Structure Outline

- Solve Structure
- Refine Structure and add all atoms
- Rename atoms
- Refine anisotropically
- Place in same asymmetric unit
- Add Hydrogens
- Deal with difficulties

Final Steps

- Adjust weight
- Eliminate outliers
- Add hydrogens from difference Fourier if needed
- Make sure all atoms are positive definite.
- If accentric make sure absolute configuration is correct.
- Refine to convergence.
- Produce final output (not done for class structures).

Adding Hydrogens

- Hydrogen atoms are generally treated as riding atoms—that is the idealized bond distance and angles are maintained.
- Idealized atoms are treated using AFIX cards.
- To generate the cards use HFIX cards—format “HFIX code atom” placed anywhere before the central atom.
- This generates AFIX cards with corrected adp's
- Adp -1.2 means U=1.2*U of bonded atom
- Some hydrogen atoms must be found from the Fourier map

HFIX CODES

- C sp3
  - 1 hydrogen 13
  - 2 hydrogens 23
  - 3 hydrogens 137(133 stop changing torsional angle)
- C sp2
  - 1 hydrogen 43
  - 2 hydrogen2 93
- C sp
  - 1 hydrogen 163
- OH 147 (143)

Refinement of Hydrogen Atoms

- Any hydrogen that is significant should be refined (at least in my opinion)
  - Hydrogen atoms involved in hydrogen bonding
  - Hydrogen atoms that are important to interpreting the structure
  - On unknown organics
  - H atoms on N or water that must be found.
- Ideally refined as isotropic atoms. May need to fix U as a negative number if U becomes too large or small.

Weight and Outliers

- Use weight button to adjust the weight—this copies the recommended weight as the new weight
- Use outlier to remove statistical outliers (data that are statistically incorrect)
  - Usually factor is -6-- this will remove all bad data where Fo<<Fc. This is usually data behind the beam stop or the chi circle.
  - For twins may want to use factor=6 to get rid of overlapped twin reflections
  - Outlier places OMIT cards in xl.ins which can be removed later.

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Disorder

- Definitions
- Site Occupancy
- Squeeze
- Multiple Conformations
- Disordered atom types on a site

http://www.molobs.caltech.edu/smallmol/download/public/shelx%20practicals_disorder.pdf

What is Disorder

- Disorder occurs when there are differences between unit cells or asymmetric units within a cell.
- The overall crystal structure displays the average of all the asymmetric units in all the unit cells.
- It is important to remember that any individual asymmetric unit is ordered.

Commensurate Crystals

- Imagine a three-fold disorder where an atom can occupy either site A or B or C.
- If the occupancy in any given cell is random then the crystal is simply disordered.
- However, the disorder can be ordered so that in cell one it is A; cell 2 B and cell 3 C, cell 4 A ...
- This is said to be a modulated or commensurate structure.
- To a first approximation it can be treated as a simple disorder

- Note that in our case the real cell is three times longer but this cell fits no known space group.
- There are programs and methods for dealing with this problem but it is beyond the scope of this course.
- The images will display satellite peaks (in this case at 1/3 the distance in reciprocal space) whose intensity is a function of 1/T.

Restraints vs Constraints

- Disorders can be treated by applying constraints and restraints
- A constraint is a rigid condition or conditions that must be satisfied exactly
  - If an atom is at x,x,z then the y value must be constrained to be the same as x.
  - An example—threat a benzene ring as a rigid planar hexagon.
  - Six parameters –3 coordinate of center 3 orientation
  - Can add a parameter for the bond distance

Restraints

- These are like springs—they try to keep parameters about equal.
- The more the parameters vary the more they are restrained.
- They require a value for the tightness of the restraint. This can be a default.
- These can be misused to correct for bad data.

Partial Occupancy

- It is possible that only some sites are occupied.
- An example is a solvent which evaporates from the crystal.
- This can be treated by refining the occupancy factor (sof).
- What to do if there are multiple atoms in the solvent. How do we refine all the individual sof's so they are all identical.

Free Variables in SHELX

- It is possible to refine additional variables called free variables.
- These are placed on the FVAR card.
  - The first variable is the overall scale factor
  - Each additional variable is numbered 2 and up
- To refine an sof for a group.
  - Place the value as a free variable on the FVAR card
  - Assign the sof of the atoms as 21.0000 (for the second free variable, 31.000 for the third, etc)

SQUEEZE

- Sometimes solvents go into cavities in a totally disordered way. Cannot make out the molecule.
- Cannot ignore these electrons as they can greatly effect the R factors.
- SQUEEZE which is in PLATON can be used to remove this density by smearing out the density across the cavity.

SQUEEZE

- The input to SQUEEZE is the SHELX atom file and the .hkl file. SQUEEZE should not be run until after all the atoms and maybe hydrogen atoms are in place.
- The output of SQUEEZE is a new .hkl file which removes the density from the cavity from the F^2 value.
- The .lis file tells you how many electrons were placed in the cavity.

