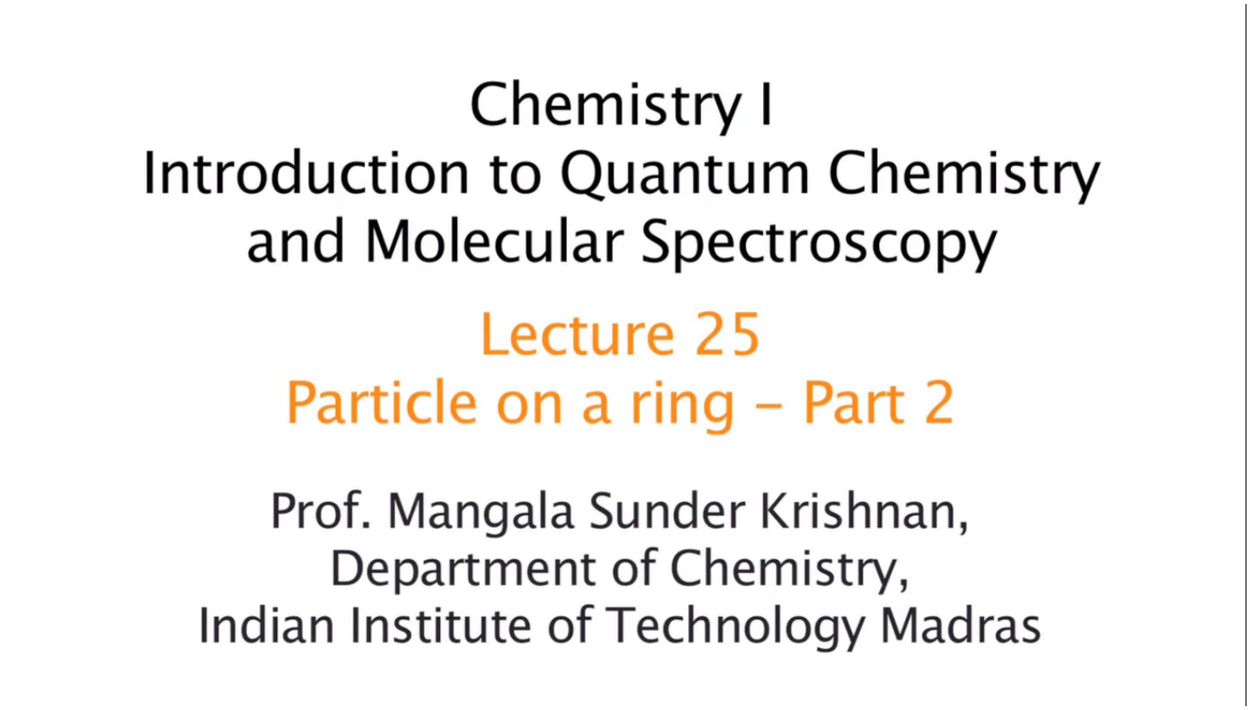

Chemistry I
Introduction to Quantum Chemistry and Molecular Spectroscopy

Lecture 25
Particle on a ring – Part 2

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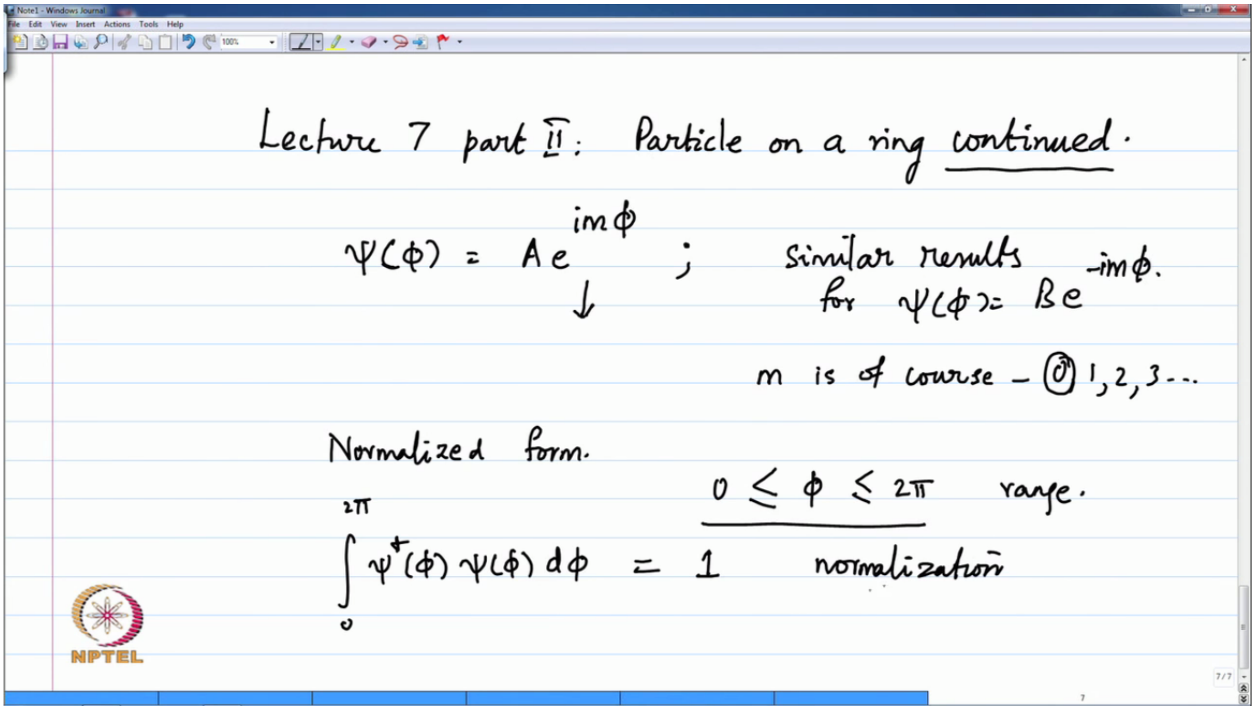
Welcome back to the lecture. We will continue with the second part that's about it I think this with this part I shall conclude the particle in a ring in a rather elementary introduction that I have given. So we shall look at a little bit more from what we left namely we have this the wave function being given by an exponential m φ or φ I mean I keep changing them but you know what it means and m is of course we are taking positive values here 0, 1, 2, 3, etc. Now 0 is something that we have to consider a little bit later. Let's worry about 1, 2, 3, and as integers. If this is the wave function what about its normalized form? A is a a normalization constant because we always concern 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 