The other face of Superflip

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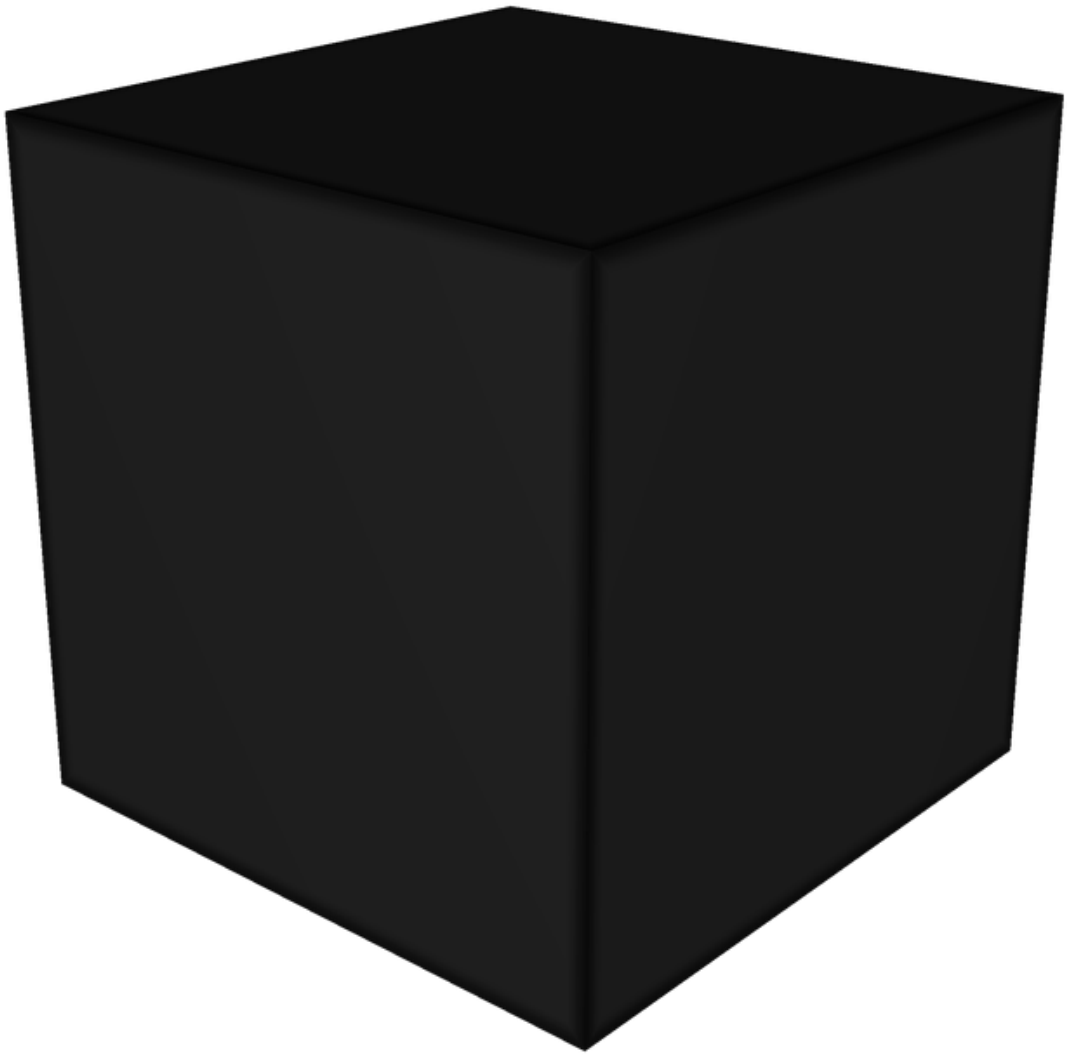
For most people Superflip is a nice game

For most crystallographers Superflip is a black box



Let's look at the inner and other side of Superflip!

Contents

Superflip and all of that

- Superflip is more than a black box
- The Superflip cards
- Applications
  - Forcing Superflip to just one spacegroup
  - Comparison of crystal structures
  - Recovering of the crystal symmetry of DFT structures
  - Fourier applications $\rightarrow$ making nice electron density maps
  - Exercises

L. Palatinus, G. Chapuis, *SUPERFLIP-a computer program for the solution of crystal structures by charge flipping in arbitrary dimensions*. J. Appl. Crystallogr. 2007, **40** 786.

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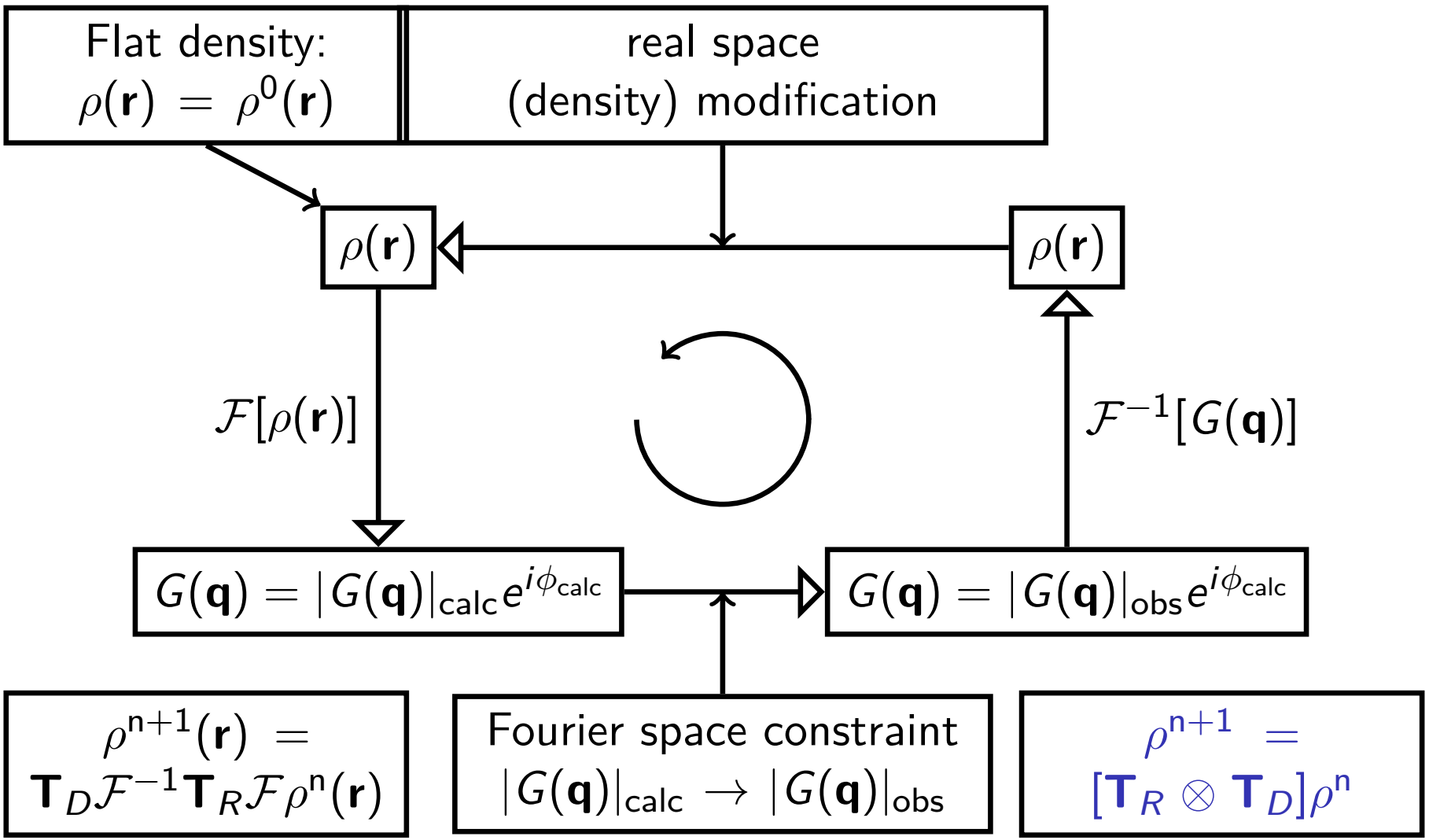
Introduction

Superflip is more than a black box!

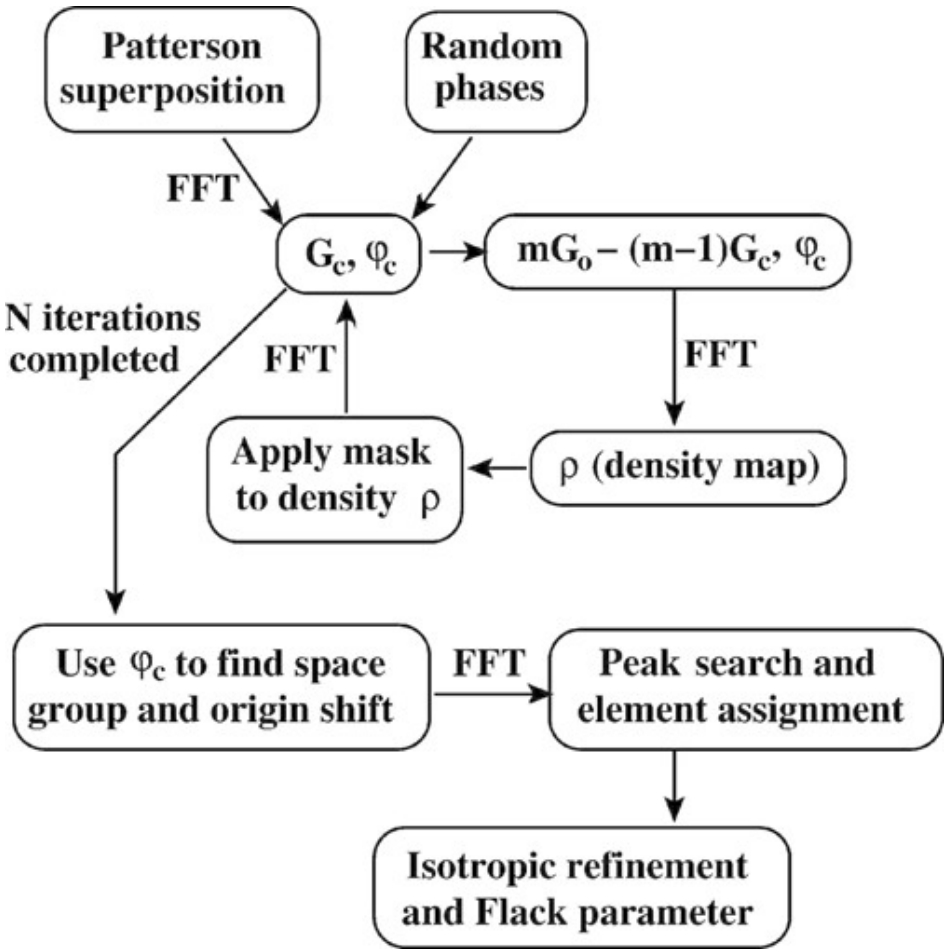
- The default parameters (nearly) always work. A. van der Lee: *Charge flipping for routine structure solution*, J. Appl. Cryst. **46**, 1306-1315 (2013)
- Symmetry recovery. L. Palatinus and A. van der Lee: *Symmetry determination following structure solution in P1*, J. Appl. Cryst. **41**, 975-984 (2008)
- → p. 983: *What we suggest is a change of paradigm: if the structure solution in P1 is equally feasible or even easier than the solution in the correct space group, then it is natural that the determination of the symmetry follows the structure solution rather than preceding it, removing thus one source of ambiguity in the structure-solution process*
- → *G. M. Sheldrick: SHELXT - Integrated space-group and crystal-structure determination*, Acta Cryst. A**71**, 3-8 (2015)

A simple flow diagram for Superflip



Eq. 1 in *Macromolecular structure solution by charge flipping*,
C. Dumas & A. van der Lee, Acta Cryst. D64, 864-873 (2008)

A simple flow diagram for Shelxt



Keywords: Patterson superposition; direct methods (??); dual-space recycling; space-group determination; element assignment.

