Introductory Quantum Chemistry
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Lecture - 4
Postulates – Part 1

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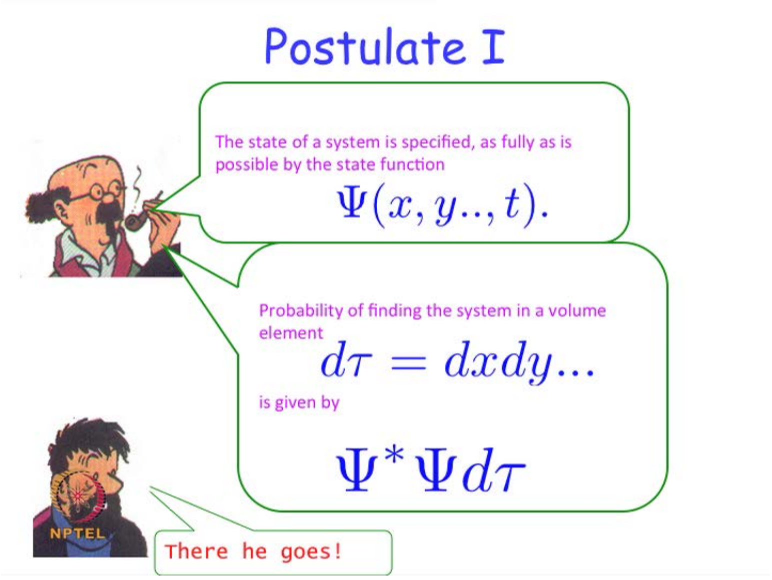

Postulate I

The state of a system is specified, as fully as is possible by the state function

$$\Psi(x, y.., t).$$

Probability of finding the system in a volume element

$$d\tau = dxdy...$$

is given by

$$\Psi^* \Psi d\tau$$

There he goes!

So, I told you it is possible for me to introduce quantum mechanics. So, starting with this particular approach which thinks of the wave function has being obtained as a sum over all possible paths right. You say that if my particle is there and if I want to calculate the wave function for the particle at this location, that location after a time ten nano seconds. Then I have to think of all possible paths not just one path all possible paths. Each path I have to calculate it is contribution then sum of all the contributions; I will get the wave function right.

So, this approach was introduced by Feynman and it is referred to as the path integral approach. So, the approach is actually due to Feynman interestingly, this was his p h d thesis this particular approach. You say quantum was developed and as you know in 1925,26 around that time, there were two of a nears effects that one was due to Schrodinger, Schrodinger was an expert on waves and he wrote down the wave equation, which we are going to see. And there was also Heisenberg, he wrote what is refer to as matrix mechanics, he developed matrix mechanics. And then within an year also

Schrodinger showed that these two mechanics which were, appeared to be very different. They were equivalent to one another that was proved by Schrodinger rarely little bit later within an year.

So, therefore, there were two approaches to quantum mechanics, which one is refer to as wave mechanics, the other was refer to as matrix mechanics and then the two together were refer to as quantum mechanics. But these approach that I have spoken about just now was introduced by Feynman in his p h d thesis around 1943 or so. And if you look into any chemistry book, you will not find this description and as I said this is the most typical the nicest approach that one can think of.

In fact, when I studied quantum mechanics, I studied it the traditional way. Traditional way means you introduce Schrodinger equation as a postulate and then go on to develop everything from there, but I never had thought that I had understood quantum mechanics until I came across this approach which made it as physical as possible.

So, this is very strongly recommended, but unfortunately as I was telling you in the previous lectures the mathematically speaking it is a little bit difficult to handle. And therefore, what we are going to do is we are not going to adopt this approach. Which is very nice, but instead we will go back to the traditional way having given you the physical ideas us to what is happening. I hope it is safe for me to go back and introduce quantum mechanics as a set of postulates which is what is usually done.

So, I am going to introduce it as a set of four postulates, but then this can be confusing because, in some books you may find five postulates. This is because you see no standard set of postulates, which have been introduced, but the five postulates in one book and four postulates in the other book, if you read the content you will find that they are all the same. So, the number of postulates does not matter, the total amount I may tell which is in there is the one that is the same. And again you may wonder why does one introduce this as a set of postulates, well you see this is as I always say this is like joining religion. If you join a religion even though is more Christianity then, there are certain things that you just have to believe you do not question them because there is no basic explanation for them.

