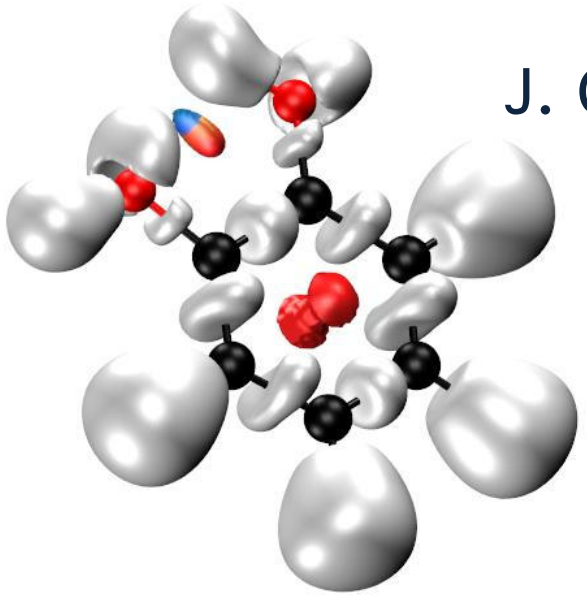
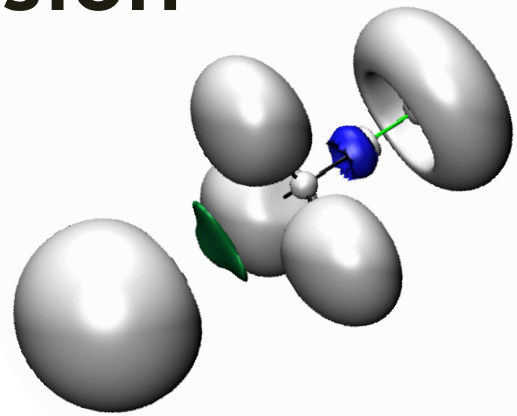
The ELF and NCI analysis

Training session



J. Contreras-Garcia

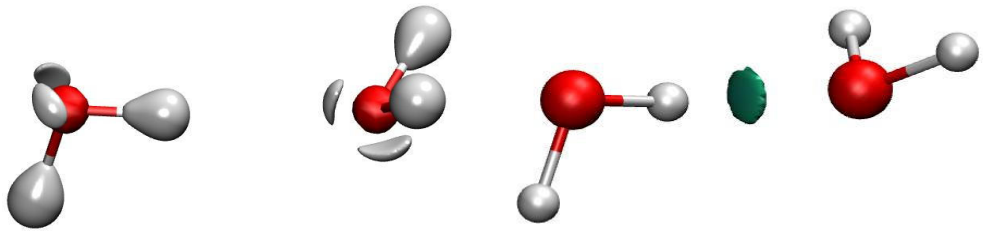
R. Chaudret



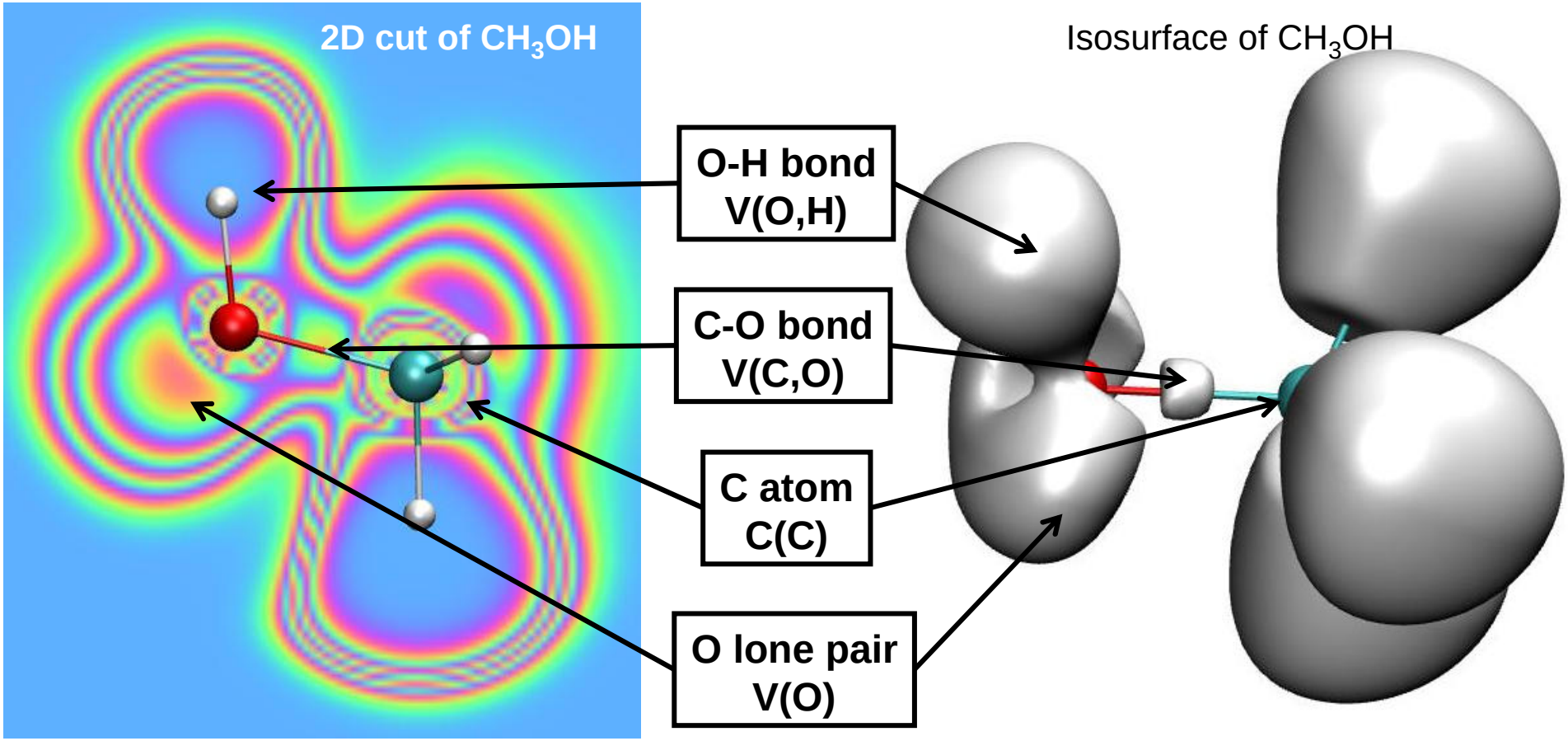
Silvi, B.; Savin, A. *Nature* **1994**, *371*, 683.
Piquemal, J. P. *Int. J. Quant. Chem.* **2008**, *108*, 1951.
Johnson, E. R. *J. Am. Chem. Soc.* **2010**, *132*, 6498.
Contreras-Garcia, J. *J. Chem. Theo. Comput.* **2011**. *7*, 625.

