Chemical Crystallography and Structural Chemistry

VO 270063-1

Lecture № 5 — 20th April 2023

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Course Schedule

2rd	March	Lecture № 1	9th	March	Lecture № 2
16th	March	Lecture № 3	23th	March	Exercise № 1
30st	March	Lecture № 4	20th	April	Lecture № 5
27th	April	Exercise № 2	4th	May	Lecture № 6
11th	May	Lecture № 7	25th	May	Exercise № 3
1st	June	**no lecture**	15th	June	Lecture № 8
22nd	June	Lecture № 9	29th	June	Exercise № 4

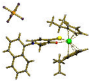
Previous Lecture

- Crystal Systems;
- choice of unit cell axes, reindexing of data
- Symmetry and diffraction data: Friedel's law and 11 Laue groups
- Experimental data collection

Contents

1 Data Integration

Data collection →



several GB

Data integration →

```
0 0 -1      2.7   0.9
0 0  1      4.0   1.0
0 0 -2 1'257.0  35.5
0 0 -2 1'600.0  42.7
```

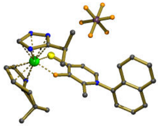
several files, 100's MB

Data Scaling

```
0 0 -1      2.8  0.55
0 0  1      3.8  0.63
0 0 -2 1'432.0  95.7
0 0 -2 1'282.0  85.9
```

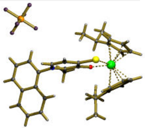
1 "hkl"-file, 50MB

→ Phasing



Starting model

→ Refinement



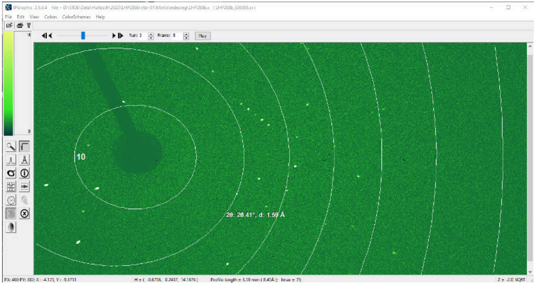
Chemically sensible model

Data Integration

Data integration comprises

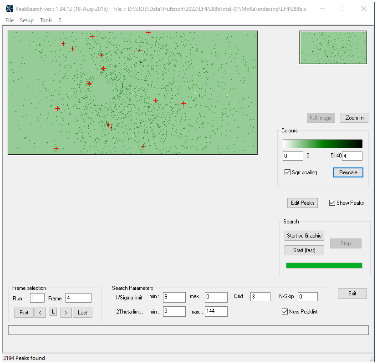
1. Indexing: Determination of unit cell dimensions, orientation of the crystal, point group
2. Extraction of spot intensities from detector images.
3. Optimisation of experimental parameters

Indexing: initial diffraction images



- typically four short runs:
- 2×10°–15°: 0°–10° and 90°–100°
- two detector settings each (low to mid resolution and mid to high resolution)

Indexing: peak finding



PeakSearch ver.: 1.34.12 (18-Aug-2015) File = D:\STOE\Data\Hultzsch\2022\LHP288b\xtal-01\MoKa\indexing\LHP288b.x

Colours: 0 0 5140 4

☑ Sqrt scaling

☑ Show Peaks

Run 1 Frame 4

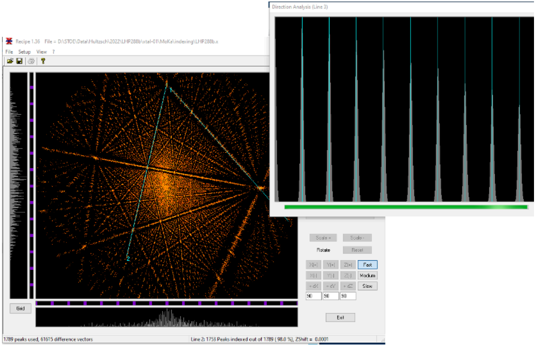
I/Sigma limit min : 9 max. : 0 Grid 3 N-Skip 0

2Theta limit : min : 3 max. : 144 ☑ New Peaklist

3194 Peaks found

- simple (non-crystallographic) pattern recognition algorithm: peak above background
- main parameter: desired peak strength (I/sigma)

Indexing: finding unit cell



Recipe 1.36 File = D:\STOE\Data\Hultzsch\2022\LHP288b\xtal-01\MoKa\indexing\LHP288b.x

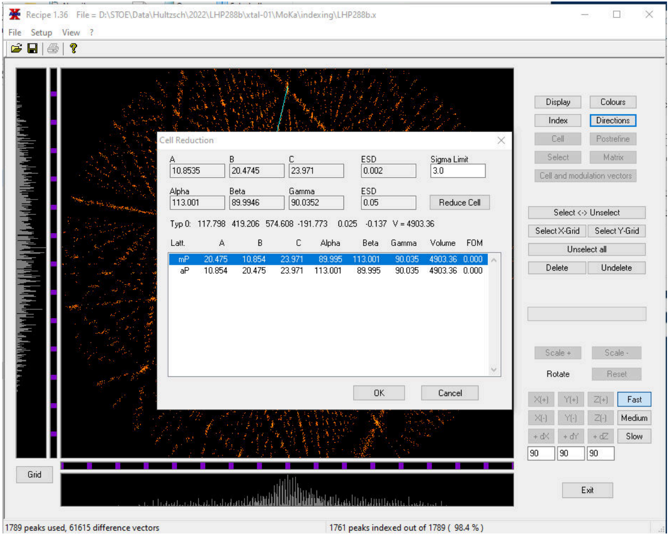
Direction Analysis (Line 3)

1789 peaks used, 61615 difference vectors

Line 2: 1753 Peaks indexed out of 1789 (98.0 %), ZShift = 0.0001

- known instrument geometry
- Calculate positions of peaks in reciprocal space (Laue equations / Ewald sphere)
- find a lattice basis

