

Modeling Disorder in SHELXL

Instructor : J. Reibenspies

V 1.0.2

Disorder is simply a lack of order or regular arrangement in the solid-state structure of a compound. The crystalline structure that is modeled is representative of the average structure of 10^{20} molecules.

see Peter Muller's tutorial on disorder at
<http://shelx.uni-ac.gwdg.de/~peterm/tutorial/disord.htm>

Detecting disorder

- Residual electron density near but not on known atomic positions.
- Unusual or elongated thermal ellipsoids
- Unusual molecular geometries, e.g. flat unsaturated ring systems.
- A "may be split" warning will appear in the *.lst file.

This work assumes that the reader is well versed in the usage of the program XP (SHELXTL). If not it is well worth a brief tutorial session in XP. It is also assumed that the reader is familiar with the program SHELXL. The appendix contains a brief table of SHELXL and XP commands.

Nomenclature

This work employs SHELXL format: label type x y z SOF U_{ij}

The generic position x,y,z will be written as xyz and will represent three independent coordinates. The site occupation factor SOF will be normally tied to a free variable.

For example

C1 1 xyz 21.000 will represent a carbon atom of type one with position x, y, z

SIMPLE DISORDERS

Simple "elbow" carbon disorder -CH₂-CH₂-CH₂- In the case of the simplest elbow carbon disorder three atoms have been located (e.g. C1, C2 and C3). A fourth atom is seen near C2 and is named C2'. It is not important that C2' is exactly in the correct disordered position, we will use restraints to correct the distances.

SHELXLT instructions

```
FVAR 1stvar 0.5  
SADI C1 C2 C1 C2' C2 C3 C2' C3  
C1 1 xyz 11.000 ...  
PART 1  
C2 1 xyz 21.000 ...  
PART 2  
C2' 1 xyz -21.000 ...  
PART 0  
C3 1 xyz 11.000 ...
```

The 21.000 links C2 to the 2nd variable on the FVAR line. -21.000 equals 1-2nd variable. The **PART** instruction separates C2 and C2' into disorder components (separate bonding schemes). A negative number for the PART is used when the disorder sits about a special position. Other restraints include **SIMU C1 C2 C2' C3** and **DELU C1 C2 C2' C3** For extreme cases use **ISOR C2 C2'**

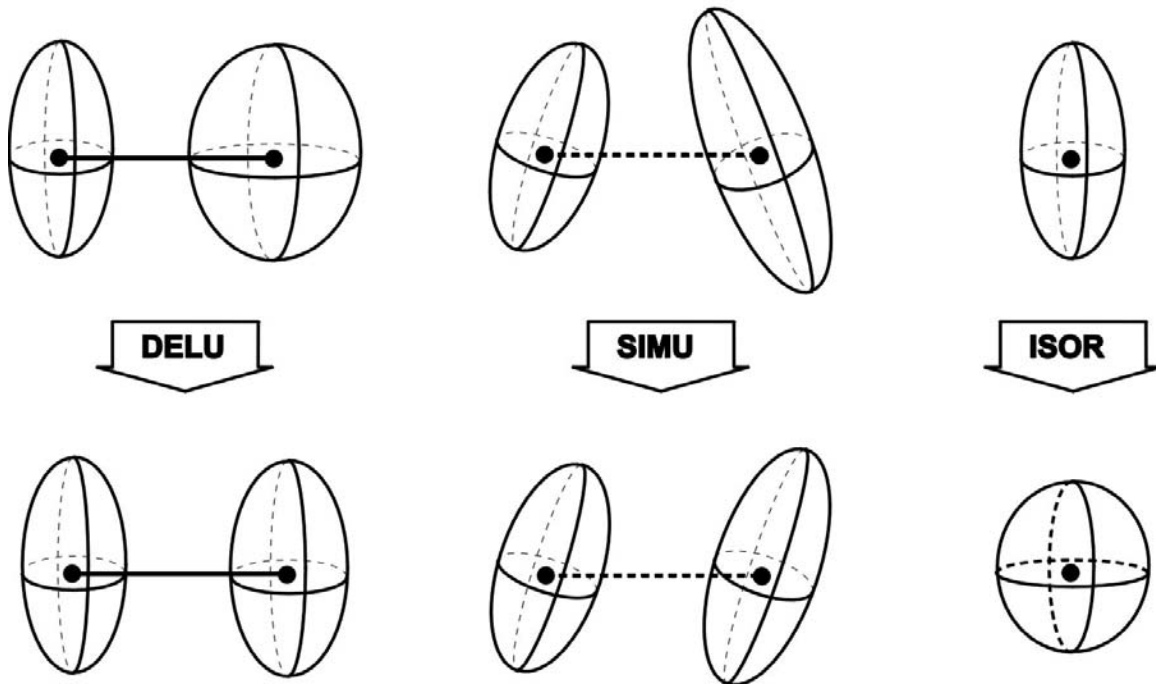


Figure taken from T.R. Schneider, *Röntgenkristallographische Untersuchung der Struktur und Dynamik einer Serinprotease*, Dissertation, Universität München **1996**.

