Introductory Quantum Mechanics and Spectroscopy

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Lecture - 7
Part 2
Particle on a Ring (Continued)

Welcome back to the lecture. We will continue with the second part; that is about I think this is with this part, I shall conclude the particle in a ring in a rather elementary introduction that I have given.

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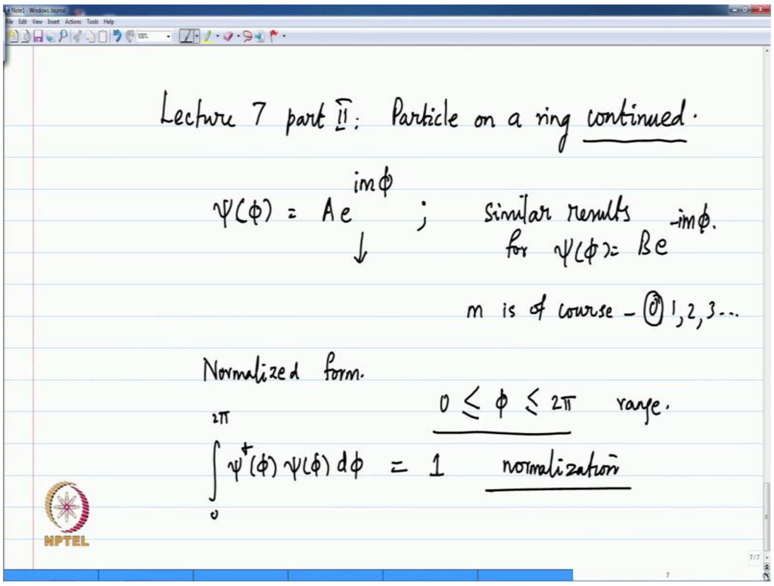

Lecture 7 part II: Particle on a ring continued.

$\psi(\phi) = A e^{im\phi}$ $\downarrow$; Similar results for $\psi(\phi) = B e^{-im\phi}$.

m is of course – ⓪ 1, 2, 3...

Normalized form.

$0 \leq \phi \leq 2\pi$ range.

$\int_0^{2\pi} \psi^*(\phi)\,\psi(\phi)\,d\phi = 1$ normalization

So, we shall look at a little bit more from what we left; namely, we have this – the wave function being given by an exponential m phi or phi; I mean I keep interchanging them, but you know what it means. And, m is of course, we are taking positive values here 0, 1, 2, 3, etcetera. Now, the 0 is something that we have to consider a little bit later. Let us worry about 1, 2, 3 as integers. If this is the wave function, what about its normalized form? A is a normalization constant, because we always concerned ourselves with making sure that, the wave functions are normalizable. Therefore, the square of the wave functions can be associated with the probability description and a probability density. In here, the normalization is done in the fashion in which I mention namely, all the values of phi for which the wave function is unique; for different values of phi, the wave function is different. It has one value for one phi. And of course, you know that, that particular range is between 0; and, a 2pi, because after that, the wave functions simply repeat itself. Therefore, this is the range; even though other values are considered, this is the range for normalization – different values. Therefore, what you have is psi star phi psi phi d phi between 0 and 2pi; that should be made equal to 1 for normalization; yes.

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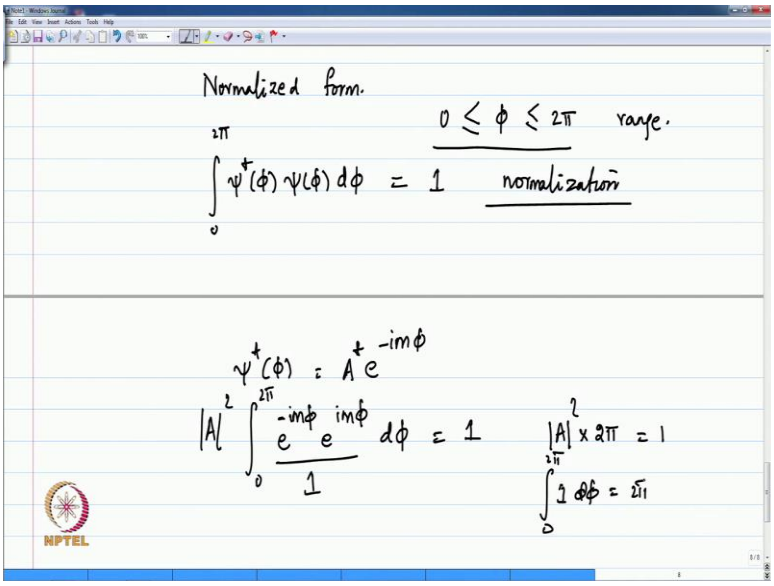

Normalized form.

