Symmetry and Structure in the Solid State

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Lecture – 52
Fourier Syntheses

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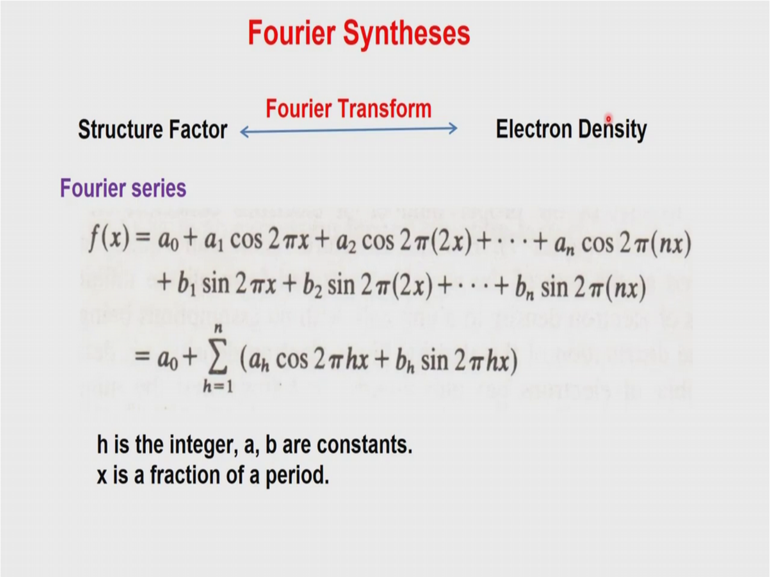

Fourier Syntheses

$$\text{Structure Factor} \xleftrightarrow{\text{Fourier Transform}} \text{Electron Density}$$

Fourier series

$$f(x) = a_0 + a_1 \cos 2\pi x + a_2 \cos 2\pi(2x) + \cdots + a_n \cos 2\pi(nx)$$
$$+ b_1 \sin 2\pi x + b_2 \sin 2\pi(2x) + \cdots + b_n \sin 2\pi(nx)$$
$$= a_0 + \sum_{h=1}^{n} (a_h \cos 2\pi hx + b_h \sin 2\pi hx)$$

h is the integer, a, b are constants.
x is a fraction of a period.

So, what is Fourier series? So, first let us learn something about the Fourier series. This is a very general expression which we have written here for Fourier series it can be f of x equals a naught plus a 1 cosine 2 pi x a 2 cosine 2 pi 2 x. So, we are now writing the cosine part of the f of x and then we write the sin part of the f of x with coefficients b 1, b 2, b 3 and b n. So, a 1, a 2, a 3 are the ones which are associated with the cosine the real part of the function and the b 1, b 2, b 3 are the ones which are associated with the sin of the function and you see that sin 2 pi x, sin 2 pi 2x, sin 2 pi 3 3x and so on sin 2 pi nx. It essentially represents a periodic function.

So, this overall is a periodic function. One is a periodicity associated with cosine, the other with the sin. Both of the cosine and the sin functions are anyway we know are periodic functions and therefore, effectively what it represents is a function like this. You see the resemblance of this with our structure factor expression in terms of the cosine and the sin being present, the only thing which is not present in this is the i, the absolute the imaginary component associated with that, but then we can also have the imaginary component brought in here with by expressing this in terms of an exponential.

So, basically the Fourier series represents a periodic function. So, if a function f which is a variable x associated with it and that value of x comes in these positions associated with the cosine function as well as the sin function. And, this periodicity is expressed in this particular form.

So, now, let us go over to a situation where we have h in this particular case is an integer, a and b are constants and x is a fraction of a period. So, this is the periodicity x is the fraction of the period.

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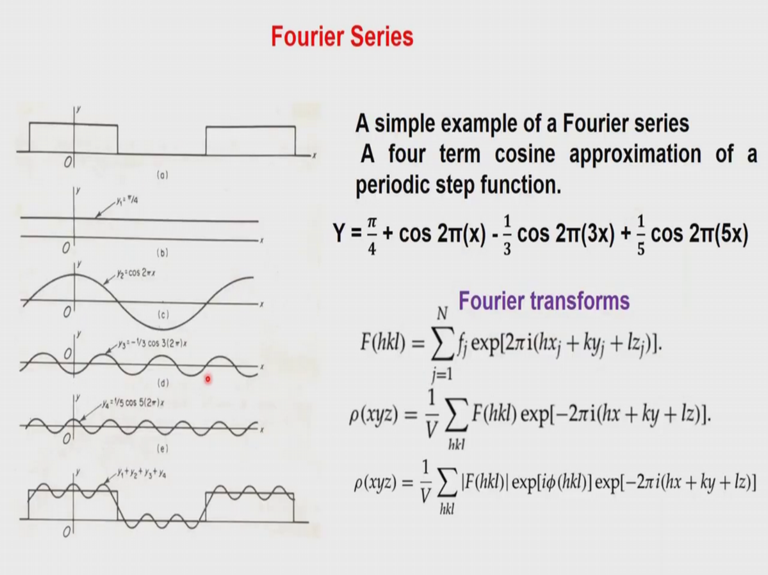