Indexing: finding unit cell



A 10.8535 B 20.4745 C 23.971 ESD 0.002 Sigma Limit 3.0

Alpha 113.001 Beta 89.9946 Gamma 90.0352 ESD 0.05

Typ 0: 117.798 419.206 574.608 -191.773 0.025 -0.137 V = 4903.36

Latt.	A	B	C	Alpha	Beta	Gamma	Volume	FOM
mP	20.475	10.854	23.971	89.995	113.001	90.035	4903.36	0.000
aP	10.854	20.475	23.971	113.001	89.995	90.035	4903.36	0.000

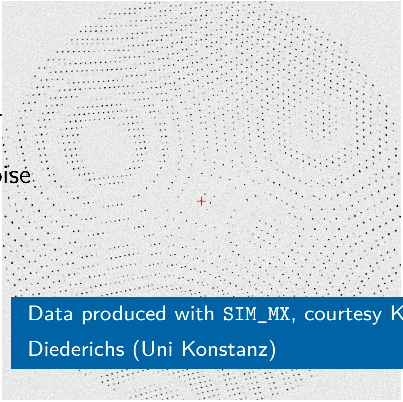
Rotation angles: 90 90 90

1789 peaks used, 61615 difference vectors

1761 peaks indexed out of 1789 (98.4 %)

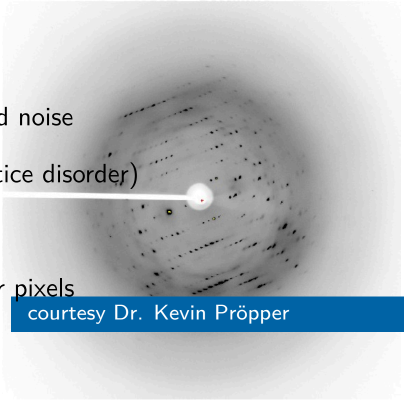
Data Extraction: Ideal diffraction image

- no lattice disorder
- no background noise
- perfect beam



Data produced with `SIM_MX`, courtesy Kay Diederichs (Uni Konstanz)

Data Extraction: Realistic diffraction image



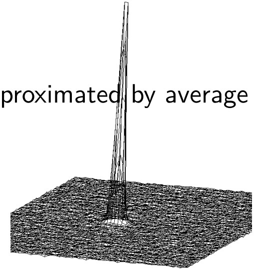
courtesy Dr. Kevin Pröpper

- strong background noise
- smeary spots (lattice disorder)
- spot overlap
- saturated detector pixels
- finite resolution

Signal extraction

1. Calculate reflex positions
2. Determine local background
3. Differentiate background from signal (spot volume, shape)
4. Different approach for strong spots and weak spots

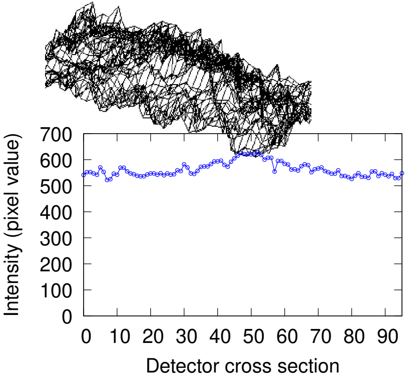
Signal extraction: strong spots



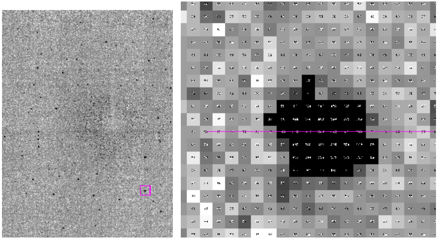
- High intensity ⇒ Small error from noise
- Spot covers large detector area: noise approximated by average
- Good spot separation
- Good spot profile (shape)

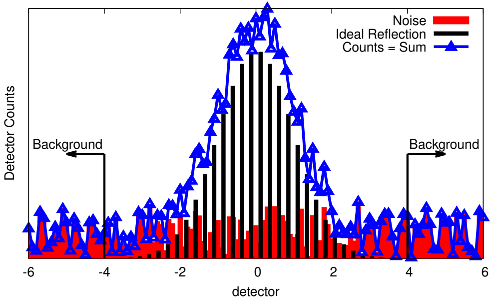
Signal extraction: weak spots

- Low intensity: ⇒ high error from noise
- Spot covers small detector area: large effect from noise
- Background difficult to determine



Cross section of a spot on the detector





Reflection profile

Most integration programs create a set of reflection profiles from strong and reliable reflections, *e.g.* a 3D Gauss function.
The profiles depend on the region on the detector and on the crystal orienation.
Advantages:

1. Measurement of weak reflections (fitting data for profile)
2. takes non-isotropic crystal shape into accoung
3. takes regions of varying detector sensitivity into account
4. produces a standard deviation of the reflection intensity: (h, k, l, I, σ_I)

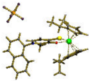
Summary Data Integration

- Starts with indexing: crystal orientation, unit cell
- Look at all images per run
- Look only at calculated spot positions on detector
- Strong spots: sum pixel values, substract background
- Strong spots: determine average reflection profile
- Weak spots: extract data based on profiles

2 Scaling

Data collection → **Data integration** → **Data Scaling**

Data collection



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Data integration

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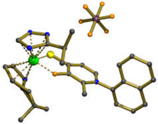
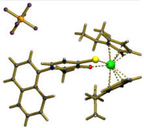
1 "hkl"-file, 50MB

→ **Phasing**



Starting model

→ **Refinement**



Chemically sensible model

Objective of the diffraction experiment

Structure elucidation of a chemical compounds

- chemical composition (*e.g.* purity after chromatography)
- Connectivity, distances between (non-) bonded atoms
- Configuration of stereochemical centres (R,S)

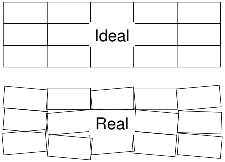
The values should be independent from the experimental setup.
Scaling makes the raw intensities (from data integration) independent from the experimental setup

Calculation of Intensities

Under consideration of the experimental, non-idealised setup, intensities are calculated as [1, Ch. Diffraction Intensities]

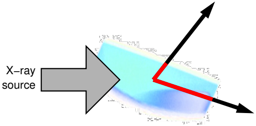
$$I_{exp}(hkl) \quad = \frac{e^4}{{m_e}^2 c^4} \frac{\lambda^3 V_{crystal}}{V_{u.c.}^2} I_0 LPTE |F_{theor.}(hkl)|^2 \qquad (1)$$

