Chemical Crystallography
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Lecture - 42
Disorder Treatment using Olex 2

Welcome back to the course of Crystallography. In the previous lecture, we were discussing about the disordered structures, and we had discussed about how to treat a disorder structure using part comments. So, now, we will see how we really do it using one particular data.

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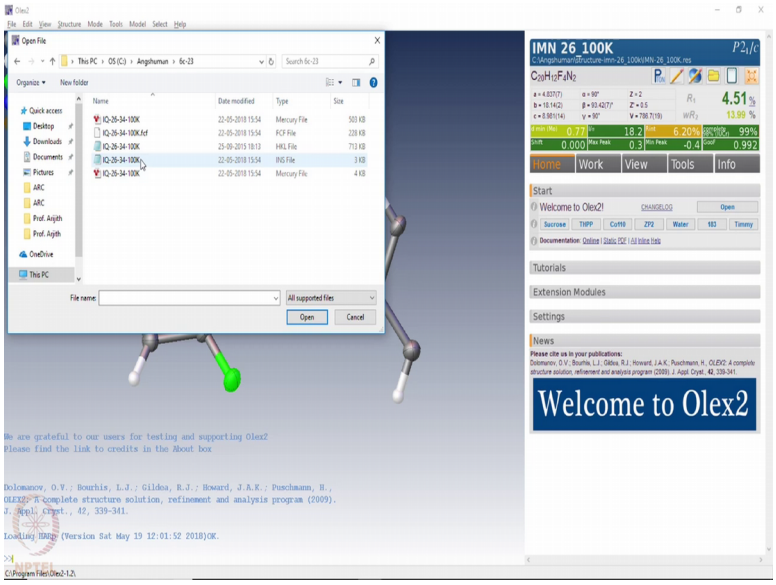

In this particular data you will see a molecule which I am going to solve from scratch, and then I will show you how the disorder is visible in that particular molecule.

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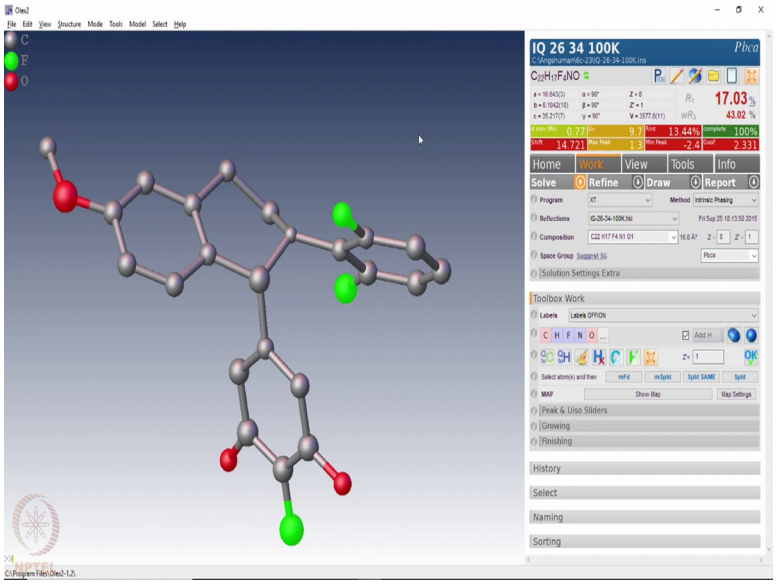

This is a model structure, but we can redo the structure solution part for all of you. So, I use the XT to solve the structure you can see it is orthodromic with space group p b c a with cell dimensions 16, 6, 35 and volume 3577.