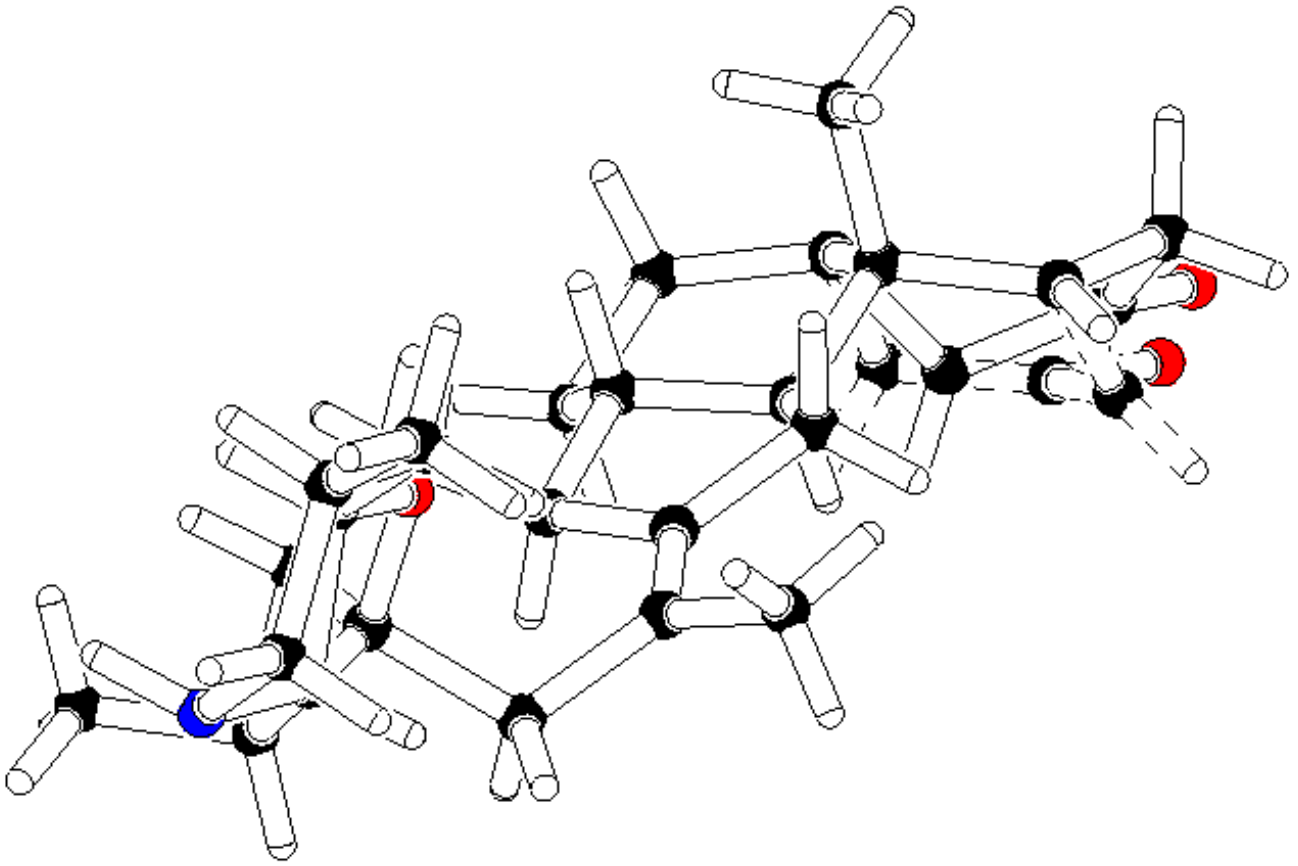
SQUEEZE

- Because SQUEEZE does not provide atoms it should be a LAST RESORT solution.
- SQUEEZE should not be used to remove chemically important parts of the structure
- Some dispute how to treat the formula of the unit cell
  - Ton Spek and I feel that if you cannot see the atoms you cannot include them in the formula
  - Others feel that from the number of electrons and the history it is possible to tell what is in the cavity.

Conformational Disorder

- A molecule can adopt two or more conformations which pack with similar efficiency.
- This can be treated by using the following concepts
  - Free variables to refine the amount of disorder and to ensure they add up to 1.
  - Part numbers to keep equivalent atoms from bonding to each other
  - Perhaps restraints to keep the distances correct.

