Using Free Variables and Restraints

Crystal structures can be divided into two classes: those in which the refinement is well behaved from start to finish, and those in which the refinement is impeded by one or more kinds of crystallographic problems. The latter variety of crystal structure is the subject of the present document.

Among the most common kinds of crystallographic problems are disorder and poor convergence of the least-squares refinement. A definition of disorder will be given below, but the presence of disorder is easy to establish: disorder is signaled by the appearance of electron density peaks (either as Q peaks in the difference maps or as unacceptably elongated thermal ellipsoids) whose locations correspond to chemically reasonable **alternative** locations for certain atoms in the structure. In order to obtain the lowest possible value for wR2 (the least-squares residual), you must determine the chemical identities of these electron density peaks and include these disordered atoms in the refinement.

Poor convergence of the least-squares refinement is a different problem, and is signaled by the fact that the maximum shift/error (a value which is calculated and reported on-screen by XL) stays large (e.g. over 1) even after many cycles of refinement.

Herein we describe the use of two tools which are invaluable for managing these problems: free variables and restraints. These tools allow the user to exercise precise control over the least-squares refinement using the SHELXTL software package. A good working knowledge of the use of free variables and restraints is crucial for the successful refinement of many crystal structures.

It should be emphasized, however, that these crystallographic problems can only be solved by thinking like a chemist; the software package will not do your thinking for you. A satisfactory match to the experimental electron density in the crystal can best be achieved by devising a chemically plausible theory of what static or dynamic processes the atoms in the crystal are engaged in.

1.   Non-Integral Site Occupancy Factors, Disorder, and Free Variables.

1.1. The site occupancy factor (SOF)

In the list of atoms found in an .ins or .res file, the first number following the x, y, and z coordinates of an atom is called the site occupancy factor (SOF). Normally, the site occupancy factor of an atom is equal to 1 -- this means that there is one atom at the location specified by the atomic coordinates (x,y,z).

In SHELXTL, if a parameter is not supposed to be varied during a least-squares refinement, then the number 10 is added to the value of that parameter. Thus, for most of the atoms in an .ins file, the default value of the SOF is 11. The SHELXTL program interprets this to

mean that SOF = 1 and don't change it. (SHELXTL knows that a SOF cannot really be 11; it must be between 0 and 1.)

There are situations, however, in which the SOF of an atom at the coordinates (x,y,z) is not equal to 1.   These situations are described in the next few sections.

1.2. SOF's and special positions

One of the most commonly encountered reasons for a non-integral SOF is that the atom sits on a special position. For example, if the atom sits on a center of symmetry, a two-fold axis, or a mirror plane, one-half of the atom is symmetry related to the other half. In this case, the SOF is equal to 0.5. If the atom sits on a special position of higher symmetry, then the SOF will be smaller than 0.5 (sometimes much smaller!). For example, in NaCl (space group Fm3m), the sodium (and chlorine) atoms reside on sites of m3m symmetry, and their site occupancy factors are $1/_{48}$ or 0.0208. The other $47/_{48}$ths of each atom is generated by the symmetry elements that pass through those special positions.

Fortunately, the site occupancy factors for atoms on special positions are automatically set to appropriate values by the SHELXTL software package, and usually it is not necessary to change them manually. One should always check to verify, however, that the value assigned by the SHELXTL software package is correct. You can do this by consulting the International Tables: the SOF for an atom on a special position should be equal to the number of positions for the corresponding Wyckoff index, divided by the order (i.e., the number of general positions) of the space group.

1.3.   Other factors that affect SOF's

Other factors, which are **not** automatically handled by SHELXTL, can also affect the SOF of an atom. Three slightly different situations are commonly encountered:

(a) In some unit cells an atom is at (x,y,z), but in other unit cells there is **no atom** at that location. This situation, which is often seen for volatile solvent molecules that occupy interstices within the crystal, is referred to as **partial occupancy**; in minerals, the phenomenon is usually referred to as a defect site or vacancy. In this case, the site occupancy factor will be an average over all unit cells, and will be less than 1.