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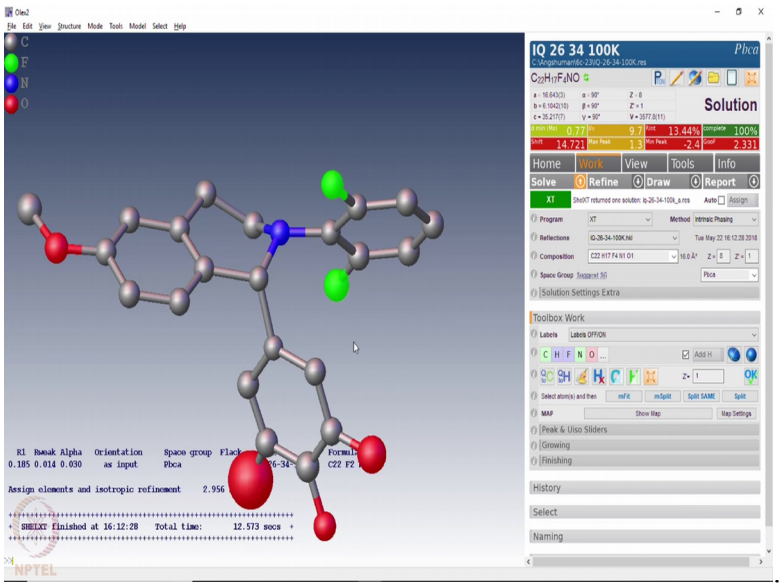

So, I am trying to solve it using the direct methods. It will quickly give you a structure which is the starting model for this solution, where you will see that the molecule is coming with one very large ellipsoid; another small ellipsoid and a very small ellipsoid here. And with my chemical knowledge because we know what molecule we made. We

now know that there are two fluorine atoms, one here and one there; only these two should have been the fluorine atoms. But here also one large density is appearing and the software is thinking that it may be oxygen, but now since we know that there is no oxygen here. What can happen is this particular fluorine because of a rotation about this particular CC bond here, the when you rotate a CC bond there by 180 degree, this fluorine can appear here. So, we write that also as fluorine and carry out this structure refinement as usual.

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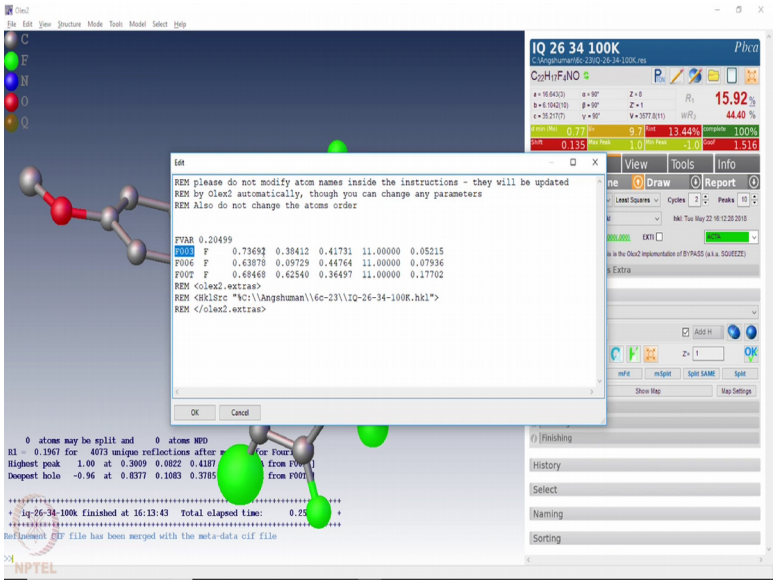

And try to reach a convergence on that. You see here what is happening is the thermal parameter of this fluorine and that fluorine are different compared to that. So, if we try to see the isotropic thermal parameters, this fluorine 3 has 0.05, fluorine 6 has 0.79 and fluorine T has this you see these are not numbered properly. So, better be number them appropriately. And if we put the labels on, then we know which is what.

