The Extended PLATON/SQUEEZE Tool in the Context of Twinning and SHELXL2014

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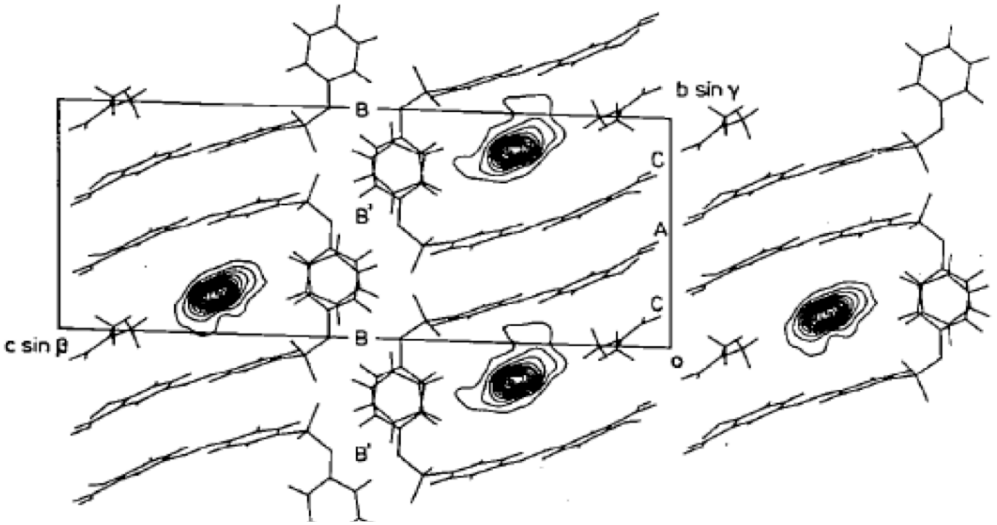
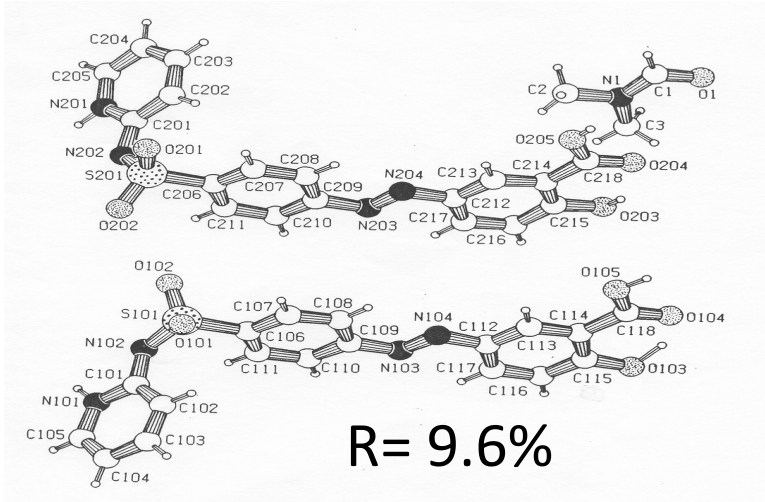
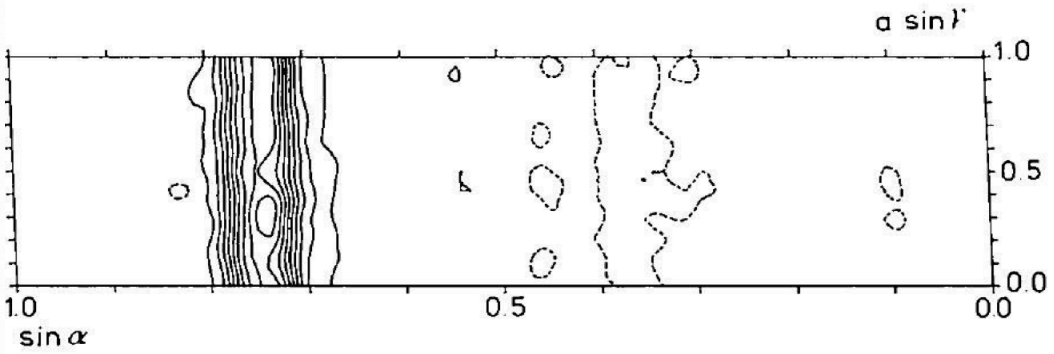
SQEEZE DEVELOPMENT STARTED AROUND 1990



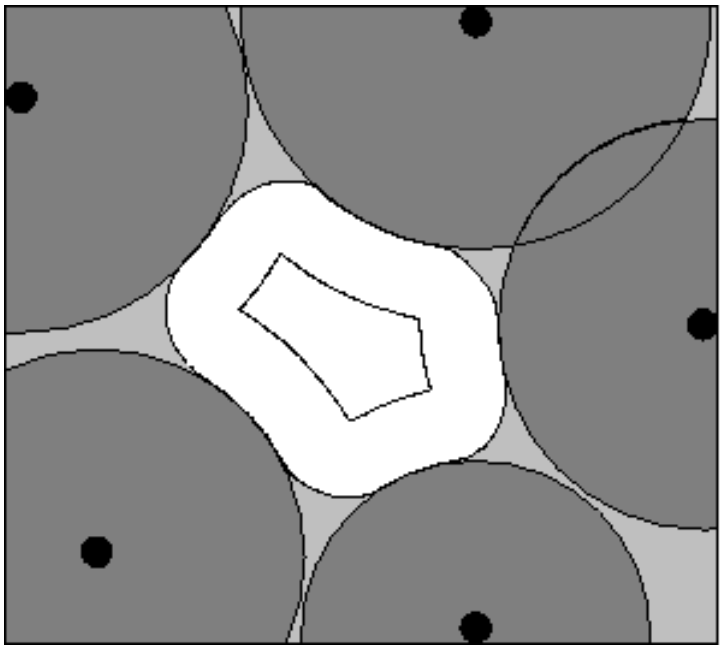




Problem: How to take the solvent contribution into account in L.S.

