Artefacts

An artefact is “a spurious observation or result arising from preparatory or investigative procedures […] any feature that is not naturally present but is a product of an extrinsic agent or method” (*Webster’s Encyclopedic Dictionary*).

In crystallography an artefact is “a method-immanent unavoidable systematic error leading to incorrect observations” (Müller in *Crystal Structure Refinement*).

Typical artefacts:
- Libration
- Short C≡C or C≡N triple bonds
- Hydrogen positions
- Fourier truncation ripples

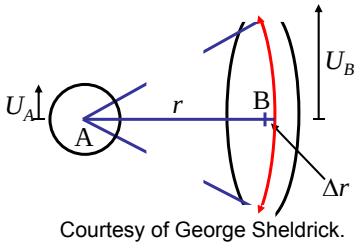
Libration

The higher the temperature, the shorter bond lengths appear to be, even though the unit cell gets slightly larger at the same time. The reason for this is libration. Especially terminal atoms show approximately circular motion. In anisotropic refinement, this motion is fitted as an ellipsoid, the center of which lies inside the circle of motion, while the atom is located on its periphery. This effect makes the bond distance appear shorter.

Depending on the movement of the atoms, the correction that needs to be applied is somewhere between 0.001 to 0.1 Å. Libration is much stronger at higher temperatures and particularly pronounced for hydrogen atoms, small ions, like NO_3^-, BF_4^-, ClO_4^-, PF_6^- and for $-CF_3$ groups.

$$\Delta r \approx \frac{\Delta U}{2r} = \frac{[U_B - U_A]}{2r}$$

For most low-temperature structures, the effects of libration are smaller than the standard uncertainties of the bond lengths and it is not necessary to correct for it.



Courtesy of George Sheldrick.
Used with permission.

CC and CN Triple Bonds

Triple bonds between light atoms are determined too short as the electron density between the nuclei is high compared to the electron density at the nuclei themselves. Therefore C≡C and C≡N bonds are determined shorter with X-ray diffraction than with neutron diffraction or spectroscopic methods.

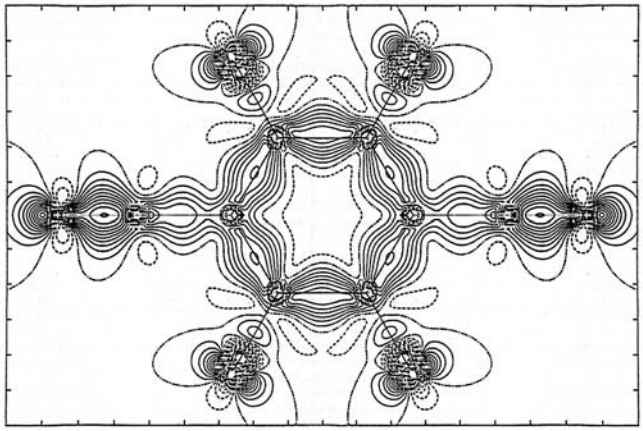
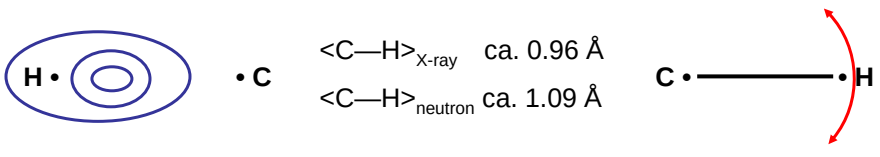


Image adapted from Hirshfeld, F. L. *Acta Cryst* B40 (1984): 613.

Hydrogen Atoms

The heavier an atom is and the more electrons it has, the stronger is its effect on the diffraction pattern. This also means that, especially in the presence of heavy atoms, light atoms are somewhat more difficult to localize. The lightest atom of all is hydrogen: it has only one electron, localized away from the nucleus. Therefore, hydrogen atoms are notoriously difficult to detect with X-ray diffraction methods.

Relatively high electron density between the atoms and libration effects make X—H bonds appear too short.



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Fourier Truncation Ripples

Artefactcual electron density maxima are both lower and closer to the true position for higher resolution data.