the probability density. In here the normalization is done in the fashion in which I mentioned namely all the values of φ for which the wave function is unique. For different values of φ the wave function is different. It has one value for one φ and of course you know that that particular range is between 0 and 2 π because after that the wave function simply repeats itself. Therefore this is the range even though other values are considered, this is range for normalization; different values therefore what you have is Ψ * φ Ψ φ d φ between 0 and 2 π that should be made equal to 1 for normalization. Yes.



Lecture 7 part II: Particle on a ring continued.

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

$\downarrow$

m is of course – ⓪ 1, 2, 3 . . .

Normalized form.

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

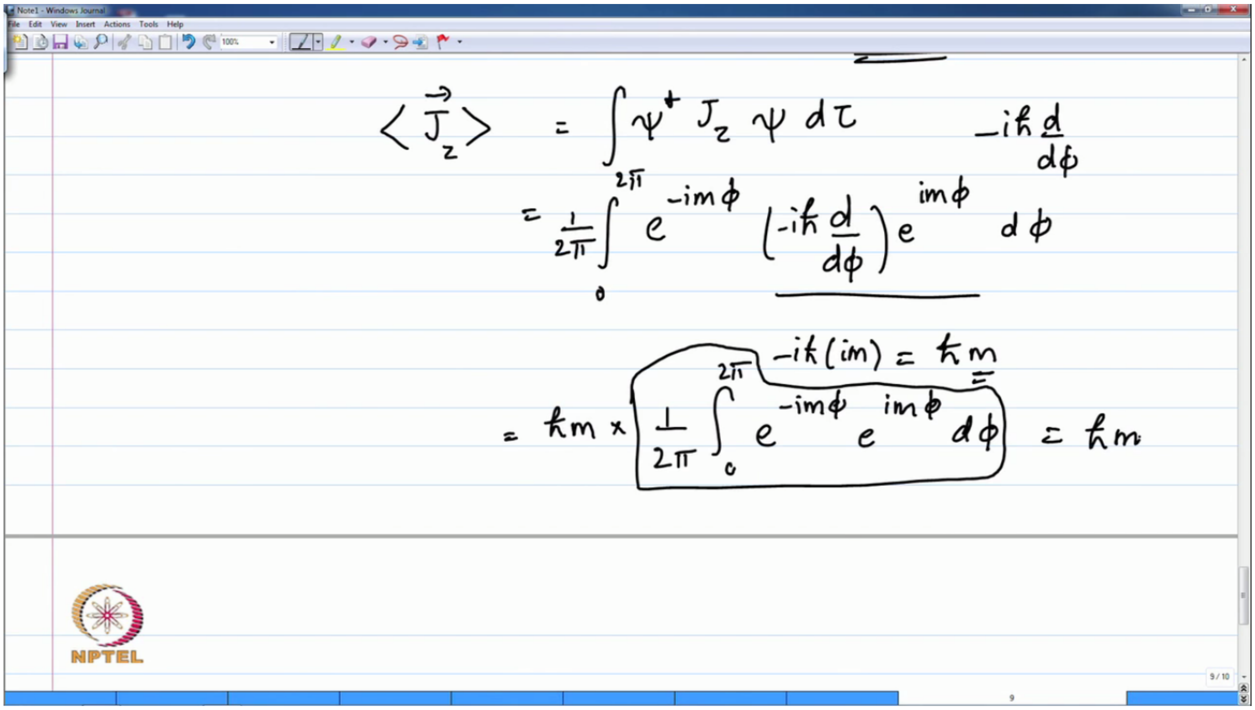
$$\int_0^{2\pi} \psi^*(\phi)\,\psi(\phi)\,d\phi = 1$$ normalization