- I_0 incoming intensity (may vary with time)
- L Lorentz factor describes trajectory through the Eqwald sphere
- P Polarisation correction; $P = (1 + \cos^2 2\theta)/2$ for unpolarised source
- T Absorption correction (esp. heavy elements)
- E extinction correction (crystal defects, mosaicity)
- $F_{theor.}(hkl)$ structure factor (calculated from structure)

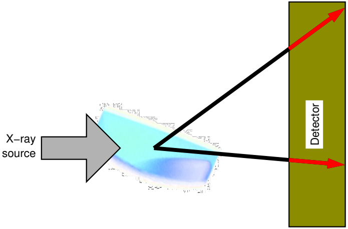


Scaling = Idealisation and correction

In order to make data as independent from the experiment as possible, data are "standardised". Some corrections are of numerical nature (polarisation), others are sample dependent (extinction: depends on elements in compounds). Two examples: absorption and angle of incidence



Absorption in the crystal depends on the path



Higher angle of incidence w.r.t. detector surface leads longer path through detector phosphor and thus to stronger signal

Basis for Scaling: Symmetry and multiple measurements

- Some corrections depend on the instrument and can be calibrated (polarisation, angle of incidence, Lorentz factor)
- Some corrections (*e.g.* absorption, extinction) are (also) sample dependent

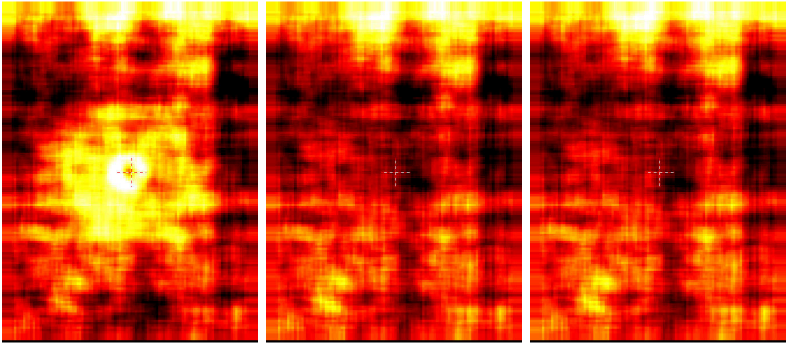
Idea: symmetry equivalent reflections, or multiply measured reflections, should have the same intensity

Scaling means

1. Determination of the measured intensity I_{obs} of a set of equivalent reflections
2. Determination of their standard uncertainties
3. Result: idealised data set

Examples for corrections

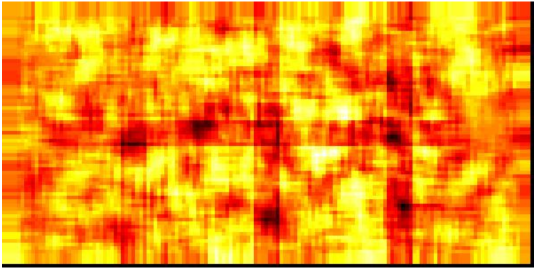
CMOS Detector (Bruker Photon II)



Detector “gain”: dark regions of the detector are more sensitive (factor between 0.97 and 1.3). Direct beam (left): indicates non-linear response at high intensity

Examples for corrections

Hybrid pixel detector (DECTRIS Eiger2 R500)

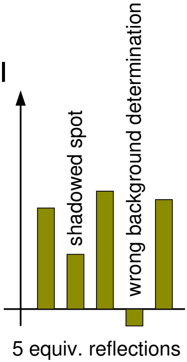


Hybrid pixel detectors are closer to ideal detectors for X-rays, with a smooth gain (factor between 0.96 and 1.02).

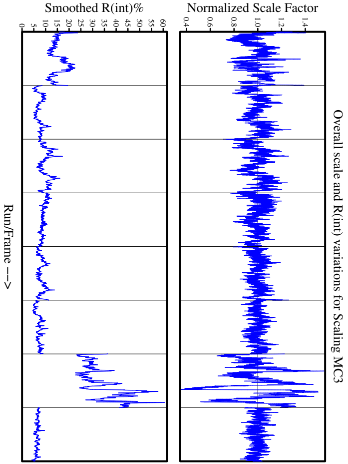
Scaling details

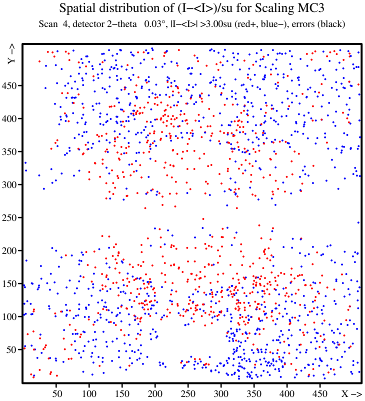
Options to find the mean intensity $< I >$ of a group of equivalent reflections

1. Statistical average: exaggerates outliers
2. Scaling of each group of equivalents independently from other groups: neglects systematic errors.
3. Instead: **One** scale factor for several groups of equivalent reflections (*e.g.* 100 groups) which are close together on the detector



Scaling plots (program SADABS)





Idealised intensities

Before Scaling

After Scaling

$$I(hkl) = \frac{e^4}{{m_e}^2 c^4}\frac{\lambda^3 V_{\text{crystal}}}{V_{\text{u.c.}}^2} I_0 LPTE|F(hkl)|^2 \qquad I(hkl) = c|F(hkl)|^2 \tag{2}$$

Before Scaling:

```
0 -1  5  1.379E+03  2.516E+02
0 -1 -5  1.367E+03  2.726E+02
0  1  5  1.184E+03  2.610E+02
0  1 -5  1.347E+03  2.674E+02
0 -1  6  1.090E+04 -1.229E+03
0 -1 -6  4.677E+03  5.733E+02
0  1  6  4.286E+03  5.488E+02
0  1 -6  9.065E+03 -1.034E+03
0 -1  7  0.204E+02  0.571E+01
```