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



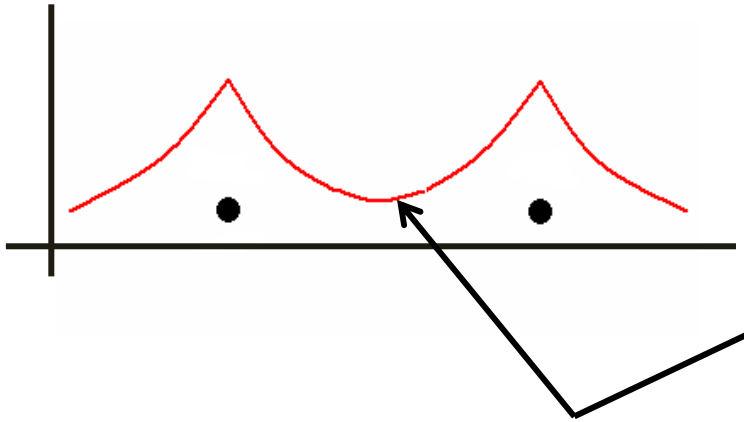
The ELF analysis

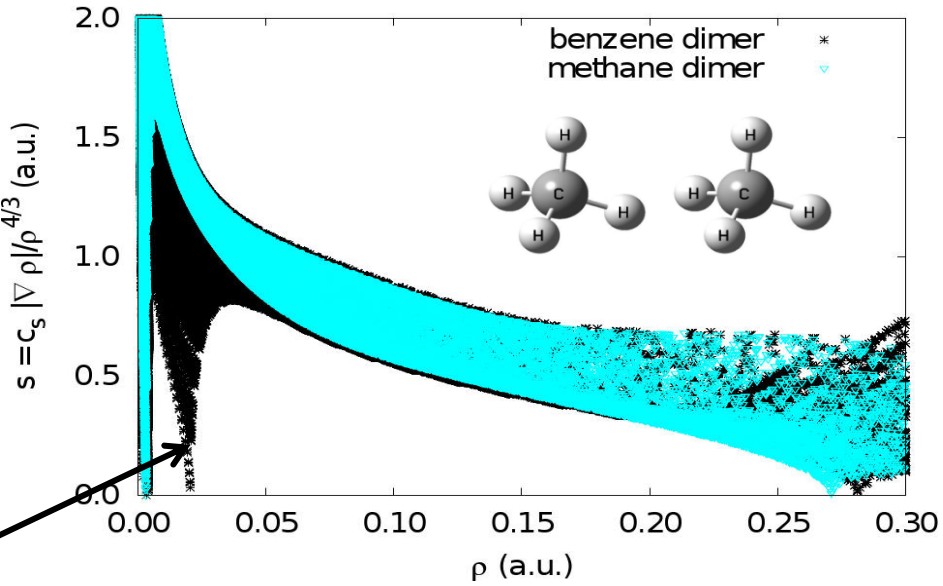


- Visualization of bonds, lone pairs and atoms
- Link with Lewis or VSEPR theory → **Easy to understand for the chemist**
- Integration of different properties on the basins (charge, dipole, volume…)

The NCI analysis

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



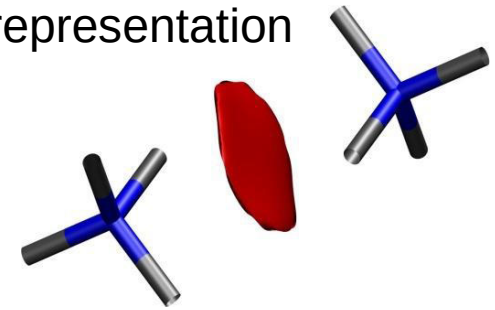


Local minimum with ρ very small and s(ρ) →0

→Interacting densities

→**Non covalent interactions**

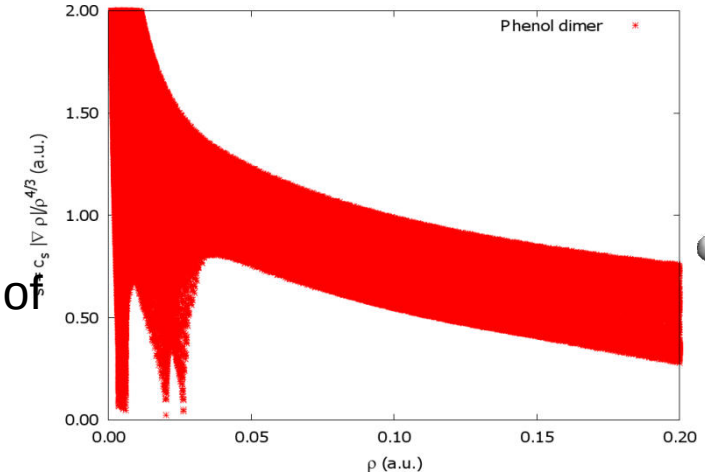
3D representation

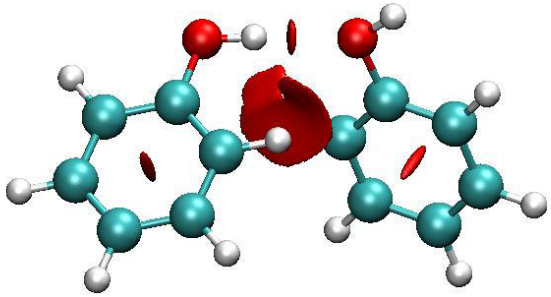


The NCI analysis

1- Strength

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



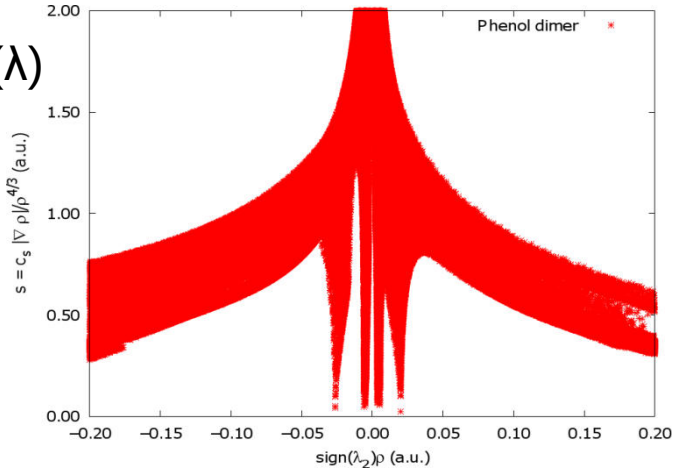


2- Nature

Multiplication by a constant (λ) based on the derivatives

λ < 0 : attractive

λ > 0 : repulsive



The NCI analysis

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

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

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

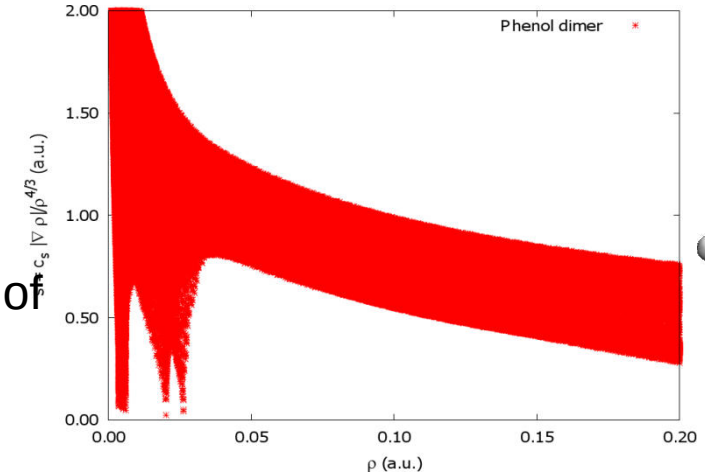
attraction **repulsion**

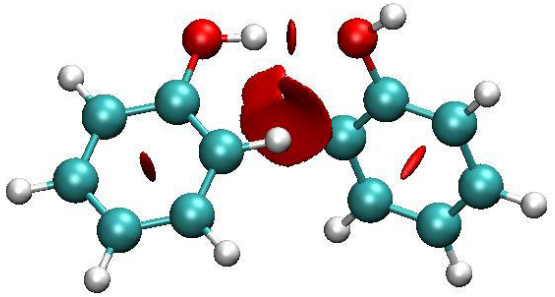
Hydrogen bond **Vdw interactions** **Steric clashes**

The NCI analysis

1- Strength

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





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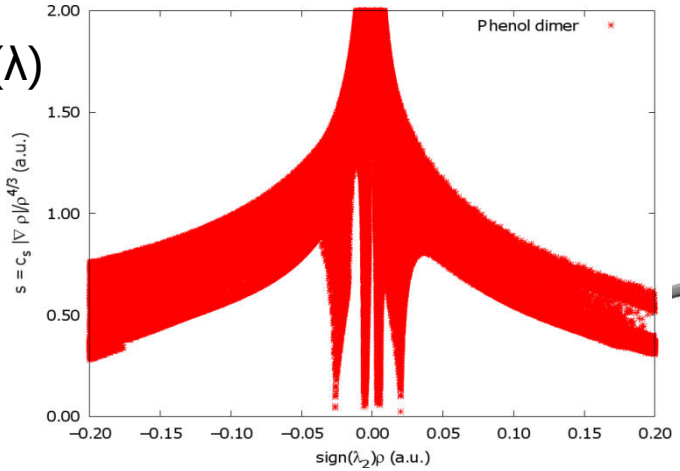
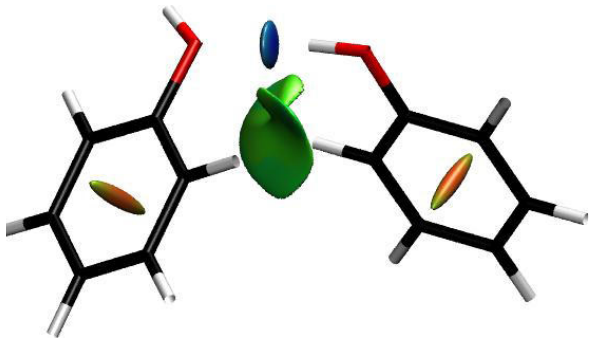




Exercices NCI

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

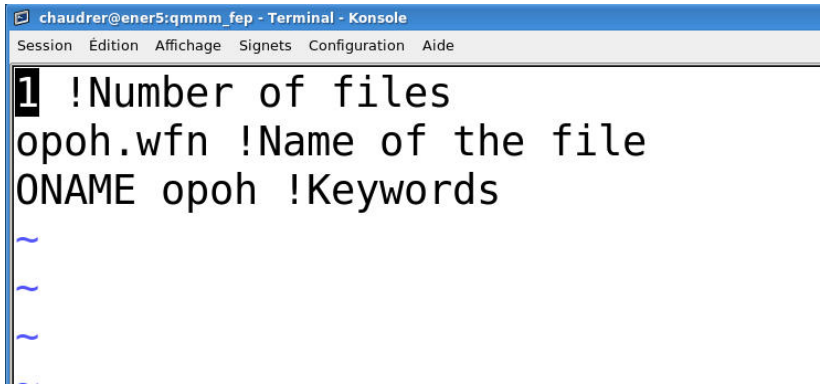
1. Run promolecular and wfn NCI analysis for catechol and comment the results. What is unexpected?
2. Associate every spike in the 2D plot to molecular interactions using gnuplot and VMD for both promolecular and wfn.

