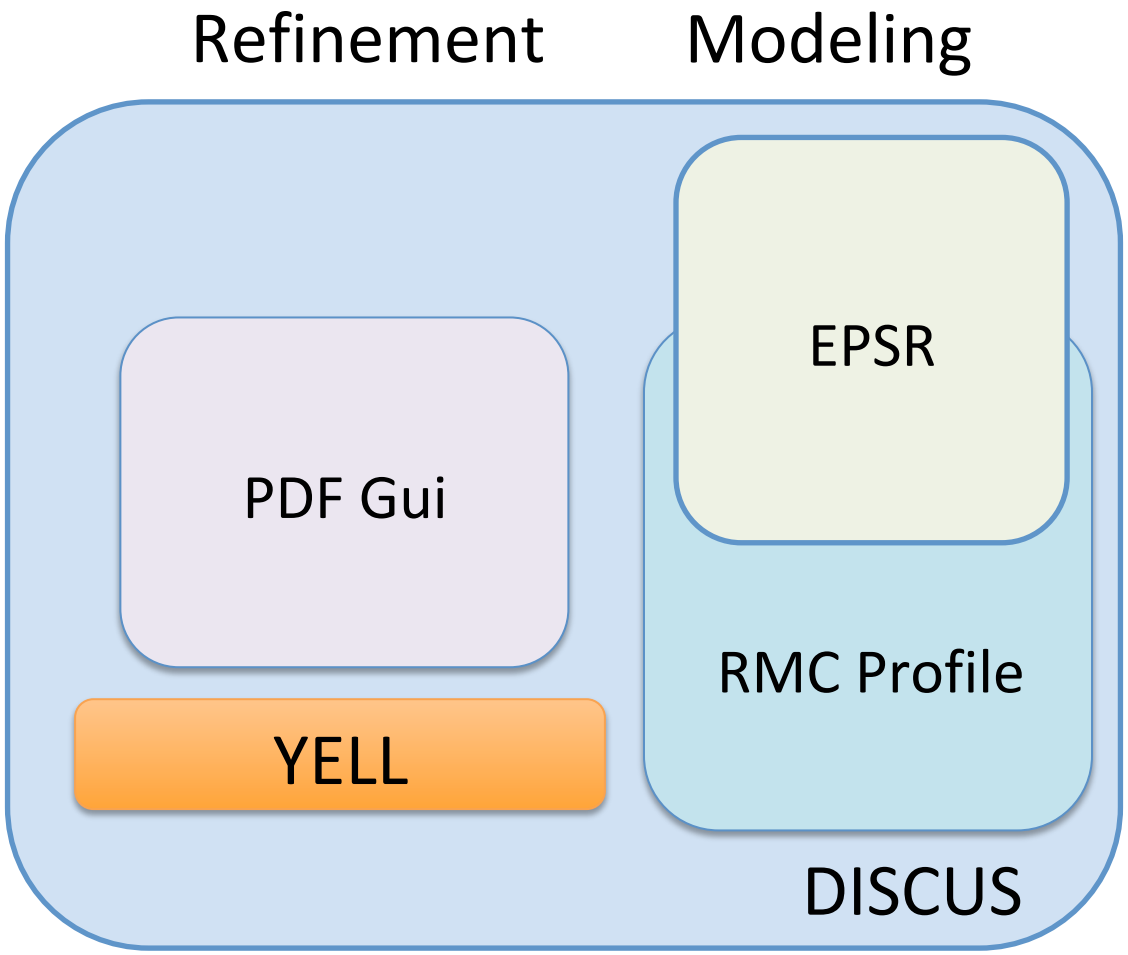
3D-ΔPDF: Pair distribution function analysis for single crystals

