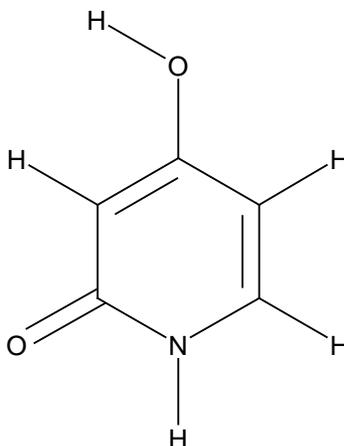


## Single Crystal Refinement using SHELX program

This work sheet consists of 2 tutorials :

The first is a simple organic compound 3-deazaauracil. This tutorial is designed for beginners to SHELX and will take you through the refinement process step by step.



The second is an inorganic compound Potassium Phosphate  $\text{KH}_2\text{PO}_4$ . This tutorial is designed for people who have some previous experience with using SHELX.

### Overview of the SHELX program

Shelx uses 4 file types

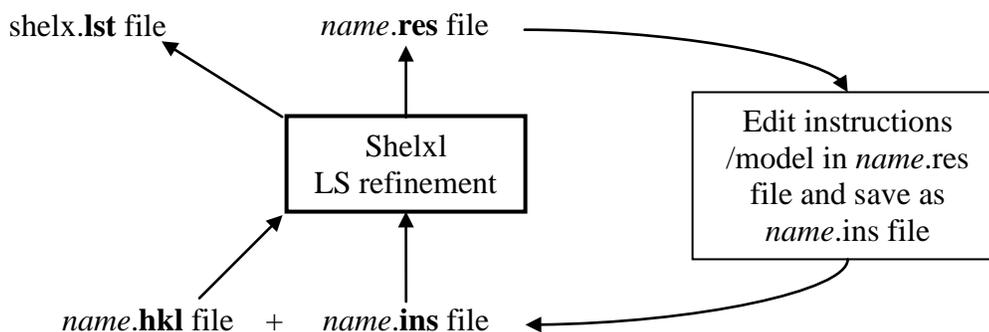
*name.ins* (input file or instructions file - contains input model and refinement parameters)

*name.res* (results file - contains model and refinement parameters)

*shelx.lst* (output of refinement details)

*name.hkl* (data file)

All these files are ASCII text files and can be read using Notepad or a similar program



Features of the shelx file format:

- Shelx ins and res files can only handle 80 characters per line so if a line is longer than this, it needs an = sign after 80 characters and the rest inserted on the next line.
- The ins and res files can be considered as consisting of 4 sections: first a series of lines containing information on the unit cell, symmetry and atom type, then a series of lines containing of 4 letter command codes that control the refinement and model, then a series of lines with the atomic coordinates etc, and finally an HKLF command to indicate the type of input data (hkl file) and the command end to signal the end of the program readable file.
- The command REM comments out a line.
- Adding 10 to any refinable parameter, stops it refining (fixes it) i.e. if the (refinable) occupancy of an atomic position is given as 1.000 then 11.000 means that the occupancy is fixed (10) at 1.000.

For full details and further information see shelx manual:

<http://shelx.uni-ac.gwdg.de/SHELX/> or under WinGX help

### **Basic differences in a SHELX refinement of Neutron data from SXD compared to a standard single crystal X-ray data refinement.**

- Atomic structure factors for neutron diffraction must be used. These need to be input explicitly as a structure factor (SFAC) command for each atom.
- The HKL file is in the format HKLF 2 (H | K | L |  $F_o^2$  |  $\sigma(F_o^2)$  | Batch number(BN) |  $\lambda$ ) not the more common HKLF 4 format (H | K | L |  $F_o^2$  |  $\sigma(F_o^2)$  | BN) you can open the HKL file using notepad to see the format.
- The command MERG 0 must be used, this tells the program not to average the intensities of reflections that have been measured more than once.
- It might be necessary to include a factor to normalise the data from different detectors in different frames this is done by including a series of BASF factors
- FMAP -2 command used instead of FMAP 2, this calculated and outputs the largest peaks and the deepest holes in the fourier difference map instead of just the largest peaks.

