Symmetry and Structure in the Solid State
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Lecture - 54
Patterson Method 2

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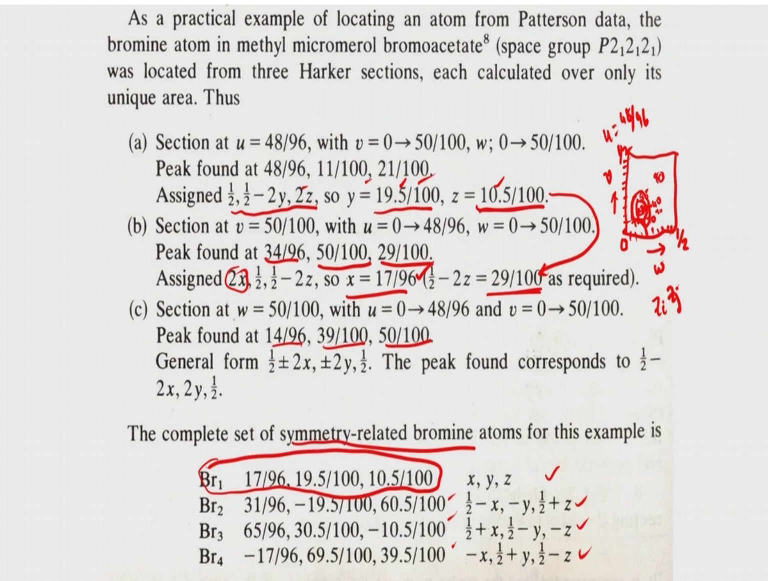

As a practical example of locating an atom from Patterson data, the bromine atom in methyl micromerol bromoacetate[8] (space group $P2_12_12_1$) was located from three Harker sections, each calculated over only its unique area. Thus

(a) Section at $u = 48/96$, with $v = 0 \rightarrow 50/100$, $w; 0 \rightarrow 50/100$.
Peak found at 48/96, 11/100, 21/100.
Assigned $\frac{1}{2}, \frac{1}{2} - 2y, 2z$, so $y = 19.5/100$, $z = 10.5/100$.

(b) Section at $v = 50/100$, with $u = 0 \rightarrow 48/96$, $w = 0 \rightarrow 50/100$.
Peak found at 34/96, 50/100, 29/100.
Assigned $2x, \frac{1}{2}, \frac{1}{2} - 2z$, so $x = 17/96$ ($\frac{1}{2} - 2z = 29/100$ as required).

(c) Section at $w = 50/100$, with $u = 0 \rightarrow 48/96$ and $v = 0 \rightarrow 50/100$.
Peak found at 14/96, 39/100, 50/100.
General form $\frac{1}{2} \pm 2x, \pm 2y, \frac{1}{2}$. The peak found corresponds to $\frac{1}{2} - 2x, 2y, \frac{1}{2}$.

The complete set of symmetry-related bromine atoms for this example is

Br_1	17/96, 19.5/100, 10.5/100	x, y, z
Br_2	31/96, −19.5/100, 60.5/100	$\frac{1}{2} - x, -y, \frac{1}{2} + z$
Br_3	65/96, 30.5/100, −10.5/100	$\frac{1}{2} + x, \frac{1}{2} - y, -z$
Br_4	−17/96, 69.5/100, 39.5/100	$-x, \frac{1}{2} + y, \frac{1}{2} - z$

So, we take it as a practical example. So, in a Patterson data, this is the structure of locating the bromine atom in methyl, micromerol, bromoacetate. This is a compound whose structure has been determined with the space group 2 1 2 1 2 1. So, it was located from three Harker sections, each calculated over only it is unique area; that means we calculated the Patterson's maps. We, we did not have to calculate the entire three-dimensional Patterson map, because we have already determined the space group earlier on by looking at the distribution of the hkl reflections when once we had the data. So, the space group is 2 1 2 1 2 1. And so we know that there are three Harker sections.

