Chemical Crystallography
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Lecture – 40
Structure Solution using Olex 2 (Rigaku Diffractometer)

Welcome back to the course of Chemical Crystallography. If you remember we were discussing about the Structure Solution and refinement using Olex 2 and in that we used to SHELX s for structure solution, SHELX l for the refinement and the other variations are SHELXt or xt which you can change from this module which is shown here the xt. And then in the refinement module you can choose SHELX l or xl or you can use the other methods of refinement where it says Olex 2 to refine it use as a different method of refinement.

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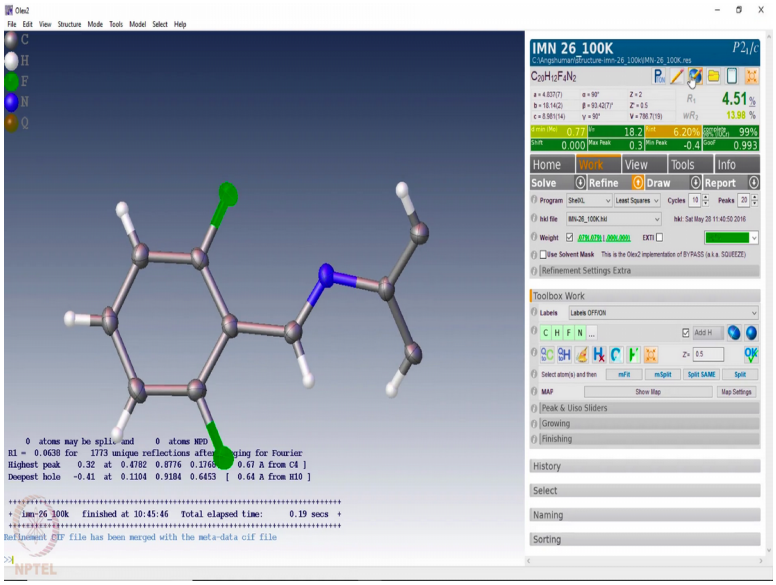

So, in that structure determination and refinement we tried to treat the hydrogens as is fixed entity.

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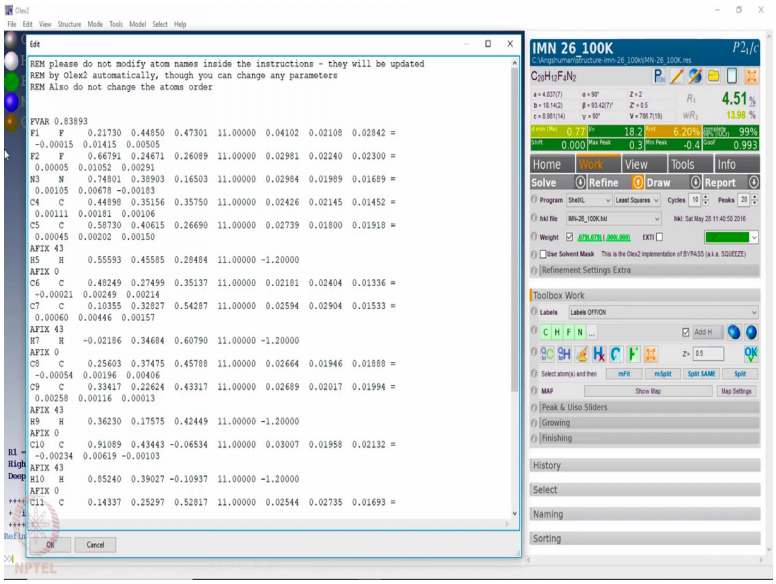

If you remember, if we try to look at the corresponding table of coordinates here what we are seeing is that we have the fluorine atoms first with the fractional coordinates that is along x y and z. Then this is the occupancy parameter which we will discuss further today. The parameter when it is 11 it means that occupancy is 100 percent, when the parameter has a fractional value in the decimal place then we write it as 10 point something.

So, 10.5 means 50 percent occupancy, 10.25 means 25 percent occupancy and so on. And then these 6 parameters which are responsible to define the thermal ellipsoid that is coming because of the thermal motion of the atoms in the molecule and that is responsible for making the molecule with making the atom instead of a sphere as an ellipse.

So, now if you look at the corresponding hydrogens, suppose the hydrogen associated to carbon 5 here, we have a term afix 43 and afix 0 indicating that this particular hydrogen 5 is connected to carbon 5. These are the fractional coordinates occupancy is 1 and this is the thermal parameter which is not going to be refined. And the thermal parameter indicates that 1.2 times the value of isotropic thermal parameter of carbon. And this is how the hydrogen is fixed that is geometrically ideal position.

So, this hydrogen is riding on the carbon and as the carbon changes its atomic position coordinates during refinement cycles the corresponding hydrogen also moves along with

it. Simultaneously if there is a change in thermal parameter of this particular carbon then the thermal parameter of the hydrogen attached to it also changes. Let us try to see what happens if we first remove this hydrogens by saying H cross; that means it has removed all the hydrogens.

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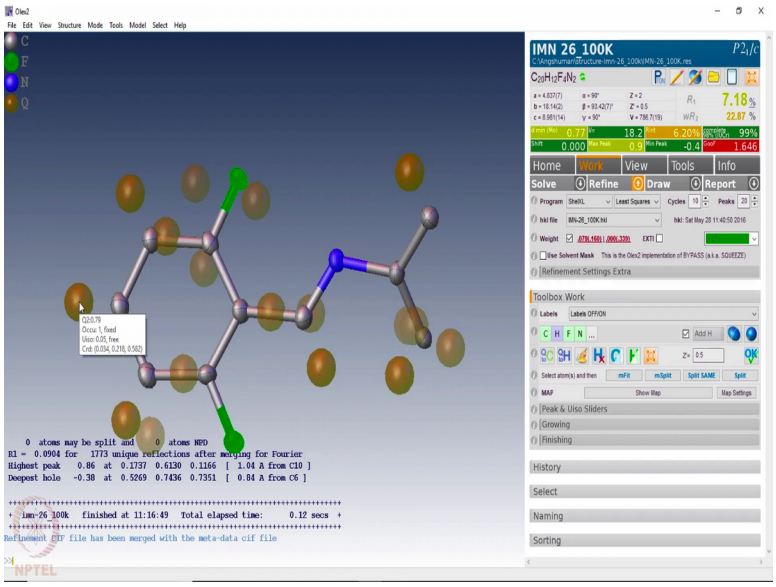

And then we do 10 cycles of refinement, which means it is doing some least squares refinement. That means, what it is doing is from the structure that we have given, it is trying to calculate the structure factors for every hkl and comparing the structure factor generated from the structure that is the calculated structure factor compares with the experimentally observed structure factor amplitudes takes the difference and that difference gives rise to difference in electron density.

So, the orange dots or orange spheres that we are getting here are the corresponding residual electron densities after assigning the heavier elements. So, now after removing some of those residual densities which were paint which means those residual densities were very less. We see some densities appearing at locations probable for the hydrogen atoms connected to those the corresponding carbons.

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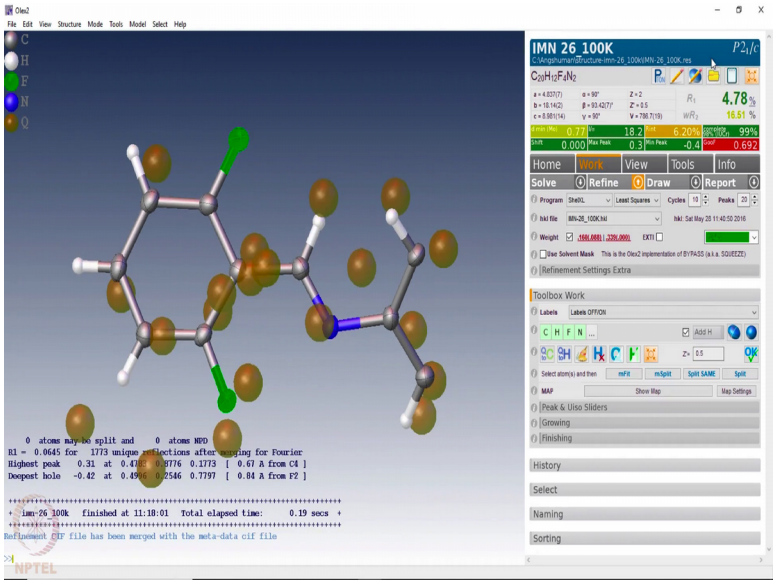

So, after selecting those hydrogens and marking those atoms and marking them as hydrogens if we tried to refine, we will see that the R factor reduces. You do it a few times till you reach a convergence so, all these weighing parameters should become green which would indicate that the refinement is reaching convergence.

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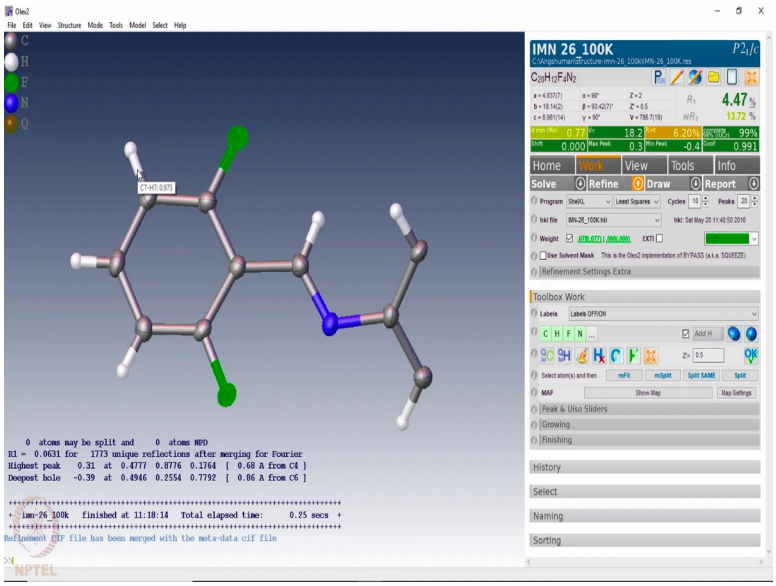

And then at this point we remove all the other residual densities and let us bring the cursor at the bond between carbon and hydrogen it shows the distance.