$\underline{0 \leq \phi \leq 2\pi}$ range.

$$\int_0^{2\pi} \psi^*(\phi)\,\psi(\phi)\,d\phi = 1 \quad \underline{\text{normalization}}$$

$$\psi^*(\phi) = A^* e^{-im\phi}$$

$$|A|^2 \int_0^{2\pi} \underbrace{e^{-im\phi}\, e^{im\phi}}_{1}\, d\phi = 1 \qquad |A|^2 \times 2\pi = 1$$

$$\int_0^{2\pi} 1\, d\phi = 2\pi$$

So, if you do that, then essentially, you know psi star phi is of course, A star e to the minus i m phi, because we do not know what A is; whether A is real or imaginary. But, we will write it as A star. Therefore, what you have is the integral is the absolute value of A square between 0 to 2pi e to the i – minus i m phi – e to the i m phi d phi. That is equal to 1. And, this of course, is 1. Therefore, you have the absolute value of A square times 2 pi is equal to 1, because the integral of 1 d phi between 0 and 2 pi is of course, 2 pi.

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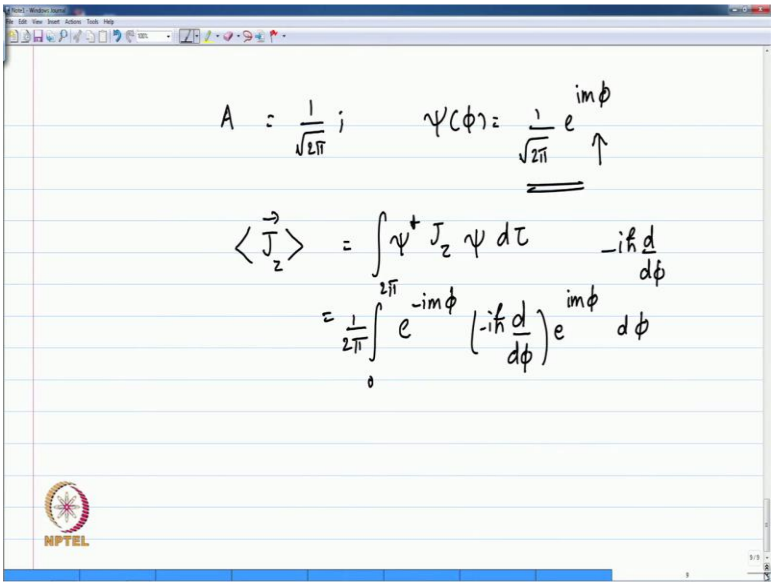

$$A = \frac{1}{\sqrt{2\pi}} ; \qquad \psi(\phi) = \underline{\underline{\frac{1}{\sqrt{2\pi}}}} e^{im\phi} \uparrow$$

$$\langle \vec{J}_z \rangle = \int \psi^* J_z \psi \, d\tau \qquad -i\hbar \frac{d}{d\phi}$$

$$= \frac{1}{2\pi} \int_0^{2\pi} e^{-im\phi} \left(-i\hbar \frac{d}{d\phi} \right) e^{im\phi} \, d\phi$$

So, you have A; we will take it as real as 1 by root 2 pi. This is the normalization constant. Therefore, the wave function psi of phi is 1 by root 2 pi e to the i m phi; it is independent. The normalization constant is independent of m, unlike the case of the harmonic oscillator, where you found out that, the normalization constant is also a function of the quantum number N because of the Hermite polynomials involved. This is the wave function. Of course, in rotational motion, the two things that we are concerned with is the rotational kinetic energy and the angular momentum of the particle.

Now, if the wave function is given by this alone as we have chosen, then it is possible for us to calculate the angular momentum J; since it points in a direction perpendicular to the actual plane of the circular motion and we shall call that as the z component if we assume x and y as the coordinates of the motion of the particle or the ring that we considered. The angular momentum is in a direction perpendicular to that. And, that you know is nothing but psi star the operator J z psi d tau; which in this case, the operator is minus ih bar d by d phi. This is the angular momentum operator that you used to actually derive this result. Therefore, if you calculate that, you see it is exponential between 0 to 2pi 1 by 2pi, because you have psi star psi. Therefore, this is square of 1 by root 2 pi. Then, you have exponential minus i m phi; you have minus h bar d by d phi exponential i m phi d phi. This is psi star psi. I do not need the denominator, because the wave function is already normalized.

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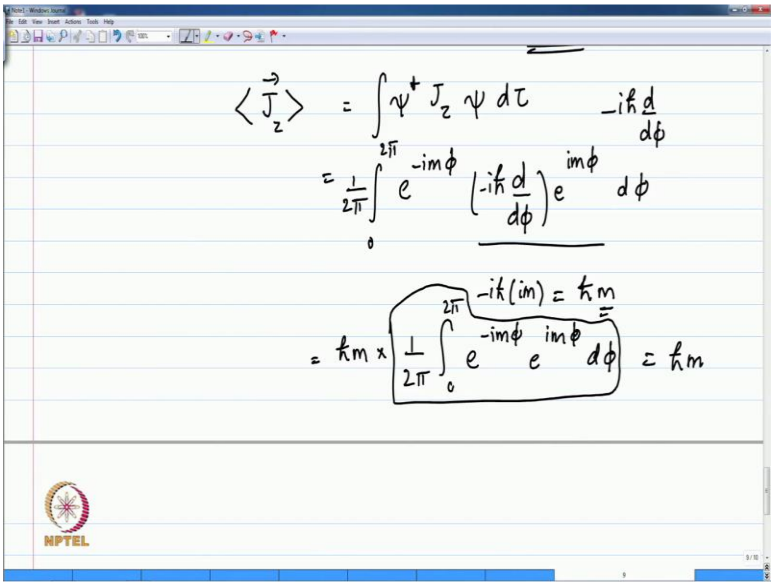