SOLUTION AND RESULT

Split-up F_c(total) = F_c(model) + F_c(solvent)



Dark area: van der Waals volume for SF parameter model

White area: solvent mask on difference map for Back-Fourier transform

Result: R dropped from 9.6 to 4.5 %

CSD(2014) Reports the use of SQUEEZE 13600 times

Development History

- Original development was based on SHELX76

P. van der Sluis & A.L.Spek (1990). Acta Cryst. C46, 883-886 and A46, 194-201 (BYPASS)

- Previously based on L.S. with SHELXL97

Drawback: need to subtract F_c(solv) from Fobs

- Current implementation around SHELXL2014

I(obs) no longer temporarily "corrected" for the solvent contribution. Handling of twinning in combination with solvent disorder now possible

SQUEEZE & SHELXL2014

- SHELXL2014 includes the new instruction, ABIN, that instructs SHELXL to read an externally supplied .fab file that contains fixed contributions to the calculated structure factors
- PLATON/SQUEEZE supplies such a .fab file containing the disordered solvent contribution + embedded squeeze details
- The new SHELXL2014 CIF file with the embedded .res and .hkl makes the use of SQUEEZE much simpler and less complicated
- The recommended input files needed for a SQUEEZE job are a .cif and .fcf from a converged SHELXL2014 refinement job
- SQUEEZE generates _sq.ins, _sq.hkl & _sq.fab for SHELXL2014
- Info on the use of SQUEEZE for archival and validation is automatically embedded in the CIF

Embedded SQUEEZE info at the end of the .fab file

```
 -1    8   20      0.33      0.05
  0    0    0      0.00      0.00
# SQUEEZE RESULTS (APPEND TO CIF)
# Note: Data are Listed for all Voids in the P1 Unit Cell
# i.e. Centre of Gravity, Solvent Accessible Volume,
# Recovered number of Electrons in the Void and
# Details about the Squeezed Material
loop_
  _platon_squeeze_void_nr
  _platon_squeeze_void_average_x
  _platon_squeeze_void_average_y
  _platon_squeeze_void_average_z
  _platon_squeeze_void_volume
  _platon_squeeze_void_count_electrons
  _platon_squeeze_void_content
   1 -0.063  0.498 -0.053       98        25 ' '
   2  0.063  0.998  0.053       99        25 ' '
   3  0.448  0.169  0.563      176        45 ' '
   4  0.552  0.669  0.437      176        45 ' '
   5  0.303  0.356  1.070       96        24 ' '
   6  0.697  0.856  0.930       95        24 ' '
_platon_squeeze_details
TITL twin5     P 21         R = 0.05
CELL   15.2996   19.9385   15.8554     90.00     97.66     90.00
SPGR P21
# Note: Atoms in Void as Cxxx and Qxxx all others
C101 0.284 0.340 0.153 !       5.30 eA-3
C102 0.296 0.355 0.087 !       4.82 eA-3
C103 0.066 1.000 0.081 !       4.67 eA-3
C104 0.061 0.985 0.987 !       4.52 eA-3
```

← h k l A(solv) B(solv)

← Void volume + electron count

← Optimized peak list

How to SQUEEZE with SHELXL2014

1. Refine a non-solvent model with name.ins & name.hkl (Include ACTA record) .
2. Run PLATON/SQUEEZE, based on *name.cif* & name.*fcf* from **1** as 'platon –q name.cif'.
3. Continue SHELXL refinement with the files *name_sq.ins*, name_sq.hkl & *name_sq.fab* from **2** as 'shelxl name_sq'
4. Inspect the .lis & .lst files and Validate