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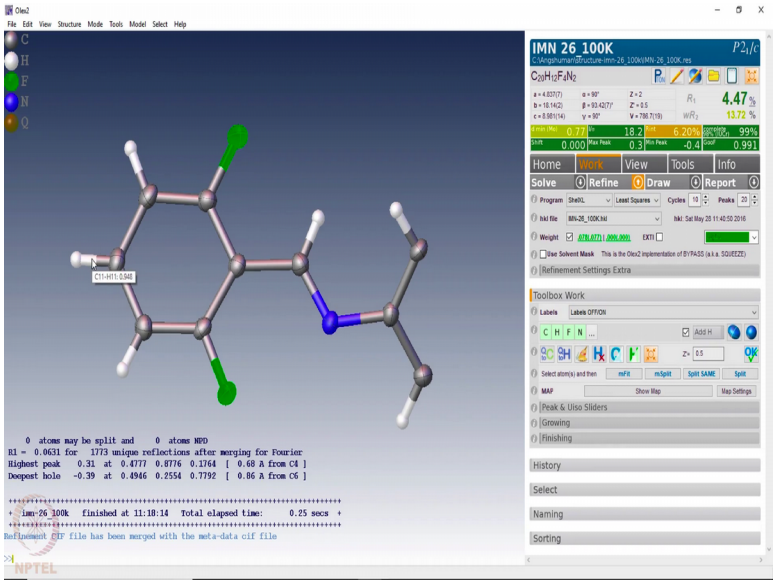

So, here now the distance between the carbon and hydrogen is 9.973, here the distance is 0.948.

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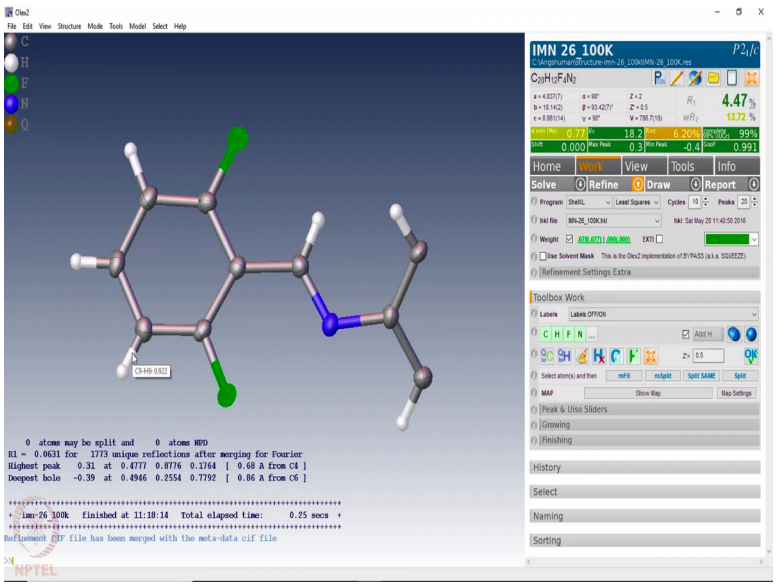

Here it is 0.922.

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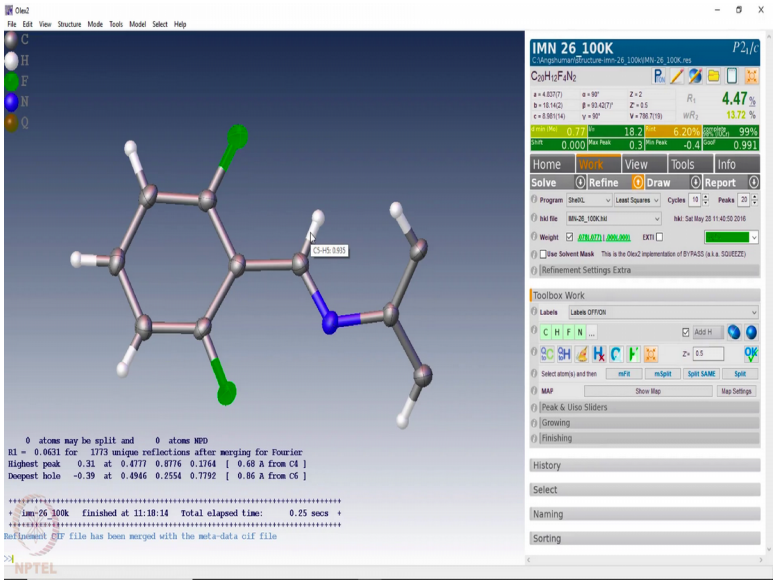

This one is 0.935.

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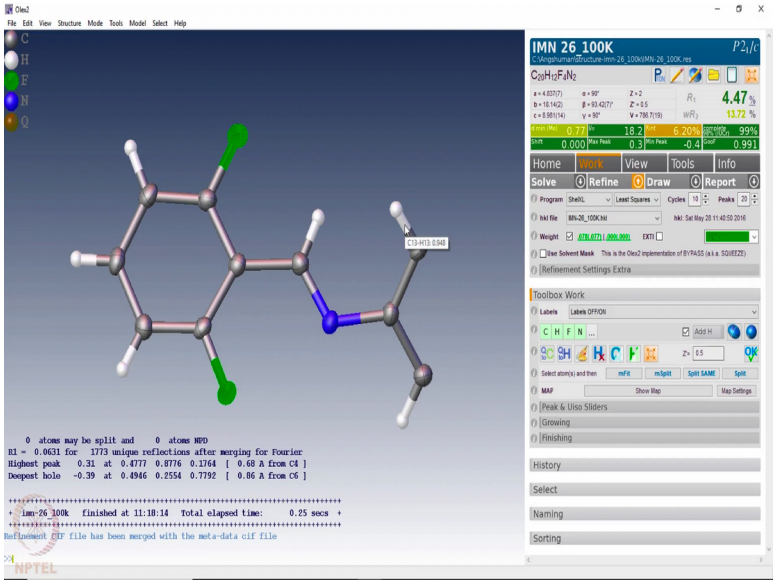

This one is about 0.948.

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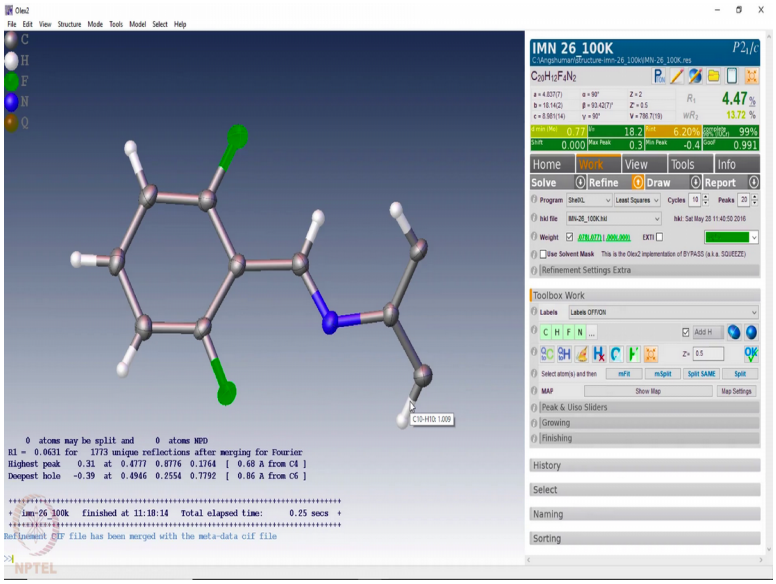

And this one is 1.009. What does it mean? It means that the electron densities which appeared after assigning the heavier elements, we have assigned those electron densities as hydrogens. And now the hydrogens are being refined independently. Those are not refined as a riding model, they are refined as independent atoms and hence the carbon hydrogen bond lengths are not fixed for all these carbon hydrogen bonds. And also if we look at the thermal parameters, if we just do go back to the atom table, now we see the hydrogen 5 is no longer associated with carbon 5.

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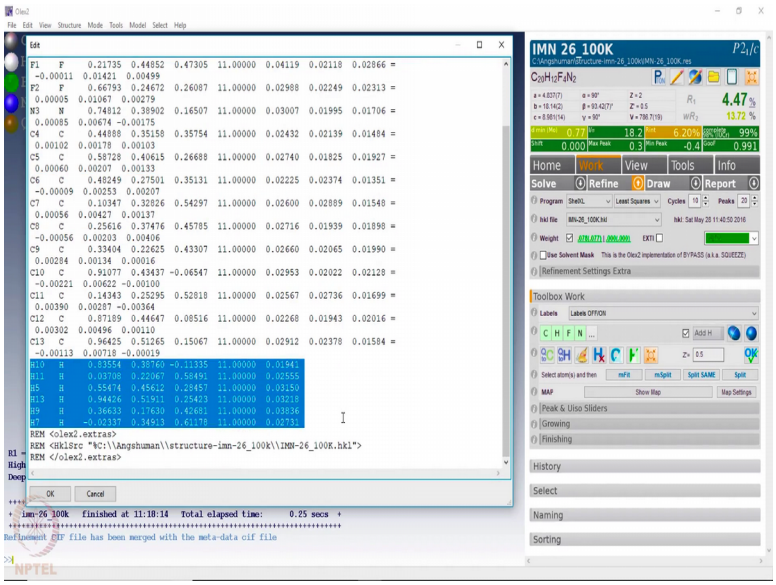

Those hydrogens are now treated separately. They have their corresponding fractional coordinates with some negative as well. And the thermal parameters, the isotropic thermal parameters are all different for different hydrogens and they are refined independently. So, this thermal parameters are not calculated based on the isotropic thermal parameter of the carbon 2 which it is attached rather this hydrogens are refined independently.

There is a problem in doing this. This particular data is a very good quality data, where this carbon hydrogen bonds are within the acceptable limits of bond length. So, the acceptable limit for carbon hydrogen bond length in case of aromatic system or carbon hydrogen bond length with sp 2 carbon and hydrogen should be between 0.9 to 1.1 angstrom.

In case of 4 quality of data, it may so happen that the bond length increases may comes 1.2 angstrom or the thermal parameter of the hydrogen becomes very large, so the sphere on hydrogen may look a very large sphere.

