# Working Session II : ELF/MESP/NCI

https://moderm2023.sciencesconf.org/

| Tuesday 5 sept.<br>T. 42-43, basement | Wednesday 6 sept.<br>T. 42-43, basement |
|---|---|
| QTAIM – IQA – REG | ELF, MESP & NCI |
| **Lunch**<br>**Brasserie l'ardoise** | **Lunch**<br>**Brasserie l'ardoise** |
| 14h30-15h30<br>QTAIM – IQA - REG | Conceptual DFT |
| 16h -17h30<br>ELF, MESP &NCI | |

# Working Session II

We provide all files needed for the session:

✓A copy of useful articles.

✓We have supplied all requisite wfn/wfx/cube input files for TopChem2.

✓Many exercises are provided with varying levels of difficulty. You can initially select exercises from the "Essential" list.

# Working Session II

Starting with Topchem2 : Summary of main commands (page 32)

1. Open a linux terminal
2. Change the directory where the input files are located:

```
cd MoDerm/TP_Exercices/Inputs_MoDerm/SessionII
```

3. and start with the command-line,

```
topchem2 ….
```

## Working Session II: ELF/CVB/NCI analysis with TopChem2

**command-line,**

- topchem2 **wfn/wfx**:your_file.wfn **function**:elf/cvb/nci **vmd** **refine**:f **proc**:4 **output**:your_file.pop

## Working Session II: ELF/CVB/NCI analysis with TopChem2

**command-line,**

- topchem2 **wfn/wfx**:your_file.wfn **function**:elf/cvb/nci **vmd** **refine**:f **proc**:4 **output**:your_file.pop

**Gaussian wfn file (or wfx)**

## Working Session II: ELF/CVB/NCI analysis with TopChem2

**command-line,**

➢ topchem2 **wfn/wfx**:your_file.wfn **function**:**elf/cvb/nci** **vmd** **refine**:f **proc**:4 **output**:your_file.pop

**ELF/CVB/NCI analysis**

## Working Session II: ELF/CVB/NCI analysis with TopChem2

**command-line,**

- topchem2 **wfn/wfx**:your_file.wfn **function**:elf/cvb/nci **vmd**
**refine**:f **proc**:4 **output**:your_file.pop

**Produce a vmd file**

## Working Session II: MESP analysis from cube files

**command-line,**

➢ topchem2 **input**:your_file_mep.cube **rho_file**: your_file_rho.cube **vmd function**:mep **proc**:4 **output**:your_file.pop

## Working Session II: MESP analysis from wfn/wfx

**command-line,**

➢ topchem2 **wfn/wfx**:your_file.wfn **function**:mep **vmd proc**:4 **output**:your_file.pop

# How to read/visualize your results ?

Results :

> vi your_file .pop ⟶

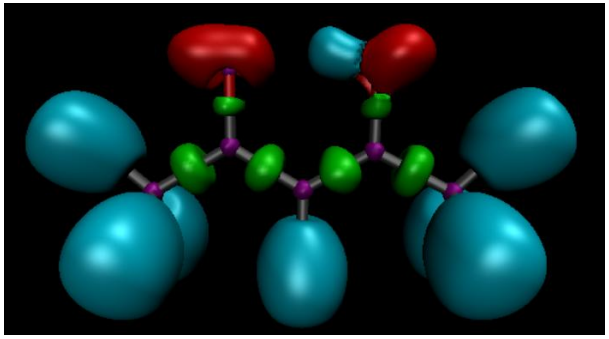
```
                    POPULATION ANALYSIS SECTION
================================================================
sum.      29.01% assigned.


 Populations
 =================


 basin                vol.      pop.      q.


  1 C(C2)           107.010     2.0672     3.9328
  2 C(O1)            93.221     2.1228     5.8772
  3 C(F4)           401.173     2.1326     6.8674
  4 V(H3,F4)        189.111     1.3105    -0.3105
  5 V(C2)           393.549     2.5571    -2.5571
  6 V(O1)           863.437     3.9723    -3.9723
  7 V(F4)           669.064     6.5752    -6.5752
  8 V(O1,C2)        124.578     3.2567    -3.2567


 total population      23.994
```

Visualize critical points locations :