   What are the differences?

   What is similar?

NCI analysis

Input file



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

Running simulation

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

Ex: setenv NCIPLOT_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(ρ)

(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

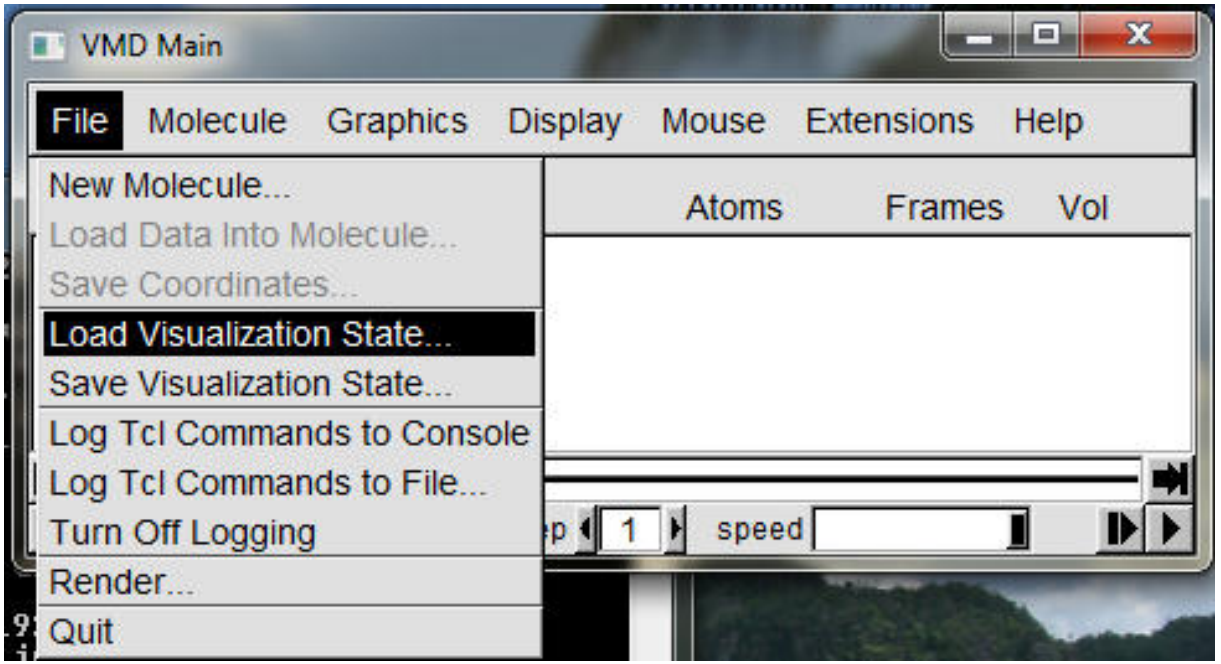
Use vmd to analyse

vmd-tutorial.pdf in the documents

Basic use of VMD

Open a file

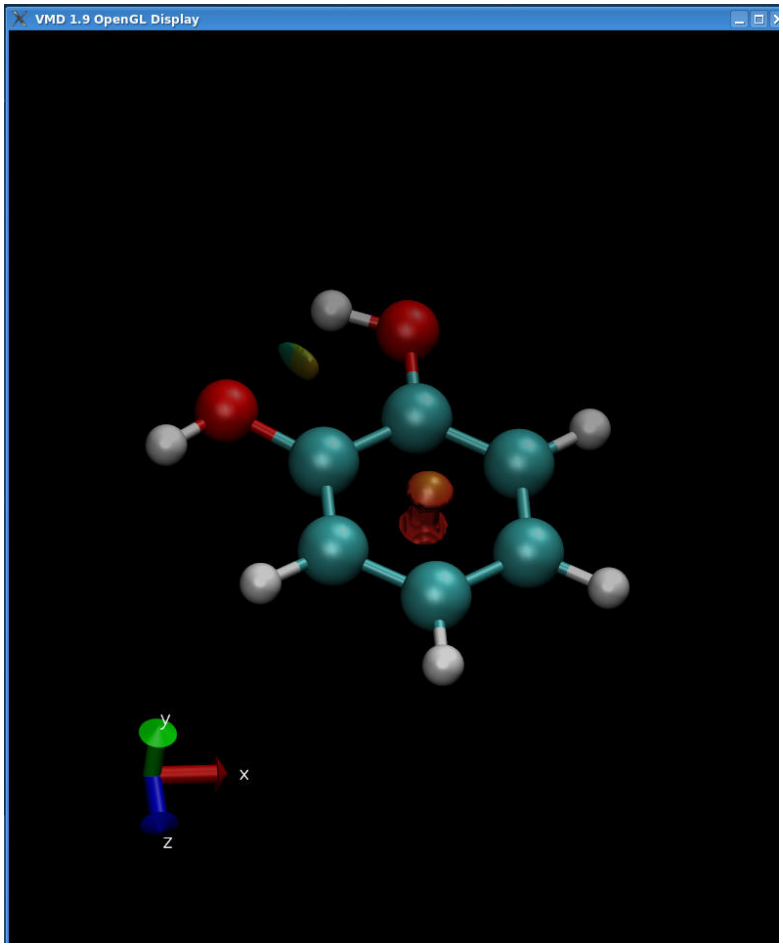
1. Open VMD : vmd
2. File > Load Visualisation State



3. Select NCI.vmd
4. Open

vmd –e NCI.vmd

Basic use of VMD



Basic use of VMD

Graphics > Representation

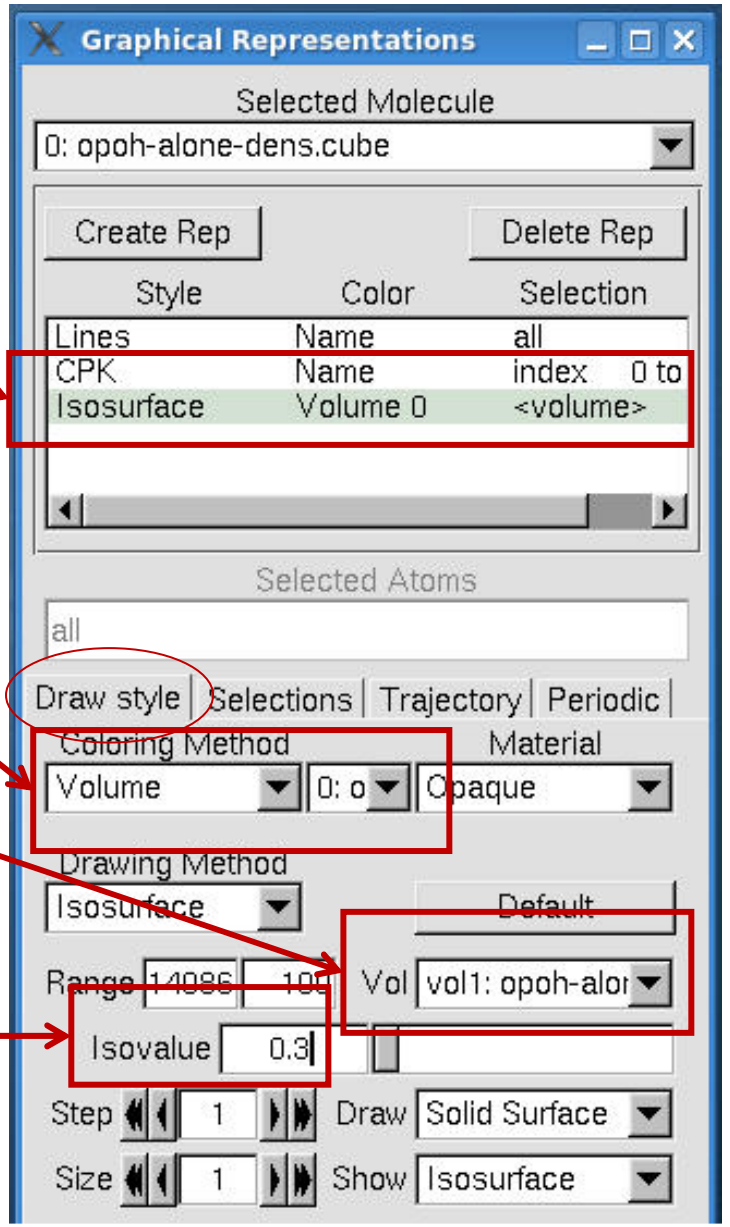
Selected representation:

represent the isosurface

The isosurfaces are colored depending on the cube selected

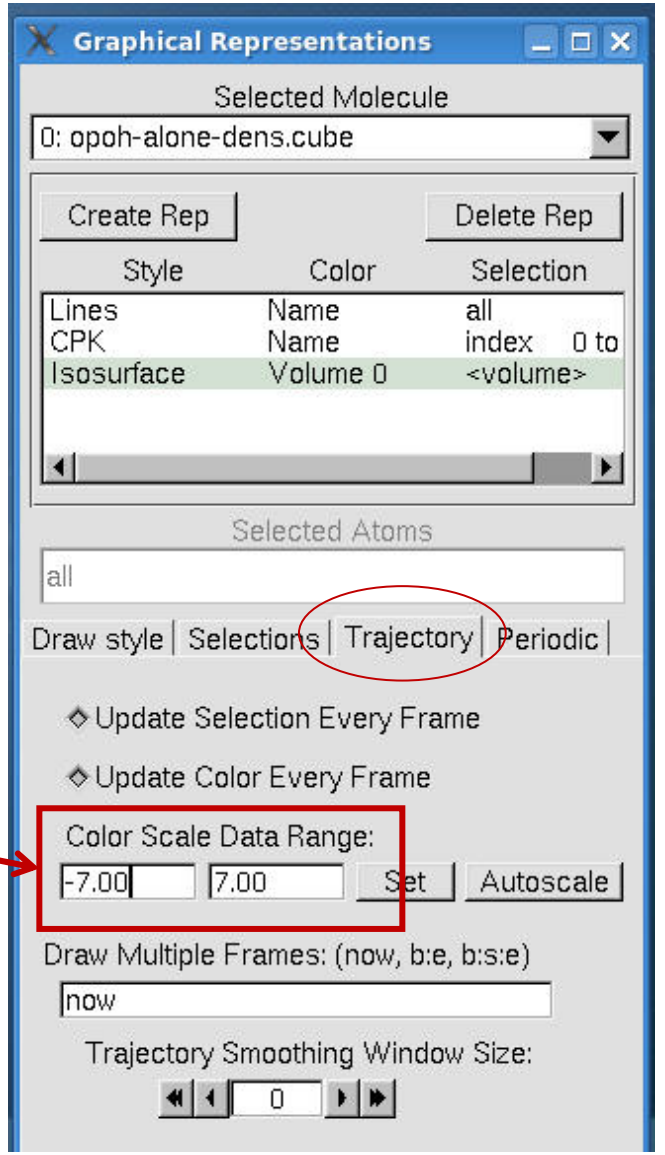
Cube file whose isosurfaces will be plotted