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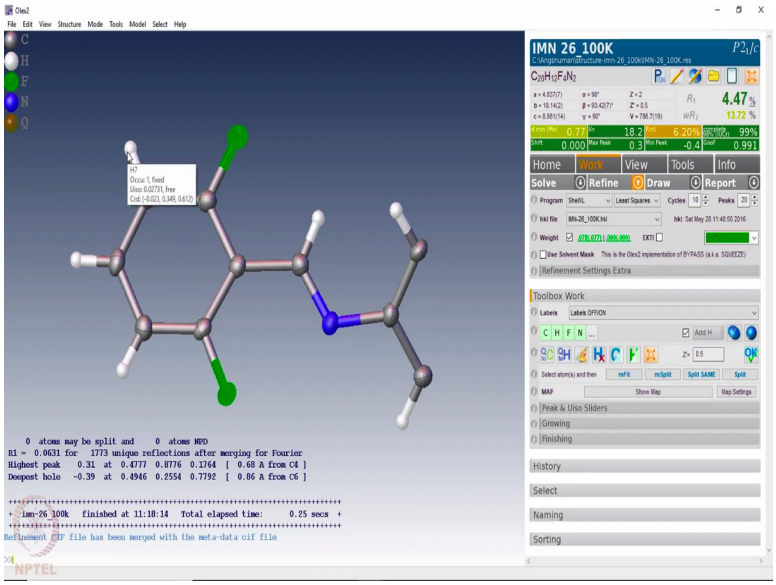

So, that is why we do not try to locate these hydrogens that is we do not assign the residual electron densities as hydrogens rather, we actually calculate those hydrogens from the carbon atoms that is being refined.

So, let us go back to the state when we had not located the hydrogens rather fix the hydrogen.

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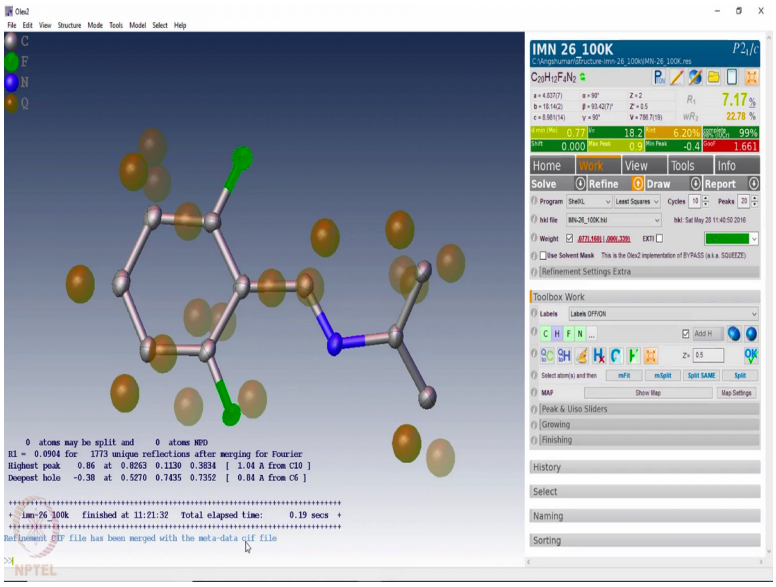

So, to go back we again remove the hydrogens, do 1 round of 10 cycles of refinement and then again click on add hydrogen. What it would do is it would correspond immediately incorporate the different afix commands. For those who are interested to learn more about afix commands, I would suggest that you should look at the SHELX manual for those specific afix command numbers because, there are different numbers for different types of hydrogens.

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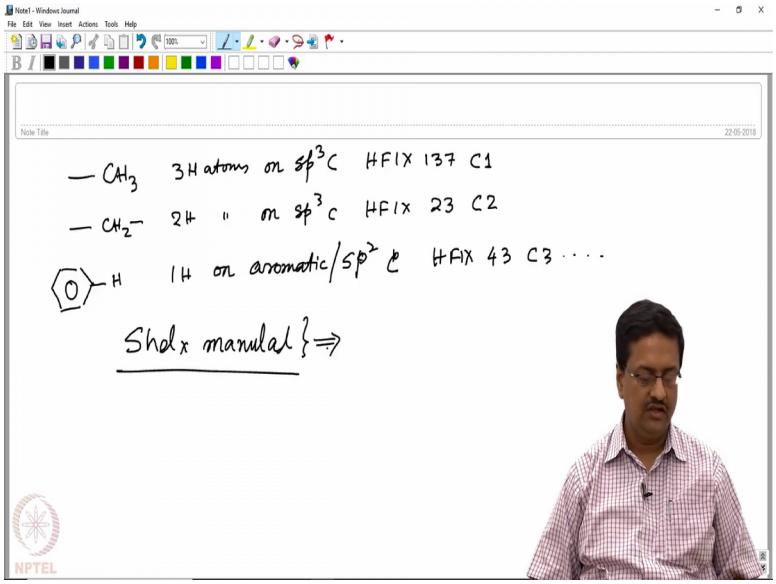

For example, some of them are routinely used. If you want CAH 3 group all the hydrogens to be added, so, it will add 3 h atoms on sp 3 carbon. So, the corresponding afix command will be H fix 137 and the corresponding carbon may be C 1.

To have 2 hydrogens on s p 3 carbon, this will be H FIX 23. You should identify the atom like this which is might be C2. Similarly, as I have indicated if it is aromatic hydrogen then it is just 1 hydrogen on aromatic or of the any other S p 2, the command is H FIX 43 C3 or whatever.

So, these are available in the SHELX manual. This part you should see from the SHELX manual and try to understand yourself how these numbers are allotted. So, now, if we just click this button here H fix, what it does is with immediately identifies what kind of atoms are there and what kind of atoms can have what kind of hydrogens and immediately pick up those H fix commands from the data base and set those atoms with the corresponding H fix command and fix the hydrogens at their refined locations.

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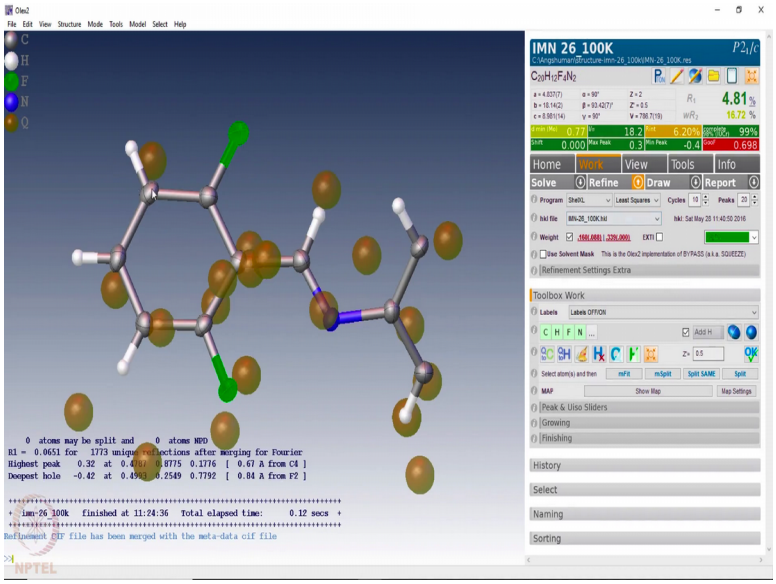

So, after doing H fix 1 has to do a few rounds of refinement to reach convergence on the weighing terms, weighing factors and till you reach the lowest possible r value for particular structure.

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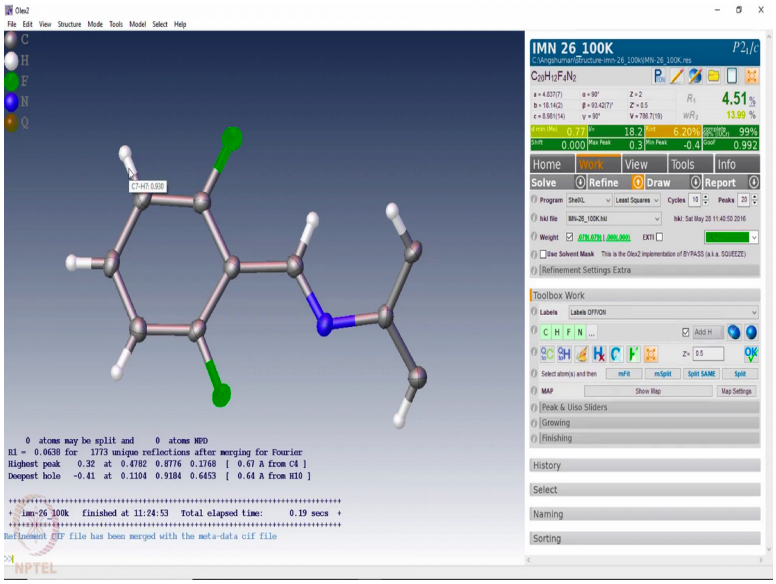

So, here once again we can see that these bond lengths are all same 0.93 angstrom 0.93 and all of them being a single hydrogen connected to sp 3 carbon they have the same bond length 0.93.

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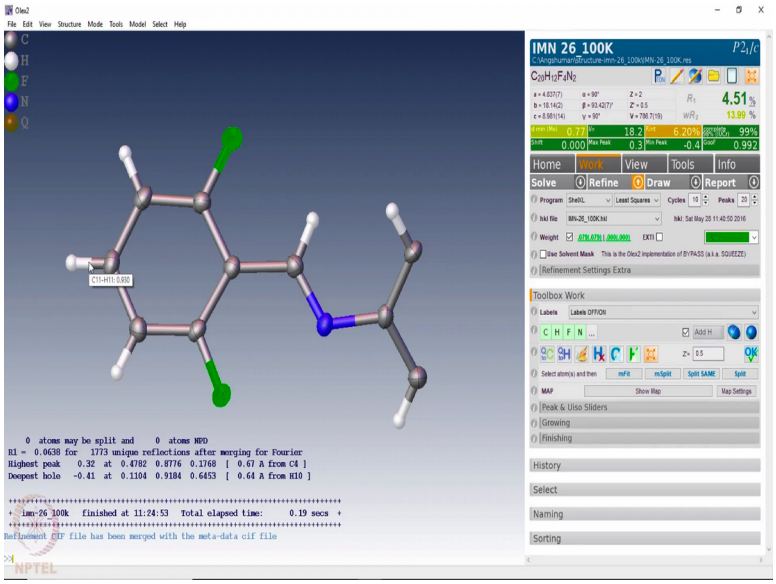

So, once we have solved the structure and refined well now we also have seen how to validate the structure solution and refinement and if we had made any mistake in this structure solution and refinement.

