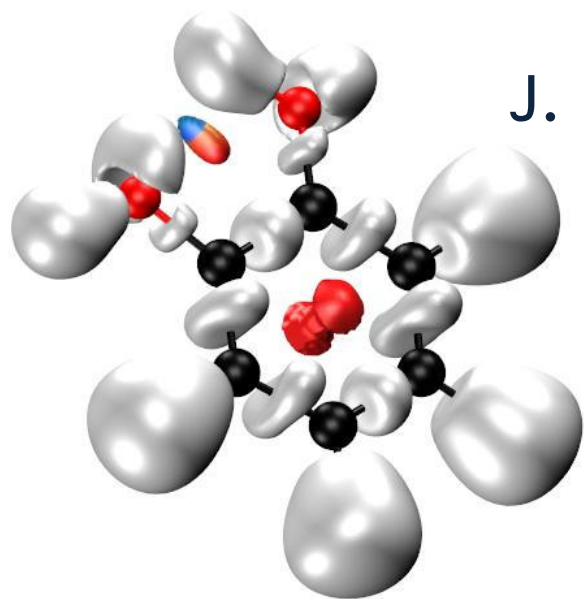


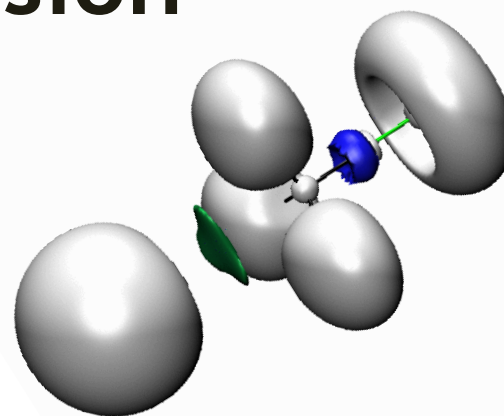


The ELF and NCI analysis

Training session



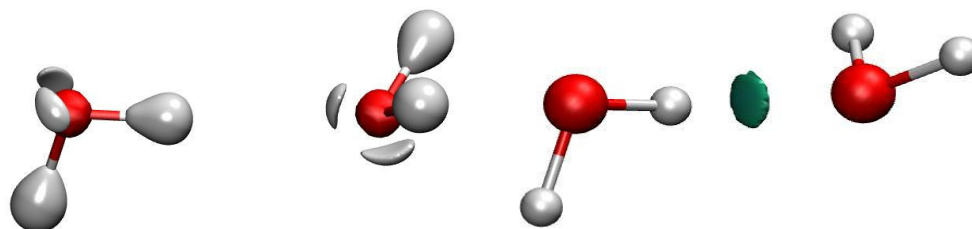
J. Contreras-Garcia
R. Chaudret



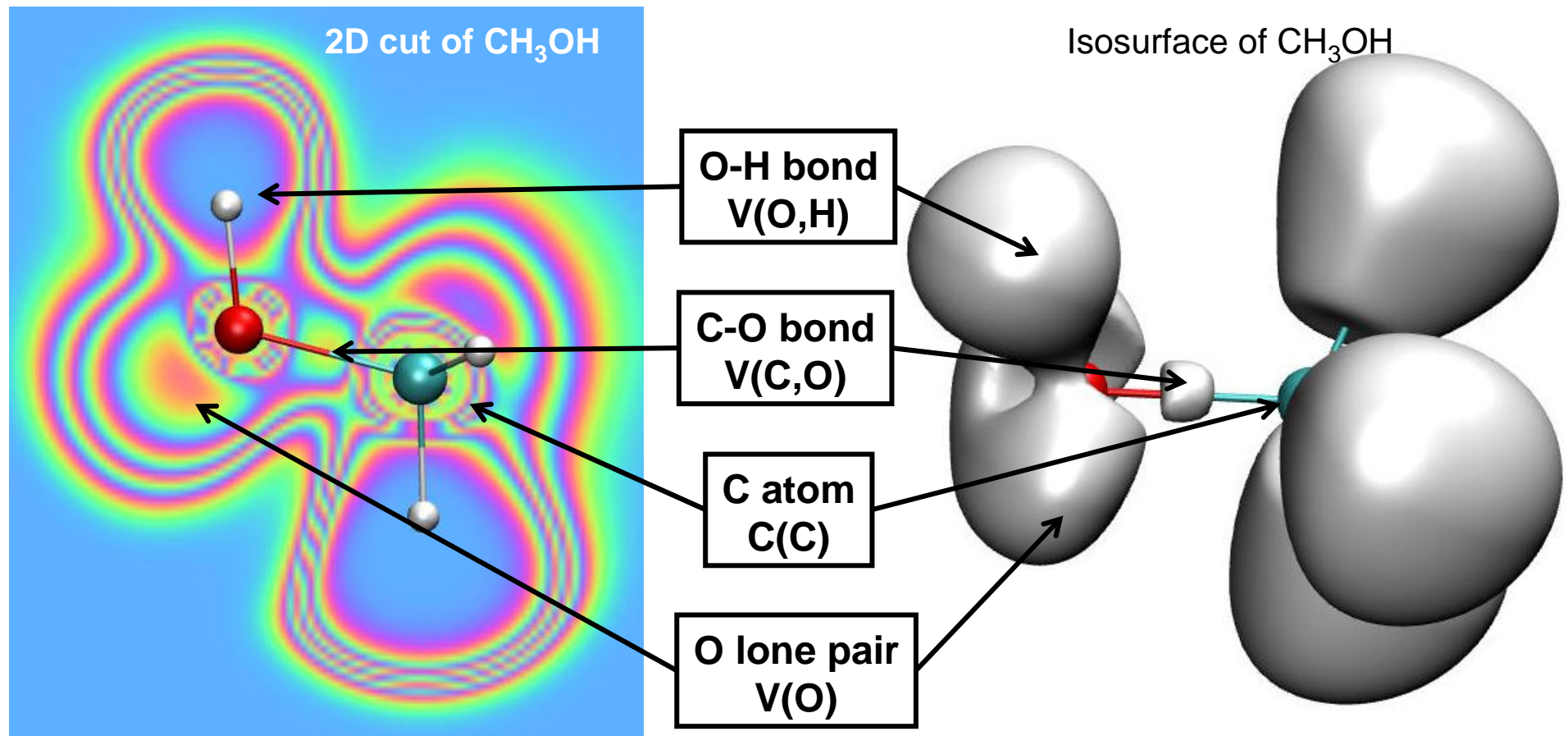
Silvi, B.; Savin, A. *Nature* **1994**, *371*, 683.
Piquemal, J. P. *Int. J. Quant. Chem.* **2008**, *108*, 1951.
Johnson, E. R. *J. Am. Chem. Soc.* **2010**, *132*, 6498.
Contreras-Garcia, J. *J. Chem. Theo. Comput.* **2011**, *7*, 625.

ELF, AIM, NCI: Summary

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

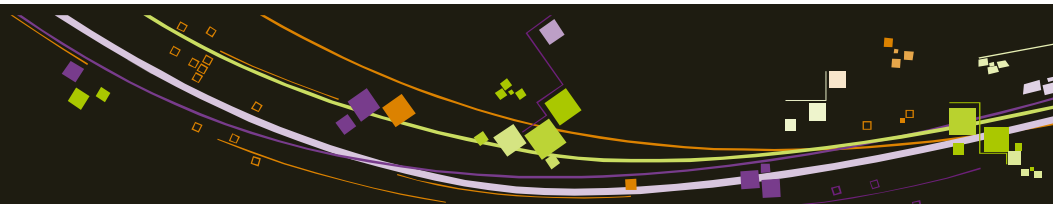


The ELF analysis

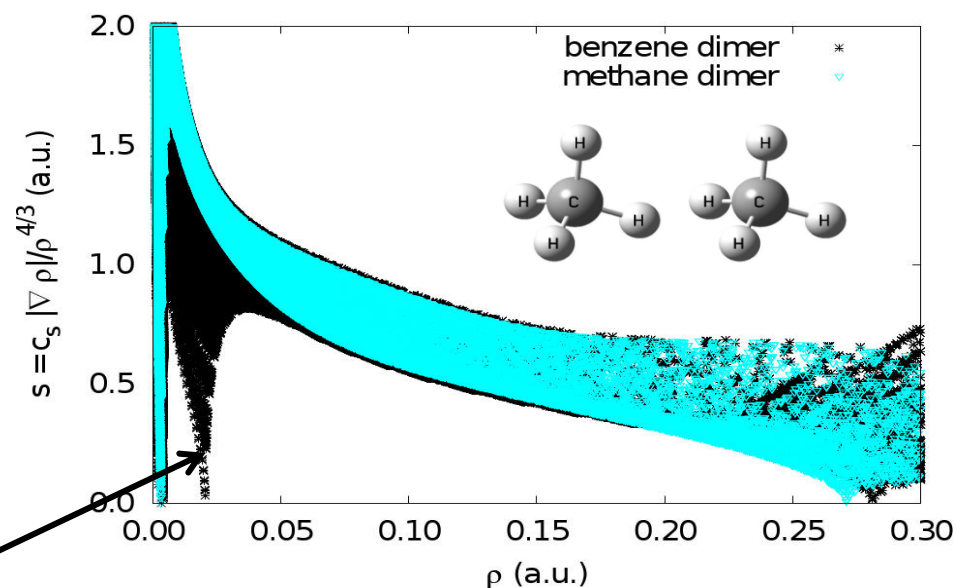
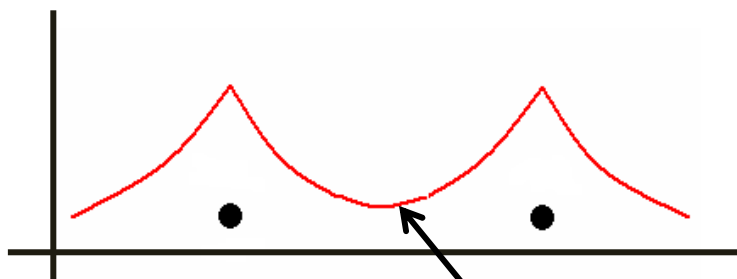


- Visualization of bonds, lone pairs and atoms
- Link with Lewis or VSEPR theory → **Easy to understand for the chemist**
- Integration of different properties on the basins (charge, dipole, volume...)

