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

Lecture - 53
Patterson Method

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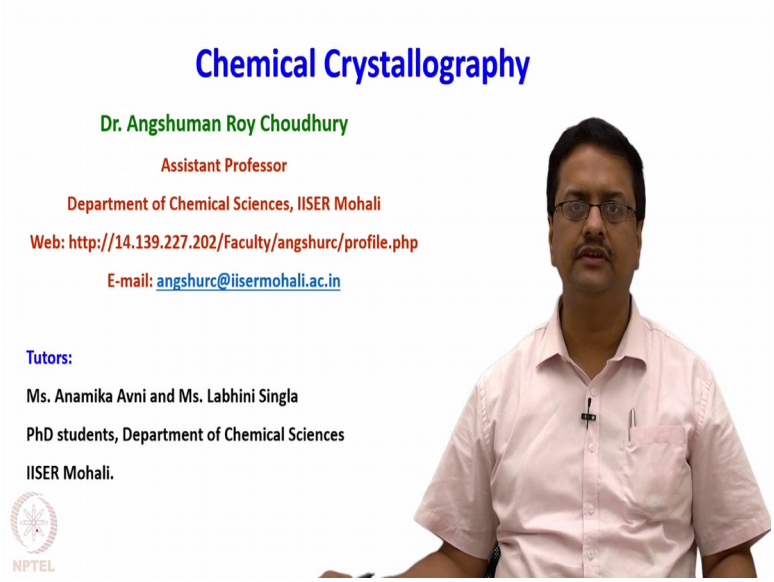

Welcome back to the course of Chemical Crystallography in the previous couple of lectures we have discussed about the direct method and the mathematical background little bit of different methods and then we talked about the practical way of doing phase determination.

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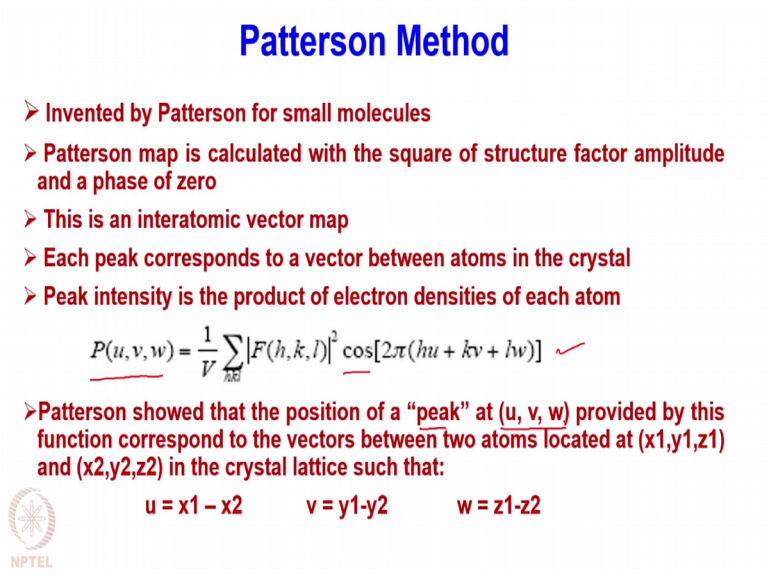

The other method of structure solution was introduced by Patterson and this is based on the presence of a heavy atom in the lattice. So, this Patterson map is calculated with the square of structure factor amplitude and a phase of 0, this is an intern atomic vector map that we will generate and in this each peak corresponds to a vector between two atoms in the lattice. So, we will also have the self vectors origin coming at the origin.

So, the peak intensity is defined as the product of electron densities of each atom. So, the Patterson function that P u v w is defined as this expression 1 by V sum of F h k l mod of F h k l square cos 2 pi h u plus k v plus l w you can see that we just have the cost term which indicates that the Patterson map is always centrosymmetric. The in case of this Patterson map he showed that the position of a peak at the coordinates u v w provided by this function corresponds to a vector between two atoms located at x 1 y 1 z 1 and x 2 y 2 z 2 in such a way that u equal to x 1 minus x 2 v equal to y 1 minus y 2 w equal to z 1 minus z 2 and the opposite vectors as well.