If there is any problem with the data itself all those are evident from the check slip report, which one has to then address.

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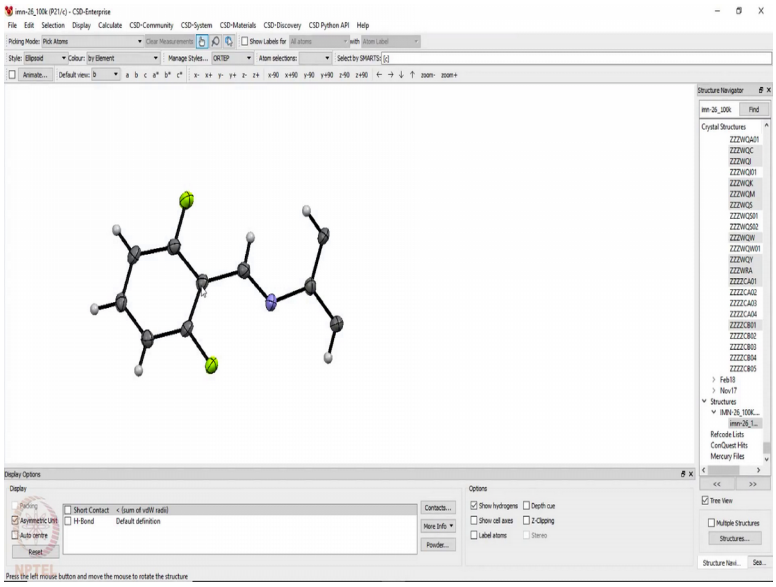

If we want to visualize the structures and then generate the packing diagram, generate the geometrical parameters and all that one can use a software called mercury, which is also

available free of cost from ccdc at particular version and the full licensed version is available with the cambridge structural database subscription which is a bit faith version of this software. So, when you click asymmetric unit it only shows what is there in the asymmetric unit.

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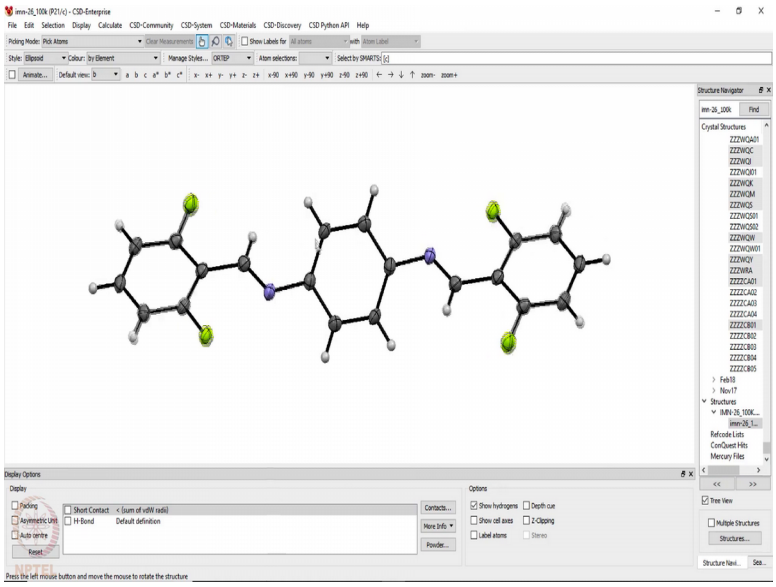

If we untick it, it shows the full molecule So, this is the full molecule for which we have determined the structure.

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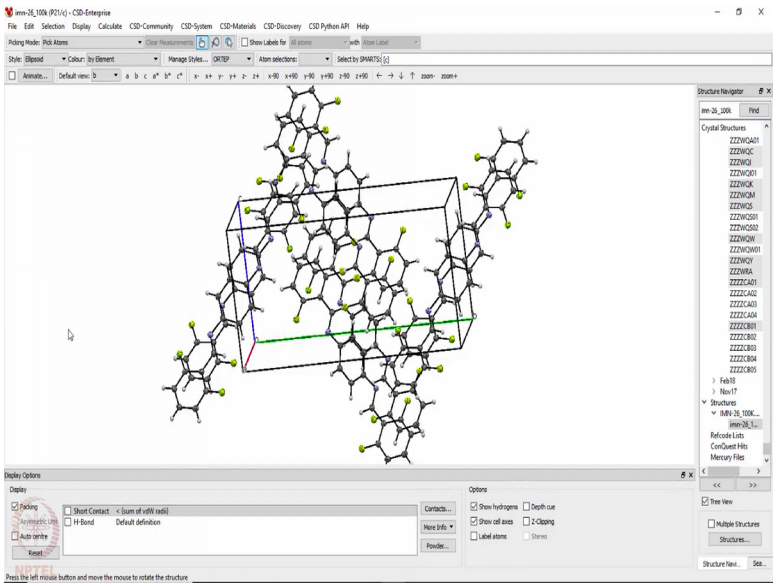

So, in this case one can draw the packing diagram and see how the molecules pack in it monoclinic unit itself, one can generate the publication material using this software for different molecules, with the different orientation of packing, one can then do analysis of short contacts.

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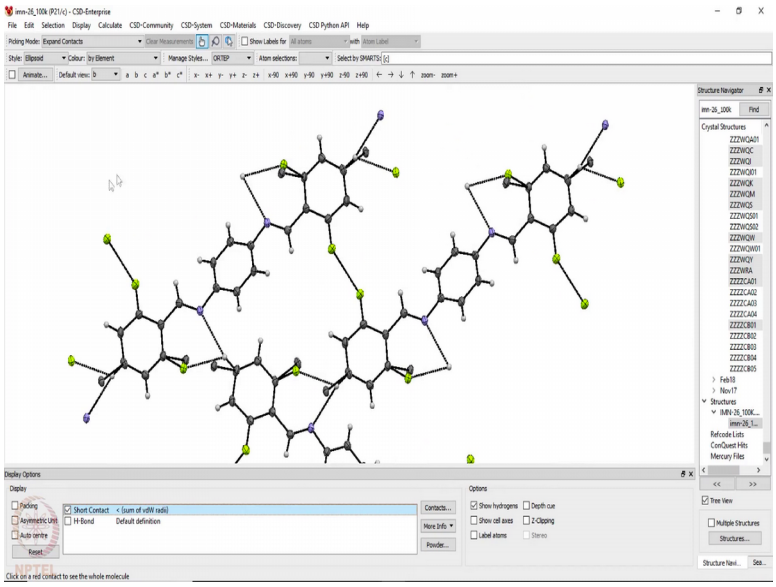

So, if you click on short contacts, it will then show what are the 3 dimensional contacts with this molecule, with other molecules, so if you can click here it generates how one molecule interacts with the other molecule, what are the hydrogen bonding possibilities, what are the other weak interactions and things like that.

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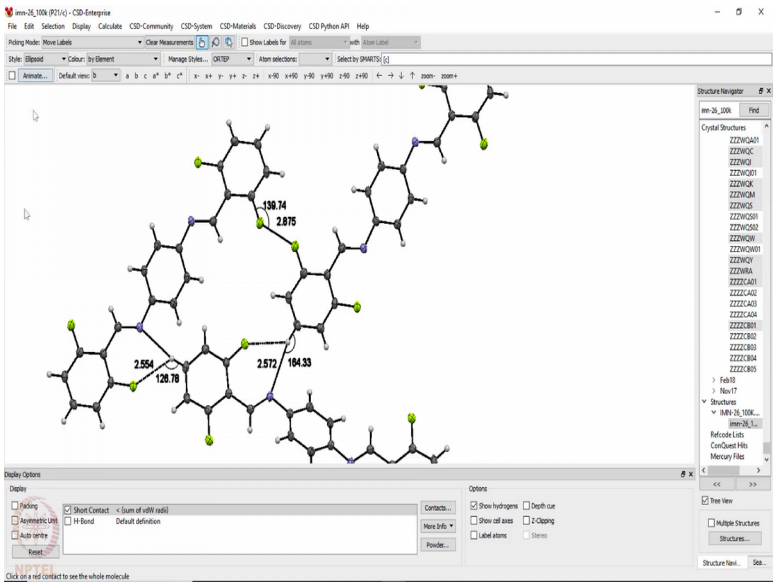

So, here what is shown here if I remove the hanging contacts, we can see that these 3 molecules which are there in the screen with appropriate orientation, you can see here that these 2 fluorines have some ff short distance.

Here 1 hydrogen has short distance with the fluorine and a nitrogen and a similar situation comes here whether when this hydrogen is connected to fluorine and nitrogen. See if someone wants to know what are the corresponding distances can calculate the distance from 1 atom to the other atom and then one can calculate the angle; that is the distance, this is the angle. So, by doing this quick calculations one can identify whether the short contacts that are being seen here are corresponding to any useful interaction or not.

So, if it is a hydrogen bond or any weak interaction one can analyze using this nice simple package. Now again if we go back to the asymmetric unit and then we have just generated the molecule which is generated by applying a mirror plane on this first molecule. So, this is the asymmetric unit, if you apply the mirror symmetric it generates the other part and suppose one if you want to know, what is the angle between this particular plane and that particular plane that kind of information also can be generated here.