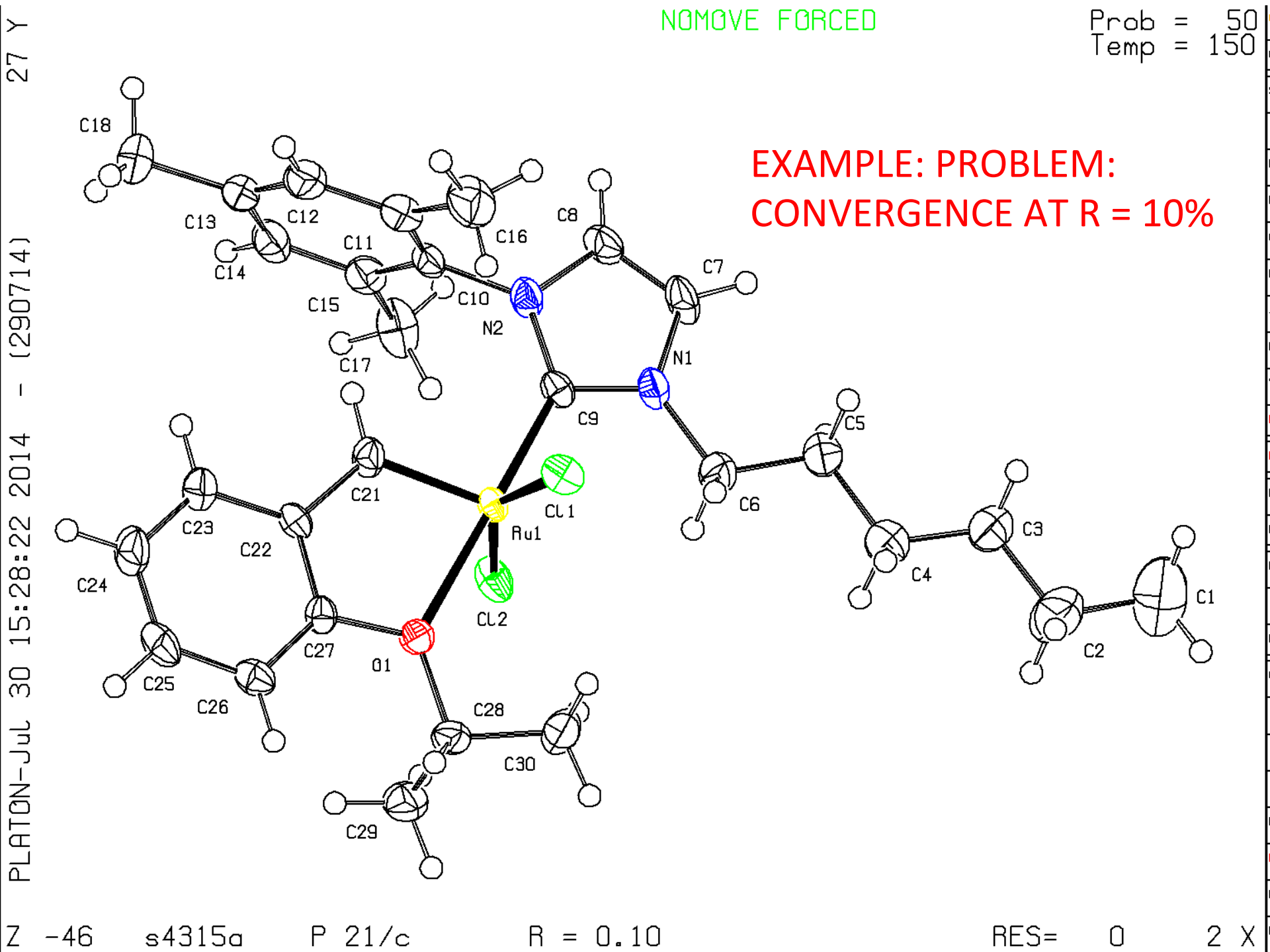
The ‘NEXTRA’ Issue

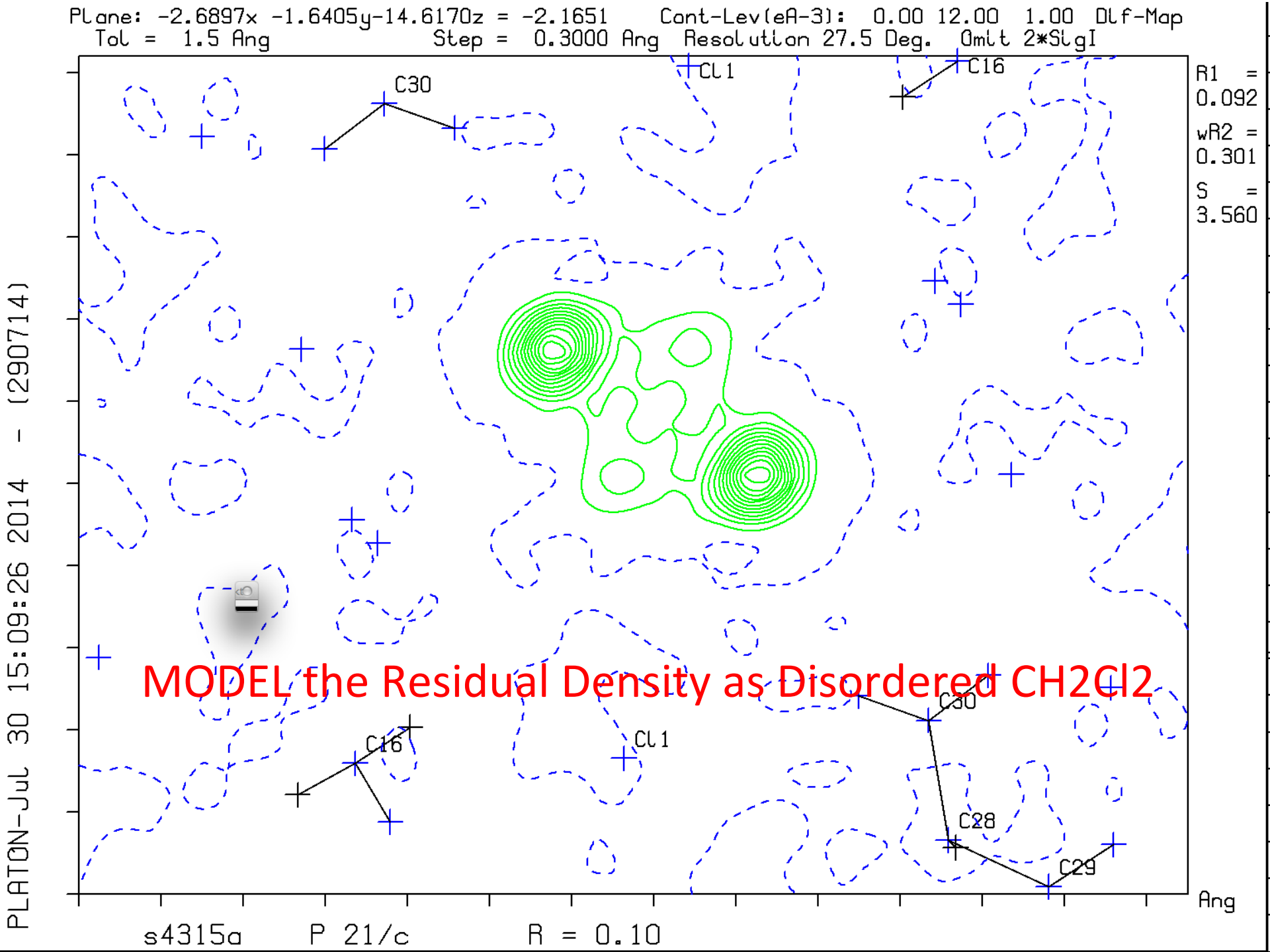
- One of the issues that needs to be addressed is the number of additional parameters to be added in the calculation associated with SQUEEZE on the SHELXL L.S. command.
- The default value is set to: (E x n) / (Z x m) where
- E = the number of recovered electrons in the unit cell
- Z = the number of asymmetric units
- m = the number of electrons in a CH2 fragment (=8)
- n = the number of parameters usually refined for a CH2 fragment (=9)

