# Advanced SHELXL

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# Link

- http://shelx.uni-goettingen.de/
  - **Wikis & manuals**
    - SHELXL - Command list (HTML version based on contribution by Lee Daniels)

- Direct link
  - http://shelx.uni-goettingen.de/shelxl_html.php

# Commands .. Card…

- SHEXL is written in subset of Fortran 4 (compatibility)
  - small Fortran program is entirely self-contained, calling no library routines. (***zero-dependency philosophy***)
- All commands have four characters
  - 8 bits/chr for 32 bits of information
  - Commands are in the Punch Card format.
    - One card per command line
      - 80 characters total
    - If command/atom information > 80 characters then two cards used with the '=' at the end of the first card


- CMND ±variable keywords
  - Where the + or – enables different functions.
    - e.g. DFIX d s[0.02] atom pairs
      - If d is positive the distance between the first and second named atom is restrained to a target value d
        - DFIX +1.5 C1 C2 (bonded)
      - If d is negative then the restraint is applied only if the current distance between the two atoms is LESS than |d|.
        - DFIX -2.5 C1 C2 (non-bonded)

www.computerhope.com/jargon/p/punccard.htm

# Landing Page

## Alphabetical list of SHELXL instructions

| | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| ABIN | ACTA | AFIX | ANIS | ANSC | ANSR | BASF | BIND | BLOC | BOND | BUMP | CELL |
| CGLS | CHIV | CONF | CONN | DAMP | DANG | DEFS | DELU | DFIX | DISP | EADP | END |
| EQIV | EXTI | EXYZ | FEND | FLAT | FMAP | FRAG | FREE | FVAR | GRID | HFIX | HKLF |
| HTAB | ISOR | LATT | LAUE | LIST | L.S. | MERG | MORE | MOVE | MPLA | NCSY | NEUT |
| OMIT | PART | PLAN | PRIG | REM | RESI | RIGU | RTAB | SADI | SAME | SFAC | SHEL |
| SIMU | SIZE | SPEC | STIR | SUMP | SWAT | SYMM | TEMP | TITL | TWIN | TWST | UNIT |
| WGHT | WIGL | WPDB | XNPD | ZERR | | | | | | | |

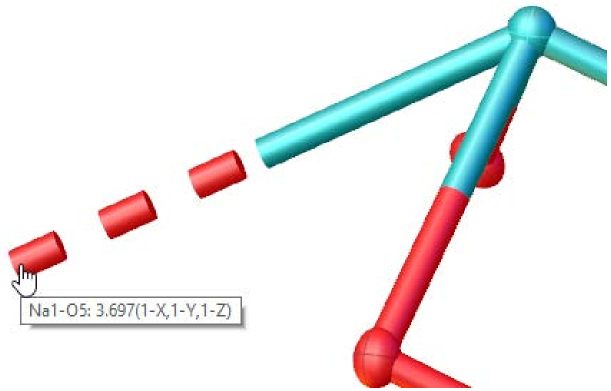
# AFIX mn d[#] sof[11] U[10.08]

- mn where first number is m : 1.. 16+ and 2nd number n: 1…9
  - Programming economy
  - Example for methyl H's mn=36 m=3,n=6 or mn=137, m=13, n=7
  - If one number is given for "mn" then m=0
    - e.g. AFIX 1 : m=0, n=1 can also be written AFIX 01
  - d is the distance
  - SOF site occupancy factor
  - U is the displacement parameter
- See HFIX for AFIX hydrogen generation

# Examples

- Hydrogen atom placement..
  - mn =36 $CH_2CX3$ :  137 : NCCX3
  - mn = 43  -C(N)X  aromatic
  - mn = 83,147 X-O-H
  - mn = 93 X=CH2 or X=$NH2^+$

# EQIV




- ✓ Add The CONN card to increase this list
  - CONN 12 2.8 $Na
    Atomic Radius  Na 2.8   (default=1.860)
- ✓ In the LST file (Covalent radii and connectivity table)

```
Na1 - O1W O1W_$3 O2W O2W_$3 O3W_$3 O3W Na2 Na2_$3 O5 O5_$3 O4W_$3 O4W
Na2 - O3W O3W_$1 O4W_$1 O4W O2W_$1 O2W Na1 Na1_$1 O5_$5 O5_$4
O1W - Na1
O2W - Na1 Na2
O3W - Na2 Na1
O4W - Na2 Na1
O1 - B1
O2 - B1 B2_$2
O3 - B1 B2
O4 - B2 B2_$2
O5 - B2 Na1 Na2_$4
B1 - O2 O3 O1
B2 - O5 O4 O2_$2 O3
```

```
Operators for generating equivalent atoms:
$1   -x+1, y, -z+1/2
$2   -x+1, y, -z+3/2
$3   -x+1, -y+1, -z+1
$4   -x+3/2, -y+1/2, -z+1
$5   x-1/2, -y+1/2, z-1/2
```

```
EQIV $3 -x+1, -y+1, -z+1
BIND Na1 O5_$3
```