> molden your_file_elf_cpelf.xyz

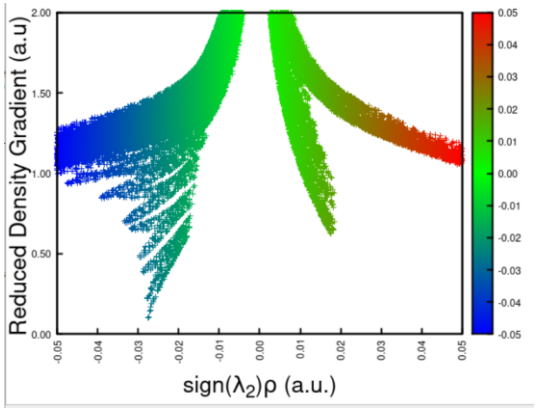
Visualize 3D Isosurfaces :

> vmd -e your_file_elf_ebas.vmd



Visualize 2D NCI :

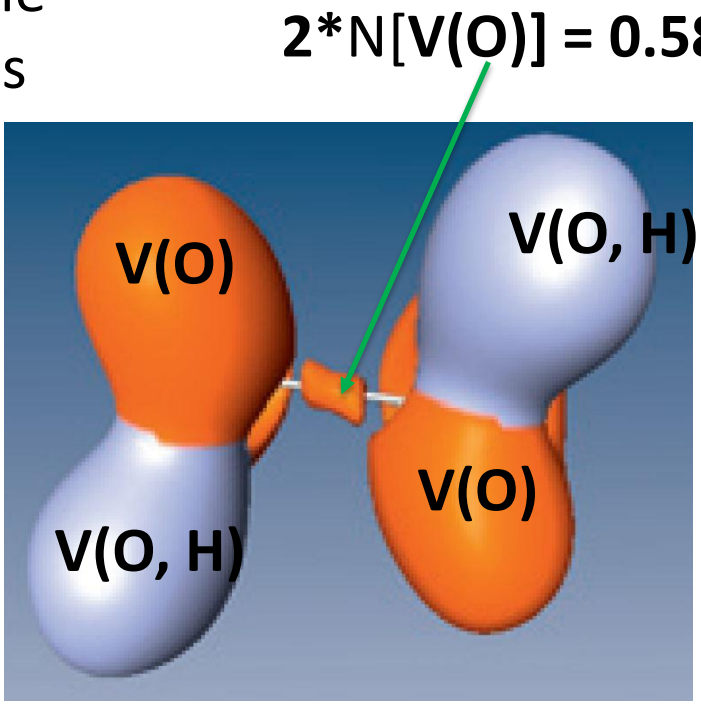
> gnuplot your_file_nci.gnu



# ELF Signature for charge-shift bond (CSB)*

- ✓ homonuclear bond X-X or common case for X = F or Cl
- ✓ depleted bond population, usually less than 1e
- ✓ large delocalization between the populations of adjacent V(X) basins

