PART 2: Structure solution and kinematical refinement in Jana2020

1.   Create new structure

Important! *The data-processing procedure is almost never perfectly reproducible. Small differences in the indexing and cell refinement procedure may result in small differences of integrated intensities. If you want to be sure that you can reproduce the following part of the tutorial, do not use the file APAP.cif_pets that you just created, but use the file APAP_reference.cif_pets provided with the example files (Copy the file to APAP.cif_pets). Using your own cif_pets file is also possible, but your results may slightly differ from the results described in this tutorial.*
Start Jana2020
In the Main menu bar, use "Structure → New" and open new structure "APAP" in directory of the Example 13.8.

2.   Import Wizard

[On the screen: Specify type of the file to be imported]
Select "Single crystal: Known diffractometer formats"; NEXT.
[On the screen: Data reduction file from]
Select "Pets electron diffractometer".
The file name automatically changes to APAP.cif_pets, which is a file produced by PETS containing all important information, including the list of intensities.

NEXT.
Change Temperature to 100 K; Leave all other settings unchanged (note the wavelength of 0.0335 Å for 120 kV electrons!); NEXT.
Leave all settings unchanged; NEXT.
The program reads 7738 reflections from the file
OK.
For absorption correction select "None or done before importing"; NEXT.
FINISH; OK to accept the data set.
You just read in the cell parameters and the intensity list. If you do not have the data in the cif_pets format, you can read them in from a general hkl file using the option "reflection file corrected for LP and absorption" at the beginning of the import wizard. You then have to input the radiation type, wavelength and cell parameters by hand.

3.   Symmetry Wizard

NEXT to close the information window and start the symmetry wizard.
Symmetry Wizard can be started separately by "Reflection file → Make space group Test". The default settings are prepared for x-ray diffraction. For electron diffraction we have to increase the tolerances. Change the tolerances according to this screenshot:

Tolerances for crystal system recognition:

Original cell parameters: 11.769 7.247 17.160 90.00 90.00 90.00

Maximal deviation for cell lengths in Ang:	0.02
Maximal deviation for cell angles in degs:	0.2
Maximal deviation for modulation vector:	0.01

Tolerances for space group recognition:

Maximal ave(I/sig(I)) for systematic extinctions induced by cell centering:	5
Maximal ave(I/sig(I)) for systematic extinctions induced by other symmetry:	100

☑ Search for higher symmetrical supercell (recommended)

☐ Introduce twin laws in case of subgroups

☑ Use old twin matrices in testing

Leave other settings default; NEXT; OK.
[On the screen: Select Laue point group]

Select Laue point group

Crystal system	Point group	Rint(obs/all)	#averaged(obs/all)	Redundancy
Triclinic	-1	8.87/12.75	1606/4116	1.88
Monoclinic-setting "a"	2/m	11.95/16.32	1134/2774	2.789
Monoclinic-setting "b"	2/m	10.28/14.72	1179/2842	2.723
Monoclinic-setting "c"	2/m	12.13/16.52	1133/2722	2.843
Orthorhombic	mmm	13.28/17.84	801/1814	4.266

Select orthorhombic mmm; NEXT.
The internal R-values would be rather high for x-rays, but are good for electron diffraction data.

Select cell centering

Centering	#obs/#all	ave(I/sig(I))	
⦿ P	0/0	0.000/0.000	Details
○ A	1231/3879	26.833/9.064	Details
○ B	1297/3862	28.218/10.012	Details
○ C	1366/3867	25.670/9.613	Details
○ I	1377/3865	26.317/9.913	Details
○ R-obverse	n.a.	n.a.	Details
○ R-reverse	n.a.	n.a.	Details
○ F	1947/5804	26.886/9.562	Details
○ X (1/2,0,0), ...	2199/6755	25.396/8.810	Details
○ X (1/3,0,0), ...	2595/7424	29.222/10.749	Details

Show/modify X centering

Select primitive unit cell; NEXT.
[On the screen: Select space group]
The window shows possible space groups.
The list of the strongest reflections contradicting the selected space group can be displayed by "Details" button.