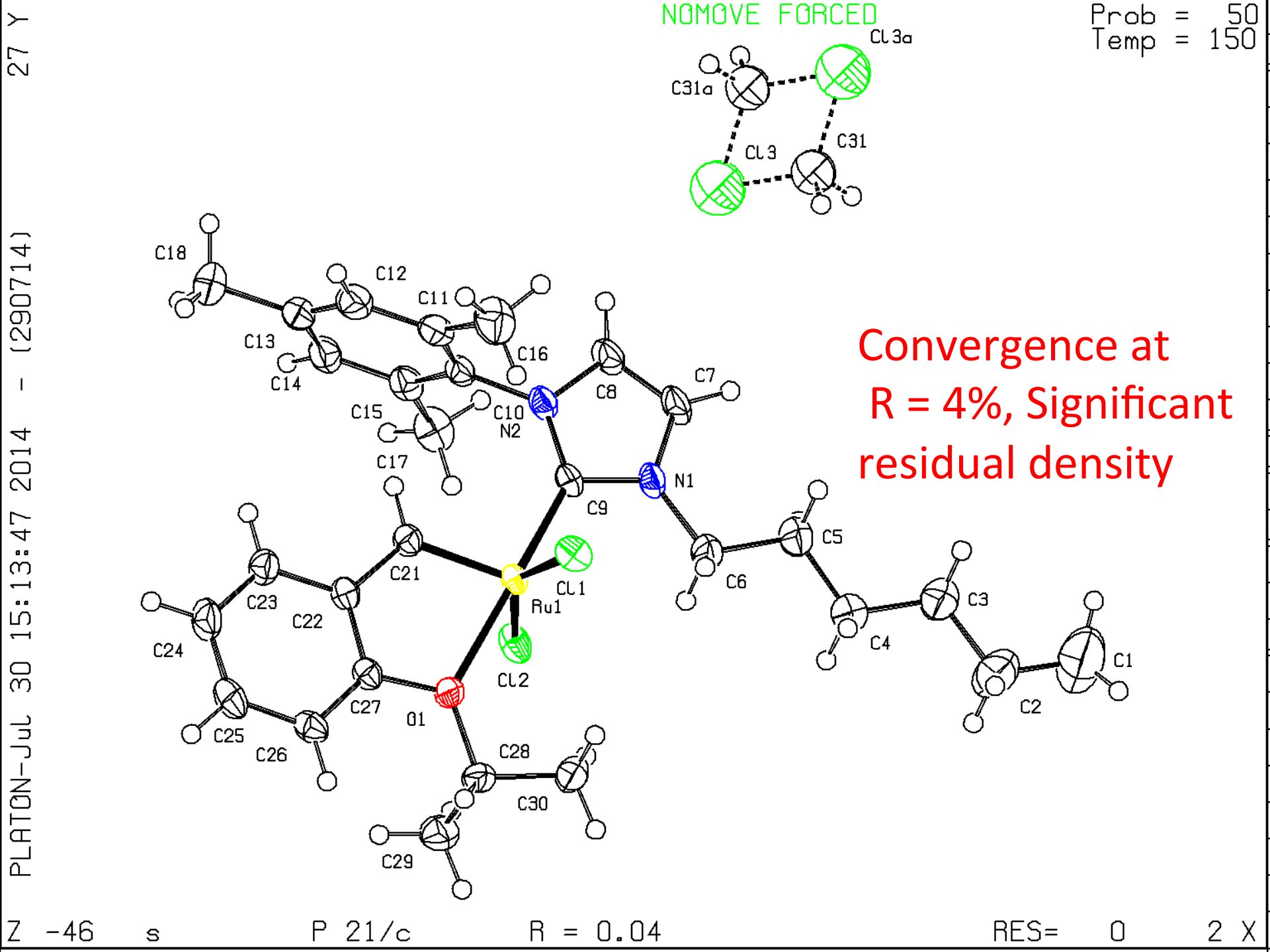
- This formula has the nice property that it vanishes when there is no residual density in the void

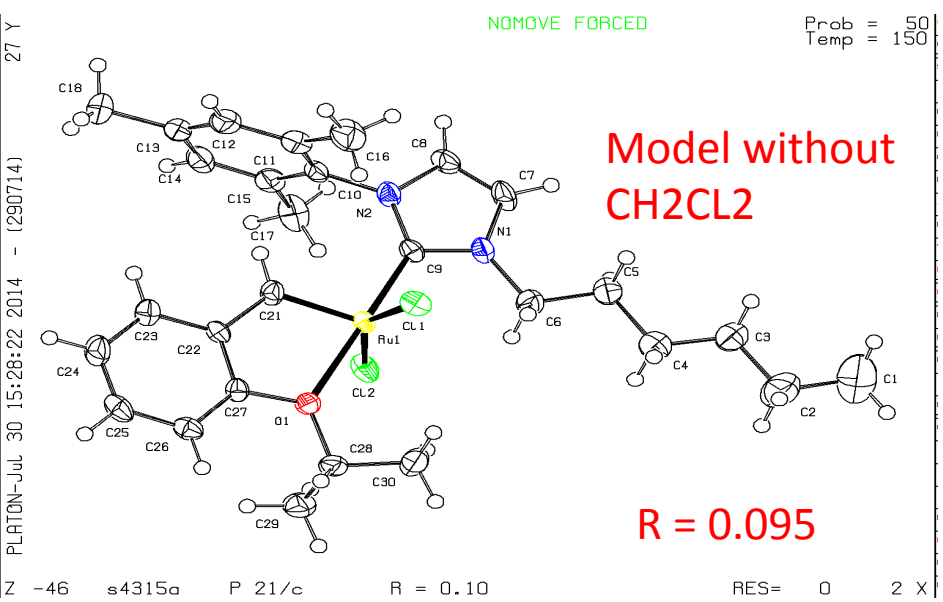
SQUEEZE EXAMPLES

- In case of unclear solvent disorder, both a disorder model with constraints/restraints and a SQUEEZE calculation should be attempted and their results compared
- Following are SQUEEZE examples without and with additional twinning complications
- Both examples are based on good data
- Note: Electron counting requires good data

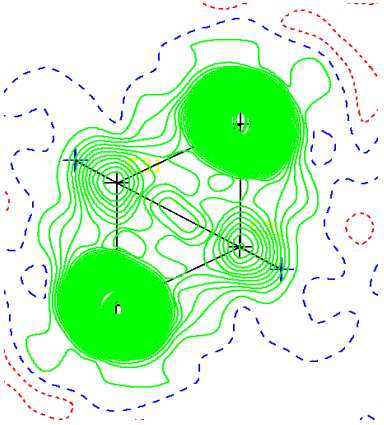

NOMOVE FORCED
Prob = 50
Temp = 150
EXAMPLE: PROBLEM:
CONVERGENCE AT R = 10%
C18
C13
C12
C16
C8
C14
C11
C7
C15
C10
N2
N1
C17
C9
C5
C21
CL1
C6
C23
Ru1
C3
C22
C4
C24
CL2
C1
C27
O1
C2
C25
C26
C28
C30
C29
PLATON-Jul 30 15:28:22 2014 - (290714)
27 Y
Z -46 s4315a P 21/c R = 0.10 RES= 0 2 X


