

Free Objects for Xtallography: Structure Solution from Powder Diffraction Data

Radovan Černý

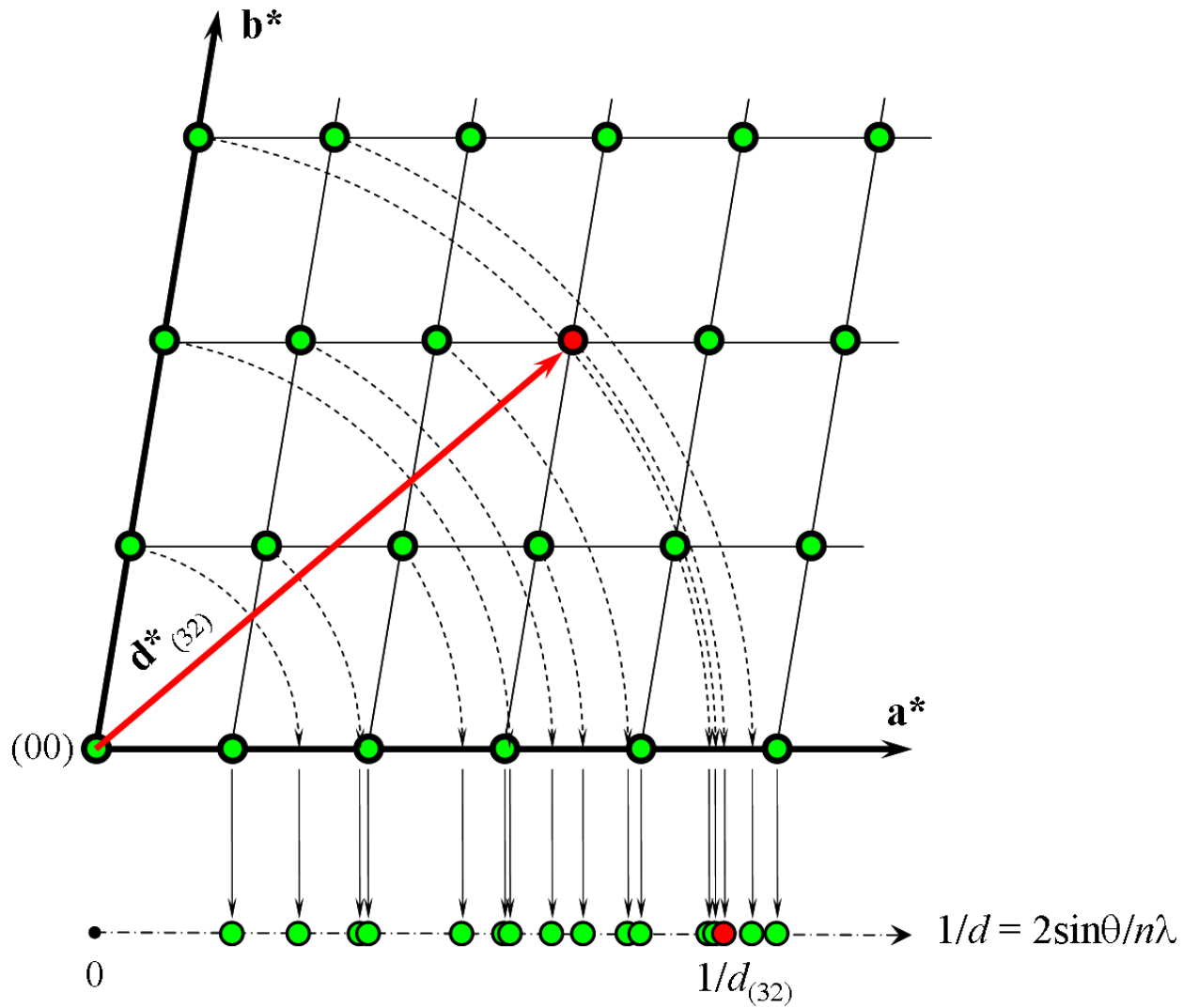
Laboratoire de cristallographie



**UNIVERSITÉ
DE GENÈVE**

FACULTÉ DES SCIENCES

Why powders more difficult than single crystals?



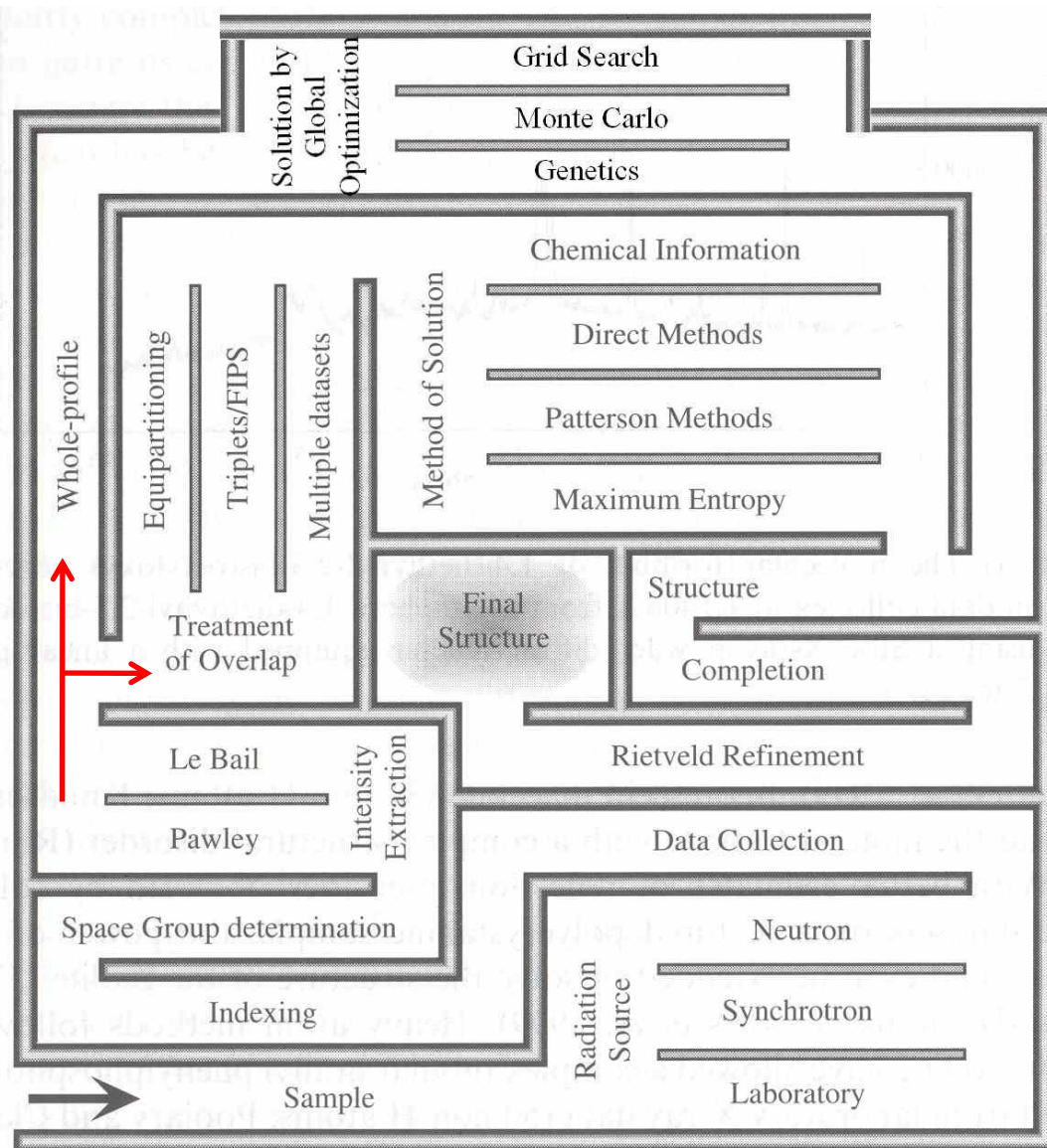
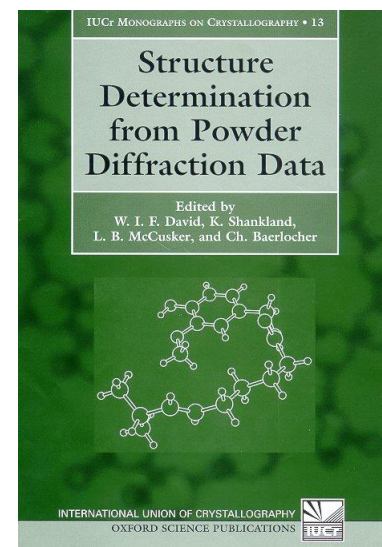
Crystal structure characterization (*ab-initio* solution and/or refinement)

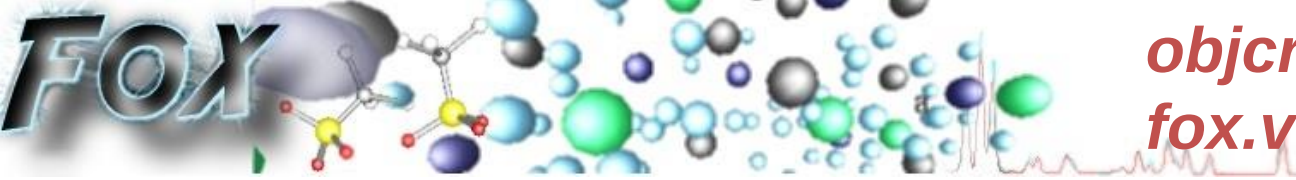
Labyrinth of the SDPD

Structure Determination from Powder Diffraction Data

IUCr Monographs on
Crystallography 13

Oxford Science
Publications (2002)





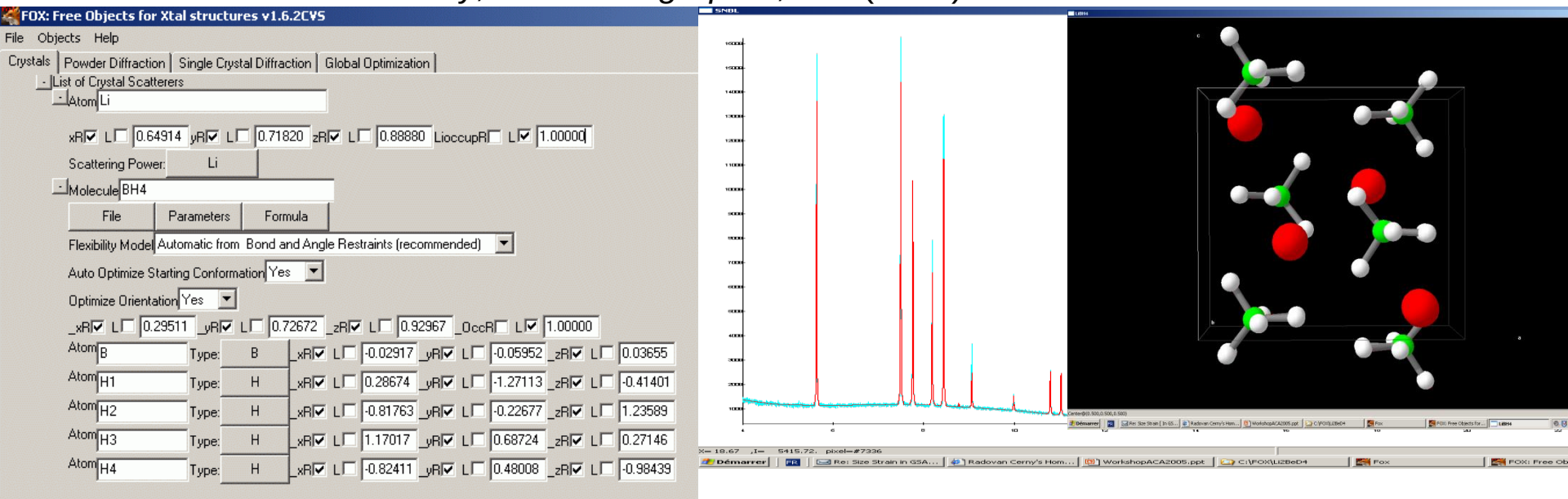
objcryst.sourceforge.net
fox.vincefn.net

FOX, "Free Objects for Crystallography": a modular approach to *ab initio* structure determination from powder diffraction.

