Methods in Chemistry III – Part 1
Modul M.Che.1101 WS 2010/11 – 11

Modern Methods of Inorganic Chemistry

Mi 10:15-12:00, Hörsaal II

George Sheldrick

gsheldr@shelx.uni-ac.gwdg.de

Calculation of the structure factors

Every atom *j* in the unit-cell makes a contribution to the structure factor $F_{hk\ell}$ of every reflection, which is expressed as a complex number:

$$A_{hk\ell} = \Sigma_j\, q\, \{ (f_j+f_j') \cos[2\pi(hx_j+ky_j+\ell z_j)] + f_j'' \sin[2\pi(hx_j+ky_j+\ell z_j)] \}$$

$$B_{hk\ell} = \Sigma_j\, q\, \{ (f_j+f_j') \sin[2\pi(hx_j+ky_j+\ell z_j)] + f_j'' \cos[2\pi(hx_j+ky_j+\ell z_j)] \}$$

$$F_{hk\ell} = A + iB; \quad \tan(\phi_{hk\ell}) = B/A; \quad F_{hk\ell}^2 = A^2 + B^2$$

The atomic scattering factors *f+f'+if"* are complex. *q* describes the thermal motion of the atom and for isotropic atoms is given by

$$q = \exp\{ -8\pi^2 U_j\, [\sin(\theta)/\lambda]^2 \}$$

and for anisotropic atoms by

$$q = \exp\{-2\pi^2[U_{11}h^2a^{*2}+U_{22}k^2b^{*2}+U_{33}\ell^2c^{*2}+2U_{23}k\ell b^*c^*+2U_{13}h\ell a^*c^*+2U_{12}hka^*b^*]\}$$

Least-squares structure refinement

Small molecule structures are normally refined by least-squares. Either

$$M_1 = \Sigma_{F>4\sigma(F)}\, w(|F_o|-|F_c|)^2 \quad \text{or} \quad M_2 = \Sigma\, w(F_o^2-F_c^2)^2$$

(these days almost always M_2) is minimized by the refinement of the atom coordinates x,y,z and the displacement parameters U or U_{ij}. M_1 has the disadvantage, that those intensities $I = F_o^2$ that were measured as negative (as a result of experimental error) cannot be taken into account.

Often weights $w = 1 / [\sigma^2(F_o^2)+gF_o^4]$ or $w = 1 / [\sigma^2(F_o^2)+g(F_o^4+2F_c^4)/3]$ are used, where $\sigma(F_o^2)$ is the standard deviation of the measured intensity F_o^2. Since with an area detector each reflection (or its equivalents) are measured several times, $\sigma(F_o^2)$ can be estimated from the scatter of the measured values. g should take systematic errors into account that are the same for all measurements of a reflection or its equivalents.

Least-squares algebra and standard deviations

In a non-linear least-squares refinement, the parameter shifts are calculated in each cycle by $\delta x = A \cdot B^{-1}$ where

$$A_j = \sum w(F_o^2 - F_c^2)(\partial F_c^2 / \partial x_j) \quad \text{and} \quad B_{ij} = \sum w(\partial F_c^2 / \partial x_i)(\partial F_c^2 / \partial x_j)$$

These sums are performed over all reflections. The esds (standard deviations, now called *standard uncertainties*) are calculated by

$$\mathrm{esd}(x_j) = [\ (B^{-1})_{jj} \sum w(F_o^2 - F_c^2)^2 \,/\, (N_R - N_P)\ ]^{1/2}$$

under the assumption that $\sum w(F_o^2 - F_c^2)^2$ is normally distributed, i.e. shows no systematic variation with the resolution etc. N_R is the number of data and N_P the number of parameters.

This only takes random errors into account. Because systematic arrors can never be completely eliminated, the esds are always under-estimated. Comparisons of independent determinations of the same structure suggest that the esds of the atomic coordinates are under-estimated by a factor of about 1.5 and those of the displacement parameters by a factor of about 2.0.