Plane: -2.6897x -1.6405y-14.6170z = -2.1651
Cont-Lev(eA-3): 0.00 12.00 1.00 Dlf-Map
Tol = 1.5 Ang
Step = 0.3000 Ang Resolution 27.5 Deg. Omit 2*Sigl
R1 = 0.092
wR2 = 0.301
S = 3.560
C30
Cl1
C16
MODEL the Residual Density as Disordered CH2Cl2
C16
Cl1
C30
C28
C29
PLATON-Jul 30 15:09:26 2014 - (290714)
Ang
s4315a P 21/c R = 0.10

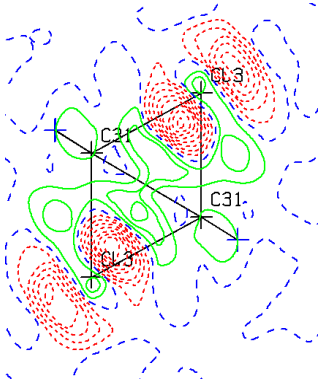

NOMOVE FORCED
Prob = 50
Temp = 150
Cl3a
C31a
Cl3
C31
C18
C12
C11
C13
C16
C14
C15
C10
N2
C8
C7
C17
N1
C9
C5
C21
Cl1
C6
C23
Ru1
C3
C22
C24
C4
C1
Cl2
C27
C2
O1
C25
C26
C28
C30
C29
Convergence at
R = 4%, Significant
residual density
PLATON-Jul 30 15:13:47 2014 - (290714)
27 Y
Z -46 s P 21/c R = 0.04 RES= 0 2 X



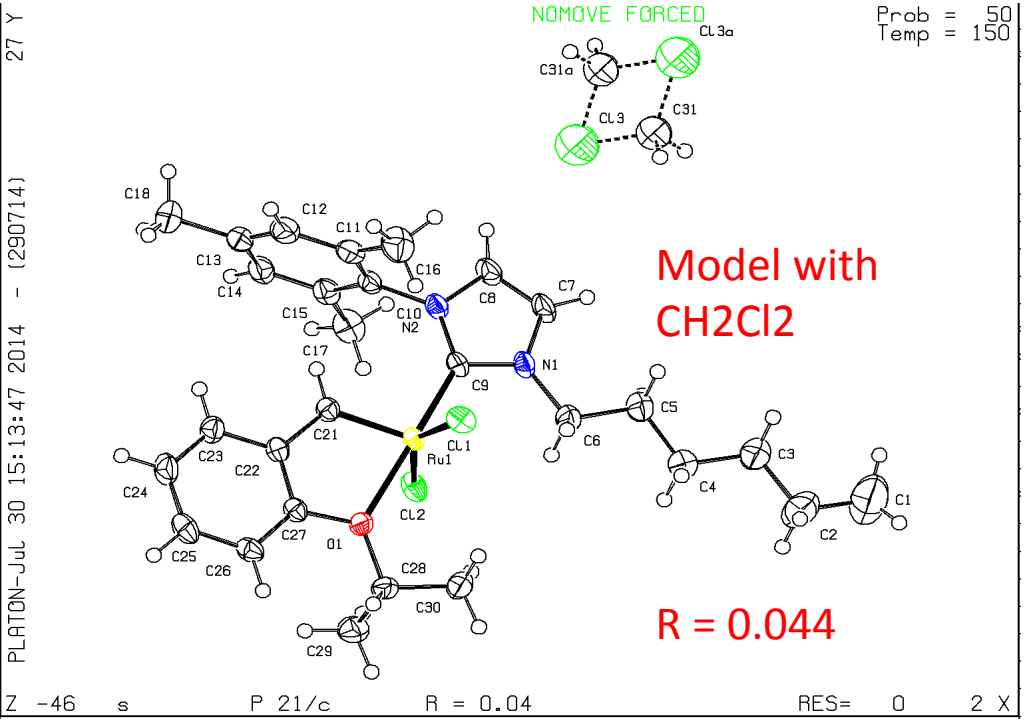
Difference Maps based on Modelled CH2Cl2

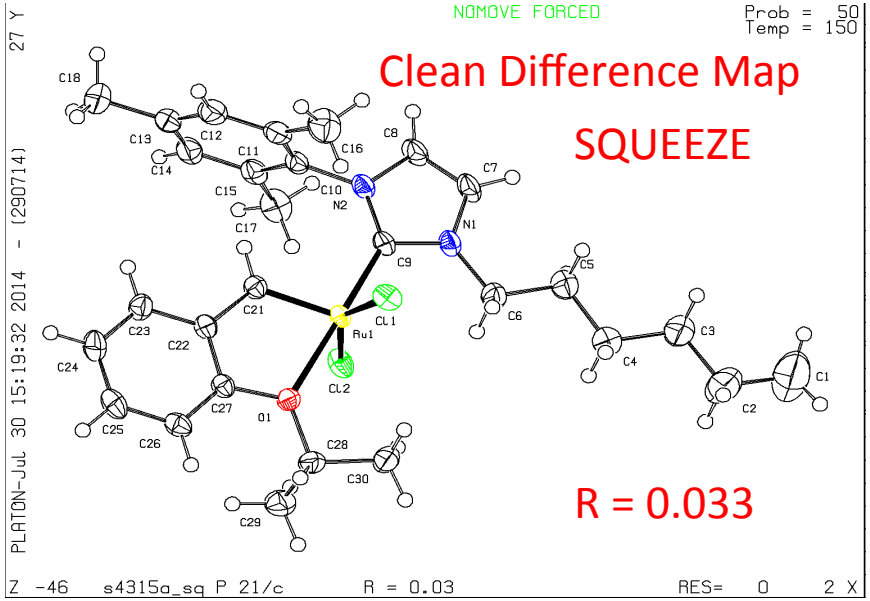


Diff. Map +/- CH2Cl2



Diff.Map + CH2Cl2





Result Summary

P21/c	2(C28 H38 Cl2 N2 O Ru, x(C H2 Cl2)		
	none	0.69(CH2Cl2)	squeeze
R	0.0954	0.0442	0.0327
wR2	0.3111	0.1315	0.0918
S	3.690	1.050	1.064
rho min/max	-0.80,12.61	-1.59,2.02	-0.43, 1.07
BP (Ang)	0.0137	0.0058	0.0042