After Scaling:

```
0 -1  5  7.014E+01  1.208E+01
0 -1 -5  6.812E+01  1.274E+01
0  1  5  5.987E+01  1.231E+01
0  1 -5  6.753E+01  1.258E+01
outlier removed
0 -1 -6  2.365E+02  2.856E+01
0  1  6  2.145E+02  2.689E+01
outlier removed
0 -1  7  1.404E+02  2.271E+01
```

Summary Scaling

- Scaling finds the mean intensity $< I >$ of symmetry equivalent reflections
- Scaling puts one or more data sets on a common scale
- Scaling removes outliers
- The result of scaling is a single (hkl)-file, which is used for all subsequent steps:
    1. Phasing, *i.e.* structure solution
    2. Model refinement

3 Intermezzo: The structure factor

The Structure Factor $F(hkl)$

- Context between atoms and diffraction intensities
- Describing the electron density with the independent atom model (“IAM”)
- Formfactor and the “fudge factor” ADP

The Structure Factor

The structure factor $F(hkl)$ is related to the **electron density** $\rho(x,y,z)$, i.e. the distribution of electrons inside the unit cell:

$$F(hkl) = \int_{\text{unit cell}} \rho(x,y,z) e^{2\pi i(hx+ky+lz)} d^3x \tag{3}$$

This equation is the Fourier transformation of the electron density.
Note: The term “Fourier transformation” is important mainly because computers are very fast in calculating Fourier transformations.

The Structure Factor

The *Independent Atom Model* (IAM, alias *isolated atom model*) is a powerful method to calculate the atomic structure factor $F(hkl)$

$$F(hkl) = \sum_{\text{in u.c.}}^{\text{atoms } j} f_j(\theta) e^{-8\pi^2 U_j(\theta,\lambda)} e^{2\pi i(hx_j + ky_j + lz_j)} \tag{4}$$

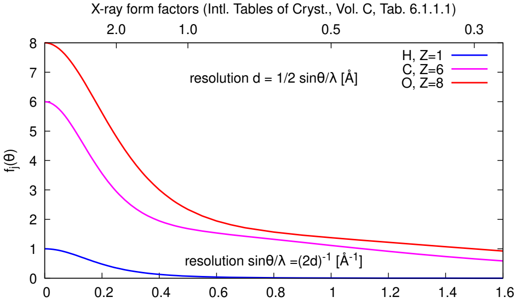
f_j atomic *form* factor. Dependent on atom element, decreases with decreasins scattering angle $\theta = \theta(hkl)$

$U_j(\theta, \lambda)$ atomic displacement parameter (ADP, alias Debye-Waller factor): models thermal vibration of atoms

$e^{2\pi i(hx_j + ky_j + lz_j)}$ phase shift of the atom relative to the origin of the unit cell

The form factor $f_j(\theta)$

Intensity of the scattered X-rays decreases with increasing scattering angle θ.



The wavelength λ is of the same order of magnitude as the size of the atoms: photons “see” the shape of atoms.

Note: hydrogen atoms do not contribute to data higher than 1 Å

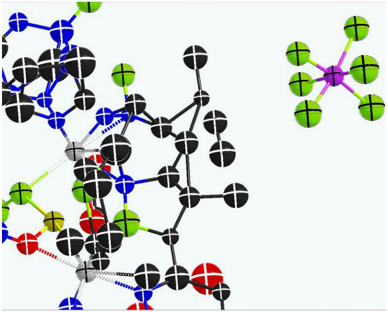
The atomic displacement parameter $U_j(\theta, \lambda)$

- Atoms vibrate at $T > 0K$
- Vibration leads to reduction of spot intensities, but not to change in spot shape
- At medium resolution: 1 parameter
- At high resolution: anisotropic description with 6 parameters as ellipsoids

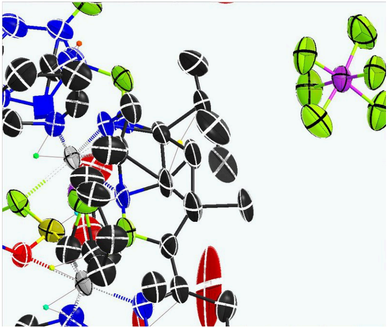
Isotropic	**Anisotropic**
$U_j(\theta,\lambda) = 4U_{\text{iso}}\frac{\sin^2\theta}{\lambda^2}$	$U_j(\theta,\lambda) = (hkl)\begin{pmatrix} U_{11} & U_{12} & U_{13} \\ U_{12} & U_{22} & U_{23} \\ U_{13} & U_{23} & U_{33} \end{pmatrix}\begin{pmatrix} a^* \\ b^* \\ c^* \end{pmatrix}$
1 parameter per atom	6 parameters per atom

- Name : ADP = isotropic or anisotropic *atomic displacement parameter*

Example images for ADP



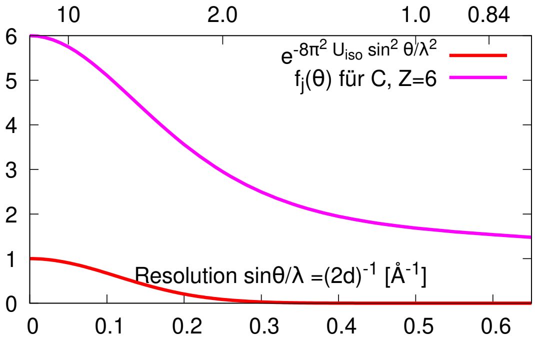
Refinement with isotropic ADPs



Refinement with anisotropic ADPs

Caveat: Anisotropic ADPs “wipe up” errors in the data.

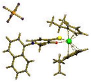
The ADP U: a fudge factor



- Sharp drop-off with resolution: can make wrongly placed atoms disappear.
- Similarity with form factor: confusion of atom types
- Risk of overfitting

4 Phasing

Data collection → **Data integration** → **Data Scaling**



several GB

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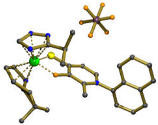
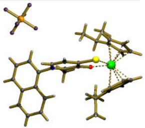
→ **Phasing** → Refinement



Starting model



Chemically sensible model

Phasing *alias* Solving the structure

- Ideally, we would measure data, run a single calculation, and get the molecular structure as result.
- our data: thousands of measured intensities $I(hkl)$.
- From Eq. 2 (p. 28) and Eq. 4 (page 33):

$$\begin{aligned} I(hkl) &= c|F(hkl)|^2 \\ &= c\left|\int_{\text{unit cell}} \rho(x,y,z)e^{2\pi i(hx+ky+lz)}d^3x\right|^2 \end{aligned}$$

- **If** we could invert this equation, we could calculate the coordinates x, y, z in one go. But we cannot ...

