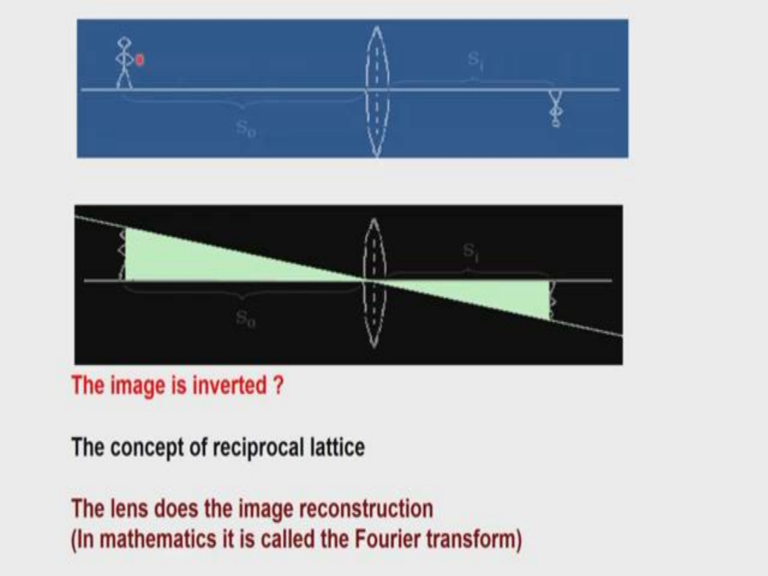
Symmetry and Structure in the Solid State
Prof. T. N. Guru Row
Solid State and Structural Chemistry Unit
Indian Institute of Science, Bangalore

Lecture – 32
X Ray Scattering; optical Analogy

(Refer Slide Time: 00:33)



The image is inverted ?

The concept of reciprocal lattice

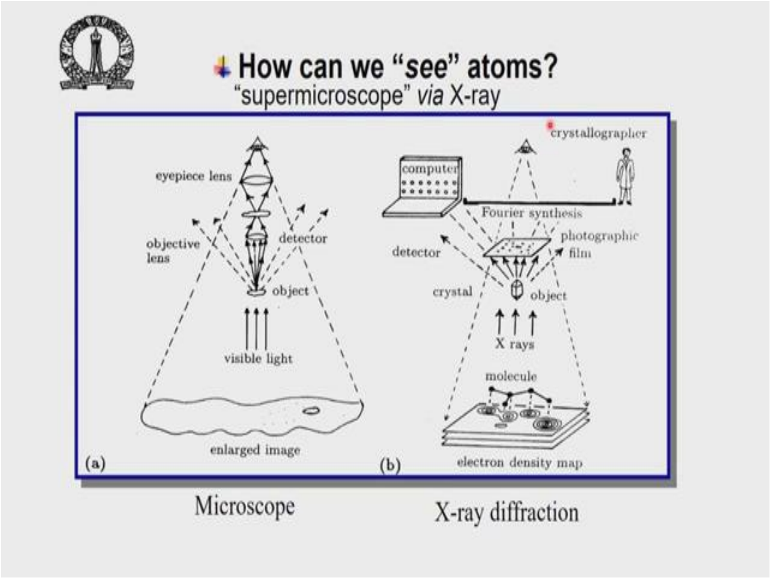
The lens does the image reconstruction
(In mathematics it is called the Fourier transform)

So, this brings us to the issue of how we can see atoms; say as we discussed in the previous slide, if we know the position of the object inside the unit cell in principal let us say this is an object inside a unit cell and we sent in an X-ray beam. If we know the positions of these atoms this edge of the elbow or leg or whatever, then it is possible to reconstruct the image by getting the amplitudes of the scattered radiation and doing a Fourier transformation. Lens is not possible, but we do the Fourier transformation; get the information of the position of the atom which is being present already.

But what happens is that we do not know where the atoms are and that is the job. So, there are two unknowns here. The positions of the atoms are not known. The associated phases are not known. So, in fact, we cannot get the image. So, we have to either guess the position of the atoms which is what was done in the earlier days of structure determination or guess the phase position and then we have to get to the; get to the this one the image of the object.

