Introduction to Quantum Chemical Topology (QCT)

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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 theses approaches have no real mathematical models behind them
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 (bond, lone pair, aromaticity, ...)

Quantum Chemistry

\[ \hat{H} \psi = E \psi \]

“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”

Quantum Chemical Topology


“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 $f(x, y, ...)$ is a (multivariate) function of real variables
**Examples:** the *pressure field*.

**Vector:** a vector field $V(x, y, ...)$ 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 \textbf{gradient} operator over a scalar-valued differentiable function \( f \) (\( C^1 \) class) of real variables \( f(x, y, z) \).

The \textbf{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

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

Bulletin Météorologique Européen
Atmospheric pressure field

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 \( f(r) \).

(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 (so-called attractor)
- \( f''(x) > 0 \), minimum
2. 2 Critical Points

Critical Points are everywhere!

hypothesical PES: a possible way starts from the energy minimum (A) to (B) via the saddle point (2)
2. 2 Critical Points

\[ f(x, y, \ldots) \] is a scalar function of several variables.

Critical points are the **nodal points** where \[ \text{grad } f = 0 \]
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:

$\lambda_1 + \lambda_2 + \lambda_3 = \nabla^2 f(x, y, z) = \text{Laplacian of } f$
Each critical point can be defined by the pair \((r, s)\):

\begin{align*}
\text{r (rank)} & \equiv \text{number of non-zero eigenvalues} \\
\text{s (signature)} & \equiv \text{difference between the number of positives and negatives eigenvalues.}
\end{align*}
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## 2.3 Classification of Critical Points

<table>
<thead>
<tr>
<th>Type</th>
<th>(rang, signature)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Attractor (local maximum)</td>
<td>(3, -3)</td>
</tr>
<tr>
<td>Repellor (local minimum)</td>
<td>(3, +3)</td>
</tr>
<tr>
<td>Saddle points</td>
<td>(3,-1), (3,+1)</td>
</tr>
</tbody>
</table>

![Diagram showing local minimum, local maximum, and saddle point](image)

- **Local minimum**: (3, +3)
- **Local maximum**: (3, -3)
- **Saddle point**: (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!

Basin 1  separatrix surface  Basin 2
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) $\nabla f(r)$ is tangent to his trajectory.

2) $\nabla f(r)$ is orthogonal to any isosurface ($f = \text{cte}$).

3) $\nabla f(r)$ 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

\[ \overline{N}[\Omega_i] = \int_{\Omega_i} \rho(r) \, dr \]

The basin population is the mean value of the electron density localized in the basin volume \( \Omega_i \).

For \( n \) basins in a molecule:

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

This should be checked for each calculation..

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/](https://gaussian.com/)

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


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](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/

- **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)**
Some references


https://www.lct.jussieu.fr/pagesperso/silvi/elfhtml/node1.html#SECTION0001100000000000


Some references

Chemical Bonding and Molecular Geometry: From Lewis to Electron Densities

Chemical bonding: From Lewis to atoms in molecules

About Lewis’s heritage: Chemical interpretations and quantum chemistry

Six questions on topology in theoretical chemistry

Nine questions on energy decomposition analysis
Thank you for your attention!