## 1<sup>st</sup> data set: 3-Deazauracil

### 1. First you need a molecular model in an ins file format to use as a starting point for the structure refinement.

The ins file can be output from sources such as Cambridge Structural Database, or from an x-ray structure refinement. Below is the ins file that you will be using here, with a brief explanation of each line. If you have not carried out single crystal refinement using Shelx programs before, it is worth having a quick read though this before you start.

The ins file for this tutorial can be found in folder SingleCrystal06\dzu.ins on your desktop or at [\\Olympic\babylon5\Public\Neutron\trainingcourse\SingleCrystal06\dzu.ins](http://Olympic\babylon5\Public\Neutron\trainingcourse\SingleCrystal06\dzu.ins).

*Copy this file into your current working directory*

#### A basic ins file for deazauracil taken from an existing refinement of X-ray (Mo K $\alpha$ ) data

```
TITL DZU
CELL 0.71073 8.638 5.279 11.22 90 90 90
ZERR 4 0.006 0.005 0.008 0 0 0
LATT -1
SYMM 1/2+x,1/2-y,-z
SYMM -x,1/2+y,1/2-z
SYMM 1/2-x,-y,1/2+z
SFAC C H N O
UNIT 20 20 4 8
FVAR 1.0
N1 3 0.325500 0.342900 0.710200 11.000000 0.05000
C1 1 0.324500 0.544100 0.634400 11.000000 0.05000
O1 4 0.441700 0.686500 0.631500 11.000000 0.05000
C2 1 0.189900 0.581100 0.565000 11.000000 0.05000
C3 1 0.067100 0.414700 0.573500 11.000000 0.05000
O2 4 -0.063800 0.443200 0.514300 11.000000 0.05000
C4 1 0.076100 0.207400 0.652600 11.000000 0.05000
C5 1 0.205500 0.177400 0.718400 11.000000 0.05000
HKLF 4
END
```

→ Title.  
→ Wavelength and unit cell parameters.  
→ Z and error on each respective unit cell parameter.  
→ Lattice type (1=P 2=I etc) -ve means that structure is non-centrosymmetric.  
→ Symmetry operators.  
→ Structure factors (if only element name is given these are set to default X-ray values, otherwise they can be defined explicitly).  
→ Number of atoms of each type in unit cell, in order listed in sfac command.  
→ Free variables. 1<sup>st</sup> variable in list is the overall scale factor, other variables can be added as needed.  
→ Atom parameters: name, type (position in sfac list), fractional coordinates, occupancy, isotropic temperature factor.  
→ Details of hkl file format where HKLF 4 = h, k, l, F<sub>o</sub><sup>2</sup>,  $\sigma$ (F<sub>o</sub><sup>2</sup>), BN  
→ For SXD data use HKLF 2 format (h, k, l, F<sub>o</sub><sup>2</sup>,  $\sigma$ (F<sub>o</sub><sup>2</sup>), BN,  $\lambda$ ).  
→ End of file.

## 2) Next you need to generate the shelx format hkl files:

In SXD2001

You should have already integrated your data

*Click on File*

*Generate SHELX reflection file*

*Browse and select the ins file dzu.ins*

*Browse and select the integration \*.int files*

*Select one histogram per crystal per detector, an appropriate scale factor and 1/sigma cutoff.*

For this tutorial the hkl has already been generated and can be found with the ins file in folder SingleCrystal06 on you desktop or at \\Olympic\babylon5\Public\Neutron training course\SingleCrystal06. *Copy this file into your current working directory*

## 3) Now you can start the wingx program

*Click on Program Files\WinGX\WinGX32*

*Select File menu*

*Change Project*

*Select New Project*

*Browse to find your files*

## 4) Now you must edit the ins file to make it suitable for neutron data refinement

*Click on Refine menu*

*Select Open INS file*

*A copy of your ins file will open for editing*

You will need to change or include:

- SFAC
- HKLF
- MERG
- BASF

**SFAC:** the scattering factor parameters in your DZU.ins file are currently set to the default X-ray radiation values. These need to be changed to explicitly define the scattering factor for each element for neutron radiation.

