Ab initio structure solution from electron precession data by charge flipping

Lukas Palatinus

Institute of Physics
AS CR, Prague

What is charge flipping?

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

- Published by Oszlanyi & Sütö (2004), Acta Cryst A
- Requires only lattice parameters and reflection intensities
- The output is an approximate scattering density of the structure sampled on a discrete grid
- No use of symmetry apart from the input intensities
- Related to the LDE (low density elimination) method (Shiono & Woolfson (1992), Acta Cryst. A; Takakura et al. (2001), Phys. Rev. Lett.) and the "difference map" (Elser (2003), Acta Cryst. A)
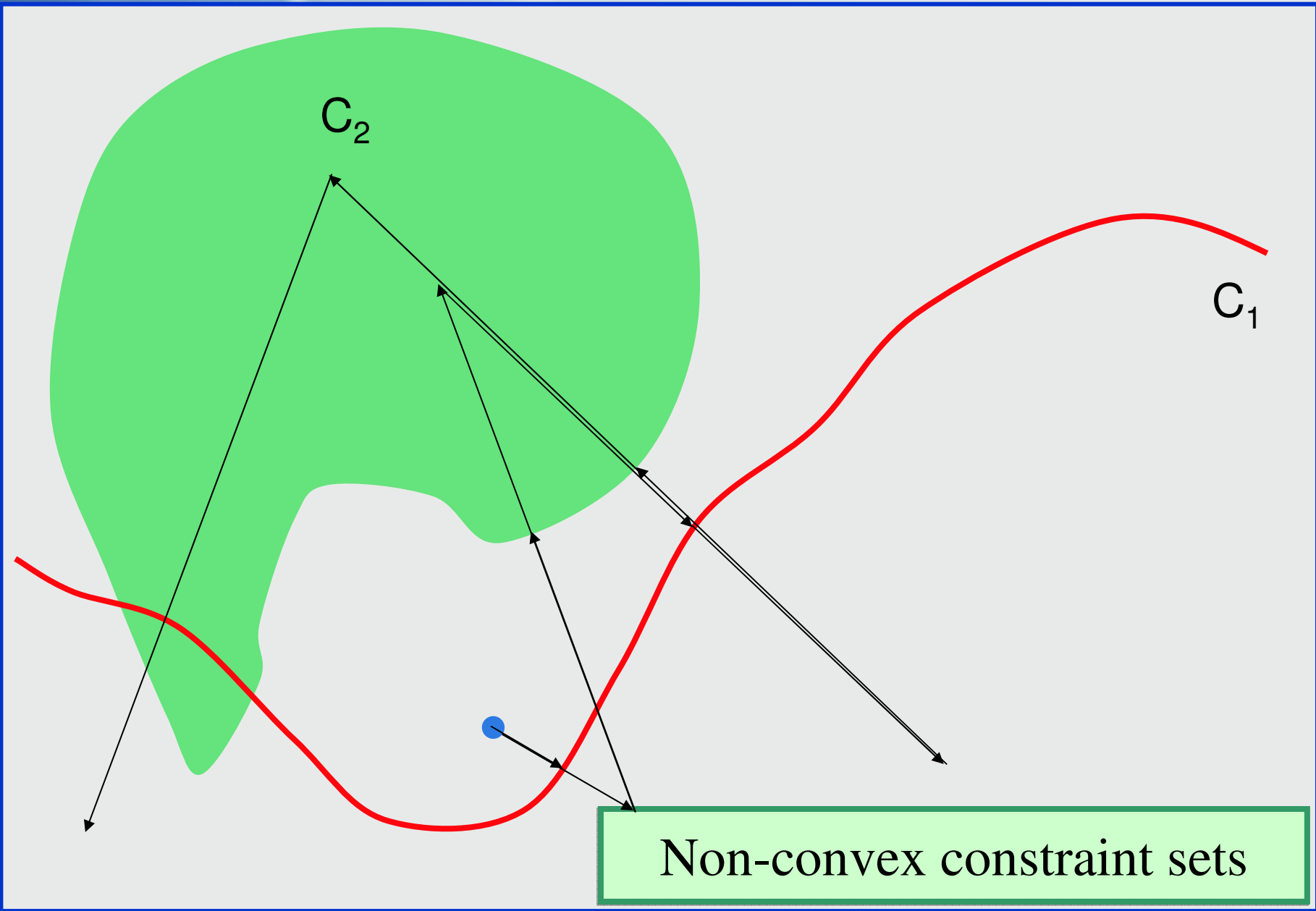
Convex feasibility problem