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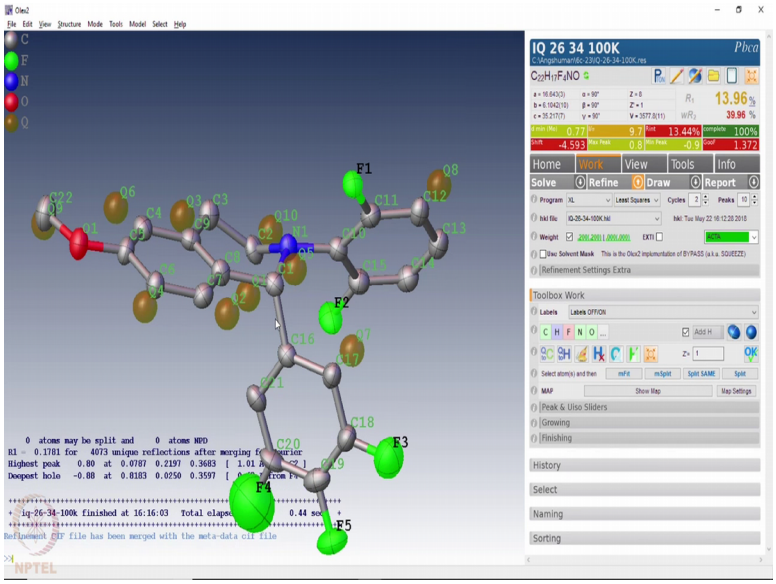

So, first thing first we should name the atoms. And refine it once again until it is easy if we try to see this thermal parameters which is higher, which is lower. So, the thermal parameter of 4 is much higher; 5 is probably the correct; 6 sorry 3 is also high this indicates that there is some disorder there. If we compare with other two fluorines on the other ring, we can see that the other two fluorines F 1 and F 2 have 0 3 and 0 4; the third fluorine on the second ring has 0 5 which is sort of ok. And 4 and 5 have higher thermal parameters. So, at the moment, we do nothing; at the moment we just try to continue the refinement as usual we do it with an isotropic refinement. And we recognise that these fluorines are disordered because they are now rotated by 180 degree.

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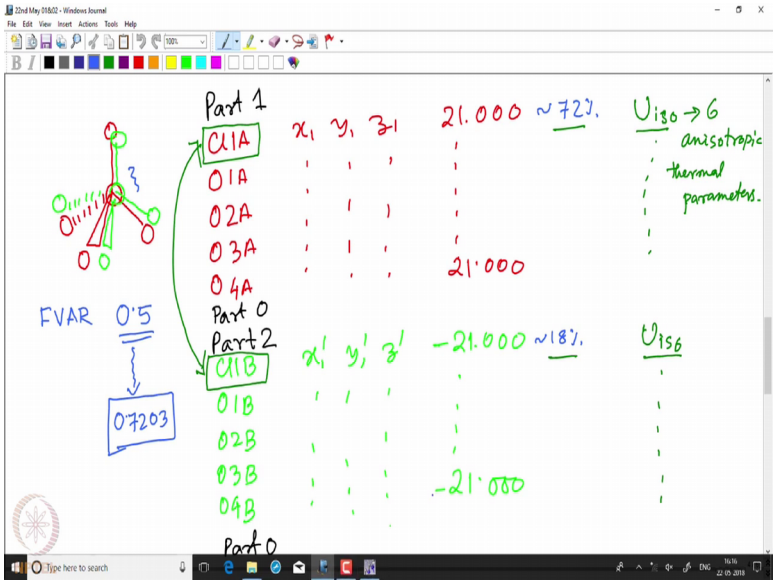

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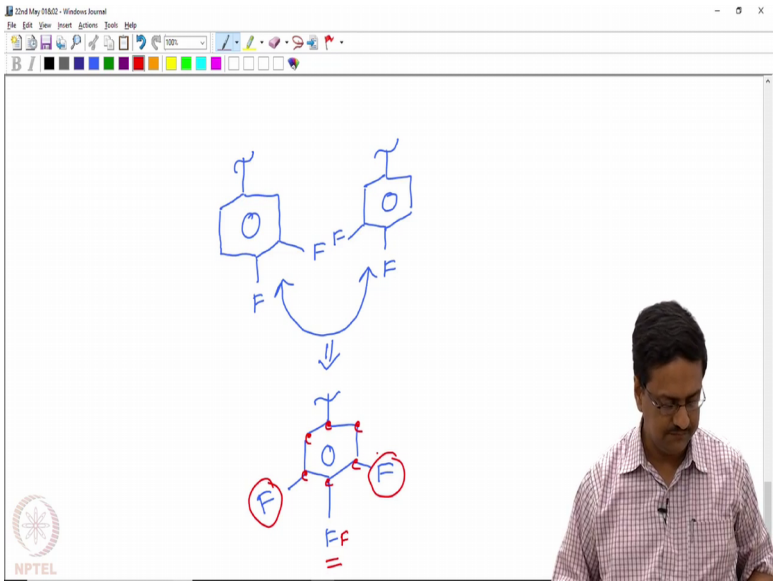