$$\langle \vec{J}_z \rangle = \int \psi^* J_z \psi \, d\tau \qquad -i\hbar \frac{d}{d\phi}$$

$$= \frac{1}{2\pi}\int_0^{2\pi} e^{-im\phi}\left(-i\hbar\frac{d}{d\phi}\right)e^{im\phi}\, d\phi$$

$$-i\hbar(im) = \hbar m$$

$$= \hbar m \times \boxed{\frac{1}{2\pi}\int_0^{2\pi} e^{-im\phi}\, e^{im\phi}\, d\phi} = \hbar m$$

And, it is easy to calculate this. This is minus ih bar d by d phi is im. Therefore, you have minus ih bar multiplying im, which gives you h bar m; and, m is a quantum number, h bar is a constant. So, you can actually take that out. Therefore, you have h bar m times 1 by 2 pi between 0 to 2pi e to the minus im phi times e to the im phi d phi. And, that is of course, you know that is nothing but the normalization of this wave function itself. So, you get h bar m. So, the angular momentum is therefore, a quantized quantity.

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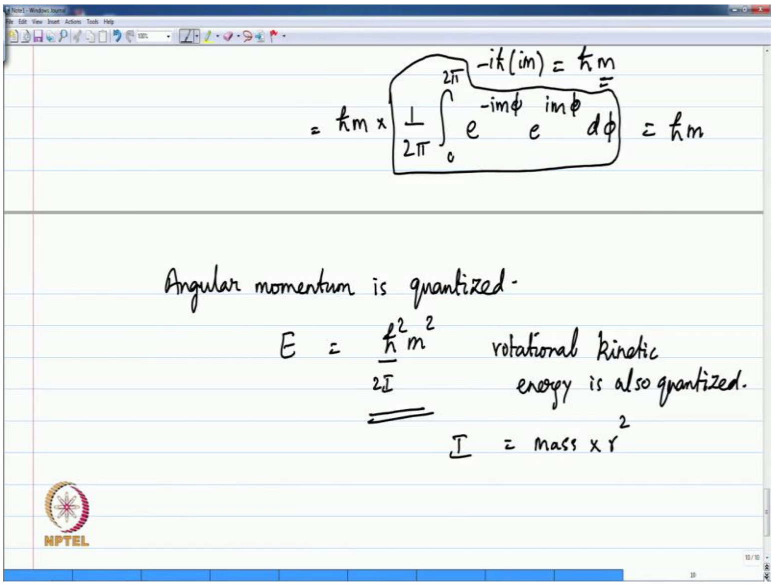

$$= \hbar m \times \boxed{\frac{1}{2\pi}\int_0^{2\pi} e^{-im\phi}\, e^{im\phi}\, d\phi} = \hbar m \qquad -i\hbar(im) = \hbar m$$

Angular momentum is quantized.

$$E = \frac{\hbar^2 m^2}{2I}$$ rotational kinetic energy is also quantized.

$I = \text{mass} \times r^2$

Angular momentum is quantized. You already have derived the energy E as h bar square m square by 2I. Thus, energy is rotational kinetic energy is also quantized – is also quantized. I have been careful enough not to include the potential energy. See there is a potential energy as I said in the last lecture; rotational motion is an accelerator motion; it is a non inertial motion. And, the particle or the system keeps moving around a point only because there is a central force directed towards the center of the rotation. Therefore the potential energy cannot be ignored. We have ignored it because we assume that, the radius of the system is a fixed value. And, for that given radius, we found out that, the energy is given by h bar square m square by 2I. Where is the information on the radius? It is actually in the value of I, because that is nothing but the mass m times the r square; where, r is the radius. Therefore, it is already given in here.

If the radius is also a variable, then the potential energy is actually a function of the radius and then whatever we have done cannot be done; you have to solve the full Schrodinger equation in which there is a kinetic energy given by whatever we did namely, minus h bar square by 2I d square by d phi square. That is one. Then, you have to actually include the potential energy. And then, it is a two-dimensional motion, because it involves radius and the angle. That is something else; we will do that if we have to study rotational motion as an internal degree of freedom in spectroscopy. Here we have not considered that. We have only worried about the rotational kinetic energy as the total energy neglecting the potential energy. And then, you find out that, the angular momentum is given by h bar m; and, that is a quantized quantity.