So if you do that then essentially you know φ * φ is of course is A * e to the minus imφ because we don't know what A is; whether the A is real or imaginary but we will write it as A * therefore what you have is the integral is the absolute value of A square between 0 to 2 π e to the i minus imφ e to the imφ d φ that's equal to 1 and this of course is 1 therefore you have the absolute value of A square times 2 π is equal to 1 because the integral of 1 d φ between 0 and 2pi is of course 2 π.

So you have A we will take it as real as 1 by root 2 π. This is the normalization constant therefore the wave function sin of φ is 1 by root 2 π e to the imφ it's 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's 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 you assumed X and Y as the coordinates of the motion of the particle or the the ring that we consider the angular momentum is in the direction perpendicular to that and that you know is nothing but Ψ * the operator JZ Ψ d tau which in this case the operator is minus ih bar d by d φ. This is the angular momentum operator that you use to actually derive this result. Therefore, if you calculate that you see it is exponential between 0 to 2 π 1 by 2 π because you have Ψ * Ψ therefore this is the square of 1 by root 2 π. Then you have exponential minus imφ. You have minus ih bar dD by d φ exponential imφ d φ. This is Ψ * Ψ.



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

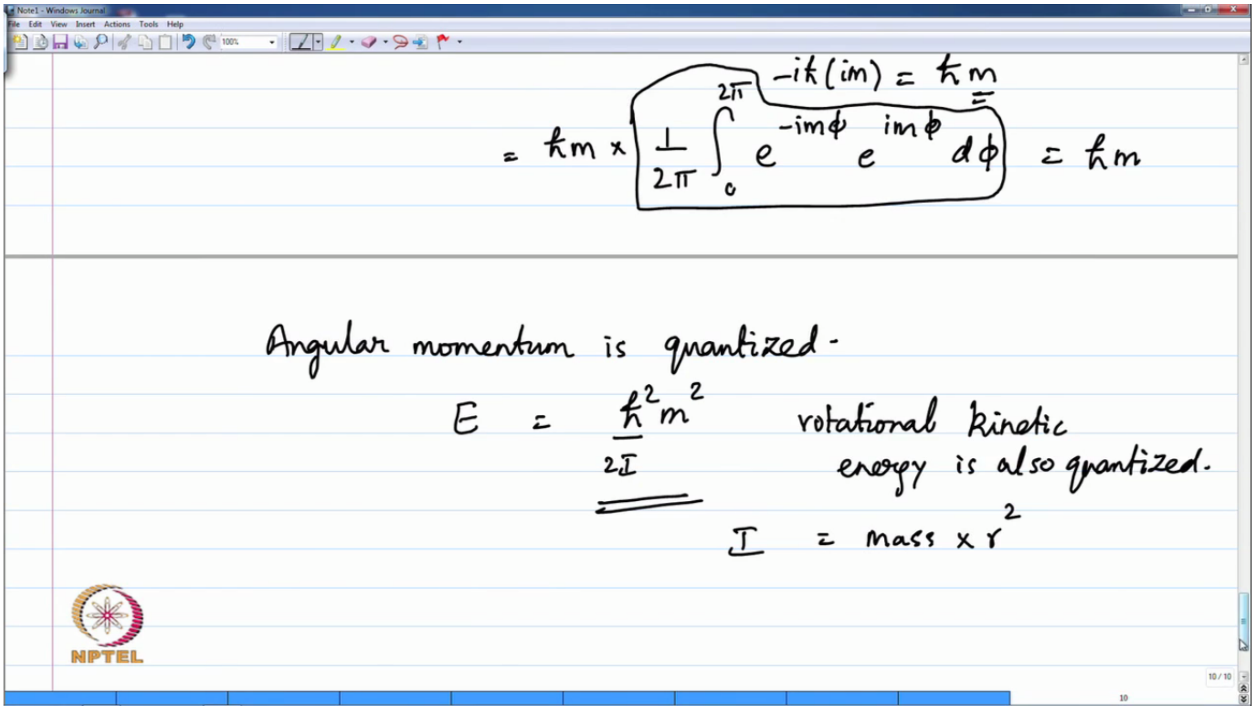
$$= \frac{1}{2\pi}\int_0^{2\pi} e^{-im\phi} \underline{\left(-i\hbar \frac{d}{d\phi}\right) e^{im\phi}} \, d\phi$$