Simonov Arkadiy

Uni Freiburg

Direct space programs



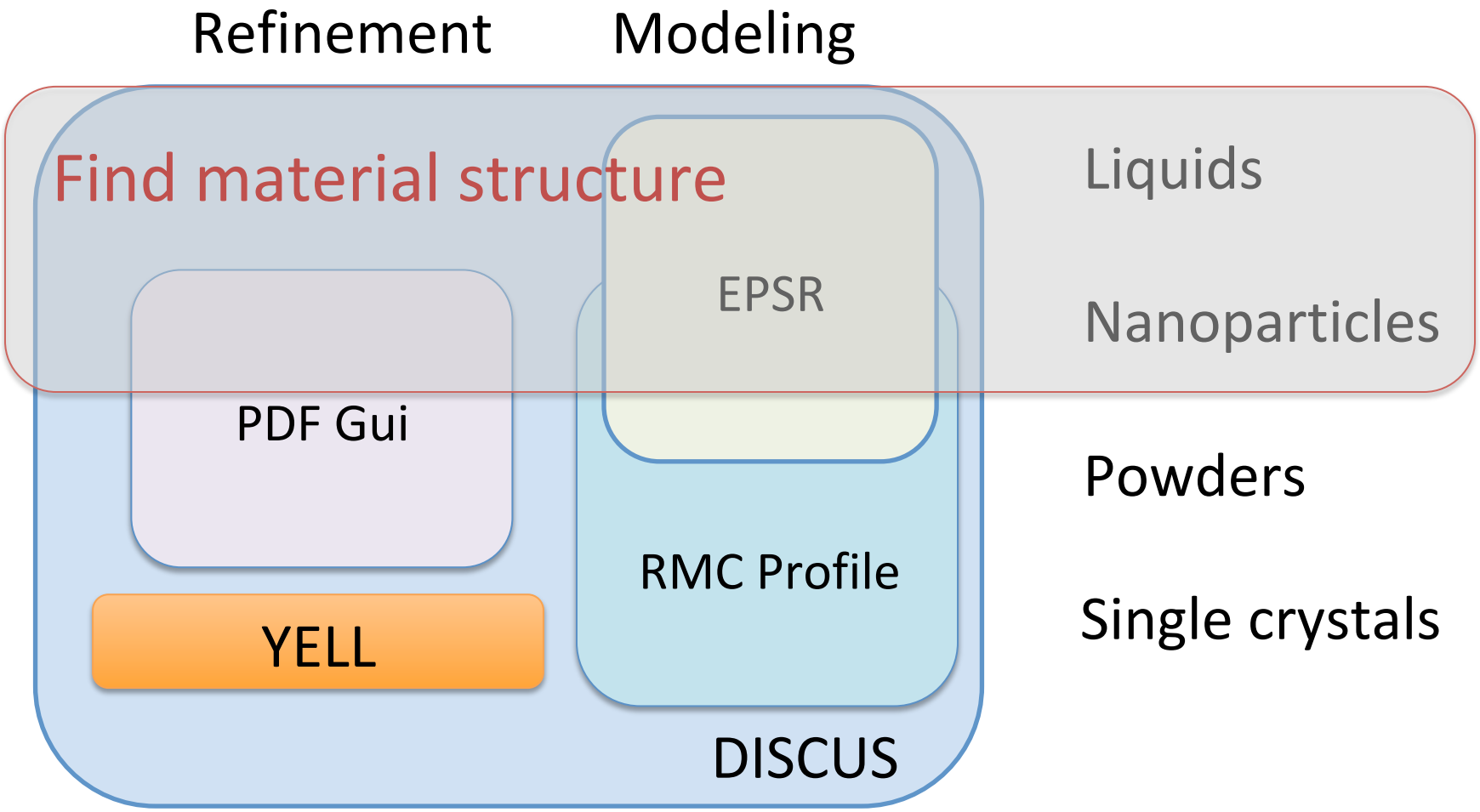
Liquids

Nanoparticles

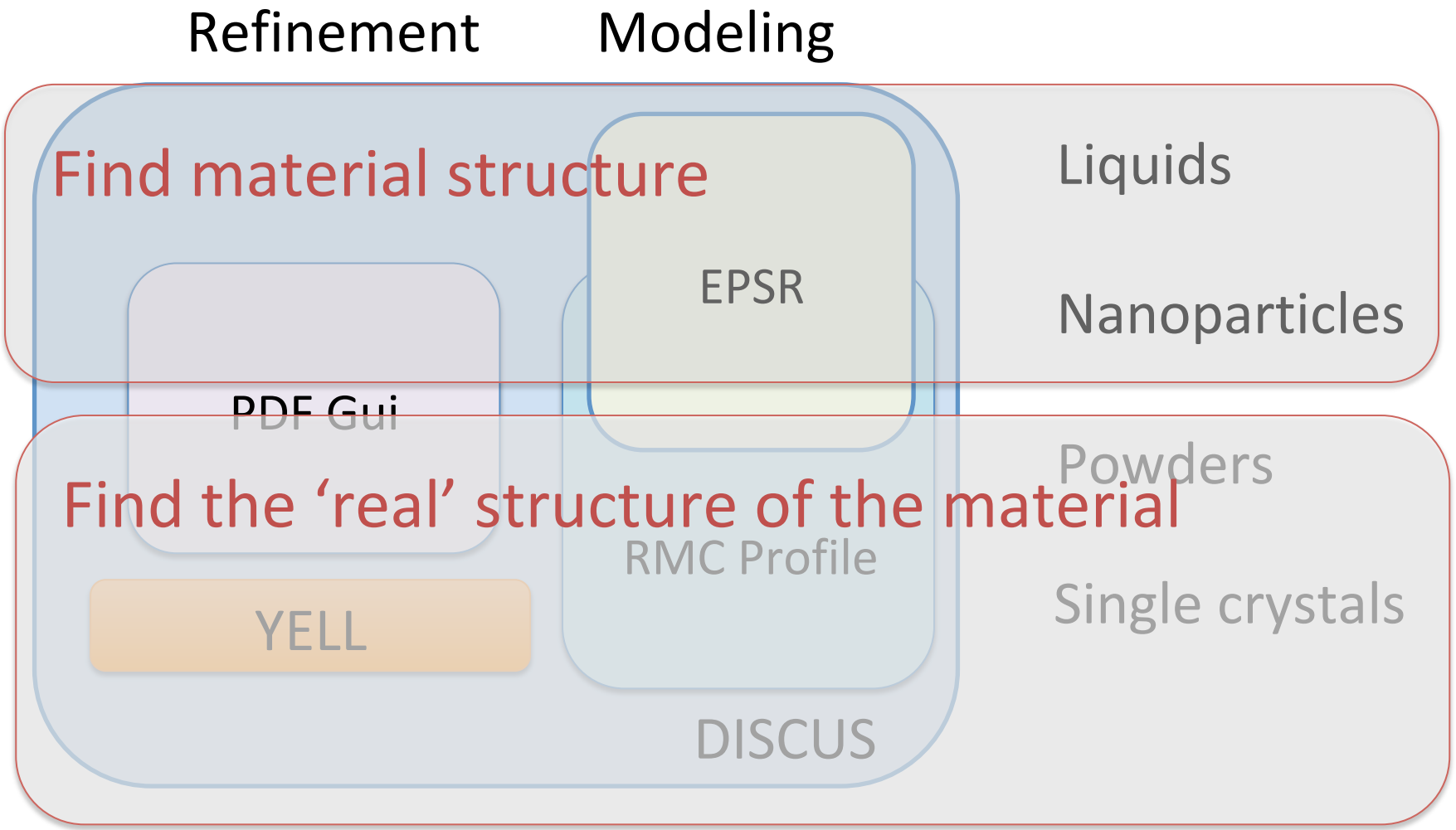
Powders

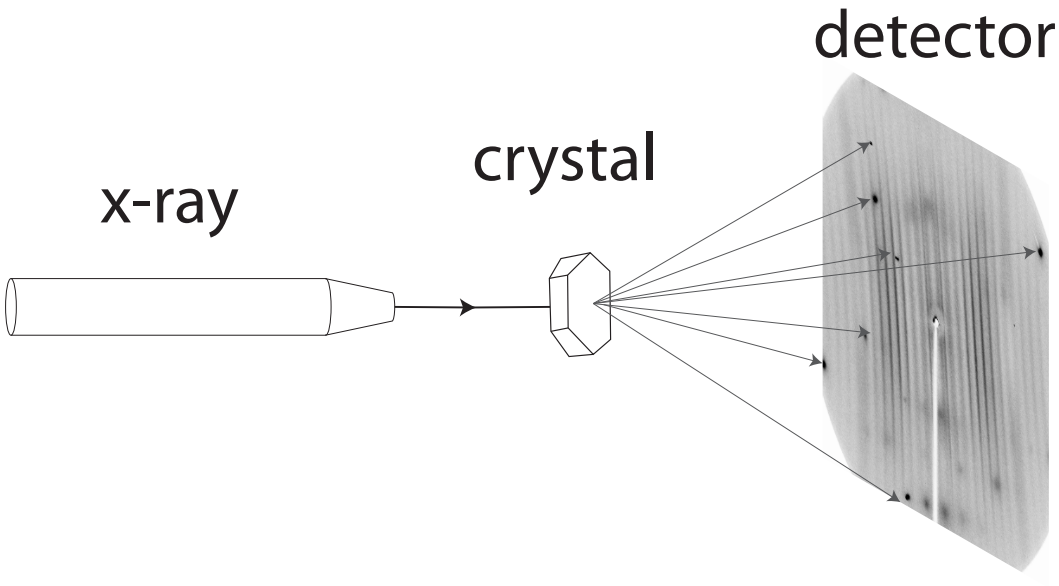
Single crystals

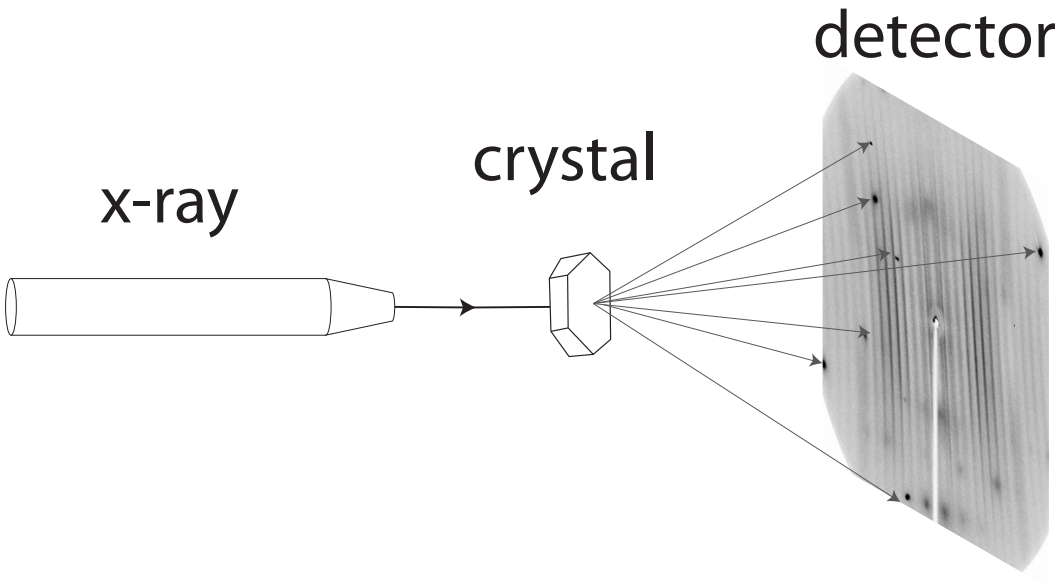
Direct space programs

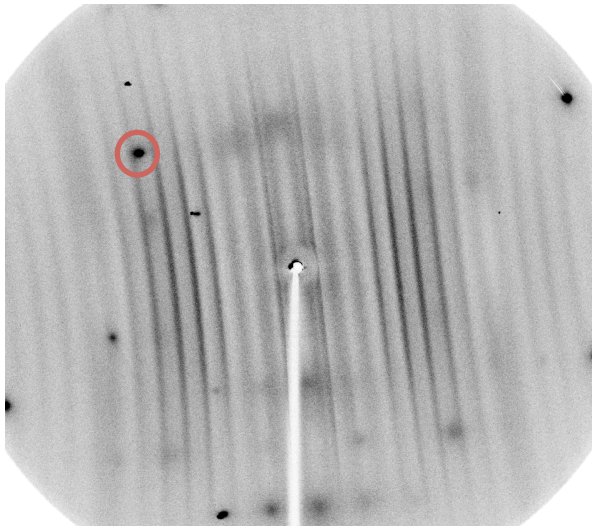


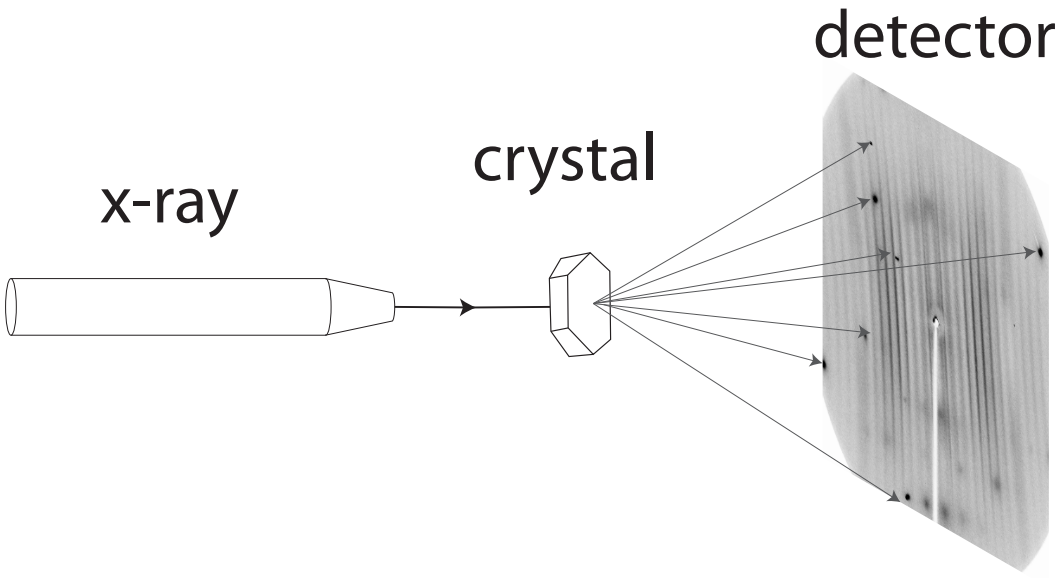
Direct space programs

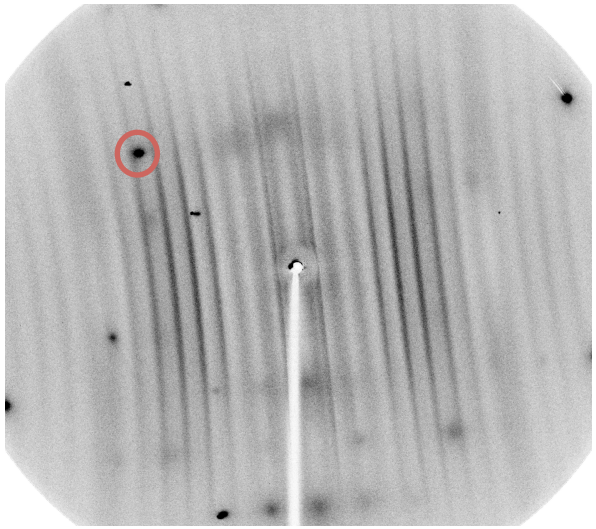


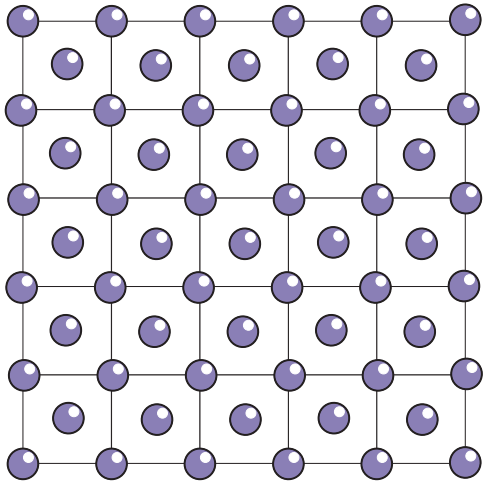

detector
crystal
x-ray


detector
crystal
x-ray









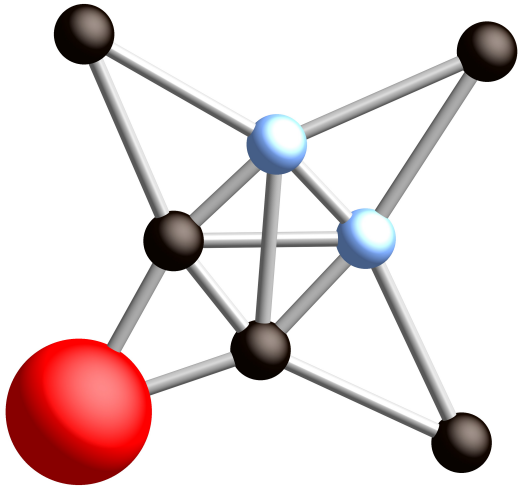
CrysAlis
SuperFlip
shelx
platon

Average structure

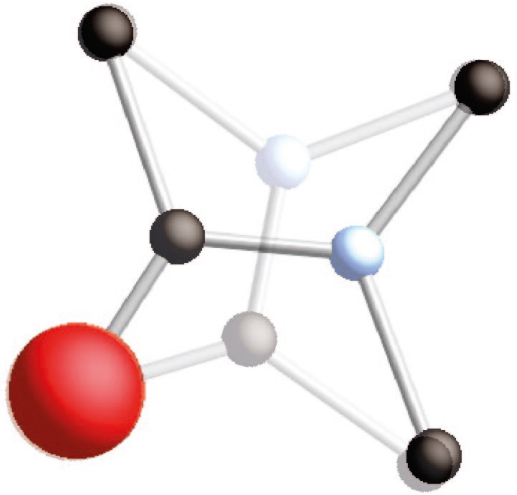
$$F(\mathbf{h}) = \sum_{m}^{M} c_m \exp\{2\pi i \mathbf{r}_m \mathbf{h}\} \exp\{-\mathbf{h}^T \beta_m \mathbf{h}\} f_m(\mathbf{h})$$

$$\langle \rho(\mathbf{r}) \rangle = \sum_{\mathbf{R}}^{\infty} \sum_{m} c_m \mathcal{N}(\mathbf{r}|\mathbf{R} + \mathbf{r}_m, \beta_m) * \varrho_m(\mathbf{r})$$

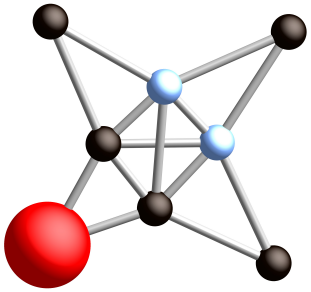
[M.Tutughamiarso, et al (2011) Acta Crystallogr C. CSD: AKEMIN]

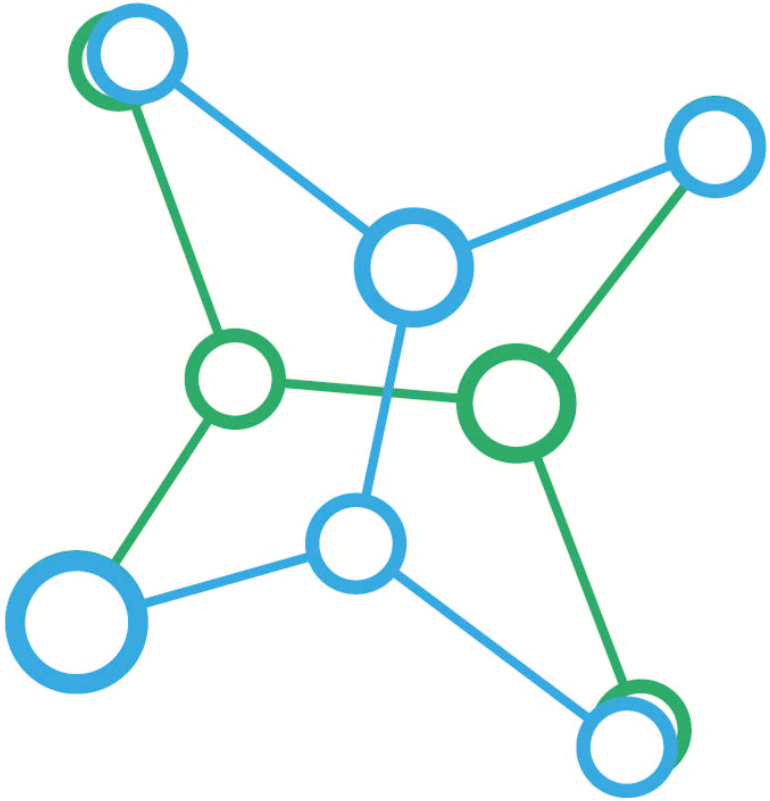


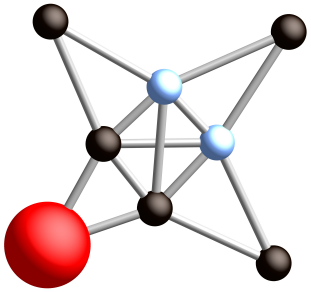
Average structure

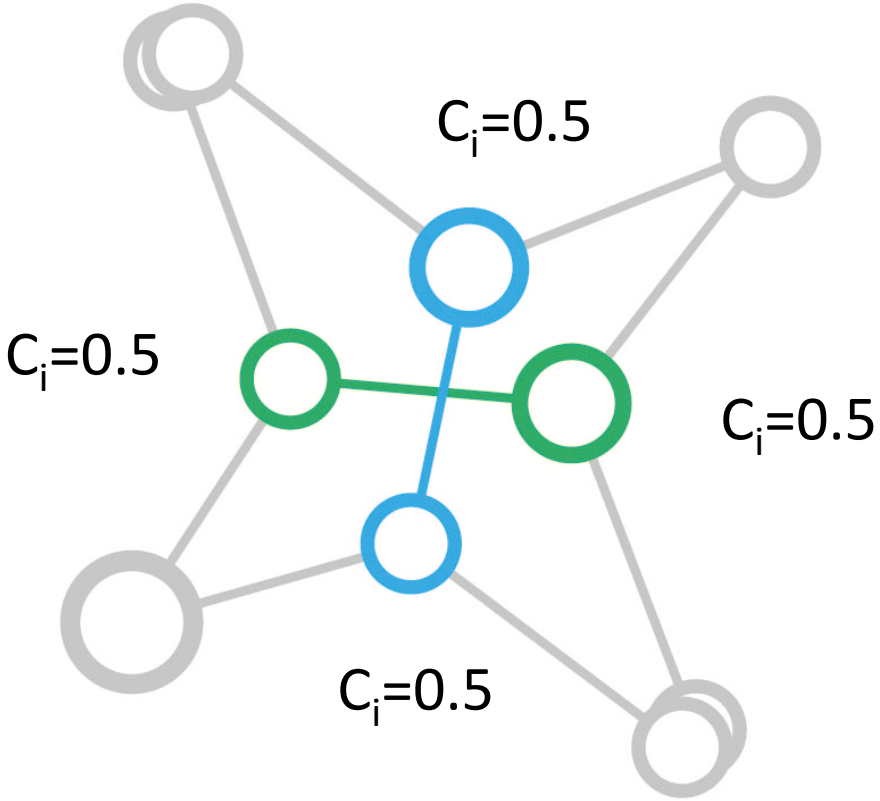


Disentanglement








C_i=0.5
C_i=0.5
C_i=0.5
C_i=0.5

Patterson function: PDF of the average structure

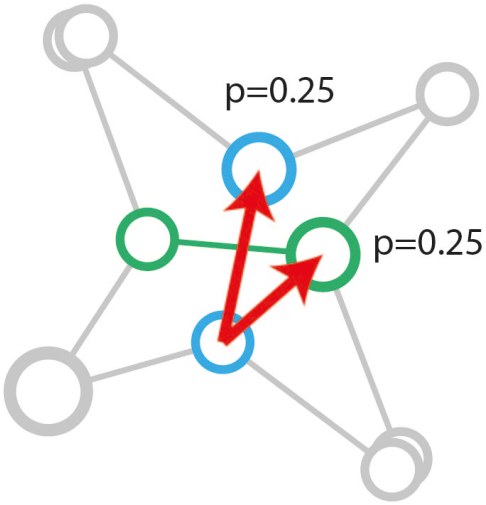
$$F(\mathbf{h}) = \sum_{m}^{M} c_m \exp\{2\pi i \mathbf{r}_m \mathbf{h}\} \exp\{-\mathbf{h}^T \beta_m \mathbf{h}\} f_m(\mathbf{h})$$

$$\langle \rho(\mathbf{r}) \rangle = \sum_{\mathbf{R}}^{\infty} \sum_{m} c_m \mathcal{N}(\mathbf{r}|\mathbf{R} + \mathbf{r}_m, \beta_m) * \varrho_m(\mathbf{r})$$

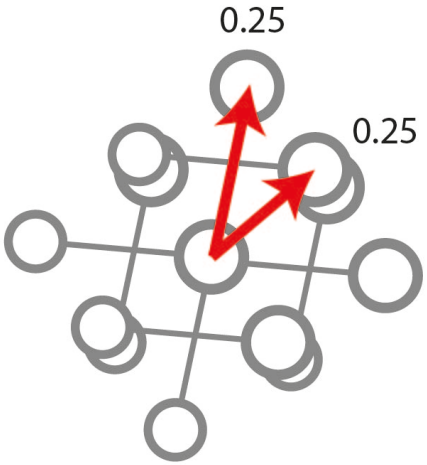
$$P_{Pat}(\mathbf{x}) = \mathfrak{F}^{-1}[I_{Bragg}(\mathbf{h})] = \langle \rho(\mathbf{x}) \rangle * \langle \rho(-\mathbf{x}) \rangle$$

$$P_{Pat}(\mathbf{x}) = \sum_{\mathbf{R}_{uvw}}^{N} \sum_{mn}^{M} c_m c_n \mathcal{N}(\mathbf{x}|\mathbf{R}_{uvw} + \mathbf{r}_n - \mathbf{r}_m, \beta_m + \beta_n) * \varrho_m(\mathbf{x}) * \varrho_n(-\mathbf{x})$$

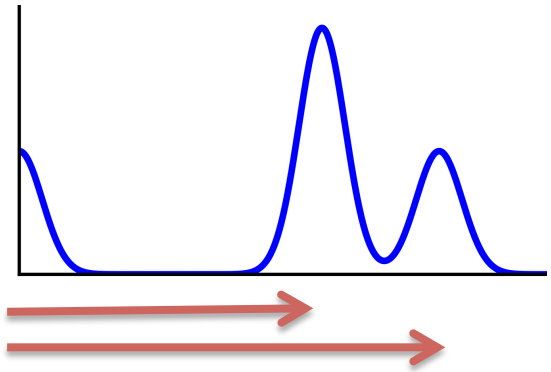
Patterson function $P_{Pat}(\mathbf{x}) = \mathfrak{F}^{-1}[I_{Bragg}(\mathbf{h})]$



Average structure

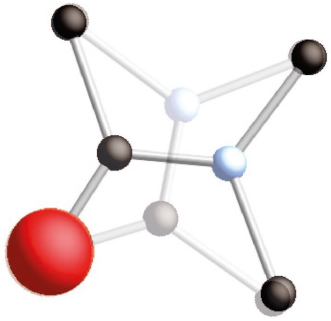


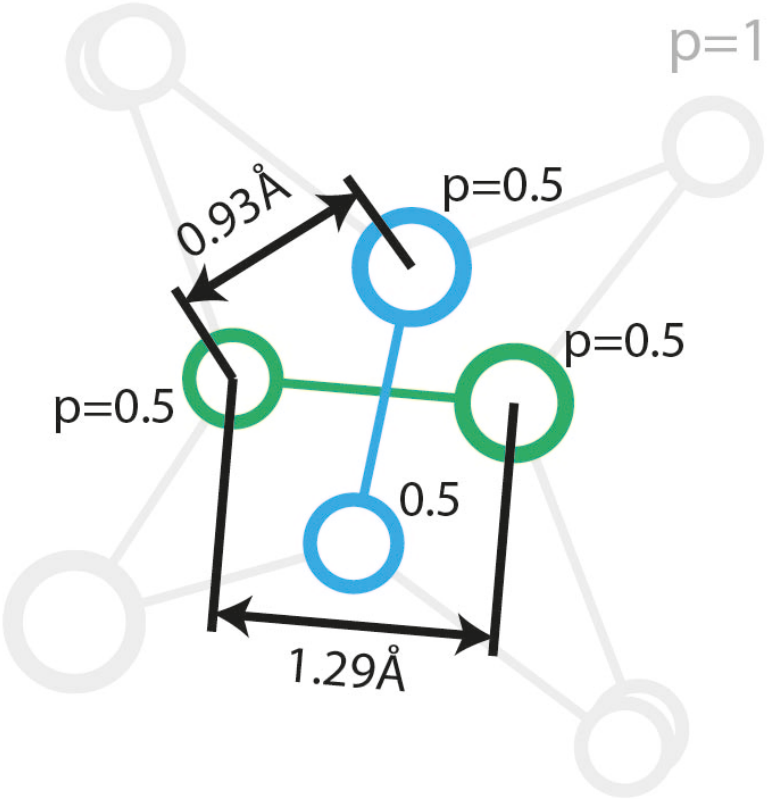
Patterson function



1D-Patterson function

TAKE AWAY MESSAGE 1:
AVERAGE STRUCTURE IS THE MOST DISORDERED MODEL OF YOUR CRYSTAL




p=1
0.93Å
p=0.5
p=0.5
p=0.5
0.5
1.29Å

Pair distribution function

$$P(\mathbf{x}) = \mathfrak{F}^{-1}[I_{Tot}(\mathbf{h})] = \langle \rho(\mathbf{x}) * \rho(-\mathbf{x}) \rangle$$

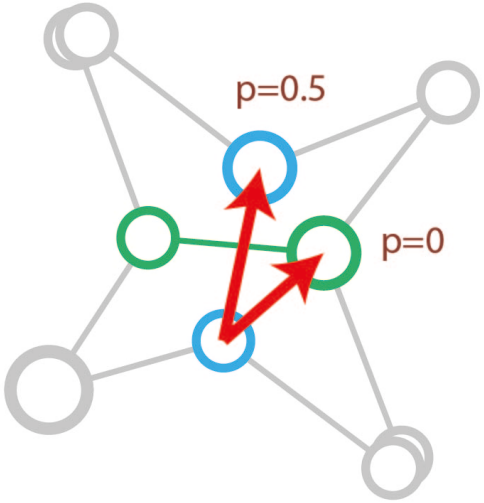
$$P(\mathbf{x}) = \sum_{\mathbf{R}_{uvw}} \sum_{mn}^{N} \sum_{mn}^{M} p_{mn}^{uvw} \mathcal{N}(\mathbf{x}|\bar{\mathbf{r}}_{nm}^{uvw}, \beta_{mn}^{uvw}) * \varrho_m(\mathbf{x}) * \varrho_n(-\mathbf{x})$$