V. Favre-Nicolin and R. Černý, *J. Appl. Crystallography* **35** (2002) 734-743

A better FOX: using flexible modelling and maximum likelihood to improve direct-space *ab initio* structure determination from powder diffraction.

V. Favre-Nicolin and R. Černý, *Z. Kristallographie*, **219** (2004) 847-856



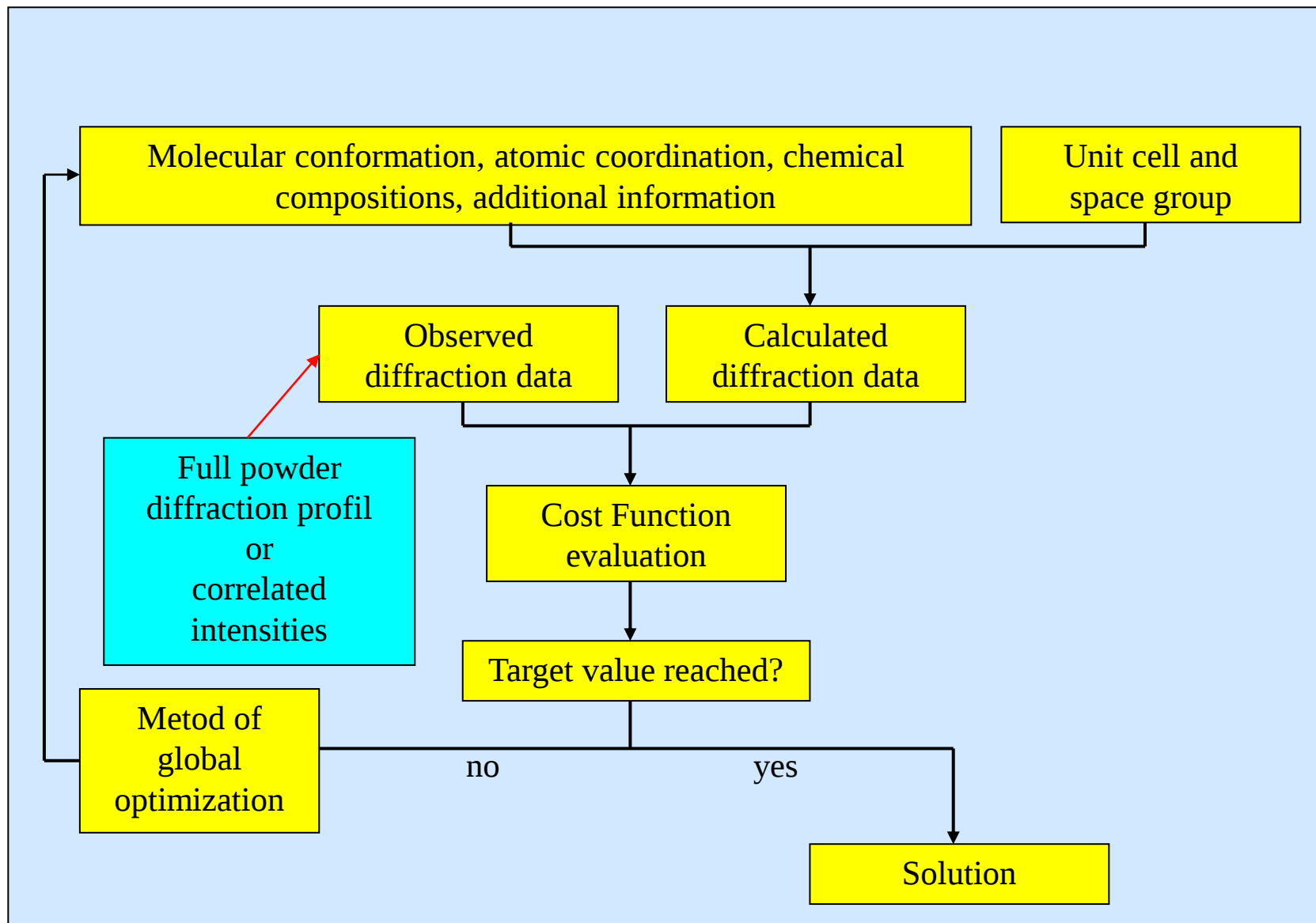
Direct space methods of Structure Determination from Powder Diffraction: principles, guidelines and perspectives.

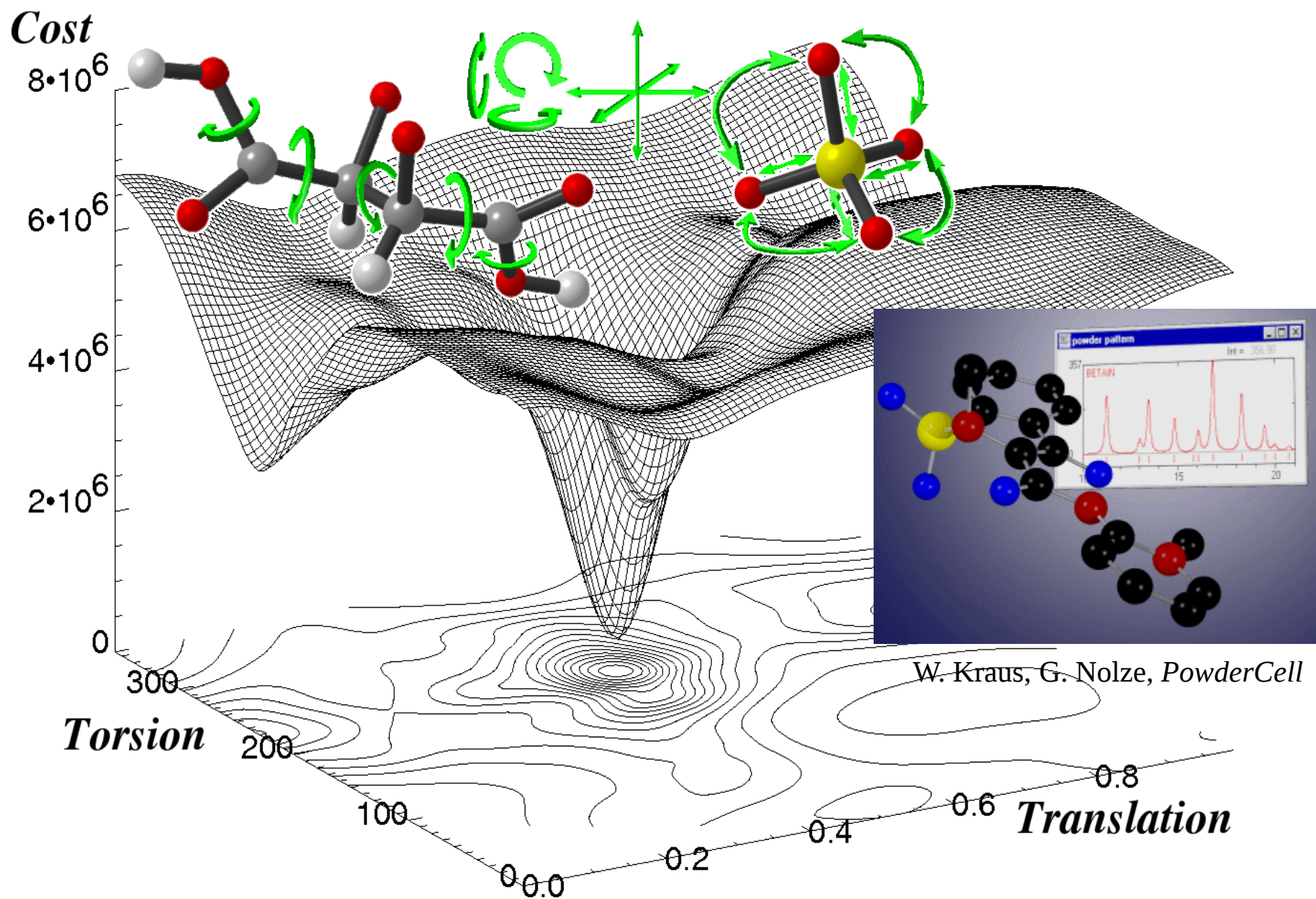
R. Černý and V. Favre-Nicolin, *Z. Kristallographie*, **222** (2007) 105-11

FOX, current state and possibilities.

