a method for the visualization of non covalent interactions based on the analysis of reduced density gradient at low densities

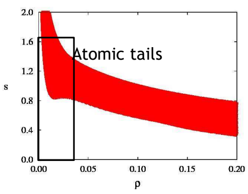
NCI

Free densities



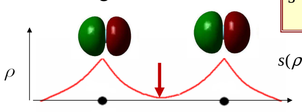
$$s = \frac{1}{2(3\pi^2)^{1/3}} \frac{|\nabla \rho|}{\rho^{4/3}}$$

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



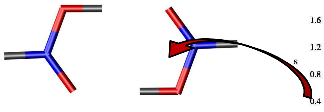
NCI

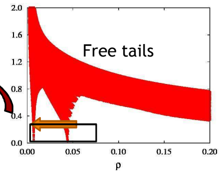
Interacting densities



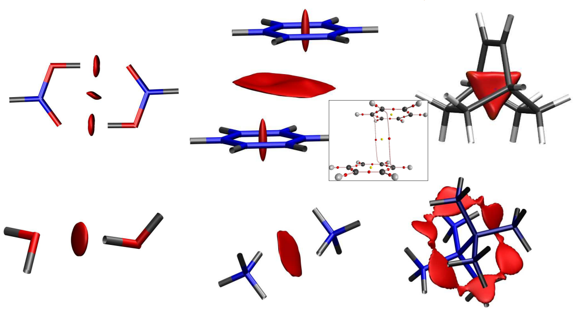
$$s = \frac{1}{2(3\pi^2)^{1/3}} \frac{|\nabla\rho|}{\rho^{4/3}}$$

$$s(\rho) \xrightarrow{r \to 0} e^{R/3} r + O[r]^3 \to 0$$





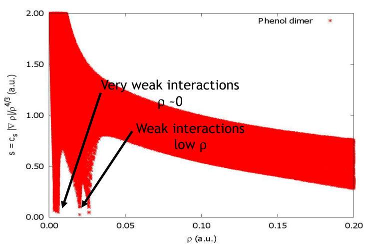
attractive → repulsive

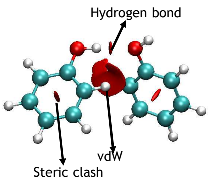


NCI

Distinguish interaction type

1 •**Density** is proportional to the strength of the interaction



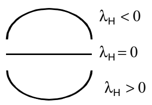


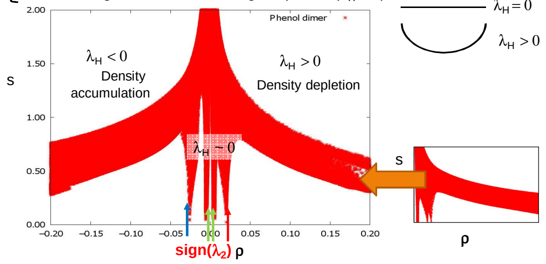
NCI

Distinguish interaction type

2 **Sign of the second eigenvalue**

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

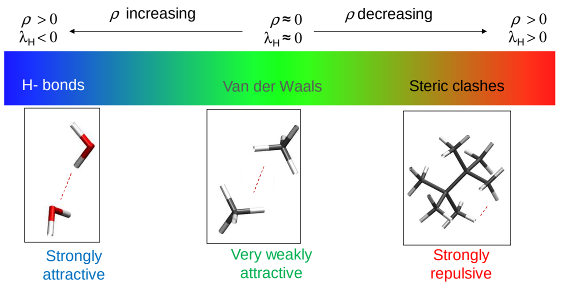




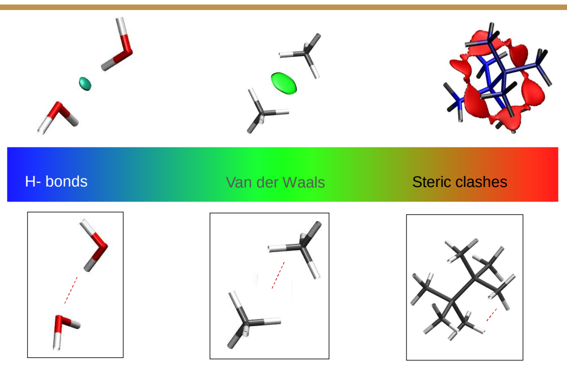
NCI

1) We distinghish 3 ranges of interaction
2) We colour the isosurfaces in a continuum 3-range scheme

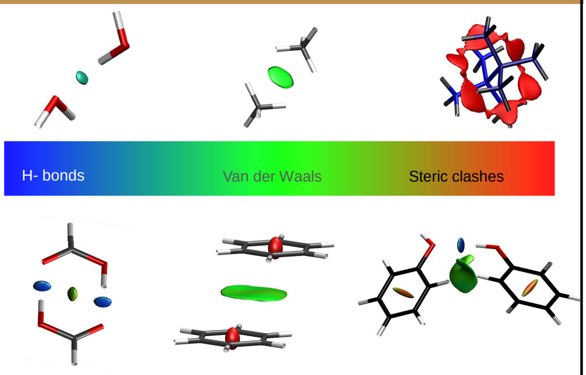
3 ranges



NCI



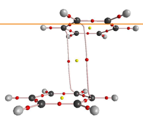
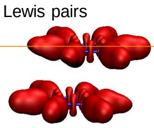
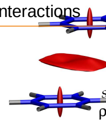
NCI