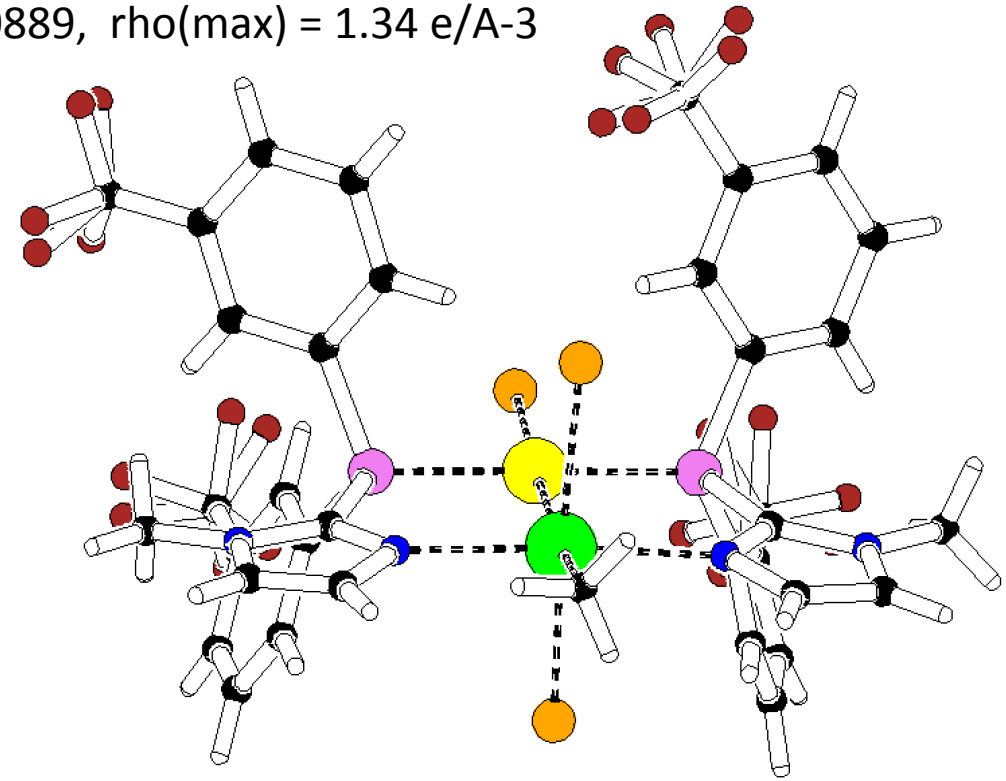
Disordered Solvent + Twinning Refinement protocol with SHELXL2014 and SQUEEZE

- Step 1: SHELXL refinement based a name.ins (that should include 'ACTA', 'LIST 8', 'BASF' and 'HKLF5' records) and a name.hkl file [merohedral: BASF/TWIN]
- Step 2: Run SQUEEZE with the name.cif and name.fcf files produced in Step 1 (i.e. run: platon –q name.cif)
- Step 3: Continue SHELXL refinement with the files name_sq.ins, name_sq.hkl and name_sq.fab produced by PLATON in step 2 ➔ name_sq.cif & name_sq.fcf
- Note: The name_sq.fab file contains the solvent contribution to the SF and the details of SQUEEZE
- name_sq_sqz contains optimized diff.map peaklist

SQUEEZE2014 Example: Coordination Compound

Acetonitril Model: R = 0.0323, wR2 = 0.0889, rho(max) = 1.34 e/A-3

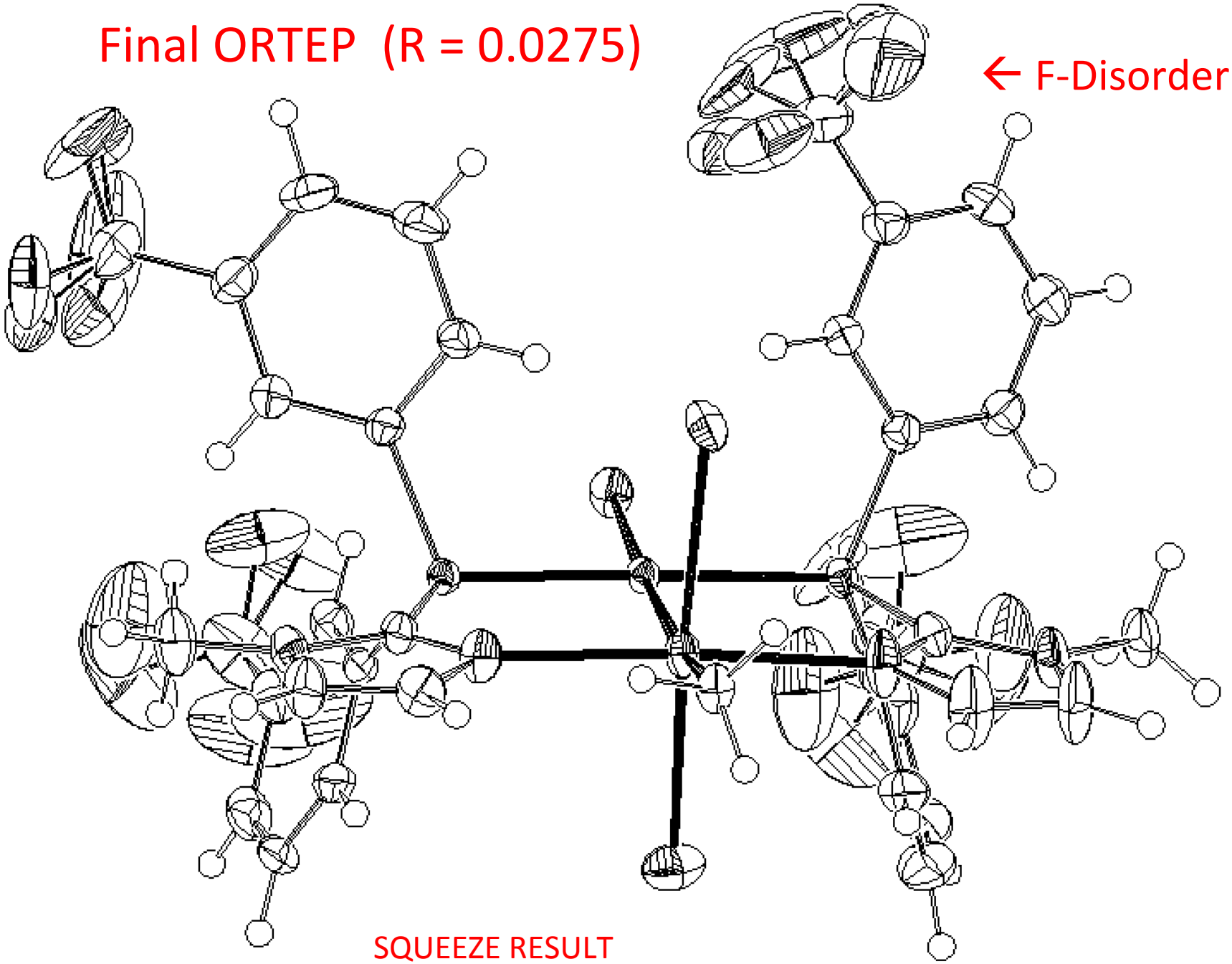
Space Group $P2_1$
Z = 4, Z' = 2
60:40 Twin
Twin axis: (0 0 1)
150 K
Twinabs hklf5 data
Acetonitril solvate