The phase problem

The inverse of the Fourier transformation

$$F(hkl) = \int_{\text{unit cell}} \rho(x,y,z) e^{2\pi i(hx+ky+lz)} d^3x$$

reads

$$\rho(x,y,z) = \sum_{(h,k,l)} F(hkl) e^{-2\pi i(hx+ky+lz)}$$

The phase problem

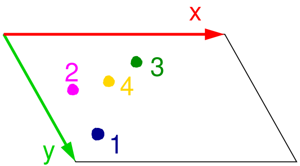
The structure factor $F(hkl)$ is a complex number. Therefore, it has

an amplitude $|F(hkl)| = \sqrt{I(hkl)/c}$

a phase $\phi(hkl) = ???$

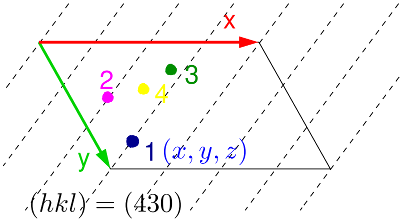
$F(hkl) = \sqrt{I(hkl)/c} \times e^{-i\phi(hkl)}$
We can measure the amplitude, but we cannot measure the phase. This is known as the **phase problem of crystallography**.

Relation between Phases and Molecule



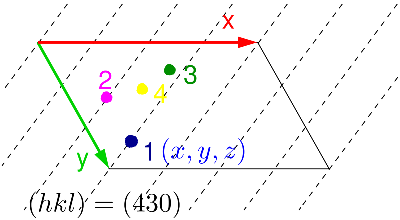
Unit cell with four atoms inside.

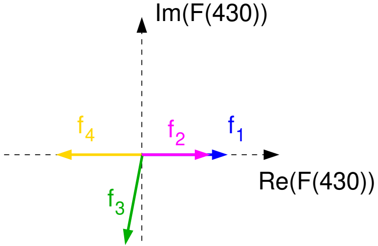
The phases are related to the chemical structure



Example reflection $F(430) = \sum_{j=1}^{4} f_j(\theta) e^{-8\pi^2 U_j(\theta,\lambda)} e^{2\pi i (4x_j + 3y_j + 0z_j)}$

The phases are related to the chemical structure





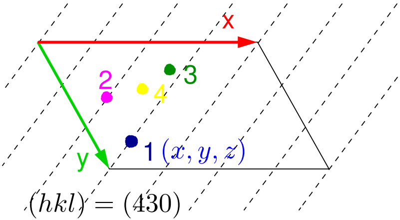
$$\phi_j = 2\pi(4x_i + 3y_i + 0z_i)$$

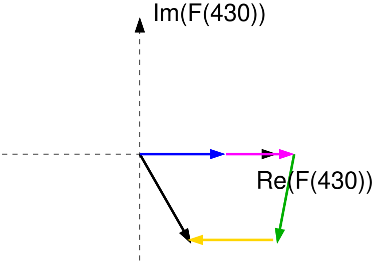
= rel. distance to origin

= rel. distance to lattice plane

$$F(430) = \sum_{\mathrm{j=1}}^{4} f_j(\theta) e^{-8\pi^2 U_j(\theta,\lambda)} e^{2\pi i(4x_j+3y_j+0z_j)}$$

The phases are related to the chemical structure

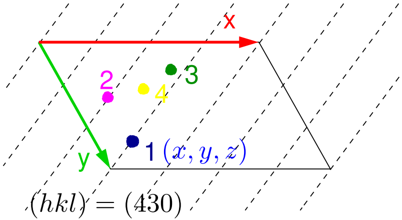


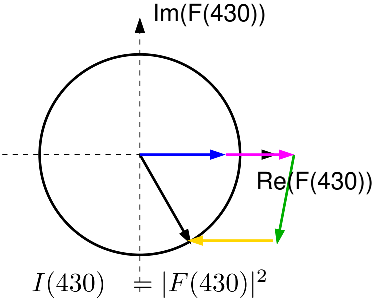


$$
\begin{aligned}
F(430) &= f_1(430) \\
&+ f_2(430) \\
&+ f_3(430) \\
&+ f_4(430)
\end{aligned}
$$

Total $F(430)$ = sum of individual vectors

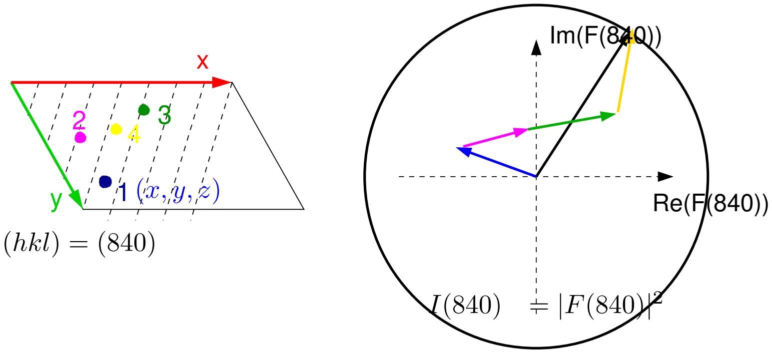
The phases are related to the chemical structure





Measurement $I(430) = |F(430)|^2$: loss of phase information

The phases are related to the chemical structure



Same coordinates, *different* contributions per atom to $F(840)$

Phases $\phi(hkl)$

- The phase problem arises, because $F(hkl)$ is a complex number.
- $F(hkl) = \sum_{\text{all atoms}} f_j(\theta) e^{-8\pi^2 U_j(\theta,\lambda)} e^{2\pi i(hx_j + ky_j + lz_j)}$
- The length f_j for each atom is independent of (hkl).
- The phase contribution $e^{2\pi i(hx_j+ky_j+lz_j)}$ varies for each reflection.
- the phases $\phi(hkl)$ is an angle between 0° and 360°
- The total phase $\phi(hkl)$ contains convoluted information from each atom. Each contribution depends on the position of the atom **relative** to the lattice planes for the reflection (hkl), *i.e.*, there are as many phases as there are reflection spots.

