Symmetry and Structure in the Solid State
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Lecture – 33
X-Ray Scattering: Fourier transforms

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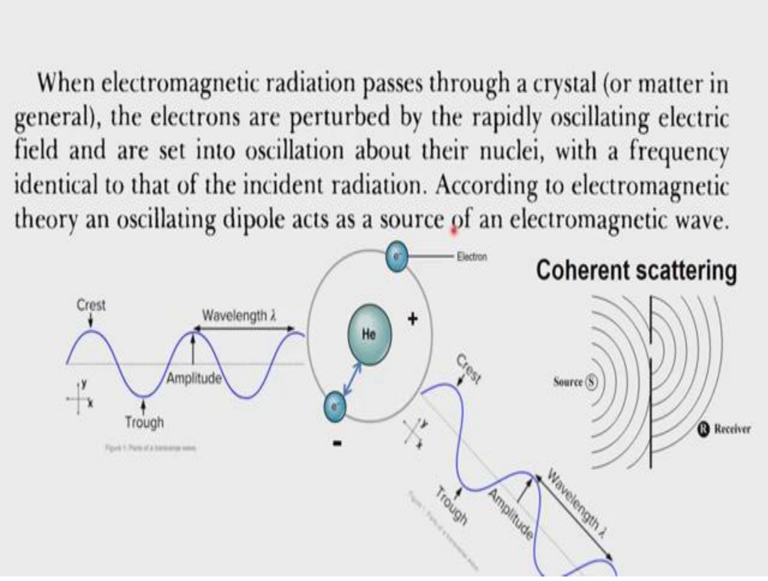

When electromagnetic radiation passes through a crystal (or matter in general), the electrons are perturbed by the rapidly oscillating electric field and are set into oscillation about their nuclei, with a frequency identical to that of the incident radiation. According to electromagnetic theory an oscillating dipole acts as a source of an electromagnetic wave.

So, we discuss this scattering theory yesterday. And it looks like that from the feedback I got from my students. It looks like an another explanation, and probably a thorough explanation of the scattering is required, particularly with the view that there are people from pharma industry, and possibly even teachers who are trying to go through this course.

And so what I thought was I will prepare some slides reorganize them. And then go through it once more, so that we get a clear feel for the scattering theory, because this is this is the basis of all scattering, and eventually the diffraction, and what happens, when X-rays fall on a crystal. And how the diffraction appears, and how the equivalent points respond, and how the atoms and molecules respond and so on.

So, what we therefore say is that when electromagnetic radiation passes through a crystal, the electrons are perturb by rapidly oscillating electric field. So, here is a wave, the wave as we know can be characterized in terms of its amplitude. And this angle at which it starts is referred to as the phase angle. The wavelength associated with the wave is now given by λ, and that is the distance from the crest to the next crest. It is also equal to the distance between the trough and the trough.

And therefore, when these electromagnetic radiation comes in and falls on an atom, this is a bloated picture of an atom, I have taken helium as an example. So, what happens is that there is a central nucleus, which is positively charged. And then there are electrons, there are two in the case of helium and these electrons carry a negative charge.

So, when this wave comes and disturbs these atom, as we see here that it generates a rapidly oscillating electric field, and this because the fact that the wave which is coming in can be described in terms of an electric field, which is $E_0 \cos 2\pi \nu t$ taking only the real part or $E_0\ e^{i2\pi\nu t}$, which is taking into account the complex nature of a wave; so these electromagnetic waves in general or complex quantities.

So, to describe this wave we make use of the complex numbers, we will go into the detail a little later. But, at this moment there is an incoming wave which comes and hits the atom, and the atom is set to vibrate. Now, because there is a heavy central nucleus, the electrons are disturbed much more the outer electrons particularly.

And as a consequence the positive and the negative charges develop, and therefore it is becomes a dipole a positive and a negative is separated by distance is a dipole. So, this dipole now oscillates with the same frequency as the incoming radiation. So, there is no change in the frequency and so we call it as coherent radiation.