So, we look at the three Harker sections. so we look at the section at u equals 48 by 96. What is 48 by 96 is half? So, we look at u half, v is now going from 0 to 50 up to 100, it just goes 50 slash 100 and w goes also from 0 to 50 slash 100. So, we look at this particular section of the Patterson, we compute only this particular section of the come of the Patterson. We get a peak at 48 by 96, 11 by 100, and 21 by 100. I think I should illustrate that with a small diagram.

How we do this? What you do is, you have a Patterson section. So, you take u equals half. So, this is now u 48 by 96 ok. We are taken the top off at u equals 48 by 96. So, this is the origin here. You now go from let us say this is the v direction, and this is the w direction. So, you mark this as 0, you mark this 0 0. So, we now go along the v direction, we go up to half, which represents 50 by 100, you go here again to half which represents 50 by 100.

Now, you compute the Patterson value at every point one let us say, just to give you an example or every 0.05. So, you get several points along the w direction, you get several points along the v direction. And then find out the peak positions, the value of the Patterson. The value of the Patterson you already know is varying as with respect to this as z i z j right that product of z i z j.

So, if it is a heavy atom, in this case bromine, it will vary as 35.5 square. So, you will start getting the peaks. The way you will get the peaks will be like this. You draw the contour diagram. This is the contour diagram of a Patterson map. So, you take let us say for example, here at this point you got a very high value let us say you got some 90. And then adjacent points you got 85 and then you got something like 70 here, then something like 40 there, and something like 70 there ok.

And then all the other points also will come like that. The various values corresponding to the value of the w as well as that of v, we are now looking at u equals half that is 48 by 96 section. And you are going from 0 to half here and 0 to half here. So, what you do is now draw the contour. The way you draw the contour is I am going to draw the contour of 80 ok. So, 80 is about this it is 85; so 85. So, I will draw this contour which is 80. And 80, 40 is midpoint, 80 will come beyond this 70 and this goes beyond the 70. So, you get a contour like that.

Then you draw the contour of 85. So, it will go something like that; and contour belonging to 90, it will go like that. So, this way we plot the contours. Taking the points of the adjacent, so the next point will be 20 let us say and there is something like 80 here. That will be another peak in the u v section corresponding to some other atom let say.

So, we take the highest peak, the highest peak now, is at 48 by 96 11 by 121 by 100 in this map. So, we what we have done is 0 to half is expressed as 50, 0 to 50 slash 100, that means, half right, 50 by 100 is half, 50 by 100 is half. So, we will calculate the corresponding value of y and z as 11 by 100, 21 by 100. This is only a computational ease, so that we plot this section. So, we have plotted the section u equals half, and we have taken the top of the u and v and w is spread out. So, you have a sheet, where you have u and w values you mark 0.1, point naught 1, point naught 2, point naught 3 and so on. At every point you calculate what is the Patterson value and that is proportional to z i z j, so that value you put it here. And then you draw the contours depending upon the strength or the weight associated with that position as far as peak is concerned.

So, you draw what are known as contours. And these contours will tell us the location of the u v and w, and that happens to be 11 by 100 and 21 by 100. So, it is 11 by 100 along the v direction, and 21 by 100 along the w direction, so that is the peak. So, you pick up that peak. You assign this peak as half, half minus 2 y, 2 z that means this is now a Harker section. And so you solve for y and z. Now, what will be the value of y and z? So, this is v is what, v is 2 y, and w is 2 z. So, you get the value of y as 19 and a half by 100 and 10 half way. So, you get the value corresponding to y as well as z.

Then you go to the section v similarly, you go to the next one which is the section along the y direction, which is v equals half and plot u and w in this following way. And pick up the peak. The peak found is at 34 96, 50 100 and 29 100, this is corresponding to 2 x half, half minus 2 z. See here the peak was found at what 48 96, 48 by 96 is half ok, and 11 by 100 is half minus 2 y. Say what you got you may be wondering, what is this going on, because you said 11 by 100 is the peak 11 by 100 corresponds to 2 y. So, you have to take half minus 2 y, so half minus 2 y will be 19.5 100 when you solve for y.