There are certain assumptions which you have to make and the ones you make this assumption ones you believe in certain things you practice the religion. So, this is like the it is exactly the same here if you want to join the religion of quantum mechanics. You have to believe in these things right. As I told you, I have made the physical by introducing the path integral approach, but these postulates that you are going to see they will appear strange and therefore, they are difficult to believe in, but it is not possible to derive these from anything else. If you want you can assume path integral approach and derive many of these things or you can assume these postulates and derive the path integral approach. So, the two are equivalent right.

But if you want to join the religion of quantum mechanics you just have to believe in these and you may ask what is the big fun? Well the big the fun is that, once you have assumed this you can make loads of predictions and all your predictions are in complete agreement with experiment and therefore, that is proof enough anything that who cares in chemistry. You can explain, you can calculate using these postulates that is the justification for the postulates.

So, I am going to introduce as it is as a set of four postulates, here is my first postulate. What it say I kind of introduce the idea of a wave functions. So, what is says is that if I have any system, in the morning or in my previous lectures you see just the electrons that was my system and to specify, where the electron is what was I doing, I was using the wave function.

So, now we generalize and says imagine, you have any system may not be one electron, may be two electrons or may be hundred electrons that is my system or may be helium atom, helium atom has three particles a nucleolus and two electrons. So, to specify that system or if I have a benzene molecule, that is my system depending upon the situation my system may be different right. So, if you have any system what is going to happen is that, I will have a wave function, which I will denote by the symbol this symbol is capital psi, notation is important this is capital psi.

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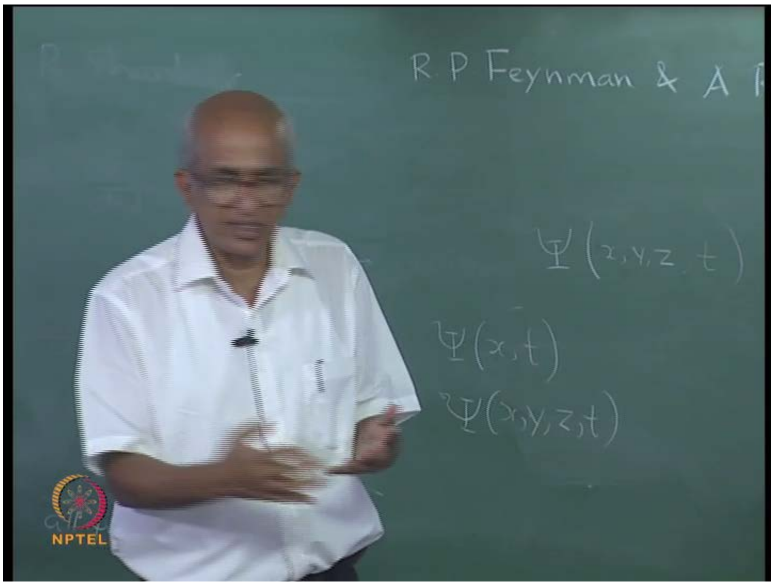

And this psi is going to be a function of position x y is the imagine. I have just one electron because, you are thinking of the electron I have one electron and one electron to specify this was electrons positioning space, I will need three coordinates Cartesian coordinates. So, if the electrons was it to specified by x y z. So, then in such a situation what will happen is that, the wave function will be a function of these three position coordinates, but not only that as time passes the wave function may change and it may therefore, depend upon, it will depend upon time.

So, therefore, you see if we have if I have an electron which is moving in three dimensional space, which is what it will do? Then it will have a wave function psi, which will depend upon the position coordinates of the electron and the time t. So, I can illustrate this may be, how let us say, I have just one particle moving constrained moving one direction. Well you may say that, there is artificial.