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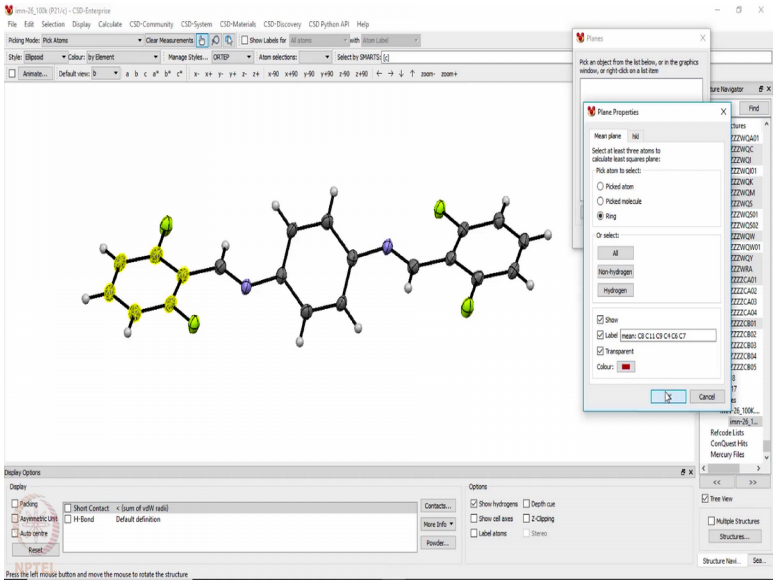

So, if we try to calculate planes, we can do that. You can select the rings, select the pick atoms and then I select all those atoms and then make a plane in red colour.

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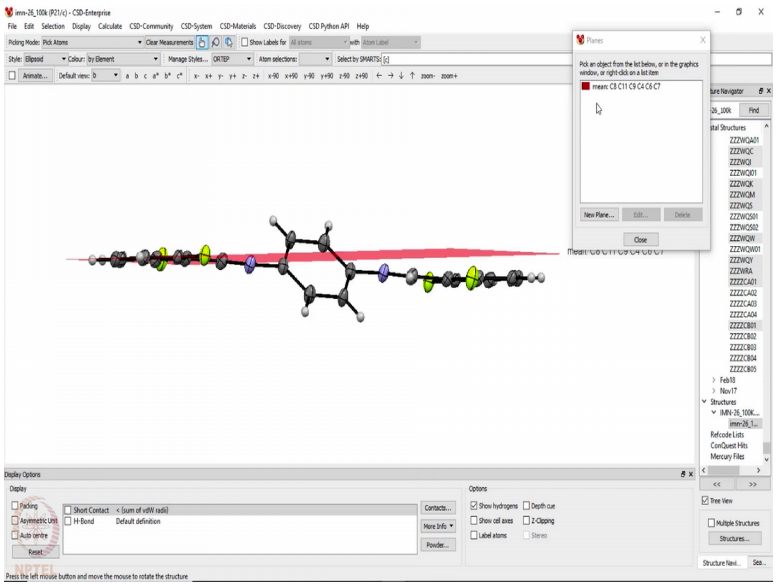

So, this red coloured plane contains that particular aromatic ring. So, now, if I want to generate 1 more plane and designated with yellow passing through the central ring we can do it like that.

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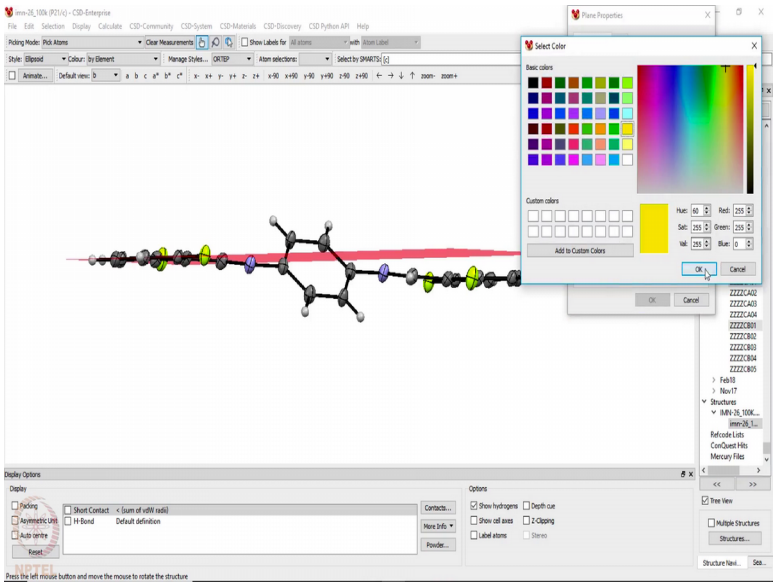

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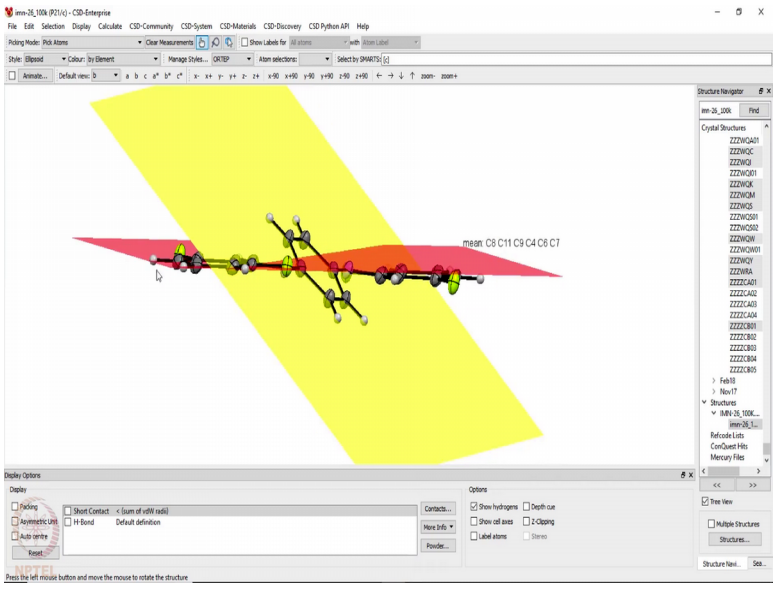

So, now, what we have a 2 planes one plane passing through the terminal carbonic ring terminal aromatic ring and 1 plane passing through the central aromatic ring.

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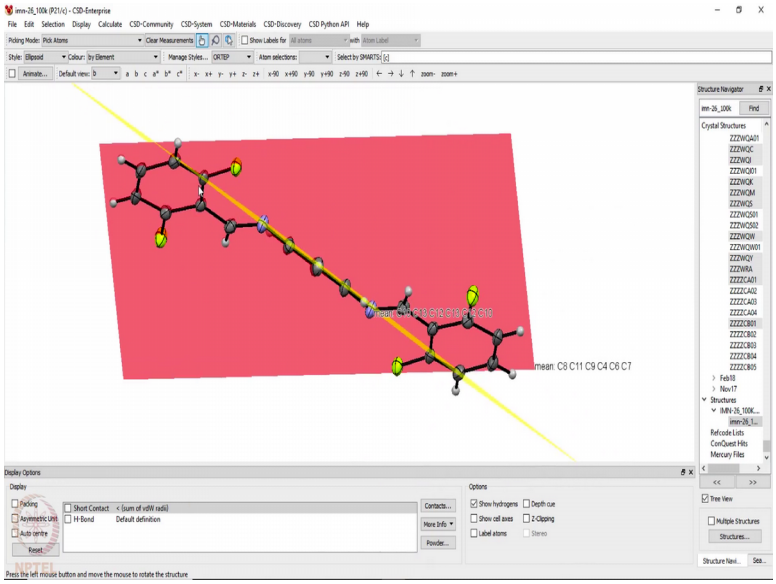

What is the angle between these 2 planes?

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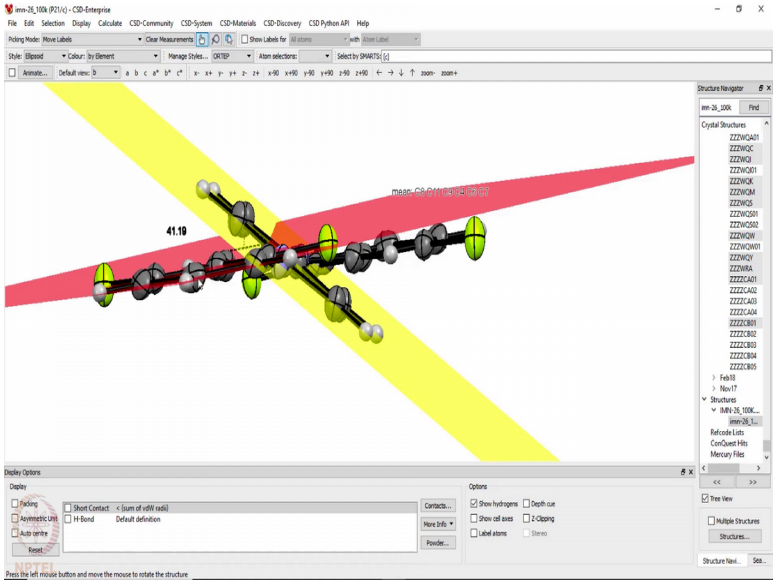

Again you go back and measure angle between the 2 corresponding planes you can move the label to a visible point and see what it is. So, the angle between the 2 planes is found to be 41 bits. So, we can clear again, clear measurement and come back.

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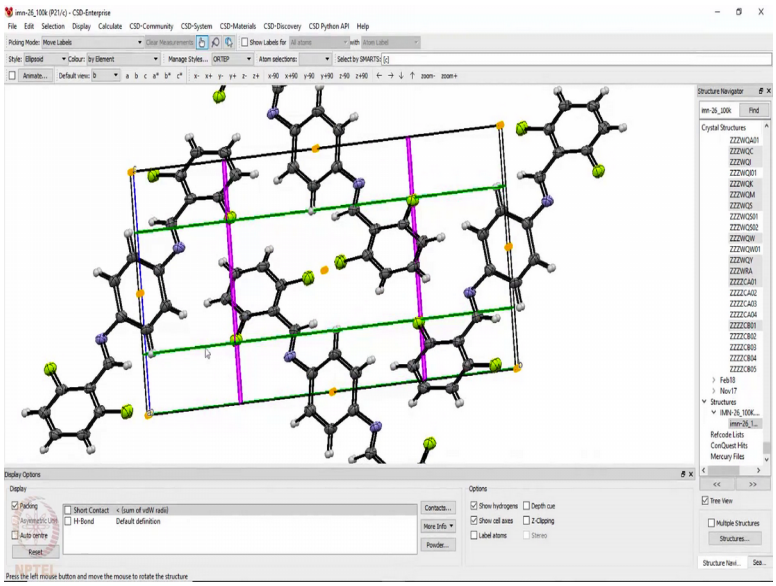

What we can do is we can do a packing diagram and then we can display the symmetry elements.