(b) In some unit cells an atom is at (x,y,z), but in other unit cells there is **a different kind of atom** (or, less commonly, several different kinds of atoms) at that same location. This situation, which is often seen in minerals, is referred to as **substitutional replacement** and is characteristic of a solid solution. In this case, the site occupancy factor for each kind of atom is less than 1, but the two (or more) SOF's add to 1.

(c) In some unit cells the atom is at (x,y,z), but in other unit cells the atom is at (x',y',z'). This situation is referred to as **disorder**. In this case, the SOF of each individual site is

less than 1, but the **sum** of the two SOF's is equal to 1. Of course, it is possible for the atom to be disordered over **more** than two sites whose SOF's sum to 1.

It is important to realize that the SOF is a number that is **averaged** over **all** the unit cells in the lattice. In any **one** unit cell, the SOF must be either 1 or 0, but you can never know this number because X-ray diffraction tells you nothing about any individual unit cell.

1.4. Partial occupancy and free variables

Let us suppose that your crystal contains a solvent molecule, and that two of the atoms in the solvent molecule are C1 and C2. The .ins file might contain the following lines:

| C1 | 1 | 0.38773 | 0.84554 | 0.17390 | **11.0000** | 0.0500 | .... |
| C2 | 1 | 0.40640 | 0.92662 | 0.11408 | **11.0000** | 0.0500 | .... |

key: ATOM CODE   X   Y   Z   SOF   U11   ....

Suppose that the solvent molecule is missing from some of the unit cells, so that the SOF for all its atoms should be less than 1. (This might be indicated, for example, by unusually large displacement parameters Uij, although large ellipsoids could also just mean that the solvent molecule is experiencing high thermal motion.) To let the SOF's vary and refine to a value different from 1, you could change the value of the SOF's from 11.0000 to 1.0000. If you set up the .ins file as follows:

| C1 | 1 | 0.38773 | 0.84554 | 0.17390 | **1.0000** | 0.0500 | .... |
| C2 | 1 | 0.40640 | 0.92662 | 0.11408 | **1.0000** | 0.0500 | .... |

and then run XL, the program will **independently** refine the SOF for C1 and C2, and in general, these SOF's will refine to slightly different (and sometimes significantly different) numbers. This is a problem, since the SOF for C1 must be **equal** to the SOF for C2 (all the atoms in the solvent molecule must have the same average site occupancy factors because in any one unit cell they either are both there or both absent). **We therefore do not recommend this approach.**

There is an alternative way to let the SOF's refine that allows you to force the SOF of C1 to equal the SOF of C2. This alternative method employs what is called a free variable. To do this, change the SOF for **both** atoms from 11.0000 to 21.0000 (the reasons for this will be explained below). The number 21.0000 is called a free variable index; it is **not** the actual site occupancy factor, but rather a number that tells the XL program where to **look for** the site occupancy factor:

| C1 | 1 | 0.38773 | 0.84554 | 0.17390 | **21.0000** | 0.0500 | .... |
| C2 | 1 | 0.40640 | 0.92662 | 0.11408 | **21.0000** | 0.0500 | .... |

You must then also change the FVAR line, which is the command that appears just before the list of atoms in the .ins file. The first number on the FVAR command (which stands for **F**ree **VAR**iables) is the overall scale factor, a number that normalizes the observed reflection

intensities. For example, if the overall scale factor is 0.16834, then the FVAR command looks like:

FVAR   0.16834

Modify the FVAR command line by adding a second number for the site occupancy factor:

FVAR 0.16834 1.0000

The free variable index of 21.0000 in the C1 and C2 atom lines means the following: let the SOF be equal to the **2nd** number on the FVAR command, times the number **1**. After you run XL, the SOF listed on the atom lines in the .res file will still be 21.0000, but the FVAR command will have changed:

FVAR 0.16832 0.7534

so that the new SOF for **both** C1 and C2 is 0.7534.

By adding more numbers to the FVAR command, you can refine as many free variables as you want.   Up to eight numbers are allowed for any one FVAR command, but you can have more than one FVAR command; the free variable indexes for the second FVAR command will start at the number 9, the indexes for the third FVAR command will start at 17, etc. For example, if the SOF of an atom is set equal to 121.0000, then the SOF is set initially to the value of the twelfth number on the FVAR commands (i.e., the fourth number on the second FVAR command).

