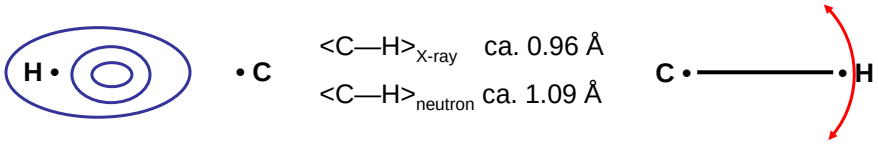
Hydrogen Atoms

It is electron density that we measure by X-ray diffraction. 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.



Courtesy of George Sheldrick. Used with permission.

George M. Sheldrick

Hydrogen Atoms

Especially for hydrogen atoms bound to carbon it is frequently possible to calculate the hydrogen positions from the coordinates of the atoms the hydrogen atoms are attached to, as the standard bond lengths and angles are well known.

Hydrogen atoms of water molecules must be detected in the experimental electron density or else they cannot be included into the model.

Even more difficult to detect can be hydrogen atoms in heavy metal hydrides. The sometimes relatively strong Fourier truncation ripples close to heavy atom positions can overpower the rather weak electron density maxima representing the hydrogen atoms. Very accurate and especially complete high quality data and proper scaling are required to distinguish those hydrogen atoms from the background noise.

Hydrogen Atoms

In most cases, the positioning of hydrogen atoms bound to carbon in an atomic model during the refinement of an X-ray crystal structure is done entirely without any or only very little direct information from the diffraction experiment. Hydrogen atoms on aromatic carbons, CH, CH_2 groups, most CH_3 groups are easy. CH_3 in acetonitrile, Cp* or toluene: torsion angle needs to be determined.

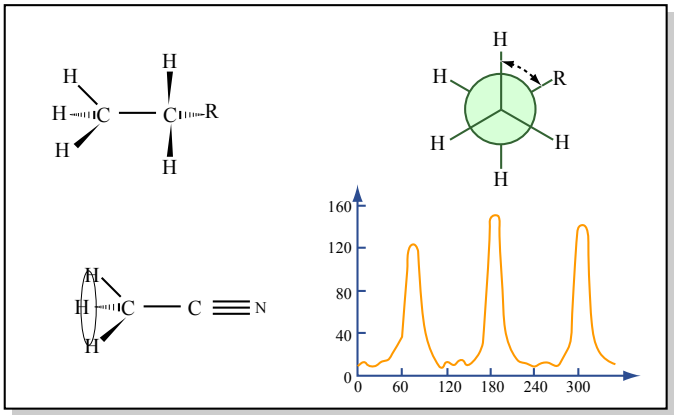


Figure by MIT OCW.

Hydrogen Atoms in SHELXL: HFIX

Hydrogen atoms are placed at **calculated positions** and refined using a **riding model**. That means rigid group constraints, in other words AFIX.

The HFIX command generates both the hydrogen atom positions and the appropriate AFIX lines.

This is good mainly for hydrogens bound to carbon, but can also be used for some N-H and O-H situations.

Hydrogens bound to metal atoms cannot be generated that way.

Hydrogen Atoms in SHELXL: HFIX

Syntax:
`HFIX mn atomnames`

`m` describes the geometry and number of hydrogen atoms.
`n` defines how the hydrogen atoms(s) are refined.

The SHELX manual has a list of all possible **`n`** and **`m`** numbers.
The book has a list of the most important combinations on page 30-31.

`atomnames` is a list of all atoms that are supposed to get hydrogen atoms.

Hydrogen Atoms in SHELXL: Semi-free refinement

Acidic hydrogen atoms could be absent and should be "seen" in the difference Fourier before they should be placed.

Good alternative: semi-free refinement:

- Take coordinates for hydrogen atoms from peaklist (list of Qs in .res file).
- Place H atom **directly under** the atom it is attached to.
- Change atom name (Q → H) and atom type (1 → 2).
- Change U-value (0.05 → -1.2 or -1.5).
- Use DFIX to restrain X-H and possibly H-H distances.
  See .lst file for target distances.

This is very elegant and less restrictive than the riding model, but requires good high-resolution low-temperature diffraction data.

Hydrogen Atoms in SHELXL: Hydrogen Bonds

If the command **HTAB** appears in the header of the .ins file, SHELXL performs a search over all polar hydrogen atoms present in the structure and examines hydrogen bonding.

The bonds listed in the .lst file are those for which the distance between acceptor and hydrogen atom are smaller than the radius of the acceptor atom plus 2.0 Å, and the angle between the donor atom, the hydrogen and the acceptor atom is larger than 110°.

Once the hydrogen bonds have been identified, the second form of the **HTAB** command can be used to calculated standard uncertainties:

HTAB donor-atom acceptor-atom

SHELXL generates hydrogen bonds with standard uncertainties and, in combination with **ACTA**, the appropriate table in the .cif file.

EQIV can be used to specify a symmetry equivalent of the acceptor atom.

Atom Type Assignment – All Electrons are Blue

We measure electron density not atomic number. The accuracy of the electron density depends on correctness of the model, which is equivalent to the interpretation of the electron density function and we are facing a nice Catch 22.

Chemical knowledge, that is geometry of molecules (bond lengths and angles, number of bonds, etc.):

Cu(I) is colorless C(II) is blue.
Carbon makes four single bonds, no more.
Pt(II) is usually planar, Pt(IV) is usually octahedrally coordinated.
Zr(III) is dark green to black, Zr(IV) pale yellow to colorless.
etc.

A crystal structure must be chemically sensible or it is wrong!

Atom Type Assignment – All Electrons are Blue

We measure electron density not atomic number. The accuracy of the electron density depends on correctness of the model, which is equivalent to the interpretation of the electron density function and we are facing a nice Catch 22.

Crystallographic knowledge or what does the thermal displacement ellipsoid look like?

Too small ellipsoid
The true element may be heavier than the one currently in you model.

Too large ellipsoid
The true element may be lighter than the one currently in you model.

Example: finding the oxygen atom in THF by refining all five atoms as C.

Atom Type Assignment – All Electrons are Blue

A sphere (or ellipsoid) is drawn around the volume corresponding to 50% of the electrons assumed in the model. If the real atom has more electrons this volume will be below average, if the real atoms has more electrons the volume will be larger than average.

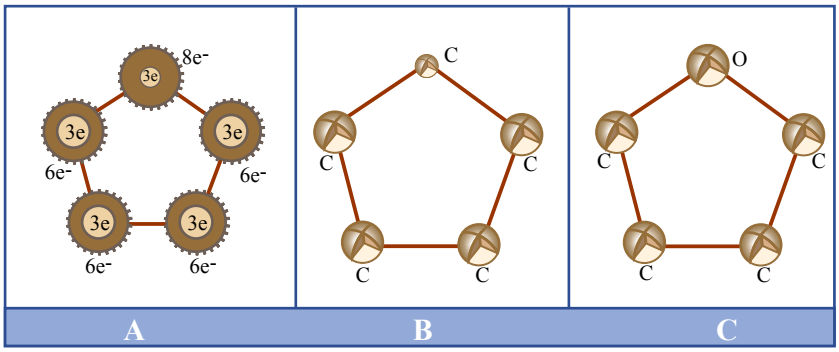


Figure by MIT OCW.

Atom Type Assignment – All Electrons are Blue

Another example...