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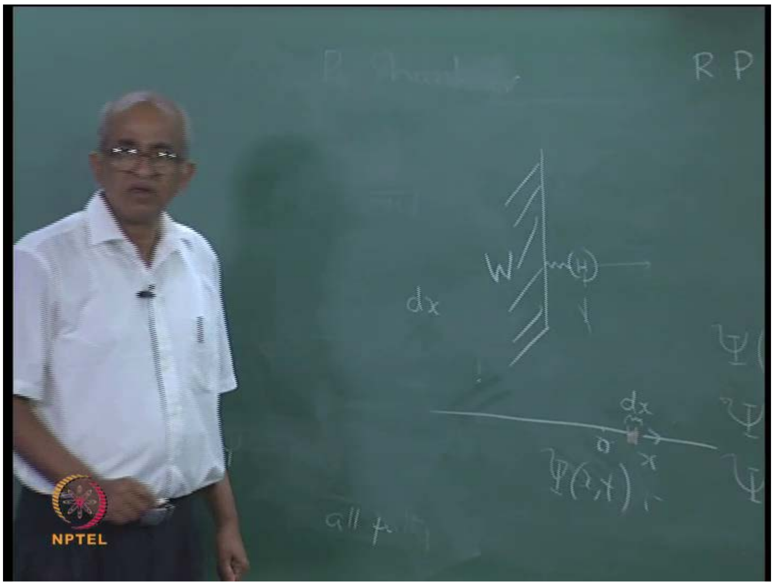

But let me give you a very physical example. Imagine I have tungsten metal, this is tungsten and imagine that I have a hydrogen atom bonded to the tungsten metal, which is a very physical thing you can have hydrogen atom, which is chemically attached, strictly speaking chemist soft down the surface of tungsten. And imagine that I displaces this hydrogen atom somehow and release it I pull it into this side and release it then; I know that it will execute vibrations in the perpendicular direction. And imagine that I am interested only in that vibrational motions.

So, then I say that is a one dimensional system why because, you need only one coordinate to specify the position of the hydrogen atom. If I say I will be interested in other can vibrate in this direction also right, if you are displaced in that direction it will execute vibration, but I am not interested in that. I am only interested in this particular vibrational motion and as long as I am interested in that vibrational motion. I can say this is a one dimensional system because, the position of the hydrogen atom can be specified by giving the value of the displacement of the hydrogen atom from it is equilibrium position that is enough. So, it is a one dimensional system.

For such a one dimensional system I mean if I was interested in the vibrational motion parallel to the surface of course, I will have to say that it is not a one dimensional system, but it vary I will need other coordinates like y and z perhaps right.

I will need y, if I am interested in only this vibrational motion, but suppose I have this other vibrational motion perpendicular to the plane of the board then, I will need all the three coordinates, but to make things simple I say only this motion is of interest to me. And in such a situation, what is going to happen is? That I will have a wave function psi and then it will depend, if you are interested only in this vibrational motion perpendicular to the surface, it will depend only upon position x right. That is all the wave function will depend only upon that and then the time t. So, that is for a one dimensional system.

On the other hand, if you had may be just imagine this room. Imagine it is completely empty, I mean, I want to make this system, my system as simple as possible completely empty. Imagine it is nice rectangular in shape and I have one helium atom in this room and what will the helium atom do? It will be moving around.

Now, my helium atom imagine this is just one particle, actually it is not just one particle because, there is a nucleolus and two electrons, but I am interested in the motion of this helium atom as I hold not I am not interested in the how the electros are moving because, I think of the helium atom as a single particle correct. And then to specify the position of the single particle in space, I will need only three coordinates right. I will have to worry about the internal structure later perhaps, but at the moment I am interested only in the motion of the system as I hold and in such a situation, what will happen? I will have my psi which is a function of because, I am thinking of helium atom as a particle I would have psi which is a function of x y and z and then time. This is how it is going to be.

On the other hand suppose I am worried about the internal structure, how the electrons are moving around the nucleolus right. Suppose I mean, I can be interested in that then what is going to happen is? I will think of a coordinate system like this x y z and I will say my nucleolus is at the origin because, I am not interested in the motion of this whole thing. I am interested in the motion of the two electrons with respect to the nucleolus then what I will do is?

