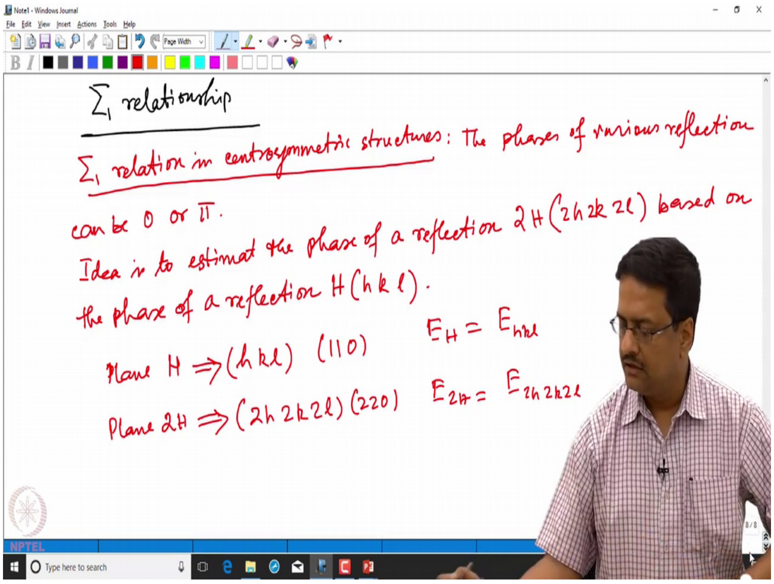
Chemical Crystallograhpy
Prof. Angshuman Roy Choudhury
Department of Chemical Sciences
Indian Institute of Science Education and Research, Mohali

Lecture - 52
Sigma 1 and Triplet Relationship

Welcome back to the course of Chemical Crystallography. In the previous lecture, we have discussed about the unitary structure factor and normalized structure factor expressions. And we are now ready to explore the different methods that are used in direct method for structure solution. So, today, we will start with a portion where we would like to see the method, where we use the method of sigma 1 relationship.

(Refer Slide Time: 00:51)



Σ_1 relationship

Σ_1 relation in centrosymmetric structures: The phases of various reflection can be 0 or π.

Idea is to estimat the phase of a reflection $2H\,(2h\,2k\,2l)$ based on the phase of a reflection $H\,(h\,k\,l)$.

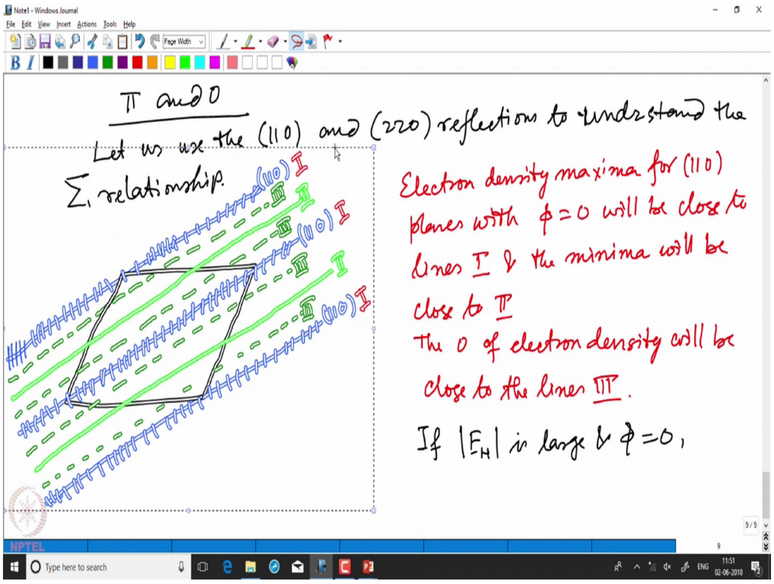
Plane $H \Rightarrow (h\,k\,l)$ $(1\,1\,0)$ $E_H = E_{hkl}$