And according to electromagnetic theory any oscillating field of this kind will generate its own wave as you shown here. So, this wave now comes out in this form, and this particular wave now is from this particular atom. So, it may so happen that there are several atoms in the crystal and all these atoms are connected to each other and so on.

As a consequence, we will get a large number of waves coming out with this interaction. The advantage again is the crystal and the symmetry and that is why you know we keep on stressing on the symmetry throughout this course. The fact that these atoms or inside a unit cell, and the unit cell obeys the laws of symmetry.

The issue of the obeying of the laws of symmetry brings in the fact that these atoms now or inside a lattice. And since, they are inside a lattice, the presence of the atoms follow the symmetry rules. And since, they follow the symmetry rules the coming out of these waves are actually in a direction, which is which is decided not just by the presence of the atom inside, but also by the presence of where the atom is present depending on where atom is present, different kinds of waves get to be coming out of the system.

And therefore, we have a several atoms giving rise to its own their own waves. And so if you see this as the equivalent of a crystal at this particular point, we see that there is a source which sends electromagnetic radiation has spherical waves, sufficiently long distances, the spherical waves can be approximated to a plane wave.

And this now in turn we will generate its own spherical waves, so this point now becomes if this is the crystals, now crystal becomes the source. So, from this we get lots of waves coming out, and therefore we have the process of interference which we recorded yesterday, and which tells us that only in certain directions, we will have the bright light coming out and the rest of the directions will be dark. So, we get in a three dimensional geometry, we get spots dark and white spots.

And these spots now will go to the receiver, which is essentially a detector. And we find out as a consequence the nature of the way in which this these; what we called as eventually reflections come up. We will get to a better understanding with as we go along.

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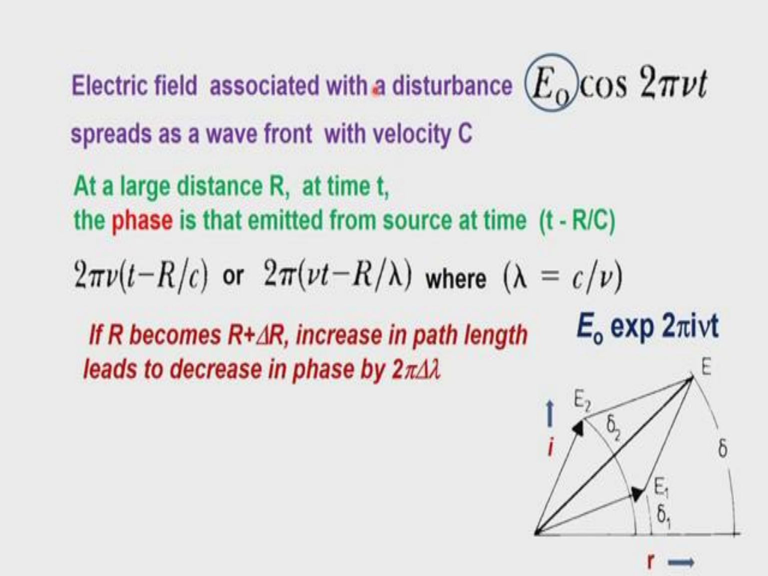

Electric field associated with a disturbance $E_0 \cos 2\pi\nu t$

spreads as a wave front with velocity C

At a large distance R, at time t,
the phase is that emitted from source at time (t - R/C)

$2\pi\nu(t-R/c)$ or $2\pi(\nu t-R/\lambda)$ where $(\lambda = c/\nu)$

If R becomes R+ΔR, increase in path length leads to decrease in phase by $2\pi\Delta\lambda$

$E_o \exp 2\pi i\nu t$

So, the electric field that is associated with the disturbance, which occurs due to the presence of the wave coming in the incoming radiation this is the wave. And that particular wave now introduces a certain disturbance at every atom position. So, wherever there is an atom, these dipoles get developed, and then we get this oscillations and these oscillations will inturn generate waves.