So, what is happening is in this particular case we have a phenyl ring with 2 fluorines at these two positions with respect to the attachment that is position 3 and 4. And this ring being rotated by 180 degree in two different locations, the fluorines are appearing on either side. The asymmetry unit represents and overall average of these two structures are these two confirmations like this. So, what we need to now understand that there are 6 carbon atoms in the ring which are falling at same place; and 1 fluorine atom which is falling at same place on rotation. So, these carbon atoms should be splitted, but then converted to e x y z and e a d p, so that they fall on that at the same place along with the

fluorine and the other two fluorines will have two independent positions with different occupancies.

So, what we need to do is we need to split the atoms which are this at two different sites. So, we will split these carbons 16, 17, 18, 19, 20, 21 and fluorine as set of 2, and then select all these fragments along with the fluorines and rewrite the atom table.

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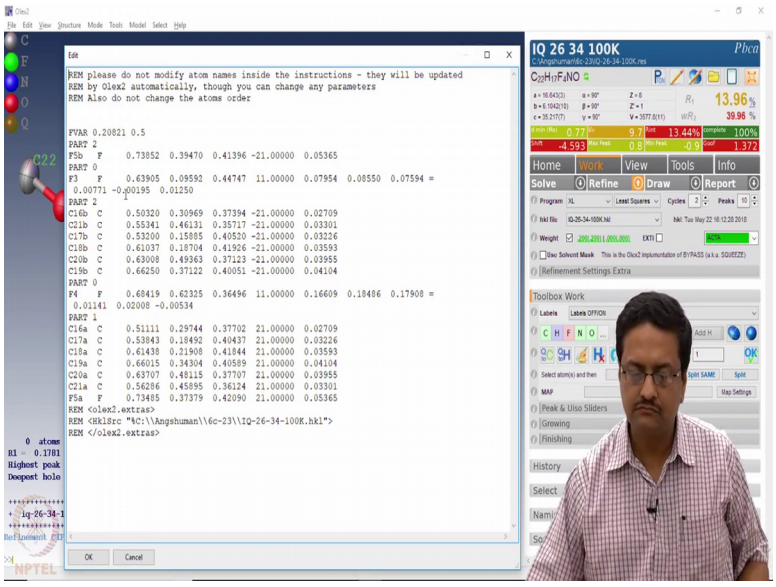

So, this is part one which has 16 a to 21a F 1a. And along with F 1 a we should have the atom F 3 as well which is this one. So, you bring that F 3 here and write this a as 21 and make it isotropic. Similarly, this atom we make it bring it here is already isotropic F 4 goes to the other part, and we make it isotropic and make it minus 21. And here it is FVAR 0.5, FVAR variable this 0.5, which means these two fractions are 50-50 populated. So, we should conclude this with part 0 and this also with part 0. Let us define once, so now, we can see two separate parts.

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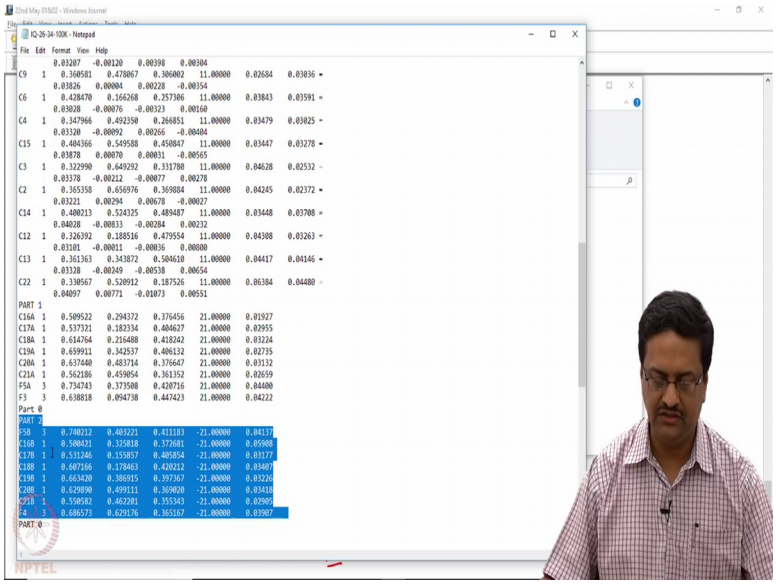