Fourier Series

A simple example of a Fourier series

A four term cosine approximation of a periodic step function.

$$Y = \frac{\pi}{4} + \cos 2\pi(x) - \frac{1}{3}\cos 2\pi(3x) + \frac{1}{5}\cos 2\pi(5x)$$

Fourier transforms

$$F(hkl) = \sum_{j=1}^{N} f_j \exp[2\pi i(hx_j + ky_j + lz_j)].$$

$$\rho(xyz) = \frac{1}{V}\sum_{hkl} F(hkl)\exp[-2\pi i(hx + ky + lz)].$$

$$\rho(xyz) = \frac{1}{V}\sum_{hkl} |F(hkl)|\exp[i\phi(hkl)]\exp[-2\pi i(hx + ky + lz)]$$

So, when we have a situation like this it is better we understand a little better in terms of actually considering a function which is periodic. So, what we do is we consider a periodic step function as is shown here. This is from the textbook of Stout and Jensen of course, what I will do is that towards the end of the course I will give acknowledgments to all the textbooks from which I have taken the pictures. I will also give references to all those textbooks and at the same time acknowledge the individual authors because, but for them this course could have could not have been compiled. So, we will come to that when we come to the end of the course.

So, this is a periodic function the periodic function is a four term cosine approximation of a periodic. So, we are dropping out the sin part, we are looking only at the cosine part and this is the expression Y equals pi by 4. Pi by 4 now defines the extent to which the step function goes. So, this is a step function. So, we step up here by pi one fourth, keep it steady come down then this is 0 for some time and then again one fourth and again 0 for some time and it repeats periodically. So, the periodicity is in terms of this to this distance. It could be any point here and any point here is a periodicity one as apply pi by 4 step associated with it.

So, this step function can get a mathematical form pi by 4 plus cosine 2 pi x minus 1 third cosine 2 pi 3x plus one fifth cosine 2 pi 5x; of course, we can add many many many more terms. We are now making an approximation by using a four term cosine function to fit this so called step function. So, we have a step function already given to us and we want to fit the coefficients in such a way and organize the expression in such a way that we fit it to this step function.

So, let us take the first part which is the pi by 4. So, if we take the pi by 4 this is represented in the diagram b here which will tell us that this is at a height of y equals pi by 4. So, this we call it as the first component y 1 which represents the period of the step which is repeated here, the amplitude of the step which is repeated here. The step size in other words is one fourth and this is told shown as this is pi 4 pi by 4 and that is shown in this first plot. The second plot takes the plots the second function which is cosine 2 pi x.

Now, what we will do is we plot the cosine 2 pi x y 2 is cosine 2 pi x and that cosine 2 pi x follows this part and similarly the minus one third cosine 3 2 pi times x is a plot which is shown here. And, the fourth function which is one fifth cosine 2 pi 5x has a function which is behaves like this in this particular plot. So, these are actual plots of individual components of these four term case. So, this is term one, this is term two, this is term three and this is term four.

So, now, we will represent a overall Y where we sum up all these four as is shown here. So, when we take the sum of all these four expressions, we will get a function which is shown here on top of the existing step function. So, our idea is to fit this step function by an equation right and we have taken four terms here and these four terms almost nearly fitted by this variation. So, this variation is showing the deviation of the fit with respect to the actual existing one.

So, suppose this you consider as your f ups ok, this will be your f calculated and you see that there is an approximation associated with it. Now, as we keep adding the functions we can add now the function one seventh minus one seventh cosine 2 pi 7x and then we can add the next function which is plus one ninth cosine 2 pi 9 x and so on. So, we keep on adding it. Take two infinite series then eventually what it represents is this function the step function.

So, the four term approximation is bringing essentially the near complete representation of the periodic function. You see the periodicity in the repeat of the four functions up there in pi 4 pi by 4 region and down below in the pi by 4 region. So, even though for example, if you add this at y one fourth throughout you see that the big dip in this function the dips associated with these functions will take it at the 0 level. So, y one fourth gets cancelled and therefore, you see that one can take additional terms we can have ten terms. The larger the number of terms the better is the fit and that is how we can now look at the Fourier series.