So, if we consider the electric field as $E_0 \cos 2\pi\nu t$, this quantity E_0 is the amplitude of the wave, and $\cos(\nu t)$ now represents the so called phase associated with the wave. So, the entire wave is described in terms of the amplitude, and the phase that is associated with the wave. And this particular this electric field now spreads as a wave front, and that wave front goes with the velocity of light the ***c*** is the velocity of light, because X-rays are photons, and they also have the velocity of light they are essentially light. So, these photons therefore will move with a velocity of light.

Now, just as we were mentioning as the spherical wave fronts, which spread from a given point at very large distances at a particular time t, what really happens is that this phase associated with that wave is at a time t, at a distance R. So, we now move to a distance R from the position of the scattering scatterer. And at time t, if we observe the behavior of the wave which is coming at a distance of R, it is actually the phase that is emitted from the source at a time $t - R/c$, because it is travelling with a velocity of c, R is the distance at which we catch it.

And therefore, whatever we measure at t is now that which originated at $t - R/c$, and that is the phase which we get at $t - R/c$. And therefore, the phase will be $2\pi\nu(t - R/c)$ or $2\pi(\nu t - R/\lambda)$, where λ is c/ν, this is something which there was a mistake yesterday while writing down, even though I explained it as λ equals c/ν, there was a mistake. So, λ is defined as the velocity of light divided by the frequency. We have also noted that the frequency will not change, after scattering that is the coherent scattering.

Now, what we do is we consider a situation, where the R distance R is now becomes $R+\Delta R$. So, if ΔR is an additional distance that means, there is an increase in the path length. Whenever there is an increase in the path length, there is a corresponding decrease in the phase. So, as we go longer and longer distances, we the phases keep on reducing associated with this scattering vector.

And therefore, we see that it leads to a decrease in the phase, and that decreases $2\pi\Delta\lambda$. So, if R+ ΔR, becomes now $2\pi\Delta\lambda$ will be the decrease in the phase. And since we already said that these are electromagnetic waves, the electromagnetic waves are indeed expressed as complex numbers. So, instead of $E_0 \cos 2\pi\nu t$, we have $E_0 \exp 2\pi i\nu t$.

So, this now is the representation, which is in the organd diagram below, we have the imaginary axis, and we have the real axis. And suppose we take two such waves coming out from this experiment, we have discussed only one here. Suppose, there are two such amplitudes which come out from a single point at taken as the origin, then we have a E_1 which has a phase of δ_1, and then we have an E_2 which has a phase of δ_2. Then what happens is that when these two combined due to interference, we will have the resultant. And the resultant is E, and their corresponding value associated with the phase is δ.

So, we noticed that as we go to higher and higher distances. So, if R becomes R+ ΔR, there is a decrease in the phase by $2\pi\delta\nu$. So, what are the consequences of these? So, we have to now see that there is a wave, the wave is represented by a complex equation which is $E_0 \exp 2\pi i\nu t$, this particular quantity represents the wave. The first part which is E_0 is the amplitude of the wave, $\exp 2\pi i\nu t$ is the phase associated with the wave. To describe the wave fully we need both these quantities, the amplitude as well as the phase.

Now, what really happens is the amplitude is the one which carries the amount of energy in the in the system. So, if we consider E_0^2, which actually represents the total energy, it is also refer to as the intensity of the wave. So, when the intensity of the wave has to be looked at, we consider the E_0^2 as the intensity of the wave; so the amplitude square.

So, what happens in a typical experiment, which we did in the last class about the interference experiment, for example is the fact that when waves coming, and two waves interact with each other, there is a interference. And that interference depends upon, where the waves originated from that means, it depends upon the δ_1 and the δ_2, which are shown here.

Depending on the value of δ_1 and δ_2, we will get a resultant which is corresponding to the phase δ and the value E. So, what is happening in this situation is that there are two waves coming out, and these two interfere. And the interference results in an addition of these two waves, which are coming in. The addition is with respect to the vector directions E_1 and E_2.

