

# Getting Started with Shelxtl-Plus

## Using XP

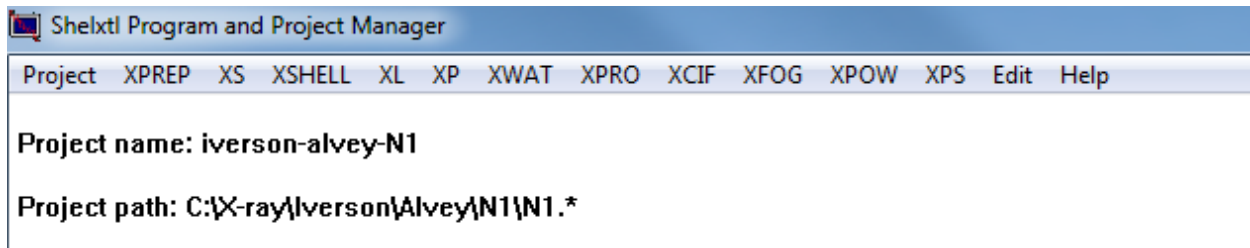
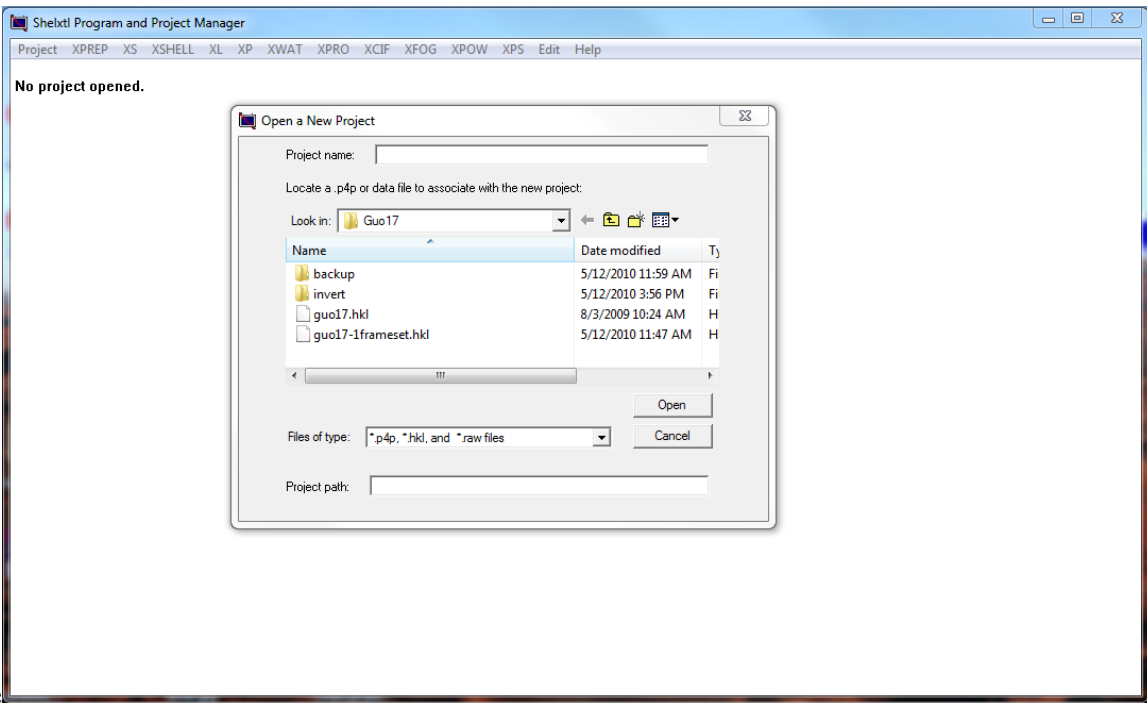
XP is a graphics program written by George Sheldrick for single crystal structure analysis. It can be used to generate publication quality figures and unit cell packing diagrams. Such figures can also be obtained elsewhere using ORTEP and Mercury, for example. XP is extremely useful in fine tuning a crystal structure model. This file describes only the basics.

It is assumed that you have Shelxtl-Plus installed properly and that you have an .hkl file and an .res file. It is also assumed that you have a structural model to work with. XP is the graphics program for use with the Shelxtl-Plus package. By default, XP will read a file, filename.res, where filename is the name of the .res, .hkl, .ins files, etc.



Double click on the Shelxtl-Plus icon

If you have already started a project, select Project and open the relevant project. This will direct you to the directory containing the necessary files. If you are starting a new project, select Project and New. Use the directory locator and find the directory where the data is located. Select either the .hkl or .ins/.res file and enter a project name.