This takes the form:

SFAC label a1 b1 a2 b2 a3 b3 a4 b4 c f' f'' mu r wt

Where a1 to b4 are set to 0 for neutron radiation

c is the bound coherent scattering length

f' and f'' are real and imaginary dispersion terms and set to 0 for neutron radiation

mu is the linear absorption coefficient in barns/atom

r is the covalent radius  
and wt is the atomic weight.

| element | Bound coherent scattering length | mu     | Covalent radius | Atomic weight |
|---------|----------------------------------|--------|-----------------|---------------|
| H       | -3.739                           | 34.237 | 0.320           | 1.008         |
| C       | 6.64600                          | 0.002  | 0.770           | 12.011        |
| N       | 9.36000                          | 1.251  | 0.700           | 14.007        |
| O       | 5.80300                          | 0.001  | 0.660           | 15.999        |
| K       | 3.67000                          | 1.100  | 2.310           | 39.098        |
| P       | 5.13000                          | 0.073  | 1.100           | 30.974        |

Table 1: values needed for scattering factor command for the various elements covered in these tutorials.

**Replace the line ' SFAC C H N O'**  
**with the following lines:**

```

SFAC C 0 0 0 0 0 0 0 0 0 6.64600 0 0 0.002 0.770 12.011
SFAC H 0 0 0 0 0 0 0 0 0 -3.73900 0 0 34.237 0.320 1.008
SFAC N 0 0 0 0 0 0 0 0 0 9.36000 0 0 1.251 0.700 14.007
SFAC O 0 0 0 0 0 0 0 0 0 5.80300 0 0 0.001 0.660 15.999

```

The order of the atom types in the sfac command is very important: the number in the second column in the atomic coordinates refers to the atomic type as given in the SFAC list, so in this case 1=C 2=H 3=N 4=O. The order is also important for the UNIT command which lists the number of atoms of each element type in the unit cell in the order given in the SFAC list.

**HKLF:** the HKLF format output from SDX2001 is type **2** (h, k, l,  $F_o^2$ , BN,  $\lambda$ ), not type 4

**Go to the end of the ins file**  
**Change the command HKLF 4 to read HKLF 2**

**MERG:** because SXD frequently collects the same reflection more than once (at different wavelengths in different positions) it is important not to merge the data. You do this by including the command MERG 0 in the dzu.ins file beneath the UNIT command line

**After the UNIT command line input the following lines:**  
**MERG 0**

**BASF:** BASF parameters are batch scale factors. SXD has 11 detectors. These detectors need to be scaled relative to each other to account for the differences in sensitivity of the detectors and changes between runs (or something to that effect).:  
total number of BASF parameters = (11 detectors x n runs) -1

If you open the hkl file in Notepad, the batch number for each reflection is the number in 6<sup>th</sup> column. You will need one less BASF parameter than there are batch numbers, since each subsequent batch is scaled relative to the first batch. Therefore for 11 detectors and

6 runs you will need 65 BASF parameters (but remember you cannot have more than 80 characters per line, so you will need more than 1 line of BASF parameter.)

The BASF factors for each detector should not vary greatly from 1. However, this parameter is likely to 'blow up' at first (i.e. absorb features of the data that should be modelled) so initially we do not want to include the BASF factors in our refinement. We can comment them out by putting REM in front of each line

*After the unit command input the following lines:*

```
REM BASF 1 1 1 1 1 1 1 1 1 1  
REM BASF 1 1 1 1 1 1 1 1 1 1  
REM BASF 1 1 1 1 1 1 1 1 1 1  
REM BASF 1 1 1 1 1 1 1 1 1 1  
REM BASF 1 1 1 1 1 1 1 1 1 1  
REM BASF 1 1 1 1 1 1 1 1 1 1
```

Further commands that are needed to set up the file for Least Squares refinement:

**L.S. 10** (sets the number of least squares refinement cycles to 10)

**WGHT 0.1** (sets the weighting scheme, for neutron data the weighting scheme is usually not refined)

**FMAP -2** (difference Fourier map (Fo-Fc) is calculated and the largest peaks and holes in this map identified – this allows the identification of atoms that have been missed from the model.