CIF

Na1 O5 3.6968(6) 5_666

ORTEP : nomenclature

5_666 = -x+1, -y+1, -z+1

-x,-y,-z #5 in the loop list

666 add +1, +1, +1

(555 is 0,0,0 : 444 is -1,-1,-1)

loop_
_space_group_symop_operation_xyz

1. 'x, y, z'
2. '-x, y, -z+1/2'
3. 'x+1/2, y+1/2, z'
4. '-x+1/2, y+1/2, -z+1/2'
5. '-x, -y, -z'
6. 'x, -y, z-1/2'
7. '-x+1/2, -y+1/2, -z'
8. 'x+1/2, -y+1/2, z-1/2'

# EXTI x[0]

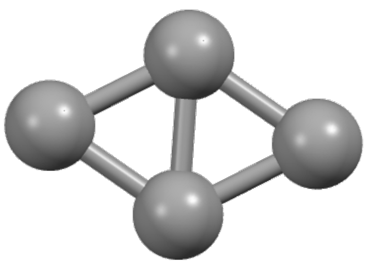
- Secondary extinction occurs when parts of the scattered X-ray beam are scattered a second time from parallel planes in the crystal which reduce the intensity measured for the singly scattered spots.
- Secondary extinction typically occurs for large crystals and is most significant for the strong, low scattering angle peaks.
- Secondary extinction is observed if the $\overline{F_c^2} > \overline{F_o^2}$ (significantly)

$$k\left[1 + 0.001 F_c^2 \lambda^3 \frac{x}{\sin 2\theta}\right]^{-\frac{1}{4}}$$

# FRAG

- Has been superseded by Disordered Structure Refinement (DSR, FRAGMENT DB/OLEX)*
- Arguslab to generate MM optimized structure
  - Save as XYZ clip/paste edit names and TYPE/SFAC (must match INS file).

```
FRAG 17 1 1 1 90 90 90
REM orthogonal coordinates
C1 1 -1.310000  0.234000  0.115000  11.000000 0.05000
C2 1 -0.031000  0.908000 -0.125000  11.000000 0.05000
C3 1  1.190000  0.098000 -0.149000 11.000000 0.05000
C4 1 -0.089000 -0.576000  0.092000 11.000000 0.05000
FEND
FVAR
….
AFIX 176  ! Fragment 17 n=6 The next atom(s) are 'dependent' atoms in a rigid group.
C1 1  0.312300  0.24000  0.15000  11.000000 0.05000
C2 1  0.031000  0.90000 -0.15000  11.000000 0.05000
C3 1  .0190000  0.09000 -0.19000  11.000000 0.05000
C4 1  0.089000 -0.56000  0.09000 11.000000 0.05000
AFIX 0
```




*D. Kratzert, I. Krossing, J. Appl. Cryst. **2018**, *51*, 928-934.
www.arguslab.com/arguslab.com/ArgusLab.html

# Make your own FRAG database

Create and edit the file **myfrag.txt** add

```
FRAG 17 1 1 1 90 90 90
REM orthogonal coordinates
C1 1 -1.310000  0.234000  0.115000  11.000000 0.05000
C2 1 -0.031000  0.908000 -0.125000  11.000000 0.05000
C3 1  1.190000  0.098000 -0.149000 11.000000 0.05000
C4 1 -0.089000 -0.576000  0.092000 11.000000 0.05000
FEND
END
```

INS file

```
TITLE
…
UNIT
+myfrag.txt
…
FVAR
..
AFIX 176  ! Fragment 17 n=6 The next atom(s) are 'dependent' atoms in a rigid group.
C1 1  0.312300  0.24000  0.15000  11.000000 0.05000
C2 1  0.031000  0.90000 -0.15000  11.000000 0.05000
C3 1  .0190000  0.09000 -0.19000  11.000000 0.05000
C4 1  0.089000 -0.56000  0.09000 11.000000 0.05000
AFIX 0
```

Create files for the most common disordered fragments ($ClO_4$  $BF_4$ etc)

Add complicated commands etc..

All with the

+filename

FYI….

++filename copies the lines to the RES file (++filename will not be copied)

Can be used for onetime comment insertion into the RES file e.g.