If Hydrogens have been added with XP then

```
FVAR 1stvar 0.5
SADI C1 C2 C1 C2' C2 C3 C2' C3
C1 1 xyz 11.000 ...
PART 1
AFIX 3
H1A 2 xyz 11.000 -1.2
H1B 2 xyz 11.000 -1.2
AFIX 0
C2 1 xyz 21.000 ...
AFIX 3
H2A 2 xyz 11.000 -1.2
H2B 2 xyz 11.000 -1.2
AFIX 0
PART 2
C2' 1 xyz -21.000 ...
PART 0
C3 1 xyz 11.000 ...
PART 1
AFIX 3
H3A 2 xyz 11.000 -1.2
H3B 2 xyz 11.000 -1.2
AFIX 0
PART 0
```

Simple CF₃ disorder.

CF₃ are normally disordered between two positions that are 60° apart. The simplest fix is the AFIX command.

In the following examples C1 is the pivot carbon atom of the CF₃. The following is a constrained refinement.

```
C1 1 xyz 11.0000 ...
AFIX 127 1.39
F1 3 xyz 21.000 ....
F2 3 xyz 21.000 ....
F3 3 xyz 21.000 ....
F1' 3 xyz -21.000 ....
F2' 3 xyz -21.000 ....
F3' 3 xyz -21.000 ....
AFIX 0
```

The restrained equivalent for CF₃ would be

```
SADI C1 F1A C1 F2A C1 F3A C1 F1B C1 F2B C1 F3B
SADI F1A F2A F1A F3A F2A F3A F1B F2B F1B F2B F2B F3B
C1 1 xyz 11.0000 ...
PART 1
F1A 3 xyz 21.000 ....
F2A 3 xyz 21.000 ....
F3A 3 xyz 21.000 ....
PART 2
F1B 3 xyz -21.000 ....
F2B 3 xyz -21.000 ....
F3B 3 xyz -21.000 ....
PART 0
```

This allows for independent angles other than those constrained to 60° apart.

A simpler method is

```
EADP C1A C1B
EXYZ C1A C1B
PART 1
SAME F3A < C1A
C1A 1 xyz 21.0000 ...
F1A 3 xyz 21.000 ....
F2A 3 xyz 21.000 ....
F3A 3 xyz 21.000 ....
PART 2
SAME C1A > F3A
C1B 1 xyz -21.0000 ...
F1B 3 xyz -21.000 ....
F2B 3 xyz -21.000 ....
F3B 3 xyz -21.000 ....
PART 0
```

Disadvantage : XP will not copy SAME command in the FILE instruction.

If there are many disorder CF₃s then one can use the **RESI** and **SAME** as well as the **EXYZ** and **EADP** instructions.

For example the CF₃ disorder can be modeled by

```
SAME_CF3 C1 > F3
EXYZ C1_1 C1_2
EADP C1_1 C1_2
PART 1
RESI 1 CF3
C1 1 xyz 21.0000 ...
F1 3 xyz 21.000 ....
F2 3 xyz 21.000 ....
F3 3 xyz 21.000 ....
RESI 2 CF3
PART 2
C1 1 xyz -21.000 ...
F1 3 xyz -21.000 ....
F2 3 xyz -21.000 ....
F3 3 xyz -21.000 ....
PART 0
RESI 0
```

Advantages

The RESI commands makes the modeling of disorder extremely simple.
One SAME (SIMU, DELU etc) instruction will work for all CF₃ residues.
Commands can be repeated as many times as needed.

Disadvantage

XSHELL will not recognize residue numbers
XSEED does not reflect the residue number in labeling scheme
SAME instruction must be added after XP file command.
CIF file does not use the same labeling nomenclature.

A one time constrained/ restrained method to model CF₃s is to use the **FRAG** and **AFIX** commands. For example in the first refinement the FRAG instruction is introduced with a CF₃ fragment (perhaps from a Molecular Mechanics program).

FRAG 17

```
C1  1  xyz  11.000 ....  
F1  3  xyz  11.000 ....  
F2  3  xyz  11.000 ....  
F3  3  xyz  11.000 ....  
FEND
```

```
FVAR ... 0.5
```

PART 1

AFIX 179

```
C1A  1  xyz  21.000 ....  
F1A  3  xyz  21.000 ....  
F2A  3  xyz  21.000 ....  
F3A  3  xyz  21.000 ....  
AFIX 0
```

PART 2

AFIX 179

```
C1B  1  xyz -21.000 ....  
F1B  3  xyz -21.000 ....  
F2B  3  xyz -21.000 ....  
F3B  3  xyz -21.000 ....  
AFIX 0  
PART 0
```

In this case C1A and C1B are pivot atoms and have the same coordinates.
In the RES file the **AFIX 179** will be replaced with the **AFIX 9**. The entire CF₃ group is now tied to only three variables.