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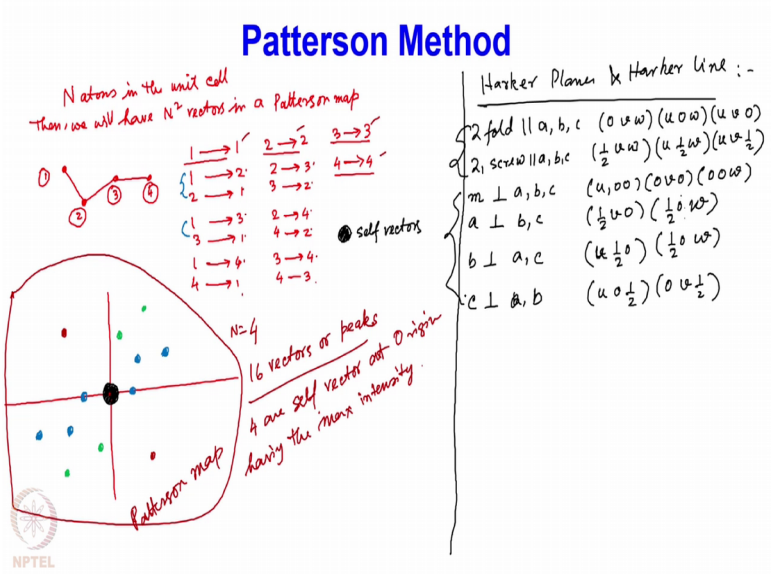

So, suppose if we have N atoms in the unit cell, then we will have N squared vectors in a Patterson map how? Suppose we have 4 atoms like this. So the Patterson man will have the vector peaks from atom 1 to atom 1 this is the cell vector and the other vectors 1 to 2 and 2 to 1 the opposite vector 1 to 3 and 3 to 1 1 to 4 and 4 to 1 like that which would have 2 to 2 the other cell vector 2 to 3 and 3 to 2 2 to 4 and 4 to 2 and you should have 3 to 4 and 4 to 3.

So, we have in addition 3 to 3 and 4 to 4, so what we see there are 4 self-vectors of length 0, so they will all appear at the origin. So, if I have a Patterson map plotted here for this particular molecule we should have a large central peak corresponding to all self-vectors, other than that now we have the opposite vectors 1 to 2.

So, if the 1 to 2 vector appears here the opposite vector of 1 to 2 will appear on the other side of the origin because, it is just opposite in sign. Similarly, if the vector 1 to 3 appears somewhere there then it is centrosymmetric opposite will come here that is 3 to 1. In the same manner if 1 to 4 appears somewhere here the corresponding 4 to 1 should appear at that point.

Now if we look for the vectors 2 to 3 and 3 to 2 suppose 2 to 3 appear somewhere there. So, the corresponding 3 to 2 will appear here 2 to 4 if it appears somewhere there it will have 4 to 2 at this point, then one can have 3 to 4 appearing at some the point whereas, the 4 to 3 will appear like that.

So, what we see in this particular map which is generated here is a Patterson map which is centrosymmetric with respect to the origin. So, always a Patterson map is centrosymmetric irrespective of the structure whether it is eccentric or non centric, how many such peaks have appeared? We have 4 self-vectors so 4 5 6 7 8 9 10 11 12 13 14 15 16.

So, for structure with N equal to 4, we have 16 vectors or peaks appeared in the Patterson map of which 4 are self-vectors at origin having the height maximum or maximum intensity and other vectors appear at different locations with the intensity of much less than the origin. So, this the most useful feature of this Patterson map is the presence of peaks at certain positions which we have drawn here and this indicates the information about the symmetry elements present in the unit cell.