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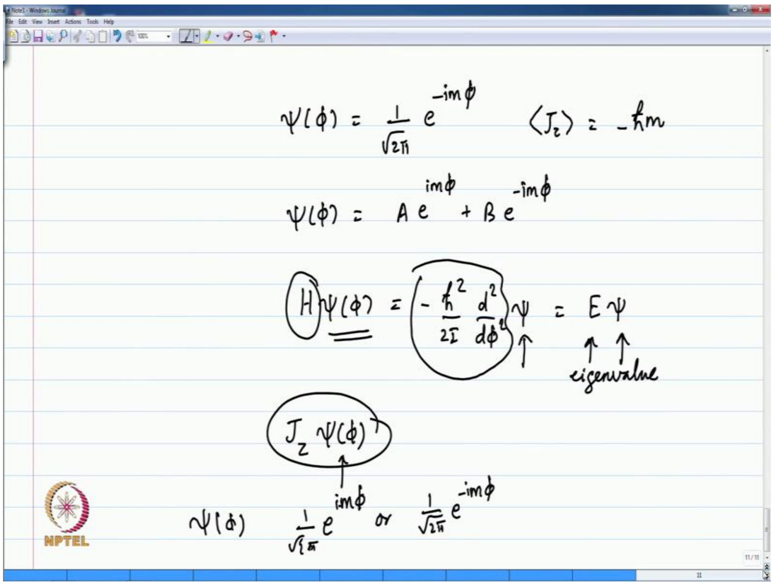

$$\psi(\phi) = \frac{1}{\sqrt{2\pi}} e^{-im\phi} \qquad \langle J_z \rangle = -\hbar m$$

$$\psi(\phi) = A e^{im\phi} + B e^{-im\phi}$$

$$\boxed{H}\underline{\underline{\psi(\phi)}} = \left(-\frac{\hbar^2}{2I}\frac{d^2}{d\phi^2}\right)\underset{\uparrow}{\psi} = \underset{\uparrow}{E}\,\underset{\uparrow}{\psi}$$

eigenvalue

$$\boxed{J_z \psi(\phi)}$$

$$\psi(\phi) \quad \frac{1}{\sqrt{2\pi}} e^{im\phi} \text{ or } \frac{1}{\sqrt{2\pi}} e^{-im\phi}$$

What about if we use the wave function e to the minus i m phi – e to the minus i m phi should be obvious that, if you calculate the angular momentum, it is obviously minus h bar m. It is a negative value. The angular momentum therefore, has a directional sense either towards perpendicular to the plane up or perpendicular to the plane down. But, what is interesting is – what is if we use the general wave function namely, A e to the i m phi plus B e to the minus i m phi, because we do not know whether the particular motion is clockwise or anti-clockwise; we do not know what it is. Then, we also do not know what the value… The J z is not a fixed quantity. Please remember when you wrote the kinetic energy h of psi phi was minus h bar square by 2I d square by d phi square psi. And, you wrote this as E psi. Therefore, you see that, the Hamiltonian acting on the wave function – the Hamiltonian operator acting on the wave function gave you the wave function and the energy. And you remember that, this was the eigenvalue equation. Therefore, the energy was an eigenvalue for this problem; and, the psi is an eigenfunction. Likewise, if you write to the J z operator and write psi phi; if psi phi is either exponential e i m phi 1 by root 2 pi or 1 by root 2 pi exponential minus i m phi.

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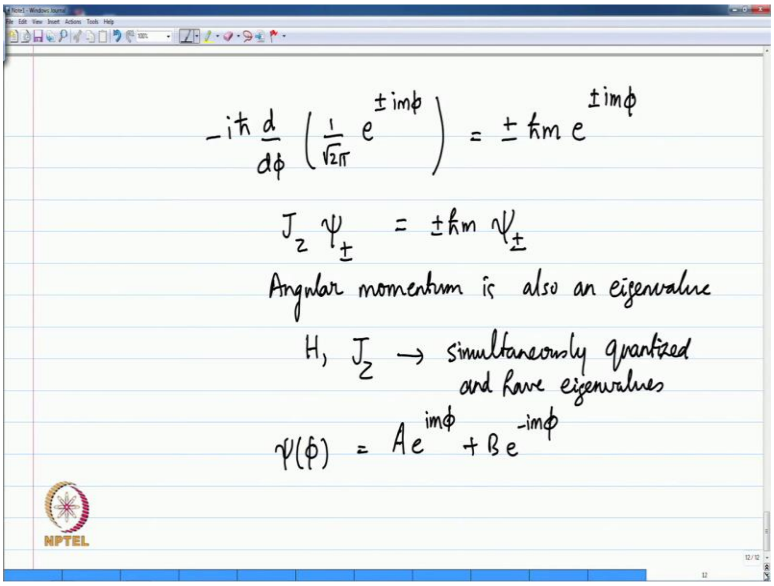

$$-i\hbar \frac{d}{d\phi}\left(\frac{1}{\sqrt{2\pi}} e^{\pm im\phi}\right) = \pm \hbar m e^{\pm im\phi}$$