RDG cutoff to represent the isosurface



Basic use of VMD

Graphics > Representation



Color range

Basic use of VMD

Graphics > Color

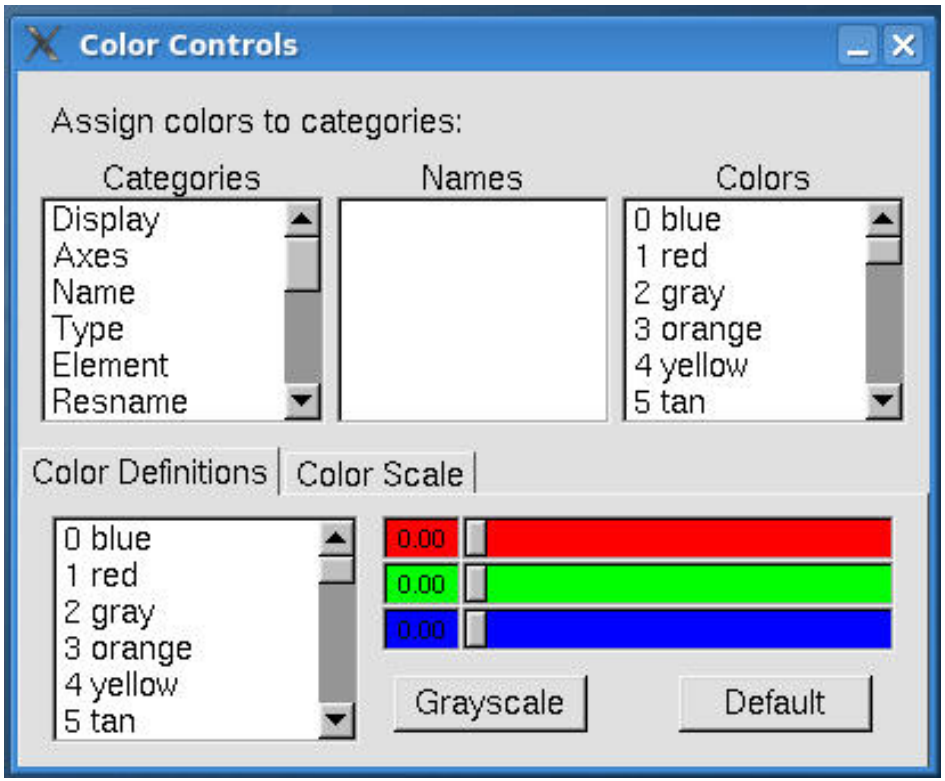
- **Display > Background > White**

→ Set the background white

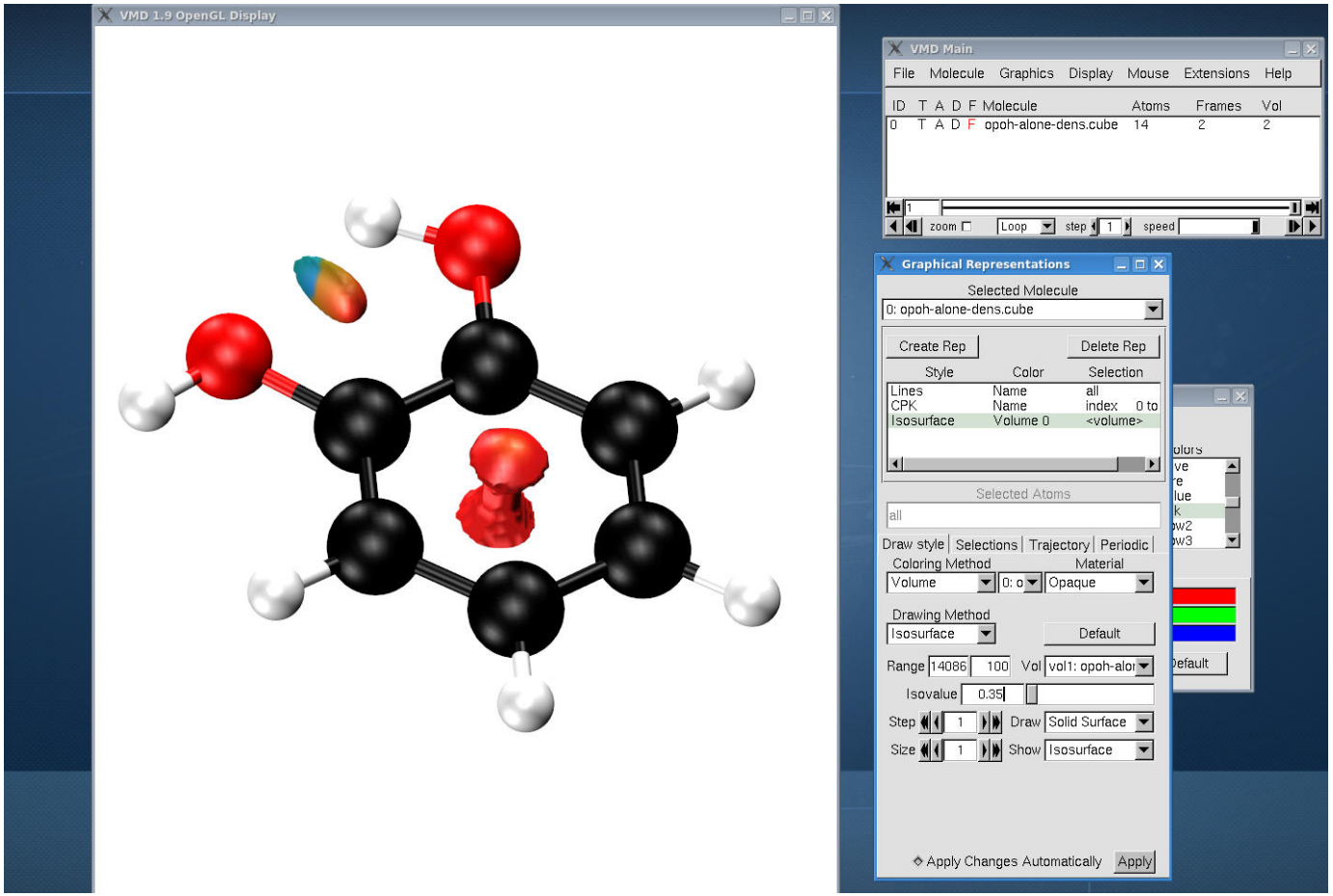
- **Name > C > Black**

→ Set the Carbon atoms black

- **Color Scale** : change the color scale of the interactions (here blue < green < red)



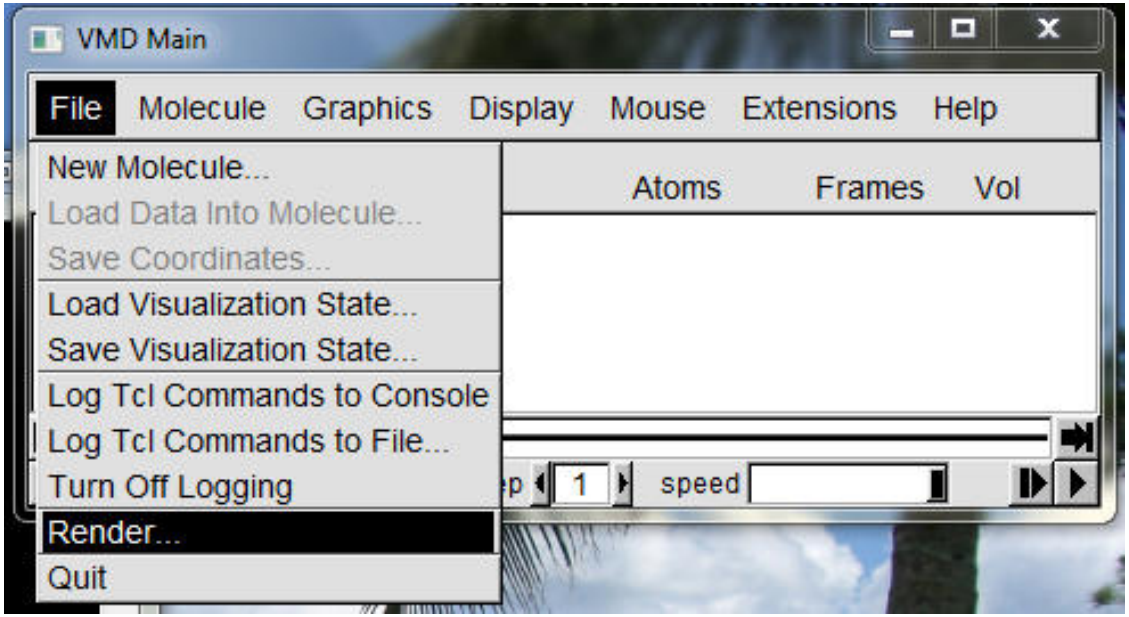
Basic use of VMD



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, choloro-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 programms:

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

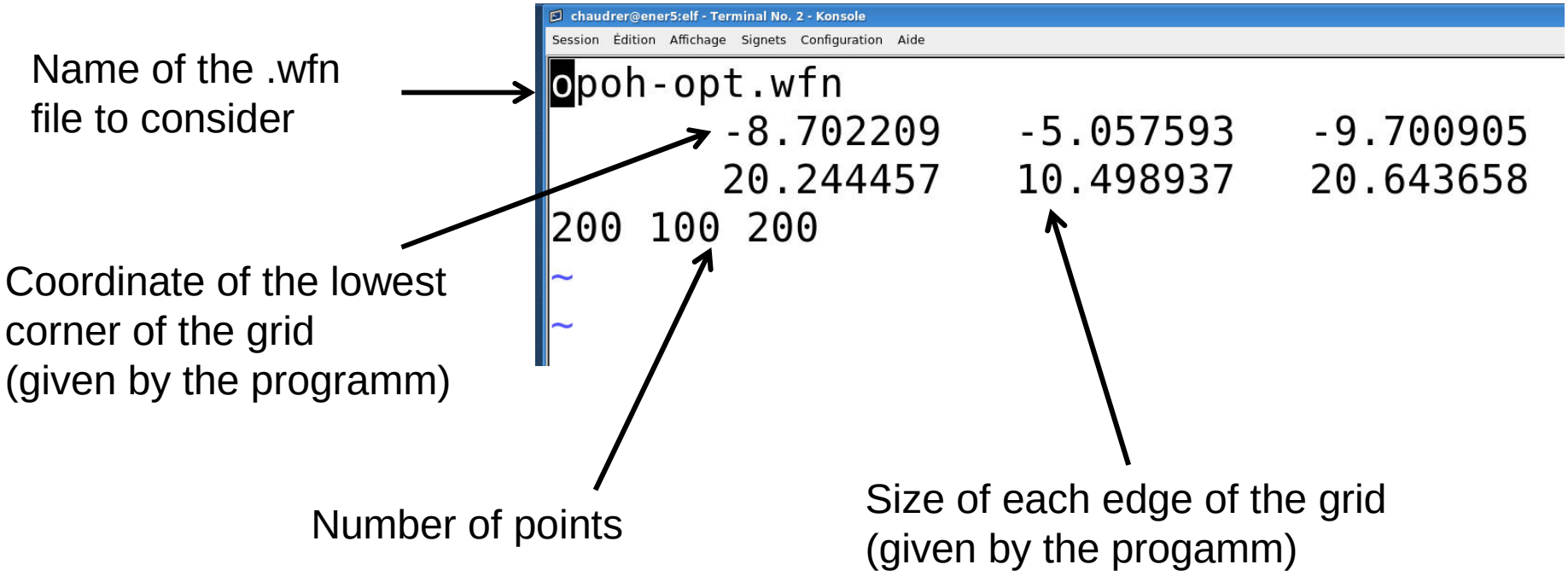
4. Integrate different properties

   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

Input file (can also be done interactively)