So, the coordinates of atoms can then be determined from these Patterson maps. So, when we draw these Patterson maps for different symmetry elements we have to draw them with their corresponding equivalent points. There are some useful features in this Paterson map we have a few lines and planes which are of particular interest to us these are called the Harker planes and Harker lines where these vectors are located that is the atoms can the location set of u v w are on those planes or on lines. So, if this the presence of these values are given line or plane indicates the presence of a particular symmetry.

So, if you have a 2 fold symmetry parallel to a b or c then, your vectors u v w will have values 0 v w when it is parallel to a when this parallel to b it will be u 0 w when it is parallel to c it will be u v 0. If it is a 2 1 screw parallel to a b or c you see here in this case there is a translation associated with the rotation. So, these points will then change to half v w u half w and u v half.

Similarly, if there is a mirror plane perpendicular to a b or c the Harker sections will then become Harker lines will then become u 0 0 0 v 0 0 0 w or the a glide perpendicular to b or c will represent a Harker line like half v 0 or 0 half. Similarly b line perpendicular to a or c we generate the Harker line at u half 0 or 0 half w similarly c line perpendicular to b or a or b will generate the Harker lines at u 0 half and 0 v half.

So, these are the corresponding Harker planes which are corresponding to the 2 fold and 2 1 screw axis and these are the Harker lines which correspond to mirror or glide plane. So, we will now investigate a few cases simple cases with the Paterson synthesis.

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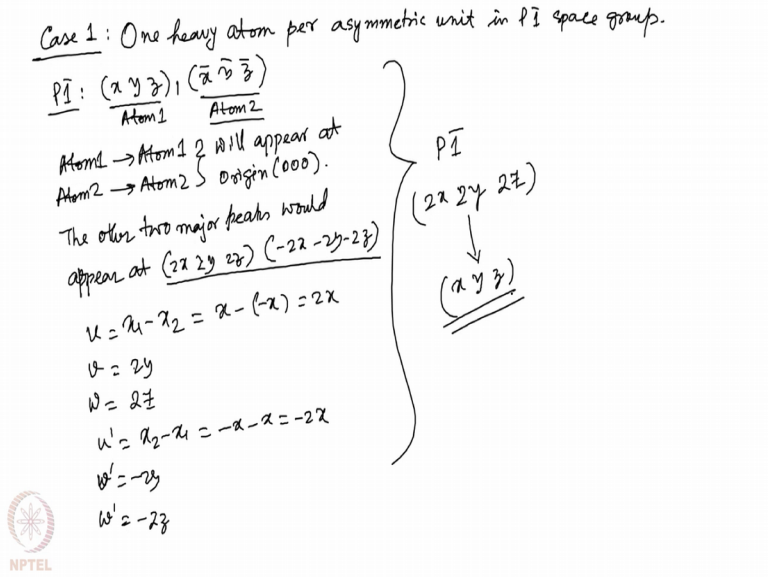

So, my our case 1 is extracted where we have one heavy atom part a symmetric unit in P 1 bar space group. So, as we know in case of P 1 bar space group the equivalent points are x y z and x bar y bar z bar. So that means, if we have one automatics y z the other heavy atom is at x bar y bar z bar. So, of course, the largest Patterson peak is the self-atom that is atom 1 to atom 1 and atom 2 to atom 2.

And these two rather some peaks will appear at origin that is at 0 0 0. The other two prominent peaks are other two major peaks would come or appear at 2 x 2 y 2 z and minus 2 x minus 2 y minus 2 z remember u is x 1 minus x 2. So, here it is equal to x minus of minus x which is equal to 2 x, so v is 2 y w is 2 z. In the same way u prime is x 2 minus x 1 which is equal to minus x minus x, so it is equal to minus 2 x similarly, v prime is minus 2 y w prime is also minus 2 z.