$$J_z \psi_\pm = \pm \hbar m \psi_\pm$$

Angular momentum is also an eigenvalue

$H, J_z \rightarrow$ simultaneously quantized and have eigenvalues

$$\psi(\phi) = Ae^{im\phi} + Be^{-im\phi}$$

If the wave function is either this or that, then you also see that, the angular momentum J z acting on psi phi gives you that angular momentum value, which is as you remember – minus i h bar d by d phi 1 by root 2 pi exponential plus or minus i m phi. If I put that in; then, you will get the answer plus or minus h bar m e to the plus or minus i m phi. So, the plus is for the plus and minus is for the minus. Therefore, you see that, the angular momentum operator J z acting on psi gives you plus or minus h bar m psi. And, I will write it as plus minus, plus minus here to say the plus component is e to the i m phi; the minus component is e to the minus i m phi. Angular momentum is also an eigenvalue – is also an eigenvalue; that is, h and the angular momentum are simultaneously quantized and are observables – and are eigenvalues of psi and have eigenvalues – simultaneous eigenvalues. If the wave function is not given by one or the other component of the exponential i m phi; if the wave function is given by a linear combination of the two; these are the two possibilities. And, the m of course takes different values and therefore, the psi is for you have infinite number of wave functions and infinite number of energies for the particle fixed to a particular radius, because that radius fixes the value of i – the momentum of inertia. Therefore, the energy is given by that unit h bar square by 2I. That is the fundamental unit for the problem. But, if the wave function is a linear combination of the plus or minus i m phi; then, the angular momentum operator does not have an eigenvalue, because if you write psi phi is A e to the i m phi plus B e to the minus i m phi, if you write that.

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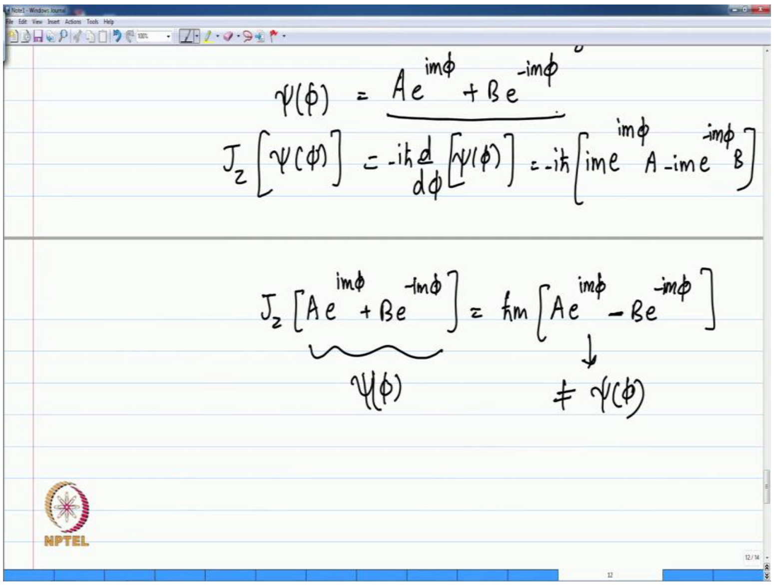

$$\psi(\phi) = \underline{Ae^{im\phi} + Be^{-im\phi}}$$

$$J_z\left[\psi(\phi)\right] = -i\hbar\frac{d}{d\phi}\left[\psi(\phi)\right] = -i\hbar\left[ime^{im\phi}A - ime^{-im\phi}B\right]$$

$$J_z\underbrace{\left[Ae^{im\phi} + Be^{-im\phi}\right]}_{\psi(\phi)} = \hbar m\left[\underset{\substack{\downarrow \\ \neq \psi(\phi)}}{Ae^{im\phi} - Be^{-im\phi}}\right]$$

And, you can normalize this. If you calculate J z acting on this psi phi; please remember J z is minus ih bar d by d phi on this wave function psi phi. And, please note that, this is going to give you the d by d phi acting on i m will give you plus i m. And therefore, you will get minus i h bar i m e to the i m phi with A of course. And then, you will have for the B, you will have minus i m e to the minus i m phi B. Therefore, you see that, you are going to get J z acting on A e to the i m phi plus B e to the minus i m phi gives you now h bar m times A e to the i m phi, but with the minus sign B e to the minus i m phi. This is psi phi; this is not equal to psi phi; this is something else. Therefore, you have an operator acting on a function giving you something else, not the function back. So, it is not an eigenvalue equation. What does that mean? Angular momentum does not have a precisely defined value if the wave function is a linear combination A to the i m phi plus B to the i m phi. Does that mean angular momentum cannot be defined? It cannot be defined as to have a unique value. An average value can always be calculated. An average value in quantum mechanics is essentially the wave function star the operator associated with the measured value and acting on the wave function integral you remember that.

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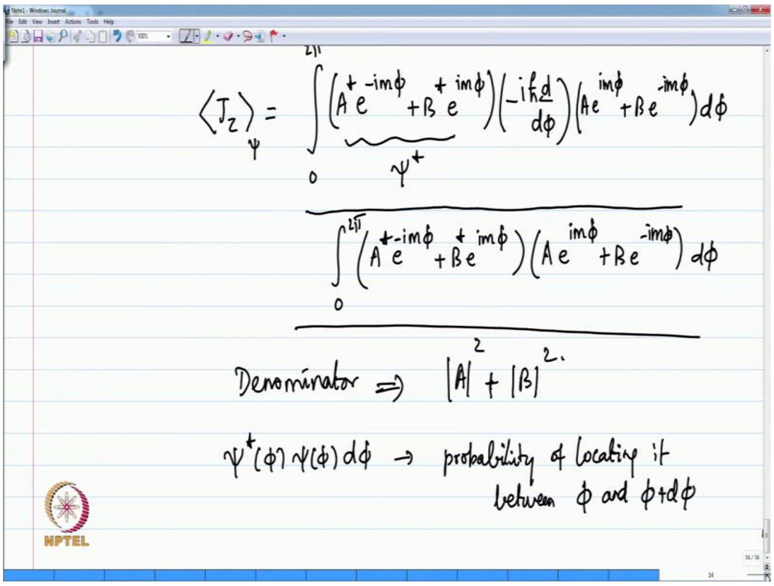