Superflip & Shelxt - differences and similarities

Similarities

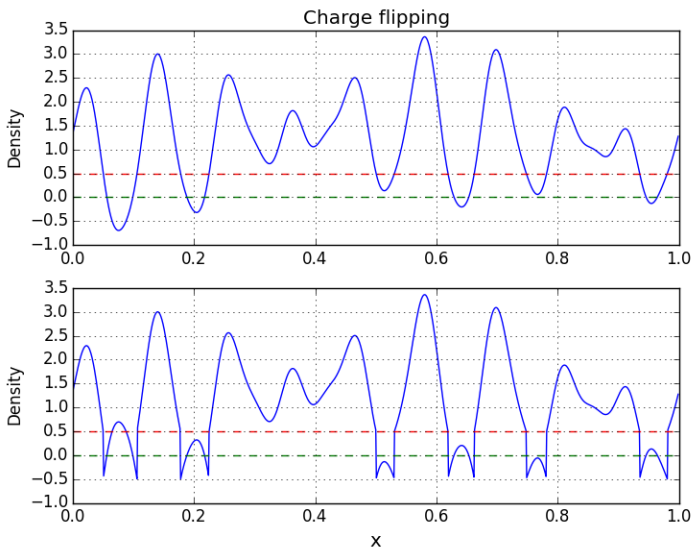
- Both are iterative dual-space methods
- Both apply *constraints* and *perturbations* in both real and reciprocal space
- Both have a very relaxed notion of atomicity
- No direct methods

Differences

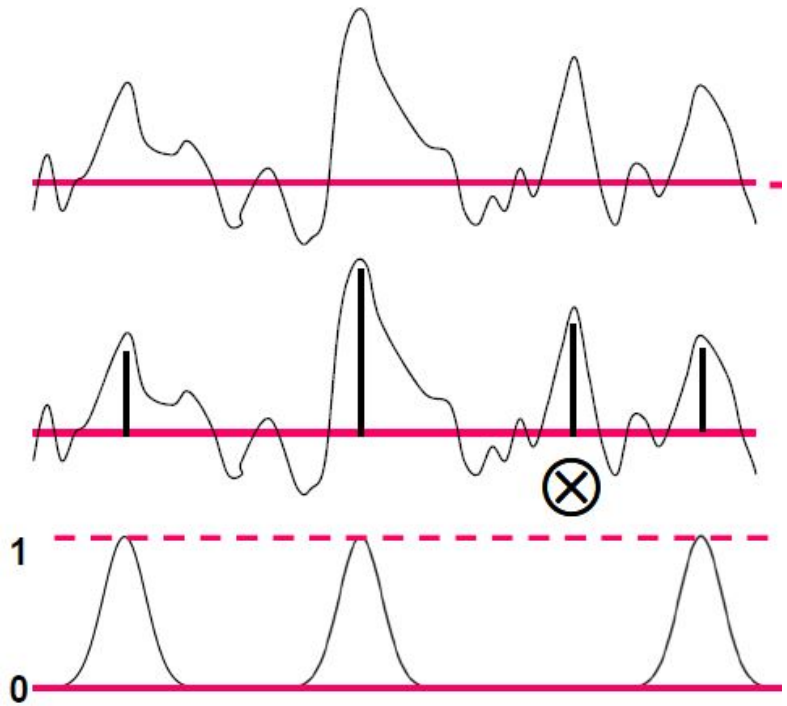
- Real space perturbation
  - Shelxt $\rightarrow$ random omit maps
  - Superflip $\rightarrow$ charge flipping
- Reciprocal space constraint
  - Shelxt $\rightarrow$ complex replacement of $|G_{\text{cal}}|$ by $|G_{\text{obs}}|$
  - Superflip $\rightarrow$ simple replacement of $|G_{\text{cal}}|$ by $|G_{\text{obs}}|$

Superflip & Shelxt - differences and similarities

Real space pertubations



$$\rho_i^{n+1} = \rho_i^n \text{ if } \rho_i^n > \delta$$
$$\rho_i^{n+1} = -\rho_i^{n+1} \text{ if } \rho_i^n < \delta$$



1. search peaks
2. omit a fraction of peaks
3. make a mask $\mathcal{M}$ of unit gaussiens
4. apply $\rho^{n+1} = \mathcal{M}\rho^n$

Superflip & Shelxt - differences and similarities

Reciprocal space constraints

Superflip

Use G_{obs}, normalized F_{obs}

$$|G^{n+1}| = |G_{obs}|$$
$$\phi^{n+1} = \phi_{cal}$$

Weak reflections pertubation:

$$\phi^{n+1} = \phi_{cal} + \pi/2$$

for `weakratio`% of the weakest reflections

Free lunch-*like* algorithm

Shelxt

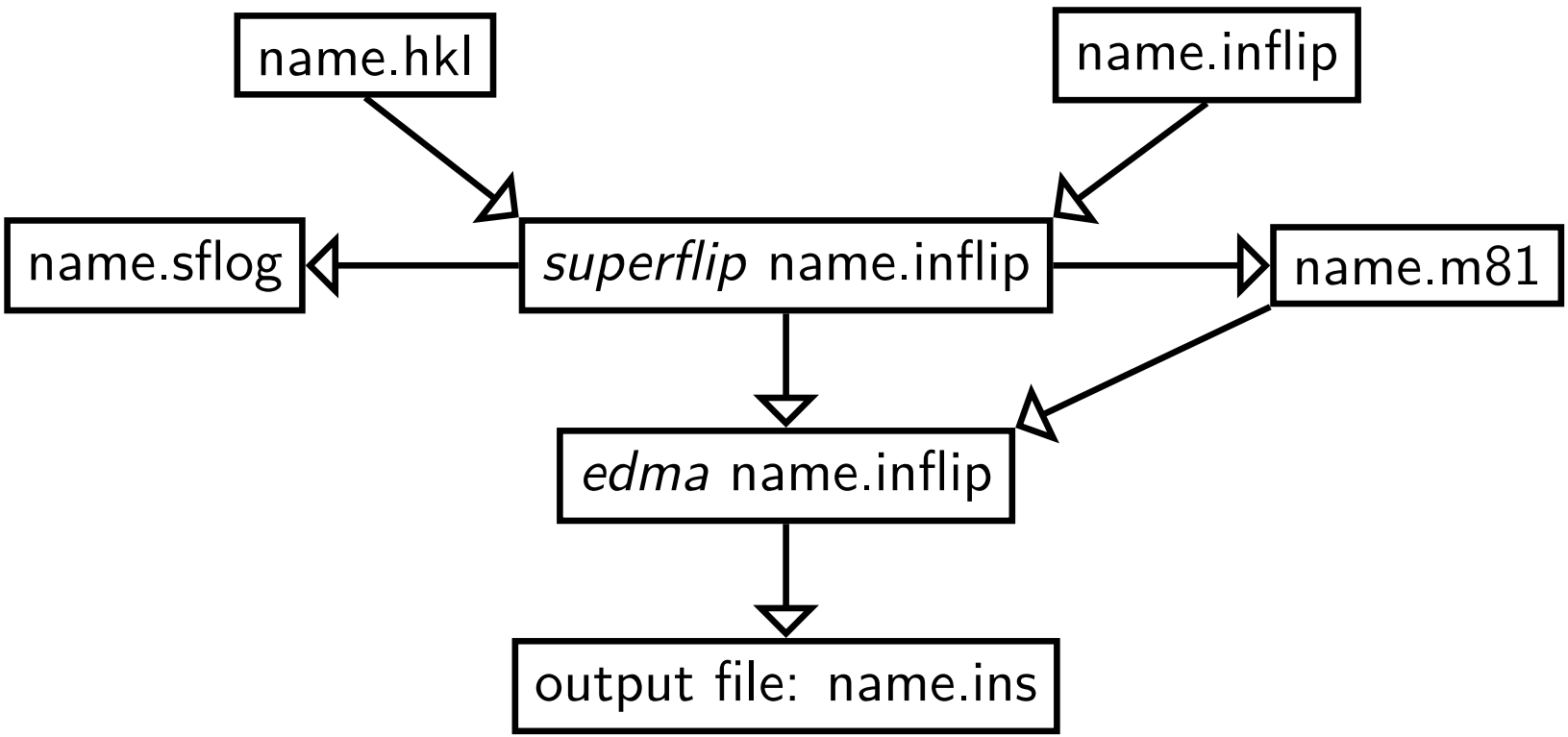
Use $G_{obs} = E_{obs}^{q} F_{obs}^{1-q}$

$$|G^{n+1}| = m|G_{obs}| - (m-1)|G_{cal}|$$
$$\phi^{n+1} = \phi_{cal}$$

m=3 and q=0.5 can be changed

Free lunch algorithm

Flow diagram Superflip



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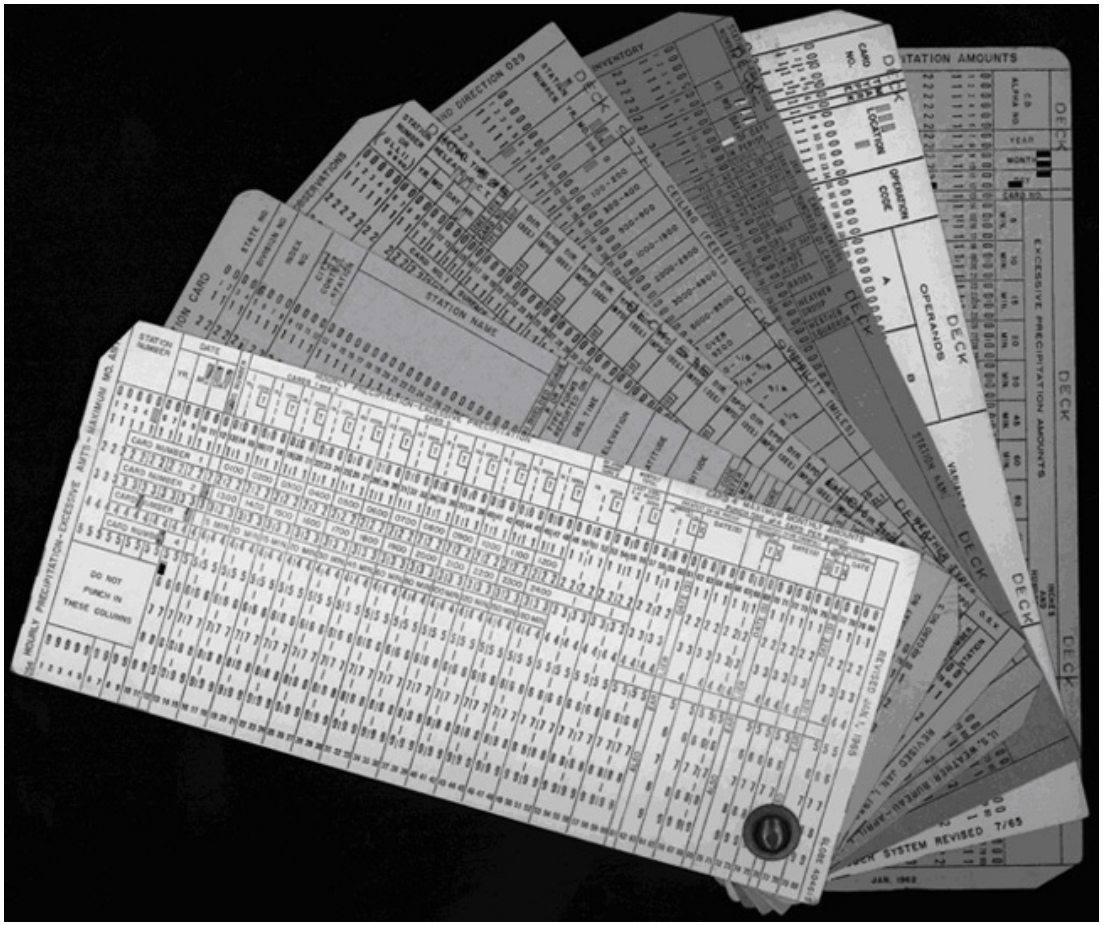
The Superflip 'cards'



The Superflip cards - I

```
# Main keywords
title exp_1614 in C2/c
perform CF                                          #or /lde/general/fourier/symmetry
outputfile sflip.m81 sflip.m80 sflip_sym.ins        #or xplor/ccp4
outputformat jana
dataformat intensity
dimension 3
voxel AUTO
cell 13.158 8.677 7.496 90.000 95.981 90.000        #Laue group used for symmetry determination
spacegroup C2/c
centers
0.0000000000 0.0000000000 0.0000000000
0.5000000000 0.5000000000 0.0000000000
endcenters
symmetry                                            #can be shelx notation
x1 x2 x3
-x1 -x2 -x3
x1 -x2 x3+1/2
-x1 +x2 -x3+1/2
endsymmetry
```

Generalized iterative algorithm

'perform general'

$$\rho^{n+1} = [(1-\beta_1-\beta_2)\mathbf{I} + \beta_1 \mathbf{T}_R^{\gamma_{R1}} \otimes \mathbf{T}_D^{\gamma_{D1}} + \beta_2 \mathbf{T}_D^{\gamma_{D2}} \otimes \mathbf{T}_R^{\gamma_{R2}}]\rho^n$$

$$\text{avec} \qquad \mathbf{T}^{\gamma} = (1+\gamma)\mathbf{P} - \gamma\mathbf{I}$$

Charge flipping: $\beta_1 = 1;\ \beta_2 = 0;\ \gamma_{R1} = 0;\ \gamma_{D1} = 1.$

$$\rho_{n+1} = [\mathbf{T}_R \otimes \mathbf{T}_D]\rho_n$$

$$\mathbf{T}_D^1 = 2\mathbf{P}_D - \mathbf{I}$$

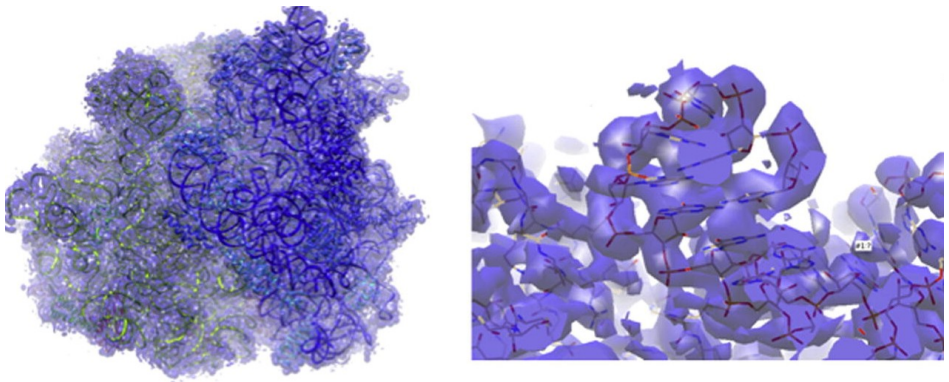
$$\mathbf{P}_D \rightarrow \rho_i^{n+1} = \rho_i^n \text{ if } \rho_i^n > \delta \quad \text{and} \quad \rho_i^{n+1} = 0 \text{ if } \rho_i^n < \delta$$

Low density elimination: $\beta_1 = 1;\ \beta_2 = 0;\ \gamma_{R1} = 0;\ \gamma_{D1} = 0.$

Use of other iterative algorithms?

