Chemical Crystallograhpy

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Lecture – 49
Phase Problem

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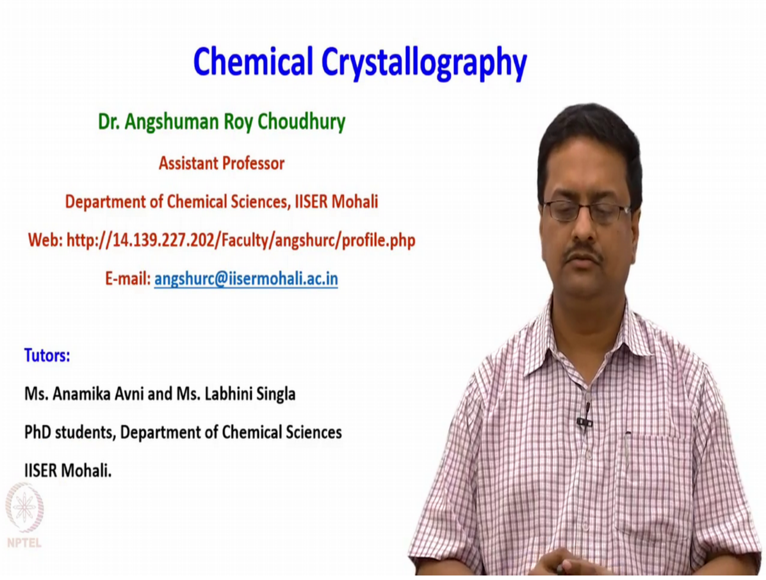

Welcome back to this course of Chemical Crystallography. We have ns learnt about the ns data collection and data reduction methodologies in previous couple of lectures and today we will start ns trying to understand how one can solve structures using different methods. So, what we have done till now is we have learnt how to do a data collection.

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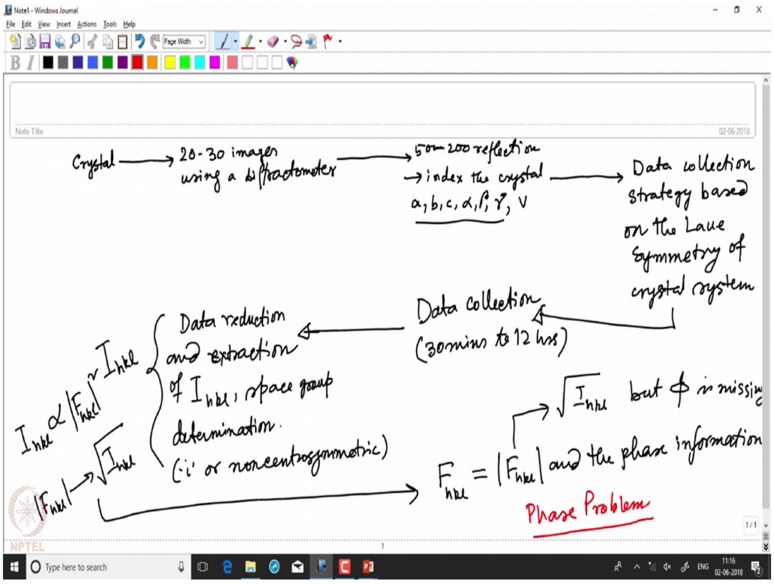

So, we should start with the crystal; we collect about 20 to 30 images using a diffractometer. And then utilize the reflections obtained in those 20 to 30 reflections maybe it will have 50 to 200 reflections we try to index the diffraction pattern. So, index the crystal and get the values for this hell dimensions that is a b c alpha beta gamma and eventually we can calculate the volume and then based on the values of alpha beta and gamma we can identify what crystal system and what Brava lattice it belongs to.

So, then we do a data collection strategy based on the lave symmetry of the lattice or of the crystal system. So, then we collected data which might take anything between 30 minutes to few hours maybe went up to 12 hours; depending on what kind of crystal it is how much is the volume what is its diffraction quality, how much exposure time you are giving and so on. And how much of data that you need to collect because as we know for triclinic we need to collect much more amount of data compared to the orthorhombic or cubic systems.