Plane $2H \Rightarrow (2h\,2k\,2l)$ $(2\,2\,0)$ $E_{2H} = E_{2h\,2k\,2l}$

This sigma 1 relationship is applied in most of the cases of centrosymmetric structures. So, we use sigma 1 relationship in centrosymmetric structures. In case of the centrosymmetric structures, the phases of various reflections can be 0 or pi. So, the phases for centrosymmetric reflect structure is restricted between 0 and pi. So, the idea is to estimate, is to estimate the phase of a reflection 2 H, which means 2 h plus 2 h 2 k 2 l based on the phase of reflection H, which means h k l.

So, when we write the plane H, it means we are talking about the plane h k l. When we write the plane 2 H, we mean that the plane is 2 h 2 k 2 l; for example, if it is 1 1 0, then it will be 2 2 0 and so on. So, if we write E H it is for the plane h k l, you can write E 2 H is for E 2 h 2 k 2 l.

(Refer Slide Time: 03:49)



π and 0

Let us use the (110) and (220) reflections to understand the Σ_1 relationship.

Electron density maxima for (110) planes with $\phi = 0$ will be close to lines I & the minima will be close to II

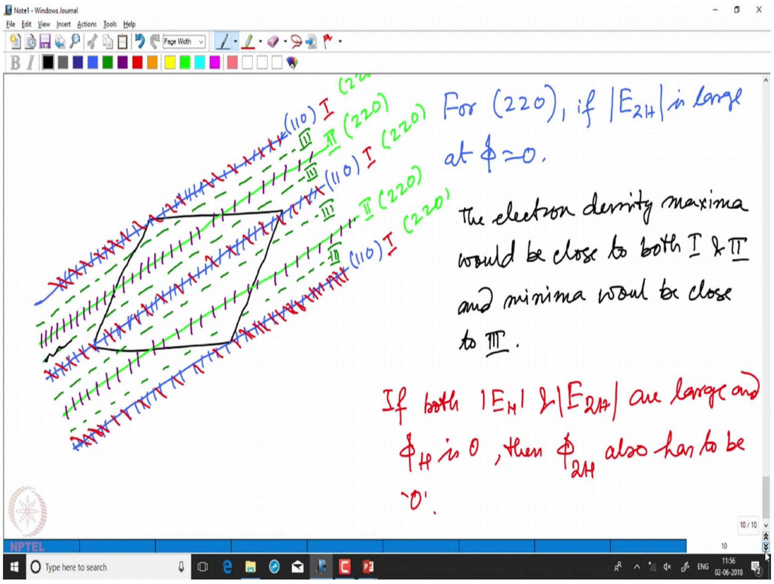
The 0 of electron density will be close to the lines III.

If $|E_H|$ is large & $\phi = 0$,

So, now as we know that the in case of centrosymmetric the phases can be just pi and 0. Now, let us use the 110 and 220 reflections to understand the sigma 1 relationship. Let us try to first draw the projection of an oblique lattice like this. And then we are trying to draw first the 110 set of planes, which are like that are the corresponding 110 set of planes we mark these lines as I, because they are identical planes. Now, in case of this 110 reflections the maxima of the electron density will appear close to I.

And the minima will appear close to the lines which I am trying in between and marking them as II. So, the electron density maxima for 110 planes with we assume the phase phi equal to 0 will be close to lines I. And the minima will be close to II, so where would the 0 of electron density lie, the 0 of electron density would lie in between I and II which I am drawing here as dashed lines, so that dashed line will indicate the 0 electron density for this 110 set of planes. So, the minima (Refer Time: 07:39) the 0 of electron density will be close to the lines marked as III. So, what will happen is the possible if the mod E H is large and phi is equal to 0, what we will see is the large electron density close to the lines marked as I, and minima will be close to II and 0 will be close to III.

(Refer Slide Time: 09:17)



For (220), if $|E_{2H}|$ is large at $\phi = 0$.

