Instructions Workshop Part 3 – Analysis of the X-ray Wavefunction Refinement

In this part you will obtain derived properties such as Bader topology, bond indices and two dimensional maps. These are only examples, since there are numerous other possibilities of analyzing the constrained wavefunction chemically.

1) **Set up folders.** Create a new folder (called, epoxide_analysis) and copy the stdin, the cif and hkl as well as the three final wavefunction files (molecular orbitals, density matrix and orbital energies) from the epoxide_XCW folder into it. Additionally, copy all files from the tonto_for_Windows folder.

2) **Write input.** Upon opening the stdin file, change the basis_directory to the path on your system (copy-paste it from the previous stdin file). Then, you can delete everything below the crystal block (except for the final curly bracket). Replace it with the following, save and close. Then run Tonto, as before.

```
read_archive molecular_orbitals restricted
read_archive orbital_energies restricted
read_archive density_matrix restricted

assign_NOs_to_MOs

write_aim2000_wfn_file

robydata= {
  kind= atom_bond_analysis
  atom_list= { 1 ... 7 }
  analyze_all_atom_pairs= TRUE
}
roby_analysis


plot_grid= {
kind= laplacian
center_atoms= { 1 2 }
x_axis_atoms= 2 3
y_axis_atoms= 2 1
use_bcube
cube_scale_factor= 0.50
n_points= 401
z_width= 0
plot_format= gnuplot.contour
contour_scale= log
contour_min_value=  -1.00
contour_increment=   0.50
contour_max_value=   3.00
contour_tic_dps=     1
contour_font_size=   9
contour_min_color=   red
contour_mid_color=   white
contour_max_color=   blue
contour_fade_factor= 0.6
}
plot


plot_grid= {
kind= electron_density
contour_scale= positive-log
```

```
contour_min_value=  -2.00
contour_increment=   0.25
contour_max_value=   0.50
contour_tic_dps=     2
contour_font_size=   12
contour_min_color=   white
! contour_max_color=   blueviolet
contour_max_color=   112 0 171
contour_fade_factor= 0.4
}
plot

plot_grid= {
kind= deformation_density
contour_scale= linear
contour_min_value=  -0.10
contour_increment=   0.01
contour_max_value=   0.10
contour_tic_dps=     2
contour_font_size=   12
contour_min_color=   purple
contour_mid_color=   white
contour_max_color=   60 160 208
contour_fade_factor= 0.5
}
plot

plot_grid= {
kind= g_kinetic_energy
contour_scale= positive-log
contour_min_value=   -2.00
contour_increment=    0.50
contour_max_value=    3.00
contour_tic_dps=     1
contour_font_size=   12
contour_min_color=   white
contour_max_color=   0 100 250
contour_fade_factor= 0.6
}
plot
```

Which new files have been written by tonto?

The file without extension is the wfn file. → Change its name by adding the extension ".wfn".

The Roby bond analysis is in the stdout file.

The files ending on "commands" are instruction files for the program gnuplot, whereas the "contour_data" and "bond_data" files are grid files to be plotted with gnuplot. Properties are the Laplacian, the electron density, the deformation density and the kinetic energy density.

3) **Analysis of the wfn file according to Bader's QTAIM**
   a. Extract the AIM2000Demo.zipfile. Do not double click it.
   b. Go into the Disk1 folder. Double-click on the Setup.exe and accept all defaults.
   c. Open the AIM2000 program. Read in the wfn file from the folder epoxide_analysis using the red wfn button (do not use File→open). A popup window with some atoms should appear. Bonds are not drawn – yet.
   d. We will only do a quick QTAIM analysis here to get the bond paths and critical points. Click on "Calculate Critical Points" (or from the menu Calculation→critical points). Then search for nuclear attractors (press the button), bond critical points (press the button) and finally ring critical points (press the button). Then click "OK, Done". When you close the window after successful generation of these points they should appear in the popup window as red- and yellow-coloured points.
   e. Open the "Record of critical points".
      Scroll down to the first (3,-1) bond critical point. Which bond does it represent if you consider the distance of the bcp to the atoms, and what is its electron-density value in atomic units?

   f. Click on "Calculate Molecular Graph" and then calculate paths uphill from (3,-1) critical points. Click OK to close the window. Bond paths should appear in the popup window.
      Describe the shape of the C-O bonds in the epoxide molecule. Is this what you expect?

   g. Close down AIM2000.

4) **Bond-index analysis according to Roby**
   a. Open the stdout file with a text editor and search for the block "Roby bond indices and populations".
      What are the C-O, C-C and C-H bond indices (=bond orders) and what are their percentage covalencies?

      What is the order of the bond types according to their covalent character?

      Close the stdout file.

5) Creating 2-dimensional maps of the epoxide ring with gnuplot
   a. Install gnuplot by double-clicking on gp466-win32-setup.exe. During installation, set the terminal type to "Windows".
   b. Install the program in a folder called, "gnuplot". Then copy all "commands", "contour_data" and "bond_data" files into the folder "bin" located within your gnuplot folder.
   c. Shorten the names of the "commands" files. A sensible name would be "ED.commands", "Laplace.commands", etc.

d. Run the program gnuplot.exe by double-clicking on it. A console-type popup window will appear.
e. Load each of the commands files consecutively by writing, e.g., *load 'ED.commands'* in the terminal window. Graphical windows with the plots will appear, and they are also saved as pdf files in the "bin" folder.
f. Type "exit" in the gnuplot window to close it.
g. Compare the maps and interpret them with respect to the strained character of the bonds in the epoxide ring.