So, in the case of the resemblance of this Fourier series to what we are doing here the Fourier transforms you see that we have a large number of observations, j it is a large number this is over all the atoms, but the observations we have or in terms of the h, k and l and we have a large number of hkl measurements from our reciprocal lattice availability. So, from the reciprocal lattice we have measured a very large number of h k l. What we have to fit of course, is are the values of x j, y j, z j which are associated with the with the atomic scattering factor f j, but if you look at the expression below you see that this is now the Fourier transform of the top expression and the Fourier transform of the top expression now, gives us the electron density.

So, if you now consider this part this now should in principle represent the electron density associated with the system. And this now is replaceable this part is replaceable by this quantity which is practical. So, we write rho of xyz as equal to 1 over V because we are now looking at a volume of the unit cell. See this again brings us back to the symmetry and structural details we have because of the periodicity we do not have to sum it over the entire crystal. The crystal can consists of a large number of unit cells thousands of unit cells. The summation can be the calculation can be restricted to the volume. So, whatever we get in the volume will repeat in the next unit cell volume and so on. So, we can calculate only for that.

So, therefore, this expression rho of xyz will get this 1 divided by V as we see in both these cases. The presence of 1 divided by V essentially tells us that we are now in a define defined the single crystal and we have the unit cell that is defined. And, so, we then I will do it over sum over all the hkl values you see you have thousands of measurements. So, every measured F of hkl modulus you have calculated you have put it on an absolute scale by the Wilson plot and then this exponential i phi hkl will give us the phases. How do we get to these values is the next step which we will consider times exponential 2 pi i hx plus ky plus lz which is a representation of the atom position xyz.

So, with respect to all the atoms we have this general expression for rho of xyz which depends upon the summation over all h, k and l. In principle if we want a perfect fit to this y one fourth curve it should be an integral value of all these terms. In other words we should have replaced this by a triple integral integration going over h, k and l minus infinity to plus infinity in principle, but in a crystal we have the advantage of limiting the number of h values to a certain values k to a certain value and l to a certain value.

So, it is now a effectively a triple summation replacing the triple integral; integration over h integration over k integration over l is replaced by summation over h summation over k summation over l. So, this is a 3-dimensional summation which now takes the F hkl value. It also takes the phase into account and therefore, the electron density can be computed this represents now a complete representation or near complete representation of the periodic function.

So, let me repeat this issue a little bit. What is happened here is that we have now a function and that function is now chosen in such a way that it will mimic the axial electron density distribution inside the crystal. If we want to remain mimic that one we have to now have it in terms of what we call as the Fourier series and this Fourier series expansion we have discussed in terms of an expression which is a four term expression here. We see that it is almost there, if you add four more terms it will become better and better. So, as we keep adding terms it will become better and better. So, the rho of xyz as we keep adding over all possible hkl's this will give the best possible identification of the electron density. So, that is the logic with which we build up a Fourier series.

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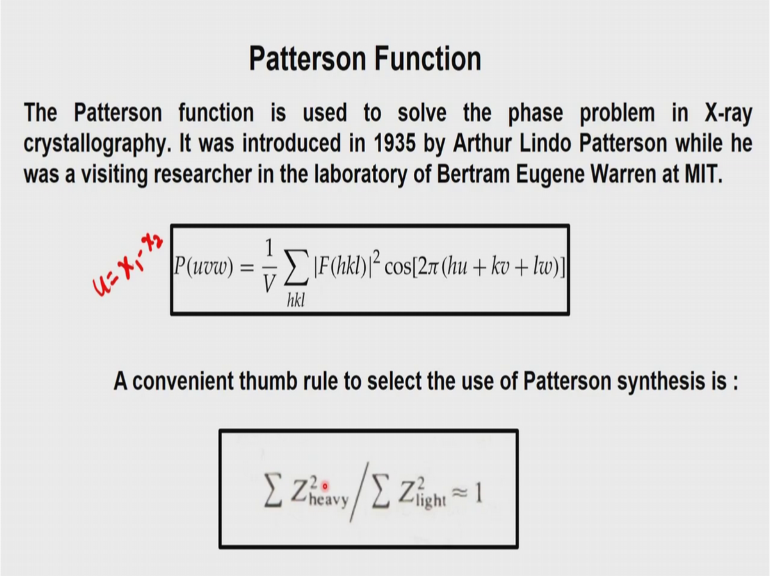

Patterson Function

The Patterson function is used to solve the phase problem in X-ray crystallography. It was introduced in 1935 by Arthur Lindo Patterson while he was a visiting researcher in the laboratory of Bertram Eugene Warren at MIT.