So, the peaks are appearing at those two points, so by looking at the Patterson map of a triclinic system and then the getting the values of 2 x 2 y 2 z 1 can easily divide it by 2 1 can divide it by 2 and get the values of x y and z. So, this is how one can get the coordinates of the heavy atoms in case of a structure where you have one heavy atom per symmetric unity P 1 bar space book.

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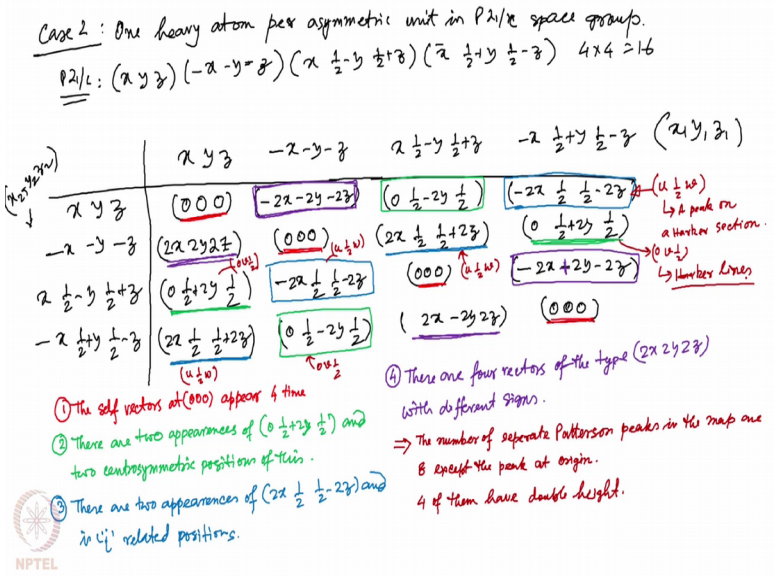

So, let us see if we have a situation which is my case 2; one heavy atom for a symmetric unit in P 2 1 by n orbit 1 by c space group. So, in case of P 2 1 by c space group the equivalent points are as we know x y z minus x minus y minus z x half minus y half plus z and x x bar half plus y minus z the vectors will be 4 into 4 that is 16. So, what are those vectors let us try to get those vectors right for all these four systems, so 4 as a metric units.

So, we write here the coordinates x y z minus x minus y minus z x half minus y half plus z and minus x half plus y half minus z and again we write the coordinates here as well x y z minus x minus y minus z x half minus half minus y half plus z and minus x half plus y half minus z. So, now if we assume that this set corresponds to x 1 y 1 z 1 and this set corresponds to x 2 minus y 2 x 1 by x 2 y 2 z 2 then what we will write in the blank space is x 1 minus x 2 y 1 minus y 2 z 1 minus z 2.

So, this matrix when we write x 1 minus x 2 is 0 y 1 minus y 2 is 0 z 1 minus z 2 0 similarly minus x 1 minus x 1 minus x 2 here it is minus x minus x so minus 2 x minus 2 y minus 2 z. This one is x minus x is 0 it becomes half minus 2 y and it becomes up this one here becomes minus 2 x half half minus 2 z.

So, if we continue the same for the next rule it becomes 2 x 2 y 2 z this point is 0 0 0 because it is minus x and then minus of minus x is classic so it becomes 0. Then this goes for 2 x half half plus 2 x, then here it is 0 half plus 2 y half in the 3rd row these becomes

0 half plus 2 y half minus 2 x half half minus 2 z. This point is 0 0 0 the origin peak and here we have minus 2 x minus 2 y minus 2 z the 4rth row is nothing, but 2 x half plus half and half plus 2 z 0 half minus 2 y half minus 2 x minus 2 y 2 z and here the last point is 0 0 0.

So, now we need to look at these vectors carefully, these are all possible vectors first for this particular special P 2 1 by c. Now point number 1; the self vectors at 0 0 0 appear 4 times, the point number 2 is there are two appearances of 0 half plus 2 y half and two centrosymmetric positions of this. So, 0 half plus 2 y half is here and also 0 half plus 2 y half is here the corresponding centrosymmetry related points are these two where it is instead of half plus it is half minus. The third point is that again there are two appearances of 2 x half half minus 2 z and it is i that is central of inverse related positions.

