The Center for X-Ray Crystallography
University of Florida
Written by Jürgen Koller, amended by Annaliese Thuijs

HOW TO GET AN X-RAY CRYSTAL STRUCTURE

Solving an X-Ray Crystal Structure with ShelXTL

I. File

- ➢ *New* (give your new project a name and highlight the *.raw file)
- ➢ *Open* (opens an already existing project)

II. XPrep

- ➢ Screen shows: P   A   B   C   I   ……
                    0.0   19.0   21.0   ……

  These symbols are abbreviations for lattices (e.g. face centered, body centered, …) You have to look for the one with the smallest value, which also determines the lattice type for your crystal. If two columns are 0 chose the one with higher symmetry.
- ➢ Select [H] and press *enter* and go through commands
- ➢ Before you type [F]: press [A] for absorption correction (only if crystal dimensions have been measured before data collection)
- ➢ This part of the program creates a new set of files: *.hkl (including the data)
                                                            *.ins (input file for next step)
                                                            *.prp (listing of what happened in XPrep)

III. XS

- ➢ Input for this program: *.ins and *.hkl
- ➢ CFOM (Combined Figures of Merit): The lower this value, the better is your collected data set (as low as 0.036)
- ➢ RE: if this value is below 10% your data is good
- ➢ The output from this program is: *.res (including the results)
                                        *.lst (listing of what happened in XS including an electron-density map)

IV. XP

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- *help* (gives you a list of all commands. Type help …. And receive a description of this specific command)
- *info* (lists all atoms and bonds of your current moiety after *fmol* has been applied)
- *fmol* (creates a list of atoms with according connectivities. If there is still *fmol* occurring in the prompt, just press *enter* until the list is complete. This command has to be applied everytime you enter XP)
- *fmol/n* (does the same as *fmol* but without showing on the screen. Later on, if you are in unique mode, by typing *fmol/n* you can go back to the entire molecule)
- *mpln* (mean least square plane: calculates the best view of the electron-density map to facilitate looking at the structure)
- *mpln/n* (again, no visual output)
- *fmol/n $n* (you will only see the nitrogen atoms)
- *fmol/n rest* (you will see the rest of the atoms without the nitrogens)
- *proj* (project: view structure: mono $\rightarrow$ 1-dimensional
  stereo $\rightarrow$ 3-dimensional)
- *eyes 1* (always view structure in 1-D)
- *eyes 2* (always view structure in 3-D)
- *uniq ho1* (unique: view only the specified atom here Ho1 and what it is connected to. If you then type *proj* you will only see Ho1 and its immediate surroundings)
- *diag* (like *proj* without a menu. If you now press *enter*, the picture of the structure will stay in the top right corner of your screen even if you are in prompt screen)
- *kill q40 q3* (deletes specified atoms here atoms q40 and q3 irreversibly. If you now type *proj*, the deleted atoms will not show up any more)
- *read kv01* (if you accidentally deleted an atom and you want it back, this command will re-read the *.res file until 'END' in the *.res file)
- *reap kv01* (reads complete *.res file. After *read* or *reap*, you type *fmol* and *proj* and all the original atoms are back)
- *bang q22 q1* (calculates all bond angles and bond distances for the selected atoms)
- *name q22 n1* (if you are sure about the identity of a specific electron density here q22 you can name it here Nitrogen1 or n1. Note: you can't give two separate atoms the same name)
- *pick* (in the window you can browse through atoms of a specific moiety and label them)
- *sort* (if you type *sort* and then *info*, you will see all the acquired information so far sorted by numbers)
- *sort $o $n* (sorts and lists all the oxygen atoms first and then all the nitrogen atoms sorted by numbers)

- *file kv01* (writes new *.ins file)
- *quit* (exits XP)
- *exit* (also exits XP)

V. XL

- Run XL (this is the first step of the refinement. After computer is done, just press any key)

VI. XP

- *info* (after *fmol* and *mpln* type *info* and look at the column with the U_{eq} values: All values for the assigned atoms should be roughly in a range between 0.02x and 0.05x.
  If you get 0.1xx → you assigned too many electrons to that peak. Kill, because it is a noise peak
  If you get 0.000 → Too little electrons assigned. Take an atom with higher atomic number
  If you then are missing an atom in your structure, take the q with the highest value, which should be much higher than all the others, and assign it an atom name)
- *proj less $q* (projects everything except q's)
- *kill $q* (kill all the remaining q's that aren't atoms)
- *file kv01*