$u = x_1 - x_2$

$$\boxed{P(uvw) = \frac{1}{V}\sum_{hkl} |F(hkl)|^2 \cos[2\pi(hu + kv + lw)]}$$

A convenient thumb rule to select the use of Patterson synthesis is :

$$\boxed{\sum Z^2_{\text{heavy}} \Big/ \sum Z^2_{\text{light}} \approx 1}$$

Now, we will see how to solve the structure. You see the we have in order to solve this structure; let me go back to the previous slide in order to solve this structure, we need this fellow and this is the phase factor. As we have been telling over and over again this phase problem is a serious problem. In fact, it is so serious that there is no solution to this problem we can only get approximate values of the phases. We cannot get the actual values of the phases.

So, we can only make an approximation closest to the right phases and from there on go and try to improve the structure. So, that is why we get a trial structure and the trial structure is taken to the full better refined structure based on the fact that we have over determined data set. So, the determination of the phase therefore, becomes very crucial in order to that is the major step for toward structure determination. So, one once we have this, we can then use this expression to calculate the electron density distribution which will tell us where the positions of the atoms inside the unit cell.

So, the summation is over the unit cell and within the unit cell we will get the information of where the atoms are sitting and since F of hkl depends upon f j the nature of the atom will also be shown one once we compute this quantity. So, we will know whether it is a carbon nitrogen oxygen depending upon the value that we can associate with f of j. So, if this is the procedure we have to now think of the methodology by means of which we can solve the phase associated with this. So, the so called solution to the phase problem.

One of the solutions to the phase problem was arrived at by a person called Patterson. Of course, I have written it here that he worked in Eugene Warrens Warrens lab at MIT 1935 he developed this expression. This expression you see has lot of similarities to the previous expressions except that we are now using modulus of F of hkl square. When we use modulus of F of hkl square after the Wilson plot, we are using absolute values of the intensities. So, F of hkl square represents is proportional to the intensity with all the constants and things like that.

So, we have therefore, F of hkl square has the component here times cosine 2 pi hu plus kv plus lw where u, v and w represent the inter atomic vectors. What we mean by inter atomic vectors? These are vectors which are between atoms. So, for example, u is suppose there are two atoms in the structure u is equal to x 1 minus x 2; the x coordinate difference. Similarly, we can get v equals y 1 minus y 2; w equals z 1 minus z 2. So, this is the distance between the two atoms and that comes in as the inter comic vector and that is the factor which comes here.

Otherwise you see the similarity between the expression we had for the structure factor and the electron density. Here instead of the electron density we have the so called Patterson function. P uvw therefore, represents the Patterson function and since these are vectors this represents a vector space. So, these are this now defines a vector space we have the direct space we have the reciprocal space and now we also have the vector space.

So, Patterson represents the vector space. What you see here is the total absence of the face. So, we do not have the phase information that is required here; it is become everything is real. We will see the properties of Patterson in a few minutes, but here the quantities are only real quantities because we are using cosine function and there is no i sin component h is associated with it and as a consequence this can be directly evaluated in real space. So, it is a vector space and vector space now represents the real space vector space.

And, so, the way in which we go about the term using this Patterson function is something which we will describe in the near in the next few slides. Even though Patterson function looked as though it can solve any structure in fact, it in principle it can. However, one once we have this Patterson expression it becomes extremely difficult to evaluate individual atom positions from the collection of all these inter atomic vectors because Patterson is by itself a centrosymmetric system and it represents a centrosymmetric map and therefore, this vector map is centrosymmetric; that means, u can be x 1 minus x 2 it can also be x 2 minus x 1.

Both are one and the same and they are expressed with respect to a common origin. So, as a consequence there will be a large number of overlapping vectors.

So, the as the crystal size increases 1 or 2 atoms 2 or 3 atoms is no problem, but as the size of the molecule increase suppose we have 20 atom, 30 atom, 40 atom structures the number of vectors will enormously increase. We will see how it all happens in the coming slides. But, one thumb rule which I will mention at the very beginning is that when you want to determine the structure using the Patterson function. It is generally recommended particularly for small molecule structures, for a successful structure determination you should look at this ratio.

The ratio of the number of heavy atoms, the square of the Z value of the number of heavy atoms; sum over all the possible heavy atoms. Suppose, there is only one heavy atom then it is depends upon this Z square of the heavy atom, Z being the atomic number. So, if we have carbon it is 6 square it is not a very heavy atom, on the other hand if we have bromine we have 35.5 square which will be a very heavy atom. So, compare it to the weight associated with it. The weight associated with bromine is much much more than the weight that is associated with carbon.

