Chemical Crystallography
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Lecture – 33
Structure Factor and Electron Density

Welcome back to the course of Chemical Crystallography. In the previous lecture we have learnt about the Friddle's law can be derived from the expression of structure factor using vector space diagram. So, from here we would like to continue, and we would like to now derive the expression for structure factor with electron density this is what is our motto for today's lecture.

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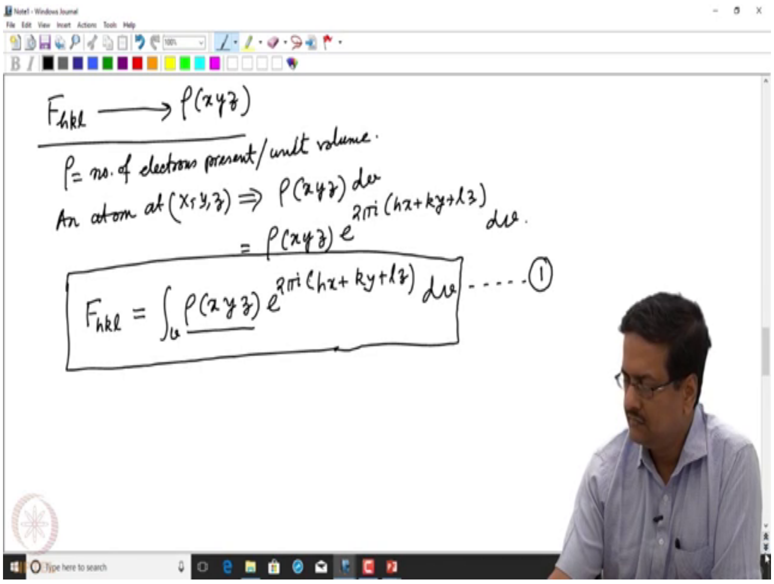

So, what we want to do is, we want to represent we have to derive an expression, which we will relate F h k l in terms of rho x y z, which means we want to establish the relationship between the structure factor with the atoms that are present at various positions in the unit cell.

Here we know the electron density rho is nothing but number of electrons present per unit volume. So, suppose we have an atom located at x y z, we have an atom at x y z. So, the electron density associated with that atom can be written as rho x y z, and if the volume element involved to accommodate that automatics y z is d v.

So, the electron density associated with that atom is rho x y z dv. So, in exponential form this density can be written as rho x y z e to the power 2 pi i hx plus ky plus l z dv. So now, we have a large number of such atoms located at various sites in the unit cell. So, when we want to add the contribution of all such atoms, and then relate it to the corresponding structure factor.

Then for scattering from all those electron density sites, that is all the sites located at various x y z. So, having the volume element dv, we can write the expression for such a factor as F h k l equal to sum over v rho x y z e to the power 2 pi i hx plus ky plus l z dv. Let us write this equation as equation number 1. We will need to refer to this equation in few challenge in next part of this lecture.

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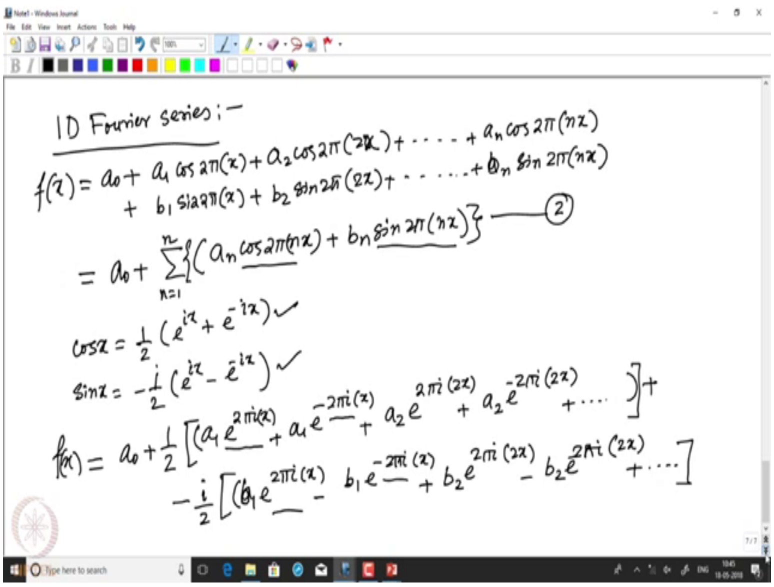

So, let us try to now understand what is 1D. Let us now try to understand, what is one dimensional Fourier series, because we will need these mathematical tools to understand the relationship between structure factor and electron density.

