Introduction to the charge flipping for powder diffraction

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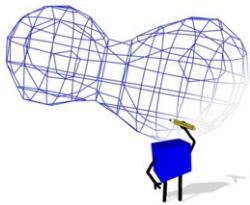
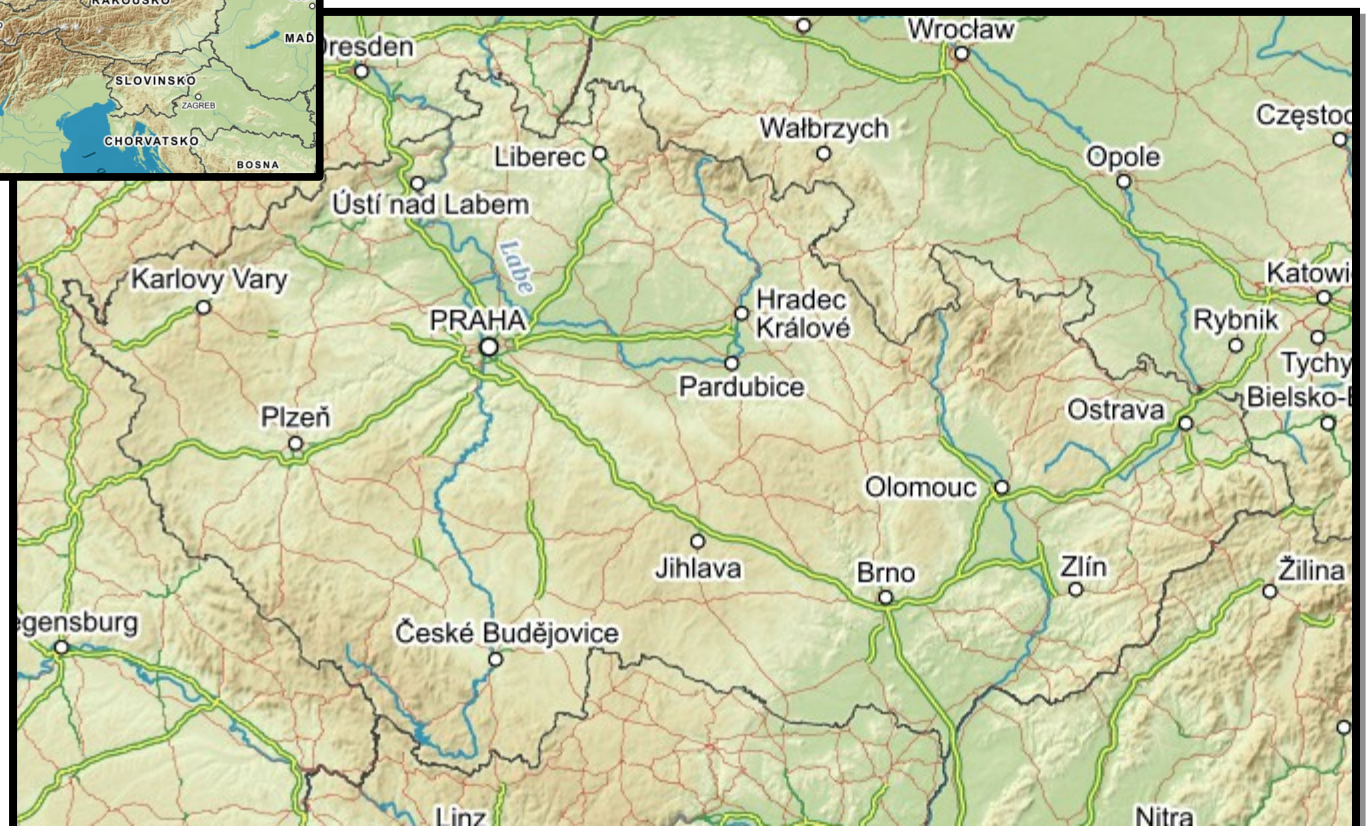
Superflip

FZÚ

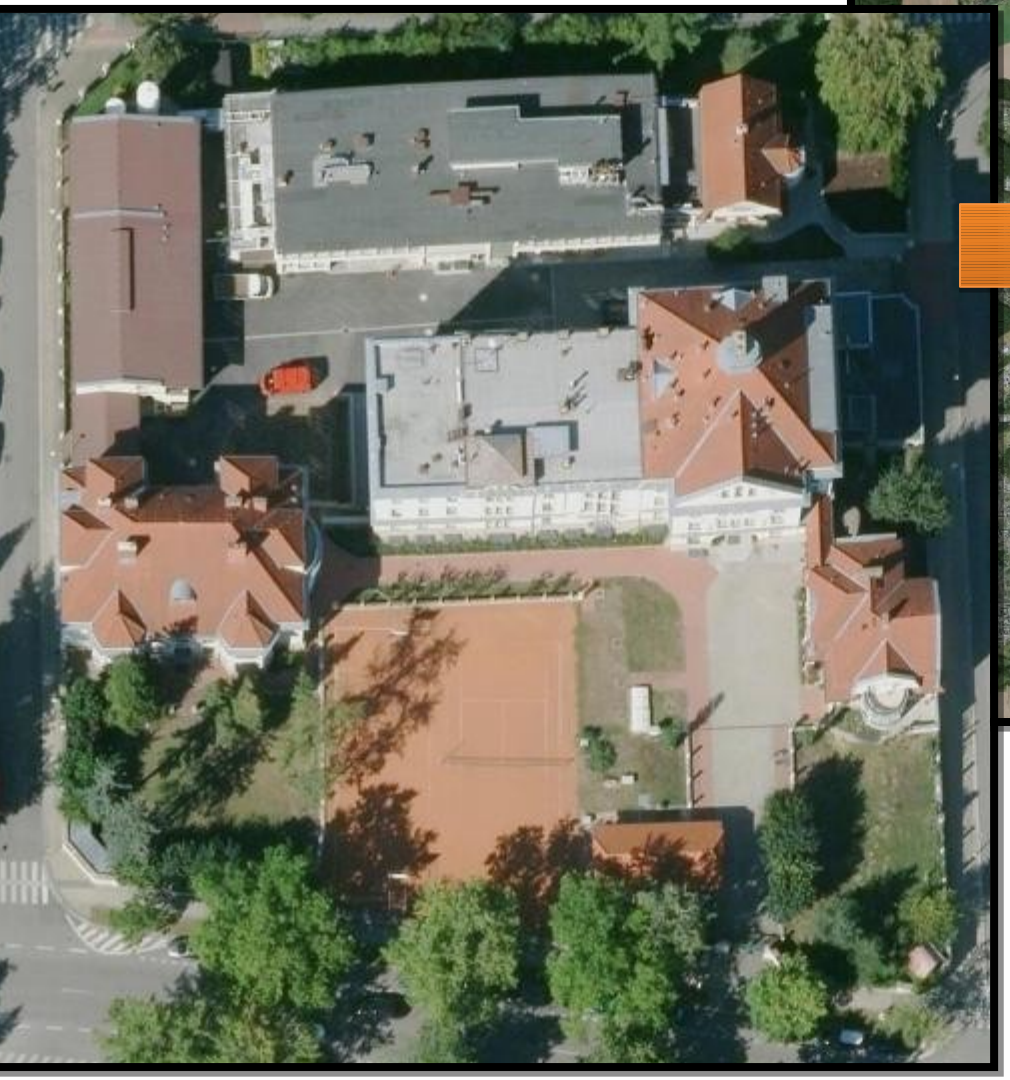


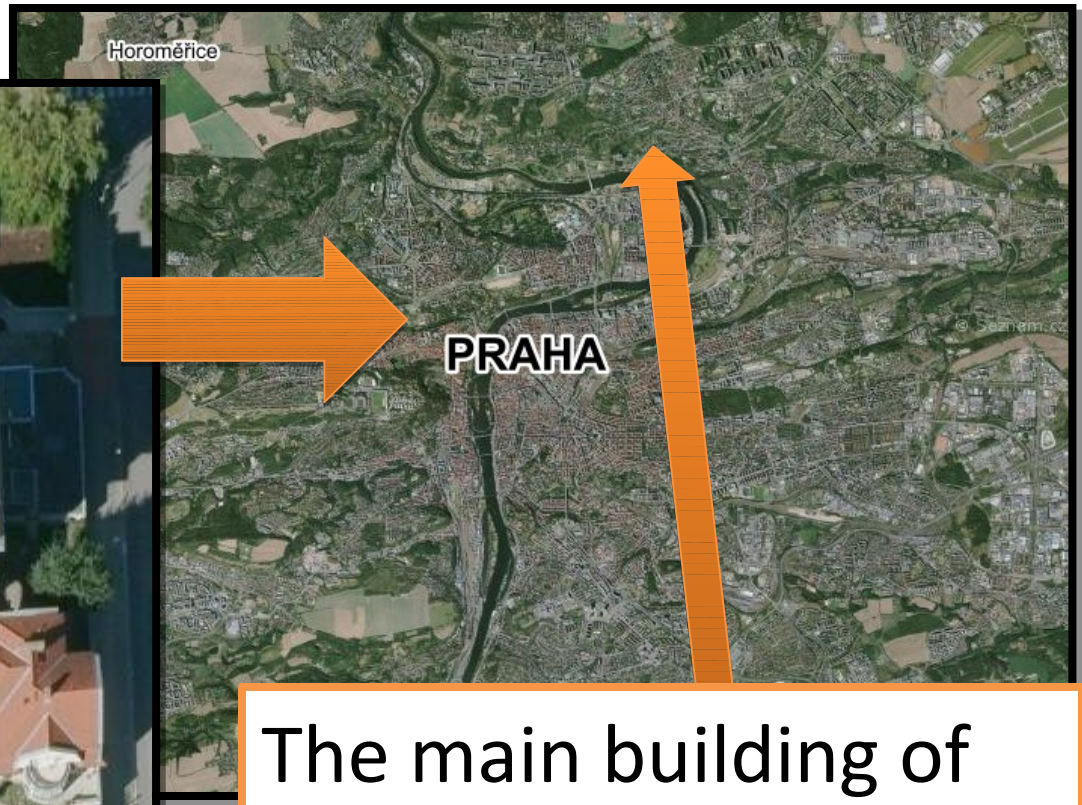
We are here

Approx. 800 km from here…



We are here

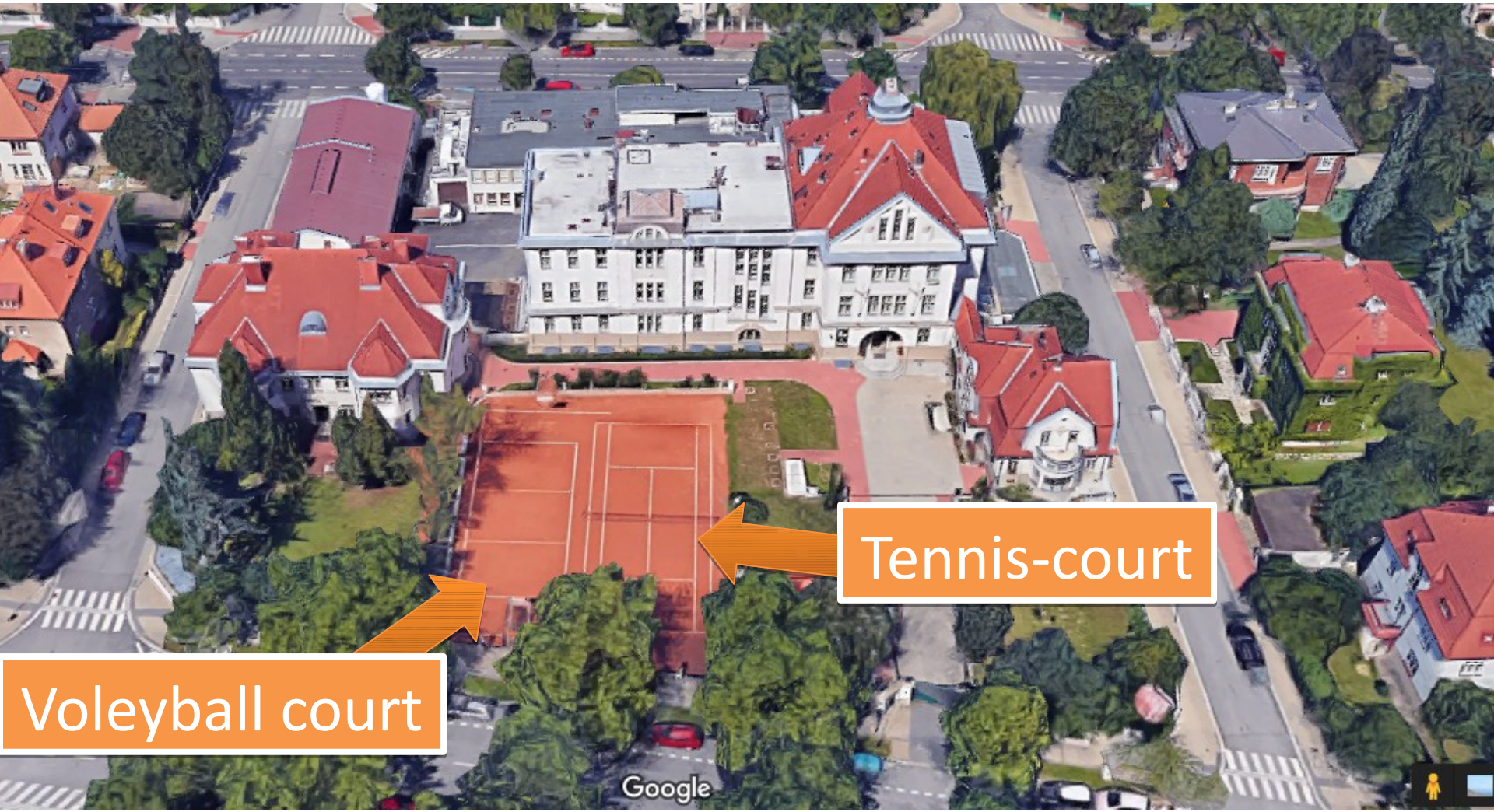




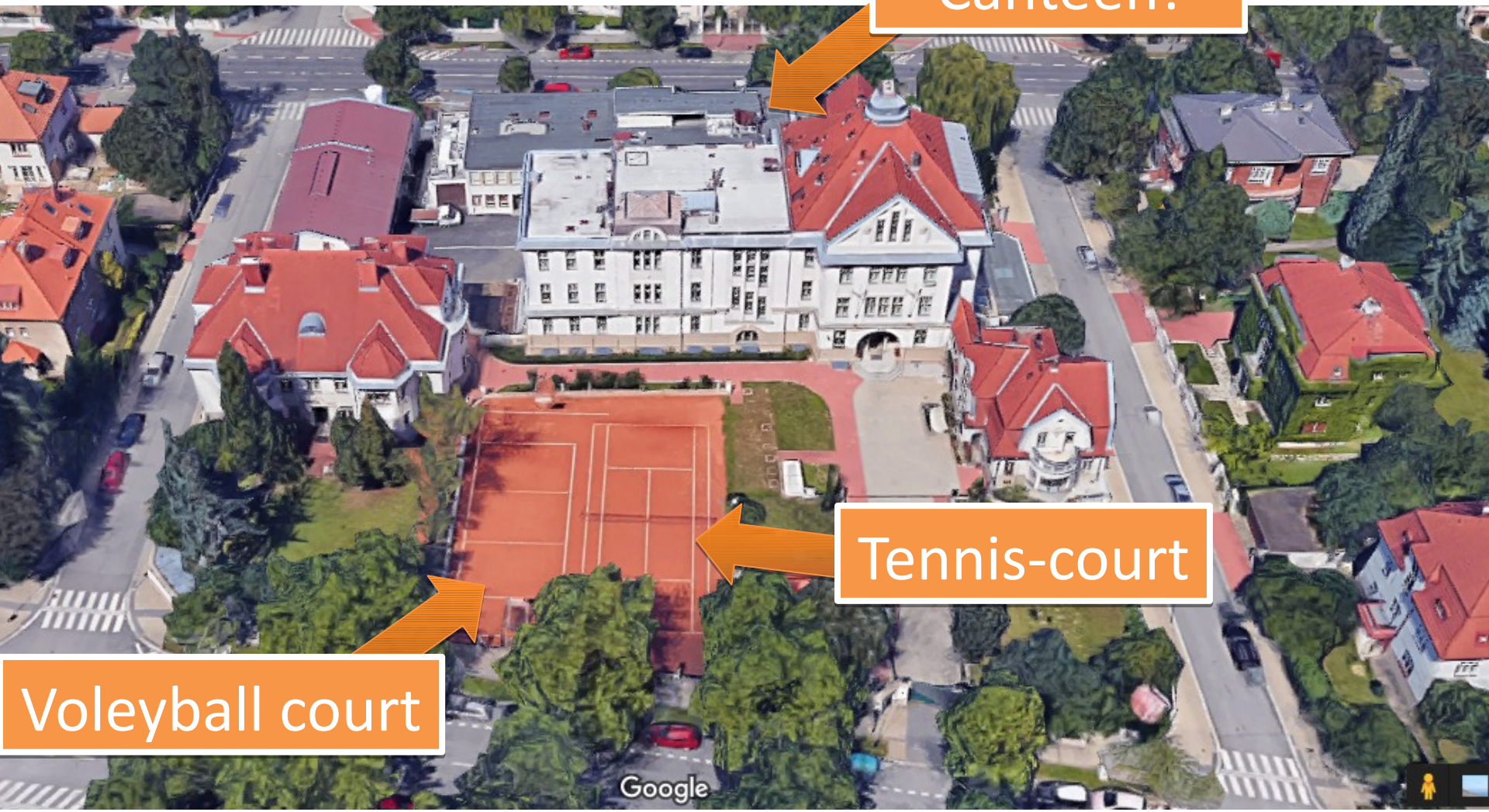
The main building of the institute is on the other side of Prague

