

Chemical bond analysis

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Theoretical background

The original definition of ELF was introduced by Becke and Edgecombe in 1990. It was then reformulated by Savin, in a much more intuitive manner. ELF can be understood as a measure of the effect of the Pauli repulsion. In order to account for the effect of Pauli repulsion, we take into account how much faster electrons move due to the fact that they are fermions in the Pauli kinetic energy density, $t_p(r)$:

$$t_p(r) = t(r) - t_b(r) \quad (1)$$

This is constructed from the positively defined kinetic energy density, $t(r)$, and $t_b(r)$, the bosonic kinetic energy density. This is the kinetic energy density associated with a system that has the same density but where electrons are bosons (i.e. they all occupy the same orbital):

$$t_b(r) = \frac{1}{8} \frac{|\nabla\rho(r)|^2}{\rho(r)} \quad (2)$$

In order to get rid of the electron density dependence of $t_p(r)$, the whole quantity is divided by the kinetic energy density of the homogeneous electron gas, t_w :

$$t_w = c_F \rho(r)^{5/3} \quad (3)$$

This leads to the ELF kernel,

$$\chi = \frac{t_p}{t_w} = \frac{t(r) - \frac{1}{8} \frac{|\nabla\rho(r)|^2}{\rho(r)}}{c_F \rho(r)^{5/3}} \quad (4)$$

Then it is mapped to be bounded and range in between 0 and 1, leading to the Electron Localization Function (ELF):

$$\text{ELF} = \frac{1}{1 + \chi^2} \quad (5)$$

The Pauli principle has a small influence on electrons alone or forming pairs, so their excess of kinetic energy density is small and ELF approaches unit. Instead, in the regions in between these regions, the probability of finding same spin electrons rises, and so does their kinetic energy density, leading to low ELF values.

When visualized in 3D ELF isosurfaces reveal in a very intuitive manner the type of bonding present in a system. Let's see some examples.

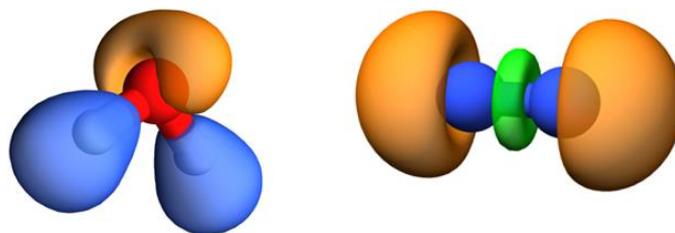


Figure 1. H₂O, N₂. Bonds with hydrogen are shown in blue, other bonds in green, and lone pairs are shown in orange. Isovalue = 0.8.

Figure 1 shows the results for the water and N_2 molecules. In both cases we can see the lone pairs in orange. In the case of the N_2 molecule we can also see the covalent bond in green. ELF is naturally conceived to identify covalent interactions. So we will analyze several CH_3X ($X=CH_3, NH_2, OH, F$) compounds (Figure 2). We can easily see in the picture how polarity is directly revealed. Homopolar covalent bonds are centrosymmetric, whereas they become smaller and more deformed towards the more electronegative atom as the bond becomes more polar. Valence basins are denoted by $V(A,B)$, where A and B are the atomic center which share the basin. Instead, $V(A)$ identifies the lone pairs. You can see in Figure 2 how the charge within ELF regions recovers the expected chemistry: close to 2 electrons for the C-C bond, which diminish as the atom becomes more electronegative.