So, a 1 dimensional Fourier series can be written as fx equal to a 0 plus a 1 cos 2 pi x plus a 2 cos 2 pi 2 x plus the sin terms. So, this should go up to a n cos 2 pi n x, and then we add the corresponding sin terms, which are b 1 sin 2 pi x plus b 2 sin 2 pi 2 x plus up to bn sin 2 pi n x. It is in one dimension.

So, in a simplified manner, one can write it as a 0 plus sum over n equal to 1 to m, a n cos 2 pi n x plus b n sin 2 pi n x. So, we write this equation as equation number 2. So now, we know that cos x is equal to half e to the power ix plus e to the power minus ix, and sin x equal to minus i by 2 e to the power ix minus e to the power minus ix.

So now if we try to rewrite the expression for fx in terms of sin and cos terms, because we it is already written in cos and sin terms and when we will represent a then using these exponential factors. So, fx will become equal to a 0 plus half is taken out, it is equal to a 1 e to the power 2 by i x plus a 1 e to the power minus 2 pi i x.

Plus, a 2 e to the power 2 pi i 2 x plus a 2 e to the power 2 pi i minus 2 x sin, minus 2 pi e to the power to 2 pi i 2 x and so on, these corresponds to the a terms plus the b terms which will have a minus i by 2 b 1 e to the power 2 pi i x plus b 1 sin minus b 1 e to the power minus 2 pi i x plus b 2 a to the power 2 pi i 2 x minus b 2 e to the power 2 minus e to the power minus 2 pi i 2 x and so on up to the n.

So, when we try to do the sum of these. We can see that there are common factors which can be taken out and rewritten. So, what we try to take out is the terms with e to the power 2 ix at 1 place, e to the power minus 2 ix at another place and so on.

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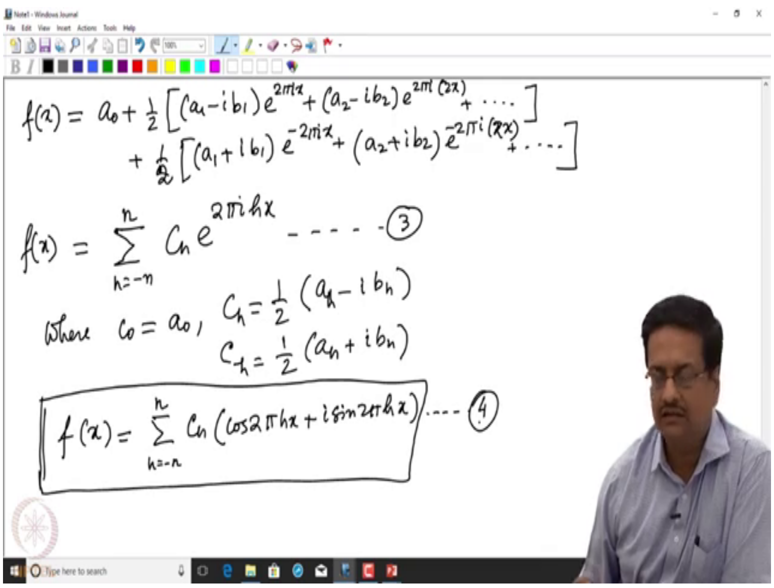

So, in the next page we will rewrite this expression for fx, we will rewrite this expression for fx equal to a 0 plus half a 1 minus b 1, a 1 minus i b 1 e to the power 2 pi x, plus a 2 minus ib 2 e to the power 2 pi i 2 2 x plus so on, plus half a 1 plus ib 1 e to the power minus 2 pi i x plus a 2 plus ib 2 e to the power minus 2 pi i 2 x and so on up to the nth term.

