Introduction to the charge flipping for powder diffraction

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We are here

Approx. 800 km from here...
We are here

The main building of the institute is on the other side of Prague.
We are here
We are here

Volleyball court

Tennis-court
We are here

Canteen!

Tennis-court

Volleyball court
Canteen
Department of structure analysis

Powder diffraction

X-ray single crystal diffraction

Electron precession diffraction
Powder diffractometers in our lab

Empyrean (PANalytical)

SmartLab (Rigaku)
Powder sample

powder = polycrystalline material
Powder diffraction pattern is a combination of a large number of the single crystal diffraction patterns.
Powder diffraction pattern of alaptide powder on the area detector
Diffracted pattern
Problems and limitations

- **Information loss** – data are projection of a 3D diffraction pattern to 1D
Problems and limitations

- **Peak overlap** – extraction of intensities.
Problems and limitations

- Peak overlap – extraction of intensities.

What is the intensity of these reflections?

Positions of reflections
Problems and limitations

- Peak overlap – extraction of intensities.

What is the intensity of these reflections?

Positions of reflections
Peak overlap
El. density – $F_{\text{calc}}$ Fourier

$\sin \Theta / \lambda = 0.2$

$\lambda = 1.5418 \, \text{Å}$

$\text{max} = 36^\circ \, 2\Theta$

$d_{\text{max}} = 2.5 \, \text{Å}$
Rozlišení ELD

\[ \sin \Theta / \lambda = 0.25 \]

\[ \lambda = 1.5418 \text{ Å} \]

\[ \text{max} = 45^\circ \]

\[ d_{\text{max}} = 2.0 \text{ Å} \]
Rozlišení ELD

\[
\sin \Theta / \lambda = 0.3
\]

\[
\lambda = 1.5418 \text{ Å}
\]

\[
\text{max} = 55^\circ 2\Theta
\]

\[
d_{\text{max}} = 1.7 \text{ Å}
\]
Rozlišení ELD

\[ \sin \Theta / \lambda = 0.35 \]

\[ \lambda = 1.5418 \text{ Å} \]

\[ \text{max} = 65^\circ \ 2\Theta \]

\[ d_{\text{max}} = 1.4 \text{ Å} \]
Rozlišení ELD

$\sin \Theta / \lambda = 0.4$

$\lambda = 1.5418 \text{ Å}$

$max = 76^\circ \ 2\Theta$

$d_{\text{max}} = 1.3 \text{ Å}$
Effect of the peak overlap

- **Dual space methods** and **direct methods** need:
  - High resolution data (~1.2 Å and better)
  - Low peak overlap
    - charge flipping combined with histogram matching may solve the „peak overlap“ issue

- **Direct Space methods**
  - Starting model
  - Time consuming process
Charge flipping is a method for \textit{ab initio} determination of an approximate scattering density from the set of structure-factor amplitudes.

- Published by Oszlányi \\& Sütő (2004), Acta Cryst A
- The output is an \textit{approximate scattering density} of the structure sampled on a discrete grid
- Requires only \textit{lattice parameters} and \textit{reflection intensities}
- No use of atomicity, only of the “sparseness” of the electron density
- \textbf{No use of symmetry apart from the input intensities}
The direct-space constraint must restrict the scattering densities to a physically meaningful subset. Typical requirements are positivity, sparseness and atomicity.
Constraints and projections

Positivity projection
Constraints and projections

Significance + positivity projection (dynamic support with positivity)
Constraints and projections

Significance projection (dynamic support without positivity)
Constraints and projections

Reflector of the significance + positivity projection – the charge flipping operation
Constraints and projections

Constraint on the number of maxima in the density
Charge flipping - applet

http://escher.epfl.ch/flip/
Charge flipping

- Assign random phases
- Flip sign of ed < $\delta$
- Back transform
- Combine $|F_{hkl}(\text{obs})|$ with $\phi_{hkl}(\text{calc})$
- R-value

$|F_{hkl}(\text{obs})|$
$\delta$ (ed threshold for flipping)

Electron density map

Perturbed electron density map
Charge flipping for powders

1. Assign random phases
2. Flip sign of $\delta$ (ed threshold for flipping)
3. Repartitioning after $n$ cycles
4. Electron density histogram

| $|F_{hkl}(\text{obs})|$ with overlap groups |
| $\delta$ (ed threshold for flipping) |
| Repartitioning after $n$ cycles |
| Electron density map |
| Flip sign of $\delta$ |
| Perturbed electron density map |
| Combine $|F_{hkl}(\text{obs})|$ with $\phi_{hkl}(\text{calc})$ |

- $|F_{hkl}(\text{calc})|$ with $\phi_{hkl}(\text{calc})$
- New $|F_{hkl}(\text{obs})|$ and new $\phi_{hkl}(\text{calc})$
- Repartition overlapping reflections
- Perturbed electron density map
- Back transform
- $R$-value
- n cycles?

- Yes: Histogram matching
- No: Repartitioning after $n$ cycles

Electron density map

R-value

n cycles?
Electron density histograms

Original idea: Zhang & Main, Acta Cryst A46, 1990 – used to improve phases, not intensities
Electron density histograms

Original idea: Zhang & Main, Acta Cryst A46, 1990 – used to improve phases, not intensities

\[ F_{\text{new}}^{\text{HM}} = F_{\text{HM}} \sqrt{\frac{\sum_k |F_{\text{h}}|^2}{\sum_k |F_{\text{HM}}|^2}} \]
Charge flipping for powders

Zeolite ZSM-5, $\text{Si}_{96}\text{O}_{192}$

without histogram matching  with histogram matching
Charge flipping for powders

• How to set up the algorithm?
• $K = 0.3$
• $\text{Biso} = 0–1$
• $\text{HM} = 20–5$
• $\delta = \delta_{\text{auto}}$
• 500 cycles
• 100 runs

Sisak et al. (2012): Optimizing the input parameters for powder charge flipping
Charge flipping for powders
Charge flipping for powders
Charge flipping for powders

Can we really interpret this map?
Charge flipping for powders
Rozlišení ELD

\[ \sin \Theta / \lambda = 0.25 \]

\[ \lambda = 1.5418 \, \text{Å} \]

\[ \text{max} = 45° \, 2\Theta \]

\[ \text{dmax} = 2.0 \, \text{Å} \]
Advantages and disadvantages

+ **Minimum assumptions** and approximations involved
+ No explicit use of **chemical composition** and form factors
+ No explicit use of **space group** symmetry
+ **Obtaining symmetry** with solution
+ Applicable to x-ray, neutron, electron diffraction

- **Requires atomic resolution** (d<1.3Å for light atoms, much more relaxed for heavier atoms)
- **Peak overlap** should not be so high
Thank you!