So, it is generally recommended that when we want to use Patterson function and do not go to any other phase determination protocol. The approach of Patterson is preferred whenever you have this ratio satisfied, at least nearly equal to 1. It is not a not a necessary requirement that is why I say it is a convenient thumb rule. But, whenever we are close to this ratio with all the remaining atoms in the structure represented by this denominator and then it is not a serious problem to use the Patterson function.

So, Patterson function will give us now the heavy atom positions uniquely and fairly accurately because this information in the Patterson is after all a development of the presence is due to the development of the presence of atoms inside the unit cell and that is what we are looking for. So, it does give us the positions of the atoms particularly the heavy atoms. And, once we have the data which is now giving us the heavy atoms we can use the over determined data set to determine the remaining light atoms by the by a procedure which we described just now the using the Fourier synthesis.

So, this is just a convenient thumb rule. Now, let us look at the other properties of the Patterson function.

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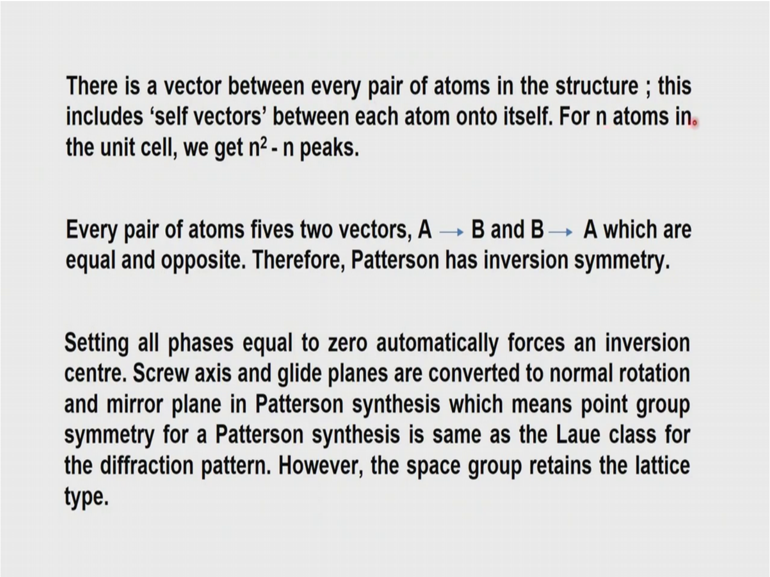

There is a vector between every pair of atoms in the structure ; this includes 'self vectors' between each atom onto itself. For n atoms in the unit cell, we get $n^2 - n$ peaks.

Every pair of atoms fives two vectors, A → B and B → A which are equal and opposite. Therefore, Patterson has inversion symmetry.

Setting all phases equal to zero automatically forces an inversion centre. Screw axis and glide planes are converted to normal rotation and mirror plane in Patterson synthesis which means point group symmetry for a Patterson synthesis is same as the Laue class for the diffraction pattern. However, the space group retains the lattice type.

So, as I mentioned there is a vector between every pair of atoms in the structure and this includes the self vectors that is x 1 on the x 1 y 1 z 1 on x 1 y 1 z 1 itself which will generate the origin peak. So, for n atoms if there are n atoms in the unit cell 20 atoms in the unit cell we get 20 square minus n minus 20 peaks. So, all these peaks now originate from the single origin and therefore, there is a severe overlap of these vectors.

So, every pair of atoms to form fives two vectors A to B and B to A which are equal and opposite. Therefore, Patterson has inversion symmetry. So, Patterson is always centrosymmetric. What is also important is the fact that all the phases, we can set them to 0 automatically forces inversion centre. So, that means, Patterson does not worry about the phase factor. What is important in a Patterson is therefore, we all these space groups which we have discussed now, now we will bring in back bring back the symmetry. See the discussion in this course is on symmetry rather than anything else symmetry and structure in the solid state.

So, we are looking at crystals and in the crystals we can now do the Patterson synthesis by calculating the Patterson map which is a vector map, but this particular Patterson map is always centrosymmetric whether the crystal is centrosymmetric or non-centric, the Patterson map is always centrosymmetric that is one issue. The second issue is that all translation involved components of our symmetry like 2, 1 screw axis, the glide planes; they will lose their translation component when we do the Patterson synthesis.

So, if it is a p 2 1 upon c the Patterson symmetry is 2 by m. So, this is already indicated in the international tables of crystallography and when we go back to the previous two classes and look at those slides which we have on the space group representation we also indicate the Patterson symmetry. So, the Patterson symmetry for p 2 1 by c will be p 2 by m. So, the Patterson will have only p 2 by m. On the other hand, if you have a c centred lattice let us say c 2 by c then the Patterson will be c 2 by m. It will lose the translation component associated with the screw axis and the glide planes, but the lattice information is preserved.

