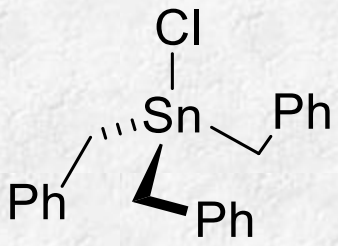
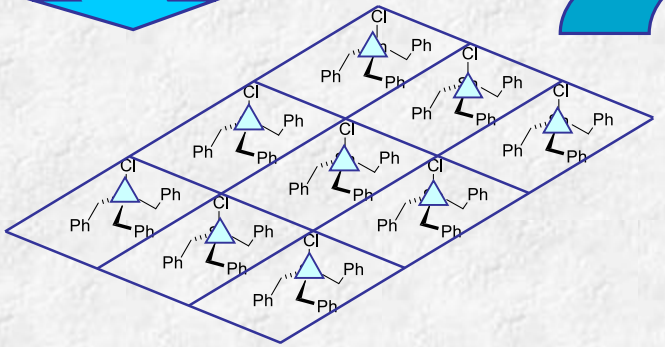
# Structure determination

**Crystallisation**

**Single crystal selection**




***Molecular structure**:*
*Atomic positions*

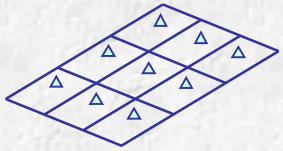
***Crystalline structure**:*
*Unit cell and space group*

***Crystal**:*
*Macroscopic dimensions*

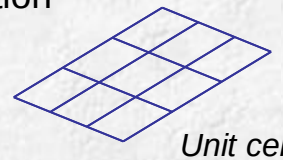
Dataset collection

**Solution and Refinement**

| H | K | L | I | σ |
|---|---|---|---|---|
| 0 | 0 | 1 | 134.4 | 12.5 |
| 0 | 0 | 2 | 0.2 | 1.2 |
| 1 | 1 | 4 | 52.4 | 2.2 |

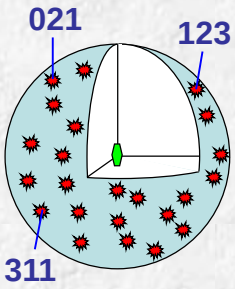


Space group determination

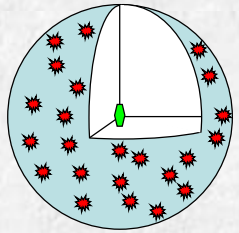


*Unit cell*

| H | K | L | I | σ |
|---|---|---|---|---|
| 0 | 0 | 1 | 134.4 | 12.5 |
| 0 | 0 | 2 | 0.2 | 1.2 |
| 1 | 1 | 4 | 52.4 | 2.2 |




Détermination of the unit cell



*Raw data*

***Unit cell + space group**:*
*Dimensions and symmetry of the crystalline structure*
***Intensity of the reflections:***
*Atomic positions*

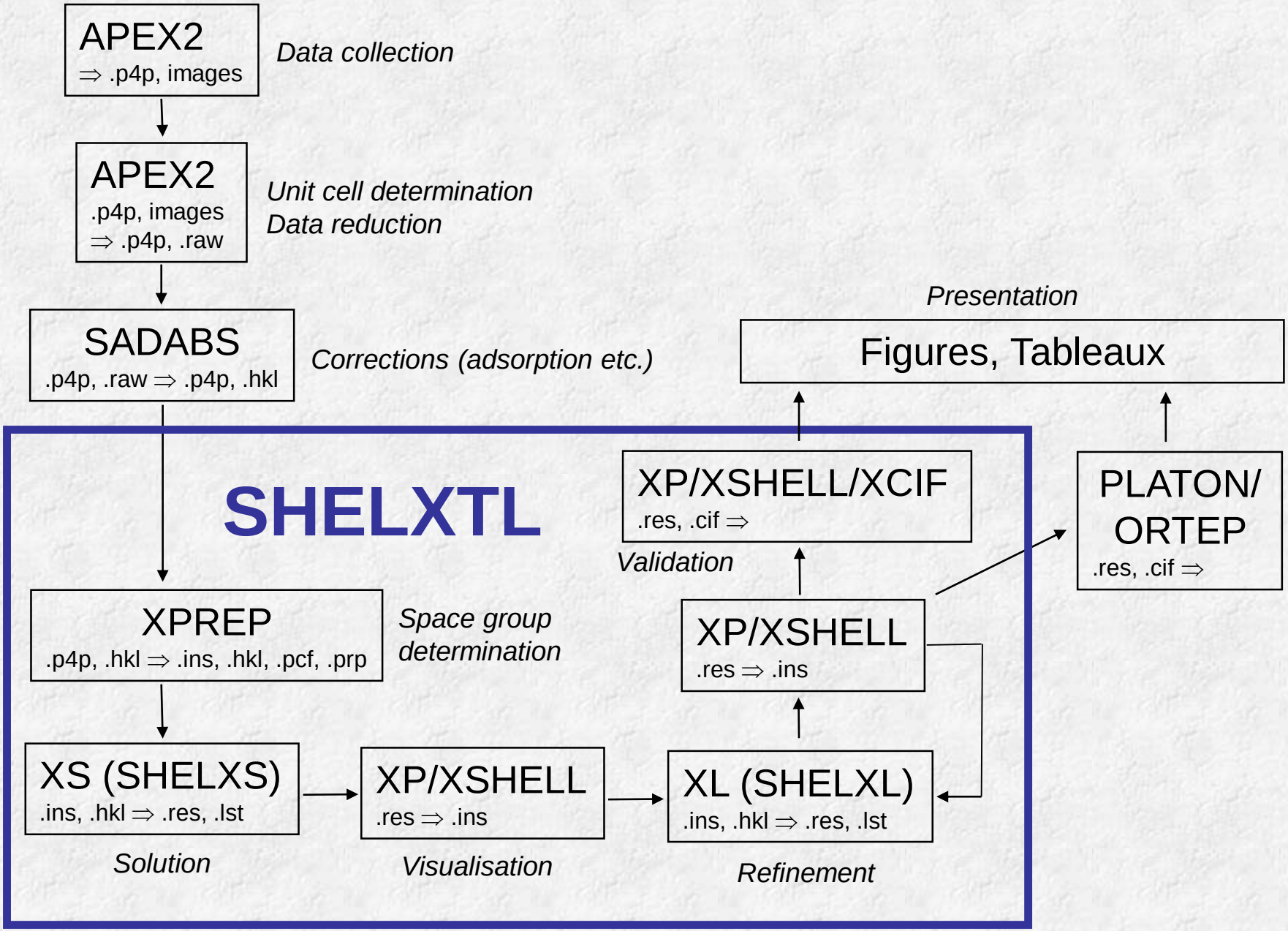
# Programs used in a single crystal diffraction study

- Grow a crystal
- Choose and mount a single crystal

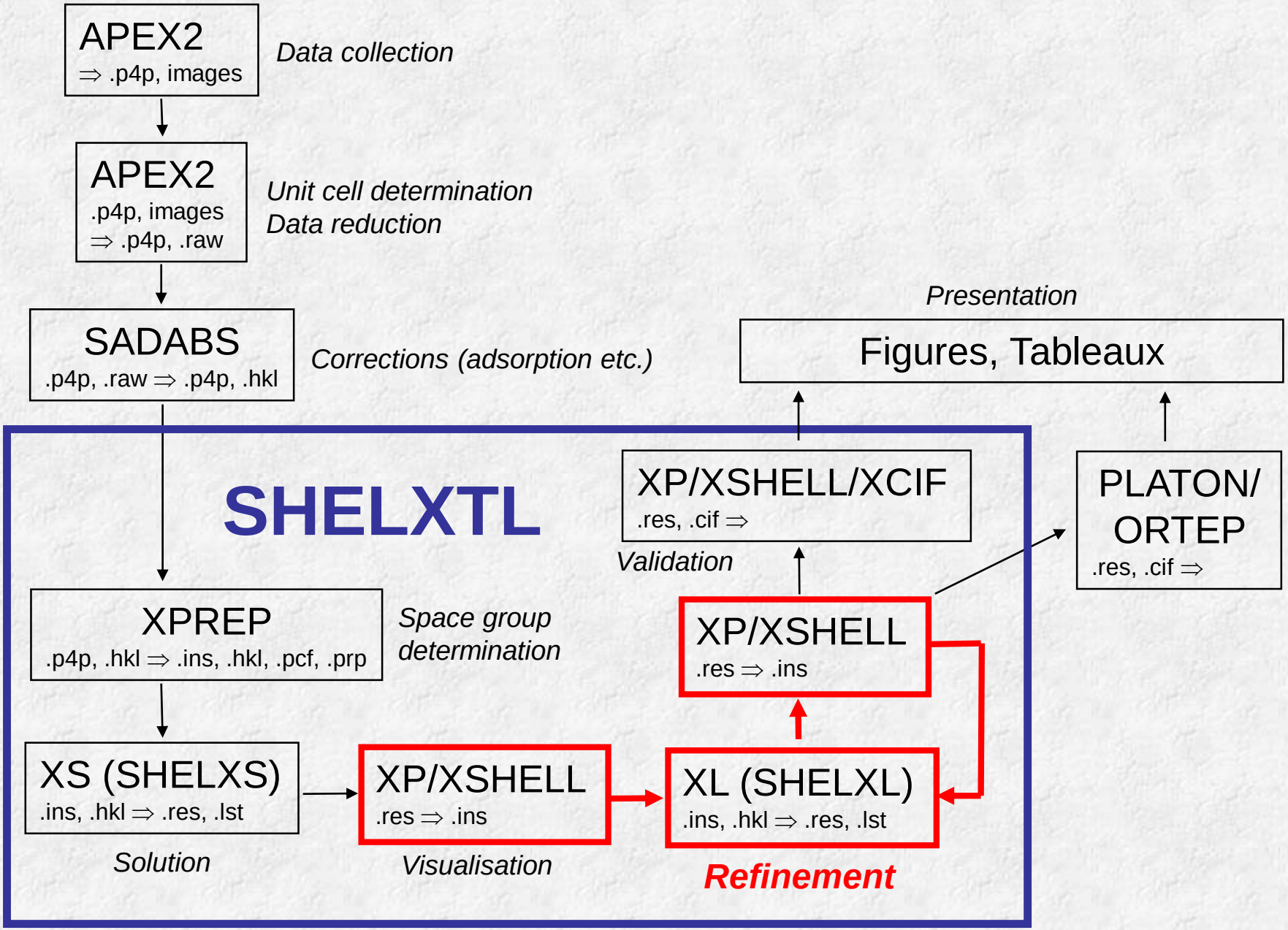
- **Collect the dataset** — **APEX2 ⇒ images**
- Determine the unit cell — **APEX2 ⇒ .p4p**
- **Integration of the image files and data reduction**
  - **Lorentz correction** — **SAINT**
  - **Polarisation correction** — **SAINT ⇒ .raw**
  - **Absorption correction** — **SADABS ⇒ .hkl**
  - **Other corrections (twinning etc.)**
- **Space group determination** — **XPREP ⇒ .ins, .hkl, .pcf, .prp**
- **Structure solution** — **XS (SHELXS) ⇒ .res, .lst**
- **Structure refinement** — **XL (SHELXL) ⇒ .res, .lst, .cif**
- **Validation** — **checkcif, PLATON**
- Preparation of tables and figures — **XP, XSHELL, PLATON etc.**
- Data backup

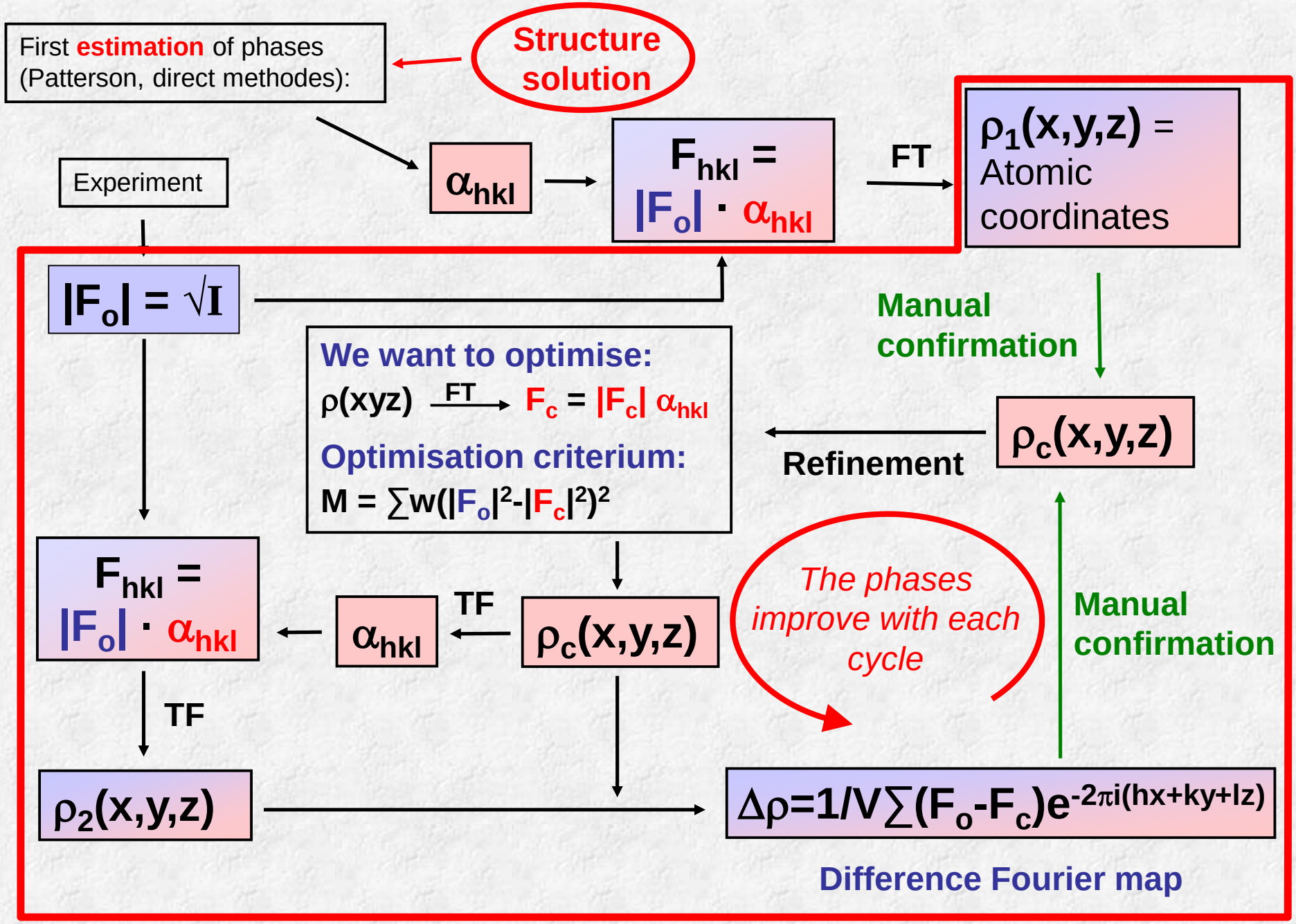
List with reflection intensities

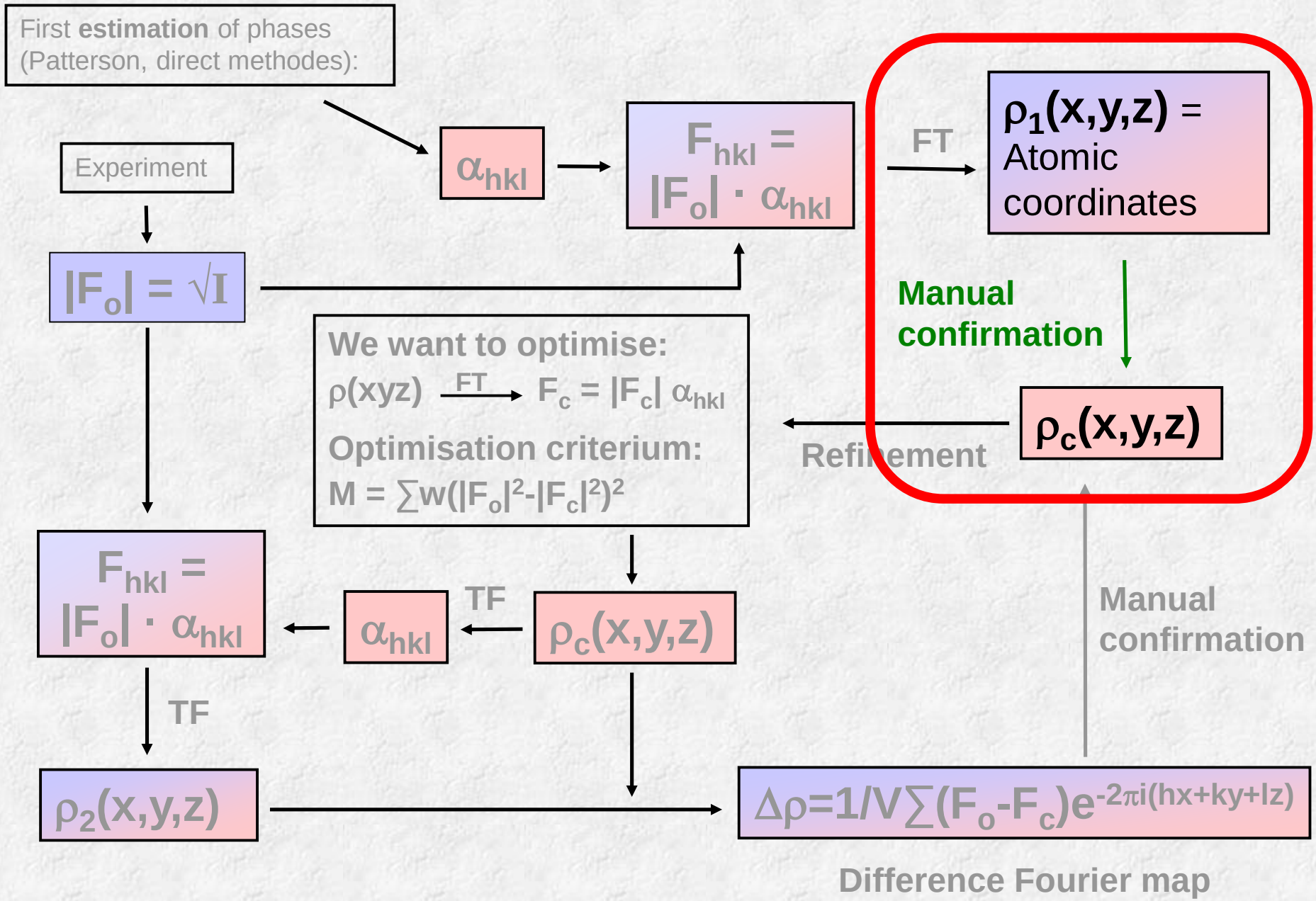
# Programs used in a single crystal diffraction study



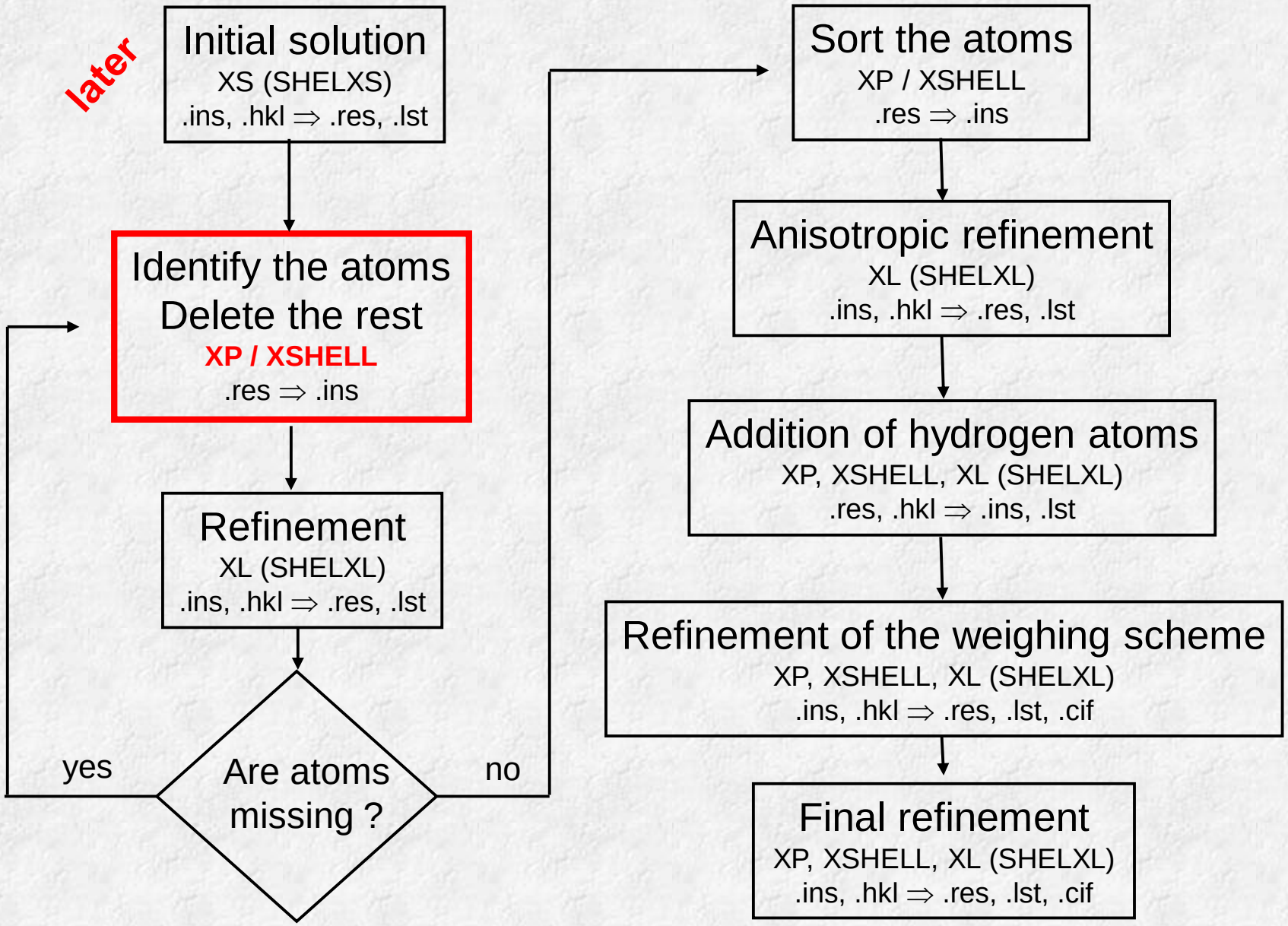
# Programs used in a single crystal diffraction study



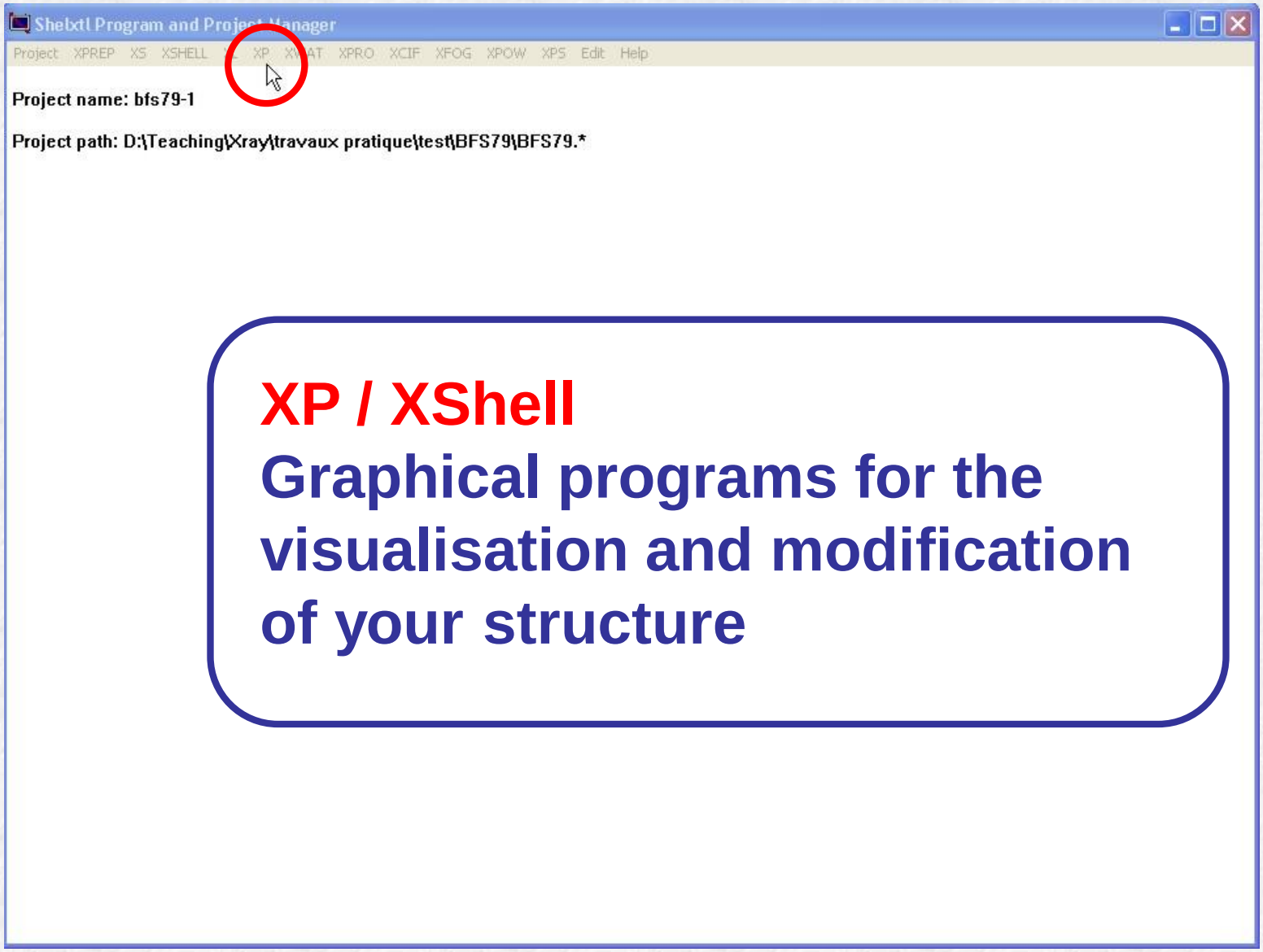

First estimation of phases (Patterson, direct methodes):
Structure solution
Experiment
$\alpha_{hkl}$
$F_{hkl} = |F_o| \cdot \alpha_{hkl}$
FT
$\rho_1(x,y,z)$ = Atomic coordinates
$|F_o| = \sqrt{I}$
Manual confirmation
We want to optimise:
$\rho(xyz)$ FT $F_c = |F_c| \alpha_{hkl}$
Optimisation criterium:
$M = \sum w(|F_o|^2-|F_c|^2)^2$
$\rho_c(x,y,z)$
Refinement
$F_{hkl} = |F_o| \cdot \alpha_{hkl}$
$\alpha_{hkl}$
TF
$\rho_c(x,y,z)$
The phases improve with each cycle
Manual confirmation
TF
$\rho_2(x,y,z)$
$\Delta\rho=1/V\sum(F_o-F_c)e^{-2\pi i(hx+ky+lz)}$
Difference Fourier map


First **estimation** of phases (Patterson, direct methodes):
Experiment
$|F_o| = \sqrt{I}$
$\alpha_{hkl}$
$F_{hkl} = |F_o| \cdot \alpha_{hkl}$
FT
$\rho_1(x,y,z)$ = Atomic coordinates
Manual confirmation
$\rho_c(x,y,z)$
Refinement
We want to optimise:
$\rho(xyz) \xrightarrow{FT} F_c = |F_c| \alpha_{hkl}$
Optimisation criterium:
$M = \sum w(|F_o|^2-|F_c|^2)^2$
$F_{hkl} = |F_o| \cdot \alpha_{hkl}$
$\alpha_{hkl}$
TF
$\rho_c(x,y,z)$
TF
$\rho_2(x,y,z)$
Manual confirmation
$\Delta\rho=1/V\sum(F_o-F_c)e^{-2\pi i(hx+ky+lz)}$
Difference Fourier map