R. Černý, V. Favre-Nicolin, J. Rohlíček, M. Husák, *Crystals* (2017), **7**, 322

Structure solution: Direct space methods

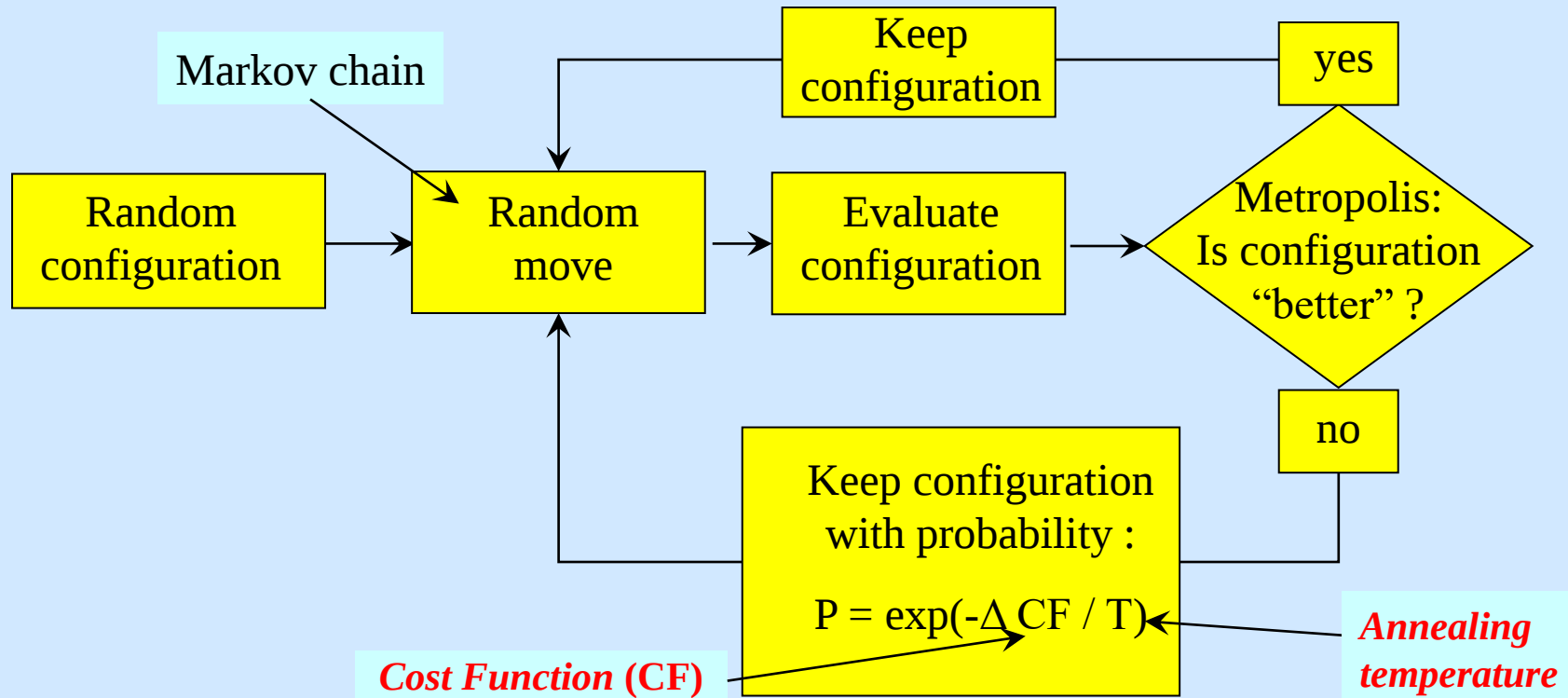




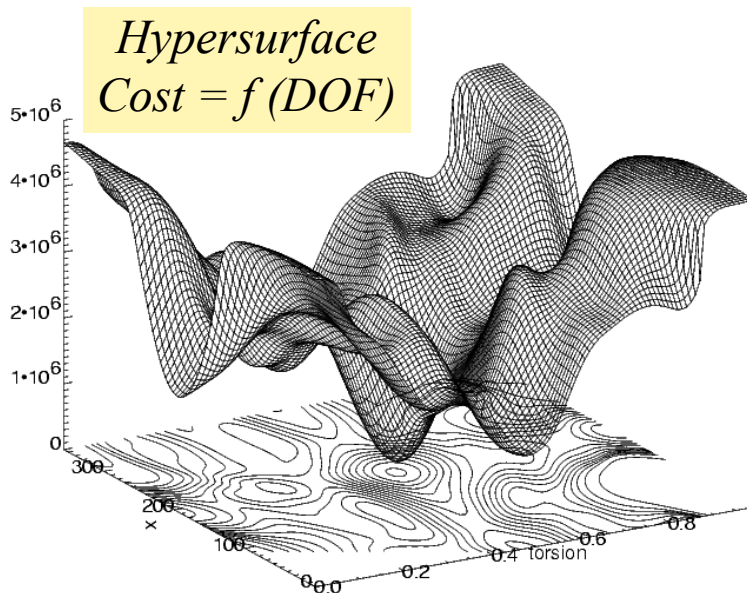
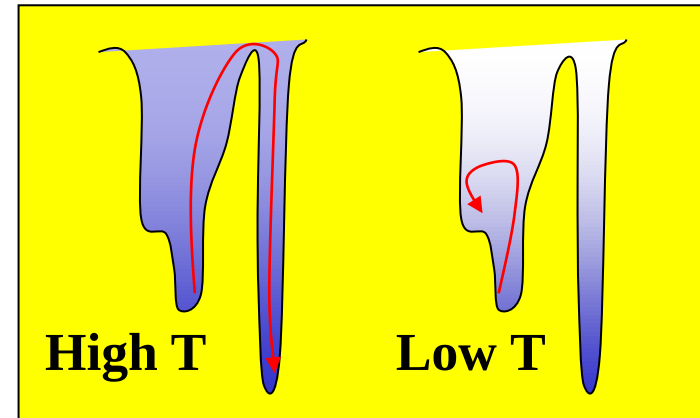
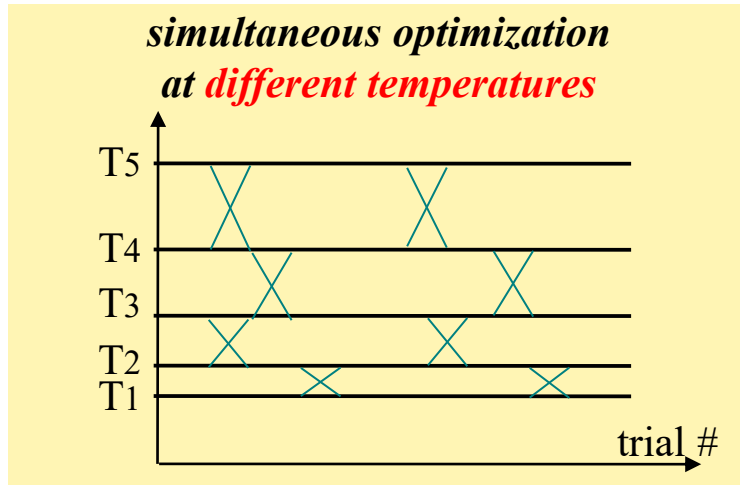
Simulated Annealing

Monte-Carlo based Optimization

Explore parameter space and generate “all” possible configurations with a Boltzmann-type distribution

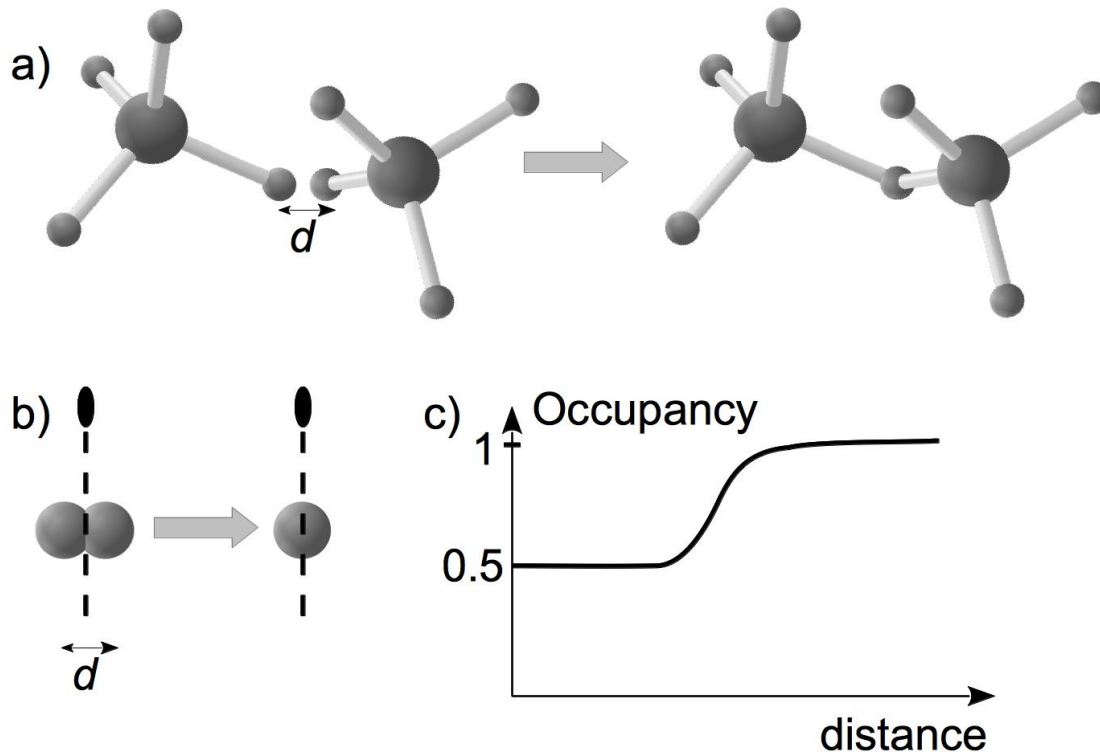


Parallel Tempering & Annealing Temperatures



To automatically choose the temperatures, in each parallel optimization **it is the average atomic displacement per random move which is imposed, from 0.01 to 1 Å**. The Temperature is then tuned so that in each “world” **the acceptance rate of new configurations is from 10 to 30%.**

Dynamical Occupancy Correction

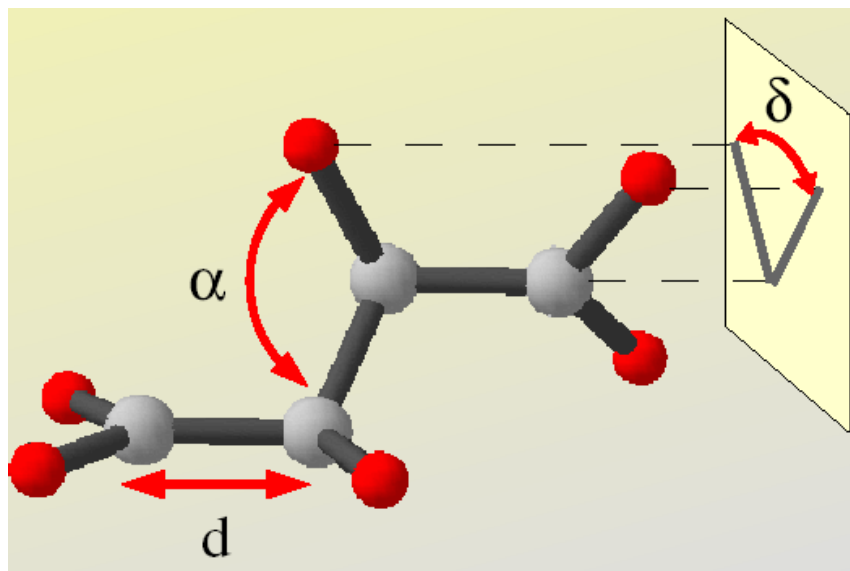


Ab initio structure solution algorithms working in direct space must be able to automatically handle (a) atoms which are shared between individual building units, and those which (b) are on a special position. In both cases, the algorithm can transform two overlapping atoms into a single one by (c) diminishing the occupancy of the atoms when their distance falls below a threshold value.

Building Units : Description

Flexible approach = isolated atoms + restraints

Idea: keep all the coordination information, but **without its pitfalls**



- this modelization is *independent from the order of the atoms*
- *any type of restraint can be introduced*
- *any type of movement can be directly done (no need to compute complex torsions)*

Introduce a Cartesian coordinate system for each Molecule object.