So, after this data collection in previous few lectures, we have learnt how to do a data reduction. And extraction of the I h k l from the absorbed data. And also it completes the data reduction with the space probe determination as well. So, when we have determined a space group we must know we then identify whether it is centrosymmetric or non centrosymmetric crystal structure.

So, now what we have in this data is just the values of I h k l for all the reflections that we have collected we just have the intensity and as we know this intensity I h k l is proportional to the square of amplitude of the structure factor. So, this intensity can be converted to the structure factor amplitude, that is the F H k l by taking a square root of I h k l, but in that process what is missing is the information, which is there in F the F H k l is a combination of mod of F H k l that is the amplitude of the structure factor and the phase information.

So, the structure factor F H k l has two parts the amplitude and the phase the amplitude of structure factor comes from the square root of intensity, but information for phi the phase is missing. So, this problem that we now encounter is called the famous phase problem in crystallography. So, what we need is we need to determine these phases for each and every reflection to be able to correlate the structure factor with the electron density.

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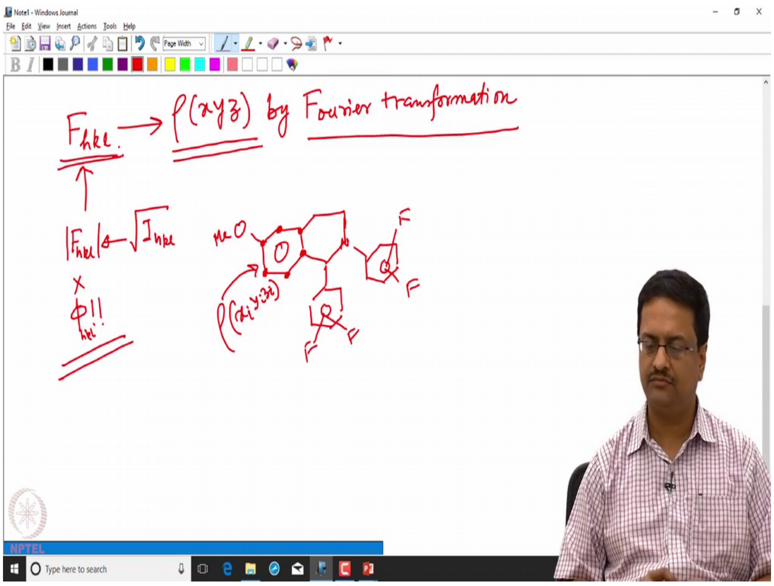

So, we know that F h k l is related to rho x y z by a Fourier transformation. So, to get this expression for F H k l what we have is just the mod of F H k l and which comes from the intensity and what we don't have is the information on phase phi h k l.

So, the structure solution problem has to work in a way to get the phases for each and every reflection that, we have measured and then only we will be able to do this Fourier transformation effectively to get the value of rho x y z which corresponds to the atom coordinates located at different locations of in the unit cell. And as a result we will be able to determine the coordinates opposed of this particular molecule which might have crystallized in a monoclinic unit cell, but we do not know the bond lengths, bond angles, torsion angles and all that.

You see this is a highly complicated molecule with lots of flexibilities and this molecule crystallizes in some space group and one wants to determine the cell dimension and then one wants to determine the its actual structure, which means we want to determine the rho x y z at every such atom locations. And to do that what we need is the expression for the structure factor F H k l which should have both the amplitude and the phase information together.

So, in the past there have been a large number of attempts, to solve this phase problem in different ways, the most efficient way of solving this phase problem on today's date is a set of methods.