The solution of structures san be formulated as a search for intersection of two constraint sets. The solution of the problem is relatively easy, if the two constraint sets are convex, i.e. if:

$$x \in C \wedge y \in C \Rightarrow \overline{xy} \in C$$

C_2

C_1

Non-convex constraint sets

C_2

C_1
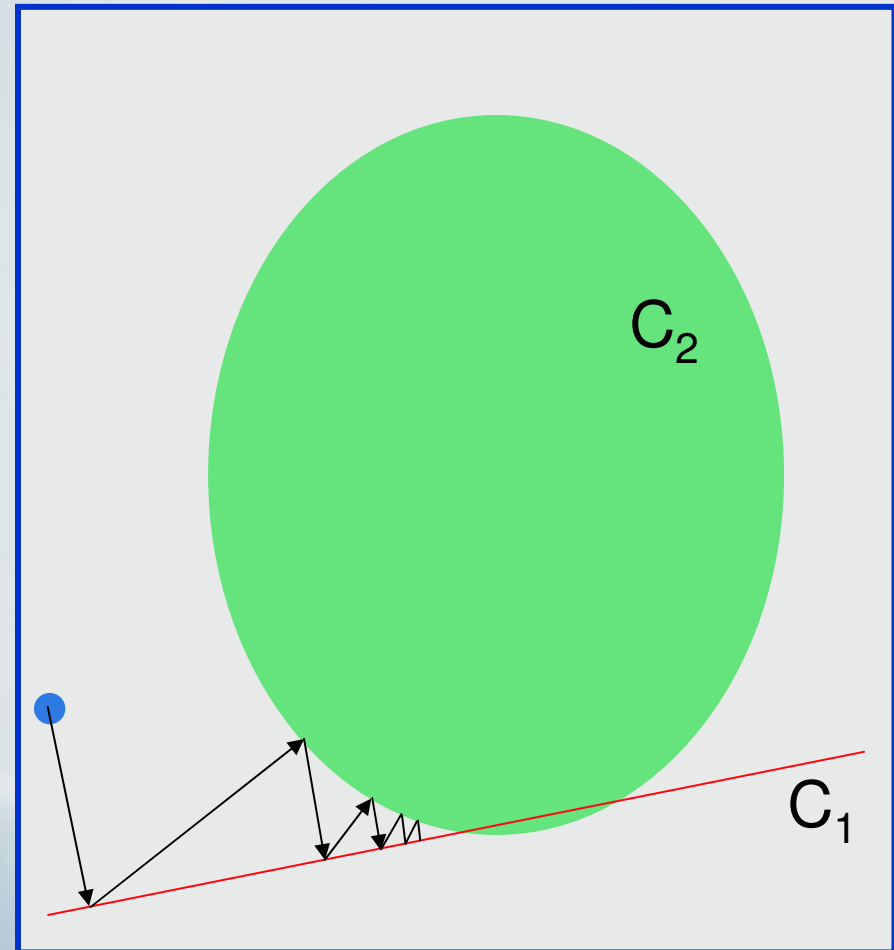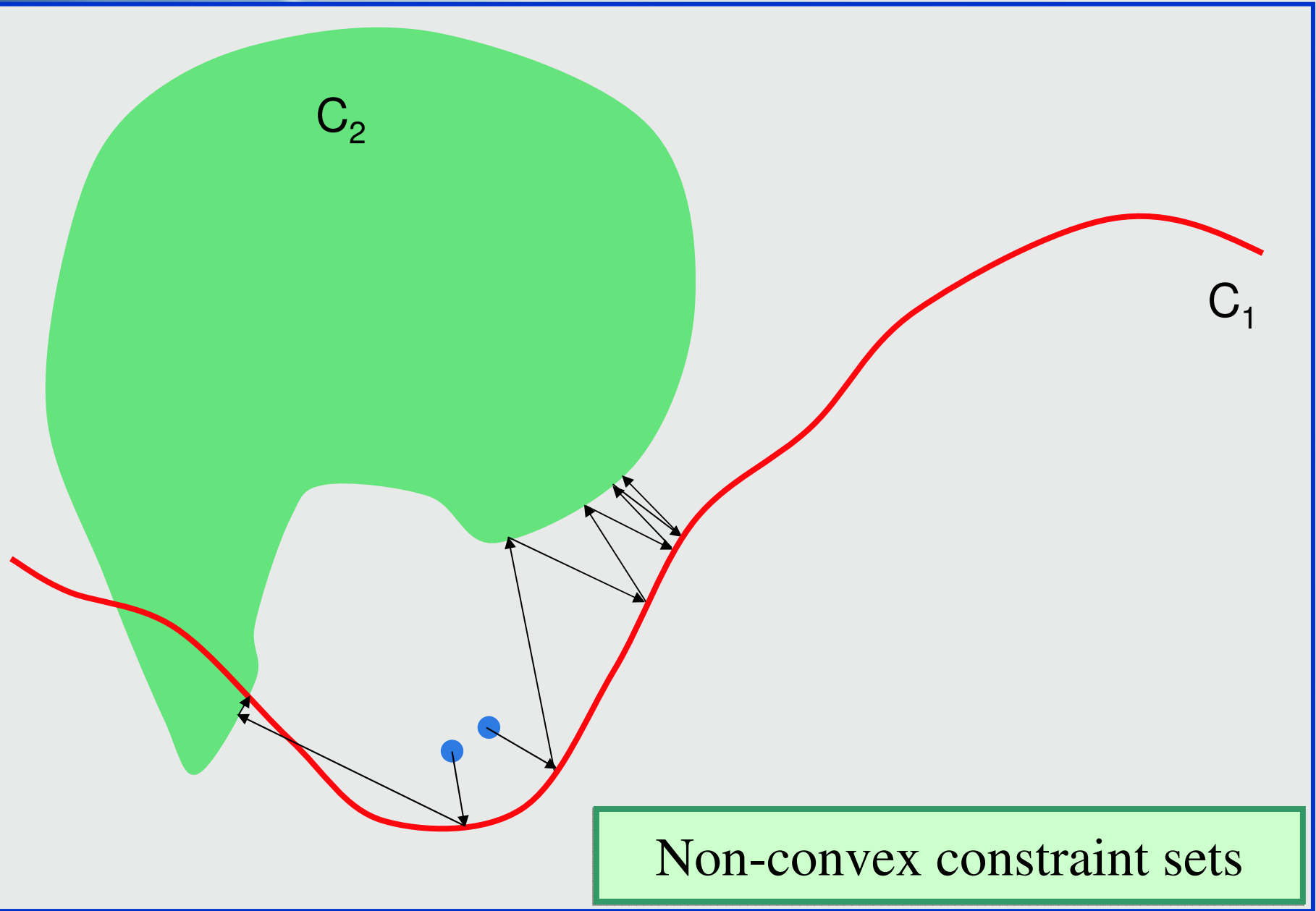
Non-convex constraint sets