# Refinement organigram



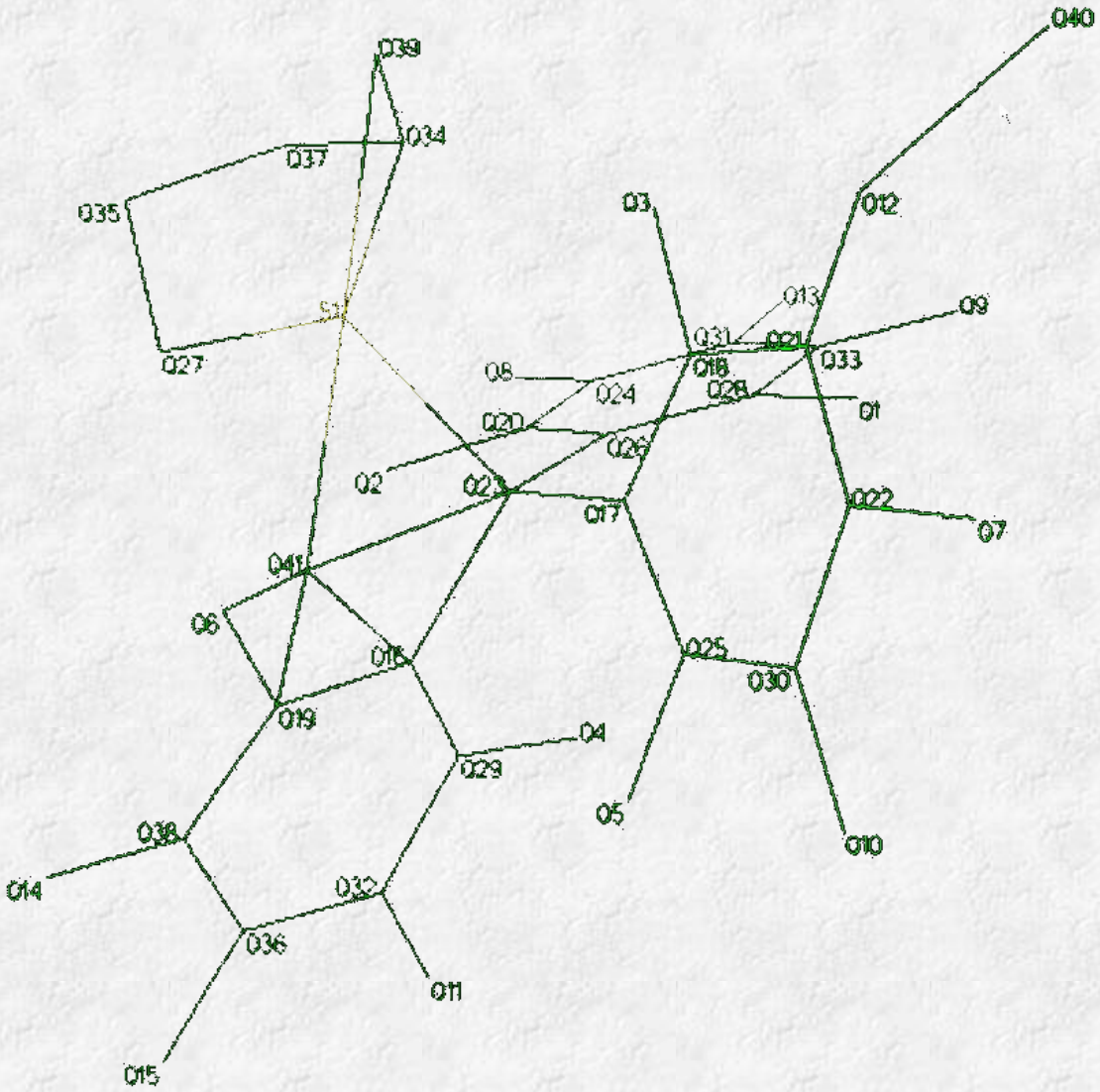
# Initial Solution

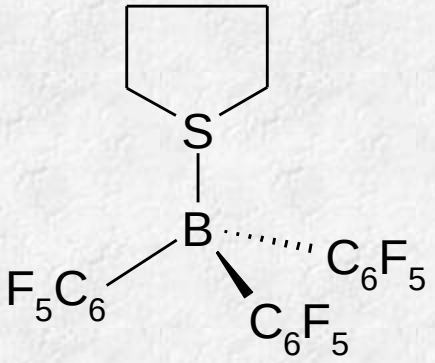



**XP / XShell**

**Graphical programs for the visualisation and modification of your structure**

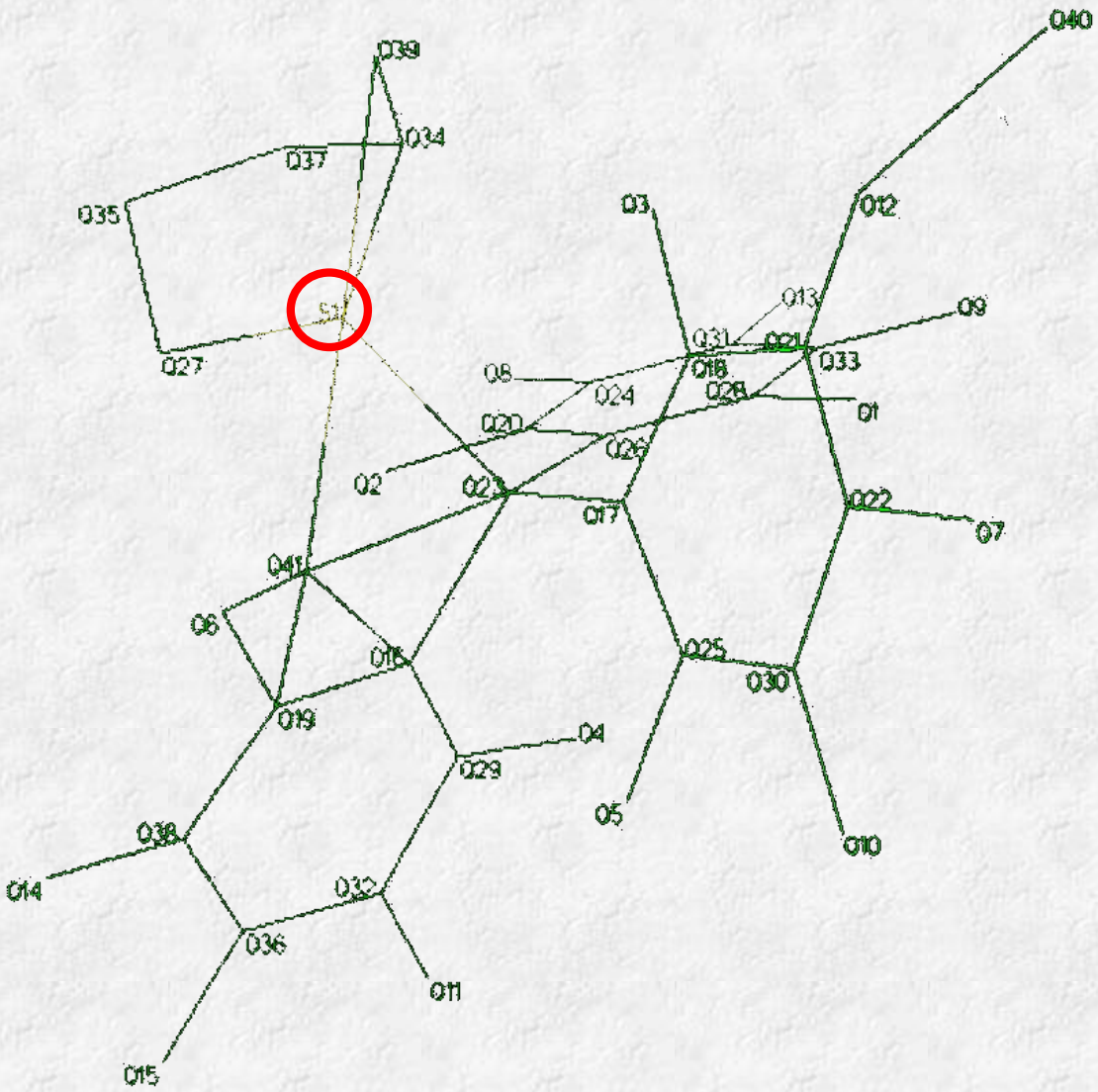
# Initial solution

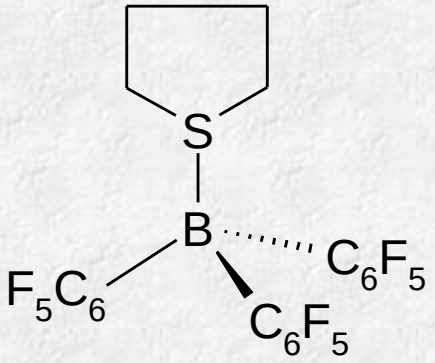



The initial solution proposes a electron density map in which the highest points of electron densities are identified (Q-peaks).

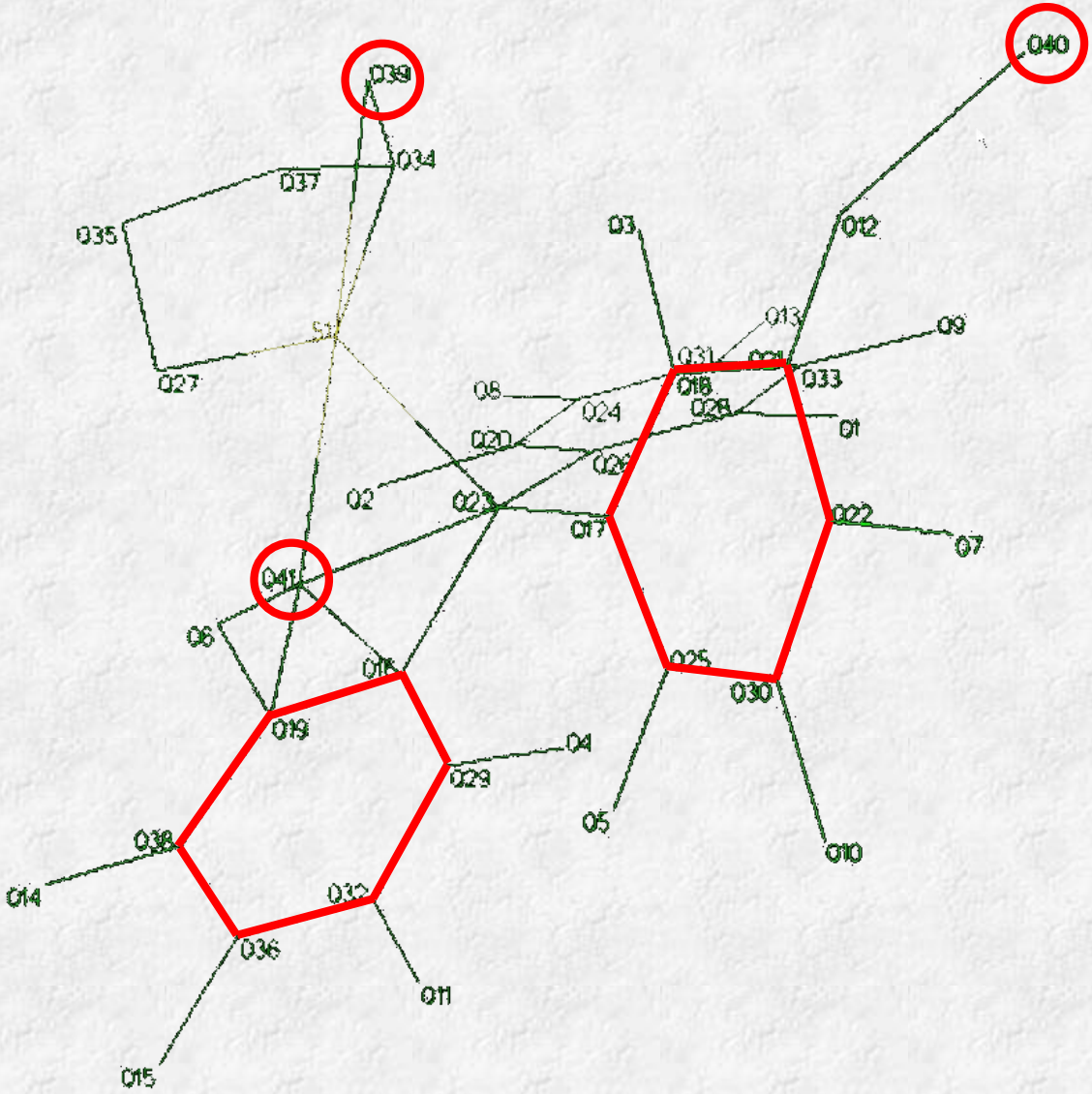
# Initial solution




For some centers of electron density an element is already proposed. You have to verify if they are correctly assigned.

# Initial solution

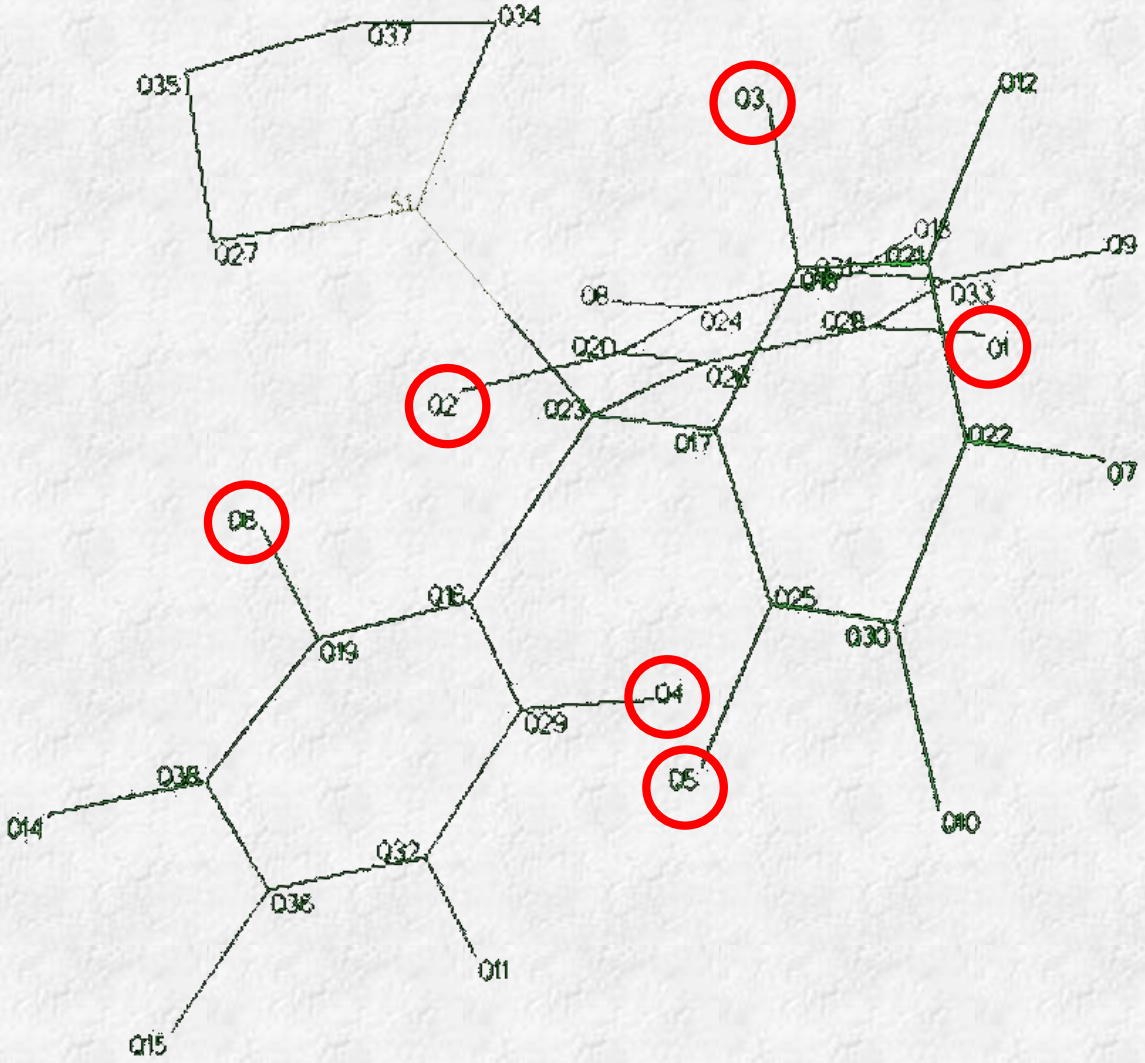


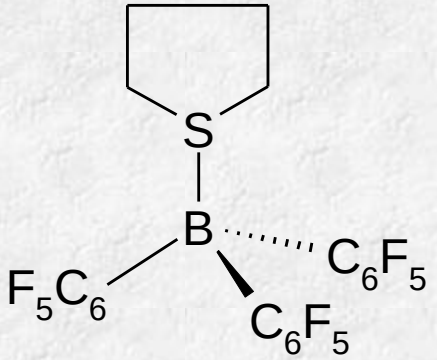

Several centers of electron densities are not related to your structure.

**Do not hesitate to delete them!** A deleted electron density will show up again in later cycles, if it is correct.

If a structure is difficult to identify, look for regular structures, such as aromatic rings etc.

# Initial solution

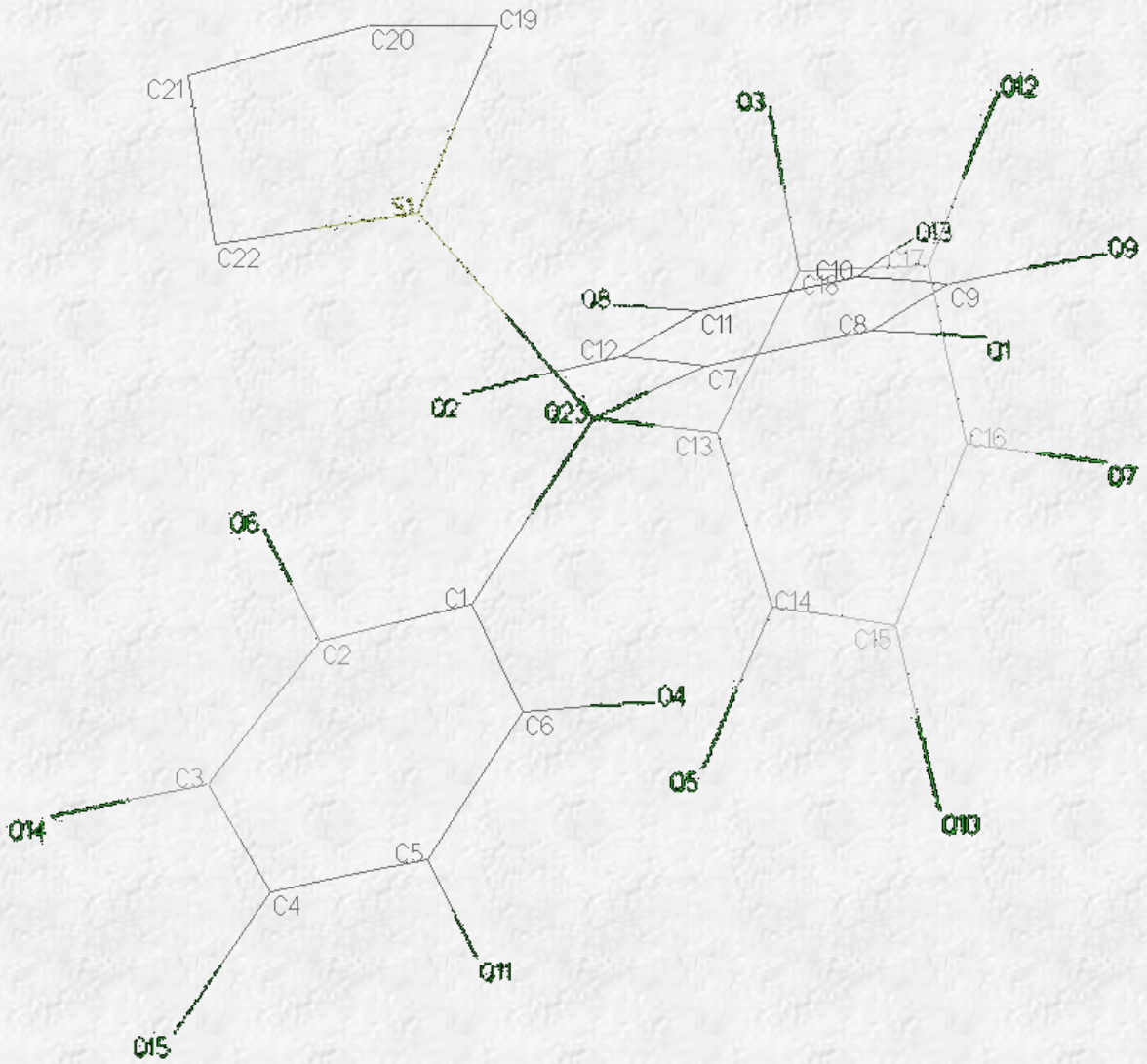



Q-peaks are sorted after their electronic density with Q1 being the highest electron density.

The peaks with the smallest numbers have the highest electron density and are thus fluorine atoms.

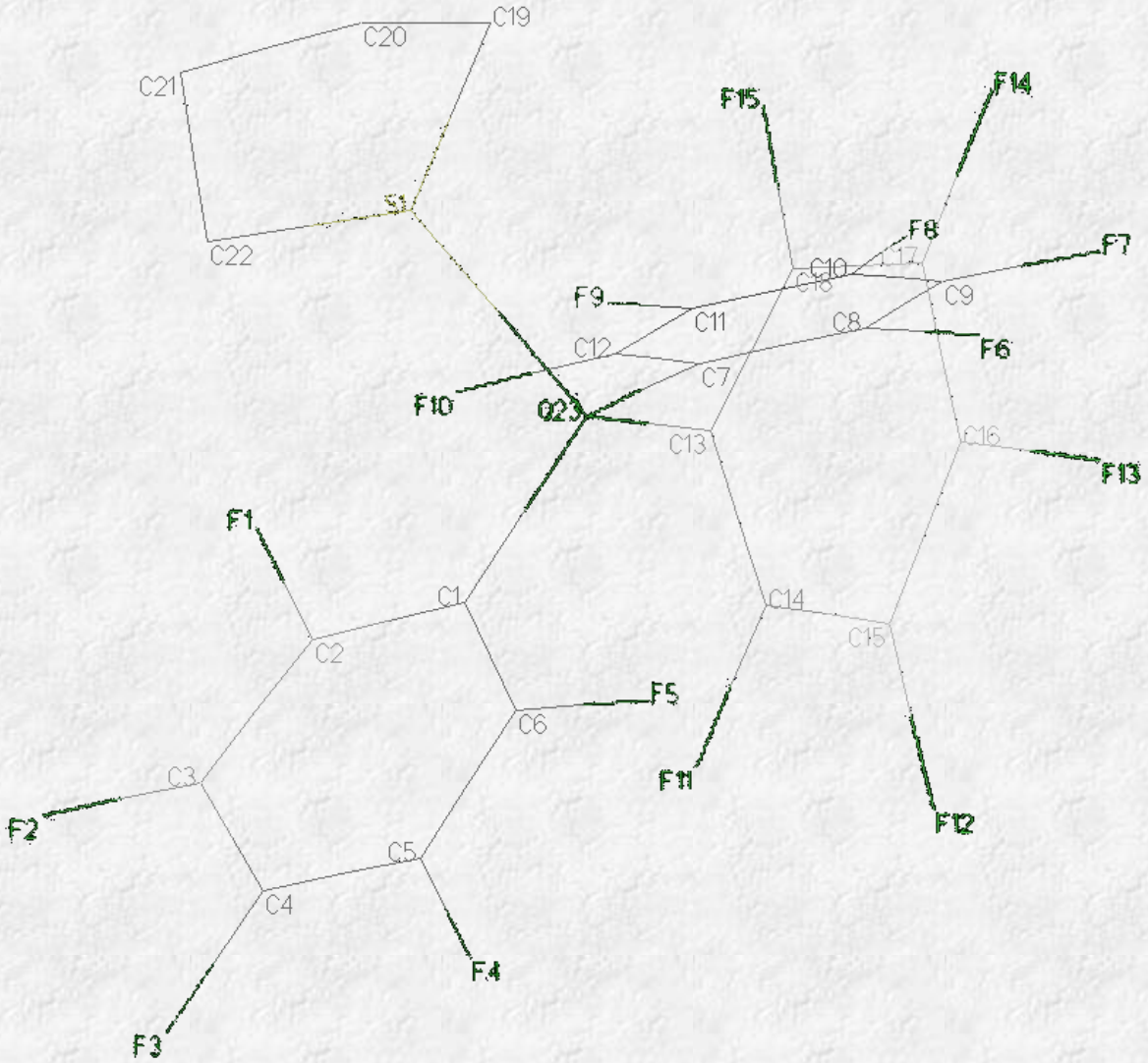
# Initial solution




Now you have to assign correct elements to the remaining electron densities:

- **Carbon**

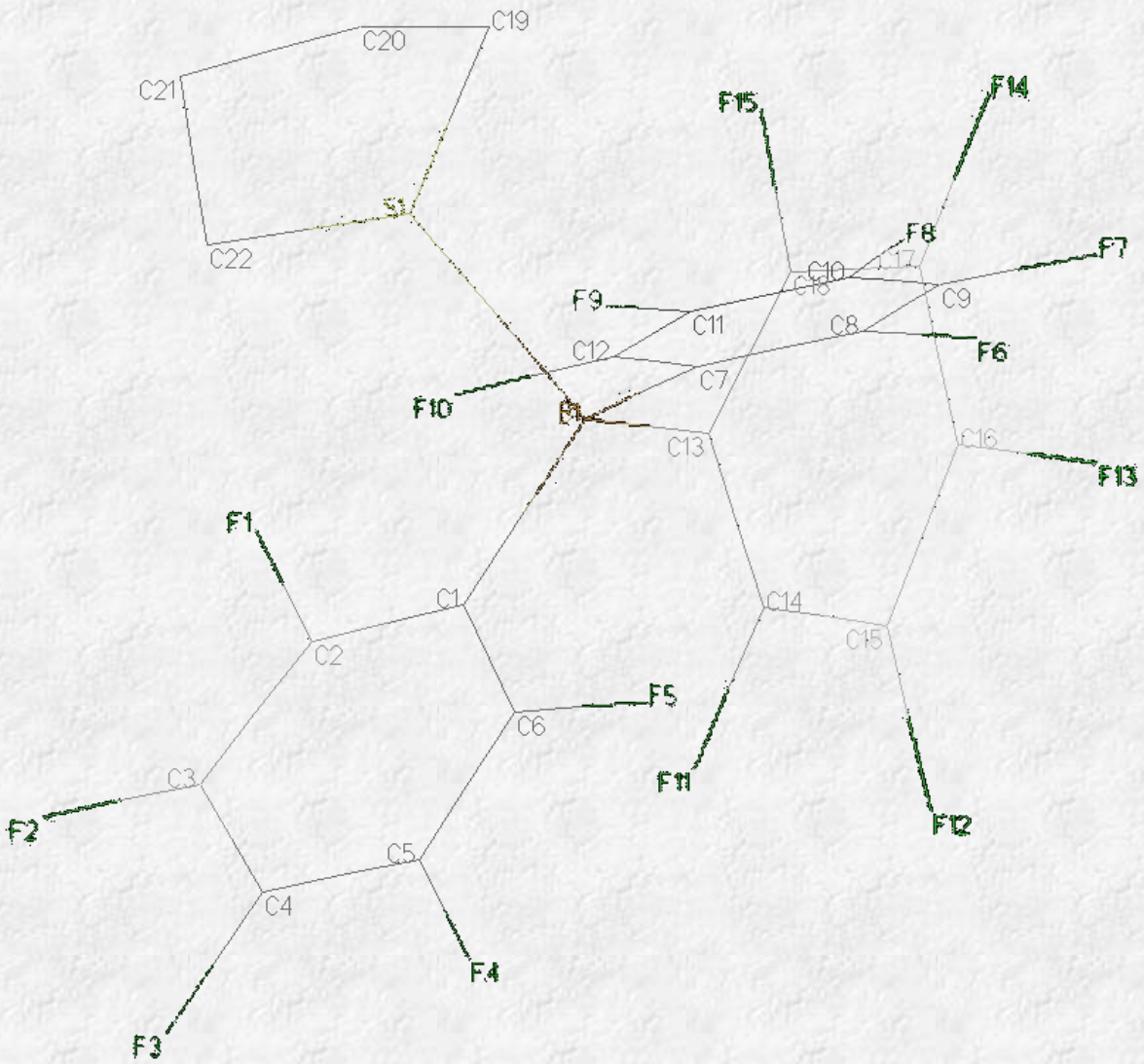
# Initial solution




Now you have to assign correct elements to the remaining electron densities:

- **Carbon**
- **Fluor**

# Initial solution

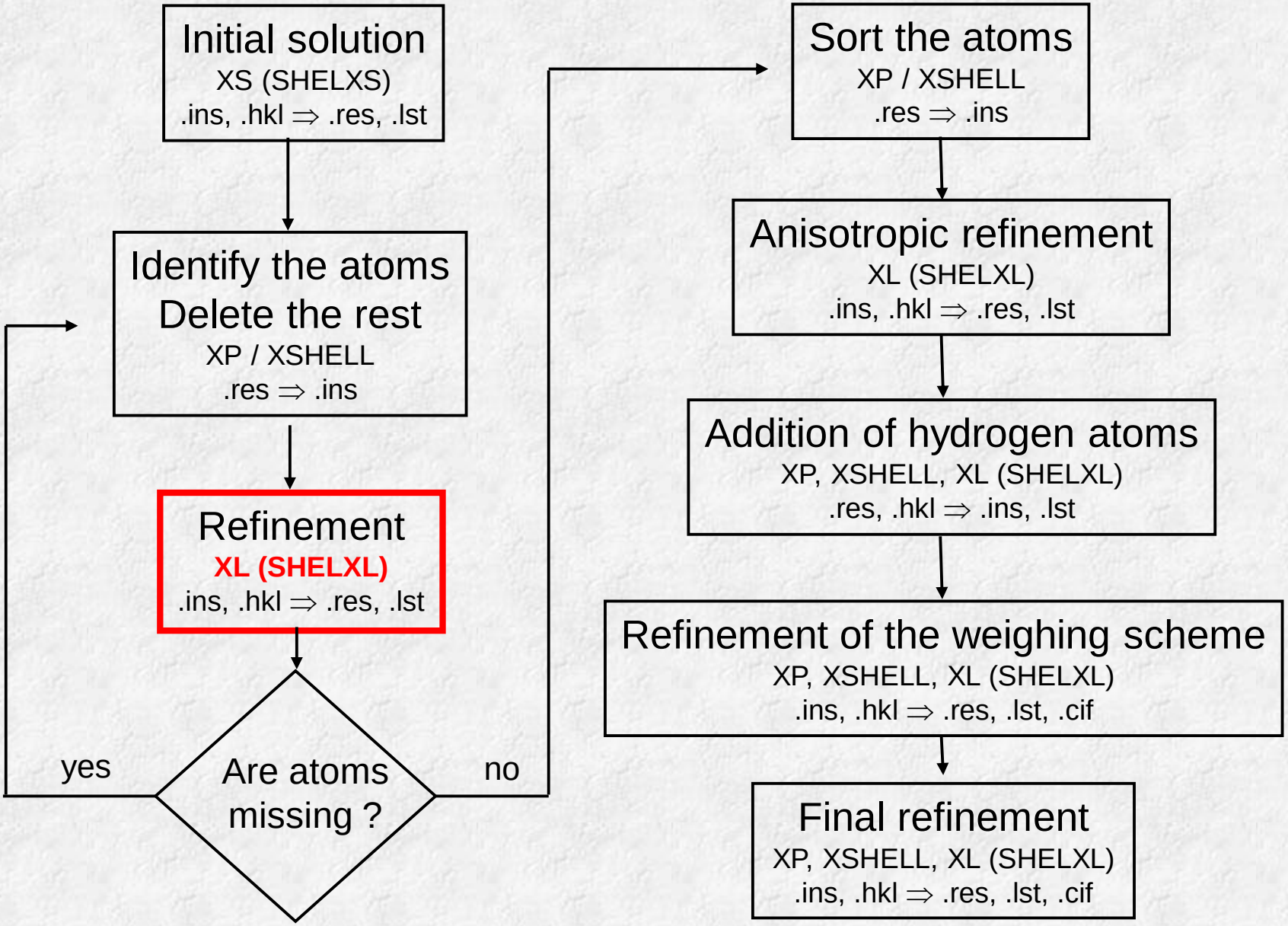



Now you have to assign correct elements to the remaining electron densities:

- **Carbon**
- **Fluor**
- **Boron**

**At the ends no Q-peaks must be left!**

# Refinement organigram



# Which parameters are refined?

Ins-file:

CELL 0.71073 8.1380 15.4444 15.1323 90 98.922 90

Sl1 4 0.16560 0.14717 0.71608 11.00000 0.03452

**Atom position**

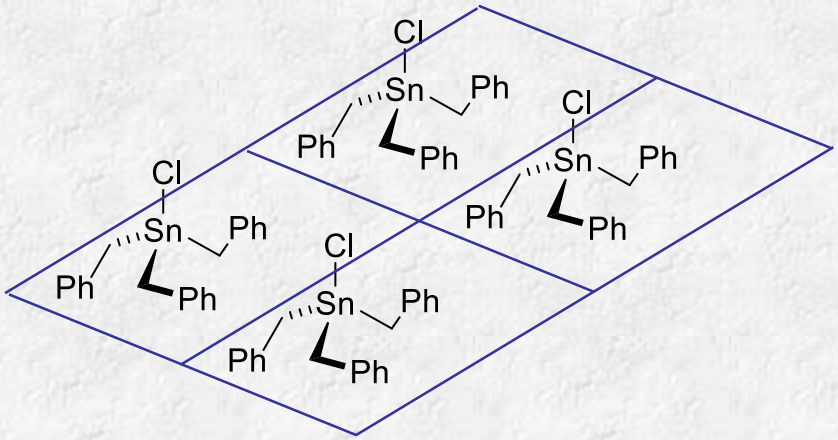
The atomic positions are given as fractions of the basis vectors. The values given are thus **not in Å** and Si1 is found at

***x* = *u*·*a*** = 0.16560·8.1380 Å = 1.3476 Å

***y* = *v*·*b*** = 0.14717·15.4444 Å = 2.2729 Å

***z* = *w*·*c*** = 0.71608·15.1323 Å = 10.836 Å

The **fractional atomic positions** are normally symbolized by the letters ***u*, *v* and *w***. Since each atom is present in the unit cell *u*, *v* and *w* have values between 0 and 1. For practical reasons, we find sometimes values <0 or >1, but never <-1 or >2.



# Which parameters are refined?

| | | | | | | |
|---|---|---|---|---|---|---|
| Sl1 | 4 | 0.16560 | 0.14717 | 0.71608 | 11.00000 | 0.03452 |

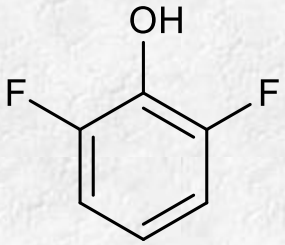
**Occupation factor**

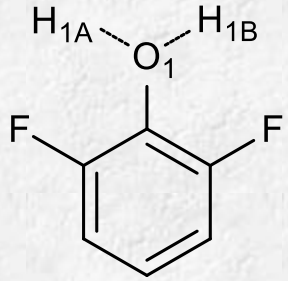
The occupation factor indicates how many atoms are occupying this position. The maximal occupation factor is 1, but in special cases, smaller numbers are possible.

- **Disorder**

Ins-file:

| | | | | | | |
|---|---|---|---|---|---|---|
| O1 | 3 | 0.12560 | 0.23453 | 0.83456 | 1**1.00000** | 0.02932 |
| H1A | 2 | 0.12864 | 0.23364 | 0.80236 | 1**0.50000** | 0.04732 |
| H2A | 2 | 0.12853 | 0.23923 | 0.85935 | 1**0.50000** | 0.04593 |



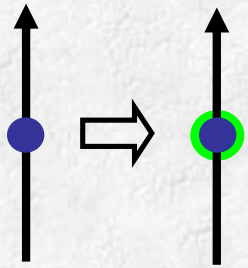
# Which parameters are refined?

Sl1 4 0.16560 0.14717 0.71608 **11.00000** 0.03452

**Occupation factor**

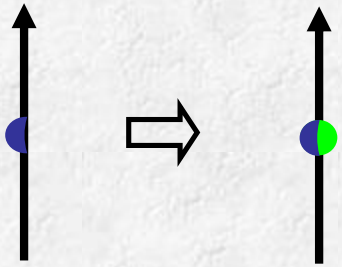
The occupation factor indicates how many atoms are occupying this position. The maximal occupation factor is 1, but in special cases, smaller numbers are possible.

- **Disorder**
- **Special positions**



**An atom on a symmetry element is duplicated on its position. To avoid this, the program would have to recognize and exclude atoms on special positions from some symmetry operations.**

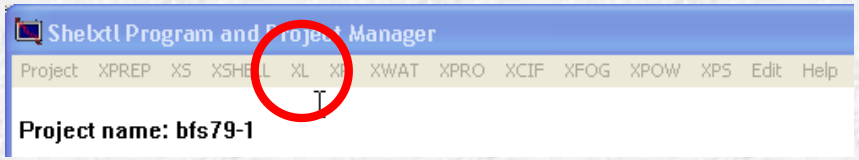
Sl1 4 0.25000 0.14717 0.25000 1**0.50000** 0.03452



**By applying an occupation factor of ½, the atom can be treated in the same way as all other atoms.**

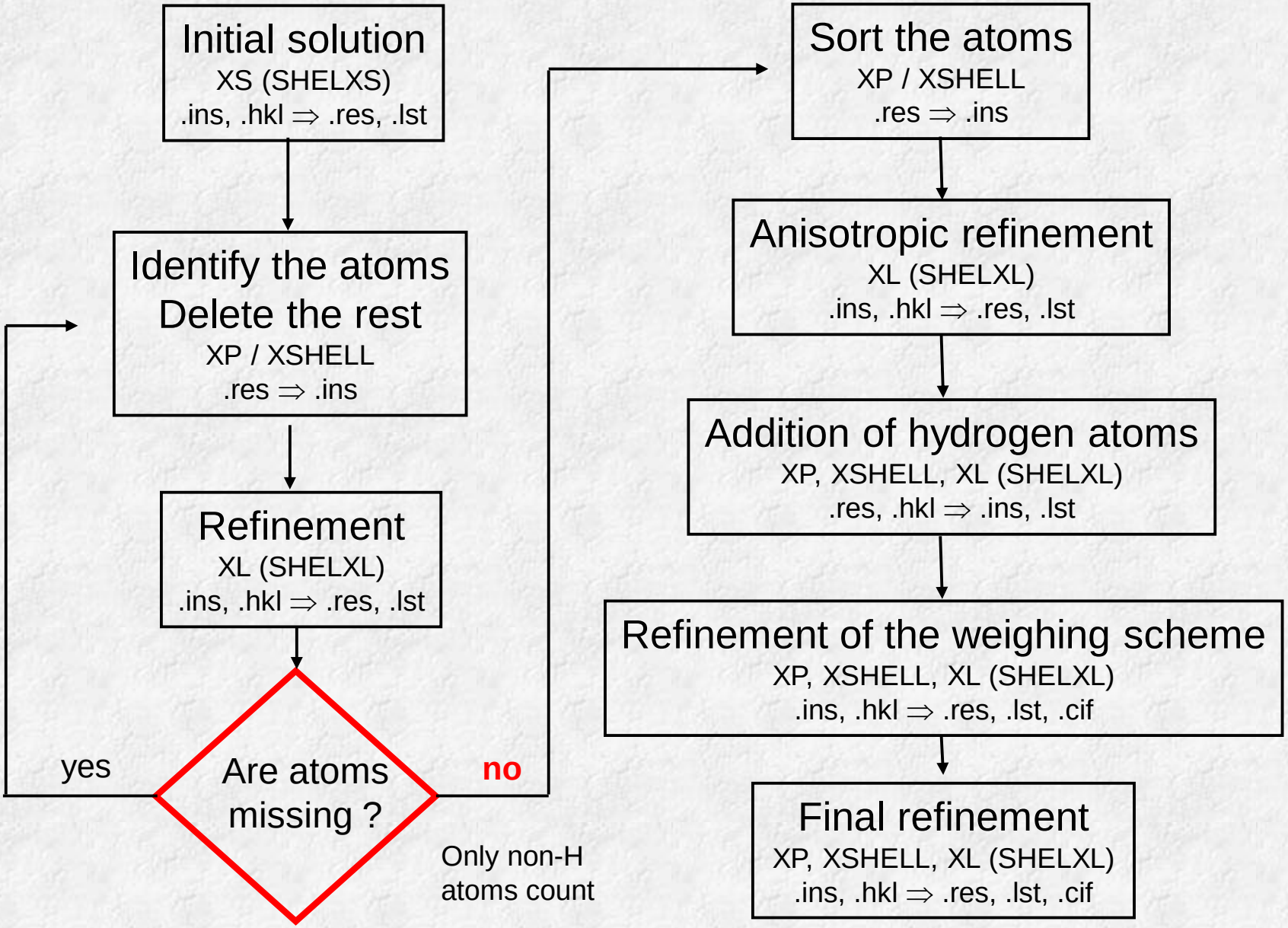
# Structure refinement

```
XP>> file bfs79

 Enter name of file from which instructions (includ
 copied [bfs79.res]:
 MOLE instruction needs to be added later by hand
 MOLE instruction needs to be added later by hand

XP>> quit_
```

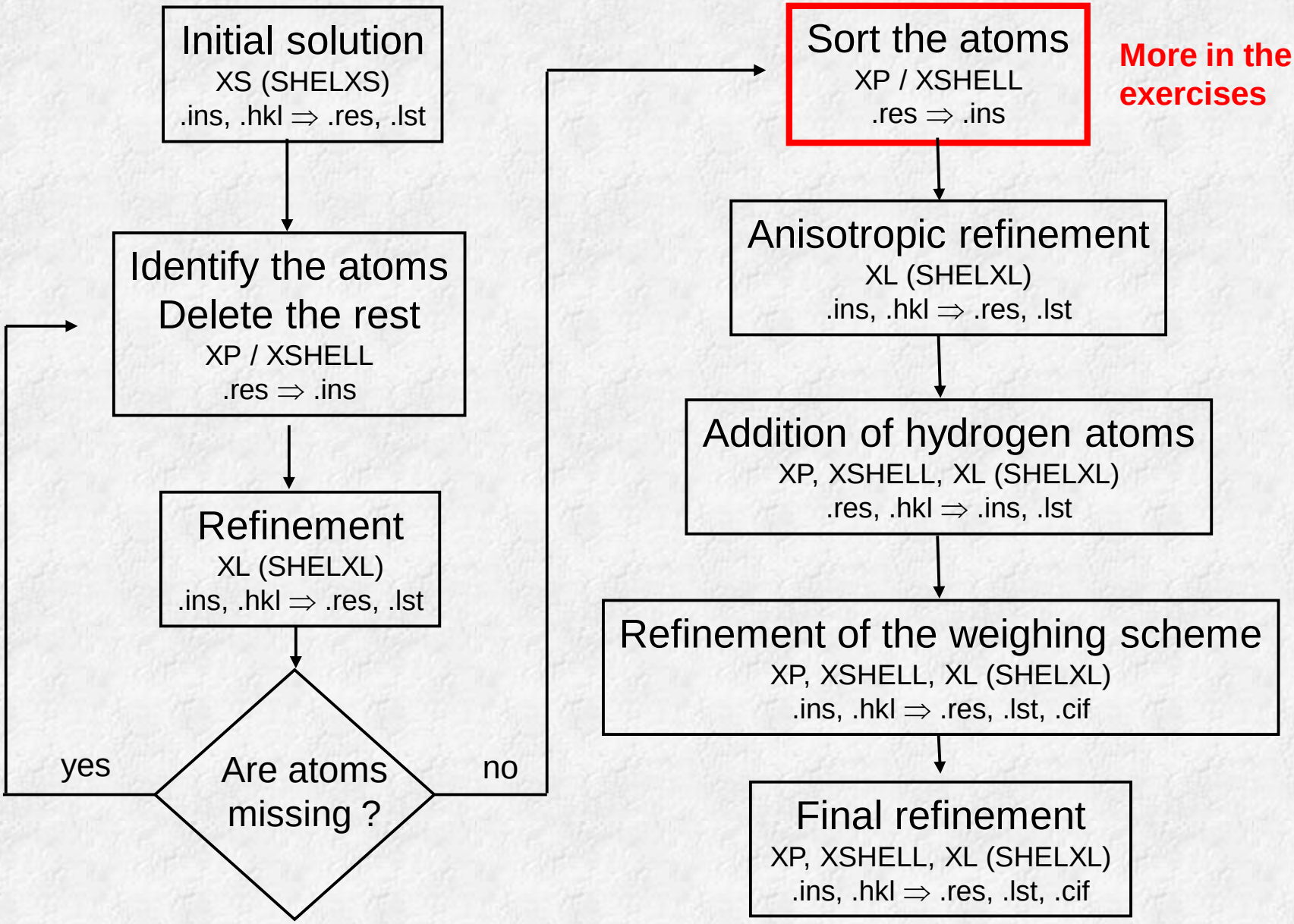



```
C:\WINDOWS\system32\cmd.exe
Max. shift = 0.033 A for C6       Max. dU =-0.013 for B1
wR2 =  0.5375 before cycle   2 for   4359 data and   157 /   157 parameters
GooF = S =      4.992;      Restrained GooF =      4.992  for       0 restraints
Mean shift/esd =   2.257    Maximum = -15.000 for  U11 S1          at 14:56:40
Max. shift = 0.034 A for C6       Max. dU =-0.012 for B1
wR2 =  0.4500 before cycle   3 for   4359 data and   157 /   157 parameters
GooF = S =      4.012;      Restrained GooF =      4.012  for       0 restraints
Mean shift/esd =   0.833    Maximum =   3.631 for  U11 F3          at 14:56:40
Max. shift = 0.015 A for F4       Max. dU = 0.004 for F3
wR2 =  0.4375 before cycle   4 for   4359 data and   157 /   157 parameters
GooF = S =      3.863;      Restrained GooF =      3.863  for       0 restraints
Mean shift/esd =   0.343    Maximum =   1.708 for  U11 F9          at 14:56:40
Max. shift = 0.006 A for C9       Max. dU = 0.002 for F9
wR2 =  0.4356 before cycle   5 for   4359 data and     0 /   157 parameters
GooF = S =      3.831;      Restrained GooF =      3.831  for       0 restraints
R1 =  0.1199 for   3938 Fo > 4sig(Fo)  and  0.1273 for all   4359 data
wR2 =  0.4356,  GooF = S =   3.831,  Restrained GooF =    3.831  for all data
R1 =  0.1270 for   4359 unique reflections after merging for Fourier
Highest peak    1.65  at  0.2299  0.0360  0.5193  [  0.57 A from F3 ]
Deepest hole   -1.84  at  0.1948  0.1040  0.5327  [  0.60 A from F3 ]

++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++
+  BFS79          finished at 14:56:41   Total elapsed time:        3.0 secs  +
++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++
Appuyez sur une touche pour continuer...
```

# Refinement organigram

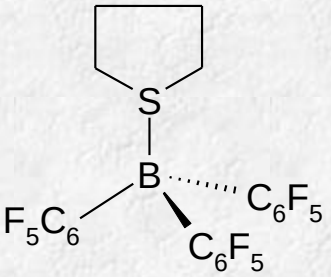


# Refinement organigram



# Atom numbering and order

Each atom has a label consisting out of its element symbol and a number

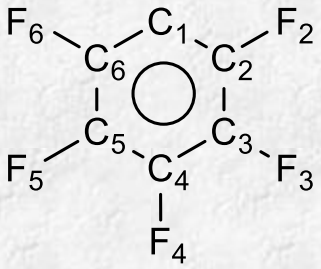



**Numbering: Two strategies**

1. The labels of each atoms start with the number 1 : ⇦
   S**1**, B**1**, F**1**…F**15**, C**1**..C**22**
2. One starts the first atom with 1 and continues counting regardless the element:
   S**1**, B**2**, F**3**…F**17**, C**18**..C**39**

**Some remarks** (in decreasing importance)**:**

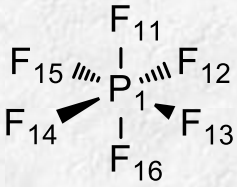
- Always use a number, even if there is only one atom present. Thus, **S1, not S**
- Follow the numbering of similar structures in your group.
- You can jump numbers to help understanding, **but do not overdo it**. Avoid numbers >100.

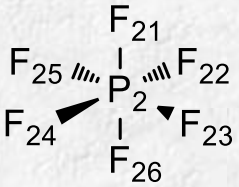


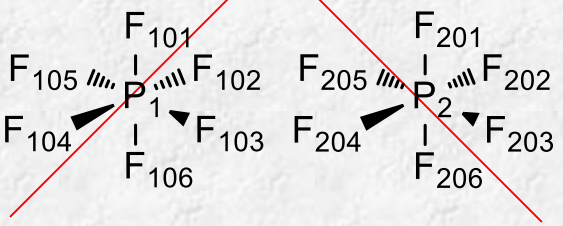

C1-C18,
F2-F6,
F8-F12,
F14-F18

C11-C16, F12-F16
C21-C26, F22-F26
C31-C36, F32-F36

C101-C106, F102-F106
C201-C206, F202-F206
C301-C306, F302-F306

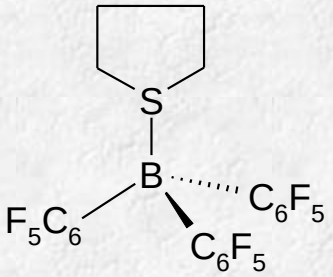


# Atom numbering and order

Each atom has a label consisting out of its element symbol and a number

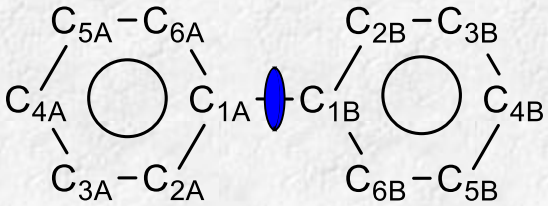


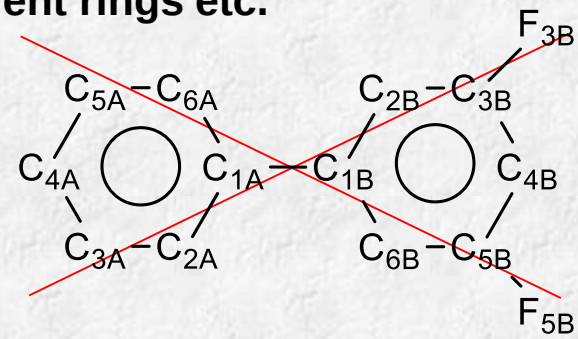

**Numbering: Two strategies**

1. The labels of each atoms start with the number 1 : S**1**, B**1**, F**1**…F**15**, C**1**..C**22**
2. One starts the first atom with 1 and continues counting regardless the element: S**1**, B**2**, F**3**…F**17**, C**18**..C**39**

**Some remarks** (in decreasing importance)**:**

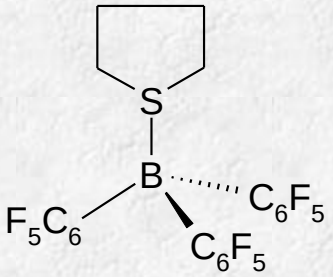
- Always use a number, even if there is only one atom present. Thus, **S1, not S**
- Follow the numbering of similar structures in your group.
- You can jump numbers to help understanding, **but do not overdo it**. Avoid numbers >100.
- Try to number cycles and chaines consecutively.
- If possible, try to follow “organic” numbering rules.
- **Do not use symbols such as: # * ‘ $ etc.**
- **The use of letters (C15A, C15B) is reserved for atoms which are identical by symmetry or disorder. Do not use them for different rings etc.**



# Atom numbering and order

Each atom has a label consisting out of its element symbol and a number




**Numbering: Two strategies**

1. The labels of each atoms start with the number 1 : ⇦
   S**1**, B**1**, F**1**…F**15**, C**1**..C**22**
2. One starts the first atom with 1 and continues counting regardless the element:
   S**1**, B**2**, F**3**…F**17**, C**18**..C**39**

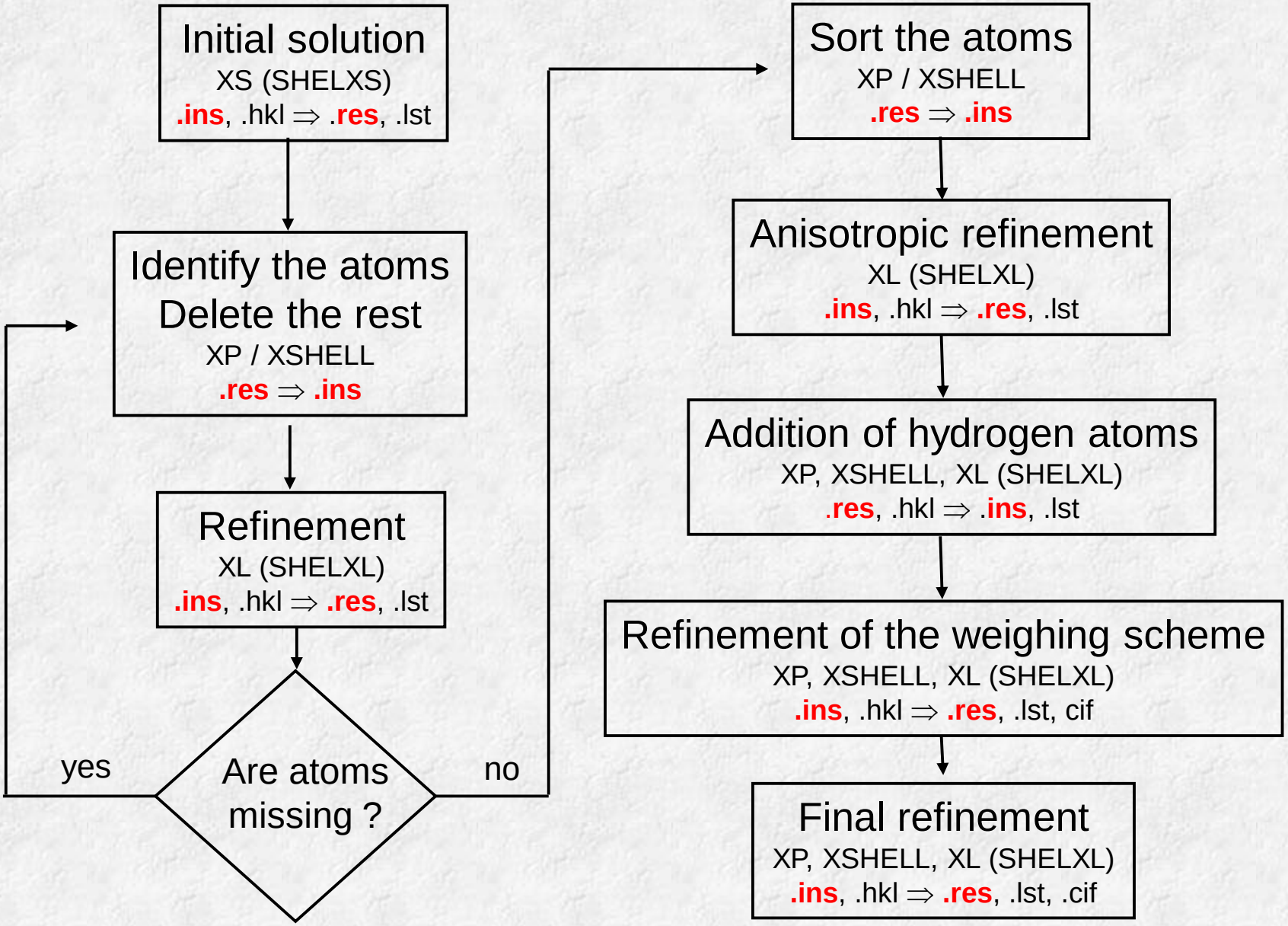
**Some remarks** (in decreasing importance)**:**

- Always use a number, even if there is only one atom present. Thus, **S1, not S**
- Follow the numbering of similar structures in your group.
- You can jump numbers to help understanding, **but do not overdo it**. Avoid numbers >100.
- Try to number cycles and chaines consecutively.
- If possible, try to follow “organic” numbering rules.
- **Do not use symbols such as: # * ‘ $ etc.**
- **The use of letters (C15A, C15B) is reserved for atoms which are identical by symmetry or disorder. Do not use them for different rings etc.**