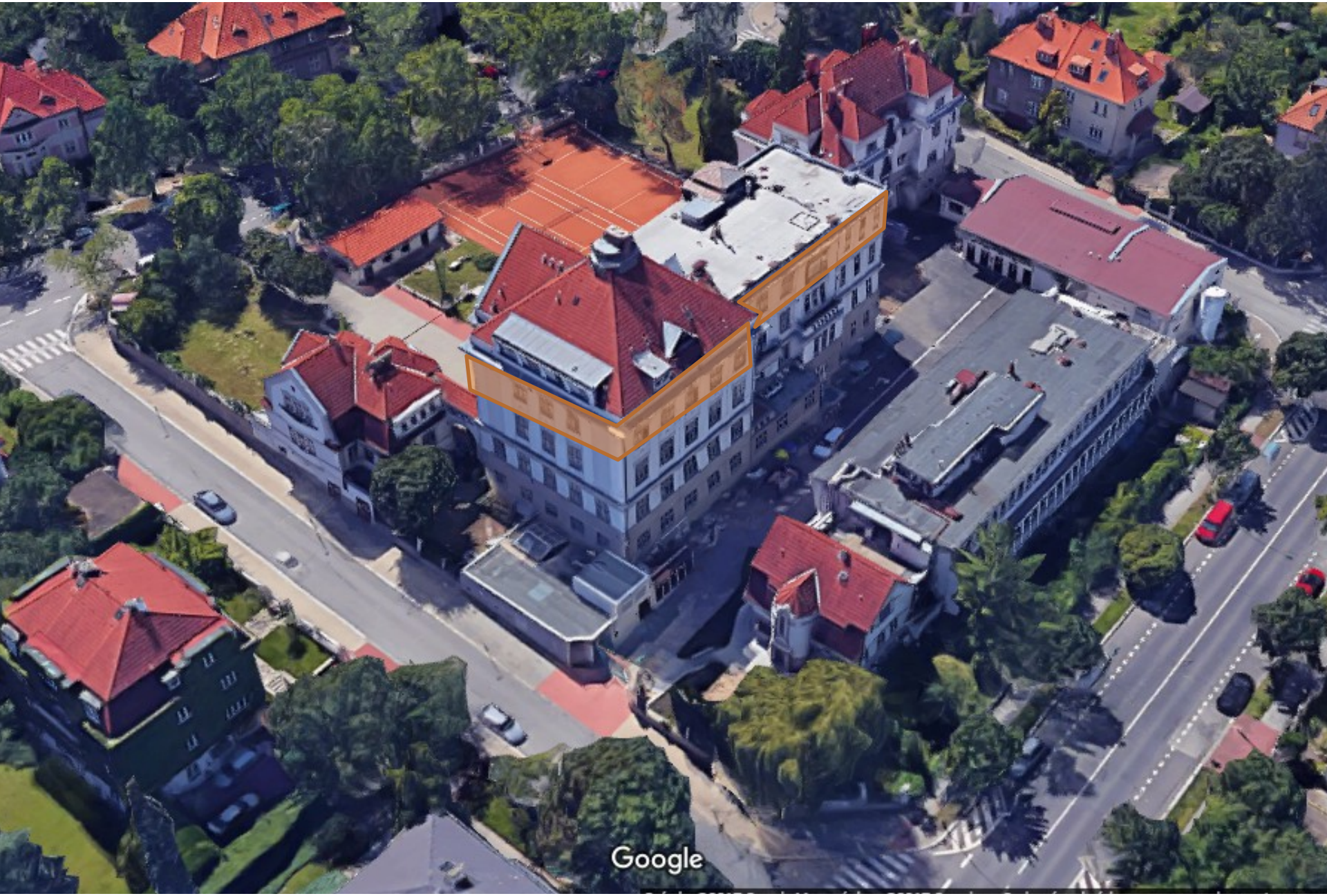
We are here

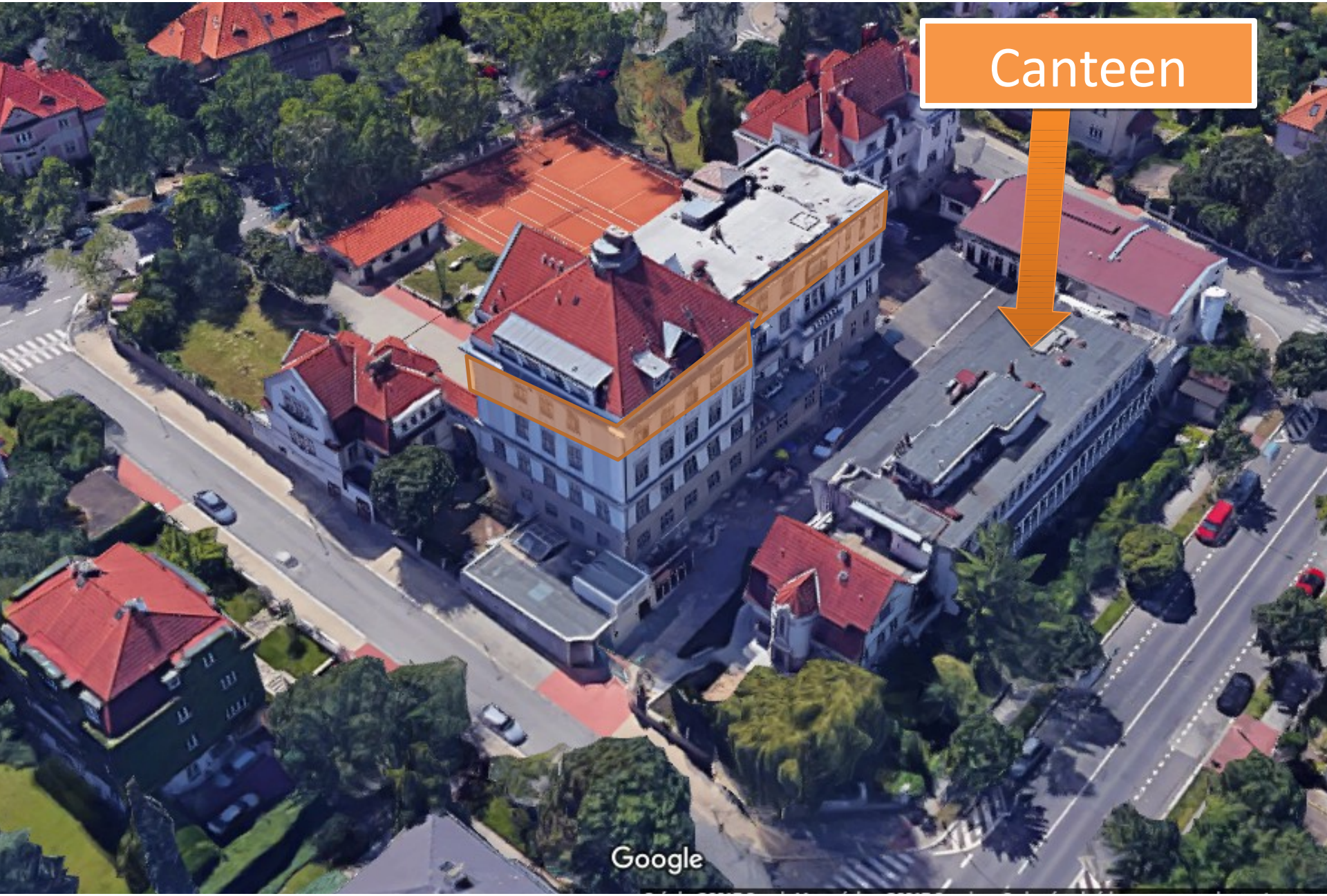
We are here



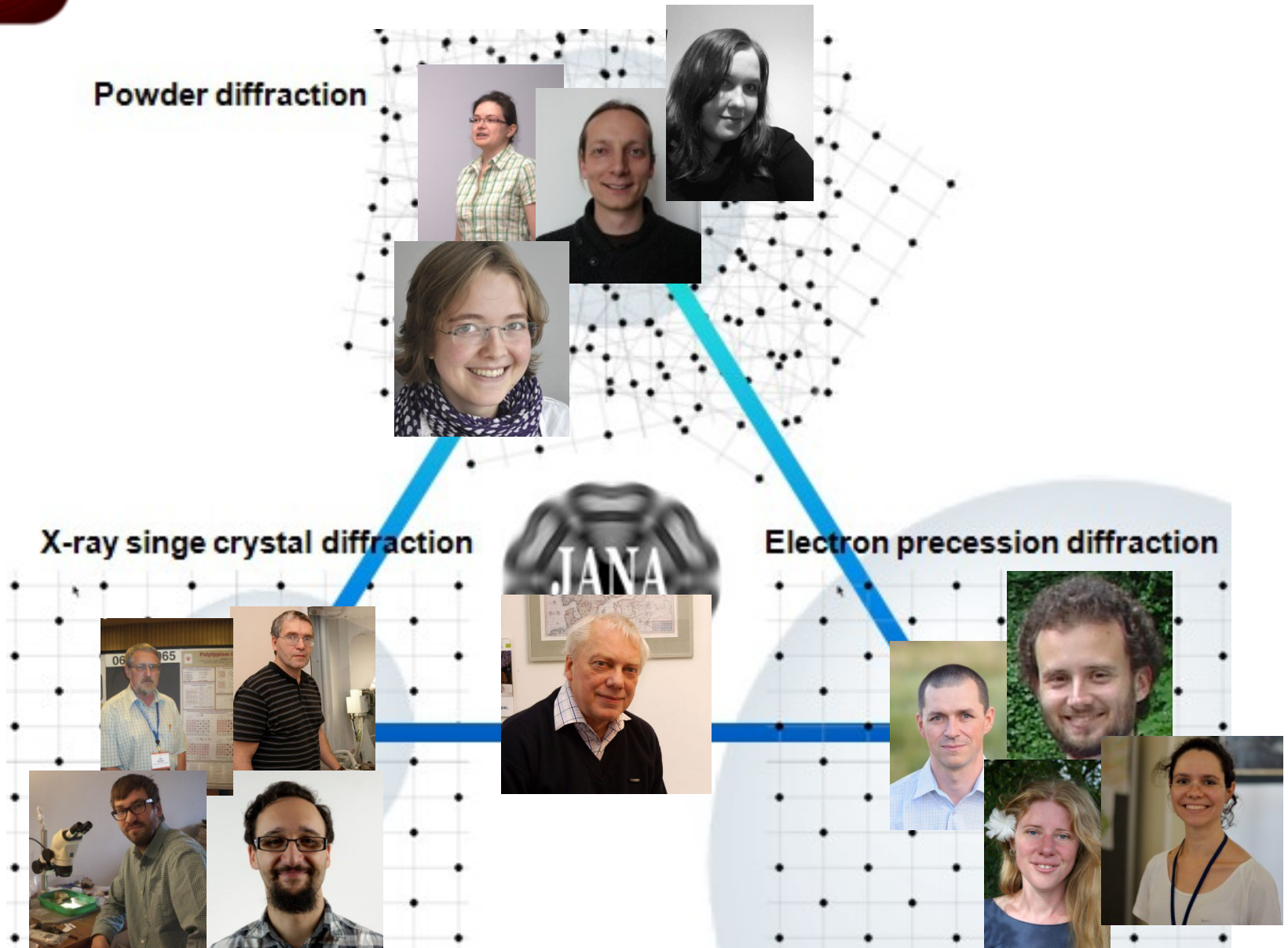
We are here




Google

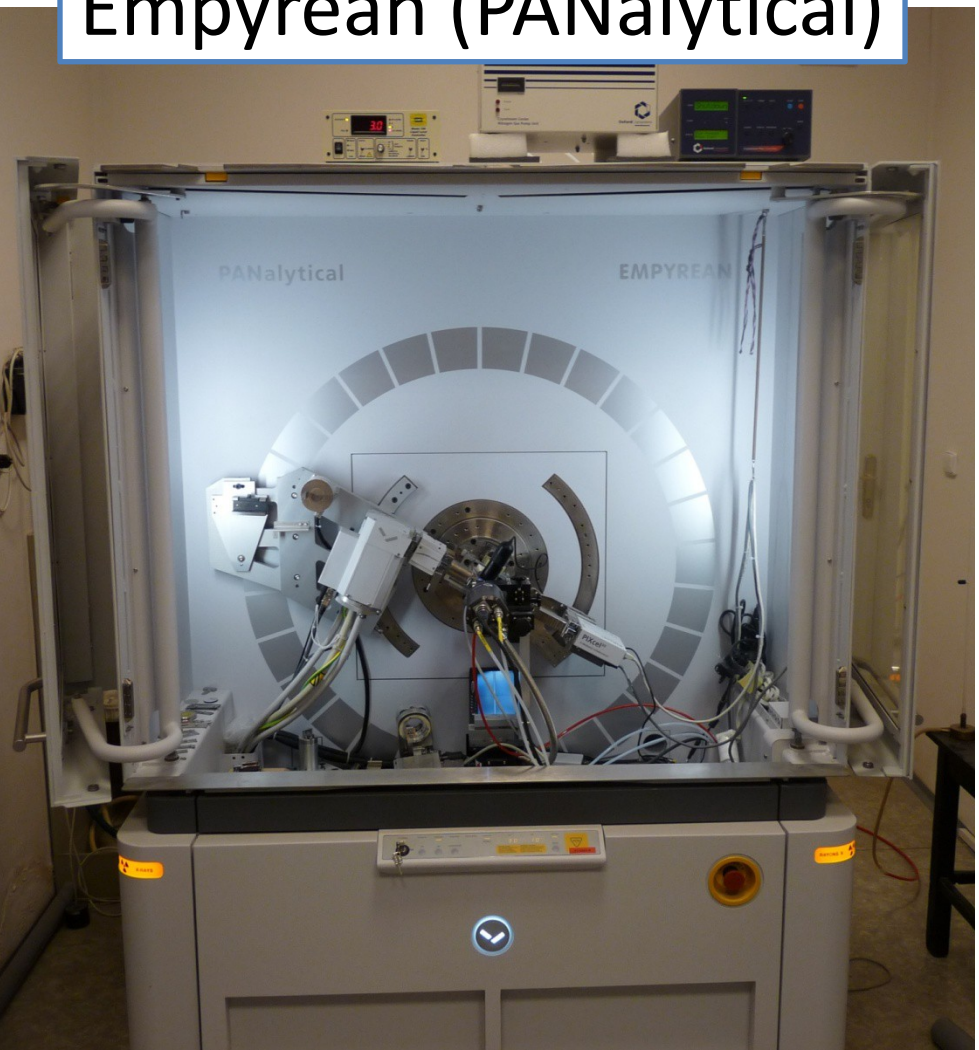

Canteen
Google

Department of structure analysis



Powder diffractometers in our lab

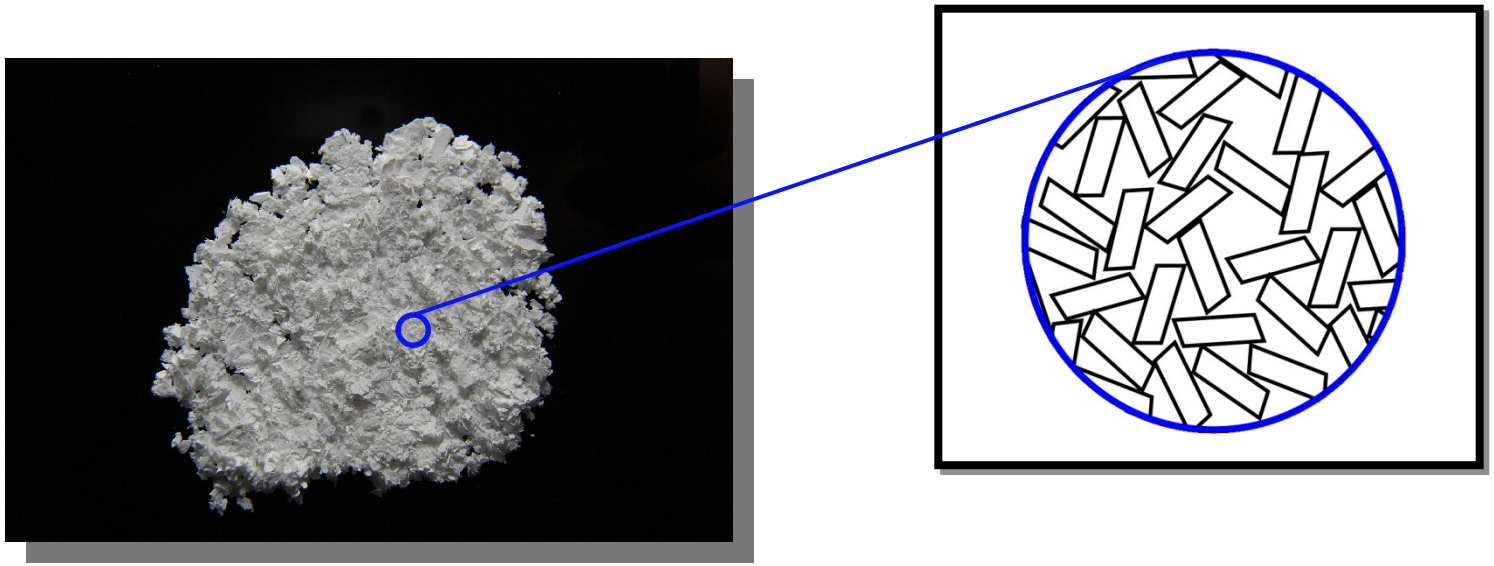
Empyrean (PANalytical)



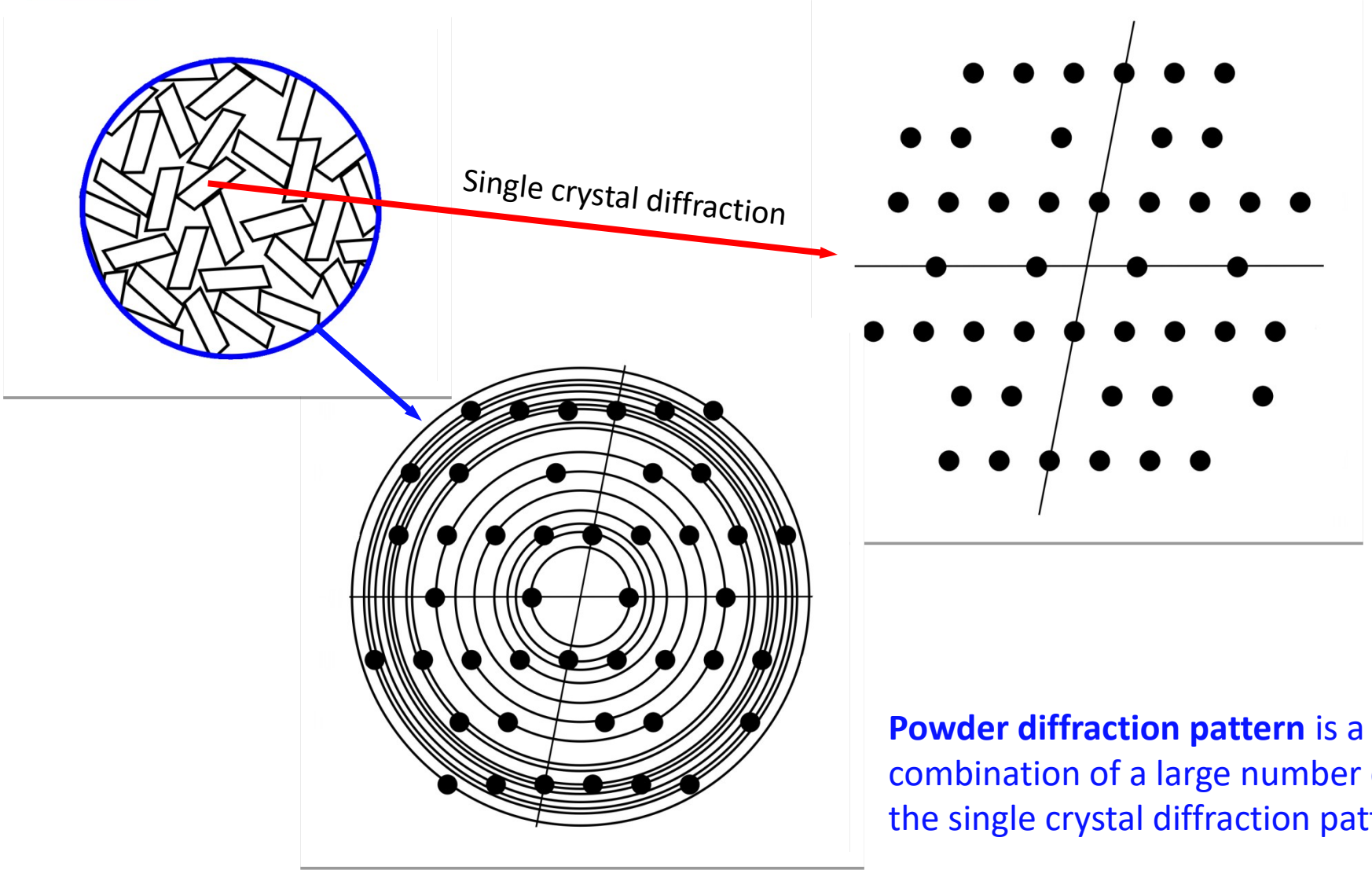
SmartLab (Rigaku)