VII. XL

- Run XL refinement cycle again
- Go back to XP and look at U_{eq} again. Make adjustments if necessary.
- Go back and forth XL and XP until all atoms and their U_{eq} values are okay

VIII. Edit

- *copy .res* → *.ins* (takes the *.res file from XL and writes a new *.ins file for further steps)
- *Edit .ins* (opens window with the data of the *.ins file)
- Below 'PLAN 20' make a new line and type in a new command:
  'ANIS' for the atoms you wish to make anisotropic
- Save and exit Editor

IX. XL

➢ Run XL refinement cycle again (now XL takes sphere representation of the atoms and calculates ellipsoid representation which is more accurate)

X. XP

➢ Now you can also see some of the protons in the structure as q's. Usually you don't need to refine protons except Hydroxide-protons or H-bonded protons. For all the other protons you just add them later in optimized calculated positions. If you want to refine the protons, just assign q's as protons and go back and forth between XL and XP to refine them. The U_{eq} values of protons are usually a little bigger than the ones for other atoms.

➢ *kill $q*

➢ *hadd $h $c*   (adds protons to all unsaturated carbons. Check if all protons are in the right postion and if there is the right number of protons on all atoms. Alternatively, protons can be added in the *.ins file. Under 'PLAN 20' write 'HFIX 137 c1 c2' to add protons to c1 and c2)

➢ *atyp 2 5 $c*   (set colors and style of all carbon atoms. First number encodes the type, second number encodes the color of the chosen atoms. Type *help atyp* to see a list of all the colors and styles)

➢ *file kv01*   (writes new *.ins file with anisotropic refinement)

XI. XL

➢ Run another XL refinement cycle

XII. Edit

➢ *Edit .ins*

➢ See 'Afix 43' (different for every atom. First number tells you the hybridization of the atom. 4 is aromatic carbon, 3 is methyl carbon, 2 is methylene carbon)

➢ See 'Afix 0' (terminates the project for one atom and moves on to the next)

➢ *copy .res → .ins*

➢ *Edit .ins*

➢ Below 'TEMP -100' make a new line and type in a new command: 'OMIT -3 55' (this tells XL to only use reflections within $2\theta = 55^{o}$)

➢ Save and exit Editor

XIII. XL

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➢ Run another XL refinement cycle (Before you exit XL look at the WR2 and R1 value)

XIV. <u>Advanced Refinement</u>
  ➢ Atoms that are not behaving properly—modify in the .ins file:
    ♦ Atom moving too much
      1. DFIX:
        a. The distance between the first and second named atom, the third and fourth, fifth and sixth etc. (if present) is restrained to a target value d with an estimated standard deviation s.
        b. Use DFIX 1.54 0.01 A B, where 1.54 is the distance, 0.01 is the standard deviation, A is the first atom, B is the second atom
      2. SADI
        a. The distances between the first and second named atoms, the third and fourth, fifth and sixth etc. (if present) are restrained to be equal with an effective standard deviation s.
        b. SADI 0.02 A B, 0.02 is the standard deviation, A is the first atom, B is the second atom
      3. SAME
        a. The list of atoms (which may include the symbol '>' meaning all intervening non-hydrogen atoms in a forward direction, or '<' meaning all intervening non-hydrogen atoms in a backward direction) is compared with the same number of atoms which follow the SAME instruction.
        b. Use for a set of atoms: SAME C1> C6 before C11 > C16, where C1 … C6 is an ideal benzoate and C11 > C16 is an unideal benzoate. Also good for t-butyl group
    ♦ Displacement parameters are too high or too low
      1. EADP
        a. The same isotropic or anisotropic displacement parameters are used for all the named atoms. The displacement parameters (and possibly free variable references) are taken from the first atom in the atom list that is linked to other atoms by EADP.
        b. Use this command for methyl groups in tert-butyl groups, F^- ions in PF_6^-
      2. RIGU