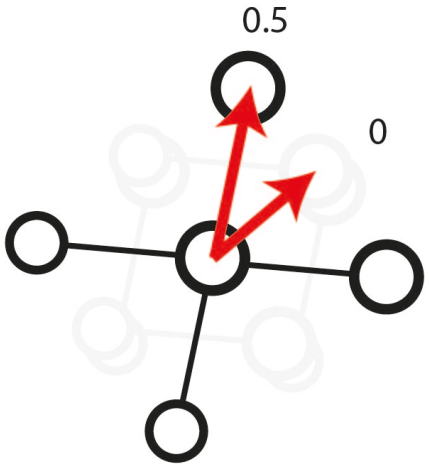
Patterson

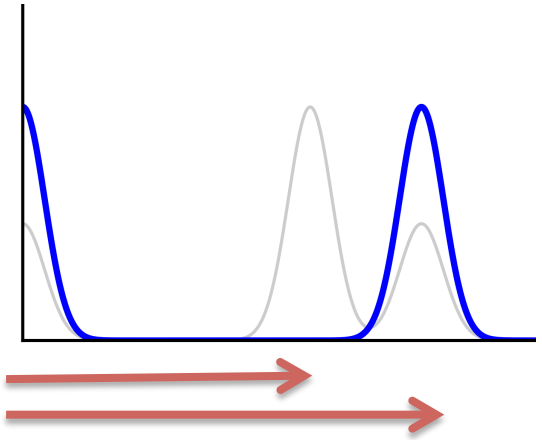
$$P_{Pat}(\mathbf{x}) = \mathfrak{F}^{-1}[I_{Bragg}(\mathbf{h})] = \langle \rho(\mathbf{x}) \rangle * \langle \rho(-\mathbf{x}) \rangle$$

$$P_{Pat}(\mathbf{x}) = \sum_{\mathbf{R}_{uvw}} \sum_{mn}^{N} \sum_{mn}^{M} c_m c_n \mathcal{N}(\mathbf{x}|\mathbf{R}_{uvw} + \mathbf{r}_n - \mathbf{r}_m, \beta_m + \beta_n) * \varrho_m(\mathbf{x}) * \varrho_n(-\mathbf{x})$$

Pair distribution function $P(\mathbf{x}) = \mathfrak{F}^{-1}[I_{Tot}(\mathbf{h})]$







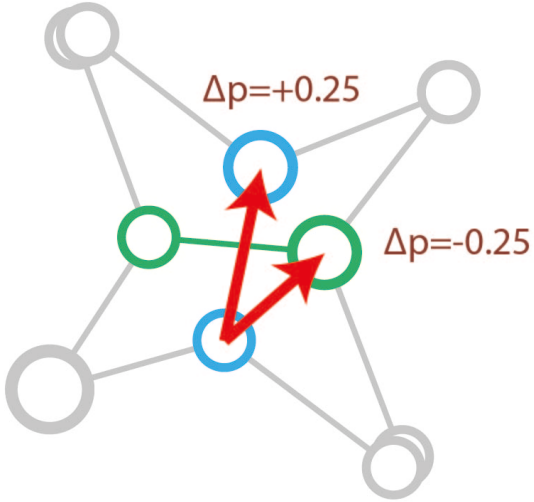
Average structure

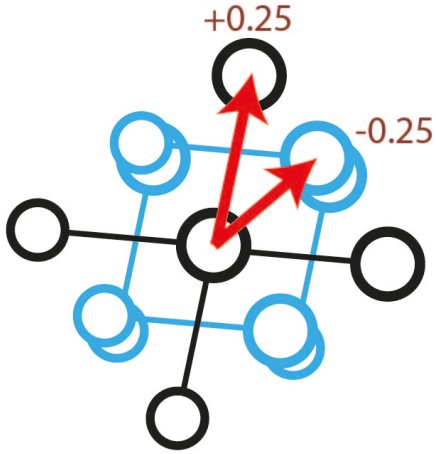
3D-PDF

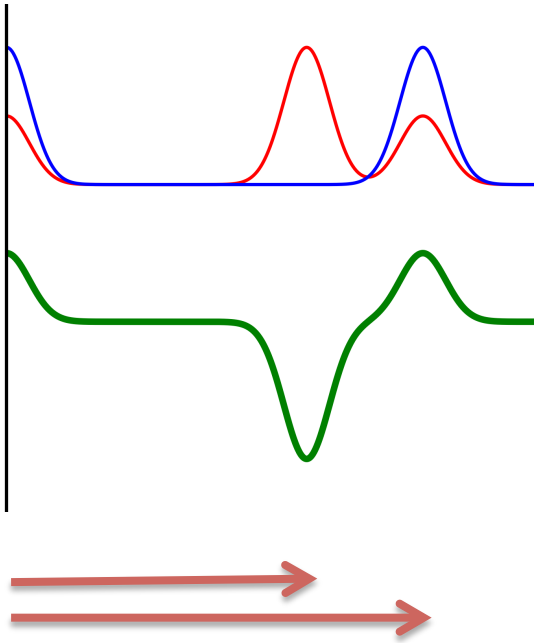
1D-PDF

Difference PDF

$$\Delta P(\mathbf{x}) = \mathfrak{F}^{-1}[I_{Diff}(\mathbf{h})]$$







Average structure

3D-ΔPDF

1D-ΔPDF

TAKE AWAY MESSAGE 2:
DIFFUSE SCATTERING CAPTURES LOCAL CORRELATIONS

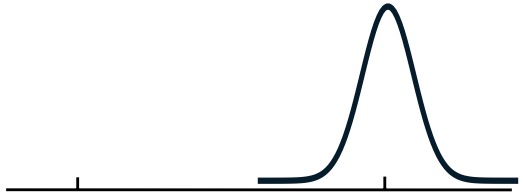
Possible correlations:

- $\Delta p_{ij} \neq 0$ - substitution correlation
- $\Delta U_{ij} \neq 0$ - ADP correlation
- $\Delta r_{ij} \neq 0$ - size effect