Constraints and restraints

The higher the data-to-parameter ratio, the better the structure can be determined.

Constraints **are exact mathematical conditions that reduce the number of refined parameters. Examples are rigid groups and the riding model for hydrogen atoms.**

Restraints **have a target value *T* and a *standard deviation* σ. They are treated like reflection data and are added to the quantity to be minimized :**

$$M = \Sigma\, w_x (F_o^2 - F_c^2)^2 + \Sigma\, w_r (T - T_c)^2$$

The X-ray weights w_x are normalized to make the average value of $w_x(F_o^2 - F_c^2)^2$ equal to one. w_x rises during the refinement as a consequence of the improved agreement between F_o^2 and F_c^2. The weights of the *restraints* $w_r = 1/\sigma^2$ should be independent of the structure and the resolution. *Restraints* increase the effective number of data but *constraints* reduce the number of parameters. In both cases the data-to-parameter ratio is improved.

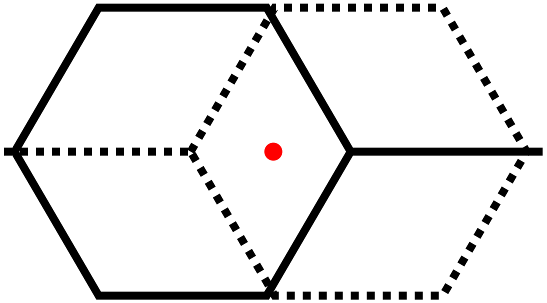
Constraints for special positions

Example: An atom on a twofold axis in the space group C2. The two positions related by this axis, x,y,z and $-x,y,-z$, are only identical when $x = 0$ and $z = 0$. In order to simplify the calculation of the structure factors, the effective occupancy is fixed at 0.5. The ellipsoid, that represents the anisotropic motion of the atoms, must also remain unchanged after a 180° rotation:

I.e. $[U_{11}, U_{22}, U_{33}, U_{23}, U_{13}, U_{12}] \equiv [U_{11}, U_{22}, U_{33}, -U_{23}, U_{13}, -U_{12}]$, with the result that $U_{23} = 0$ and $U_{12} = 0$.

Toluene on an inversion center

Toluene has a long liquid range and so is especially suitable for growing crystals. Unfortunately toluene simply cannot resist inversion centers!