Solving the structure = Solving the phase problem

- The phase problem prevents us from calculating the electron density map directly from our data
- Phases can be calculated from a chemical model (its coordinates)
- "Phasing" means to find a model close enough to the proper model
- Once a good enough molecule has been found, it needs to be improved: "model building" and "refinement"

Solving the structure = Solving the phase problem

> In the beginning, crystallographers worked on the structures of simple molecules and they could often make a good guess of the conformation of a molecule and even how it might pack in the crystal lattice. The guesses could be tested by calculating a diffraction pattern and comparing it to the observed one. If a guess places the atoms in about the right place, then the calculated phases will be approximately correct and a useful electron density map can be computed by combining the observed amplitudes with the calculated phases. If the model is reasonably accurate, such a map will show features missing from the model so that the model can be improved. You can remind yourself how this works by looking at Kevin Cowtan's cats.

Randy Read, [2]

Phasing and then?

- "phasing" estimates the phase $\phi(hkl)$ for each reflection of the dataset
- the estimates are often quite poor
- the initial average phase errors can be several 10s of degrees $(10, 20, 30, \dots{}^\circ)$
- initial phases means
    1. finding **some** atom positions
    2. some correct, some incorrect element types
    3. often fixed, isotropic ADP values
- model building and refinement improves these phases by correcting these approximations

Phasing methods [3, 4, 5]

There are several methods to solve the phase problem. This lecture will cover to most popular ones

1. Patterson map
2. Direct methods

Patterson maps are common for small molecules, which contain a mixture of heavy and light atoms.
Direct methods are particularly useful for structure with similar elements, *e.g.* organic compounds.

5 The Patterson map

The Patterson map

- since 1934, Arthur Lindo Patterson (1902–1966)
- good for very small structures with some heavy elements
- direct determination of atom positions

Calculation of the Patterson map

The Patterson map ignores phases and calculates the Fourier transformation from the intensities:

$$P(uvw) = \sum_{(hkl)} I(hkl) e^{-2\pi i(hu+kv+lw)}$$

This can be calculated without knowing the phases $\phi(hkl)$, only from the measured intensities.
It turns out this map is the "auto-convolution" of the electron density with itself ($(uvw) = \vec{u}$):

$$\begin{aligned} P(uvw) &= \rho(\vec{x}) \star \rho(\vec{x} - \vec{u}) \\ &= \int_{\text{unit cell}} \rho(\vec{x})\rho(\vec{x} - \vec{u}) d^3x \end{aligned}$$

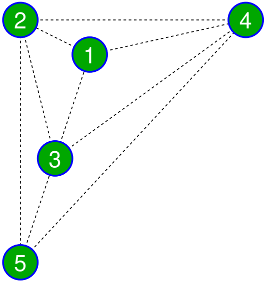
Meaning of the Patterson map

It can be shown that the Patterson map

$$\begin{aligned} P(uvw) &= \rho(\vec{x}) \star \rho(\vec{x} - \vec{u}) \\ &= \int_{\text{unit cell}} \rho(\vec{x})\rho(\vec{x} - \vec{u}) d^3x \end{aligned}$$

has its peaks at vector (positions) $\vec{u}$ that corresponds to the connecting vector between two atoms in the molecule in the unit cell.

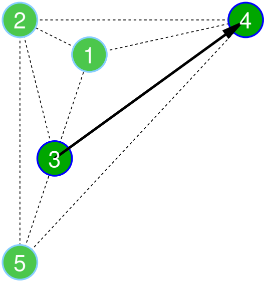
Illustration of the Patterson map in 2D



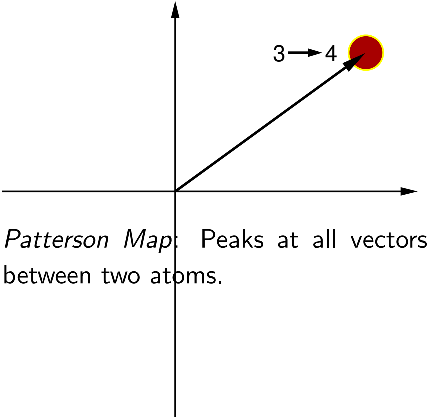
"2D molecule, 5 atoms"

peaks of Patterson map

Illustration of the Patterson map in 2D



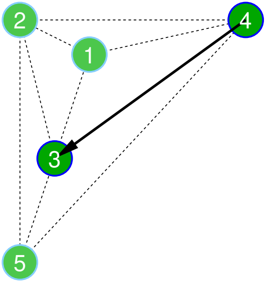
"2D molecule, 5 atoms"



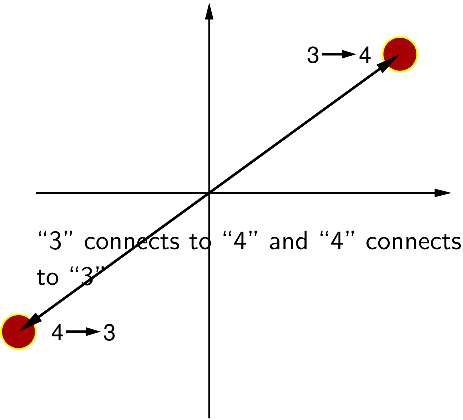
Patterson Map: Peaks at all vectors between two atoms.

peaks of Patterson map

Illustration of the Patterson map in 2D



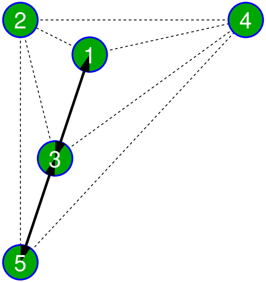
“2D molecule, 5 atoms”



