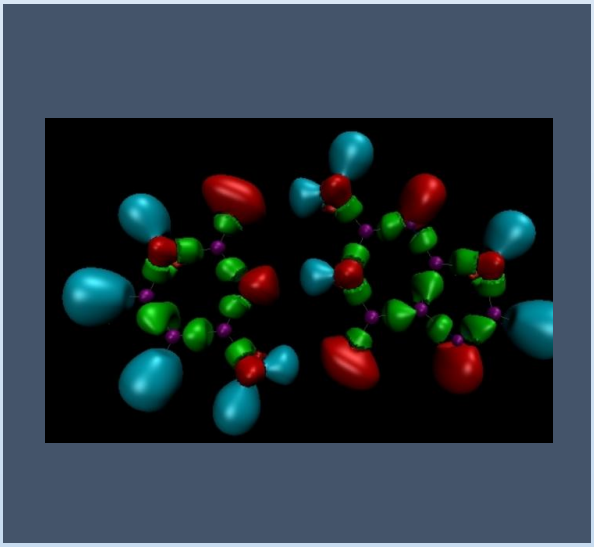

Starting with TopChem2

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Starting with TopChem2

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I. Generalities and Quick Introduction

TopChem2 is a standalone program which allows for advanced and robust topological analyses of the electron localization function, the electron density and the molecular electrostatic potential from 3D- cube or from wfn/wfx gaussian files. The Non Covalent Interaction (NCI) index is also computed. The program is easily usable in command-line offering a user-friendly experience.

Dependencies:

- Linux Intel/AMD x86, 64 bit operating systems

Installation:

A] Open a linux terminal and extract the files from the tar archive:

```
> tar -xvf TopChem2_cube64.tar.gz
```

B] Change the directory to where the files are located:

```
> cd INSTALL_TOPCHEM64
```

C] Run the bash script installer, it does not require administrative privileges to run:

```
> bash installer.sh
```

The setup installer is an easy-to-follow dialog. Please follow the corresponding instructions for installing TopChem2.

Several fortran binaries are provided in the package:

`topchem2` : the main program
`vasp_to_cube` : utility for generating cubes from CHGCAR/ELFCAR VASP files.
.

II. Quick-Start in command-line

Just open a terminal window, and type *topchem2* with optional parameters. Default parameters for critical points search and integration procedure are in general of sufficient quality to afford reliable results. The program runs through three different sections: critical points search, basin analysis and population analysis.

Analysis from wfn/wfx files

For a rapid start of *topchem2*, using the default parameters setup options and the wfn file example h2o.wfn (assumed to be in the current directory),

For a QTAIM analysis, enter the following at a command prompt:

```
> topchem2 wfn:h2o.wfn function:rho output:output.txt proc:6
```

ELF topological analysis from wfn, enter the following at a command prompt:

```
> topchem2 wfn:h2o.wfn function:elf output:output.txt th_assign:0.0001 dist_cp:0.2 proc:6
```

Analysis from cube files

For a rapid start of *topchem2*, using the default parameters setup options and the cube files examples h2o_rho.cube and h2o_elf.cube (assumed to be in the current directory),

QTAIM analysis from cube file, enter the following at a command prompt:

```
> topchem2 input:h2o_rho.cube function:rho output:output.txt proc:6
```

For the ELF topological analysis from cube file, enter the following at a command prompt:

```
> topchem2 input:h2o_elf.cube function:elf output:output.txt cp:y th_assign:0.0001
th_cp:0.001 dist_cp:0.2 rho_file:h2o_rho.cube
```

III. Output Files

A calculation can produce several output files:

- ✓ One output text file where the main numerical values are gathered. All values are given in atomic units.
- ✓ *file_elf_cpelf.xyz* or *file_cprho.xyz* : xyz file format containing the xyz coordinates (Å) of found critical points.
- ✓ *file_rbas.sbf* or *file_ebas.sbf* : binary Fortran files: Contains assignment basin codes of 3D-grid points. These files are needed to compute populations and integrated quantities.

- ✓ *topmod_rbas*.sbf or topmod_ebas.sbf **:** These files format are compatible with the TopMod program.
- ✓ *file_elf_esyn.cube*: cube file containing color basin code of grid points. Needed to visualize ELF basin colors (see below content VI.)