Powder sample

powder = polycrystalline material



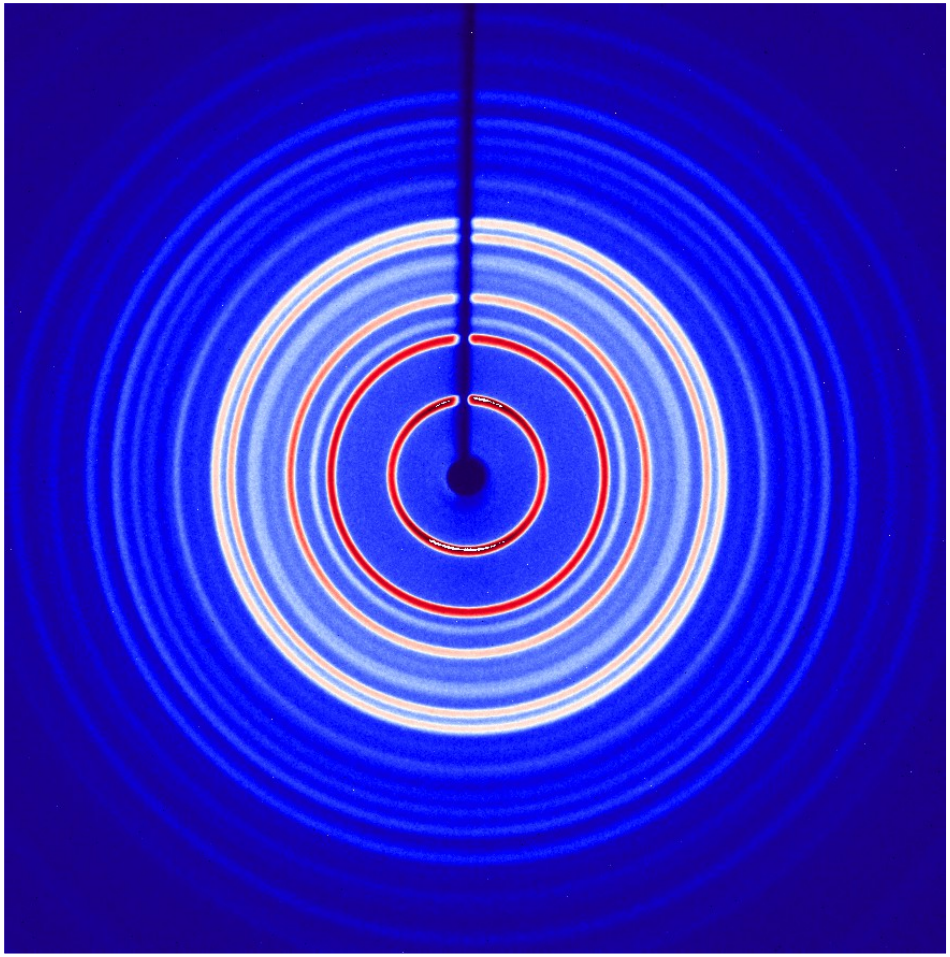
Diffraction of the powder sample



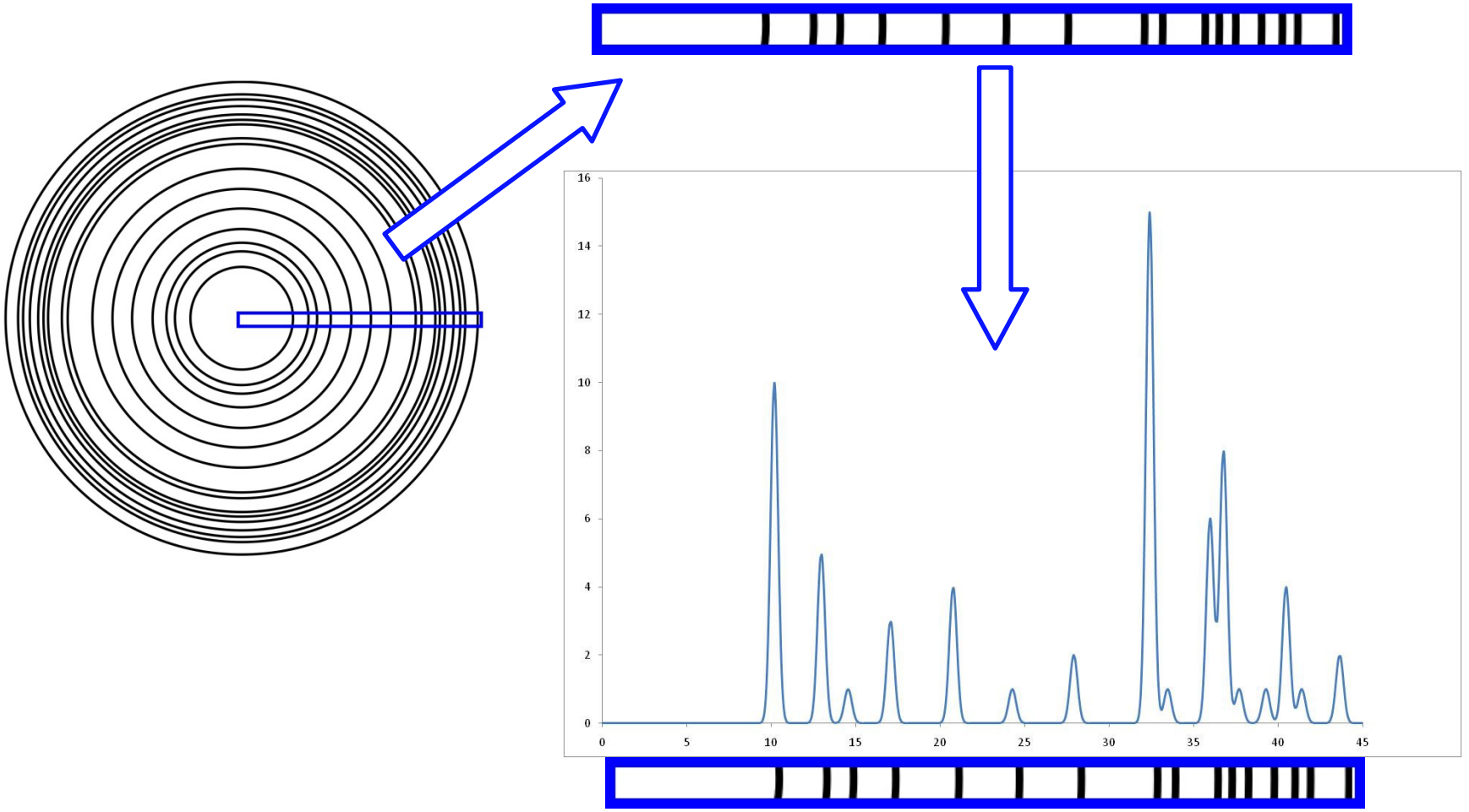
Powder diffraction pattern is a combination of a large number of the single crystal diffraction patterns

iffracted pattern

Powder diffraction pattern of alaptide powder on the area detector

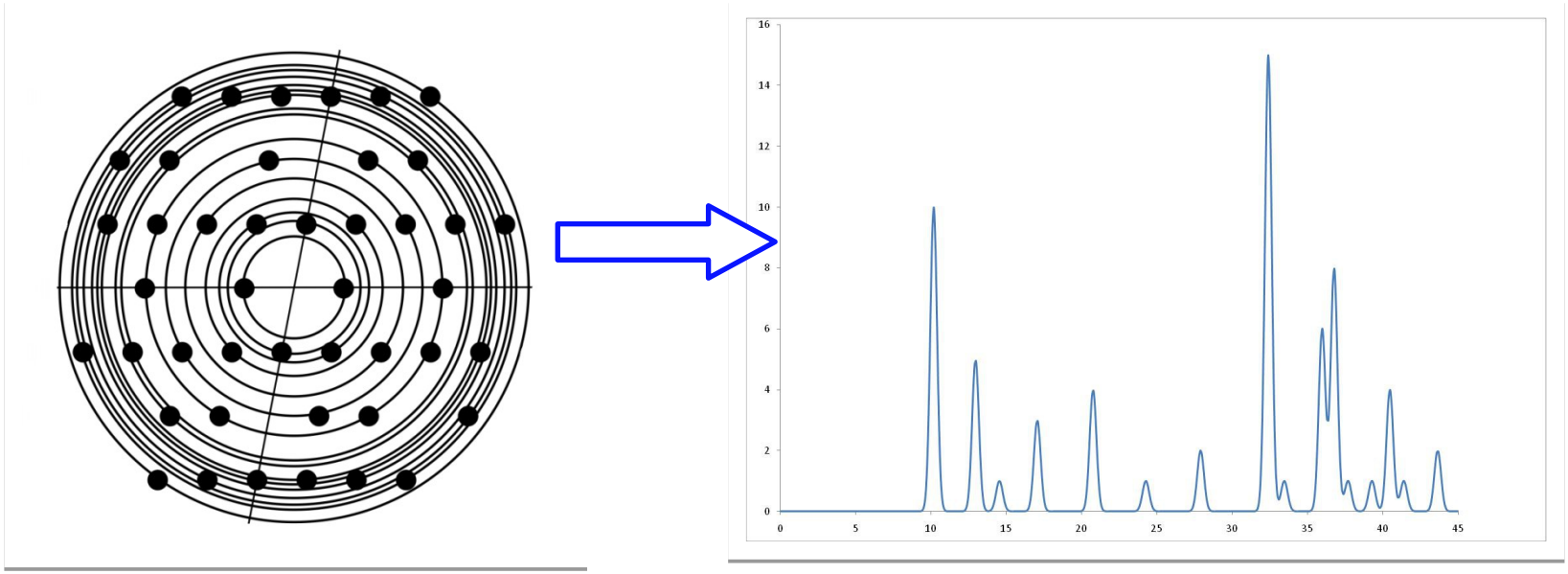


Diffracted pattern



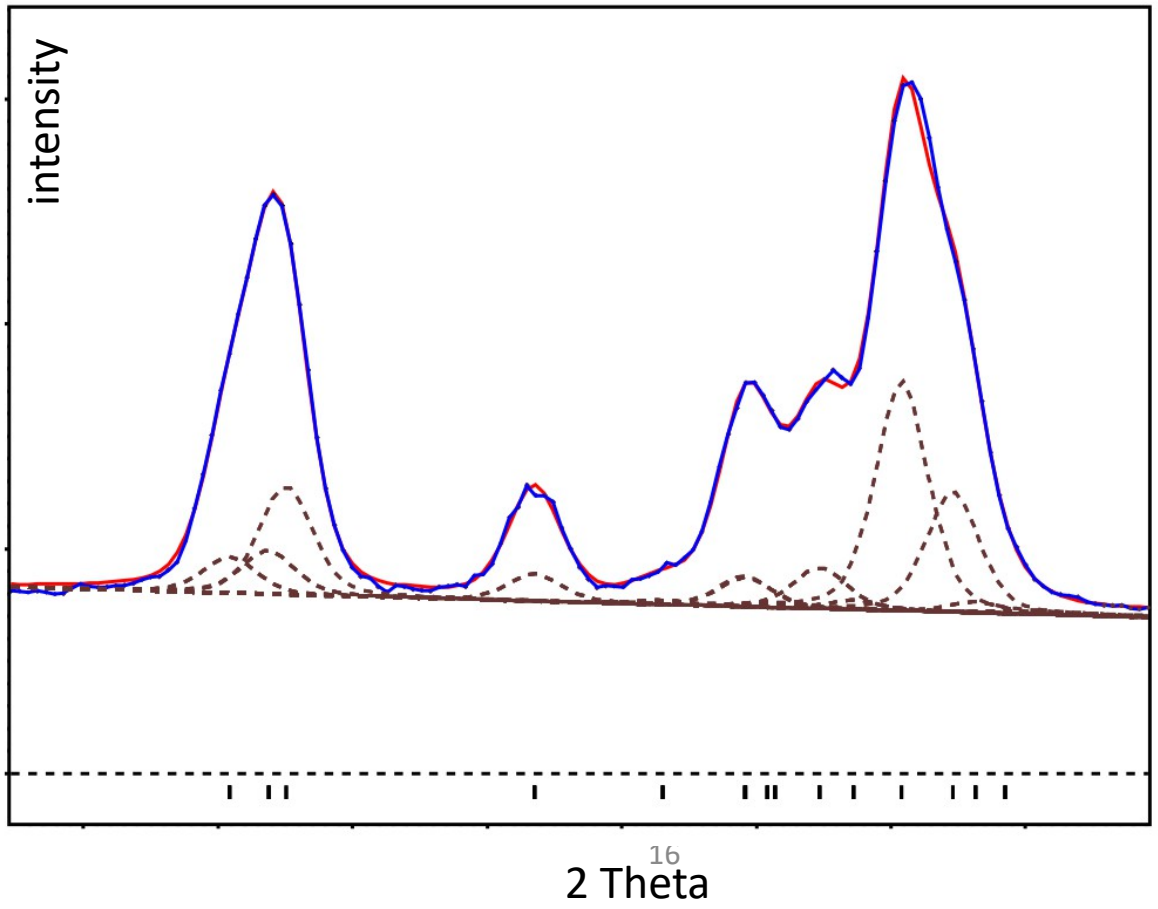
Problems and limitations

- Information loss – data are projection of a 3D diffraction pattern to 1D



Problems and limitations

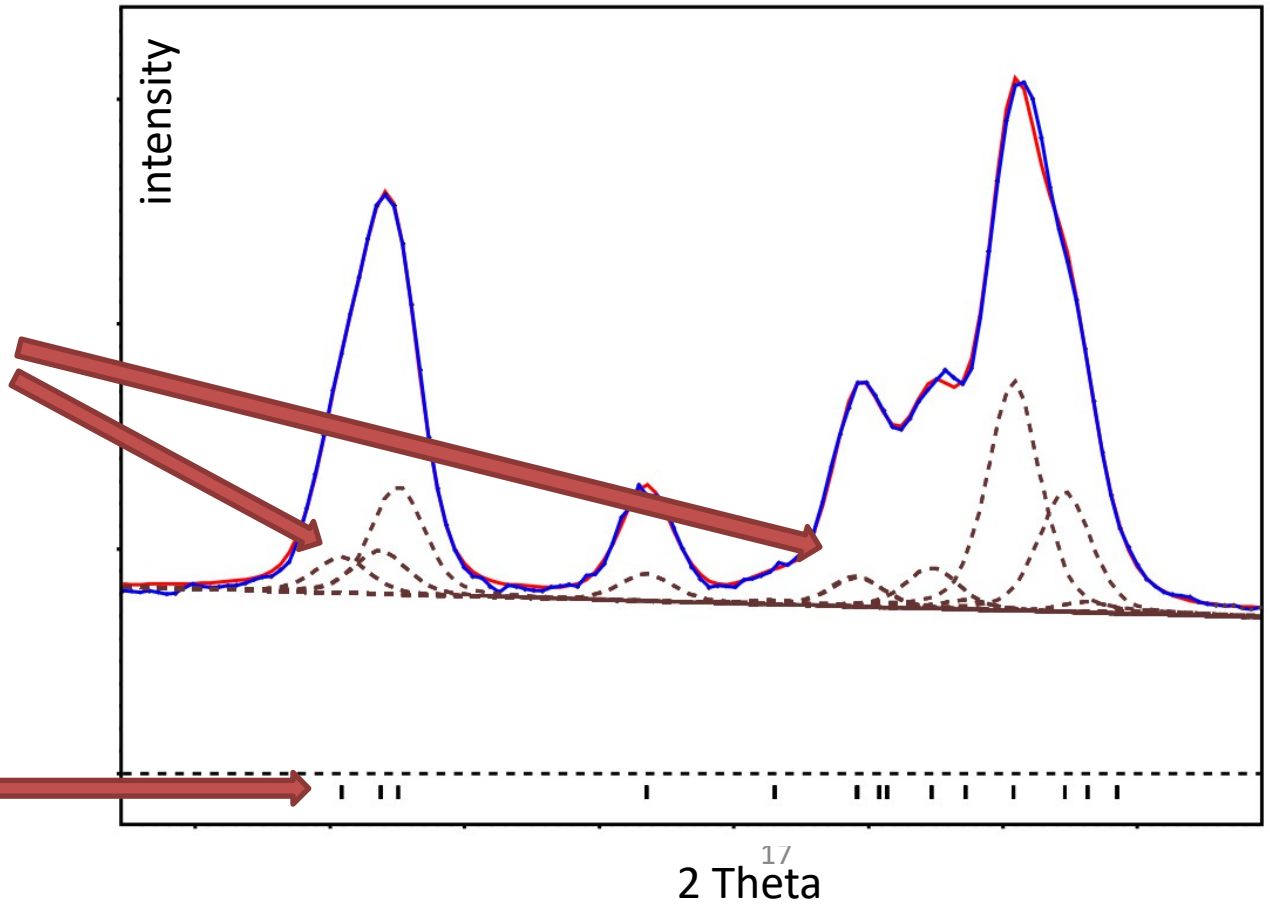
- Peak overlap – extraction of intensities.