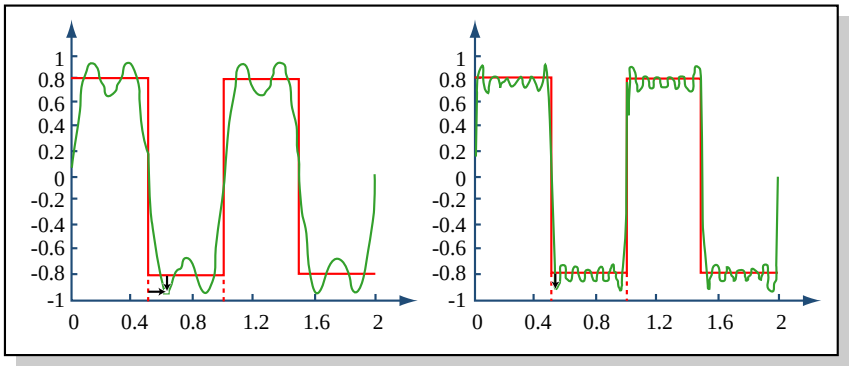

Figure by MIT OpenCourseWare.

Fourier Truncation Ripples – Famous Example

Low resolution structure of nitrogenase Mo-Fe Cofactor was hiding atom in center of metal atom cluster: Einsle et al. (2002). *Science* **297**, 1696-1700.

Nitrogen Fixation:

$N_2(g) + 8\ e^- + 8\ H^+ + 16\ ATP \rightarrow 2\ NH_3 + H_2(g) + 16\ P_i$

Two proteins involved: Fe-protein and MoFe-protein.

Three basic steps:

1. Reduction of Fe-protein by ferrodoxin or flavodoxin.
2. SET from Fe- to MoFe-protein hydrolizing two ATP.
3. Electron transfer to the substrate at the **MoFe cluster**.

Simpson, F. B., Burris, R. H. (1984): *Science* **224**, 1095.

Calculated Electron Density Near the Fe Atom

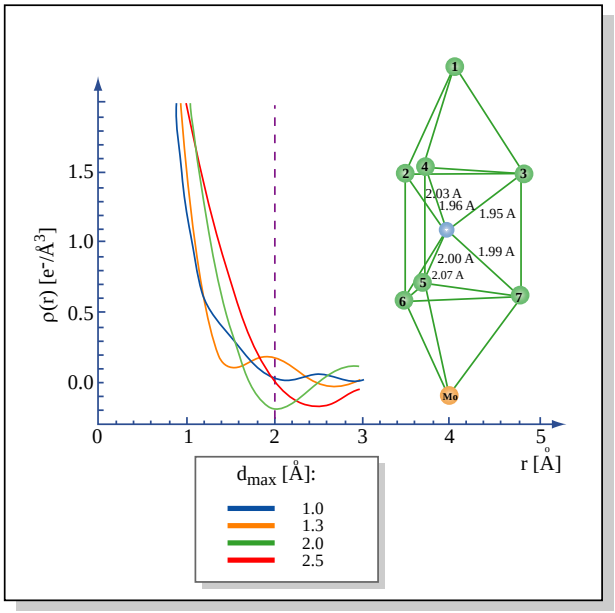

Figure by MIT OpenCourseWare.

What is NOT an Artefact?

Roland Boese (University of Essen): Three types of errors

> Unavoidable errors aka artefacts

> Avoidable errors
- wrong unit cell dimensions
- twinning refined as disorder or vice versa
- wrong atom type assignments
- wrong space group
- Fourier truncation peaks mistaken for hydrogens or vice versa

> Really avoidable errors
- typos in unit cell dimensions
- mis-adjustments of the diffractometer
- wrong data collection strategy (low completeness and/or MoO)
- refinement errors
- data collection at room temperature

Do not use the term artefact to explain/excuse an avoidable or really avoidable error!

Check Your Results = Structure Validation

Automated validation checks for completeness of reported information, quality of the analysis and correctness of the structure.

Missed symmetry (correct space group?)
Voids (overlooked solvent?)
Anisotropic Displacement Ellipsoids (atom types, disorders?)
Bond lengths and angles (comparison with tabulated values)
Intermolecular contacts (clashes with symmetry equivalents?)
Hydrogen Bonds (all O-H moieties hydrogen bond to acceptor?)
Connectivity (no isolated atoms allowed)
Reflection Data (completeness, resolution, merging *R*-values)
Refinement Parameters (final *R*-values, GooF, difference density)

Use CHECKCIF and/or PLATON
http://checkcif.iucr.org

It is a good idea to validate early on (as part of the refinement) and not only when it comes to writing up the structure.

What to do with the Reminder of the Semester?

November 1: Lecture artefacts etc.

November 3: Refinement of whatever you want to refine.

November 8: Lecture / demo on Ortep-32, POVRay, etc.

November 10: Coffee??

No lectures the week before Thanksgiving and none during Thanksgiving week either. After Thanksgiving:

November 29: General Q&A

December 1: Final (most probably take home)
December 4: 12:00 noon (sharp). Final due (if take-home)

5.067 Crystal Structure Refinement
Fall 2009