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

sbf_to_cube

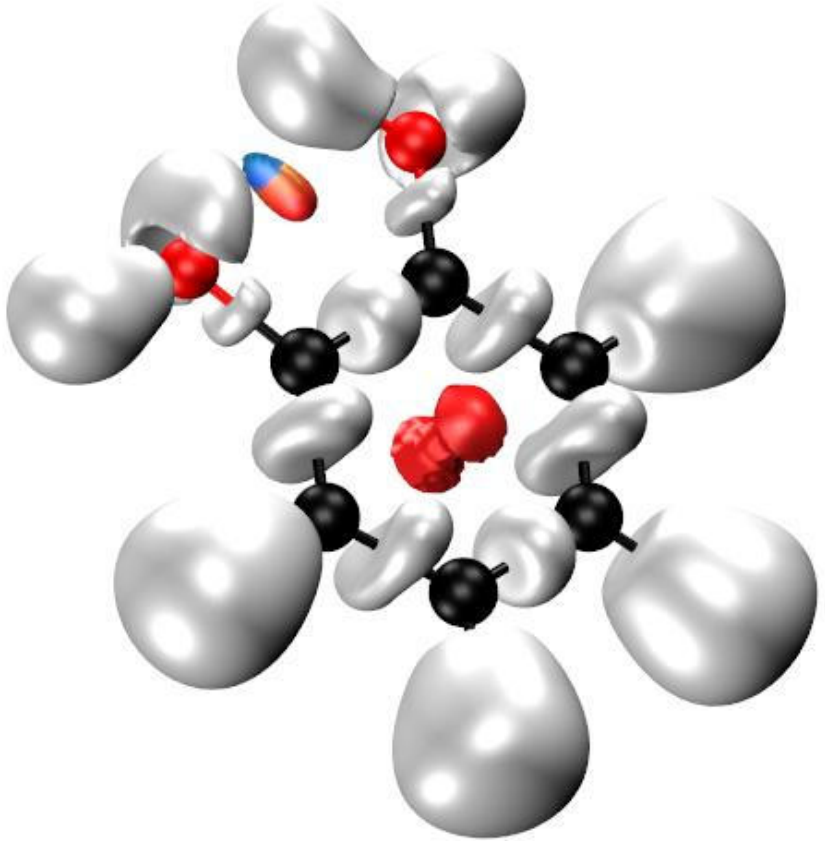
Output files

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

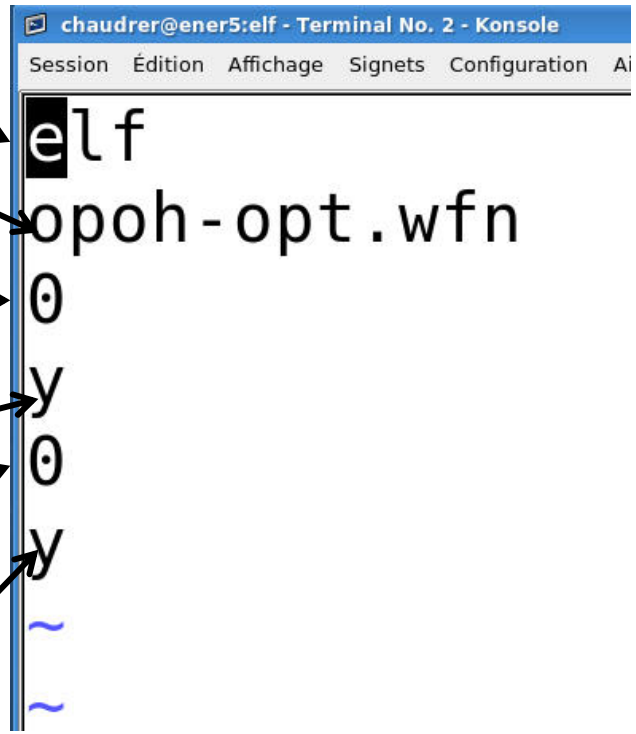
Name of the wfn file (same as precedent)

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



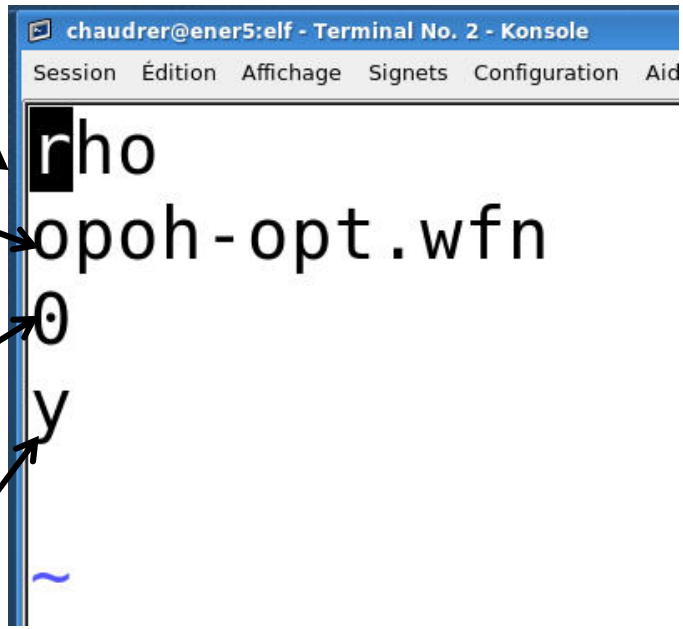
Input file for density (can also be done interactively)

Selection between elf or rho

Name of the wfn file (same as precedent)

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

Assign grid point to decompose
the volume into bassins



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

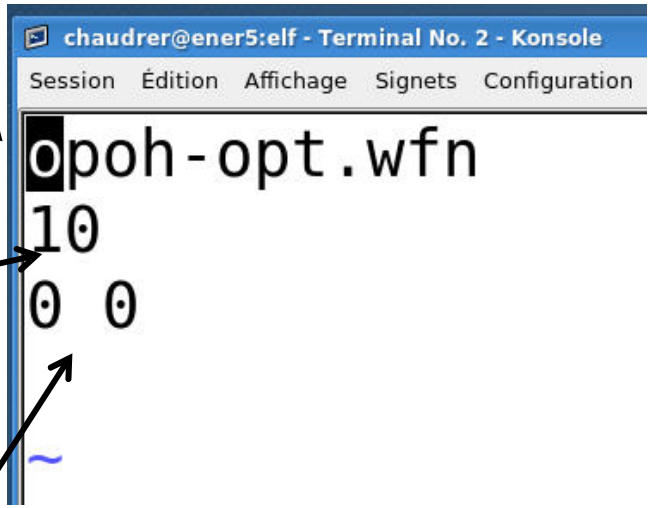
Pop09

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)



Pop09 output file

Output files

First ELF then AIM

1.Integrated properties for all basins: **volume, population**, pαβ, pαα, pββ, …

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

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.

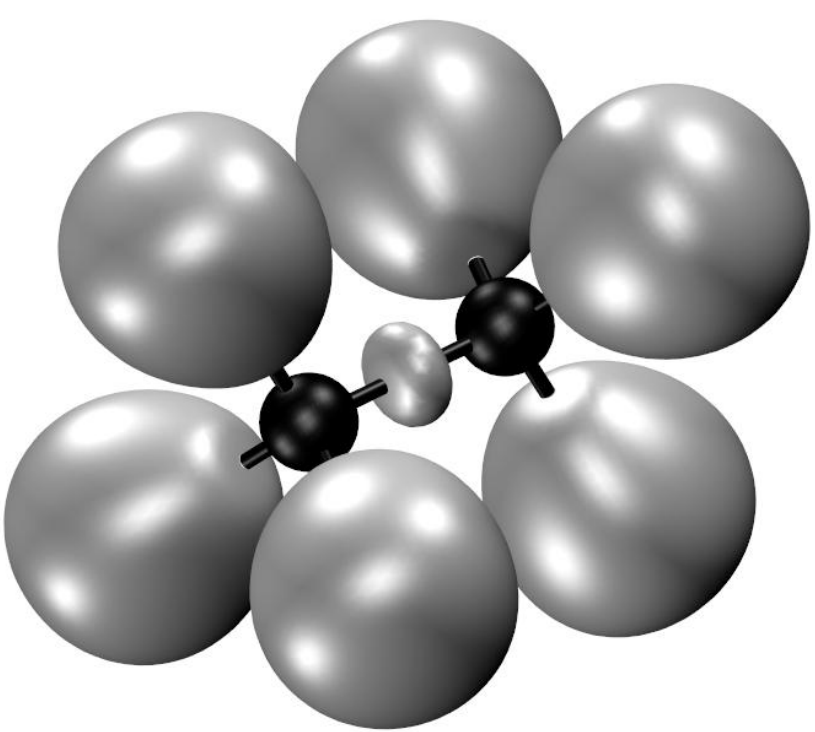
3. Look at the different ELF output. What is the evolution of the populations of the different important basins? Does that correspond to the NCI analysis evolution?

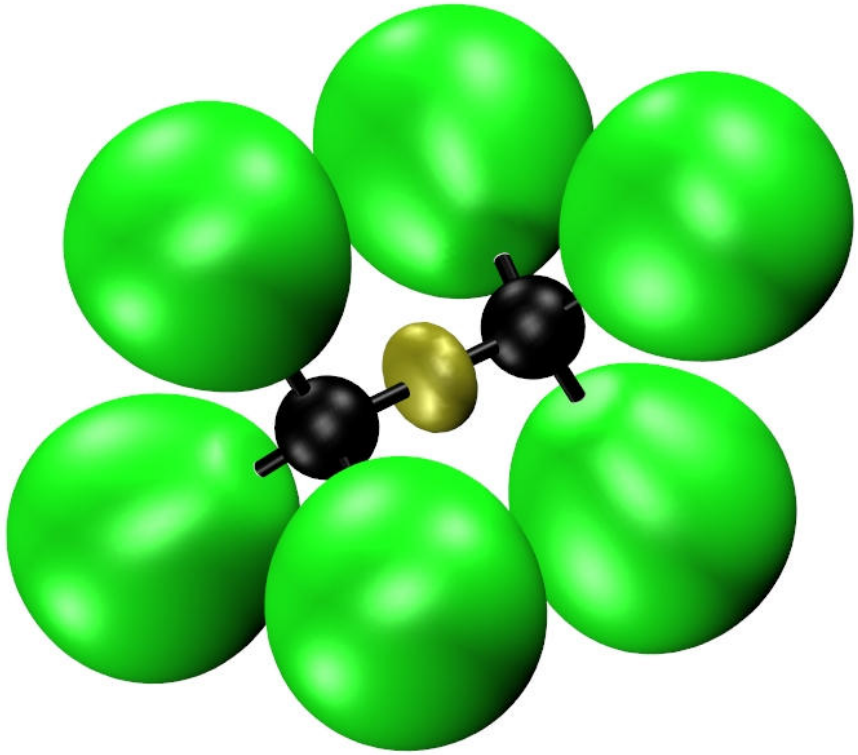
Congrats!