So, these 2 x half half minus 2 z is here 2 x half there should be 2 z let me correct it here. So, this is one point which is 2 x half half plus 2 z similarly here it is 2 x half plus 2 z and it is corresponding centrosymmetric related ones are here which is minus 2 x half half minus 2 z minus 2 x half of minus 2 z. And then in the point number four we can note that there are four vectors of the type 2 x 2 y 2 z with different signs.

So, for example, this is a 2 x 2 y 2 z and it is inversion related is minus 2 x minus 2 y minus 2 z these two are inverse unrelated. Similarly, these two 2 x minus 2 y plus 2 z is inversion related here this should be plus 2 y, if you correct it because this is half plus y minus half minus y half gets cancelled minus y becomes plus y so it becomes plus 2 y. So, what we have is the following, the number of separate Patterson peaks in the map are 8 x except the peak at origin 4 of them have the double height as well.

So, in this case there are different types of peaks at different location, so what we see is that we have some peaks of the type u half w which is which are here u half w is located at that point u half w type of peaks. Similarly, here we have u half w set of this one is also u half w type of peaks and this one u half w set of peaks.

These u half w set of peaks represent the peak on a Harker section and the peak of type 0 v half that is some things like that 0 v half here it is 0 v half and so on. There are other peaks also it is here 0 v half so this 0 v half set of peaks are located on the Harker lines.

So, by identifying these peaks and getting their coordinates determined from the Patterson map one can then calculate the coordinates of x y and z from the various values of u v and w determined from the Harker lines and Harker sections and then calculate the position of the heavy atom.

So, once we determine the position of the heavy atom accurately that information can be fed into the refinement program. And the phases of other reflections which were not determined before can be determined and by doing a delta f synthesis one can complete the structure solution for the other lighter atoms. So, as a homework I would like to give the problem that you identify the vectors in Patterson map with one heavy atom.

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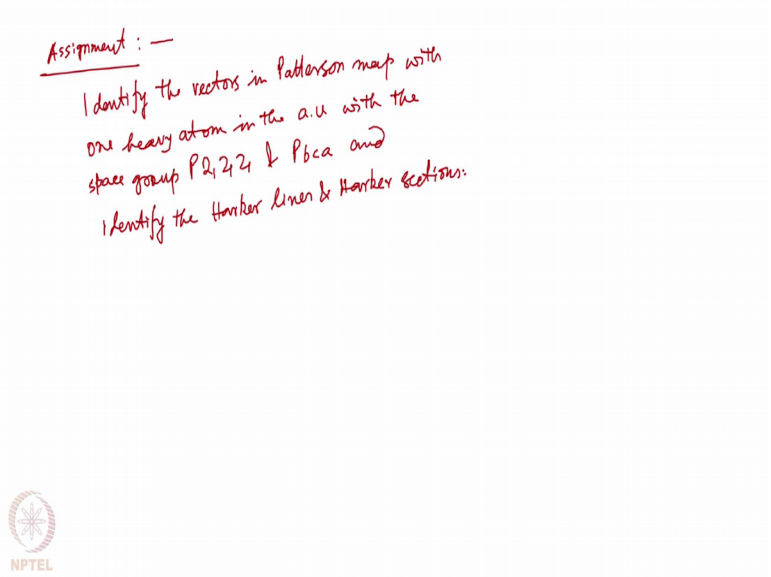

So, the assignment is like this, identify the vectors in Paterson map with one heavy atom in the a symmetric unit with the space group P 2 1 2 1 2 1 and P b c a separately and identify the Harker lines and Harker sections. In the next lecture we will discuss about another case where you have two heavy atoms in the a symmetric unit in a case of a P 1 bar structure and then we will discuss one practical example how to use these Paterson maps and the heights of the peaks to get the coordinates of the heavy atom.