Create : **myinfo.txt**

```
REM  Data collected on a Bruker QUEST
REM  Bruker QUEST purchased with funds
REM     from NSF Grant 000-000-000
END
```

++**myinfo.txt**

# HKLF n[0] s[1] r11…r33[1 0 0 0 1 0 0 0 1] wt[1] m[0]

Common transformation : Convert **C***c* to **I***a* or **C**2/*c* to **I**2/*a*

Convention* *a<c* and $\beta$ *near 90.*

If the **C** cell has a>c and β > 120 then convert to the **I** cell

Use direct HKL transformation matrix‡ (if data was reduced in the **C** lattice, transform the unit cell too!)

$$\begin{pmatrix} 0 & 0 & \bar{1} \\ 0 & 1 & 0 \\ 1 & 0 & \bar{1} \end{pmatrix}$$

Example C2/c to I2/a

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| Original | CELL | 14.7440 | 8.8500 | 10.0620 | 90.000 | 131.609 | 90.000 |
| Transformed | CELL | 10.0620 | 8.8500 | 11.0273 | 90.000 | 91.410 | 90.00 |

WINGX TRANSFORM : Farrugia, L.J. (2021) J.Appl.Cryst. 45, 849.

FYI OLEX2 use : **sgs b3 i2afile.hkl**
(sgs [unique axis][cell choice] [name.hkl])

HKLF 4 1 0 0 -1 0 1 0 1 0 -1

REM HKLF 4 1 (00-1 010 10-1)

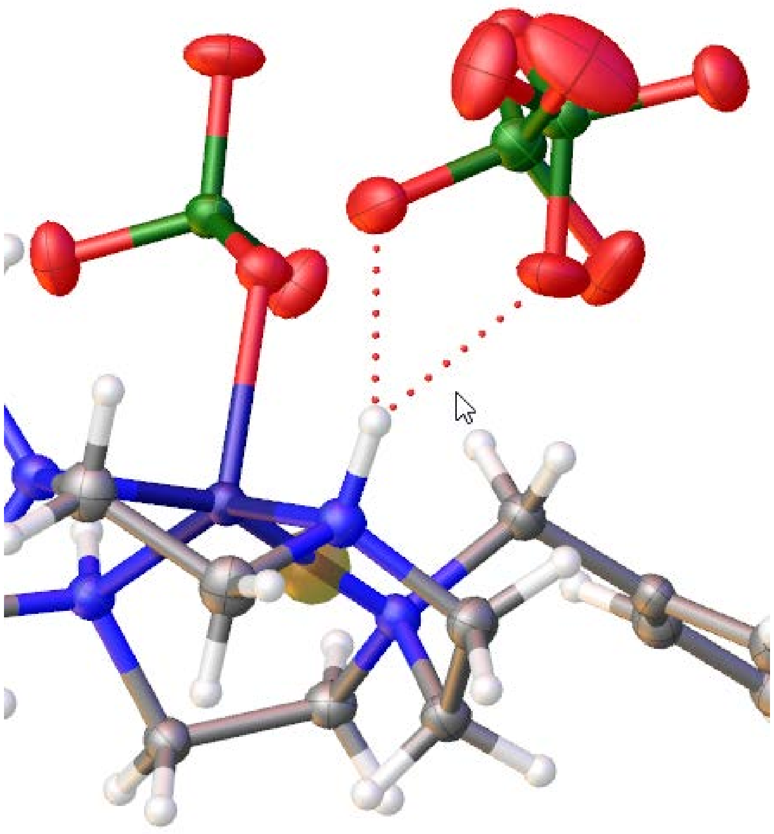
*Mighell A. D. (2002). Conventional Cells-The Last Step Toward General Acceptance of Standard Conventional Cells for the Reporting of Crystallographic Data. *Journal of research of the National Institute of Standards and Technology*, *107*(4), 373–377.
‡Inter. Tables. for Cryst. (2005) Springer, Dordrecht, The Netherlands page 86

# OMIT s[-2] 2θ(lim)[180]

- If s is given as zero or negative, all reflections with $Fo^2 < 0.5s\sigma(Fo^2)$ are replaced by $0.5s\sigma(Fo^2)$.
  - $s = 2$ $Fo^2 < \sigma(Fo^2)$
- If *s* is positive it is interpreted as a threshold for flagging reflections as ‘unobserved’
  - An OMIT instruction with a positive s value is not allowed in combination with ACTA
- 2θ(lim) defines a limiting 2θ above which reflections are totally ignored; they are rejected immediately on reading in
  - OMIT -2 55 – ACTA or use SHEL command