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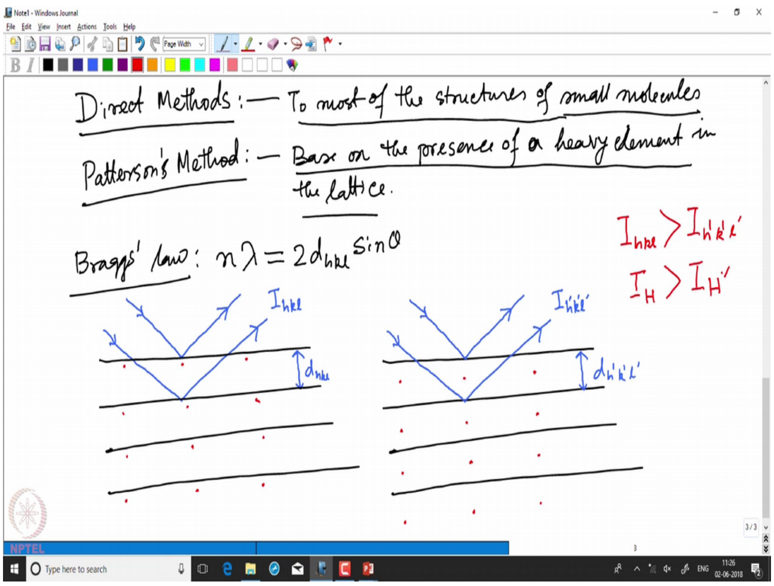

We called together as direct methods, which are combination of different individual methods which we will discuss one by one if you of them. And then these applies to most of the structures of small molecules. One may ask what are small molecules, these are all kinds of organic organometallic inorganic molecules of small size having a decent unit cell like a small unit cell up to about 1 lakh, 1 and a half lakh cubic angstrom volume for metal organic frameworks two compounds, which has volumes like a few 100 cubic angstrom like sodium chloride which has a volume of about 250 cubic angstroms.

So, these range of molecules fall in the class of small molecules and adequate and is the most useful method in determining their structures. The other method which was established much before direct method is the method of heavy atom. So, this method is named after the name of the scientist Patterson it is called Patterson's method which is based on the presence of and presence of a heavy element in the lattice.

So, we will discuss these two methods one after another in these coming few lectures and then we will be able to understand the structure solution that happens. So, quickly now on a computer as we have seen in one of those presentations in a lecture. So, what we know about the X ray diffraction from Braggs law we know that the constructive interference happens, when the diffracted intensity diffracted beam has a path difference same as the integral multiple of wavelength. So, when the path difference in the diffracted beam is integral multiple of the wavelength you get a diffraction.

So, now suppose if we have set of h k l planes as I am drawing and the atoms that we are trying to look at are placed very close to the plane that we are trying to probe with the X ray beam. So, in that case when we have the X ray diffraction to occur from such planes the incident beam and the diffracted beam art I am drawing them like this. So, the distance here if I write it as d h k l the intensity of these diffracted beams I write it as I h k l. There will be a situation where the atoms that we are trying to look at are significantly away from the concern planes the way I am drawing it is somewhere in between the planes are not exactly on the planes.

So, once that kind of situation happens with this particular set of h k l which I want to write as the d h prime k prime l prime where the intensities are also I h prime k prime l prime. So, there are two situations side by side in one case the atoms are very close to the plane of diffraction the plane of in contact, and in our case the atoms are far away from the planes in consideration and from both the planes the diffraction is occurring. So, what would happen what would we see is that the intensity of h k l that I h k l would be greater than I h prime k prime l prime because the atoms the scattering centers are far away from the plane of this particular different diffraction.

So, this I h k l can be represented as simply I h and the other one can be represented as I h prime. So, for two different reflections two different sets of planes these intensities will be largely different. So, our aim is to compare the diffracted intensities from different set of planes and try to find relationships between them. And we will try to see if we can get to know the phase of one such reflection whether can we get the phase of the other reflections of either another large intensity or another small intensity p.