Problems and limitations

- Peak overlap – extraction of intensities.

What is the intensity of these reflections?



Problems and limitations

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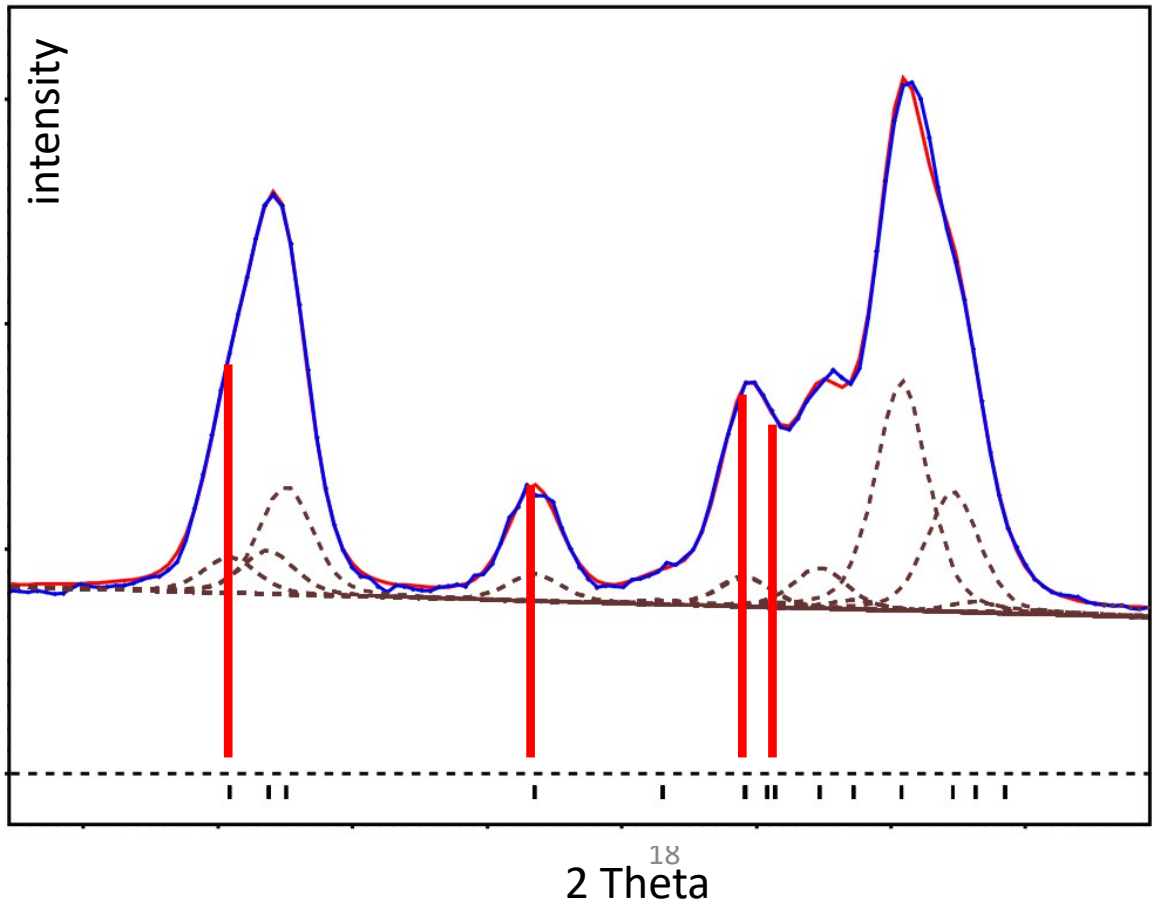
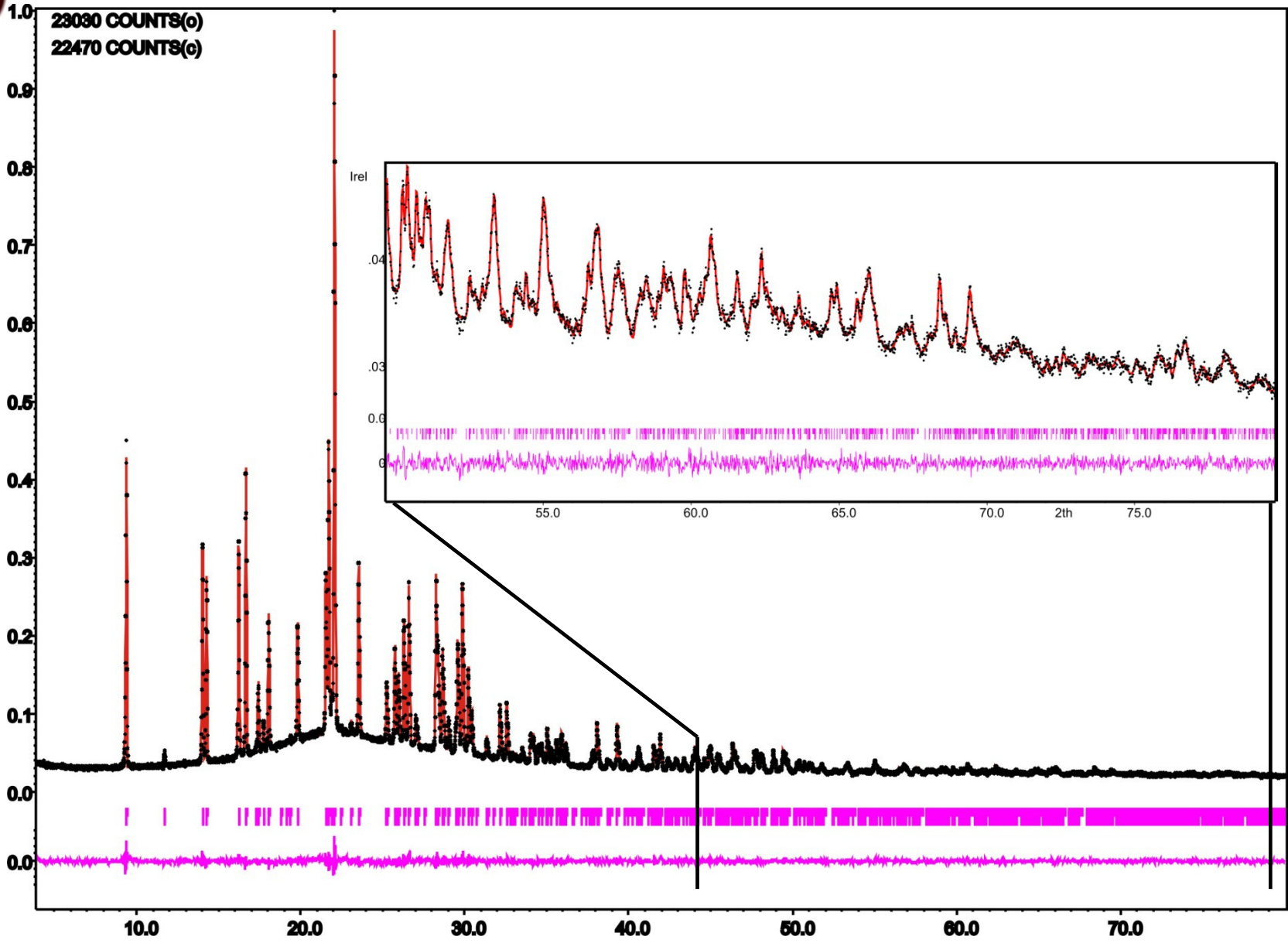
What is the intensity of these reflections?