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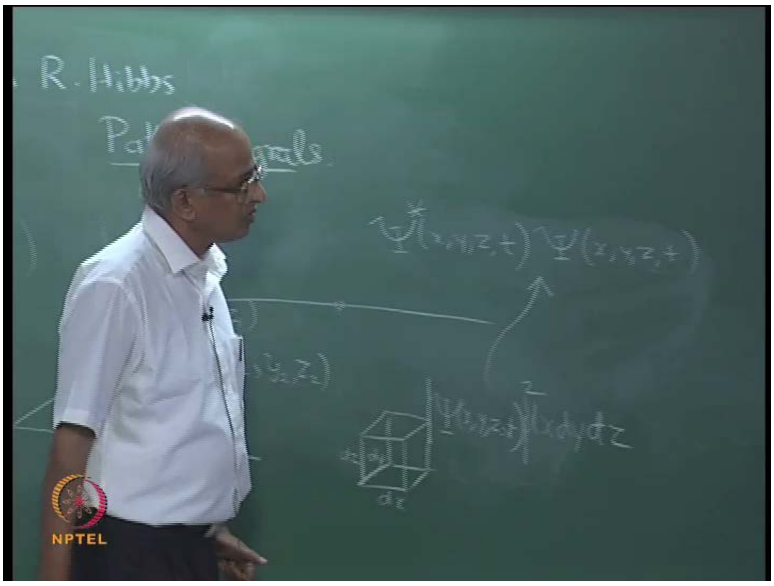

I will have the nucleolus and I will have one electron here perhaps and the other electron, there the first electron will be specified by it is coordinates which will be denoted by x 1 y 1 z 1 and the second electron will be specified by it is own coordinate x 2 y 2 z 2 . So, therefore, if I am interested in the motion of the two electrons around the nucleolus, I will need six coordinates. So, I can say, this is a six dimensional system why because; I need six coordinates to specify the positions of the two electrons in space.

And the wave function will then depend upon what psi, x 1 y 1 z 1. I am lazy, I do not want to write the whole thing, but x 1 y 1 z 1 x 2 y 2 z 2, z 2 finally, and then it depends upon time. So, this is how it is. So, depending upon the situation, you see, your wave function will be a function of as many position coordinates as you need at the time. The number of position coordinates will depend upon what you think of as your system.

But then you have the natural question what is the use of the wave function, you are just saying, if you have a system there is this function, which we refer to as the wave function. Another way it is used for the same thing is state function and in fact, that is what is used here. The state of a system is specified as fully as is possible by the state function instead of using the write a state function you could also write wave function their mean the same thing ok.

And then what is the use of this that is mentioned in this part of the postulate one so, the postulate one actually continues. Well let me illustrate this postulate with an example, you think of this hydrogen atom, which is vibrating perpendicular to the surface like this.

So, as I told you the position of this hydrogen atom to specify, it you need only one coordinates if you are thinking of vibrational motion. So, this is that coordinates and I shall refer to that as x and if the atom is not vibrating you say what is going to happen is I would expect it to be at the equilibrium position. Somewhere here, which I may denote as zero, zero is the equilibrium position and if it is moving what will happen it is moving away from zero to that side or may be to the other side.

So, suppose I think of the wave function for this, the wave function for this will be psi which is x a, function of x alone only one position variable and the time t. So, what is the use of this function? The answer is that, you think of a small interval along this axis remember our descriptions of earlier wave function is going to give me the information contained in the wave function is the probability.

So, therefore, we wanted to calculate the probability of finding the electron in this small tiny interval, in this interval how much is the length of that interval? The length of that interval is d x. So, using the wave function you can actually calculate this probability how will you calculate it? The answer is very simple; if you think of the probability physically, see if this width of this interval is large, you would expect that the probability also will be large, well if the width is small the probability will be small.

So, therefore, the probability definitely has to be proportional to that distance. So, if this interval is small definitely, I will have d x in my probability because, it has to be proportional and our earlier discussions imply that, they it has to be proportional to square of psi right. So, therefore, I would expect that the probability will be given by an expression which, I shall write as psi of x t magnitude square, this is the probability according to this postulate this is actually postulate. This is the probability that the particle will be found in a small interval of length d x ok.