Select space group

Characteristics for systematically absent reflections

Space group	#obs/#all	ave(I/sig(I))	Figure of merit
Pmcm	27/624	6.621/0.819	0.02257
P2cm	27/624	6.621/0.819	0.02257
Pmc21	27/624	6.621/0.819	0.02257
Pbcm	52/738	6.684/1.037	0.03127
Pbc21	52/738	6.684/1.037	0.03127
Pccm	42/718	7.467/0.987	0.03657
Pcc2	42/718	7.467/0.987	0.03657
Pbca	76/842	7.660/1.277	0.05162
Pmca	51/728	8.105/1.127	0.05444
P21ca	51/728	8.105/1.127	0.05444
Pncm	61/720	7.575/1.179	0.05461
Pnc2	61/720	7.575/1.179	0.05461
Pcca	66/822	8.306/1.239	0.05932
Pnca	85/824	8.196/1.406	0.07316
Pbma	49/218	8.233/2.588	0.64151
Pb21a	49/218	8.233/2.588	0.64151
Pbmm	25/114	6.753/2.232	0.67707
Pbm2	25/114	6.753/2.232	0.67707
Pb21m	25/114	6.753/2.232	0.67707
Pmmm	0/0	--------/--------	1.00000
Pm2m	0/0	--------/--------	1.00000
P2mm	0/0	--------/--------	1.00000
Pmm2	0/0	--------/--------	1.00000
P2212	0/0	--------/--------	1.00000
P222	0/0	--------/--------	1.00000
Pcma	42/222	10.473/2.678	1.05361
Pc2a	42/222	10.473/2.678	1.05361
Pnma	61/224	9.644/3.279	1.20950
Pn21a	61/224	9.644/3.279	1.20950
P22121	3/24	23.473/3.628	2.02661

It is difficult to select the correct space group. In particular, presence or absence of the glide planes and screw axes is hard to asses, knowing that kinematically absent reflections may have significant intensities due to dynamical diffraction effects.
Select *Pbca*; NEXT.
Accept the space group in the standard setting; FINISH.
Symmetry is saved in file APAP.m50.

4. Creating refinement reflection file

In this step the program creates file APAP.m90 containing the data set merged by symmetry and with discarded forbidden reflections. This file will be used for refinement.
NEXT;
7738 reflections were read, 842 reflections were rejected as systematically extinct, 6885 reflections were written to the output file.
OK; OK; NEXT
The Rint(obs/all) is 13.18%/16.99% for 1574 unique reflections averaged from 6896 reflections.
OK; FINISH

5. Structure Solution Wizard

OK to close the information window and start the solution wizard
 [On the screen: window of Commands for Superflip] Structure solution wizard can be executed separately through the Command tree "Structure solution → Commands for Superflip".

Jana2020 does not contain solution procedures, it calls external programs. By default, Jana uses Superflip (using charge flipping as the solution method). Superflip is distributed with Jana2020.
In "Formula" textbox type the list of elements: C8 H9 N O2.
Superflip does not need information about chemical composition but it will be required for peak assignment based on electrostatic potential map calculated by Superflip. If Jana2020 is used for peak assignment, a list of expected chemical elements is sufficient. If you know the expected formula, you may enter it and use EDMA for peak picking (at the bottom of the window). If the formula is correct, EDMA often gives cleaner and more complete interpretations of the solution.
Click the checkbox next to "Use a specific random seed" and enter the value 111.
Choose AAR as the iteration scheme.

AAR tends to give better results than CF for electron diffraction data, although in many cases the difference is negligible.

Select "EDMA – fixed composition" for peak search.
"Run Superflip".

The specific random seed is used just to guarantee reproducibility of the results. For standard work random seed need not be defined.

[On the screen: window of Superflip appears with iteration running. After ten runs, listing of Superflip log file is displayed].

A window pops-up with the information about space group and symmetry match after the trials finished. The result of the structure solution may slightly differ.

Click OK.

Click on "Replace the result with tutorial files" for reproducibility of the results;OK.

You can switch between your solution and tutorial one by clicking on the same button.

Click on "Open the listing" for reproducibility of the results;OK.

At the bottom you find the result of the structure solution:

Properties of the saved density:

```
 Run  Rvalue  Peaks  Symm.   Der.SG
  8   45.42   2.47   12.73    Pbca
```

The space group proposed by Superflip is the same as our initial guess.

"Close" the listing

Click "Draw 3D map".

VESTA opens with a density shown as isosurfaces, and an atomic model overlaid. Rotate the view to inspect the structure (C - brown, N - blue, O - red).

Click in VESTA "Edit", "Bonds…"

Select the list entry number 1 (C-O) and switch the "Search mode" to "Search molecules" and use, OK.