So when you solve for z, you again take the value 2 z. So, 2 z is 20 y by 100, and therefore, this will be 10.5 by 100, half of that. So, 2 z is 21 by 100 that is half of that and this is half minus 2 y; so 11 by 100 now gives you 19.5. So, the peaks corresponding to y and z are at 19.5 by 100, 10.5 by 100. You get a solution in the second section at two axis. Now, you get a solution for x. Here we got a solution for y and z. So, here we get a value for x. And we also get a value for half minus 2 z from this position, and the value for half minus 2 z is now 29 by 100, which is a requirement coming from up they up here, because z value is 10.5 by 100. So, half minus 2 z if you calculate, it will be 29 by 100. So, there is a peak corresponding to that as well.

So, similarly you work out the w section. And therefore, you get the value 14 96 39 100 50 100 as the 2 x, 2 y, 2 z are the solution as a half plus minus 2 x. half plus minus 2 y and half, and then you get the values corresponding to that. So, what I suggest is you go through this table. And then you consider the first one as a Harker section corresponding to x equals half. The second one is the value corresponding to y equals half. The third is corresponding to z equals half. And you have the corresponding values of y and z in every case in this case y and z sorry in this case, x and z and in the third case it is x and y.

So, effectively two of them are common between these. In other words, you have the value of 2 z here and a half minus 2 z here. So, z can be uniquely determined between these two. Similarly, the value of x can be determined between these two, and the value of y can be determined between 1 and 3. So, you get the value of x, y, z, which is unique. So, the complete set of symmetry, then you get you see remember this is a 2 1 2 1 2 1 system. And therefore, there will be not just one bromine atom; we will have 4 bromine atoms. And therefore, you have to find the positions of 4 bromine atoms. And those four bromine atoms should be related by the equivalent point relationships.

So, when you get this solution as 17 by 96, 19.5 and 10.5. 10.5 came from here; and 19.5 came from there; and 17 96 came from where? 17 96 came from here the value of x. So, then we had the second position of the bromine. So, when once you have this solution coming from the two three peaks which we have located, you can now generate the equivalent points in the space group, and look for peaks corresponding to those values. These three peaks will correspond to these values, that means you have let us leave out the lower part, then we will keep the 96 or 100 let us say for arguments sake.

So, we have a bromine sitting at 0.17, 0.195, 0.105, then you use half minus x minus y half plus z half, then generate these points which is coming now to be 0.31, minus 19.5 and minus 60.5, minus 0.605 sorry. So, these values now will correspond to each one of these bromine, and these bromines are symmetry related bromines, these only one bromine in the structure but you get four bromines in the entire unit cells.

So, this corresponds therefore to the 4 bromine atoms in the unit cell. So, you can determine all their positions. So, Harker section utilization along with the symmetry that is available in the Patterson map will allow us to find the positions of the heavy atoms fairly uniquely. And particularly in systems which offer unique finding of the position of the atom. I hope I have made it clear, but just for the sake of revision, let us go through it once.

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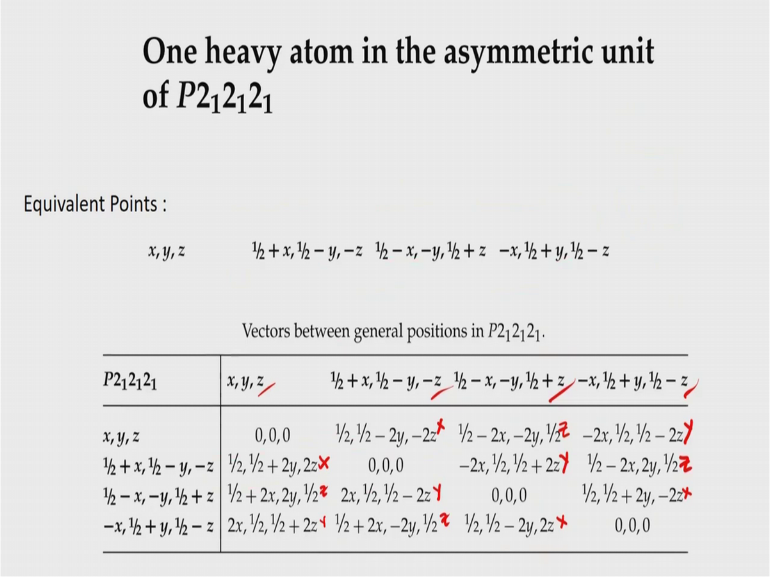