So, this expression can further be simplified as a 0 ;plus; this expression can be further simplified as h equal to minus n 2 plus n C h e to the power 2 pi i h x. We write it as expression number 3; where c 0 is equal to a 0 and C h is equal to half a h minus ib h. And c minus h equal to half a h plus ib h. So, one can write the same as f x equal to sum over h equal to minus n 2 plus n C h cos 2 pi h x plus i sin 2 pi h x. So, this is the expression for a 1 one dimensional Fourier series in along x axis say.

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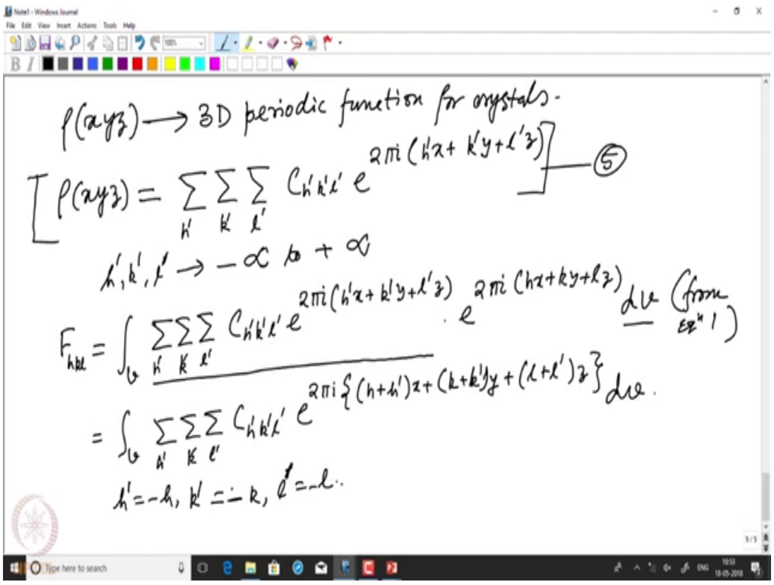

So, what we know is that the electron density which is rho x y z is a 3 dimensional periodic function for crystals.

So, the overall rho x y z can be represented as a sum of this Fourier series in 3 dimensions with h prime, k prime sum over l prime C h prime, k prime, l prime e to the power 2 pi i h prime x plus k prime y plus l prime z. So, this is the expression number 5. These values of h prime k prime and l prime can be from anything from minus infinity to plus infinity, plus there are infinite number of planes that one can consider within an unit cell.

So, what one can write in that case for F h k l is nothing but sum over v triple sum over h prime k prime and l prime C h prime k prime l prime e to the power 2 pi h prime x plus k prime y plus l prime z into e to the power 2 pi i h x plus ky plus lz dv, which is my equation number, now we do not write n number for this.

This equation comes from the equation number 1, because if you see the equation number 1 we have rho x y z. This rho x y z is now represented in expression number 5. And now rho x y z is placed in case of equation number 1 and we can write F h k l equal to the a triple sum over h prime k prime l prime C h prime k prime l prime e to the power 2 pi i h prime x k prime y l prime z and so on.

So, we can write this as sum over v h prime sum of over k prime sum over l prime C h prime k prime l prime e to the power 2 pi h plus h prime x plus k plus k prime y plus l plus l prime z dv.

So, if this is a periodic function. So, the exponential function is a periodic function here, and what happens is when we do the integration over a period, then it is 0 for all the terms, the integral over a period of an exponential function is 0 for all the terms, except for the terms where h prime equal to minus h, k prime equal to k prime equal to minus k and l prime equal to minus l.