All atom positions are directly defined by their xyz coordinates
and
the coordination information is introduced by **restraints** on:

- **bond lengths** $\chi^2 = \frac{(d - d_0)^2}{\sigma_d^2}$

- **bond angles** $\chi^2 = \frac{(\alpha - \alpha_0)^2}{\sigma_\alpha^2}$

- **dihedral angles** $\chi^2 = \frac{(\delta - \delta_0)^2}{\sigma_\delta^2}$

Main FOX interface

FOX: Free Objects for X

2(C16 H22 F Fe2 N2 O13), Fe H12 O6, 14(H2 O) [P -1]

Crystals Powder Diffraction Single Crystal Diffraction

☒ Crystal 2(C16 H22 F Fe2 N2 O13), Fe H12 O6, 14(H2 O)

File Parameters Scatterers Display

Constrain Lattice to SpaceGroup Symmetry Yes (Default)

Use Dynamical Occupancy Correction Yes

Display Enantiomer No

AntiBump 0,00 Scale 1,0000

Bond Valence Cost 0,00 Scale 1,0000

a:R ☐ L ☒ 10,8238 b:R ☐ L ☒ 11,3967 c:R ☐ L ☒ 13,409

SpaceGroup: P -1

List of Crystal ScatteringPowers

☐ ScatteringPowerAtom Fe Symbol: Fe

☐ ScatteringPowerAtom O Symbol: O

☐ ScatteringPowerAtom H Symbol: H

☐ ScatteringPowerAtom C Symbol: C

☐ ScatteringPowerAtom N Symbol: N

☐ ScatteringPowerAtom F Symbol: F

List of Crystal Scatterers

☐ Atom Fe3

X: R ☒ L ☐ 0,000000 Y: R ☒ L ☐ 0,500000 Z: R ☒ L ☐ 0

Scattering Power: Fe

☐ Atom O5W

X: R ☒ L ☐ 0,092980 Y: R ☒ L ☐ 0,510760 Z: R ☒ L ☐ 0

Scattering Power: O

☐ Atom H5W1

X: R ☒ L ☐ 0,060000 Y: R ☒ L ☐ 0,545000 Z: R ☒ L ☐ 0

Scattering Power: H

ConnectAtoms: found Molecule: H2 O1
ConnectAtoms: found Molecule: H2 O1
ConnectAtoms: found Molecule: H2 O1
CIF: updating graphical user interface for Crystal
Automatically opening 3D Crystal view
Finished opening 3D Crystal view
CIF: finished updating graphical user interface for Crystal (Crystal creation= 0.393s total)

0,000<x<1,000
0,000<y<0,500
0,000<z<1,000
Mouse
left-click & drag: change orientation
middle-click & drag: zoom (vert) change depth perception (horiz)
wheel: rotate
Trackpad
two-finger drag: change orientation
Keyboard (all lowercase)
+,-: change zoom
2,4,6,8,D,C,F,R: rotate
F1,F2,F3,F4,F5,F6: increase/decrease display area
shift+F1,F2,F3,F4,F5,F6: shift display area
F7,F8: increase/decrease fade distance
F9,F10: display area=asymmetric or full unit cell
H: toggle help display
L: toggle atom labels
M: toggle full molecules
Y: toggle hydrogens

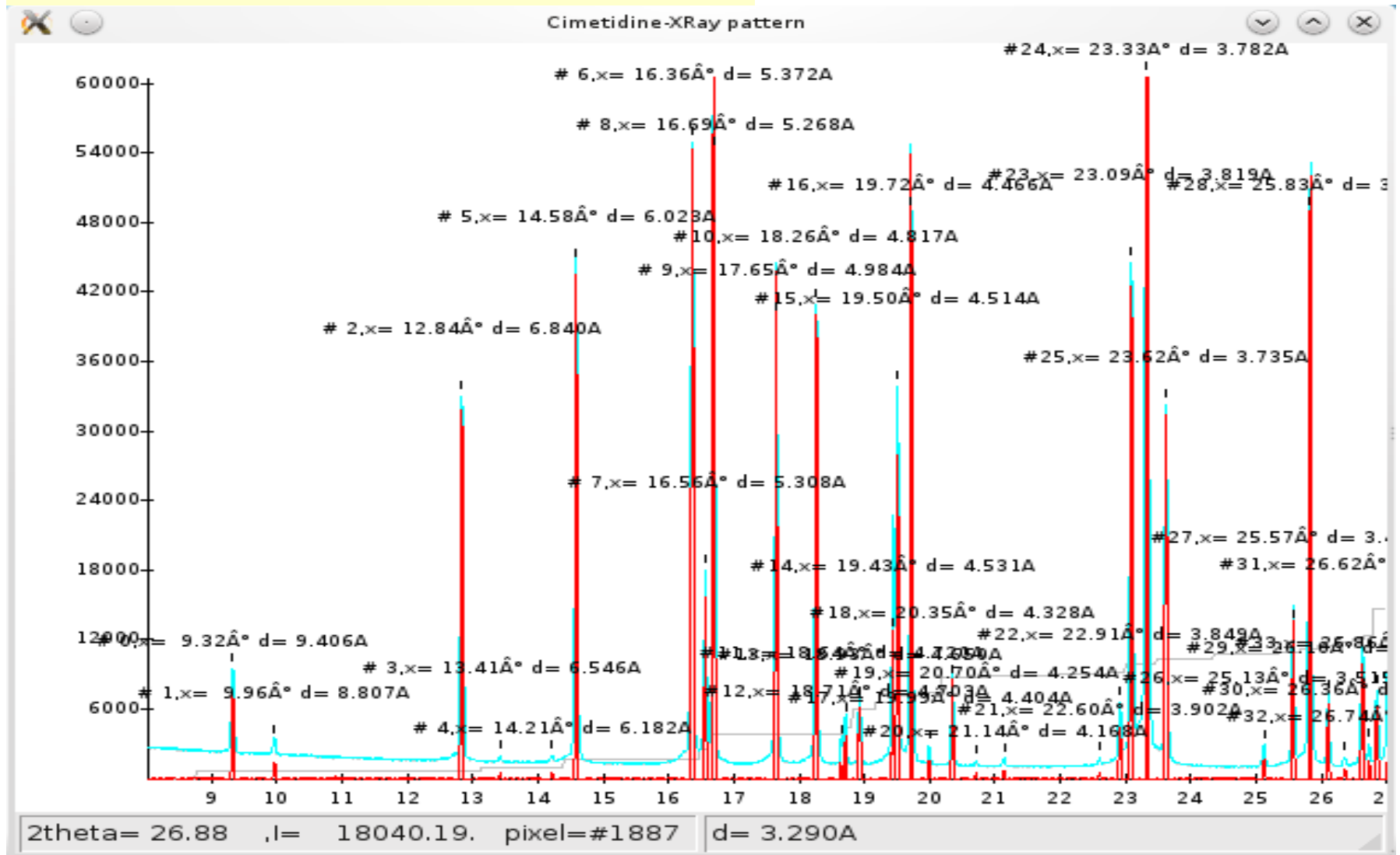
Center@10,500,0,250

Crystallography Open Database results (double-click on formula to load CIF)

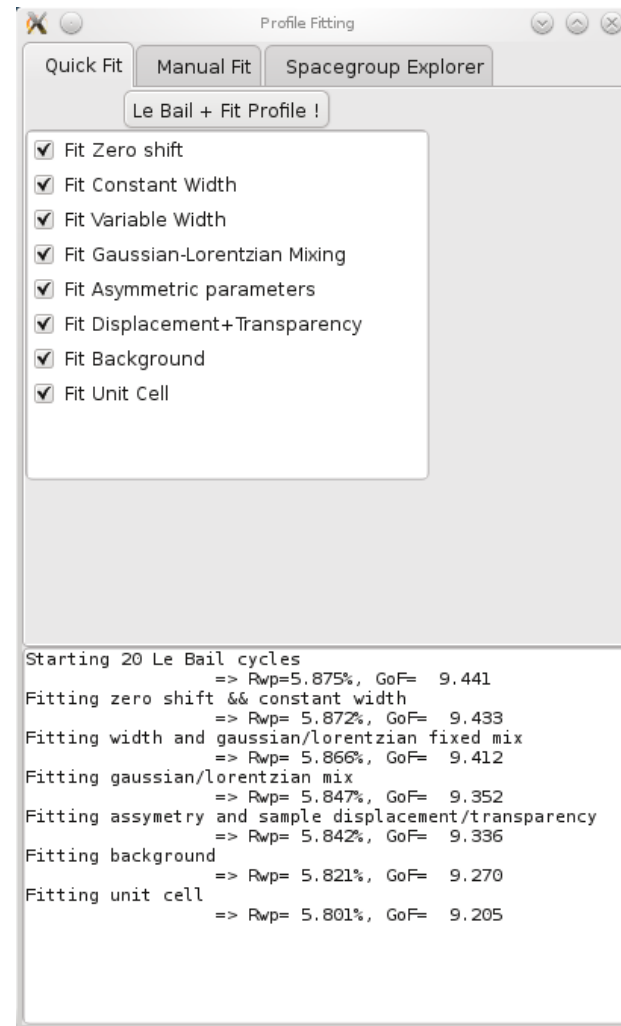
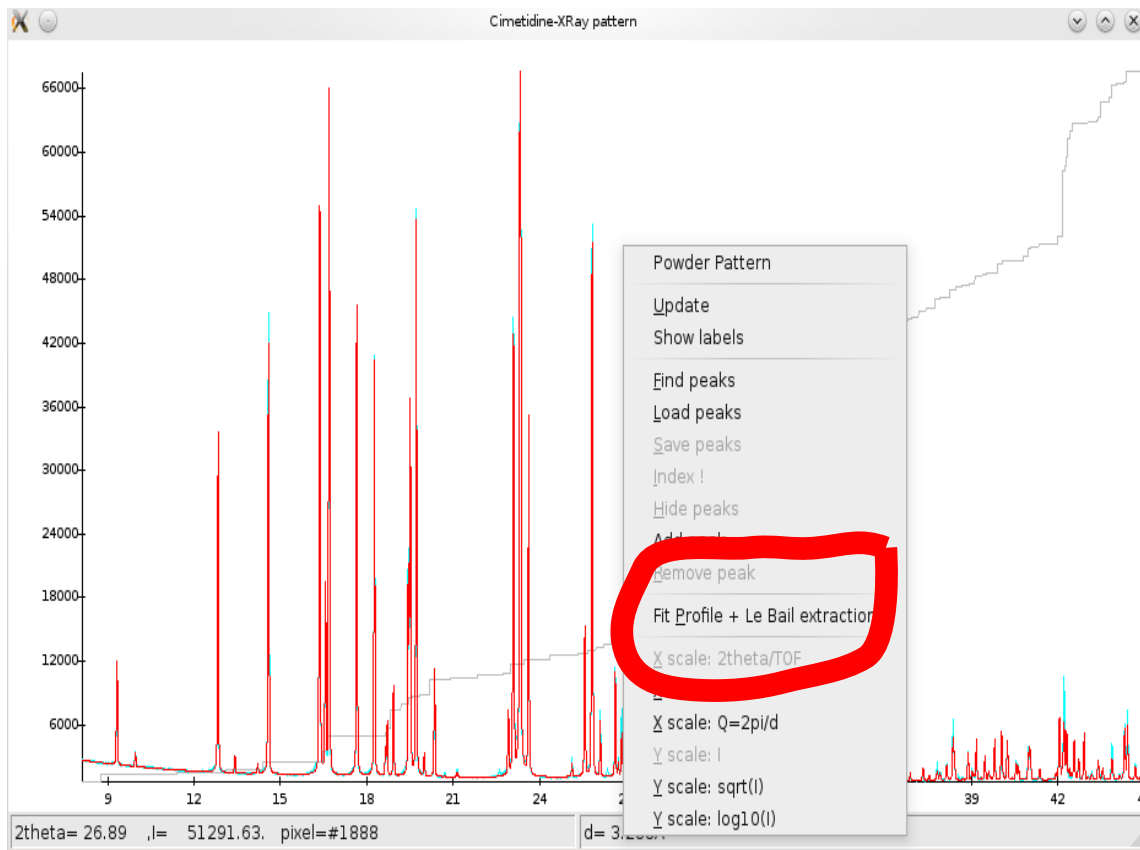
C31 H34 F6 Fe2 N2 O4	Acta Crystallographica Section E 65 (2009), m961: Chen, Fang 1,4-Diferrocenyl-2-methylpiperazine-1,4-dium bis(trifluoroacetate)
C32 H84 F2 Fe5 N4 O46	Inorganic chemistry 55 (2016), 848: Kerber, William D.; Goheen, Joshua T.; Perez, Kaitlyn A.; Siegler, Maxime A. Enhanced Stability of the Fe(II)/Mn(II) State in a Synthetic Model of Heterobimetallic Cofactor Assembly.
C36 H24 F12 Fe N2 O8	Organometallics 21 (2002), 1111: Enders, Markus; Kohl, Gerald; Pritzkow, Hans (null)
C38 H12 F20 Fe N6 O4	Journal of the American Chemical Society 134 (2012), 8310: Michael J. Rose; Harry B. Gray; Jay R. Winkler Hydrogen Generation Catalyzed by Fluorinated Diglyoxime-Iron Complexes at Low Overpotentials