So, how do we go about it? We go about it in such a way that the image reconstruction has to be monitored by actually solving the phase problem. Now, how do we solve the phase problem? We solve the phase problem by guessing what the phases are. There is the only way we can get to the image of the object which means the positions of atoms.

(Refer Slide Time: 02:09)



How can we "*see*" atoms?

"supermicroscope" *via* X-ray

Microscope

X-ray diffraction

So, how do we really see atoms this is a picture which I have taken from the book of Glusker and True blood; a remarkably good quality book which I make I suggest that all of you go through it. Here, this is a picture from the older version of Glusker and True blood as you can see that we here have written photographic film. In modern days, we do not use the photographic film we use different kinds of modern day detectors like the CCD cameras or the EOS and so on, the photon detectors and so on.

Nowadays, a very high quality detectors are there to measure this. So, what is the thing we need to construct, we see if we have the knowledge of the phase as well as the amplitude information like in the case of a normal microscope, where we have the visible light as the probe and visible light falls on an object. The objects scatters radiation in all possible directions and we take now this scattered radiations and put the convex lens in front of it the so called objective lens.

We get an image of the object. So, the main object generates the image just like the previous slide we had and this image of course, can be made to enlarge by what is known as an eyepiece lens and this now enlarges the image.

So, suppose let us say this was a piece of the bread which we had and I put this here and put it under a microscope. I will get an enlarged image of the object of that piece of bread and you see some of these little pieces here that could be the pieces which we talked about in terms of cashews and badam and things like that.

So, effectively, we see they enlarge the image and therefore, we get an information about the nature of the object much better and this is how the typical microscope works a like microscope. We can use of course, different kinds of radiation and make the corresponding microscope, we can use electrons and make a electron microscope and we can use the electron microscope to fall on the object scattering will occur.

Now, instead of the lens we can have a measuring device like a CCD or something. So, in this particular example, we are using X rays, if the object is the crystal. Now one of the property is which the crystal has which I have not mentioned so far which you have learnt so far, but I have not mentioned it. Is the fact that there is a systematic arrangement of objects inside the crystal and this is governed by symmetry and because it is governed by symmetry the scattering they occurs not in all possible directions. But scattering occurs in only predetermined directions; predefined directions depending upon where the nature of the crystal.

So, we have let us say the crystal lattice known. We know where the equivalent points are; we know what are all the atoms which are there in the system. In principle what we measure or the scattering which is coming from individual crystal planes and therefore, it is not in all possible directions like our interference experiment told, if you have two slits; the two slit experiment gives you the interference pattern dark and bright images. If it is a three dimensional one you get spots week and dark spots and therefore, you do not get the continuous scattering as is as it happens here. But you get discrete directions. Now, the fact that this happens in discrete directions helps us to identify the spots.

So, we can identify the spots; we can also identify the coordinates of the spots and we when we identify the coordinates of the spots, then we identify the nature of the way in which the spots are distributed and this is referred to as the reciprocal lattice because what we get is before the image reconstruction and we get the intensities of each and every spot which is the intensity of the reciprocal lattice point. Then, we solve the phase problem by some means and do a Fourier synthesis using the help of a crystallographer in earlier days, but nowadays its only computer which can do the job.

So, we do not need a crystallographer; we just do these computers, use the computer and do the image reconstruction and then, one once we do that, we will get the image of the object. The image of the object now just like here, we saw all the additives; we will see the positions of the atoms. What we see are not the positions of the atoms per say we see the so called electron density distribution. The heavier the atom the more is the electron density; the lighter the atom the less is the electron density. So, you get what is known as an electron density map.

So, this in a nutshell tells you what we do in X-ray diffraction techniques. So, we have a crystal, the crystal obeys all the rules which we have formulated for the symmetry information and therefore, the scattering occurs in only specified directions, these specified directions now can be caught on a screen it could be a photographic film; it could be a detector. Then, we do the image reconstruction through Fourier synthesis. After solving the phase problem and we get the image of the object.