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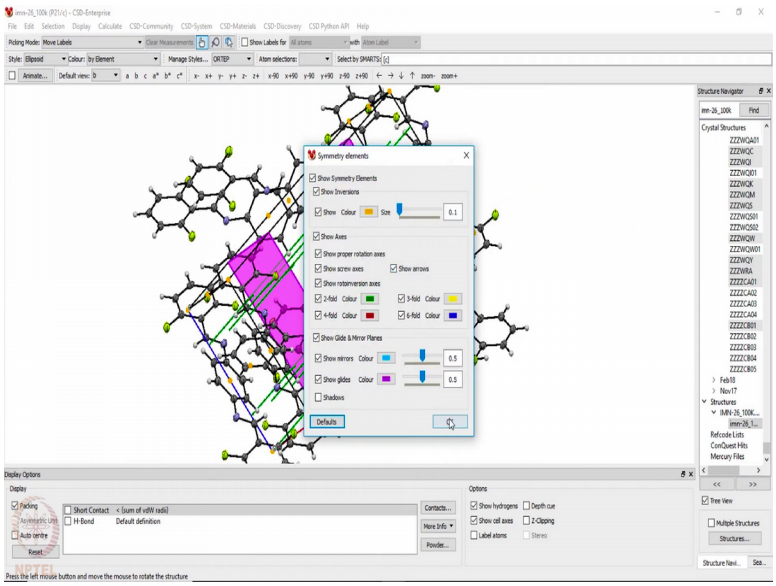

So, here what we can see is that the orange dots that we are seeing here are the inversion centers. So, in case of p 2 1 by c as we have learnt in our class that if you consider the origin at 000, which is the centre of inversion then with respect to that origin the screw axis which is shown here, this green lines are screw axis. Those screw axis are one forth shifted along c, if you look at that from oc, the origin is here the screw axis which is

green line is one forth shifted along c and the mirror plane that is the p 21 by c that light which is shown as purple is one forth shifted along ob.

So, if you remember the space group diagram of p 21 by c, then it is like clear here that the origin is not coinciding with the screw axis or is not coinciding with the light plane; rather both screw axis and light plane are one forth shifted with each other.

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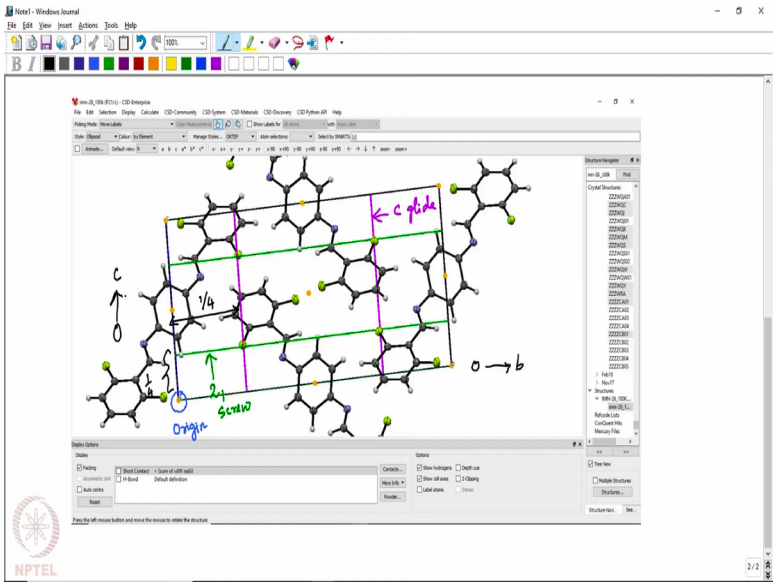

So, this is just the screenshot that I have pasted here. So, that I can write that where is the origin, which is this is the origin, these green once are 2 1 screw and the purple indicates the c glide. Note that if 2 1 screw is one forth shifted along oc and the mirror plane is one forth shifted along ob. So, this is what we learned, when we were trying to draw the space group backgrounds for various space groups in 2 dimension.

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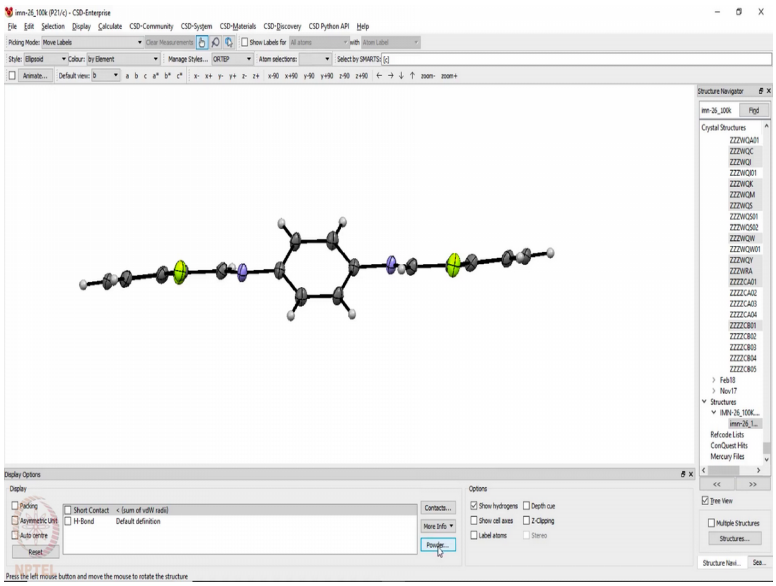

So, now this is the (Refer Time: 21:42) here the structure that we have solved from a single crystal x ray diffraction data. What else we can do with it, see a single crystal is grown from a starting bulk material that was a polycrystalline powder to start with what we have done is that, we have taken that powder dissolved it in a particular solvent and then tried to evaporate this out and slowly at about 4 degree centigrade in a refrigerator or at minus 20 degree centigrade in a refrigerant.

In this process, the solute solvent interactions are different based on what the solvent is and what the solute is. So, what may happen is from a given bulk sample of a particular crystal structure of a particular crystal system on dissolving and re crystallizing, it may give you a completely different three dimensional packing. If this new packing may or may not contain a solvent and that structure is what we have determined using single crystal x ray diffraction method.

One can ask you, how do you know that this structure that you have determined from a single crystal is the same as that of powder X-ray diffraction rate. The answer should be given by doing a simulation of powder X-ray diffraction data from the single crystal data. So, that is done again using this very smart software called mercury.

One can use mercury to simulate the powder X-ray diffraction pattern manipulate the simulated pattern in terms of FWHM full width at half maximum you can change the

wavelength. See the thing is we have, we have done the X-ray diffraction single crystal X-ray diffraction experiment using molybdenum radiations.

So, this is the data which we have got from molybdenum radiation, but then you might have recorded the powder pattern of this particular sample using copper radiation. So, if you want to compare these 2 data sets then the powder pattern that I am going to simulate from the single crystal structure I should simulate it for copper wavelength normally. So, here at the bottom if you see at this point, we have option called simulation of powder pattern.

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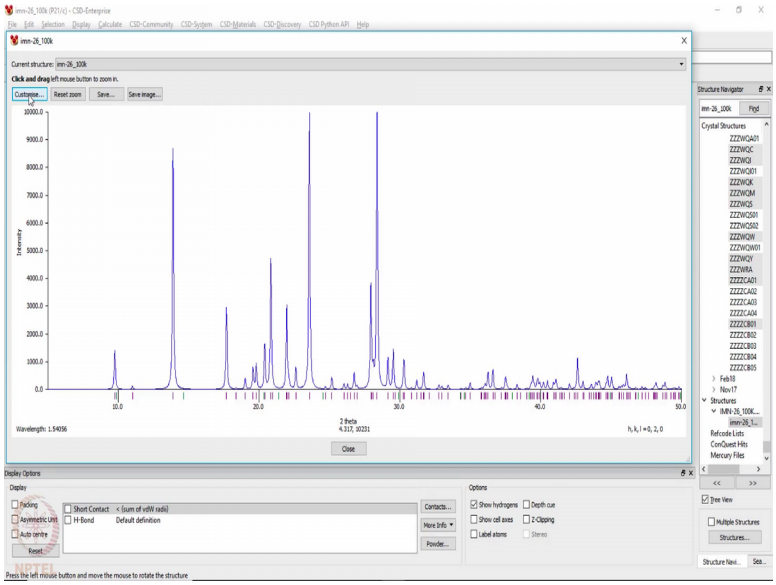

With a single click it generates, it gives you a simulated powder pattern. You see the simulated pattern the peaks are very very sharp. In your observed pattern these peaks may not be so sharp.

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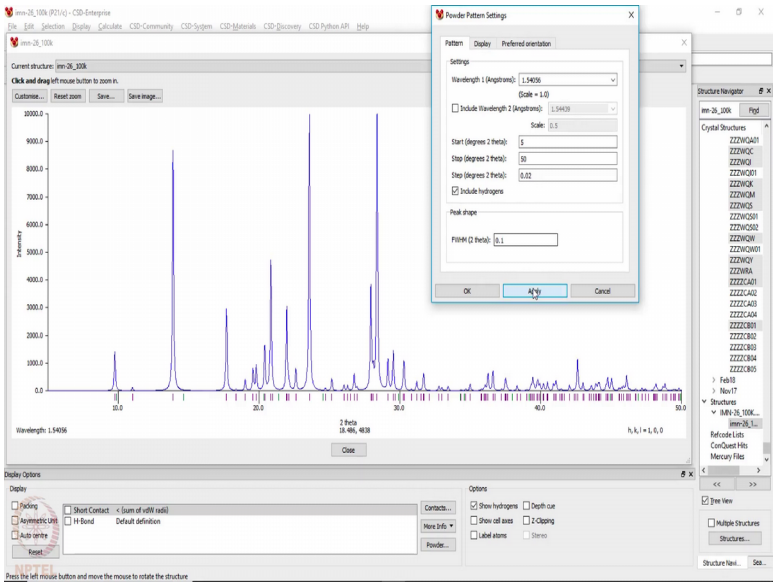

To be able to a correctly compare or accurately compare, you can go and customize, you can increase the FWHM to about 0.25, which is a generally case for routine data collections. And see here this is determined using the copper k alpha radiation.