So, the number of possible symmetries that Patterson represents can easily be calculated and I wish I want you to calculate that. I would not tell you how many possible Patterson space groups are possible in principle. I want you to find out. So, what is happening is that the primitive lattices remain primitive, the centred lattices remains centred; that means, the c lattice remains c lattice, f remain f, i remains i and so on and all the translation components like in a structure of p 2 1 2 1 2 1 the Patterson symmetry becomes p 2 by m 2 by m 2 by m which is p mmm.

So, the symmetry reduces the neglects the translation components associated with the operations like screw axis and glide planes. However, it retains the centring information; the lattice information is retained. So, this is something which one should remember that is what is written in this paragraph. So, whatever I described just now is written up here. So, the Laue class the Patterson syntheses is the same as the Laue class for the diffraction pattern. However, the space group retains the lattice type.

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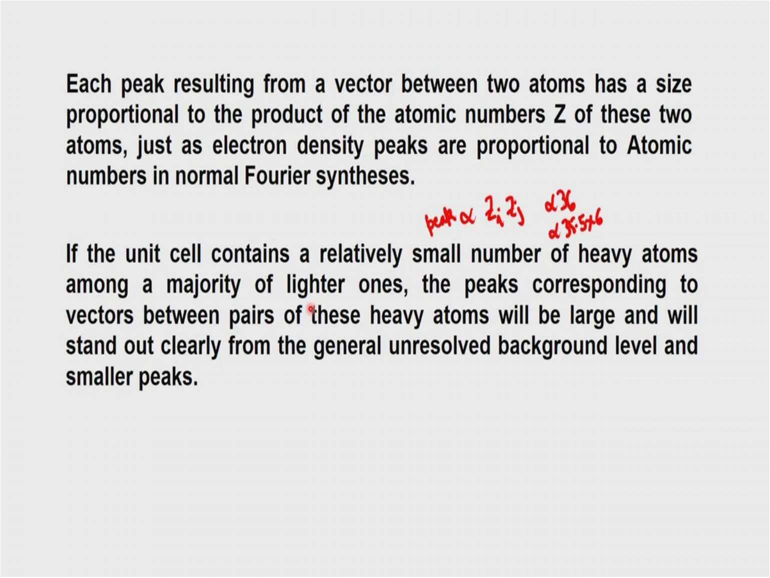

Each peak resulting from a vector between two atoms has a size proportional to the product of the atomic numbers Z of these two atoms, just as electron density peaks are proportional to Atomic numbers in normal Fourier syntheses.

peak $\propto Z_i Z_j$ $\propto 36$ $\propto 35.5 \times 6$

If the unit cell contains a relatively small number of heavy atoms among a majority of lighter ones, the peaks corresponding to vectors between pairs of these heavy atoms will be large and will stand out clearly from the general unresolved background level and smaller peaks.

Now, each peak resulting from a vector between two atoms as a size which is proportional to the atomic number ah; that means, to say that; that means, to say that if we have let us say a Z i, and Z j then the two atoms the product of the atomic numbers will be now proportional to the height peak height of the peak value. So, if there are two carbon atoms the Patterson peak will be proportional to 36, 6 and 6. If there are there is a bromine atom it will be proportional to 35.5 and we are now considering the vector between the carbon atom and the bromine atom this will be 35.5 times 6.

So, you see that the peaks that appear in the Patterson function are very sensitive to the Z value and therefore, if you have heavy atoms that is the logic of using that Z heavy square divided by Z square as a thumb rule because it is possible now when we compute the Patterson map. The peaks associated with the heavy atoms will stand out particularly if your if both Z and Z j.

Now we are looking at the bromine to bromine vector, it will be not only be longer as far as the bond distance is concerned because between bromine and bromine it will be very long distance compared to the distance between carbon and carbon which is a covalent distance of 1.54. Bromine and bromine may not have a covalent distance C to Br will have which is longer than C to C, but bromine to bromine distance will be more than 3, 3 and a half angstroms.

So, this vector therefore, will not only appear at 3 and a half angstroms from the origin it will also come with a Z i, Z j proportional to 35.5 square which is a very large value. And, so, it is therefore, possible to use the Patterson synthesis to identify the vectors that occur between bromine and bromine the vector that occur between carbon and bromine and so on. So, once you identify those vectors in principle, we can find out where these atoms are. So, this is known as the heavy atom approach and Patterson synthesis is basically used when we have a heavy atom along with a large number of small atoms.