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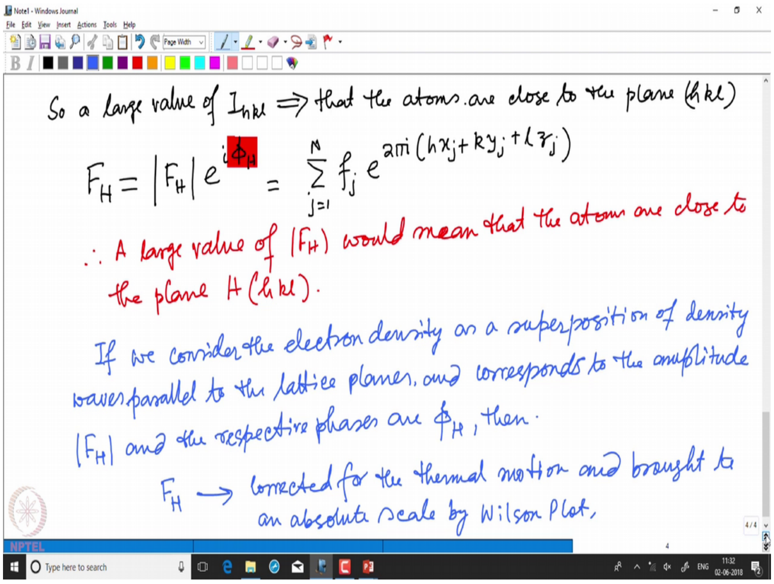

So, a large value of I h k l would mean that the atom are close to the plane h k l. So, in that case if we try to write what is the value of F H is equal to mod of F H e to the power i phi h this quantity phi is my phase associated with that particular reflection.

So, which can also be written as the sum over j equal to 1 to n f j suppose there are j different atoms at different places e to the power 2 pi i h x j plus k y j plus l z j. Therefore, a large value of mod F H would mean that the atoms are close to the plane H that is h k l. If we consider the electron density as a superposition of density waves parallel to the lattice planes and corresponds to the amplitude F H and the respective phases are phi H.

Then we can write the normalized structure factor F H, which is corrected for the thermal motion and brought to an absolute scale by the method of Wilson Plot.

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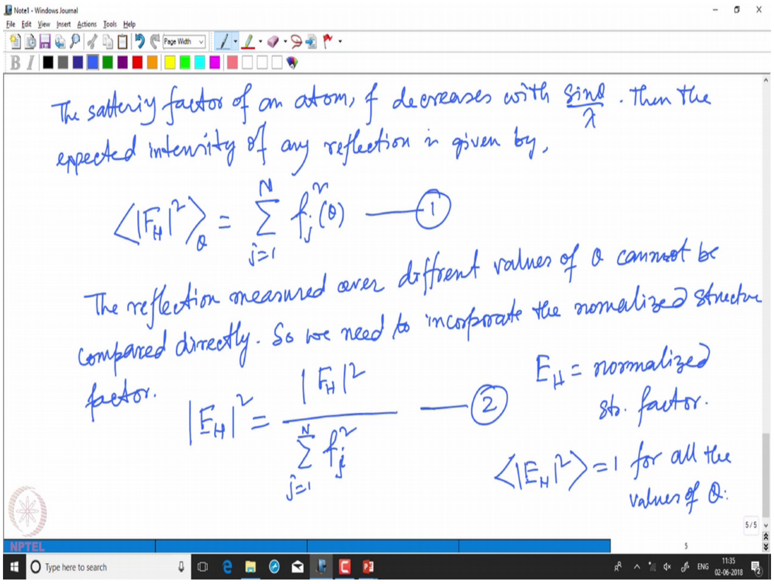

Then the scattering factor F of an atom the scattering factor of an atom if of an atom f decreases with sin theta by lambda. Then the expected intensity of any reflection is given by mod of F H square over the entire theta is equal to sum over j equal to 1 to N f j squared, which is a function of theta.

Now, the reflections measured over different values of theta cannot be compared directly. So, we need to incorporate the normalized structure factor as the E H square which is equal to mod of F H square by sum over j equal to 1 to N f i f j square where E H is the normalized structure factor.

So, now if you compare the equations 1 and 2 we can write that the expectation value for E H square is equal to one for all the values of theta it is independent of theta.