On the tab "Style", button "Boundary…" you can restrict the "Ranges of fractional coordinates" for "y(max)" to 0.5 for a better visualization of the molecule(s).
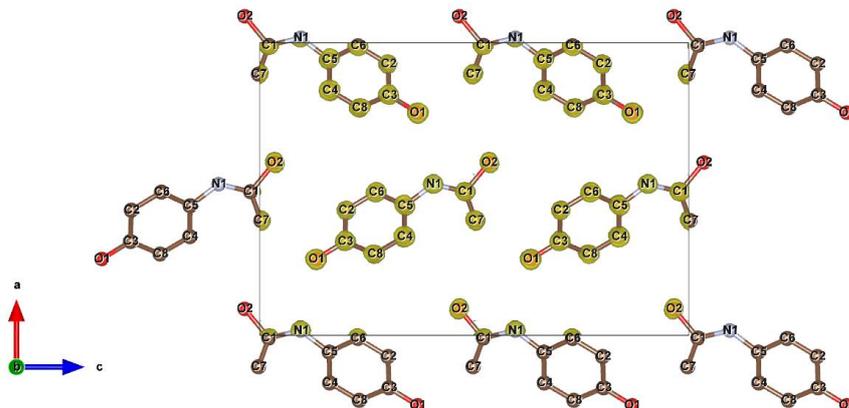

At first glance the structure looks very good. The only problem are some wrongly interpreted atoms due to the very similar atom scattering factors of C, N and O. We will therefore correct the structure using our chemical knowledge about N-Acetyl-p-aminophenol. Here is the scheme of the molecule:
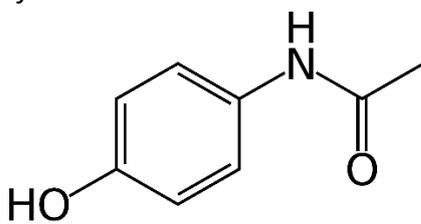
Close VESTA (do not save the file).
Press "Accept last solution".

Click on Edit atoms, select all atoms click on "Action" button and choose "Make symmetrically contiguous motifs";OK.
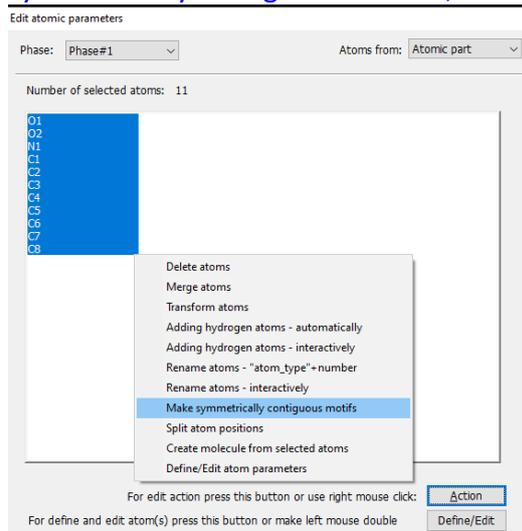
Switch to JanaDraw.

Click the icon to draw just one molecule

Comparing the shown structure with the scheme we see that we need to change C7 to O2.

Double click atom C7.

In the dialog that opens change the atomic type to O, rename it to Ox to avoid the clash with the O2, which is in fact C7; OK.
Repeat for atom O2 (change to C7).
Now you can rename the Ox to O2.
The next step changes the names of atoms according to their chemical type and assigns a sequential number to each atom.

Click on the quick button "Edit Atoms" ⚛.
Select all atoms, click "Action" and select "Rename selected atoms to atom_type + number"; OK. YES.
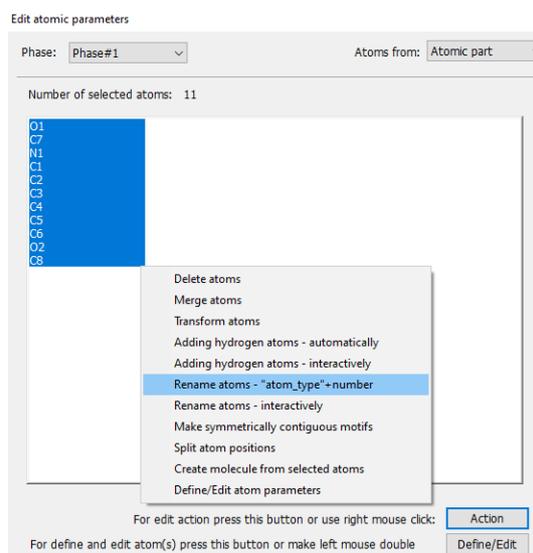
The corrected model should look like this:
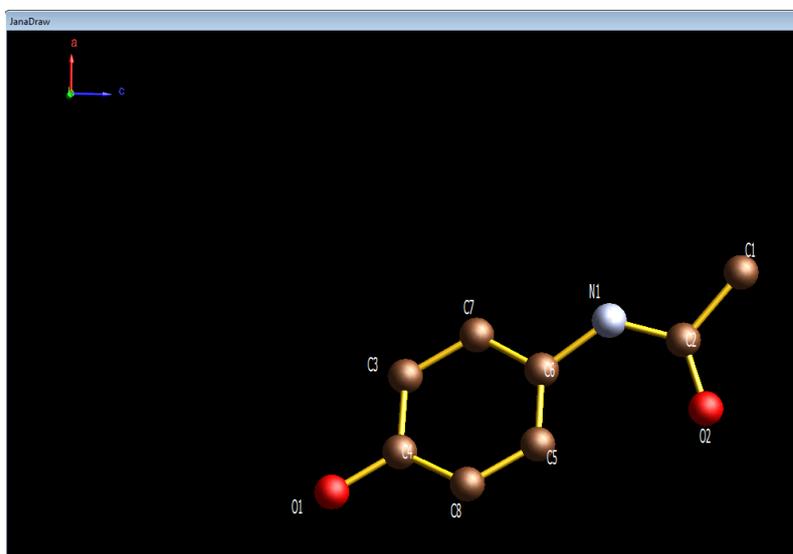
6.   *Initial Refinement*