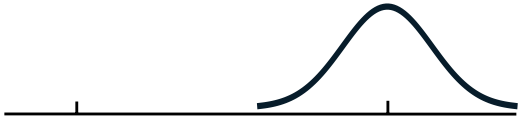
Displacement correlation

Structure

PDF



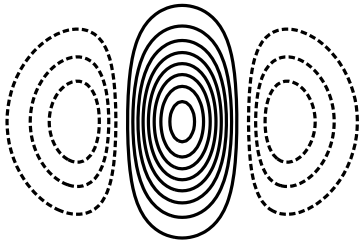
Patterson



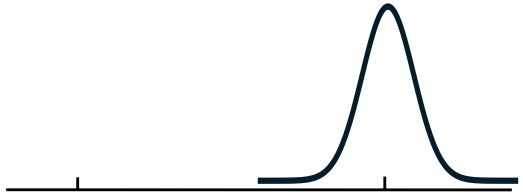
ΔPDF

Displacement correlation

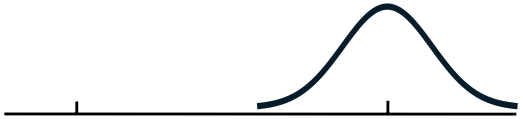
Structure



PDF



Patterson



ΔPDF

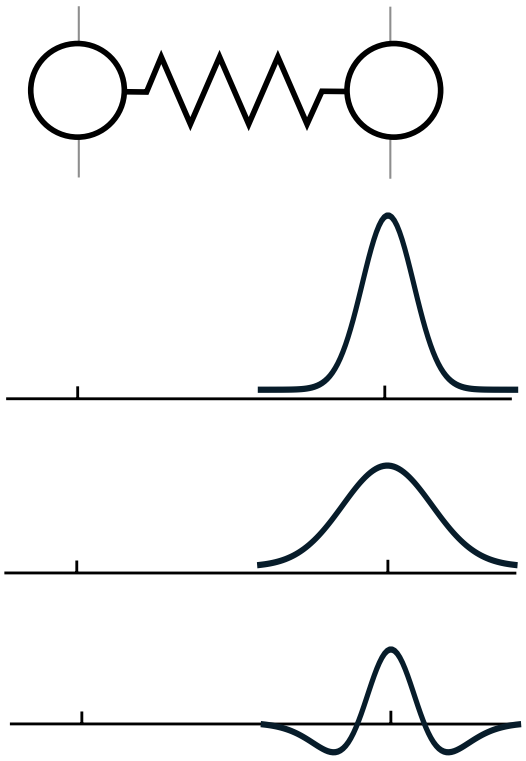
Displacement correlation

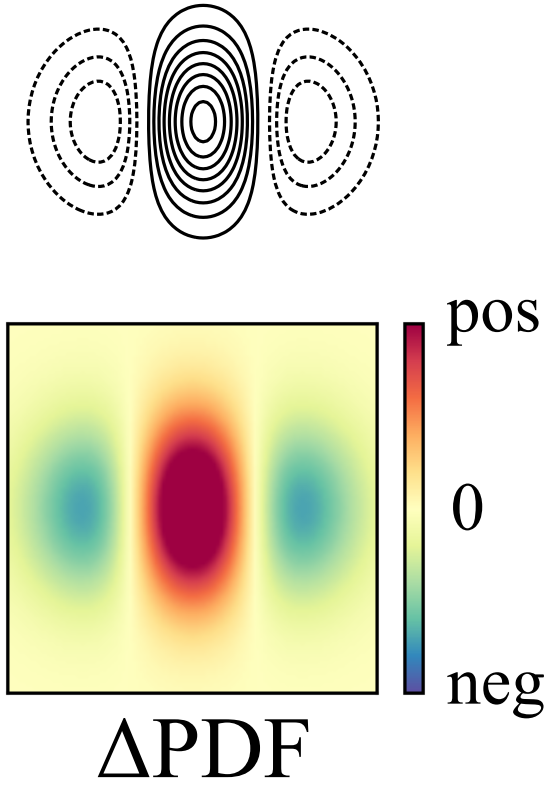
Structure

PDF

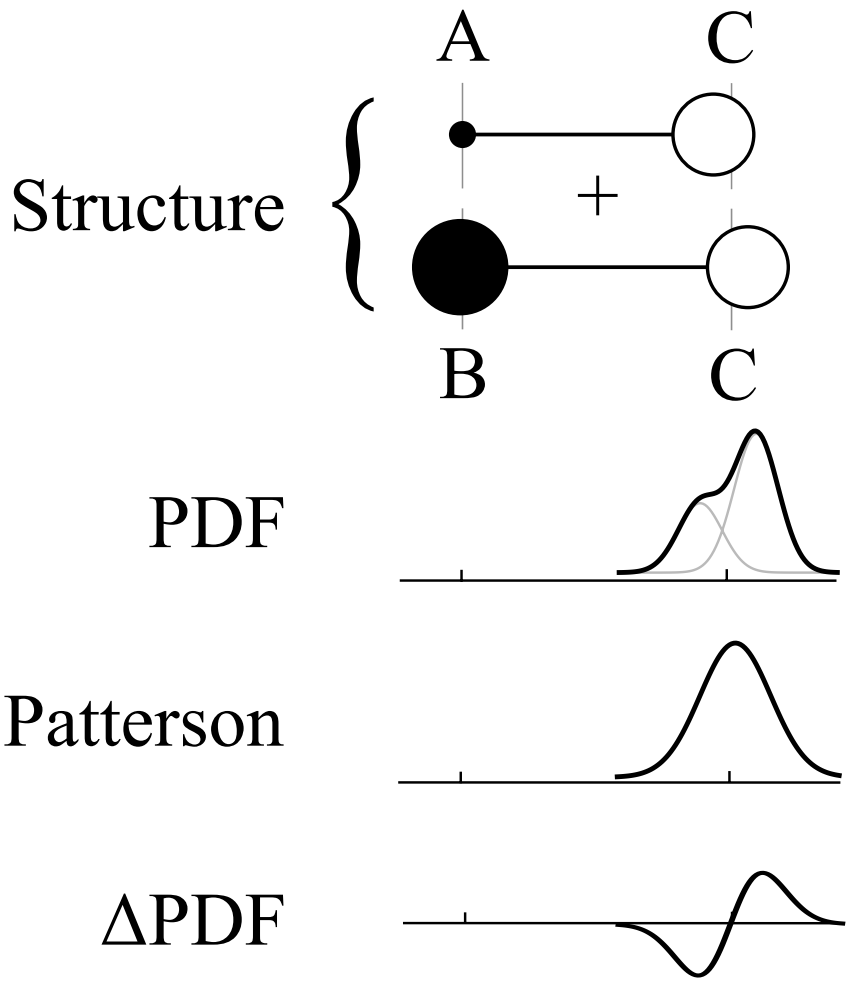
Patterson

ΔPDF

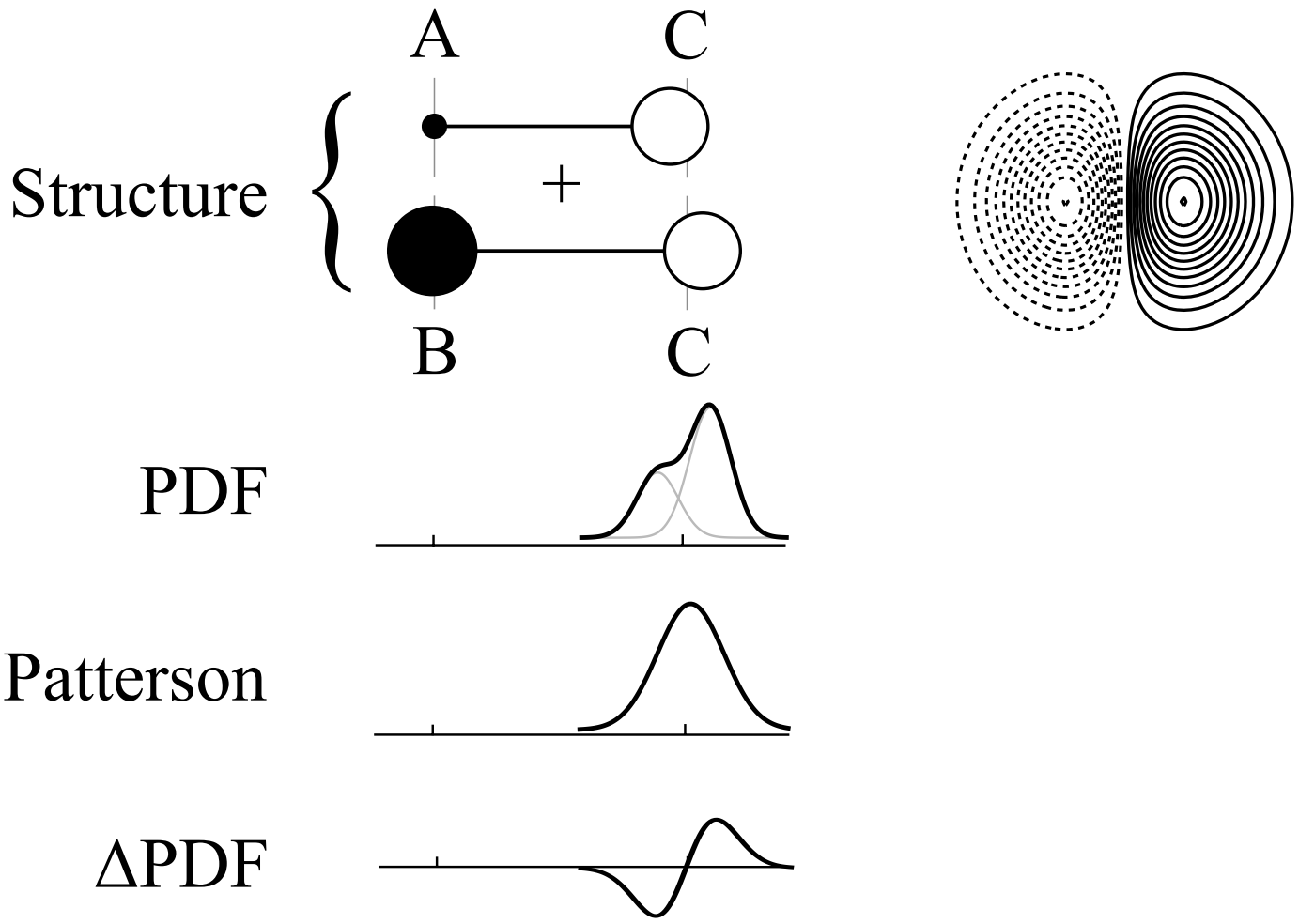




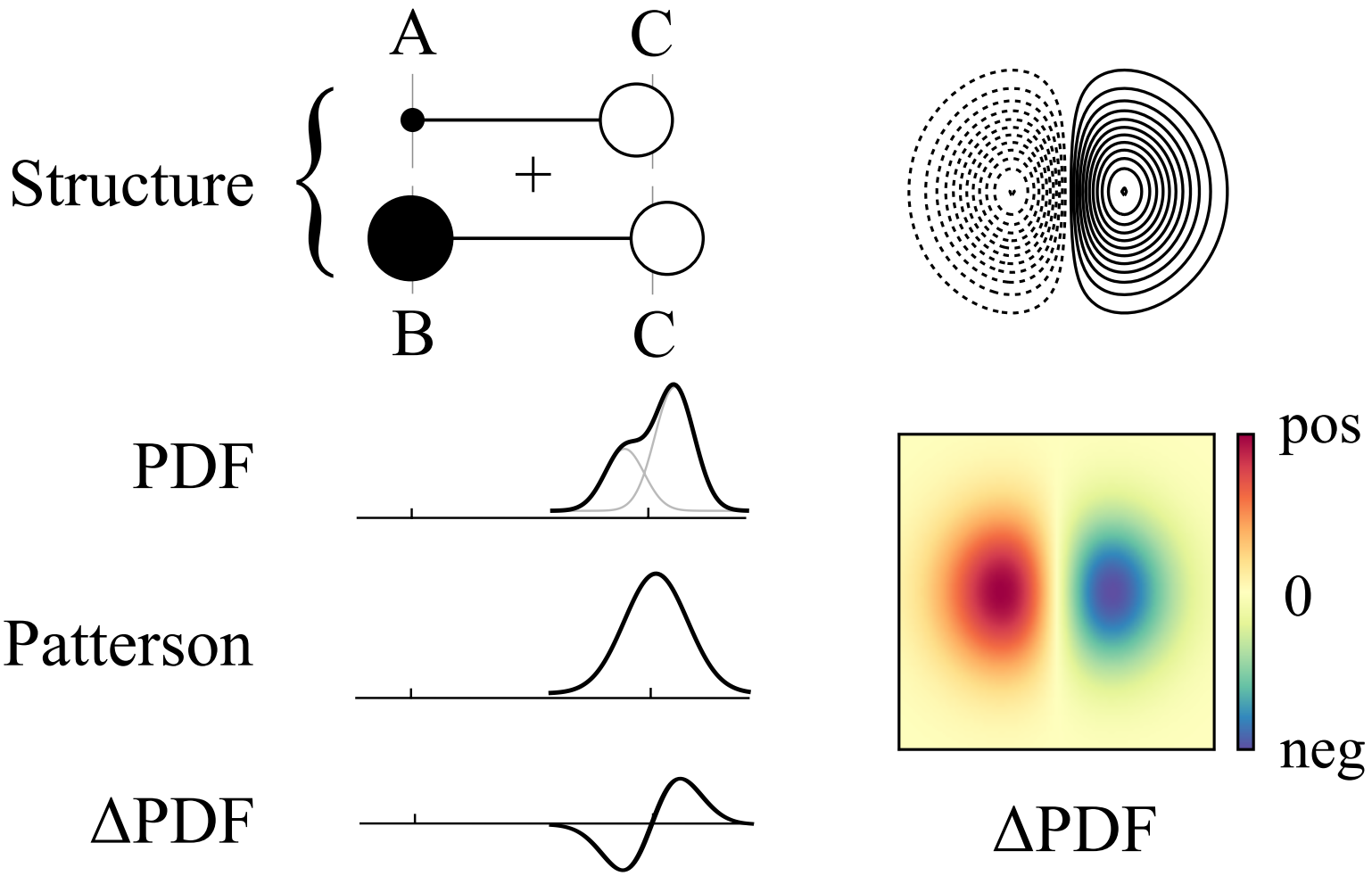
Size Effect



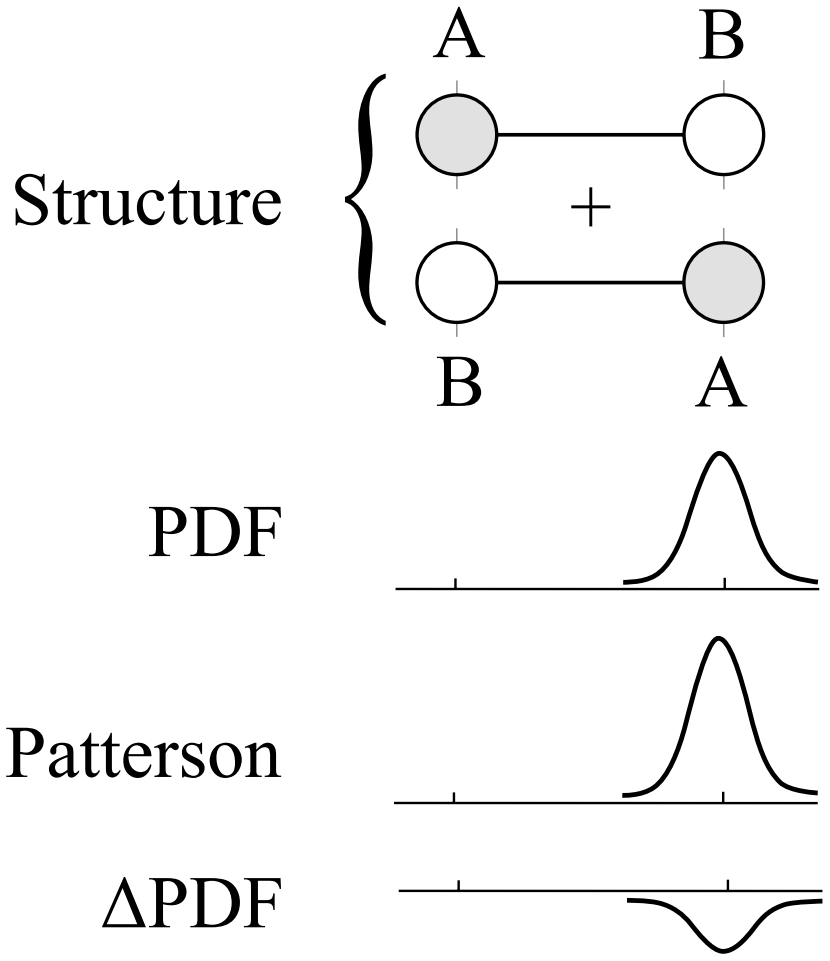
Size Effect



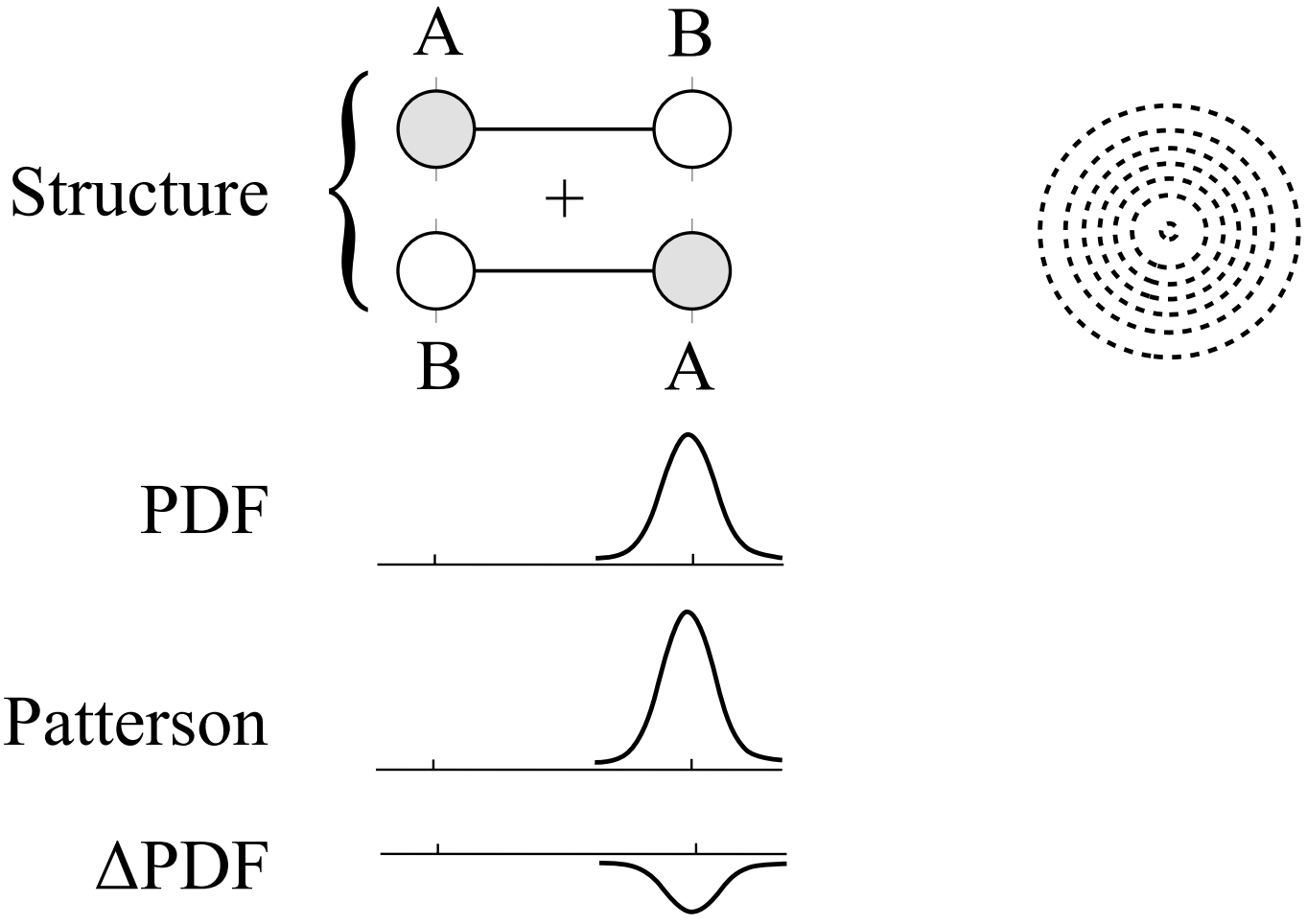
Size Effect



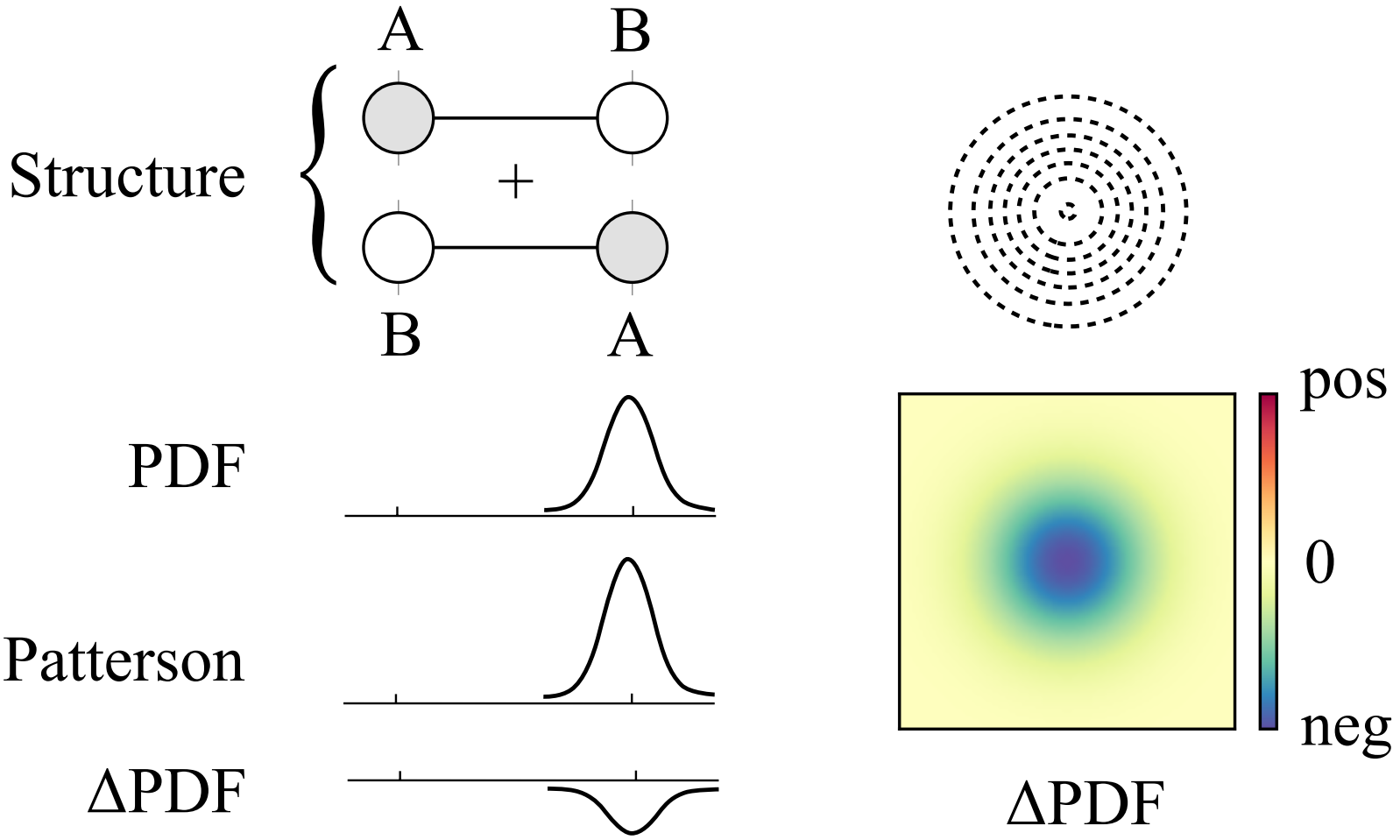
Substitutional correlation



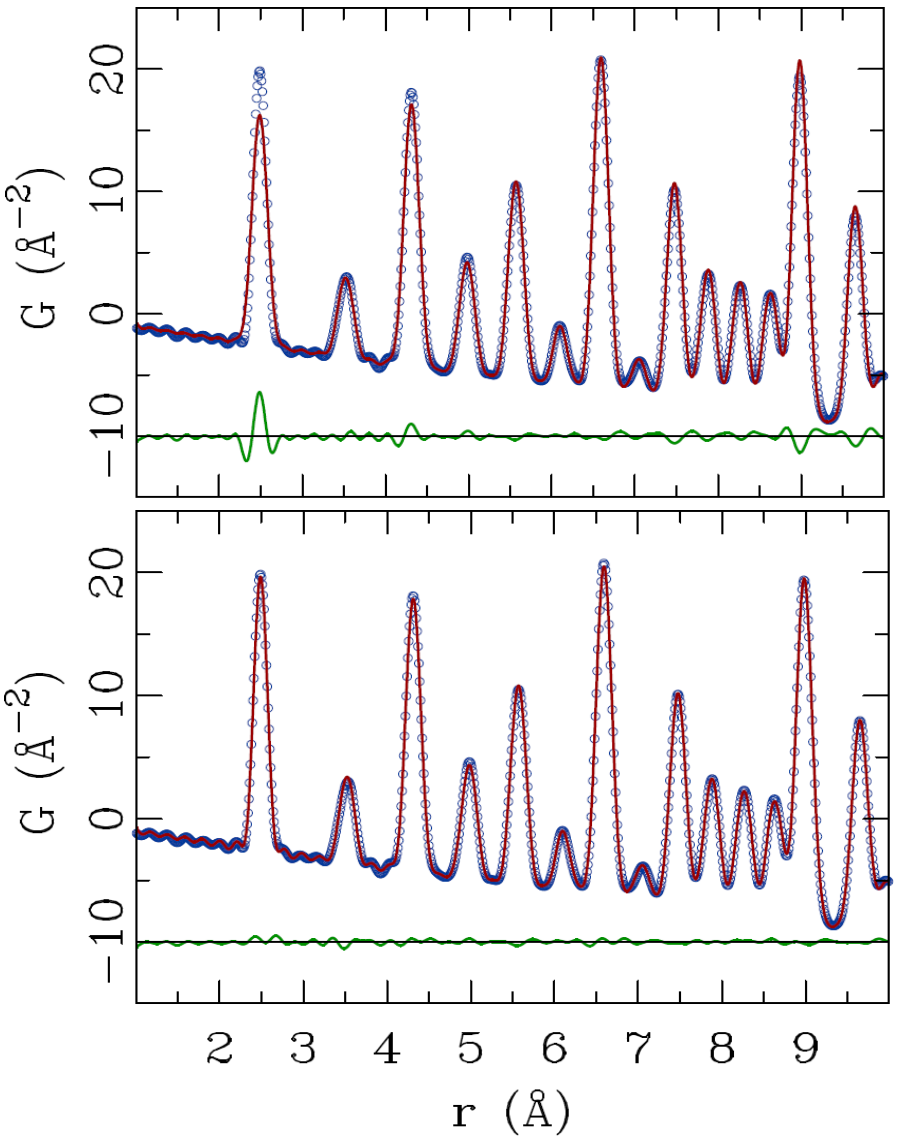
Substitutional correlation



Substitutional correlation

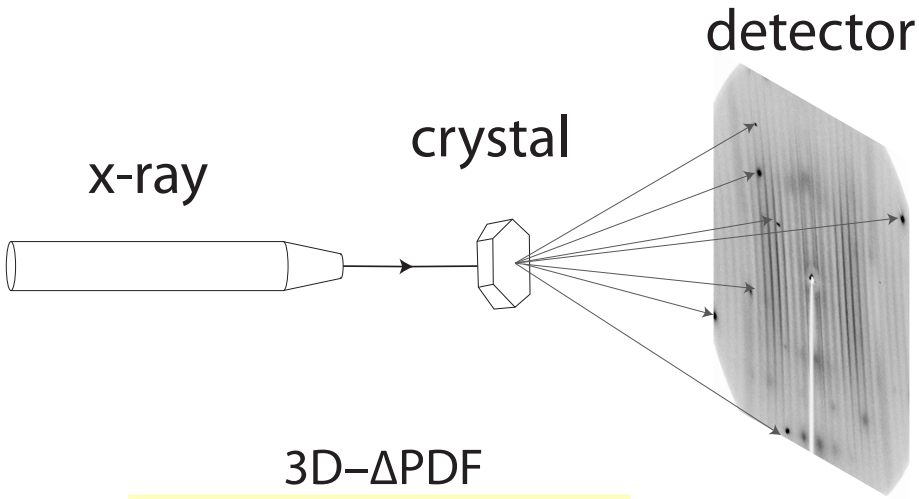


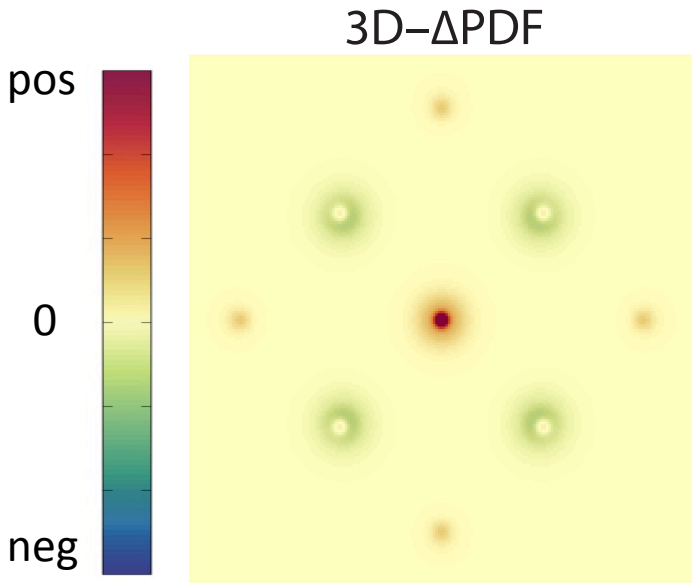
Why calculate delta PDF



Nickel PDF,
Emil Božin

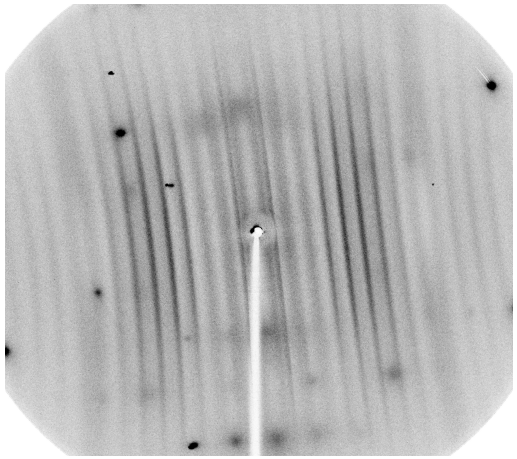
Three dimensional difference pair distribution function (3D-ΔPDF)