IV. TopChem2 USAGE

Type *>topchem2 help* :

```
|=============================================================================================================|
|            TopChem2.  v. 3. 2022.                                                                           |
| J. Pilmé. Requests and bugs : julien.pilme@sorbonne-universite.fr                                           |
|                                                                                                             |
|  The Command-line Usage is:                                                                                 |
|=============================================================================================================|
| topchem2 help : this help                                                                                   |
| topchem2 input:[*.cube] wfn/wfx:[*.wfn/wfx] output:[file] function:string  OPTIONS(see below)               |
|                                                 string:[rho] Electron density                               |
|                                                 string:[elf] Electron Localization Function                 |
|                                                 string:[mep] Molecular Electrostatic Potential              |
|                                                 string:[dld] Dual Descriptor FMO approximation              |
|                                                 string:[fp]  Fukui f+ FMO approximation                     |
|                                                 string:[fm]  Fukui f- FMO approximation                     |
|                                                 string:[fwv] Fast analysis of the Wavefunction              |
|                                                                                                             |
| 1. input    :[string]   input cube file.                                                                    |
|    wfx/wfn  :[string]   input gaussian wfn file.                                                            |
| 2. output   :[string]   output file (txt format).                                                           |
| 3. function :[string]   function choice, string:rho/elf/mep/dld/fp/fm/fwv                                   |
|=============================================================================================================|

|================================ GENERAL OPTIONS ============================================================|
|=============================================================================================================|
|* 4.  cp:[y/n/o]     y(enabled)/n(disabled) the search of critical points.                                   |
|                     o(enabled) but basin analysis and populations are skipped                               |
|                     Default: electron density: n  elf: y.                                                   |
|                                                          current file "file_cpelf.xyz" will be              |
|                                                          used for the basin analysis.                       |
|* 5.  th_assign:[real] threshold of the function for the basin analysis.                                     |
|                       Default value: electron density: 0.0001 a.u. ; elf: 0.01                              |
|* 6.  th_cp:[real]   Minimal threshold of the function at critical points locations.                         |
|              Default value: electron density: 0.001 a.u.; elf:0.75; mep, positive:1d-7                       |
|* 7.  dist_cp:[real] Enforced minimal distance (bohr) between 2 critical points.                             |
|              Default value: electron density: 0.25 bohr ; elf:0.5 bohr/mep:0.6 bohr                         |
|* 8.  periodic:[y/n] y(enabled)/n(disabled) Use periodic cell properties for the basin analysis.Def:n        |
|* 9.  grad:[y/n]     y(enabled)/n(disabled) Use gradients for the basin analysis. Default: y                 |
|* 10. steep_grad:[low,medium,high,vhigh] : accuracy for the steepest gradient process. Default:medium       |
|* 11. bas :[y/n]     y(enabled)/n(disabled) the basin analysis. Default: y                                   |
|* 12. voronoi        Voronoi charge distribution instead f QCT distribution                                  |
|* 13. refine:[y/n/f] y(enabled)/n(disabled)/f(full) Additional refinement step at the final stage            |
|      of the basin analysis.  full: all points are assigned (Voronoi scheme). Default: y                     |
|* 14. proc:[integer] Number of used processors for the basin & population analysis. Default: 1               |
```

.....

The main argument parameters have the following meaning:

1. *input*: [string] Input Current **electron density/ELF/MESP cube file**.
2. *wfn/wfx*: [string] Input Current **Gaussian wfn/wfx file**.
3. *output*: [string] output text file. **Main numerical results** are gathered in this file.
4. *function*: [string]. Compute the three-dimensional grid and enable the basin analysis.