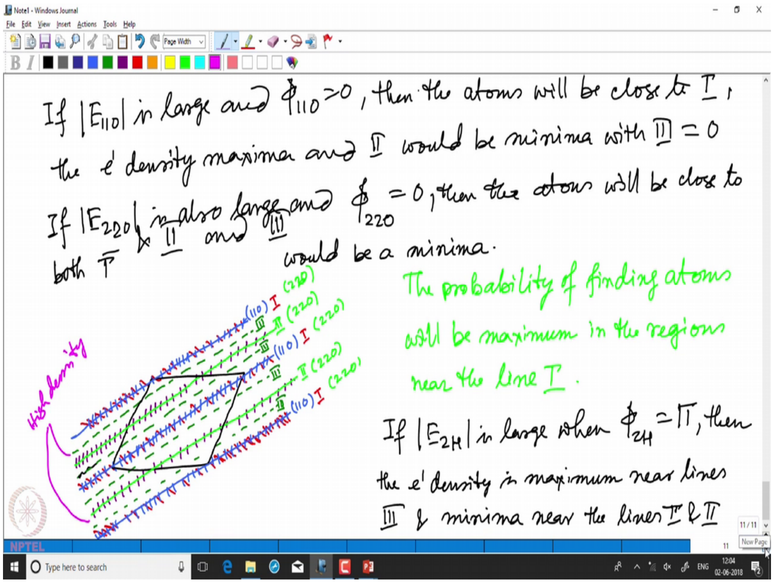
The electron density maxima would be close to both I & II and minima would be close to III.

If both $|E_H|$ & $|E_{2H}|$ are large and ϕ_H is 0, then ϕ_{2H} also has to be '0'.

So, now if we try to see what happens for the planes 220 the reflexion 220, if again for 220 E 2 H is large, at phi equal to 0. So, what are 220 lines the 220 lines are, now the lines which are marked as green the number II. And eventually this middle line also becomes the 220 as well and so on So, now for 220 set of reflections the electron density maxima would be close to both lines 1 and lines 2, because you can see both lines I and lines II correspond to the same 220 set of planes. So, the maxima will be close to lies I and lines II and minima would be close to III.

So, if both E H and E2H are large and phi H is 0, then phi 2 H also has to be 0, which means that the electron density for this particular crystal were both E H and E 2 H are large. We should see a large electron density associated with the lines, which are marked here as 1 where these are coincident where the electron density maximized for both 110 and 220 will have a lesser density near the II, because in case of the line in case of 110 reflection the lines along II will have minima whereas, in case of 220 will have maxima So, these lines will have intermediate density, and the lines III will have 0 intensity, because line III is now minima for 2 and 0 for 1 that is it is 0 for 1 0 0 set of reflections, and it is a minima for the 200 set of reflections. So, there would not be any density close to that.

(Refer Slide Time: 14:25)



If $|E_{110}|$ is large and $\phi_{110} = 0$, then the atoms will be close to I, the e' density maxima and II would be minima with III = 0

If $|E_{220}|$ is also large and $\phi_{220} = 0$, then the atoms will be close to both I & II and III would be a minima.

The probability of finding atoms will be maximum in the regions near the line I.

If $|E_{2H}|$ is large when $\phi_{2H} = \pi$, then the e' density is maximum near lines III & minima near the lines I & II

So, one can conclude that if E 110 is large and phi 110 is 0, then the atoms will be close to I, the electron density maxima, and II would be minima with III as 0 density. Similarly, if E 2 0, 2 2 0 is also large, and phi that is the face of 220 is also 0, then the atoms will be close to both I and II and III would be a minima, which indicates that. The plot we had drawn in the previous slide which I am trying to bring it here as well indicates that