Summary

- We have complementary functions to describe all the chemical entities of our systems
  - The density, which usually has a one-to-one correspondence with the atoms in the system
  - However, the charge density alone does not describe bonding in its entirety, especially the mechanism of electron pairing: we use ELF
  - However, the density and ELF do not show non covalent interactions, foundamental in molecular crystals: NCI

59

Method	**AIM**	**ELF**	**NCI**
Function	density	Pauli kinetic energy density	Reduced density gradient
Chemical meaning	Atoms	Lewis pairs	Non covalent interactions
Critical points	Maxima=atoms	Maxima=Lewis pairs	Minima=NCIs
Regions	Atoms	Lewis pairs	Non covalent interactions
		 ELF = 0.9	 s = 0.6, ρ < 0.05

Applications

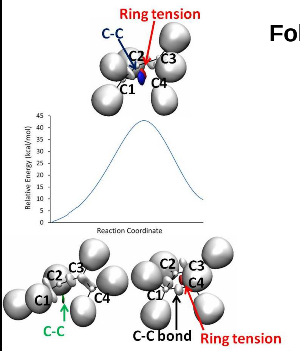
Reactivity

Protein structure

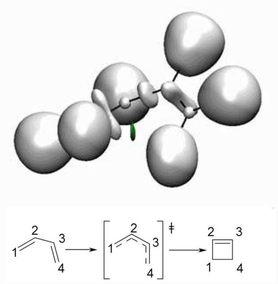
New materials

61

Reactivity

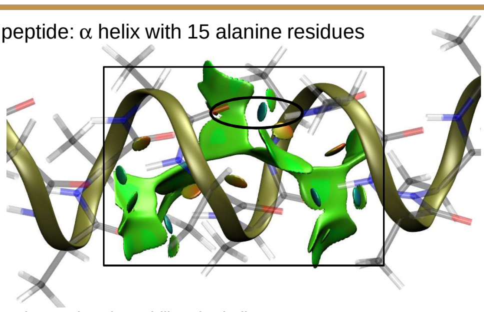


Following organic reactions



Proteins

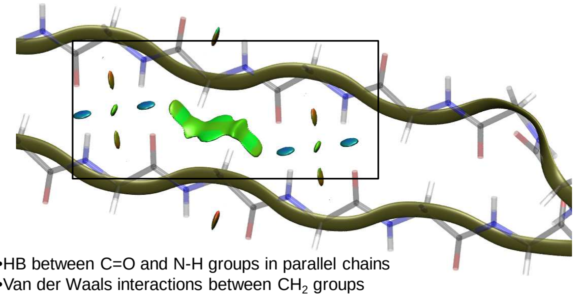
Polipeptide: α helix with 15 alanine residues



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

63

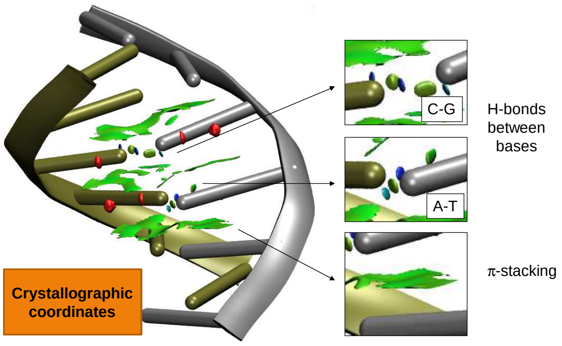
Proteins



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

64

DNA



19/01/2017 J. Chem. Theor. Comp. 7, 625 (2011) 65

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.

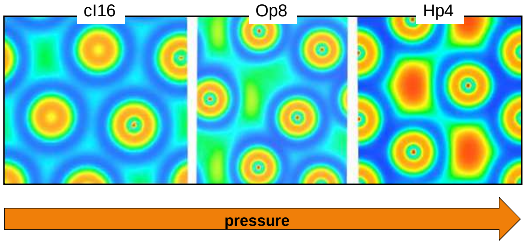
➢However, recent experiments have shown a pressure-induced transformation of Na into an optically transparent and insulating phase at 200 GPa (5.0-fold compression)

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

66

Na

Localization of valence electrons is again observed under pressure

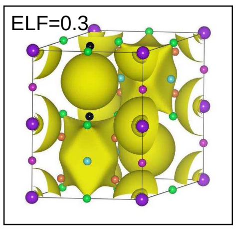


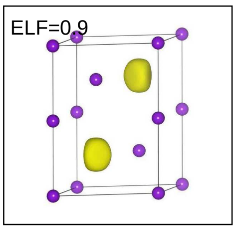
K

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

COUPOUND→IONIC-LIKE

ELECTRONS→PSEUDOANIONS





27 GPa

Thanks to the topological approach we have been able to …

- Understand the electronic structure of a new class of materials beyond historical classifications of materials types and bonding types.
  - We have understood the microscopic nature of a new electronic property (insulating state of metals)
- We have connected strong and weak chemical bonding with reactivity
  - We have shown that weak interactions enable us to foresee the outcome of a reaction mechanism
- We have visualized the interactions that stabilize protein structure and provide them with different properties and functionalities