$$\langle J_z \rangle_\psi = \frac{\int_0^{2\pi} \underbrace{\left(A^+ e^{-im\phi} + B^+ e^{im\phi}\right)}_{\psi^+} \left(-i\hbar \frac{d}{d\phi}\right) \left(A e^{im\phi} + B e^{-im\phi}\right) d\phi}{\int_0^{2\pi} \left(A^+ e^{-im\phi} + B^+ e^{im\phi}\right) \left(A e^{im\phi} + B e^{-im\phi}\right) d\phi}$$

Denominator $\Rightarrow |A|^2 + |B|^2$.

$\psi^+(\phi)\psi(\phi)\,d\phi \rightarrow$ probability of locating it between ϕ and $\phi + d\phi$

Therefore, the angular momentum does not have the unique value; but, an average value of the angular momentum can always be calculated for such linear states – linear combination states by the same thing 0 to 2 pi. You will have A star e to the minus i m phi, because this is psi star plus B star e to the i m phi. This is the psi star acting on now with the operator minus i h bar d by d phi acting on the psi, which is A e to the i m phi plus B e to the minus i m phi d phi. But, please remember this wave function we have not yet normalized. Therefore, we have to make sure that, we write the psi star psi in the denominator namely, 0 to 2 pi A start e to the i m phi plus B star… A star e to the minus i m phi plus B star e to the i m phi multiplied by A e to the i m phi plus B e to the minus i m phi d phi. This is a very elementary integral. Anybody you can calculate there. I think with all the mathematics that you have done so far, you should be able to calculate this.

It is easy to see that, this will give you – the denominator will give you A square – absolute A square minus absolute B square – plus B square – B star e to the… – plus B square. But, the numerator will give you something else. The average value can be defined; but, an eigenvalue does not exist. What does that mean? That means that, if the wave function – if the particles motion is not very clearly known as anti-clockwise or as clockwise; then, we do not know whether the angular momentum vector is pointing upward or pointing downward. This is an average value; that is, I mean you can only do this many many times. And, every measurement gives you some result and then you take the average. And, that is the sense in which the angular momentum plays a very definite role when you come to particle in a box – particle on a ring. I think this exists also in a particle in a box. If the wave function for a particle in a box is not a precise eigenstate of the energy, but it can be linear combinations of the multiple eigenstates of energy. As you have here, you have a similar problem. Therefore, please remember this is also the first instance in which I am giving you a slightly more difficult problem that the eigenvalues and the expectation values need not have to be the same when the state of the system is not precisely defined to be an eigenstate.

Is this state an eigenstate of the energy operator – this linear combination? Of course, it is. Please remember the energy operator has d square by d phi square – second derivative operator. The minus m, which comes in when you operate the derivative on this function once, it is cancelled – becomes plus m square. Therefore, you get the energy. Of course, that is how you solve the Schrodinger equation. And, I gave this as the general solution. Therefore, this is a general solution what you have written here namely, the A e to the i m phi plus B e to the minus i m phi; that you have here on the screen. This is also an eigenfunction of the energy operator, but it is not an eigenfunction of the angular momentum operator. Therefore, particle in a box, a particle on a ring, I mean, motion on a ring comes out with something unique.

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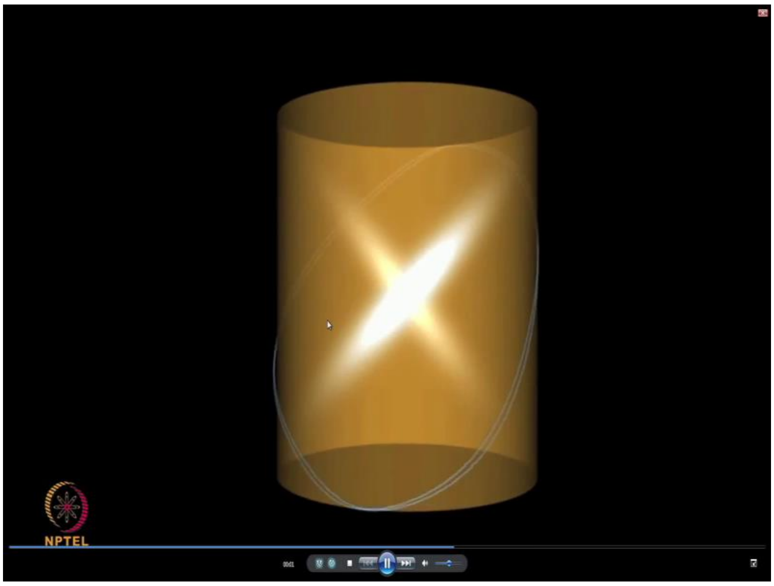

Now, what are the wave functions like? Let us just look at some of the pictures. The ring is of course the cylinder. Let me just say if you draw a straight line here; that is a cylinder. And, the circle in that plane, the wave function is the particle. You have to see me that is why; the particle on a wave – the particle on a box if you remember, it is a linear coordinate system x. And therefore, there is a sine wave. Now, when you have a particle on a ring, this line actually closes into a circle; the starting point 0 and the n-th point l sort of closes into a circle of radius r. And, that is a circle on which we are trying to describe. Therefore, this wave function, that is, the sine wave corresponding to the quantum number 1 is actually the wave function that is now described as a sine wave on a ring. And that is what you see here.