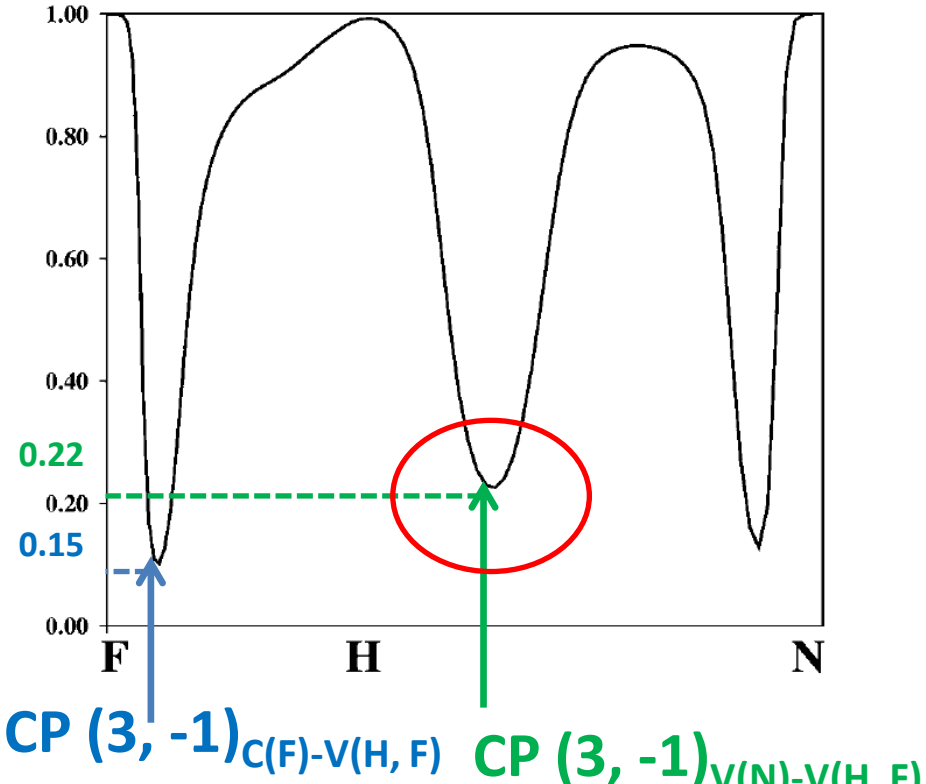
$H_2O_2$

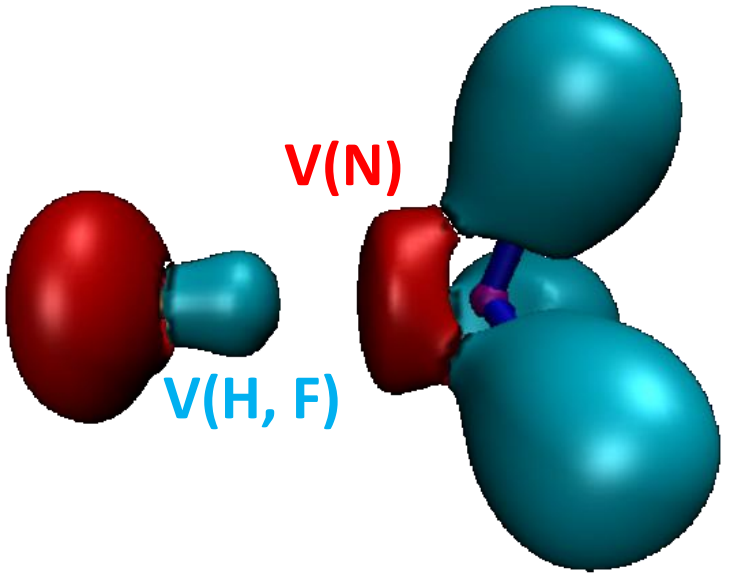



* Shaik S., Danovich D., Silvi B., Lauvergnat D., Hiberty P. Charge-Shift Bonding—A Class of Electron-Pair Bonds That Emerges from Valence Bond Theory and Is Supported by the Electron Localization Function Approach *Chem. Eur. J.* 21, pp. 6358–6371 (**2005**)

# ELF Core-Valence Bifurcation index (CVB) index *

The core-valence bifurcation index (CVB)* is designed to classify the A-H••• B hydrogen bonds :




→ CVB = 0.22 - 0.15 = 0.07 > 0

Correlation with the interaction energy FH-$NH_3$

* Fuster, F. and Silvi, B. Does the topological approach characterize the hydrogen bond ? *Th. Chem. Acc.* 104, p 13–21 (2000)

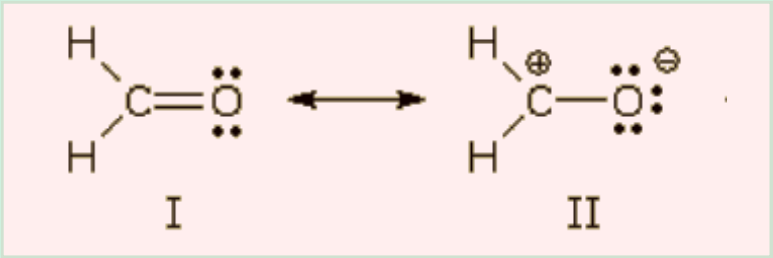
# Practical calculation

**Bond polarity index (bpi)** : Gives the contributions of A and B QTAIM basins, respectively, to the total population of the V(A, B) disynaptic basin. bpi is always restricted to [-1, 1]