Auto-indexing

- Search for peaks

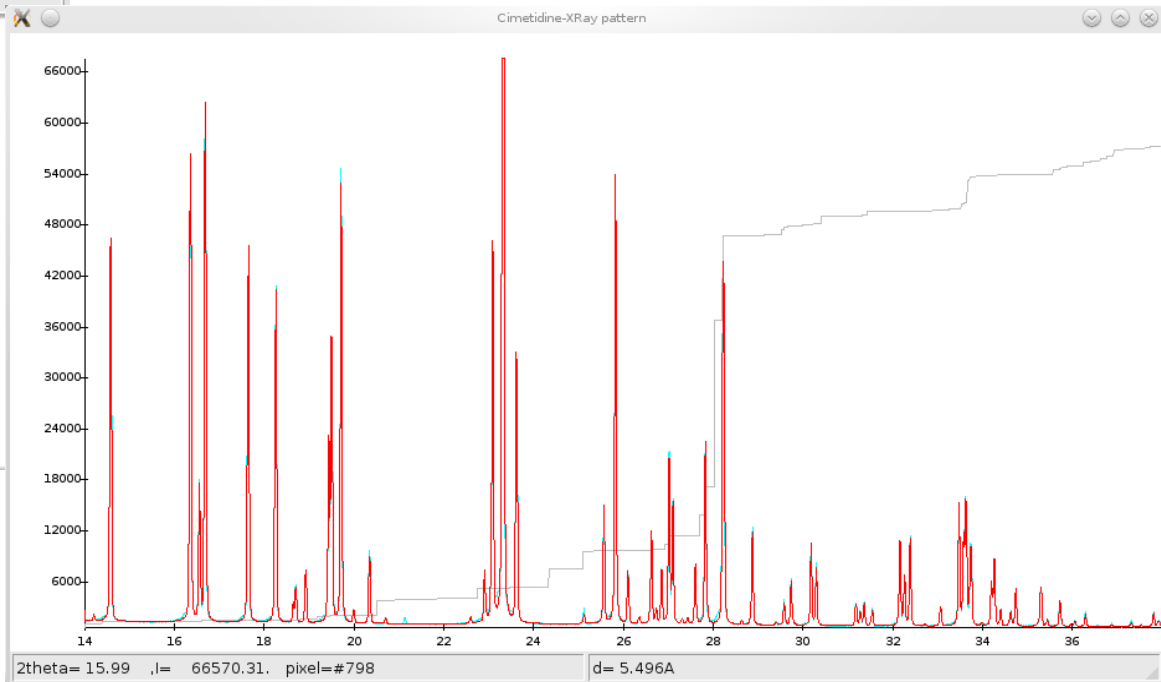
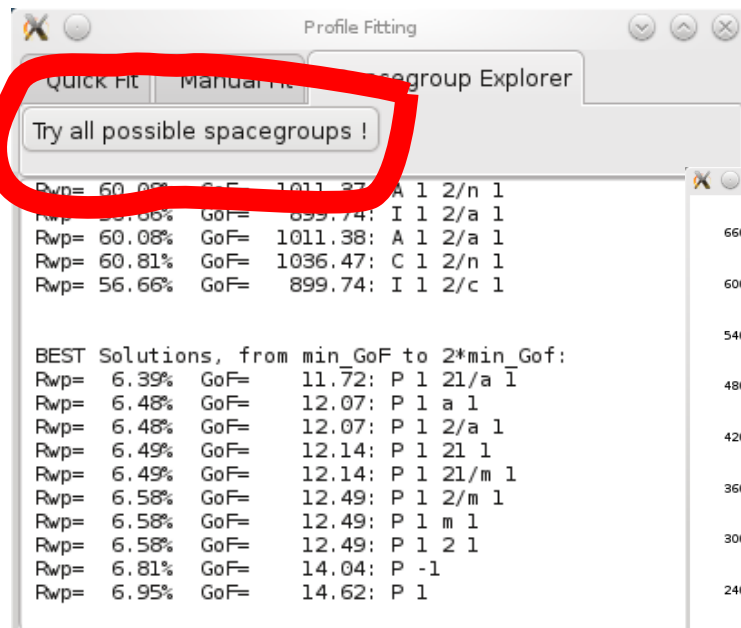


Profile fitting & Le Bail extraction



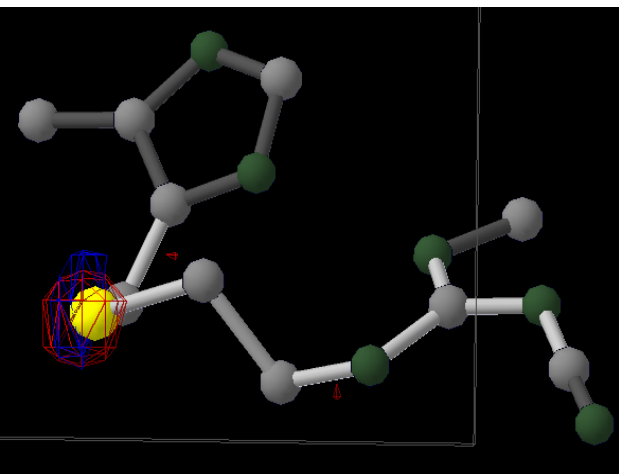
Profile fitting: spacegroup explorer

- Performs a profile fitting for all spacegroup settings allowed by the unit cell (37 for monoclinic cells, 478 for cubic cells... it can take a while).
- Spacegroups are listed by increasing GoF up to $2 \cdot \min(\text{GoF})$

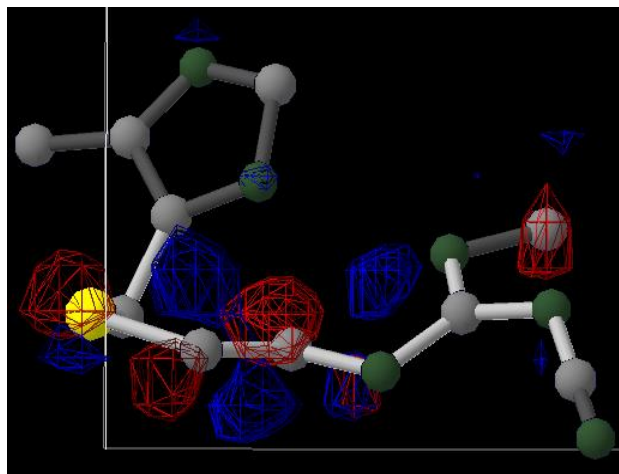


Fourier maps

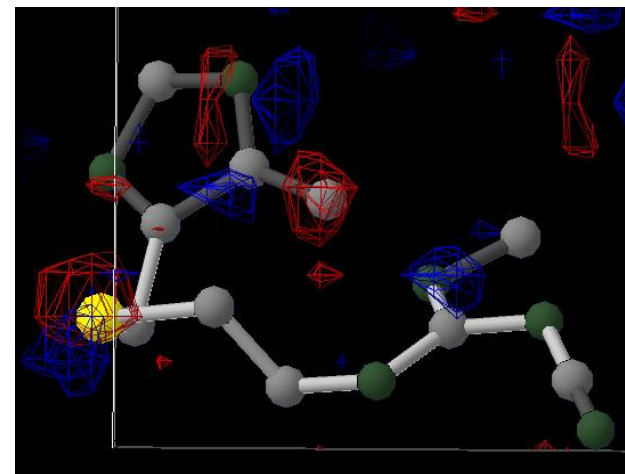
- Display Fourier maps (calc, obs, obs-calc)
- Fourier maps are included in the POV-Ray output



Correct



*Wrong conformation
of internal chain*



*Wrong position
for side CH₃ group*

Available Fourier maps for Cimetidine

Update 3D View ☒ Wireframe ☒ Show Fourier ☒ Sharpen maps

Available Maps	Displayed Maps
(Fc)P: Xray: 1.529A: Cimetidine-XRay pattern	(Fo-Fc)S: Xray: 1.529A: LeBail (d=1.00A): Cimetidine
(Fc)S: Xray: 1.529A: LeBail (d=1.00A): Cimetidine	(Fo-Fc)S: Xray: 1.529A: LeBail (d=1.00A): Cimetidine
(Fo)S: Xray: 1.529A: LeBail (d=1.00A): Cimetidine	
(Fo-Fc)S: Xray: 1.529A: LeBail (d=1.00A): Cimetidine	

min=-7.14 max= 3.90 sigma= 0.82

New Contour: -2

Add

Contour:

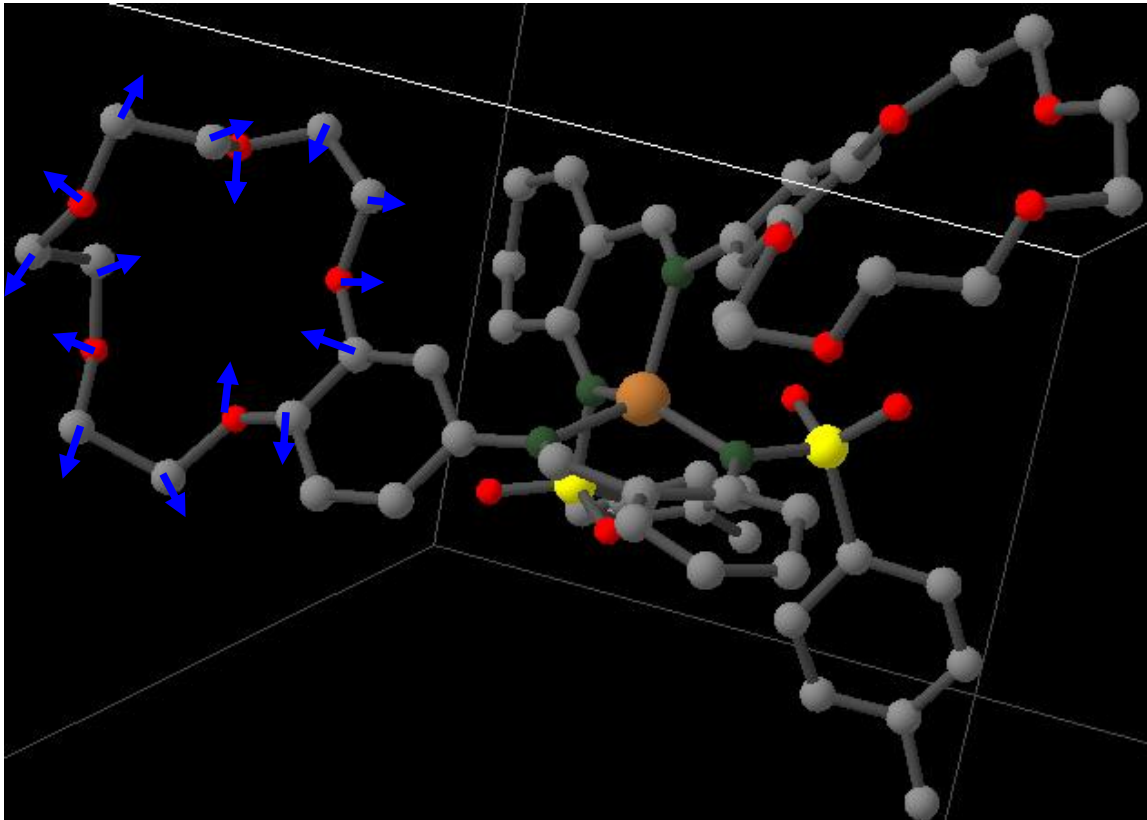
red

Remove

Kolokvium 2023

15

Using Molecular Dynamics



Atoms in “restrained” groups are moved using molecular dynamics principles :

- Each atom is given a random vector speed*
- The overall Energy is $E_{kinetic} + E_{restraints}$*
- Atoms are moved according to standard mechanics (force=gradient of $E_{restraints}$)*

Using Molecular Dynamics

Molecule mpf-9+h.fhz

File Parameters Formula & Restraints Manipulate Geometry

Flexibility Model Automatic from Restraints, strict

Auto Optimize Starting Conformation No

Optimize Orientation Yes

Rotation Center Geometrical center (recommended)

_xR ☒ L 0.432748 _yR ☒ L 0.253980 _zR ☒ L 0.458472 _OccR ☐ L ☒ 1.0

MD moves frequency 0.000000 MD moves Energy 40.0000

Center Atom: No atom !

	Name	Type	X
1	N1	N	-4.5425
2	N2	N	-3.239250

Energy of Molecule for Molecular Dynamics Moves

Standard amplitude=40.
Small amplitude=10. (small distortion of the Molecule)
Large amplitude=400. (large distortion of the Molecule)

*MD moves are **computationally expensive***

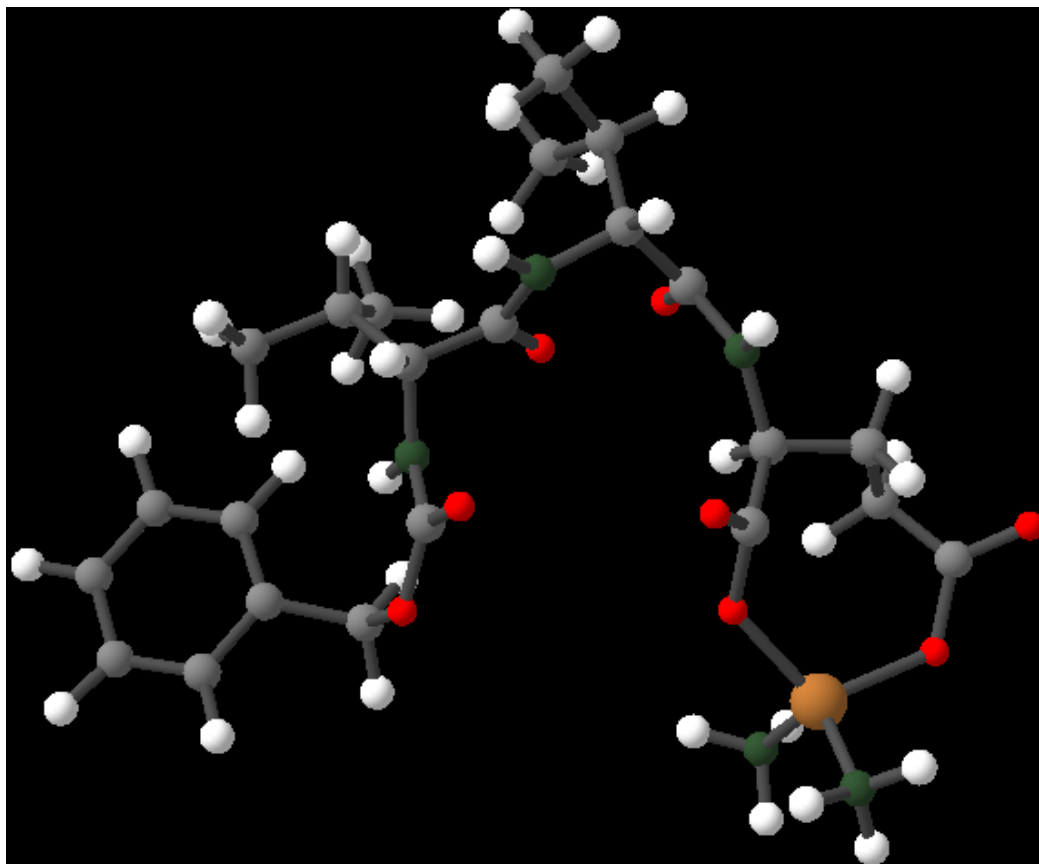
=> they are only tried once in a while

*=> the **frequency** can be chosen (by default: 0=never)*

*=> the **relative energy** of the molecule can be chosen to avoid too much distortion*

*... But remember that **SOME DISTORTION IS NECESSARY** to reach the 'true' conformation of the Molecule, starting from an incorrect one...*

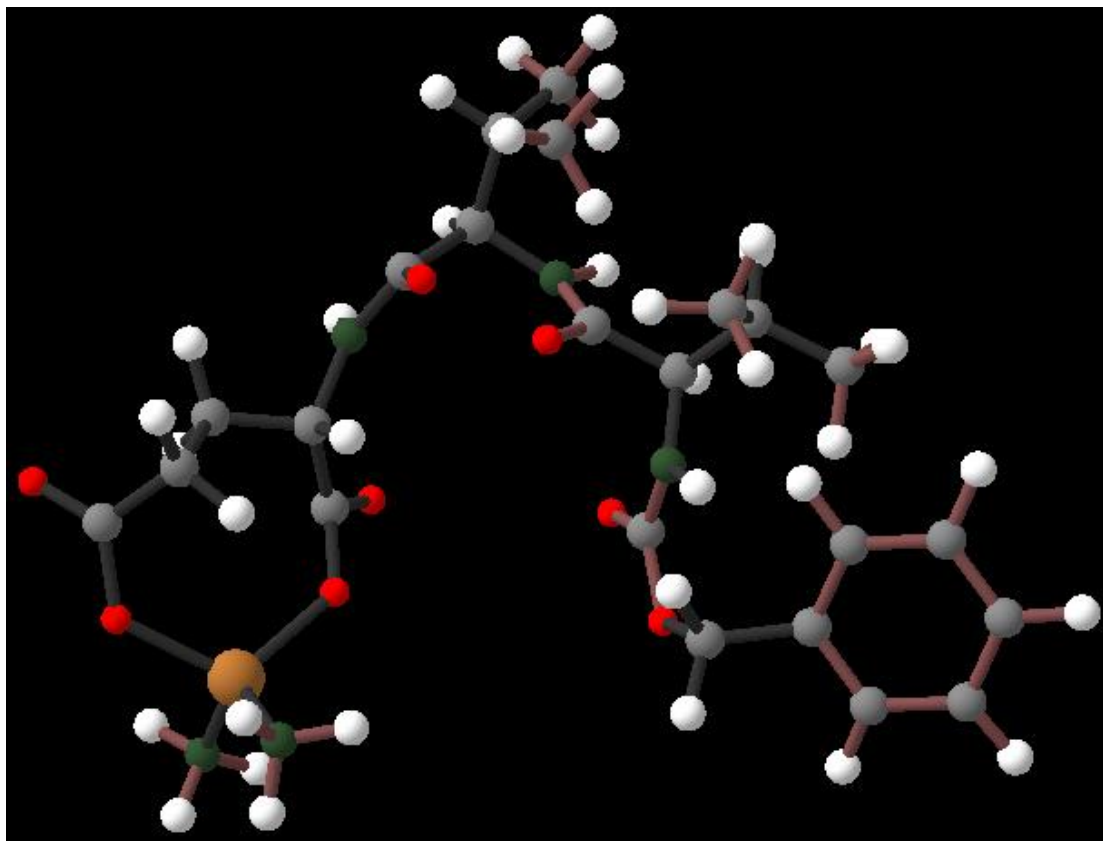
Using Molecular Dynamics + least squares



***MD moves allow to solve complex, flexible structures with large cycles...
...but it can take a long time !***

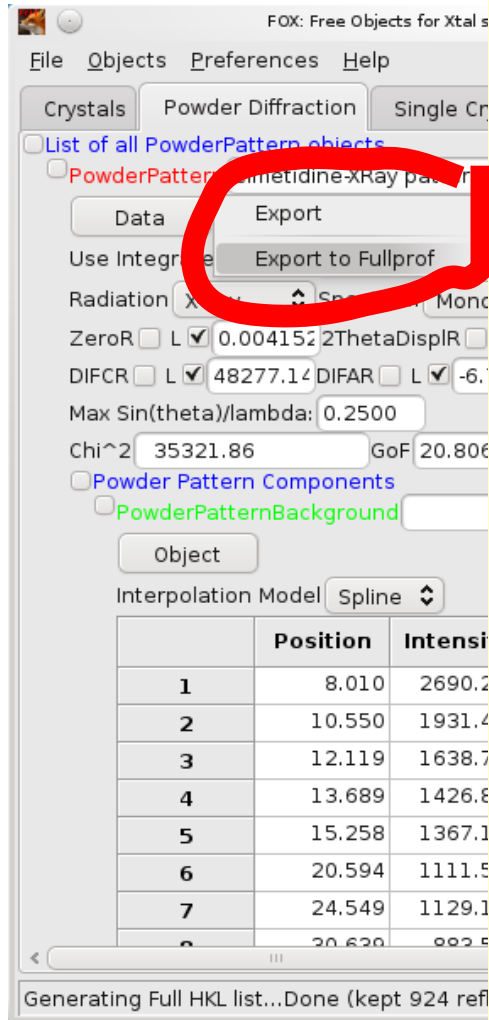
Using periodic least squares greatly help the convergence, as the least squares algorithm moves all the atoms individually (taking into account restraints) and is not limited by simple moves, or a Z-matrix description