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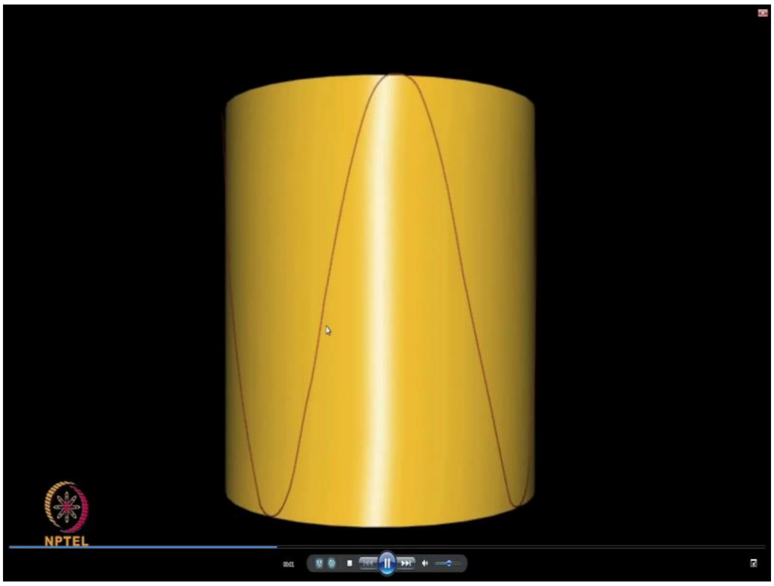

Let us look at the some other quantum number. You see that, now, if the sine waves that you have written down; now, you have many sine waves for if the quantum number of an n for a particle in the box is very large; there are many components. Now, take all the sine waves and eventually then just you close them down by bringing the two points – n points together. That is a wave function. Actually, it does not make any difference; I mean it is not very important beyond a point of being able to visualize what the wave functions are. The probability here is a problem, because you know psi star psi is 1. Therefore, it is 1 by root 2 pi. And, the probability of finding the particle on a circle in any region is precisely proportional to that region and it is a constant. It does not vary like what you have for a particle in a box. If you say psi star psi d phi, is the probability of locating the particle between phi and phi plus d phi – phi and phi plus d phi between.

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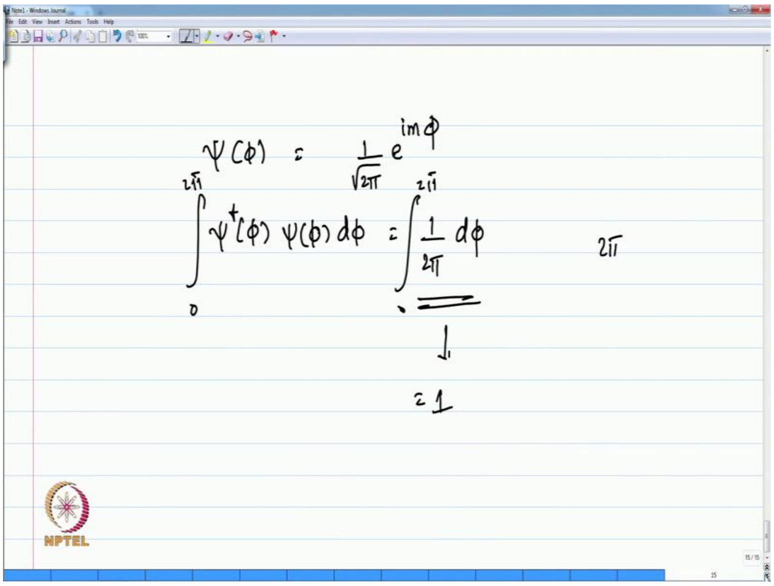

$$\psi(\phi) = \frac{1}{\sqrt{2\pi}} e^{im\phi}$$

$$\int_0^{2\pi} \psi^*(\phi)\, \psi(\phi)\, d\phi = \underline{\int^{2\pi} \frac{1}{2\pi}\, d\phi}$$

$$\downarrow$$

$$= 1$$

2π

Then, you know that, if the wave function is psi of phi is 1 by root 2 pi e to the i m phi; then, psi star phi psi phi d phi is 1 by 2 pi d phi, because the exponentials cancelled each other. Therefore, you see that, the probability is proportional to the part of the ring – the length of the arc in a ring that we look at. What is the total length of the arc on the ring? What is the circumference? 2 pi. Therefore, you see that, the probability of locating the particle in any region is uniformly the same and is purely proportional to the length of the arc unlike the particle in the one-dimensional box, where it is quite different. So, there is a subtlety here.