The NCI analysis

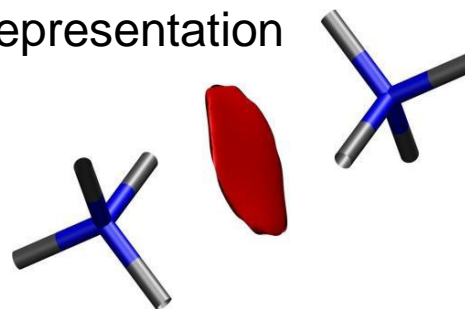


$$s = \frac{1}{2(\pi^2)^{1/3}} \frac{|\nabla\rho|}{\rho^{4/3}}$$



Local minimum with ρ very small
and $s(\rho) \rightarrow 0$
→ Interacting densities
→ **Non covalent interactions**

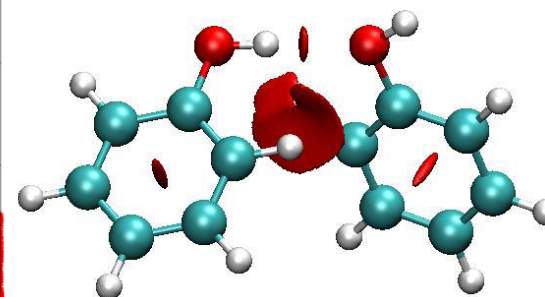
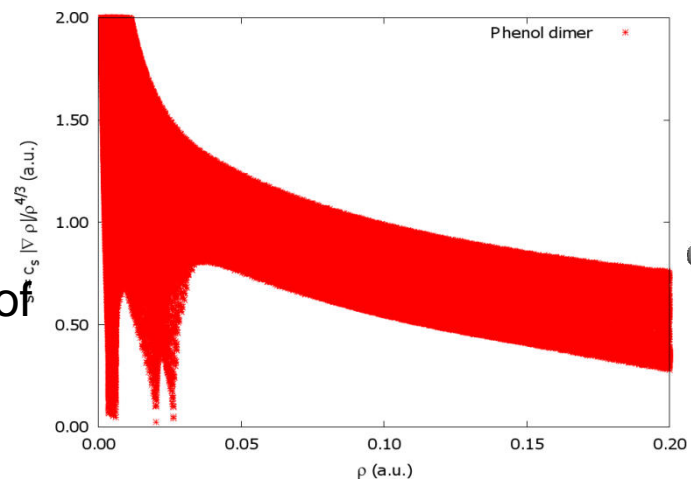
3D representation



The NCI analysis

1- Strength

The electronic density is proportional to the strength of the interaction (AIM)



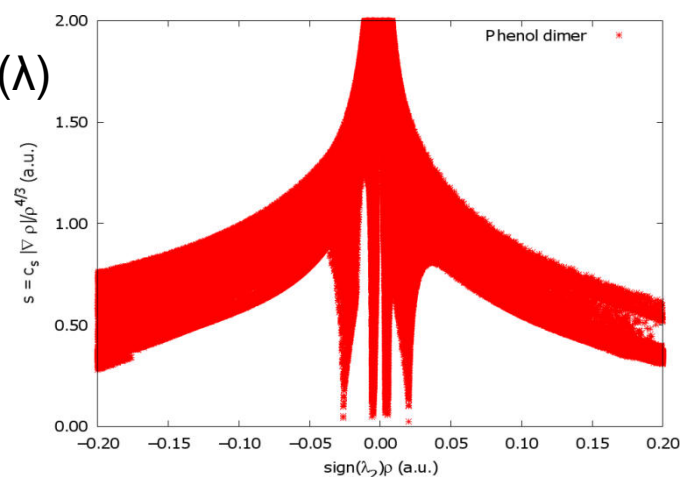
2- Nature

Multiplication by a constant (λ)

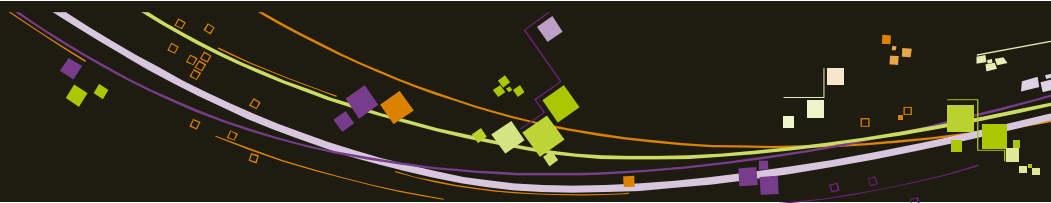
based on the derivatives

$\lambda < 0$: attractive

$\lambda > 0$: repulsive



The NCI analysis



$$\rho < 0$$
$$\lambda < 0$$

$$\rho \approx 0$$
$$\lambda \approx 0$$

$$\rho > 0$$
$$\lambda > 0$$



attraction

repulsion

Hydrogen bond

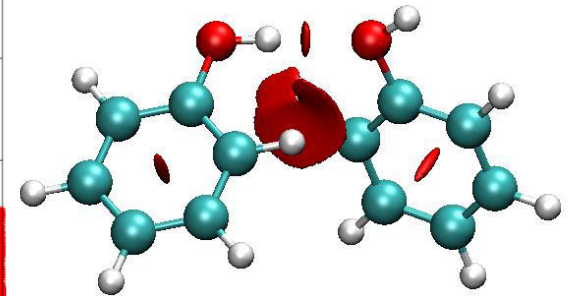
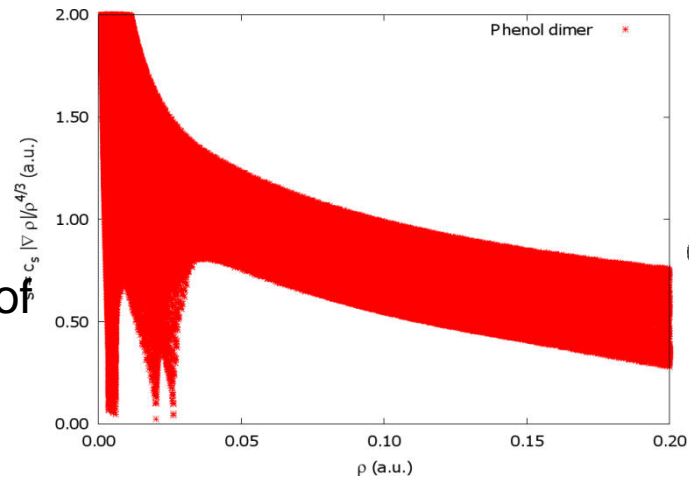
Vdw interactions

Steric clashes

The NCI analysis

1- Strength

The electronic density is proportional to the strength of the interaction (AIM)



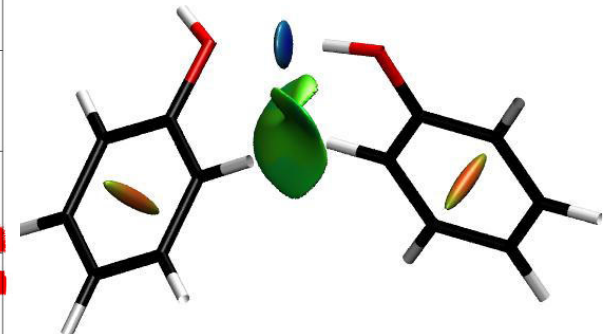
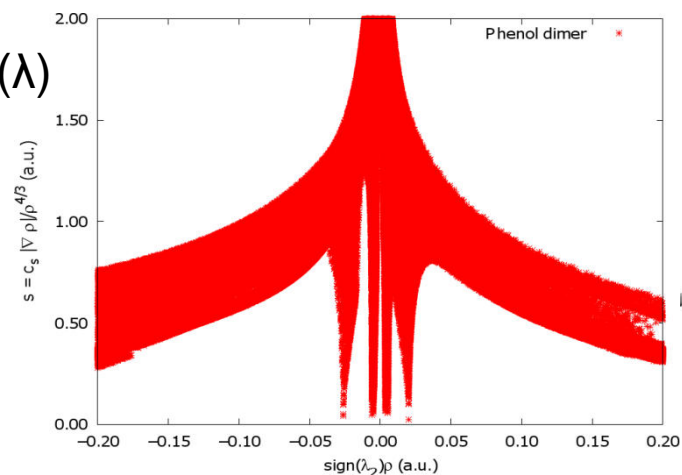
2- Nature

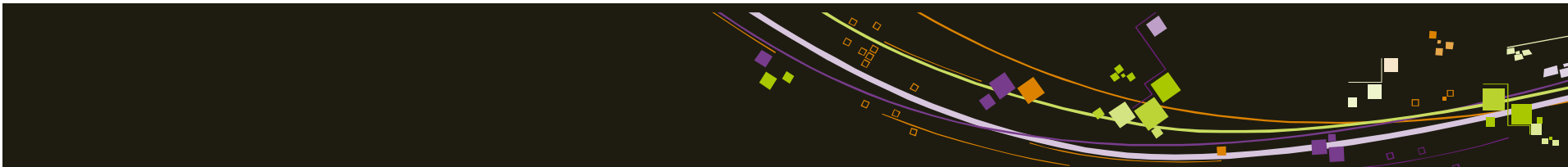
Multiplication by a constant (λ)

based on the derivatives

$\lambda < 0$: attractive

$\lambda > 0$: repulsive

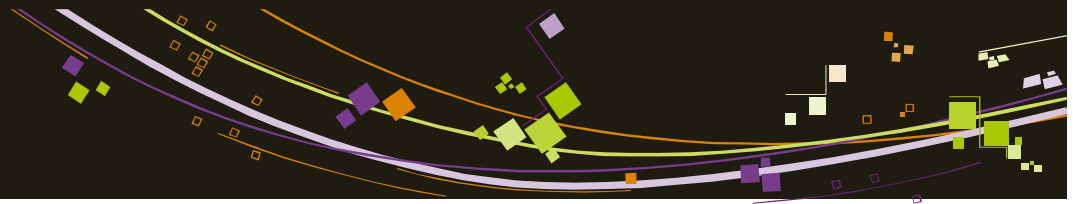




Exercices NCI

Silvi, B.; Savin, A. *Nature* **1994**, *371*, 683.
Piquemal, J. P. *Int. J. Quant. Chem.* **2008**, *108*, 1951.
Johnson, E. R. *J. Am. Chem. Soc.* **2010**, *132*, 6498.
Contreras-Garcia, J. *J. Chem. Theo. Comput.* **2011**, *7*, 625.