You finished

Correction ELF

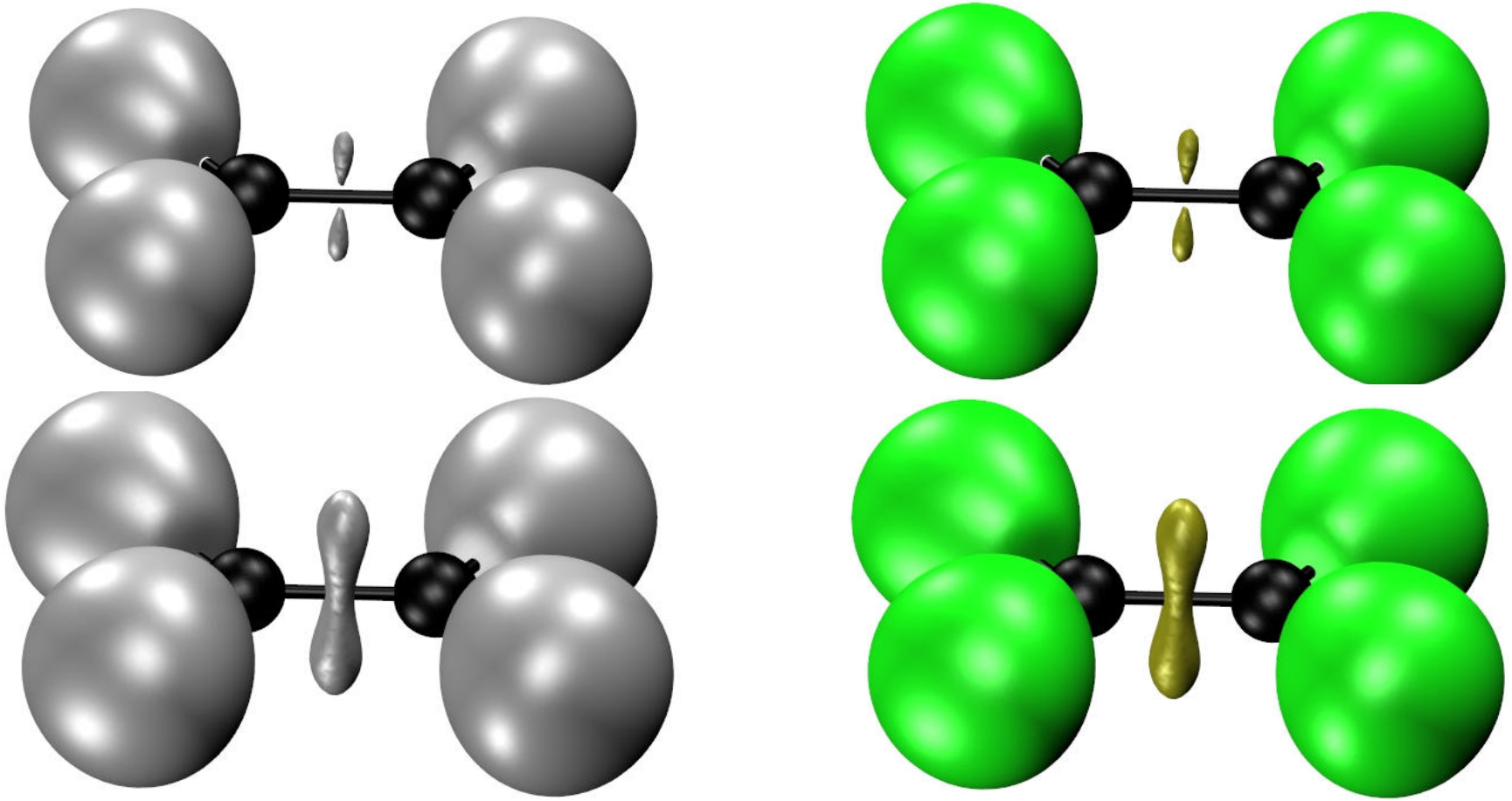
Ethane





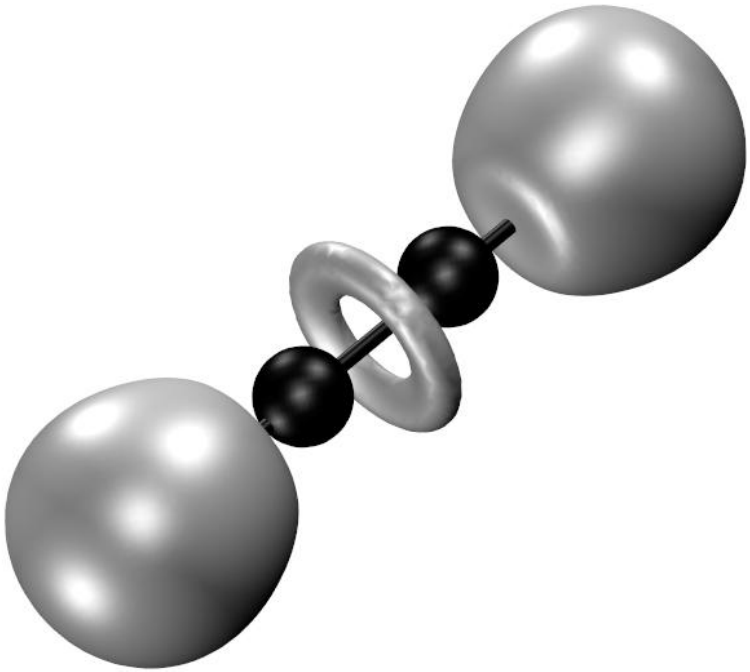
Correction ELF

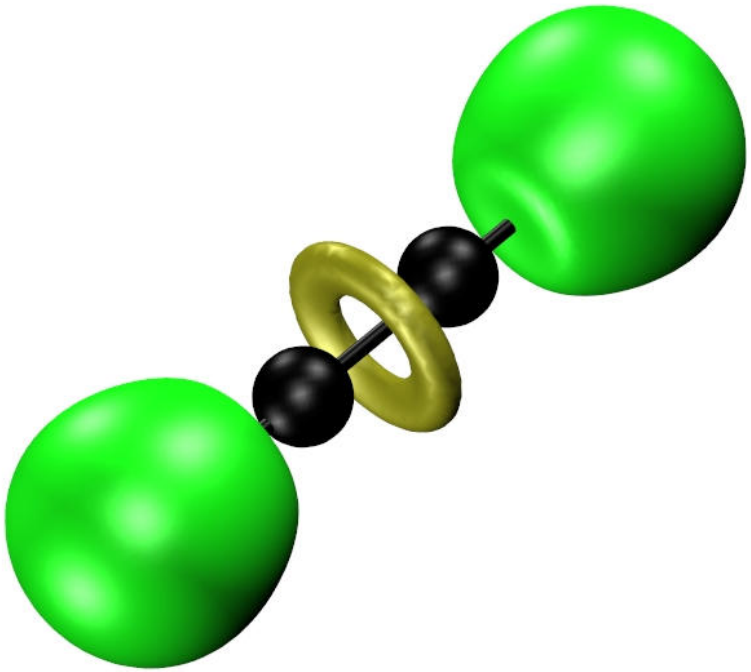
Ethylene



Correction ELF

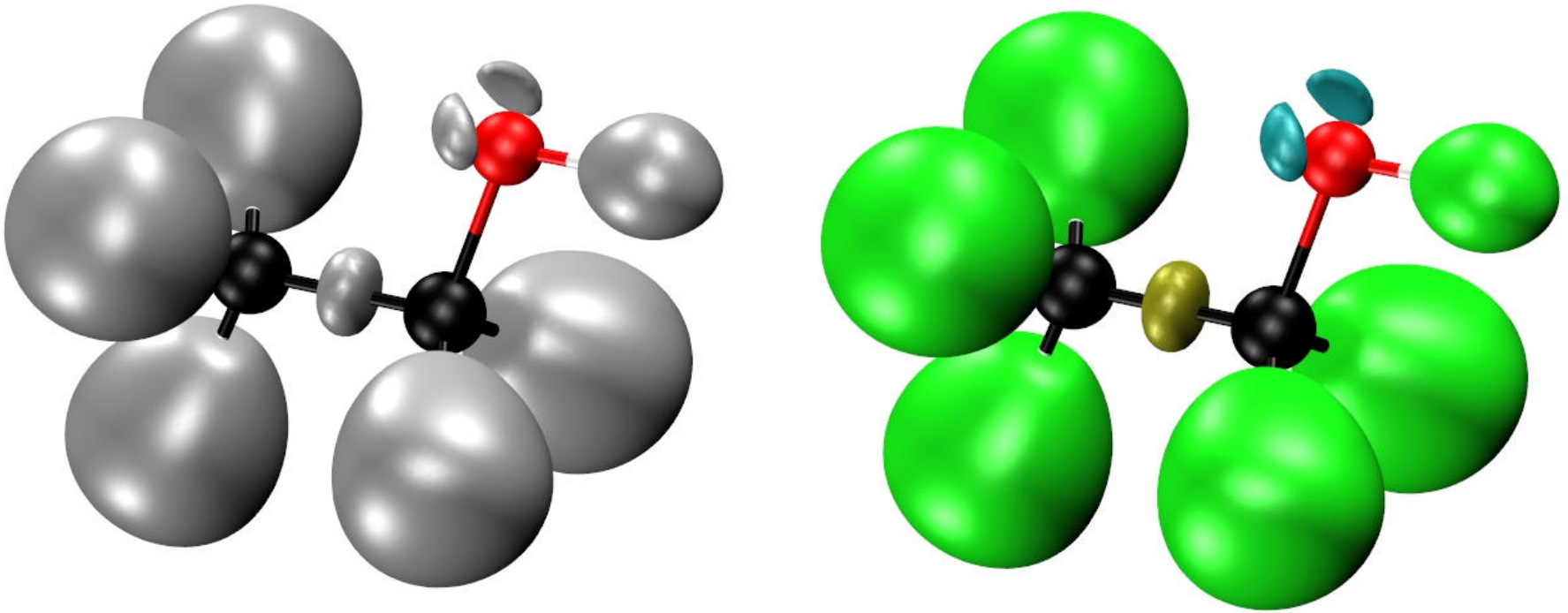
Ethine





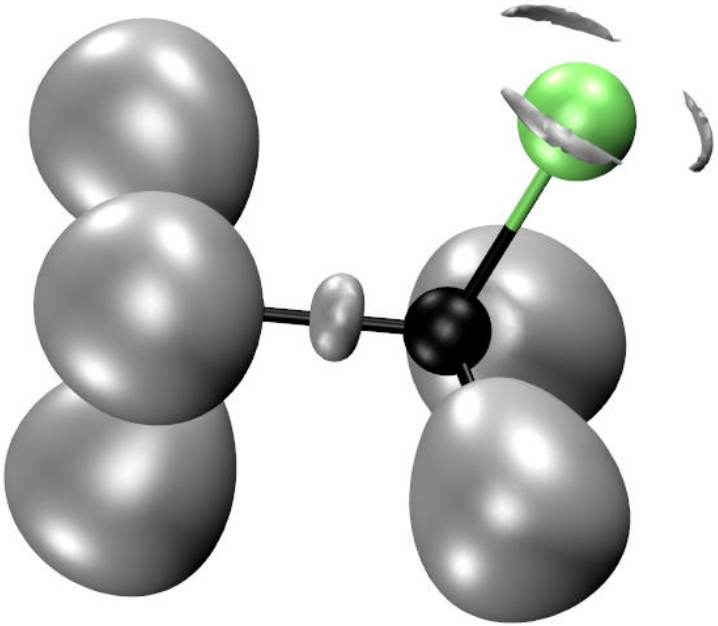
Correction ELF

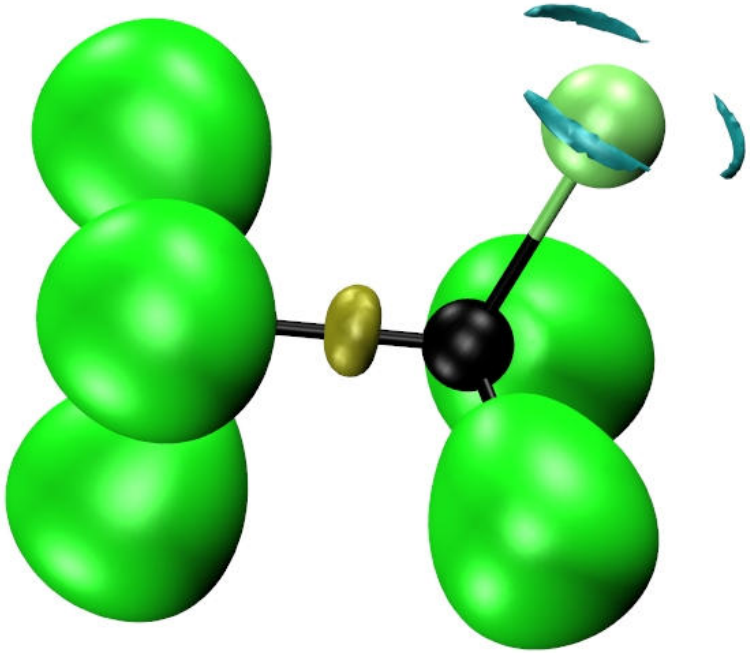