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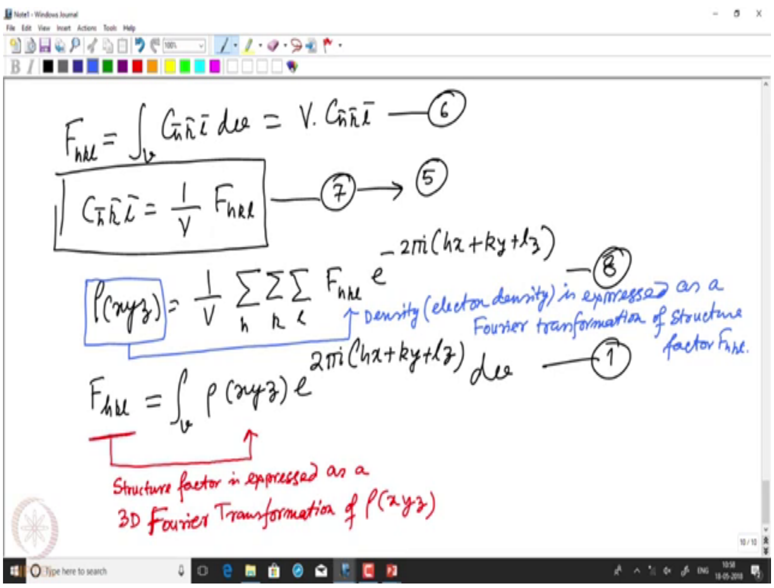

So, what happens when we arrive at those 2 situations? In a situation when it is h prime equal to minus h k prime equal to minus k and l prime equal to minus l, we can we should we can write F h k l is equal to sum over v C h bar k bar l bar dv; which is equal to V into C h bar k bar l bar.

So, this is the expression number 6. So, one can write the constant C h prime k h bar k bar l bar; is equal to 1 by V F h k l, we write it as equation number 7. So now, we substitute this equation number 7 to equation number 5. What is equation number 5? The equation number, now we substitute now we substitute this express value for C h bar k bar l bar to the equation number 5 and rewrite the expression for rho. So, what is rho x y z? It is equal to 1 by v triple sum over h k and l, F h k l e to the power minus 2 pi i hx plus ky plus lz; which is the equation number 8.

So now, if you try to compare this equation number 8 with the equation number 1 that we wrote; so, I am again rewriting that F h k l is equal to sum over v rho x y z e to the power 2 pi i hx plus ky plus l z dv. So, this was my equation number 1. What do we see here in these 2 very important expressions? In case of equation number 1, we are expressing structure factor as a Fourier transformation of rho x y z.

So, here the structure factor is expressed as a 3 dimensional Fourier transformation of rho x y z which is a periodic function in 3 dimension. But in the equation 8 we see the reverse here the rho is expressed in terms of F h what does it mean? Here the density that is the electron density is expressed as a Fourier transformation of structure factor F h k l.

So, what does it mean? If we have a set of structure factors, if we do a Fourier transform of structure, factor we get to know the electron density at various places. And if we do the reverse, we take the electron density and do a Fourier transformation; we get to know the structure factors.

So, this food Fourier transform and inverse Fourier transforms are is done every now and then when we try to refine and compare the structure and the modified structure along with the model; which we will discuss in future. So, in this lecture we have learnt till now, how one can express the structure factor F h k l in terms of rho h k l, and how one can represent rho h k l in terms of F h k l. So now, let us extend our understanding of structure factor using the exponential form.

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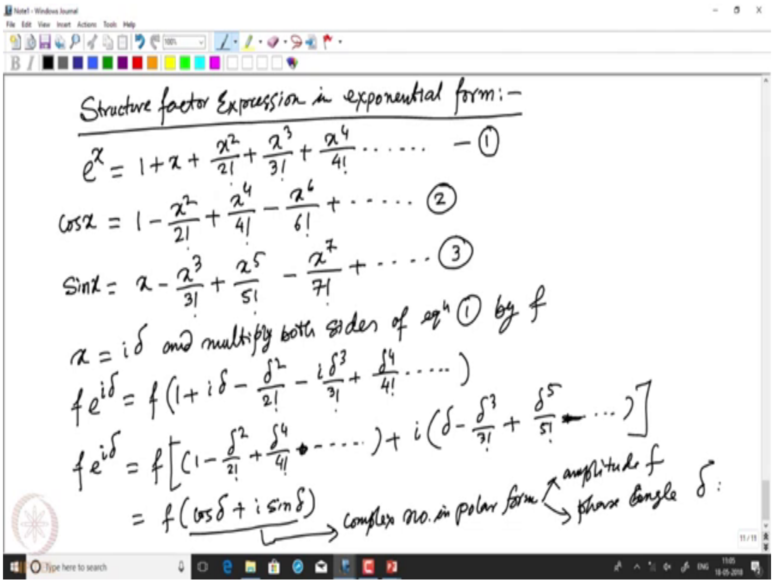

So, today now we would like to learn the structure factor expression in exponential form. So, once again for our use we need to know a few mathematical expressions, we need to know the expressions for e to the power x; which is 1 plus x plus x square by 2 factorial plus x cube by 3 factorial plus x to the power 4 by 4 factorial and so on is now the equation number 1.