   a. Apply enhanced rigid bond restraints with esds s1 for 1,2-distances and s2 for 1,3 [Thorn, Dittrich & Sheldrick, *Acta Cryst.* A**68** (2012) 448-451].
   b. Use RIGU for all atoms
3. Modeling disorder
   a. Use parts with defined occupation factor
      i. PART 1 10.6 C1 > C6 PART 2 10.4 C1' > C6'
      ii. Where 10.6 is the occupation factor of part 1, 10.4 is the occupation factor of part 2, C1 > C6 are the main atoms, C1' > C6' are the disordered atoms
   b. Use parts and use a free variable
      i. PART 21 C1 > C6 PART 0
      ii. PART -21 C1' > C6' PART 0
      iii. FVAR line 0.08 0.6
      iv. 21 defines part1, -21 defines part2, PART 0 end the command line so only a set list of atoms are included in the disorder
   c. 0.08 is the free variable for all atoms (already in the .ins) 0.60 is the 2nd Free variable linked to 21. To use further parts just add further lines (i.e. part 31 part -31 part 41 part -41, FVAR 0.08 0.60 (#fvar3) (#fvar4)

➢ Adding hydrogen atoms to non-carbon atoms (modify in XP)
   ♦ Use HADD:
      1. HADD 8 O1 (adds 1 hydrogen atom to O1, making it a hydroxide)*
      2. HADD 9 O1 (add 2 hydrogen atoms to O1, making it a water)*
      3. HADD 4 C4 (add one proton to C4 because it is aromatic, can be used if hadd $c does not add correct number of hydrogens)
      4. For more information on hydrogen codes type HELP HADD
      **applicable for either group (i.e. N, C, etc.)

XV. Edit

➢ *copy .res → .ins*
➢ *Edit .ins*
➢ Go down (all the way to the bottom) and look for a line with: 'WGHT ...'
➢ Copy this line
➢ Go back up and look for another line with 'WGHT …' under 'PLAN 20'

- ➢ Overwrite this line with the other line from the bottom (This tells XL to use a weighting-scheme of the reflections including errors which is proposed by the computer)
- ➢ Save and exit Editor

XVI. XL

- ➢ Run another XL refinement cycle (Now WR2 and R1 value should have gone down)
- ➢ Go back into *.ins file, copy the 'WGHT …' line again, run XL again… Go back and forth until WR2 value doesn't change significantly any more)

XVII. XP

- ➢ *kill $q*
- ➢ *info less $h*   (you can see that the labels are not in order)
- ➢ *pick*   (rename all the atoms in an orderly fashion)
- ➢ *sort*   (now atoms are sorted in info-list)
- ➢ *sort $cl $n*   (sort in order of atomic numbers)
- ➢ *hadd $c*   (H's are placed after the Carbon they are attached to)
- ➢ *save kv02*   (Saves this session. Take a name different from the overall project name. This is a good point the save because all the atoms are labeled, refined, …)
- ➢ *next kv02*   (To continue where you left from with the *save* command)
- ➢ *fmol*   (creates a list of atoms with according connectivities. If there is still *fmol* occurring in the prompt, just press *enter* until the list is complete)
- ➢ *file kv01*

XVIII. Edit

- ➢ *Edit .ins*
- ➢ Below 'L.S. 4' make two new lines and type in the new commands:
  'ACTA' and
  'BOND $H'
- ➢ Save and exit Editor

XIX. XL

- ➢ Run another XL refinement cycle (now XL creates a new set of files: *.cif crystallographic information file and *.fcf)

XX. Edit

- *copy .res → .ins*
- Below 'PLAN 20' make a new line and type in a new command:
  'CONF' (this adds a list of torsion angles to the *.ins file)
- Save and exit Editor