So, to recapitulate again, we have a crystal, X-rays are falling on the crystal. The crystal now we will scatter only in certain specific directions. We will find out what are those specific directions in a in the next couple of classes and then, these now create dark and white images we can say the so called reciprocal lattice will be created.

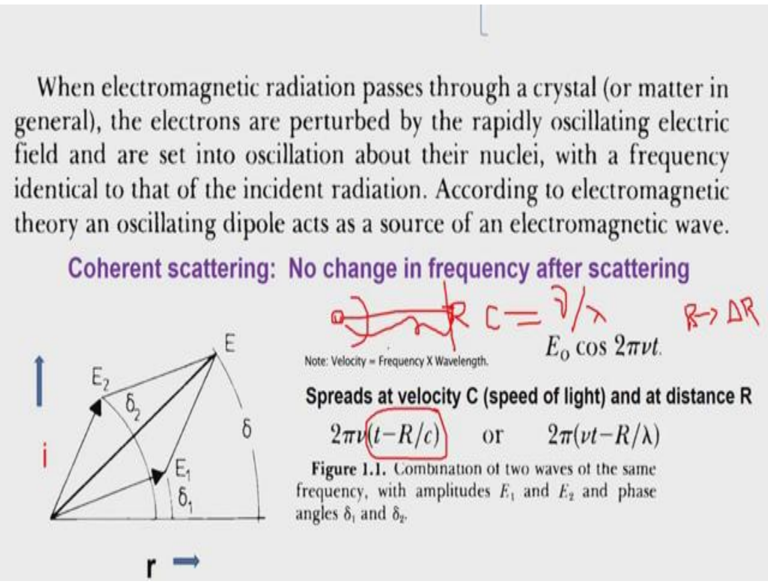
Because we have a lattice in the crystal, the crystal lattice will now create the reciprocal lattice, we have just seen why it should be reciprocal from the previous diagrams. And therefore, we this reciprocal lattice information can be now used. We measure the intensity of every one of the spots. We also estimate the phases associated with these spots.

We measure the coordinates of these spots in reciprocal space and then, do a Fourier synthesis after guessing what the phases are and then, we get an image of the output. And the crystallographer we will do the manipulations and the changes that are required based on the Fourier synthesis in order to get a final electron density map and this can be now done through computers. We have the synthesis Fourier refinement programs, where we improve the phase information such that we get to the final electron density.

So, what we get finally is the electron density map; the distribution of electron density associated with atom positions, wherever there is an atom we have a large amount of electron density as you all know. And therefore, depending on the strength of the electron density, we can also find out which atom is what. Therefore, we get the entire structure. And the structure now will come in a situation of a single units under the single unit cell, we know the equivalent points and therefore, we can determine the structure associated with the asymmetric unit.

So, what we eventually look for is the structure that is associated with the asymmetric unit in the unit cell right. So, how is the whole thing done?

(Refer Slide Time: 09:57)



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.

Coherent scattering: No change in frequency after scattering

R $C = \nu/\lambda$ R→ΔR

Note: Velocity = Frequency X Wavelength.

$E_0 \cos 2\pi\nu t.$

Spreads at velocity C (speed of light) and at distance R

$2\pi\nu\boxed{(t-R/c)}$ or $2\pi(\nu t-R/\lambda)$

Figure 1.1. Combination of two waves of the same frequency, with amplitudes E_1 and E_2 and phase angles δ_1 and δ_2.

So, this is the whole logic of how this whole thing has being carried out. So, let us go through it very slowly and systematically. So, when electromagnetic radiation passes through a crystal. So, we now have a crystal we are sending electromagnetic radiation now we know it is X-rays. So, X-rays are falling on the crystal or matter in general as we discussed so far the electrons are the ones which are perturbed that are disturbed by the rapidly oscillating electric field.