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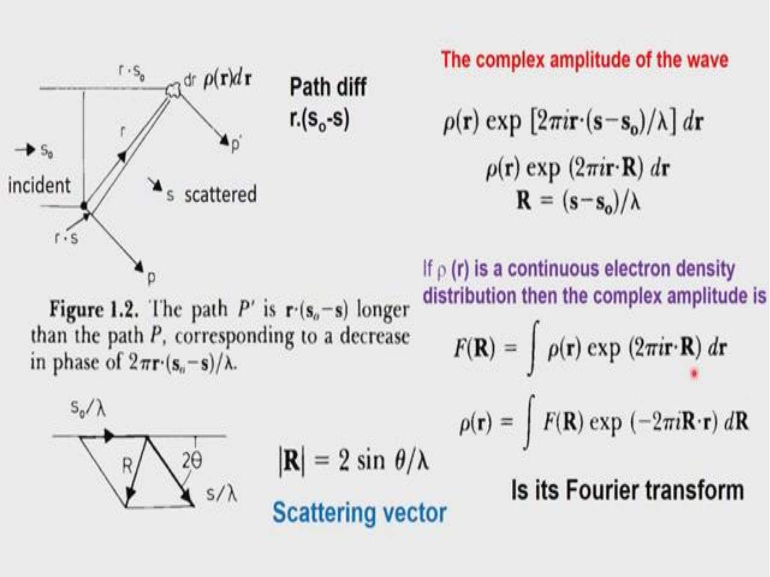

Path diff
r.(s$_0$-s)

The complex amplitude of the wave

$$\rho(\mathbf{r})\exp\left[2\pi i\mathbf{r}\cdot(\mathbf{s}-\mathbf{s}_0)/\lambda\right]d\mathbf{r}$$

$$\rho(\mathbf{r})\exp(2\pi i\mathbf{r}\cdot\mathbf{R})\,d\mathbf{r}$$

$$\mathbf{R} = (\mathbf{s}-\mathbf{s}_0)/\lambda$$

Figure 1.2. The path P' is $\mathbf{r}\cdot(\mathbf{s}_0-\mathbf{s})$ longer than the path P, corresponding to a decrease in phase of $2\pi\mathbf{r}\cdot(\mathbf{s}_0-\mathbf{s})/\lambda$.

If ρ (r) is a continuous electron density distribution then the complex amplitude is

$$F(\mathbf{R}) = \int \rho(\mathbf{r})\exp(2\pi i\mathbf{r}\cdot\mathbf{R})\,d\mathbf{r}$$

$$\rho(\mathbf{r}) = \int F(\mathbf{R})\exp(-2\pi i\mathbf{R}\cdot\mathbf{r})\,d\mathbf{R}$$

$$|\mathbf{R}| = 2\sin\theta/\lambda$$

Scattering vector

Is its Fourier transform

So, what is the consequence of this? The consequence of this can be seen in the next slide, where we see that we have the complex wave coming in. So, the incident wave which is coming in this is a wave, as we have imagined before. So, it has an amplitude and a phase. Now, this incident wave which is representing the energy associated with the incoming radiation which is E_0^2 is the energy, so that is referred to as the intensity.

So, there is a certain intensity of the wave that is how the light intensity comes up. And that intensity is now incident on, let us say a small volume dr in the in a in matter. It could be a crystal, it could be any other state of matter, but we will consider a crystal. So, inside the crystal that is a small elemental volume dr which we consider, where it has ρ(r)dr as the electron density that means, there is a certain amount of electron density, which stays inside this little piece.

And because this electron density is there, when the incident radiation falls on that it undergoes a the scattering because of the presence of the electron as we discussed earlier. There is an atom, atom is attached to the electrons, and the electrons are the ones which interact with the X-rays. Please notice that whatever interactions that occur in an X-ray diffraction experiments are more or less or we can say almost entirely due to the interaction of X-rays with electrons, this is the point which we should never forget.

And therefore, depending upon the electron density, we will get the scattering variations. And that will eventually interfere and generate the scattering. So, the incident radiation which is coming in which is generated from an X-ray source can be taken as in terms of a unit vector s_0, s_0 is referred to as the unit vector. And this unit vector s_0 now represents the incoming radiation, and this if we if we sit at an origin O (0, 0, 0), here we decide that this is the origin.