**PLAN 10** (tells the program how many of the largest peaks or holes in the difference Fourier map (Fo-Fc) to output, in this case 10. The positions of these peaks are given as a list of dummy atoms (Q1, Q2 etc) at the end of the dzu.res file.)

**Question.** Why do you need FMAP -2 (identifies peaks and holes) for neutron data refinement but FMAP 2 (identifies peaks only) for X-ray data refinement?

*Between the unit command and the BASF command lines input the following lines:*

```
L.S. 10  
FMAP -2  
PLAN 10  
WGHT 0.1
```

Your final ins file should look like this:

```
TITL DZU
CELL 0.71073 8.6380 5.2790 11.2200 90.000 90.000 90.000
ZERR 4.00 0.0060 0.0050 0.0080 0.000 0.000 0.000
LATT -1
SYMM 1/2 + X, 1/2 - Y, - Z
SYMM - X, 1/2 + Y, 1/2 - Z
SYMM 1/2 - X, - Y, 1/2 + Z
SFAC C 0 0 0 0 0 0 0 0 6.64600 0 0 0.002 0.770 12.011
SFAC H 0 0 0 0 0 0 0 0 -3.73900 0 0 34.237 0.320 1.008
SFAC N 0 0 0 0 0 0 0 0 9.36000 0 0 1.251 0.700 14.007
SFAC O 0 0 0 0 0 0 0 0 5.80300 0 0 0.001 0.660 15.999
UNIT 20 20 4 8

MERG 0
L.S. 10
FMAP -2
PLAN 10
REM BASF 1 1 1 1 1 1 1 1 1 1 1
REM BASF 1 1 1 1 1 1 1 1 1 1 1
REM BASF 1 1 1 1 1 1 1 1 1 1 1
REM BASF 1 1 1 1 1 1 1 1 1 1 1
REM BASF 1 1 1 1 1 1 1 1 1 1 1
REM BASF 1 1 1 1 1 1 1 1 1 1 1
WGHT 0.1
FVAR 1.00
N1 3 0.325500 0.342900 0.710200 11.000000 0.05000
C1 1 0.324500 0.544100 0.634400 11.000000 0.05000
O1 4 0.441700 0.686500 0.631500 11.000000 0.05000
C2 1 0.189900 0.581100 0.565000 11.000000 0.05000
C3 1 0.067100 0.414700 0.573500 11.000000 0.05000
O2 4 -0.063800 0.443200 0.514300 11.000000 0.05000
C4 1 0.076100 0.207400 0.652600 11.000000 0.05000
C5 1 0.205500 0.177400 0.718400 11.000000 0.05000
HKLF 2
END
```

## 5) now you are ready to start refining the model

*In the Refine menu select SHELXL-97*

At this point your dzu.ins file will be read in, 10 cycles of refinement carried out, dzu.res file written.

Compare the dzu.res file to the dzu.ins file.

To see the results of the refinement in more detail, open the SHELXL.lst file from the Refine menu.

## Locating the Hydrogen atoms

The model of dzu that you are using is missing the hydrogen atoms. A missing hydrogen atom will only have a small effect on an X-ray data refinement but will have a very detrimental effect on the refinement of neutron data.

They will identify the 20 largest peaks or holes in the difference Fourier map (Fo-Fc) will be listed at the end of the dzu.res file. Their positions are given as a list of dummy atoms (Q1, Q2 etc). These dummy peaks are generally referred to as Q-peaks.

Use SXGRAPH to look at the structure

*Open menu Model*

*Select SXGRAPH*

*Use options on right hand side to label atoms and to display or hide the Q peaks*

*Decide which Q peaks correspond to H atoms (if you are unsure check the diagram on page 1)*

*Select Q peaks by clicking on them, then right click to edit properties*

*Change scattering factor type to Hydrogen, and give each peak a unique name (e.g. H1, H2)*

*When you have identified all H's delete remaining Q peaks using the Delete menu options*

*Click Save INS file button*

*Open the new dzu.ins file using options Refine, Open INS file*

*You will see the new hydrogen atoms have been added.*

*Unfortunately a fault in the SXGRAPH program means that the following commands have been lost:*