1.5. Free variables and disorder

Occasionally, you will find that an atom or group of atoms is disordered over two or more locations in the unit cell. For example, a cyclopentadienyl ring or a CF_3 group may exist in two two different rotameric conformations, or an ethyl group may sometimes be kinked "up" and sometimes kinked "down". The presence of disorder is signaled by the appearance of Q peaks in the electron density map at locations that form a chemically sensible alternative conformation (or location) of the molecule.

For the examples cited above, the electron density maps before adding the second disordered component might look as follows:
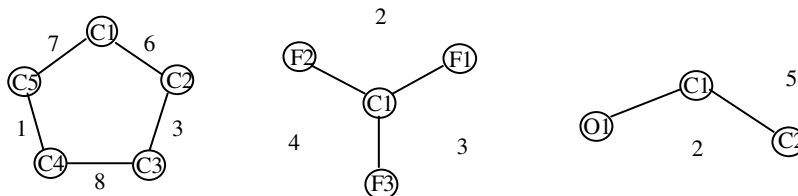
In these cases, the Q peaks (shown here without the Q prefix) form chemically sensible structures that correspond to different conformations or different locations of these groups. Although these

examples show disorder over two sites, it is possible for a group of atoms to be disordered over three (or even more) sites.

Often, the presence of disorder will also show itself in the form of unusually elongated ellipsoids for nearby atoms; this occurs because the SHELXTL program is doing its best to "cover" the electron density due to the disordered component. Unusually-elongated ellipsoids are flagged in the .lst file, in a table that just follows the table of atomic coordinates after refinement. The message "may be split into x1 y1 z1 x2 y2 z2" will follow those atoms that have unusually elongated (sausage-like) ellipsoids, where (x1,y1,z1) and (x2, y2, z2) are suggested coordinates for the two disordered components (partial atoms).

It is important to note that the site occupancy factors for the disordered components do not need to be equal. Often, one finds that one disordered component will be the "major" component, and the rest will be "minor" components. Only if the disordered components are related by a symmetry element must the SOF's be equal.

When an atom is disordered, the SOF for any one location (x,y,z) may be less than one, but the **sum** of the SOF's over all possible locations for the atom is usually **equal** to 1. In other words, if an ethyl group is disordered over two locations and 71% of the ethyl groups are kinked up (SOF = 0.71), then the remaining 29% of the ethyl groups will be kinked down (SOF = 0.29).

Suppose that atom C1 is disordered over two sites; call them C1A and C1B. If you set up the following commands in the .ins file:

```
FVAR  0.16832
C1A    1    0.38773   0.84554    0.17390    0.7100   0.0500     ....
C1B    1    0.36640   0.81662    0.20408    0.2900   0.0500     ....
```

and then run XL, the program will independently refine the SOF's for C1A and C1B, and in general, these SOF's will not add up to exactly 1. **For this reason, we do not recommend the above approach.**

To force the SOF's for C1A and C1B to add to exactly 1, you can again use a free variable. Set up the following commands in the .ins file:

```
FVAR  0.16832  0.7534
C1A    1    0.38773   0.84554    0.17390    21.0000   0.0500     ....
C1B    1    0.36640   0.81662    0.20408   –21.0000   0.0500     ....
```

As before, the numbers 21.0000 and –21.0000 are not site occupancy factors, but are numbers that tell XL where to **look** for the SOF. In this case, for C1A the number 21.0000 tells XL that the SOF for this atom (at the beginning of the least-squares refinement) should be set equal to the **2nd** number on the FVAR command, times **1**. This means that for atom C1A, the site occupancy factor will be 0.7534 to begin with.

For C1B, the number –21.0000 tells XL that the SOF for this atom should be set equal to the following value: (**2nd** number on the FVAR command minus 1) times **–1**. While this is a

little weird, it accomplishes what you want: for C1B, the site occupancy factor will be 0.2466 to begin with:

$$(0.7534 - 1) \times (-1) = 0.2466$$

As the least squares refinement proceeds, the value on the FVAR command is changed, but it will still be true that (SOF for C1A) + (SOF for C1B) will equal 1.