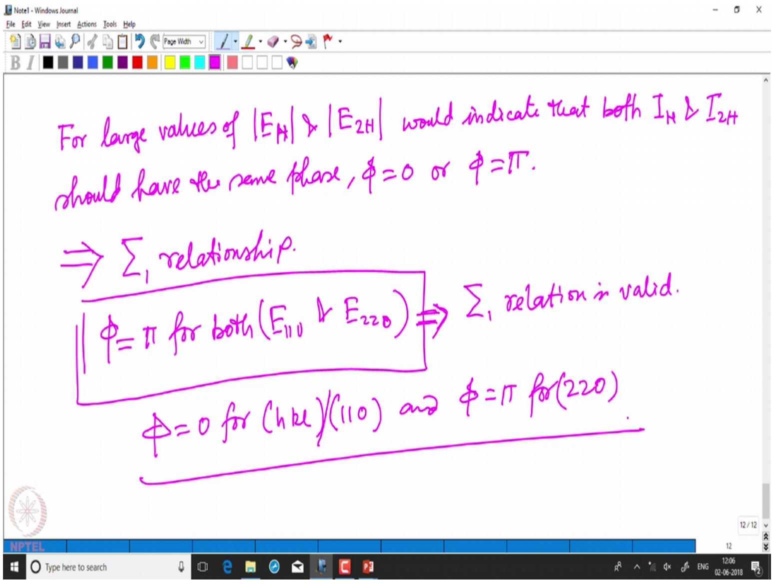
So, this plot here then describes what I have written here. So, the probability the probability of finding atoms will be maximum in the regions near the line 1, if both the conditions are satisfied. If a different situation arises so, if E 2 a sorry. If E 2 H is large when phi to H is 0 sorry phi 2 H is pi, then the electron density is maximum near the lines marked as III, and minima near the lines I and II.

So, this represents a situation where there is no overlap regions. If you can see in this figure, if we have additional electron density if it is E2H is maxima at phi equal to pi, then the regions marked as III will have high density and regions marked as I and II will have low density. So, overall the 110 and 220 sets or reflections will not have any overlap of intensity, and hence a different scenario will be represented.

So, by looking at the high values of E H k l and then incorporating two different values of the phi that is phi 2 H, we get two different scenarios. And from that we can conclude whether it is the phi for 220 is 0 or phi based on the electron densities that we can see by doing the corresponding Fourier transformation. So, what is then done is first you assume that the phi for 110 reflection is 0 and do a Fourier transformation get the density plot.

Then you do it for phi the for the h k l, which is 220 as you need to be 0 and do the Fourier transformation, and see the electron densities. And then if you do it again for phi equal to pi for 220 reflection. and see that there is a difference and based on this one then can solve the values for the electron density for the coordinates for the atoms close to these particular two reflections So, this method is then applied to all possible reflections, which are related by just integral multiple of h k l.

(Refer Slide Time: 21:13)



For large values of $|E_H|$ & $|E_{2H}|$ would indicate that both I_H & I_{2H} should have the same phase, $\phi = 0$ or $\phi = \pi$.

$\Rightarrow \Sigma_1$ relationship.

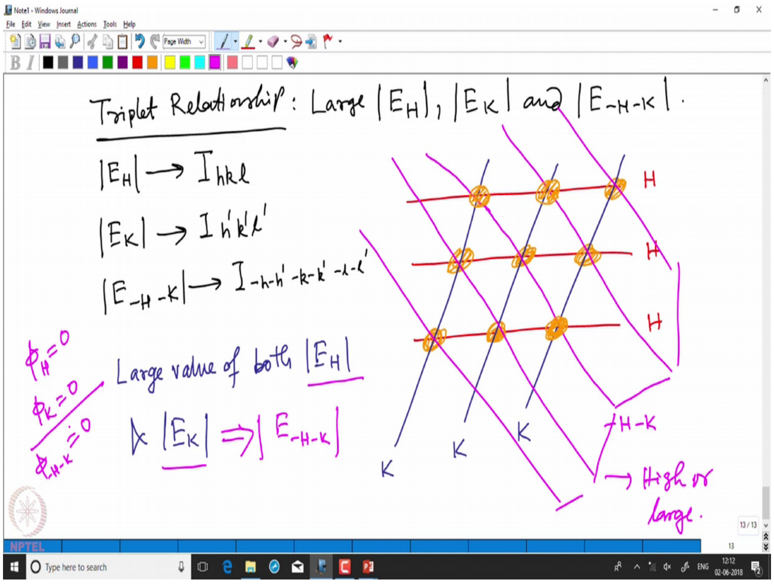
$\phi = \pi$ for both $(E_{110}$ & $E_{220}) \Rightarrow \Sigma_1$ relation is valid.