*FMAP -2*

*PLAN 10*

*REM BASF 1 1 1 1 1 1 1 1 1 1*

*REM BASF 1 1 1 1 1 1 1 1 1 1*

*REM BASF 1 1 1 1 1 1 1 1 1 1*

*REM BASF 1 1 1 1 1 1 1 1 1 1*

*REM BASF 1 1 1 1 1 1 1 1 1 1*

*REM BASF 1 1 1 1 1 1 1 1 1 1*

*re-enter these commands in the dzu.ins file.*

*Run the refinement again (select Shelx97 in Refine menu).*

## 6) Various ways to improve on your refinement:

- Remember to use the shelx.lst file to check on your refinement and to check for problems with the data.
- Use the options under the Graphics menu to look at your model.
- Use GEOM option in Analyse menu to check that the bond lengths and angles are refining to sensible values.
- Use Maps to check the Fourier difference map.

A) Make the atoms anisotropic:

***In the res file:***

***Type: ANIS \$H \$C \$N \$O (just before or after line L.S. 10)***

***Select Save as INS in File menu.***

***Run the refinement again (select Shelx97 in Refine menu).***

**Question.** Are the thermal ellipsoids describing each atom sensibly, in terms of shape and size?

(hint: use shelx.lst file and CAMERON graphics program to check this)

B) Refine the extinction parameter:

***In the res file:***

***Near line L.S. 10***

***Type EXTI***

***Select Save as INS in File menu***

***Run the refinement again (select Shelx97 in Refine menu)***

***N.B. This parameter also can have a tendency to 'blow up' so check that this parameter remains at a sensible value.***

C) Include the BASF parameters in the refinement.

***In the res file:***

***Remove REM commands from in front of the BASF commands***

***Select Save as INS in File menu***

***Run the refinement again (select Shelx97 in Refine menu)***

The BASF parameters should remain close to 1, check this is the case

D) Check the shelx.lst file carefully.

Especially check:

Principal mean square atomic displacements U.

→ Gives a measure of the atomic displacement parameters of each atom.

Analysis of variance for the reflections employed in the refinement.

→ Gives an analysis of the data-to-model agreement as a function of resolution and reflection intensity.

Most Disagreeable Reflections

→ Gives a list of the most poorly fitting reflections, check carefully for any patterns or trends.

E) Check your model carefully using the various graphical packages available:

***Graphics ORTEP***

***Model SXGRAPH (allows you to edit model and output changes to the ins file)***

***Graphics CAMERON***

***Graphics MERCURY***

In the second 2 graphical packages, use the 'pack' or 'packing' option to see how the model builds up to give the full crystal structure.

F) Adjust the weighting scheme

*In the res file:*

*Copy WGHT command from end of file this is the suggested weighing scheme*

*Replace WGHT command at top of file with suggested weighting scheme copied from end of file.*

*Select Save as INS in File menu.*

*Run the refinement again (select Shelx97 in Refine menu).*

*Repeat until weighting scheme stops changing.*

G) Finally you can create a crystallographic information file (CIF) suitable for publishing

*In the res file:*

*Type the command ACTA*

*Select Save as INS in File menu.*

*Run the refinement again (select Shelx97 in Refine menu).*

*This will output a dzu.cif file.*

*Select options in the Publish menu to look at, edit, and produce tables from this file*

*Publish Open CIF to edit cif file*

*Publish CIF TABLES*

*Answer 'No' to question about creating ARCHIVE.CIF file*

*Select 'Crystal/atom tables from cif' option, select OK*

*Select OK for next table, then 'Yes' and 'Quit' in following message windows*

Tables will be written to dzu.tex file

## 2<sup>nd</sup> data set: KH<sub>2</sub>PO<sub>4</sub>

Copy the starting model and data files to your work area. The files you need are KH2PO4.ins and KH2PO4.hkl located in the folder SingleCrystal06 in you desktop or at <\\Olympic\babylon5\Public\Neutron training course\SingleCrystal06>.