If an atom is disordered over **three or more** positions, then you will have to assign separate free variables for each SOF, and then use a SUMP command. See the SHELXTL manual for more information about the SUMP command.

1.6. Free variables and substitutional replacement

The approach above is also useful to handle substitutional replacement, i.e., cases in which two (or more) **different kinds** of atoms occupy the same site. Suppose that you have told the SHELXTL program that the atom at the location (x,y,z) is a magnesium atom, but that in actuality this site is occupied by a magnesium atom in only 80 % of the unit cells, and in the remaining 20 % by iron. Because iron has more electrons than magnesium, the presence of the iron atoms makes the electron density at (x,y,z) greater than expected for a magnesium atom. The SHELXTL program does its best to match the observed and calculated electron densities, and it will do this by artificially reducing the size of the displacement parameters for the Mg atom, so that its electron density will be "concentrated" in a smaller volume of space. Careful inspection of the displacement parameters will show that the Mg atom has a suspiciously small ellipsoid compared to other atoms in its vicinity.

If the substitutional replacement had involved an atom with fewer electrons than Mg, then the opposite situation would have been seen: the Mg atom would be artificially "spread out" and would have a suspiciously large ellipsoid compared to other nearby atoms.

If you suspect, for example, that in a particular crystal, a certain location (x,y,z) is occupied in some unit cells by a magnesium ion and in other unit cells by an iron atom, you should set up the atom lines in the .ins file as follows:

```
FVAR  0.16832  1.000
MG     1     0.38773   0.84554    0.17390    21.0000    0.0500     ....
FE     1     0.38773   0.84554    0.17390   –21.0000    0.0500     ....
```

If the free variable is set to 1.00 (as in the above example), the initial values of the SOF's will be 1.00 for MG and 0.00 for FE. Running XL will refine the value of the SOF's for both atoms, and they will continue to sum to 1 even after refinement.

In cases of substitutional replacement, the atomic coordinates of the two atoms are (by definition) identical. But if the .ins file is set up with commands as shown above, the least squares refinement will vary the coordinates of MG and FE **independently**, and the two atoms will tend to drift apart from one another. You could force the coordinates of the two atoms to be identical by adding appropriate free variables, but it is easier to add the command EXYZ MG FE to the .ins

file between the UNIT and WGHT commands (see section 2.3 below). Similarly, the displacement parameters for MG and FE should be set equal, and this can be done either with a free variable, or by using an EADP MG FE command (see section 2.4).

1.7. Free variables applied to atoms on special positions

Free variables can also be used for atoms on special positions, but some care is required. For example, suppose you have a solvent molecule that lies in some of the unit cells but not others, and that it contains two atoms C1 and C2. Let us suppose that C1 lies in a general position, away from any symmetry element. The SOF for atom C1 will be non-integral, say 0.7534. This number will appear in the FVAR command, and the SOF in the atom lines for C1 will be set to 21.0000. Let us suppose that C2 sits on (for example) a two-fold axis. The SOF for C2 should be **half** of those of the atoms in general positions (i.e., 0.7534 / 2 = 0.3762). To make sure that this happens, set the SOF for C2 equal to 20.50000. This tells the program to set the SOF for that atom initially to the **2nd** number on the FVAR command, times **0.5**.

```
FVAR  0.16832  0.7534
C1      1    0.38773   0.84554   0.17390   21.0000   0.0500     ....
C2      1    0.50000   0.92662   0.11408   20.5000   0.0500     ....
```

The following table may be helpful; n is a number between +5 and -5:

free variable index	meaning
20 + n	2nd number on the FVAR command, times n
20 – n	2nd number on the FVAR command times –n
–20 + n	(2nd number on the FVAR command minus 1) times n
–20 – n	(2nd number on the FVAR command minus 1) times –n

Free variables can also be used when atoms involved in substitutional replacement reside on special positions. Thus, to constrain two SOF's to add up to 0.25 (e.g., for two elements occupying the same fourfold special position), they could be given at 20.25 and -20.25:

```
FVAR  0.16832  0.8
MG      1    0.50000   0.50000   0.11408   20.2500   0.0500     ....
FE      1    0.50000   0.50000   0.11408  –20.2500   0.0500     ....
```

For the example above, the initial values of the SOF's (i.e., before the next cycle of least-squares refinement) are $0.8 \times 0.25 = 0.20$ for MG, and $(0.8 – 1) \times –0.25 = 0.05$ for FE.