Since these electrons are now connected to the nuclei, the nucleus and the electron density gets disturbed in such a way that the positive and the negative signs there is a displacement and this displacement causes a dipole and this dipole now oscillates with the incoming radiation.

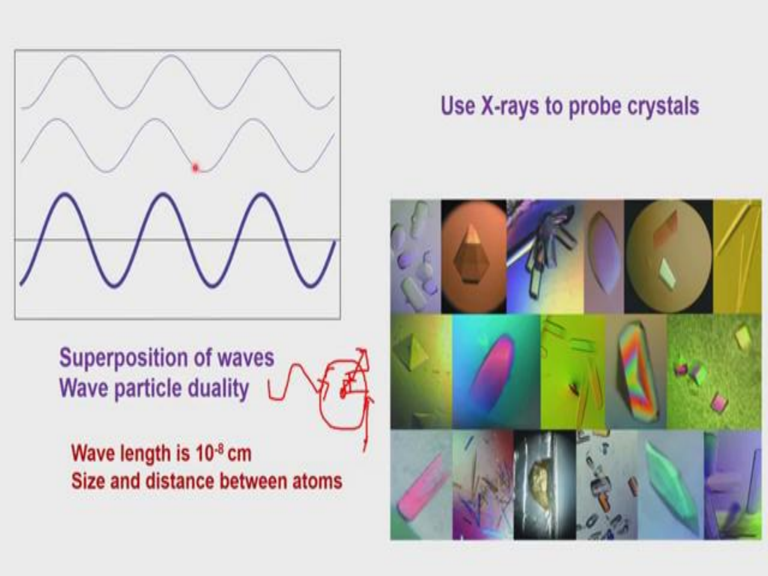
And therefore, it emits its own radiation and we have already made an assumption as I mentioned that it is coherent scattering. So, there is no change in the frequency after the scattering experiment is done. So, we shall take the electric field as $E_0 \cos 2\pi\upsilon t$ and if we take that as the electric field or the electric disturbance which occurs at the origin and whenever it falls on that object, we have to see when and where it falls on the object.

So, what is happening is that these now emanate as spherical waves as we saw from the previous diagrams, where we had an object and a slit experiment. So, it these emanate as spherical wave fronts. In general instead of using only the real part we also bring in the imaginary part of the axis which is mainly because electromagnetic radiation and the theory of electromagnetism essentially involves complex waves; waves expressed as cosine + i sine.

So, E_0 is therefore, $E_0\, e^{i2\pi\upsilon t}$. So, the $e^{i2\pi\upsilon t}$ can be expanded further into $E_0 [\cos 2\pi\upsilon t + i \sin 2\pi\upsilon t]$. So, it is a cosine and a sine function and therefore, we write this what is known as the organd diagram, where we have the imaginary axis along the y direction and the real axis along the r direction.

So, suppose we have two waves E_1 and E_2 and they are now coming out from this system and E_1 is at a phase which is δ_1 and E_2 has a phase which is δ_2, then these two now we will combine and the way in which the resultant is taken is very well known in mathematics. So, we take the resultant and the resultant of these two waves E_1 and E_2 is E which is now has a separate phase which is δ. This can be in fact, illustrated with a diagram here.

(Refer Slide Time: 12:58)



Use X-rays to probe crystals

Superposition of waves
Wave particle duality

Wave length is 10^{-8} cm
Size and distance between atoms

So, if we now say that this is the E_1 and this is E_2. So, depending upon the phase associated with E_2, this wave will develop either constructively or destructively as it happens here. So, this particular wave now is overlapping a different positions along the incident wave or we can take this wave as E_1 which is emanating from the origin which is the electron density position.

And E_2 is another wave which originates from some other atom, but we associate that with the origin, then we can combine E_1 and E_2 and get the average the resultant associated with E_1 E_2. And therefore, you see that if this is the phase associated with E_1 δ_1; this is the phase associated with δ_2, then we see that the phase associated with this will be δ which is a combination of δ_1 and δ_2.

