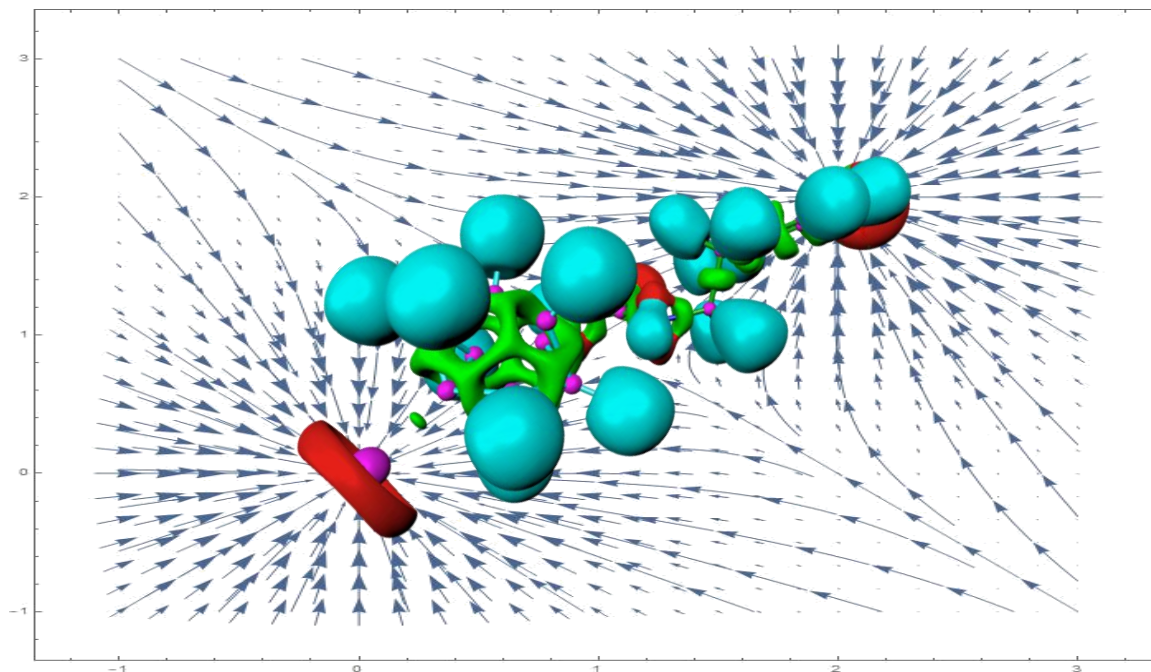
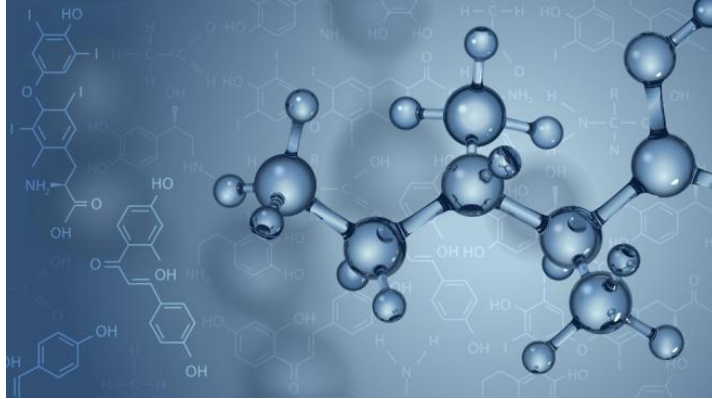


Introduction to Quantum Chemical Topology (QCT)

Julien Pilmé

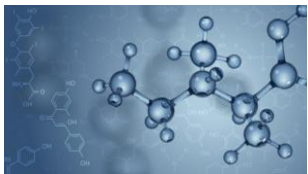


FOREWORD What is a chemical bond ?



FOREWORD What is a chemical bond ?

The point of view of (empirical) chemistry



molecules are made of atoms linked by bonds that lead to the formation of stable compounds (Dalton, 1803-1808)

- A covalent bond is formed by a **localized electron pair** (Lewis, 1916) and some molecular geometries can be predicted by the VSEPR model (Gillespie and Nyholm, 1957)
- Molecular interactions are **classified** into several categories based on their nature of their strengths : covalent, dative, ionic, hydrogen bond, VdW, etc..

but these approaches **have no real mathematical models behind them**

FOREWORD What is a chemical bond ?

The point of view of quantum chemistry (QC)

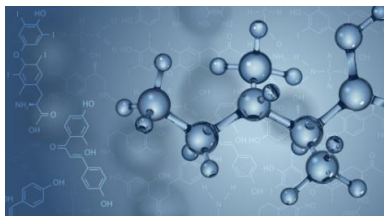
QC gives the three-dimensional arrangement of atoms in the stable compounds (and in the transition states) but **it tells nothing on the chemical bond.**

Gives a physical meaning to the,

- Molecular orbital approaches (Pauling 1930's ,Mulliken 1950's)
- Later Conceptual DFT (Parr and Yang, 1990's)
→ **Successful for semi-quantitative predictions**
Example: the Woodward-Hoffmann rules

MOTIVATION: Is it possible to design a mathematical model with the chemistry we want to represent?