# RESI example

REM !!! AFTER REFINEMENT !!!!



```
SAME_CLO4 0.01 Cl1 > O4
DELU_CLO4 0.01 Cl1 > O4
SIMU_CLO4 0.01 Cl1 > O4
REM   !!!   BEFORE REFINEMENT !!!!
RESI CLO4 1
Cl1   3     0.62217  0.35166  0.90800  11.00000  0.01746
O1    6     0.56365  0.32114  0.80755  11.00000  0.02095
O2    6     0.76386  0.31947  0.92229  11.00000  0.02508
O3    6     0.65518  0.49086  0.94273  11.00000  0.04555
O4    6     0.49753  0.27380  0.95549  11.00000  0.02702
RESI CLO4 2
PART  1  21
Cl1   3     0.75223  0.28725  0.56960  11.00000  0.04724
O1    6     0.67045  0.37649  0.56405  11.00000  0.07819
O2    6     0.84283  0.30865  0.65894  11.00000  0.03107
O3    6     0.74673  0.17383  0.50973  11.00000  0.11249
O4    6     0.88973  0.36817  0.51377  11.00000  0.12744
RESI CLO4 3
PART 2 -21
Cl1   3     0.7223  0.28725  0.56960  11.00000  0.04724
O1    6     0.6045  0.37649  0.5405  11.00000  0.07819
O2    6     0.8283  0.30865  0.6894  11.00000  0.03107
O3    6     0.7673  0.17383  0.5973  11.00000  0.11249
O4    6     0.8973  0.36817  0.5377  11.00000  0.12744
RESI 0
PART 0
```

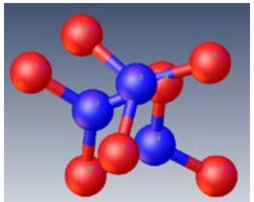
# SIZE dx dy dz

- dx, dy and dz are the three principal dimensions of the crystal in mm, as usually quoted in publications. This information is written to the *.cif* file. If a SIZE instruction is present in the *.ins* file, SHELXL uses it to write the estimated minimum and maximum transmission to the *.cif* file.
- EXAMPLE

```
_exptl_absorpt_correction_T_max        0.7466
_exptl_absorpt_correction_T_min        0.6720   ! Difference 0.075
        _exptl_crystal_size_max        0.250
        _exptl_crystal_size_mid        0.100
        _exptl_crystal_size_min        0.010
_shelx_estimated_absorpt_T_max         0.997
_shelx_estimated_absorpt_T_min         0.934    ! Difference 0.063
```

# SUMP c sigma c1 m1 c2 m2

- The linear restraint:
  - c = c1*fv(m1) + c2*fv(m2) + ...
  - Enables more than two atom (groups) to be assigned with the sum of site occupation factors restrained to be a constant with sigma s.u.



- Example
  - 3 $NO_3$ anions disordered over 3 sites total charge of -1

```
PART 2
N1A   5 .... 21.000
O1A   4 ...  21.000
O2A   4 ...  21.000
O3A   4 ...  21.000
PART 3
N1B   5 .... 31.000
O1B   4 ...  31.000
O2B   4 ...  31.000
O3B   4 ...  31.000
PART 4
N1C   5 .... 41.000
O1C   4 ...  41.000
O2C   4 ...  41.000
O3C   4 ...  41.000
```