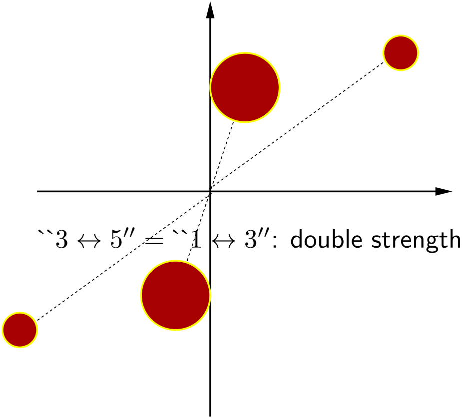
“3” connects to “4” and “4” connects to “3”

peaks of Patterson map

Illustration of the Patterson map in 2D



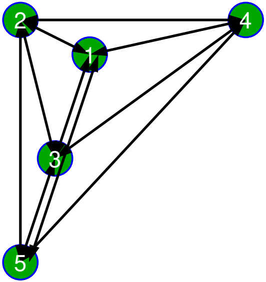
“2D molecule, 5 atoms”



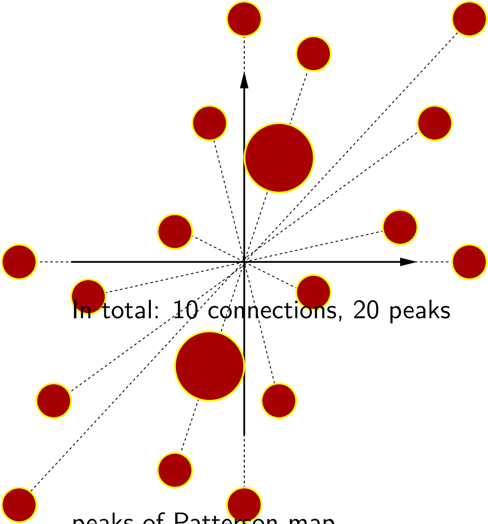
$``3 \leftrightarrow 5'' = ``1 \leftrightarrow 3''$: double strength

peaks of Patterson map

Illustration of the Patterson map in 2D



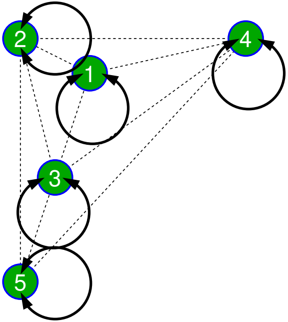
"2D molecule, 5 atoms"



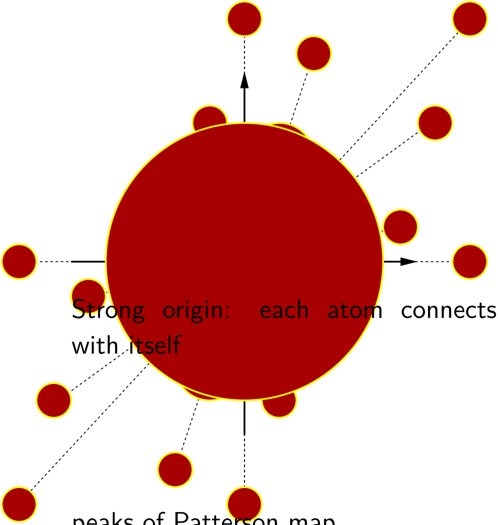
In total: 10 connections, 20 peaks

peaks of Patterson map

Illustration of the Patterson map in 2D



“2D molecule, 5 atoms”



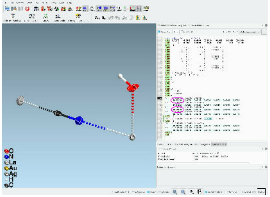
Strong origin: each atom connects with itself

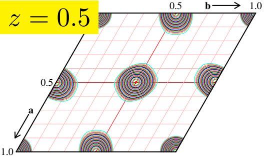
peaks of Patterson map

Patterson map observations

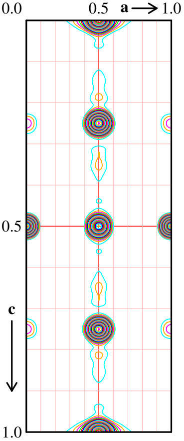
- heavy elements have stronger peaks (high density $\rho(x,y,z)$)
- with too many atoms: origin peak overwhelms: non-interpretable
- with too many atoms: too many peaks, overlap
- Patterson map always centro-symmetric (peak at $(x,y,z) \Leftrightarrow$ peak at $(-x,-y,-z)$)
- the Patterson map does not **directly** reveal the molecule shape

Patterson map for $La[Au(CN)_2]_3 \cdot 3H_2O$



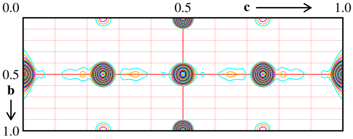


$z = 0.5$



$y = 0.0$

$x = 0.0$



- La(III): $54e^-$, Au(I): $78e^-$, O^{2-}: $10e^-$
- 54*78 $=$ 4’212 $\gg$ 78*10=780: 1 dominating peak
- Patterson maps: typically “origin peak removed”

Summary Patterson map

- Patterson map calculated from intensities, without phases
- Patterson map corresponds to convolution of density $\rho(x, y, z)$
- Peaks correspond to connecting vectors between atoms
- Peak height corresponds to product of number of electrons
- Atom coordinates can be deduced from map in case of few atoms, or few heavy atoms
- The more atoms (of similar weight), the harder to interpret

6 Direct methods

Direct methods

- Well suited with molecules of similar atom types (organic compounds with $C, N, O, \ldots$)
- Can work with thousands of atoms
- Requires atomic resolution, better than 1.2 Å (Sheldrick's rule, [6])

Concept of direct methods

1. Generate roughly the number of expected atoms at arbitrary positions
2. Calculate phases of this pseudo-molecule
3. Improve phases based on **tangent formula**
4. Improved phases produce an improved electron density map
5. Peak picking from improved map
6. Repeat
7. Best solution: assign atom types