Small versus large assemblies

- When the standard algorithm does not work
- For extremely large assemblies it has been shown that AAR* and FDF algorithms perform better - the XFEL context!



Lensless coherent imaging of proteins and supramolecular assemblies: Efficient phase retrieval by the charge flipping algorithm, C. Dumas, A. van der Lee, L. Palatinus, *J. Struct. Biol.* **182**, 10–116 (2013)

*AAR = Average Alternating Reflections → `perform general 0.5 1.0 1.0 0.0 0.0 0.0`

The Superflip cards - II

```
# Keywords for charge flipping
delta AUTO                              #or value sigma, e.g.  '1.3 sigma'
weakratio 0.200
Biso 0.000
randomseed AUTO
normalize local                         #wilson/local/atoms/no (default no)
nresshells 100
missing float 0.4                       #handling missing reflections

searchsymmetry average                  #no/shift
derivesymmetry use                      #yes/no/use [limit agreement
factor]

fastftt yes

dataformat shelx                        #shelx/amplitude/intensity
fbegin name.hkl
endf
# End of keywords for charge flipping
```

The value of δ .... depends on the scale factor

$$\begin{aligned} \rho^{i}_{n+1} &= \rho^{i}_{n} \text{ if } \rho^{i}_{n} > \delta \\ \rho^{i}_{n+1} &= -\rho^{i}_{n+1} \text{ if } \rho^{i}_{n} < \delta \end{aligned}$$

Use the standard deviation (square root of the variance) σ of the electron density instead:

$$\sigma = \sqrt{< \rho^{i} - \bar{\rho} >} = (1/V^2) \sum_{\mathbf{q} \neq \mathbf{0}} |F_{obs}(\mathbf{q})|^2 \quad \text{Parseval's theorem!}$$

Then we can write:

$$\begin{aligned} \rho^{i}_{n+1} &= \rho^{i}_{n} \text{ if } \rho^{i}_{n} > k_{ed}\sigma \\ \rho^{i}_{n+1} &= -\rho^{i}_{n+1} \text{ if } \rho^{i}_{n} < k_{ed}\sigma \end{aligned}$$

Handling of symmetry in Superflip

The cards

- symmetry - endsymmetry → is used for averaging the reflections in the input file; reflections are then expanded in $P1$
- searchsymmetry no/shift/average → given symmetry elements are searched for and eventually the density is shifted and/or averaged accordingly
- derivesymmetry yes/no/use → symmetry compatible with cell metrics and centering can be determined and applied or not

The symmetry agreement factor ϕ_{sym}

$$\begin{aligned} \phi_{\text{sym}}(\mathcal{S}) &= C \cdot \frac{\sum_{\mathbf{h}} |F_{\mathbf{h}} F_{\mathbf{hR}}| \Delta^2_{\mathbf{h},\mathcal{S}}}{\sum_{\mathbf{h}} |F_{\mathbf{h}} F_{\mathbf{hR}}|} \\ \text{avec } \Delta_{\mathbf{h},\mathcal{S}} &= |\varphi(\mathbf{h}) - \varphi(\mathbf{hR}) - 2\pi \mathbf{h} \cdot \boldsymbol{\tau} + 2\pi n| \end{aligned}$$

Definition

- if $\Phi_{\text{sym}}(\mathcal{S}) = 0.00$ then $\rho(\mathbf{r})$ is perfectly symmetrical with respect to $\mathcal{S}$
- if $\Phi_{\text{sym}}(\mathcal{S}) = 1.00$ then $\rho(\mathbf{r})$ is completely random with respect to $\mathcal{S}$

Example (sflog-file)

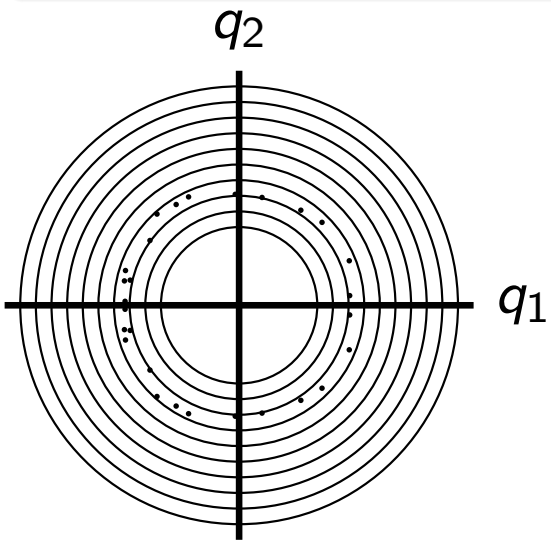
	Symmetry operations			Symmetry operation agreement factor	
c(0,1,0):	x1	-x2	1/2+x3	0.193	xxxxxxxxxxxxxxxxxxxxxxxxxxxxxxxxxxxxxxxxxxxxxxxxx
2(0,1,0):	-x1	x2	-x3	2.022	xxxxxxxxxxxxxxxxxxxxxxxxxxxxxxxxxxxxxxxxxxxxxxxx
-1:	-x1	-x2	-x3	2.200	xxxxxxxxxxxxxxxxxxxxxxxxxxxxxxxxxxxxxxxxxxxxxxxx
m(0,1,0):	x1	-x2	x3	68.937	xxxxxxxxxxxxxxxx

```
-------------------------
Space group derived from the symmetry operations:
-------------------------
HM symbol:  C2/c
Hall symbol:  -C 2yc
Fingerprint:  33122260n0321 (0,0,0)
Centering vectors:
0.000 0.000 0.000
0.500 0.500 0.000
Symmetry operations:
1:  x1 x2 x3
2(0,1,0):  -x1 x2 1/2-x3
-1:  -x1 -x2 -x3
c(0,1,0):  x1 -x2 1/2+x3
```

Normalizing structure factors - I

No, Wilson, atoms, or local?

- No → slower convergence (default)
- Wilson → in contradiction with *ab initio* character of charge flipping!
- atoms → wilson, but only for atoms of composition
- local → gives *in general* the best results (Karle approach)



$$E_{\mathrm{obs,i}} = \frac{|F_{\mathrm{obs,i}}|/\sqrt{\epsilon_{\mathrm{i}}}}{\sqrt{\sum^{N}[|F_{\mathrm{obs,i}}|^2/N\epsilon_{\mathrm{i}}]}}$$

N is the number of reflections in resolution shell; the number of reflection shells is determined by the Superflip keyword nresshells.

Normalizing structure factors - II

Wilson

$$E_{\mathrm{obs,i}} = \frac{|F_{\mathrm{obs,i}}|}{\sqrt{\epsilon_{\mathrm{i}} \sum^{M} [|f_{\mathrm{j}}|^2]}}$$

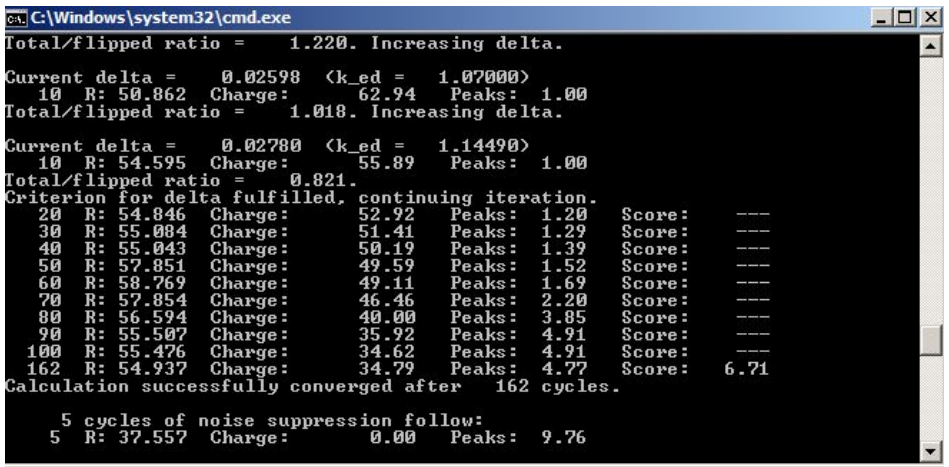
M is the number of different elements in the unit cell.

Local

$$E_{\mathrm{obs,i}} = \frac{|F_{\mathrm{obs,i}}|/\sqrt{\epsilon_{\mathrm{i}}}}{\sqrt{\sum^{N} [|F_{\mathrm{obs,i}}|^2/N\epsilon_{\mathrm{i}}]}}$$

N is the number of reflections in the resolution shell.

What do I see when the program is running?

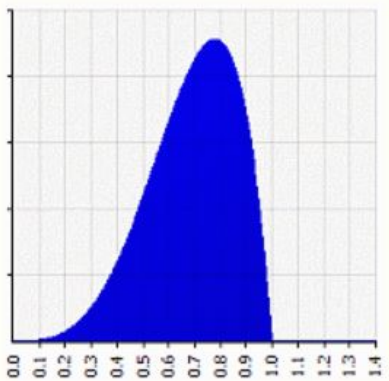


The flipped charge is $\sum |\rho_i|$ summed over all pixels for which $\sum |\rho_i| < \delta$

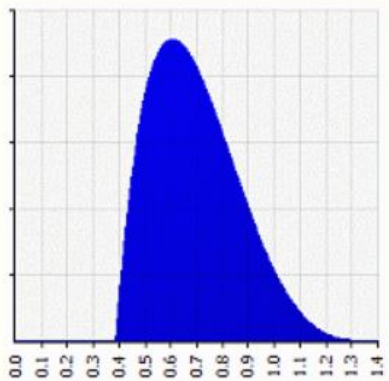
Peaks = peakiness = skewness of the histogram of the density = $\frac{1}{A}\sum_i(\rho_i - \bar{\rho})^3$ (third moment of data set)

Electron density histograms

A density histogram is a probability distribution of values of the electron density sampled at regular intervals (grid points) throughout the 3-dimensional map



Beta(α=4.5, β=2)
skewness = −0.5370



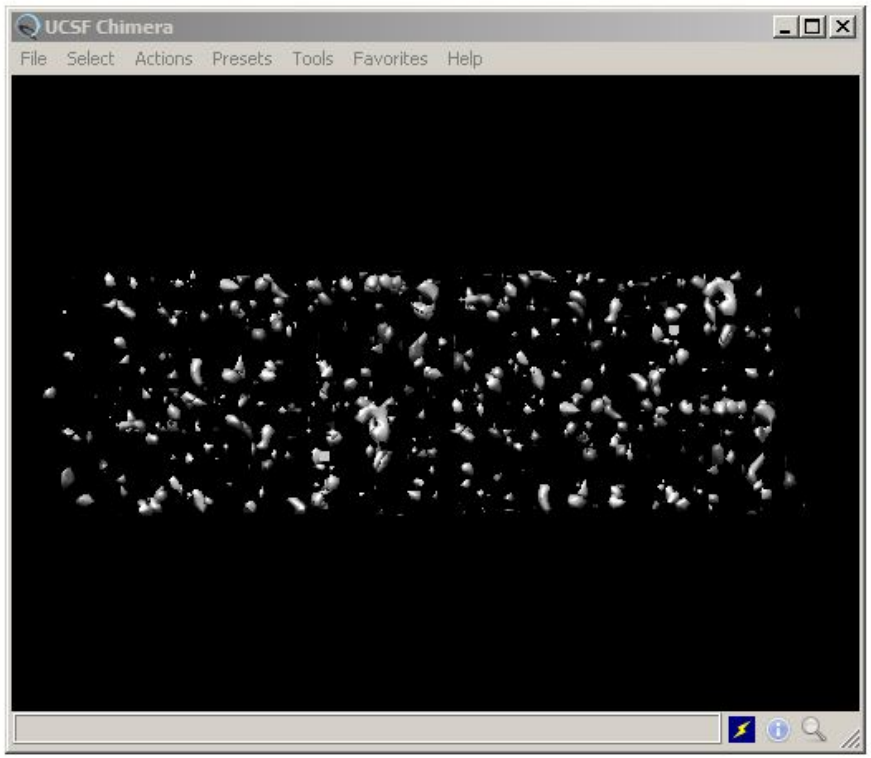
1.3846 − Beta(α=4.5, β=2)
skewness = +0.5370