Chemical objects \longleftrightarrow Quantum Chemistry
(bond, lone pair, aromaticity, ...)



$$\hat{H}\Psi = E\Psi$$

Hamiltonian Operator (Energy operator) Energy eigenvalue

“Our understanding is still far from complete and, as new molecules are discovered and synthesized, established ideas often need to be modified. So the nature of the chemical bond is a subject that continues to intrigue chemist”

From the book: “Chemical Bonding and Molecular Geometry From Lewis to Electron Densities” R. J. Gillespie and P. Popelier, 2001

Quantum Chemical Topology

P. Popelier (book chapter [Applications of Topological Methods in Molecular Chemistry](#), pp.23-52):

“Quantum Chemical Topology (QCT) is a branch of theoretical (**quantum**) chemistry that uses the language of (**gradient**) dynamical systems (e.g. **attractor**, **basin**, homeomorphism, **gradient path**/phase curve, **separatrix**, **critical points**) to partition chemical systems and characterise them via associated quantitative properties. This methodology can be applied to a **variety of quantum mechanical functions**, the oldest and most documented one being the electron density (**Bader analysis = Quantum Theory of atoms in molecules QTAIM**)”

1.1 Scalar and Vector Fields: Definitions

Definition. A **field** is a quantity - represented by a number (or a vector or a tensor)- defined for each point of the space region. For example, the temperature of the atmospheric pressure is described by assigning a real number to each point on a map.

Scalar : a **scalar field** $f(x, y, \dots)$ is a (multivariate) function of real variables

Examples: the *pressure field*.

Vector: a **vector field** $\mathbf{V}(x, y, \dots)$ connects a **vector** to each space point.

Examples: the *electric field* or the *velocity field*

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1.1 Scalar and Vector Fields: Definitions

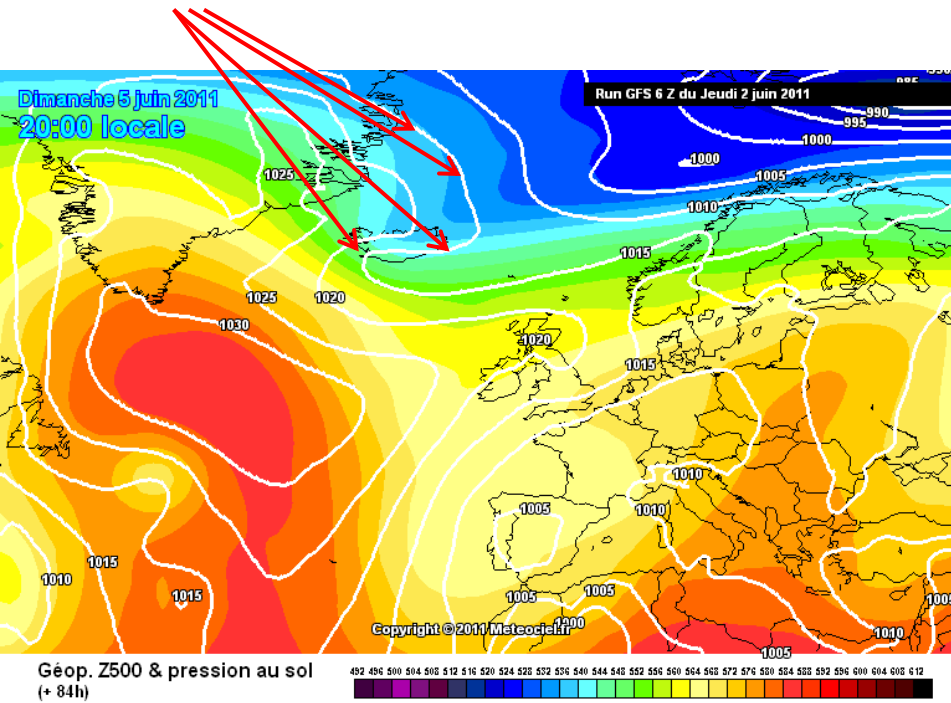
The action of the **gradient** operator over a scalar-valued differentiable function f (C^1 class) of real variables $f(x, y, z)$.

The **gradient field** is an assignment of a vector gradient to each point of space :

$$\text{grad } f(x, y, z) = \nabla f = \frac{\partial f}{\partial x} \mathbf{i} + \frac{\partial f}{\partial y} \mathbf{j} + \frac{\partial f}{\partial z} \mathbf{k} = \begin{pmatrix} \frac{\partial f}{\partial x} \\ \frac{\partial f}{\partial y} \\ \frac{\partial f}{\partial z} \end{pmatrix}$$