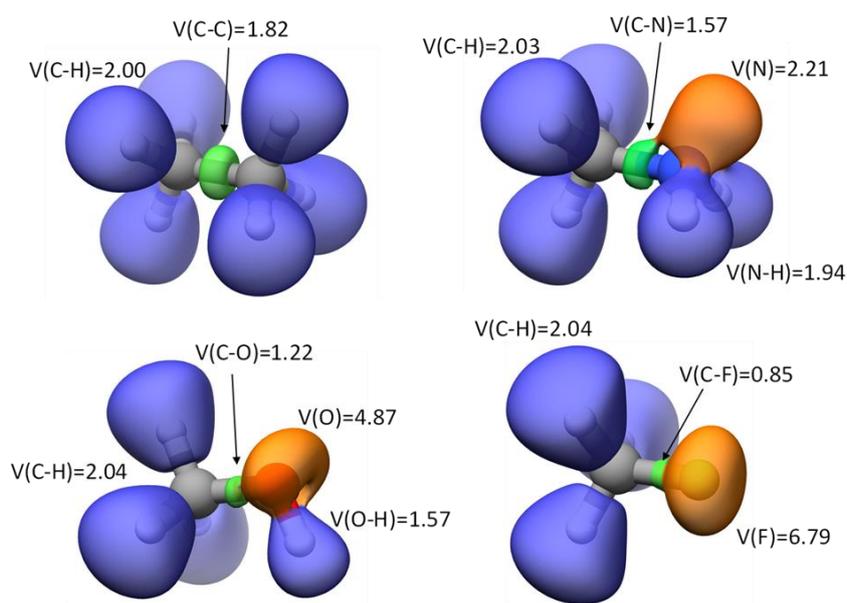


Figure 2. CH_3-X ELF basins and population. Bonds with hydrogen are shown in blue, other bonds in green, and lone pairs are shown in orange. Isovalue = 0.8.

When the basin completely migrates to one atom, so that basins are all surrounding the respective cores, we arrive to the extreme of an ionic bond. This leads to spherical basins, at least in the harder atom (e.g. Li in LiH in Figure 3). This effect is further enhanced in solid state (see periodic LiF). Ionic compounds are also easy to identify by looking at the charges.

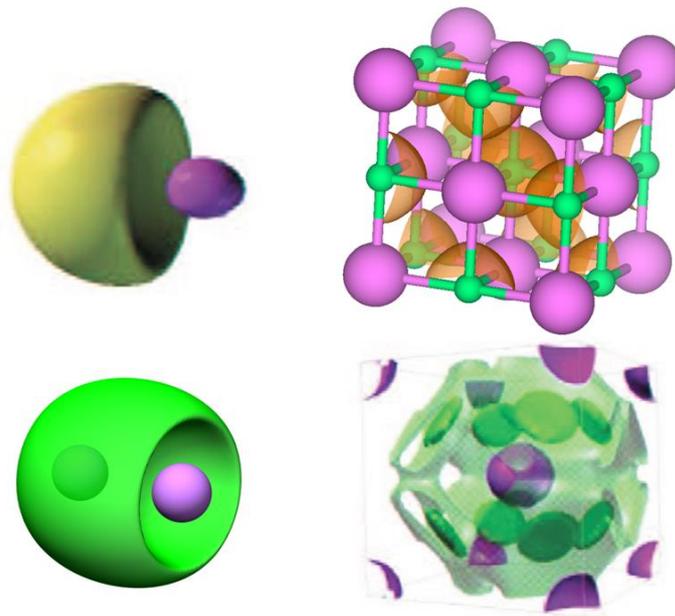


Figure 3. ELF surfaces in LiH (molecular); LiF (solid); Li₂; Li (solid).

The ELF function not only qualitatively predicts the atomic structure with a number of shells and charges that coincides with those predicted by the Aufbau principle. Figure 4 shows the results for the Cl⁻ anion with the K, L and M shells.

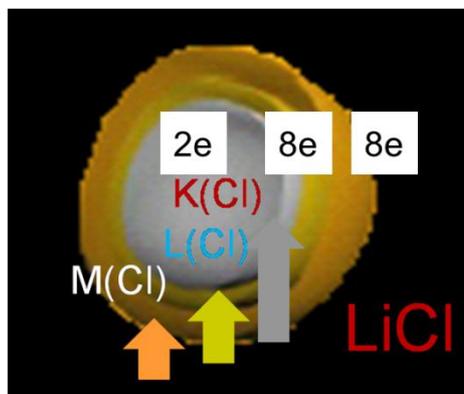


Figure 4. ELF structure and charges for Cl⁻ in LiCl.

Finally, let's see look at simple models of delocalized bonds. Figure 3 shows the Li₂ molecule. Li₂ is remarkable due to the huge volume of the V(Li-Li) basin (compare for example with the ethane!). Also, the isosurface is very flat along the bond. This provides a good idea of how to go towards the definition of metals in periodic systems. In a 3D metal, we expect a flat ELF surface crossing the solid.

Manual

I will give you several options for calculating and visualizing ELF in solids, depending on which codes you are more acquainted with. I will go through the example with VASP and VMD, but you can find tips on how to proceed with QE and vesta right after the example.