$$-i\hbar(im) = \underline{\underline{\hbar m}}$$

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

I don't need the denominator because the wave function is already normalized and it's easy to calculate this. This is minus ih bar d by d φ 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 h bar m times 1 by 2 π between 0 to 2 π e to the minus imφ times e to the imφ d φ and that's of course you know that's nothing but the normalization of this wave function itself. So you get h bar m.

So the angular momentum is therefore a quantized quantity. 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've been careful enough not to include the rotational, the potential energy. See there is a potential energy as I said in the last lecture rotational motion is in – is an accelerated motion. It's a non inertial motion and the 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 assumed 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's actually in the value of I because that's nothing but the mass m times the r square where r is the radius. Therefore it's 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 that is the kinetic energy given by whatever we did namely minus h bar square by 2I d square by d φ square that's one. Then you have to actually include the potential energy and then it's a two-dimensional motion because it involves radius and the angular. That's something else we will do that if we have to study rotational motion as an internal degree of freedom in spectroscopy.



$-i\hbar(im) = \underline{\underline{\hbar m}}$

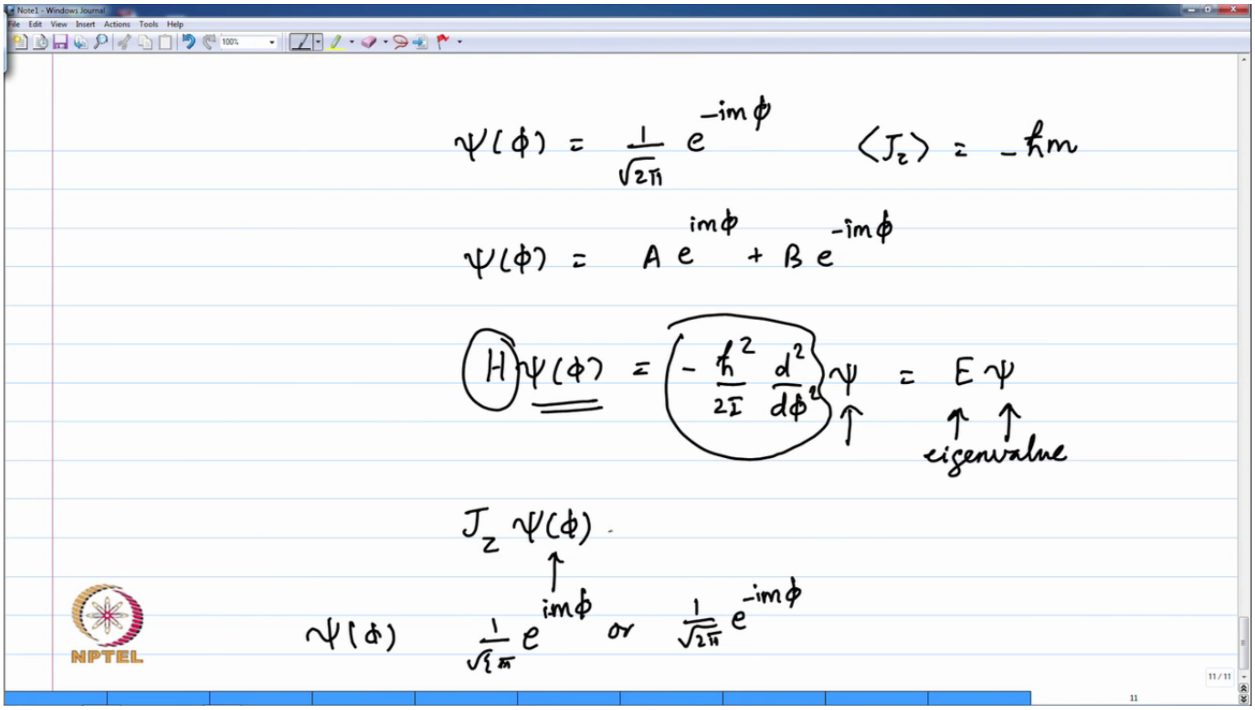
$$= \hbar m \times \boxed{\frac{1}{2\pi}\int_0^{2\pi} e^{-im\phi}\, e^{im\phi}\, d\phi} = \hbar m$$

Angular momentum is quantized.