Now, if you think of a helium atom in this room we can generalize this very easily. If you think of a helium atom in this room and imagine that, I have a rectangular small rectangular parallelepiped region in this room, which I am going to draw on the board. Well because, you are thinking of the helium atom remember the wave function is given by psi, which is a function of x y z and this is helium atom and for that imagine in three dimensional space. You have three dimensional space and you think of a small rectangular parallelepiped region in this room and because it is small I will say that the sides of this small volume are d x d y and d z. So, this is going to be d x the height is going to be d z and the one of the sides, the other side is going to be d y.

So, that the total volume contained in this rectangular parallelepiped; obviously, is d x into d y into d z and it is obvious, I hope that the probability that my helium atom will be found inside this rectangular parallelepiped, which is somewhere in this room right. May be here a rectangular parallelepiped with sides d x d y d z the probability that my helium atom will be in that inside that small volume has to be proportional to that volume. So, it has to be proportional to d x d y d z and then naturally what would you expect you would also expect psi x y z t magnitude square.

So, this will be the probability that the helium atom will be within this room sorry, not within this room, but within that small rectangular parallelepiped region. Now, in general say, what is going to happen is? That this psi will be a complex number it will not be even be a real number, it will be a complex number with a real and an imaginary part. And that is why I had been putting this magnitude square, but instead of taking the magnitude and squaring it. If you like you can also do the following you take the wave function take it is complex conjugate right. And multiply the two together and that is nothing but the square of the magnitude of the wave function.

So, instead of writing magnitude of psi square, you can as well write psi star psi, this object is nothing but psi star psi. Now, as I told you depending upon the problem that I consider for example, here I was thinking of a hydrogen atom then you have d x while if I am thinking of a helium atom in this room what happens is? This is my probability right, this is my probability.

Now, if you look at this expression say there is d x d y d z, that is a volume. And you multiply that volume by this factor you are going to get the probability density sorry, not the probability density, but probability. Take the volume multiply it by this object you are going to get the probability. And therefore, this object is referred to as the probability density; I mean you would take volume I made a mistake. So, it may not be clear, I take a volume and multiply it by density I will get the mass.

So, similarly you take the volume multiply it by this object you are going to get the probability of finding it in that small volume. So, therefore, this object it should be referred to as a probability density.

So, psi star psi is a probability density. And what is usually done is, you see your psi may depend upon several variables depending upon what your problem is. So, therefore, you do not normally write all the variables. So, you just write psi then multiply it by psi star right. And if it is a helium atom you will say you will have to multiply it by d x d y d z to get the probability, while if it is just this hydrogen atom vibrating perpendicular to the surface then you just have to multiply it by d x.

So, depending upon the problem you have to modify whether it is d x or d x into d y into d z and so on. So, we simply adopt a general notation, you say that the probability that the system may be in a volume d tau, d tau stands for d x if it is a simple one dimensional problem. Well it will stand for d x into d y into d z because it is a three dimensional problem. So, therefore, this is going to be the probability, psi star psi into d tau is going to be the problem, where what is d tau? d tau is written there it is actually d x into d y, it is not complete because, you may have more things there are dots there were dots there which say sometimes disappeared, so d x into d y into d z, if you have ten variables there. If it is a product of all of them and so again it is natural to refer to this as probability density.

Now, I want to describe to you some very interesting consequences of this postulate, this is the first postulate in all details. Let us take this one dimensional system hydrogen atom perhaps vibrating perpendicular to the surface. In that case the probability that the hydrogen atom is between x and x plus d x let me be very clear this is the point x that is the point to be having position coordinate x plus d x, I am thinking of the probability that the particle is in this interval d x and that may be obtained as psi star x psi x t into d x this is the probability.

That is what we have assumed we have postulated now, but if that is the way it is. Suppose, I want to calculate the probability that the particle is anywhere between minus infinity and plus infinity, but how will I calculate the total probability that if it is somewhere between minus infinity and plus infinity.

