Chemical bond analysis 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 is 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?

c) Now let's try to analyze new materials. Obtain the files for potassium and look at it. Integrate the basins. Compare what you obtain with Na and Diamond. Which one does it look more alike? This is a high-pressure structure called an electride. They are insulating metals. Try to explain this property from the localization of electrons you have observed.

SG	Cell param	All positions
$P6_3mmc$ (#194)	a=7.9608 a.u. c=10.882 a.u.	K 0.0 0.0 0.0 K 0.0 0.0 0.5 K 1/3 0.25 2/3 K 2/3 1/3 0.75

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!)