Molecular Dynamics + least squares + rigid bodies



***SOME DISTORTION IS NECESSARY... but sometimes you really want to avoid it
=> You can create 'rigid groups' of atoms that will only be translated/rotated as a
rigid body, even during least squares.***

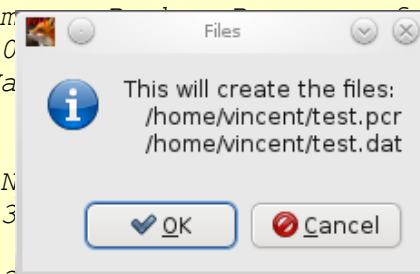
Fullprof export



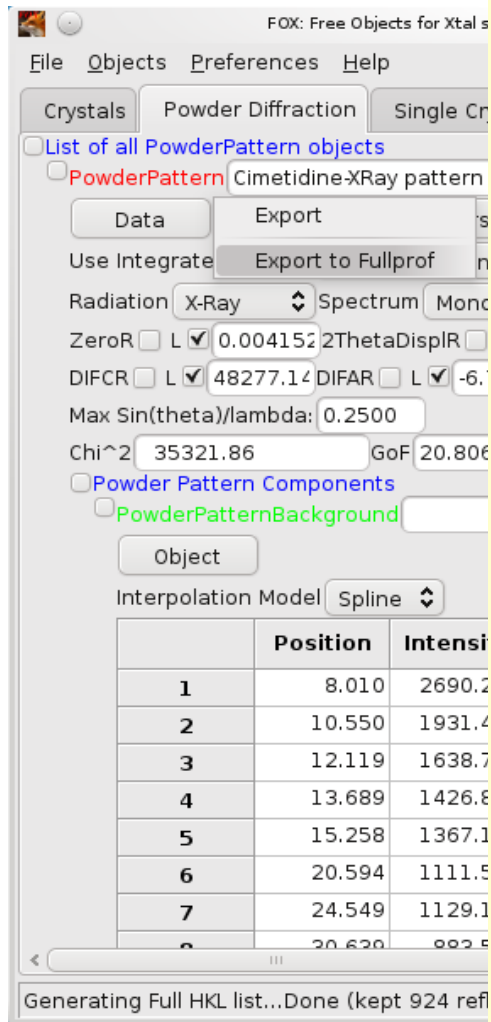
```

. 1 !Number of refined parameters
.! Zero Code Sycos Code Sysin Code Lambda Code More -> Patt #1
. 0.00415153 0.0 0.00119514 0.0 0.00105758 0.0 0.000 0.0 0
.!-----
---
.! Data for PHASE number: 0 ==> Current R_Bragg for Pattern# 1: 0.00
.!-----
---
.Cimetidine
.!Nat Dis Ang Jbt Isy Str Furth ATZ Nvk More
.17 17 20 0 0 0 0 1.0 0 1
.!Jvi Jdi Hel Sol Mom Ter N_Domains
. 0 3 0 0 0 0 0
.!Contributions (0/1) of this phase to the patterns
. 1
.!Irf Npr Jtyp Nsp_Ref Ph_Shift for Pattern#0
. 0 0 0 0 0
.! Pr1 Pr2 Pr3 Brind. Rm
. 1.0 1.0 1.0 1.0 0
.! Max_dst(dist) (angles) Bond-Va
. 2.7000 1.5000 0
.P 1 21/a 1
.!Atom Typ X Y Z Biso Occ In Fin N
.C1 C 0.566876 0.342198 0.343369 3
. 0 0 0 0 0
.N2 N 0.448664 0.371933 0.388352 3 1 0 0 0 0
. 0 0 0 0 0
.C3 C 0.454253 0.405903 0.550729 3 1 0 0 0 0
. 0 0 0 0 0
.N4 N 0.586007 0.407123 0.696493 3 1 0 0 0 0
. 0 0 0 0 0
.C5 C 0.624978 0.44932 0.859614 3 1 0 0 0 0
. 0 0 0 0 0
.N6 N 0.663486 0.486503 1.01791 3 1 0 0 0 0
. 0 0 0 0 0
.N7 N 0.367983 0.448348 0.627608 3 1 0 0 0 0
. 0 0 0 0 0
.C8 C 0.233019 0.464033 0.453323 3 1 0 0 0 0

```



Fullprof export



```

!      U      V      W      X      Y      GauSiz      LorSiz      Size-Model
0.00341898 8.85951e-05 0.00156559 0.0 0.0 0.0 0.0 0.0
!      a      b      c      alpha      beta      gamma      #Cel
Info
10.3942 18.819 6.82503 90 106.437 90
0.0 0.0 0.0 0.0 0.0 0.0 0.0
! Pref1 Pref2 alpha0 beta0 alpha1 beta1 ?
0.0 0.0 0.0 0.0 0.0 0.0
0.0 0.0 0.0 0.0 0.0 0.0

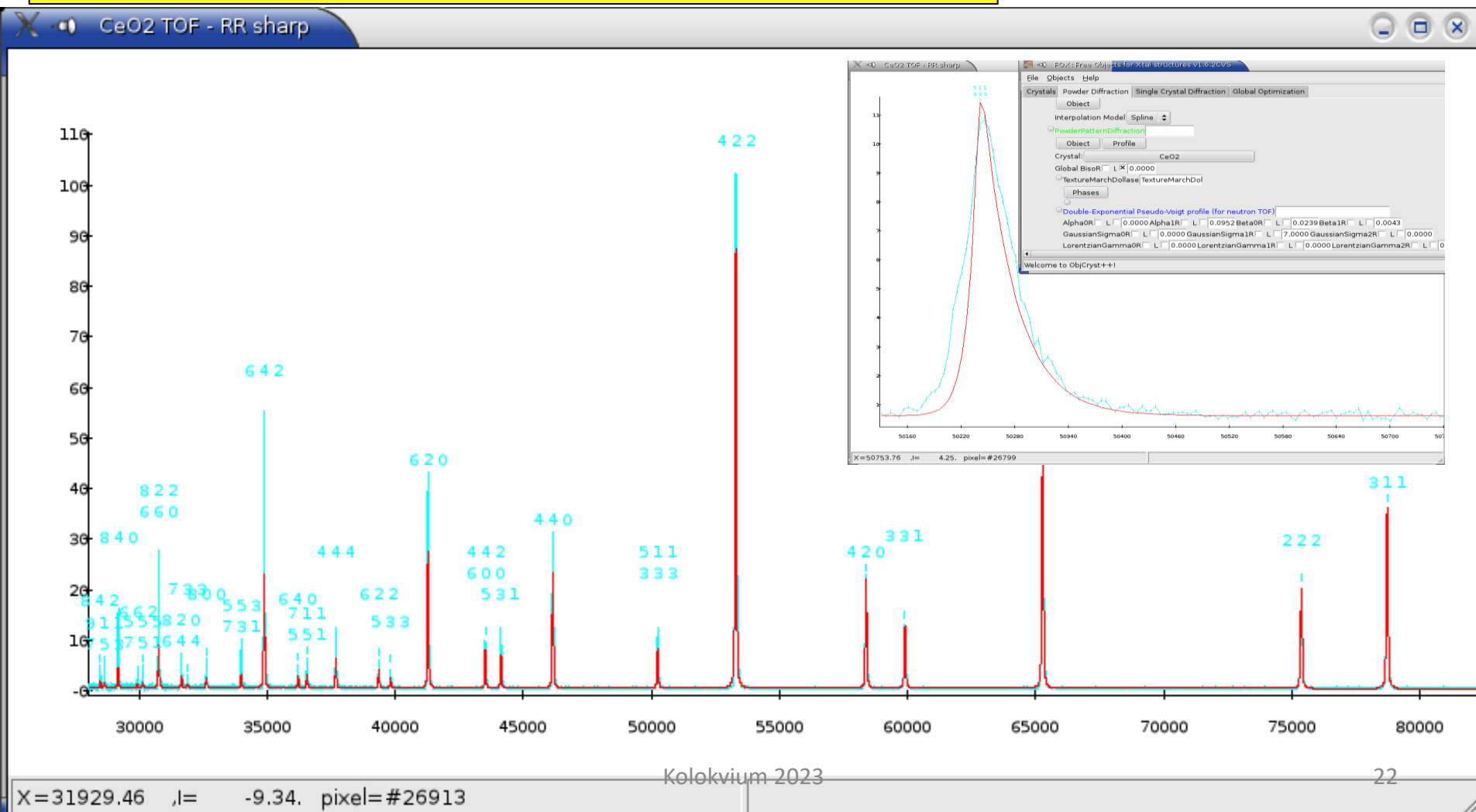
!Soft distance constraints
C1 N2 1 0 0 0 1.47 0.01
N2 C3 1 0 0 0 1.4 0.01
C3 N4 1 0 0 0 1.4 0.01
N4 C5 1 0 0 0 1.37 0.01
C5 N6 1 0 0 0 1.13 0.01
C3 N7 1 0 0 0 1.4 0.01
N7 C8 1 0 0 0 1.47 0.01
C8 C9 1 0 0 0 1.54 0.01
C9 S10 1 0 0 0 1.82 0.01
S10 C11 1 0 0 0 1.82 0.01
C11 C12 1 0 0 0 1.5 0.01
C12 N13 1 0 0 0 1.37 0.01
N13 C14 1 0 0 0 1.37 0.01
C14 N15 1 0 0 0 1.37 0.01
N15 C16 1 0 0 0 1.37 0.01
C16 C17 1 0 0 0 1.5 0.01
C16 C12 1 0 0 0 1.45 0.01

!Soft angle constraints
C1 N2 C3 1 1 0 0 0 0 0 0 108.862 0.572958
N2 C3 N4 1 1 0 0 0 0 0 0 119.748 0.572958
C3 N4 C5 1 1 0 0 0 0 0 0 119.748 0.572958
N4 C5 N6 1 1 0 0 0 0 0 0 180 0.572958
N2 C3 N7 1 1 0 0 0 0 0 0 119.748 0.572958
N4 C3 N7 1 1 0 0 0 0 0 0 119.748 0.572958
C3 N7 C8 1 1 0 0 0 0 0 0 108.862 0.572958
N7 C8 C9 1 1 0 0 0 0 0 0 108.862 0.572958
C8 C9 S10 1 1 0 0 0 0 0 0 108.862 0.572958