[On the screen: basic window of Jana]
In the Command tree, double click "Refinement → Refinement commands"
[On the screen: Refine commands]
Change the number of cycles to 100.
Go to "Select/Listings".

Remember, in part 1 step 9c we point out, based on the camel plots at I>3σ(I), that the averaged rocking curve at 1.3 to 1.4 Å⁻¹ was already relatively noisy. For this reason, it is advisable to limit the resolution for the data used for structure refinement to 1.3 Å⁻¹. For this tutorial we will cut the resolution down to 1.2 Å⁻¹ just for saving computing time.

Check the box "Apply sin(th)/lambda limits" and set for "max." the value 0.6.
OK. Click "Yes+start".

Refinement converges with R(obs)= 22.09%. At this moment you may check the refinement listing (Refinement→ view refinement listing) with a lot of information about the refinement procedure and the results.

7. Difference Fourier map

Difference Fourier map is used to check if there is any missing electrostatic potential that has not been described by the structure model yet.
[On the screen: basic window of Jana]
In Command tree, expand "Fourier synthesis" and double click "Fourier commands".
Select the following parameters to calculate the Fourier map.
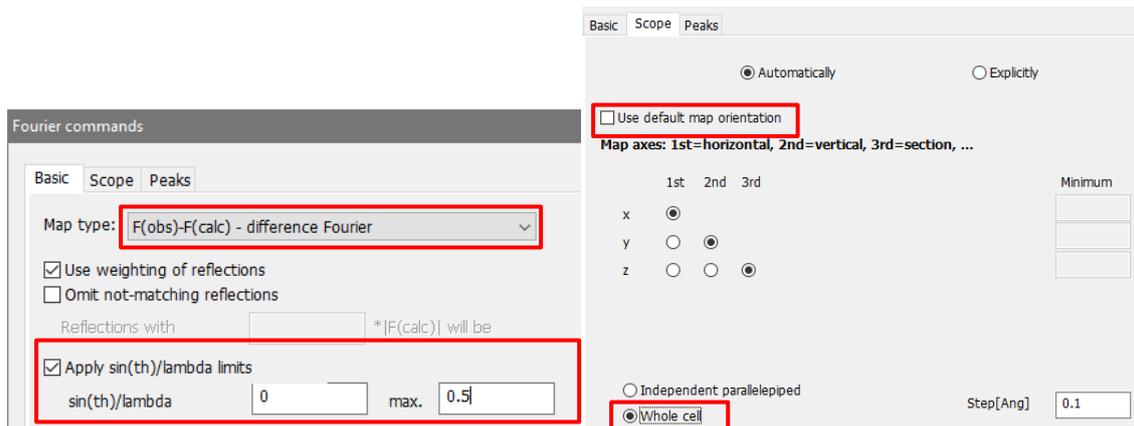
Click "OK".

"Yes+start".

Choose "NO" to avoid the procedure for including new atoms.

Choose "NO" to avoid opening the listing.

Have a look at the calculated map using VESTA as when looking at the solution.

Click "Run Contour", expand "Use old Fourier map", and double click "draw maps as calculated"; OK.

On the upper menu, go to "Run→Vesta" (alternatively click the Vesta icon in the bottom toolbar)

Go to "Properties", tab "Isosurfaces".