Exercice 1



Analysis of the intramolecular hydrogen bond in catechol molecule

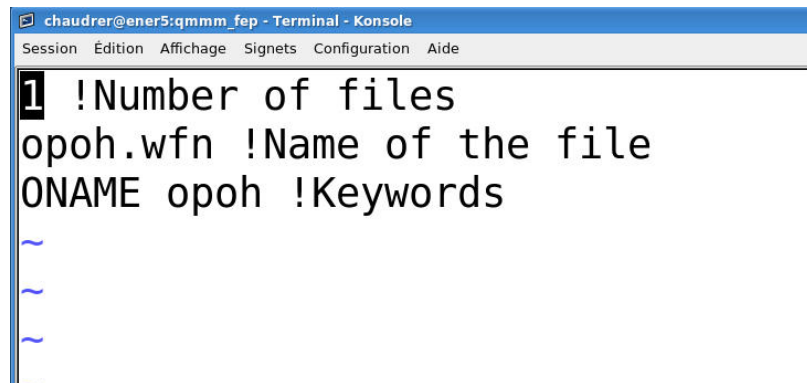
1. Run promolecular and wfn NCI analysis for catechol and comment the results. What is unexpected?
2. Associate every spike in the 2D plot to molecular interactions using gnuplot and VMD for both promolecular and wfn.

What are the differences?

What is similar?

NCI analysis

Input file



```
chaudrer@ener5:qmmm_fep - Terminal - Konsole
Session  Édition  Affichage  Signets  Configuration  Aide
1 !Number of files
opoh.wfn !Name of the file
ONAME opoh !Keywords
~
~
~
```

- Different type of input: wfn / xyz
- Different possible keywords
- **More information in NCI-manual.pdf**

NCI analysis



Running simulation

1- (already done but don't forget to set up the NCI environment)

Ex: setenv NCI_PLOT_HOME /home/irsrvhome1/R07/chaudrer/programmes/nciplot

(Needed to find the promolecular densities stored)

2- Run NCI : **nciplot NCI.inp >NCI.out**

NCI analysis

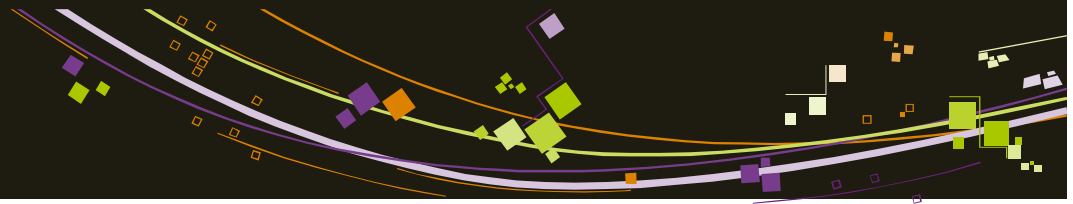


Output files

NCI.out :

1. Opening
2. If promolecular : look for the atomic densities
3. Display the input information (keywords)
4. Display the parameters for the calculation
 - Coordinates of the starting point of the grid
 - Coordinates of the ending point of the grid
 - Step (x, y, z)
 - Number of steps (x, y, z)
5. Display the name of the other output files

NCI analysis



Output files

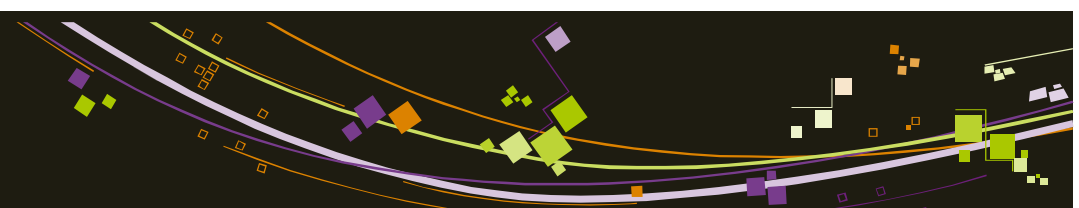
NCI.dat:

Contains all the values of ρ and $s(\rho)$
(to plot the 2D graph)

To plot NCI.dat with gnuplot:

1. Open gnuplot
2. Enter: plot "NCI.dat"
3. The 2D graph should appear

NCI analysis



Output files

NCI-*.cube

NCI.vmd

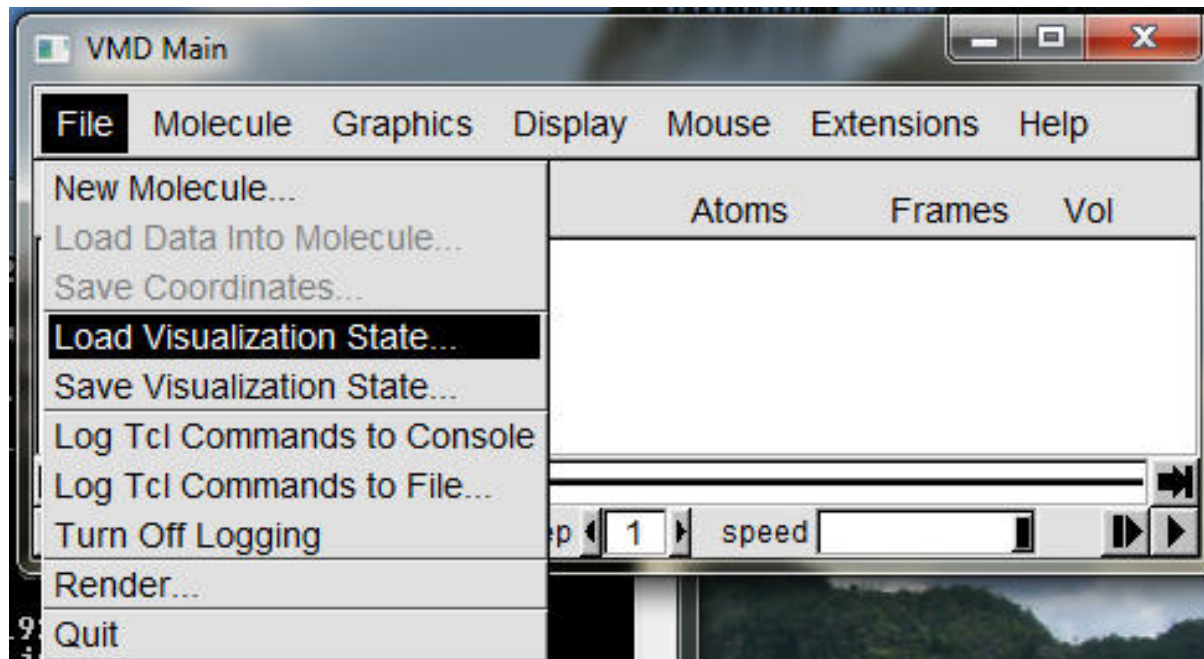
Use vmd to analyse

vmd-tutorial.pdf in the documents

Basic use of VMD

Open a file

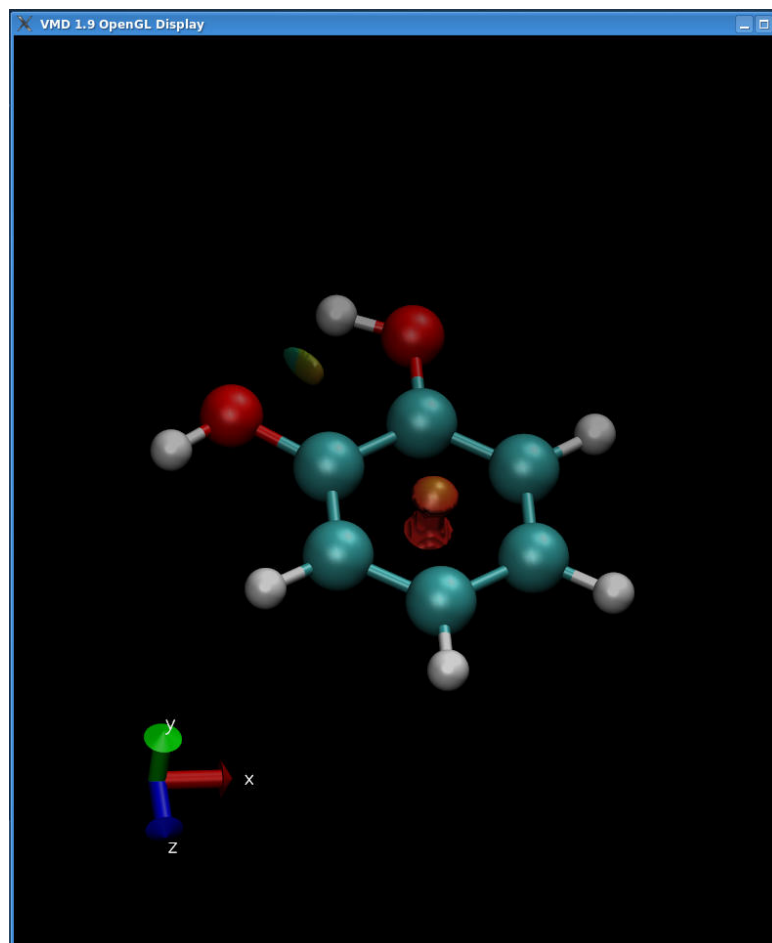
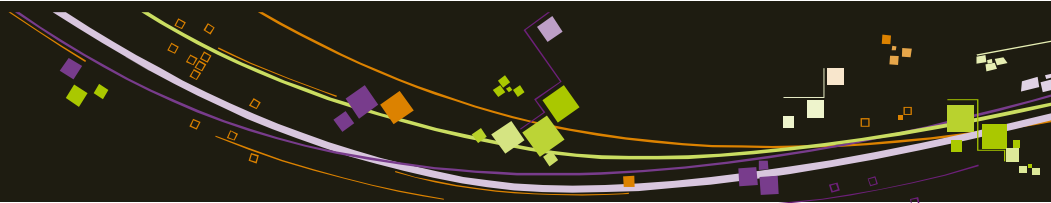
1. Open VMD : vmd
2. File > Load Visualisation State