One can change this So, let us first do it with copper and you can see by changing the FWHM from 0.1 which has the peaks very sharp, I change it to 0.3 the peaks are becoming bit broader which looks more like the data that is generally collected using a powder X ray diffractometer.

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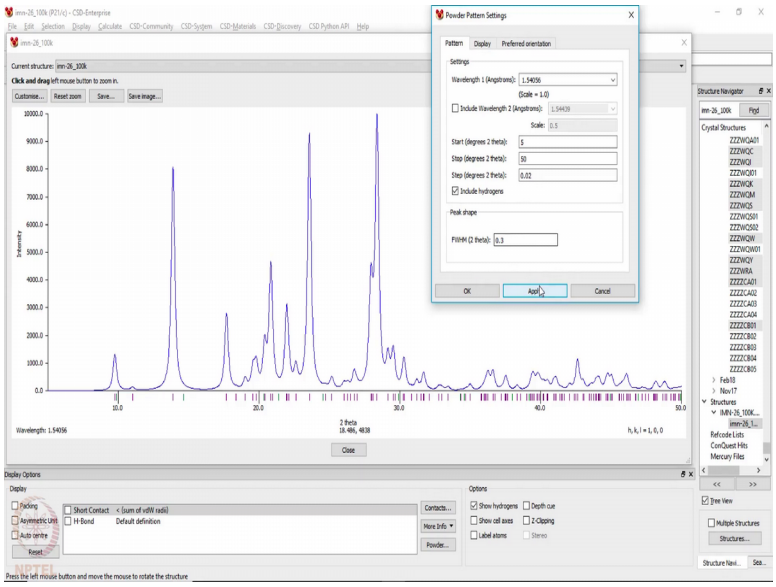

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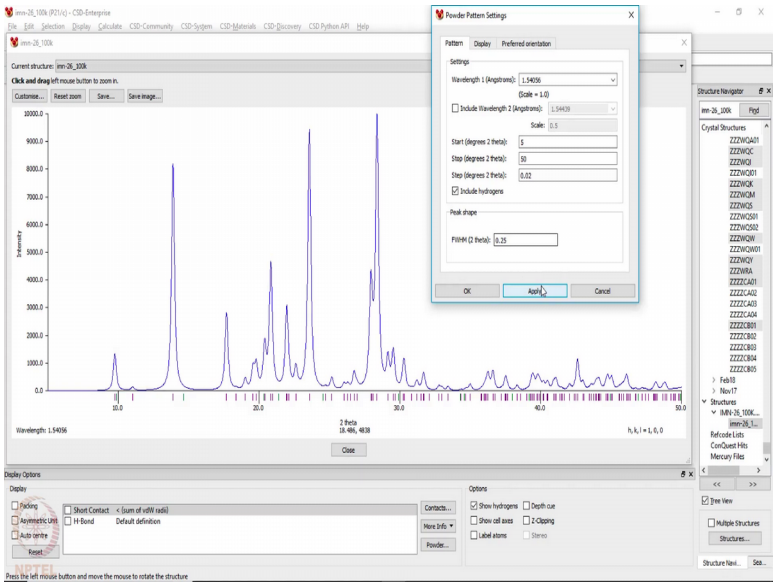

So, a an (Refer Time: 25:29) fw between 0.25 and 0.3 is something what one should use and then simulate the powder pattern. You see here this powder pattern is spread from about 10 degree into theta, to about 45 degree into theta and beyond 50 45 the peaks are very small.

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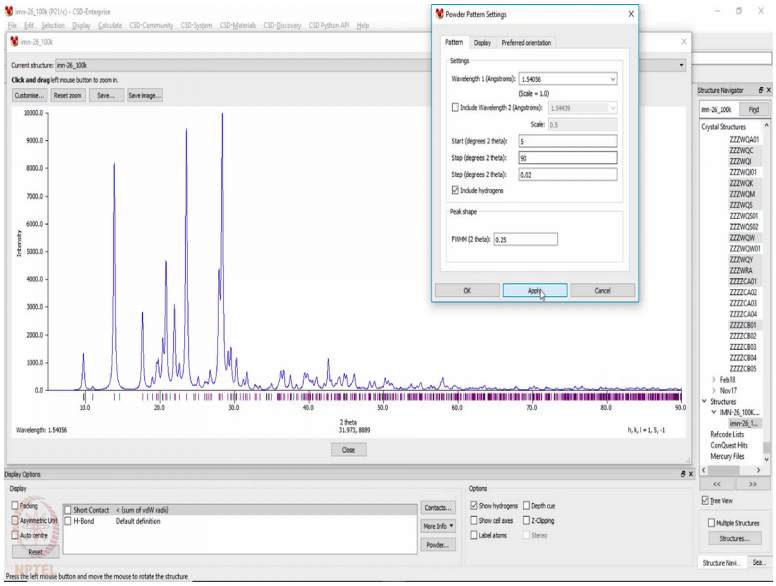

You can change that stop angle to maybe 90 degree and if you would say apply what we say is, see is beyond 60 degree there are nothing much that is diffracting might that point.

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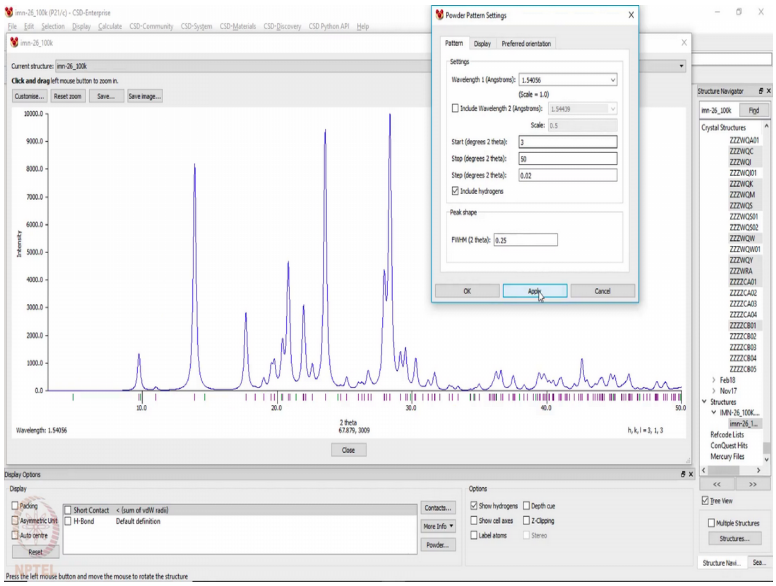

So, generally we simulate up to 50 degree into theta and generally from 30 degree to theta as well. And we see here there is no peak below 10 degree to theta.

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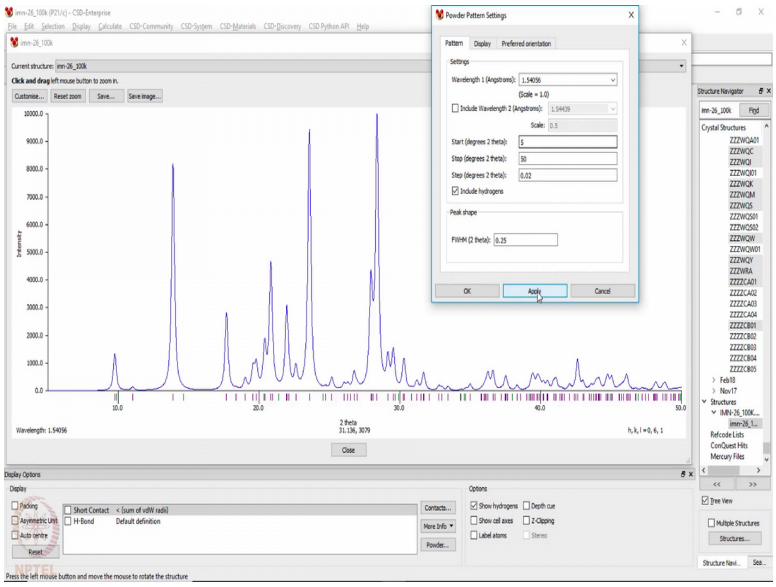

So, we can chop it at even 5 degree does not make any harm.

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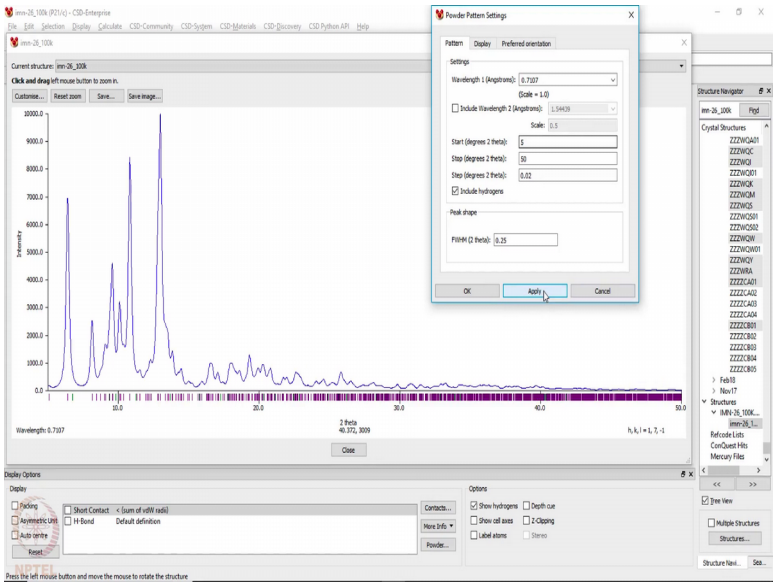

So, now if I change this wavelength to the molybdenum wavelength, which is 0.7109 angstrom or 7.07 angstrom and apply you see the entire pattern which was spread over a large 2 theta value is now squeezed, most of the peaks have merged and it has become more featureless.