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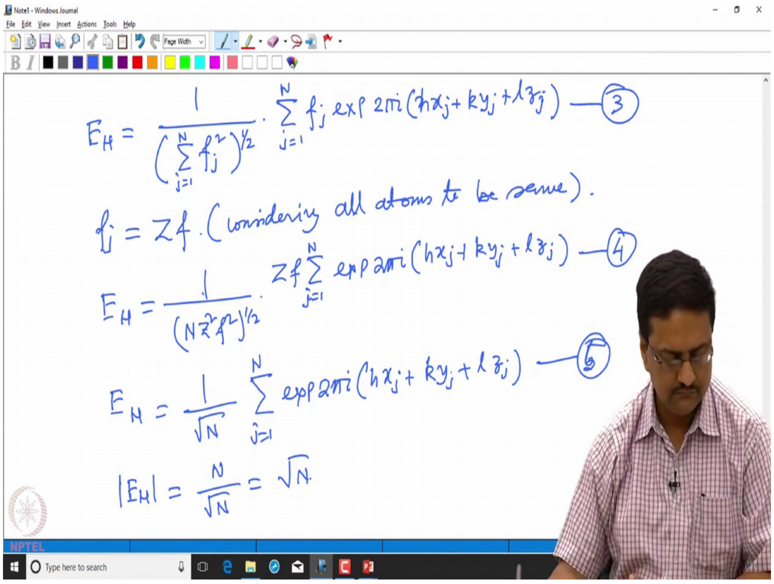

So, one can write E H as equal to 1 by sum over j equal to 1 to N f j square with a square root here into sum over j equal to 1 to N f j exponential 2 pi i h x j plus k y j plus l z j this equation number three. If we assume that this is a structure which contains only one type of atom then all the f js can be written as Z into f that is all atoms being same.

So, then in that case we can write E H equal to 1 by N Z square f square with a square root on top into z f some of us i j equal to 1 to N exponential to pi i h x j plus k y j plus l z j is my equation number four. And on simplification what we can write E H is equal to 1 by square root of N equal to into sum over j equal to 1 to N exponential 2 pi i h x j plus k y j plus l z j.

So, the maximum possible value for the E H is nothing, but it is equal to N by square root of N which means is equal to root N.

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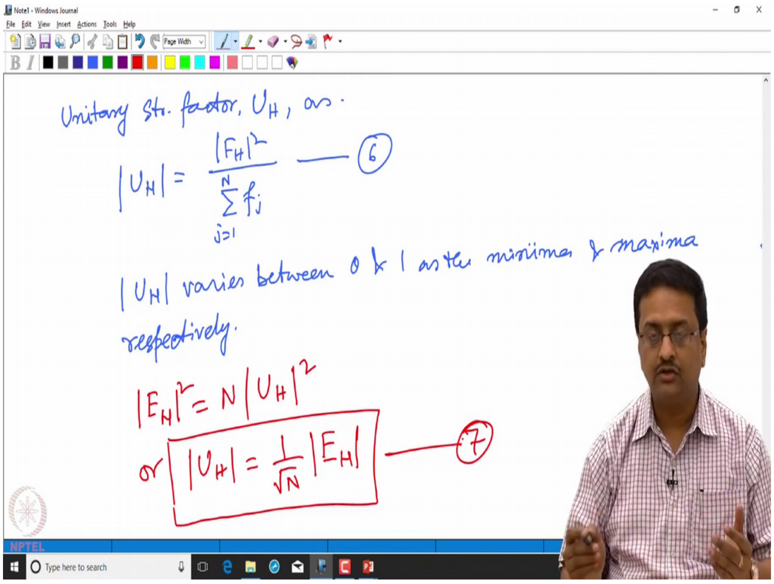

So, from using this expression we can write the expression for unitary structure factor that is U H as mod U H is equal to mod F H square divided by sum over j equal to 1 to N f j we write it as equation number 6. And this mod U H varies between 0 and 1 as the maxima and minimum or rather I should write where is as minima and maxima respectively.

So, combining these two expressions for unitary structure factor and the normalized structure factor we can write the E H square is nothing, but N into U H square or U H square is equal to 1 by square root of N sorry mod U H is equal to is E H. So, introduce this part of the lecture we have tried to understand how one can derive some expressions related to the structure factor and we can use normalized and unitary structure factors in future classes to see, how this can be utilized for to get the phases of unknown reflections.