Once started, you should see a menu like the one shown above. Click on XP. By default, the .res file will be read in. Unlike the graphics program in WinGX, you have to issue a command to generate a connectivity list. Like XL (SHELXL-97 or SHELXL-2014 in WinGX), all instructions have four letters, which can be modified with additional information. Like XL, these commands are not case sensitive. I use uppercase letters for clarity here. To create the connectivity list, FMOL is typed, followed by hitting the enter key. FMOL is the first command you will enter.

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XP>> fmo1
O1 - C1 Q4 Q5 Q8 Q10
O2 - C5
N1 - C1 C5 C8 Q4 Q5 Q10
C1 - O1 N1 C2 Q1 Q4 Q5 Q6 Q8 Q9 Q10
C2 - C1 C3 C6 Q1 Q2 Q3 Q4 Q5 Q6 Q7 Q9 Q10
C3 - C2 C4 Q1 Q2 Q3 Q4 Q5 Q6 Q7 Q9
C4 - C3 C5 C7 Q1 Q2 Q3 Q7
C5 - O2 N1 C4 Q2 Q3 Q10
C6 - C2 H6 Q1 Q4 Q5 Q6 Q9
C7 - C4 H7 Q2 Q3
C8 - N1 C9 H8B H8A Q10
C9 - C8 C10 H9A H9B
C10 - C9 C11 H10B H10A
C11 - C10 H11C H11A H11B
H10B- C10
H6 - C6 Q6 Q9
H11C- C11
H8B - C8
H11A- C11
H9A - C9
H9B - C9
H7 - C7
H8A - C8
H10A- C10
H11B- C11
Q1 - C1 C2 C3 C4 C6 Q2 Q3 Q4 Q5 Q6 Q7 Q9
Q2 - C2 C3 C4 C5 C7 Q1 Q3 Q5 Q7
Q3 - C2 C3 C4 C5 C7 Q1 Q2 Q7
Q4 - O1 N1 C1 C2 C3 C6 Q1 Q5 Q6 Q8 Q9 Q10
Q5 - O1 N1 C1 C2 C3 C6 Q1 Q2 Q4 Q6 Q8 Q9 Q10
Q6 - C1 C2 C3 C6 H6 Q1 Q4 Q5 Q9
Q7 - C2 C3 C4 Q1 Q2 Q3
Q8 - O1 C1 Q4 Q5
Q9 - C1 C2 C3 C6 H6 Q1 Q4 Q5 Q6
Q10 - O1 N1 C1 C2 C5 C8 Q4 Q5
XP>>

```

The available commands can be listed using HELP. The syntax for each command is listed by typing HELP FMOL, for example. All XP commands are case insensitive, upper or lowercase instructions work the same way.

Some of the more commonly used commands are:

PROJ – generates a wireframe view of the structure with features for rotating the figure

UNIQ – for structures with multiple components (ion pairs, for example). You can isolate one component by issuing UNIQ C1 (or any atom in that component). Only atoms bound to C1 or atoms in the same group as C1 are included in the connectivity list for display. You will need to issue FMOL to get back to the full connectivity list. UNIQ is also useful to group atoms together that may be part of the same molecule but listed in different parts of the unit cell due to some symmetry operation. SUPERFLIP sometimes has portions of a molecule separated in different parts of the cell. UNIQ will group these together.

MPLN/N – generates a plane through the atoms in the current connectivity list. MPLN/N followed by PROJ will provide a view perpendicular to the plane. To view the equation of the

plane and the distance of individual atoms from that plane, you can leave off the /N qualifier. MPLN follow by a list of atoms will generate a least-squares plane through the atoms in the list.

DIAG – shows a wireframe view of the structure with atom labels. Follow this command with an enter command and you will retain the figure in the upper right hand corner of the screen.

INFO – lists all the atoms in the connectivity list

BANG – lists the bond lengths and angles. BANG C1 will list only bond lengths and angles for C1.

ENVI – lists the bond lengths and angles as above but includes symmetry related atoms and the symmcode for the listed atoms

SRCH – similar to ENVI but with symmcode specified for the named atom in the SRCH command.

Both SRCH and ENVI assume that the distance between bonded atoms is less than the van der Waals' radii of the atoms plus 0.5Å. To look for longer contacts, this value can be increased. For H-bonding interactions involving an atom, O1, for example, use something like ENVI 1.8 O1.