One heavy atom in the asymmetric unit of $P2_12_12_1$

Equivalent Points :

x, y, z $\quad$ $\frac{1}{2}+x, \frac{1}{2}-y, -z$ $\quad$ $\frac{1}{2}-x, -y, \frac{1}{2}+z$ $\quad$ $-x, \frac{1}{2}+y, \frac{1}{2}-z$

Vectors between general positions in $P2_12_12_1$.

$P2_12_12_1$	x, y, z ✓	$\frac{1}{2}+x, \frac{1}{2}-y, -z$ ✓	$\frac{1}{2}-x, -y, \frac{1}{2}+z$ ✓	$-x, \frac{1}{2}+y, \frac{1}{2}-z$ ✓
x, y, z	$0,0,0$	$\frac{1}{2}, \frac{1}{2}-2y, -2z$ x	$\frac{1}{2}-2x, -2y, \frac{1}{2}$ z	$-2x, \frac{1}{2}, \frac{1}{2}-2z$ y
$\frac{1}{2}+x, \frac{1}{2}-y, -z$	$\frac{1}{2}, \frac{1}{2}+2y, 2z$ x	$0,0,0$	$-2x, \frac{1}{2}, \frac{1}{2}+2z$ y	$\frac{1}{2}-2x, 2y, \frac{1}{2}$ z
$\frac{1}{2}-x, -y, \frac{1}{2}+z$	$\frac{1}{2}+2x, 2y, \frac{1}{2}$ z	$2x, \frac{1}{2}, \frac{1}{2}-2z$ y	$0,0,0$	$\frac{1}{2}, \frac{1}{2}+2y, -2z$ x
$-x, \frac{1}{2}+y, \frac{1}{2}-z$	$2x, \frac{1}{2}, \frac{1}{2}+2z$ y	$\frac{1}{2}+2x, -2y, \frac{1}{2}$ z	$\frac{1}{2}, \frac{1}{2}-2y, 2z$ x	$0,0,0$

Let us take the case of 2 1 2 1 2 1 and that is where we have taken the example right. So, 2 1 2 1 2 1 has four equivalent points. The equivalent points are x, y, z, half minus x, this one and this one before recalling. So, you generate the matrix. So, when you generate the matrix, you see that you get both Harker is all three Harker sections will appear corresponding to the 2 1 axis. So, with respect to x, there is a Harker section coming at x equals to half; with respect to y, there is a Harker section coming y equals half and z equals half.

So, if you take the Harker section coming with respect to x equals half, what are the equivalent points we find in that particular Harker section? One is this half, half plus 2 y minus z, another is let us me point a put an x here, half where else is half here, half, half minus 2 y, 2 z; then half half minus 2 y, 2 z; and then half half half plus 2 y 2 z. So, these four will correspond to the Harker section 1. So, in principle, these are the 4 bromine atoms related by equivalent points So, you see that each one of them now in separate columns, each separate column is under each separate equivalent point. So, you get the Harker sections corresponding to x equals half in these 4 marked as x.

Now, what about y? y will come for example here. I am marking it as y and then this is half y equals half then y equals half is here, then y equals half is there, and y equals half is there. So, once again you see it belongs to 4 equivalent points.

Now, the question comes up which x corresponds to which y and which y corresponds to which z that can be easily sorted out when once we now find out what are the z values. So, these z values are here; this is a z value, this is a z value, because z equals half, and z equals half, and z equals half. Apart from them as the requirement of the Patterson, you get 0 0 0 0 along the diagonals. So, therefore, you have x, y, z, all three located with respect to all 4 bromine ok.