Advantages and disadvantages

\+ Minimum assumptions and approximations involved

\+ No explicit use of chemical composition and form factors

\+ No explicit use of space group symmetry

\+ Pseudosymmetry does not hamper solution

\+ High quality of solutions

\+ Tolerant to noise

\- Requires atomic resolution (d<1.1A for light atoms, d<1.5 for heavier atoms)

\- Requires reasonably complete data

\- Requires presence of the strongest reflections

Symmetry

Charge flipping calculates density always in $P1 \rightarrow$ density is randomly shifted in the unit cell. Symmetry must be recovered in the resulting density.

Consequence: the space grup can be determined after the structure solution

Symmetry determination

Palatinus & van der Lee (2008), J. Appl. Cryst. **41**

Charge flipping calculates density always in $P1 \rightarrow$ density is randomly shifted in the unit cell. Symmetry must be recovered in the resulting density.
Consequence: the space grup can be determined after the structure solution

```
Symmetry operations compatible with the lattice and centering:
                          Symmetry operation              agreement factor
      c(0,1,0):            x1          -x2      1/2+x3      0.035
    2_1(0,1,0):           -x1       1/2+x2         -x3      0.443
           -1:            -x1          -x2         -x3      0.483
      n(0,1,0):         1/2+x1          -x2      1/2+x3     97.026
      a(0,1,0):         1/2+x1          -x2          x3     97.833
      2(0,1,0):            -x1           x2         -x3    110.029
      m(0,1,0):             x1          -x2          x3    114.562


--------------------------------------------------
Space group derived from the symmetry operations:
--------------------------------------------------

    HM symbol:      P21/c
    Hall symbol:    -p 2ybc
    Fingerprint:    3300220n{03}23 (0,0,0)
    Symmetry operations:
             1:             x1           x2          x3
    2_1(0,1,0):            -x1       1/2+x2      1/2-x3
           -1:             -x1          -x2         -x3
      c(0,1,0):             x1       1/2-x2      1/2+x3
```

