Chemistry I
Introduction to Quantum Chemistry and Molecular Spectroscopy

Lecture 24
Particle on a ring – Part 1

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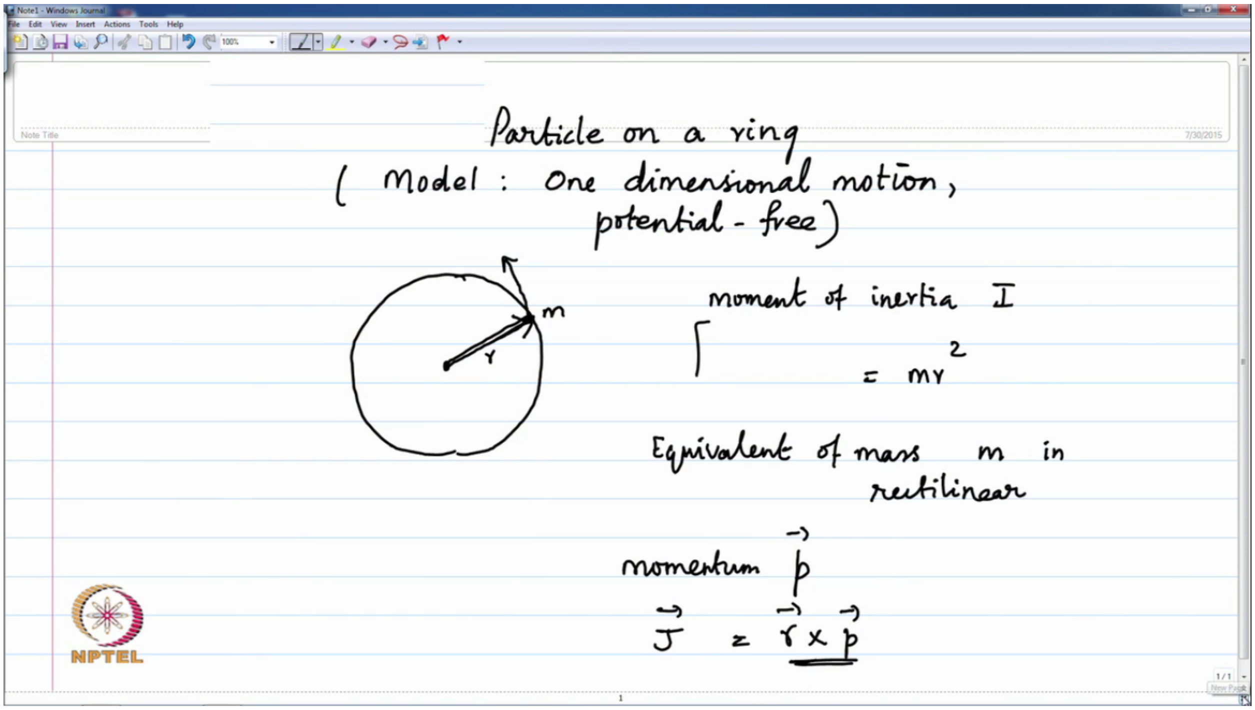
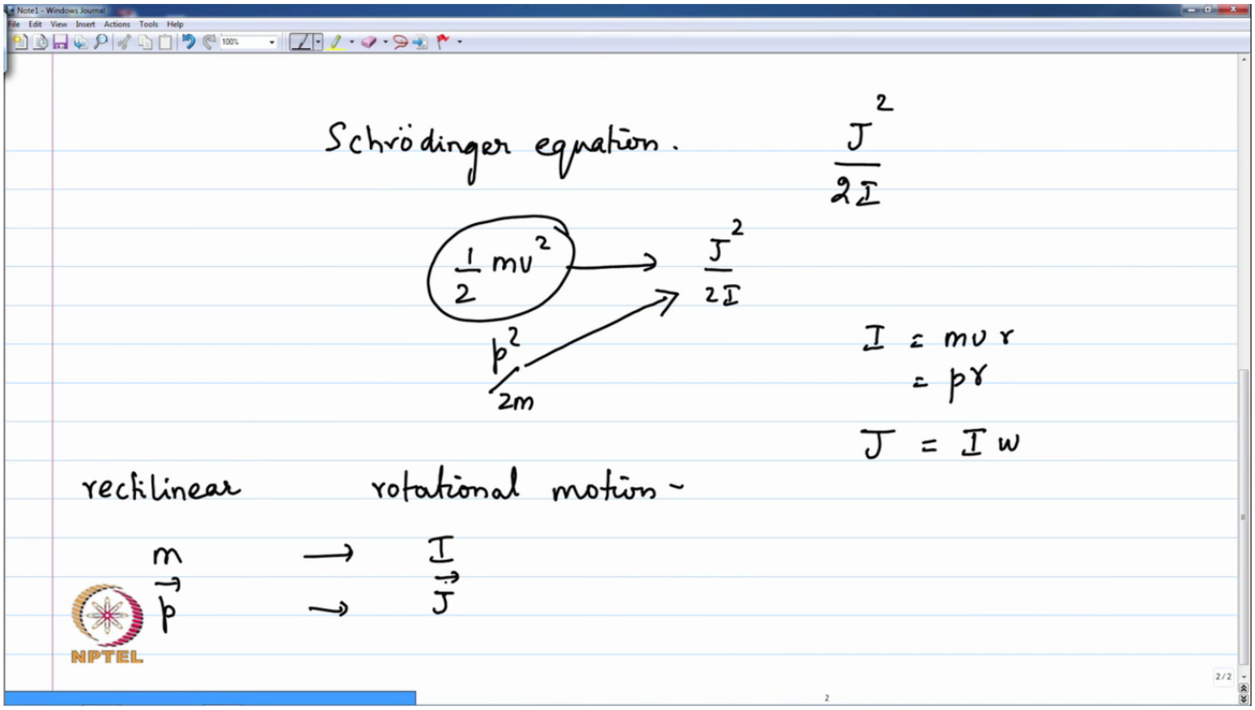
Welcome back to the lectures in chemistry. We shall deal with one more model namely the model of a particle on the ring before we close the lecture that's on the introductory quantum chemistry and move on to the lectures on introductory molecular spectroscopy.