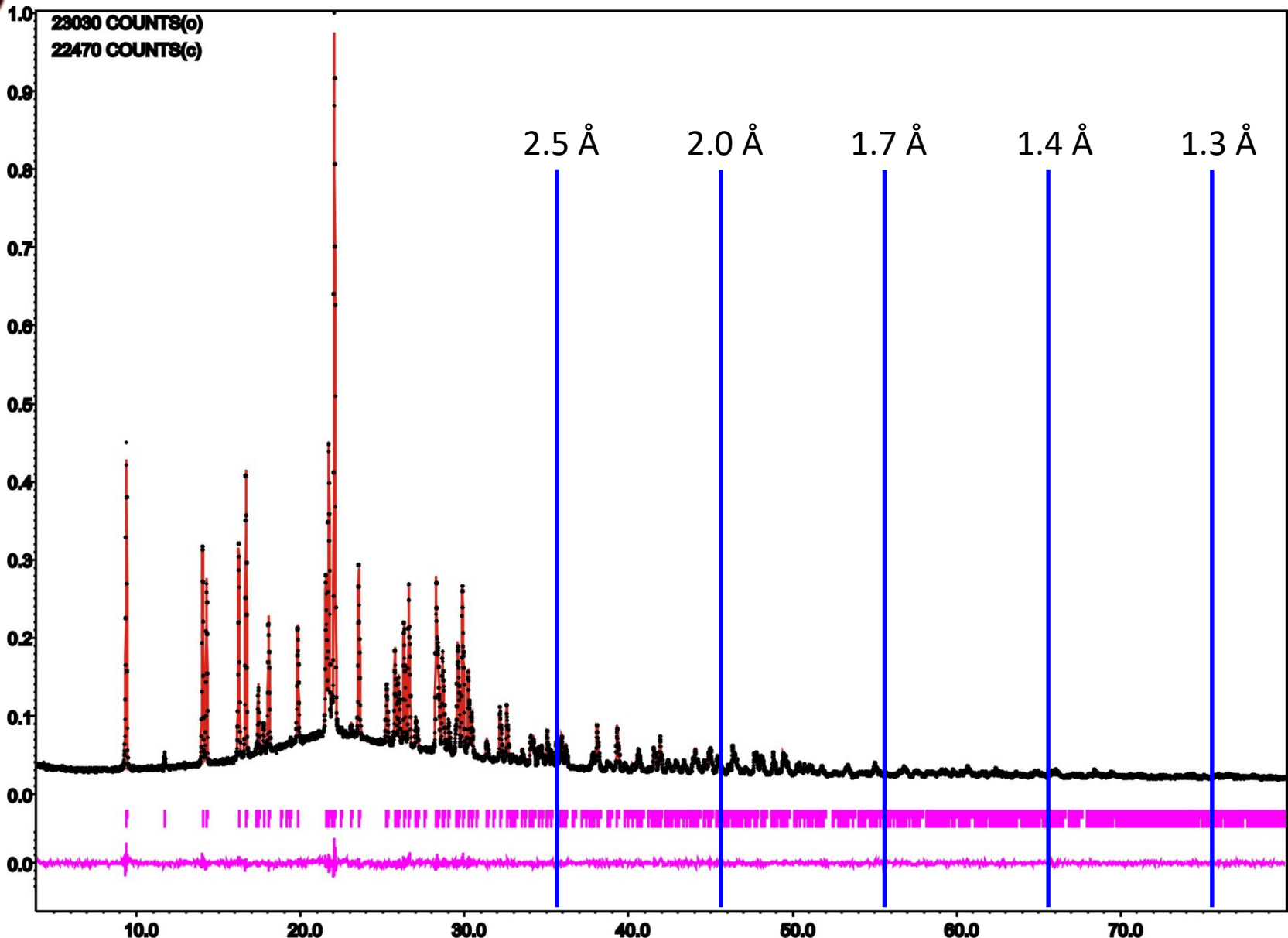


Positions of reflections

Peak overlap



Peak overlap



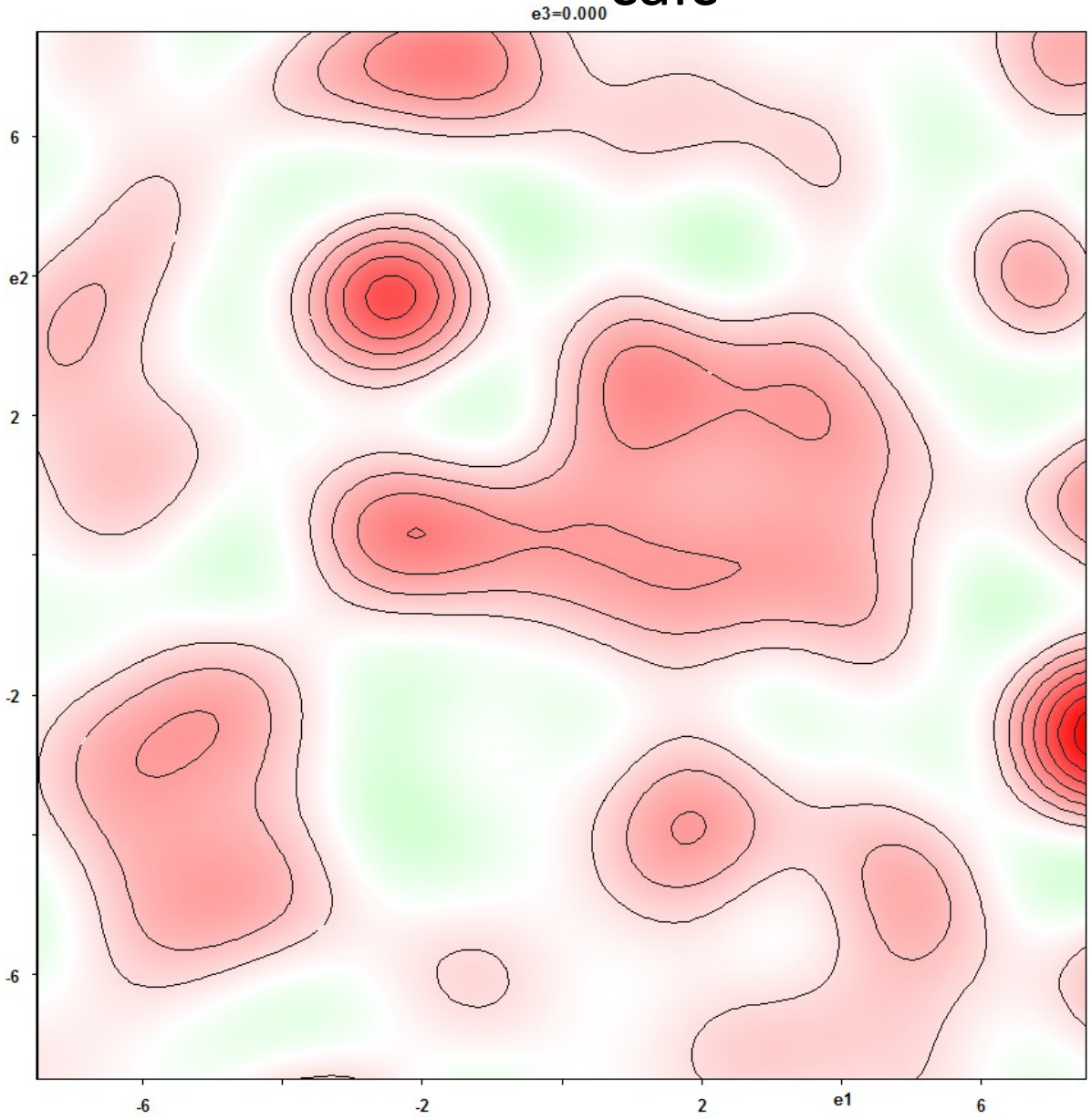
El. density – F_{calc} Fourier

sin Θ / λ = 0.2

λ = 1.5418 Å

max = 36° 2Θ

dmax = 2.5 Å



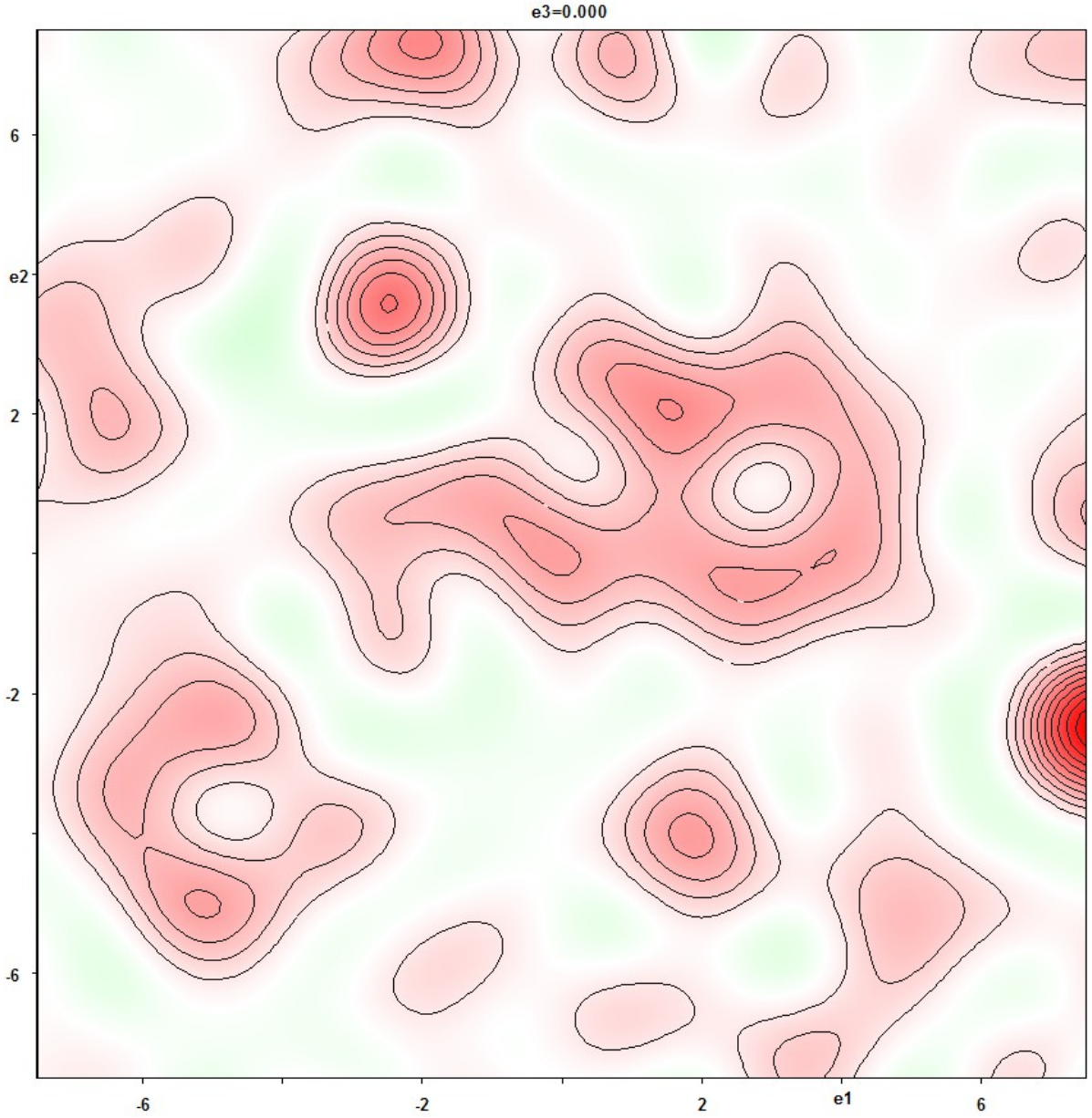
Rozlišení ELD

sin Θ / λ = 0.25

λ = 1.5418 Å

max = 45° 2Θ

dmax = 2.0 Å



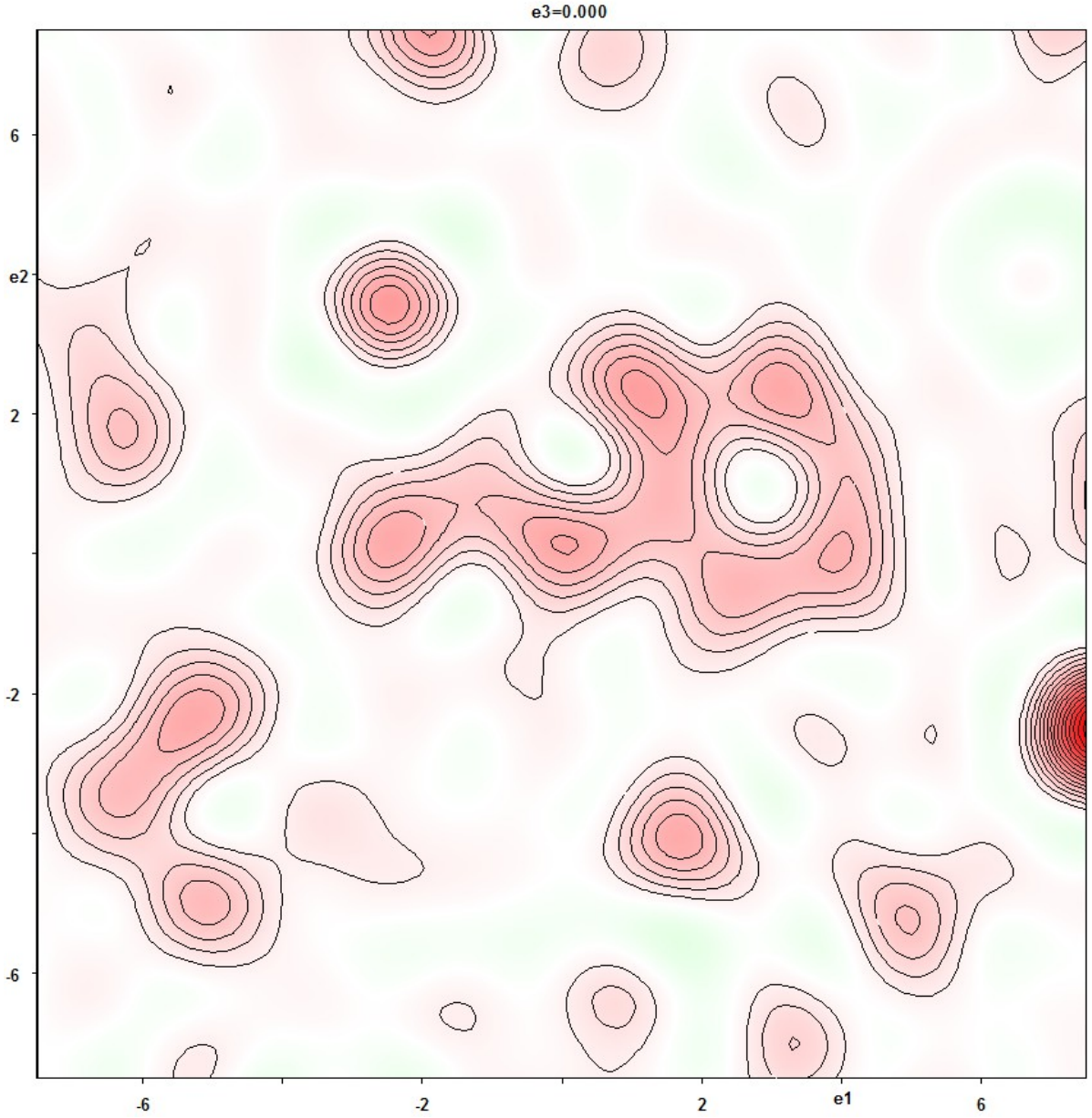
Rozlišení ELD

sin Θ / λ = 0.3

λ = 1.5418 Å

max = 55° 2Θ

dmax = 1.7 Å



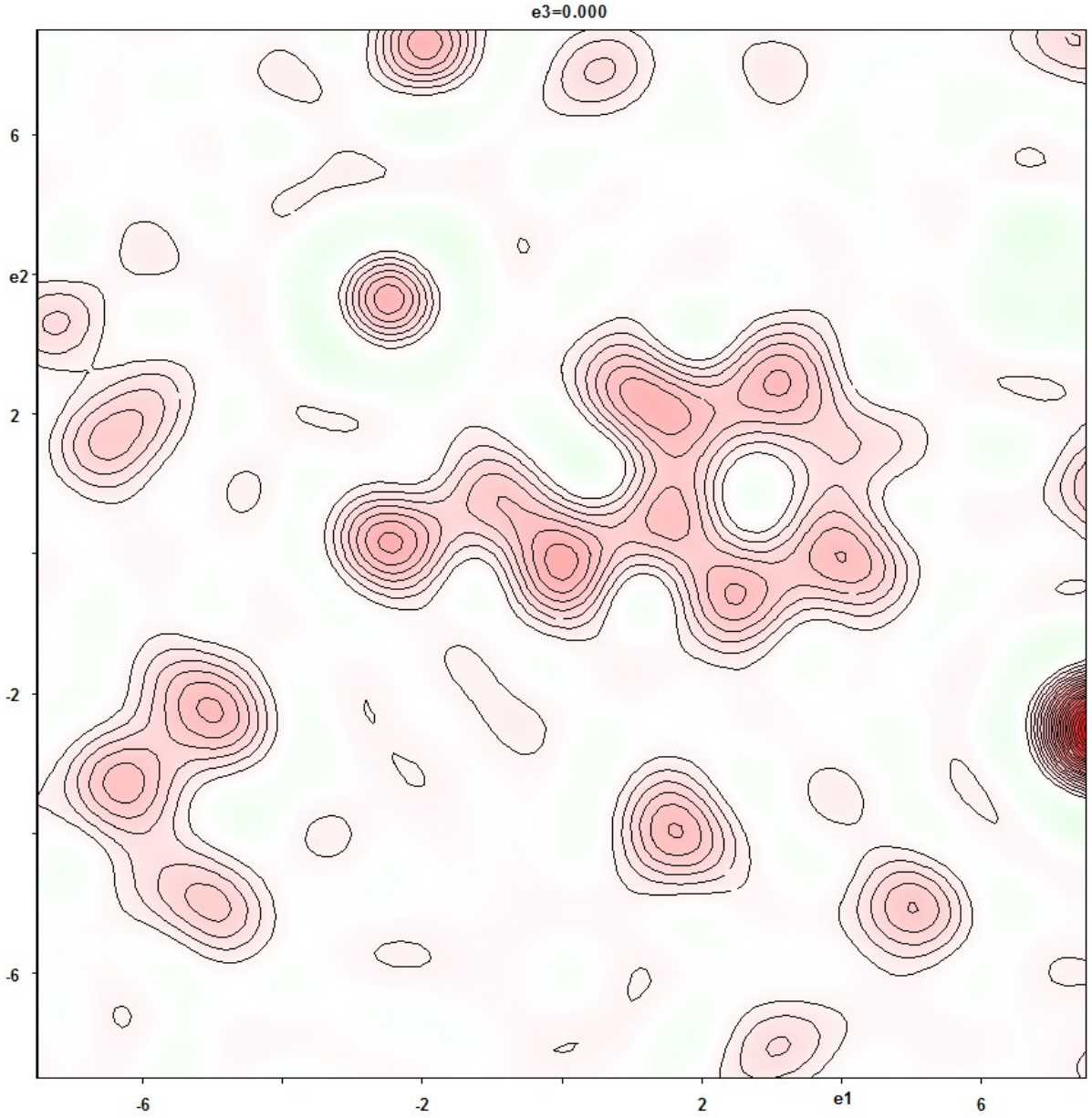
Rozlišení ELD

sin Θ / λ = 0.35

λ = 1.5418 Å

max = 65° 2Θ

dmax = 1.4 Å



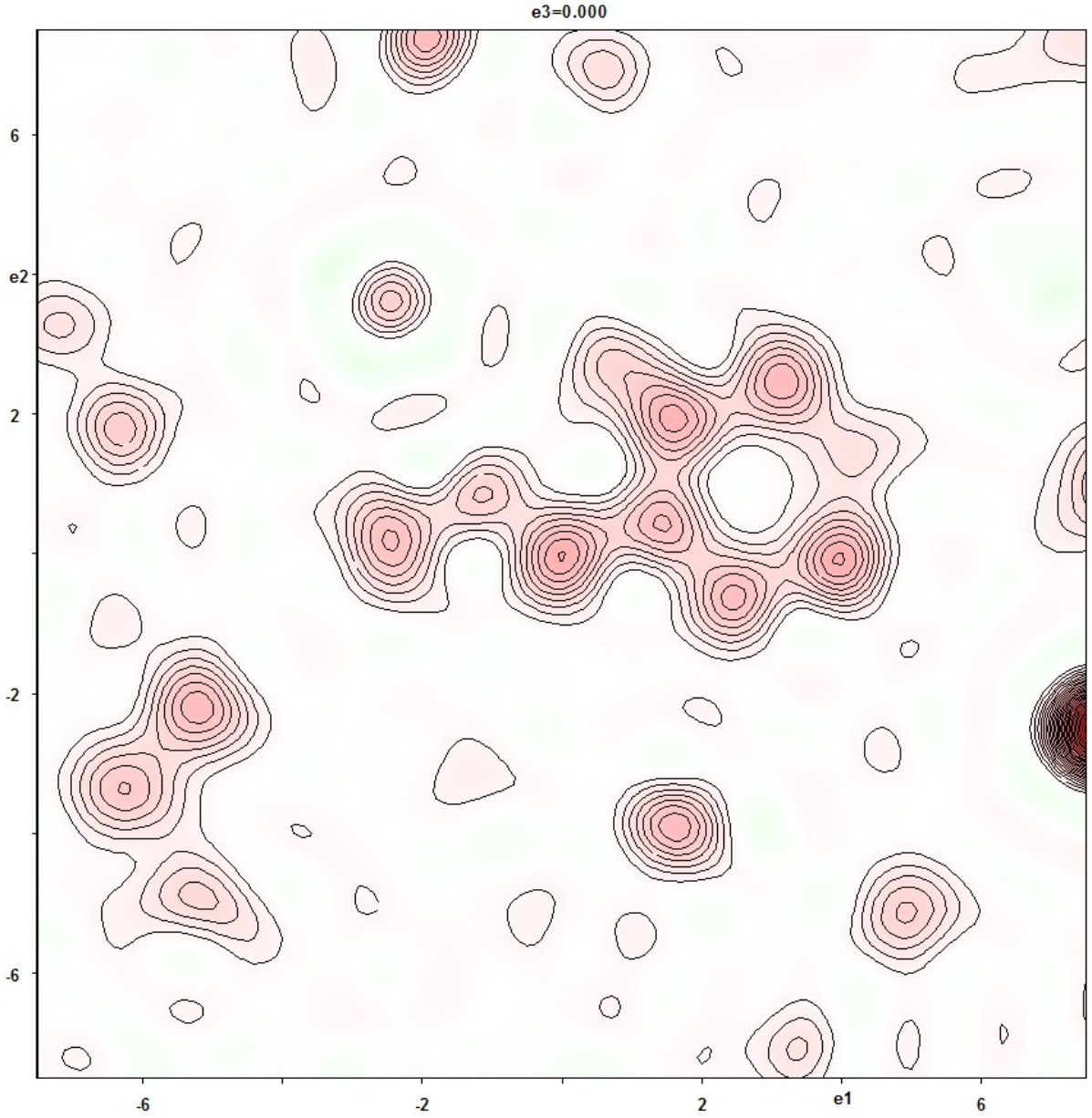
Rozlišení ELD

sin Θ / λ = 0.4

λ = 1.5418 Å

max = 76° 2Θ

dmax = 1.3 Å



Effect of the peak overlap

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

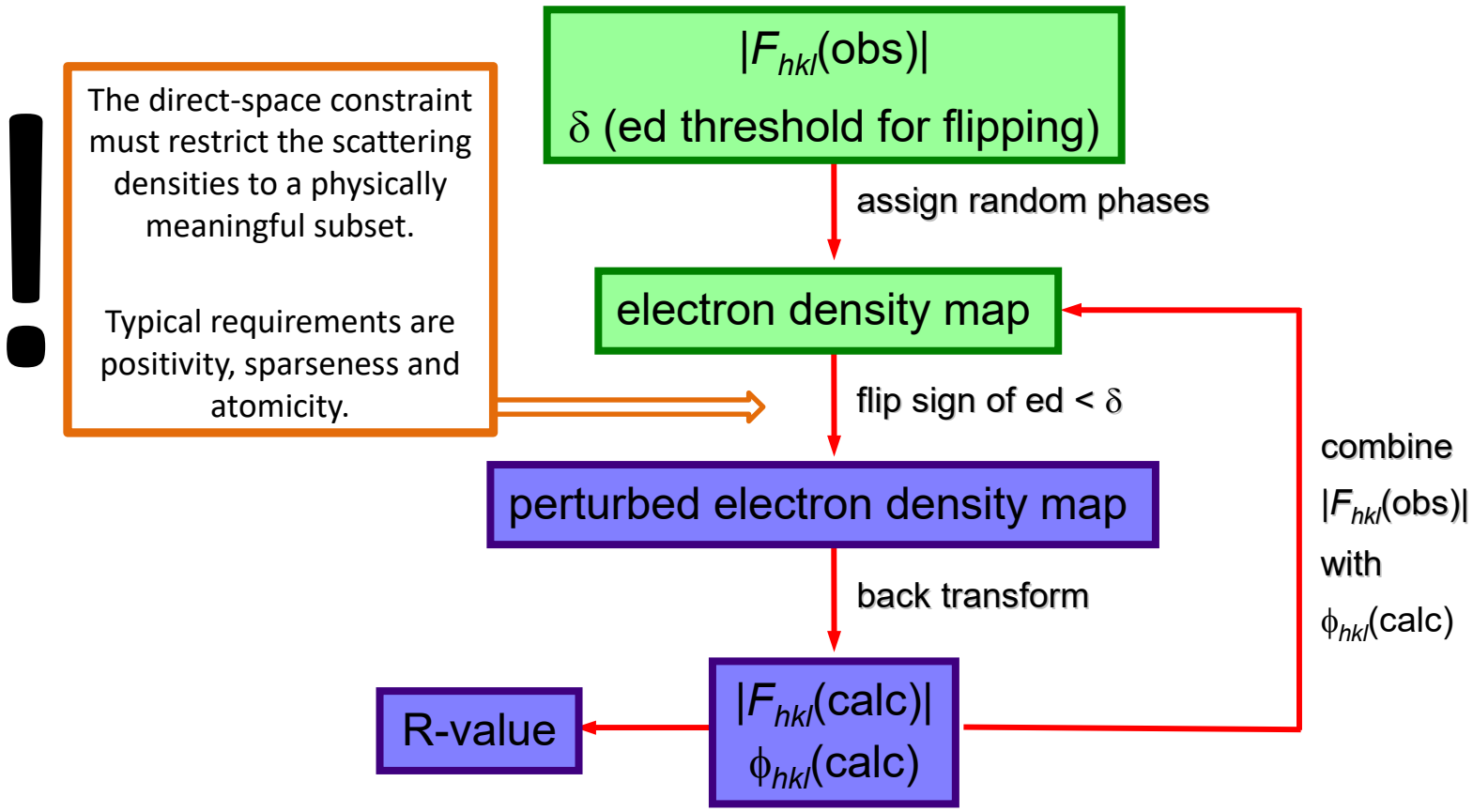
- Direct Space methods
  - Starting model
  - Time consuming process

What is charge flipping?

