Instructions Workshop Part 2 – X-ray constrained wavefunction fitting

In this part, for the epoxide, you will refine the wavefunction, i.e. the Hartree-Fock molecular orbitals, so that they fit the X-ray diffraction data. This is done by successively increasing the weight factor "lambda" for the least squares error. The positions and the ADPs are fixed at the values you obtained in Part 1.

1) **Look at the input files.** Open the input file "stdin" that Olex2 wrote for the Hirshfeld atom refinement in the epoxide_HAR folder with a text editor. Identify the different blocks "cif", "crystal", and "scfdata" (2x). These blocks specify the input needed for the calculations. The keywords "scf" and "refine_hirshfeld_atoms" are the commands that instruct the quantum chemical calculation and the least-squares refinement.
2) **Set up XCW folders.** Now we need to modify this input to perform an X-ray constrained wavefunction fitting. Create a new folder (e.g. "epoxide_XCW") and copy the stdin from the "epoxide_HAR" folder into the new folder. Additionally copy the files "tonto.epoxide.hkl" and "tonto.epoxide_epoxide.molecule.cif" over, and all files in the "tonto_for_Windows" folder.
3) **Modify the stdin input file.** Open the stdin file with a text editor and try to think about what needs to be modified.
   a. We want to read in the new cif file that contains the experimental geometry after HAR. In the new cif file, the name of the data block (keyword data_'name') has changed which needs to be updated in the stdin file (keyword data_block_name= 'name').
   b. We also want to change the basis set to 3-21G to make the calculation run faster (check that the path to the basis_directory is still valid). And we need to change the scf procedure. Use the following procedure after the becke_grid block (copy-paste the following text, instead of the procedure for the HAR). Keep the final curly bracket.

```
scfdata= {
   kind = rhf
   initial_density= promolecule
   convergence= 0.001
   diis= { convergence_tolerance= 0.01 }
  }
  scf

 scfdata= {
    initial_density=   restricted
    kind=           xray_rhf
    convergence= 0.001
    use_SC_cluster_charges= TRUE
    cluster_radius= 8 angstrom
    diis= {
      save_iteration=  2
      start_iteration= 4
      keep=          8
   }

    max_iterations=  200       ! The maximum number of SCF interation
    use_damping=     YES       ! These are used to damp the SCF interation process
    damp_factor=     0.50      ! by including 20% of the previous result
    damp_finish=     3
    use_level_shift= YES
```

```
    initial_lambda=  0.00     ! These specify the "lambda value"
    lambda_step=     0.05     ! used to mix the energy with the chi^2
    lambda_max=      0.05
  }
  scf
}
```

The constrained wavefunction fitting is controlled via the Lagrangian multiplier λ, which can be increased stepwise.
How many lambda-steps do we use in this example?

4) **Run Tonto.** Save the stdin, close the editor, and run Tonto in the same folder by double-clicking on it.
   a. A black terminal screen will appear when Tonto is running. If there is no warning in the black terminal, then you probably have not set the data_block_name= correctly. See 3a above.
   b. If you want to check the progress of the calculation, you have to make a copy of the stdout file every time you want to check and open it with a text editor.
   c. When the calculation is finished, the terminal window should disappear. It will take more than 30 mins. This is too long for this workshop. Therefore, we give the results in folder "epoxide_XCW_results". Move to the "epoxide_XCW_results" folder now.
   d. Be careful if you use the stdin you copy from us for the next step because the path to the basis set directory will not correspond to the location on your computer.

Which new files are written by Tonto?

You now have an X-ray constrained wavefunction based on a HAR geometry, both obtained by embedding into a field of point charges and dipoles. The full procedure is called X-ray wavefunction refinement (XWR) and the result (refined geometry plus constrained wavefunction) can be understood as an alternative to a multipole modeling. The constrained wavefunction can now be chemically analyzed, i.e. that the analysis is not restricted to an electron density analysis. All kinds of properties can be deduced with Tonto or with external programs which can read a wavefunction. See part 3.

References:

HAR:
a. D. Jayatilaka, B. Dittrich, Acta Cryst. A 2008, 64, 383.
b. S. C. Capelli, H.-B- Bürgi, B. Dittrich, S. Grabowsky, D. Jayatilaka, IUCrJ 2014, 1, 361.

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a. D. Jayatilaka, Phys. Rev. Lett. 1998, 80, 798.
b. D. Grimwood, D. Jayatilaka, Acta Cryst. A 2001, 57, 87.

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a. S. Grabowsky, P. Luger, J. Buschmann, T. Schneider, T. Schirmeister, A. N. Sobolev, D. Jayatilaka, Angew. Chem. Int. Ed. 2012, 51, 6776.