SYMM – lists the symmetry operators for the space group. For triclinic P-1, the symmcodes are 1555 and 2555 corresponding to x,y,z and -x, -y, -z. The 555 coding refers to the default unit cell where fractional coordinates are those listed in the .res file. For P-1, the symmcode 1565 C1 refers to the atom C1 with coordinates at x, 1+y, z; symmcode 2666 refers to atom C1 at 1-x, 1-y, 1-z. This syntax dates back to the early ORTEP programs.

SGEN – can be used to generate symmetry related atoms with the symmcode listed. From the above example, SGEN 1565 C1 creates a new atom, C1A, at position x, 1+y, z. So if C1 is at 0.55, 0.35, 0.11, a new atom C1A will be placed at 0.55, 1.35, 0.11. SGEN 2666 C1 will generate a new atom, C1A, at position 1-x, 1-y, 1-z, which will be at 0.45, 0.65, 0.89. The new atom usually retains the same label as the old atom with a letter appended. The label for the new atom will be listed. The command SGEN -1565 (note the – sign) moves C1 to its new position at x, 1+y, z without creating a new atom, C1A.

GROW – for molecules and complexes lying around symmetry positions, GROW will complete the molecule or complex by generating the symmetry related atoms. Mercury does this by default.

FUSE will remove symmetry equivalent atoms generated by GROW and get back to the original asymmetric unit.

PRUN – prunes (removes) all bonds from the connectivity list. PRUN C1 removes all the bonds to C1. You can clean up the projection this way. PRUN \$Q is a useful example.

LINK atom1 atom2 – draws a bond from atom1 to atom2 and includes the bond in the BANG/ENVI output.

CENT – calculates the center of a group of atoms. CENT/X calculates the center of a group of atoms and places a dummy atom at that position with label X1A, X1B, etc. This can be useful for displaying metallocenes. You can use PRUN to remove the bonds from the metal to the ring atoms and add a bond to the centroid with the LINK command. LINK 5 Fe1 X1A (draws a fine line from Fe1 to X1A).

HADD – will calculate hydrogen atoms in idealized positions for the atoms listed. The type of H added is based on the geometry of the carbon atom. You should check that this is done correctly.

VIEW plotfile – will show the plotfile on screen

TELP will generate a figure for printing/saving using the view displayed with the DIAG command.

TELP 0 30 .01 – generates a ball-and-stick figure with bond radii of 0.01Å.

TELP 0 -50 .01 generates a displacement ellipsoid figure with percentage probability of 50% and bond radii of 0.01Å. You are prompted for a filename and then proceed to the figure with the option of placing labels. A square box will appear where the label is to go. The atom label is shown in the lower right corner of the screen. Clicking the mouse places the label. Typing N on the keyboard, skips that atom, type C moves back to the previous atom. Typing H halts the process and exits without saving the file. Typing B halts the process and saves the plotfile.

DRAW plotfile – starts the process of creating a plotfile formatted for generating a file that can be inserted into MS\_Word. At the prompt, enter A for Adobe postscript, give a plotfile name for the output file and follow that by typing C for a color plot or enter for a black and white figure. The file is written to filename.PS. Rename this file to filename.EPS if you wish to insert the figure into a Word document.

The .res file is composed of atoms in the model plus a number of Q peaks. These Q peaks, which are listed at the end of the .res file, represent the regions of highest electron density in the cell that are not included in the model and may represent missing atoms. The number of such peaks is determined by the PLAN nn instruction on the .ins file where nn is some number and is the number of additional Q peaks generated. These Q peaks could be noise peaks or they could represent atoms that have not been included in the model. By default, the Q peaks are assigned the bond radius of C. So if you have chloroform as solvent, you will see three large Q peaks that