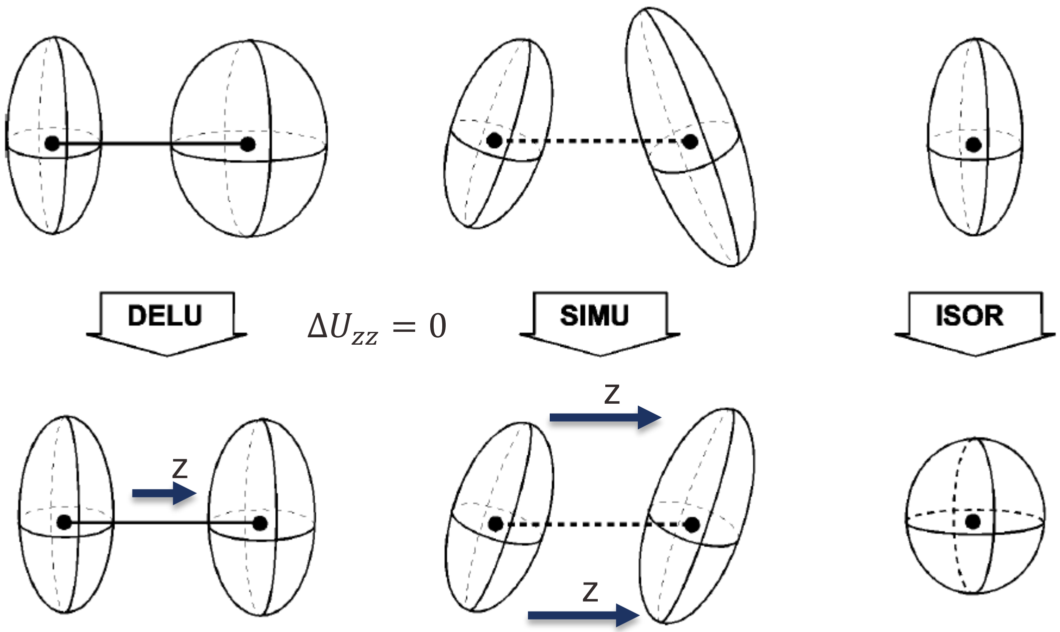
SUMP 1.0 0.01 1 21 1 31 1 41

FVAR scale factor 0.5 0.3 0.2

# Restraints on Displacement

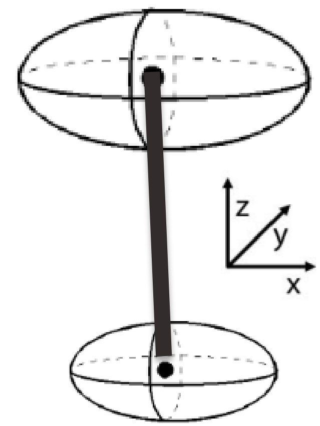
- DELU s1[0.01] s2[0.01] atomnames
  - Soft restraint (total 2/atom pair)
- SIMU s[0.04] st[0.08] dmax[2.0] atomnames
  - Soft restraint (total 6/atom pair)
- ISOR s[0.1] st[0.2] atomnames
  - 5 restraints per atom
- RIGU s1[0.004] s2[0.004] atomnames
  - Hard 3 restraints for 1-2
  - 3 for 1-3 parameters

# Restraints on Displacement DELU, SIMU, ISOR, RIGU




$\Delta U_{zz} = 0$

Restraints along *z*




$\Delta U_{zz} = 0, \Delta U_{yz} = 0, \Delta U_{xz} = 0$

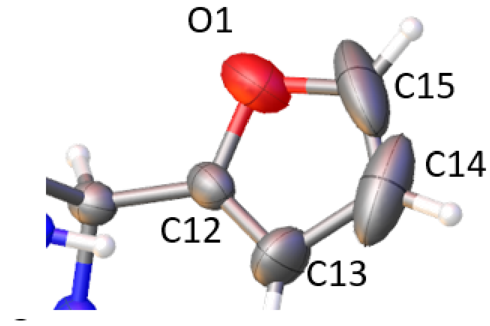
**RIGU***

Restraints along *zz, yz and xz*

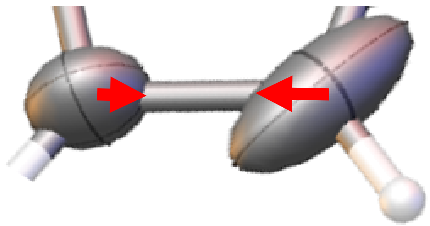
Schneider, T.R. (1996) Röntgenkristallographische Untersuchung der Struktur und Dynamik einer Serinprotease, Thesis (Ph.D.), Universität Mücnchen, Germany
*Thorn, A., Dittrich, B. & Sheldrick, G. M. (2012). Acta Cryst. A68, 448-451.

# Hirshfeld Rigid-Bond Test

- The components of the anisotropic displacement parameters along chemical bonds are assumed to be equal in magnitude.
- Large differences might indicate contamination of these parameters
  - Disorder
  - model or data errors
  - over-refinement




**PLAT230_ALERT_2_B Hirshfeld Test Diff for C13 --C14 . 11.0 s.u.**



Multiple Choice.
Which restraint would best be employed to rectify the ALERT B (above) with fewest restraints?

a. SIMU
b. DELU
c. ISOR
d. RIGU

F.L. Hirshfeld Acta Cryst (1976),A32,239-244

# References


- Müller, P., Herbst-Irmer, R., Spek, A.L., Schneider, T., and Sawaya, M.R. (2006) “Crystal Structure Refinement: A Crystallographer's Guide to SHELXL “ International Union of Crystallography Texts on Crystallography, Oxford, U.K.
- http://shelx.uni-goettingen.de/shelxl_user_guide.pdf
- SHELX-97 shelx.uni-goettingen.de/shelx97.pdf