Start up the wingx program

**Edit the KH2PO4.ins file to prepare for a neutron data refinement:  
Adjust SFAC (using the information in table 1), HKLF and MERG for  
neutron data**

**Include BASF commands but comment them out for the time being**

**Include L.S. 10, WGHT 0.1, FMAP -2, PLAN 10 commands**

If you are unsure about how to carry out the steps above see 3-Deazauracil tutorial parts 1-4 for more details.

You should end up with an ins file that looks like this:

```
TITL   KH2PO4 300 K line integrals
CELL   0.71073  7.4659  7.4659  6.9888  90.0000  90.0000  90.0000
ZERR   16  0.0026  0.0026  0.0033  0.0000  0.0000  0.0000
LATT   -2
SYMM   +X,1/2-Y,1/4-Z
SYMM   -X,-Y,+Z
SYMM   -X,1/2+Y,1/4-Z
SYMM   1/2-Y,-X,3/4+Z
SYMM   -Y,+X,-Z
SYMM   +Y,-X,-Z
SYMM   1/2+Y,+X,3/4+Z
SFAC   K  0  0  0  0  0  0  0  0  0  3.67000  0  0  1.100  2.310  39.098
SFAC   P  0  0  0  0  0  0  0  0  0  5.13000  0  0  0.073  1.100  30.974
SFAC   O  0  0  0  0  0  0  0  0  0  5.80300  0  0  0.001  0.660  15.999
SFAC   H  0  0  0  0  0  0  0  0  0 -3.73900  0  0  34.237  0.320  1.008
UNIT   4  4  16  8
MERG   0
L.S.   10
FMAP   -2
PLAN   10
WGHT   0.100000
FVAR   1.0
REM   BASF 1 1 1 1 1 1 1 1 1 1
REM   BASF 1 1 1 1 1 1 1 1 1 1
REM   BASF 1 1 1 1 1 1 1 1 1 1
REM   BASF 1 1 1 1 1 1 1 1 1 1
K1     1  0.00000  0.00000  0.50000  10.25000  0.01
P1     2  0.00000  0.00000  0.00000  10.25000  0.01
O1     3  0.14833  0.08256  0.12586  11.00000  0.01
HKLF   2
END
```

## 5) now you are ready to start refining

*In the Refine menu select SHELXL-97*

At this point your KH2PO4.ins file will be read in, 10 cycles of refinement carried out, KH2PO4.res file written.

Compare the KH2PO4.res file to the KH2PO4.ins file.

To see the results of the refinement in more detail, open the SHELXL.lst file from the Refine menu.

### Locating the Hydrogen atom

The model of KH2PO4 that you are using is missing the hydrogen atom. A missing hydrogen atom will only have a small effect on an X-ray data refinement but will have a very detrimental effect on the refinement of neutron data.

The 10 largest peaks or holes in the difference Fourier map (Fo-Fc) will have been output to the KH2PO4.res file. Their position as a list of dummy atoms (Q1, Q2 etc), these dummy peaks are generally referred to as Q-peaks.

Use SXGRAPH to look at the structure

*Open menu Model*

*Select SXGRAPH*

*Use options on right hand side to label atoms and to display or hide the Q peaks*

*Select menu Model, then Grow Fragments to look at full structure*

**Question.** Can you identify which Q peak corresponds to the hydrogen atom? In deazauracil this is easy from the geometry. In this case it is not immediately obvious.

*Open the KH2PO4.res file.*

Q1 should be the largest hole and in principle should correspond to the location of the hydrogen atom.

**Question.** What do you notice about the atomic coordinates of Q1?

*Copy Q1 into the list of atomic parameters, Does it matter if you were to copy the peak height in as well?*

*Change the name from Q1 to H1*

*Change the atom type (in column 2) to correspond to the position of H in your list of SFAC commands.*

*Select Save as INS in File menu.*

*Run the refinement again (select Shelx97 in Refine menu).*

**Check the model:**

The R-factors have probably decreased but are still high - lets find out why:

a) Check bond lengths:

*Click on Analyse.*

*Select PARST and ok.*

*Scroll down though the output until you reach the bond distances.*

*Alternatively:*

*Input command 'BOND \$H' into KH2PO4.ins file below the L.S. command.*

*Run the refinement again (select Shelx97 in Refine menu)*

*Bond lengths are output at the end of the shelx.lst file*

**Question.** Do these distances look reasonable?

Hopefully you will have noticed that the O-H distance seems a bit long.