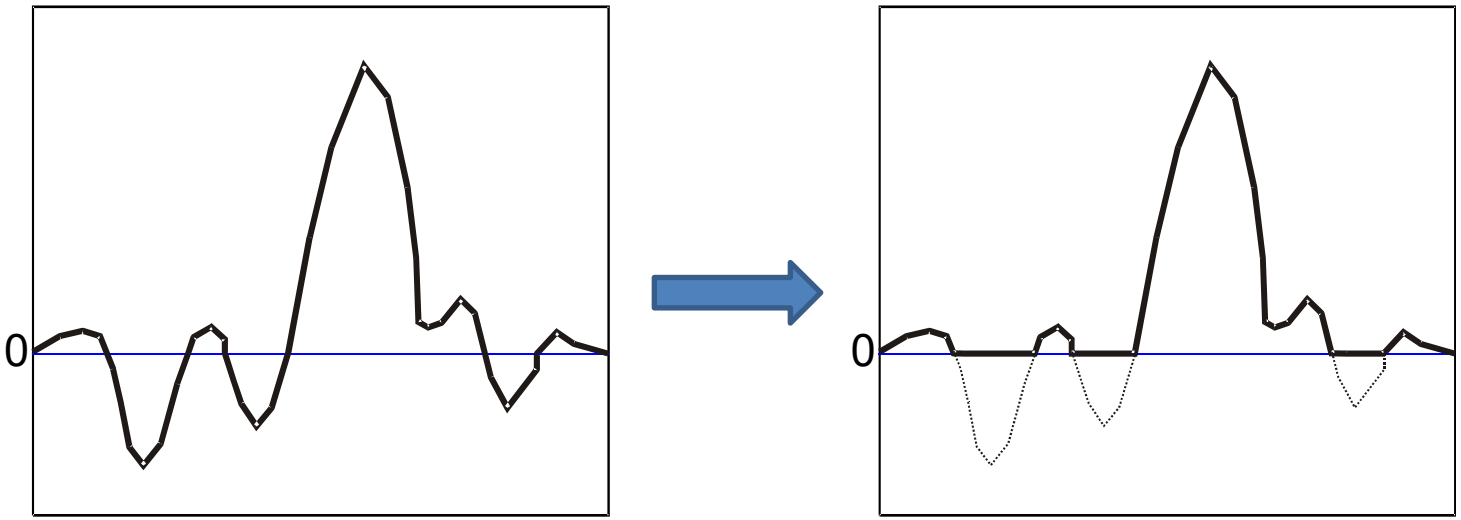
Charge flipping is a method for *ab initio* determination of an approximate scattering density from the set of structure-factor amplitudes

- Published by Oszlányi & Sütő (2004), Acta Cryst A
- The output is an **approximate scattering density** of the structure sampled on a discrete grid
- Requires only **lattice parameters** and **reflection intensities**
- No use of atomicity, only of the “sparseness” of the electron density
- **No use of symmetry apart from the input intensities**

Charge flipping

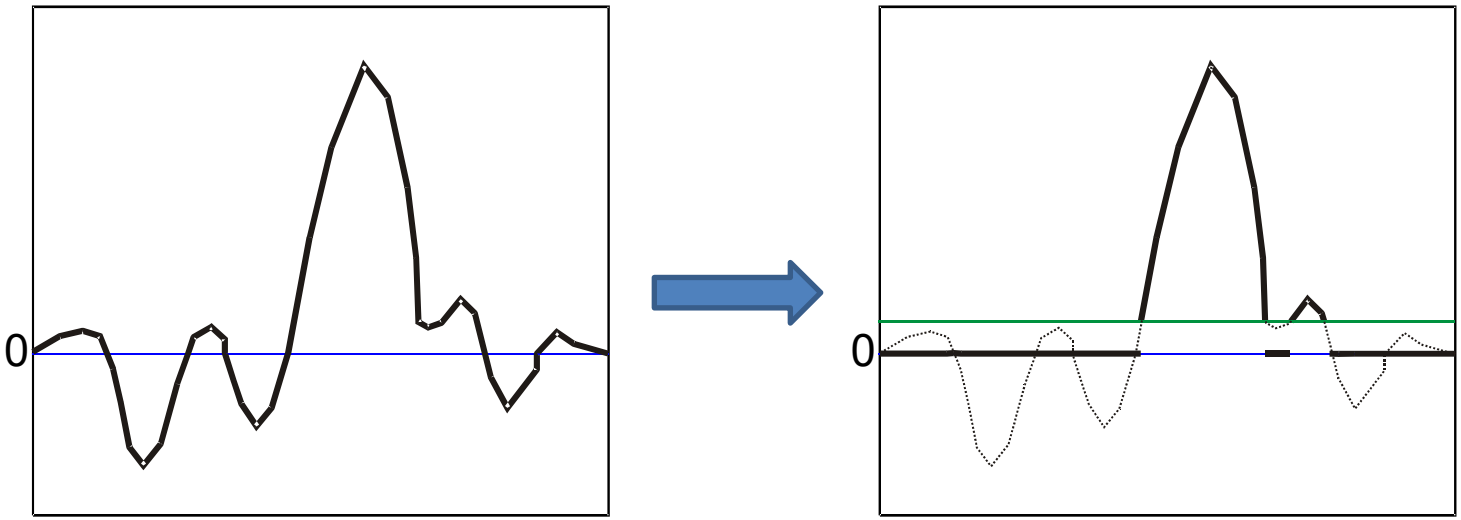


Constraints and projections



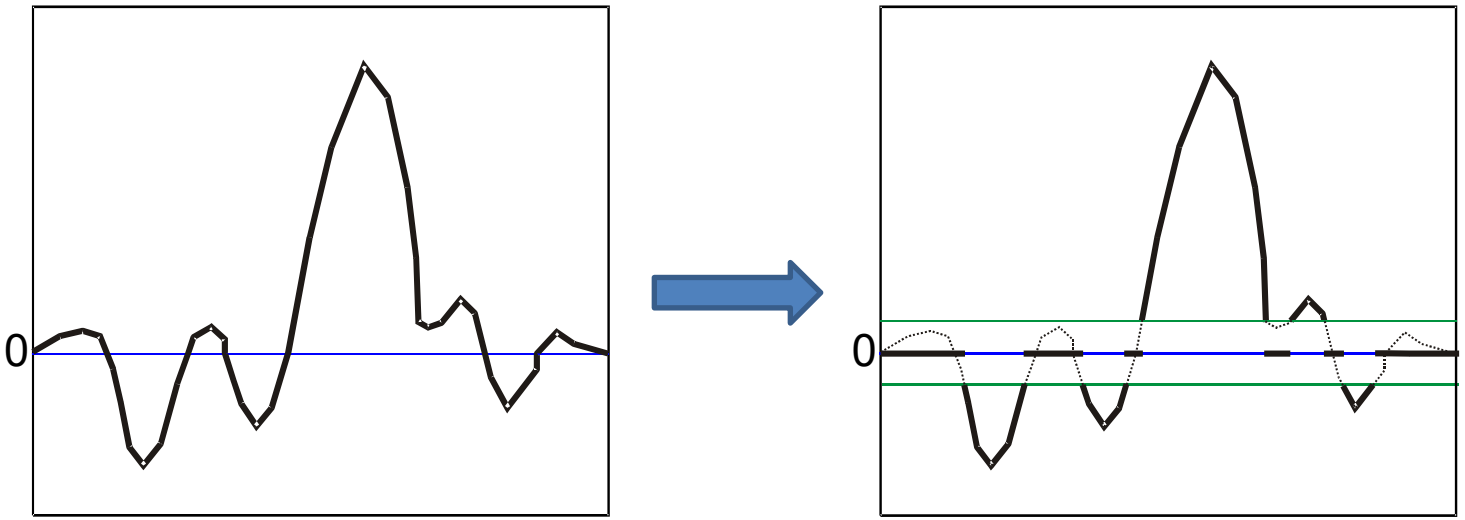
Positivity projection

Constraints and projections



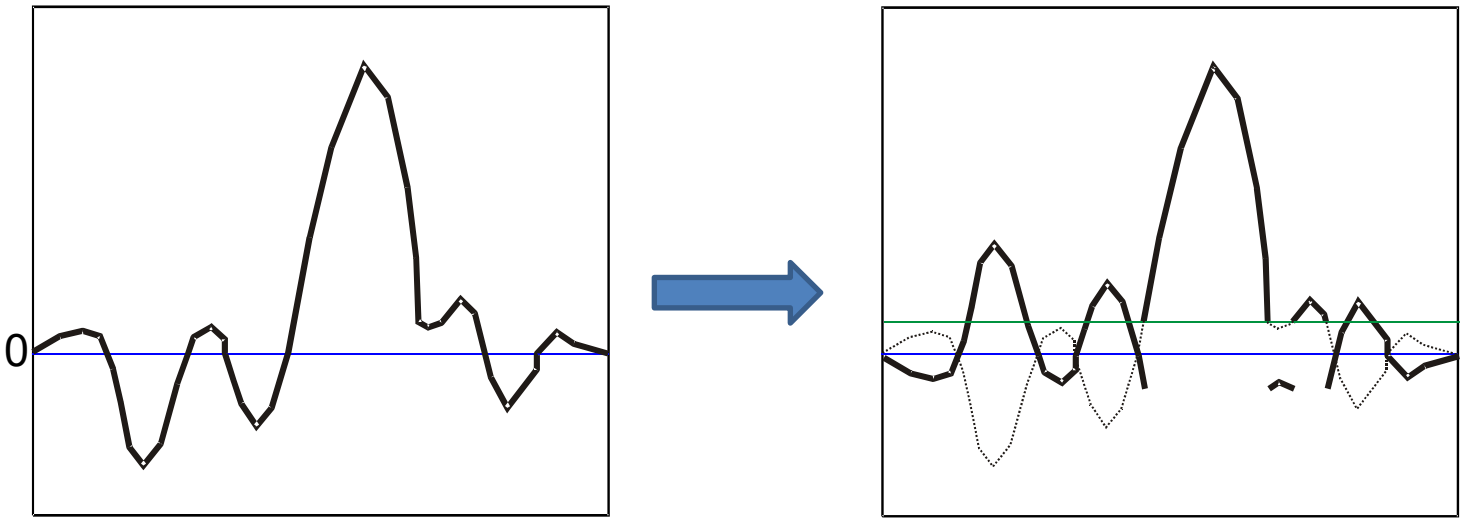
Significance + positivity projection (dynamic support with positivity)

Constraints and projections



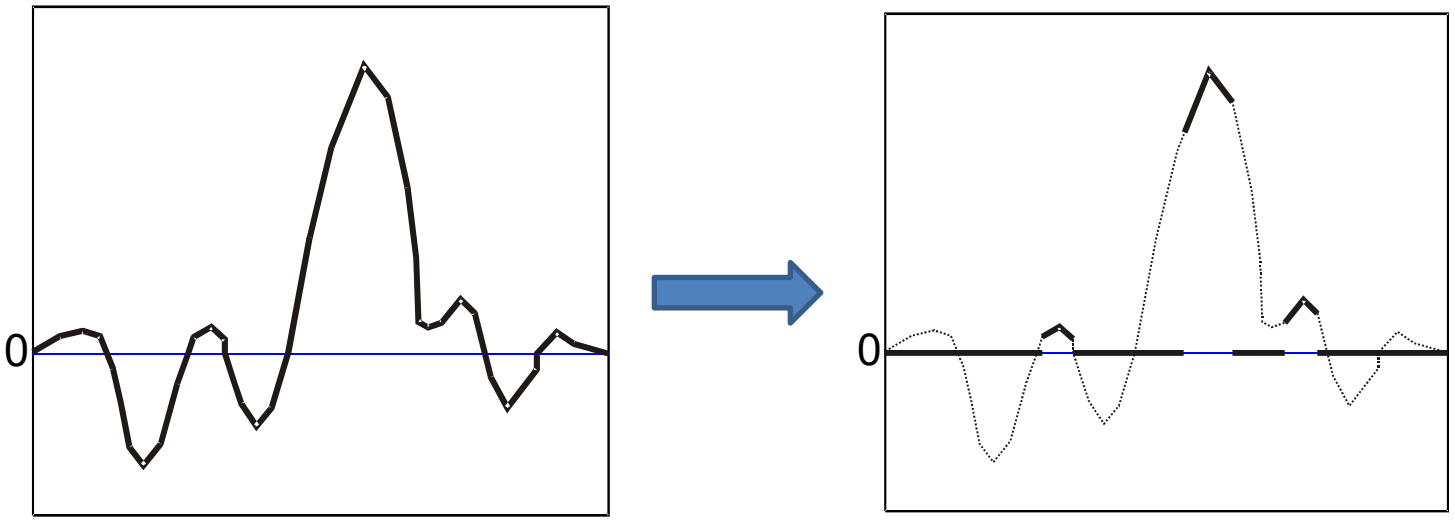
Significance projection (dynamic support without positivity)

Constraints and projections



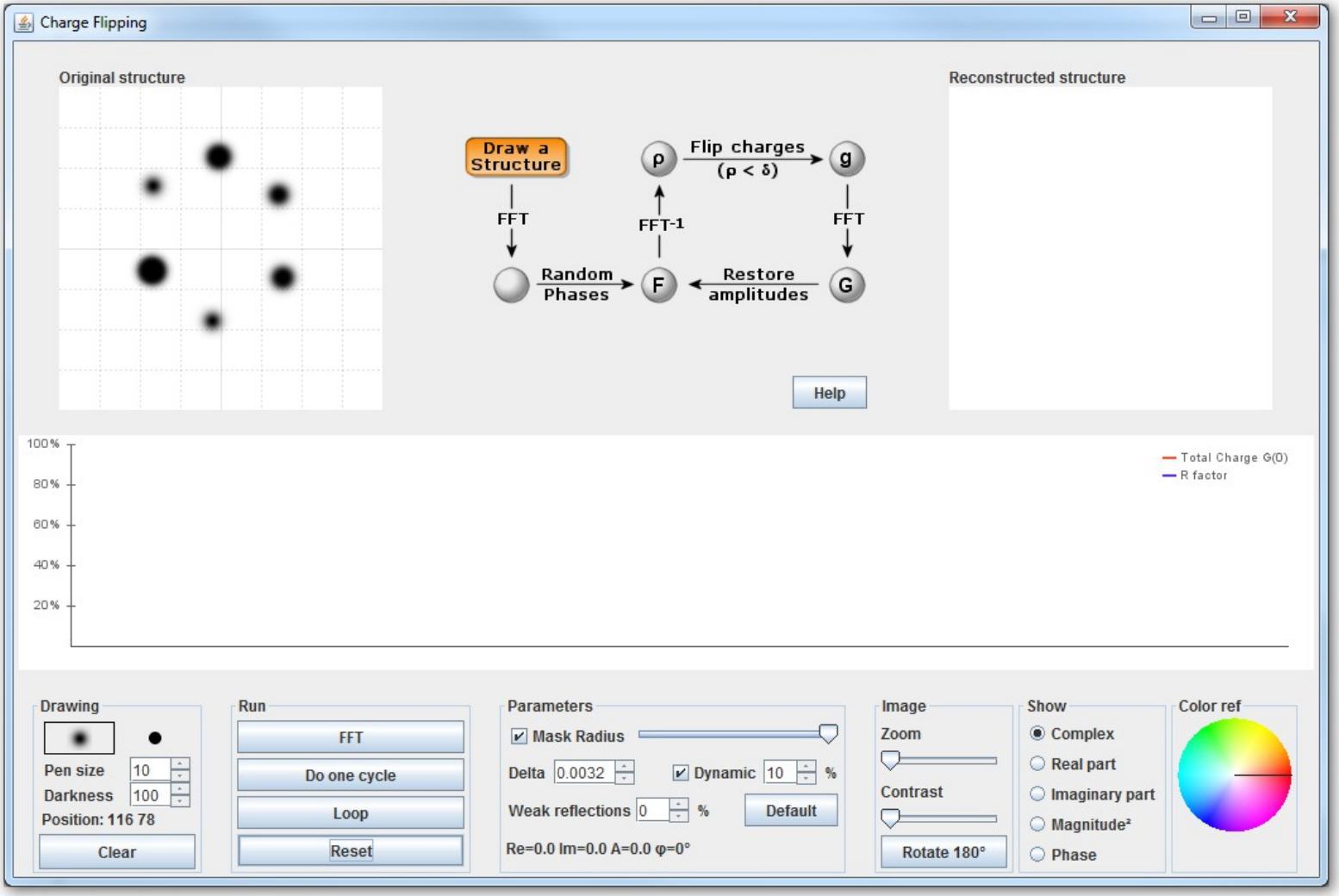
Reflector of the significance + positivity projection – the charge flipping operation

Constraints and projections



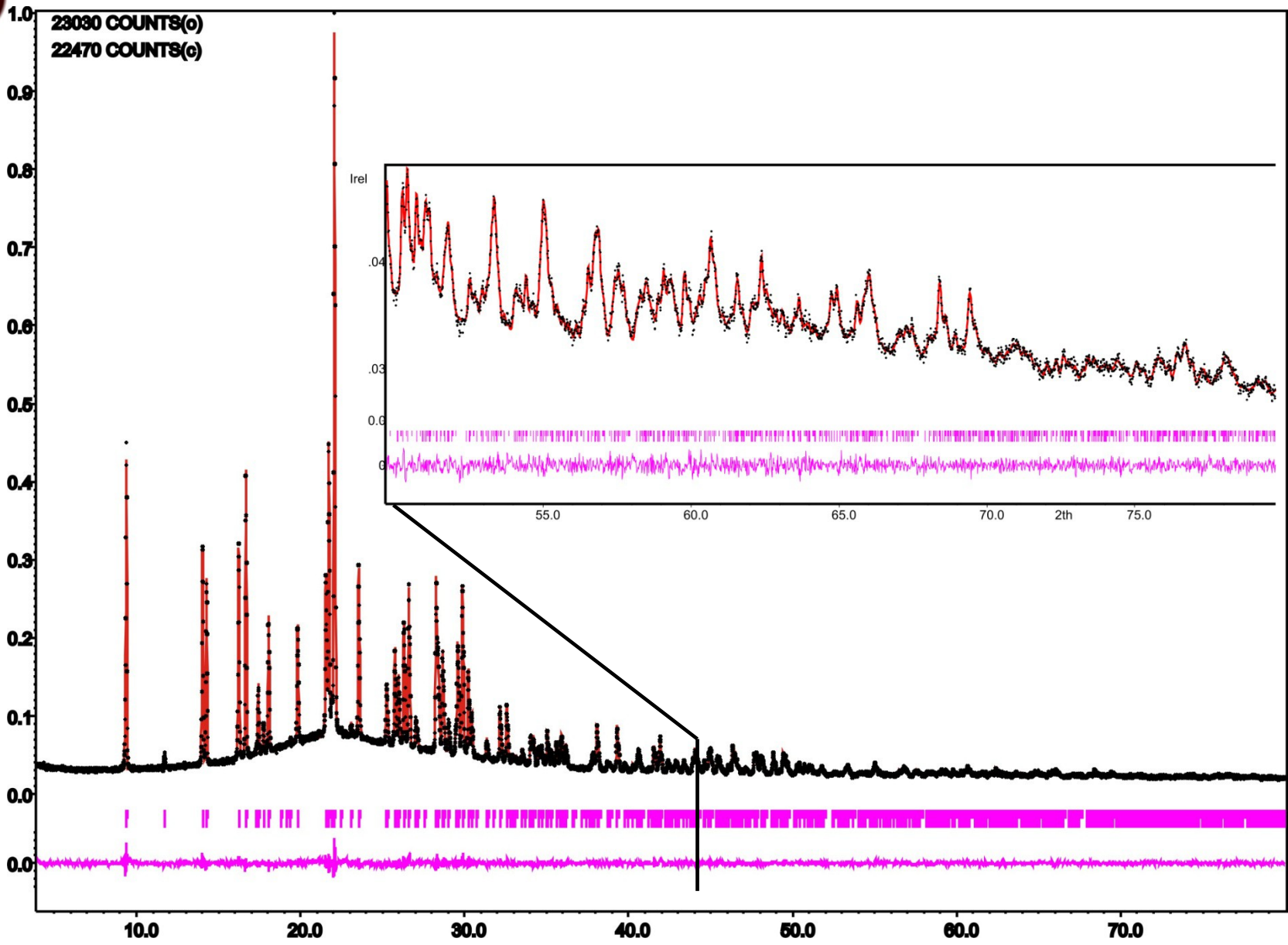
Constraint on the number of maxima in the density