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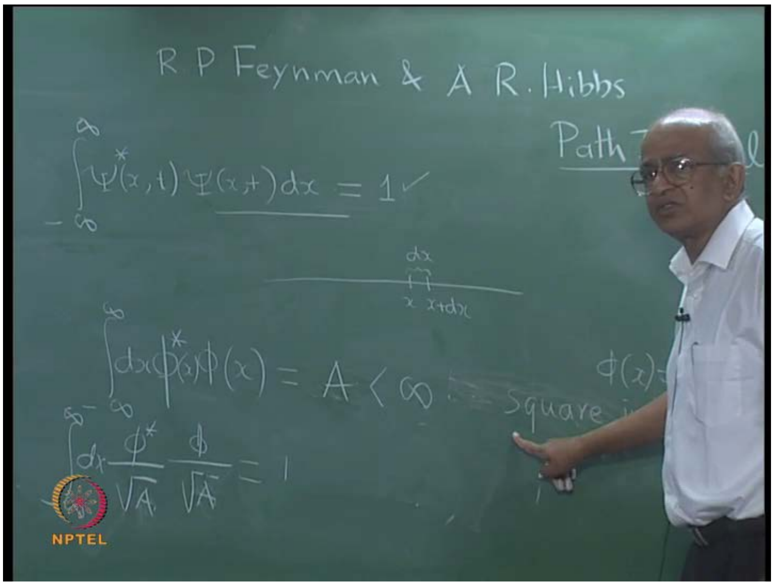

The answer is that I have to integrate this from minus infinity to plus infinity to get the total probability. But again basically I know that, if I calculate the total probability as far as I am concerned the particle is sure to be in that interval because, it cannot be anywhere else. So, the particle is sure to be in that interval and therefore, if I calculated this I know that it should be equal to unity.

So, my state function or my wave function should be such that, this integral must be equal to unity. So, this is a condition that my state function would have to satisfy otherwise I am going to say that it is not acceptable. Because, I am saying that postulating that psi star psi d x must be the probability that it is in a small length the d x. So, total probability has to be equal to 1. So, therefore, this integral has to be equal to 1.

But suppose, I have a function for which it is not equal to 1, for example, may be I have a function and I can think of any simple function, but let me just take a function phi of x I am not going to write the time dependents anyway, let us not worry about that. I want to just illustrate the points.

Suppose it is such that phi star phi x multiply it by d x integrate it from minus infinity to plus infinity this will be an acceptable function. If the answer is equal to 1, but suppose the answer is 10 and; obviously, this does not satisfy the condition. That I wanted to satisfy correct, but then if you think about this, from phi suppose, I construct it phi divided by square root of 10 this is a new function. It is not phi, but a new function which I have constructed from phi, what I have done? I have multiplied it by 1 by square root of 10 and now this new function if it took it multiplies it by it is own complex conjugate and the volume element d x and integrate it from minus infinity to plus infinity what would be the answer? The answer will be 1.

So, even if my phi does not satisfy the normalization condition and hence this is not an acceptable function from phi, I can construct a new function right. I just multiply my phi by a number and the new function is such that it is satisfying this condition. This process is referred to as normalization and any function which satisfies this condition, we will say that it is normalized any function satisfying that condition normalized and if a function is not normalized. It is possible for you to normalize it what you do, you multiply it by an appropriate constants.

So, suppose this is not 10, but if it is equal to 8. A constant which I denote as A, then what we do? You will multiply it by, you will take phi multiply it by 1 by square root of A that is all that you need to do and the new function is normalized. So, it appears as if I can if you have any function it appears as if I can normalize it right. Well how can you normalize it, I take phi multiply it by phi star integrate it from minus infinity to plus infinity, I find whatever that answer is take 1 by square root of that number and multiply phi with that right.

So, it seems that I can do this, it does not matter what the function is, but that is not true. Because suppose, it so happens that this number when I did the integral, the number turns out to be infinity right. I mean I can if you want I can give you examples for this a function like e to the power of, suppose a function is e to the power of x by 2. Well I do not think work this out, but if you would actually perform the integral you will find that phi star phi integral from minus infinity to plus infinity actually is infinity.