a) string ≡ rho: Electron density ρ(**r**) (QTAIM analysis): **3d-Grid and Analysis**. Of all the possible ways to analysis the electron density in a molecule or in a solid, the Quantum Theory of Atoms in Molecules (QTAIM) is probably the most used for discussing the nature of chemical bonding . The pioneering works are due to Richard F. W. Bader and coworkers in the 70s. this methodology can be applied to both experimental and computed electron densities, the topological atoms being defined as the union of a nucleus and of its atomic

basin. The topology of the density gradient field is characterized by critical points and their connectivity. Among the saddle points, a bond critical point (BCP) plays an essential role because the values of some local descriptors based on the electron density are usually related to the nature of the chemical bond.
See R. Bader, *Chem. Rev*. 91, pp. 893-928 (1991)

b) string ≡ elf: Electron localization function (ELF): **3d-Grid and Analysis.** The electron localization function (ELF) topological analysis was intensively used for studying of the bonding schemes in molecules and in solids, or for rationalizing the chemical reactivity. It relies on the Laplacian of the conditional same spin pair probability scaled by the homogeneous electron gas kinetic energy density. ELF is usually interpreted as a signature of the electron-pair distribution. Its topological analysis represents a bridge between the traditional pictures of the chemical bond derived from the Lewis theory, and first principles quantum-mechanical methodologies. Overall, the spatial distribution of the valence basins closely matches the non-bonding and bonding domains of the VSEPR model. ELF was expressed in the framework of the density functional theory by Savin et al. and rationalized in terms of the local excess kinetic energy due to the Pauli repulsion. ELF can be computed at each grid point as follows:

$$\chi = \frac{\tau - \frac{1}{8}\frac{|\nabla\rho|^2}{\rho}}{c_f\rho^{5/3}} \text{ and } ELF = \frac{1}{1+\chi^2}$$

where τ is the kinetic energy density .

See for definitions: *J. Chem Phys*, 92, 5397-5403 (**1990**). Savin, *Angewandte* 31,187–188 (**1992**) and its topological analysis with *Nature* 371, 683 (**1994**)

c) string ≡ mep: Molecular Electrostatic Potential**: 3d-Grid and location of (3,+3) critical points.** The MESP is an interesting travel guide assessing the chemical reactivity of molecules towards positive (electrophilic) or negative (nucleophilic) sites of reactants. The MESP is typically visualized using mapping its values onto the electron density isosurface reflecting the molecular sites boundaries.
See H. Suresh, Geetha S. Remya, Puthannur K. Anjalikrishna, WIREs Comput Mol. Sci 12:e1601 (2022)

d) string ≡ fm, fp, dld : Frontier Molecular orbital and orbital-weigthed approximations for Fukui $\mathbf{f}^+$ and $\mathbf{f}^-$ functions and Dual descriptor: **3d-Grid and Analysis.**
The Fukui functions and the Dual Descriptor are suitable tools of the conceptual DFT designed to describe and predict the chemical reactivity. They describe how the electron density is modified after adding or removing some amount of electrons. They can predict where are the electrophilic/nucleophilic molecular sites. $f^-(\mathbf{r})$ indicates which are the preferred sites for an electrophilic attack while $f^+(\mathbf{r})$ indicates which are the preferred sites for a nucleophilic attack. Dual Descriptor combines the both properties of the Fukui functions.
See P. Geerlings, F. De Proft, and W. Langenaeker *Chem. Rev.* 103, 5, pp. 1793-1874 (2003). *J. Phys. Chem. A* (**2005**), 109, 1, 205–212, *J. Comput. Chem.*, 38, 481 (**2017**) and *J. Phys.*

Chem. A, 123, 10556 (**2019**). The orbital weighted definition is useful in order to study the local reactivity of molecular systems whose frontier molecular orbitals are degenerated.

e) string ≡ nci: 3d-Grid and of sign(λ_2)*ρ(r) mapped onto RDG isosurfaces.

The non-covalent interaction index (NCI) method relies of the properties of the reduced density gradient (RDG),

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

RDG is very used for studying the weak interactions : The « strength » of weak interaction can be visualized using a mapping of sign(λ_2)*ρ(**r**) onto RDG isosurfaces, sign(λ2) being the sign of the second density Hessian eigenvalue (λ_2). Typically, the attractive and repulsive interactions are identified as regions where $\lambda_2 < 0$ and $\lambda_2 > 0$, respectively. Weak van der Waals interactions when λ_2 becomes nul.
See *J. Am. Chem. Soc.*, **132**, 6498 (2010).

f) string ≡fmw: No grid is computed. Fast analysis of the wavefunction.