vmd -e NCI.vmd

3. Select NCI.vmd
4. Open

Basic use of VMD



Basic use of VMD

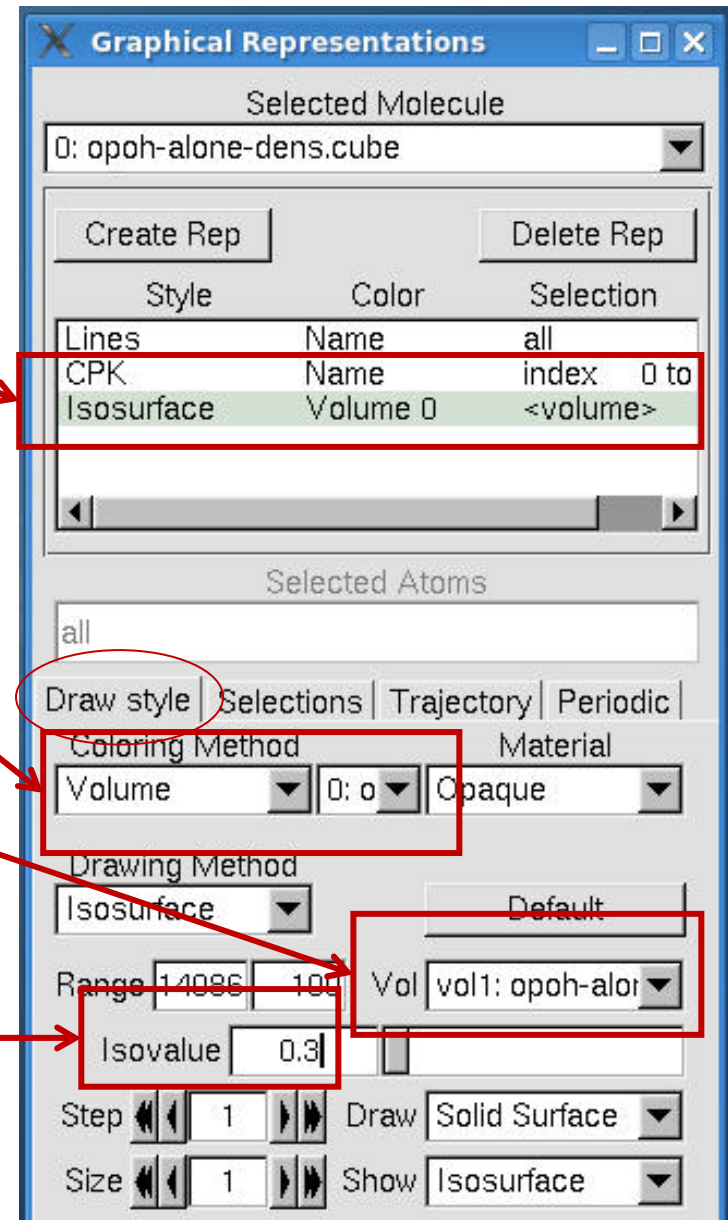
Graphics > Representation

Selected representation:
represent the isosurface

The isosurfaces are colored depending
on the cube selected

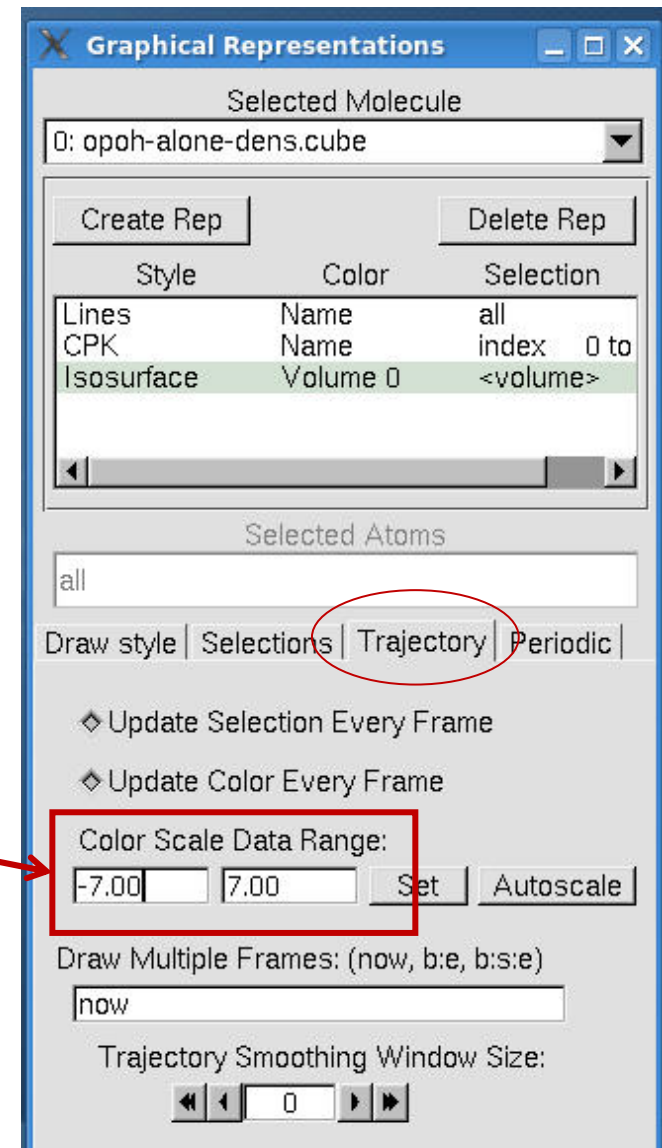
Cube file whose isosurfaces will be plotted

RDG cutoff to represent the isosurface



Basic use of VMD

Graphics > Representation

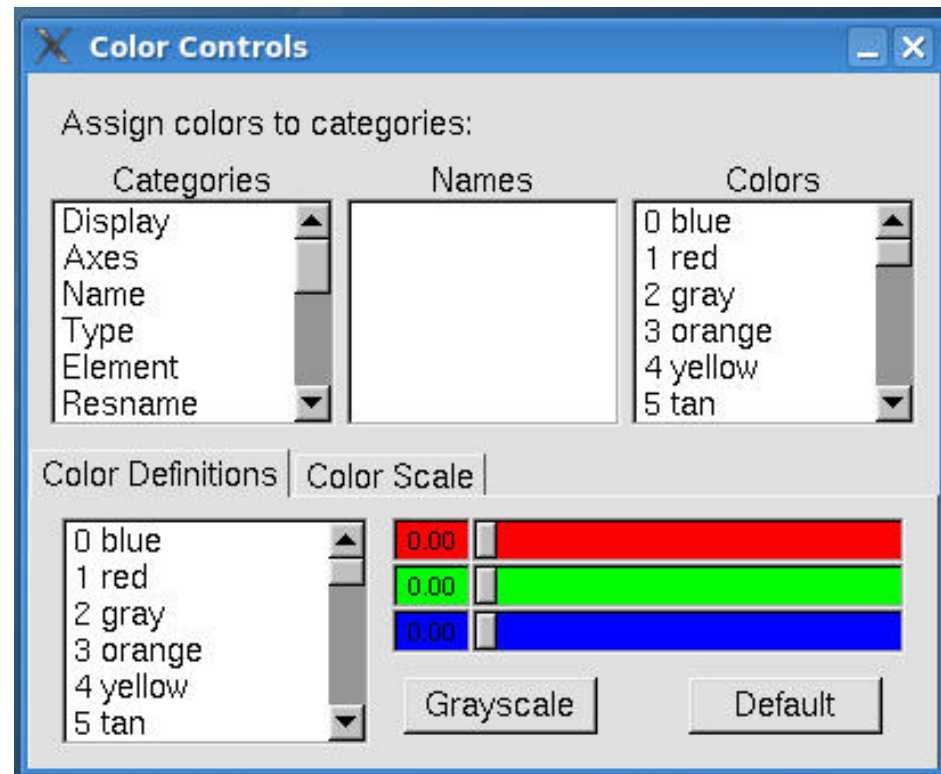


Color range

Basic use of VMD

Graphics > Color

- **Display > Background > White**
→ Set the background white
- **Name > C > Black**
→ Set the Carbon atoms black
- **Color Scale** : change the color scale of the interactions (here blue < green < red)



Basic use of VMD

The screenshot displays the VMD 1.9 OpenGL Display window. The main view shows a ball-and-stick model of a molecule with black carbon atoms, red oxygen atoms, and white hydrogen atoms. A red isosurface is overlaid on the molecule, and a small rainbow-colored volume is visible above it.

The VMD Main window is open, showing a menu bar (File, Molecule, Graphics, Display, Mouse, Extensions, Help) and a table of loaded molecules:

ID	T	A	D	F	Molecule	Atoms	Frames	Vol
0	T	A	D	F	opoh-alone-dens.cube	14	2	2

The Graphical Representations window is also open, showing settings for the selected molecule '0: opoh-alone-dens.cube'. It includes options for creating and deleting representations, a table for defining representations, and various drawing and display controls.

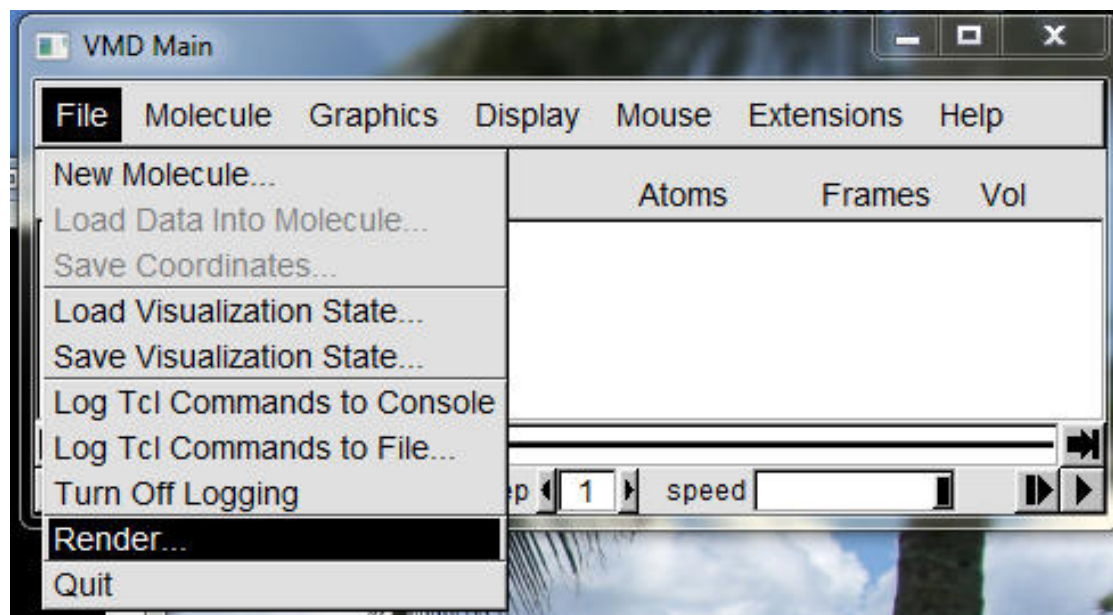
Style	Color	Selection
Lines	Name	all
CPK	Name	index 0 to
Isosurface	Volume 0	<volume>

The Graphical Representations window also features a 'Selected Atoms' list (currently 'all'), drawing style options (Volume, CPK, Isosurface), coloring methods (Volume, CPK, Isosurface), and drawing methods (Isosurface, Solid Surface). It includes controls for Range (14086, 100), Isovalue (0.35), Step (1), and Size (1). A color palette is visible on the right side of the window.