Superflip

Superflip = charge FLIPping in SUPERspace

A freely available program for application of charge flipping in arbitrary dimension

Some properties:

- Keyword driven free-format input file

- Determination of the space group from the solution

- Includes essentially all "flavors" and recent developments of charge flipping

- Continuous development

- Interfaced from several crystallographic packages: Jana2006, WinGX, Crystals

- Applicable to solution of 2D, 3D and nD structures

Charge flipping and precession electron diffraction

No atoms are placed in the unit cell

No normalization is needed

No refinement performed

} No modifications to the basic charge flipping formalism

Applications of charge flipping:

- reconstruction of 2D projections from a single diffraction image of one zone axis

- phasing the structure factors for combined use with other techniques

- solution of 3D structure from 3D diffraction data

2D structure projections

Advantages:

- Getting PED pattern from one zone axis is relatively straightforward
- No scaling problems
- Often provides sufficient information

2D structure projections

Advantages:

- Getting PED pattern from one zone axis is relatively straightforward
- No scaling problems
- Often provides sufficient information
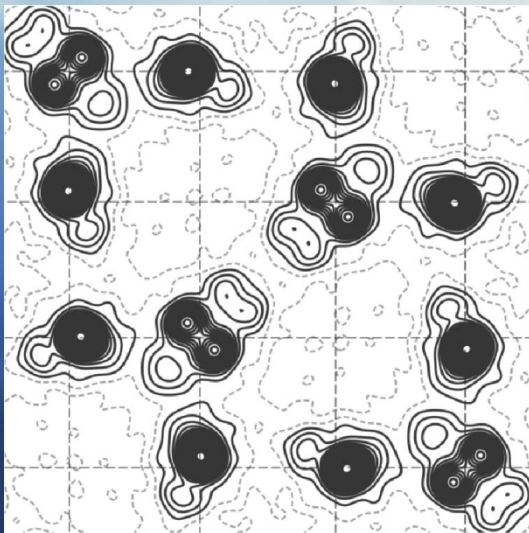
Calculated projected potential of
$Er_2Ge_2O_7$
*p*4*gm*, a=b=6.78A
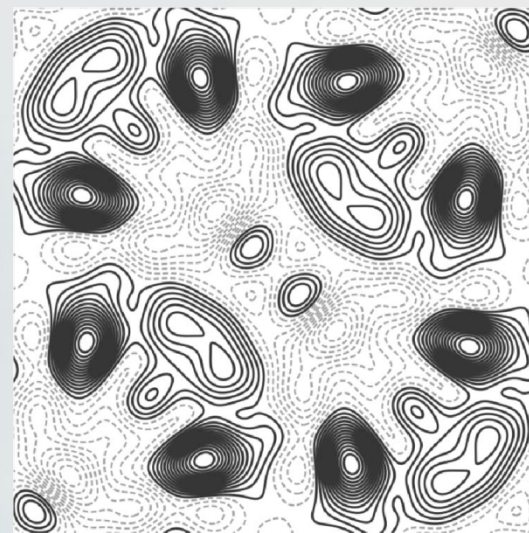
Potential reconstructed by charge flipping from experimental data.
thickness 55nm, prec. angle 42 mrad

Eggeman, White & Midgley, Acta Cryst. A65, 120-127

2D structure projections

2D projections (and small 3D structures) have one common problem. The number of reflections is small, and the iteration minimum is very shallow:

- Indicators of convergence do not work
- The solution is not always stable
- The solution is not perfect
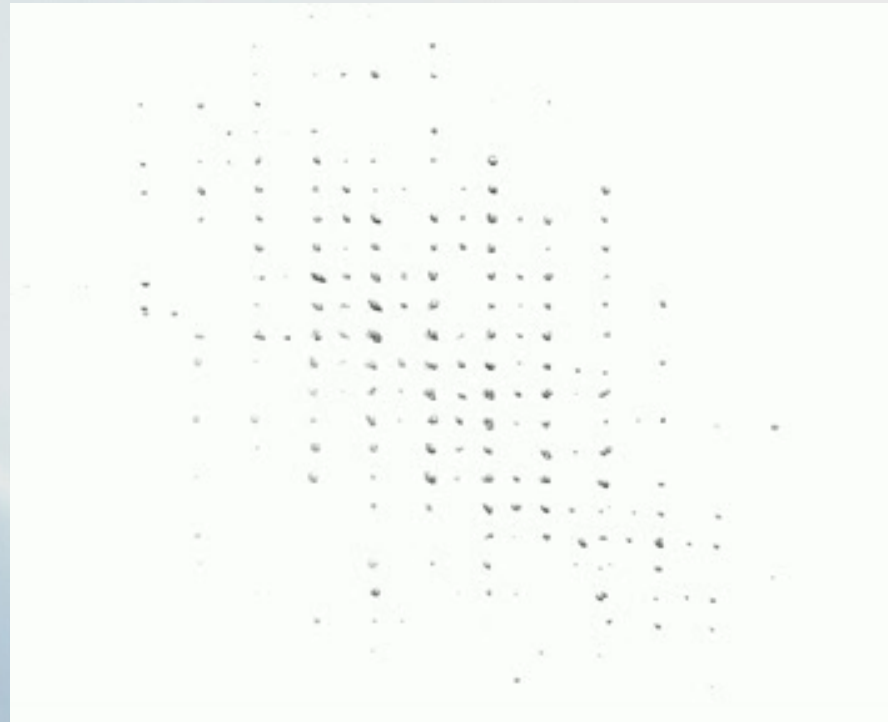

Large number of reflections
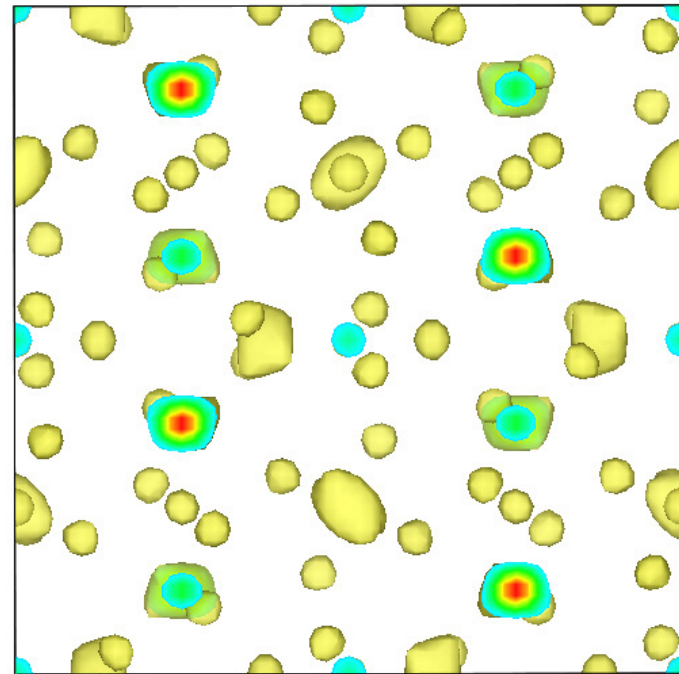
Small number of reflections

Solution from 3D diffraction data

Advantage: Data easily obtained, scaling possible, lattice parameters „for free", general approach

Disadvantage: zonal systematic absences less obvious, integration issues

Spessartine ($Mn_3Al_2Si_3O_{12}$):
cubic, a=11.68, *Ia-3d*
Data from tilt series (-50°,50°)
steps of 1°
precession angle 1°

Solution from 3D diffraction data

Advantage: Data easily obtained, scaling possible, lattice parameters „for free", general approach