Step 1 (SHELXL2014) ➔ R1 = 0.047, wR2 = 0.1445
Step 2 (SQUEEZE) ➔ 188 electrons found in unit cell
Step 3 (SHELXL2014) ➔ R1 = 0.0275, wR2 = 0.0679, S = 1.064

Final ORTEP (R = 0.0275)

← F-Disorder



SQUEEZE RESULT

SQUEEZE optimizes the Difference map by Fourier Recycling. Refinement is done with SHELXL

SQUEEZE + L.S. Recycling is rarely needed but can be done as:

platon –q3 name.cif (by calling SHELXL from within PLATON)

SQUEEZE-SHELXL LOOP RESULTS

CYC	R1	wR2	S	RhoMax	RhoMin	Electrons	Volume
1	0.0669	0.2037	2.6450	3.97	-0.49	177.3	624.4
2	0.0304	0.0747	0.9560	0.47	-0.35	177.6	623.3
3	0.0303	0.0746	0.9550	0.47	-0.35	177.7	623.3

Requirements

- There should be no residual unresolved density in the discrete model region of the structure because of its impact on the difference map in the solvent region.
- The data set should be reasonably complete and with sufficient resolution [i.e. sin(theta)/lambda >0.6].
- Low temperature data help a lot.
- There should be no unresolved charge balance issues that might effect the chemistry involved (e.g. The valency of a metal in the ordered part of the structure)

Limitations

- The reported electron count in the solvent region is meaningful only with the supply of a complete and reliable reflection data set
- The SQUEEZE technique can not handle properly cases of coupled disorder effecting both the model and the solvent region.
- The solvent region is assumed not to contain significant anomalous scatterers (Friedels averaged)
- Designed for 'small molecule structures'
- Using SQUEEZE as part of the MOF soaking method where the interest lies in the solvent region can be very tricky and should be done with extreme care

PLATON runs from a terminal window under LINUX, MAC-OSX and MS-Windows (Louis Farrugia's, UK)

(http://www.cryst.chem.uu.nl/spek)
(http://www.platonsoft.nl/xraysoft)
(including a copy of this presentation)

Suggestions & Comments (with data) are welcome: send to a.l.spek@uu.nl

Thank You

LISTING OF FINAL SQUEEZE CYCLE RESULTS

```
:: Cycle =  4, R(F) = 0.04, Nref(Hemi) =  8811, R(F > 4SIGF) = 0.03 Nref =  7380

Unique Density Maxima in Enhanced  Difference Map (CutOff level =  0.50 eA-3)
=============================================================================
      x     y     z  (e/A^3)     Shortest Contacts within 3.2 Angstrom (Excl. H)
=============================================================================
  1 0.490 0.220 0.281  4.57 void
  2 0.552 0.266 0.301  4.41 void
  3 0.475 0.379 0.212  3.54 void
  4 0.441 0.356 0.252  3.39 void
  5 0.499 0.297 0.252  0.89 void
  6 0.953 0.184 0.125  0.55      C16  0.68; C11  0.75; C15  1.90; C12  1.90; Cu2
  7 0.408 0.253 0.501  0.51      C13  0.61; C12  0.90; C14  1.85; C17  1.97; C11
  8 0.358 0.170 0.717  0.50      Cu1  1.11; C21  1.53; C22  2.11; C27  2.37; Cu2
  9 0.283 0.085 0.613  0.50      C18  0.77; N1   1.75; C19  2.46; Cu1  2.82; C17

VOID   Volume Ang^3 Electron-Count (e-) Volume per electron Vol/Atom
=============================================================================
    A          155              43          3.6                    29
    B          155              43          3.6                    29
    C          155              43          3.6                    29
    D          155              43          3.6                    29

Total (Positive) Electron Count in Voids/Cell =   172

Total (Fo-Fc)map Electron Count in  Unit Cell =   171

VOID-Fo-Fc-Map:     Rho(min) =   -0.28, Rho(max) =    4.57, RhoCutOff =    0.00
PeaksCloseToAtoms: Rho(min) =   -0.63, Rho(max) =    0.55, RhoCutOff =    0.50

:: Fo-scale =0.210538E+01 - SinT/L-Min = 0.20 for Fo/Fc-Scaling


:: Cycle =  5, R(F) = 0.04, Nref(Hemi) =  8811, R(F > 4SIGF) = 0.03 Nref =  7380
```