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

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

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's a quantized quantity. What about if you use the wave function e to the minus imφ, e to the minus imφ it should be obvious that if you calculate the angular momentum it's obviously minus h bar m. So negative value. The angular momentum therefore has a directional sense either towards the perpendicular to the plane up or perpendicular to the plane down but what's interesting is what is if we use the general wave function namely Ae to the imφ plus Be to the minus imφ because we do not know whether the particular motion is clockwise or anti-clockwise we don't know what it is. Then we also don't know what the value the Jz is not a fixed quantity. Please remember when you wrote the kinetic energy h of Ψ φ was minus h bar square by 2I d square by d φ square Ψ and you wrote this as E Ψ. 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 thus Ψ an eigenfunction. Likewise if you write the Jz operator and write Ψ φ, if Ψ φ is either exponential e imφ 1 by root 2 π or 1 by root 2 π minus sorry, 1 by root 2 π exponential minus imφ if the wave function is either this or that.



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

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

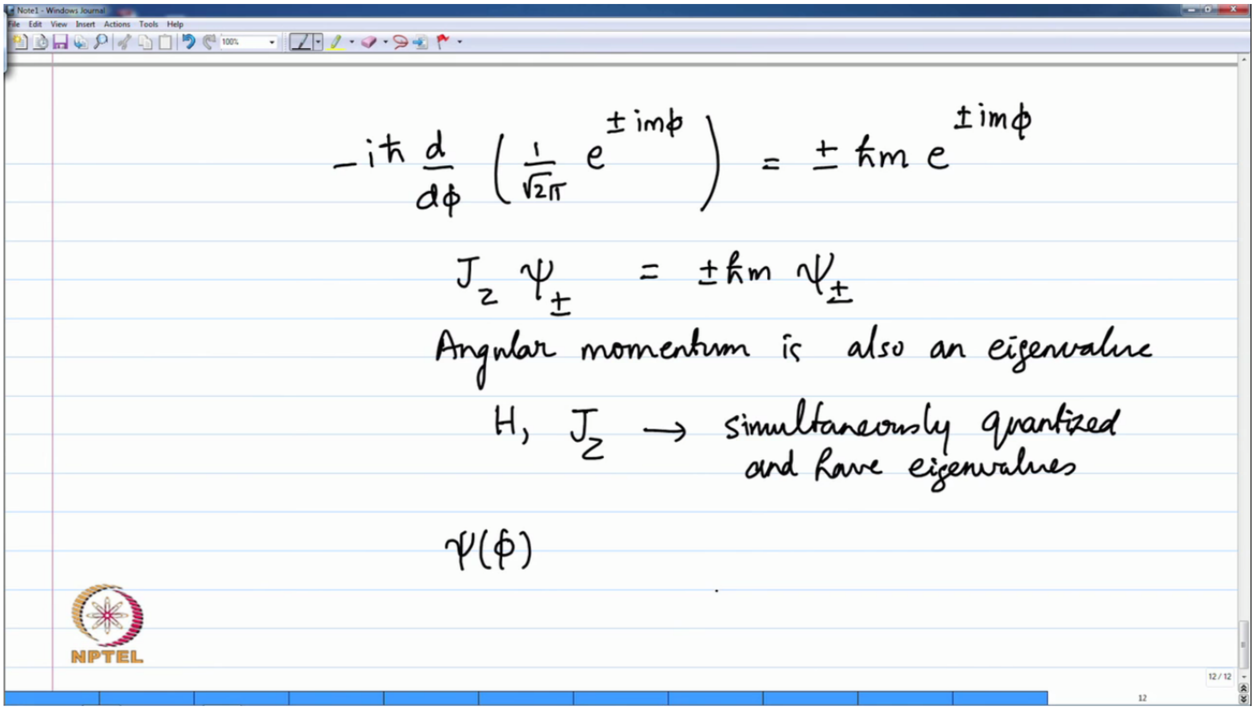
$$\boxed{H} \underline{\underline{\psi(\phi)}} = \left(-\frac{\hbar^2}{2I} \frac{d^2}{d\phi^2} \right) \underset{\uparrow}{\psi} = \underset{\uparrow}{E} \underset{\uparrow}{\psi}$$