As long as the particle is moving on a circle, its probability of locating it in a certain region is simply proportional to the length of the region. And of course, the total probability is 1. Therefore, anywhere on the circle, if you want to calculate, you have to do for all values of phi; it becomes obviously 2 pi. And therefore, psi star d phi between the entire region is of course that, 0 to 2 pi. And, that is equal to 1. So, the probability does not come up with. But, please remember this is for e to the i m phi at the same thing for e to the minus i m phi. And, I will ask you to calculate the problem – the inner problem in one of the quizzes; what is the probability if it is a linear combination of the wave function? The mathematics is very simple; you should be able to do that.

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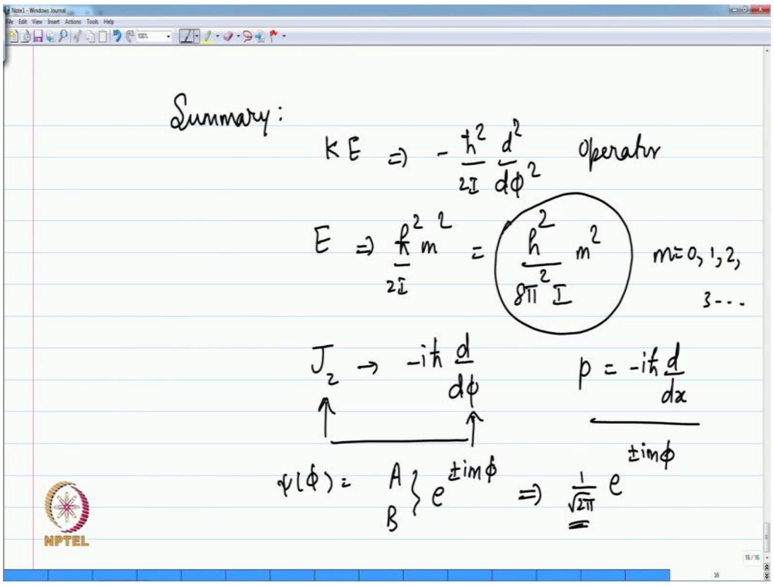

Summary:

$$KE \Rightarrow -\frac{\hbar^2}{2I}\frac{d^2}{d\phi^2} \quad \text{Operator}$$

$$E \Rightarrow \frac{\hbar^2 m^2}{2I} = \boxed{\frac{h^2}{8\pi^2 I} m^2} \quad m = 0, 1, 2, 3 \ldots$$

$$J_z \rightarrow -i\hbar\frac{d}{d\phi} \qquad p = -i\hbar\frac{d}{dx}$$

$$\psi(\phi) = \left.\begin{matrix}A\\B\end{matrix}\right\} e^{\pm im\phi} \Rightarrow \underline{\frac{1}{\sqrt{2\pi}}}\, e^{\pm im\phi}$$

So, particle on a ring has two or three important summarized results. One – Let me… Summary – let me write the final summary here. Kinetic energy – we wrote this as minus h bar square by 2I d square by d phi square operator – kinetic energy operator. Energy is h bar square m square by 2I; which if you have to write is h square by 8 pi square i m square; m is 0, 1, 2, 3, etcetera. m is equal to 0 is a perfectly acceptable quantum number here, because all it means is that, the particle does not have a rotational kinetic energy; it stays somewhere on the circle; it does not violate the uncertainty principle, because if we say that, m is 0, we say that, it is angular momentum is exactly 0. If the angular momentum is 0, please remember – angular momentum is given by this operator minus i h bar d by d phi. And therefore, the angular momentum and the angular coordinate have the same relation like the linear momentum and the linear coordinate that you have for a particle in a one-dimensional box. They satisfy a commutation relation. Therefore, the location of the particle cannot be specified precisely if we know a precise value for the linear momentum.

The same thing here; if we know precisely the value of angular momentum, we do not know exactly where the particle is. It is anywhere on the ring. Therefore, it is as uncertain as the dimension that you are worried about. Therefore, uncertainty principle does not violate; it does not violate. So, m is equal to 0 is allowed; which means rotational energy is equal to 0; particle is stationary. But, you do not know on what part of the circle, what arc of the circle that it is in. So, the uncertainty rules are not violated in anyway unlike the particle in a box; where, since you do not have the possibility of the particle in a box having a very precise position and a very precise momentum for a particle in a ring; we do not have that part. So, this is the other important variation from the particle in a box.

And finally, the wave functions are given by A or B if you want to write e to the plus or minus i m phi and m is of course… – plus m is with the notation constant A. Essentially, it is 1 by root 2 pi e to the plus or minus i m phi, which is a normalization constant. So, these results are important, but this particular result will be very useful in what is known as the microwave or rotational spectroscopy. I do not know whether I will talk about that in this course, but the particle in a ring is an extremely important model for understanding the elementary rigid body rotations of diatomic and polyatomic molecules. Therefore, I hope I have introduced you to something slightly different from the usual – the quantum results that, you see particle in a ring is slightly more subtle than any other model and that has to be kept in mind.

We will complete the course of… With this, we come to the end of the quantum mechanics parts of this course, the algebraic part of it. The next few lectures for the remaining weeks of this course will be on molecular spectroscopy. And, I will start with the introduction to molecular spectroscopy in my next lecture.

Until then, thank you very much.