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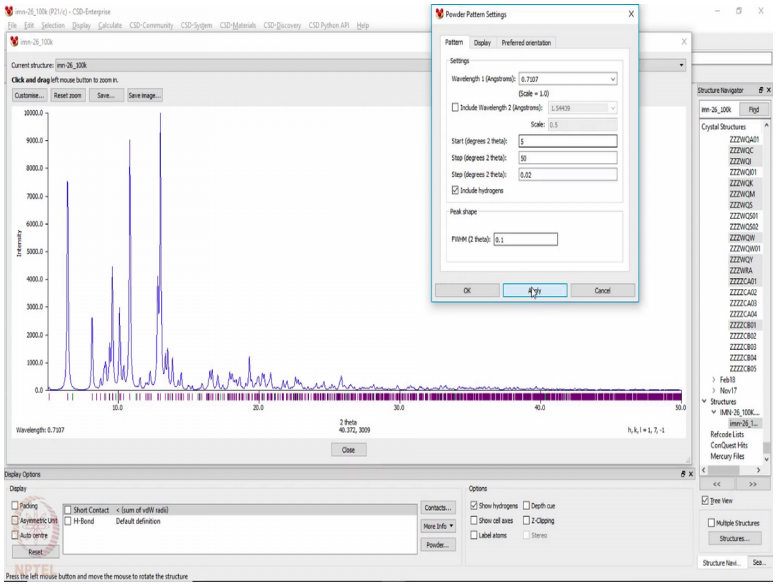

Even if I make it FWHM 1 the peaks are very very close and they are sort of merged. So, that is why we do not record any powder X ray data using molybdenum.

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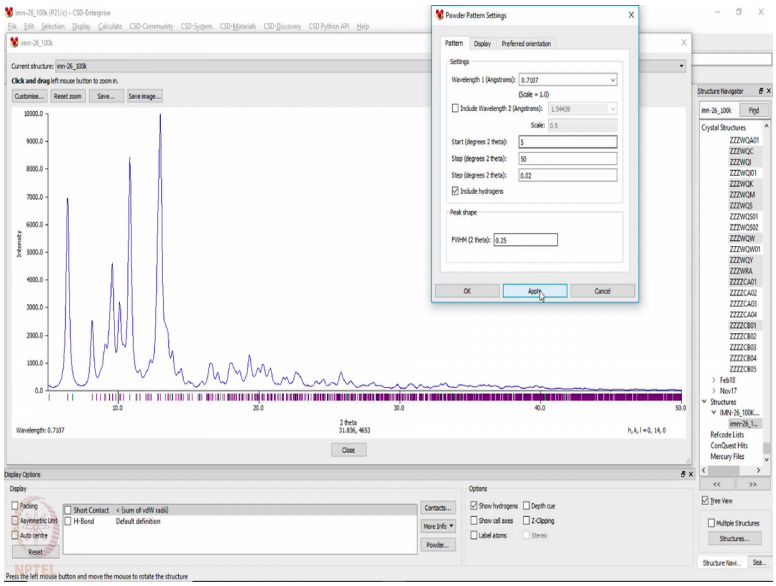

So, by default you will have the FWHM about 0.25 degree into theta and we will get a more featureless or rather merged powder X-ray diffraction data using molybdenum radiation.

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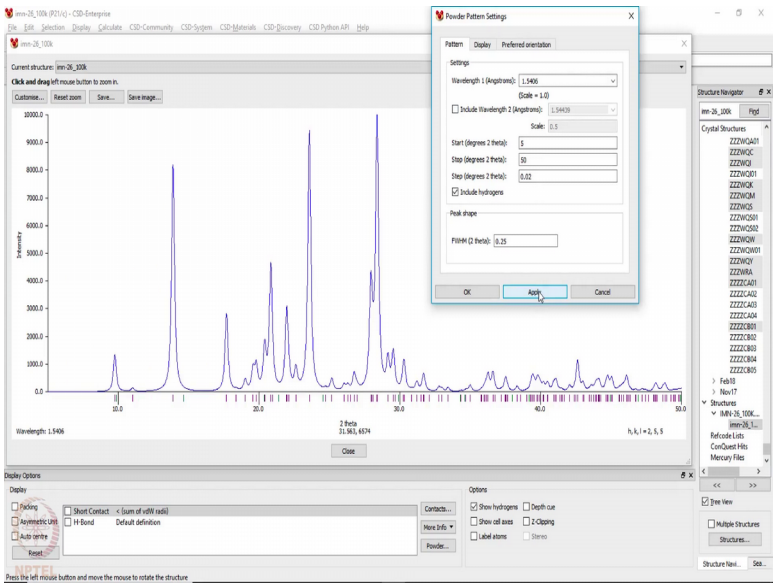

But the same if we use copper 1.5406 angstrom wavelength and then we apply it you see that the peaks are well spread, they are not merged and with the same FWHM there are several peaks which can be distinguished from the other. All these peaks completely disappeared or merged through a wavelength.

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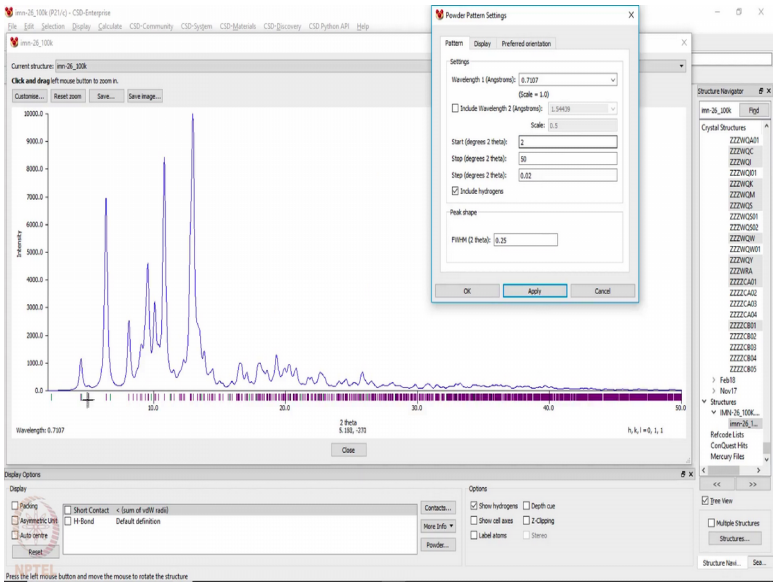

So, if I make it again 0.7107 and we start it from 2 degree then, you see that the peak which was at 10 is now appearing about 5, slightly below 5 So, this calculation we had done in one of our earlier classes where we try to understand, why should one use molybdenum copper for powder X-ray diffraction and molybdenum (Refer Time: 28:23) single crystal X-ray diffraction, here is a direct evidence that one should not use the molybdenum radiation for powder X-ray diffraction and while simulating we also should simulate using the powder X-ray using the molybdenum radiation for powder X-ray diffraction

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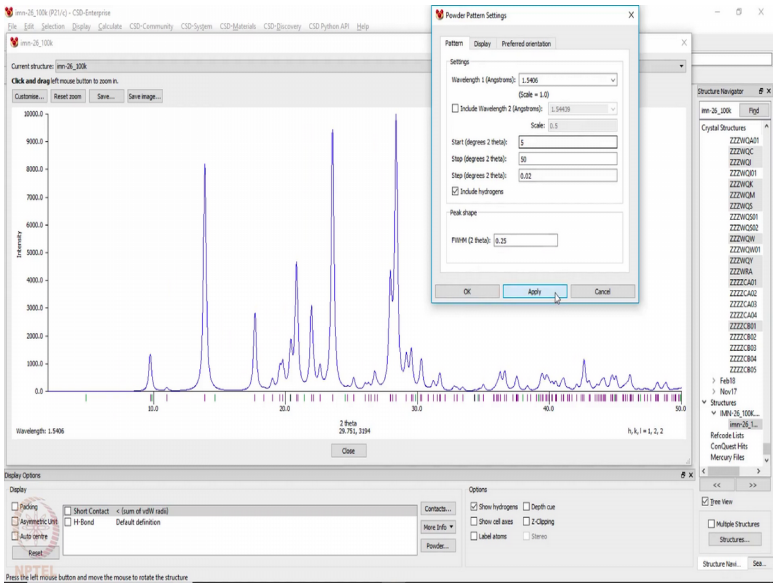

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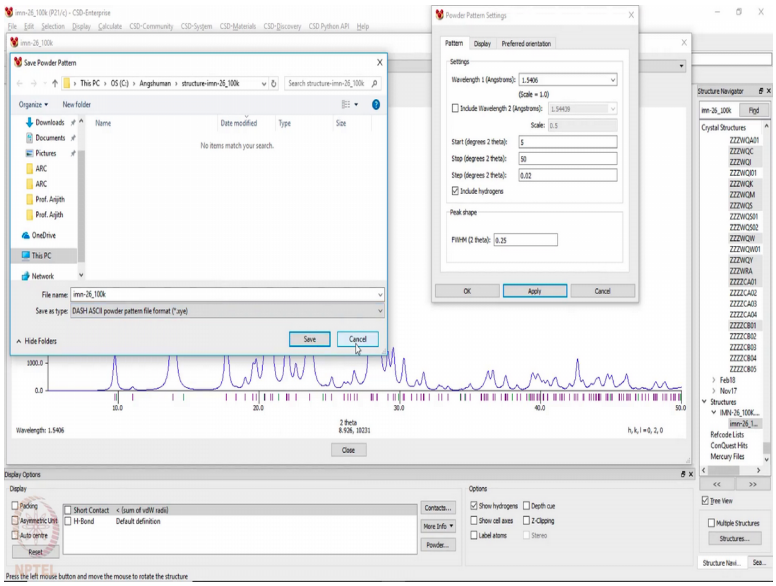

So, then this can be saved. In multiple formats one can save it as the xyz format, if one can save it as a raw format and then converted to a suitable other format, so that this can be plotted using different other packages, which also we should discuss in one of those classes will I will show you when we talk about powder X-ray diffraction handling the powder data and so on.

One can simply save the image as bmp jpeg or whatever for any publication purpose for this. So, today with this we would like to conclude the section of discussion on structure solution and refinement using Olex 2 and how one can determine the packing features parameters using mercury.

In the next lecture we will continue to discuss about the disorder in structures, how to fix the disorder how to treat the disorder structures and do the refinement for those disordered structures.