So, the position of the heavy atom can be determined and when once we determine the position of the heavy atom we can put the heavy atom into the expression for F calculated and therefore, the phase that is associated with the bromine atom the heavy atom is now considered to be the phase associated with the rest of the structure, even it is it is an approximation, but you see the phase modification will be maximum in case of a heavy atom than compared to the lighter atoms and so, it will be a dominant factor.

So, one once we use that information and then go and do the F naught minus F c the more delta F synthesis or the difference Fourier synthesis then we will get the rest of the structure. So, heavy atom position first determined and using the heavy atom determined position we compute the F calc and then do a difference Fourier between F naught minus F calc. The heavy atom position disappears. The rest of the atoms one now will show up ok.

So, if you have for example, looking for a particular person who is thin among a large number of a few heavy people you remove the heavy person, then you can identify the thin person. So, just get rid of the heavy person and then you get the thin person. So, that is the idea of locating the rest of the atoms and when we locate all these atoms in principle we will get to the structure determination.

So, if the relay unit cell contains a relatively small number that is what I have written here among a majority of lighter ones the peaks corresponding to the vectors between pairs of these heavy atoms. Remember, we do not get the position of the heavy atom, we get the vector distance between the atoms will be large and will stand out clearly from general unresolved background level of the smaller peaks. So, it is possible therefore, to use the Patterson synthesis in case you have a heavy atom and in case the heavy atom is following our thumb rule. The presence of the heavy atom in the structure follows the some thumb rule. It can be more than one heavy atom, it is not necessary just to have one heavy atom, but this ratio should be reasonably satisfied.

However, very very many complex structures have been determined by Patterson synthesis because the development of the next method which we are going to discuss later in the class is the so called direct methods. By definition itself direct methods mean that we directly determine the phases. So, until the development of that took place and it matured into a very useful and straightforward computable methodology Patterson was the only preferred method. So, the preferred Patterson method therefore, is the one which in fact, sort of took care of everything.

So, the preferred Patterson method was determining many many structures. So, in initial days what people did particularly the organic chemists did was to have a heavy atom derivative of that compound which they want to get this structure of. So, suppose they make a structure and they want to determine the structure and there is no heavy atom what they do is for suppose there is a phenyl ring and a nitro group attached to it. To the nitro group they will attach a bromine atom, so that the structure of the molecule can be determined.

Very little did they realize at that particular time, that the two compounds will be very different in their properties. If one is looking for a property the heavy atom the substitution is not a very good idea because it is changing the nature of the compound, but you will get the structure, alright. So, initial days of structure determination if you look at literature people put heavy atom derivatives and determine the heavy atom position and thereby solve the structure. And, then they assume that without the heavy atom also the structure may be very nearly the same.

So, many of the early days structures therefore, use the Patterson methodology to determine the structure of heavy atom derivatives of organic compounds that is there plenty in literature, but then one once they realize that the property which your looking for is completely disappearing there is no point in introducing a heavy atom derivative. They had to live with light atoms. By that time the direct methods evolved and direct methods evolved into such a situation that, it could be easily programmed in. So, the development of high speed computers and modern technology for data collection enable the takeover of structure determination procedure by the direct methods over and over the Patterson function.

So, the Patterson methods are still used in various circumstances. In fact, they are very much useful in determining the structure of proteins as we will discuss later on very briefly because we are now coming towards the end of the course. So, we cannot now go into the detail of that. However, we will discuss it briefly other than that direct methods is the most preferred one because it is easy to program and what all you have to do now in the modern day structure determination protocol is to present enter button after getting these structures after getting the observed structure factors on an absolute scale and the rest of it is done by the machine using the direct methods.

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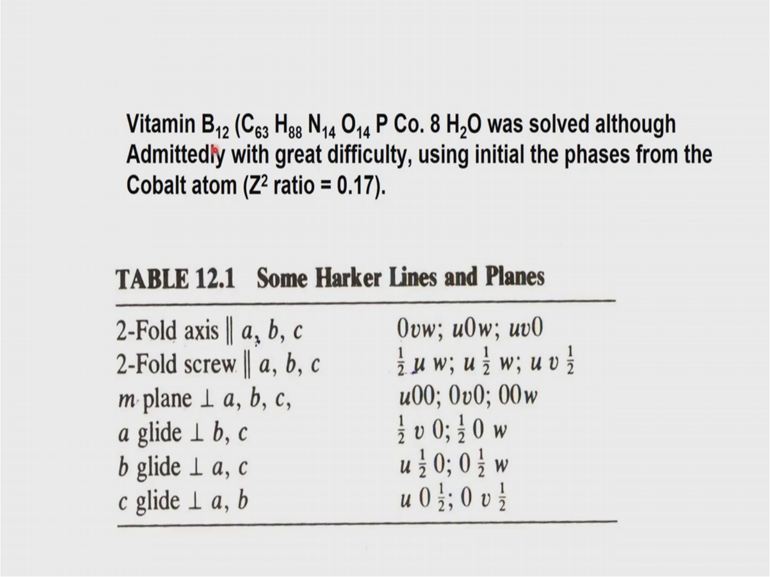