If more than two kinds of atoms are involved in a substitutional replacement at a special position, then individual free variables should be assigned to the SOF's, and a SUMP command should be used to make them add up to the desired value. See the SHELXTL manual for more information about the SUMP command.

1.8. Use of the PART command

If you have disordered groups of atoms, the SHELXTL programs will see the disordered atoms as all lying near one another, and the distances and angles involving atoms in **different** disordered components will be included in the tables of bond distances and angles. These distances are chemically non-meaningful, and will often make it impossible to use AFIX commands (see section 2.1) to include hydrogen atoms in fixed positions. For these reasons, it is advantageous to delete the chemically non-meaningful interatomic distances between disordered atoms from the tables. This can be done by inserting PART commands at appropriate places in the atom list. To do this, insert PART 1 before the atoms in the first disordered set, PART 2 before the atoms in the second disordered set, etc. If the atoms in a disordered part are followed by atoms that are **not** disordered, you must insert a PART 0 command.

For example, suppose that you have a diethyl ether molecule in which one ethyl group (atoms C1 and C2) is disordered over two sites A and B, while the other ethyl group (atoms C3 and C4) is ordered. The following set of commands would divide the disordered atoms of the first ethyl group into the appropriate sets:
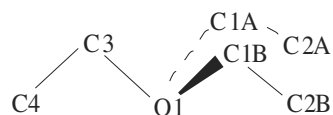
O1	3	0.36593	0.83884	0.20722	**11.0000**	0.0500	....
PART 1							
C1A	1	0.38773	0.84554	0.17390	**21.0000**	0.0500	....
C2A	1	0.39554	0.92662	0.11408	**21.0000**	0.0500	....
PART 2							
C1B	1	0.39002	0.86181	0.17066	**–21.0000**	0.0500	....
C2B	1	0.40767	0.93777	0.12556	**–21.0000**	0.0500	....
PART 0							
C3	1	0.40022	0.83992	0.23056	**11.0000**	0.0500	....
C4	1	0.41229	0.92933	0.25819	**11.0000**	0.0500	....

This set of commands will ensure, for example, that the distance between C1A and C1B is not included in the table of bond distances.

If the disordered molecule resides on or near a symmetry element, it is often helpful to insert PART -1 and PART -2 commands to separate the disordered components. The negative numbers will delete all distances and angles that involve symmetry-related atoms generated by the symmetry operation. See the SHELXTL manual for more details.

1.9. The relationship between SOF and Uij

The SOF and the displacement parameters Uij are mutually compensating. For example, suppose that you locate an atom and include it in your atom list with SOF = 11 (i.e., SOF = 1 and the value is non-variable). If the SOF of the atom is actually less than 1, then the calculated electron density at that location will be **larger** than the experimental electron density. The least-

squares program will try to minimize the wR2 factor (i.e., to match the calculated and experimental electron densities) by "smearing" the atom out: it will make the displacement parameter(s) for that atom artificially large. If you realize that this atom actually has a SOF which is less than 1, and you allow the SOF value to refine to a lower value, then the least squares program will no longer have to smear out the atom to match the calculated and experimental electron density. The displacement parameter(s) will usually become smaller as a result.

There is one important consequence of the fact that the SOF and the Uij factors are mutually compensating. If both the SOF and Uij are allowed to vary simultaneously, sometimes the compensating effect will make it impossible for the least-squares refinement to converge: no matter what value is assigned to the SOF, the computer can find a value of Uij that will match the observed electron density. In such cases, one of the two parameters must be given a fixed (i.e., unchangeable) value in order to obtain a satisfactory convergence. Usually, it is better to set the SOF to a fixed value and let Uij vary.