And we look at the what happens, when these electron density presents itself in front of the incident beam. So, in the incident beam comes up here, and falls on this ρ(r)dr, and then it is scatters in this direction *P-P'*. So, this direction which in which it scatters can also be considered in terms of a unit vector S. So, s_0 is the incident unit vector, and s is the scattered unit vector.

So, if you consider now the two paths, the path traversed by this line, and the path traversed by that line, you see that there is a difference in the path length. The path length is in terms of so what we do to take this origin drop a perpendicular to this point, which is now representing the incident radiation.

And take this point and from the electron density which is present at dr we drop a perpendicular, so that is r . s and this is r . s_0. So, the path difference therefore will be r . (s_0 - s) that is the additional distance with this wave this line has traveled representing the wave compared to this particular line. Since there is no electron density here, and there is a electron density there the extra distance that is (Refer Time: 15:38) is the path difference.

We already saw that a path difference of δ, we will introduce a if it is positive, it will introduce a negative change in the path in the phase difference. So, we can always calculate the phase difference in this particular case. So, the path difference is r . (s_0 - s), so the phase difference will be 2π, $2\pi(s-s_0)/\lambda$, where λ is the wavelength. So, the phase difference for the path difference of r . (s_0 - s), the phase difference is 2π, $2\pi(s-s_0)/\lambda$.

So, when we now decide to represent, what is the amplitude associated with this electron density ρ(r)dr. We bring in the issue of E_0 that E_0 is ρ(r)dr as given here, and this now becomes the so called phase term. So, the phase term you see is now saying s, $(s - s_0)/\lambda$, which is now the path difference $2\pi(s - s_0)/\lambda$. Since, this is a complex quantity, and it is with respect to r . $(s - s_0)/\lambda$. So, this is r . (s_0 - s) the path difference. So, the phase difference should be the phase difference should be smaller.

So, larger the path difference larger the phase difference, and therefore there is a change of sign. The change of sign is incorporated by changing s and s_0 positions. So, we have therefore the complex amplitude expressed in this following wave. So, ρ(r)dr this part will explain the will consist of giving the E_0 part the amplitude part, and this is the phase that is associated with the wave.

So, therefore we can now express the complex amplitude the associated with the wave in terms of ρ(r)dr exp 2πir . (s - s_0)/λ is the phase difference. Now, we make an approximation here is not an approximation, we give a nomenclature for this quantity (s - s_0)/λ. Notice that (s - s_0)/λ is representing a distance, which is in inverse space or reciprocal space, because λ is the wavelength, and it is measured as a distance. The difference (s - s_0) is also a distance.

So, therefore the we now replace (s - s_0) by a value R. And this R is referred to as the scattering vector. And this scattering vector will be equal to (s - s_0)/λ. So, therefore this quantity R has dimensions of reciprocal length remember this, because we are now going to worry about what are the types of possibilities this vector R can take in a situation, where we have the scattering occur occurring inside a crystal. So, this vector R and its properties are what we will worry about as we go along.

So, to summarize this part of the discussion, we have any incident radiation. And then a scattered radiation, it falls on a certain electron density ρ(r)dr, which is a small elemental volume inside the crystal let us say. So, as a consequence we get a path difference associated with the path in which the wave traverses, and that is r . (s_0 - s), which leads to a phase difference which is - (r . (s_0 - s)), which is (s - s_0) r . (s - s_0)/λ multiplied by 2πi indicating that this is a complex quantity.

So, we therefore get the expression for the complex amplitude as ρ(r) exponential this. And we now define (s - s_0)/λ in terms of a vector R. And this particular vector R, therefore has dimensions of reciprocal length. So, what you noticed in this expression is very interesting, there are two vectors r and R. The r is refer to the direct space distance, the distance from the origin to the electron density. So, this is indirect space and R is in the reciprocal space.

And therefore, r . R now is a product which represents a product of a distance and a quantity which has the dimensions of reciprocal distance or inverse distance. And so r . R will turn out to be a simple number, we will show that later on. But, in this particular case you see that as I have written here, the caption to the figure the path p' is $r \cdot (s_0 - s)$ longer than the path p. And therefore, the corresponding to a decrease in the phase, which is $2\pi r \cdot (s - s_0)/\lambda$, and we take it take this as a complex quantity; so i gets enough there.

