Part 1 – HAR through Olex2

Ammonia:
8f) What is the R1 value that you observe? Answer: 1.30%.
8g) Where does the Q peak of highest residual electron density appear (the one that disappears last when you turn the mouse wheel), and what does it mean? Answer: It is above the nitrogen atom. It is the lone pair on nitrogen.
8h) What is the N-H bond distance? Answer: 0.822 Å.
8i) What happens if you try to refine the hydrogen displacements anisotropically, too? Answer: They are elongated along the bond axis, which is physically not meaningful.
What is the N-H bond length now? Did it change significantly towards the neutron result? Answer: 0.799 Å. The bond has become even shorter.
What happens to the R-value? Answer: It becomes smaller (1.18%), which obviously doesn't present a physically more meaningful result. Conclusion: a lower R1 value is not always better.

9f) How do the anisotropic hydrogen atoms look like? Answer: Now they look physically reasonable because they are perpendicular to the bond axis.
9g) What is the N-H bond distance now? And how big is the improvement relative to the neutron result? Answer: 0.990 Å. This is basically identical to the neutron result.
9h) What is the R-value? Answer: 0.99%, reflecting a true improvement this time.

Epoxide:
Answers corresponding to 8)
f: R-value: 3.50%
g: The highest Q peak is in the C-C bond, shifted a bit outside the bond axis which represents the banana-bond character.
h: C-H bond distances are 0.955, 0.965, 0.982, 0.990 Å.
i: They are very oblique, C-H 0.960, 0.971, 0.982, 0.996, R-value 3.46 %.

Answers corresponding to 9)
f: reasonable
g: 1.071, 1.091, 1.101, 1.103, elongation observed as expected.
h: 5.88%.

Part 2 – X-ray constrained wavefunction fitting

3b) How many lambda-steps do we use in this example? Answer: There are two steps, one for lambda= 0.0 and then lambda = 0.05.

4d) Which new files are written by tonto? Answer: Except for the output files "stdout", "stderr" and "stdout.fit_analysis", there are files containing the density matrix, the molecular orbitals, and the orbital energies for each lambda step and for the finalized calculation (which is identical with the maximum lambda).

Part 3 – Analysis of the X-ray Wavefunction Refinement

2) Which new files have been written by tonto? Answer: Except for the stderr and stdout output files, there is a file tonto.epoxide_epoxide.molecule_tonto.epoxide_epoxide without extension and several files ending on *gnuplot.bond_data, *gnuplot.commands, and *gnuplot.contour_data.
3e) 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? Answer: It represents one of the C-O bonds with an ED value of 0.11 au.
3f) Describe the shape of the C-O bonds in the epoxide molecule. Is this what you expect? Answer: The shape is not outwards-bent like in the orbital picture of a banana bond, but the bond paths rather have an S-type shape which expresses the bond strain.
4a) What are the C-O, C-C and C-H bond indices (=bond orders) and what are their percentage covalencies? Answer: C1-O2 = 0.93, 92%; C4-O2 = 0.92, 91%; C4-C1 = 1.07, 100%; H1-C1 = 0.93, 97%; H2-C1 = 0.93, 97%; H3-C4 = 0.93, 97%; H4-C4 = 0.93, 97%.
What is the order of the bond types according to their covalent character? Answer: C-C > C-H > C-O.