eigenvalue

$$J_z \underset{\uparrow}{\psi(\phi)}$$

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

Then you also see that the angular momentum Jz acting on Ψ φ gives you that angular momentum value which is as you remember minus h bar d ih bar d by d φ 1 by root 2 π exponential plus or minus imφ if i put that in then you will get the answer minus, sorry what do you get plus or minus yes plus or minus h bar m e to the plus or minus imφ. So the plus is for the plus and the minus is for the minus. Therefore you see that the angular momentum operator Jz acting on Ψ gives you plus or minus, sorry yeah plus or minus h bar m Ψ and I will write it as plus minus plus minus here to say the plus component is e to the imφ the minus component is e to the minus imφ. Angular momentum is also an eigenvalue, is also an eigenvalue. That is H and the angular momentum are simultaneously quantized and/or observables and/or eigenvalues of Ψ and have eigenvalues, simultaneous eigenvalues if the wave function is not given by one or the other component of the exponential imφ okay.



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

$$J_z \Psi_\pm = \pm \hbar m \Psi_\pm$$

Angular momentum is also an eigenvalue

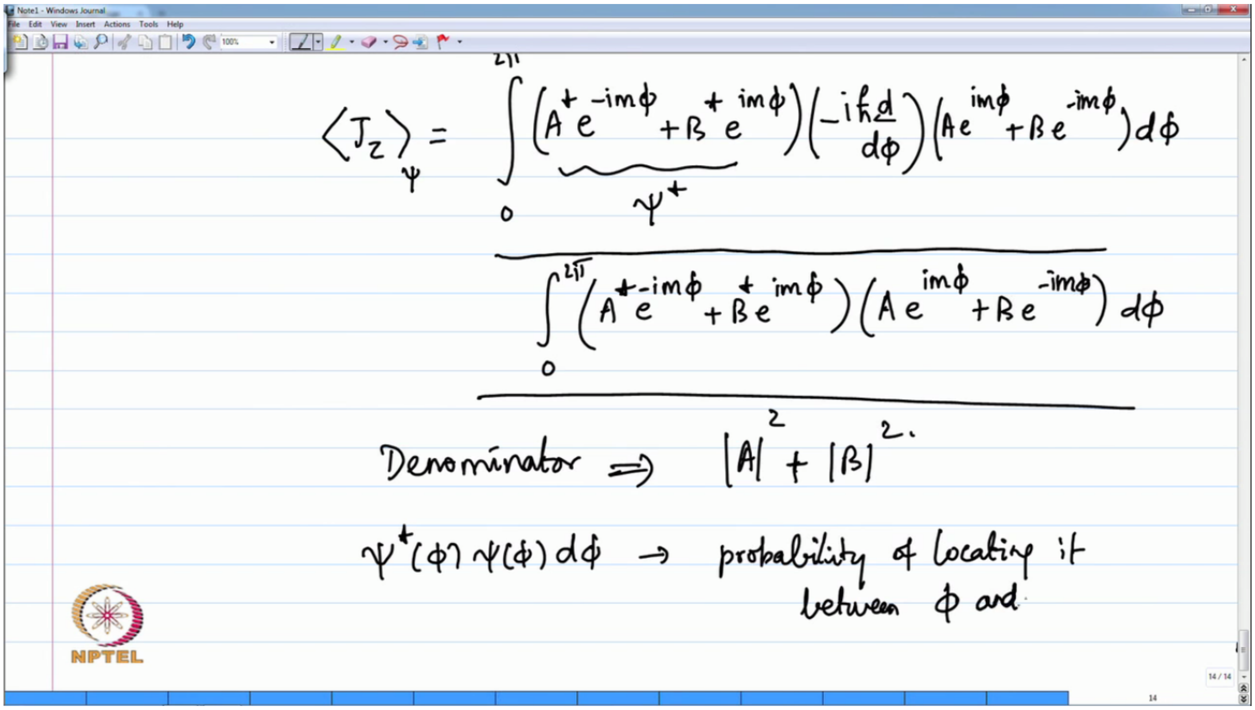
$H, J_z \rightarrow$ simultaneously quantized and have eigenvalues