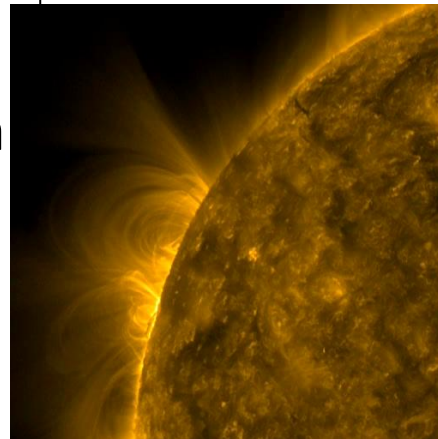
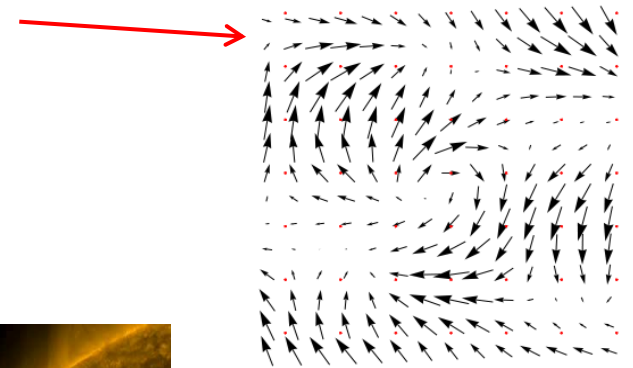
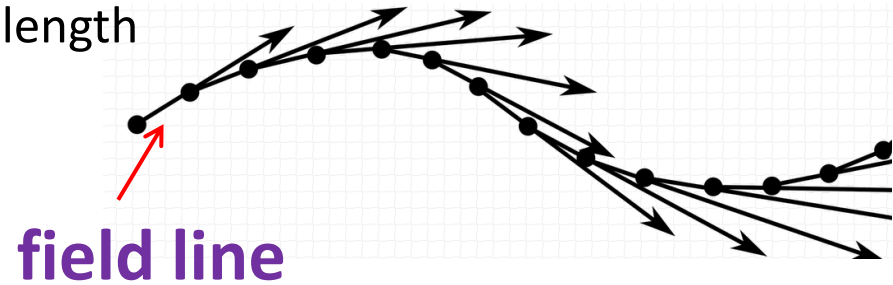
1.2 Scalar and Vector Fields: Viewing

Isoline : the function has a constant value



Bulletin Météorologique Européen
Atmospheric pressure field

field line: symbolic curve that is tangent to the vector at every point along its length



The solar plasma reveals the **field lines** of the magnetic field.

2. 1 Gradient Dynamical System

Mathematically speaking, a gradient dynamical system is a topological space (means a manifold, see for example <https://mathworld.wolfram.com/Manifold.html>)

The dynamical system is generated by a **gradient vector field** of $f(\mathbf{r})$.

(for example, $f \equiv$ electron density or $f \equiv$ the electron localization function)

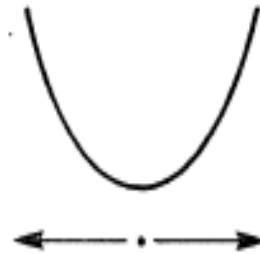
2. 2 Critical Points

CP for a differentiable function (derivatives exist) is a stationary point i.e. $f'(x) = 0$.

The nature of CP is given by the sign of $f''(x)$



$f''(x) < 0$, maximum

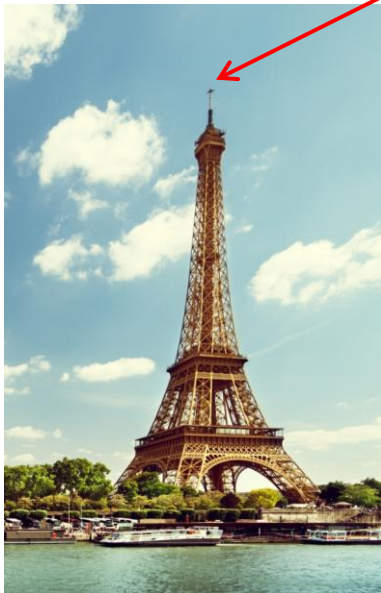


$f''(x) > 0$, minimum

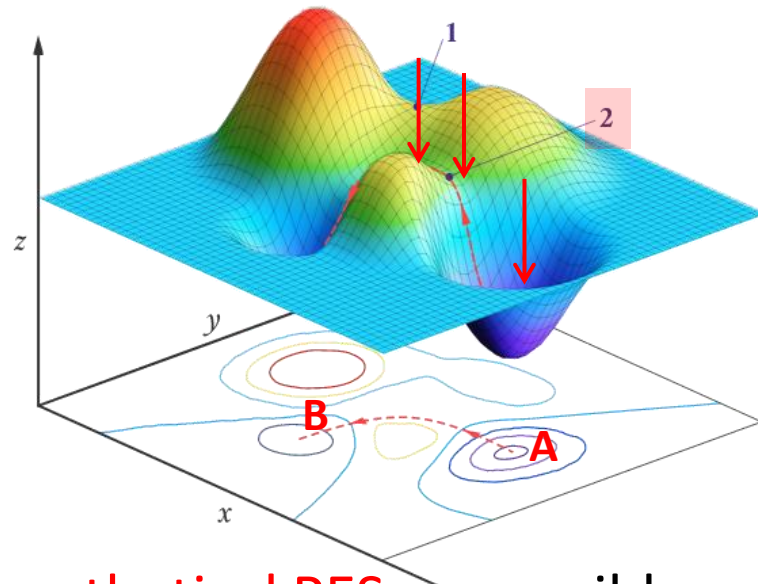
(so-called **attractor**)

2. 2 Critical Points

Critical Points are everywhere!



Attractor !



hypothetical PES : a possible way starts from the energy minimum (A) to (B) via the saddle point (2)

2. 2 Critical Points

$f(x, y, ..)$ is a scalar function of several variables.