So, if we consider it that way, we go back to that picture and we see therefore, we have an E_1 and then E_2, the resultant vector is along the E direction and so, this is the corresponding δ value. What is happening in a scattering experiment is one more issue which we have to consider, that is the issue of what we see and where it happens because if the electrical disturbance is associated with let us say E_0 $e^{i2\pi\upsilon t}$ and that is occurring at a particular origin 0 0 0 and then, we actually look at what happens at a distance which is R from the origin.

This particular wave which we are now talking about, which is a now a complex wave, it spreads at a velocity of light. So, it spreads at a velocity of light and it spreads as a spherical wave front; both we have seen and had sufficiently large distances r we have already decided, it will be a plane wave. So, it will go as $E^{i.(k.r)}$, where k is the wave vector and r is the position vector. So, that is associated with the amplitude E_0 and this will be the phase.

So, the phase now if it is real is cos $2\pi\upsilon t$, but since we are considering electromagnetic radiation, the phase will be $e^{i2\pi\upsilon t}$. Now, the frequency we have assuming is not going to change and therefore, even if we now look at a distance R, we are not looking at the disturbance which we are now looking at a disturbance which originated at a time t - R/*c*, because we are now measuring the intensity at a position which is at a distance R from the source.

So, if this is the source and we measure the distance at a distance R, then it is already travelled that distance with the speed of light and therefore, what we are measuring is that which occurred t - R/*c* before. Let me explain it a diagram. Suppose, this is our position of the object; this is the position of the object from which these scattering is emanating, we are now measuring it at a distance let us say R.

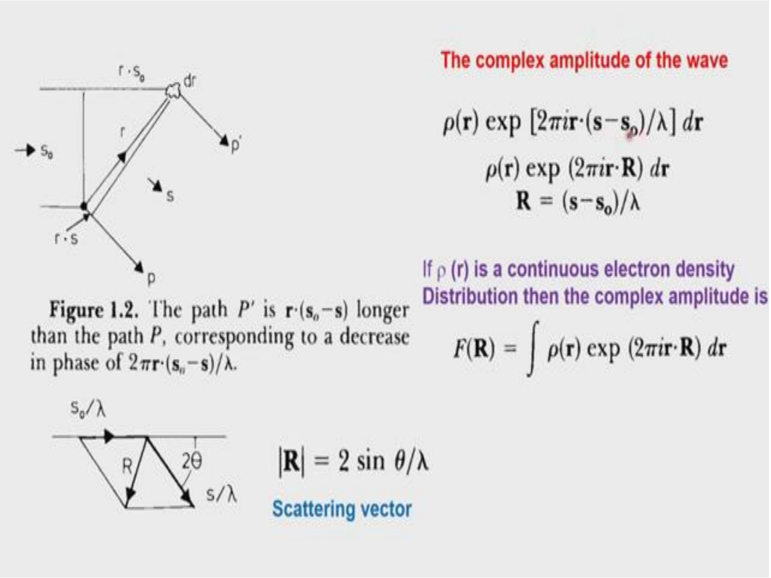
So, this distance is R now. So, the wave front is spherical to start with and somewhere here it is almost a plane wave. So, as we measure it at a distance R, we are now sitting at this position and measuring. Now, what we are measuring is not a t, but t - R /*c* because the wave started t – R/*c* times before at that particular position. Let me make it clear again, what is happening is that if we are measuring at a time t with respect to the position R, we are actually looking at the wave which originated t – R/*c*, where c is the velocity of light and R is the distance at which it has travelled.

So, light has already travelled by that distance and therefore, this is therefore, what is known as the path difference. This introduces a difference in path and the path difference is now can be expressed in terms of wavelength as well because *c* is equal to; *c* is equal to υ/λ. So, therefore, we see that it is dependent upon λ. So, we introduce this expression it is either $2\pi\upsilon(t - R/c)$ or $2\pi(\upsilon t - R/\lambda)$ and this is therefore, the extra path which it has traveled at any given time t.