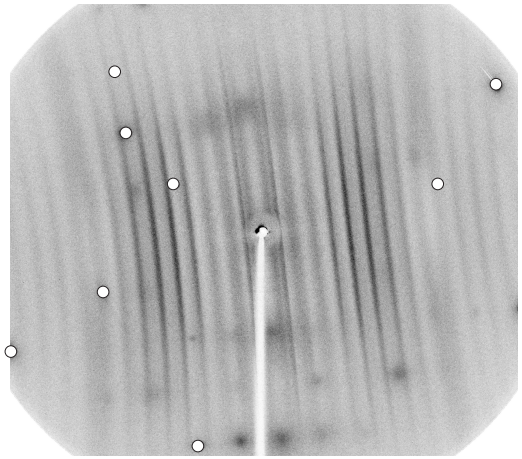




FFT

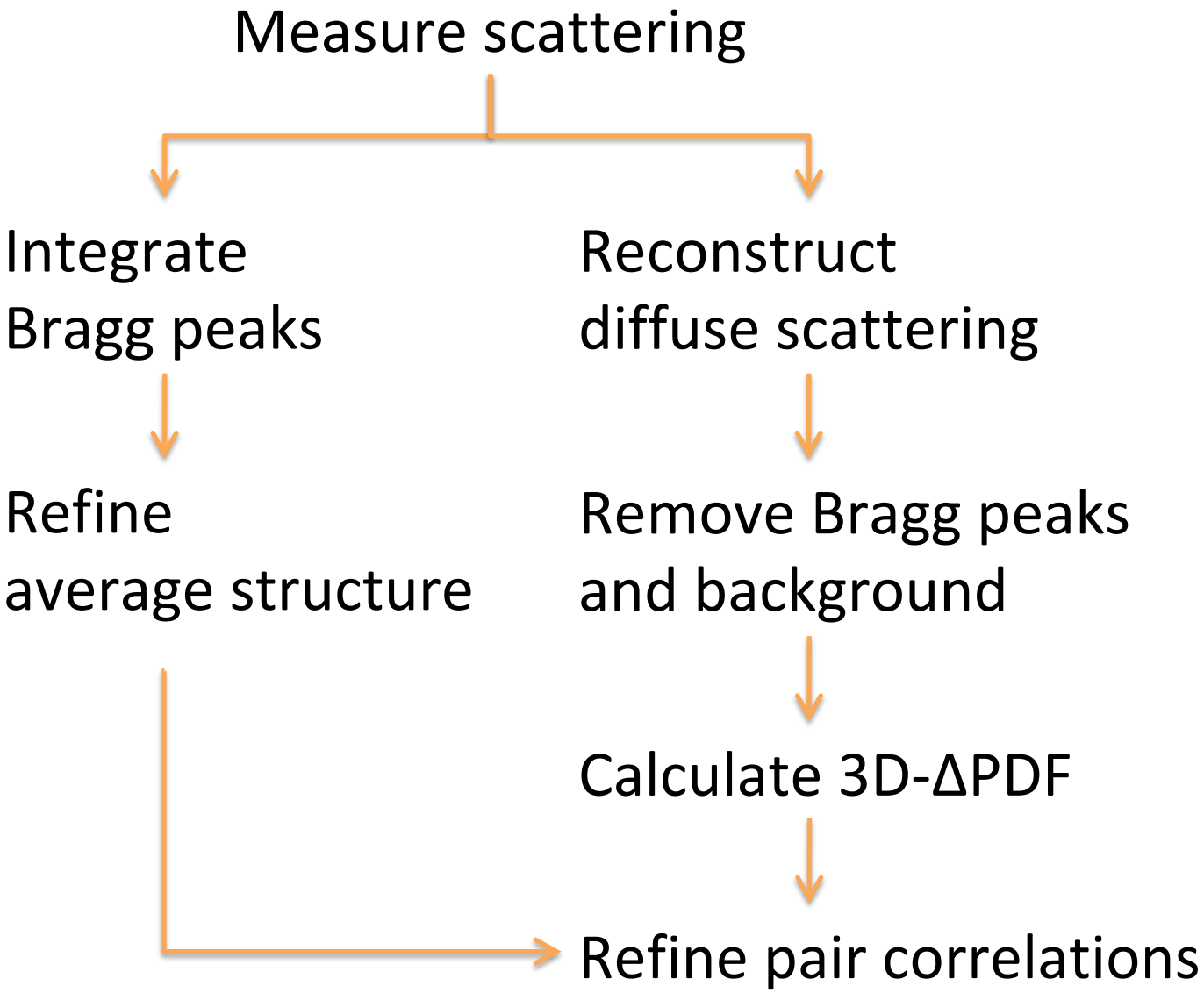
Total scattering

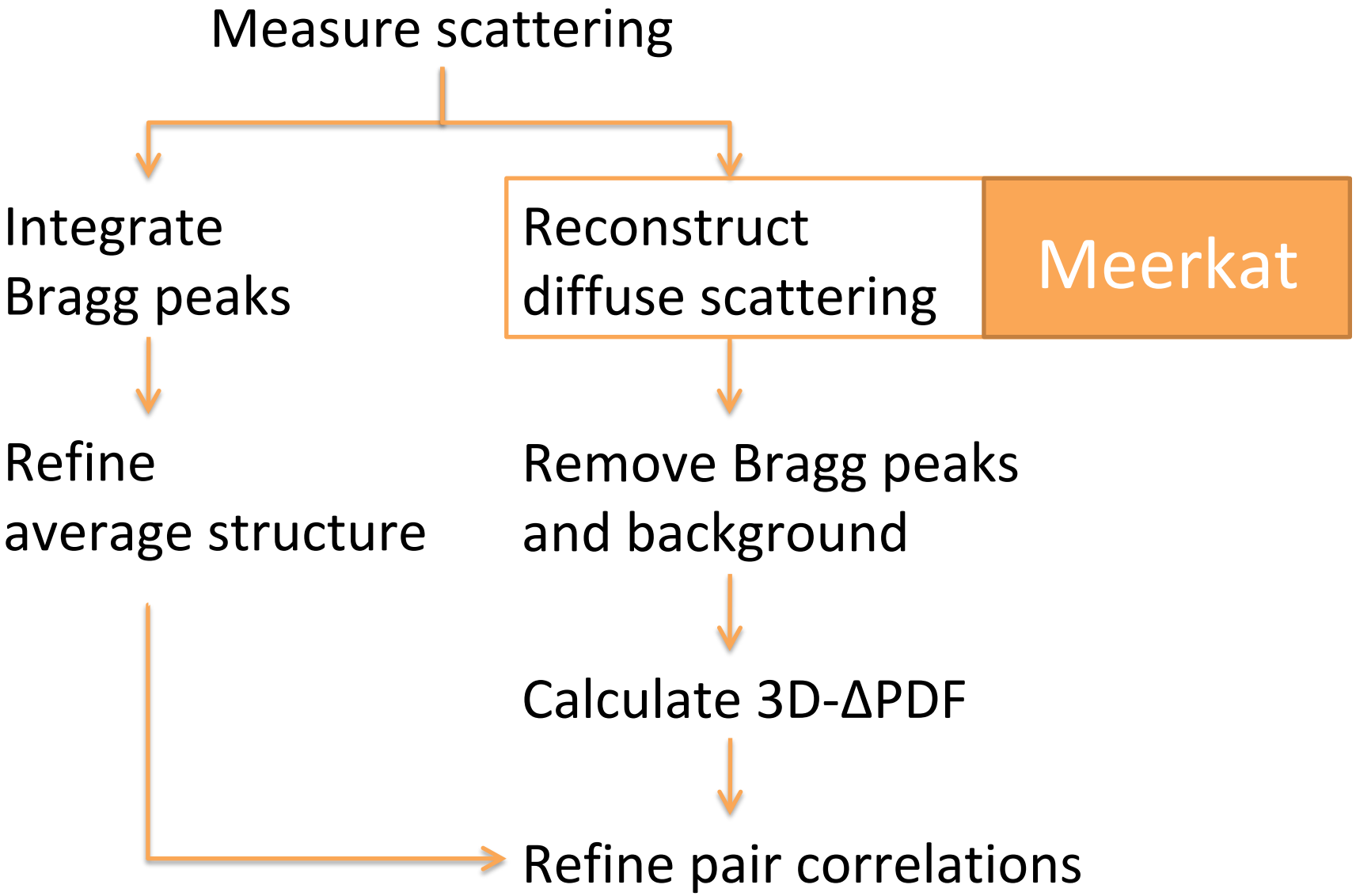


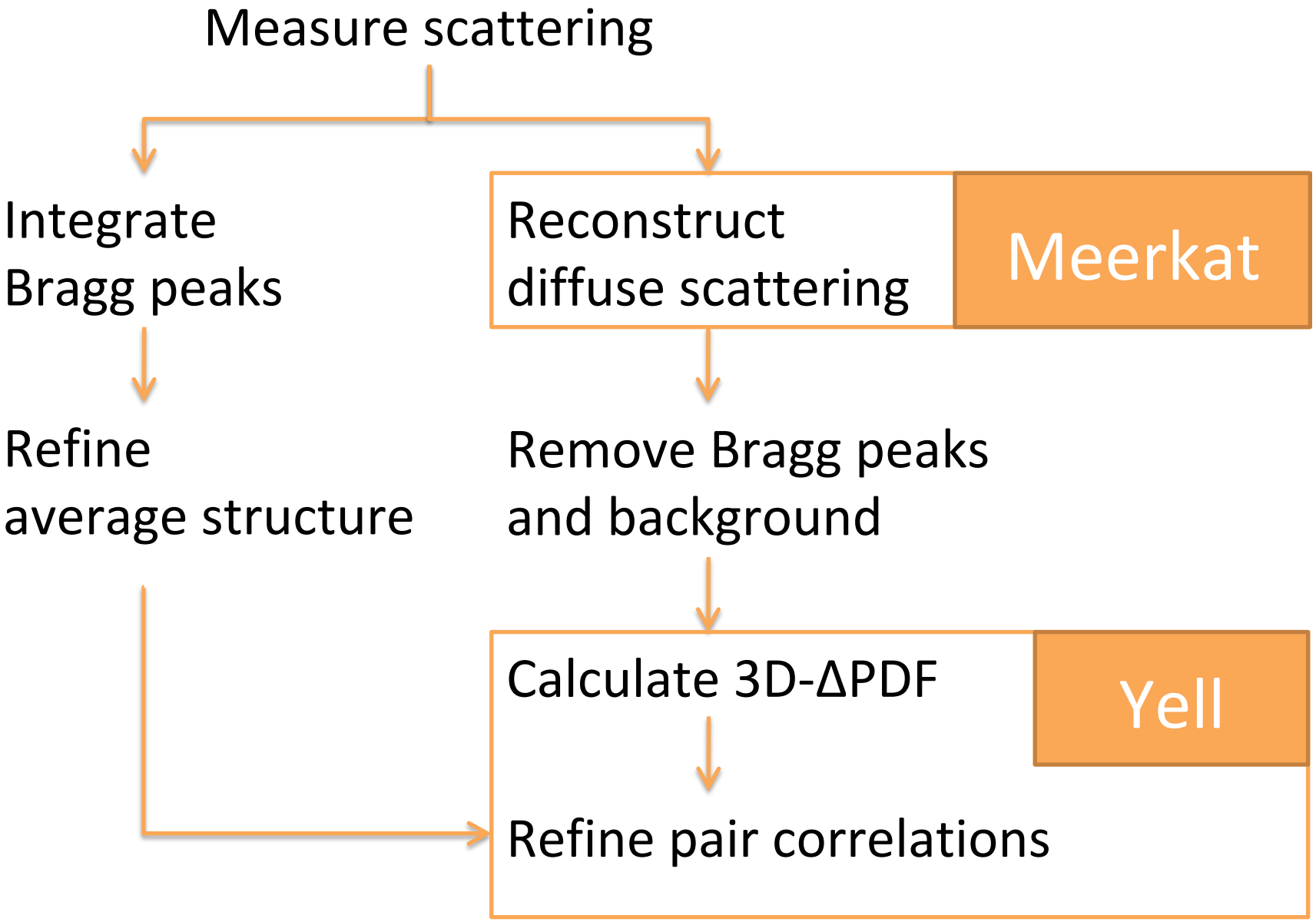


Diffuse scattering only

B. E. Warren, X-ray Diffraction. Courier Dover Publications, 1969.
Schaub, P., Weber, T. & Steurer, W. (2007). Phil. Mag., 87(18-21), 2781–2787.


Measure scattering
Integrate
Bragg peaks
Refine
average structure
Reconstruct
diffuse scattering
Remove Bragg peaks
and background
Calculate 3D-ΔPDF
Refine pair correlations

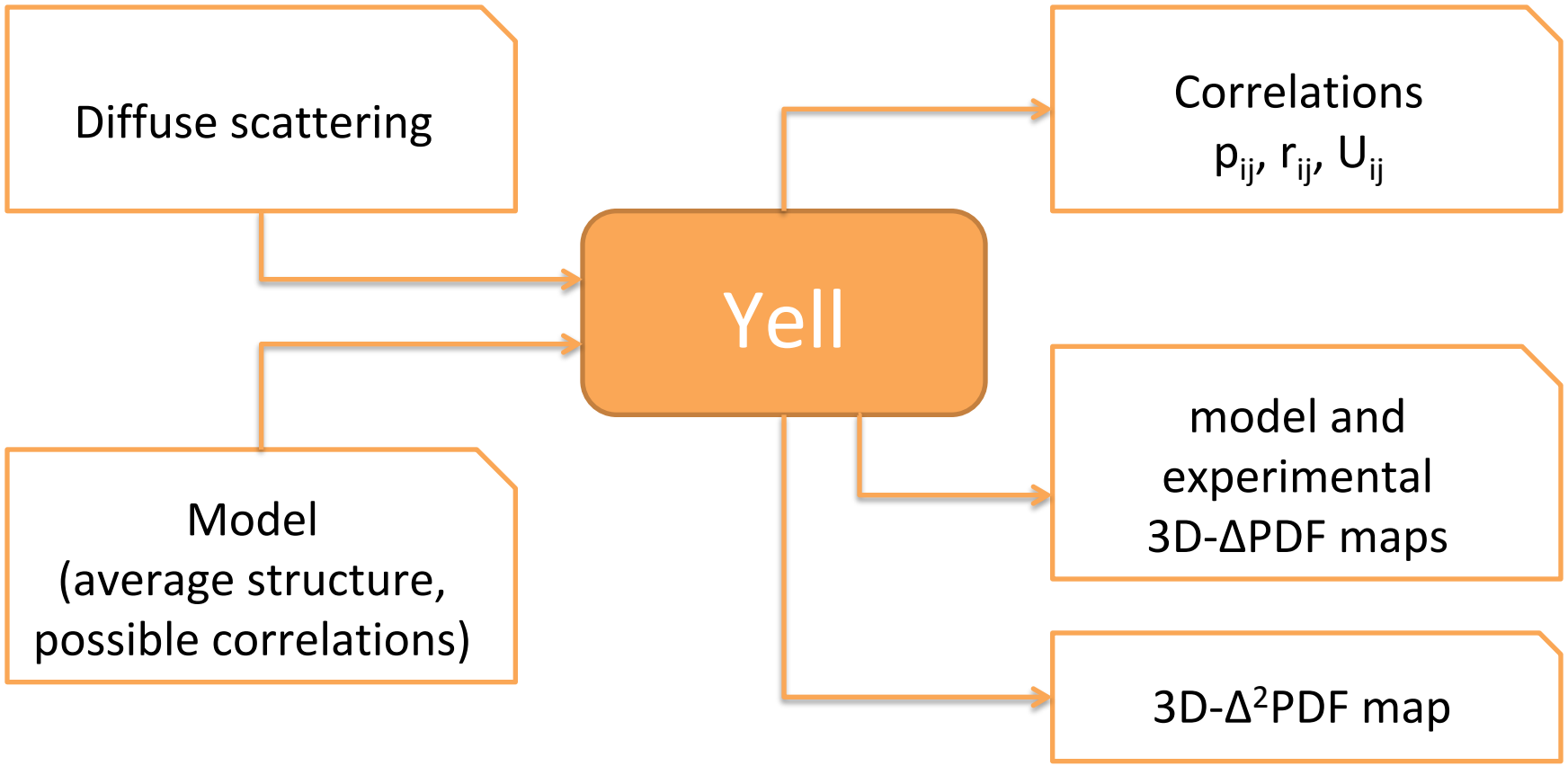

Measure scattering
Integrate
Bragg peaks
Reconstruct
diffuse scattering
Meerkat
Refine
average structure
Remove Bragg peaks
and background
Calculate 3D-ΔPDF
Refine pair correlations