may not be bound to anything because the C-Cl bond length is longer than the expected C-C bond length. To see the electron density associated with these Q peaks, type INFO \$q.

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XP>> info $q
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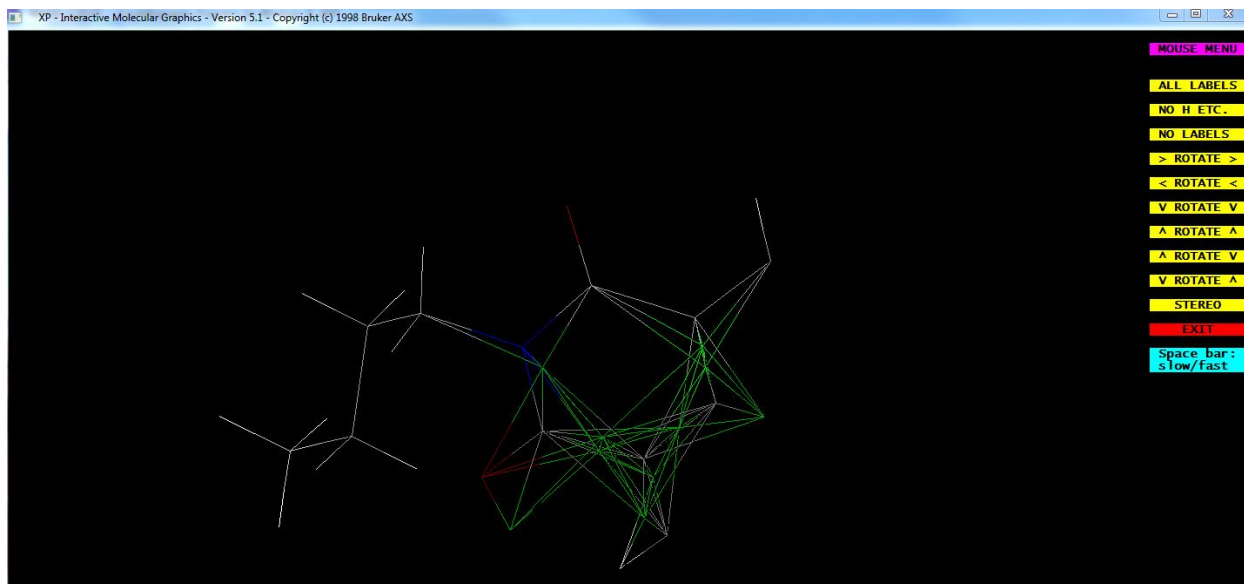
Atom	SFAC	x	y	z	ATYP	Color	ARAD	BRAD	SRAD	Ueq	Peak
Q1	1	0.52880	0.63340	0.46170	1	1	0.20	0.77	1.27	0.050	0.23
Q2	1	0.30770	0.55630	0.44000	1	1	0.20	0.77	1.27	0.050	0.22
Q3	1	0.36730	0.51220	0.40700	1	1	0.20	0.77	1.27	0.050	0.21
Q4	1	0.59230	0.73740	0.40650	1	1	0.20	0.77	1.27	0.050	0.20
Q5	1	0.55510	0.75600	0.42810	1	1	0.20	0.77	1.27	0.050	0.20
Q6	1	0.66740	0.76010	0.51990	1	1	0.20	0.77	1.27	0.050	0.19
Q7	1	0.50000	0.50000	0.50000	1	1	0.20	0.77	1.27	0.050	0.19
Q8	1	0.81670	0.95980	0.42540	1	1	0.20	0.77	1.27	0.050	0.18
Q9	1	0.77660	0.71850	0.46880	1	1	0.20	0.77	1.27	0.050	0.17
Q10	1	0.36550	0.79900	0.35830	1	1	0.20	0.77	1.27	0.050	0.17

35 atoms and 94 bonds in current lists

In the list above, the INFO \$q instruction lists only the information for atoms starting with Q. Most of the information in the list is self explanatory. The value for **Peak** is the electron density at that x,y,z position. In the example above, these Q peaks are noise peaks. Typically, H atom peaks are in the range 0.5 – 0.9 or so. By default, the Ueq (equivalent isotropic displacement parameter) is set to 0.05 for the Q peaks but represents the refined value for atoms in the model.

The Ueq is a useful number to keep track of during refinement. With a good crystal, low-temperature structures, this number is usually in the range 0.025-0.05 for well behaved atoms. A very large value for Ueq could mean that the atom assigned to that position is too large (a chlorine atom where a carbon atom should be) or that atom is disordered over two or more positions, effectively reducing the electron density at that position. A very small value (0.001 is the minimum that will be listed) means that an atom with a higher electron density is more appropriate at that position.

After FMOL, you can view the molecule by issuing the PROJ instruction. The screen below appears.



The atoms are color coded. The Q peaks are green with green bonds. Here the green peaks show up in regions where there may be bonding e- density not accounted for in the model. If H atoms were missing, the Q peaks should, with good data, correspond to the H atom positions.

You use the menu bar on the side to rotate the figure. To get rid of the Q peaks, exit the viewer. You can permanently delete the Q peaks by KILL \$Q. Or you can remove them from the working set of atoms by issuing: FMOL less \$Q. This command will create a new connectivity list with the Q's left out. Issuing FMOL again will add all the atoms back into the working connectivity file.

Once you have made all the changes you intend to make to your model, you need to save the changes to a new .ins file. Enter the FILE instruction followed by the filename. You will be prompted for the name of the .res file from which the instructions are to be copied. The instructions are the list of commands in the .res file. Typically, this is all the information excluding the atom positions. These instructions include but are not limited to the lines from the TITL line to the FVAR line. You can enter SADI, ISOR, DFIX, etc. instructions anywhere in the file. These instructions will also be included in the new .ins file. SAME instructions are not copied into the new .ins file and will have to be added manually.

Typically, you will run XL (or SHELXL-2014/7 from WinGX) many times before you are completely satisfied with the refinement model.