Charge flipping - applet



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

Charge flipping for powders



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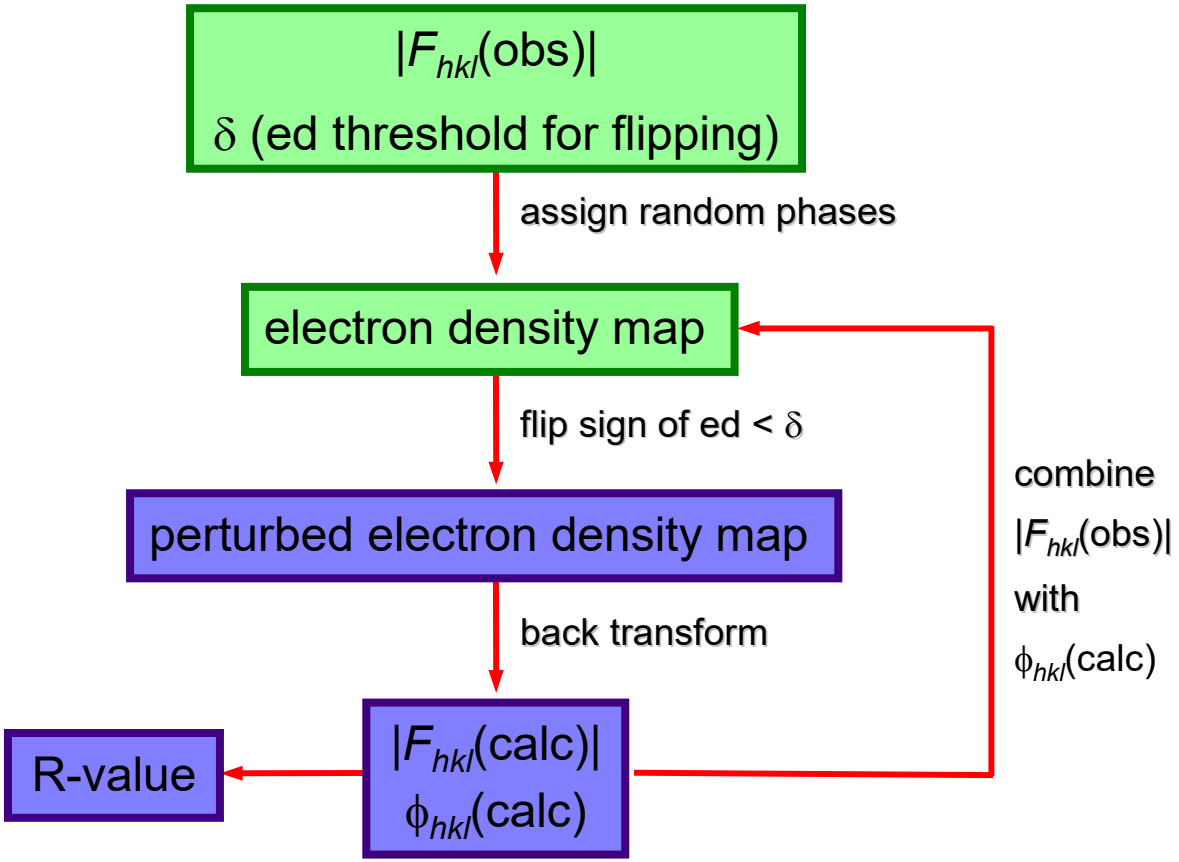

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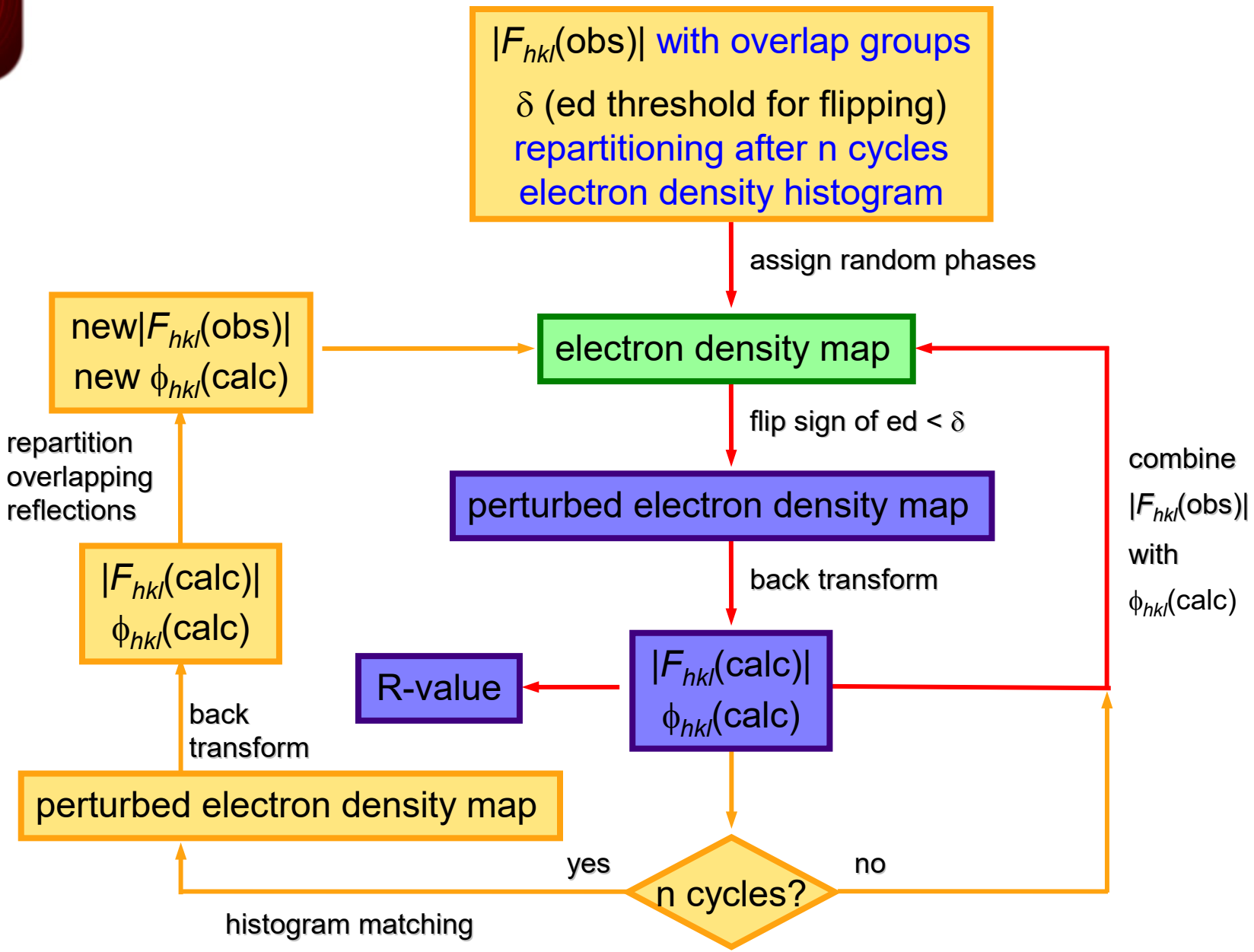
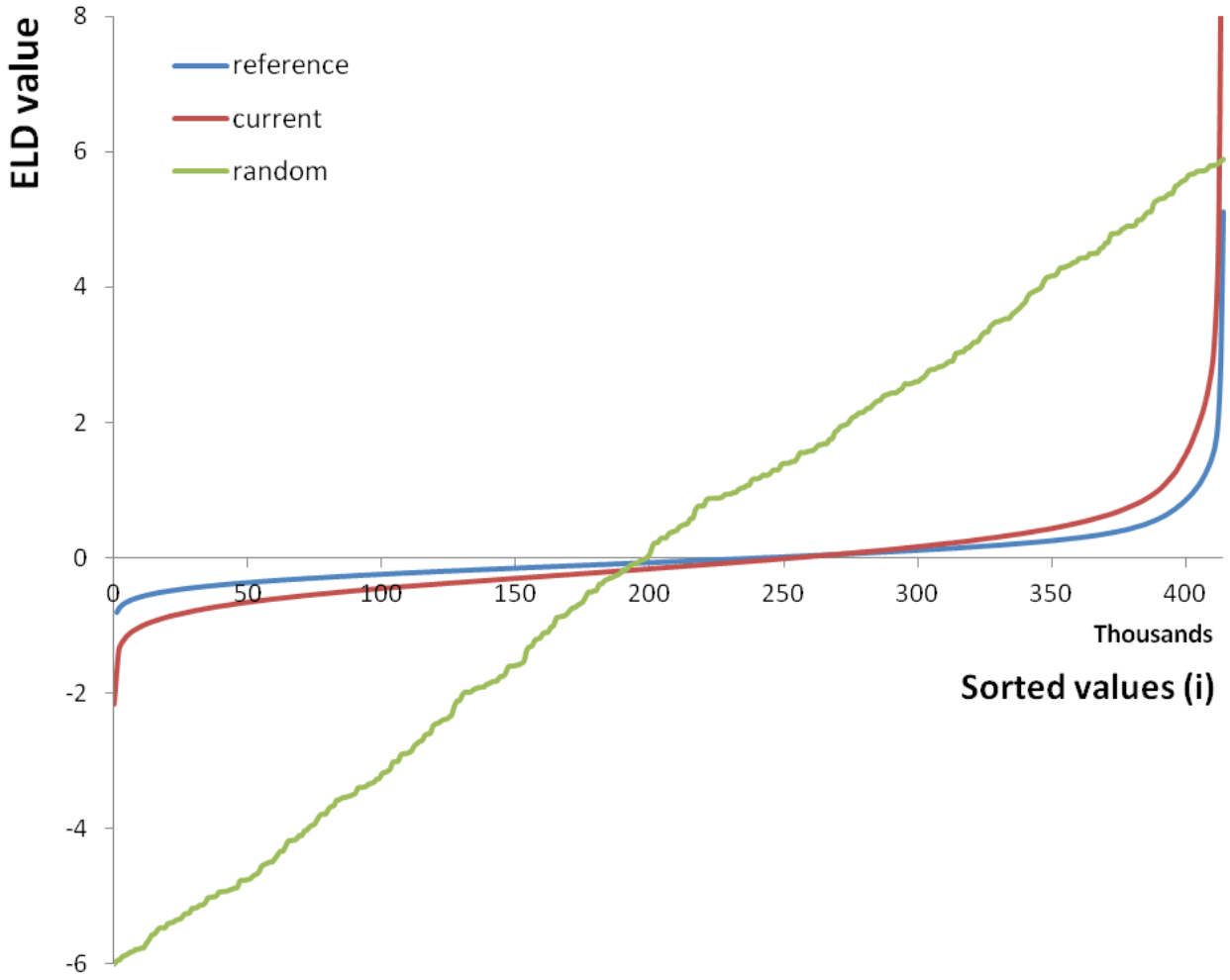
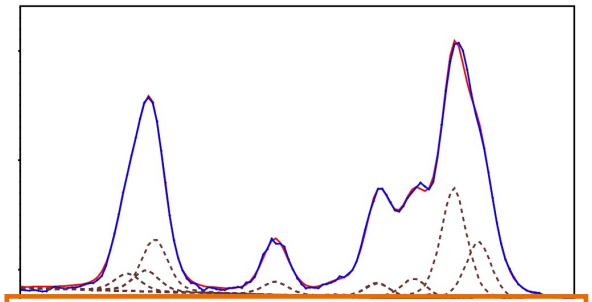


Electron density histograms

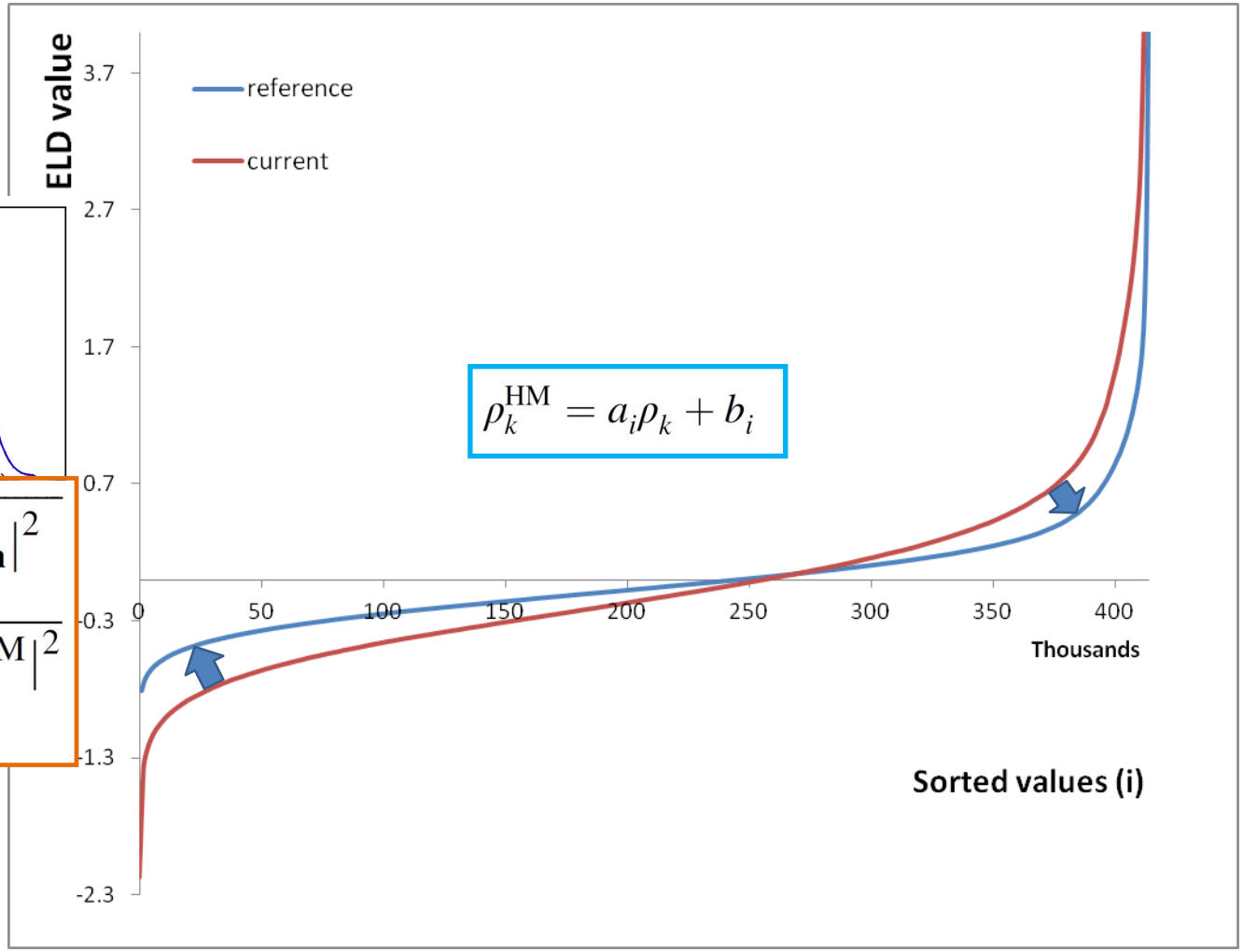


Original idea: Zhang & Main, Acta Cryst A46, 1990 – used to improve phases, not intensities

Electron density histograms



$$F_{\mathbf{h}}^{\text{new}} = F_{\mathbf{h}}^{\text{HM}} \sqrt{\frac{\sum_{\Gamma_k} |F_{\mathbf{h}}|^2}{\sum_{\Gamma_k} |F_{\mathbf{h}}^{\text{HM}}|^2}}$$



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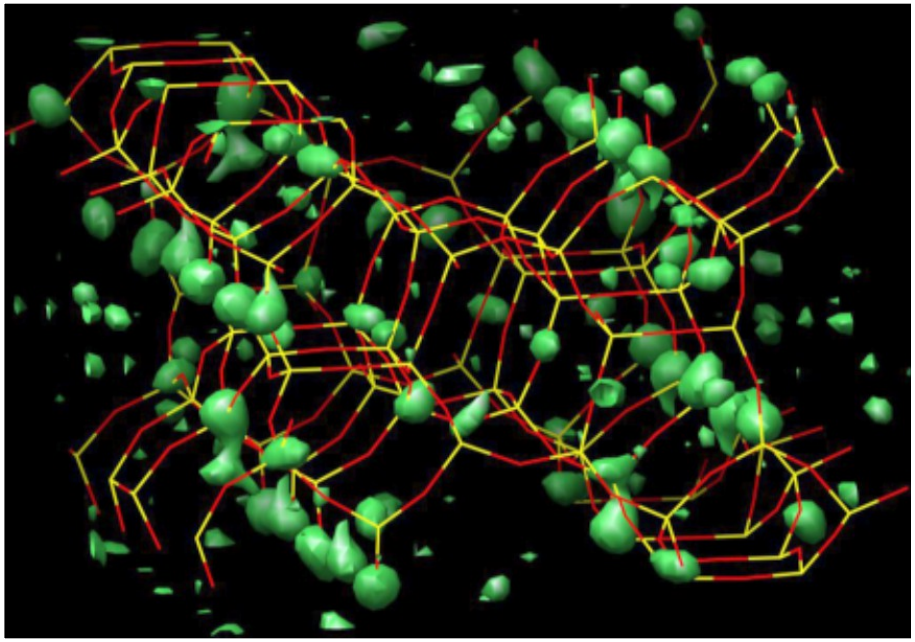
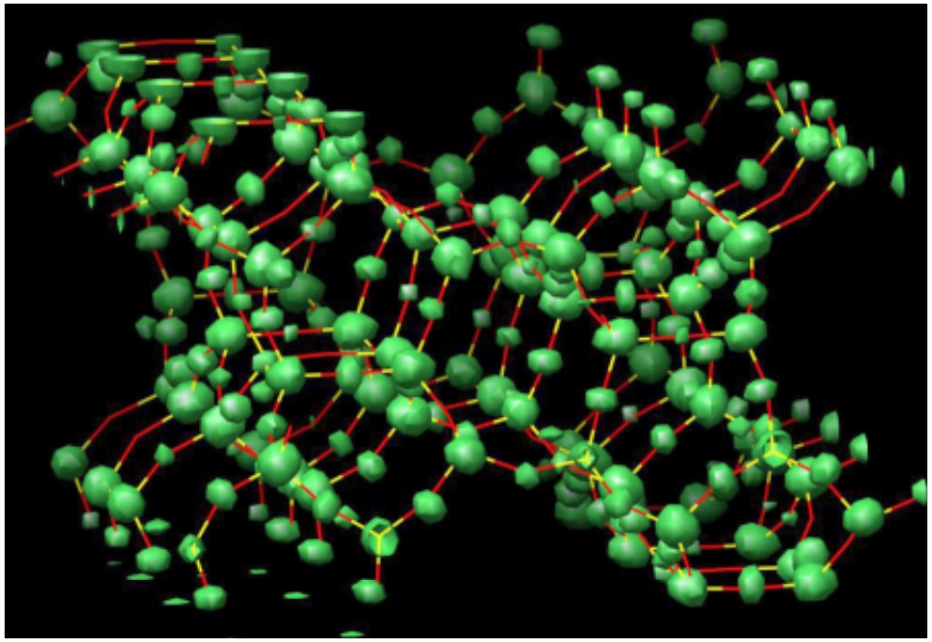
Charge flipping for powders