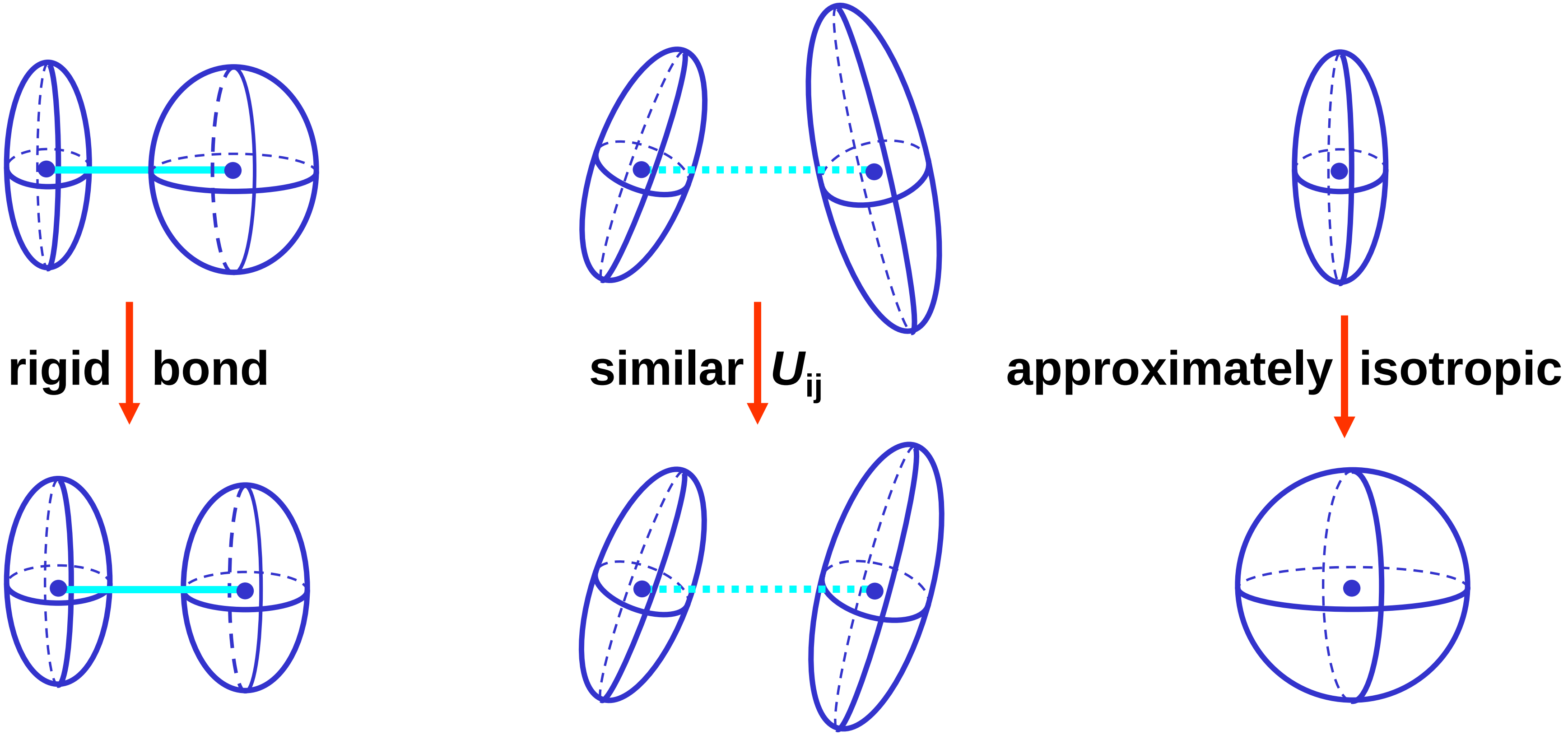
The refinement of such a disorder is only possible with the help of restraints and constraints.

***Constraints*: All atoms in the toluene molecule have fixed occupancies of 0.5; one molecule is refined as a rigid group with standard geometry.**

***Restraints*: All non-hydrogen atoms in the toluene molecule lie approximately in a plane; chemically equivalent bond lengths and angles are approximately equal; the displacement parameters of two bonded atoms are approximately equal along the bond and the 6 U_{ij} parameters of two strongly overlapping atoms are about the same.**