Disadvantage: zonal systematic absences less obvious, integration issues

Spessartine ($Mn_3Al_2Si_3O_{12}$):
cubic, a=11.68, *Ia-3d*
Data from tilt series (-50°,50°)
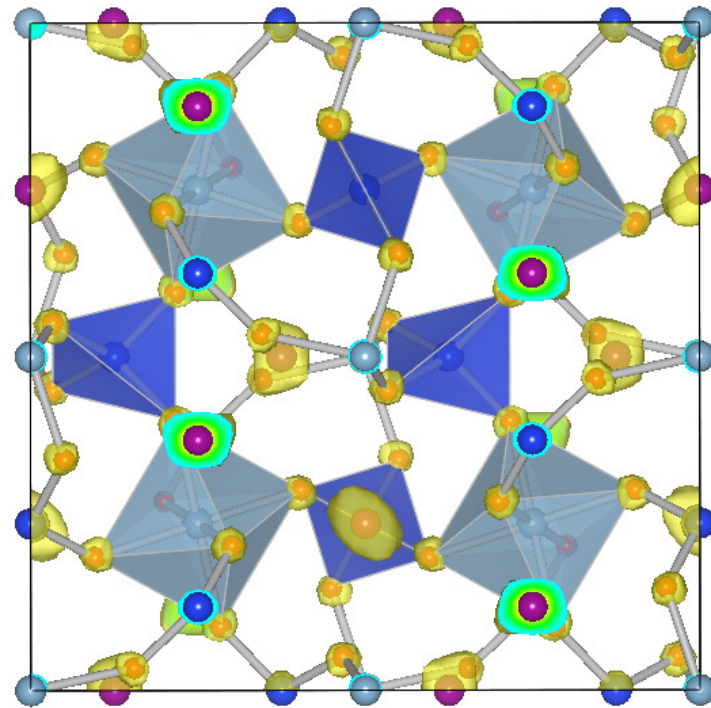steps of 1°
precession angle 1°

Solution from 3D diffraction data

Advantage: Data easily obtained, scaling possible, lattice parameters „for free", general approach

Disadvantage: zonal systematic absences less obvious, integration issues

Spessartine ($Mn_3Al_2Si_3O_{12}$):
cubic, a=11.68, *Ia-3d*
Data from tilt series (-50°,50°)
steps of 1°
precession angle 1°

What to do after the solution?

Very often the PED data are not kinematical enough to provide full structural model, and difference Fourier maps do not help either.

Traditional difference Fourier map:

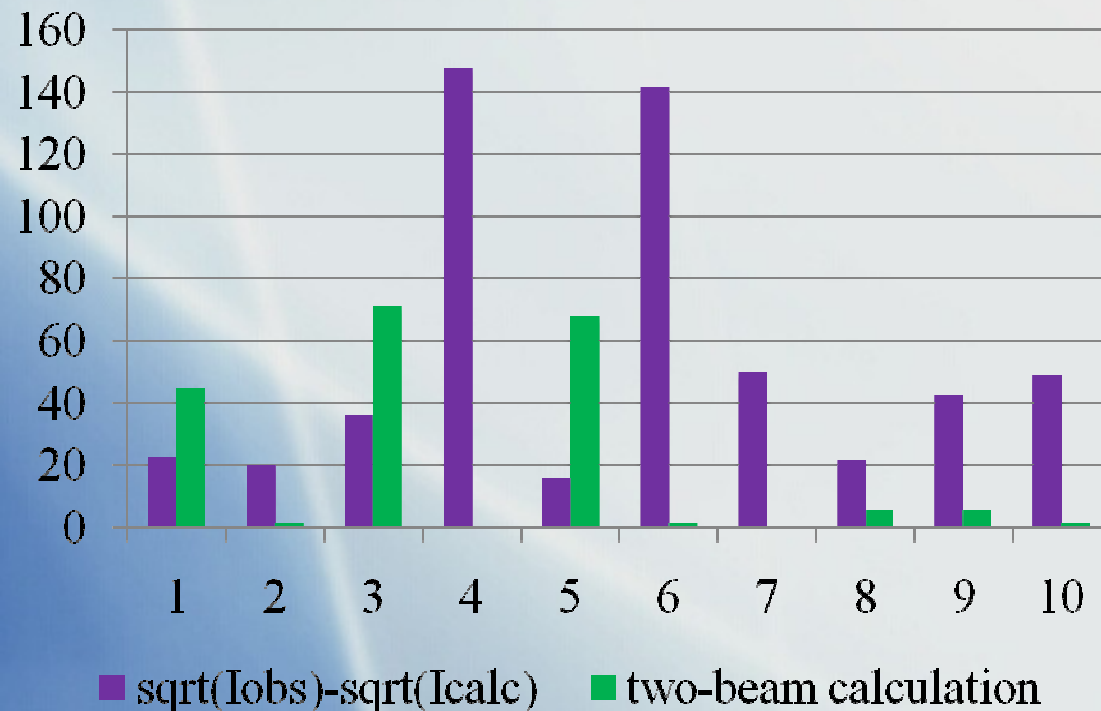use $\Delta\rho = FT^{-1}(\Delta F)$ such that $F_{calc} + \Delta F = F_{obs}$

A more general formulation:

use $\Delta\rho = FT^{-1}(\Delta F)$ such that $I(F_{calc} + \Delta F) = I_{obs}$

What to do after the solution?