We try to modify this atom table. So, now, here we have arrange the two parts in the less file as part 1 and part 2. And you can see now all of them have isotropic thermal parameters and 16 AB 16 BC 16B, 17B to 21B is here and 16A to 21A is there. F 3 is one component which is only present in part 1. F 4 is a component which is only present in part 2, whereas all others are present in their same location

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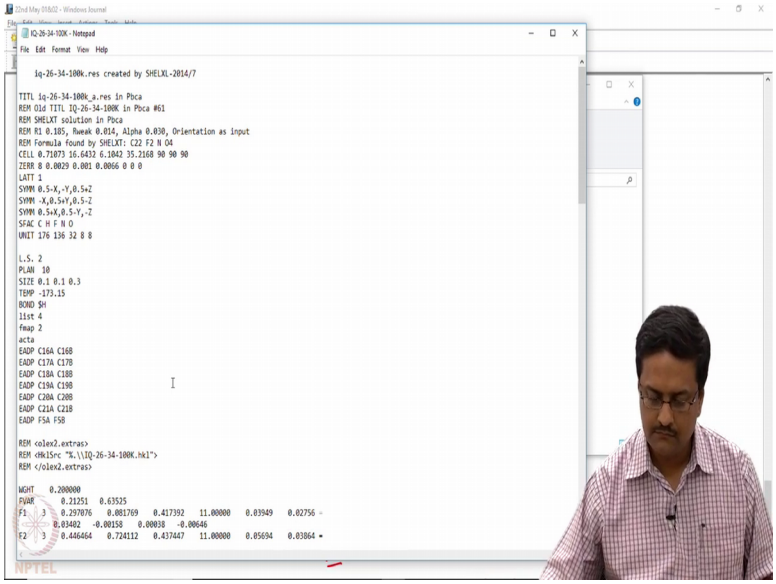

So, to incorporate that what we need here in this instructions that we should have a certain number of EADP and E XYZ comments. So, we should also right EADP C 16A is equal to C 16B. EADP C17A is equal to C17B, C18A equal to C 18B.

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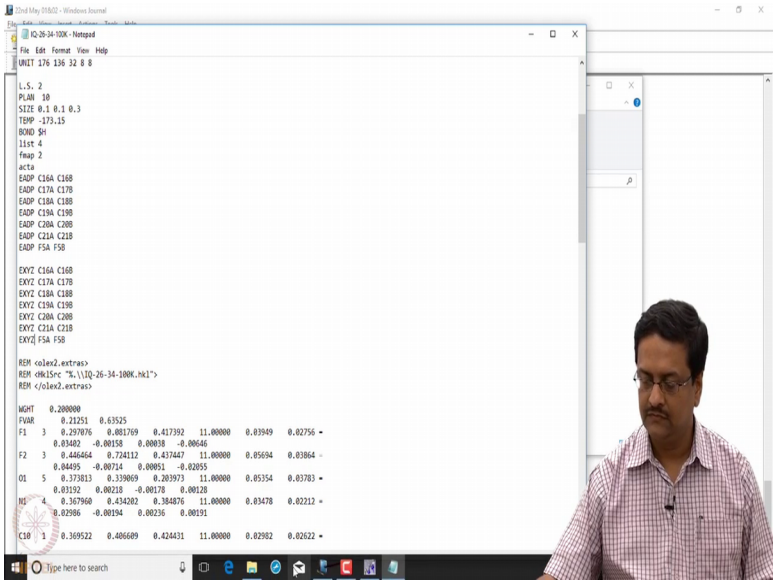

And simultaneously we should write the corresponding E XYZ for all of these set of atoms, group of atoms. So, copy and paste it here and change the ADP to XYZ and save this arias file and now we go back to our structure solution.