Vitamin B_{12} (C_{63} H_{88} N_{14} O_{14} P Co. 8 H_2O was solved although Admittedly with great difficulty, using initial the phases from the Cobalt atom (Z^2 ratio = 0.17).

TABLE 12.1 Some Harker Lines and Planes

2-Fold axis $\parallel a, b, c$	$0vw$; $u0w$; $uv0$
2-Fold screw $\parallel a, b, c$	$\frac{1}{2}\,u\,w$; $u\,\frac{1}{2}\,w$; $u\,v\,\frac{1}{2}$
m plane $\perp a, b, c,$	$u00$; $0v0$; $00w$
a glide $\perp b, c$	$\frac{1}{2}\,v\,0$; $\frac{1}{2}\,0\,w$
b glide $\perp a, c$	$u\,\frac{1}{2}\,0$; $0\,\frac{1}{2}\,w$
c glide $\perp a, b$	$u\,0\,\frac{1}{2}$; $0\,v\,\frac{1}{2}$

So, continuing with the Patterson we see that very complicated structures of course, were determined. In fact, the structure of vitamin B 12 which got the Nobel Prize to Dorothy Hodgkins was solved by the by the location of the cobalt atom. You see that my thumb rule will not be valid here anymore because there are so many other atoms, but still the structure could be done by identifying the cobalt position. In fact, this structure was done by a group of people who are working under Dorothy Hodgkins and I take pride in announcing that one of them happened to be an Indian and that Indian happens to be professor Venkateshan with whom I did my PhD. So, there is a connection.

So, this is one of the very difficult structures which was done in those days and the admittedly with lot of difficulty no it was not a straightforwardstructure solution and the phases from the cobalt atom were used. The Z square ratio I have given here just for yourwonder the Z square ratio was 0.17. We said it should be nearly 1, but if you take the Z square ratio here it is 0.17 and that shows the effort put by that group in order to determine the structure of vitamin B 12. But, no matter what this was a very crucial structure determined in those days, one of the biggest structures of those days which got the Nobel Prize to Dorothy Hodgkins who did wonderful things later on, but then this is where things worked out the way.

There is one little issue with Patterson and that issue is where is the symmetry? We have been talking about symmetry and structure in 3-dimensions unfold and then we are looking at projections we are looking at possibilities of translational periodicity is getting involved and so on, but what we said was done in Patterson the symmetry associated with to the 2, 1 screw axis becomes twofold the glide planes become mirror. So, where did where did the information of symmetry which we have in all these the crystal systems go away? It did not go away. It stayed in the Patterson and that is known as a Harker line and planes.

So, the information that is contained in Harker lines and planes will tell us the space group information whether they have the translation components associated with the space group which we have. So, even though the Patterson now has reduced the symmetry the information regarding the translation involved components which are present with that particular space group is incorporated into what we call as Harker lines and planes.

So, Harker of course, also should have walked away with a Nobel Prize. He did so many other things. In fact, he is the one who actually initiated work in the direct methods the. So, called Harker Kasper inequalities actually heralded the protocol which was eventually which eventually became direct methods, that is something which is remarkable. Harker also contributed to. So, many other things and the one of the things which Harker contributed was the structural determination of proteins.

So, I think we will discuss these issues with the Harker lines planes and contribution of Harker because it so happens that I overlapped with Harker, when I was a postdoc in

SUNY Buffalo and he unless I talk about him no course on symmetry and structure is complete because the fact that Patterson this took away the information on the symmetry. However, the fact that it retain the symmetry was discovered by Harker and that helped in solving many many structures.

Suppose, a heavy atom derivative gets into a p 2 1 2 1 2 1 structure and then the 2 1 2 1 2 1 information disappeared in the Patterson. You determine the position of the heavy atom all right, but how do you determine the rest of the atoms? Now, where is that information that is associated with the heavy atom position? In fact, the heavy atom position the location of the heavy atom position is contained in the so called Harker lines and planes.

In fact, we use these to determine the structure and that is why this contribution from Harker is enormously significant. So, we can say that you know there are so many people who are listed under those who did not get the Nobel Prize. So, Harker is one such.