"Proof of principle": two-beam calculation on zone 001 of Al_2O_3:

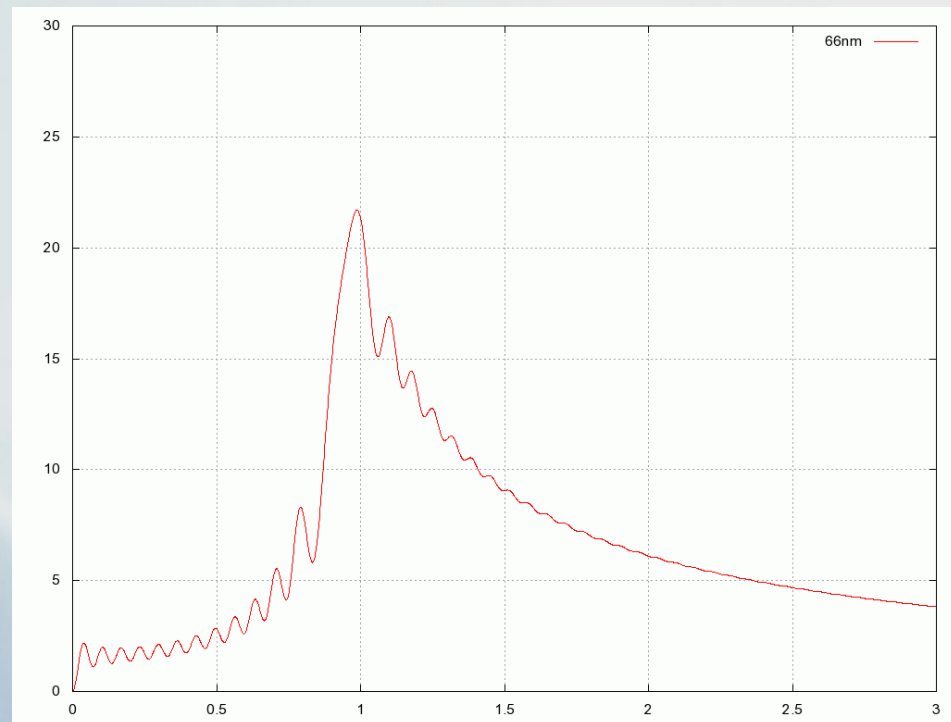Relative errors on Fobs-Fcalc [%]

■ sqrt(Iobs)-sqrt(Icalc)   ■ two-beam calculation

Thickness determination

Dynamical calculations require the crystal thickness to be known.

PED provides access to „CBED-like" properties of the reflections without actually performing the CBED experiment!

Conclusions

- Charge flipping does not strictly require the knowledge of chemical composition and symmetry

- Charge flipping is applicable also to 2D and 3D electron diffraction data

- 3D data sets obtained from manual or automatic tilt series are preferable for the structure solution step

- Steps beyond the pseudokinematical approximation are necessary for successful solution of complex structures

Acknowledgements:

Gabor Oszlányi, Hungarian Academy of Science, Budapest

Christian Baerlocher, Lynne McCusker, ETH Zürich

Walter Steurer, ETH Zürich

Michal Dušek, Vaclav Petricek, Institute of Physics, Prague

Gervais Chapuis, EPFL, Lausanne

Sander van Smaalen, University of Bayreuth

EDMA

Palatinus & van Smaalen, University of Bayreuth

EDMA = Electron Density Map Analysis (part of the BayMEM suite)

Program for analysis of discrete electron density maps:

- Originally developed for the MEM densities

- Analysis of periodic and incommensurately modulated structures

- Location of atoms and tentative assignment of chemical type based on a qualitative composition

- Several interpretation modes depending on the degree of certainty about the composition

- Export of the structure in Jana2006, SHELX and CIF formats

- Writes out the modulation functions in a form of a x_4-x_i table