$\Psi(\phi)$

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 Ψ 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 moment of inertia. Therefore the energy is given by that unit h bar square by 2I that is the fundamental unit for that problem but if the wave function is the linear combination of the plus or minus imφ then the angular momentum operator does not have the eigenvalue because if you write Ψ φ is Ae to the imφ plus Be to the minus imφ if you write that and you can normalize this. If you try to calculate the expectation value, sorry, if you calculate Jz acting on this Ψ φ please remember Jz is minus ih bar d by d φ on this wave functions Ψ φ and please note that this is going to give you the d by d φ acting on im will give you plus im and therefore you will get minus ih bar ime to the imφ with A of course and then you will have for the B you will have minus ime to the minus imφ B. Therefore you see that you are going to get Jz acting on Ae to the imφ plus Be to the minus imφ gives you now h bar m times Ae to the imφ but with a minus sign Be to the minus imφ. This is Ψ φ. This is not equal to Ψ φ. This is something else. Therefore you have an operator acting on a function giving you something else not the function back. So it's 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 imφ B to the imφ. Does that mean angular momentum cannot be defined? It cannot be defined as to have a unique value and average value can always be calculated. An average value in quantum mechanics is essentially the wave function * the operator associated with the measured value and acting on the wave function integral you remember that.

Therefore, the angular momentum does not have a 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 π you will have Astar e to the minus imφ because this Ψ * plus B * e to the imφ this is the Ψ * acting on now with the operator minus ih bar d by d φ acting on the Ψ which is Ae to the imφ plus Be to the minus imφ d φ but please remember this wave function we have not yet normalized. Therefore we have to make sure that we write the Ψ * Ψ in the denominator namely 0 to 2 π A * e to the imφ plus B * to the, A * minus imφ plus B * A to the imφ multiplied by A to A to the imφ plus Be to the minus imφ d φ. This is a very elementary integral. Anybody can calculate that. I think with all the mathematics that you have done so far you should be able to calculate this. It's easy to see that this will give you the denominator will give you A square absolute A square minus absolute B square. Sorry, plus B square I guess. B * A to the – yeah 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 particle's motion is not very clearly known as anti-clockwise or as clockwise then we don't know whether the angular momentum vector is pointing upward or pointing downward. This is an average value that means you can only do this many many times and every measurement gives you some result and then you take the average and that's the sense in which the angular momentum plays a very definite role when you come to particle in the box, particle on a ring.

I think this exists also in the 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 eigenstates of 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 φ square. Second derivative operator. The minus m which comes in when you operate the derivative on this function once it cancels. It becomes plus m square therefore you get the energy. Of course that's how you solve the Schrodinger equation and I gave this as a general solution. Therefore this is a general solution what you have written here namely the Ae to the imφ plus Be to the minus imφ that you have here on the screen. This is also an eigenfunction of the energy operator but it's not an eigenfunction of the angular momentum operator for particle in the box, particle on a ring I mean motion on the ring comes out with something unique.



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

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

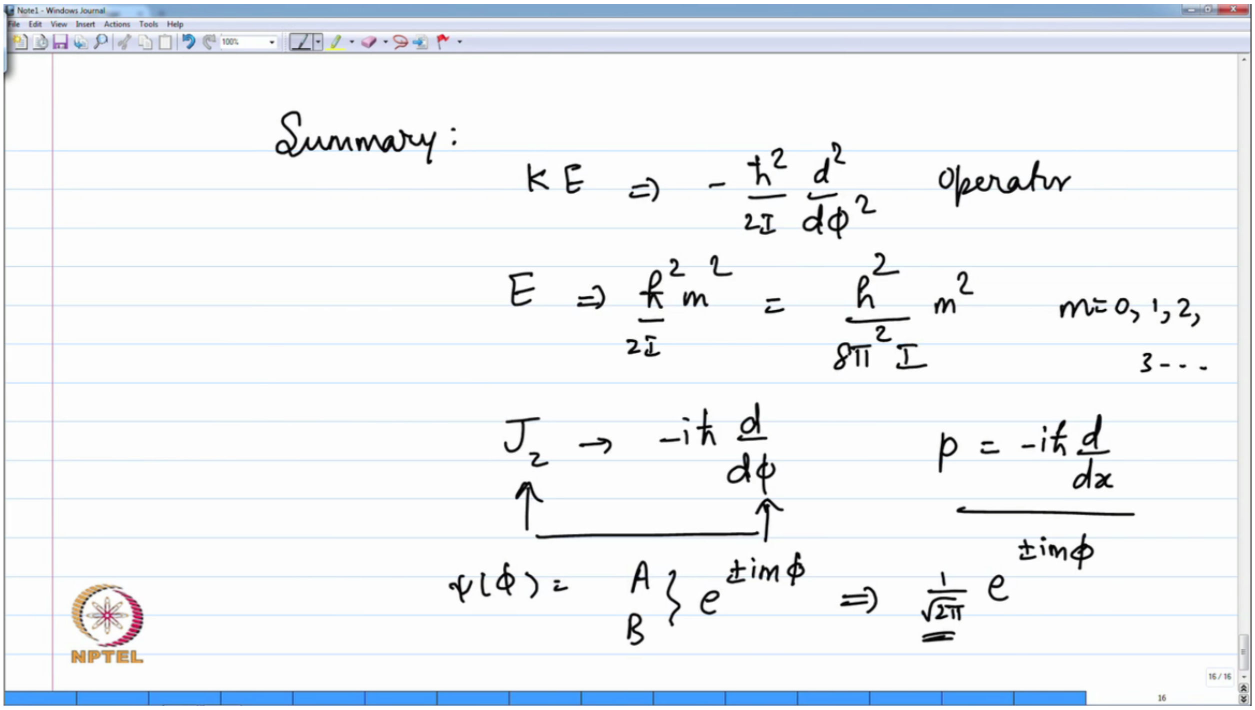
$\psi^{+}(\phi)\psi(\phi)\,d\phi \rightarrow$ probability of locating it between ϕ and