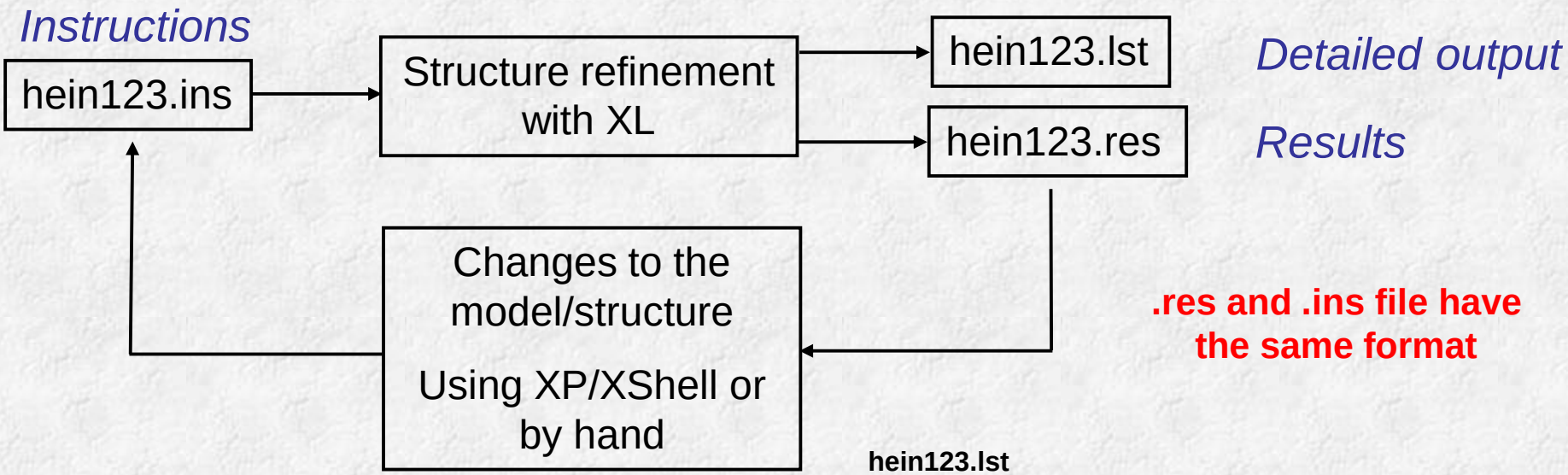
**Sorting atoms:**

- It is preferable to group atoms into the respective molecuels, e. g. cation, anion 1, anion 2, solvant
- Sort the elements first after their elements, then after their number, the heavy elements first. E. g. triflate : S1, F1, F2, F3, O1, O2, O3, C1

# A short detour: The res/ins file



# A short detour: The res/ins file




**.res and .ins file have the same format**

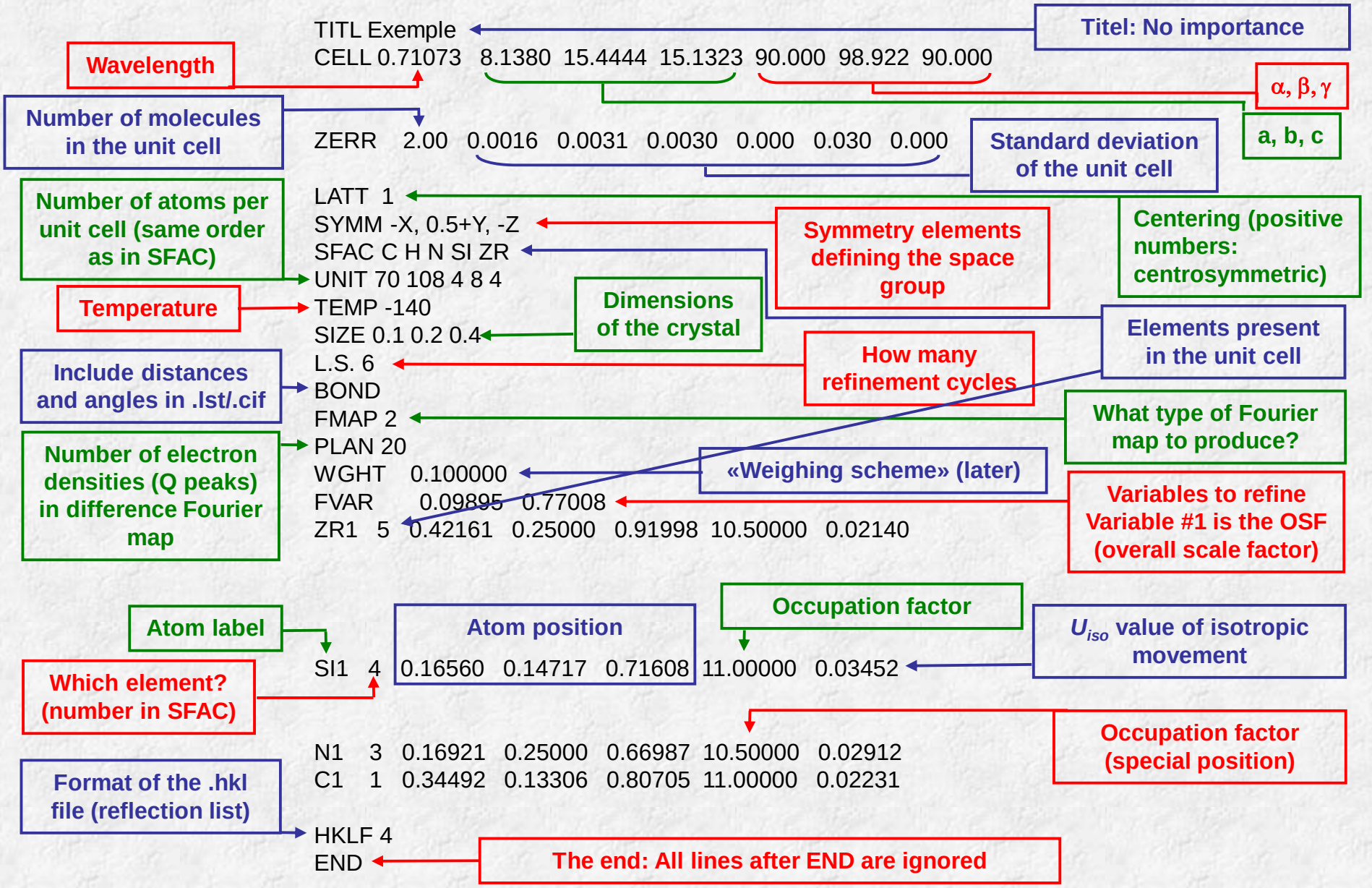
**hein123.res/hein123.ins**

```
TITL Hein123
CELL 0.71073   8.1380  15.4444  15.1323  90.000  98.922  90.000
ZERR    2.00   0.0016   0.0031   0.0030   0.000   0.030   0.000
LATT  1
SYMM -X, 0.5+Y, -Z
SFAC C H N SI ZR
UNIT 70 108 4 8 4
L.S. 6
WGHT    0.100000
FVAR       0.09895
ZR1   5   0.42161   0.25000   0.91998  10.50000   0.02140
SI1   4   0.16560   0.14717   0.71608  11.00000   0.03452
N1    3   0.16921   0.25000   0.66987  10.50000   0.02912
C1    1   0.34492   0.13306   0.80705  11.00000   0.02231
…
HKLF 4
END
```

**hein123.lst**

```
 50091  Reflections read, of which 26152  rejected

     39  Systematic absence violations
      0  Inconsistent equivalents
   4013  Unique reflections, of which      0  suppressed
R(int) = 0.0363     R(sigma) = 0.0207

Least-squares cycle   1
 wR2 =  0.4060 before cycle   1 for   4013 data and   189 /
189 parameters,  GooF = S =     7.187;     Restrained
GooF =      7.187  for      0 restraints

N      value       esd    shift/esd  parameter
    1     0.36649     0.00352  -210.419    OSF
    2     0.00205     0.00032     2.885   EXTI
    5     0.02660     0.00068     3.314    U22 Zr1
 Mean shift/esd =   1.629    Maximum =-210.419 for  OSF
 Max. shift = 0.029 A for C25      Max. dU = 0.003 for C14
```

# A short detour: Fichier *.res / fichier *.ins



# Thermal motion of atoms / Temperature factor

| | | Atom position | | | Occupation factor | $U_{iso}$ |
|---|---|---|---|---|---|---|
| Sl1 | 4 | 0.16560 | 0.14717 | 0.71608 | 11.00000 | 0.03452 |

**$U_{iso}$ ?**

- The distribution of the electronic density depends on the thermal motion of the atoms
- Thermal motion is not identical for all atoms
- An X-ray experiment takes significantly more time than thermal motion

⇒ **we obtain an averaged distribution of the electron density**

**Isotropic motion:**

- The vibration of an atom is identical in all directions
- It is described by a Gaussian function

$$\rho(r') = \sqrt{2\pi U}\, e^{\frac{-r'^2}{2U}}$$

$\rho$ : distribution of the electron density

$r'$ : distance from the equilibrium position

# Thermal motion of atoms

**Fourier transformation:**

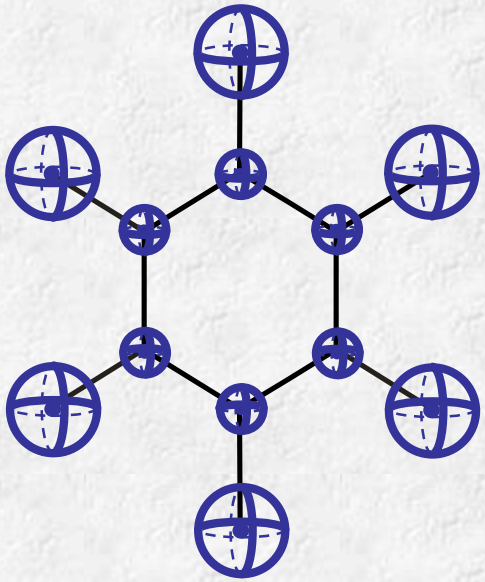
$$q(r^*) = e^{-2\pi^2 U r^*} = e^{-8\pi^2 U \frac{\sin^2\theta}{\lambda^2}} = e^{-B\frac{\sin^2\theta}{\lambda^2}}$$

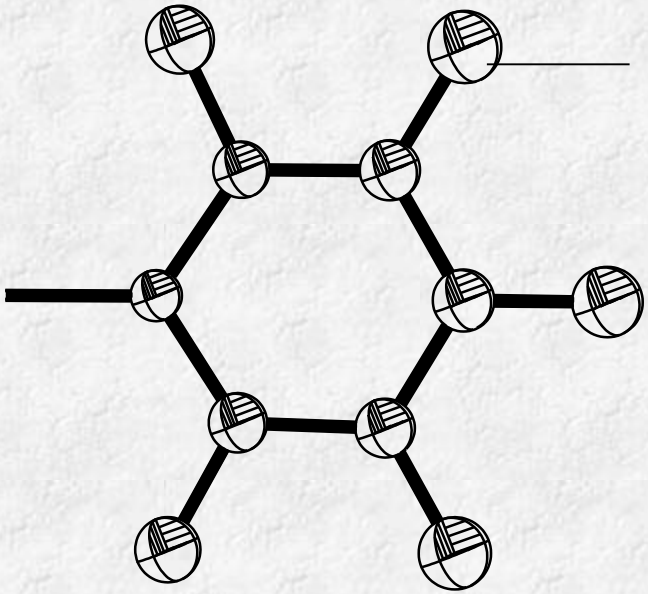
$$U = \langle r'^2 \rangle \quad [\text{Å}^2]$$

Average squared displacement

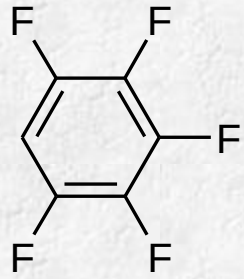
$$B = 8\pi^2 U \quad [\text{Å}^2]$$

Atomic temperature factor
(Debye-Waller factor)





x% probability that the atom is found inside the radius of the indicated sphere

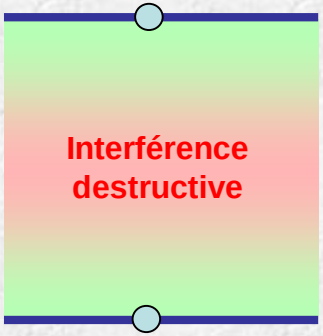


# Thermal motion of atoms

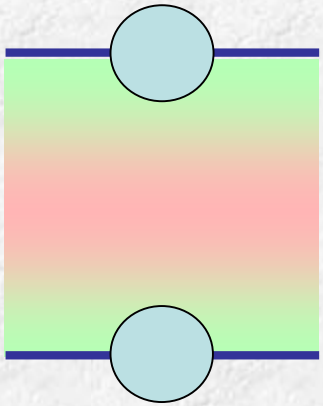
**Fourier transformation:**

$$q(r^*) = e^{-2\pi^2 U r^*} = e^{-8\pi^2 U \frac{\sin^2\theta}{\lambda^2}} = e^{-B\frac{\sin^2\theta}{\lambda^2}}$$

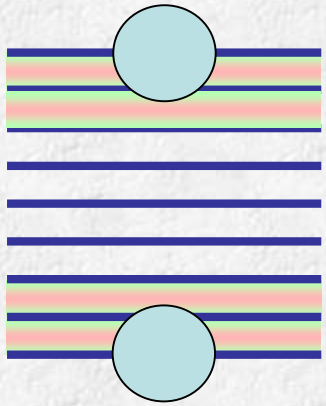
**More pronounced for reflections at high θ**




$(I_{100})^{1/2} = f^2$



$(I_{100})^{1/2} = 0.5f + 0.5f \cdot \sin 20°$



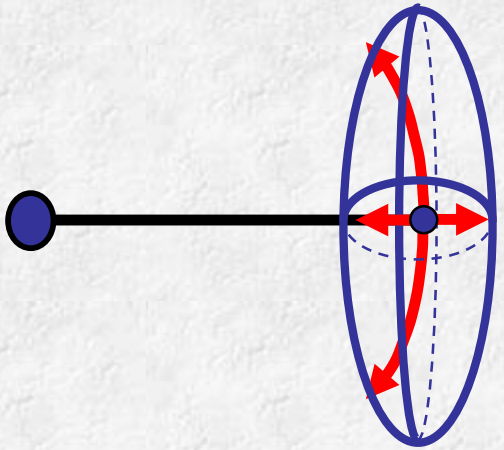
$(I_{800})^{1/2} = 0.5f + 0.5f \cdot \sin 180° = 0$

Another reason why reflection intensities decrease at high theta angles. (What was the first one ?)

# Thermal motion of atoms

**Anisotropic motion:**

- The atomic motion is not isotropic, i. e. identical in all directions.



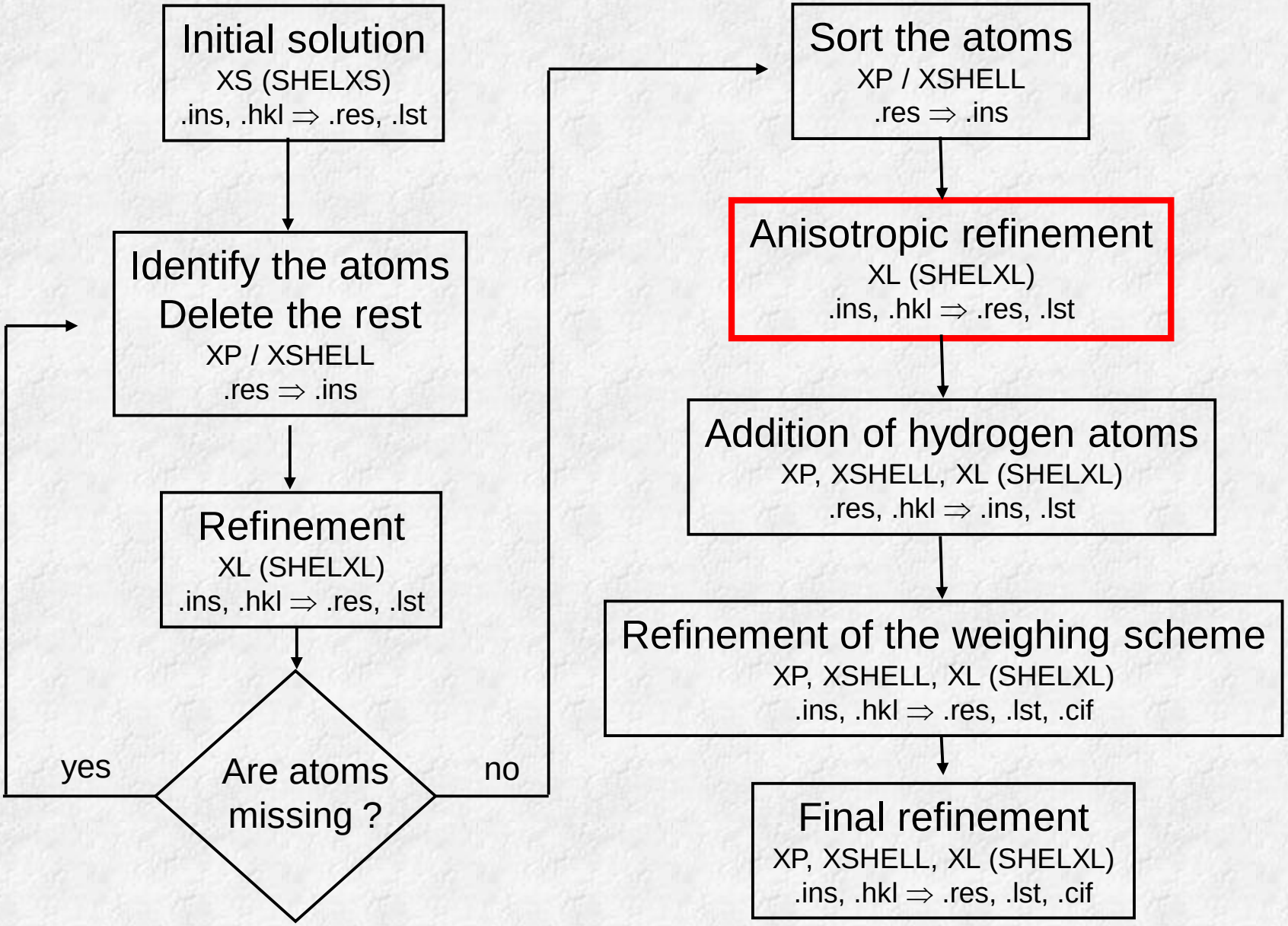
- It is described in our model by an ellipsoid (different Gaussian functions in three dimensions) or, mathematically speaking, by a symmetric tensor:

$$U = \begin{pmatrix} \langle x'^2 \rangle & \langle x'y' \rangle & \langle x'z' \rangle \\ \langle x'y' \rangle & \langle y'^2 \rangle & \langle y'z' \rangle \\ \langle x'z' \rangle & \langle y'z' \rangle & \langle z'^2 \rangle \end{pmatrix}$$

- Instead of **1 parameter ($U_{iso}$)** we require **6 parameters for the ellipsoid** (3 radii and the direction of the principal axis).

$$q(r^*) = e^{-2\pi^2(U_{11}x'^2 + U_{22}y'^2 + U_{33}z'^2 + 2U_{12}x'y' + 2U_{13}x'z' + 2U_{23}y'z')}$$

# Refinement organigram



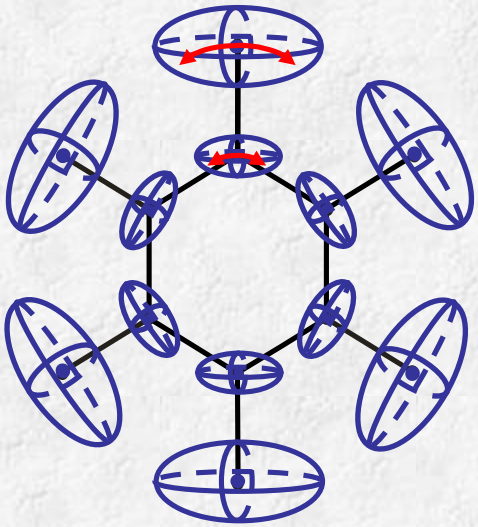
# Thermal motion of atoms

***.ins:**

```
ANIS
WGHT    0.100000
FVAR       0.71880
S1    5    0.277586    0.724064    0.718741    11.00000    0.02858
B1    3    0.366643    0.625301    0.823380    11.00000    0.02507
F1    4    0.079477    0.474487    0.653317    11.00000    0.03965
```

***.res:**

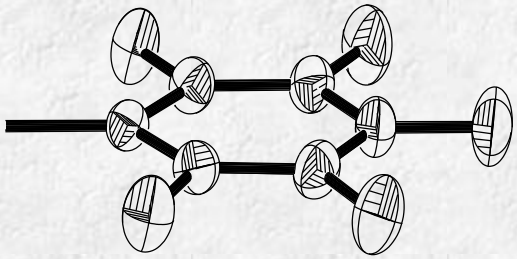
```
WGHT    0.100000
FVAR       0.73527
S1    5    0.277751    0.724339    0.718759    11.00000    0.03304    0.02854 =
        0.02460    0.01056    0.00663    0.01163
B1    3    0.366302    0.625285    0.823440    11.00000    0.02772    0.02171 =
        0.02300    0.00834    0.00485    0.00625
F1    4    0.079086    0.473686    0.653072    11.00000    0.02849    0.03982 =
        0.04679    0.01366    0.00319    0.00667
```

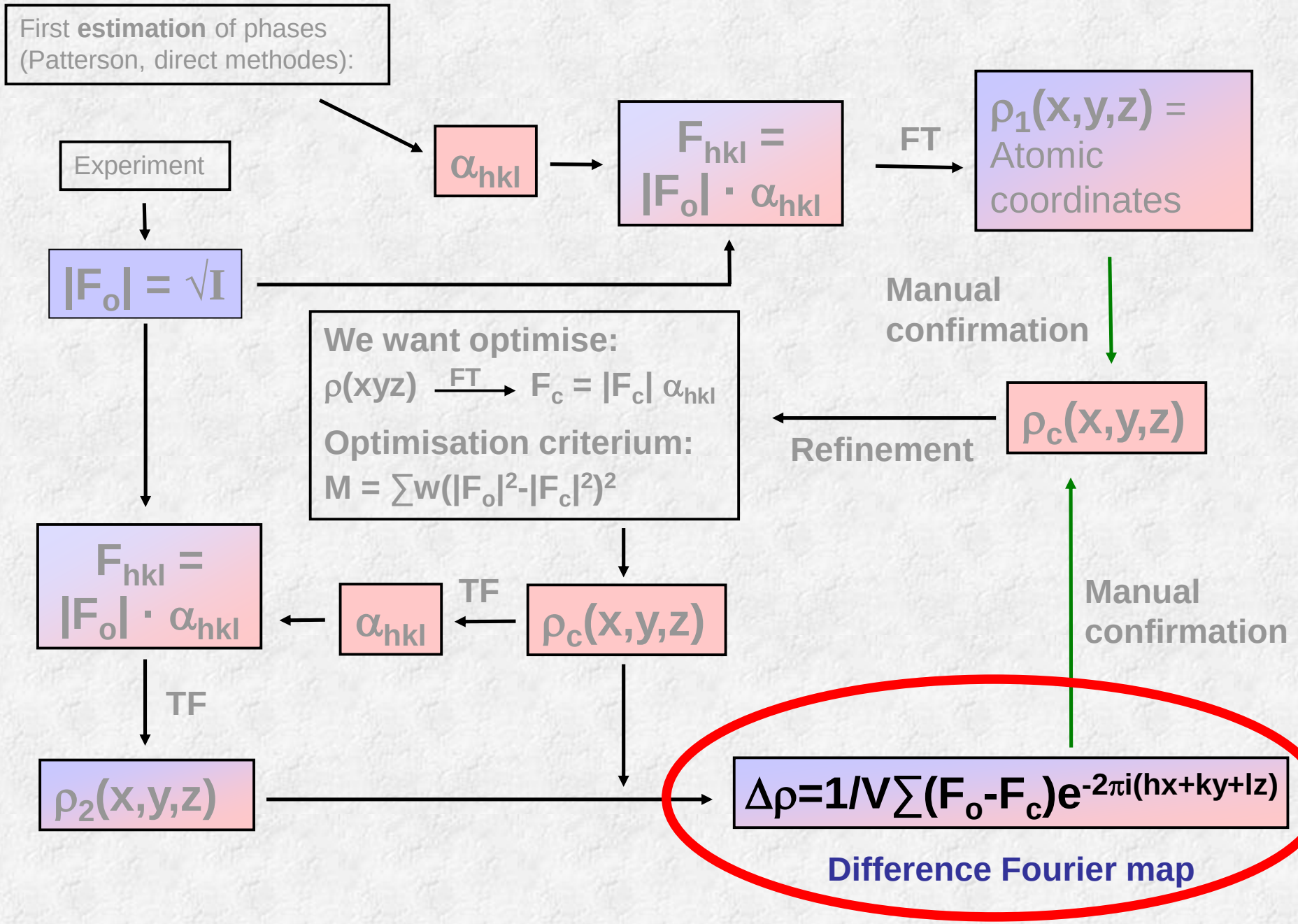


$U_{eq}$: is the equivalent $U_{iso}$ value giving the same volume, calculated for comparison

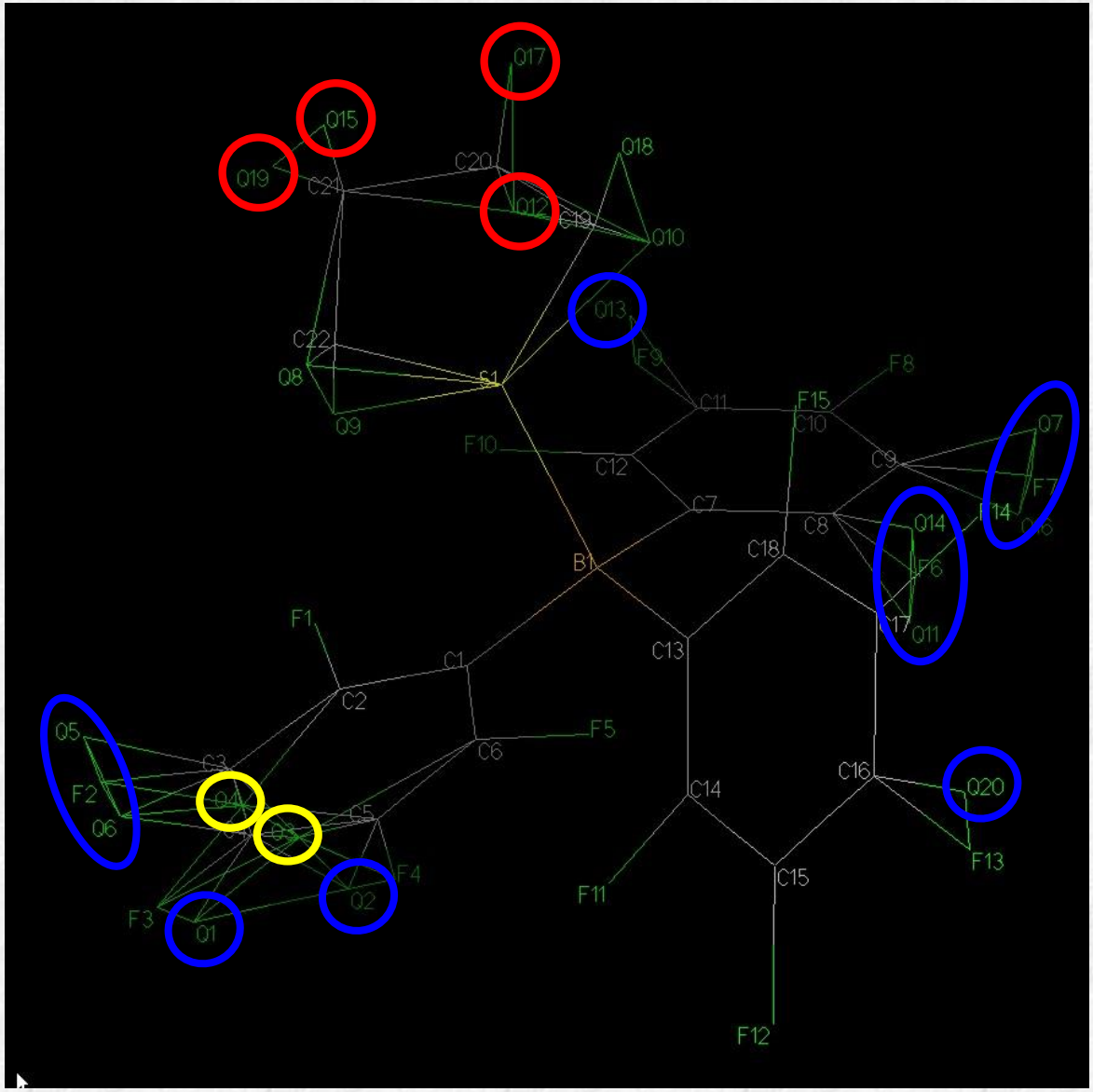
**Typical $U_{iso}$ values:**

| | |
|---|---|
| Heavy atoms: | 0.005-0.02 Å$^2$ |
| Light atoms (H-F): | 0.01-0.06 Å$^2$ |
| Terminal atoms: | 0.03-0.2 Å$^2$ |




