Modeling Disorder in SHELXL

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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 sight 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 forth 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.

SHELXTL instructions

FVAR 1st var 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'

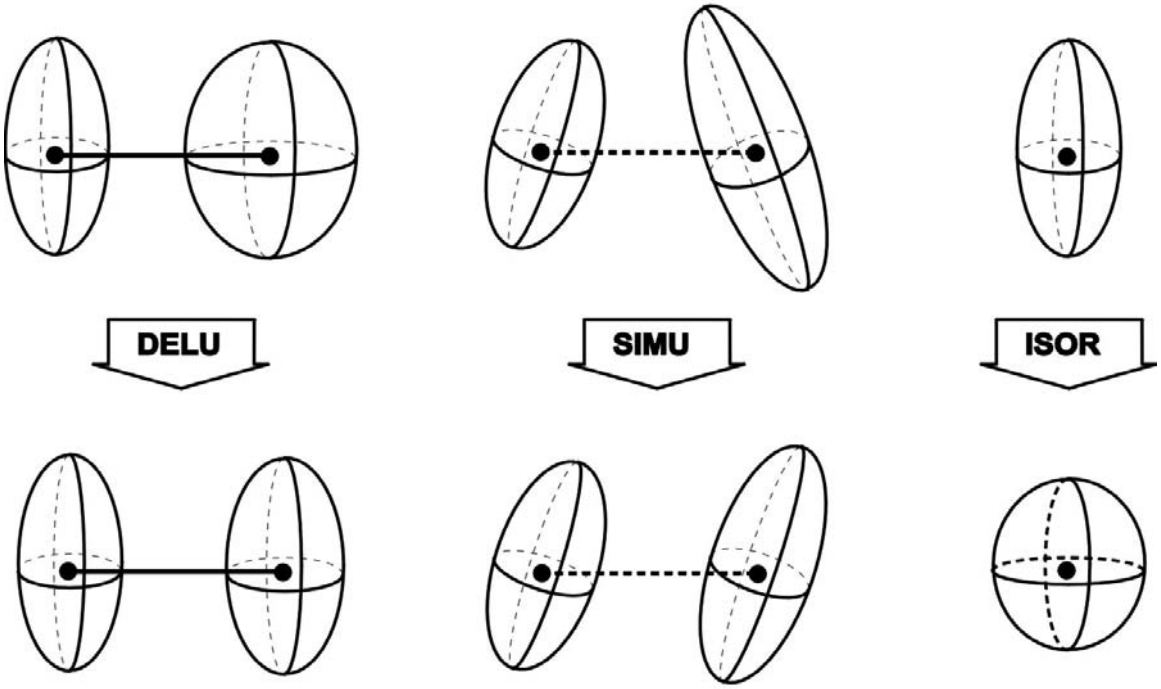

Figure taken form T.R. Schneider, *Röntgenkristallographishe Untersuchung der Struktur und Dynamik einer Serinprotease*, Dissertation, Universität München **1996**.

If Hydrogens have been added with XP then

```
FVAR   1st var    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 CF_3 disorder.

CF_3 are normally disordered between two positions that are 60^o apart. The simplest fix is the AFIX command.

In the following examples C1 is the pivot carbon atom of the CF_3. 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 CF_3 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^o 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 CF_3s then one can use the RESI and SAME as well as the EXYZ and EADP instructions.

For example the CF_3 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 CF_3s is to use the FRAG and AFIX commands. For example in the first refinement the FRAG instruction is introduced with a CF_3 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 CF_3 group is now tied to only three variables.

Disordered included solvents and counter ions are very common. A ClO_4 anion can be modeled as described for CF_3 groups. In the case of independent molecules such as ClO_4 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 ½ 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).