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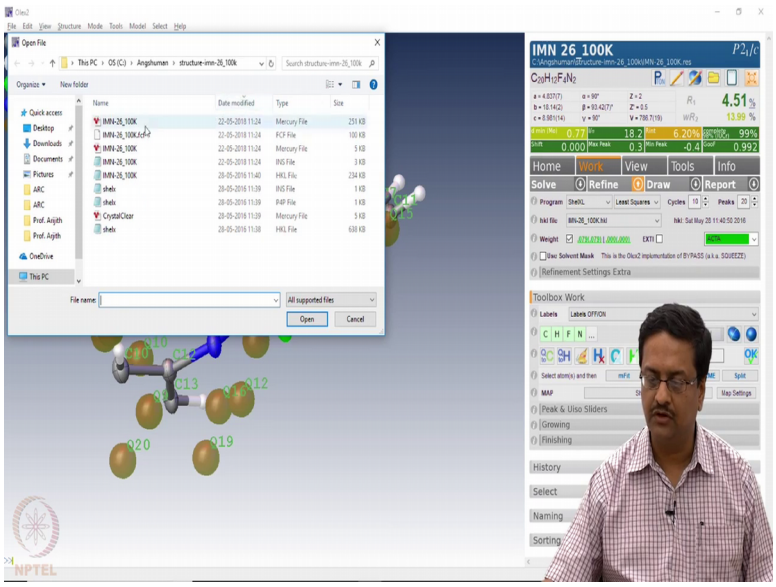

And select the arias file that we have just now modified. And then refine it a couple of times. What do we see now is that the atoms which are having near the EADP and EXYZ comments are having those symbols embedded in those atoms. And the atoms which are refine general they are not having any information of EADP or EXYZ. And at the moment these are all in an isotropic format. The top part of the molecule and the bottom part of the molecule has only isotropic thermal parameters.

So, to make everything anisotropic then we can click on the anisotropic option. So, now, it is defined anisotropically you can see the ones which were initially spheres has now become ellipsoids. The R factored has slightly fallen and now we should do this refinement a few cycle of tens each till it gets converged and the shift is coming down to green. If it is not coming, do not worry we just add hydrogens because that is not done here.

So, until and unless we add hydrogens, the structure is not complete. So, now, when we added hydrogens and we try to refine it a few more cycles you can see that the shift is coming close to 0. And R factor has come down to about 9 percent which is showing here. Now, look at the atom you can look at the part of the molecule here which is now disorder treated. We have part one which looks like that 0 and 2 which looks like this. So, all the parts if you show it looks like that which means this particular fluorine is on right hand side and has occupancy of 64 percent and this has occupancy of about 35 percent.

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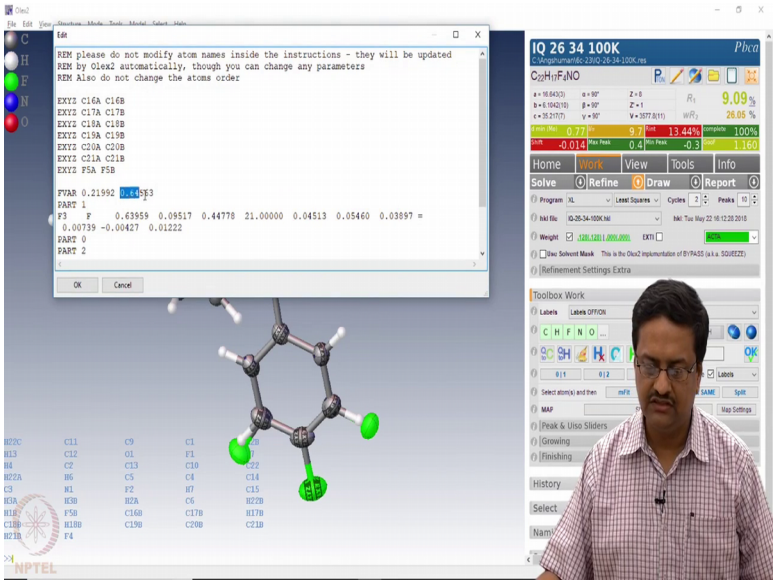