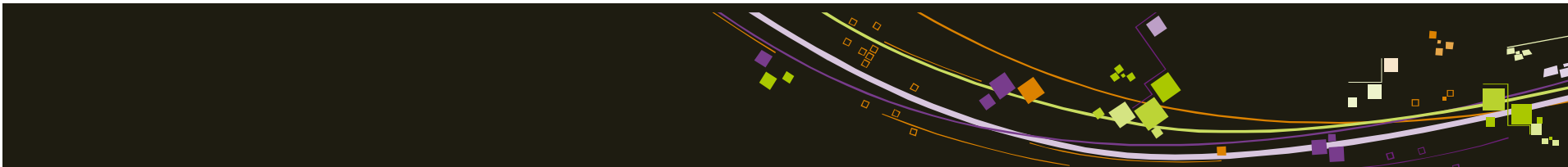
Basic use of VMD

Rendering

Print an image:



Select the rendering mode you prefer (snapshot for exemple)
Give a file name (NCI.tga for exemple)
Click on "Start Rendering"



Exercices ELF

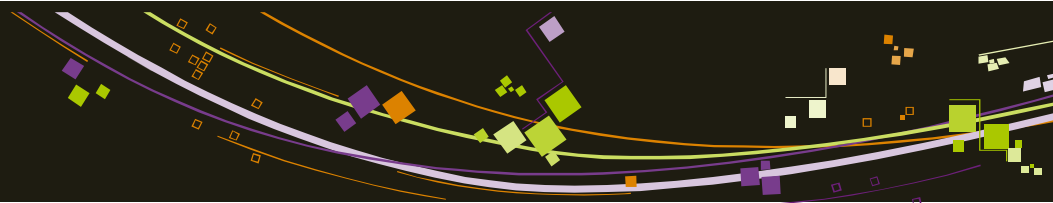
Silvi, B.; Savin, A. *Nature* **1994**, *371*, 683.

Piquemal, J. P. *Int. J. Quant. Chem.* **2008**, *108*, 1951.

Johnson, E. R. *J. Am. Chem. Soc.* **2010**, *132*, 6498.

Contreras-Garcia, J. *J. Chem. Theo. Comput.* **2011**, *7*, 625.

Exercice 2



1. Perform ELF analysis and obtain the elf and esyn cubes for ethane, ethylene (ethane), ethyne, chloro-ethane and ethanol molecule.
2. Visualize the cube files using VMD and color then using the esyn cubes. How is the C-C bond evolving? Visualize the lone pairs for ethanol and chloro-ethane molecules. Can you explain the differences?

ELF input files

General presentation

To run a complete ELF analysis there are 4 different steps using 3 programmes:

1. Compute ELF and AIM fonction on every point of a grid
Use top_grid or grid09
2. Decompose the ELF volume
Use top_bas or bas09
3. Decompose the AIM volume
Use top_bas or bas09
4. Integrate different properties
Use top_pop, top_chem or pop09

} Can be interverted



Here the name of the .wfn and the title within the wfn should be similar

Grid09

Input file (can also be done interactively)

Name of the .wfn file to consider

Coordinate of the lowest corner of the grid (given by the programm)

Number of points

Size of each edge of the grid (given by the progamm)

```
chaudrer@ener5:elf - Terminal No. 2 - Konsole
Session Edition Affichage Signets Configuration Aide
opoh-opt.wfn
-8.702209 -5.057593 -9.700905
20.244457 10.498937 20.643658
200 100 200
~
~
```

The output are sbf files that can be transformed into cube files :

sbf_to_cube

Grid09

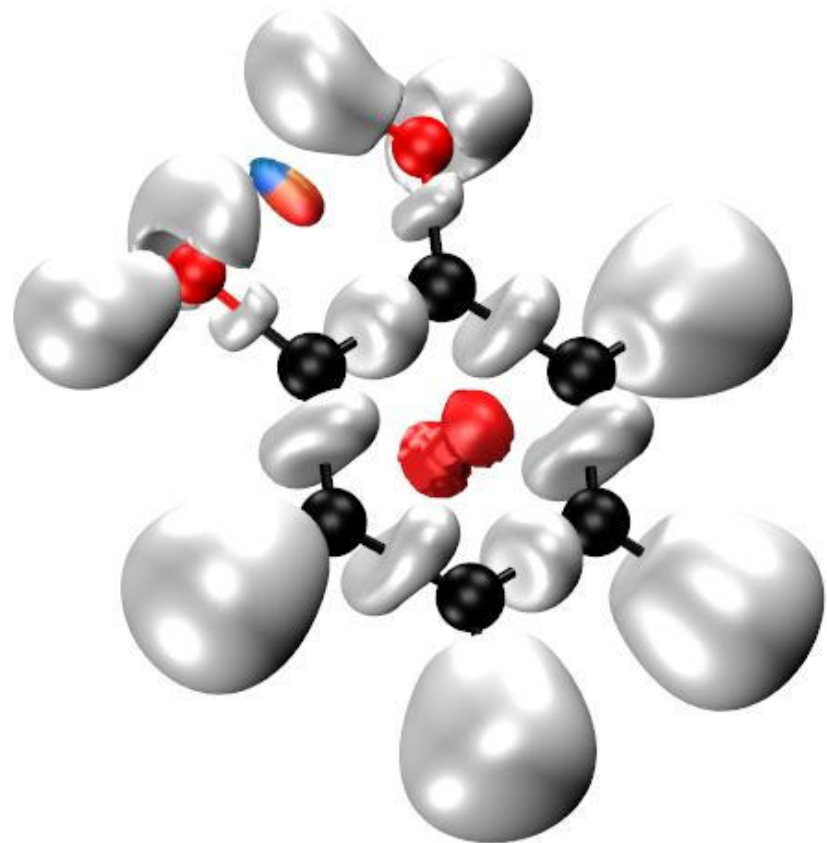
Output files

Grid09 output files are .sbf files


Use **sbf_to_cube**

Visualize cube file with vmd:

File > New Molecule...



Input file for ELF (can also be done interactively)



Selection between elf or rho

Name of the wfn file (same as precedent)

Accuracy desired
(0=very high, 1=high, 2=medium)

Find external core shell attractors

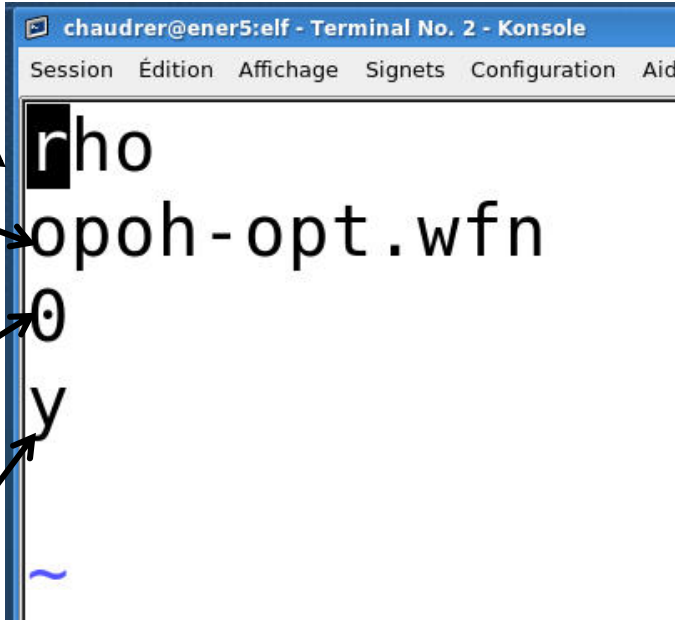
Search mode
(0=automatic)

Assign grid point to decompose
the volume into bassins

```
elf
opoh-opt.wfn
0
y
0
y
~
~
```

The image shows a terminal window titled 'chaudrer@ener5:elf - Terminal No. 2 - Konsole'. The terminal displays the following input sequence: 'elf', 'opoh-opt.wfn', '0', 'y', '0', 'y', followed by two tilde characters '~'. Arrows from the text on the left point to these specific lines in the terminal output.

Input file for density (can also be done interactively)

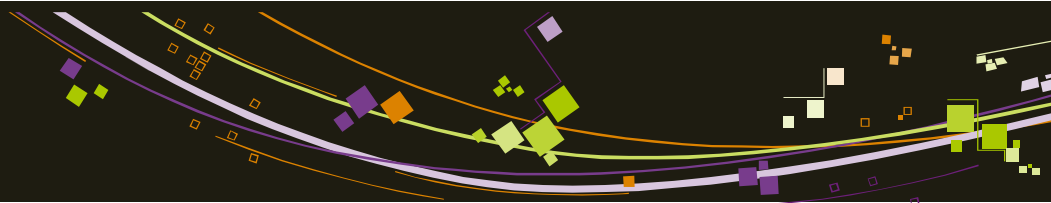


The image shows a terminal window titled "chaudrer@ener5:elf - Terminal No. 2 - Konsole" with a menu bar containing "Session", "Édition", "Affichage", "Signets", "Configuration", and "Aid". The terminal content is as follows:

```
rho
opoh-opt.wfn
0
y
~
```

Annotations with arrows pointing to the terminal content:

- "Selection between elf or rho" points to the first line "rho".
- "Name of the wfn file (same as precedent)" points to the second line "opoh-opt.wfn".
- "Accuracy desired (0=very high, 1=high, 2=medium)" points to the third line "0".
- "Assign grid point to decompose the volume into bassins" points to the fourth line "y".