How to obtain ELF data

1. With QE

For QE, you have to ask to produce cube files for the charge and ELF. For example, you will need to run `pp.x` with the following input type for obtaining the ELF (we assume it is the same directory where you run the electronic structure calculation):

```
&INPUTPP
  prefix      = 'C'
  outdir      = './'
  plot_num    = 8
  filplot     = 'C.ELF.dat'
/

&PLOT
  iflag       = 3
  output_format = 6
  fileout     = 'C.ELF.cube'

  nx = 500
  ny = 500
  nz = 500
/
```

This is interpreted as follows:

<code>filplot</code>	file "filplot" contains the quantity selected by
<code>plot_num = 8</code>	ELF
<code>iflag=3</code>	3D plot
<code>output_format = 6</code>	format as gaussian cube file (3D)
<code>fileout</code>	name of the file to which the plot is written
<code>nx, ny, nz</code>	number of points in the parallelepiped

It suffices to change the variable `plot_num` in order to obtain cube files for other fields. Noticeably, `plot_num = 0, 19, 21` are the valence density, NCI and the total density, respectively.

2. With VASP

ELF can be calculated for solids with most packages nowadays.

Within the program: In VASP it suffices to set the option in the INCAR

```
CHGCAR=.True.  
ELFCAR=.True.
```

ELFCAR (and CHGCAR) are 3D grids that can be read directly by many visualization programs

ELF critical points

ELF populations and critical points can be analyzed for example with the CRITIC code:

https://www.lct.jussieu.fr/pagesperso/contrera/critic2_julia.tar

Quick installation guide: <https://www.lct.jussieu.fr/pagesperso/contrera/notes-4-critic.pdf>

Before creating your input

You will need the POTCAR you used in the calculation in order to retrieve the core charge in the pseudopotentials.

You can find it with the following command once the POTCAR file is open:

```
grep ZVAL POTCAR
```

ZCORE and ZPSP are the numbers you obtain. However, unlike in the POTCAR, they should be input as natural numbers!

Remember to keep the same order in the `typat` and `zcore` should respect the order in which they appear in the POTCAR.

With this information, you have all the information you need to create your input. For our diamond example this would look like (which we will name "Diamond.critin"):

```
crystal ./Diamond.density.cube  
load ./Diamond.density.cube  
zpsp C 4  
yt
```

Input explanation:

crystal	Crystal structure information is read from this file
zpsp	valence charge (see above) in the same order
load Diamond.density.cube	density data to be read from the file Diamond.density.cube. In case you are using vasp files, you load the CHGCAR
yt	Find critical points and integrate basins

You can run critic as follows:

```
> critic2g < Diamond.critin > Diamond.critout ↓
```

If you now open `Diamond.critout` you can find the electron density maxima, which are at the atoms:

#	Id	cp	ncp	Name	Z	mult	Volume	Pop	Lap
1	1	1	1	C_	6	--	3.94220678E+01	4.06810382E+00	1.55745279E-04
2	2	1	1	C_	6	--	3.87861006E+01	3.99998518E+00	-2.66899515E-06
3	3	1	1	C_	6	--	3.87861006E+01	3.99998518E+00	-2.66899515E-06
4	4	1	1	C_	6	--	3.87861003E+01	3.99998518E+00	-2.66010002E-06
5	5	1	1	C_	6	--	3.81490555E+01	3.93175568E+00	-1.47155141E-04
6	6	1	1	C_	6	--	3.87860693E+01	3.99998191E+00	-1.94384189E-07
7	7	1	1	C_	6	--	3.87860693E+01	3.99998191E+00	-1.94384188E-07
8	8	1	1	C_	6	--	3.87860696E+01	3.99998191E+00	-2.03279329E-07

You see all atoms hold ca. 4 valence electrons (column `Pop`) and have a volume of 38 a.u.

If we want to see the bonds, we have to look at the topology of ELF with an input like this:

```
crystal ./Diamond.den.cube
load ./Diamond.den.cube id rho
load ./Diamond.ELF.cube id elf
zpsp C 4
reference elf
integrable rho
yt nnm
cpreport Diamondcps.xyz cell
```

Since now we are using the ELF field to partition space and we integrate the density, we have added the keywords:

```
reference elf
integrable rho
```

We will now have maxima out of the nuclei, so we add the keyword `nnm` (non-nuclear maxima) to the integration line:

```
yt nnm
```

Indeed, the cell shows maxima at the carbon cores and at the C-C bonds:

#	Id	cp	ncp	Name	Z	mult	Volume	Pop	Lap	\$rho
1	1	1	1	C_	6	--	0.00000000E+00	0.00000000E+00	0.00000000E+00	0.00000000E+00
2	2	1	1	C_	6	--	0.00000000E+00	0.00000000E+00	0.00000000E+00	0.00000000E+00
3	3	1	1	C_	6	--	0.00000000E+00	0.00000000E+00	0.00000000E+00	0.00000000E+00
4	4	1	1	C_	6	--	0.00000000E+00	0.00000000E+00	0.00000000E+00	0.00000000E+00
5	5	1	1	C_	6	--	0.00000000E+00	0.00000000E+00	0.00000000E+00	0.00000000E+00
6	6	1	1	C_	6	--	0.00000000E+00	0.00000000E+00	0.00000000E+00	0.00000000E+00
7	7	1	1	C_	6	--	0.00000000E+00	0.00000000E+00	0.00000000E+00	0.00000000E+00
8	8	1	1	C_	6	--	0.00000000E+00	0.00000000E+00	0.00000000E+00	0.00000000E+00
9	--	--	--	??	--	--	1.93929563E+01	8.67913250E+00	6.09898962E-06	1.99998184E+00
10	--	--	--	??	--	--	1.93929563E+01	8.67913250E+00	6.09898961E-06	1.99998184E+00
11	--	--	--	??	--	--	1.93929659E+01	8.67914141E+00	5.92496041E-06	1.99998533E+00
12	--	--	--	??	--	--	1.93929976E+01	8.67915843E+00	-7.28836495E-06	1.99998825E+00
13	--	--	--	??	--	--	1.93929659E+01	8.67914141E+00	5.92496042E-06	1.99998533E+00

14	--	--	??	--	--	1.93929563E+01	8.67913250E+00	6.09898962E-06	1.99998184E+00
15	--	--	??	--	--	1.93929976E+01	8.67915843E+00	-7.28836495E-06	1.99998825E+00
16	--	--	??	--	--	1.93929563E+01	8.67913250E+00	6.09898961E-06	1.99998184E+00
17	--	--	??	--	--	1.93929659E+01	8.67914141E+00	5.92496042E-06	1.99998533E+00
18	--	--	??	--	--	1.93929563E+01	8.67913250E+00	6.09898961E-06	1.99998184E+00
19	--	--	??	--	--	1.93929976E+01	8.67915843E+00	-7.28836497E-06	1.99998825E+00
20	--	--	??	--	--	1.93929976E+01	8.67915843E+00	-7.28836496E-06	1.99998825E+00
21	--	--	??	--	--	1.93929976E+01	8.67915843E+00	-7.28836496E-06	1.99998825E+00
22	--	--	??	--	--	1.93930121E+01	8.67915827E+00	-1.06386292E-05	1.99998425E+00
23	--	--	??	--	--	1.93929563E+01	8.67913250E+00	6.09898961E-06	1.99998184E+00
24	--	--	??	--	--	1.93929976E+01	8.67915843E+00	-7.28836496E-06	1.99998825E+00

Maxima 1-9 are the carbon atoms, and 10-21 are the bonds. Carbon atoms are bare cores, all electrons are now in the bonds, which hold ca 1.9999 electrons each (column ρ).

Finally, we will probably want to know where the non-nuclear maxima (in this case bonds) are, so we print the list of critical points as an xyz file that we can open with visualization software:

```
cpreport Diamondcps.xyz cell
```

We will visualize their position in the next section.

In the case of molecular crystals, very low densities appear throughout the crystal, so you might need to discard spurious maxima. This can be done adding a cutoff on the ELF value:

```
yt nnm discard "$elf < 0.2"
```

Also, you might want to print all the critical points within a molecule, even if outside the unit cell, it suffices to make a run with the keyword `molmotif`:

```
crystal urea.scf.in
```

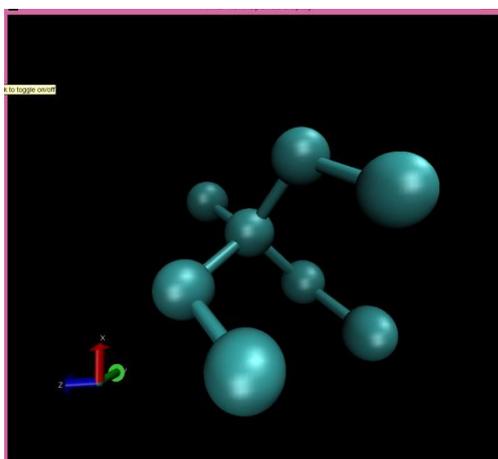
```
write ureamolecs.xyz molmotif
```

Visualization

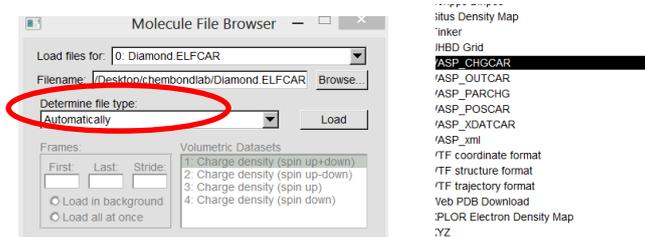
1. With VMD

Let's see the example of `Diamond.ELFCAR`.