So, if it so, happens that if A is infinity then, what will you do? You will take your phi multiply it by 1 by square root of A, but A itself is infinity. So, 1 by square root of A will be sorry, square root of A itself will be infinity and therefore, 1 by that is going to be 0. So, your new normalized function is 0, which is totally meaningless because, you cannot say that I have a particle and it is wave function is identically equal to 0. If the wave function is equal to 0 then the probability of finding the particle anywhere in space is 0, but I know that the particle is there.

So, therefore, you see a wave function equal to 0 is something that I do not want that is not the acceptable for me. So, therefore, the condition is that, this A has to be less than infinity. If A is less than infinity then, I can normalize the function and a function which satisfies this condition. That it is integral actually phi star phi is less than infinity is referred to as a square integrable function.

Now, if the word is itself obvious, you take the square of the function roughly speaking integrate it from minus infinity to plus infinity the answer is, if the answer is less than infinity then you say that it is a function that is square integrable right. The word square integrable means this integral equal to A is less than infinity. So, you can carry out this process of normalization only if the function is square integral only if A is less than infinity can we carry out process of normalization. So, we therefore, what we will do is we will not impose this condition it is not really necessary to impose this condition. It is enough if I impose a condition that the function is square integrable because as long as the function is square integrable, I can carry out the process of normalization in and get a wave function which is satisfying that condition ok.

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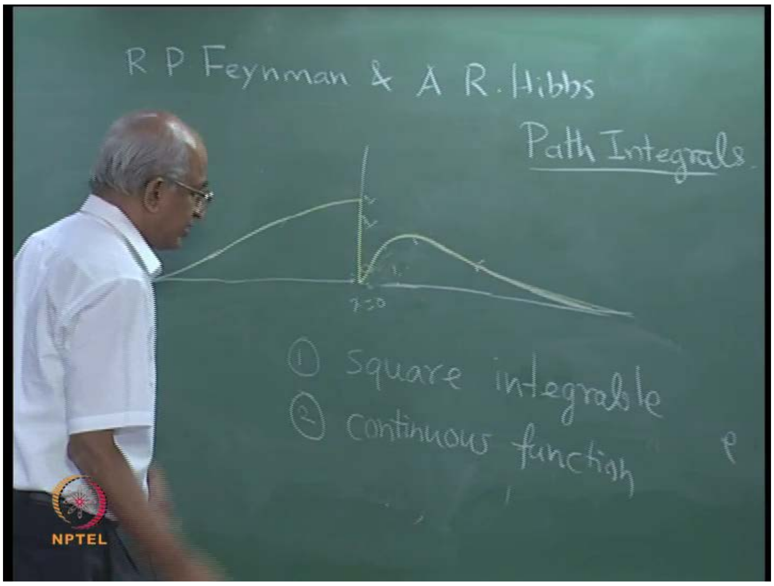

So, that is one result and another result that, I would like to speak about is the following. Suppose I say, I have a function phi of x and I am going to say that it is of the form sin inverse of x, well of course, I mean you will have to say x is between 0 and well minus 1 and plus 1. This is only for the sake of illustration essentially. So, if you think of this interval running from minus 1 to plus 1, imagine I am evaluating this is x running from minus 1 to plus 1. Suppose, I put x is equal to 0 then what will happen is? That I will have sin inverse of 0 as my wave function.

Now, sin inverse of 0, it has a problem, what is the problem? Sin inverse of 0, one possible answer is 0 itself right, but there are other possible answers, it may be pi. Sin inverse of theorem may be pi or it may be 2 pi, it maybe 3 pi, it may be 4 pi all these are possible answers. So, therefore, this is a function sin inverse of x is not a single valued function. It has multiple values at this same location at the same point it has a large number in fact, infinity number of values.

So, suppose your straight function happen to be a multiple valued function then you are going to run into problems, what is the problem? See suppose, I want to calculate the probability density at this point x is equal to 0 then what I will have to do is, I will have to take sin inverse of 0, take it is magnitude and square it right.

Now, which value am I going to take here, would I take the value 0 or would I take the value pi or would I take the value 2 pi and so on right, that is not clear. So, therefore, we do not want such a problem, we know that probability density is a number which has to be unique. It is something which is physically meaningful which I can perhaps measure.