Zeolite ZSM-5, $Si_{96}O_{192}$



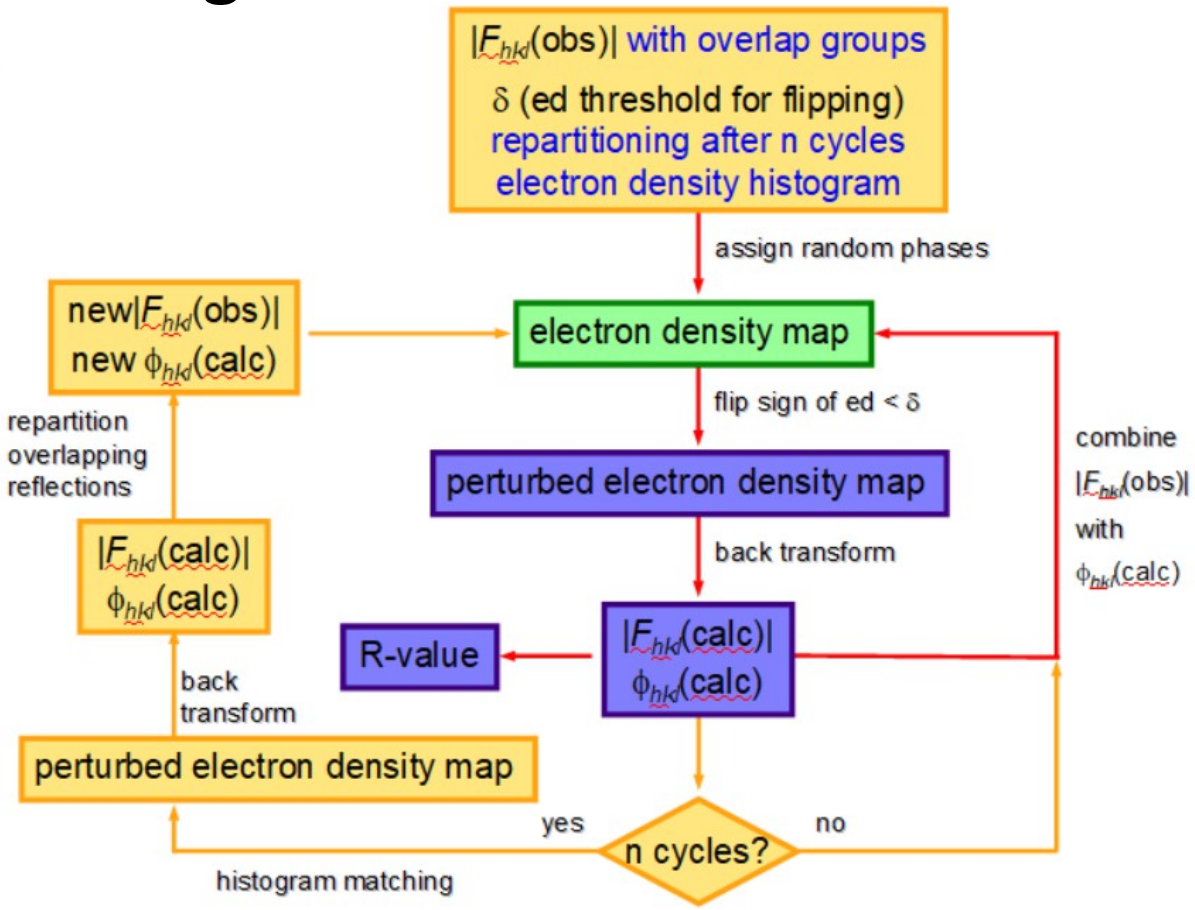
without histogram matching



with histogram matching

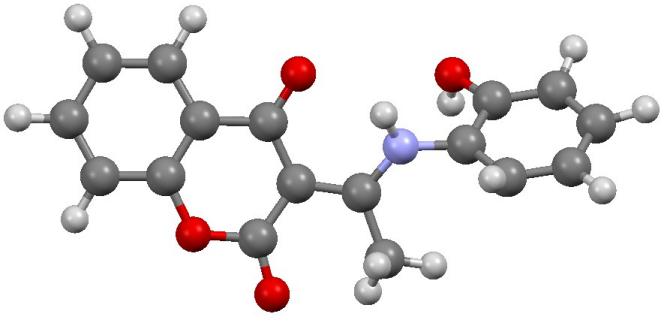
Charge flipping for powders

- How to set up the algorithm?
- K = 0.3
- Biso = 0–1
- HM= 20–5
- δ = δauto
- 500 cycles
- 100 runs



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

Charge flipping for powders



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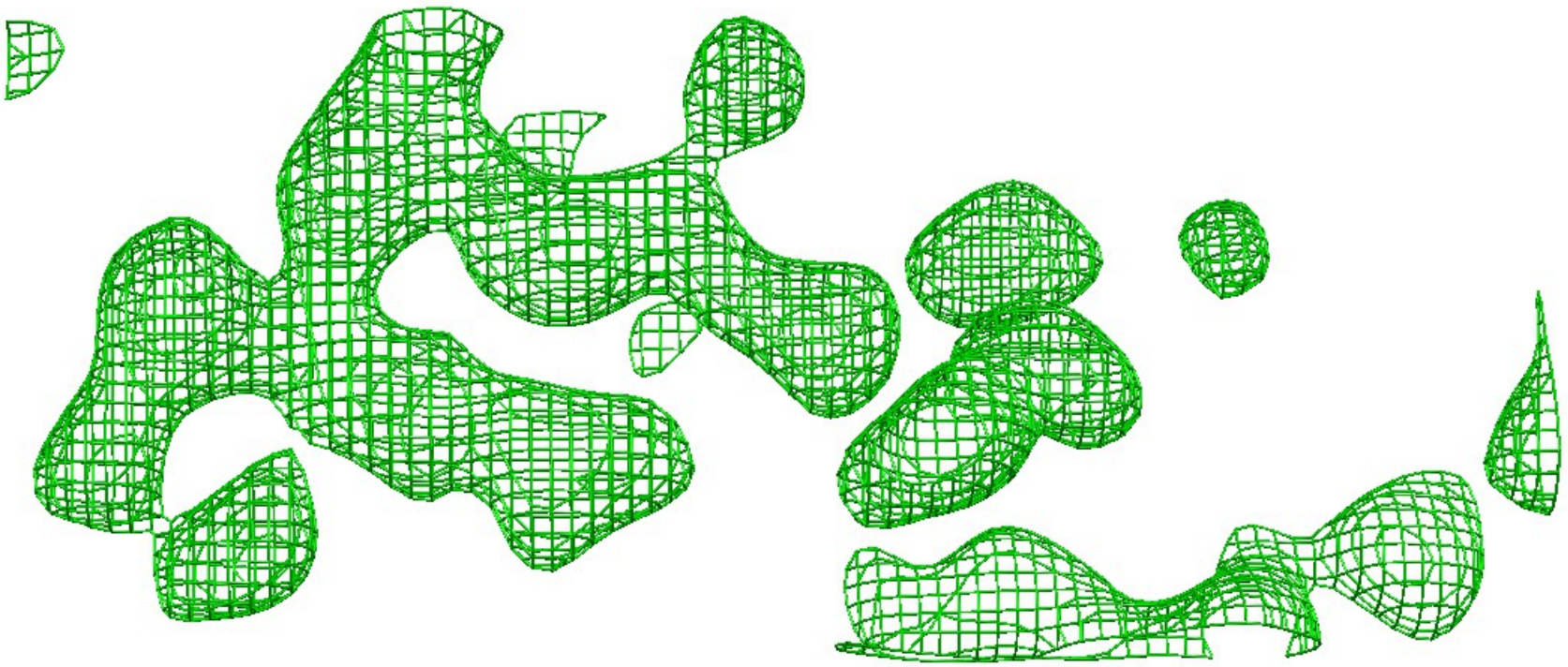

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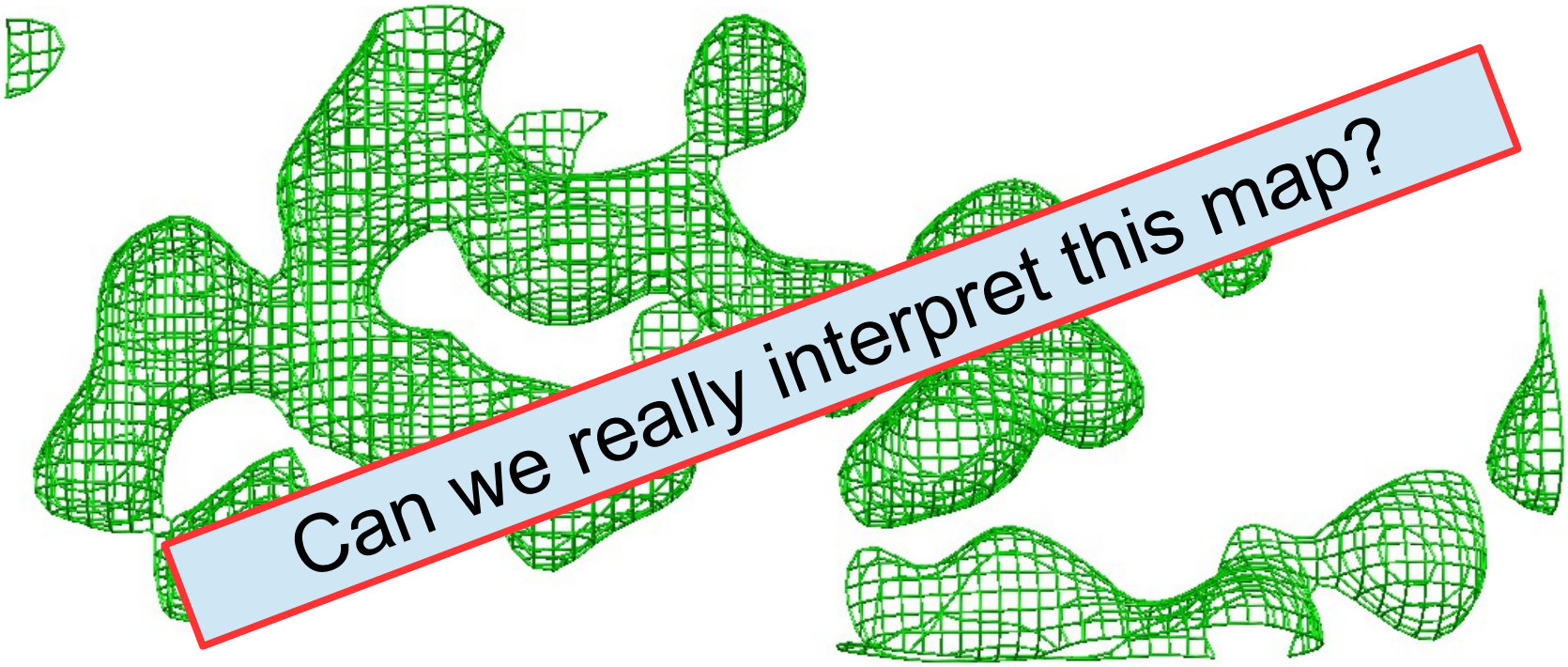

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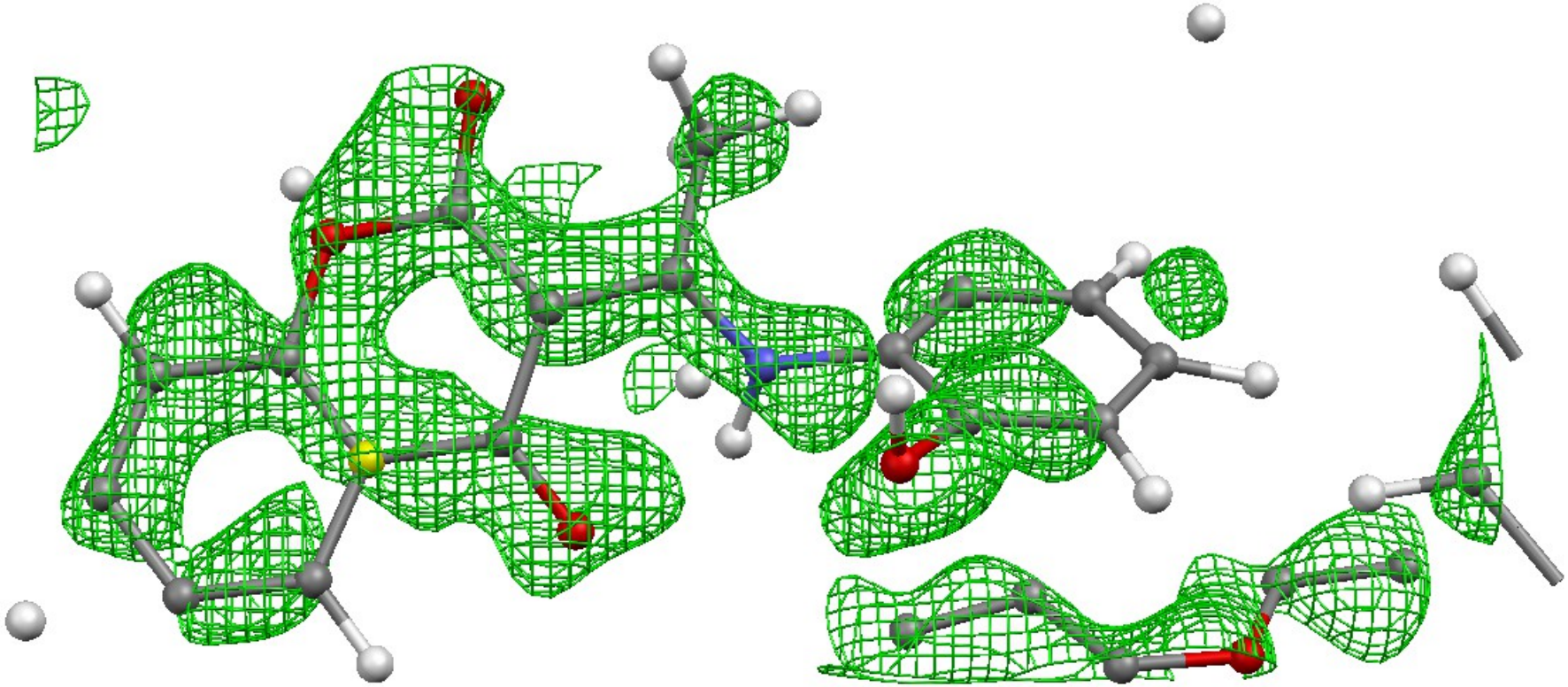

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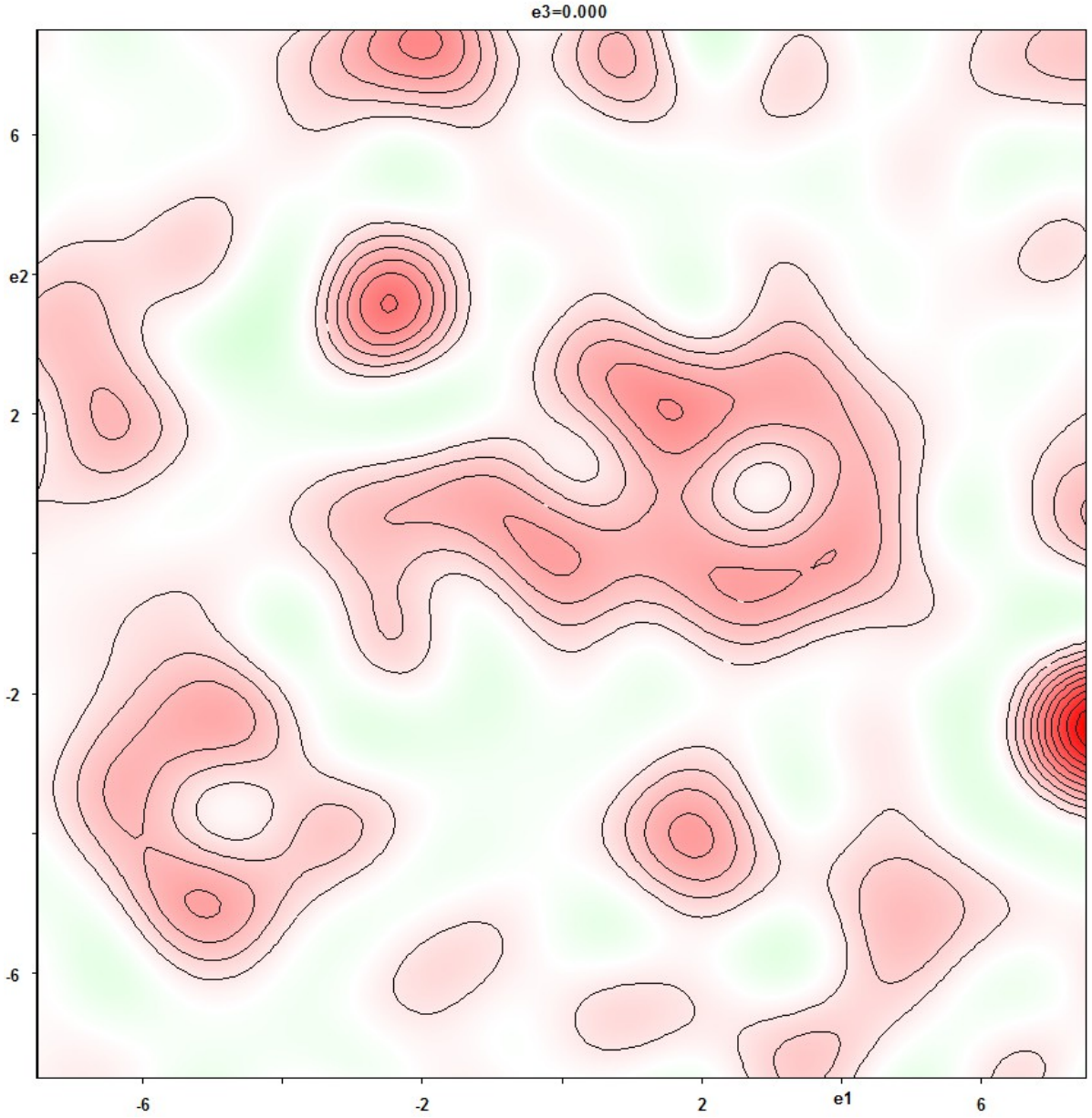

Advantages and disadvantages

+ 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<1.3A for light atoms, much more relaxed for heavier atoms
- Peak overlap should not be so high

End

Thank you !