Critical points are the **nodal points** where **grad $f = 0$**

2.3 Classification of Critical Points

The critical points of $f(x, y, z)$ are ranked according to their **exponents** which are **the three eigenvalues** $\lambda_1, \lambda_2, \lambda_3$ of the hessian matrix.

$$\begin{pmatrix} \frac{\partial^2 f}{\partial x^2} & \frac{\partial^2 f}{\partial x \partial y} & \frac{\partial^2 f}{\partial x \partial z} \\ \frac{\partial^2 f}{\partial y \partial x} & \frac{\partial^2 f}{\partial y^2} & \frac{\partial^2 f}{\partial y \partial z} \\ \frac{\partial^2 f}{\partial z \partial x} & \frac{\partial^2 f}{\partial z \partial y} & \frac{\partial^2 f}{\partial z^2} \end{pmatrix}$$

Trace of the Hessian matrix:

$$\lambda_1 + \lambda_2 + \lambda_3 = \nabla^2 f(x, y, z) = \text{Laplacian of } f$$

2.3 Classification of Critical Points

Each critical point can be defined by the pair (r, s) :

r (rank) \equiv number of non-zero eigenvalues

s (signature) \equiv difference between the number of positives and negatives eigenvalues.

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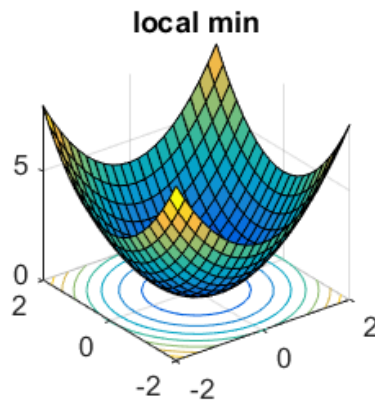
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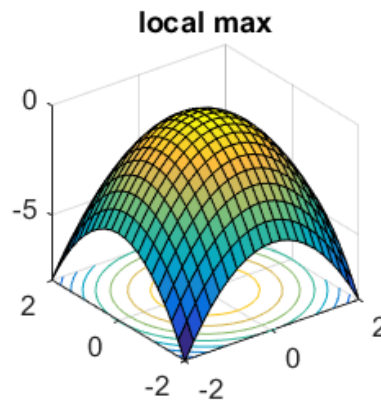
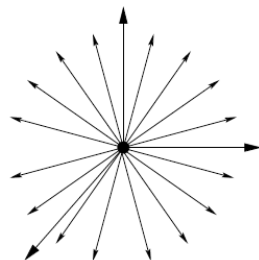
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2.3 Classification of Critical Points

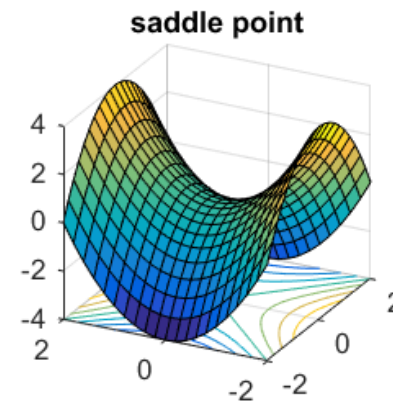
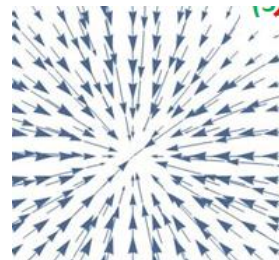
	(rang, signature)
Attractor (local maximum)	(3, -3)
Repellor (local minimum)	(3, +3)
Saddle points	(3,-1), (3,+1)



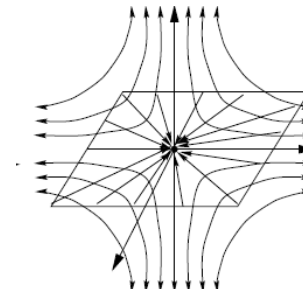
(3, +3)



(3, -3)



(3,-1), (3,+1)



2.3 Classification of Critical Points

Hopft-Poincaré Theorem

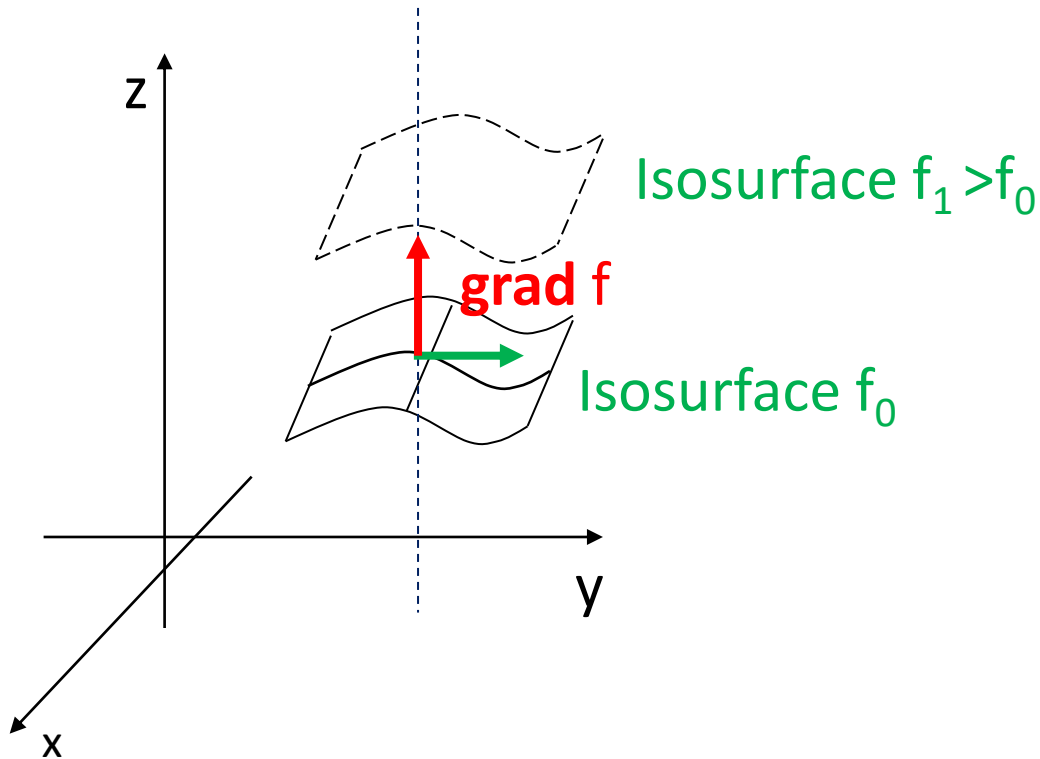
For a non-periodic system (molecule) in \mathbb{R}^3 , the number of critical points must fulfill the following sum rule :