First **estimation** of phases (Patterson, direct methodes):
Experiment
$|F_o| = \sqrt{I}$
$\alpha_{hkl}$
$F_{hkl} = |F_o| \cdot \alpha_{hkl}$
FT
$\rho_1(x,y,z)$ = Atomic coordinates
Manual confirmation
$\rho_c(x,y,z)$
Refinement
We want optimise:
$\rho(xyz) \xrightarrow{FT} F_c = |F_c| \alpha_{hkl}$
Optimisation criterium:
$M = \sum w(|F_o|^2-|F_c|^2)^2$
$\rho_c(x,y,z)$
TF
$\alpha_{hkl}$
$F_{hkl} = |F_o| \cdot \alpha_{hkl}$
TF
$\rho_2(x,y,z)$
Manual confirmation
$\Delta\rho=1/V\sum(F_o-F_c)e^{-2\pi i(hx+ky+lz)}$
Difference Fourier map

# Difference Fourier map



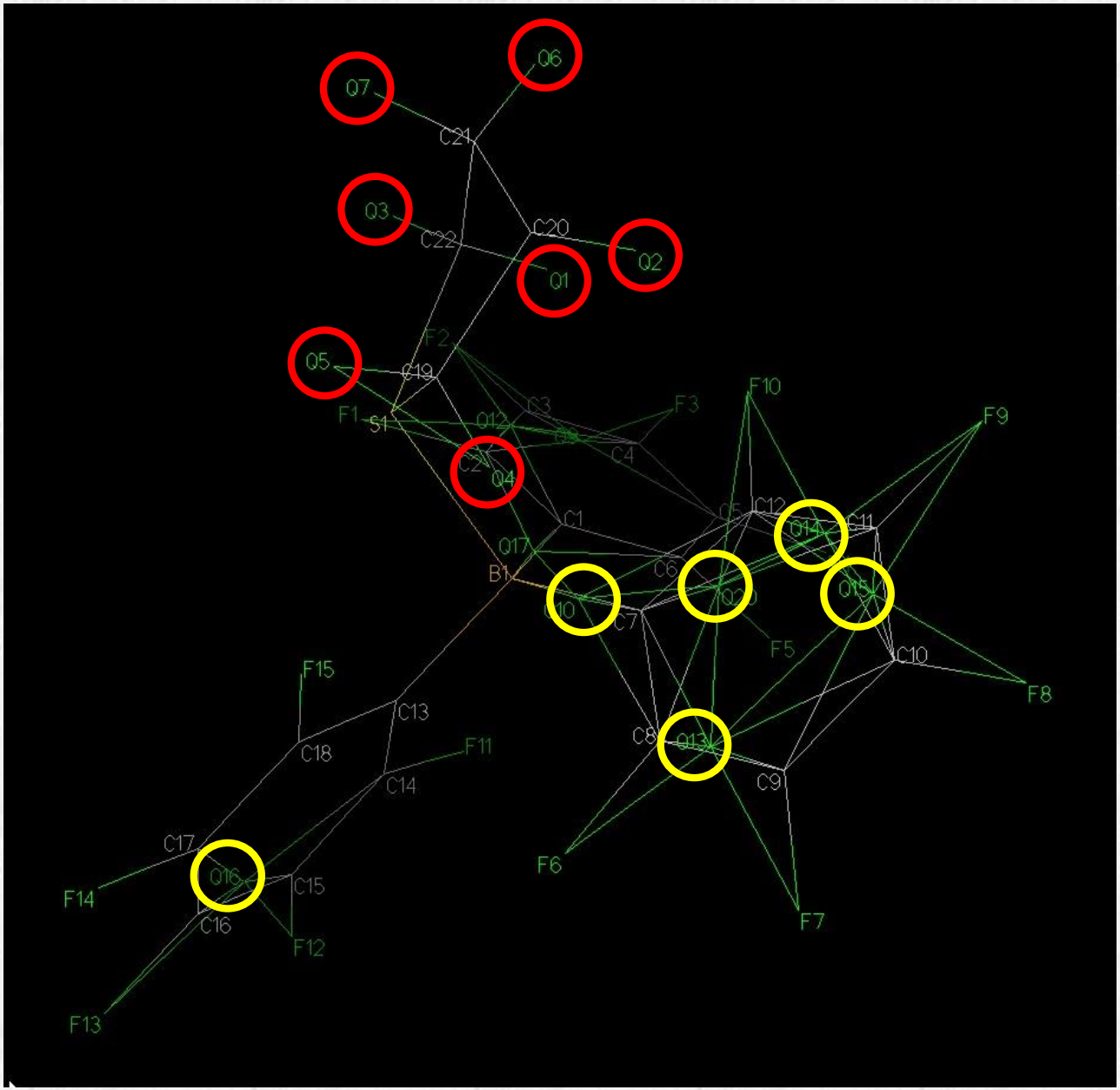

The refinement result does not show any new atoms.

There are no missing atoms

The remaining peaks can be attributed to:

- **Thermal motion of atoms**
- **Hydrogen atoms**
- **Errors**

# Difference Fourier map

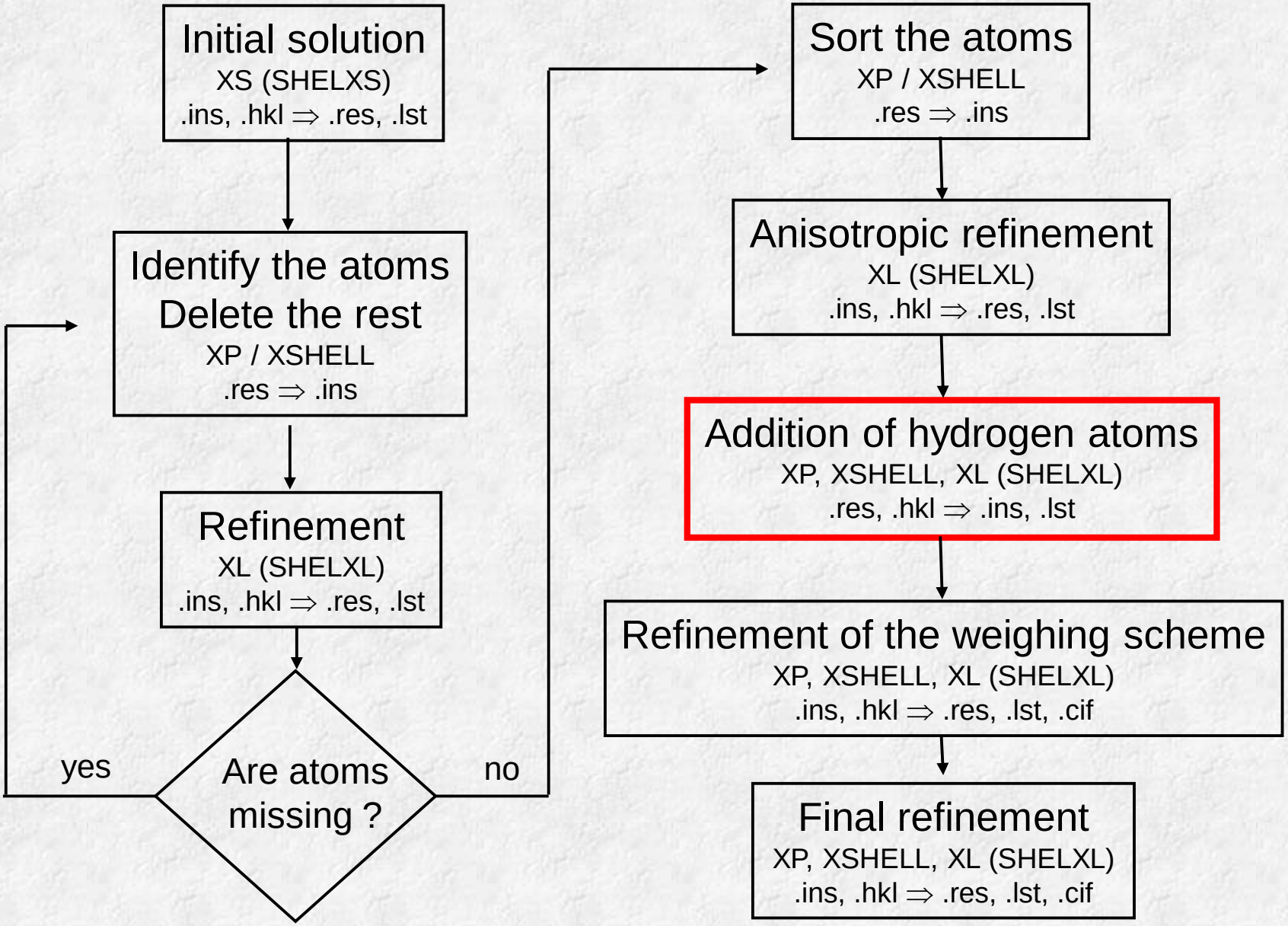



**After anisotropic refinement**:
Les pics restants peut être attribués aux:

- ~~**Thermal motion of atoms**~~
- **Hydrogen atoms**
- **Errors**

**The 8 highest Q-peaks (Q1-Q8) correspond to hydrogen atoms!**

# Refinement organigram



# Constraints and restraints

**Constraint:** Exact mathematical condition, which results in a reduction of the number of parameters. A constraint cannot be violated. Example: rigid groups and “riding” hydrogen atoms.

**Restraint:** Additional observations/restraints which are added to the data during refinement. Restraints can be violated to a certain degree.

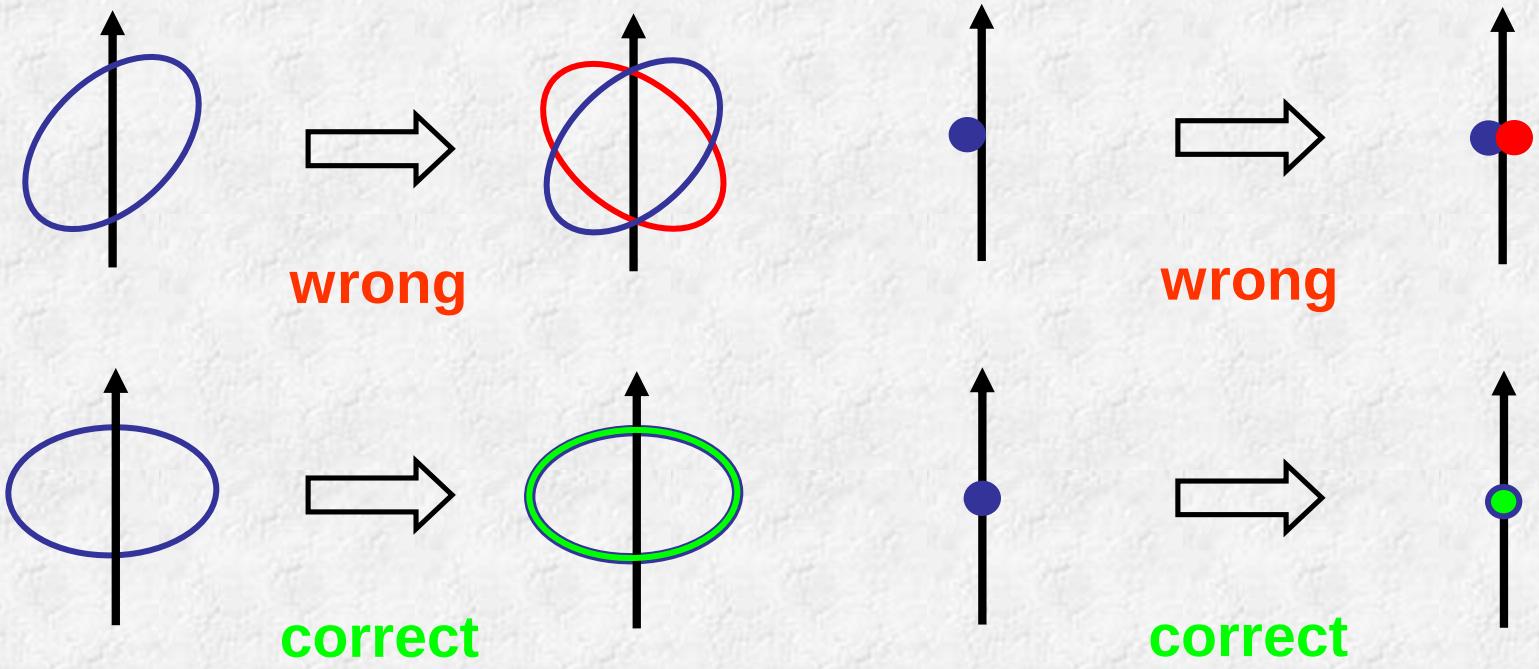
$$M = \sum w_x(F_o^2 - F_c^2)^2 + \sum w_r(T_{target} - T_c)^2$$

**Both, constraints and restraints increase the data/parameter ratio.**

# Types of constraints used in the SHELX program package

- **Special positions** (generated automatically)

**These constraints, which are necessary for atoms positioned on symmetry elements, are automatically generated by the program.**




File *.lst:

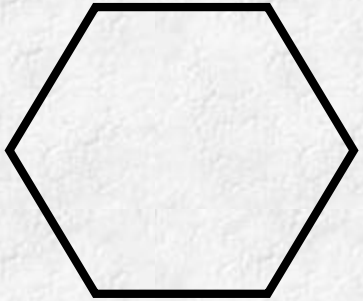
**Special position constraints for Zr1**

**x = 0.0000 z = 0.2500 U23 = 0 U12 = 0 sof = 0.50000**

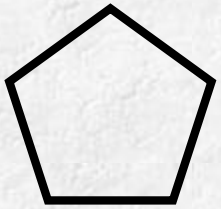
# Types of constraints used in the SHELX program package

- **Special positions** (generated automatically)
- **Rigid groups (e. g. AFIX x6 … AFIX 0)**

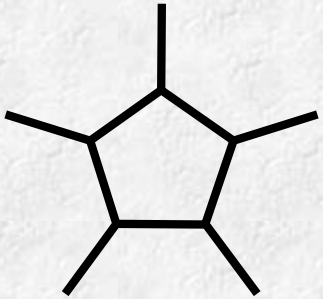
In rigid groups the parameters for all atomic positions (3 x n) are replaced by 3 rotations and 3 translations for the complete group. The idealized geometry of the group is fixed and the atoms cannot move independently. *AFIX x**6***: completely rigid group; *AFIX x**9***: group can grow and shrink keeping its relative geometry.



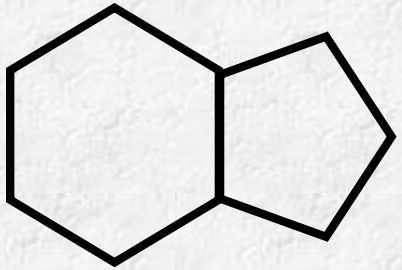
**AFIX 66**
**C1 x y z**
**:**
**C6 x y z**
**AFIX 0**



**AFIX 56**
**C1 x y z**
**:**
**C5 x y z**
**AFIX 0**



**AFIX 106**
**C1 x y z**
**:**
**C10 x y z**
**AFIX 0**



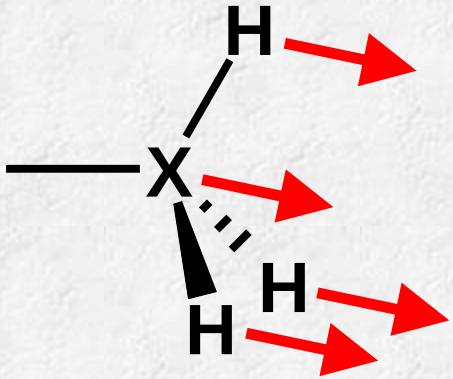
**AFIX 116**
**C1 x y z**
**:**
**C11 x y z**
**AFIX 0**

# Types of constraints used in the SHELX program package

- **Special positions** (generated automatically)
- **Rigid groups (e. g. AFIX x6 … AFIX 0)**
- **"Riding model" for hydrogen atoms (AFIX mn)**

$$xH = xC + \Delta x$$
$$yH = yC + \Delta y$$
$$zH = zC + \Delta z$$
$$U_H = 1.2 \cdot U_X$$

No additional parameters are refined for the hydrogen atoms, if they are treated by a riding model!



# Types of constraints used in the SHELX program package

- **Special positions** (generated automatically)
- **Rigid groups (e. g. AFIX x6 … AFIX 0)**
- **“Riding model” for hydrogen atoms (AFIX mn)**
- **Fixed parameters**

Addition of 10 excludes a value from the refinement.

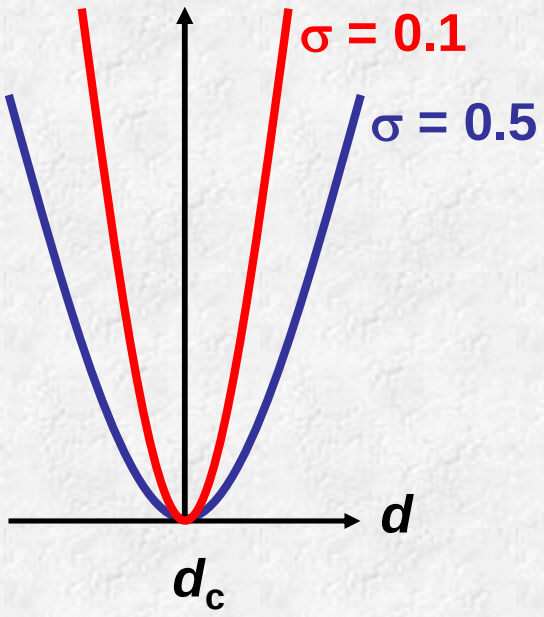
Normally occupation factors are not refined.

```
C1    1   0.31357   0.46194   0.73087  11.00000   0.03221   0.02339 =
       0.02334   0.00728   0.00820   0.00568
C2    1   0.17696   0.50000   0.65307  10.50000   0.03174   0.02909 =
       0.02961   0.01051   0.00909   0.00550
C3    1   0.13022   0.26106   0.57225  11.00000   0.03871   0.02965 =
       0.03073   0.00631   0.00674  -0.00625
```

(The program adds automatically the constraints for atoms on special positions.)

# Types of constraints used in the SHELX program package

In contrast to constraints, which cannot be violated, restraints define only a target value for some parameters. They are associated with a standard deviation σ, which describes how much a violation of the target value is penalised. The smaller σ, the more the parameter is forced to be close to the targeted value $d_c$. A σ = 0 yields a constraint.




$$M = \Sigma\, w_x(F_o^2 - F_c^2)^2 + \Sigma\, 1/\sigma\,(d - d_c)^2$$

**Restraints in SHELX**

**DFIX, DANG, SADI, SAME:** distances and angles (1,3-distances)

**DELU, SIMU, ISOR:** thermal motion parameters

**FLAT, CHIV, BUMP, NCSY, SUMP**

# Free variables

In SHELXL, each value is provided in the form of ***x* = 10*m* + *p*.**

*p*: value, which is refined; *m*: refinement mode

***m* = 0: normal refinement, *x* = *p***

***m* = 1: no refinement, *x* is fixed at *p***

**Values fixed at 1.0000**

```
C1    1   0.31357   0.46194   0.73087  11.00000    0.03221
C2    1   0.17696   0.39844   0.65307  11.00000   10.035
C3    1   0.13022   0.26106   0.57225  11.00000   10.035
CL1   2   0.25000   0.17682   0.50000  10.50000    0.05684
Br1   3   0.25000   0.19763   0.50000  10.50000    0.05110
```

**Values fixed at 0.035**

**Values fixed at 0.5000**

- We can exclude any value from refinement by adding 10.
- For atoms on special positions, the program does this automatically without our intervention.

```
C1    1   0.31357   0.46194   0.73087  11.00000    0.03221
C2    1   0.17696   0.39844   0.65307  11.00000   10.035
C3    1   0.13022   0.26106   0.57225  11.00000   10.035
CL1   2  10.25000   0.17682  10.50000  10.50000    0.05684
Br1   3  10.25000   0.19763  10.50000  10.50000    0.05110
```

# Free variables

In SHELXL, each value is provided in the form of ***x* = 10*m* + *p***.

*p*: value, which is refined; *m*: refinement mode

***m* = 0: normal refinement, *x* = *p***

***m* = 1: no refinement, *x* is fixed at *p***

***m* > 1: *x* = *p*·"free variable no. *m*"**

***m* <-1: *x* = *p*·(1 - "free variable no. *m*")**

**The same value is refined for all three atoms**

```
FVAR          0.73503  0.0239   0.2365
C1     1    0.31357    0.46194    0.73087   11.00000    21.00000
C2     1    0.17696    0.39844    0.65307   11.00000    21.00000
C3     1    0.13022    0.26106    0.57225   11.00000    21.00000
CL1    2    0.25000    0.17682    0.50000   31.00000     0.05684
Br1    3    0.25000    0.19763    0.50000  -31.00000     0.05110
```

**Using the m<-1 option, a ratio can be defined with a fixed sum of the two variables:**

**31.000 + -31.0000 = 1**
**30.500 + -31.5000 = 0.5**

***(10m)p* + *(-10m)p* = *p***
**Free variable no. *m*, targetvalue *p***

# Free variables

In SHELXL, each value is provided in the form of ***x* = 10*m* + *p*.**

*p*: value, which is refined; *m*: refinement mode

***m* = 0: normal refinement, *x* = *p***

***m* = 1: no refinement, *x* is fixed at *p***

***m* > 1: *x* = *p*·"free variable no. *m*"**

***m* <-1: *x* = *p*·(1 - "free variable no. *m*")**

```
FVAR        0.73503 0.0239  0.2365
```

- There is no "free variable no. 1", since adding 10 is used to exclude values from refinement.
- The first position of the FVAR command is thus occupied by the "overall scale factor" (OSF).
- The OSF scales our (arbitrary) intensities, which depends on crystal size, detector sensitivity etc., to the theoretical diffraction by a single unit cell.

# Free variables

In SHELXL, each value is provided in the form of ***x* = 10*m* + *p*.**

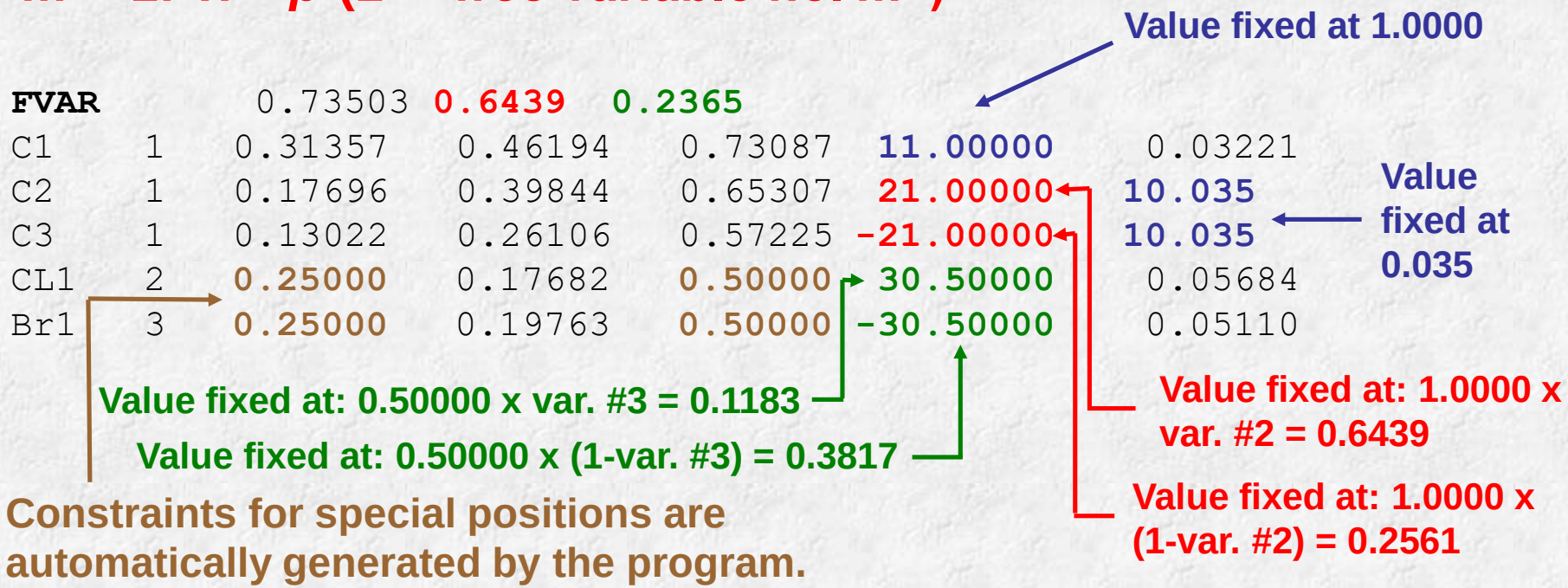
*p*: value, which is refined; *m*: refinement mode

***m* = 0: normal refinement, *x* = *p***

***m* = 1: no refinement, *x* is fixed at *p***

***m* > 1: *x* = *p*·"free variable no. *m*"**

***m* <-1: *x* = *p*·(1 - "free variable no. *m*")**

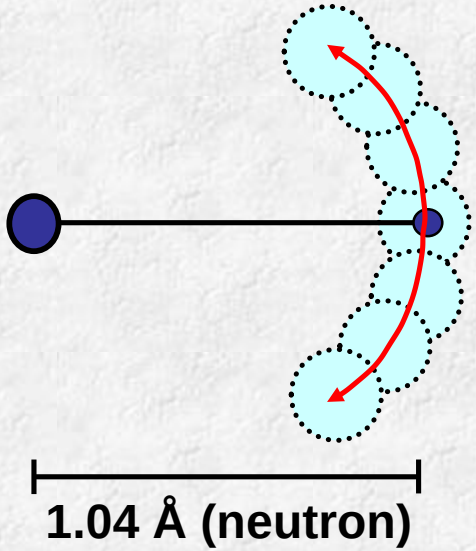


# Using constraints and restraints: Hydrogen treatment

The position of hydrogen atoms is a challenge in X-ray diffraction studies due to their low electron density. In addition, the C-H (and OH, NH etc.) distances are determined systematically to short for two reasons:

## 1.«Libration»

The effect is especially strong for hydrogen atoms (very light atoms)



# Using constraints and restraints: Hydrogen treatment

The position of hydrogen atoms is a challenge in X-ray diffraction studies due to their low electron density. In addition, the C-H (and OH, NH etc.) distances are determined systematically to short for two reasons:

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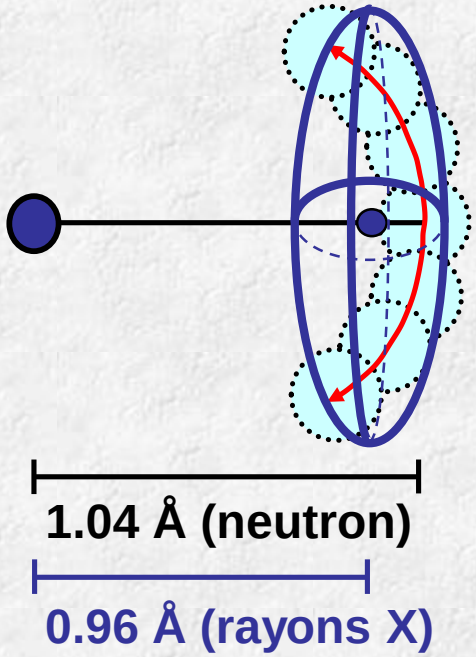
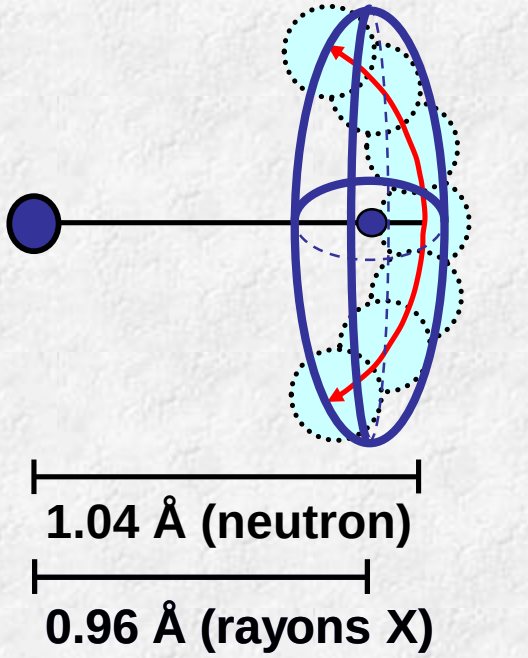


# Using constraints and restraints: Hydrogen treatment

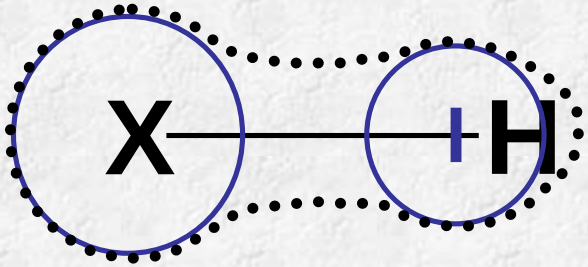
The position of hydrogen atoms is a challenge in X-ray diffraction studies due to their low electron density. In addition, the C-H (and OH, NH etc.) distances are determined systematically to short for two reasons:

## 1.«Libration»

The effect is specificially strong for hydrogen atoms (very light atoms)

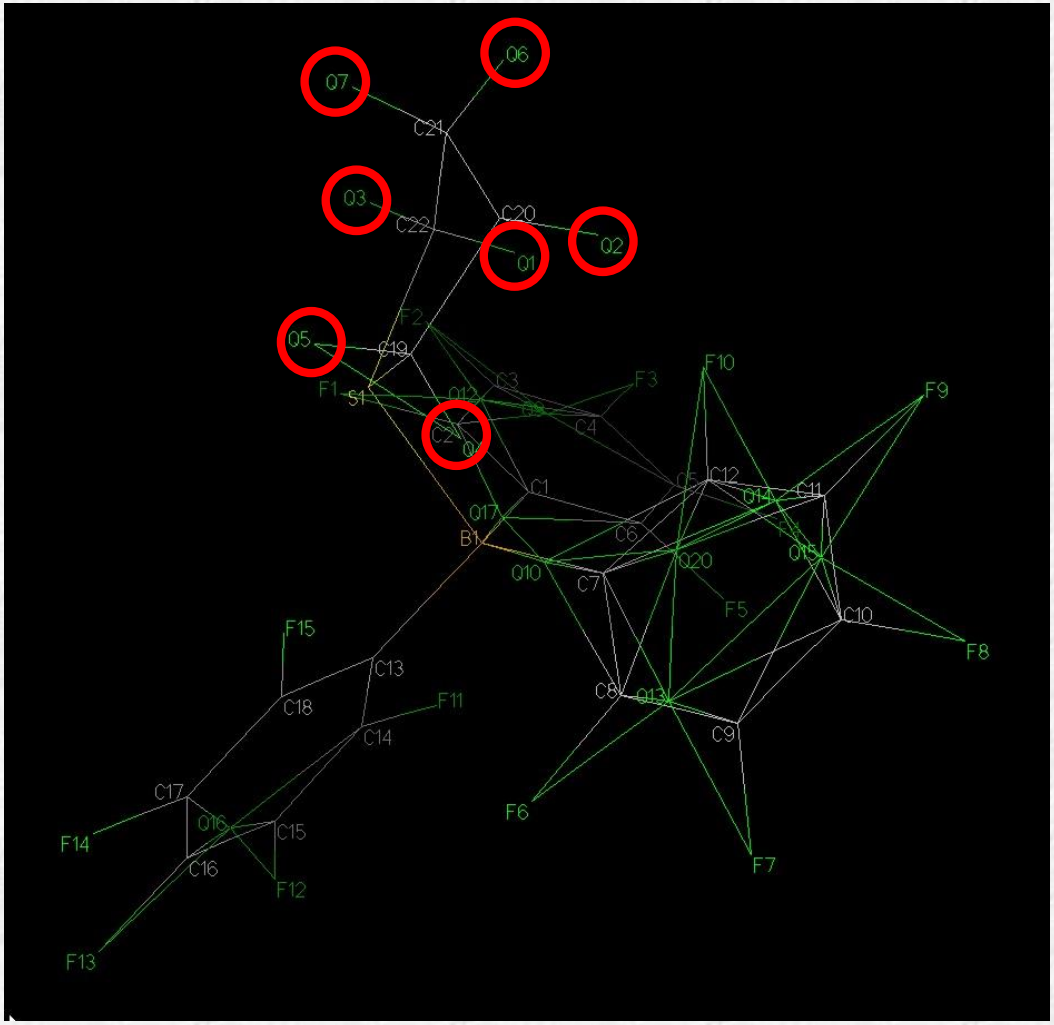



2. The maximum of the electron density is located in the bond, not on the nucleus.



# Hydrogen treatment

**With data of moderate quality, you can find the hydrogen atoms in the difference Fourier map.**



# Hydrogen treatment : 1. Free refinement

## 1. Free refinement

The anisotropic refinement of hydrogen atoms requires 9 parameters per hydrogen atom.