So, I want only one value for probability density I do not want multiple values. And therefore, what should I do I will have to impose the condition that my straight function is a single valued function, I do not want it to be a multiple valued function because that is going to give me a problems. So, at any point it can have only one value not more than one value only one value. So, therefore, I say that my statement function has to be a single valued function.

Now, suppose I have a function phi of x which I will write this may appear a little bit complicated, but if you think about it is a nice example. I want you to think of this function, I know it is a I mean for some people it can be difficult function, but this is an nice example for a function which has a peculiar behavior.

Now, if you look at this function you have e to the power of minus x square. So, as x becomes large then finally, what will it do? It will decrease the function to 0. So, therefore, I know that here the function is going to be vanishing on the other side also the function is going to be vanishing, but the behavior is behavering between what is very interesting ok.

This is x is equal to 0. So, suppose you are somewhere here very close to x equal to 0, but on the right side of x is equal to 0 because, the value of x is very small, may be let us say, I think of this point which is at 0.01. So, this x is going to be 0.01; that means, I am going to have e to the power of 100 here correct. Here I am going to have e to the power of 100, e to the power of 100 plus 1. It is e to the power of 100 itself because, it is such a huge number and if x is very close to 0, this is almost 0. So, the e to the power of that will be 1.

So, you will have 1 by e to the power of 100 it is extremely small. So, as you are approaching x is equal to 0 from this side what will happen? The function actually deceases and it approaches 0 right. That is what happens with this function as you approach x is equal to 0 from above the function far away of course, the function is 0, but as you approach the function actually increases, but very close to x is equal to 0. The function has value 0 as we have seen. So, therefore, it should turn around that it should approach 0 like this correct.

Now, suppose you think of x very close to 0, but on the negative side. So, here you are going to have let us say, minus 0.01 right. A point where the value of x is minus 0.01 what will happen? You will have x equal to minus 0.01 so, you are going to have e to the power of minus 100 there.

So, e to the power of minus 100 plus 1, e to the power of minus 100 is almost 0. So, therefore, this one you cannot neglect. So, you will have 1 and in the numerator you see x is very small. So, e to the power of minus x square is almost 1.

So, you will have 1 divided by 1 plus e to the power of minus 100 and how much is that it is 1. So, as you approach x is equal to 0 from the negative side, what happens the function actually behaves like this it approaches unity, if you are approaching from the negative side. While it approaches 0, if you are approaching from the positive side right

Now, this is a function that is very interesting because what it does is when you cross the point x is equal to 0. The value of the function jumps, it jumps from 1 to 0, say if you are going in this direction, the value of the function steadily increases until it reaches the value 1 very close to x is equal to 0.

And also it cross x is equal to 0, the value of the function suddenly jumps and therefore, this is the behavior of the function. It suddenly jumps and then it does this. So, you say that this function is a function which is in this continuous it has a sudden discontinuous behavior at x is equal to 0 right. Suppose I say that this is my wave function this function is my wave function.

Then what it means is that the probability also, probability of finding the particle will also change discontinuously and usually is now physical reason for that to happen right, unless you have some peculiar situation and so on. In fact, there is no peculiar situation which will make the probability change in their discontinuous fashion probability always has to vary smoothly and continuously in all physical problems that I know of.

So, therefore, what is the way out you cannot have such a function. A function in which the probability will change in a discontinuous fashion is not acceptable and therefore, what we will do? We say that, my wave function has to be or our wave function has to be varying smoothly and continuously it cannot be a discontinuous function.

So, the wave function it has to satisfy two conditions actually. One it has to be square integrable and the second is that it has to be a continuous function. Oh well there are three conditions not two, third being it has to be single valued at any point it can have only one value. So, these three conditions have to be satisfied by any wave function which is acceptable.

If these conditions are not satisfied then, I will say that my wave function is not acceptable and I am not going to take such a wave function. These are all physically motivated requirements right. So, if I have some equations which I will have later like the Schrodinger equation which you solve and find your wave functions and if you get a solution which does not satisfy any of these conditions. Then you will say that is not something that is acceptable and simply throughout that function.

Thank you for listening.