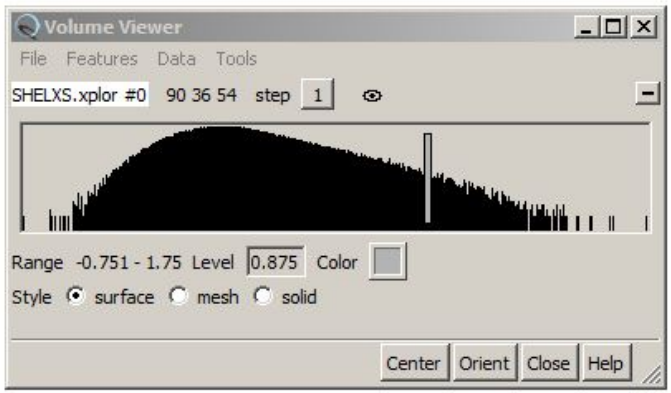
$$\overline{x} = \sum_{N} x_i$$

$$\overline{x_2} = \frac{1}{N} \sum_{N} (x_i - \overline{x})^2$$

$$\overline{x_3} = \frac{1}{N} \sum (x_i - \overline{x})^3$$

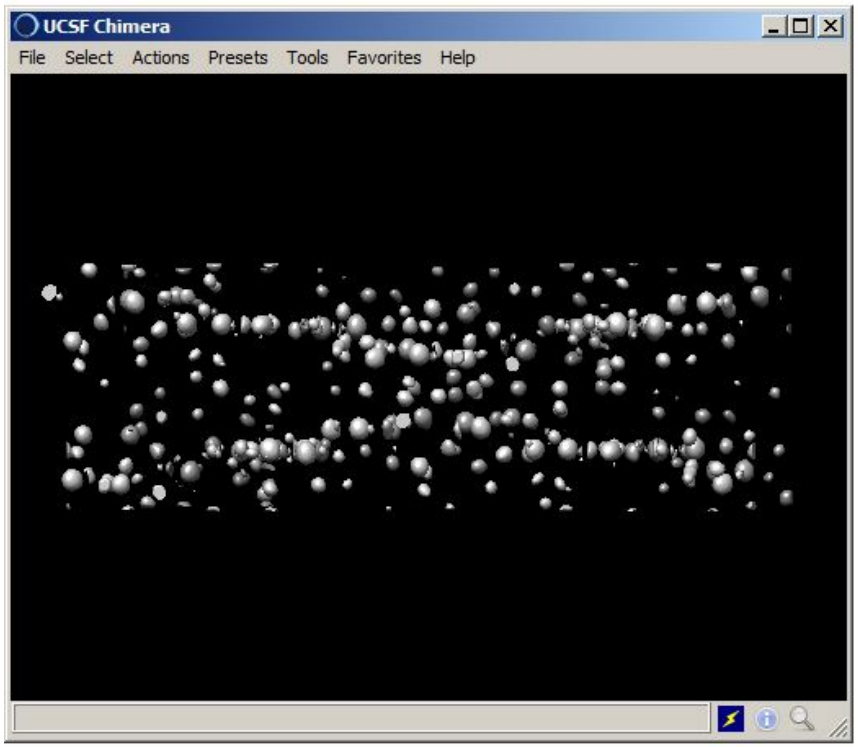
Electron density histograms - 'bad'

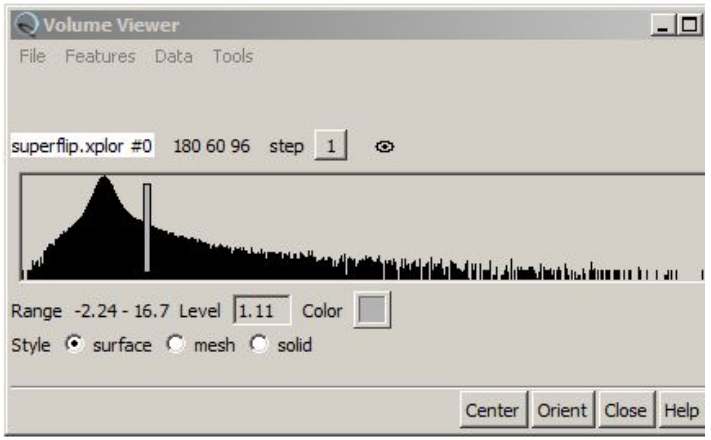




peaks ≈ 1

Electron density histograms - 'good'





peaks ≈ 6

Detection of convergence & solution

Superflip

Parameters

- `Convergencemode peakiness/charge/rvalue/symmetry/normal [value]`
  - peakiness 3.0
  - charge
  - rvalue 30%
  - symmetry
  - normal → CFOM 0.8

Detection of convergence & solution

Shelxt

Parameters

- CC,R(weak),CHEM
  - CC → correlation coefficient between G_{obs} and G_{cal} (100%)
  - R(weak) = $< E^2 >$ for 10% smallest E_{cal}: has to be close to 0.0
  - CHEM → fraction of angles for peak-peak distances between 1.1 and 1.8 Å lying between 95°and 135°(not for inorganics)
  - CFOM = 0.01CC - R(weak)
- $\alpha \rightarrow$ symmetry agreement factor
- $R_1 \rightarrow$ after isotropic refinement

The 'cards' of Superflip - III (EDMA)

```
# EDMA-specific keywords
inputfile sflip.m81
outputbase sflip
export sflip.ins                #cif, ins, m40
numberofatoms 0                 #guess/composition; 0 = guess
composition C H N O             #with composition C2 H5 N2 O2
maxima all                      #none/all/atoms
fullcell no
scale fractional
plimit 1.5 sigma                #real number [absolute/relative/sigma]
centerofcharge yes              #useful in case of anharmonicity etc.
chlimit 0.2500                  #only pixels > ρmax are used
# End of EDMA-specific keywords
```

L. Palatinus, S. J. Prathapa, S. van Smaalen, *EDMA: a computer program for topological analysis of discrete electron densities.* J. Appl. Cryst. 2012, **45**, 575-580

The 'cards' of Superflip - IV (EDMA)

Input file EDMA

- If `derivesymmetry use` then new `symmetry` ··· `endsymmetry` cards are needed!
- `cell` card also needed
- critical points can be determined with `criticalpoints` keyword

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Forcing Superflip to analyze only one spacegroup

Why and how ?

- Why?
  - Organometallic structures with heavy element on special position often confuse Superflip
  - Moderately twinned structures often confuse Superflip (example follows)
- How?
  - Superflip → `searchsymmetry average & derivesymmetry no`
  - Shelxt → `shelxt -s"P2(1)_c"`

Comparing crystal structures

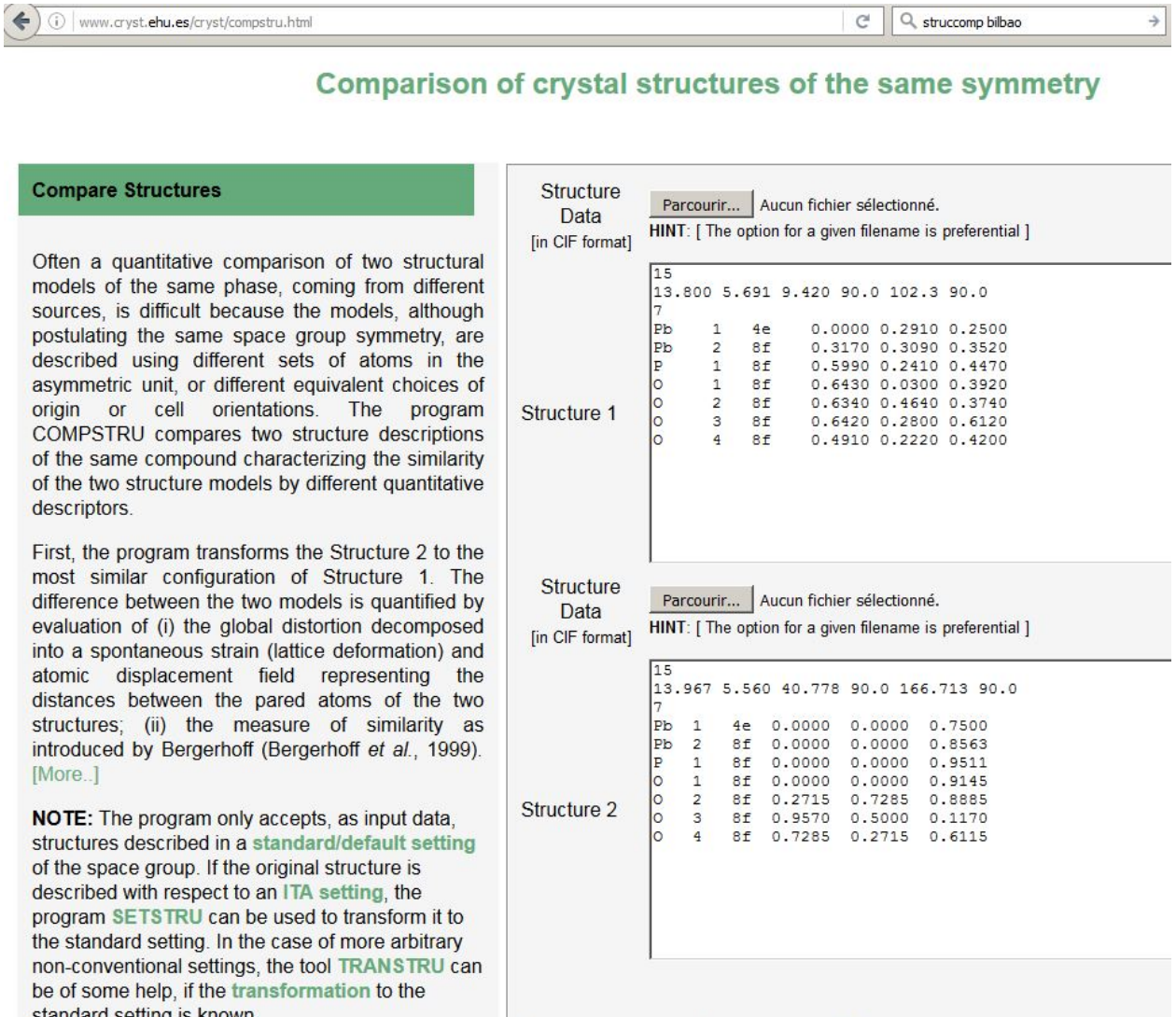
"The DFT calculations have validated the crystal structure ···"

- DFT crystal structures (not gas-phase molecules!) have been optimized in $P1$
- Need to go back to original space group symmetry
- Need for comparison with the structure determined with X-ray diffraction

Problem is also recurrent in ab initio crystal structure predication: how to remove duplicates?

Solutions - Bilbao's *COMPSTRU*

http://www.cryst.ehu.es/cryst/compstru.html



Solutions: Bilbao's *COMPSTRU* - II

http://www.cryst.ehu.es/cryst/compstru.html

WP		Atom	Atomic Displacements			
			u_x	u_y	u_z	|u|
4a	(x,y,z)	C1	0.0087	0.0303	0.0042	0.3295
4a	(x,y,z)	C2	-0.0263	-0.0059	0.0012	0.3474
4a	(x,y,z)	C3	-0.0308	0.0083	-0.0024	0.4112
4a	(x,y,z)	C4	-0.0001	0.0510	-0.0046	0.5064
4a	(x,y,z)	C5	0.0035	0.0432	-0.0022	0.4254
4a	(x,y,z)	C6	0.0028	0.0372	-0.0001	0.3636
4a	(x,y,z)	C7	-0.0031	0.0314	0.0015	0.3097
4a	(x,y,z)	C8	0.0101	-0.0313	0.0024	0.3355
4a	(x,y,z)	C9	0.0213	-0.0355	0.0019	0.4442

Solutions: Bilbao's *COMPSTRU* - III

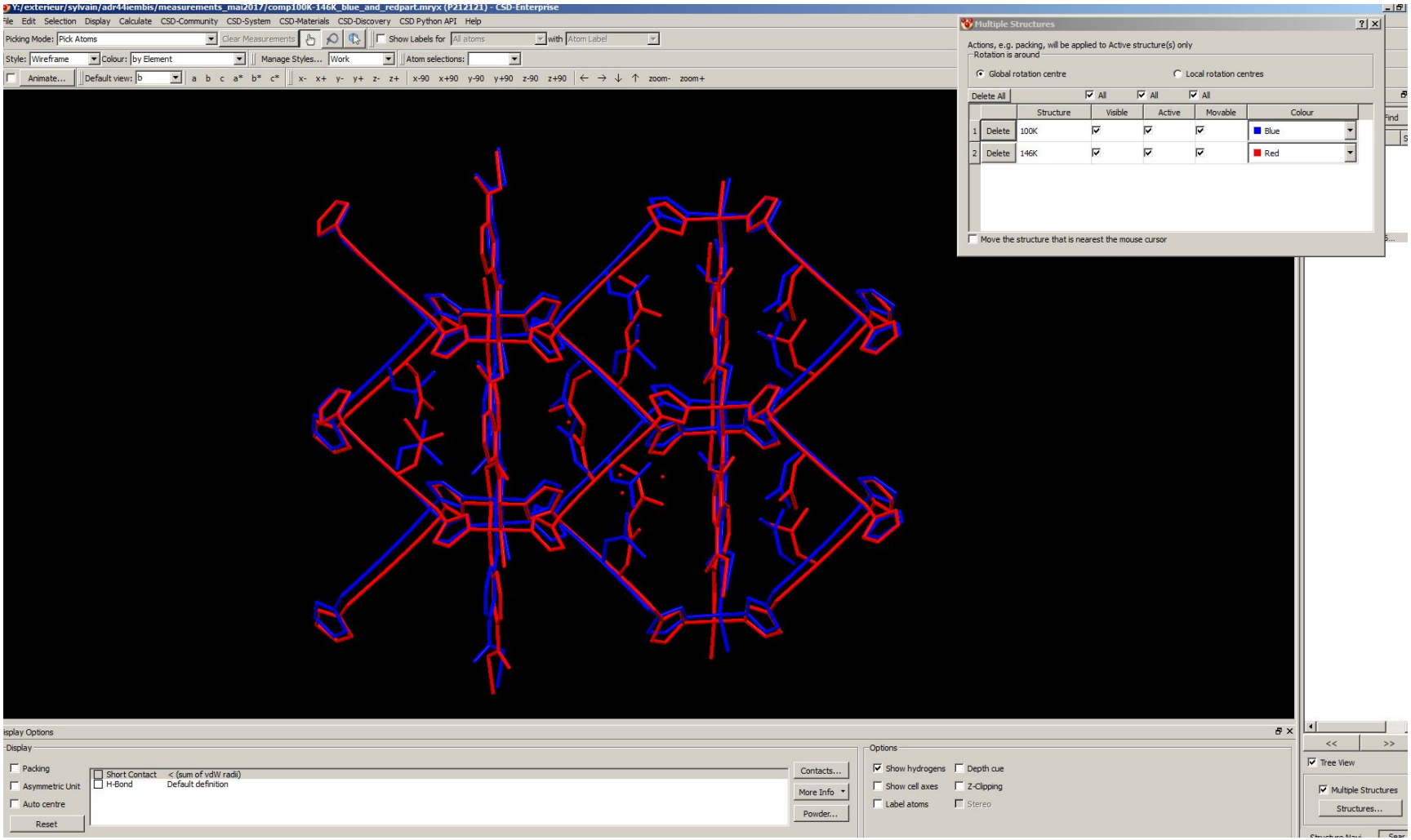
http://www.cryst.ehu.es/cryst/compstru.html