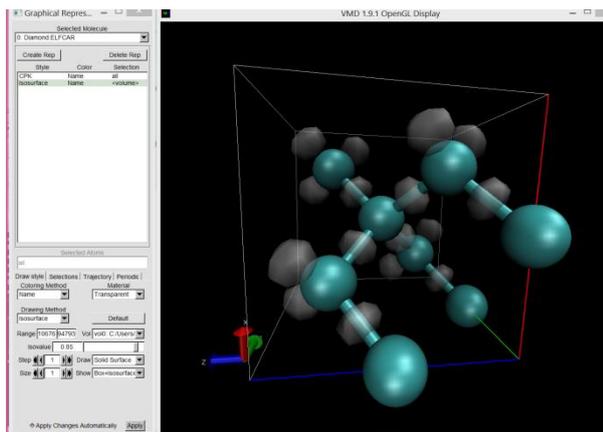
1. First you will have to load the xyz coordinates of the atoms, `Diamond.xyz`. Choose CPK to visualize them.



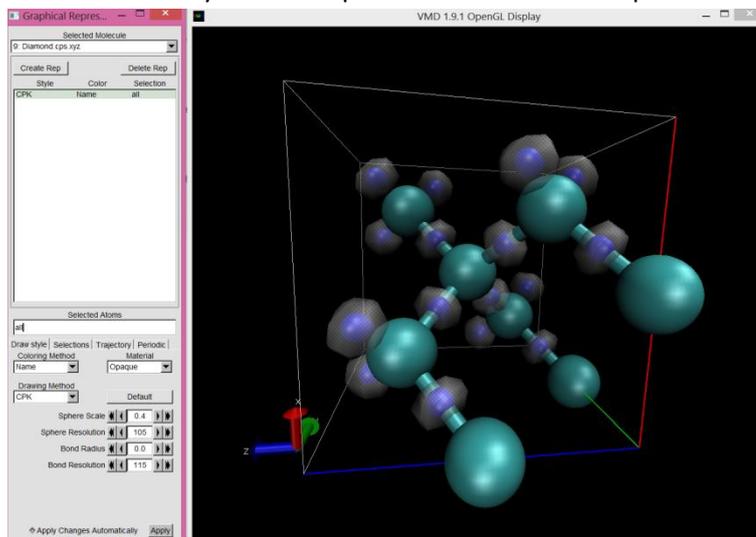
- Now we can load the ELF surface. The file type is not automatically detected, so you will have to choose the type of file as “vasp CHGCAR”.



Choose “Transparent surface” and Isovalue:0.85:



- You can also visualize the position of the ELF maxima (bonds, lone pairs, etc) from the previous section (remember we asked for the list as `Diamondcps.xyz`). It suffices to load the file as xyz. You can plot them with smaller spheres:



You can see that the maxima are at the center of the bond isosurfaces. Now you can also check the charges on the C cores and the C-C bonds.