The particle on a ring is an important one dimensional model which was not discussed until now for the simple reason that it wasn't necessary until now but if you have to study the rotational motion of a molecular system it is important to see how the angular momenta or quantized and particle in the ring model illustrates that in very simple terms.



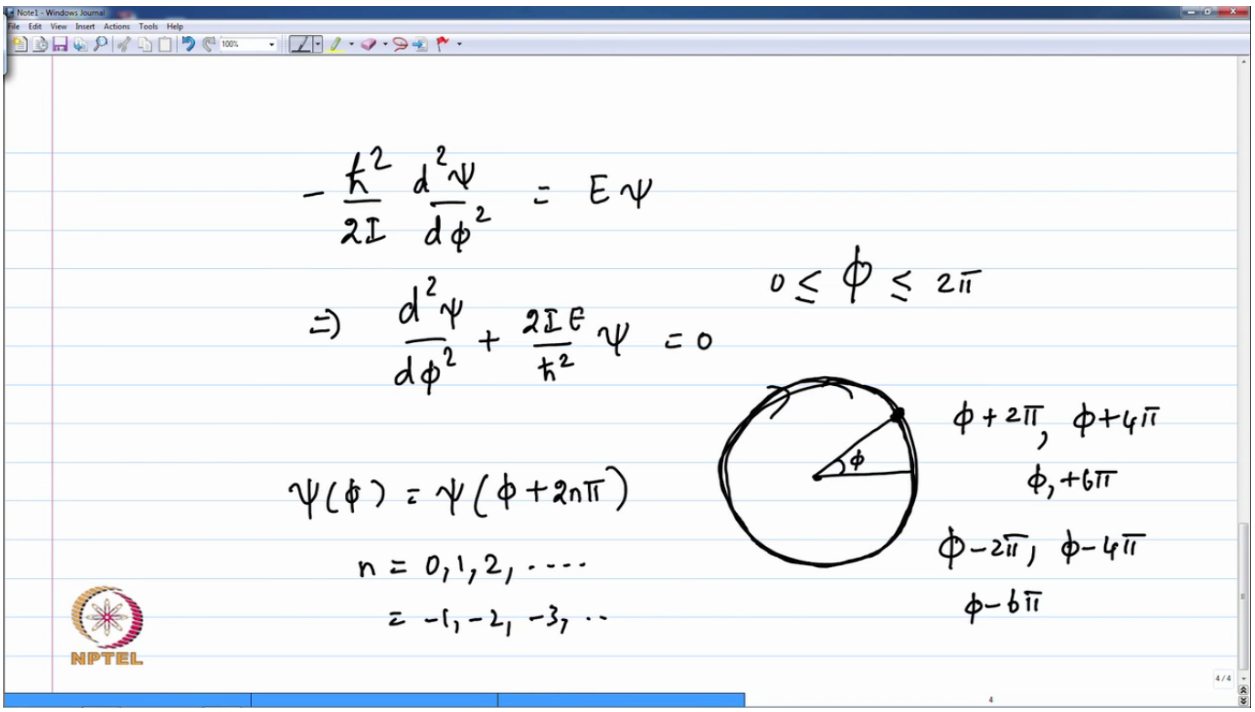
So it's a one-dimensional motion and when I say potential free you have to take this with a bit of a salt because any accelerated motion is not independent of potential. Therefore if you talk about a particle in the ring will be moving on a ring or motion around the point obviously there is a certain force which keeps that motion contained to that ring. Therefore there is a potential energy. What we will do is to neglect that component and only look at the particle with its rotational kinetic energy and the rotational kinetic energy of a very simple mass of say m moving in a circle around a point r sorry moving in a circle with radius r if you have to draw a simple circle around and the particle is moving on the circle with the radius r and its mass is m and it's a non-relativistic motion then we talk about the moment of inertia, I and that's given by mr square. The moment of inertia is essentially the equivalent of the mass in rectilinear motion m in rectilinear that is motion in a frame in which there is no external potential. The Newton's first law says that an object which is at rest will remain at rest and object which is moving at a the certain velocity will continue to move with the constant velocity as long as no forces act on them and so on. So that's the inertia, the concept of inertia came from that and in the case of circular motion it's the moment of inertia which is the moment about an axis in this case the axis is perpendicular to the plane of the motion and there is an angular momentum and if you put in the velocity, the momentum P as tangential to the motion on the circle then the angular momentum J is the vector r cross P. The vector is pointing outward or cross P. And in this case of course you know r & P you can use the right-hand thumb rule to show that the angular momentum is pointing towards you that is in a plane perpendicular but the vector is facing you, towards you and r cross P this angular momentum is quantized when you use Schrodinger equation for studying the circular, for studying the motion about a point. You remember the kinetic energy is of course in classical terms for a particle it is the angular momentum square divided by 2I or if you use the standard kinetic energy form that hal mv square you remember that transfers to J square by 2I because this goes to P square by 2m and you know that I is mvr which is P times r and therefore you can see that and also that the angular momentum J being given in terms of the angular velocity I Omega it is very easy to see that J square by 2I is equivalent to P square by 2m.



Therefore in rotational motion and if you say rectilinear Cartesian xy motion in one direction the mass the analogous quantity is I for the particle the moment of inertia. The velocity sorry, the momentum the linear momentum the analogous quantity is the angular momentum G and let's see we will get rid of that. And the kinetic energy half mv square goes over to J square by 2I. The one-dimensional motion you remember the momentum was replaced in quantum mechanics by the derivative operator minus ih bar d by dx where P is obviously sorry if you put the vector arrow you should not put the subscript here because of the component of the momentum. If you put the vector arrow this is gradient operator that process is also a vector. So the momentum P is associated with the coordinate X. In a similar way if you look at the angular momentum for the particle in circular motion as we will start with that as a simple example what's the coordinate associated with the angular momentum operator that's essentially with reference to an axis called the X-axis that's essentially the angle φ. So let me just write that that's the angle φ. Therefore with respect to the angle φ if we have to write correspondingly the angular momentum operator J. We have to write that the angular momentum operator is given by ih bar d by d φ.