So, now you can go to the next slide and see these four are the four bromine which we have located based on these three Harker sections. So, I want you to spend some time off you on your own rather than me going and explaining it, because these two are very clearly given slides through which you can now go back and forth and check up the coordinates, which we have got with respect to the Harker sections and Harker lines. So, 21 2 1 2 1 is going to give us a unique solution. What we want is only 1 bromine position, the rest of them we can generate by symmetry operation. This is just to see that Patterson will contain that symmetry information, we have illustrated this particular example.

Now, that is about all I want to say about Patterson method 6. So, the there is lot of things which one can say about Patterson methods, but there is no time which is left now we are coming towards the end of the course all together. So, I have to go to the next methodology, which is the direct methods. Once again at this particular point, let me stress that I am not going through the entire direct methods protocol. In fact, I am going to really rush through the direct methods, because of lack of time, but I will give you the basic physical meaning associated with direct methods.

And this is extremely important, because what you see when you do a structural determination is when you go to the stage where you have to determine the phases or solid structure, you essentially put up a inter mark and they were there it is written either Patterson of direct methods, you just say direct methods and put the enter button. So, the enter button now will take you to the direct methods. After a few minutes, you will get the solution to the problem. And you see the map the so called e-map we will discuss what is e the e-map which will tell you the positions of the atoms which you are rotating now as point atoms. So, the all the electron density associated with that atom will be there, but it is located as a point atom.

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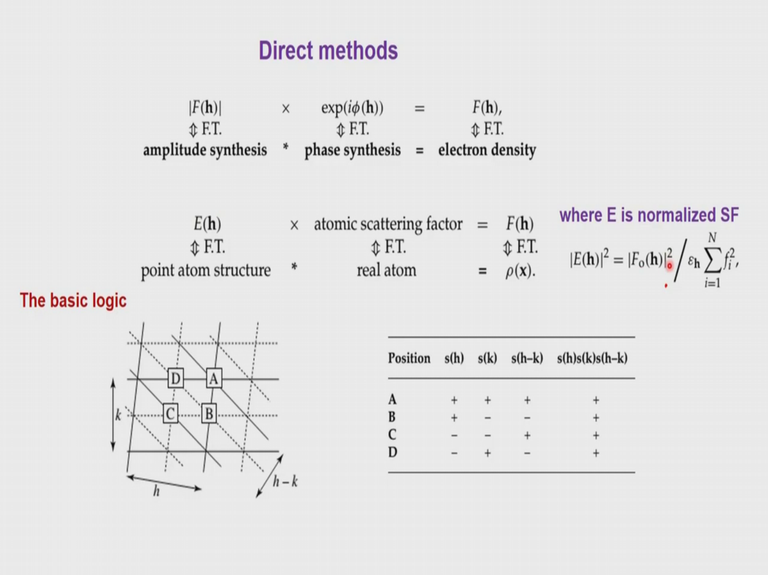

Direct methods

$$\begin{array}{ccccc} |F(\mathbf{h})| & \times & \exp(i\phi(\mathbf{h})) & = & F(\mathbf{h}), \\ \Updownarrow \text{F.T.} & & \Updownarrow \text{F.T.} & & \Updownarrow \text{F.T.} \\ \textbf{amplitude synthesis} & * & \textbf{phase synthesis} & = & \textbf{electron density} \end{array}$$

$$\begin{array}{ccccc} E(\mathbf{h}) & \times & \text{atomic scattering factor} & = & F(\mathbf{h}) \\ \Updownarrow \text{F.T.} & & \Updownarrow \text{F.T.} & & \Updownarrow \text{F.T.} \\ \text{point atom structure} & * & \text{real atom} & = & \rho(\mathbf{x}). \end{array}$$

where E is normalized SF

$$|E(\mathbf{h})|^2 = |F_0(\mathbf{h})|_0^2 \Big/ \varepsilon_{\mathbf{h}} \sum_{i=1}^{N} f_i^2,$$