- ✓ Add to the command-line: contrib:y
- ✓ Directly given in the your_file.pop

```
Bond Polarity Index (electrons)

=======================
                        1- O          2- C
 1 C(C2)                0.000         1.000
 2 C(O1)                1.000         0.000
 3 C(F4)                0.000         0.000
 4 V(H3,F4)             0.000         0.000
 5 V(C2)               -0.886         0.871
```

# Weigths of Lewis resonant structures (hands on Session II )




B3LYP/6-311+G(d,p) level of theory

populations → N[V(C, O)] = 2.43e ; N[C(C)]=2.08e ; N[C(O)]= 2.15e

C-O linear system → $\begin{cases} 8\ w_I + 6\ w_{II} = 2.43 + 2.08 + 2.15 \\ w_I + w_{II} = 1 \end{cases}$

Solution:

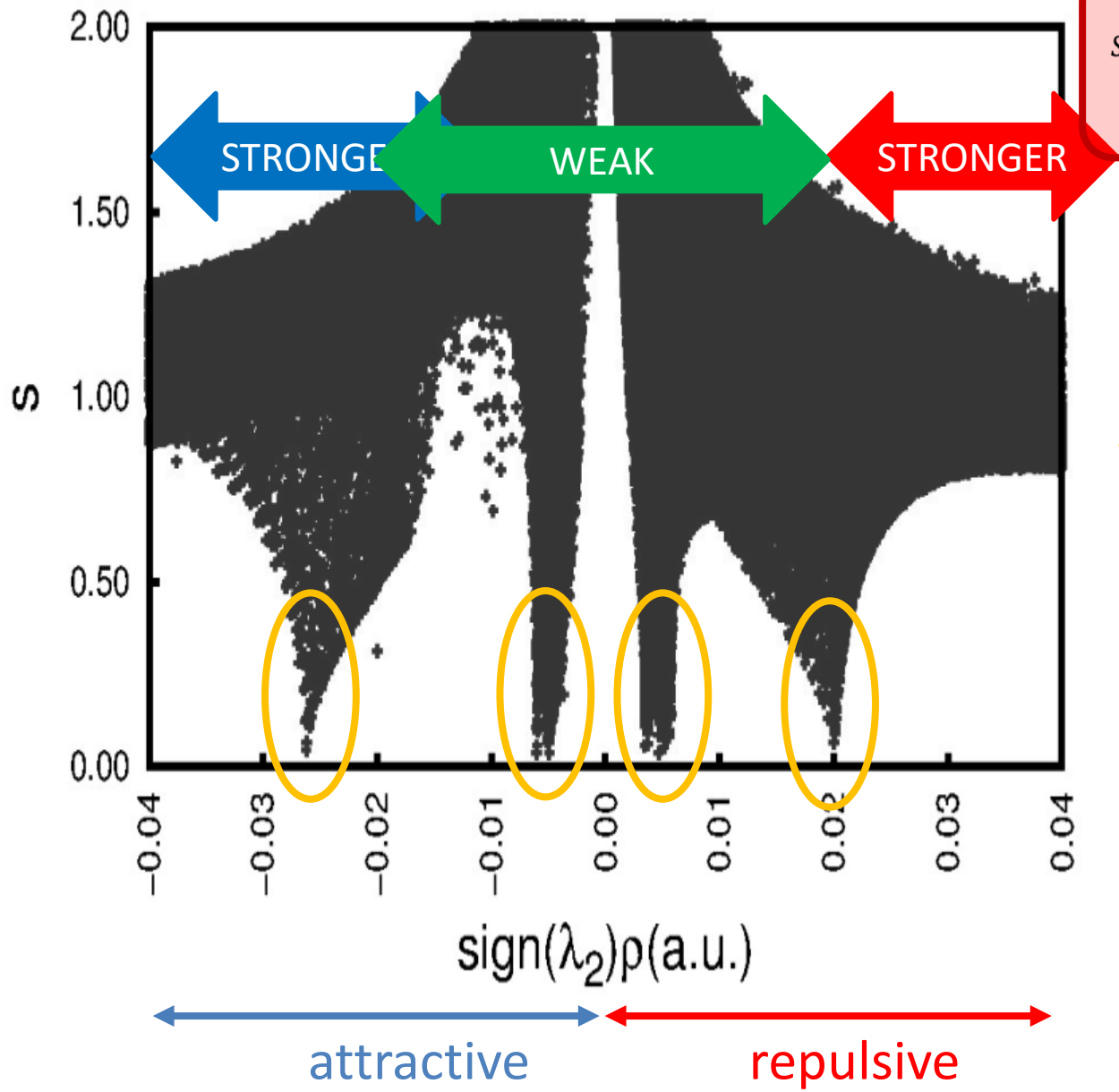
$\begin{cases} w_I = 0.33 \\ w_{II} = 0.67 \end{cases}$ → strong contribution of the polarized structure $C^+\ O^-$