Evaluation of the structure similarity

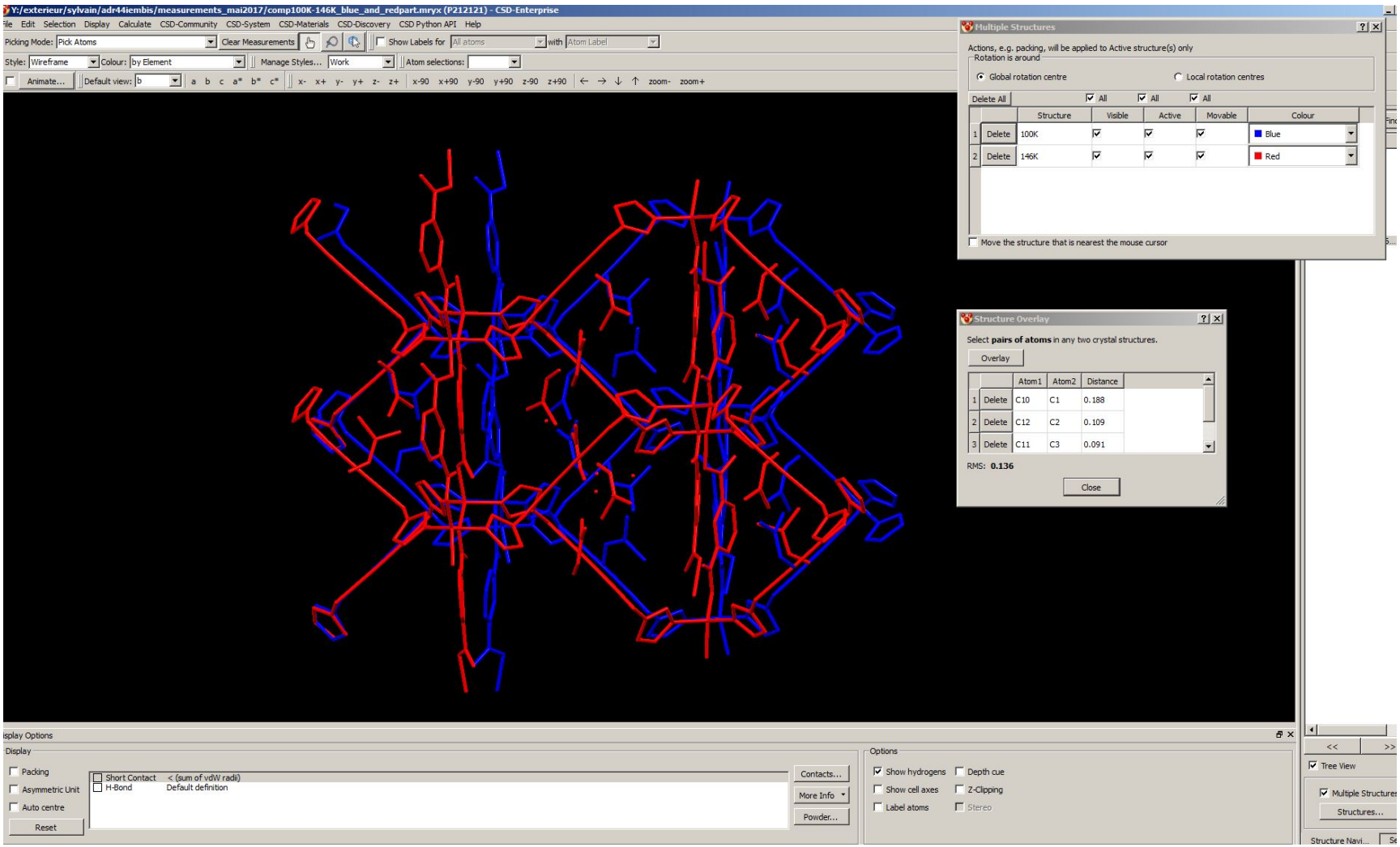
S	$d_{max.}$ (Å)	$d_{av.}$ (Å)	Δ
0.0085	1.7441	0.4059	0.106

- Lattice and atomic position criteria:
  - The degree of lattice distortion (S) is the spontaneous strain (sum of the squared eigenvalues of the strain tensor divided by 3). For the given two structures, the **degree of lattice distortion (S)** is **0.0085**.
  - The maximum distance ($d_{max.}$) shows the maximal displacement between the atomic positions of the paired atoms. The **maximum distance ($d_{max.}$)** in this case is: **1.7441 Å**
- The arithmetic mean (d_{av}) of the distance. In this case, the **arithmetic mean (d_{av})** is **0.4059 Å**
- The measure of similarity (Δ) (Bergerhoff *et al.*, 1998) is a function of the differences in atomic positions (weighted by the multiplicities of the sites) and the ratios of the corresponding lattice parameters of the structures. The **measure of similarity (Δ)** calculated for this case is **0.106**.

Solutions: Mercury's "Structure Overlay" option - I



Solutions: Mercury's "Structure Overlay" option - II

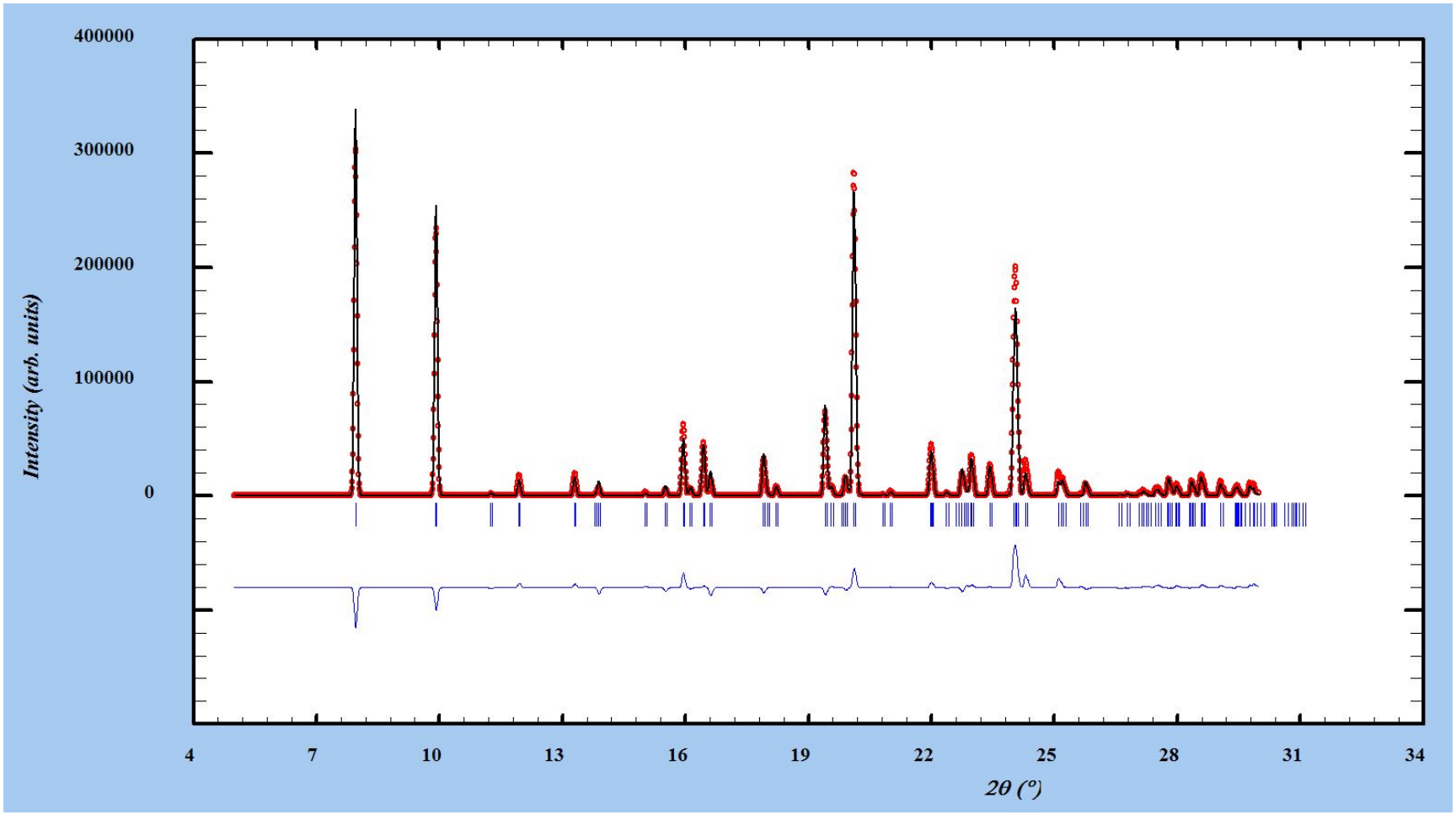


Solutions: Powder diffractogram comparison - I

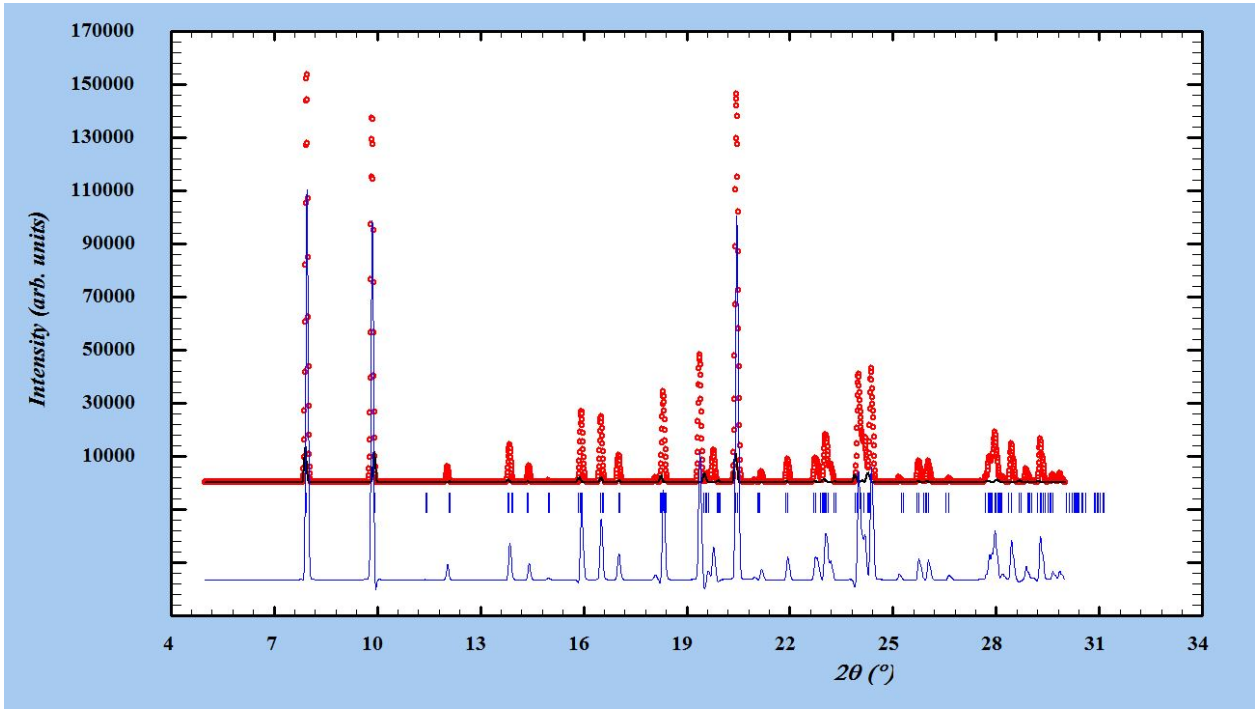
Recipe

- Manual alignment of cell parameters from DFT and X-ray structure
- Calculate X-ray diffractogram for experimental structure
- Calculate X-ray diffractogram for DFT structure
- Refine scale factor and compare

Solutions: Powder diffractogram comparison - II



Solutions: Powder diffractogram comparison - III



- DFT cell parameters: 12.786199 22.237999 9.808199 90.0 90.0 90.0
- X-ray cell parameters: 12.826199 22.337999 9.728199 90.0 90.0 90.0

A. Duarte Rodrigues, K. Fahsi, X. Dumail, N. Masquelez, A. van der Lee, S. Mallet-Ladeira, R. Sibille, J.-S. Filhol, S. G. Dutremez, *Chem. Eur. J.*, accepted (2017).