Now, if $\rho(r)$ is a continuous electron density, suppose we have a little element of volume considered, and we said it is $\rho(r)dr$, but it is there now in the entire crystal. So, $\rho(r)$ now represents the continuous electron density distribution. Then the amplitude will be and integration over this quantity. So, this complex amplitude which we are talking about, the complex amplitude associated with the wave now coming out from a crystal, which has a continuous electron density distribution.

So, we assume that inside the crystal, we have all these atoms and molecules and so on. And the electron density that is associated with all these atoms, molecules, and so on or distributed in such a way that there is continuous electron density distribution, this is an assumption we are going to make. So, the whole entire crystal is now filled with electron density. Of course, the electron density will be more, when there is an atom position. Much more, when there is a bigger atom. Very less, when there is a smaller atom. And between molecules and there is some space in which the electron density will be reduced considerably.

But, essentially the whole unit cell now is filled with electron density. If that is the case, then the complex amplitude for the entire crystal will turn out to be $F(R) = \int \rho(r) \exp(2\pi i\, r \cdot R)\, dr$. So, this is an expression which we call as the structure factor. I have not written it down here, because we are going to bring it again and again throughout our discussion. But, please note that F(R) is referred to as the structure factor that is because it represents the strength that is associated with the amplitude of the structure, so because of the fact that there is electron density $\rho(r)dr$ inside the crystal, this quantity F(R) gains strength.

Now, we define what we call as a Fourier transform, we will define at this moment. And we will see that the Fourier transform is essentially a value of $\rho(r)$ taken outside now, so that means F(R) can be converted to $\rho(r)$ by this expression. And $\rho(r)$ can be converted to F(R) or F(R) can be converted to $\rho(r)$ by this expression, $\rho(r)$ can be converted to F(R) while this expression. And these two together form what are known as Fourier transforms of each other.

We will be spending considerable amount of time in understanding this quantity, but essentially what we say here what we see here is that a $\rho(r)$ is in the real space that is the electron density. So, if we want to calculate electron density, we need to have the F(R) values. And these F(R) values are in what we call as the reciprocal space.

So, the R vector is in reciprocal space R vector, and r vector is in the direct space. So, you also see that there is a change of sign here $\exp(-2\pi i\ R\ .\ r)\ dR$ that is the representation of the electron density. So, given the value of F(R) in principle we should be able to get $\rho(r)$, provided we know about this quantity which is the phase. On the other hand if we are given the F(R) and the phase value, it should be possible to get $\rho(r)$. It is also indicative that if we know $\rho(r)$ the electron density distribution, where the atoms are sitting and so on. We can easily calculate the quantity F(R) exponential, this the whole thing can be calculated.

So, if we know the structure, we can get the structure factor. If we know the structure factor in principle, we should able we able to get the electron density. The only catch here is that we need to find the phase. The problem is referred to as the phase problem, because the finding of the phase is not going to be straight forward, because the waves which are scattered emanate from different points in the entire crystal, and we do not know from where it is coming from. It also depends upon where the atoms are sitting.

Even though we now can imagine the crystal to be consisting of a of several planes, and then we can actually look at the possibility of sending an X-ray beam want to a given plane, and trying to get the intensity out of that plane. The actual scattering is done by the electrons, and therefore the atom positions. So, whenever we refer to as *x, y, z,* and say there is an atom in that particular position or an object in that position. It is the object which scatters, it is not the plane inside the crystal which scatters.

But, we will see as we go along, because this is something which we will always be confusing, when people talk about the scattering coming from planes. So, we have to sort out, what is the relationship between the scattering that comes from the planes. And what is the relationship between that and the electron density that is associated with the entire unit cell; so the entire unit cell has atoms and molecules and so on. And it is these electron density associated with these atoms and molecules, which cause these scattering.