So, the path that is travelled by the wave is covered by t - R/*c*. So, if that is the case then we have to consider that as the so called path difference or the phase sorry so called phase difference. So, if R becomes $R + \Delta R$ and this ΔR is very small let us say. So, if R becomes $R + \Delta R$, then there is a increase in the path since this is $t - R/c$; you see $t - R + \Delta R / c$. This is now the distance which is which has added a ΔR to that, we will make the value of the phase associated with that wave a little longer.

So, there is a phase difference which is negative here and therefore, the path difference is positive. So, for every additional path the phase difference is more. So, as we keep adding, the phase difference will become more and more. So, it is inverse of the two.

(Refer Slide Time: 19:24)



The complex amplitude of the wave

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

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

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

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

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

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

Scattering vector

And therefore, we see that the expressions can be worked out now, the way we have seen here. So, we now look at the complex amplitude of the wave the so called E_o. The E_o can be equal to if there is an electron density ρ(r); if there is an electron density ρ(r) dr that is present in space. Let us say and then you are sending in the X-ray beam the X-ray beam is coming in these particular direction and we call this quality as s_0 which is the unit vector of the representation of the so called wave front. Remember the wave front now which originated as a spherical wave front has become a plane wave.

So, therefore, we are writing a single line here showing the wave front. So, as the wave front approaches in this direction, we sit here at an origin and observe what happens to the presence of a little amount of electron density at this point. So, we put a little bit of electron density there and then the rays are coming in and we are sitting at this origin and observing what happens to that.

As we have said earlier that the electron density now will change the direction of the wave, it will start its own wave and that wave we will now originate in the direction *P'*. So, the original one is going in the in the direction of *P*, this scattered one is going in the direction of *P'*.

So, now *P P'* will define the so called scattered direction. So, incoming direction is referred to by the unit vector s_0. The scattered direction is referred to by the scattering vector s. So, what is happening is the fact that whenever you find this electron density, this electron density is located at a distance of r from the origin. So, we have an electron density which is located at a distance of r from the origin and we see therefore, that this wave travels an extra distance of $r \cdot (s - s_0)$.

So, since this travels and additional distance of $r.(s - s_0)$, this is the additional distance. This has travelled (r.s), it goes up like that; whereas, the $r.(s - s_0)$ is the additional distance. This will be the one which causes the phase change. So, the phase change therefore, is $2\pi\upsilon t$ that is $2 \pi i\, r.(s - s_0)/\lambda$.

We are assuming that there is no change in the frequency. So, the frequency factor does not appear here. It is only the change in the path length. So, the change in the path length is introduced as $\rho(r)$ exponential $2 \pi i\, r.(s - s_0)/\lambda$ and this is occurring due to the presence of an electron density which is $\rho(r)\, dr$.

So, E_o is equal to this quantity. The $(s - s_0)/ \lambda$ we replace it by a R which we call as the scattering vector. We will look at some of the properties of the scattering vector as we go along. The scattering vector has dimensions of reciprocal length; λ is the wavelength. So, R has dimensions of reciprocal length; that means, this scattering vector is something which could be a representation of the reciprocal lattice vector in some way. We have to find out it what is the representation of R because it is proportional to $1/\lambda$?

So, the fact that our image gets inverted after the scattering experiment is done, using the analogy of a convex lens experiment of the light waves. We see R is proportional to $1/\lambda$ and therefore, R could be utilized to define the coordinates associated with the reciprocal lattice. I am going to do this again one more round so, that there is no confusion associated with the understanding of this phenomena.

This is the basic phenomena of scattering. So, this quantity R can also be if you do a construction of this kind shown below here, s_0/λ is the incoming radiation s/λ defines the scattering direction radiation and then, this scattering is due to the presence of the electron density which is $\rho(r)$ dr. Then, the scattering vector is in a direction perpendicular to these two.

So, it is actually a bisector of s_0/λ and s/λ and I take this angle as 2θ, then it is usually shown that modulus of $|R|$ is equal to $2\sin\theta/\lambda$ and this is the scattering vector. You see the scattering vector modulus is proportional to $1/\lambda$ and therefore, this represents a quantity in reciprocal space.