Measure scattering
Integrate
Bragg peaks
Reconstruct
diffuse scattering
Meerkat
Refine
average structure
Remove Bragg peaks
and background
Calculate 3D-ΔPDF
Yell
Refine pair correlations

Meerkat

- reconstructs 3D space
- works in crystallographic coordinates
- hard-drive backed if needed
- polarization, solid angle corrections

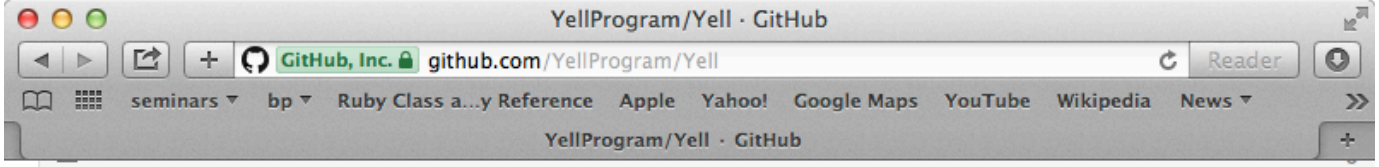
written in python,
uses fabio and hdf5 libraries


Diffuse scattering
Model
(average structure,
possible correlations)
Yell
Correlations
p_{ij}, r_{ij}, U_{ij}
model and
experimental
3D-ΔPDF maps
3D-Δ^2PDF map

Yell

- Yell finds short range order correlations which are not captured by the average structure
- Contains fast FFT-based calculation algorithm
- Works on Windows, Mac and Linux
- No installation required

https://github.com/YellProgram/Yell



README.md	Published with https://stackedit.io/	2 months ago
gpl.txt	Added license	2 months ago

README.md

Yell: a program for diffuse scattering interpretation

Yell is a program for analyzing diffuse scattering from single crystals using Three Dimensional Difference Pair Distribution Function (3D-ΔPDF) method.

Executable binary files

You can download the latest version of Yell for Mac and Windows here.

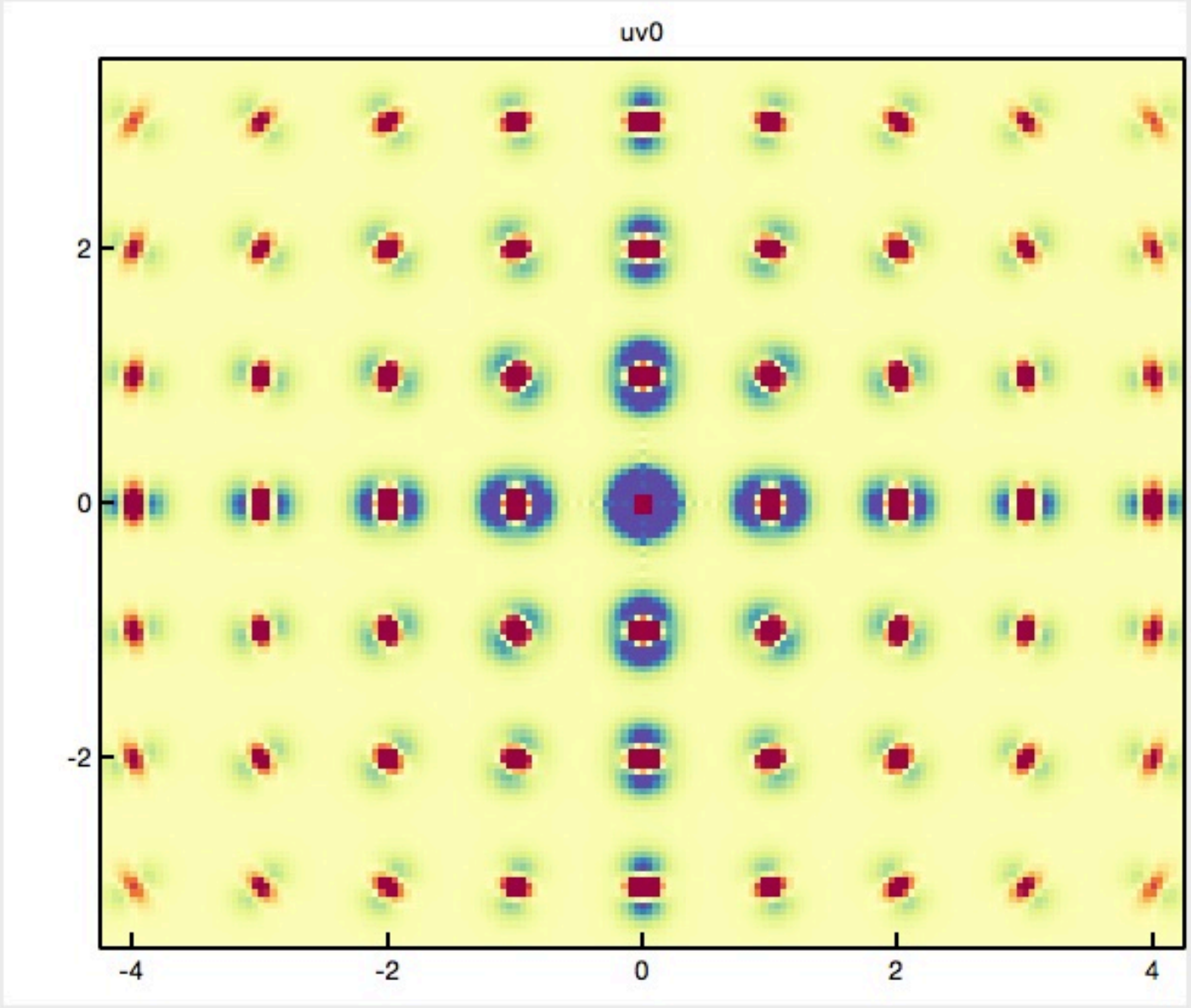
Documentation

The documentation can be accessed at this link. The pdf version is also available at the latest release here.

Examples

The hypothetical iron-void example. Additional scripts for visualizing diffuse scattering and 3D-ΔPDF maps are available for python and Matlab.

Viewer: /Users/arkadiy/ag/reports/ADD2016/simple_examples/ADPCorrelation/delta-pdf.h5



zoom out | zoom in

Color saturation

1.00

RedYellowGreenBlue

Select section:

uvx

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grid

info

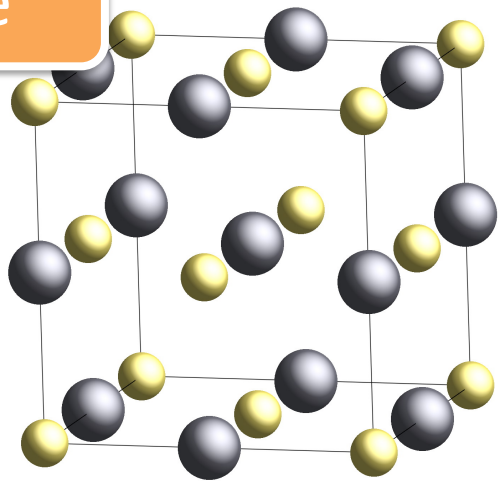
pan

zoom

home

update

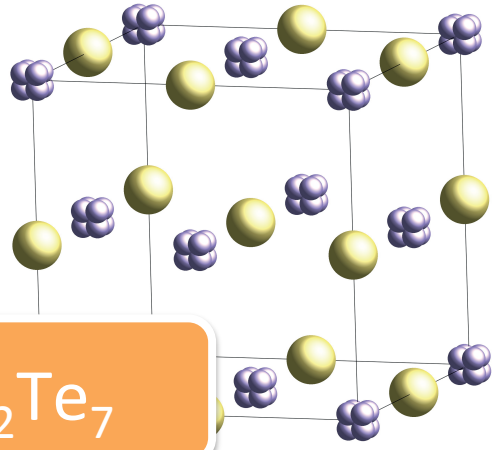
PbTe



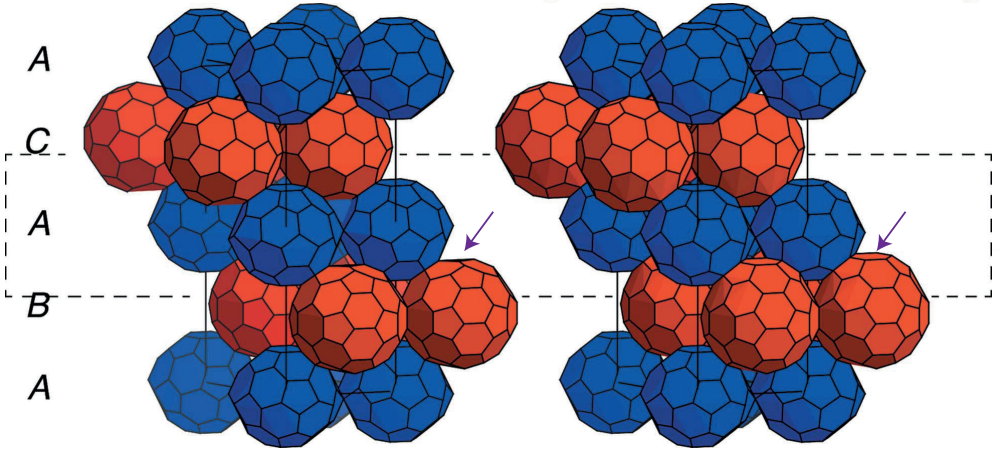
Sangiorgio B. et al. (2018)
PRM. 2(8), 085402.

Urban, P., et. al (2015).
J. Appl. Cryst., 48(1), 200-211.

$Ge_4Bi_2Te_7$

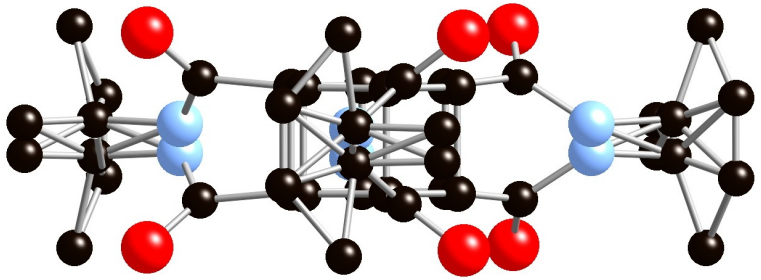


*hP*386-$Al_{57.4}Cu_{3.5}Ta_{39.0}$



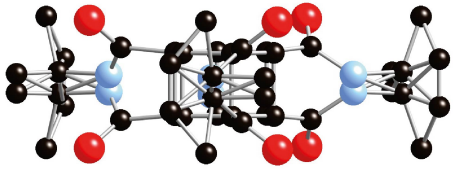
J. Dshemuchadse et. al. Acta. Crystallogr. B.,
vol. 69, pp. 238–48, (2013).

Simonov, A., Weber, T., & Steurer, W. (2014).
J. Appl. Cryst., 47(6), 2011-2018.



tris-t-butiltricarboxamide

Tris-t-butyl-benzene-tricarboxamide



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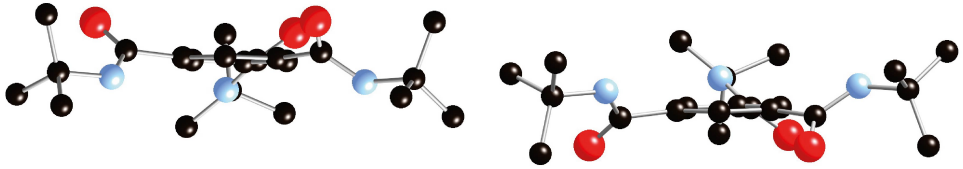
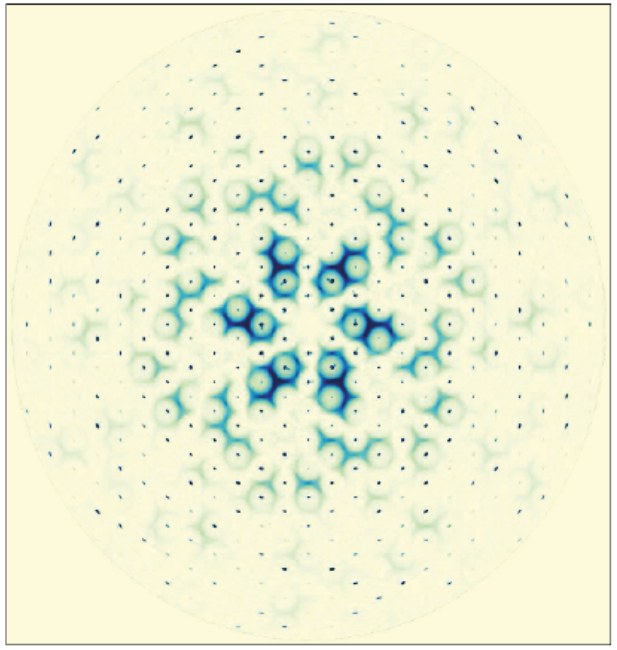


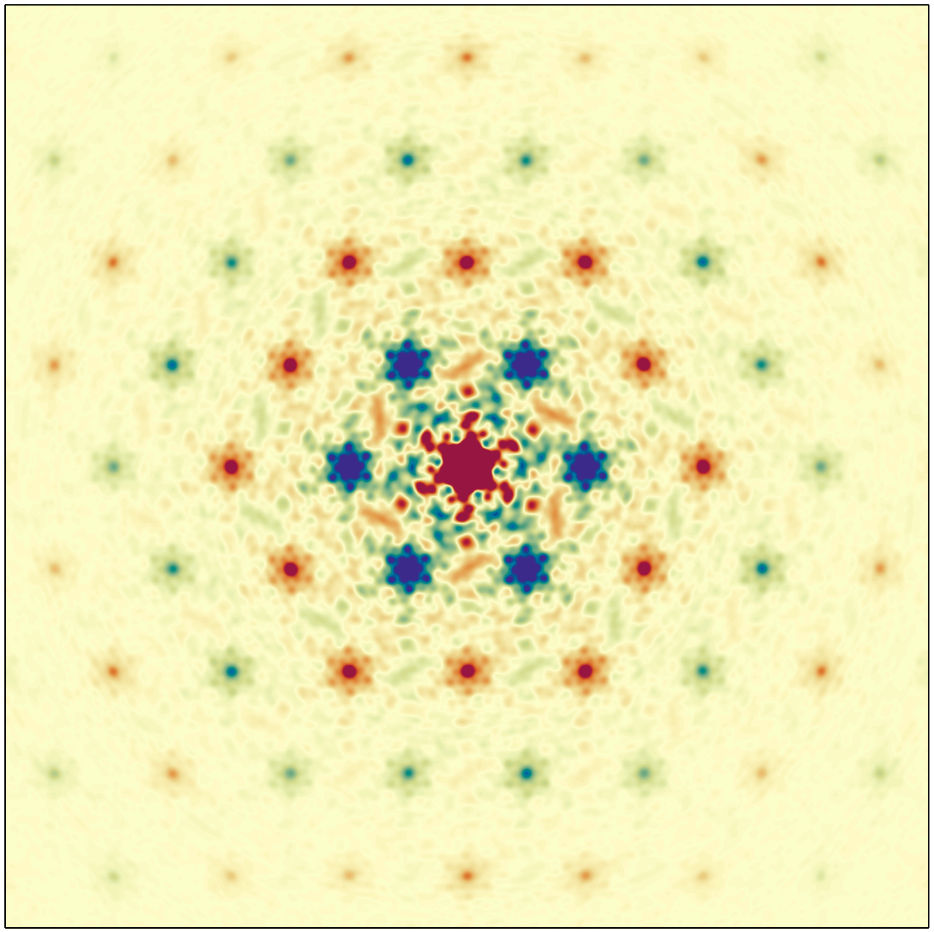
Real



X-ray scattering, hk1 layer

Simonov, A., Weber, T., & Steurer, W. (2014). J. Appl. Cryst., 47(6), 2011-2018.