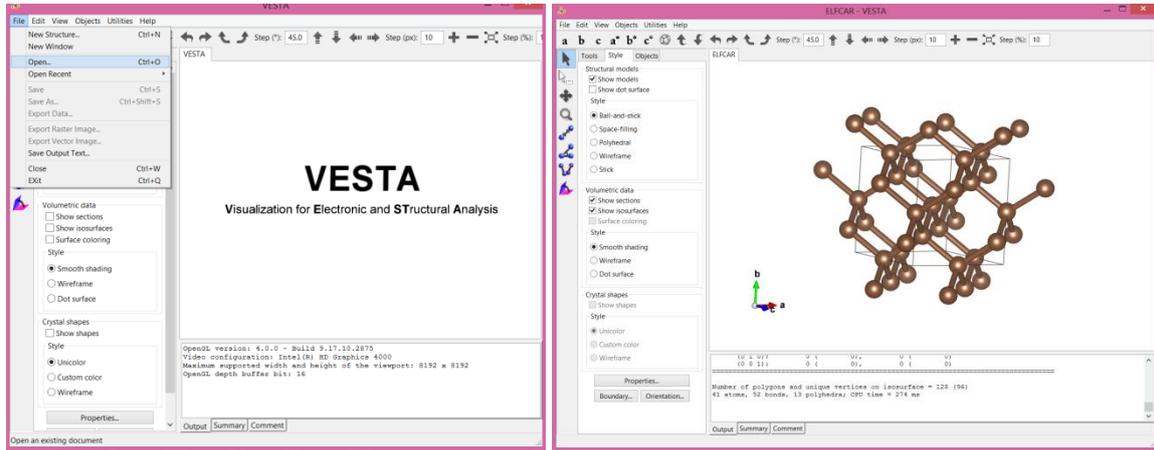
2. With VESTA

You can download VESTA at:

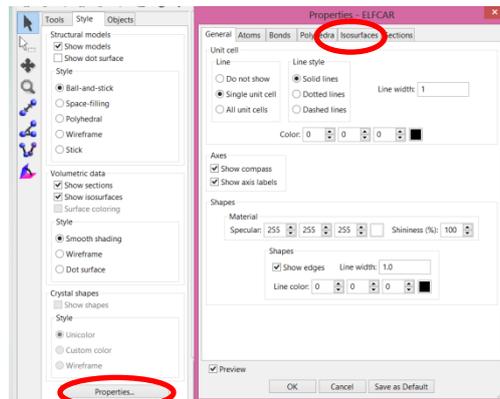
<http://jp-minerals.org/vesta/en/download.html>

IMPORTANT: If you use VESTA, remember to change the name of the file to ELFCAR. Only this name is recognized by VESTA!!!!

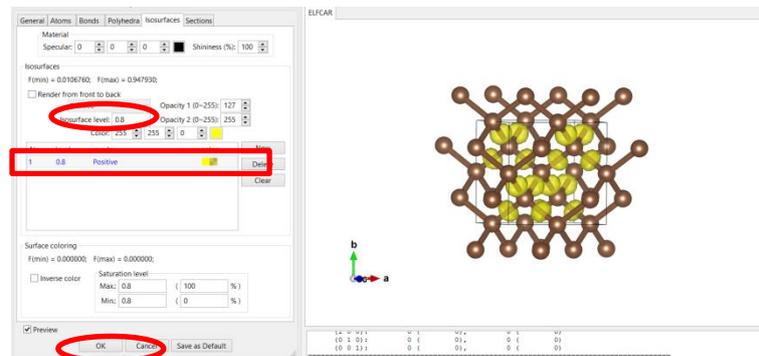
First of all you open the ELFCAR file:



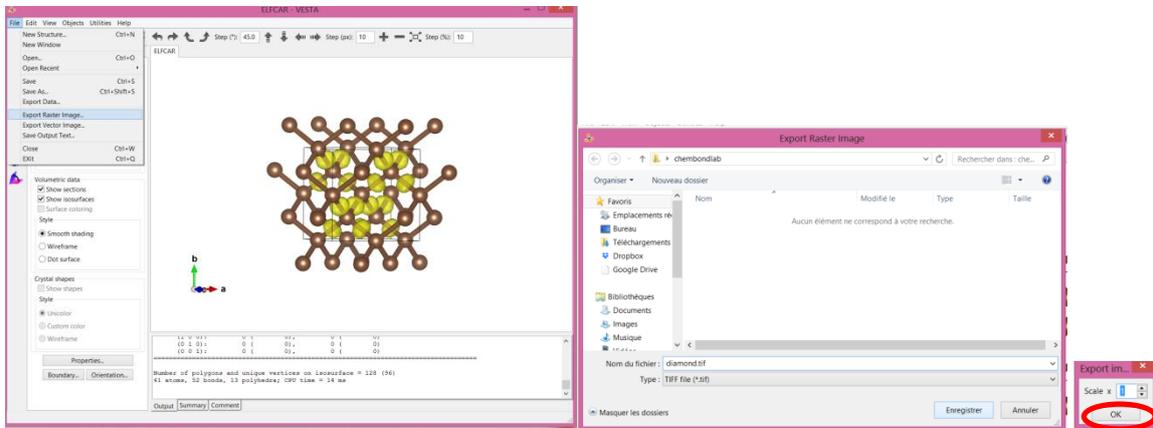
Once the ELFCAR loaded, you go to Properties > Isosurfaces:



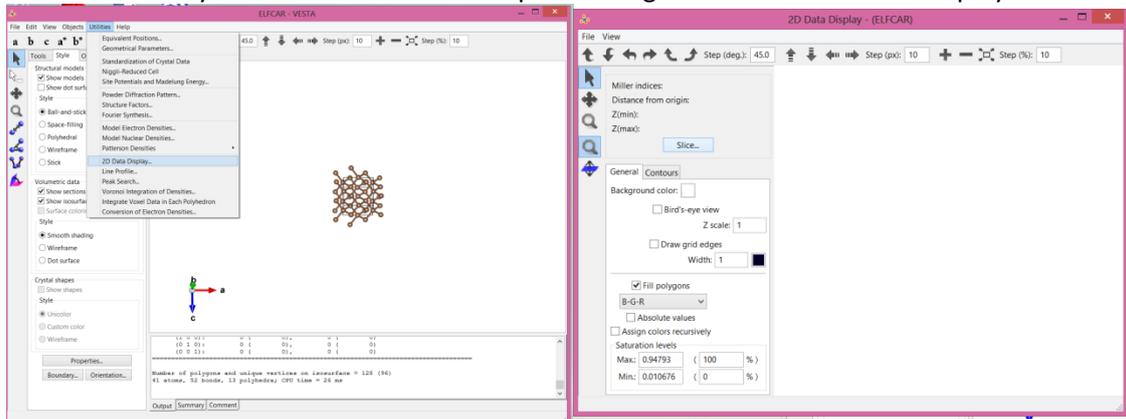
Click on the isosurface No1 line (it will become blue) and introduce the isovalue at "Isosurface level" (or at "level"), then click on OK



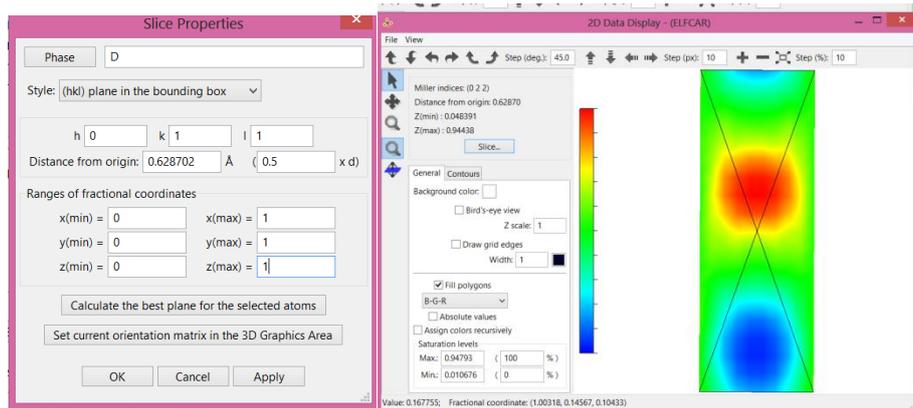
To save your picture go to File > Export Raste Image (or Export Vector Image), you introduce the name of the file, you say OK to Scale x=1:



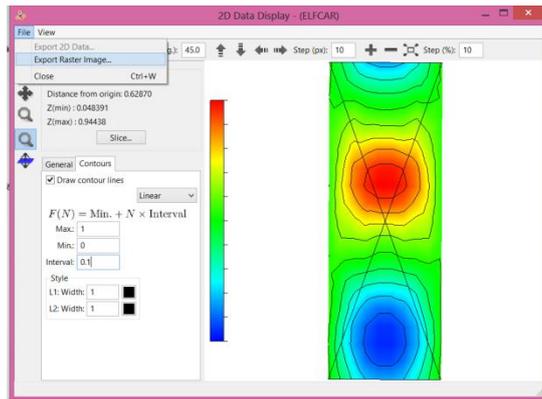
With VESTA it is easy to make also 2D contour plots. You go to Utilities>2D Data Display>Slice



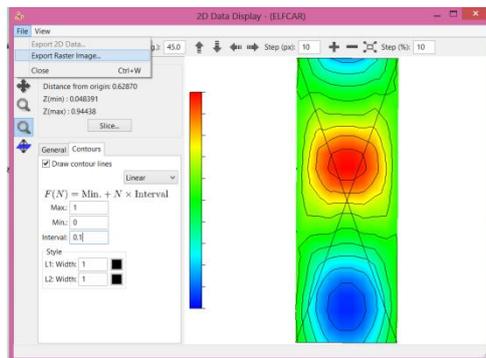
You choose your slice and press OK:



You can also add Contour lines:



To save the image, you go to File>Export Raster Image:



Exercises

You can download all files from

<https://www.lct.jussieu.fr/pagesperso/contrera/zcam2020/zcam2020.tar.gz>

The questions below will help you interpret your results.