ADP restraints

Diagrams by Thomas R. Schneider



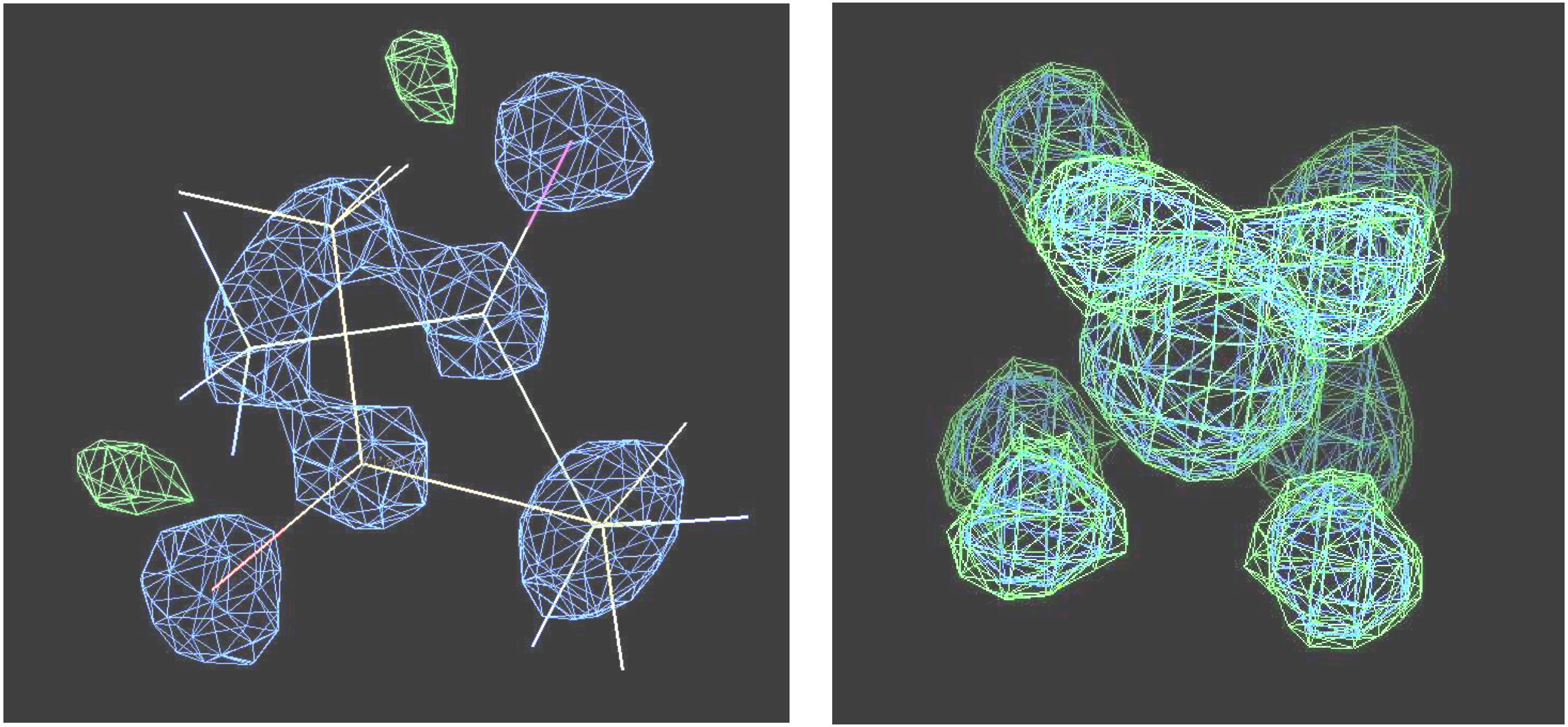
rigid bond

similar U_{ij}

approximately isotropic

The *rigid bond* restraints are given small standard deviations (large weights) becuase they fit relatively exactly (with the exceptions of hydrogen and heavy atoms). The *similar U_{ij}* and *approximately isotropic* restraints on the other hand are assigned large esds (small weights) because they only fit approximately.