$\Rightarrow$ We encounter problems with the data/parameter ratio

$\Rightarrow$ The electron density of hydrogen is very low

$\Rightarrow$ **Isotropic refinement**

**Conditions for free refinement of hydrogen atoms:**

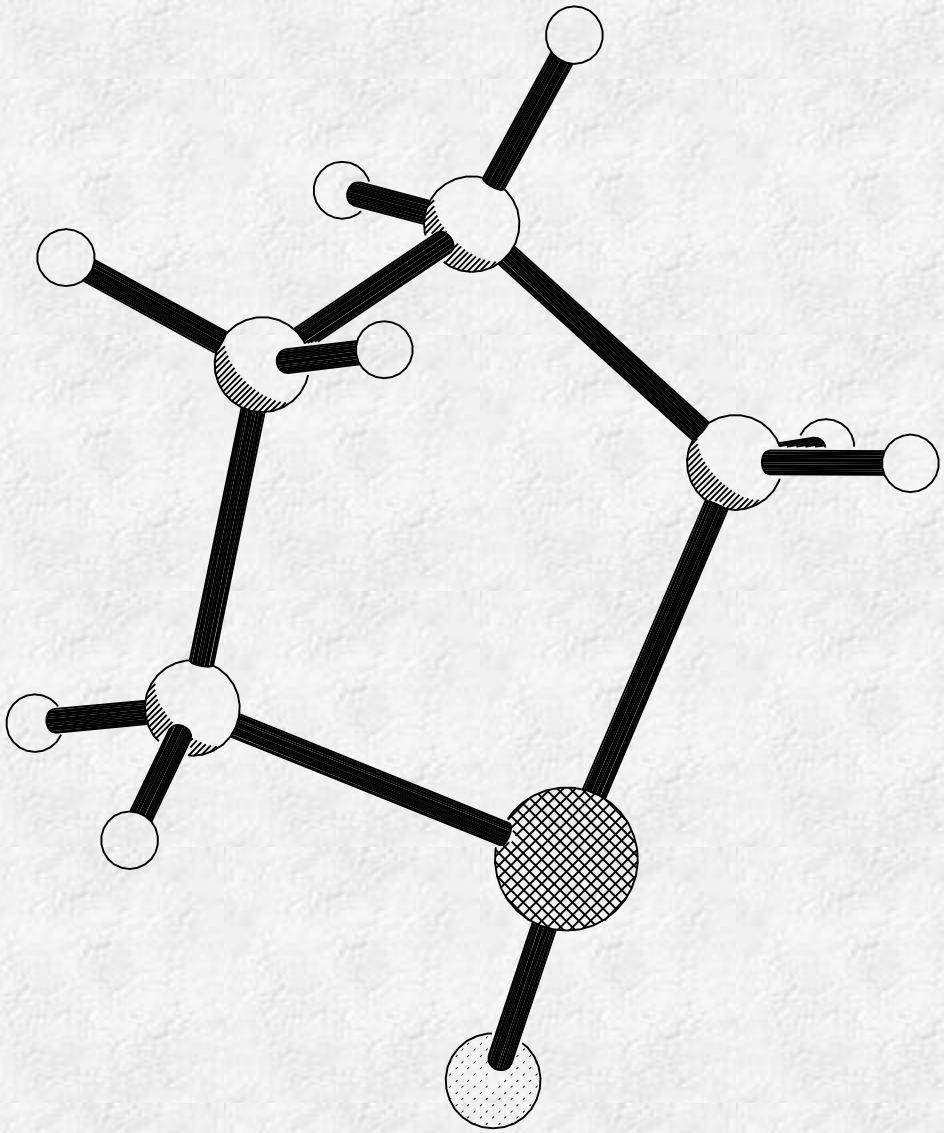
- Sufficient data quality
- The obtained distances, angles and $U_{iso}$ must be reasonable:

CH $\approx$ 0.96 Å ± 10% = 0.86-1.06

HCX $\approx \angle_{ideal}$ ± 10%

$U_{iso} < 0.2$ Å$^2$ and not too varied

# Hydrogen treatment : 1. Free refinement



**XP: BANG C19 to C22**

```
C19   S1       1.830
C19   C20      1.514   107.0
C19   H19A     0.957   110.6 113.9
C19   H19B     1.001   100.3 115.0 109.1
                        S1    C20   H19A
-------------------------------------

C20   C19      1.514
C20   C21      1.514   106.8
C20   H20A     1.015   109.9 109.7
C20   H20B     0.940   105.7 112.9 111.5
                        C19   C21   H20A
-------------------------------------

C21   C22      1.520
C21   C20      1.514   107.6
C21   H21A     0.945   108.2 114.1
C21   H21B     0.994   111.9 106.6 108.5
                        C22   C20   H21A
-------------------------------------

C22   S1       1.827
C22   C21      1.520   104.9
C22   H22A     0.954   107.6 112.1
C22   H22B     0.989   109.2 112.7 109.9
                        S1    C21   H22A
-------------------------------------
```

**.lst: $U_{iso}$ = 0.033 - 0.064**

# Hydrogen treatment : 2. $U_{iso}$ constraint

## 2. Free refinement of atomic positions, but constraint $U_{iso}$ values

⇒ $U_{iso}$ of all hydrogen atoms are restraint to the same value

⇒ One might use different values (free variables) for hydrogen atoms in $CH_3$, $C(sp^2)H$ or ($CR_2H_2$,$CR_3H$) groups.

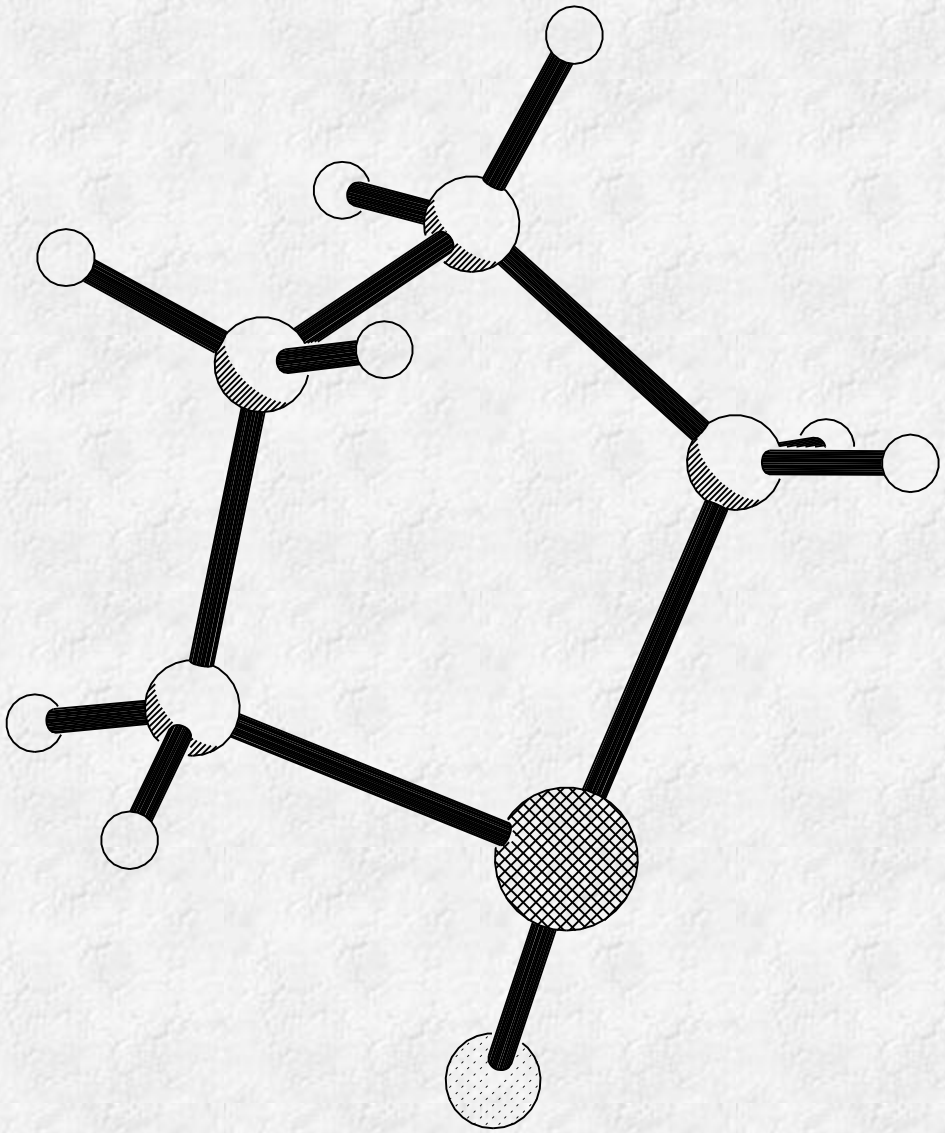
8 H ⇒ **32** paramètres

```
FVAR        0.73503
...
H19A  2   0.49363   0.89888   0.80474  11.00000   0.03671
H19B  2   0.35967   0.94429   0.75075  11.00000   0.05698
H20A  2   0.54456   0.78518   0.60379  11.00000   0.04391
H20B  2   0.49706   0.91807   0.59605  11.00000   0.05058
...
```

8 H ⇒ **25** paramètres

```
FVAR        0.73503  0.045
...
H19A  2   0.49363   0.89888   0.80474  11.00000  21.0000
H19B  2   0.35967   0.94429   0.75075  11.00000  21.0000
H20A  2   0.54456   0.78518   0.60379  11.00000  21.0000
H20B  2   0.49706   0.91807   0.59605  11.00000  21.0000
...
```

# Hydrogen treatment : 2. $U_{iso}$ constraint



**XP: BANG C19 to C22**

```
C19   S1      1.830
C19   C20     1.514   107.0
C19   H19A    0.962   110.7 113.8
C19   H19B    0.999   100.2 115.0 109.2
                        S1    C20   H19A
-------------------------------------

C20   C19     1.514
C20   C21     1.514   106.9
C20   H20A    1.020   109.9 109.7
C20   H20B    0.935   106.0 113.5 110.8
                      C19   C21   H20A
-------------------------------------

C21   C20     1.514
C21   C22     1.520   107.6
C21   H21A    0.939   113.9 108.6
C21   H21B    0.992   106.7 111.9 108.3
                      C20   C22   H21A
-------------------------------------

C22   S1      1.828
C22   C21     1.520   105.0
C22   H22A    0.951   107.5 112.2
C22   H22B    0.986   109.5 112.6 109.8
                      S1    C21   H22A
-------------------------------------
```

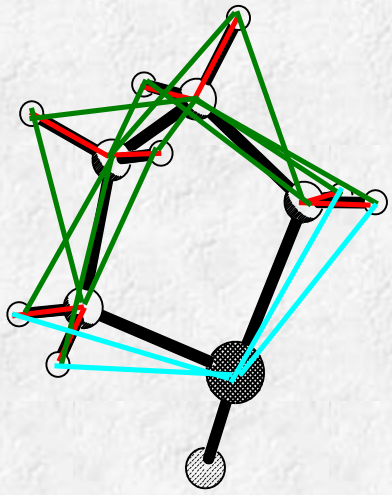
**.lst: $U_{iso}$ = 0.0462**

# 3. Restraints on distances and angles

**C-H distances are restraint to equal values ($U_{iso}$ stays fixed)**
**1,3-distances are also restraint to be equal («angle restraints»)**

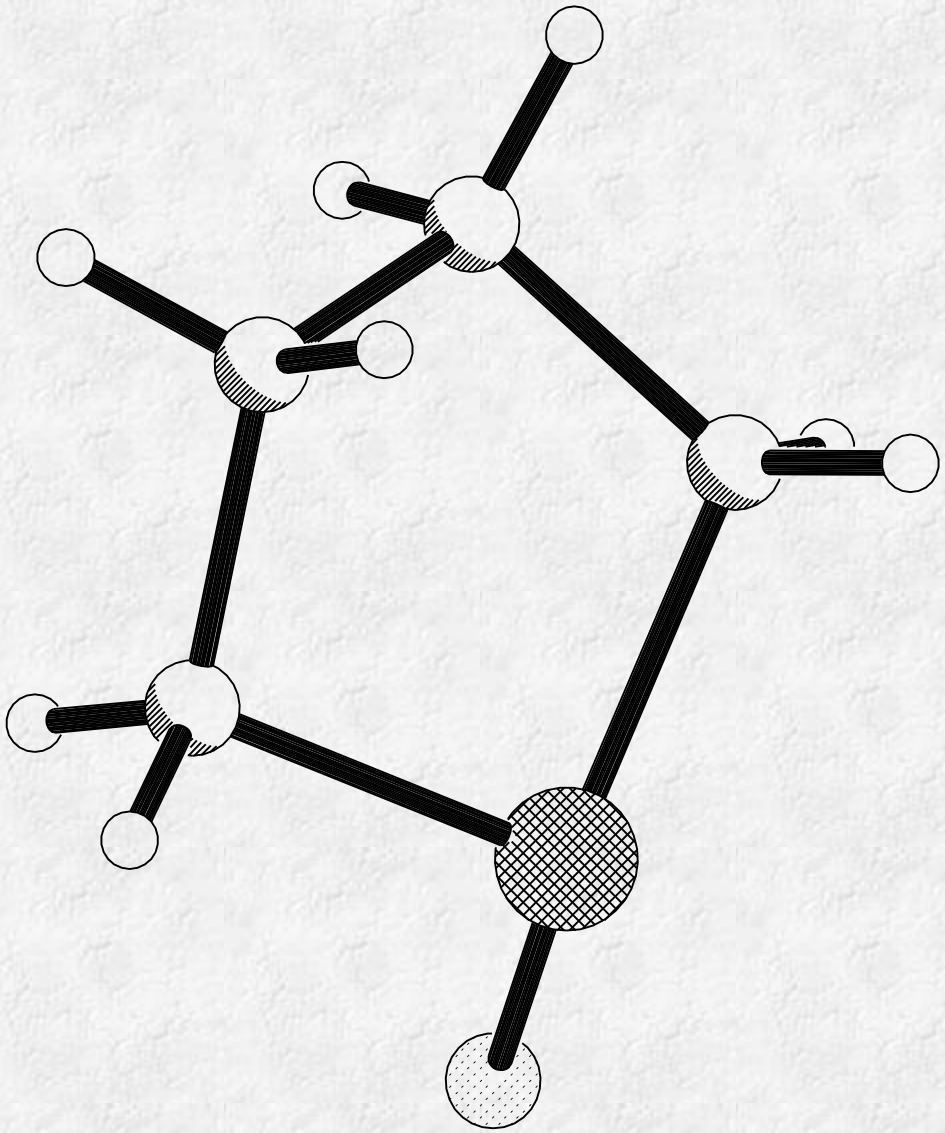
```
SADI C19 H19a   C19 H19b   C20 H20a   C20 H20b   C21 H21a   C21 H21b   =
     C22 H22a   C22 H22b

SADI C19 H20a   C19 H20b   C20 H19a   C20 H19b   C20 H21a   C20 H21b   =
     C21 H20a   C21 H20b   C21 H22a   C21 H22b   C22 H21a   C22 H21b

SADI S1 H19a   S1 H19b   S1 H22a   S1 H22b

FVAR        0.73503  0.045
...
H19A  2   0.49363   0.89888   0.80474  11.00000   21.0000
H19B  2   0.35967   0.94429   0.75075  11.00000   21.0000
H20A  2   0.54456   0.78518   0.60379  11.00000   21.0000
H20B  2   0.49706   0.91807   0.59605  11.00000   21.0000
...
```

**24 restraints ⇒ + 24 data**
8 H ⇒ 25 parameters



**Disadvantage: A lot of work**

# 3. Restraints on distances and angles



**XP: BANG C19 to C22**

| | | | | | | |
|---|---|---|---|---|---|---|
| C19 | S1 | 1.829 | | | | |
| C19 | C20 | 1.514 | 107.1 | | | |
| **C19** | **H19A** | **0.951** | **109.6** | **113.7** | | |
| **C19** | **H19B** | **0.978** | **104.4** | **112.6** | **109.0** | |
| | | | S1 | C20 | H19A | |

| | | | | | | |
|---|---|---|---|---|---|---|
| C20 | C19 | 1.514 | | | | |
| C20 | C21 | 1.515 | 106.8 | | | |
| **C20** | **H20A** | **0.985** | **109.9** | **109.8** | | |
| **C20** | **H20B** | **0.970** | **108.7** | **111.3** | **110.3** | |
| | | | C19 | C21 | H20A | |

| | | | | | | |
|---|---|---|---|---|---|---|
| C21 | C20 | 1.515 | | | | |
| C21 | C22 | 1.520 | 107.6 | | | |
| **C21** | **H21A** | **0.961** | **112.3** | **110.2** | | |
| **C21** | **H21B** | **0.980** | **108.9** | **110.7** | **107.1** | |
| | | | C20 | C22 | H21A | |

| | | | | | | |
|---|---|---|---|---|---|---|
| C22 | S1 | 1.827 | | | | |
| C22 | C21 | 1.520 | 105.0 | | | |
| **C22** | **H22A** | **0.960** | **107.6** | **111.9** | | |
| **C22** | **H22B** | **0.962** | **108.7** | **112.3** | **111.0** | |
| | | | S1 | C21 | H22A | |

**.lst: $U_{iso}$ = 0.0463**

# 4. Constraints / Riding model

Hydrogen atoms are included as rigid groups

⇒ no new parameters

**AFIX mn**: m = type of rigid group; n = treatment during refinement
(see SHELXL manual)

m = 1 : Y-**CH**(-Y)$_2$
2 : Y-**CH$_2$**-Y
3 : Y-**CH$_3$**
4 : **C(sp$^2$/arom.)-H**
8 : X-**OH**
9 : X=**CH$_2$**
12 : Y-**CH$_3$** (désordonné)
13 : Y-**CH$_3$** (angle dièdre optimisé)
14 : X-**OH** (angle dièdre optimisé)
15 : X$_{4/5}$**BH**
16 : X≡**CH**

**n = 3** : the parameters of the hydrogen atoms are derived from the parameters of the central atom and not refined.

**4** : same as n=3, but the C-H distance is refined.

**7** : Only for $CH_3$: same as n=3, but with rotation around Y-$CH_3$.

**8** : same as n=7, but the C-H distance is also refined.

**We normally use: AFIX 33, AFIX 23, AFIX 13, AFIX 43, AFIX 137, AFIX 127**

# 4. Constraints / Riding model

The command AFIX can be introduced:

- manually
- using HADD in XP
- using HFIX in the .ins-file

**Il n'y a pas de nouveau paramètre introduit à l'affinement!**

```
…
HFIX 23 C19 C20 C21 C22
(or  HFIX 23 C19>C22  or  HFIX 23 C22<C19)

S1    5    0.277756    0.724342    0.718753 …
…
C19   1    0.416258    0.872768    0.732035 …
C20   1    0.464406    0.834804    0.604059 …
C21   1    0.333324    0.739317    0.500426 …
C22   1    0.264745    0.631186    0.545540 …
```

***.res:**

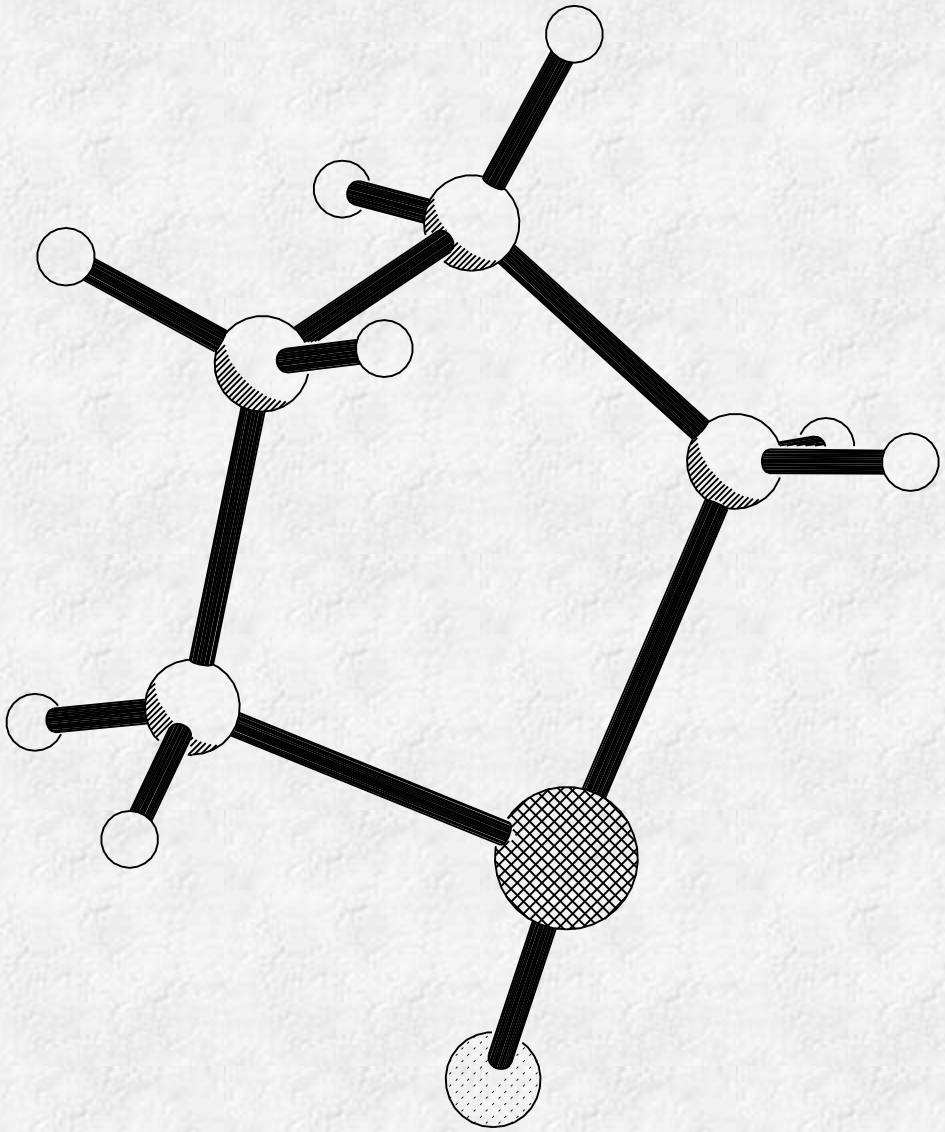
```
...
C19   1    0.416148    0.872772    0.732124    11.00000    0.05241    0.02307 =
         0.03436    0.01261    0.01026    0.00819
AFIX  23
H19A  2    0.375974    0.953289    0.750305    11.00000   -1.20000
H19B  2    0.498548    0.894564    0.802368    11.00000   -1.20000
AFIX   0
C20   1    0.464415    0.834821    0.604090    11.00000    0.04754    0.03455 =
         0.03890    0.01871    0.01419    0.01115
AFIX  23
H20A  2    0.543131    0.788600    0.603916    11.00000   -1.20000
H20B  2    0.499198    0.917434    0.588814    11.00000   -1.20000
AFIX   0
...
```

identique

= 1.2 * $U_{iso}$ (C19)

**= x(C20) + Δx** (Δx does not change)

# 4. Constraints / Riding model



**XP: BANG C19 to C22**

```
C19   S1      1.828
C19   H19A    0.980   110.3
C19   H19B    0.980   110.3  108.6
C19   C20     1.515   107.1  110.3  110.3
                        S1     H19A   H19B
---------------------------------------------

C20   C19     1.515
C20   H20A    0.980   110.4
C20   H20B    0.980   110.4  108.6
C20   C21     1.515   106.8  110.4  110.4
                        C19    H20A   H20B
---------------------------------------------

C21   C20     1.515
C21   H21A    0.980   110.2
C21   H21B    0.980   110.2  108.5
C21   C22     1.521   107.6  110.2  110.2
                        C20    H21A   H21B
---------------------------------------------

C22   S1      1.826
C22   C21     1.521   105.0
C22   H22A    0.980   110.8  110.8
C22   H22B    0.980   110.8  110.8  108.8
                        S1     C21    H22A
---------------------------------------------
```

# Comparison

| | Free refinement | fixed $U_{iso}$ | restraints (SADI) | riding model |
|---|---|---|---|---|
| **$wR_2$** | 12,91% | 12,96% | 13,01% | 13,14% |
| **Residual $e^-$ dens.** | 0,29 $e^-/Å^3$ | 0,29 $e^-/Å^3$ | 0,29 $e^-/Å^3$ | 0,29 $e^-/Å^3$ |
| **C-H distances** | 0,95-1,02 | 0,94-1,02 | 0,95-0,99 | 0,98 |
| **X-C-H angles** | 100-115 | 100-115 | 104-114 | 110-111 |
| **Parameters added** | 32 | 25 | 25 + 24 data | 0 |

# Which method to choose ?

**My personal view:** (and obligatory for this class)

C-H distances and angles do not show much variations.