Click on Isosurfaces No 1 and change it to Positive and its level to 0.22 (3σ level); OK.

Go to "Boundary" and set the y(max) to 0.5; OK.
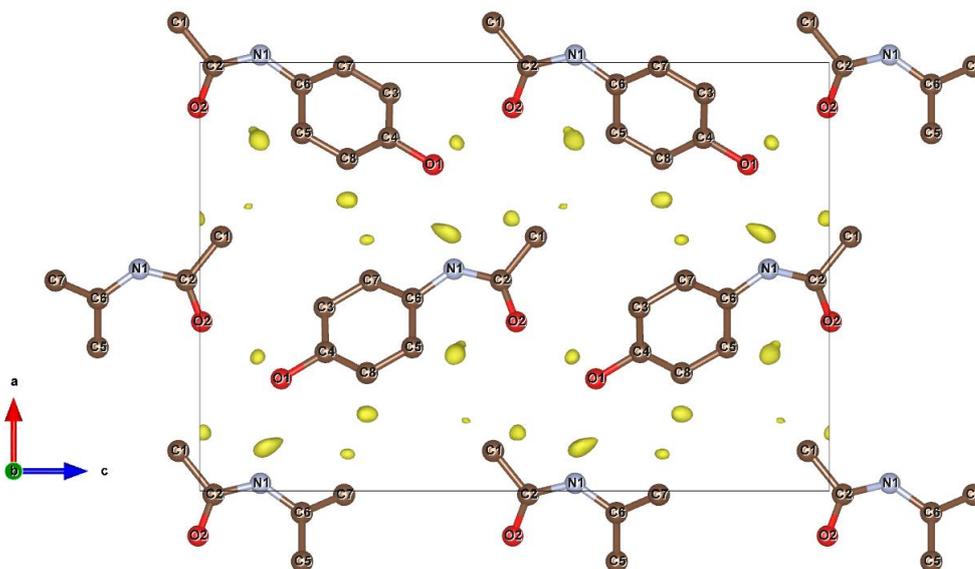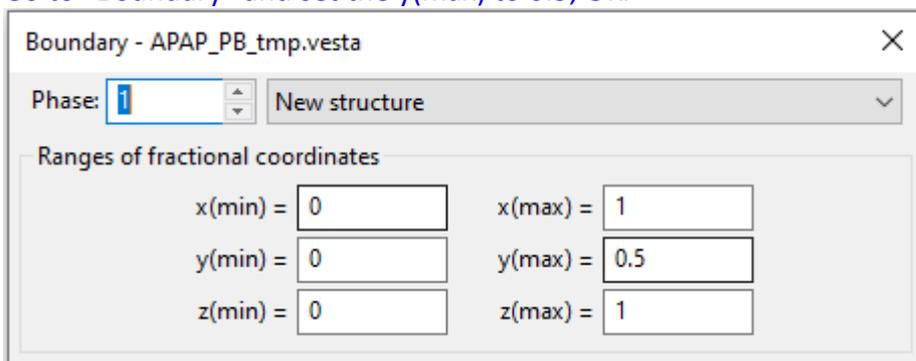
A few weak positive peaks can be observed close to the atoms where we expect hydrogen atoms. It seems that at least 6 out of 9 hydrogens are visible in the difference Fourier map of the kinematical structure refinement.

Close VESTA.

Close Contour and return to the main window of Jana.

We will add the hydrogen atoms on O1 and N1 as freely refined atoms, and add the hydrogens on the carbon atoms as riding.

First, we will add the hydrogen atoms to O1 and N1

Expand the Command tree for "New", double click "New atom"; OK.

Select Max1 and click "Include the peak at the specified position".

Fill in Name of the Atoms as H*.

Set the "Atomic type" to "H"; Accept.

Repeat with the maximum close to O1 (Max10).

Click "Finish" and "Yes" to include the two new atoms.

Edit structure parameters → Edit atomic parameters

Select carbon atoms C1, C3, C5, C7 and C8.

Press Action→Adding hydrogen atoms interactivelly.

Set ADP ext. factor to 2; OK.

Set H distance to 1.08; Apply => Go to next; Apply => Go to next; Apply => Go to next; Apply =>
Go to next; Apply.
Confirm changes by clicking OK; Yes.

Seven hydrogen atoms were added.
Replot the structure in JanaDraw to see the molecule with added hydrogen atoms

8.   *Final kinematical refinement*

Run refinement by the quick button or by Refinement →Run refinement
Refinement converges with an Robs value of about 18.35%