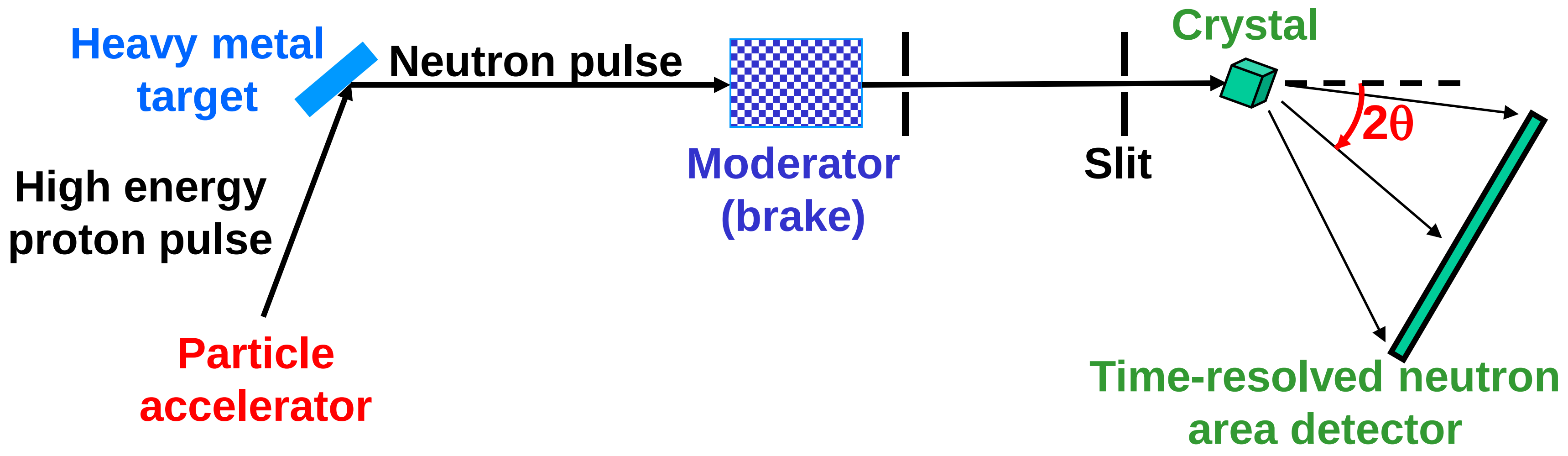
Disorder



The picture on the left shows a disordered acetone molecule and its interpretation. The perchlorate ion on the right should be interpreted in the exercises! The electron density is shown in blue and the difference density in green; in the right hand picture they are the same, because the atoms were not included in the structure factor calculation.

Neutron diffraction

Neutrons can be considered to be either particles or waves. When the neutrons come from an atomic reactor, it is necessary to select a narrow wavelength range (usually around λ = 1 Å) using a crystal monochromator, with the loss of many of the neutrons. Since the diffraction is weaker, much larger crystals are needed than for X-ray diffraction. ***Spallation sources*** with ***time-of-flight*** detection are an attractive alternative. In contrast to the usual procedure, 2θ rather than λ is varied in the Bragg equation $\lambda = 2d\cdot\sin(\theta)$. The neutrons in the same pulse arrive at different times at the detector; the shorter the wavelength, the greater the energy and velocity.