Ethanol



Correction ELF

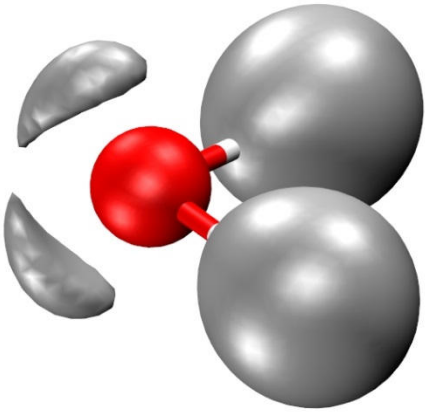
Chloro-ethane

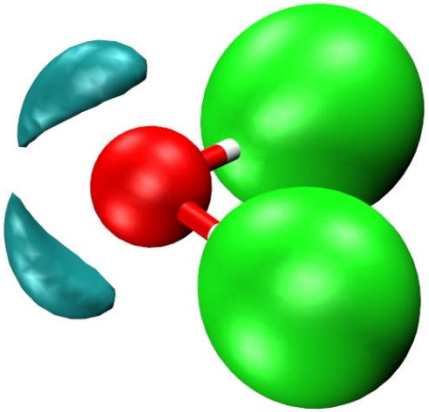




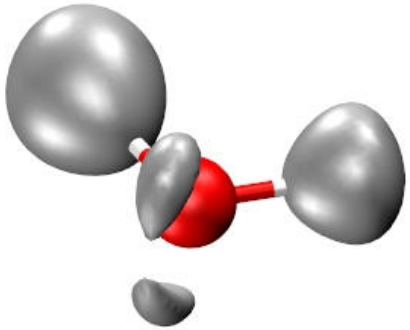
Correction ELF

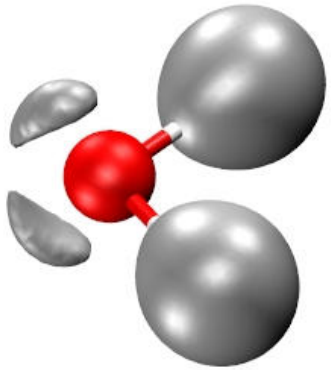
Water

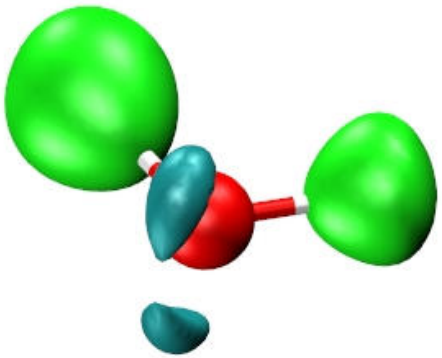


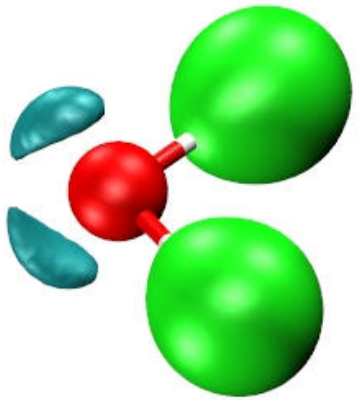


Water dimer









Correction ELF

Catechol