1.10. Other uses of free variables

Free variables can also be used for the displacement parameters or atomic coordinates. This is useful when you wish to restrict the number of parameters, or when light atoms are involved in disorder (if the disordered atoms are overlapping, it can be very difficult to refine independent displacement parameters for them). For example, look at the following commands:

```
FVAR  0.16832  0.7534  0.0500
C1      1    0.38773   0.84554    0.17390    21.0000    31.0000      ....
C2      1    0.40640   0.92662    0.11408    21.0000    31.0000      ....
```

In this case, the SOF's for both atoms are initially set to 0.7534 and then are refined **together** in the next cycle of least squares, and will still be equal to one another after the refinement is finished. In addition, the U11 parameters for both atoms are initially set to 0.0500 (the third number on the FVAR command) and are also refined together in the next cycle of least squares. 0.05 is a good starting value for U11.

2. Poor Convergence of the Least-Squares Refinement; Using Restraints

If the number of variables used to model the structure becomes too large, then the least-squares refinement tends to become unstable and convergence can be slow or impossible to achieve. The reasons for this are clear: for example, if you have measured 1000 X-ray intensities and have 1001 variables, it will always be possible to "fit the data", even with a model structure which is completely fictitious. A good rule of thumb is that the number of variables should never exceed one-tenth of the number of "observed" reflections with $I > 2\ \sigma(I)$; this latter number can be found in the .lst file generated by XL. If the number of variables begins to approach this limit, one should strongly consider reducing the number of variables. This can be accomplished with skillful use of what are called AFIX commands.

Least-squares refinements can also become unstable if a parameter (such as a coordinate or displacement parameter) is added to the model, but the intensity data are insufficient in some way and do not allow a "best-fit" value for that parameter to be calculated. For example, hydrogen atoms scatter X-rays very poorly, and the locations of the hydrogen atoms in many cases cannot be established by analysis of the X-ray intensities. Trying to perform a least-squares refinement with hydrogen coordinates included as parameters may cause the refinement to converge slowly or not at all. In this case, it is often possible to include restraints which "fix" the hydrogen atom in "idealized" locations calculated from the C-H bond distances and angles that they must make. These restraints can also be applied with AFIX commands.

Restraints are also useful to handle certain refinement instability problems that accompany the partial occupancy, disorder, and substitutional replacement phenomena discussed in the previous section. Unlike the AFIX constraints, these restraints generally do **not** reduce the number of variables (exceptions include the EXYZ and EADP commands).

NOTE: most of the command commands described below have adjustable parameters (bond distances, estimated standard deviations, etc.), although this is often not indicated in our discussion. If these parameters are not specified by you, then the SHELXTL program assigns "default" values to them. While these default values are often reasonable, they may not suit your particular situation. Consult the SHELXTL manual for more information about these commands and the adjustable parameters that apply to each one.

2.1. Special restraints

Special commands (called AFIX commands) have been set up in SHELXTL to handle certain commonly-needed restraints. A short summary of the most useful of these commands is given below. If used, the AFIX commands must be inserted in the atom list just before the atoms to which they refer. See Section 8.8 of the SHELXTL manual for more details.

IMPORTANT: if restrained atoms are followed in the atom list by atoms that are NOT subject to the special restraint, an AFIX 0 command must be inserted after the restrained atoms. The AFIX 0 command tells the program not to apply the restraint to the atoms after the command. Failure to insert AFIX 0 commands at the appropriate locations will cause the restraints to be applied (inappropriately) to the following atoms. This is a common cause of error in crystallographic refinements, and thus it is important to inspect the .ins file carefully to make sure that the appropriate AFIX 0 commands are included.

AFIX 13   next atom is an idealized tertiary C-H hydrogen atom
AFIX 23   next two atoms are idealized secondary CH_2 hydrogen atoms
AFIX 33   next three atoms are idealized non-rotating CH_3 hydrogen atoms (see also AFIX 137)
AFIX 43   next atom is an idealized aromatic C-H or amide N-H hydrogen atom
AFIX 59   next five atoms form a regular pentagon whose size is allowed to shrink or expand; the atoms must be listed in cyclic order
AFIX 69   next six atoms form a regular hexagon whose size is allowed to shrink or expand; the atoms must be listed in cyclic order

AFIX 83   next atom is an idealized hydrogen-bonded OH hydrogen atom with tetrahedral X-O-H angle