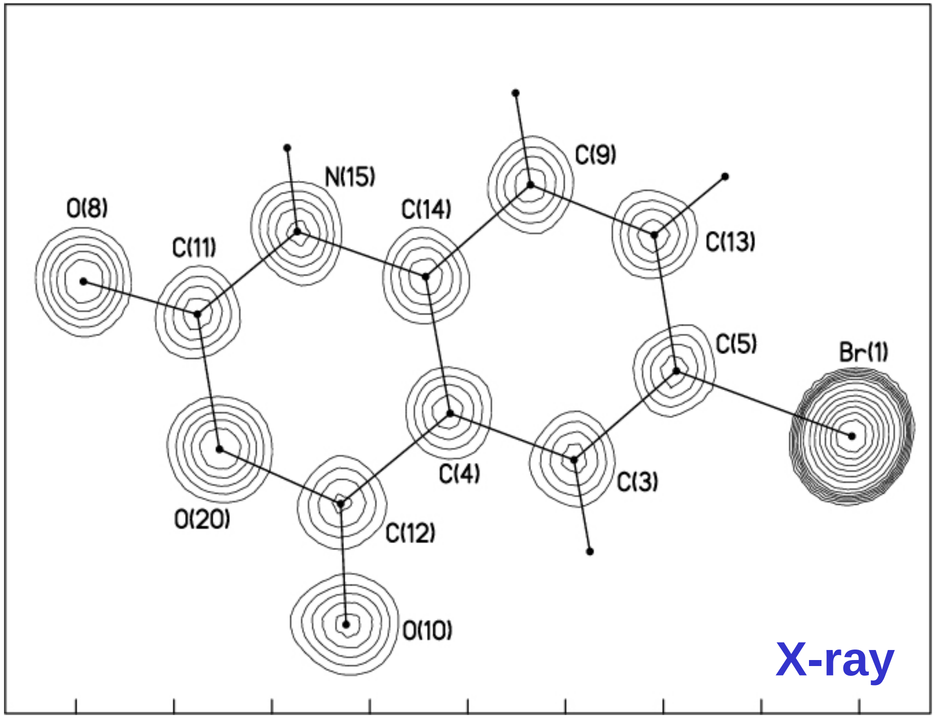


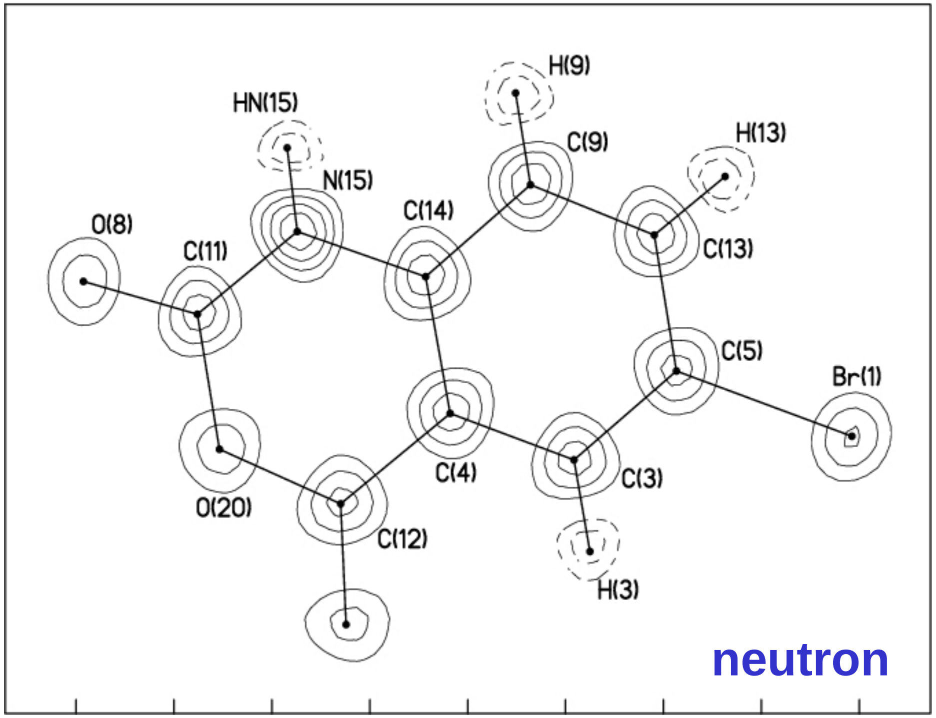
Neutron scattering factors

Although there are many similarities in the analysis of neutron and X-ray data, a big difference is that neutron scattering factors vary irregularly through the periodic table rather than increasing with atomic number:

^{1}H –3.7, ^{2}H 6.7, ^{7}Li –2.2, ^{12}C 6.6, ^{14}N 9.4, ^{16}O 5.8, ^{35}Cl 11.7, ^{37}Cl 3.1, ^{51}V –0.4, ^{56}Fe 9.9, ^{79}Br 6.8, ^{81}Br 6.8, ^{238}U 8.4 fm.

Because neutrons are diffracted by atomic nuclei rather than electrons, these values are resolution independent (in contrast to X-ray diffraction).





Exercises

1. The crystal structure of the product of the proposed reaction

$$CuCl + 5F_2 \longrightarrow [ClF_6]^+ \ [CuF_4]^- \quad (?)$$

was given as a proof. The reaction was carried out in a quartz tube. Why was the crystal light blue and surprisingly stable in moist air?

2. Interpret the disorder of the ClO_4^--Ions!

3. Why can hydrogen atom positions be determined more precisely by neutron diffraction of deuterated compounds than by (a) X-ray diffraction or (b) neutron diffraction of the corresponding ^1H-compounds? Is this also the case when only a third of the ^1H atoms can be replaced by ^2H?