Now what are the wave functions like? Let's just look at some of the pictures. The ring is of course the cylinder okay let me just say if you draw the straight line here that's a cylinder and the circle in that plane the wave function is the particle. You have to see me that's why the particular wave, the particle on a box if you remember it's a linear coordinate system X and therefore there is a sin wave.

Now when you have a particle on a ring this line actually closes into a circle. The starting point 0 and the end point l sort of closest into a circle of radius r and that's a circle on which we are trying to describe. Therefore this wave function that's a sin wave corresponding to the quantum number 1 is actually the wave function that is know described as a sin wave on a ring and that's what you see here. Let's look at some other quantum number.

You see that know if the sine waves that you have written down, now you write you have many sine waves for if the quantum number of 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, the endpoints together. That's a wave function. Actually it doesn't make any difference. I mean it's not very important beyond a point of being able to visualize what these wave functions are. The probability here is a problem because you know Ψ * Ψ is constant, is 1 therefore it's 1 by root 2 π and the probability of finding the particle on a circle in any region is precisely proportional to that region and it's a constant. It does not vary like what you have for a particle in a box. If you say Ψ * Ψ d φ is the probability of locating the particle between φ and φ plus d φ between then you know that if the wave function is Ψ of φ is A sorry it's 1 by root 2 π e to the imφ then Ψ * φ Ψ φ d φ is 1 by 2 π d φ because the exponential cancel 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's the time – what's the circumference? 2 π 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's quite different. So there is a subtlety here. As long as the particle is moving on a circle its probability of locating it in some certain medium 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 it for all values of φ it becomes obviously 2 π and therefore Ψ * Ψ d φ between the entire region is of course that 0 to 2 π and that's equal to 1. So the probability does not come up with but please remember this is for e to the imφ. It's the same thing for e to the minus imφ and I will ask you to calculate the problem, the inner problem in one of the quizzes what is the probability if it's a linear combination of the wave function. The mathematics is very simple you should be able to do that.

So particle on a ring has two or three important summarized results. Summary let me write the final summary here. Kinetic energy. We wrote this as minus h bar square by 2I d square by d φ square operator, kinetic energy operator. Energy is h bar square m square by 2I which if you have to write it's h square by 8 π square I m square, m is 0, 1, 2, 3,. etc. M is equal to 0 is a perfectly acceptable quantum number here because all it means is that the particle does not have the rotational kinetic energy. It stays somewhere on the circle. It doesn't violate the uncertainty principle because if you say that m is 0 we say that its angular momentum is exactly zero. If the angular momentum is 0 please remember angular momentum is given by this operator minus ih bar d by d φ 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 me the linear momentum. The same thing here if we know precisely the value of angular momentum we do not know exactly where the particle sits anywhere on the ring therefore it's as uncertain as the dimension that you are worried about. Therefore uncertainty principle doesn't violate, is not violated. So m is equal to zero is allowed which means rotational energy is equal to zero, particle 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 any way 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 at a very precise momentum for a particle in the ring don't have that problem.



Summary:

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

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

$J_z \to -i\hbar \frac{d}{d\phi}$ $\underline{p = -i\hbar \frac{d}{dx}}$

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

So this is the other important variation from the particle in the box and finally the wave functions are given by A or B if you want to write e to the plus or minus imφ and m is of course plus m is with the notation constant A. essentially it's 1 by root 2 π e to the plus or minus imφ which is the 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 don't know that I will talk about that in this course but the particle in the 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 quantum results that you see partnering 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. Then ext 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.