The basic logic

Position	s(h)	s(k)	s(h−k)	s(h)s(k)s(h−k)
A	+	+	+	+
B	+	−	−	+
C	−	−	+	+
D	−	+	−	+

So, what is the logic of direct methods? These two this particular entry here will tell you what we are doing. Suppose, we take modulus of h and do what is known as a Fourier transform on just the modulus of h, it is known as amplitude synthesis. If you take exponential, I filed and use the Fourier transform, it will be the phase synthesis. So, this will do the amplitude synthesis, this will be do the phase synthesis, but we want to do these two together, and then do it on the F of h we get a Fourier transform which will give us the electron density.

A very beautiful experiment was done by a Ramachandran and his associates in this case. What was done was we took the structure of a compound, whose positions were known. And then they use the modulus of F of h, and did then amplitude synthesis of compound A. They also did the phase synthesis, because they know the structure of A, they did the face synthesis using the A, and then kept it aside. So, we have the amplitude synthesis, the phase synthesis and of course, the electron density of compound A. For compound B, what they did was to take the amplitude of compound B and put it into the phase of A. This was done in 1963 fantastic experiment. G N Ramachandran was a genius. I think he should have got a Nobel prize in India, you know he was never given. He also did the phi site map as most of the people know for the protein structures; he did the Fourier synthesis of different kinds of Fourier analysis. One of them is this and he also did several other things in crystallography, which included some work in anomalous dispersion and so on.

So, he did this exercise. So, you have a compound A, and you have the amplitude as well as phase, and then you calculated electron density. You now have the compound B, compound B only the amplitude was taken, but the phase of A was put on that. And what happened when you did the electron density calculation, you got back the structure of A. You took the amplitude of B, and put it on the structure of A, it did not give us any meaningful Fourier.

So, what it means is the importance of phase is very input very crucial. So, the structure essentially depends upon how the phases are rather than on the amplitudes. And so you got the structure of A in B, because you use the phase associated with A very beautiful experiment, which tells you that both these quantities are equally important, but the phase information is extremely crucial to determine the structure. And so we have to solve the phase problem, unless we solve the phase problem it is not possible to get to the structure.

So, what is done in direct methods is to take instead of F of h, we use the value of what we call as normalized structure factors E of h. And of course, with the phases it will be giving us the point atom structure. Now, this is the logic, which we use in case of the direct methods that we use E of h, which is the normalized structure factors. How do we do the normalization, that expression is given here. E of h square is equal to F naught of h square, which is our intensity that we have measured divided by the sum over i equals 1 to N of all the atoms whose atomic scattering factor is known at that under that particular structure.

So, if we know the number of the variety of number of atoms or molecular formula, we can calculate this quantity. This epsilon h is something which is referred to as the symmetry balancer. So, we actually use this to balance the symmetry, so some reflects some of the reflections are having a weight of 1, some have a weight of half depending upon the symmetry associated with the crystal system. So, at this moment, let us say epsilon h is equal to 1, but it can be 2, it can be 3 and so on depending on the equivalences of the h k l reflections.

We have not discussed that in this course. So, I am not going into the detail of it except to say that there is a value for epsilon x. For our discussion, we can take it as 1. So, effectively the normalization of the structure factor is done with respect to all the electrons in the system in principle, and therefore, we get E h of square. So, this now when we do a Fourier transform on that, it will give you a point atom structure as though the atoms are all points, which is wrong we know that it has a thermal ellipsoid, it has distribution of the electron density and so on.

But we will have a situation where we will have E of h it go undergoing a Fourier transform to get to the point atom structure. If we now multiply this by atomic scattering factor F of h and do a Fourier transform, we will get the real atom. So, because this part now we again multiply, so this Fourier transform therefore, will now have the F naught of h with the phase solution, and so we get the real atom that means, if we take F of h do the Fourier transform we get the electron density as h. So, this is what we are going to do in case of direct methods, but what do we need we need the phase of course. So, how do we find the phases? So, we will stop here.