If we just take those two atoms and try to see what we see is 0.64. So, 0.64 is for class 21 which is F 3; and the other one is minus 21, so that is 1 minus 0.64 is about 0.36. This is not reducing. So, we may try to see the bad reflections. Here we do not see much of bad reflections. So, we cannot do much here. And we should leave it with it and try to complete the refinement if at all to a very small shift.

So, this is how one can do a disorder treatment using the EADP and EXYZ comments. See this is how the EADPs are written, this is how the EXYZs are written. And then we have two parts which are disordered.

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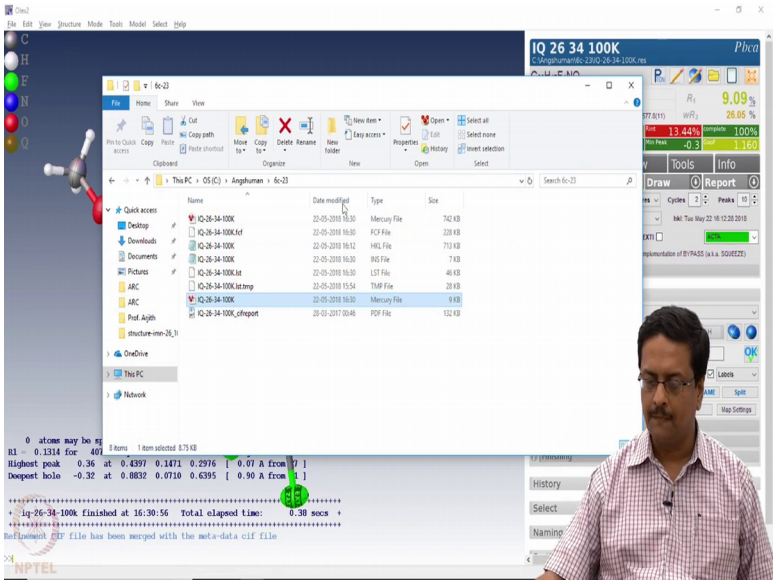

So, now, if I tried to open the res file which now will have the disordered sections.

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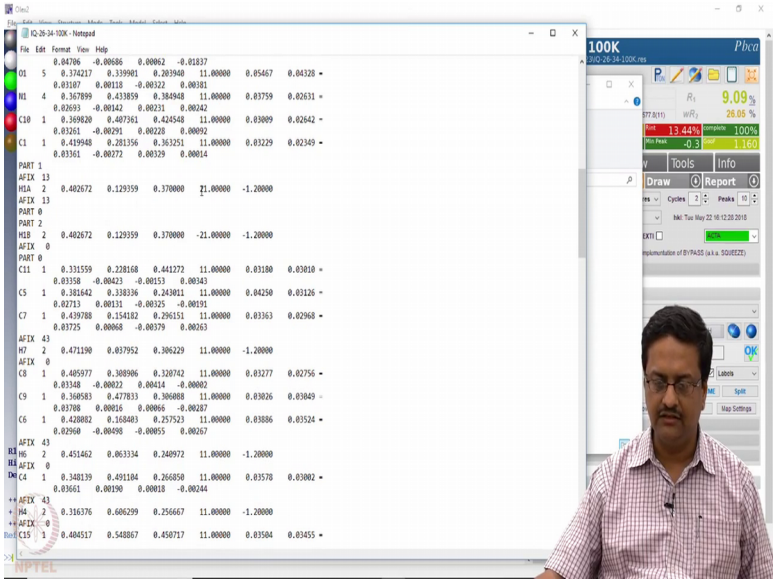

Again got segregated, but now are with the corresponding hydrogens.