AFIX 93   next two atoms are idealized NH_2 hydrogen atoms

AFIX 109   next ten atoms form an idealized C_5Me_5 group whose size is allowed to shrink or expand; atoms must be listed in cyclic order, ring carbons first, methyl carbons last

AFIX 127   next six atoms are the hydrogen atoms of a disordered methyl group with the two conformations rotated by 60°

AFIX 128 1.32   useful if next six atoms are the fluorine atoms of a disordered CF_3 group with the two conformations rotated by 60° (the 1.32 parameter is the C-F bond distance); a CONN 0 $F command must be added between the UNIT and FVAR lines

AFIX 137   next three atoms are idealized rotating CH_3 hydrogen atoms

AFIX 138 1.32   useful if next three atoms are the fluorine atoms of a CF_3 group (the 1.32 parameter is the C-F bond distance); a CONN 0 $F command must be added between the UNIT and FVAR lines

AFIX 147   next atom is an idealized rotating O-H hydrogen atom with a tetrahedral X-O-H angle

AFIX 153   next atom is a X-H hydrogen atom where X is connected to 4 or 5 other atoms (useful for polyhedral boranes)

AFIX 163   next atom is an idealized acetylenic hydrogen atom

If your goal is to apply restraints to **hydrogen** atoms, you can use HFIX commands inserted between the UNIT and WGHT lines to add the appropriate hydrogen atom lines to the atom list and to add the appropriate AFIX commands in the appropriate places. For example, if you insert an HFIX 43 C1 command between the UNIT and WGHT lines in the .ins file, and then run XL, the output .res file will contain the following lines after the line for C1:

    AFIX 43
    H1   1   0.38773   0.84554   0.17390   11.0000   -1.2
    AFIX 0

The (x,y,z) coordinates will be calculated based on the known C-H distance for (in this case) aromatic hydrogen atoms, and the SOF will be set equal to that of the atom it is attached to (i.e., C1). The value of -1.2 for U11 instructs SHELXTL to set the U11 for this hydrogen atom equal to 1.2 times the equivalent isotropic displacement parameter U_{eq} for the atom it is attached to (C1). See the SHELXTL manual for more information about HFIX commands.

2.2. Restraints on bond distances and angles

The following commands can be used to restrain bond distances and angles. They are useful if certain bond lengths or angles refine far from their chemically expected value (and you have made the correct elemental assignments for the atoms involved!). If these commands are used, they should be inserted in the .ins file between the UNIT and FVAR commands. In the following section, dist = the desired bond distance, and esd = the desired estimated standard deviation in the desired bond distance. Formats for these commands follow:

DFIX   dist esd atom pairs [default esd = 0.03 Å.]
    The DFIX command can be used to assign a specific value for the distance
    between pairs of atoms.

SADI   esd atom pairs [default esd = 0.03 Å.]
    The SADI command can be used to make the distance between two or more
    different pairs of atoms equal; the command does not, however, specify in
    advance what that distance should be.

SAME (see SHELXTL manual for more details)
    The SAME command can be used to make two or more different groups of atoms
    adopt the same shape.

Examples follow.

DFIX 1.54 0.01 C1 C2 C3 C4
    makes the C1-C2 and C3-C4 distances equal to 1.54 ± 0.01 Å. You can add as
    many atom pairs to the command line as you like; all of them will be forced to be
    1.54 Å apart.

DFIX 21 0.01 C1 C2 C3 C4
    makes the C1-C2 and C3-C4 distances equal to the 2nd free variable within ± 0.01
    Å. You can add as many atom pairs to the command line as you like.

SADI 0.01 C1 C2 C3 C4
    makes the C1-C2 and C3-C4 distances equal to within ± 0.01 Å. You can add as
    many atom pairs as you like to the SADI command; all the pairs on the same
    SADI command will have the same distance. The SADI command "costs" one
    less variable than the above DFIX command, but the DFIX command gives an esd
    for the refined distance, whereas the SADI command does not.

The FLAT and CHIV commands can be used to enforce planarity on groups of atoms. If
used, these commands should be inserted in the .ins file between the UNIT and FVAR lines.
Formats and descriptions follow:

FLAT atom names
    The FLAT command will force a group of four or more atoms to be co-planar.