g) string ≡cvb: Automatically search of ELF Core-Valence bifurcation (cvb) indexes.
see DOI 10.1007/s002149900100

GENERAL OPTIONAL KEYWORDS:

5. *cp*: [y/n/o] y(enabled)/n(disabled) the search of critical points. "o" enables only the search of critical points but both basin analysis and populations will be disabled. The default is "n" for the electron density and "y" for ELF.
6. *th_assign*: [real] All grid points where the value of the function remains below the given threshold will be ignored in the basin analysis. The **default** threshold is 0.001 a.u. for the electron density and 0.75 for ELF.
7. *th_cp*: [r(eal] Below the threshold, all found critical points are dismissed.
8. *dist_cp:* [real] Enforced minimal distance between 2 critical points. **Default** threshold of 0.25 bohr for the electron density and 0.6 bohr for ELF.
9. atom_dist:[real] Enforced minimal distance (bohr) between critical points and atoms. Default value: 0.3 bohr
10. *periodic*: [y/n] y(enabled)/n(disabled) the periodic cell properties for the basin analysis. Default: n
11. *voronoi* Voronoi charge discrete distribution instead of topological basin analysis. see J. Chem. Phys. **139**, 071103 (2013).

12. *grad:*[y/n] y(enabled)/n(disabled) the use of numerical gradients for the basin analysis. Default: y
13. *proc*: [integer] Number of used processors for the basin analysis. Default: 1
14. *rho_file*: [string] Electron density cube file needed to compute ELF populations and moments.
15. *bas_file*: [string] Binary file provided by TopChem or TopMod which will be used to compute QTAIM atomic contributions to ELF basins.
16. *refine*: [y/n/f]: y(enabled)/n(disabled)/f(full). Additional refinement step at the final stage of the basin analysis. full: all points are assigned. Default: y
17. *val*: [real,real,real] x,y,z (bohr): value of some descriptors computed at the (x,y,z) point.
18. *print*: enable the verbose mode.
19. *algo:*[offgrid/neargrid/ongrid] : used algorithm for the basin analysis

    offgrid: see DOI : 10.1002/jcc.27105. *Computers & Chemistry* 1999, 23, (6), 597-604 (default)

    neargrid: see *Journal of Physics: Condensed Matter* **2009**, 21(8), 084204, *J. Comput. Chem.* **2011**, 32(15), 3207.

    ongrid: see *Comput. Mater. Sci.* **2006**, 36(3), 354

✓ *descriptor* Enable the calculation of the values of some local descriptors at the critical points locations (by default if cp="o" or cp="y"): Electron density, Shape Function, Radial distribution, ellipticity, bond metallicity, Shannon entropy and gradients, Laplacian of the electron density and Hessian eigenvalues. Local energy densities are also computed at bond critical points. The Kirzhnits approximation used in DFT is applied here to compute the kinetic energy density from the electron density only [D. A. Kirzhnits, *Sov. Phys.* JETP ,5 , 64, **1957**].

WFN OPTIONAL KEYWORDS:

20. level: [rhf/uhf/rohf/nat] level of theory. Default: rhf.

    nat is the natural orbitals approximation for correlated post-HF wavefunction (MP_n, CI or CCSD level of theory)

21. pop: [pop/cov/pol/orb/ken] Compute integrated quantities over the basin volume.

    pop: basin volumes and populations (Default).

cov: variance and covariance analysis. For QTAIM: localization and delocalization indices and LDM matrices.

pol: condensed dipole and quadrupole basins.

orb: orbital contribution to basin populations.

ken: integration positive defined kinetic energy.

22. sizebox: [large/medium]: Size of the parallelepipedic box. The function is calculated on a 3-D grid parallel to the standard axis defined in the ab initio calculation.
23. sizegrid: [low/medium/high/vhigh] step between the grid points. low: 0.2 bohr, medium: 0.1 bohr, high: 0.075 bohr, vhigh:0.05 bohr. Default: medium.
24. num_int: use numerical integrations to compute basin integrated quantities (populations). Very fast process.
25. fukui: [fp,fm,dd] Frontier Molecular Orbital Fukui **basin Condensation**, fp:Fukui f+, fm:Fukui f-, dd:Dual Descriptor LUMO-HOMO (DOI: 10.1021/jp046577a).
26. mathematica : produce a mathematica notebook (*.nb) for the electron density calculation.

