NCI Exercises

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Instructions

In these exercises we will analyze non-covalent interactions in real molecules, following the models done in Jupiter.

You need to connect to deuterium (example with tp3):

1. Connect to tccm_tp3@liliput.lct.jussieu.fr
2. Type d3 (=ssh deuterium)
3. Create a repertory with your name and work only within it

Exercise 1. Looking at the hydrogen molecule

This exercise is a connection with the model system in the previous exercise. We will now study H_2 molecule at several distances.

1. Calculate NCI at d=2.0 and 2.5Å. You can download the wfn files at https://www.lct.jussieu.fr/pagesperso/contrera/label2022/H2-wfn.zip

Example

```
1
file.wfn/xyz
```

Once the input constructed, the code is invoked as follows:

nciplot.x < inputfile [> outputfile]

The main results are collected in four output files:

– name.dat file collects rho vs. RDG

– name-grad.cube file with RDG

– name-dens.cube file with sign(λ2) × ρ × 100

– name.vmd is a script for visualization of the results in VMD

2. The s(ρ) files are obtained from plotting name.dat.
   The resulting plots are available at
   https://www.lct.jussieu.fr/pagesperso/contrera/label2022/H2-datfiles.zip
   How do the peaks change from d=2.0 to 2.5?

3. The .cube files allow visualization of isosurfaces. You can view instructions on how to do it at https://www.lct.jussieu.fr/pagesperso/contrera/nci/vmd-instructions.webm
   You can download the cube files at
   https://www.lct.jussieu.fr/pagesperso/contrera/label2022/H2-cubefiles.zip
   Visualize the isosurface s=0.3 and a range in between -3 to 3. What kind of interaction do you see for each distance?

4. As we have seen in the H2 model, we can also use NCI to visualize covalent interactions. It suffices to look at higher densities. You can do that by adding the CUTPLOT keyword in NCIPLOT:[1]

```
1
File.wfn
CUTPLOT 2.0 0.3
```

   The difference from non-covalent to covalent is easy to visualize in the shape. What changes in s(ρ) and in the isosurface do you observe?

5. Summarize the results in the following table:

	Color	**Shape**	**Density at s=0**	**Interaction type (non-covalent/covalent)**
d=0.7 Å				
d=2.0 Å				
d=2.5 Å				

[1] The value 2.0 corresponds to the density up to which interactions will be analyzed, i.e. ρ=0-2.0 au will be plotted. The value 0.3 corresponds to the isosurface that will be analyzed if the vmd file is used.

6. Instead of using wavefunction files, you can use `xyz` files with promolecular densities. This is easily done for example for 2.0 Å as:[2]

```
2

H 0.0 0.0 0.0
H 0.0 0.0 2.0
```

Do the same for d=0.7 and d=2.5 Å. Evaluate the agreement between the promolecular approximation and the real wavefunction. Do they agree better at long or short distances? Why?

What is the difference between the functions used to describe the atoms with the promolecular approximation and the approach used with Python?

Exercise 2. Analysis of different non-covalent interaction types

Download the methane files at:

https://www.lct.jussieu.fr/pagesperso/contrera/label2022/Methanedimers-wfn.zip

This exercise will enable you to see the difference between localized and delocalized interactions. Whereas localized interactions are mainly between two atoms (like the ones we saw for H_2), delocalized one are between several atoms (so the surface spreads out).

1. Visualize Methane dimer, CH_4-H_2O, CH_4-HF and CH_4-NH_3. Which interaction is local (mainly between two atoms) or delocalized? You can download the cube files at: https://www.lct.jussieu.fr/pagesperso/contrera/label2022/Methanedimers-cubes.zip
   Fill the data in the following table:

Dimer	**NCI shape**	**Interaction type (localized/delocalized)**
CH_4- CH_4		
CH_4-H_2O		
CH_4-HF		
CH_4-NH_3		

[2] The "2" corresponds to the number of atoms, then there is a blank line and finally, the list of xyz atom positions

Exercise 3. Towards bigger systems and NCI size dependency

Download the xyz files for benzene, naphthalene and anthracene at:

https://www.lct.jussieu.fr/pagesperso/contrera/label2022/benzeneunits-xyz.zip

These systems have one, two and three fused rings.

1. Calculate NCI. Since in this case we are using rather big systems, we will choose promolecular densities, faster to calculate. We will further accelerate the calculation with an adaptative grid:

```
2
BD_P_1.xyz
BD_P_2.xyz
INTERMOLECULAR
CG2FG 3 4 2 1
```

   where `BD_P_1` is the first monomer (`1`) in the parallel (`P`) benzene dimer (`BD`).

2. You can download the cube files at
   https://www.lct.jussieu.fr/pagesperso/contrera/benzeneunits-cubes.zip
   Visualize the non-covalent interactions in the parallel conformation (`P`) and the T-shape conformation (`T`) for benzene and classify them as delocalized or localized.

3. Visualize now naphthalene and anthracene `P` and `T` conformations. Do parallel and T-shape surfaces size increase at the same pace?

4. You can quantify the different sizes with NCIPLOT-4.0. Use the following input type to obtain the charge involved in the NCI surface:

   INPUT EXAMPLE:

```
2
BenzeneA.xyz
BenzeneB.xyz
INTERMOLECULAR
RANGE 3
-0.07 -0.01
-0.01 0.01
0.01 0.07
```

OUTPUT EXAMPLE:

```
---------------------------------------------------------------------

                INTEGRATION DATA

---------------------------------------------------------------------

 Integration  over the volumes of rho^n

---------------------------------------------------------------------

 n=1.0         :       0.70727487
```

According to this output, the volume of the NCI region in benzene dimer is 0.70727487 au.

Collect the NCI charge for the parallel and T-shape series with respect to the number of units (from 1 unit in benzene to 3 in anthracene).

Benzene units	**Parallel conformation volume integral**	**T-shape conformation volume integral**
1		
2		
3		

Plot the charge vs. the number of units for P and T series. What interaction becomes favored with size? Check the fit to a straight line of the local interaction, what does this mean?