You have to have a physical presence of the electron density to scatter these wave, but it is not necessary that these electron density should be associated inside the crystal with a plane, because we have been deriving equivalent points in the earlier classes. And equivalent points clearly tell us that the objects are generated by symmetry operations. And these objects which are generated by symmetry operations either are associated with general positions or they are associated with special positions. The general positions and the special positions, we have refer to refer to the possibility of having atoms associated with planes, it is not telling as or planes or axis or whatever.

So, if there is an atom sitting on a two old axis, we will get a special position. Atom sitting on a mirror plane, we get a special position. This analysis we have done in the last classes, but we have not done an analysis where the atom has been restricted to sit on a given particular plane. And that particular plane need not be having a mirror symmetry, but what we are going to do as a measurement of the scattered radiation because of the fact that the scattering now is in very loose terms quantized with respect to the crystal, because these measurements will come now with respect to where the scattering material is located, and this is located by symmetry rules.

So, the laws of interference will tell us that where these spots will come, so it is not a continuous distribution of intensities, we get discrete distribution of intensities. So, this is where we have to get a very clear understanding. And we will make an effort to get a clear understanding of this aspect as in the future classes, and in this class onwards. But, what is very important is the or these two equations, these two equations now are the key equations in structure determination.

So, either we get to measure F(R), we know that we can measure F(R) from whatever discussion we have had now, because we can measure the intensity of the spot, which is coming out after the diffraction, after the scattering. And scattering is now giving a spot because of the interference rules, which we have put in on a three dimensional object.

So, the scattering is now coming on to that particular spot. So, we can measure the intensity of the spot. The square root of the intensity will give F(R), but it gives only the |F(R)|. So, we need to get the phases. So, we need to get the phases in, and we will put these phases in one once we evaluate the phases, we should be able to get to the electron density. And that is the way in which we approach. Of course, the other approach is to have the electron density already known, we know where the atoms are and so on; we can calculate the corresponding F(R).

Now, you see the advantage here. The advantage here is the following, see since we have a problem of determining the phases experimentally, we cannot assure the accuracy associated with the phases because of the fact that we cannot assure the accuracy of the phases associated. The first calculation of using F(R) estimated phases to give a ρ(r) will be very approximate. So, we may not have the correct electron density. We may have a nearly correct electron density, but not the perfect electron density.

So, what we have to therefore do is use these two equations alternately. So, when we use these two equations alternately, so one once we have this information of approximate F(R) corresponding to the actual F(R). This approximate F(R), now is fitted into this equation. The F(R) the |F(R)| is accurately measured by experiment. The approximation comes only in the phase.

So, one once we lock into these phases, we can go back and calculate the electron density; so the way in which we process this protocol is known as refinement; so we go back and forth, and as we see go back and forth we can get more and more accuracies associated with the ρ(r) calculated. And therefore, the ρ(r), the F(R) which is calculated from the ρ(r), which is now going to be the calculated ρ(r) will be very nearly the correct structure. And we keep on repeating until the ρ(r), which is measured and the ρ(r) which is calculated eventually go towards 0. They may not go exactly to 0, but they go towards 0. And then we say we have determine the structure accurately.

So, therefore please remember that these two equations which are Fourier transforms of each other or actually lifelines, during the structure determination protocol. So, we must have an idea of how to use this, and everything originates from the fact that we have the scattering come in from the electron density that is associated with the material in this particular case with the crystal.

So, if there is large number of atoms inside the crystals that is one way in which the scattering can come, of course it automatically increases the volume, because each atom will occupy approximately 18 $Å^3$ in a general calculation. So, if you have that kind of a volume, if you depending upon the size of the molecule, and the size in which it has to grow into the unit cell, the unit cell size changes.

So, if you have a single atom, that single atom now will essentially occupy 18 $Å^3$ that is a space it generally occupy. So, here with the assumption is that atoms are spherical number 1. And they remain spherical even inside the crystal, even after they become parts of the molecule. And these molecules now going, and set in the unit cell. Under these circumstances, therefore we have to be we are making an very serious approximation, because we are neglecting the chemistry of the whole situation. The atoms are not going to be spherical in a molecule situation, because they get deformed.

But, we are now telling that the deformation is so small as a first approximation, we can still use these two equations to get to the final structure with respect to that ok. At this time we can stop.