Electron localization Function and Electrostatic Potential OPTIONS:

- ✓ contrib : [y/n] y(enabled)/n(disabled) QTAIM contributions to basin populations. Default: n
- ✓ rho_file: [string] Electron density cube file needed to compute ELF/MEP basin populations.
- ✓ bas_file: [string] Binary file used to compute QTAIM atomic contributions (*_rbas.sbf).
- ✓ merge : [y/n] y(enabled)/n(disabled) Merge degenerated attractors. Default: y
- ✓ noh : Provide additional output cube files without protonated basins.
- ✓ vmd : Provide a vmd visualization state file. Only available for ELF.

V. Critical Points section

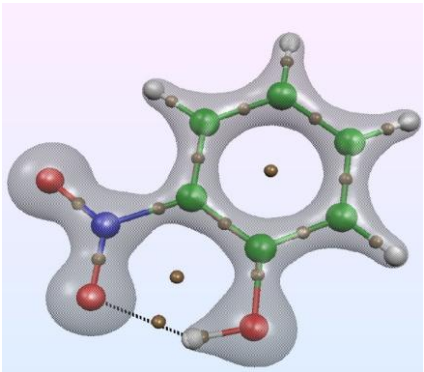
Critical points are searched and printed following the conventional ranking:

Displaying of the xyz critical points of the electron density gradient field for the ortho-nitrophenol molecule.

Color code: location of critical points are displayed with brown spheres.

- (3,-3): The three Hessian eigenvalues are all negative. This is a maxima (attractor) of the density function field.
- (3,-1): Two negative and one positive Hessian eigenvalues. This is a saddle point of the field, maxima in two directions and minimum in the other. If the density function is the electron density, it is termed as *Bond Critical Point* (BCP).
- (3,+1): One negative and two positive Hessian eigenvalues. This is a saddle point, maximum in one direction and minima elsewhere. If the density function is the electron density, the critical point is called *Ring Critical Point* (RCP).
- (3,+3): All the three Hessian eigenvalues are positives. This critical point is a minimum of the field. If the density function is the electron density, the critical point is called *Cage Critical Points* (CCP).

- **For ELF, only the attractors (3, -3) are kept. For MEP, only the minima (3,+3) are kept.**



Electron density and ELF analysis using pseudopotentials

When pseudopotentials are used, the gaussian wfx files use additional core density function data to represent the electron density of the ECP-modeled core electrons (EDF primitive functions). See http://aim.tkgristmill.com/wfxformat.html#edfsforecps

For wfn or cube files generated without recovering of the core regions, the electron density can be recovered in the core regions using a simplistic tight core gaussian function. Enabled by default when pseudo keyword is added to the command-line of TopChem2. See details by reference herein, Todd A. Keith and Michael J. Frisch, *J. Phys. Chem. A*, **115**, pp. 12879-12894, 2011.

The syntax is,

pseudo:[Atom1=Z1,Atom2=Z2,..] Enable pseudopotentials for specified atoms

When pseudopotentials are used, the ELF core basin radii (given in Bohr) are looking for for both the critical points section and the basin analysis. No critical points are sought inside the atomic sphere defined by this radius. However, this shell radius can be specified in a user file located in the work directory. This file needs to be termed as *pseudo_radius_ELF.txt*. Each line of this file corresponds to a specification of a radius given in the following format:

Atomic_ number (integer) *radius (real in Bohr)*

VI. Basin Analysis section

TopChem2 looks for all basins of the gradient scalar field along the descent trajectories from attractor points. The algorithm is similar to the one used by the TopMod program [*Computers & chemistry, 23 (6), pp. 597-604, 1999*].Each grid point is assigned to basin volumes and assignment codes are stored in binaries files *file_elf_ebas.sbf (Electron density) or file_elf_ebas.sbf (ELF)*. For ELF, color codes are assigned as basin types and stored in the cube file *file_elf_esyn.cube.* The basin type can be:

1: lone pair, usually shown in red

2: protonated bonds C-H, N-H, shown in turquoise

3: bonding, green

4: H-, white or yellow

5: core, purple

Displaying ELF color isosurfaces by means of VMD

1. Loading the file

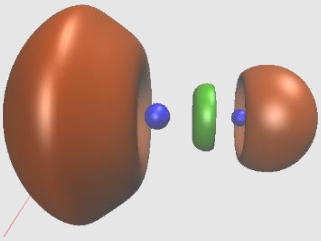
a. File > New Molecule>Browse : You choose the *name-elf.cube* file

b. Button LOAD

c. Select *name-elf.cube file* in the **VMD main Window**

d. File/Load Data into Molecule>Browse : You choose the *name-syn.cube* file

e. Button LOAD



2. Drawing/coloring ELF isosurfaces

Menu : Graphics > Representation

A. Drawing Surface

a. Drawing Method: Isosurface

b. Vol: Select *name_elf.cube* file

c. Isovalue: Using cursor to select isosurface value upper than *0.80*

d. Draw*:* Solid Surface

B. Coloring Surface

a. Coloring Method: Volume

b. Material: Select *name_esyn.cube*

3. Saving your picture

a. File > Render > Filename: file.bmp

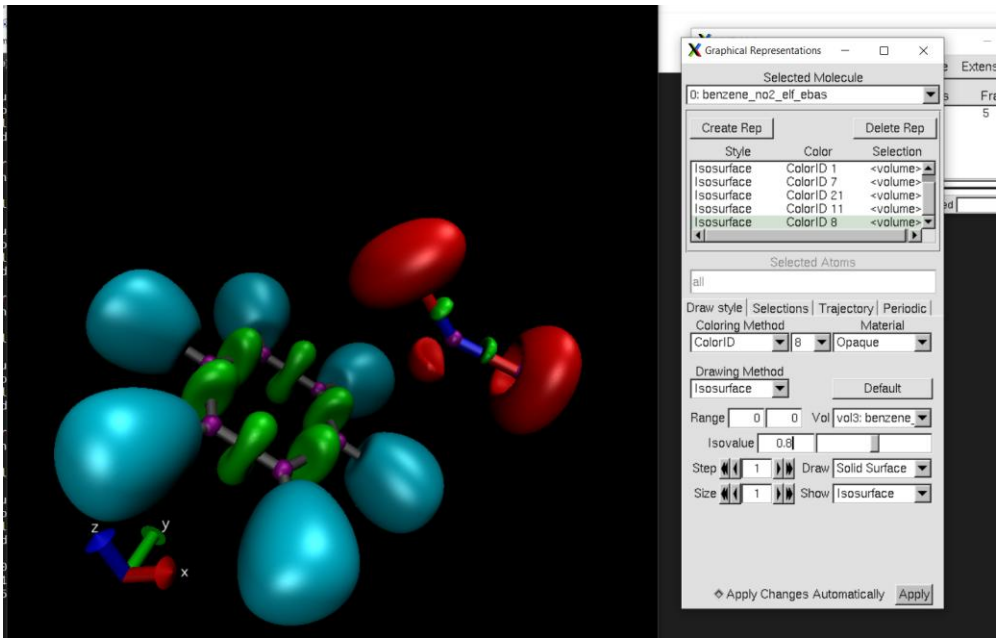
b. Start Rendering

Nice ELF, MEP and NCI Visualizations Using VMD

Alternatively, use “vmd” option in the command-line for the ELF analysis. The color types (see above) will be automatically assigned and stored in five separated cube files. A vmd file called, *file_elf_ebas.vmd* will be also created. This can be directly read in VMD as a “Load visualization file” using :