Solutions: Powder diffractogram comparison - IV

Journal of COMPUTATIONAL CHEMISTRY

A Generalized Expression for the Similarity of Spectra: Application to Powder Diffraction Pattern Classification

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Solutions: Superflip - *referencefile & modelfile*

- referencefile: Superflip *aligns* (≈ *compares*) the charge flipping density with a reference density (format .m81, .cif, .xplor)
  - can be used to fix the location of the symmetry operations there where you want them to be
  - can be used to diminish noise on successive CF runs (`repeatmode` *n*)
  - can be used to compare two structures - in conjunction with `perform symmetry` and modelfile *name*
- modelfile:
  - can be used for setting starting phases - with `perform cf`
  - can be used for determining the symmetry in a density - with `perform symmetry`

The Minimum Superposition Method revisited

Shelxt & Superflip

- Shelxs
  - based on the *Patterson superposition minimum function* (Buerger, 1959; Sheldrick, 1991)
  - instructions PATT (instead of TREF) & VECT
  - default starting map in Shelxt
- Superflip
  - use the card `modelfile superposition 0.05`

How does it work? [from the Shelxs manual]

The Patterson function is calculated twice, displaced from the origin by +U and -U, where U is the superposition vector. At each grid point the lower of the two values is taken, and the resulting superposition minimum function is interpolated to find the peak positions. This is a much cleaner map than the original Patterson and contains only 2N (or 4N etc. if the superposition vector was multiple) peaks rather than $N^{\check{s}}$. The superposition map should ideally consist of one image of the structure and its inverse; it has an effective space group of $P\bar{1}$ (or $C\bar{1}$ for a centered lattice etc).

Solutions: perform symmetry I

Or: bringing back DFT structures to their actual spacegroup symmetry

```
title alpha235K symmetrized
perform symmetry
outputfile sflip.m81 sflip_edma.ins
outputformat jana
modelfile alpha235K.cif
dimension 3
voxel AUTO
cell 7.9191 5.8957 49.6875 90.0 95.9899 90.00
#DFT cell 7.9191 5.8957 49.6875 90.0553 95.9899 89.9097
spacegroup P 1
centers
0.5000000000 0.5000000000 0.5000000000
endcenters
symmetry
x, y, z
endsymmetry
searchsymmetry average
derivesymmetry use
```

Solutions: perform symmetry II

```
# begin EDMA
inputfile sflip.m81
outputbase sflip
export alpha235K_symmetrized.ins
numberofatoms 0
composition C O S
maxima all
fullcell no
scale fractional
plimit 1.5 sigma
centerofcharge yes
chlimit 0.2500
# End of EDMA-specific keywords
```

Comparing two structures - I

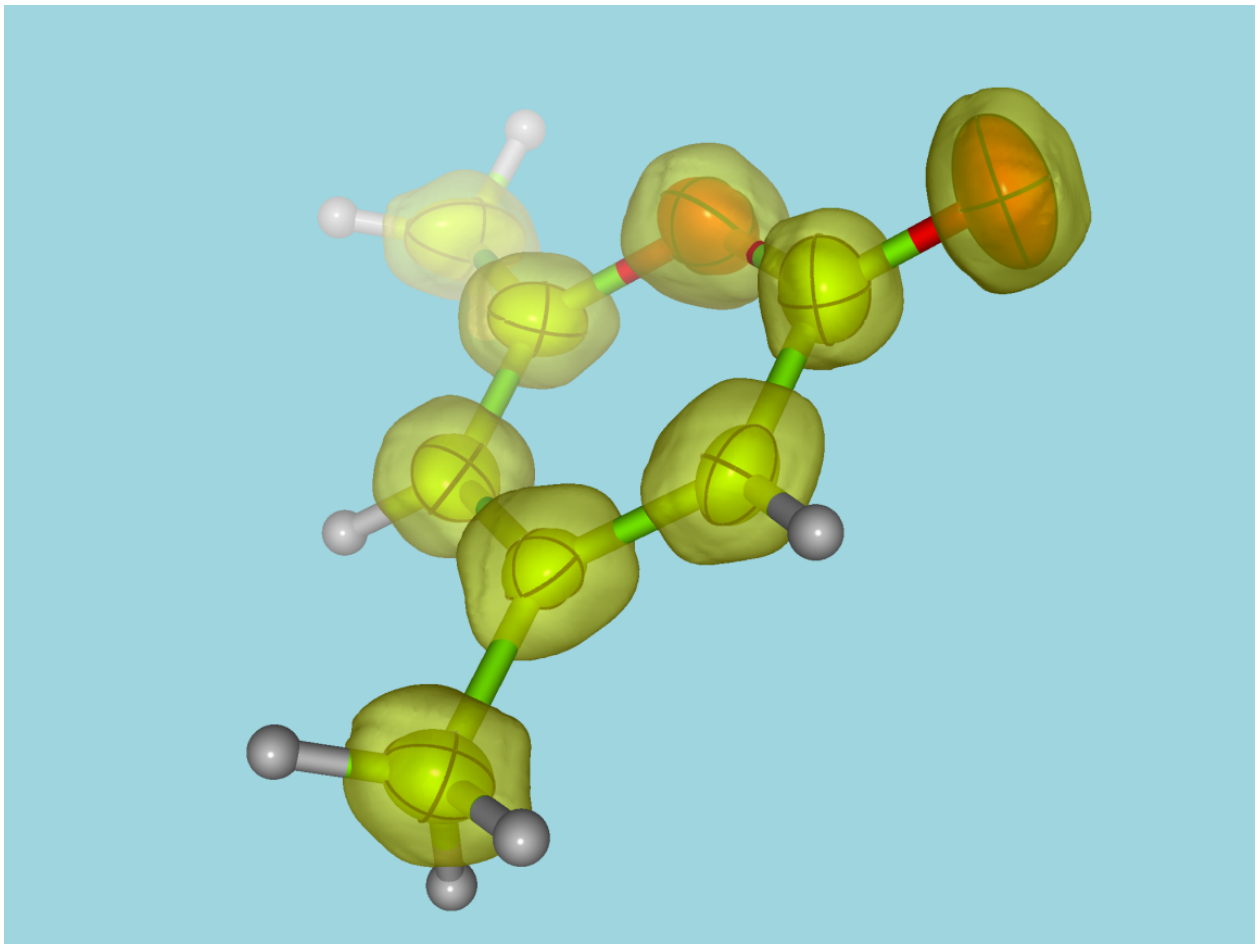
```
#Compare structures name1 and name2
#=========================================
perform symmetry
title compare two structures in Pna21
# Basic crystallographic information
cell 10.9732 12.7636 20.7212 90.0000 90.0000 90.0000
symmetry
x,y,z
-x,-y,0.5+z
1/2-x,1/2+y,1/2+z
1/2+x,1/2-y,z
endsymmetry
centers
0.00 0.00 0.00
endcenters
voxel 24 32 48
# Output density map and compare structures
searchsymmetry average
derivesymmetry use
modelfile name2.m81
referencefile name1.cif
outputfile out.m81
```

Comparing two structures - II

checking .sflog file

```
........
The resulting density will be shifted and averaged according to the
symmetry operations given above.
Following symmetry operations will be used to locate the origin of
symmetry:  3 4
The resulting density will be shifted so that is matches the reference
density.
The density was aligned with the reference file, agreement 14.86%.
Shift:  0.00000 0.00000 0.18833
........
```

Superposing an electron density map on a cif structure



Superposing an electron density map on a cif structure

Problems

- SHELXL and CRYSTALS do not output electron density maps
- JANA does output the electron density map, but in the 'wrong' format
- Using external programs, e.g. VMD or VESTA, one is faced with the 'alignment problem'
- Solution $\rightarrow$ get it all-right with SUPERFLIP

`perform fourier` and `referencefile name` are your friends!

Superposing an electron density map on a cif structure

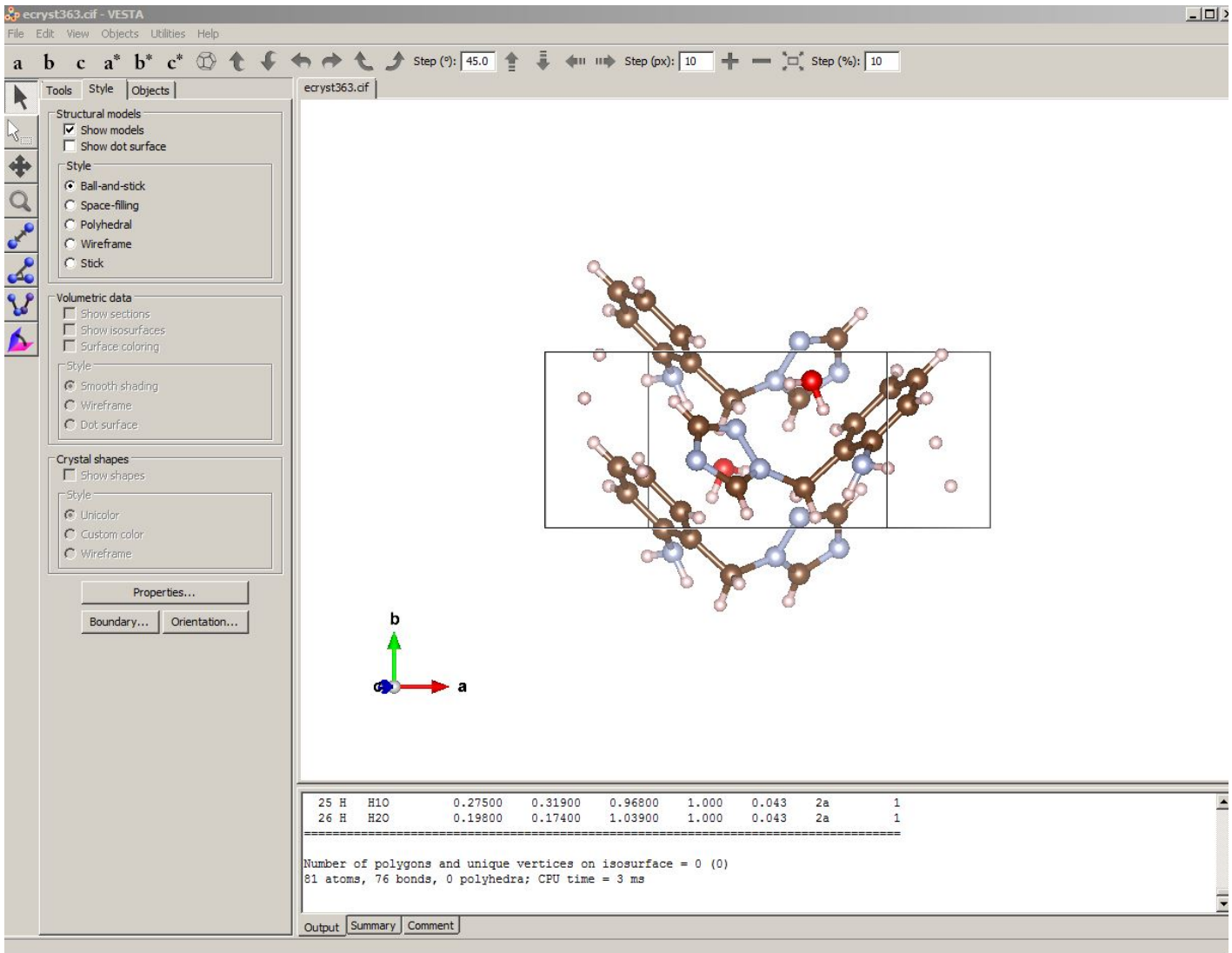
```
#=============================================
# Fourier transformation of structure factors
#=============================================
title Fourier transform of Crystals phased structure factors
perform fourier
# Basic crystallographic information
cell 13.6203 13.0436 28.5132 90.00 94.708 90.00
symmetry
x y z
-x -y -z
-x y+1/2 -z+1/2
x -y+1/2 z+1/2
endsymmetry

# Keywords influencing the CF algorithm
voxel AUTO
terminal no

# Output density map and phased hkl reflections
searchsymmetry average
derivesymmetry yes
outputfile yml47b.xplor
referencefile yml47b.cif

# Input reflections and normalization
dataformat amplitude phase                    phase is expressed as a multiple of 2π
#dataformat a b                               real and imginary part of the structure factor
fbegin fort.12
endf
```