An Example



.ins File

```
FVAR       0.44119   0.61890
part 1
O3A   4    0.439710    0.094445    0.433164
21.00000    0.09346    0.06752 =
       0.04190    0.02003    0.00617   -0.04905
C2A   1    0.410656   -0.035466    0.471886
21.00000    0.05308
AFIX  23
H2A1  2    0.542984   -0.039683    0.476927
21.00000   -1.20000
H2A2  2    0.354274   -0.010591    0.498388
21.00000   -1.20000
AFIX   0
C3A   1    0.374897    0.022451    0.433850
21.00000    0.04463
C4A   1    0.239454   -0.010792    0.400100
21.00000    0.04105
AFIX  43
H4A   2    0.254027   -0.007882    0.369348
21.00000   -1.20000
AFIX   0
part2
O3B   4    0.448410    0.066233    0.414082
-21.00000    0.10574
C2B   1    0.444405   -0.082786    0.433167
```

Some Comments

- Parts are used to keep meaningless bonds and angles out of the list
  - PART 0 is the main part
  - PART 1 interacts with PART 0 and PART 1
  - PART 2 interacts with PART 0 and PART 2
- Negative free variable means the values is 1-the free varaiable
  - -21.000 means 1- free variable 2
  - -20.500 means 0.5-free variable 2

Positions for Conformational Disorder

- Need the positions for the atoms in the disorder
- Sometimes the atoms are far enough apart that they are observed in the Fourier map
- Can be found also by splitting very oblong adp's.
- In general atoms less than 0.4A apart are best left unsplit as the resolution of the experiment is typically 0.7A or greater.
- Can use the SPLIT option in the REFINE GUI.

Restraints

sadi c1 c2a c5 c4b
sadi c1 c2b c5 c4a
sadi c3a c2a c3a c4a
sadi c3b c2b c3b c4b

SADI means same distance.

Other restraints

DFIX -- restrain to a specific bond distance

ISOR -- restrain adp to isotropic (sphere)

SAME -- used to make two fragments identical. Applies sadi

Extreme Disorder

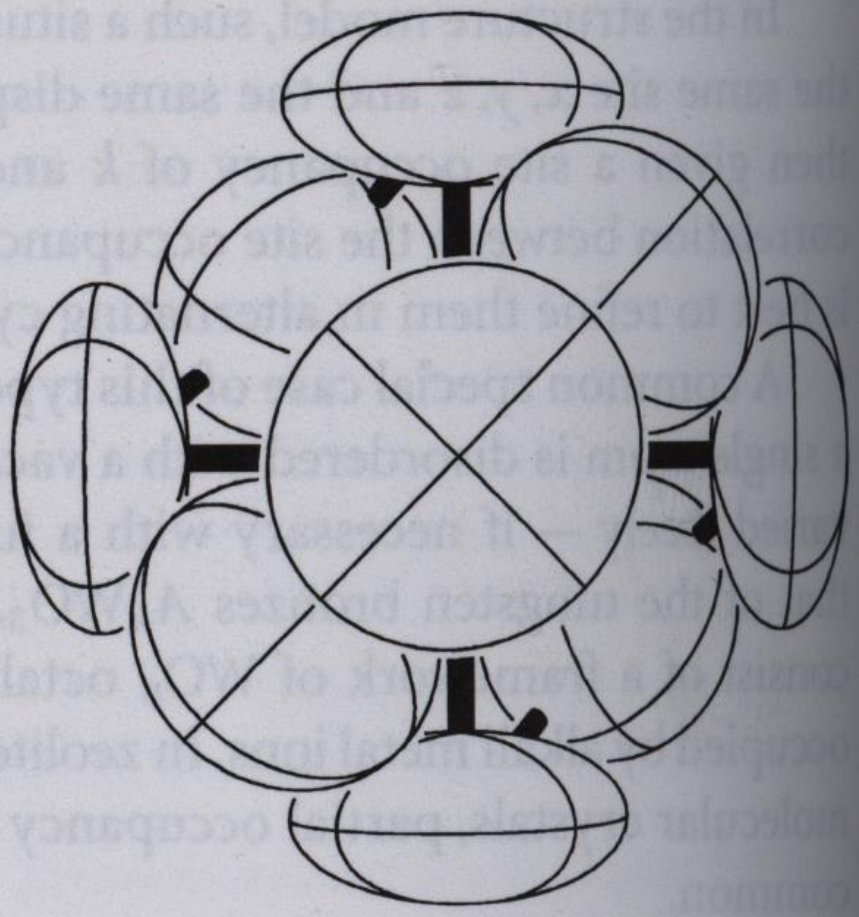


Fig. 10.1. Representation of a disordered BF_4-anion using 10 partially occupied F-sites.

Two different atoms on one site

- Sometimes two different elements occupy the same site in a structure.
  - Zn and Cu complexes co-crystallize
  - In minerals random placement
- Use EXYZ and EADP to tell the program that atoms have identical xyz's and adp's.
- Use Free variables to adjust the sof.
- If there are more than 2 different atom types on a site there is a way in SHELX to force the sum to one.