XXI. XL

- Run another XL refinement cycle

XXII. XP Codes

- *envi $cl*   (calculates environment around specified atom)
- *envi $cl 1.5*   (gives environment around specified atom but with higher tolerance. You can see a larger number of atomic interactions. With this tool you can see if there are any interactions of the specified atom to any atoms that are not directly bonded to it. If an interaction is present, that atom will have a symmetry label different from 1555)
- *symm*   (tells you what symmetry you have. The 555 represents the asymmetric unit. Example: 1555: first 5 is x- coordinate, second 5 is y, third 5 is z. 1 is symmetry operation. → 1655 is a translation in the x-direction. 1565 is a translation in the y-direction. A 2 means inversion, which you can also see with the presence of –x, -y and –z)
- *proj cell*   (see the molecule and the unit cell)
- *sgen 2666*   (generates a symmetry-equivalent molecule. Here: inversion (2) followed by a translation in all directions (666)→ result: 1-x, 1-y, 1-z)
- *fuse*   (fuses all the symmetry-equivalent molecules → Back to one molecule. By typing fuse cl1 cl1a you can fuse atoms that are symmetry-equivalent)
- *envi $cl*   (here: see that one Cl has interaction with another molecule symm 2775. Create second molecule with *sgen 2775* and see interaction)
- *link cu1 cl1a*   (creates a dashed bond between specified atoms of the two interacting molecules)
- *undo c1 c7*   (kills the bond between specified atoms)
- *link1 cu1 cl1*   (makes a dashed bond solid, if you accidentally made a real bond dashed)
- *prun cu1*   (removes all the bonds from the specified atom)
- *matr1*   (makes a-axis perpendicular to the screen in a projection. *matr2* makes b-axis perpendicular, …)

- ➢ *matr 1 1 1*   (makes the diagonal of the unit cell perpendicular to the screen)
- ➢ ↑   (up-arrow on keyboard brings back old commands)
- ➢ *cell*   (displays unit cell parameters. Put shortest axis perpendicular to screen with *matr* command)
- ➢ *pack*   (packs molecules in unit cell. Dashed lines represent intermolecular interactions.
  'Scan Mols.' → unit cell blinks (like *pick* command)
  'scan non-B' → scans dashed lines and delete what you don't need or want
  'sgen/fmol' → displays what you constructed in packing diagram)
- ➢ *info*   (all those symmetry operations added new labels to the atoms)
- ➢ *name ???a ???*(renames atoms that had an XXXA label back to XXX)
- ➢ *mpln*   (gives the best plane with deviations of atoms from that plane)
- ➢ *nopl*   (undoes all *mpln* commands and deletes all previous planes)
- ➢ *mpln n1 c1 …* (creates best plane including specified atoms)
- ➢ *mpln n2 c6 …* (creates this plane and shows you the dihedral angle between this plane and the previous plane. The numbers on the left side of an atoms show how far the atom is away from the plane. Good way to check the planarity of a ring. If numbers are really small you know that the specified atoms are in plane)
- ➢ *telp 0 -50 0.025*(*telp* creates a drawing of the molecule. In the drawing, put labels next to atoms. First number encodes type of drawing, second number is %age of thermal ellipsoids, and third number is thickness of the bonds. After you are done, press 'Esc' or 'h' to exit without saving, press 'Enter' or 'b' to exit with saving)
- ➢ *exam *.plt*   (*exam* works like a directory command and shows you a list of all files with .plt extension)
- ➢ *labl 1 400*   (determines which atoms get labeled and in what style they get labeled)
- ➢ *link 5 $h*   (makes all bonds to hydrogen atoms a line to distinguish them from other bonds)
- ➢ *view drawing1* (to see the drawing on screen)
- ➢ *draw drawing1*(chose 'h' for hpgl-file and then go through commands. Now you can insert this *.hpgl file into word and see it as a picture)
- ➢ *cent n1 c1…*   (calculates the center of the specified ring)
- ➢ *cent/x n1 c1…* (calculates the center of the specified ring and puts an imaginary atom in that position. If you need to calculate the distance between two rings, this is a good method)

XXIII. <u>Edit</u>

- ➢ Since XP can't calculate the error of a value (which you need in publications), you have to do this in the *.ins file

- ➢ Below 'PLAN' make a new line and type in a new command:
  'MPLA 6 n1 c1 > c6 cu' (this will calculate the ring n1 through c6 and will then calculate the distance of Cu to that specific ring. The 6 means that the first 6 atoms are included in the ring calculation but not Cu. You can use this to determine if for example a given molecule is square planar or not)
- ➢ Save and exit Editor, run XL refinement cycle and see the result in *.lst file
- ➢ Below 'PLAN 20' make a new line and type in a new command:
  'EQIV $1 1-x 1-y -z' (this will define a certain symmetry operation and give it the name $1)
- ➢ Then type:
  'RTAB ang1 cl2_$1 cu1 n1' (calculate the angle between the specified atoms linked through the specified symmetry operation)
- ➢ Below 'PLAN 20' make a new line and type in a new command:
  'HTAB' (htab is for calculating Hydrogen-bonds if present. You can see the hydrogen bonds in the *.lst file)
- ➢ If your hydrogen bond is within the same symmetry unit, add the following under the 'HTAB':
  'HTAB o1 n2' (calculates the H-bond between o1-H….n2)
- ➢ If your hydrogen bond is in a different symmetry unit, you have the specify the symmetry operation first (which can be found in the *.lst file behind that specific H-bond) by typing:
  'EQIV $1 x-1, y, z+1' (You can just copy and paste the symmetry operation from the *.lst file. $1 is now the name of that specific symmetry operation)
- ➢ Now add:
  'HTAB o1 n2_$1' (calculates the specified H-bond between o1-H….n2 with n2 being from a symmetry related molecule)