Direct methods: the tangent formula

Tangent formula[1] was derived by H. A. Hauptman and J. Karle — chemistry Nobel prize 1985

$$\tan(\phi_{\mathbf{h}}) \approx \frac{\sum_{\mathbf{h}'} |E_{\mathbf{h}'} E_{\mathbf{h}-\mathbf{h}'}| \sin(\phi_{\mathbf{h}'} + \phi_{\mathbf{h}-\mathbf{h}'})}{\sum_{\mathbf{h}'} |E_{\mathbf{h}'} E_{\mathbf{h}-\mathbf{h}'}| \cos(\phi_{\mathbf{h}'} + \phi_{\mathbf{h}-\mathbf{h}'})}$$

creates a network of phase relationships between (hkl) and $(h-h', k-k', l-l')$. Historically based on Sayre-Equation (1952)

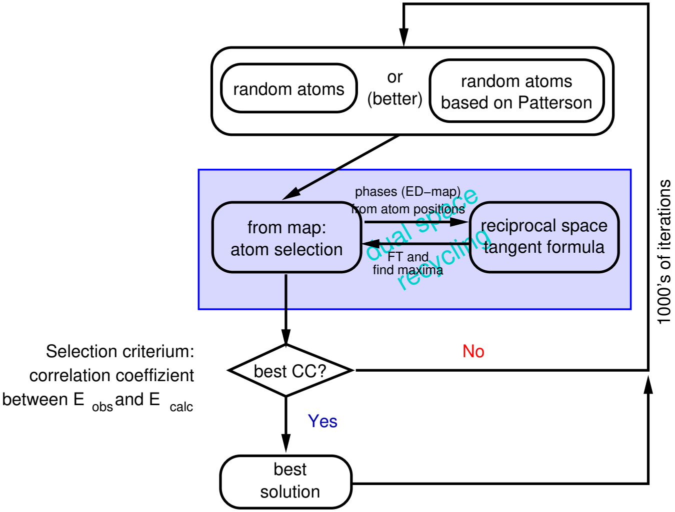
$$F(hkl) = q(\sin\theta/\lambda) \sum_{(h'k'l')} F(h'k'l') * F(h-h', k-k', l-l')$$

Sayre equation is exact for cases of only one atom type in crystal (diamond, silicon, *etc*). That is why the tangent formula works best for similar-atoms-compounds.

---

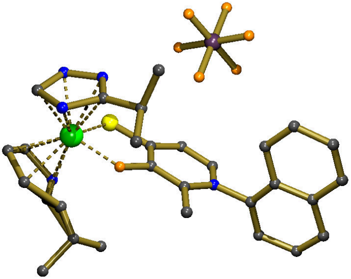
[1] $E(hkl)$: normalised structure factors, derived from measured $F(hkl)$

Direct methods: dual space recycling

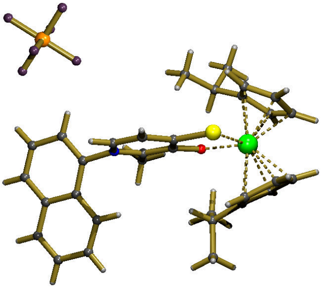


Amazingly, it works

Example (courtesy Florian hausmayr, AK Keppler)

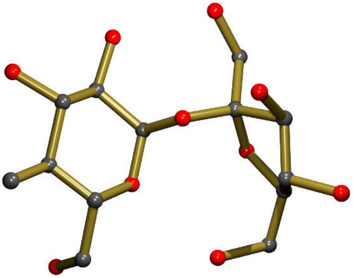


solved with automated atom assignment (SHELXT)

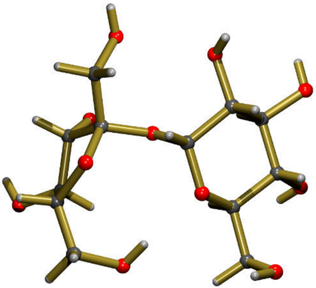


Final structure

Example: Sucrose



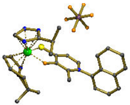
Sucrose, solved with automated atom assignment (SHELXT)



Final structure

7 Structure Refinement

Data collection → **Data integration** → **Data Scaling**



several GB

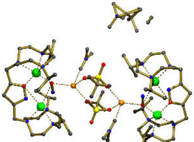
```
0 0 -1      2.7  0.9
0 0  1      4.0  1.0
0 0 -2 1'257.0 35.5
0 0 -2 1'600.0 42.7
```

several files, 100's MB

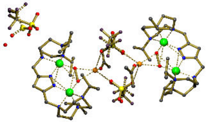
```
0 0 -1      2.8 0.55
0 0  1      3.8 0.63
0 0 -2 1'432.0 95.7
0 0 -2 1'282.0 85.9
```

1 "hkl"-file, 50MB

→ **Phasing** → **Refinement**



Starting model



Chemically sensible model

Model Building & Refinement

- Refinement optimises computationally the parameters of the structure with respect to the data
- Model building make modifications that are too large for computer optimisation, e.g.
    1. Addition or removal of atoms
    2. correction of atom types
    3. modelling of disorder and multiple conformations

References

[1] C. Giacovazzo, ed. *Fundamentals of Crystallography*. Oxford University Press, 1985.

[2] R. Read. *Protein Crystallography Course. The phase problem: introduction to phasing methods*. URL: `https://www-structmed.cimr.cam.ac.uk/Course/Basic_phasing/Phasing.html` (visited on 07/06/2022).

[3] C. Giacovazzo. *Phasing in Crystallography. A Modern Perspective*. Oxford University Press, 1998.

[4] Lukáš Palatinus and Gervais Chapuis. 'SUPERFLIP – a computer program for the solution of crystal structures by charge flipping in arbitrary dimensions'. In: *J. Appl. Crystallogr.* 40 (2007), pp. 786–790. DOI: 10.1107/S0021889807029238.

[5] George M. Sheldrick. 'SHELXT – Integrated space-group and crystal-structure determination'. In: *Acta Crystallogr* A71 (2015), pp. 3–8. DOI: 10.1107/S2053273314026370.

[6] Richard J. Morris and Gérard Bricogne. 'Sheldrick's 1.2Å rule and beyond'. In: *Acta Crystallogr* D59 (2003), pp. 615–617. DOI: 10.1107/S090744490300163X.