- For high quality data, there is not much difference between free refinement and the riding model with calculated hydrogen atoms.
- For low quality data, agreement factors are often better with free or semi-free refinement. But in most cases, this is only due to the additional parameters introduced in the refinement, not due to a better description of the hydrogen atoms.

⇒ **Use the riding model for all CH and $CH_2$ groups (AFIX 13, AFIX 43, AFIX 23).**

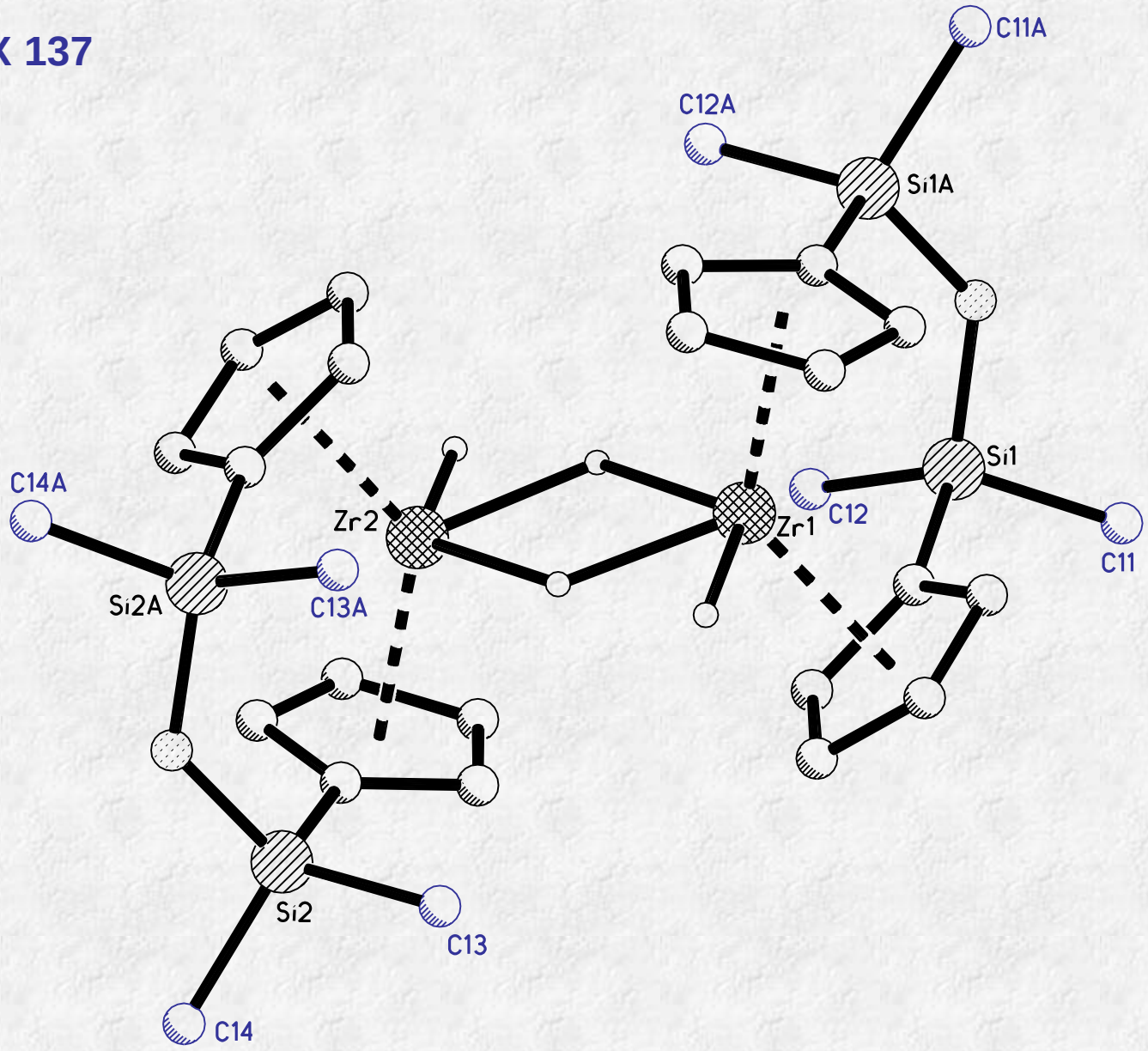
⇒ **Use the riding model with rotation (AFIX 137) for all methyl groups. Particularly important for methyl groups connected to a planar moieties.**

⇒ **If you observed electron densities between hydrogen atoms refined with AFIX 137, you have to use the rigid group for a disordered methyl group, AFIX 127.**

⇒ **For "special hydrogen atoms" (metal bound hydrides and all other hydrogen atoms not described above), use the semi-free refinement using appropriate restraints (SADI). If needed, constrain $U_{iso}$ to be equal using free variables.**

# Example: A dimeric zirconium hydride

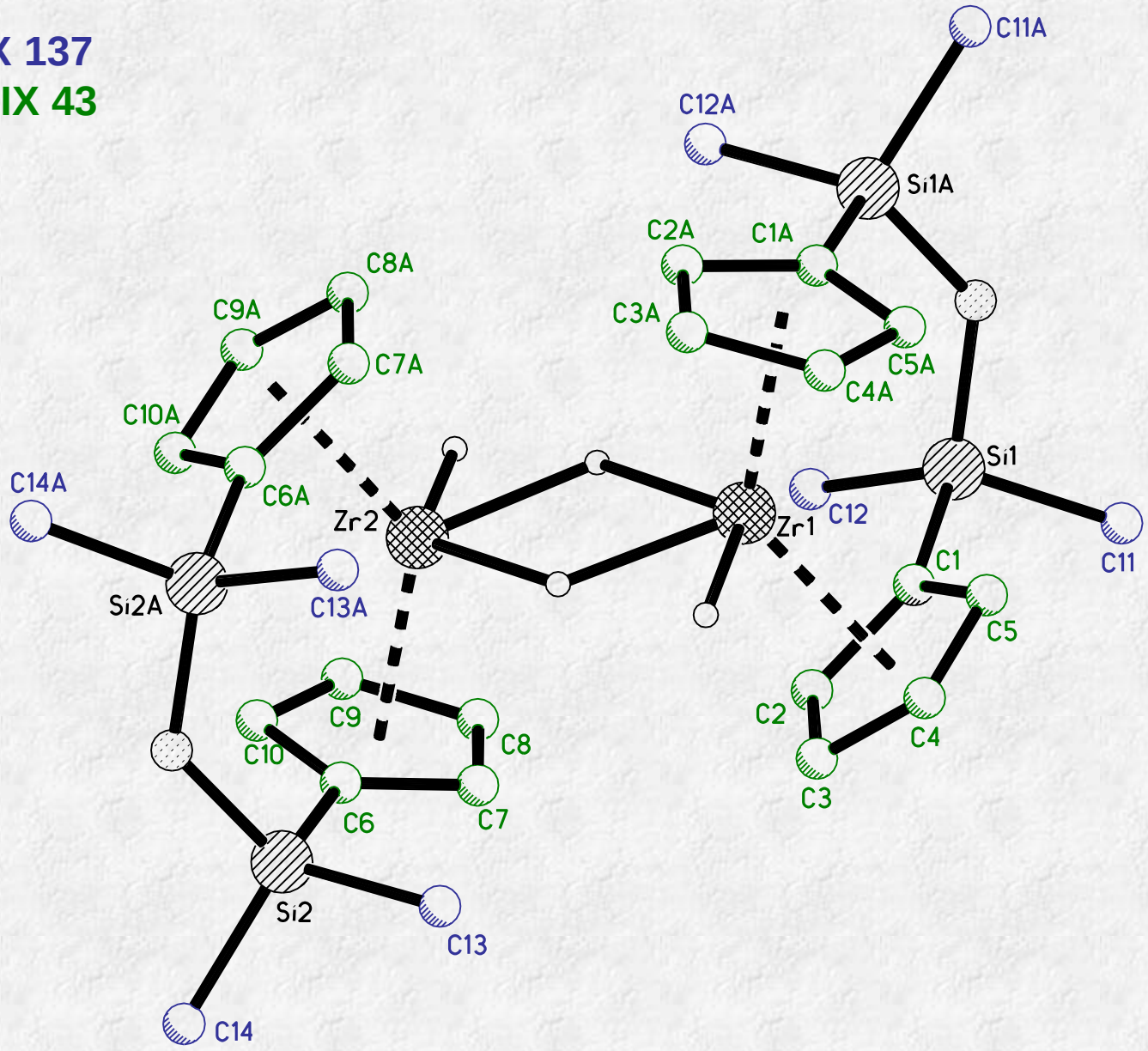
**Me: AFIX 137**



# Example: A dimeric zirconium hydride

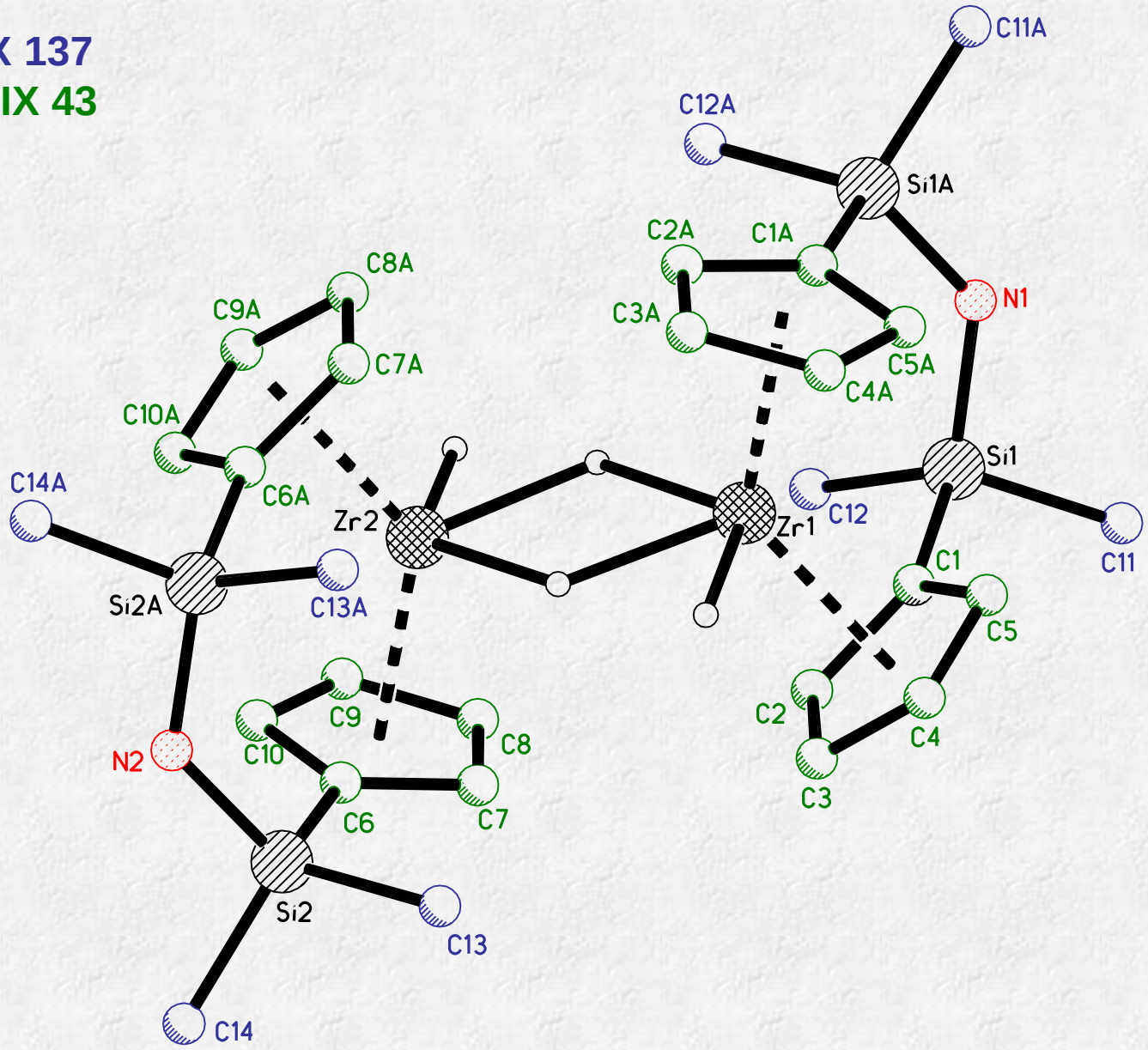
**Me: AFIX 137**

**CpH: AFIX 43**



# Example: A dimeric zirconium hydride

**Me: AFIX 137**
**CpH: AFIX 43**
**NH: ???**



# Example: A dimeric zirconium hydride

We do not have a rigid group for $Si_2NH$. We thus have to assign this hydrogen atom from the difference Fourier map (Q peaks) and refine using appropriate restraints.

XP: PICK Q9

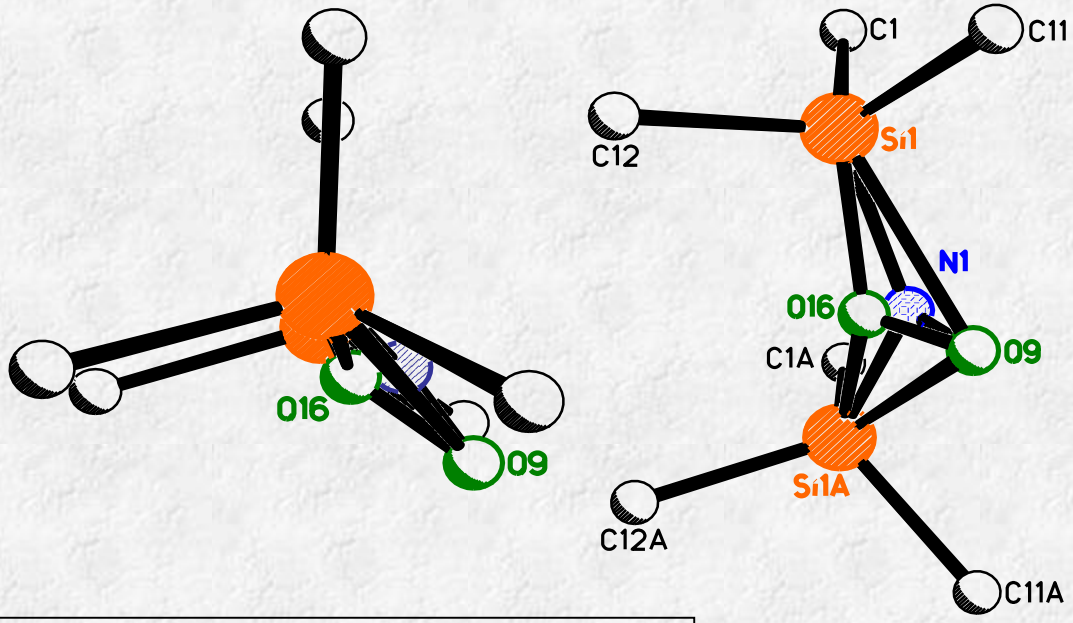
.ins: DFIX 0.91 N1 H1A N2 H2A

SADI Si1 H1A Si1A H1A

SADI Si2 H2A Si2A H2A

Angle restraints (1,3 distance restraints)

```
N1    SI1      1.737
N1    SI1A     1.737  132.2
N1    Q9       0.897  112.6 112.6
N1    Q16      0.365   74.8  74.8 111.5
                      SI1   SI1A  Q9
```

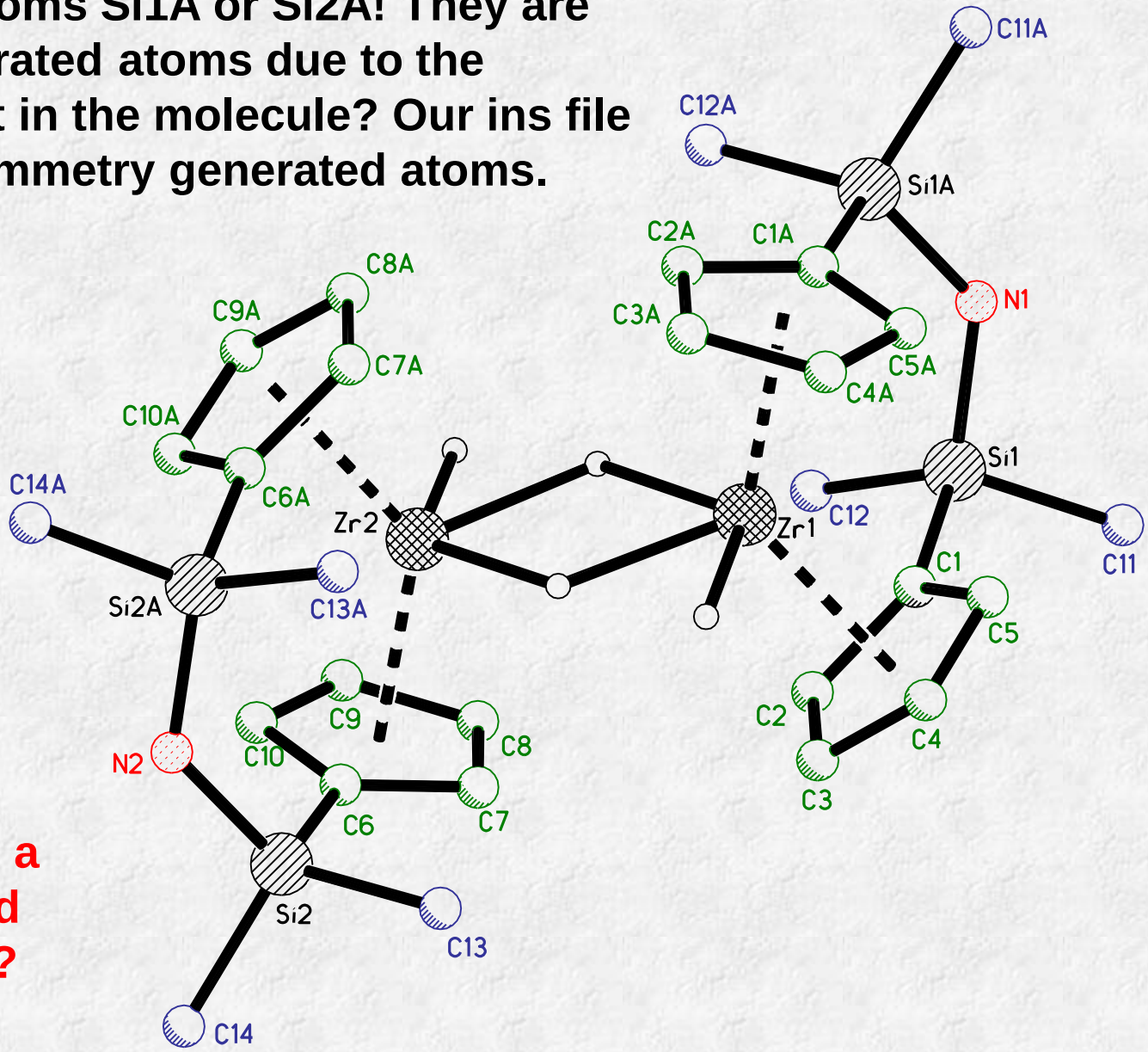



***.lst:**

```
Default effective X-H distances for T = -140.0 C
AFIX m =    1     2     3     4    4[N]   3[N]   15[B]   8[O]    9    9[N]   16
d(X-H) =  1.00  0.99  0.98  0.95  0.88   0.91   1.12    0.84   0.95  0.88  0.95
```

# Example: A dimeric zirconium hydride

**But: There are no atoms Si1A or Si2A! They are just symmetry-generated atoms due to the mirror plane present in the molecule? Our ins file does not contain symmetry generated atoms.**



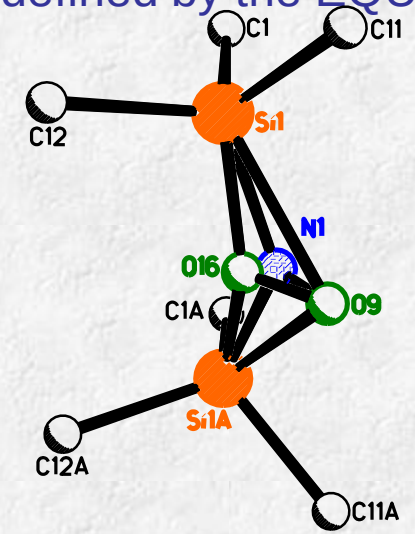

**How do we address a symmetry generated atom in the .ins-file?**

# The EQIV command

An atom generated by a symmetry operation can be adressed in the .ins-file as «atom label »_$n, where $n is the symmetry operation defined by the EQUIV :

EQIV $n *<opération de symétrie>*

EQIV $1 **x, 0.5-y, z**
SADI Si1 H1A Si1_$1 H1A




But how to find the correct symmetry operation ?

**XP:**
`> SRCH Si1`

Search finds symmetry operations, which bring the requested atom in binding contact to other atoms.

```
 SI1   (  1555) ... N1      1.737
 SI1   (  1555) ... C1      1.857
 SI1   (  1555) ... C11     1.874
 SI1   (  1555) ... C12     1.866
 SI1   (  4565) ... N1      1.737
```

`> SYMM`

SYMM displays the symmetry available symmetry operations.

```
Symmetry codes and operators

   1555. = +X, +Y, +Z
   2555. = -X, -Y, -Z
   3555. = -X,  0.500000+Y, -Z
   4555. = +X, -0.500000-Y, +Z
```

SYMM 4555 = +X, -0.500000-Y, +Z
0, +1, 0

---

SYMM 4565 = +X, 0.500000-Y, +Z

SYMM 3555 = -X, 0.500000+Y, -Z
-1, 0, +1

---

SYMM 3456 = -1-X, 0.500000+Y, 1-Z

# Example: A dimeric zirconium hydride

We do not have a rigid group for $Si_2NH$. We thus have to assign this hydrogen atom from the difference Fourier map (Q peaks) and refine using appropriate restraints.

XP: PICK Q9

.ins: DFIX 0.91 N1 H1A N2 H2A

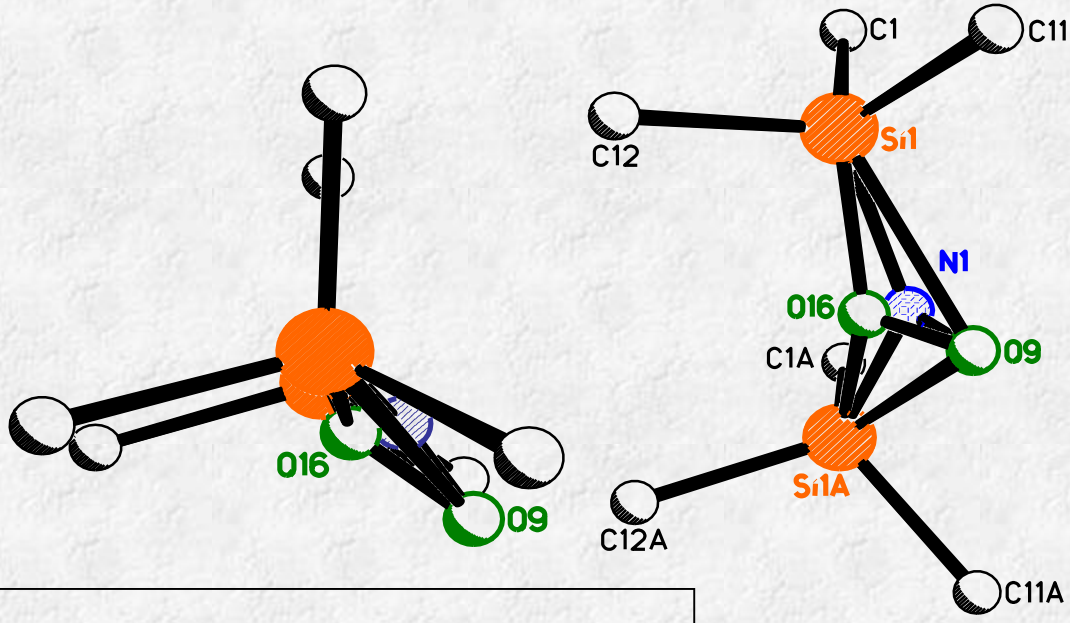
EQIV $1 x, 0.5-y, z

SADI Si1 H1A Si1_$1 H1A

SADI Si2 H2A Si2_$1 H2A

Angle restraints (1,3 distance restraints)

```
N1    SI1      1.737
N1    SI1A     1.737  132.2
N1    Q9       0.897  112.6 112.6
N1    Q16      0.365   74.8  74.8 111.5
                      SI1   SI1A  Q9
```




***.lst:**

```
Default effective X-H distances for T = -140.0 C

AFIX m =    1     2     3     4    4[N]   3[N]   15[B]  8[O]    9    9[N]   16
d(X-H) =  1.00  0.99  0.98  0.95  0.88   0.91   1.12   0.84   0.95  0.88  0.95
```

# Example: A dimeric zirconium hydride

#1: XP: PICK Q9

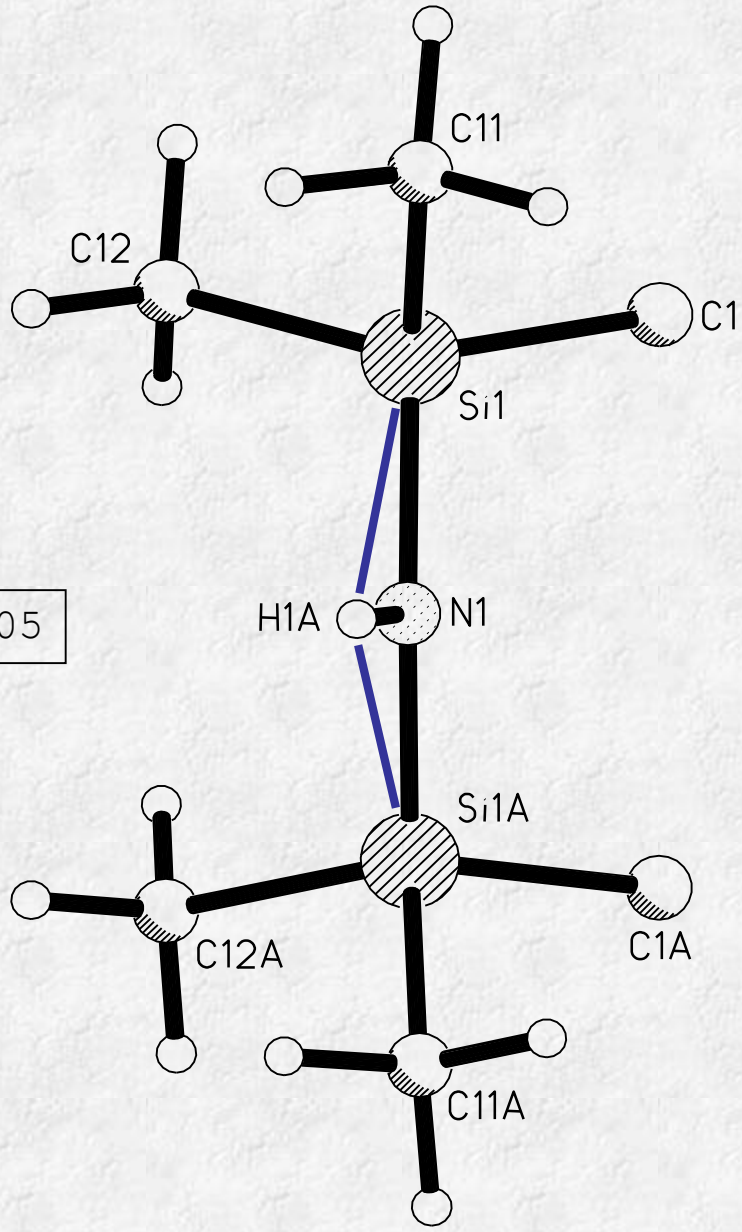
DFIX 0.91 N1 H1A N2 H2A

~~EQIV $1 x, 0.5-y, z~~

~~SADI Si1 H1A Si1_$1 H1A~~

```
H1A 2 0.13770 0.25000 0.61040 10.5000 0.05
```

**Due to the mirror plane, the Si1-N1-H1A and the Si1A-N1A-H1A angle are always identical. Thus here, we do not need the restraint.**