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

This should be checked for each calculation ..

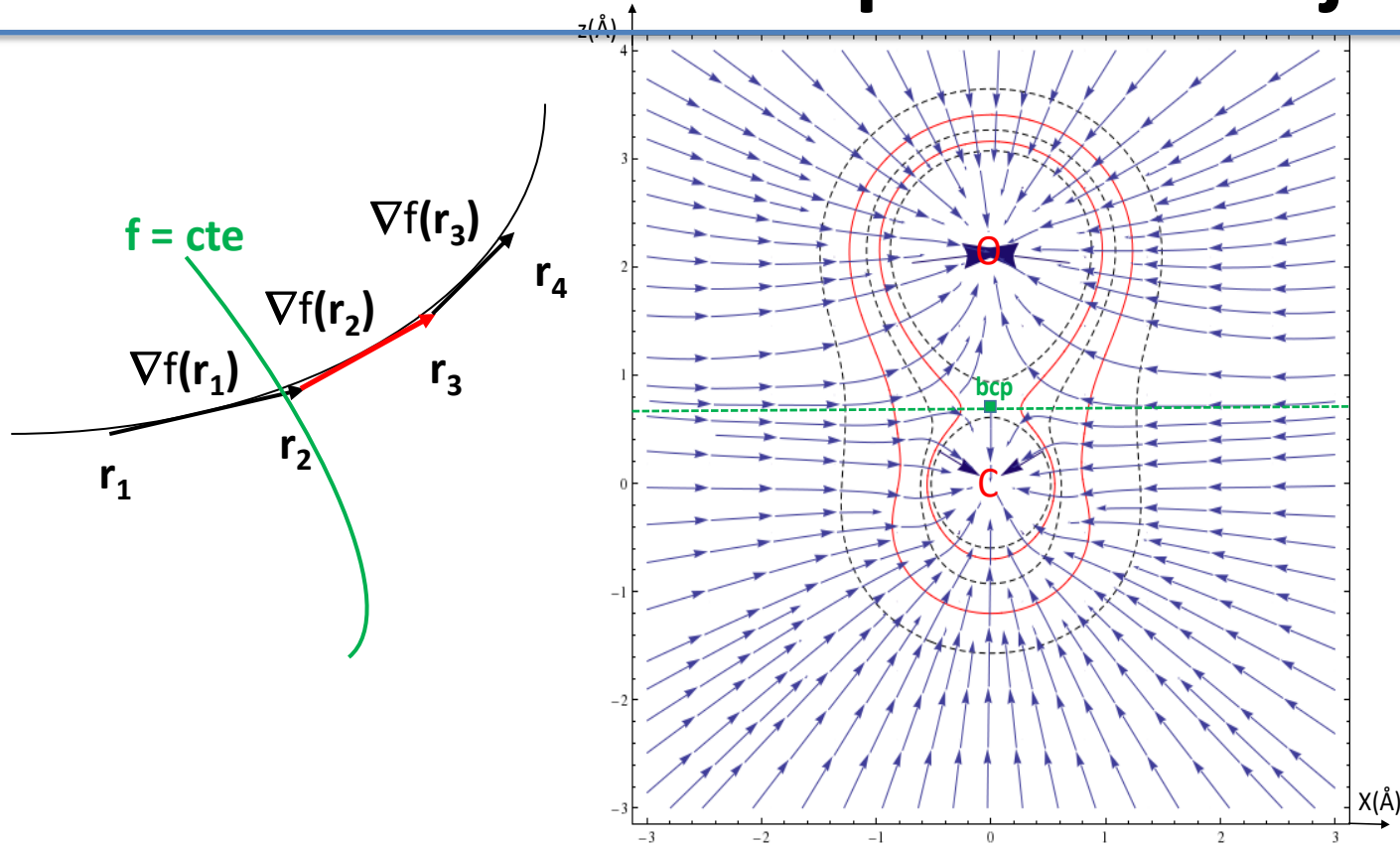
3. Gradient Field Properties

3.1 Gradient Field Properties : Trajectories



The gradient vector is always **orthogonal to the isosurface** and goes to the direction of **the steepest ascent**