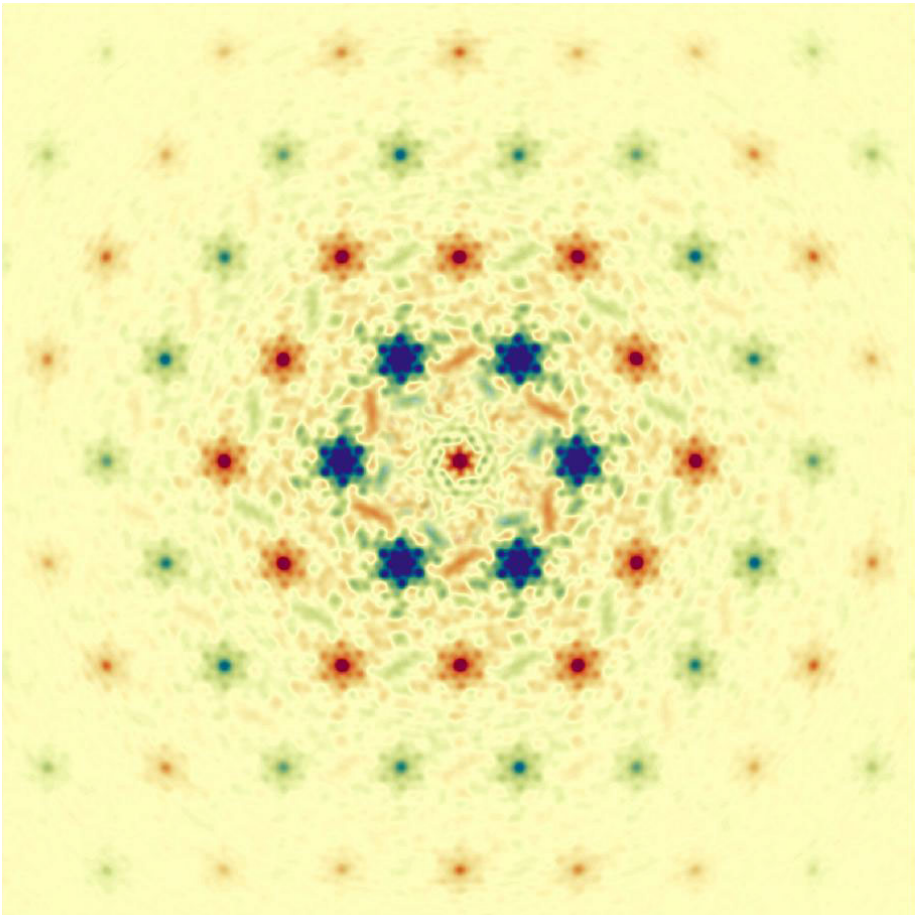
Experimental ΔPDF



ΔPDF, UV0 cut

tris-t-butyl-benzene-tricarboxamide

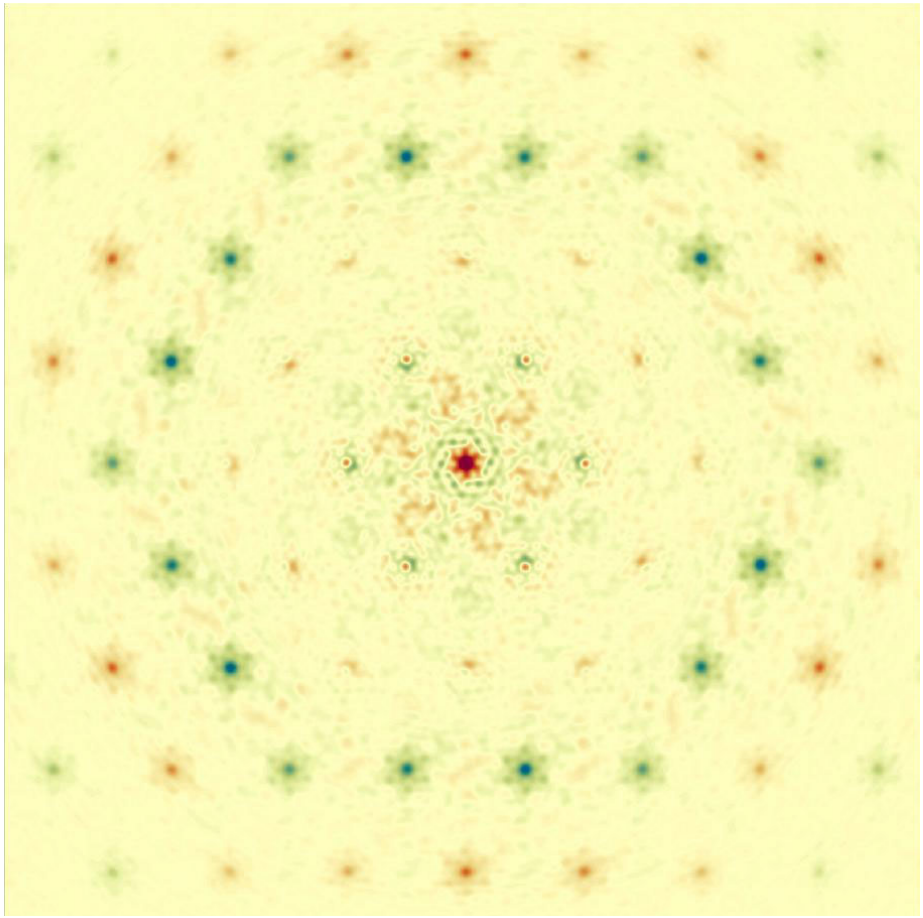
Refinement



Δ^2PDF, UV0 cut

tris-t-butyl-benzene-tricarboxamide

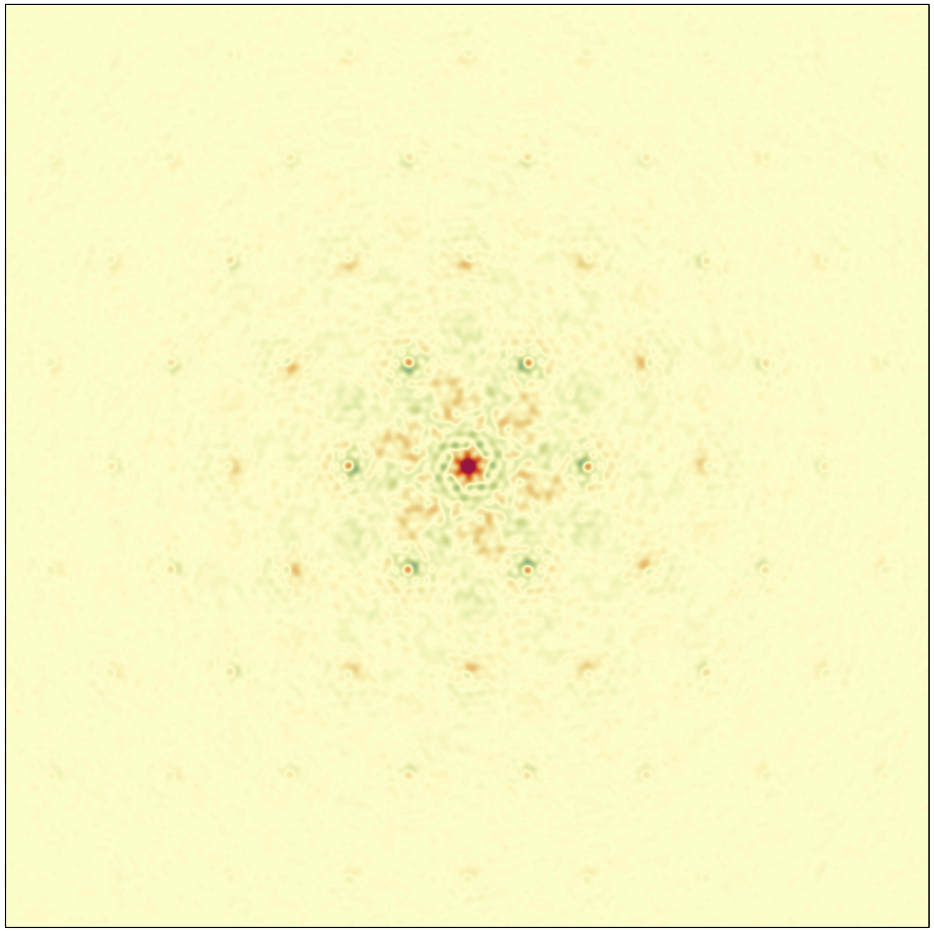
Refinement



Δ^2PDF, UV0 cut

tris-t-butyl-benzene-tricarboxamide

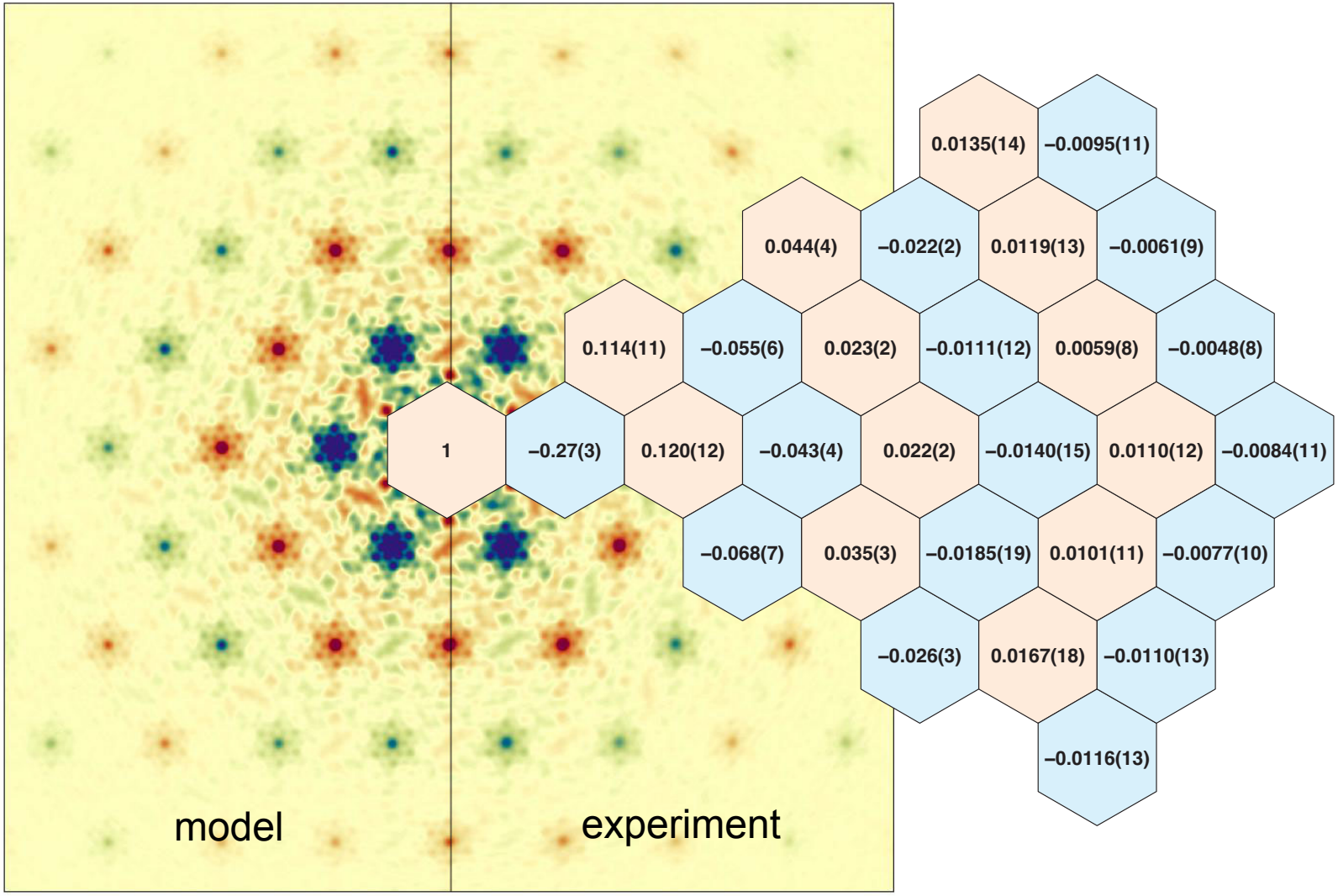
Refinement



Δ^2PDF, UV0 cut

tris-t-butyl-benzene-tricarboxamide

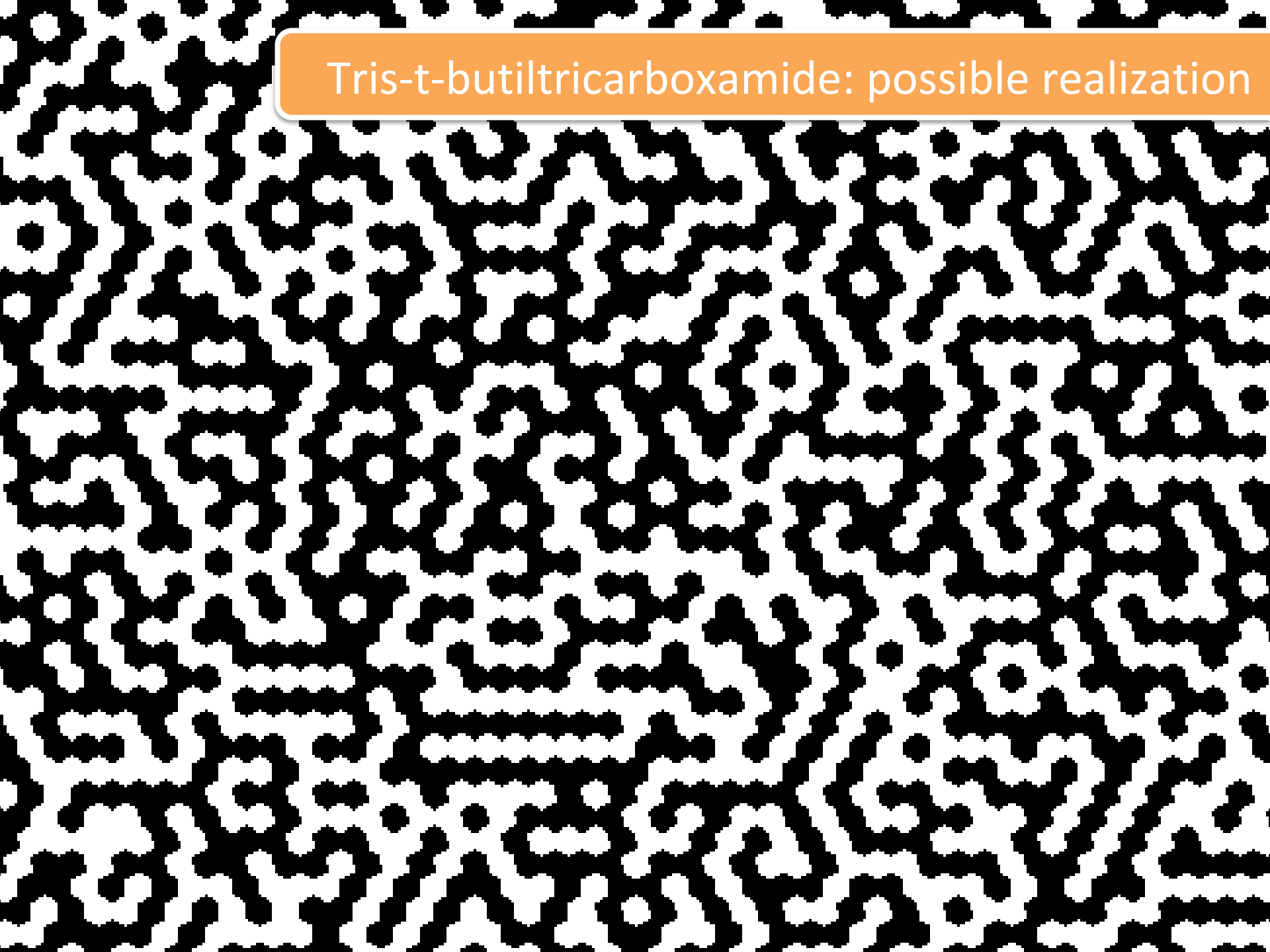
Results



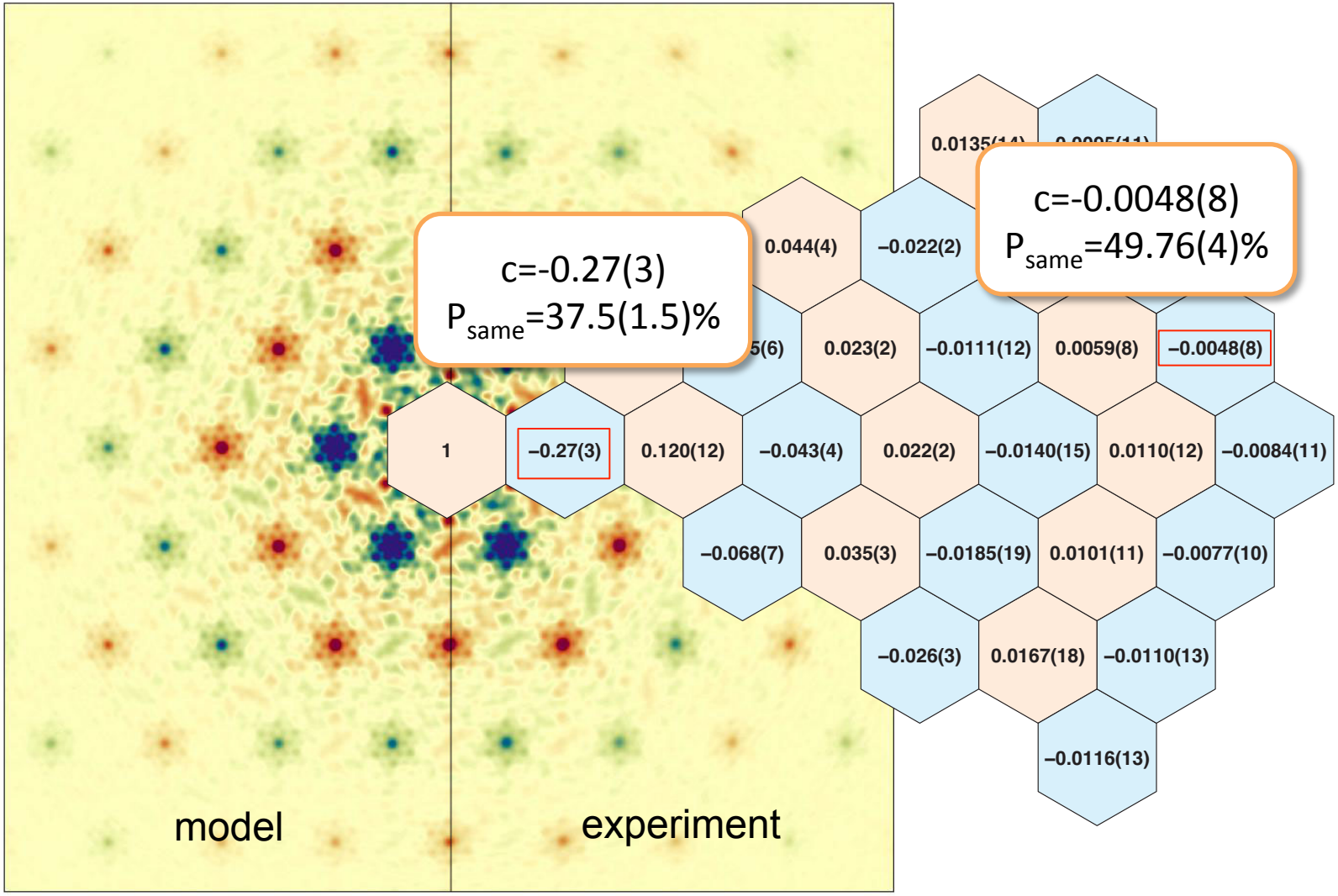
Refined correlation coefficients

Simonov, A., Weber, T., & Steurer, W. (2014).
J. Appl. Cryst., 47(6), 2011-2018.