CHIV atom name(s)
    The CHIV command will impose a planarity restraint on an atom which is bonded
    to three others; only the atom that is to have the planar geometry needs to be
    named. If more than one atom appears on a CHIV command, each one will be
    forced to have a planar local geometry.

2.3. Restraints on atomic coordinates

The EXYZ command sets the coordinates of the named atoms equal. You can add as many atoms to the EXYZ command as you like; all of the atoms named on the same EXYZ command will be forced to have the same atomic coordinates. The EXYZ command is useful when two (or more) different kinds of atoms occupy the same site (i.e., substitutional replacement or a solid solution). If used, this command should be inserted in the .ins file between the UNIT and FVAR lines. The format is as follows:

EXYZ atom names

For example, if you have a case of substitutional replacement in which the general position (x,y,z) is occupied by a magnesium atom in some unit cells, and by an iron atom in others, then you should set up the restraints on the SOF's as detailed in section 1.6, and add the following command to the .ins file:

EXYZ MG FE

2.4. Restraints on displacement parameters

Displacement parameters (which are often incorrectly called thermal parameters) are the U_{ij} values that describe the shape of the ellipsoid for each atom. For an atom which is being refined **isotropically**, there is only one displacement parameter, U_{11}, and this parameter defines the radius of the sphere used to represent the vibrational excursions that that atom experiences in the crystal. For an atom that is being refined anisotropically, there are six displacement parameters, U_{11}, U_{22}, U_{33}, U_{12}, U_{13}, and U_{23}, and these parameters define the shape and orientation of an ellipsoid.

Sometimes, two or more atoms have similar anisotropic displacement parameters. This is often true for CF_3 groups disordered as shown at the right: fluorine atoms F(1) and F(1A), which are "opposite" fluorine atoms, can profitably be refined by restraining their displacement parameters to be equal. This is because rotation about the C-C bond will make these atoms experience similar excursions about their equilibrium positions (i.e., elongated in the left-right direction).
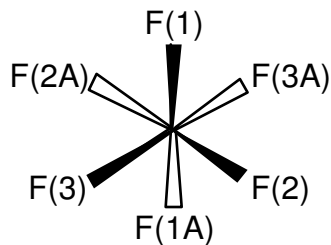
The EADP command sets the displacement parameters of the named atoms equal. You can add as many atoms to the EADP command line as you like; all of the atoms named on the same EADP command will be forced to have the same displacement parameters. If used, this command should be inserted in the .ins file between the UNIT and FVAR lines. The format is as follows:

EADP atom names.

For the example above, if you wanted to set the displacement parameters of opposite atoms equal, you would add the commands

        EADP F1 F1A
        EADP F2 F2A
        EADP F3 F3A

The following commands can be used to restrain the displacement parameters (i.e., Uij) of the named atoms. The descriptions below are not intended to be self-explanatory but are given to make you aware of some of the available tools at your disposal; for more information, see the SHELXTL manual or consult an expert.

   DELU atom names.
          DELU is a "rigid bond" restraint which is useful for restraining the anisotropic displacement parameters of chains of atoms (2 or more atoms long) in which one end of the chain has reasonable U's (but the other end does not).

   SIMU esd1 esd2 atom names [default esd's: 0.05, 0.1]
          SIMU is useful for forcing the anisotropic displacement parameters of partially-overlapping disordered atoms to be roughly equivalent in size.

   ISOR esd1 esd 2 atom names [default esd's: 0.1, 0.2]
          ISOR is useful for restraining the anisotropic displacement parameters of atoms that tend to become "non-positive definite" so that the Uij parameters do not stray too far from isotropic behavior. (Generally, the default esd's for this command are too large and often need to be smaller to give satisfactory ellipsoids.)

For SIMU and ISOR, the parameters esd1 and esd2 control how much the U's for adjacent atoms can differ: smaller numbers mean that the U's of adjacent atoms must be alike. Also, esd1 refers to the U's for the non-terminal atoms, while esd2 refers to the U's for terminal atoms (ignoring hydrogen atoms). DELU, SIMU, and ISOR commands, if used, should be inserted in the .ins file between the UNIT and FVAR commands.