Informal Theory of the SQUEEZE Procedure

$$F_H = \int_V \rho(\vec{r})\, e^{2\pi i \vec{H}\cdot\vec{r}}\, dV$$

$$= \int_V \left(\rho^M(\vec{r}) + \rho^S(\vec{r})\right) e^{2\pi i \vec{H}\cdot\vec{r}}\, dV$$

$$\rho^M(\vec{r}) = \sum_{j=1}^{N} \rho(\vec{r} - \vec{r}_j)$$

$$F_H^M = \sum_{j=1}^{N} f_j\, e^{2\pi i \vec{H}\cdot\vec{r}_j}$$

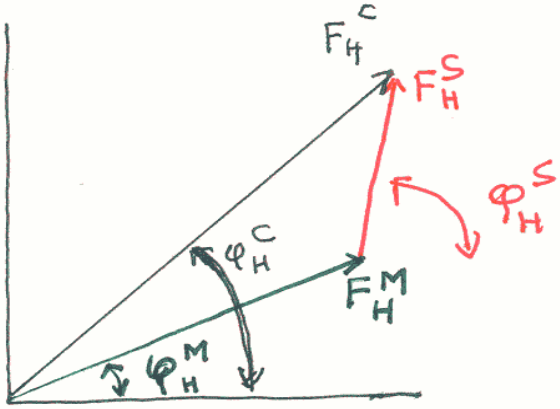
$$\rho^S(\vec{r}) \approx \Delta\rho(\vec{r}_k) \text{ on grid}$$

$$F_H^S = V_q \sum_S \Delta\rho(\vec{r}_k)\, e^{2\pi i \vec{H}\cdot\vec{r}_k}$$

$$F_H^C = F_H^M + F_H^S \Longrightarrow$$

M = Ordered

S = Solvent



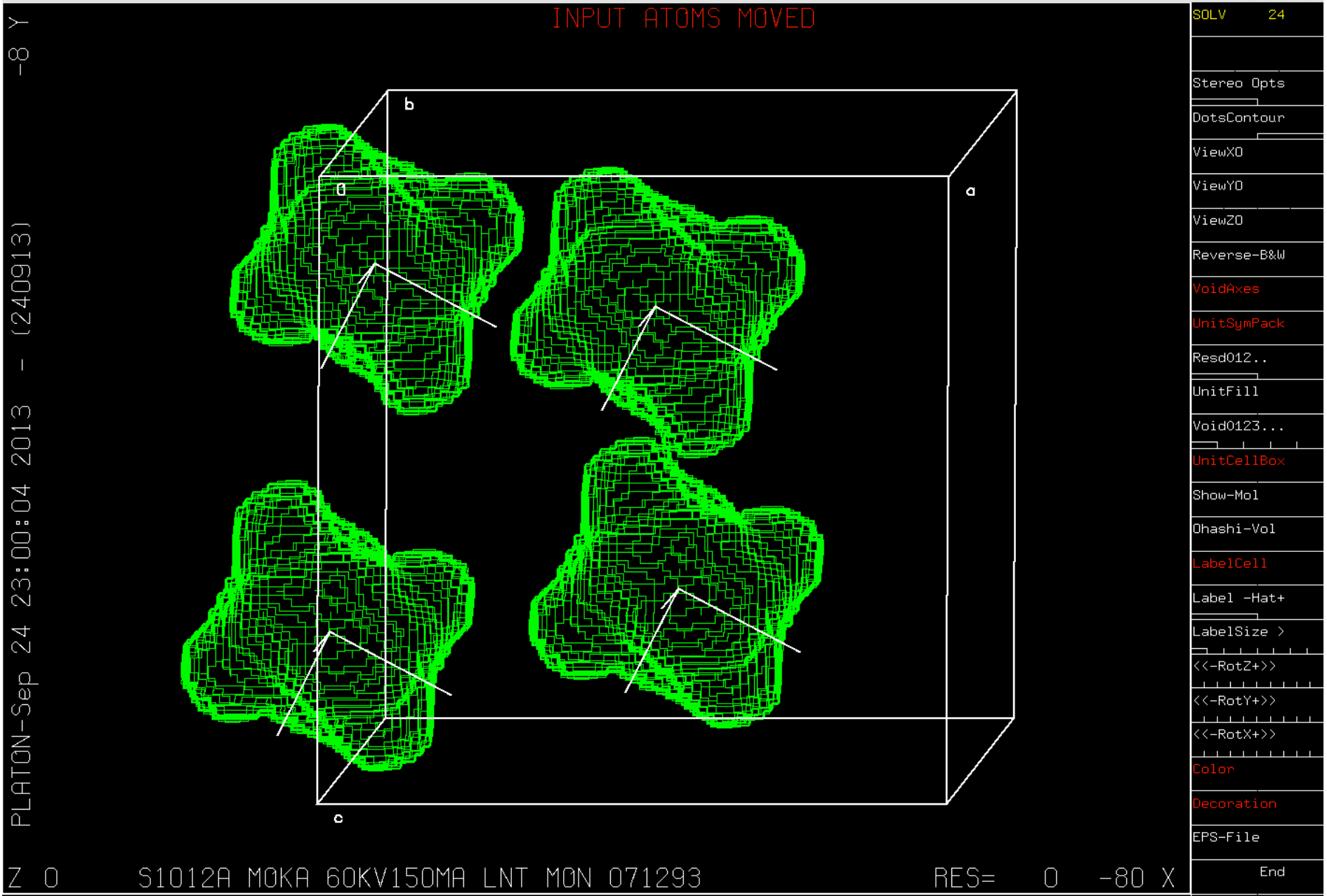
Iterate (Initially $\rho_H^S = \rho_H^M$)

$$\Delta\rho(\vec{r}) = \frac{1}{V} \sum_H \left(s|F_H^o| e^{i\varphi_H^C} - |F_H^M| e^{i\varphi_H^M}\right) e^{-2\pi i \vec{H}\cdot\vec{r}} + \frac{F_o^S}{V}$$

Solvent Free ElectronCount

$$F_H^o : F_H^{o'} = |F_H^o| e^{i\varphi^C} - |F_H^S| e^{i\varphi^S}$$

$$: V_q \sum_S \Delta\rho(\vec{r}_k)$$


P.L.A.T.O.N
INPUT ATOMS MOVED
-8 Y
PLATON-Sep 24 23:00:04 2013 - (240913)
b
a
c
Z 0 S1012A MOKA 60KV150MA LNT MON 071293 RES= 0 -80 X
SOLV 24
Stereo Opts
DotsContour
ViewXO
ViewYO
ViewZO
Reverse-B&W
VoidAxes
UnitSymPack
Resd012..
UnitFill
Void0123...
UnitCellBox
Show-Mol
Ohashi-Vol
LabelCell
Label -Hat+
LabelSize >
<<-RotZ+>>
<<-RotY+>>
<<-RotX+>>
Color
Decoration
EPS-File
End
INSTRUCTION INPUT via KEYBOARD or LEFT-MOUSE-CLICKS (HELP with RIGHT CLICKS)
>> Continue (Y/N[Y])
Exit
MenuActive