# NCI : Hands-on

- For several systems showing non covalent interactions :
  - trace **s versus sign($\lambda_2$)$\rho$ (2D NCI plot)** ;
  - look at **s isosurfaces** in the molecular space **(3D NCI plot)**
- Relate the shape / spatial extention of the NCI isosurface to the type of interaction (localized / delocalized character)
- Reveal the dual character (attractive / repulsive) of some interactions
- Confront QTAIM analysis to NCI analysis.
  - s spikes revealing the presence of an interaction do not necessarily goes to s = 0 (no QTAIM cp)
  - A single non covalent interaction can be associated with several QTAIM critical points

**Reduced Density Gradient** (RDG)

$$s(r) \propto \frac{|\nabla\rho(r)|}{\rho(r)^{4/3}}$$




s spike

Sign($\lambda_2$) :

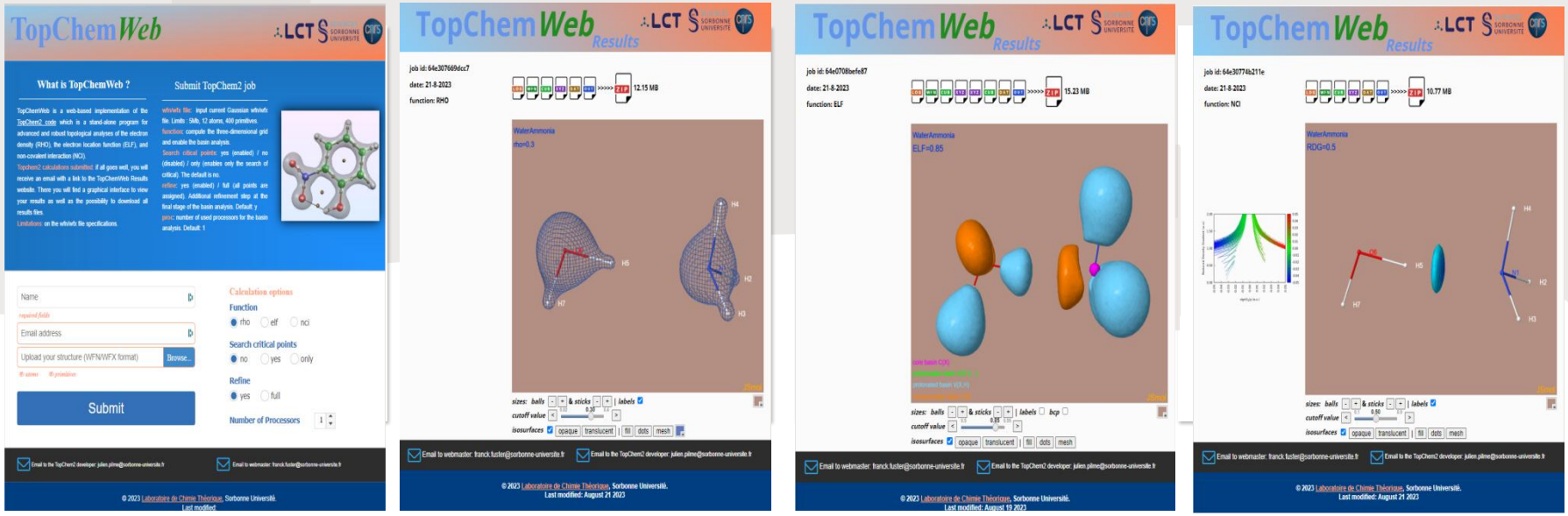
attractive / repulsive character of the interaction

ρ :

Strength of the interaction

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

**http://topchemweb.sorbonne-universite.fr/**




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