Finalizing a project

I. Modify *.cif

- ➢ Open modify.cif
- ➢ Open *.cif
- ➢ Replace the specified line with those from the modify.cif file
- ➢ The 'number of reflection used' can be found in the *.p4p file
- ➢ Save *.cif

II. XCIF

- ➢ Table of choices:

➤ Chose [R] then *enter*
        name of *.ref file → *enter* (reference file)
        [y] → *enter*
        select modified *.cif file → *enter*
        name of file needs to be modified → *enter*
➤ Chose [C] here you can set the compound name (usually you don't change the
        name, because it has been assigned correctly at data collection)
➤ Chose [T] here you create all the necessary tables
        take *.cif file → *enter*
        [y] → *enter*
        filename: here, type: *.rtf
        filename extension: rtf
        (don't add 'hydrogen atom coordinates table','torsion angles table'
        and 'hydrogen bond table' unless you specifically want them)
➤ [F]: tabulation of intensity data (usually not required)
➤ Chose [Q] *enter* (to quit the program)

III. *.rtf file

➤ Open the *.rtf file
➤ Run the 'tbl' macro
➤ Save document as *.tbl.doc

IV. *.exp.doc

➤ Open the generic experimental file
➤ Replace the bold values with the real values for your compound
➤ Unbold the numbers
➤ Save document as *.exp.doc

V. XShell

➤ Open your project
➤ Kill the q's
➤ Save file as *.pdb (If you have to create a symmetry equivalent, chose 'save all'
 command)

VI. Drawings

➤ Make one black and white and one colored drawing of the molecule in XP
➤ Insert the drawings into a word document and save it as *.drw.doc
➤ Link 5 $h

- Labl 1 400
- Telp 0 -50 0.025

VII. Send Project Back

- Go to x-ray management site
- Chose submission editor
- Enter project code and search
- When project is found, click on the project number to open project
- Go to 'Status' and change it to 'Write Experimental'
- Go to 'Assigned to' and change it to 'Khalil Abboud'

Adding a project to the database

I. Create Files

- Go to the project folder on the X-drive
- Create a new folder inside the project folder with the project name
- Copy important files into this new folder: *.cif
     *.tbl.doc
     *.exp.doc
     *.drw.doc
     *.fcf
     *.pdb
     *.res
- Create a *.zip file from this folder
- Move files to the 'Final Projects to be added' folder: *.pdb
     *.zip
     Entire project folder

II. Database

- Open the 'Final Projects to be added' folder
- Open the 'X-ray secure data' folder
- Add the *.pdb file under the professors name (change security variables)
- Add the *.zip file into the download folder (change security variables)
- Add the *.zip file to 'Archived Projects' folder under 'Zipped'
- Add the entire project folder to 'Archived Projects' folder under 'Unzipped'

III. Update Database

- ➢ Go to x-ray management site
- ➢ Chose submission editor
- ➢ Enter project code and search
- ➢ When project is found, select the 'Update Database' button
- ➢ In the next window, browse for the *.cif on the X-drive, open it and press 'go'
- ➢ Email student

IV. <u>Finish</u>

- ➢ Go to x-ray management site
- ➢ Chose submission editor
- ➢ Enter project code and search
- ➢ When project is found, click on the project number to open project
- ➢ Go to 'Status' and change it to 'Done'
- ➢ Go to 'Assigned to' and change it to 'Not assigned'
- ➢ Click the 'Generate Invoice' button
- ➢ Click on 'email' to send an email to the business office and confirm