Superposing an electron density map on a cif structure

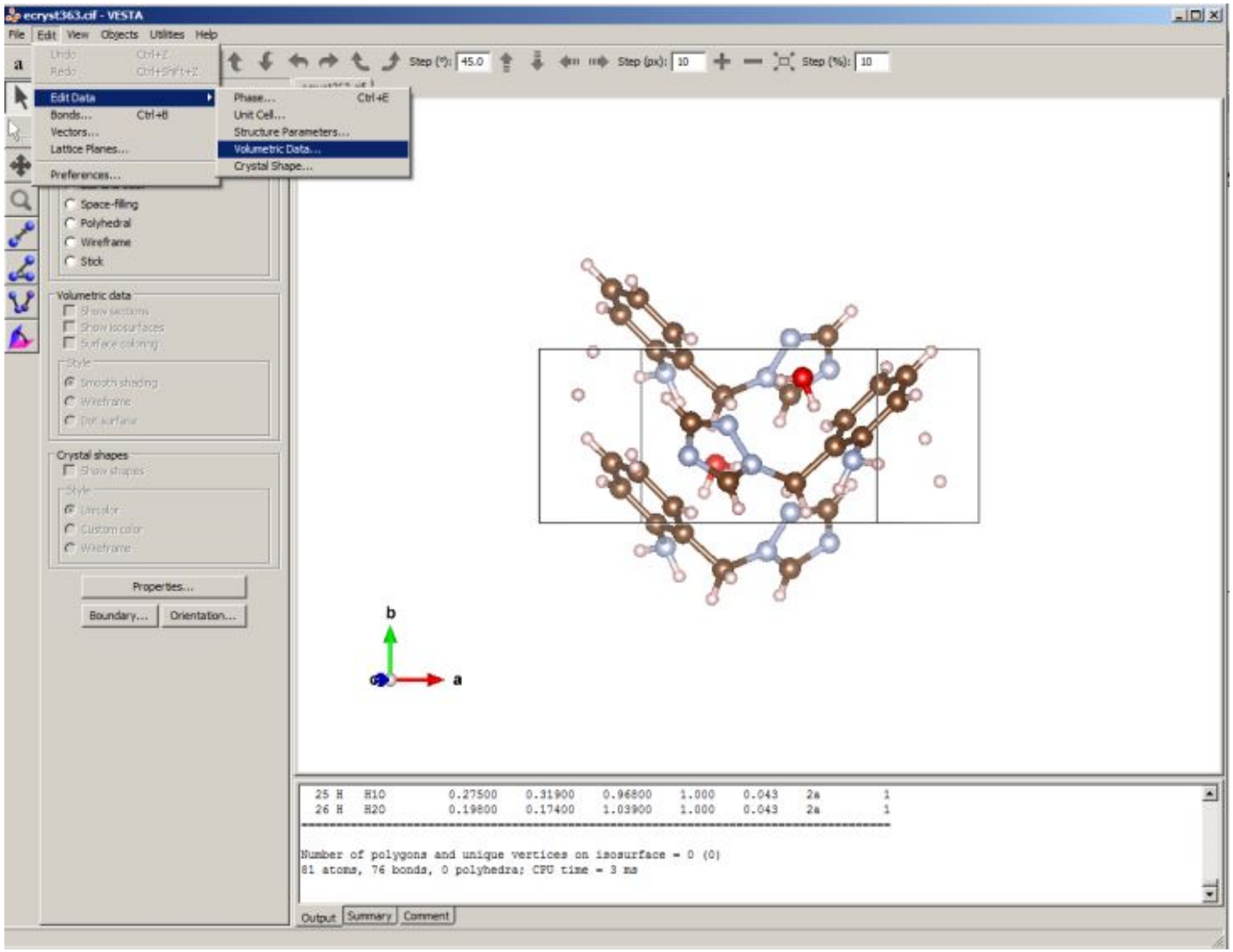
From SHELXL or CRYSTALS to VESTA

- SHELXL
  - LIST 3 → Write h,k,l, Fo, sigma(Fo), A(real) and B(imag) in FORMAT(3I4,4F8.2)
  - LIST 5 → Write h,k,l, Fo, Fc, and phase in degrees in FORMAT(3I4,2F10.2,F7.2)
  - if LIST5 convert phase to multiples of 2π
- CRYSTALS (phase is in radians)
  - type on the command line: `\punch 6 C` (this creates bfile.pch)
  - convert phase to multiples of 2π
  - `read(10,'(3I4, F10.2, F8.2, F10.2, F8.4, G12.5, F10.5)')IH, IK, IL,FO, SIGMAFO,FC,PHASE,SQRTW,CORRECT`
- JANA → run Fourier (F(obs)) in order to obtain name.m81

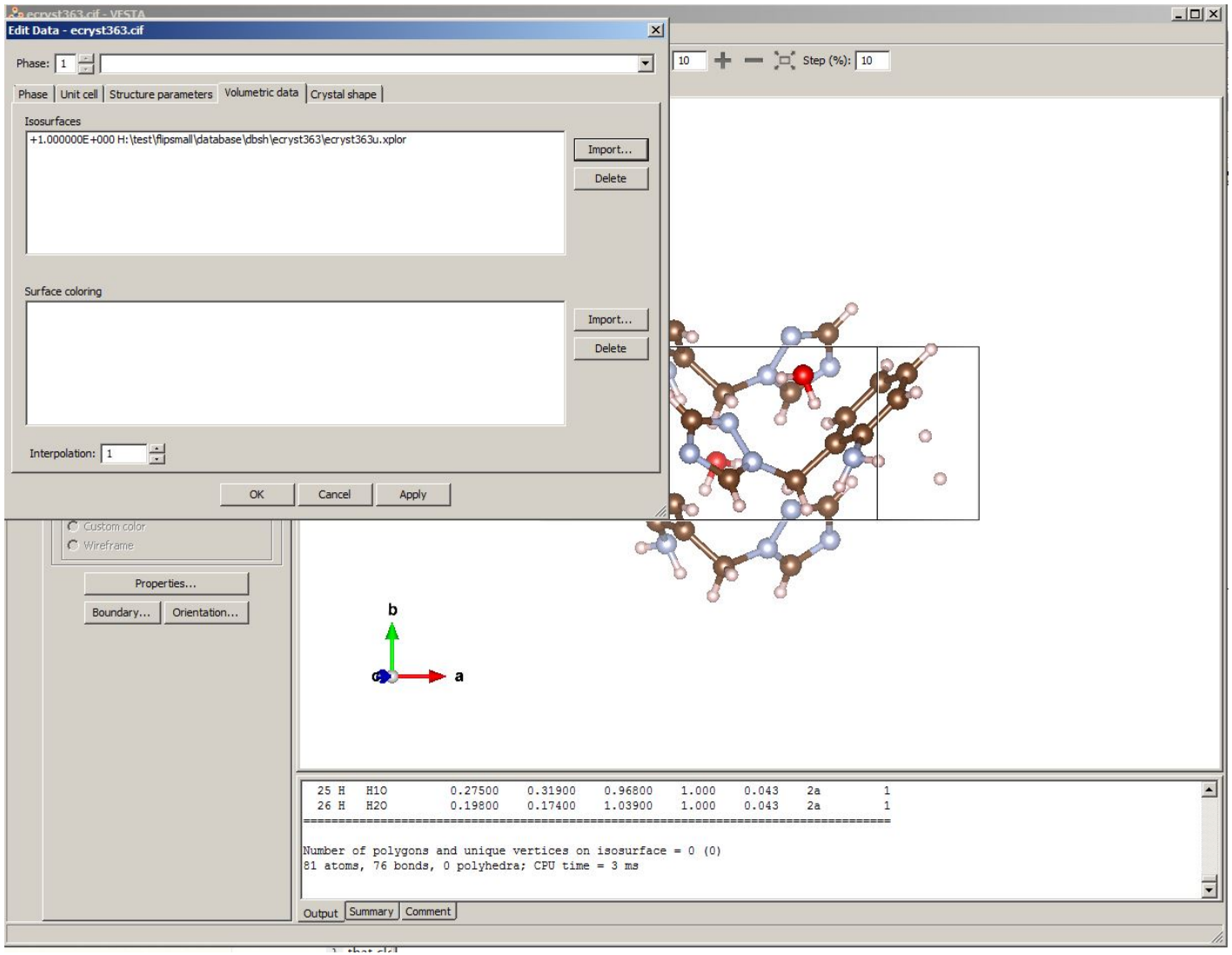
Superposing an electron density map on a cif structure



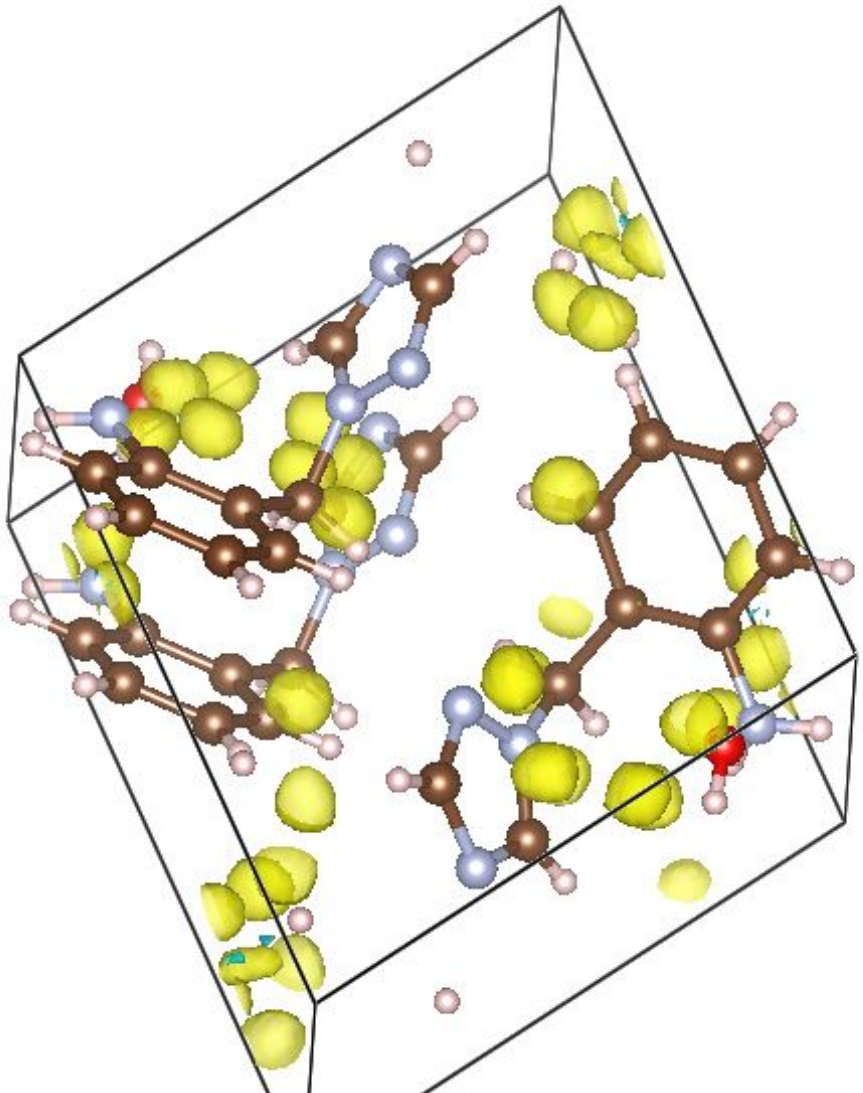
Superposing an electron density map on a cif structure



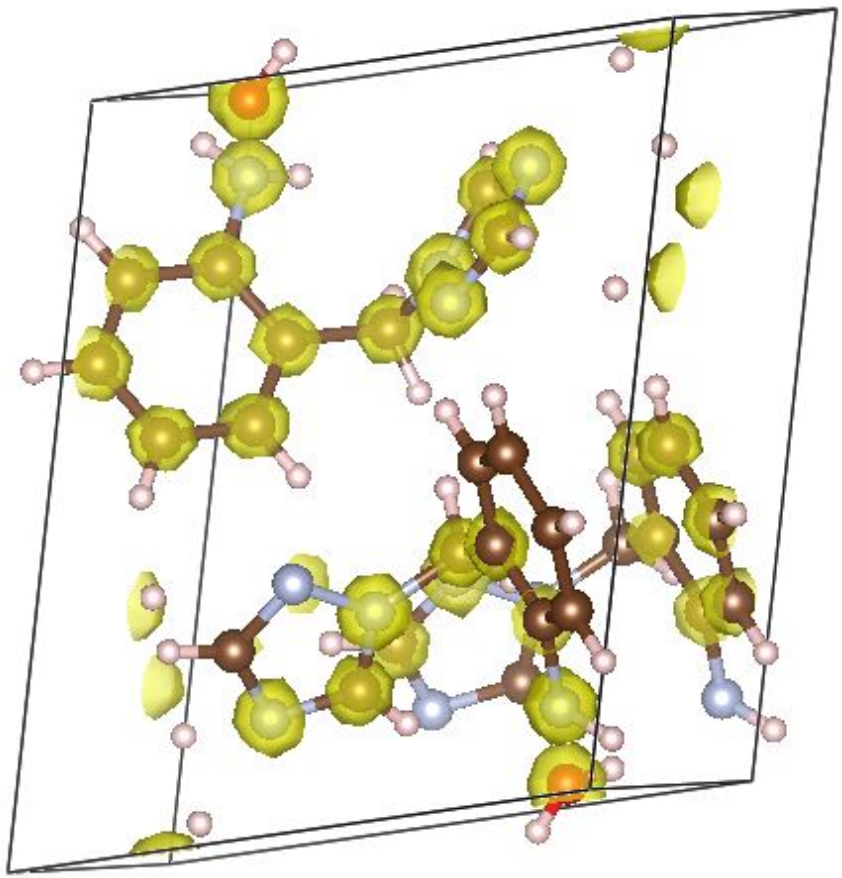
Superposing an electron density map on a cif structure



Superposing an electron density map on a cif structure



Superposing an electron density map on a cif structure



Tips & tricks

SHELXT

E.g. `shelxt -s"P2(1)_c` *name*

Change command-line options

- -q change q in $G_{\text{obs}} = E_{\text{obs}}^{q} F_{\text{obs}}^{1-q}$
  - $q = 0.5$
  - make q smaller for structures with heavy atoms
  - make q larger for large equal atom structures
- -m number of $P1$ dual space iterations (default 100)
- -s fix solutions to one space group
- -aX search all spacegroups within Laue group with $\alpha <$ X

Tips & tricks

Superflip

Change cards

- repeatmode n/nosuccess [sumgood] → first good density is used as referencefile to which subsequent good densities are aligned
- maxcycles 100000
- normalize local
- missing bound [resolution_limit] → default resolution_limit 1.25; could be an idea to extend reflections beyond the experimental resolution (free lunch)
- histogram matching
- low resolution data: AAR scheme → perform general 0.5 1.0 1.0 0.0 0.0 0.0

CRYSCALC

Superflip & Shelx

CRYSCALc

(CRYSTALLOGRAPHIC CALCULATIONS)

makes the crystallographer life easier !