Output files

1. Attractor (ELF or density) x,y,z coordinates

2. Time spent for the calculation

3. Distance of each (valence) attractor from nuclei (ELF only)

4. Angle between attractors (ELF only)

} AIM: only atomic attractors

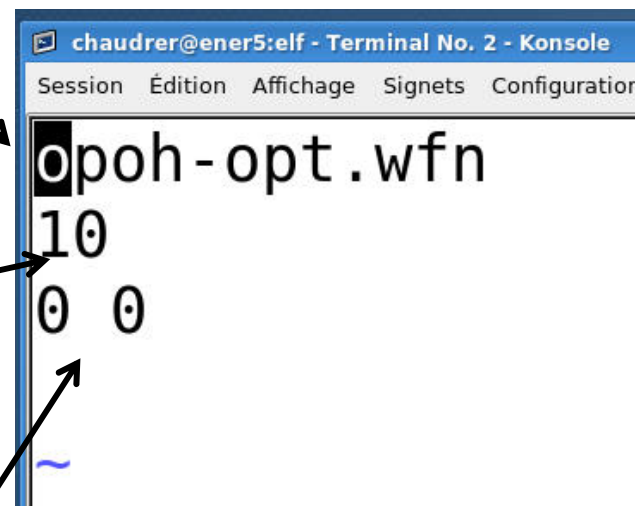
Pop09

Input file (can also be done interactively)

Name of the wfn file (same as precedent)

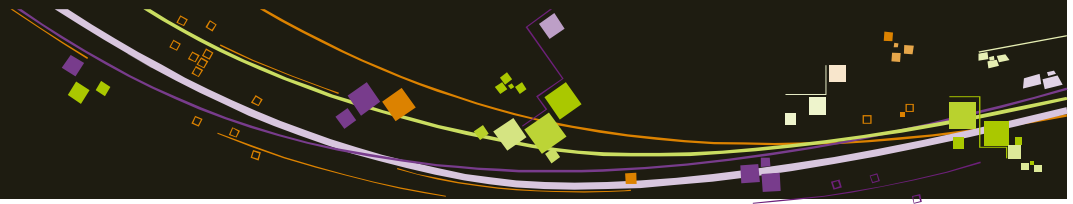
Threshold for integration
(10 = most precise)

Number of ELF and AIM basins considered
(0 0 = all)



```
chaudrer@ener5:elf - Terminal No. 2 - Konsole
Session  Édition  Affichage  Signets  Configuration
opoh-opt.wfn
10
0 0
~
```

Pop09 output file



Output files

First ELF then AIM

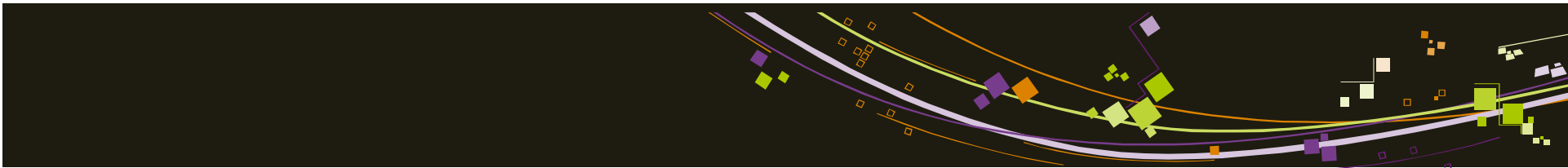
1. Integrated properties for all basins: **volume, population**, $\rho_{\alpha\beta}$, $\rho_{\alpha\alpha}$, $\rho_{\beta\beta}$, ...

2. Orbital contribution for all basins

3. Atomic contribution for all basins (ELF only)

4. α spin covariance matrix and its correlation coefficients

5. Total covariance matrix and its correlation coefficients



Exercices ELF/NCI

Silvi, B.; Savin, A. *Nature* **1994**, *371*, 683.
Piquemal, J. P. *Int. J. Quant. Chem.* **2008**, *108*, 1951.
Johnson, E. R. *J. Am. Chem. Soc.* **2010**, *132*, 6498.
Contreras-Garcia, J. *J. Chem. Theo. Comput.* **2011**, *7*, 625.

ELF/NCI for reaction mechanisms

Running calculations

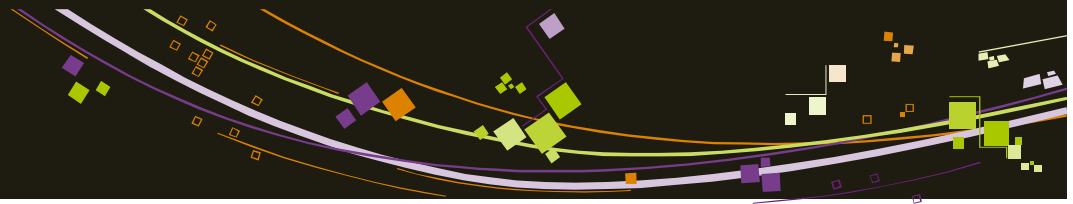
- Need the different wfn files from the reaction coordinate
- Run several small scripts to get the calculation automated
- ATTENTION: For ELF prepare the grid input so that it includes all the atoms of all the structures (get a larger grid)
- Modify the “general” input files
- Run scripts: `sh make_elf.sh` (do all the ELF calculations)
`sh make_nci.sh` (do all the NCI calculations)
- Creation of several new folders to store out, dat, sbf and cube files

ELF/NCI for reaction mechanisms

Getting the films

- copy result/elf_nci_visualization.pl and result/example-input-vmd-file in cube
- modify input file :
 - NAME name: put the wfn names (NAME-[number].wfn)
 - GEOM n1 n2 n3: [number] going from n1 to n2 by step of n3
 - REPRESENTATION [CPK/line/licorice]: VMD representation
 - ELF n: ELF cutoff = n
 - NCI n1 n2 n3: density cutoff = n1, density ranking from n2 to n3
 - set viewpoint...: use vmd to get the desired view of the system
- ./elf_nci_visualization.pl input output vmd-surface-output (vmd-attractor output)
- run vmd to get the tga files: vmd -e vmd-surface-output
- copy, modify and run result/tga2gifanim

Exercice 3



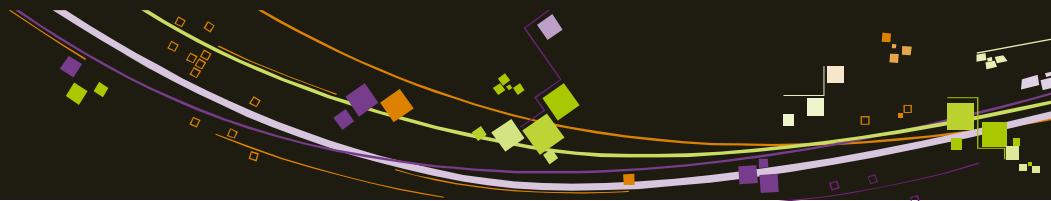
1. Perform the ELF/NCI scripts.
2. Obtain the film with your selected cutoffs, color range and view.
3. Look at the different ELF output. What is the evolution of the populations of the different important basins? Does that correspond to the NCI analysis evolution?



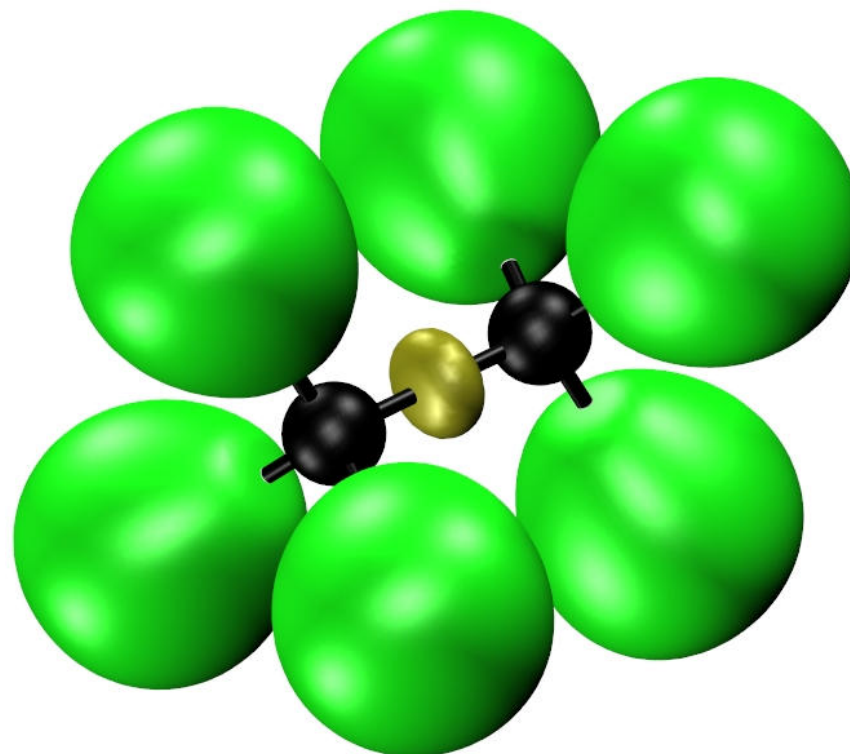
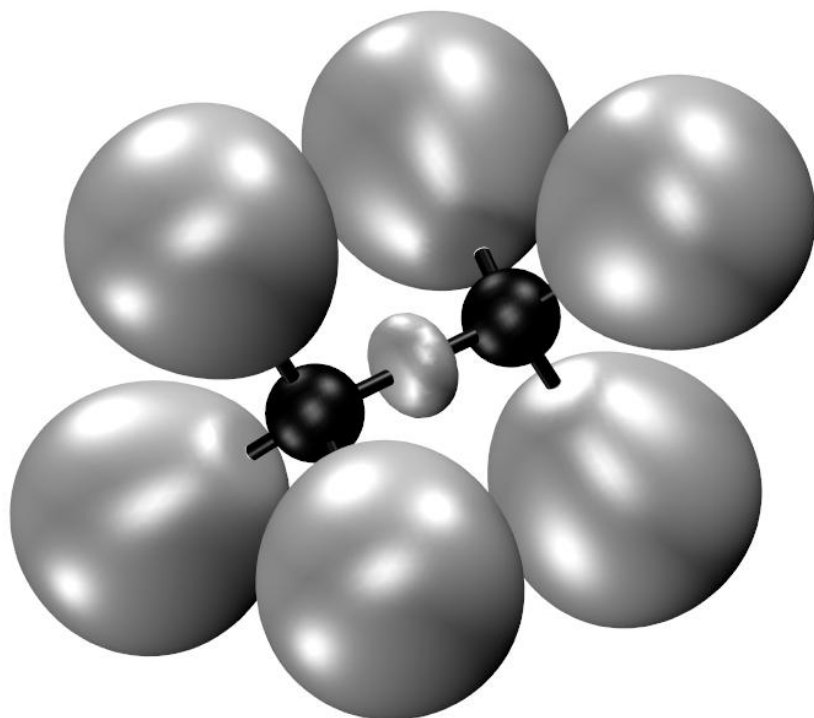
Congrats!