Tris-t-butiltricarboxamide: possible realization



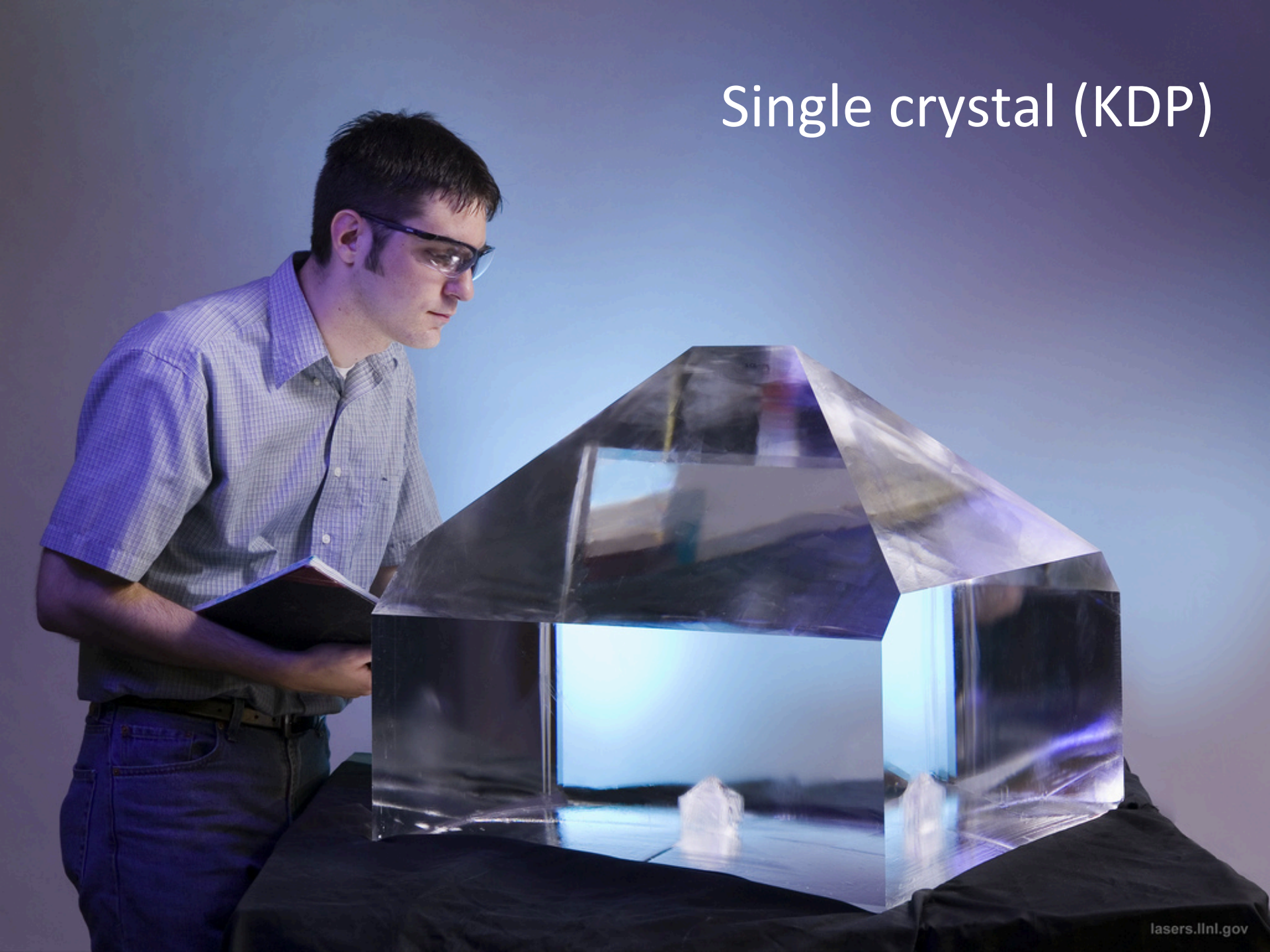
Results

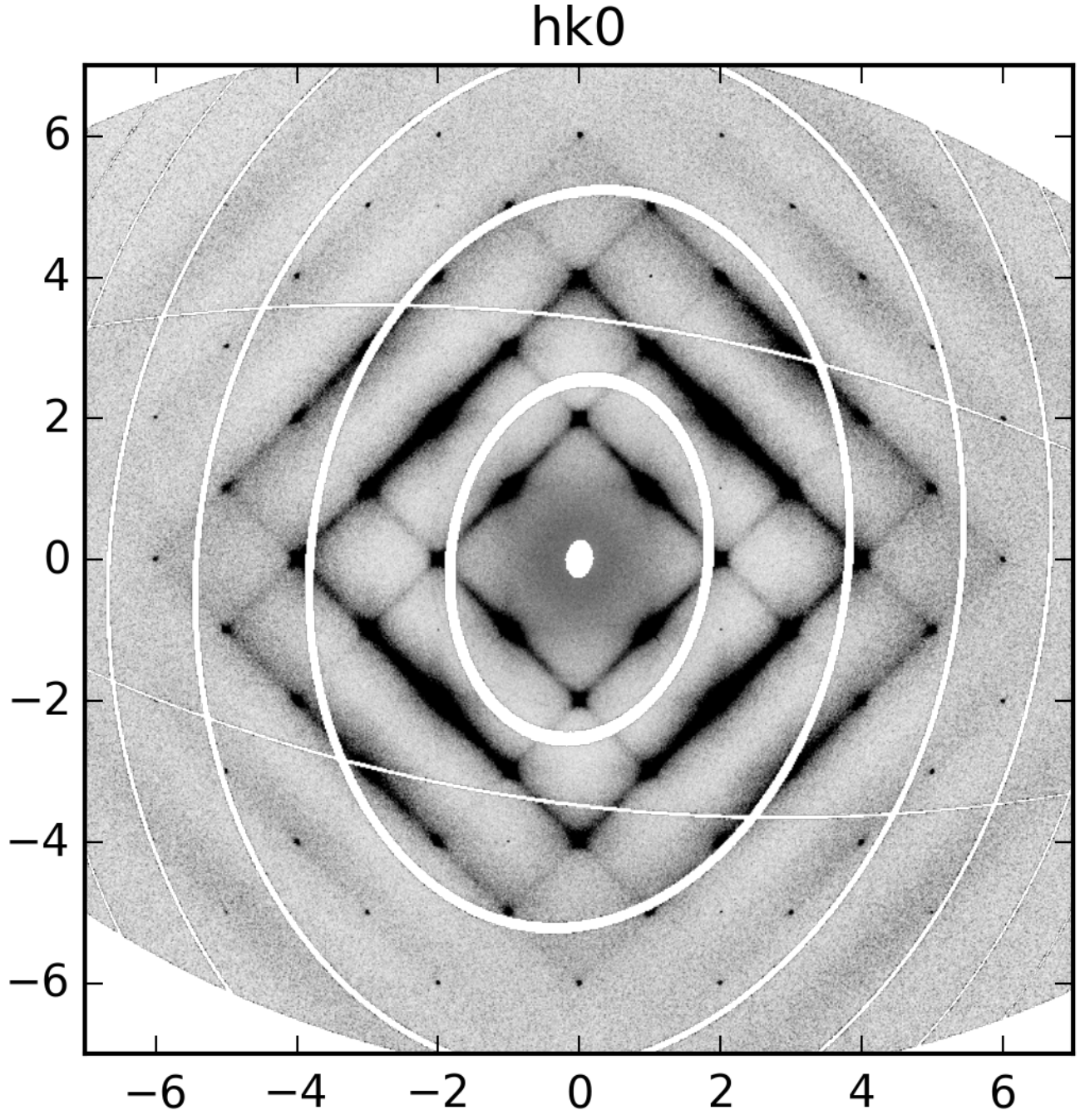


Refined correlation coefficients

Simonov, A., Weber, T., & Steurer, W. (2014).
J. Appl. Cryst., 47(6), 2011-2018.

Single crystal (KDP)

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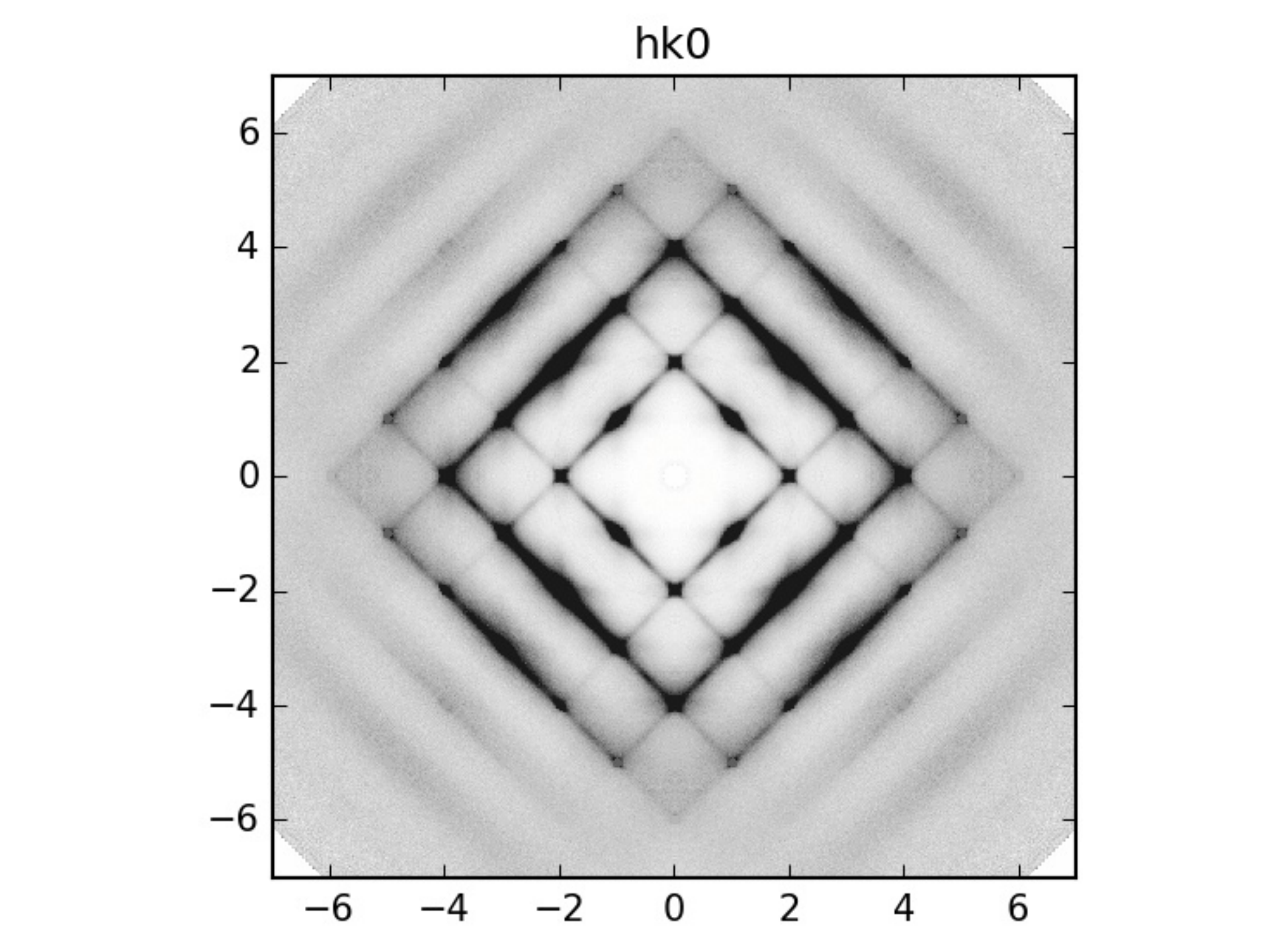
0
2
4
6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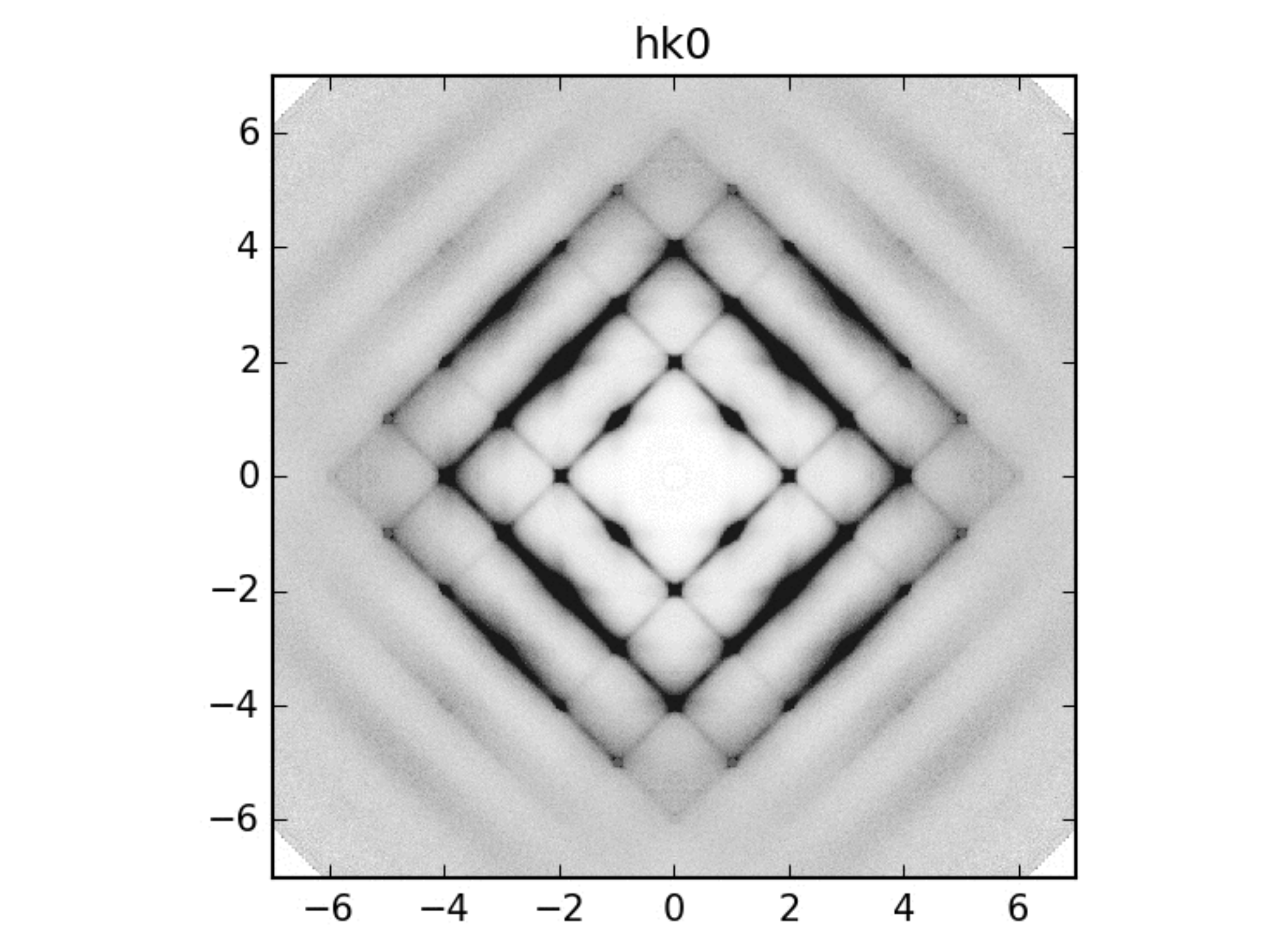
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THANK YOU