```

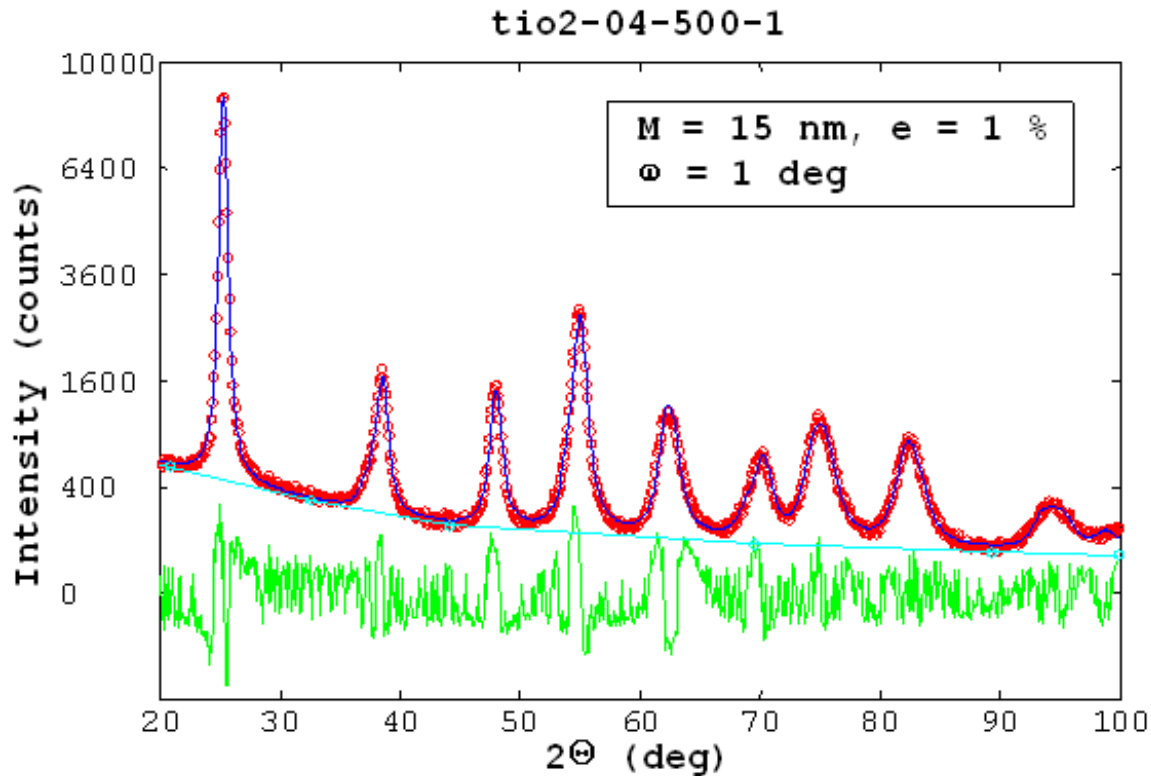
Time-Of-Flight

- Support for neutron TOF data
- Support for non constant-step data
- Double-Exponential Pseudo-Voigt profile (*M. Pitt*)



Profile fitting with Fox

(Zdenek Matěj from Charles University in Prague)



The idea was to extend **Fox** for the **Rietveld refinement** including calculation of diffraction intensities based on both the crystal structure and the microstructure models.

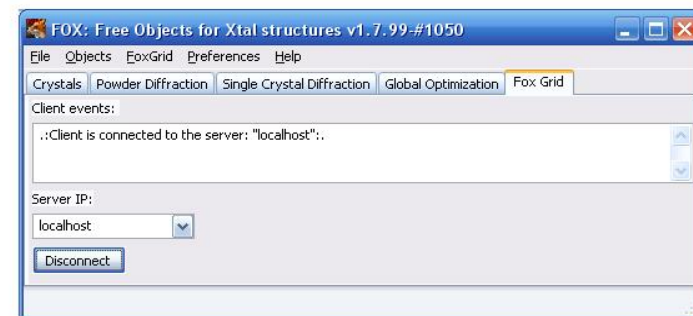
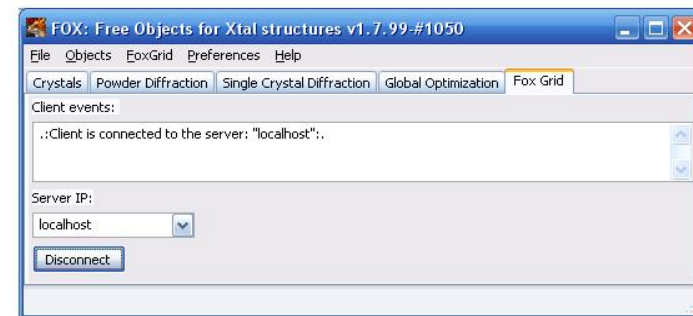
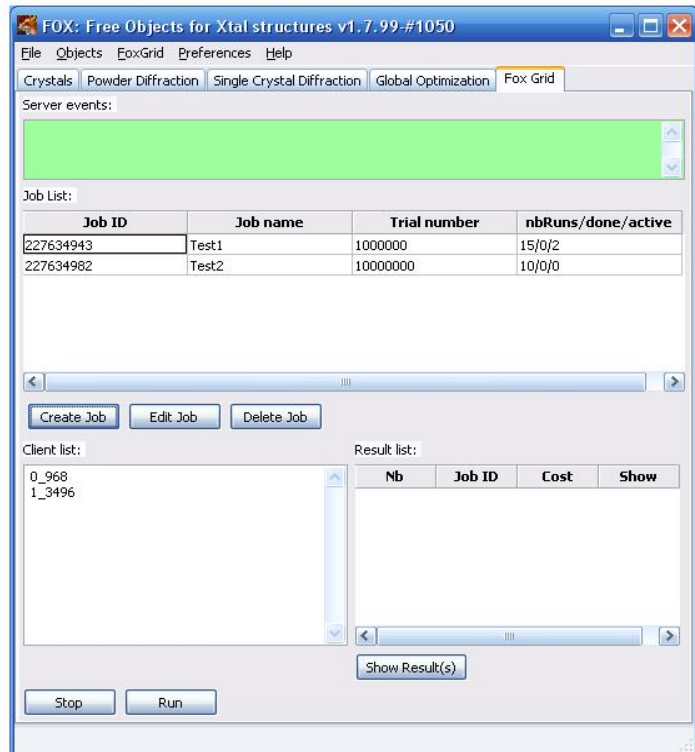
A general interface for description of various **line broadening models** was introduced by convolution of (physically relevant) profile functions (calculated in direct or reciprocal space) like: *stacking faults* model, *grain shape* function used for calculation of *size-broadening*, *dislocation broadening*, analytical or measured instrumental functions, physically based *micro-deformation (strain) broadening*. The least-square algorithm hidden in the ObjCryst++ was started, and Fox runs as a Rietveld program.

Grid-Computing for Fox

<http://tresen.vscht.cz/min/en/foxgrid>

Server

Clients



For complex structures, a 'grid-computing' version of Fox has been developed (Jan Rohlíček, Michal Hušák (ICT Prague))

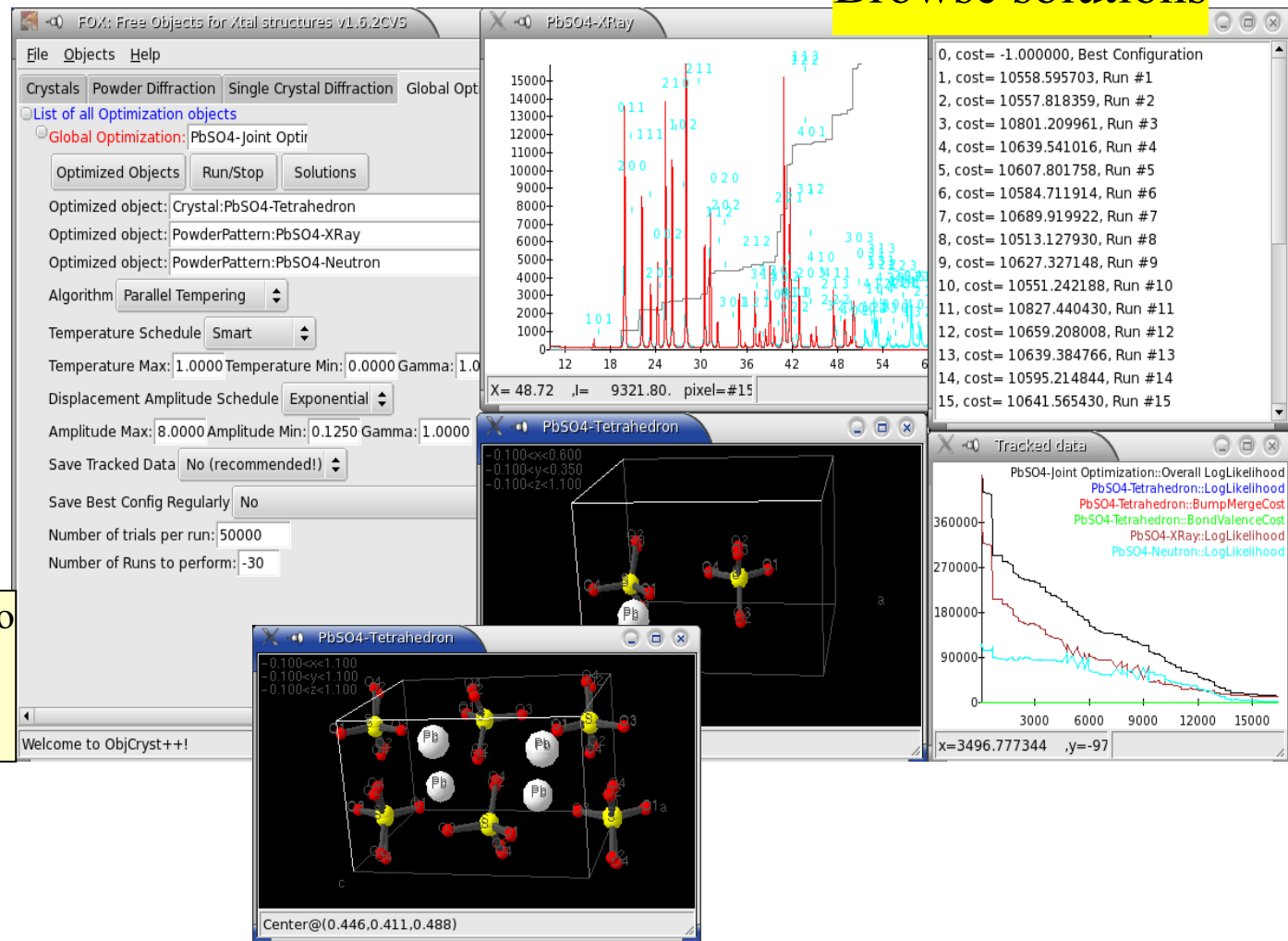
***=> xml files can be uploaded to a server, which distributes the jobs to clients
=> N PCs with 4 cores => speedup of ~ 4N compared to a single instance of Fox***

The server & clients are integrated with Fox... And now we need more testers !

Multiple Solutions

(1)
Make multiple runs
(*Dash-like*)

Multiple solutions allow to
see how “*stable*” the
solution is



(2)
Browse solutions

Conclusion & Acknowledgements

*After 20 years... Fox can now index, fit profiles,
... and still solve structures !*

- *Current Fox version allows to solve more flexible structures*

Thanks to:

- ***Vincent Favre-Nicolin***
(CEA and J. Fourier University, Grenoble)
- *Jan Rohlíček, Michal Hušák (ICT Prague)*
- *Lachlan Cranswick... for so many reasons...*



*Improvements depend on **user feedback** !!! Send feedback, feature requests !*
open-source project => add your contribution
=> help by testing "development" versions (subscribe to the
mailing list!)