You finished

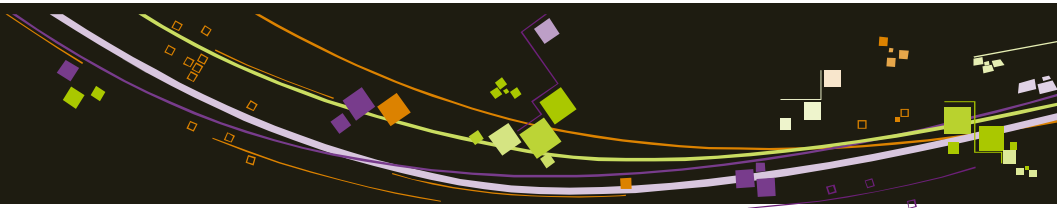
Correction ELF



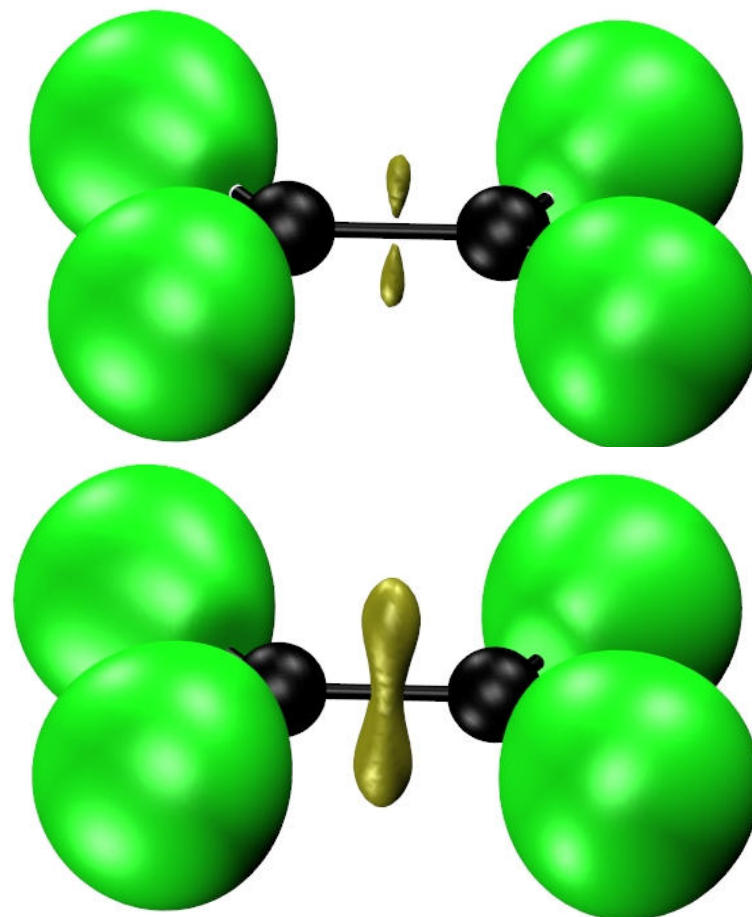
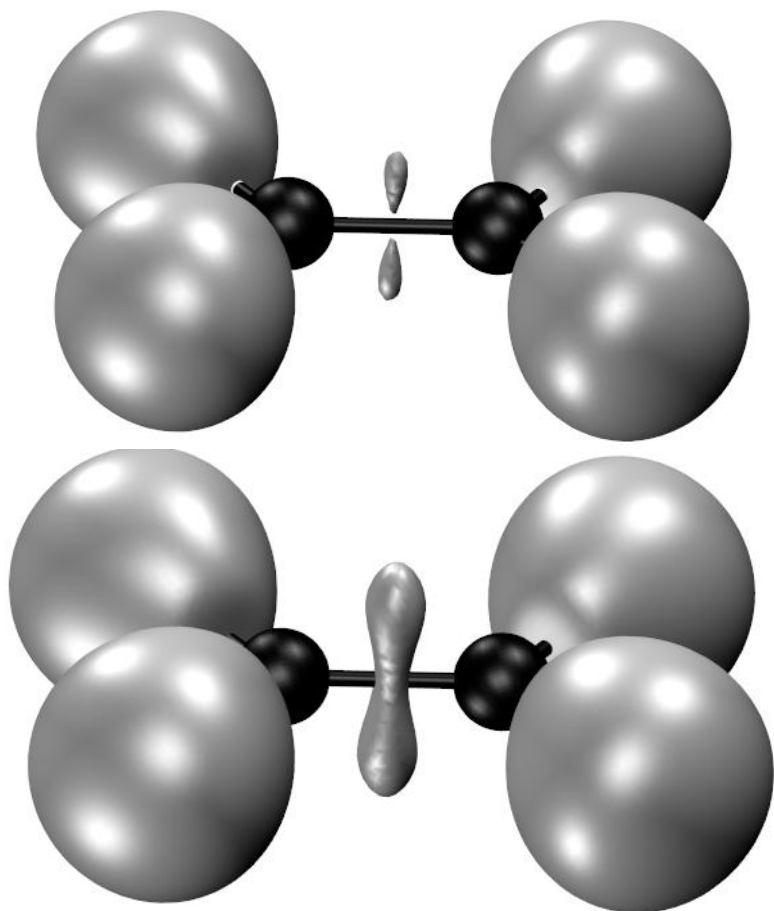
Ethane



Correction ELF



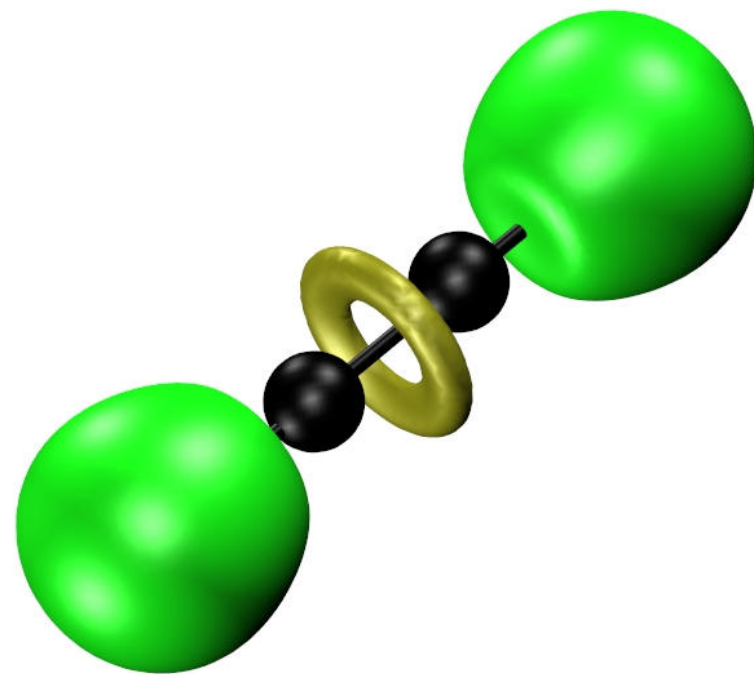
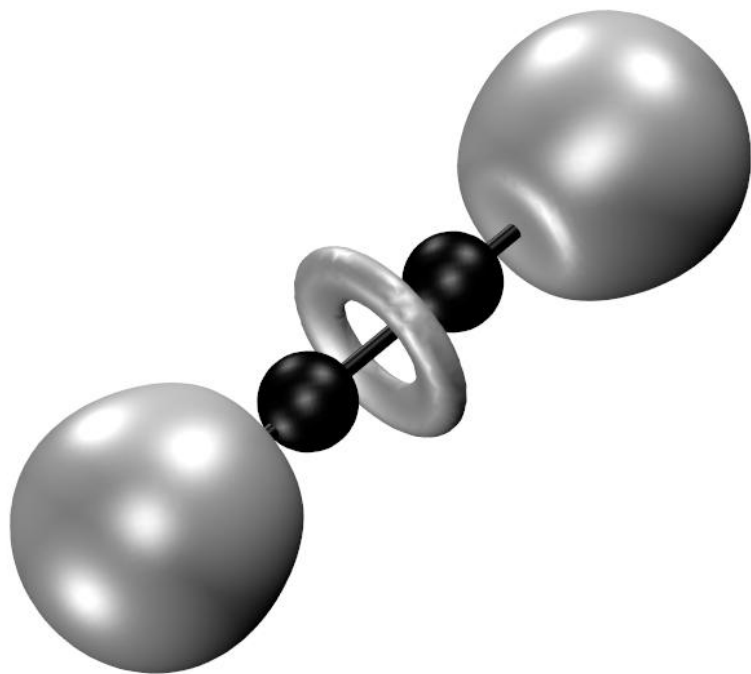
Ethylene