Ver. Nov. 2017

---*

T. Roisnel

CDIFX/PRATS/ISCR
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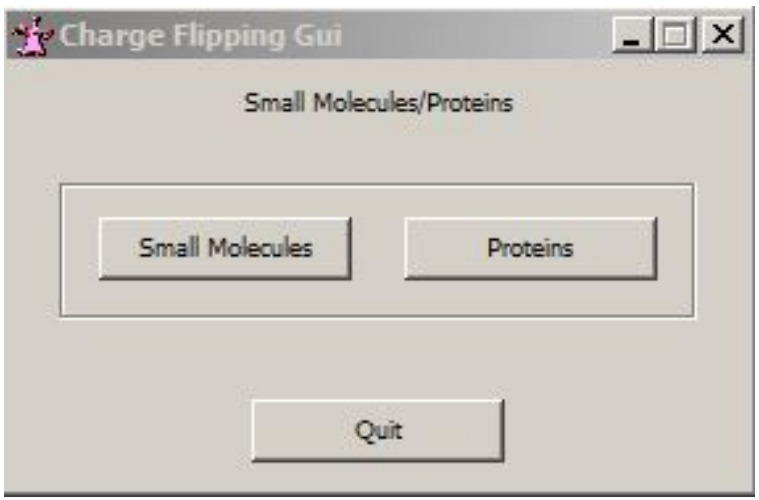
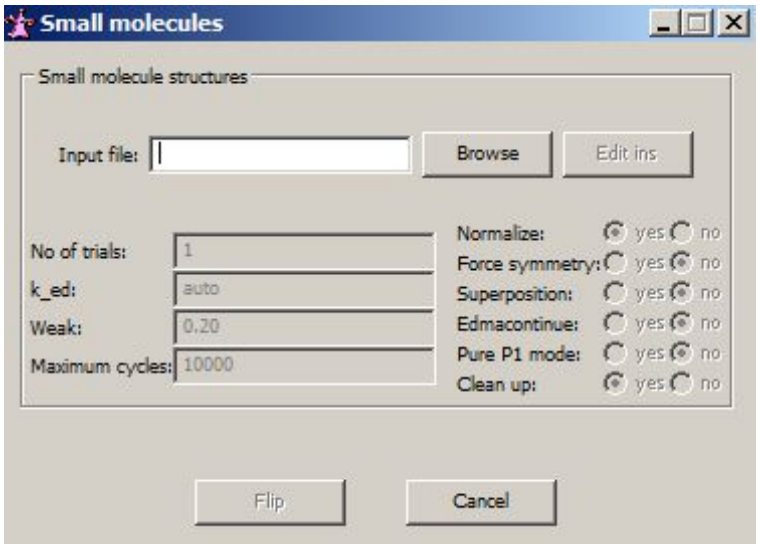
[with courtesy of JRC and JGP for CFML]

contact : thierry.roisnel@univ-rennes1.fr
Web site : www.cdifx.univ-rennes1.fr/cryscalc

CFGui

Superflip

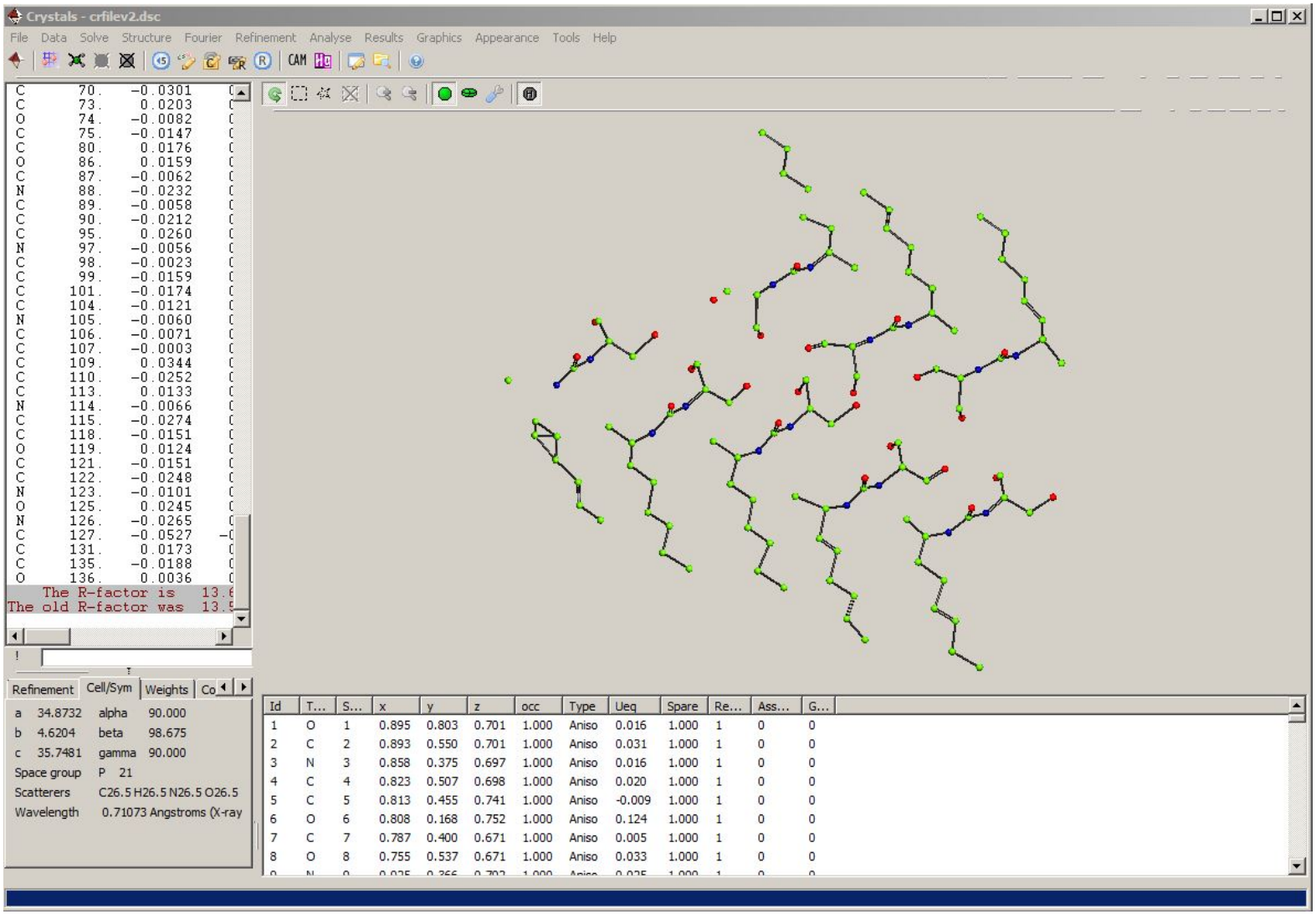




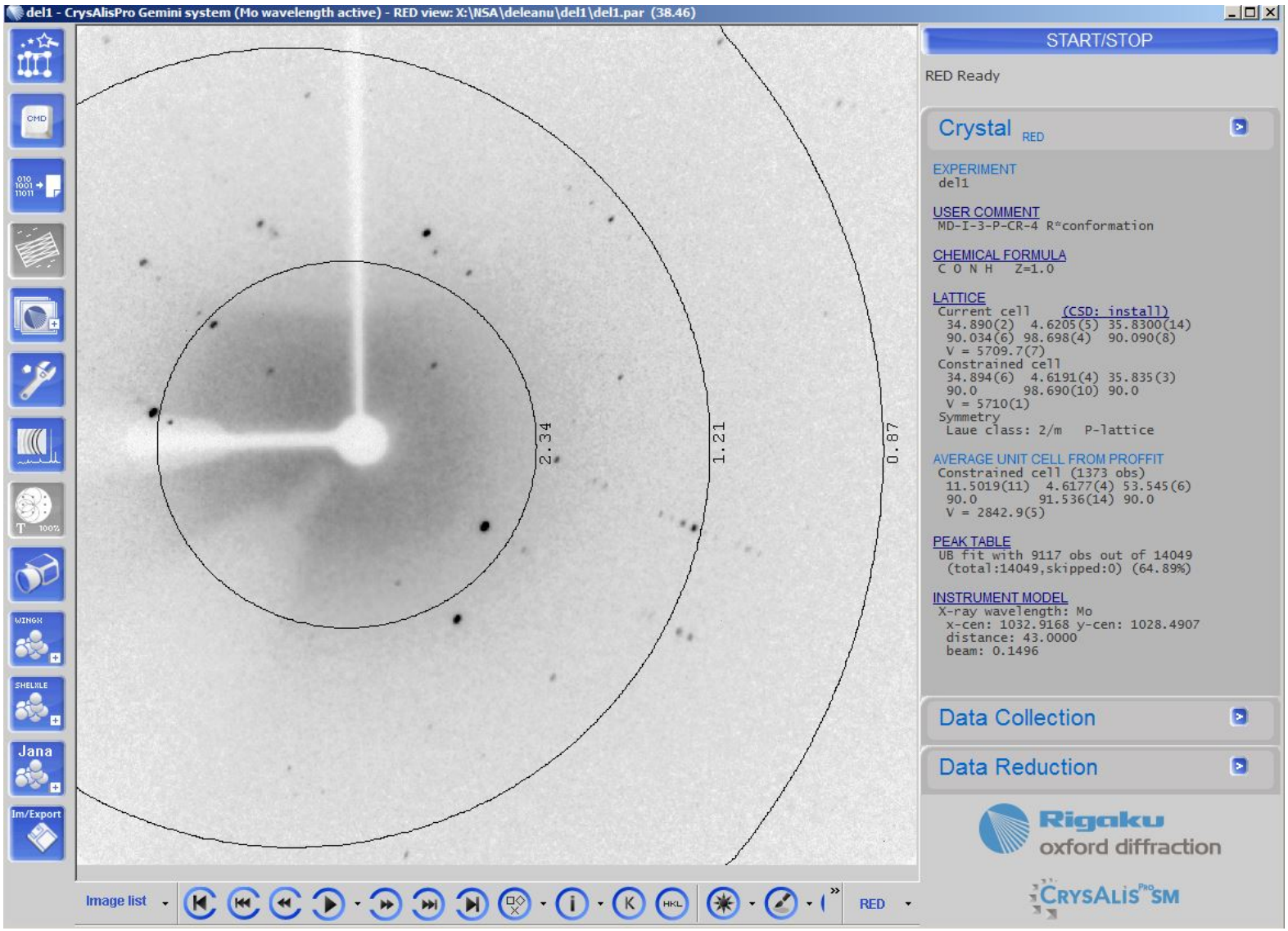
Exercises for Superflip & Shelxt

1. Resolution of a twinned molecular crystal structure with Superflip & Shelxt (LB05)
2. Resolution of a twinned molecular crystal structure with Superflip & Shelxt (HR186)
3. Structure solution of a very small protein with Superflip & Shelxt (1a7y)
4. Structure solution of a small protein with Superflip & Shelxt (2anv)
5. DFT structures - *perform symmetry* (alpha295K, beta235K)
6. Superposition of electron density maps on cif structures - *perform fourier* (ecryst35)

del1


Crystals - crfilev2.dsc
File Data Solve Structure Fourier Refinement Analyse Results Graphics Appearance Tools Help
The R-factor is 13.6
The old R-factor was 13.5
Refinement Cell/Sym Weights
a 34.8732 alpha 90.000
b 4.6204 beta 98.675
c 35.7481 gamma 90.000
Space group P 21
Scatterers C26.5 H26.5 N26.5 O26.5
Wavelength 0.71073 Angstroms (X-ray
Id T... S... x y z occ Type Ueq Spare Re... Ass... G...
1 O 1 0.895 0.803 0.701 1.000 Aniso 0.016 1.000 1 0 0
2 C 2 0.893 0.550 0.701 1.000 Aniso 0.031 1.000 1 0 0
3 N 3 0.858 0.375 0.697 1.000 Aniso 0.016 1.000 1 0 0
4 C 4 0.823 0.507 0.698 1.000 Aniso 0.020 1.000 1 0 0
5 C 5 0.813 0.455 0.741 1.000 Aniso -0.009 1.000 1 0 0
6 O 6 0.808 0.168 0.752 1.000 Aniso 0.124 1.000 1 0 0
7 C 7 0.787 0.400 0.671 1.000 Aniso 0.005 1.000 1 0 0
8 O 8 0.755 0.537 0.671 1.000 Aniso 0.033 1.000 1 0 0

del1


del1 - CrysAlisPro Gemini system (Mo wavelength active) - RED view: X:\NSA\deleanu\del1\del1.par (38.46)
START/STOP
RED Ready
Crystal RED
EXPERIMENT
del1
USER COMMENT
MD-I-3-P-CR-4 R*conformation
CHEMICAL FORMULA
C O N H Z=1.0
LATTICE
Current cell (CSD: install)
34.890(2) 4.6205(5) 35.8300(14)
90.034(6) 98.698(4) 90.090(8)
V = 5709.7(7)
Constrained cell
34.894(6) 4.6191(4) 35.835(3)
90.0 98.690(10) 90.0
V = 5710(1)
Symmetry
Laue class: 2/m P-lattice
AVERAGE UNIT CELL FROM PROFFIT
Constrained cell (1373 obs)
11.5019(11) 4.6177(4) 53.545(6)
90.0 91.536(14) 90.0
V = 2842.9(5)
PEAK TABLE
UB fit with 9117 obs out of 14049
(total:14049,skipped:0) (64.89%)
INSTRUMENT MODEL
X-ray wavelength: Mo
x-cen: 1032.9168 y-cen: 1028.4907
distance: 43.0000
beam: 0.1496
2.34
1.21
0.87
Data Collection
Data Reduction
Rigaku
oxford diffraction
CrysAlis Pro SM
Image list
RED

del1

Data

- Gemini-S diffractometer - $T = 175$K - Mo-wavelength
- $< I/\sigma(I) >= 7.91$; $R_{\text{int}} = 0.085$ at 0.85 Å resolution - 99.7 % completeness
- $a = 34.87 \quad b = 4.62 \quad c = 35.74 \quad \beta = 90.0 \quad \beta = 98.67 \quad \gamma = 90.0$; $V = 5694$ Å^3; space group $P2_1$
- refined structure: $R_{\text{F}} = 0.136$