So this is the coordinate which is an angle referenced to an axis system called the X-axis or whatever that you started with 0 axis and with respect to that how far the particle has drifted on the circle that the angle and then the angular momentum is in quantum mechanics the derivative operator containing the derivative d by d φ and you notice that the dimension of the angular momentum J is captured in the dimension of the h bar because φ is dimensionless it's an angle and therefore the angular momentum is obviously given in terms of the units h bar. Please remember this is something that Niels Bohr, his the discovery on the hydrogen atom he said that the angular momentum J is mv or which is quantized by nh bar where n is the quantum number 1, 2, 3, etc. because as long as the particle circulates I mean it's rotates in a circular motion its angular momentum is non-zero therefore the quantum number n has to be 1, 2, 3, for that part. However, we will see that en can actually take a value of zero which means that the particle doesn't have any angular momentum. It's stationary but we can't find out where it is. We will see those things in a few minutes.

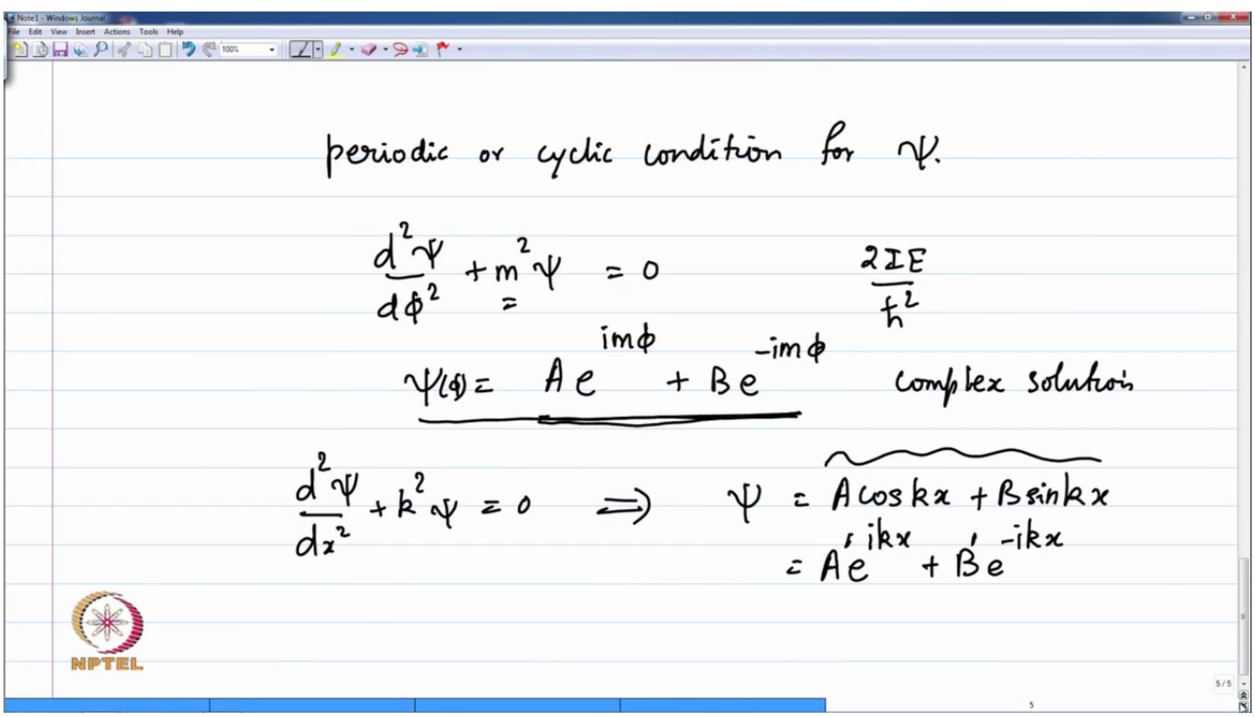
This is the angular momentum operator and therefore J square by 2I becomes the operator minus h bar square by 2I be square by d square by d φ square. This is the operator for kinetic energy and we shall assume that we are taking the particle moving or being fixed in a circle of radius r the r doesn't change let's assume that because if that is fixed then the potential energy due to that radius is a constant and they can ignore that in this simple exercise on the particle on a ring and we shall only worry about the kinetic energy operator. Therefore when you solve this equation h Ψ φ is equal to e Ψ this Ψ is now a function of the angle φ. It's a wave function which is actually represented by the value of Ψ at every given angle φ as it goes along the circle.