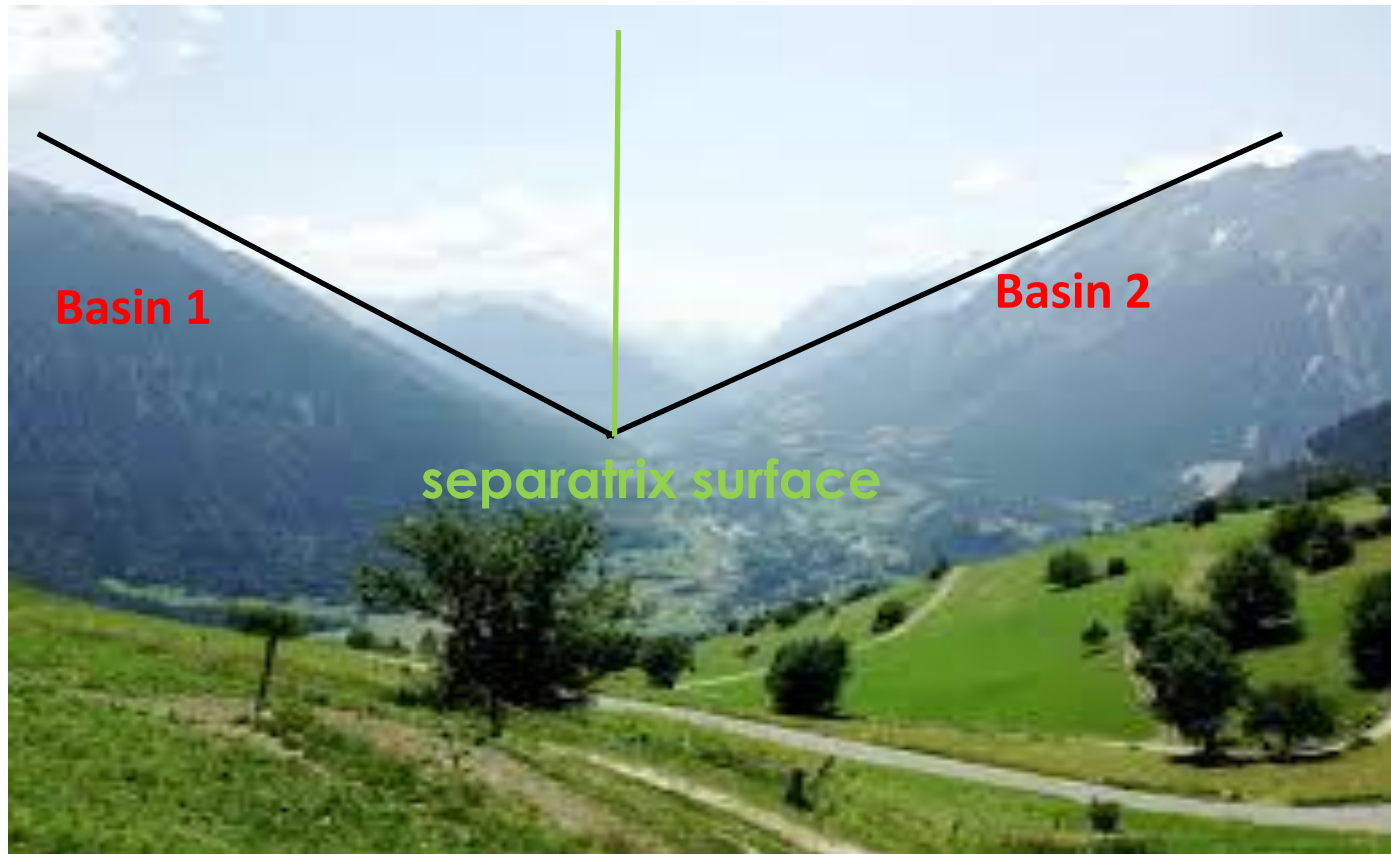
3.1 Gradient Field Properties : Trajectories