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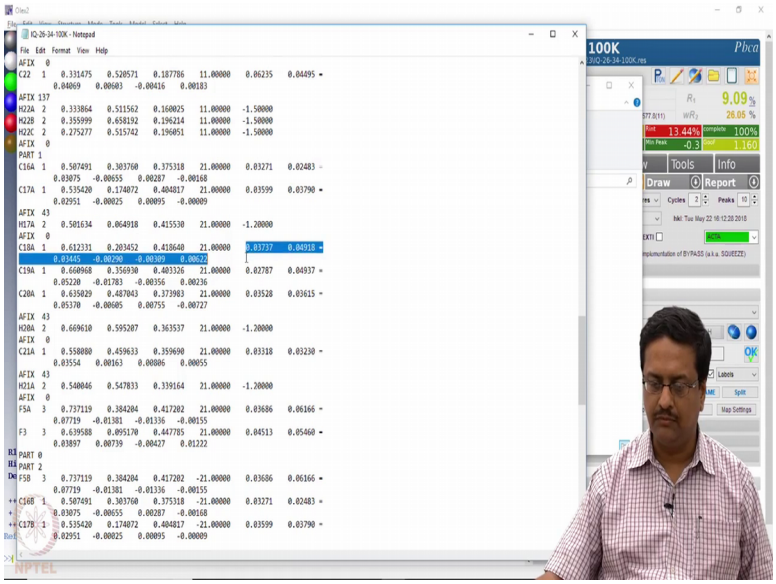

And you can see this 21 and minus 21, they have the anisotropic thermal parameters also associated with it and this structure is complete.

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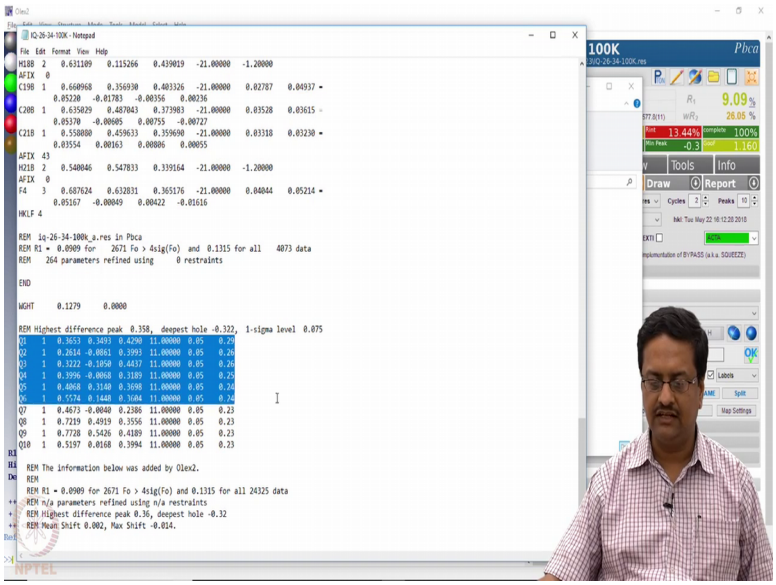

The residual electron dense it is that are coming here are extremely small, these are all very small values for a slight atom structure. And hence we do not need to do anything further this indicates the structure is fully solved and refines the well and we have the all factor of about 9 percent.

So, with this we conclude this section of our discussion on structure solution and refinement using a standard data using different crystals data sets which we have learned now. We have done data analysis using the Rigaku and Bruker software, those who are users of these packages if you have any doubt or query you can write back to me, I can help you out in solving those structures. And if you have any problem in using Olex 2 or Shell x or any such things you are free to write to me, we can discuss all these over emails.

So, with this we conclude this section of our discussion, I mean the next lecture we will now move to another part where we would discuss about the Cambridge structural database which is very useful tool for all of us in doing this search on X-ray crystallography data which we is already reported in literature, how to do the databases, how to do the analysis using database these are all parts of our day to day life due in extra crystallography laboratory. So, those who are interested in joining X-ray diffraction laboratory in future will, they should have a knowledge of usage of Cambridge structural database.