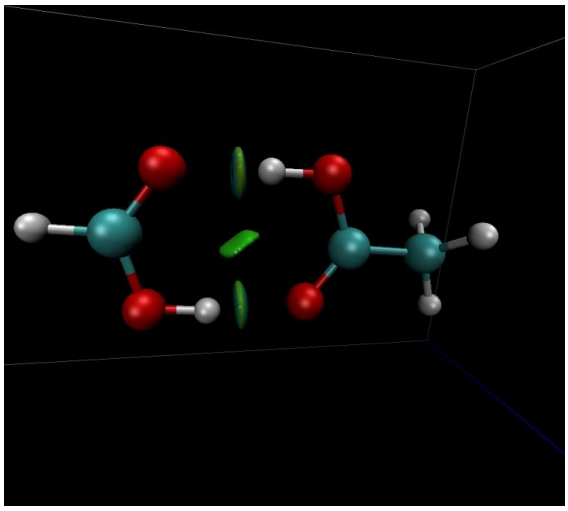
- *vmd –e file_elf_ebas.vmd*

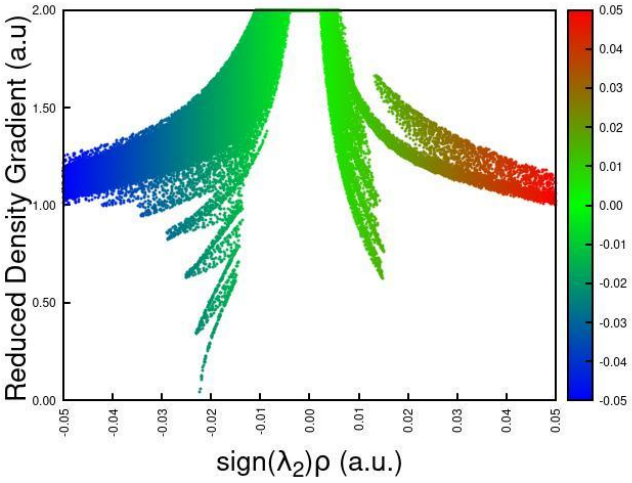
Loading all cube files might take a while, but you end up with a nice display ☺. As all cube files are read sequentially for all basins, you can delete the basins that you do not want to plot.



For NCI, a vmd (3D) and a gnnuplot are automatically produced by TopChem2

- *vmd –e file_nci.vmd*
- *gnuplot file_nci.gnu*





VII. The population Analysis section

If only cube files are used, the basin populations and distributed electrostatic moments are automatically computed. In addition to the ELF cube file, it is noted that the electron density cube file is also needed in order to obtain ELF populations & moments.

```
=====================================================================
                  POPULATION ANALYSIS SECTION
=====================================================================

 basin                vol.       pop.       q.

 1 C               255.805     4.815     1.185
 2 O               267.062     9.186    -1.186

total population      14.000

========================== Distributed Electrostatic Moments ========================
 First Moments (au).

  basin                   X.         Y.         Z.       |M1|
 1              C      -0.000     -0.000     1.641     1.641
 2              O      -0.000     -0.000     0.916     0.916

  sum                  -0.000     -0.000     2.556

 Second Moments (au).

  basin                  XX.        YY.        ZZ.        XY.        XZ.        YZ.       |M2|
 1 C                   -0.038     -0.038      0.077     -0.000      0.000      0.000      0.077
 2 O                    0.007      0.007     -0.015     -0.000      0.000      0.000      0.015

  sum                  -0.031     -0.031      0.062     -0.000      0.000      0.000
```

If a wfn file is used, analytical integrations are performed. Computed quantities depends of the *pop* optional keyword:

pop: basin volumes and populations (Default).

cov: Variance and covariance analysis. For QTAIM, it provides the localization and the **delocalization indices** (DI).

pol: integrated dipole and quadrupole topological moments.

orb: orbital contribution to basin populations.

ken: integrated positive defined kinetic energy over the basin volume.

VIII. vasp_to_cube utility

TopChem2 package includes a standalone command-line utility for generating cubes from CHGCAR and ELFCAR VASP files. The utility is termed *vasp_to_cube*. It has the following syntax:

```
> vasp_to_cube VASP_File Function ntype
```

The parameters have the following meanings:

VASP_File (string) : CHGCAR/ELFCAR
Function (string) : rho/elf
ntype (only one integer) : Number of each atom type

Example for the case of a benzene molecule in the cubic cell:

```
> vasp_to_cube CHGCAR_benzene rho 2
```

Produces cube file from CHGCAR_benzene.cube, CHGCAR contains only two different types of atoms (C and H). The considered cell in the produced cube file.