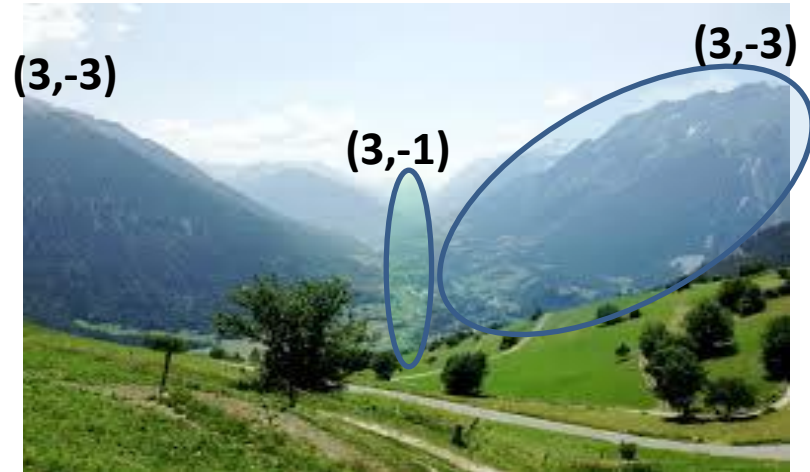
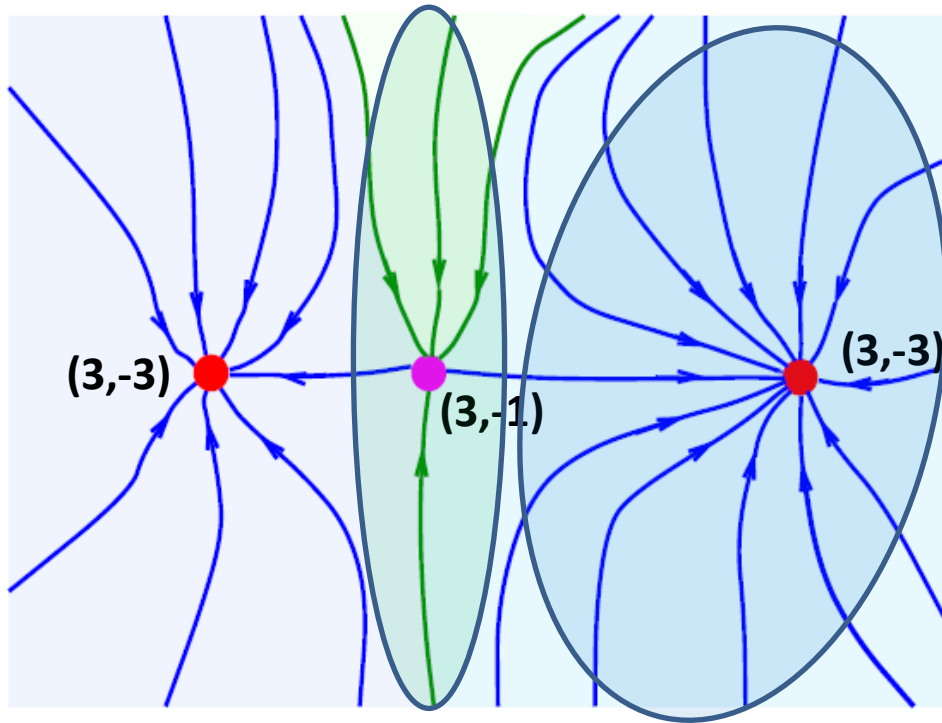
A trajectory (or gradient path or field line) is an infinitesimal sequence of gradient vectors orthogonal to the isosurfaces (steepest ascent)
Ending on a critical point

3.2 Gradient Field Properties : Basins

Basins are everywhere!



3.2 Gradient Field Properties : Basins



- ✓ All the trajectories ending on a same attractor $(3, -3)$ **define a basin volume** (blue on the picture) → **basins are non-overlapping volumes**
- ✓ The trajectories ending on a saddle point $(3, -1)$ define a surface, so-called **separatrix** (green on the picture)

3.3 Gradient Field Properties : A summary

- 1) $\nabla f(\mathbf{r})$ is tangent to his trajectory.
- 2) $\nabla f(\mathbf{r})$ is orthogonal to any isosurface ($f = \text{cte}$).
- 3) $\nabla f(\mathbf{r})$ point to the direction of **the steepest ascent**.
- 4) Each trajectory begins and terminates **on a critical point**, a trajectory cannot be crossed by another trajectory.
- 5) **The trajectories ending on a attractor define the basin (non-overlapping volumes in the molecular space).**

3.4 Gradient Field Properties : Integrated Properties

$$\bar{N}[\Omega_i] = \int_{\Omega_i} \rho(\mathbf{r}) \, d\mathbf{r}$$

The basin population is the mean value of the electron density localized in the basin volume Ω_i .

For n basins in a molecule :

$$\sum_{i=1}^n \bar{N}[\Omega_i] = N \text{ total population}$$

This should be checked for each calculation ..

$$\text{Atomic charge } q[\Omega] = Z_{\Omega} - N[\Omega]$$

Programs Used for Hands-on Sessions

Three software will mainly be used for training:

- **Gaussian**, <https://gaussian.com/>

It is the most widely used commercial research software in quantum chemistry which offers a range of varied methods.



- **ADF**: <https://www.scm.com/doc/ADF/>.

Generalist quantum chemistry software that allows direct analyzes of molecular interactions, in particular those using the QTAIM/IQA approach and the descriptors of the conceptual DFT.

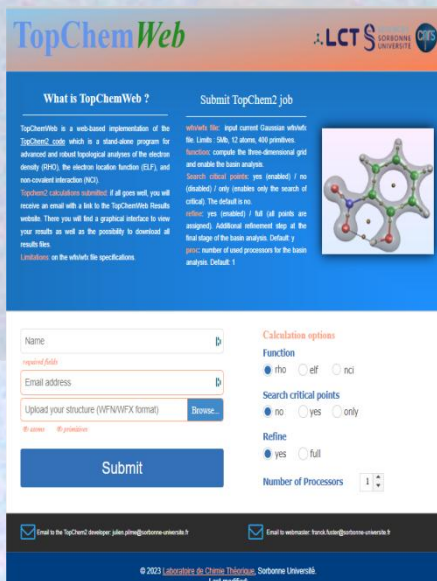
- **TopChem2**: <https://www.lct.jussieu.fr/pagesperso/pilme/topchempage.html>

It is a software for analyzing interactions using topological approaches and conceptual DFT. It is developed at the Laboratory of Theoretical Chemistry at Sorbonne University. It is free and the license allows free use for teaching or research activities.

Quick Starts are available in the Exercise book !