We write cos x equal to 1 minus x square by 2 factorial plus x cube x should be power 4 by 4 factorial minus x to the power 6 by 6 factorial and so on. We write it as equation number 2. And then we write sin x equal to x minus x cube by 3 factorial plus x to the power 4 by 4 factorial, sorry, plus x to the power 5 by 5 factorial minus x to the power 7 by 7 factorial and so on as equation number 3.

Now if we substitute x by i delta and multiply both sides of equation 1 by f, we can write f e to the power i delta is equal to f into 1 plus i delta minus delta square by 2 factorial minus i delta cube by 3 factorial plus delta to the power 4, 4 factorial and so on.

So, one can this f e to the power i delta equal to f 1 minus delta square by 2 factorial, plus delta to the power 4 4 factorial minus and so on, plus take i out delta minus delta cube by 3 factorial, plus delta to the power 5 by 5 factorial and so on. So, this can now be written as f cos delta plus i sin delta. So now, this is nothing but a complex number in polar form. So, this complex number has an amplitude of f and phase angle delta.

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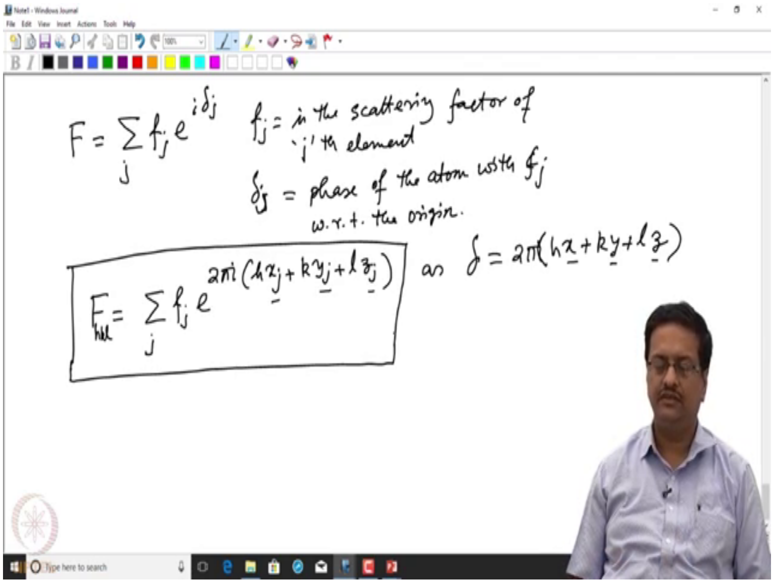

So, we can write the structure factor f is equal to sum over j f j e to the power i delta j; where if j is the scattering factor of j at element and delta j is equal to the phase of the atom with scattering factor f j with respect to the origin.

So, this is the phase of that diffracted beam because of that f j. So now, we can write f the structure factor F h k l as equal to sum over j f j e to the power 2 pi i hxj plus kyj plus lzj; as the phase delta is nothing but, 2 pi h x plus ky plus lz and here since we are doing the sum over all possible if x y and z, the subscript j's I have come in.

So, this is the expression for structure factor which we have already seen in our previous lectures; how this is represented in terms of the exponential form? So, in today's lecture we have learnt how to represent the structure factor, using the exponential form, using the polar form and so on. And then we have learnt how to correlate the structure factor with the electron density.

So, what we now know is the structure factor is the Fourier transform of electron density, and electron density is a Fourier transform of structure factor. So, in the next class we will learn about special structure factor expressions, and then we will try to derive the systematic absence conditions.