Correction ELF

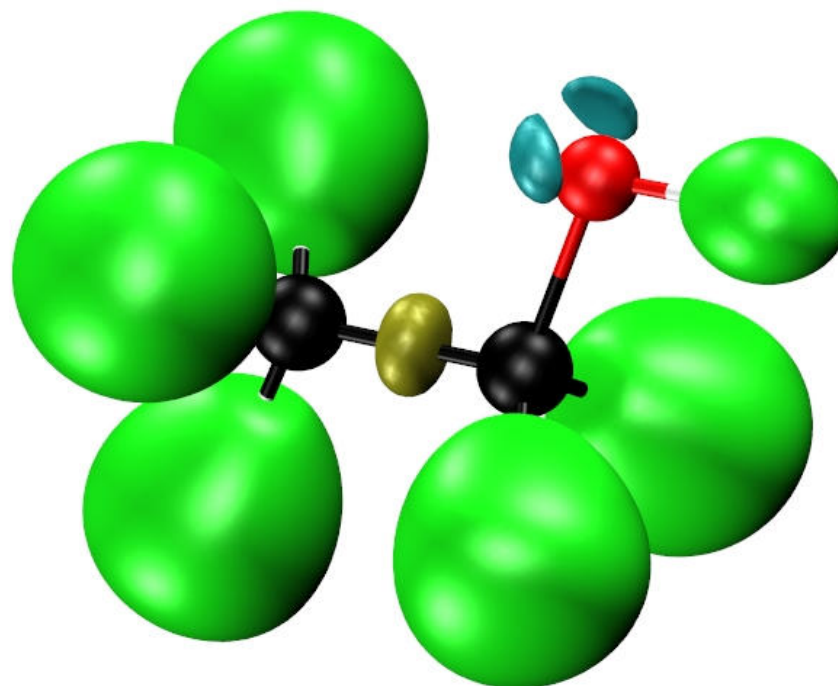
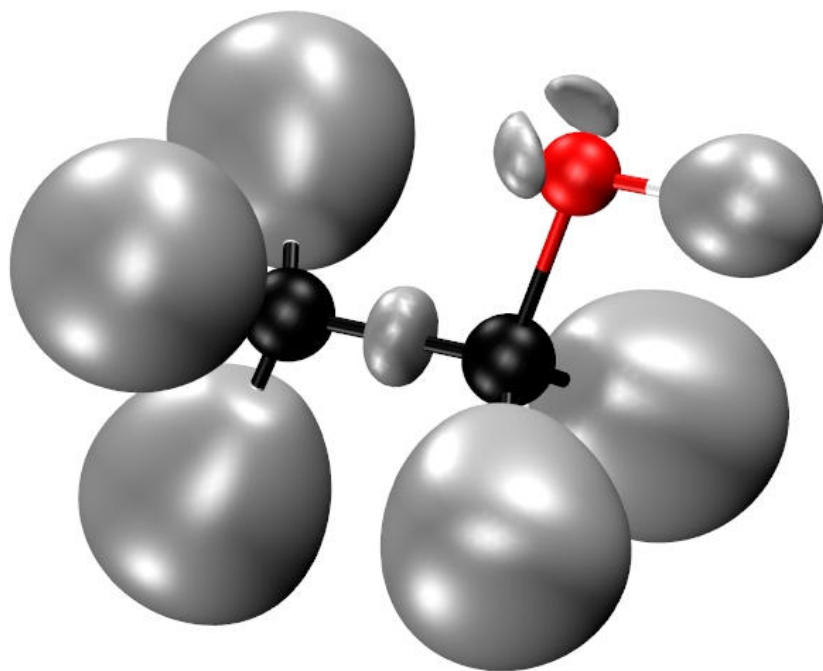


Ethine



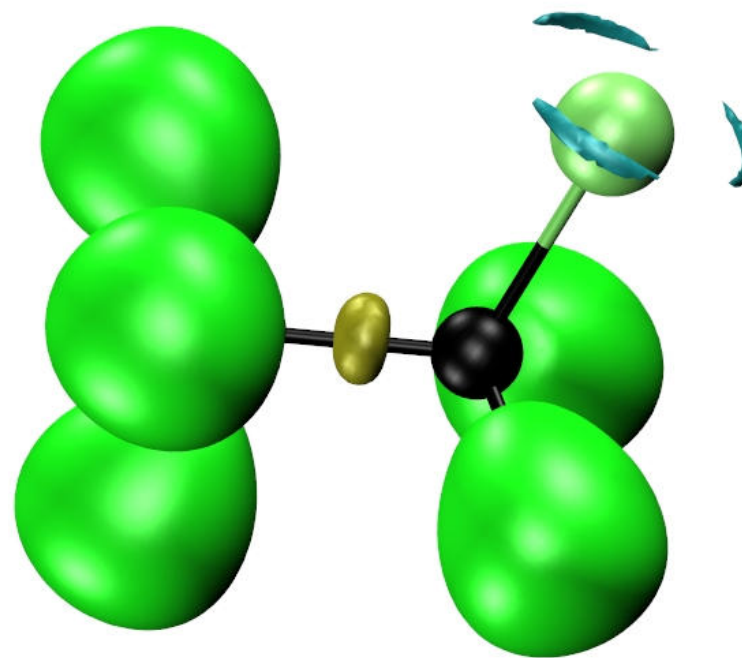
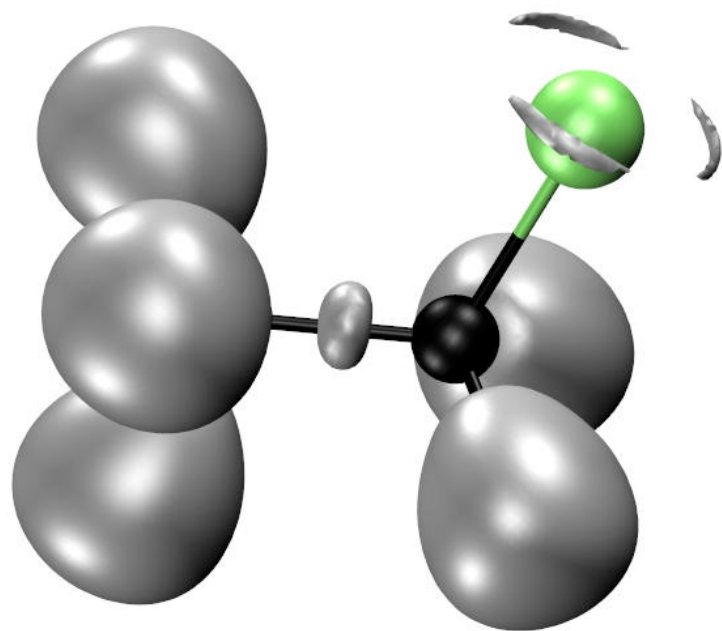
Correction ELF

Ethanol

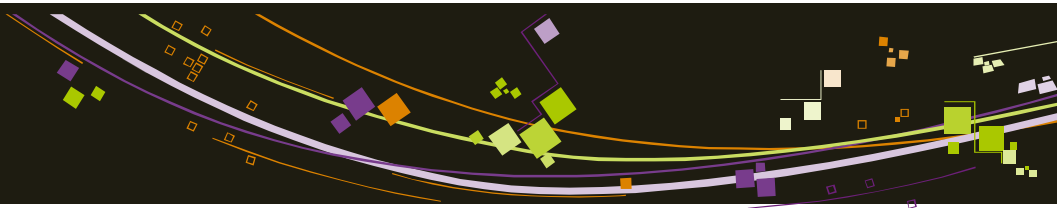


Correction ELF

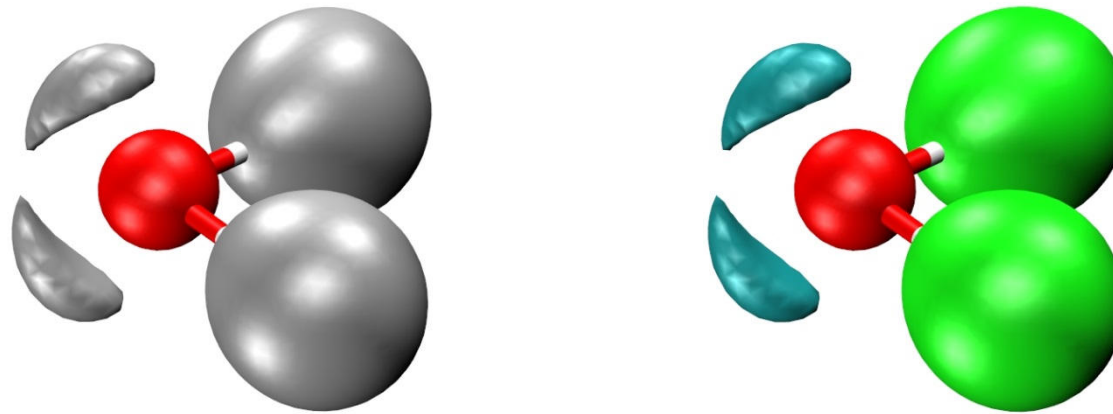
Chloro-ethane



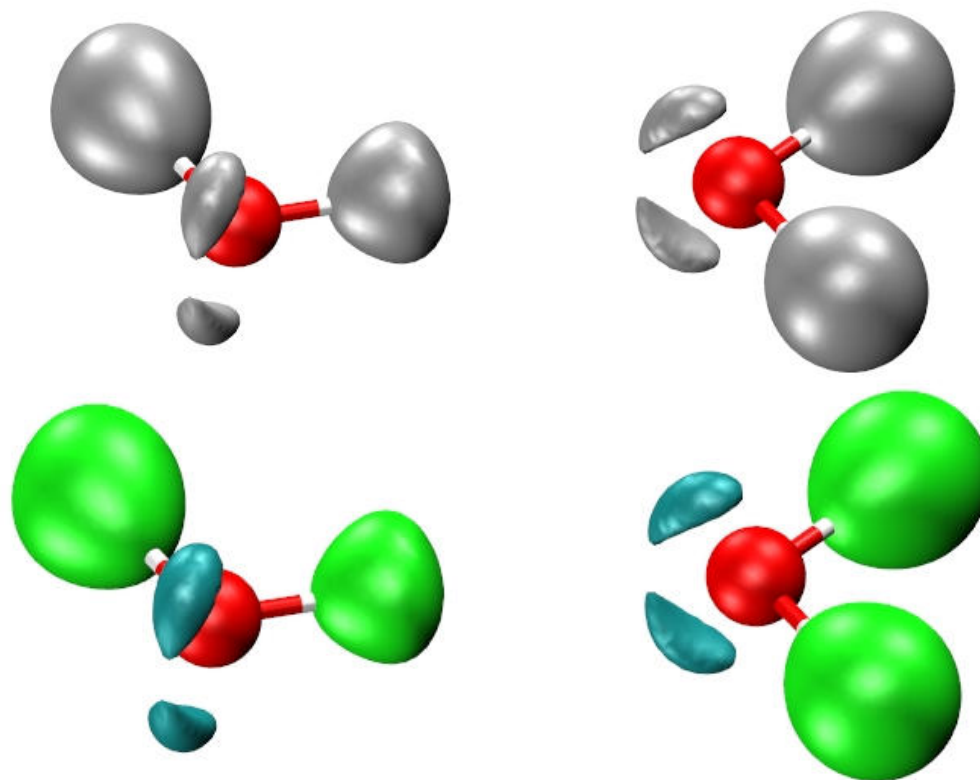
Correction ELF



Water



Water dimer



Correction ELF

Catechol

