Chemical bond analysis Exercises QM+topology

https://www.lct.jussieu.fr/pagesperso/contrera/nci-exercises.html#erice2025

Exercise 1. Identifying bonding patterns with ELF

a) Characterization of bond types. Calculate the structures (diamond, Al and NaCl) with the following crystalline structures with QE/vasp. If you use QE, do not forget to copy the *.save repertories and calculate the ELF cube files. If you use vasp you will need the ELFCAR files.

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

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

b) Analysis of a new materials. Calculate the ELF cube file for the potassium cell below. Compare what you previously obtained 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 2. Quantification

a) Atomic charges. Integrate the density basins in NaCl. You will need the CHGCAR file. What charges do you obtain? Is it what you expected? (remember you are using pseudopotentials)

b) Bond charges. Integrate the ELF basins in Diamond. Note that in this case you will need both the density and the ELF cube files (or CHGCAR+ELFCAR)! 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) and visualize them.

c) Plot NCI (`plot_num`=19 in QE). How many hydrogen bonds do you obtain for each N? (don't forget periodicity!)

d) Challenge: Calculate ELF. Where are the lone pairs in urea and how does their position relate to the hydrogen bonds?