TopChemWeb v1.0 by F. Fuster and J. Pilmé

<http://topchemweb.sorbonne-universite.fr/>



TopChemWeb LCT SORBONNE UNIVERSITÉ CNRS

What is TopChemWeb ?

Submit TopChem2 job

TopChemWeb is a web-based implementation of the TopChem2 code which is a stand-alone program for advanced and robust topological analysis of the electron density (RDG), the electron localization function (ELF), and non-covalent interaction (NCI).

TopChem2 calculations submitted. If all goes well, you will receive an email with a link to the TopChemWeb Results website. There you will find a graphical interface to view your results as well as the possibility to download all results files.

Limitation: on the widgets file specifications.

widgets file: input current Cartesian widgets file (max: 50k). 12 atoms, 400 primitives. function: compute the three-dimensional grid and enable the basin analysis.

Search critical points: yes (enabled) / no (disabled) / only enables only the search of critical. The default is no.

refine: yes (enabled) / full (all points are assigned). Additional refinement step at the final stage of the basin analysis. Default: y.

procs: number of used processors for the basin analysis. Default: 1.

Name:

Email address:

Upload your structure (WFN/WFX format): Browse...

Submit

Calculation options

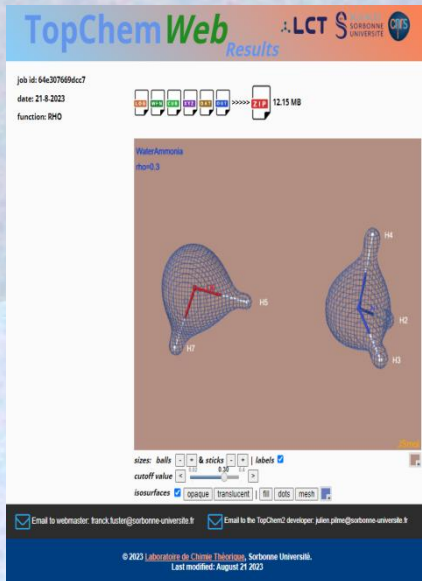
Function: rho elf nci

Search critical points: no yes only

Refine: yes full

Number of Processors:

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job id: 64e307609dec7

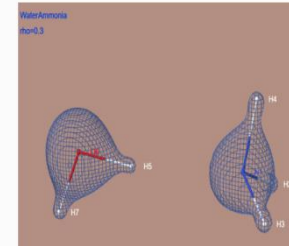
date: 21-8-2023

function: RHO

12.15 MB

Water Ammonia

Proc=3

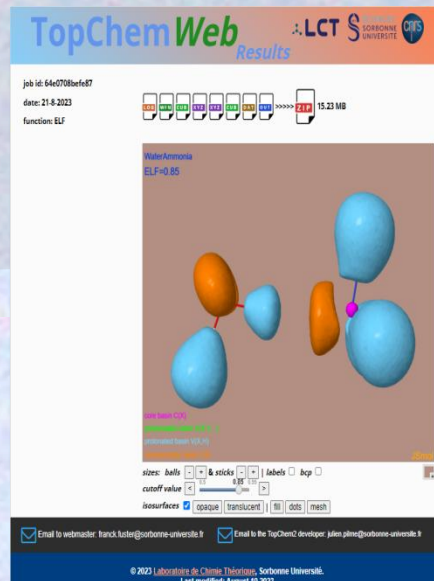


size: balls & sticks labels

cutoff value:

isosurfaces: opaque translucent dots mesh

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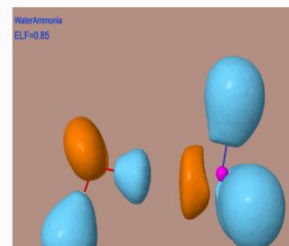
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function: ELF

15.23 MB

Water Ammonia

ELF=0.65

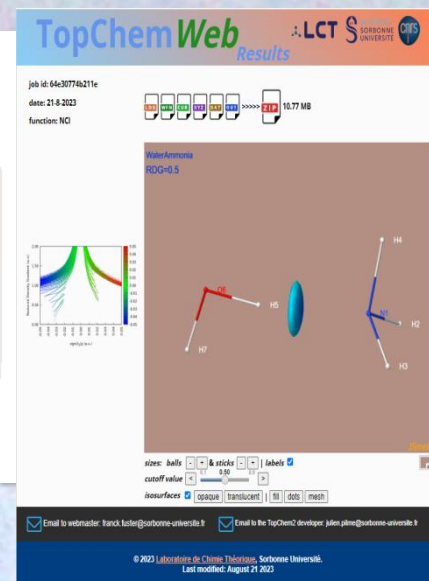


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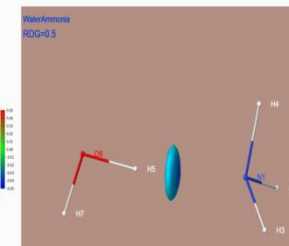
date: 21-8-2023

function: NCI

10.77 MB

Water Ammonia

RDG=0.5




size: balls & sticks labels


cutoff value:


isosurfaces: opaque translucent dots mesh

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 A free online trial implementation of the TopChem2 code

 PROAIMS wavefunction (wfn or wfx) file for input, limited to 12 atoms and 400 primitives

 Electron density, ELF and NCI functions are currently available for calculations

 Graphical interface to view your results and download all topchem2 results files (available 48 hours)

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Thank you for your attention !