Exercise 1. Identifying bonding patterns

- a) Calculate the structures (diamond, Al and NaCl) with the following crystalline structures. Do not forget to create the ELFCAR (VASP) or cube (QE) files.

Note you can recover diamond and Al from Practical session 1. Nonetheless, I recommend using conventional (ibrav=1) instead of the face centered cells in Al and Diamond for a better visualization. For this you will have to introduce all the atomic positions in the conventional unit cell. You can easily obtain them from the Bilbao Crystallographic Server (https://www.cryst.ehu.es/cryst/get_wp.html). In this case, they are provided in the table:

System	NaCl	Al	Diamond
SG	Fm-3m (#225)	Fm-3m (#225)	Fd-3m (#227)
Cell param (a.u.)	a=11.08	a=7.64	a=6.77
All atomic positions	Na 0.0 0.0 0.0 Na 0.0 0.5 0.5 Na 0.5 0.0 0.5 Na 0.5 0.5 0.0 Cl 0.5 0.5 0.5 Cl 0.5 0.0 0.0 Cl 0.0 0.5 0.0 Cl 0.0 0.0 0.5	Al 0.0 0.0 0.0 Al 0.0 0.5 0.5 Al 0.5 0.0 0.5 Al 0.5 0.5 0.0	C 0.125 0.125 0.125 C 0.125 0.625 0.625 C 0.625 0.125 0.625 C 0.625 0.625 0.125 C 0.875 0.875 0.875 C 0.875 0.375 0.375 C 0.375 0.875 0.375 C 0.375 0.375 0.875

- b) Look at Diamond isosurface ELF=0.8. Where do you obtain the basins? What are their chemical meaning? How many electrons do you expect in each basin?
- c) Look at NaCl isosurface ELF=0.7. Where do you obtain the basins? What is their chemical meaning? How many electrons do you expect in each basin?
- d) Look at Al. What does ELF=0.5 mean? Play with the ELF value around ELF=0.5 (0.5,0.55,0.6). Where do you obtain ELF basins? What happens at ELF=0.6? What does this mean (i.e. profile is steep or flat)? How are these electrons? What model does it remind you of?

- e) For the three structures, justify which chemical bond is present in diamond, Al and NaCl from their ELF picture.

Exercise 2. Quantification

- a) Integrate the density basins in NaCl. What charges do you obtain? Explain
b) Integrate the ELF basins in Diamond. What charges do you obtain? Explain. What would you have obtained if you had integrated the density basins?

Exercise 3. Molecular crystals

- a) Calculate the orthorhombic urea crystal [data are in file `urea.gen` for you to copy-paste]:

```
a= 10.516311 a.u.  
c= 8.851464 a.u.  
C 1.00000000 0.50000071 0.32600054  
C 0.50000071 0.00000143 0.67400105  
O 1.00000000 0.50000071 0.59530085  
O 0.50000071 0.00000143 0.40470074  
N 0.14590021 0.64590092 0.17660028  
N 0.64590092 0.85410121 0.82340130  
N 0.35410050 0.14590164 0.82340130  
N 0.85409979 0.35410050 0.17660028  
H 0.25750037 0.75750109 0.28270047  
H 0.75750109 0.74250105 0.71730112  
H 0.24250034 0.25750180 0.71730112  
H 0.74249963 0.24250034 0.28270047  
H 0.14410025 0.64410096 0.96200143  
H 0.64410096 0.85590118 0.03800015  
H 0.35590047 0.14410167 0.03800015  
H 0.85589975 0.35590047 0.96200143
```

- b) Obtain the atoms that complete the molecules in the cell (keyword MOLMOTIF)
c) Calculate the ELF critical points and obtain the list (keyword CPREPORT). Visualize them. Are they where you expected?
d) Integrate them. Do you obtain the correct total number of valence electrons? Are the oxygen lone pairs where you expected? How would you explain the unusual distribution of nitrogen lone pairs (think about nearby molecules!)
e) Plot NCI (`plot_num=19` in QE). How many hydrogen bonds do you obtain for each N? (don't forget periodicity!)