Disordered included solvents and counter ions are very common. A ClO₄ anion can be modeled as described for CF₃ groups. In the case of independent molecules such as ClO₄ the central Cl atom does not need to be constrained to equivalent positions (i.e. the **EXYZ** and **EADP** are not needed or desired. Thus the following could be used to describe a ClO₄ anion disordered over THREE positions.

```
SUMP 1.0 .01 1.0 2 1.0 3 1.0 4
```

```
FVAR ... 0.33 0.33 0.33
```

```
SAME_CLO4 CL1 > O4
```

```
PART 1
```

```
RESI 1 CLO4
```

```
CL1 4 xyz 21.0000 ...
```

```
O1 3 xyz 21.000 ....
```

```
O2 3 xyz 21.000 ....
```

```
O3 3 xyz 21.000 ....
```

```
O4 3 xyz 21.000 ....
```

```
RESI 2 CLO4
```

```
PART 2
```

```
CL1 4 xyz 31.0000 ...
```

```
O1 3 xyz 31.000 ....
```

```
O2 3 xyz 31.000 ....
```

```
O3 3 xyz 31.000 ....
```

```
O4 3 xyz 31.000 ....
```

```
RESI 3 CLO4
```

```
PART 3
```

```
CL1 4 xyz 41.0000 ...
```

```
O1 3 xyz 41.000 ....
```

```
O2 3 xyz 41.000 ....
```

```
O3 3 xyz 41.000 ....
```

```
O4 3 xyz 41.000 ....
```

```
PART 0
```

```
RESI 0
```

If necessary the **DELU_CLO4 CL1 > O4** and **SIMU_CLO4 CL1 > O4** instructions can be employed to restrain thermal parameters. Or in a worse case scenario use the **ISOR_CLO4 CL1 > O4**.

An included molecule such as a THF can be modeled in a manner similar to the CLO4 molecule.

```
SAME_THF O1 > C4
PART 1
RESI 1 THF
O1 3 xyz 21.0000 ...
C1 1 xyz 21.000 ....
AFIX 23
H1A 2 xyz 21.000
H1B 2 xyz 21.000
AFIX 0
C2 1 xyz 21.000 ....
AFIX 23
H2A 2 xyz 21.000
H2B 2 xyz 21.000
AFIX 0
C3 1 xyz 21.000 ....
AFIX 23
H3A 2 xyz 21.000
H3B 2 xyz 21.000
AFIX 0
C4 1 xyz 21.000 ....
AFIX 23
H4A 2 xyz 21.000
H4B 2 xyz 21.000
AFIX 0

RESI 2 THF
PART 2
RESI 2 THF
O1 3 xyz -21.0000 ...
C1 1 xyz -21.000 ....
AFIX 23
H1A 2 xyz -21.000
H1B 2 xyz -21.000
AFIX 0
C2 1 xyz -21.000 ....
AFIX 23
H2A 2 xyz -21.000
H2B 2 xyz -21.000
AFIX 0
C3 1 xyz -21.000 ....
AFIX 23
H3A 2 xyz -21.000
H3B 2 xyz -21.000
AFIX 0
C4 1 xyz -21.000 ....
AFIX 23
H4A 2 xyz -21.000
H4B 2 xyz -21.000
AFIX 0
RESI 0
```

This method has unlimited potential. Whole molecule disorder can be quickly modeled employing the RESI, SAME, SIMU and DELU instructions.

```
SAME_MOL1 C1 > C99
```

```
SIMU_MOL1 C1 > C99
```

```
DELU_MOL1 C1 > C99
```

```
PART 1
```

```
RESI 1 MOL1
```

```
C1 1 xyz 21.0000 ...
```

```
C2 1 xyz 21.000 ....
```

```
C3 1 xyz 21.000 ....
```

```
.....
```

```
C98 1 xyz 21.000 ....
```

```
C99 1 xyz 21.000 ....
```

```
RESI 2 MOL1
```

```
PART 2
```

```
C1 1 xyz -21.0000 ...
```

```
C2 1 xyz -21.000 ....
```

```
C3 1 xyz -21.000 ....
```

```
.....
```

```
C98 1 xyz -21.000 ....
```

```
C99 1 xyz -21.000 ....
```

```
RESI 0
```

Missing atoms ...

In some case an atom will be missing from an included molecule, counter ion or the main molecule. If you are positive the atom should be there (for example the terminal carbon atom of a tetraethylene amine) then you can place it there with XP.

Start XP in the usual manner. Find the atom next to the missing atom. Use HADD to add hydrogens to that atom. Select one of the new hydrogens and use HIMP to move it to the desired distance. Rename that hydrogen to the missing atom element. FILE the results.

In the new INS file find the new atom. Remove the AFIX instructions. With SADI fix the distances to something reasonable. Change the U_{ij} from the negative number to 10.1. Run a few cycles to minimize the structure.

To add an atom $\frac{1}{2}$ distance between two other atoms in XP use the
CENT/X Atom1 Atom2

Rename the resulting X atom and use HIMP to move the atom if necessary (see above).