So, if r is in the direct space, where the electron density is located in our object; the R is the representation of the reciprocal lattice vector which corresponds to the real space vector r. The R arises because of the real space vector r having an electron density associated with it and a phase which is defined as exponential $2\pi i\, \mathbf{r}.(s - s_0)/\lambda$.

And so, as a consequence the path *P*’, the extra path that is travelled is $\mathbf{r}.(s_0 - s)$ this; that means, when the wave is coming up here, it finds the electron density it travels an extra path which is $\mathbf{r}.s_0$ that is because this is the perpendicular direction which we have taken. From here, we draw another perpendicular.

So, therefore, $\mathbf{r}.(s_0 - s)$ is the path difference and we have already seen the path difference being longer now, the phase difference will be decreasing accordingly and the decrease in the phase is $2\pi i\, \mathbf{r}.(s - s_0)/\lambda$ and that is what is substituted here it. It is $2\pi i\, \mathbf{r}.(s - s_0)$, the decrease in the phase. The decrease in the phase can be represented as $(s - s_0)/\lambda$ and therefore, this is the path difference which occurs on the path difference is a consequence of the definition of the scattering length. So, R therefore, is a $\mathbf{r}.(s - s_0)/\lambda$

We will study this in little more detail and probably in the next class, but at this particular point we notice R is $(s - s_0)/\lambda$ and now we have to consider the entire crystal. If you consider the entire crystal there is electron density distribution depending upon how many atoms are there inside the crystal. So, what we do is we assume that the electron density is continuous in the entire crystal. It is not going to become negative, 0 and all that.

So, we assume that even if it becomes negative, 0 and all that, it is going to be a continuous function. Since, ρ(r) is a continuous function, we therefore, see that we can take the ρ(r) is the continuous electron density distribution; what all we have to do is to express the overall amplitude which comes out of the crystal.

See what is it we are looking for, we are now getting a we get back to this picture. We are getting the scattering coming from the crystal in a certain direction and this particular direction is due to the scattering which occur due to the presence of the electron density inside the crystal. And the presence of the electron density inside the crystal has now resulted in the change in the path length and any additional path length results in decrease in the phase associated with the wave.

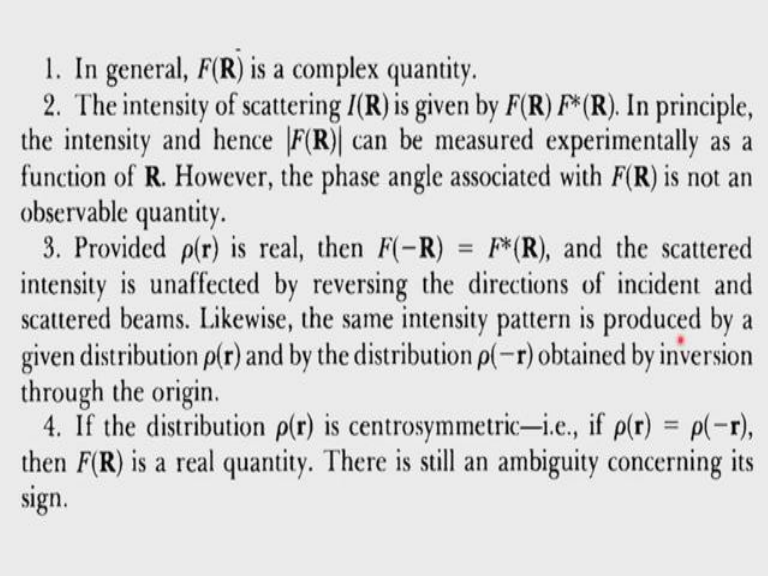
And so, we can calculate the complex amplitude which is in fact, if we measure the intensity the square root of that intensity will give us the amplitude. The complex altitude can be calculated by these expression and this is an expression which is associated with a element of a space which is representing ρ(r) dr. But if the electron density is continuous in the entire crystal space, this can now be obtained in the as the integration over the entire space the entire crystal.