b) Look at the O-H bond in a Fourier difference map:

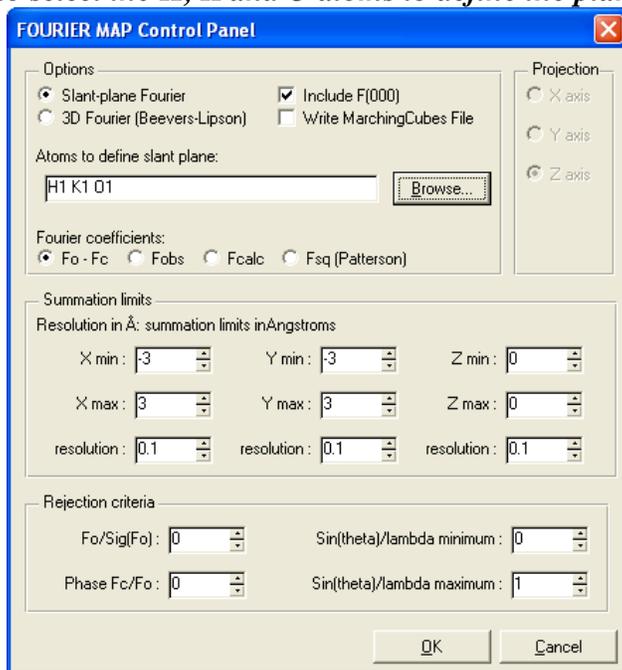
*In the KH2PO4.ins file*

*Type LIST 3 after the PLAN 5 command.*

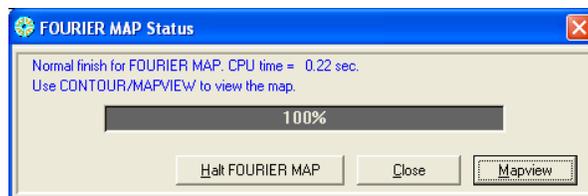
*Run the refinement again (select Shelx97 in Refine menu).*

*In the Maps menu select FOURIER MAP, Slant Plane.*

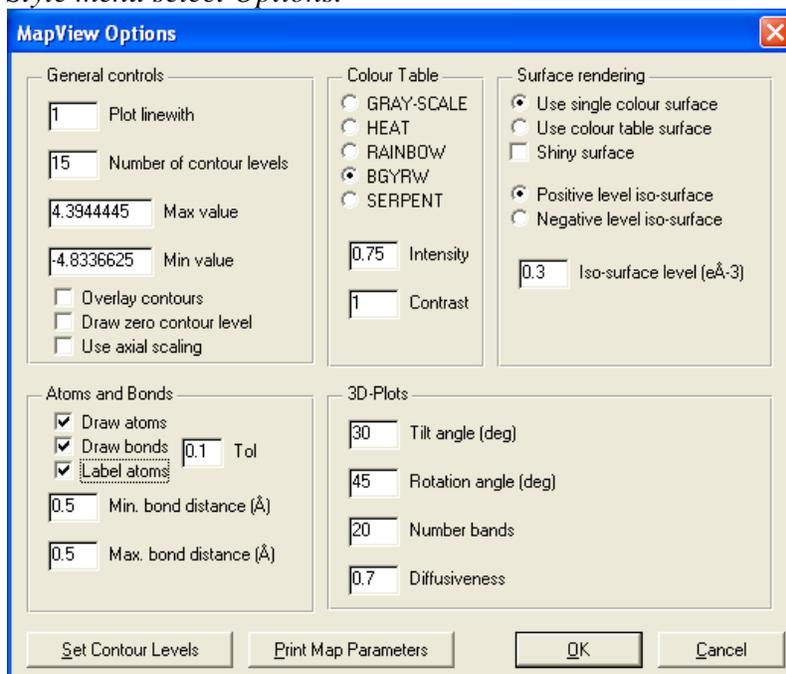
*Use browse to select the H, K and O atoms to define the plane and click OK*



*Select Mapview.*



*In the Style menu select Options.*



*Select the Draw atoms, Draw bonds and Label atoms tick boxes.  
In the Style menu select 2D-BitMap.*

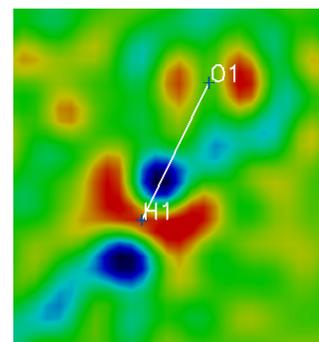
So what is happening?