$\phi = 0$ for $(hkl)(110)$ and $\phi = \pi$ for (220).

So, for large values of E H and E 2 H would indicate that both I H and I 2 H should have the same phase phi equal to 0 or what should have phi equal to pi. So, this conclusion that we are drawing here is called the sigma 1 relationship. So, I would like to practice or to do this exercise for phi equal to phi for both E 110, and E 220 set of reflections at E 220 structure.

And draw the situation scenario that I have drawn and make sure that the sigma one relation is still valid. You can also try when phi equal to 0 for h k l maybe for 110 and phi equal to pi for 220 reflection, and see what kind of electron density distributions that you get. So, this is one of the methods for getting the phases of one particular reflection compared to the phase of another reflection having same or large intensity.

(Refer Slide Time: 23:59)



Triplet Relationship: Large $|E_H|$, $|E_K|$ and $|E_{-H-K}|$.

$|E_H| \rightarrow I_{hkl}$

$|E_K| \rightarrow I_{h'k'l'}$

$|E_{-H-K}| \rightarrow I_{-h-h'-k-k'-l-l'}$

$\phi_H = 0$

$\phi_K = 0$

$\phi_{H-K} = 0$

Large value of both $\underline{|E_H|}$ & $\underline{|E_K|} \Rightarrow |E_{-H-K}|$

→ High or large.

So, now I would like to also introduce you to another relationship which is called the triplet relationship. This triplet relationship is based on the values of large values of E H E K and E minus H minus K. Remember E H corresponds to I h k l. E K corresponds to I h prime k prime l prime. And E minus H minus K corresponds to I minus h minus k corresponds to i minus h minus h prime minus h minus h prime minus l minus l prime.

So, what we are trying to visualize this the four way. If we have set of h k l planes drawn like that as E H or the planes I mark them as simply H. And then we mark another set of planes like that and write them as case and what we are trying to say is that we have large value of both mod of E H and mod of E K

So, both the planes h k l and h prime k prime l prime have large electron densities so that means when these two sets of planes interact the way that the intersect the way I have drawn here. The points of intersection are the points where the electron density should be the maximum. Our electron densities will be very high, because we are saying that both the E H and E K have very high magnitude of structure factor amplitude that is the scattering is very high in those two planes.

So, the plane which actually bisects these two planes; I am drawing it in a different colour for easy understanding the planes which are, now marked in purple are passing through the points of intersections of these planes the miller indices of these planes are nothing but minus H minus K. So, from this observation of the values of E H and E K one can also conclude that the value of E minus H minus k that is the diffraction from those set of power purple coloured planes will also be high or large.

So, this is represents a situation where by observing two different reflections of different h k l. One can then say that a third reflection will also have a very high value of E H. And if the phases of E H and E K are same the phase of E minus H minus K will also be the same. So, in a single symmetric structure if we see that the phi H is 0, and phi K is also 0, then one can conclude that phi of minus H minus K will also be 0, and all three will be of very high intensity.

So, this is what is called a triplet relationship in x ray crystallography, which also takes part helps us in structure solution by direct methods. So, today we have learned about two relationships one is sigma 1 relationship, and another one is triplet relationship in direct methods.

So, we will continue in this direction and try to understand the basics of direct methods in the next few lectures.