So, the integration over the entire crystal of ρ(r) dr this is the phase factor and this is the quantity which contributes to the overall complex amplitude and therefore, we get F(R) which is referred to as the scattering factor. Notice that this quantity F is a function of the scattering length R and this particular scattering vector has the dimensions of reciprocal lattice. So, when we measure the so called intensity we are actually measuring the intensity coming due to the presence of the reciprocal lattice point.

So, the intensity is coming from a reciprocal lattice point identified with respect to the scattering vector R and therefore, we get F(R) and this is a complex quantity again and this is an integration over ρ(r) dr which is the overall electron density now inside the crystal and this is the modification which gets introduced in ρ(r) dr due to the fact that the object that is located inside the ρ(r) dr the atoms are located at different positions inside the unit cell.

So, you will get different phase changes causing this so, called path differences which are represented by the scattering vector R. So, R is $(s - s_0)/\lambda$ and we get F(R) is equal to this quantity.

(Refer Slide Time: 29:22)



1. In general, $F(\mathbf{R})$ is a complex quantity.
2. The intensity of scattering $I(\mathbf{R})$ is given by $F(\mathbf{R})\,F^*(\mathbf{R})$. In principle, the intensity and hence $|F(\mathbf{R})|$ can be measured experimentally as a function of **R**. However, the phase angle associated with $F(\mathbf{R})$ is not an observable quantity.
3. Provided $\rho(\mathbf{r})$ is real, then $F(-\mathbf{R}) = F^*(\mathbf{R})$, and the scattered intensity is unaffected by reversing the directions of incident and scattered beams. Likewise, the same intensity pattern is produced by a given distribution $\rho(\mathbf{r})$ and by the distribution $\rho(-\mathbf{r})$ obtained by inversion through the origin.
4. If the distribution $\rho(\mathbf{r})$ is centrosymmetric—i.e., if $\rho(\mathbf{r}) = \rho(-\mathbf{r})$, then $F(\mathbf{R})$ is a real quantity. There is still an ambiguity concerning its sign.

Let us go to the next slide and define find out the properties of F(R). We will do this derivation once again a little later in a slightly different way so that it becomes very clear of how the scattering is occurring. But before we go to that we just look at the possible properties of this F(R). F(R) is a complex quantity as we see already and the intensity of the scattering as I mentioned is given by F(R) times F*(R).

Now, this F*(R)is referred to as the complex conjugate F(R) and F*(R)in fact, essentially define I(R). So, if we measure the I(R) and we take the square root of this quantity, we will in principle get the magnitude of F(R). In principle, the intensity and hence F(R) modulus can be measured experimentally; therefore, as a function of R. However, the phase angle associated with F(R) is not an observable quantity.

So, then of course, a special property of a F(R) is that if there is a if $\rho(r)$ is real. F(- R) can be written as F*(R) and the scattered intensity is unaffected by reversing the direction of the incident and scattered beams. Likewise the same intensity pattern is produced by a given distribution of $\rho(r)$ and by the distribution of $\rho(-r)$ obtained by inversion through the origin that means, when you have a inversion centre and the electron density is measured, this inversion centre we will ensure that you will get a quantity which is actually a real quantity.

So, F(R) in that situation of a centro symmetric positioning of the atoms will become a real quantity. So, if the that is what is written here if the distribution ρ(r) is Centro symmetric, if ρ(r) = ρ(-r) let us say in $P\,\bar{1}$; then F(R) is a real quantity. So, this again we will now refer to the organ diagram and in the organd diagram we will represent what happens when there is a centro symmetry and what happens when there is no presence of an inversion centre and that is something which we probably we will take up in the next class.

So, at this moment just to revise what we have done so far in this class; what I will do is we have taken the scattering issue and we have now considered the scattering process in detail. So, what we have done in this particular case is to look at two possible waves which are interfering with each other; two possible ways which are interfering with each other; one is represented by E_1, the other represented by E_2 and then, the resultant one is represented by E. So, we depends upon what is the corresponding phase angles associated with E_1 and E_2.