First consider the atomic coordinates of your hydrogen atom

H1 2 0.146526 0.250000 0.125000

The hydrogen atom is on a special position at  $\frac{1}{4} b$  and  $\frac{1}{8} c$  ie on a screw axis

Consider the region of the difference map around the hydrogen atom. The hydrogen atom has actually been located on a peak (red) but there is a hole (blue) slightly closer to the O atom and another in a symmetry related position.



**Question.** Can you identify the problem with the current atomic model and decide where the hydrogen is really located?

The real position of the hydrogen atom is slightly displaced from the screw axis. It is in fact disordered about the screw axis. It is located 50% in one blue hole and 50% in the other blue hole.

To identify which of the Q peaks corresponds to the blue hole in the map:

*Copy the list of Q peaks from the bottom of the KH<sub>2</sub>PO<sub>4</sub>.res file*

*Paste this list into the KH<sub>2</sub>PO<sub>4</sub>.ins file below atom H1*

*Save the KH<sub>2</sub>PO<sub>4</sub>.ins file*

*Run Maps → Fourier Map → Slant Plane, again selecting K1, H1 and O1 as the atoms to define the plane.*

Any Q peak that lies within the plane defined by the K O H atoms will now be labelled.

*Identify the Q peak (Qx) that corresponds to the true H atom position.*

*Open the KH<sub>2</sub>PO<sub>4</sub>.res file*

*Copy Qx and past it into the atomic parameters below H1*

*Remove the old H1 and rename Qx to H1*

*Set the atom type (in column 2) to correspond to the position of H in your list of SFAC commands*

*Set the occupancy from 11.00000 to 10.50000 i.e. 50% occupancy*

*Save file as KH<sub>2</sub>PO<sub>4</sub>.ins*

*Run the refinement again (select Shelx97 in Refine menu).*

The various R-factors (R1 and wR2) should improve (decrease).

*Run PARST to check O-H bond length.*

*Run Maps → Fourier Map → Slant Plane again to check difference map.*

Hopefully you will see an improvement.

**You can now follow instructions step 6 (page 8) from the deazauracil refinement to improve you KH<sub>2</sub>PO<sub>4</sub> refinement:**

- A) Make the atoms anisotropic:
- B) Refine the extinction parameter:
- C) Include the BASF parameters in the refinement
- D) Check the shelx.lst file carefully.
- E) Check your model carefully using the various graphical packages available:
- F) Adjust the weighting scheme
- G) Create a crystallographic information file (CIF) suitable for publishing

## **7) Exploring the effect of different parameters on the refinement**

a) Use the REM command to comment out each atom in turn.

**Question.** Where is the largest peak/hole? Note the size of the largest peak in each case. How does the size of the largest peak relate to the atom that has been omitted?

*NB: in X-ray diffraction a refinement is generally only considered complete when the highest peak in the difference map is less than  $1e/A^3$  i.e. smaller than a hydrogen atom. Of course, in neutron diffraction the difference map is not measured in  $e/A^3$ .*

**Question.** What would be an appropriate corresponding parameter to quote for neutron diffraction?

b) Try changing the covalent radius term in the SFAC command of an atom.

**Question.** What is the effect on the refinement and the structural model?

c) Try changing other parameters in the SFAC command.

**Question.** What is the effect on the refinement and the structural model?

d) **Question.** What happens if the occupancies are allowed to refine?

e) Try increasing the errors on the unit cell parameters (line ZERR in KH<sub>2</sub>PO<sub>4</sub>.ins)

**Question.** What is the effect on the output bond lengths