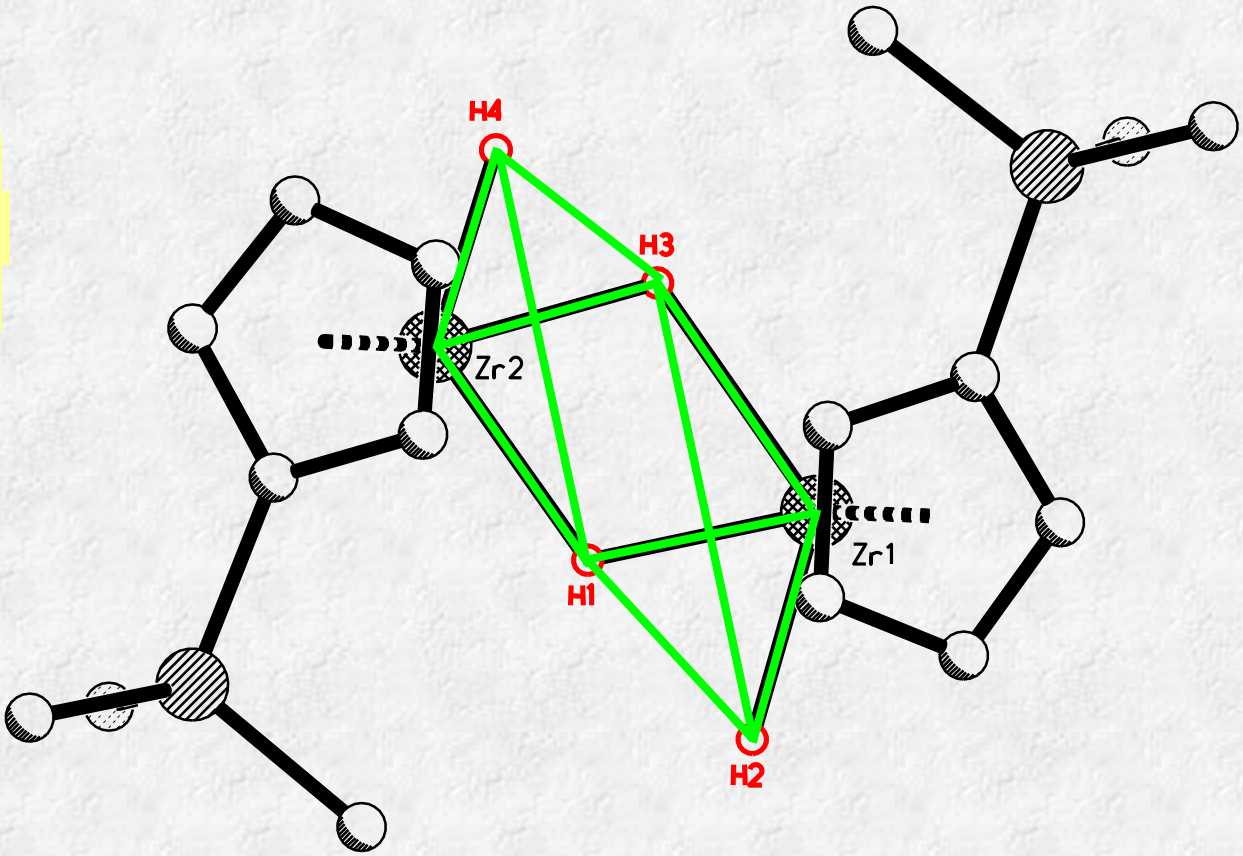
# Example: A dimeric zirconium hydride

**Me: AFIX 137**
**CpH: AFIX 43**
**N-H: DFIX 0.91**
**ZrH: ????**

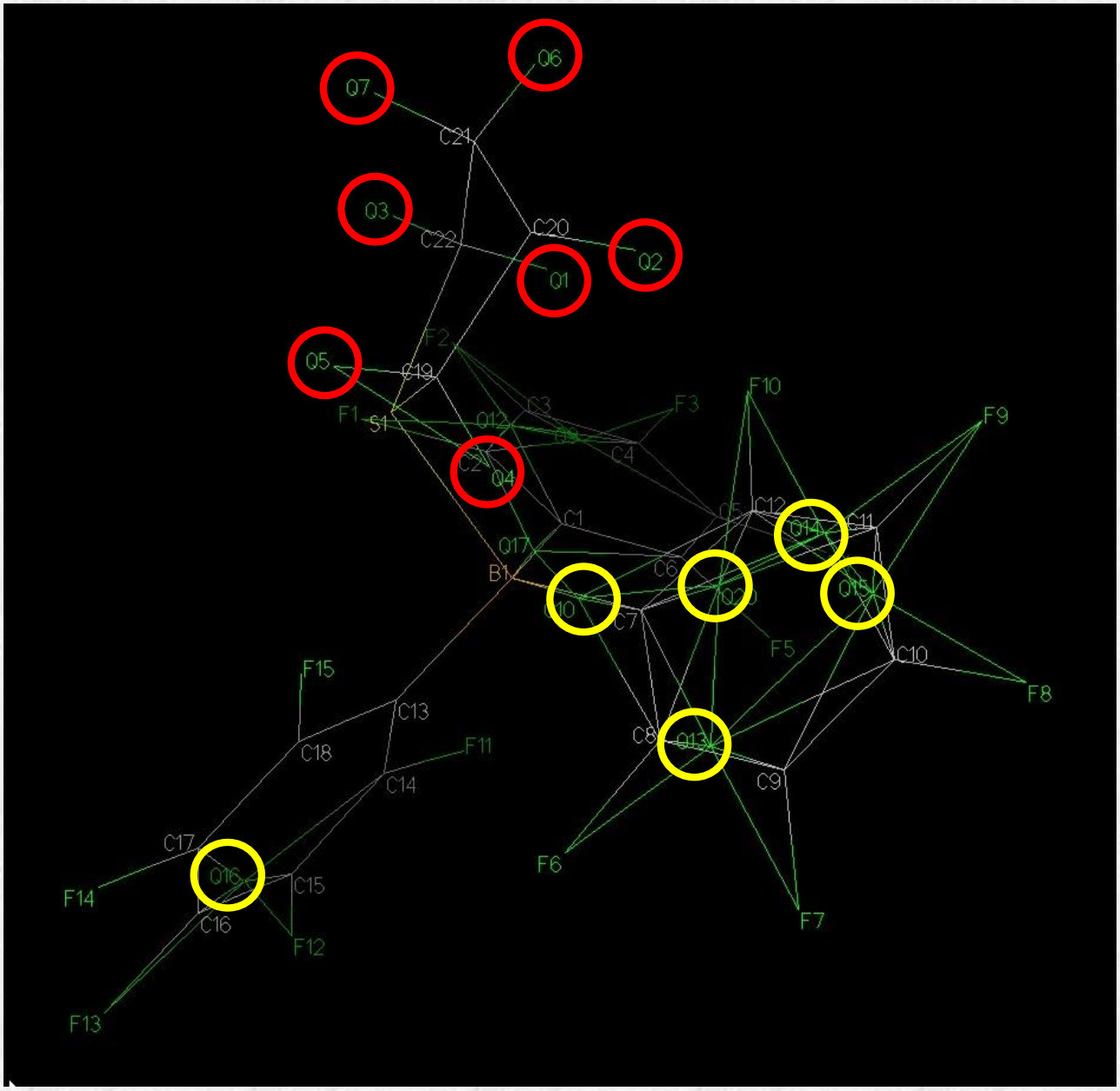
```
ZR1   H1        1.950
ZR1   H2        1.969    62.1
ZR1   H3        2.317    67.1  129.2
                          H1    H2
---------------------------------
ZR2   H1        2.189
ZR2   H3        1.923    70.3
ZR2   H4        1.704   127.2   56.9
                         H1     H3
```

**Refinement without restraints yields inacceptable deviations!**

```
SADI  Zr1 H2    Zr2 H4
SADI  Zr1 H1    Zr2 H3
SADI  Zr1 H3    Zr2 H1
SADI  H4 H3     H1 H2
SADI  H2 H3     H1 H4
```



# Back to our example

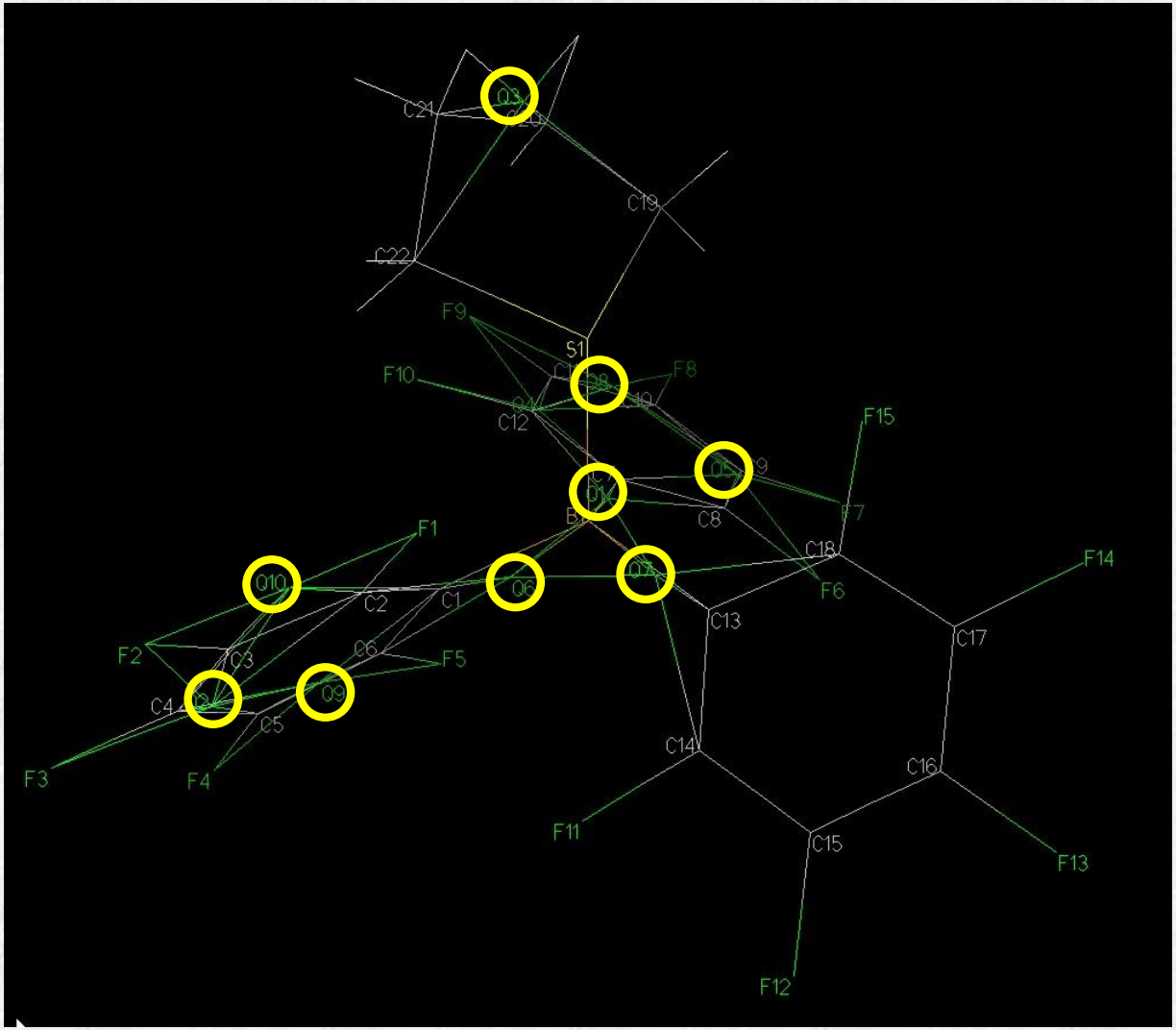



**After anisotropic refinement**:
Les pics restants peut être attribués aux:

- ~~**Thermal motion of atoms**~~
- **Hydrogen atoms**
- **Errors**

**The 8 highest Q-peaks (Q1-Q8) correspond to hydrogen atoms!**

# Back to our original example



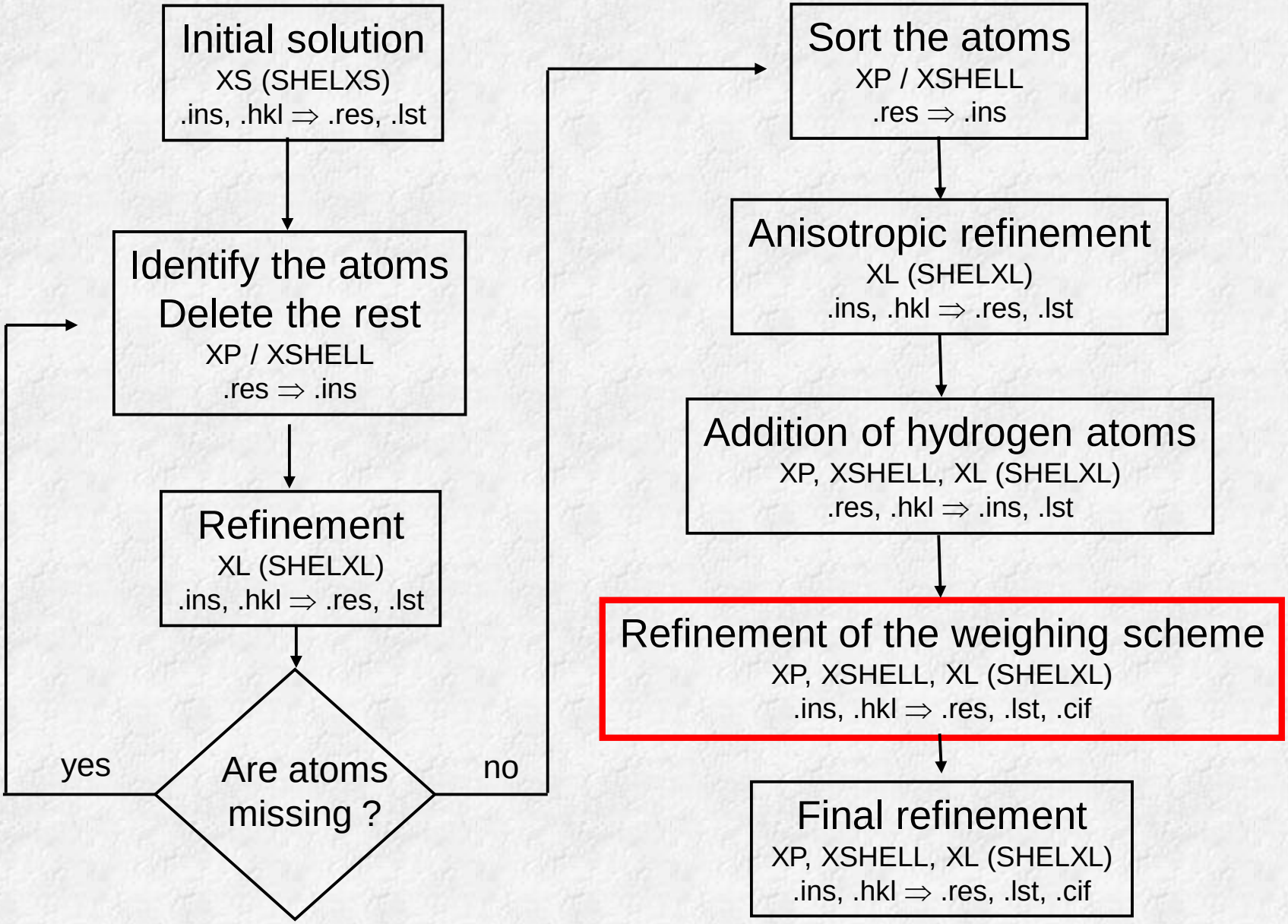

**After anisotropic refinement**:
The remaining peaks can be attributed to:

- ~~**Thermal motion of atoms**~~
- ~~**Hydrogen atoms**~~
- **Errors**

The remaining electron density ($Q1 = 0.29\ e^-/Å^3$) can be neglected.

Look at the position of the errors. Are they arbitrary?

# Refinement organigram



# Refining the weighing scheme

***.lst:**

| Fc/Fc(max) | 0.000 | 0.012 | 0.023 | 0.034 | 0.047 | 0.061 | 0.079 | 0.101 | 0.135 | 0.201 | 1.000 |
|---|---|---|---|---|---|---|---|---|---|---|---|
| Number in group | | 463 | 423 | 422 | 475 | 397 | 439 | 438 | 433 | 430 | 439 |
| GooF | | **1.406** | **1.493** | **1.414** | **1.317** | **1.076** | **1.029** | **0.813** | **0.734** | **0.633** | **0.453** |
| K | | 1.690 | 1.053 | 1.022 | 1.020 | 1.008 | 1.011 | 1.012 | 0.997 | 1.002 | 0.990 |

**Refine the weighing scheme so that the GooF is independent from the intensity.**

$$w = 1/\sigma^2(F_o^2) + (aP)^2 + bP \qquad P = 1/3\left(F_o^2 + 2F_c^2\right)$$

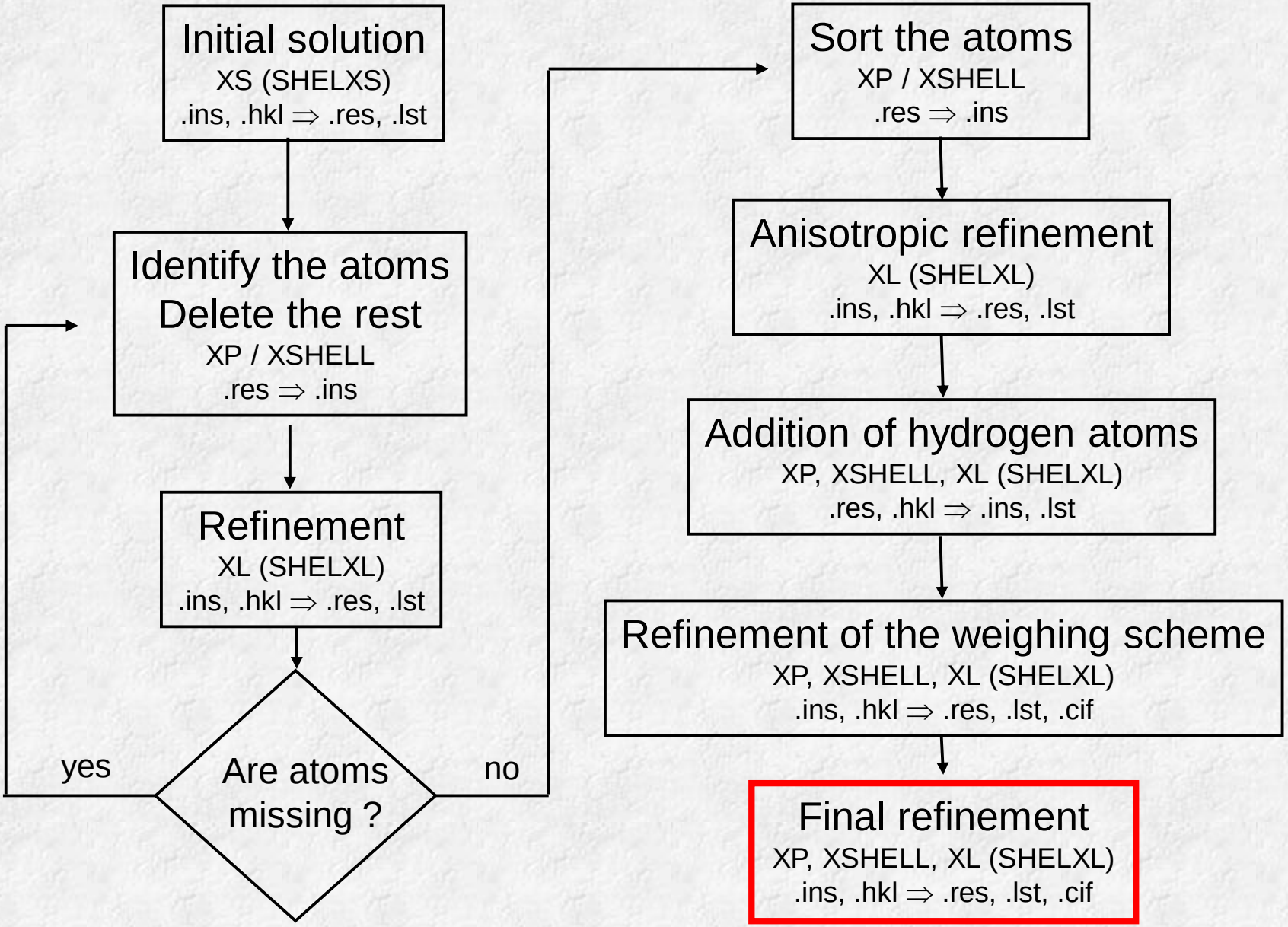
***.res:**

```
...
WGHT    0.1000
FVAR 0.3234
...
HKLF 4
END
WGHT    0.0342    0.4326
```

1. Copy and replace the command WGHT to the beginning of the file.
2. Refine (XL).
3. Repeat until the values remain constant.

| Fc/Fc(max) | 0.000 | 0.012 | 0.023 | 0.035 | 0.047 | 0.062 | 0.079 | 0.101 | 0.135 | 0.202 | 1.000 |
|---|---|---|---|---|---|---|---|---|---|---|---|
| Number in group | | 466. | 418. | 459. | 438. | 419. | 417. | 442. | 435. | 427. | 438. |
| GooF | | **1.117** | **1.023** | **1.008** | **1.059** | **0.974** | **1.102** | **0.990** | **1.064** | **1.056** | **0.993** |
| K | | 1.732 | 1.049 | 1.028 | 1.018 | 1.008 | 1.011 | 1.013 | 0.997 | 1.004 | 0.992 |

# Refinement organigram



# Final refinement

- Prepare for publication

***.ins:**

…

```
SFAC C  H  N  F  P
UNIT 56 60 16 24 4
```

- **Make sure that the sum formula is correct**

***.lst:**

…

** Cell contents from UNIT instruction and atom list do not agree **

Unit-cell contents from UNIT instruction and atom list resp.

| | | |
|---|---|---|
| **C** | **224.00** | **240.00** |
| **H** | **240.00** | **272.00** |

…

# Final refinement

- Prepare for publication

***.ins:**

…
SFAC C H N F P
UNIT 56 60 16 24 4

**L.S. 40**

- **Make sure that the sum formula is correct**
- **Let the structure converge completely**

.lst:

Least-squares cycle 4
wR2 = 0.2372 before cycle 4 for 9920 data and 879 / 879 parameters
GooF = S = 0.981; Restrained GooF = 0.983 for 174 restraints
Weight = 1 / [ sigma^2(Fo^2) + ( 0.1609 * P )^2 + 81.13 * P ] where P = ( Max ( Fo^2, 0 ) + 2 * Fc^2 ) / 3

| N | value | esd | shift/esd | parameter |
|---|---|---|---|---|
| 1 | 0.29295 | 0.00082 | 0.017 | OSF |
| 2 | 0.51134 | 9.99999 | 0.000 | FVAR 2 |
| 790 | 2.00000 | 0.49066 | 1.861 | U22 F55A |
| 791 | 0.49170 | 0.11402 | 1.331 | U33 F55A |
| 792 | 1.04633 | 0.21776 | 1.874 | U23 F55A |

**Mean shift/esd = 0.042 Maximum = 1.874 for U23 F55A**
**Max. shift = 0.011 A for F55A Max. dU = 0.205 for F55A**

**The max. shift has to be < 0.003 Å**

# Final refinement

- Prepare for publication

***.ins:**

…
SFAC C H N F P
UNIT 56 60 16 24 4

L.S. 40

**ACTA**

- **Make sure that the sum formula is correct**
- **Let the structure converge completely**
- **Generate .cif and .fcf files**

- **ACTA imposes certain conditions**
  - OMIT >0 is not allowed
  - FMAP 2 is enforced
  - LIST 4 is enforced
- **You can specify a 2θ limit, e. g. ACTA 120**
  - If there are missing reflections at high angle 2θ
  - When you encoutered problems with the completeness of the dataset.

# Final refinement

- Prepare for publication

***.ins:**

…
SFAC C H N F P
UNIT 56 60 16 24 4

L.S. 40

ACTA

**BOND $H**

- **Make sure that the sum formula is correct**
- **Let the structure converge completely**
- **Generate .cif and .fcf files**
- **Generate bond distances and angles tables**

**Use always BOND $H instead of BOND! A simple BOND does not include hydrogen atoms, which causes problems when if you want to publish the structure.**

# Final refinement

- Prepare for publication

***.ins:**

```
…
SFAC C  H  N  F  P
UNIT 56 60 16 24 4

L.S. 40

ACTA

BOND $H

CONF
```

- **Make sure that the sum formula is correct**
- **Let the structure converge completely**
- **Generate .cif and .fcf files**
- **Generate bond distances and angles tables**
- **Generate torsion angles table**

**If you want to cite a torsion angle with an error (esd), you have to include this command here. You cannot estimate errors from atomic positions later.**

# Final refinement

- Prepare for publication

***.ins:**

```
…
SFAC C  H  N  F  P
UNIT 56 60 16 24 4

L.S. 40

ACTA

BOND $H

CONF

MPLA 6 N1 C1 C2 C3 C4 C5
MPLA 3 C6 C7 C8
```

- **Make sure that the sum formula is correct**
- **Let the structure converge completely**
- **Generate .cif and .fcf files**
- **Generate bond distances and angles tables**
- **Generate torsion angles table**
- **Calculate angles between planes**

**Again, you can obtain angles with an error (esd) only for planes refined during the refinement in the *.ins file!**

# Final refinement

- Prepare for publication

***.ins:**

```
…
SFAC C  H  N  F  P
UNIT 56 60 16 24 4

L.S. 40

ACTA

BOND $H

CONF

MPLA 6 N1 C1 C2 C3 C4 C5
MPLA 3 C6 C7 C8
```

**EQIV $1 –x, -y, -z**
**HTAB N1 C8_$1**

- **Make sure that the sum formula is correct**
- **Let the structure converge completely**
- **Generate .cif and .fcf files**
- **Generate bond distances and angles tables**
- **Generate torsion angles table**
- **Calculate angles between planes**
- **Define and calculate hydrogen bonding distances and angles**

**Same, same: only hydrogen distances defined by HTAB in the *.ins file can be obtained with an error (esd).**

**Since hydrogen bonding is often intermolecular, you might have to find and define the correct symmetry operation.**

# Final refinement

- Prepare for publication

***.ins:**

```
…
SFAC C  H  N  F  P
UNIT 56 60 16 24 4

L.S. 40

ACTA

BOND $H

CONF

MPLA 6 N1 C1 C2 C3 C4 C5
MPLA 3 C6 C7 C8

EQIV $1 –x, -y, -z
HTAB N1 C8_$1
```

**WPDB -1**

- **Make sure that the sum formula is correct**
- **Let the structure converge completely**
- **Generate .cif and .fcf files**
- **Generate bond distances and angles tables**
- **Generate torsion angles table**
- **Calculate angles between planes**
- **Define and calculate hydrogen bonding distances and angles**
- **Generate a pdb-file with your atomic positions**

**This is completely facultative and not really necessary.**

# Final refinement

- Prepare for publication

***.ins:**

```
…
SFAC C  H  N  F  P
UNIT 56 60 16 24 4

L.S. 40

ACTA

BOND $H

CONF

MPLA 6 N1 C1 C2 C3 C4 C5
MPLA 3 C6 C7 C8

EQIV $1 –x, -y, -z
HTAB N1 C8_$1

WPDB -1

SIZE  .15 .15 .2
```

- **Make sure that the sum formula is correct**
- **Let the structure converge completely**
- **Generate .cif and .fcf files**
- **Generate bond distances and angles tables**
- **Generate torsion angles table**
- **Calculate angles between planes**
- **Define and calculate hydrogen bonding distances and angles**
- **Generate a pdb-file with your atomic positions**
- **Add you crystal dimensions to the CIF file.**

**Attention: If you use SIZE, it enforces the calculation of theoretical values for the absorption ($T_{min}$,$T_{max}$), which appear in the CIF file. Those have to be replaced by the real values or deleted if no absorption correction was performed.**

# Final refinement

- Prepare for publication

***.ins:**

```
…
SFAC C  H  N  F  P
UNIT 56 60 16 24 4

L.S. 40

ACTA

BOND $H

CONF

MPLA 6 N1 C1 C2 C3 C4 C5
MPLA 3 C6 C7 C8

EQIV $1 –x, -y, -z
HTAB N1 C8_$1

WPDB -1

SIZE  .15 .15 .2

TEMP -123
…
```

- **Make sure that the sum formula is correct**
- **Let the structure converge completely**
- **Generate .cif and .fcf files**
- **Generate bond distances and angles tables**
- **Generate torsion angles table**
- **Calculate angles between planes**
- **Define and calculate hydrogen bonding distances and angles**
- **Generate a pdb-file with your atomic positions**
- **Add you crystal dimensions to the CIF file.**
- **Include the temperature in the CIF file.**

# *End of Refinement*

***Next thing to do: How to make sure that we did everything correctly?***