You have a classical model in mind that is you are actually trying to trace the particle and then you talk about the wave function. I think by now you must have gotten over this this kind of feeling what's wave function associated in the particle we are always going to talk about the wave function and the square of the wave function as the probabilities even though we will call the particle model every now and then. The wave function is a function of the angular coordinate φ and therefore the solution that you have to worry about is the solution of the equation minus h bar square by 2I d square Ψ by d φ square is equal to e Ψ which is if you write that d square Ψ by d φ square plus 2IE by h bar square Ψ is equal to 0 but there is one additional requirement namely that the value of φ is between 0 and 2 π. If it's more than 2 π what is it? It does not matter. When you say if this angle is φ and this is the particle's position or the wave function at this point if you calculate the wave function for this angle what happens after you go around and increase φ by 2 π the wave function is unique to that value of φ or φ plus 2 π or φ plus 4 π or φ plus 6 π and what about going around this way if you go around the opposite direction that is 5 minus 2 π φ minus 4 π, φ minus 6 π doesn't matter all these things refer to this point. Therefore if the wave function is unique for the particle's position or the system's position at a given value of φ it should be the same for all values therefore we simply write Ψ of φ is the same thing as Ψ of φ plus 2n π where n is 0 ,1 ,2 ,3, etcetera. if you want that in the positive direction n can also be -1, -2, -3 etcetera.

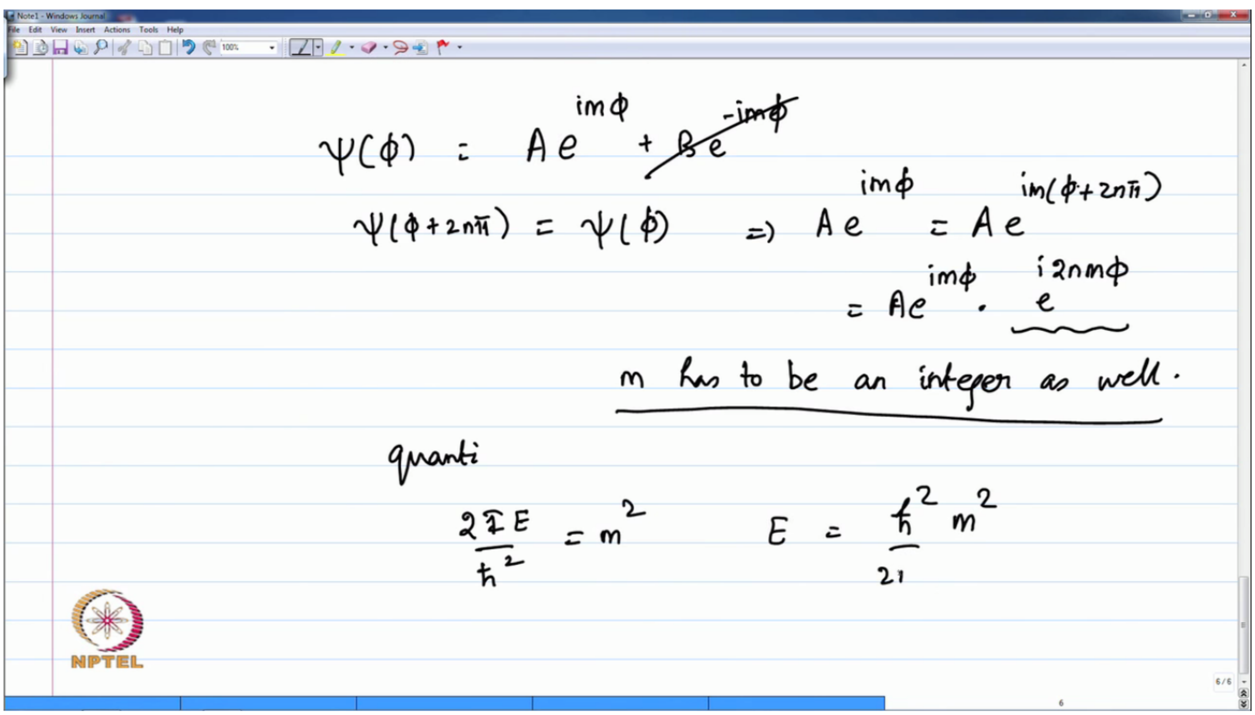
So the wave function now satisfies not a boundary condition but what is called a periodic or a cyclic boundary condition. It's called a cyclic condition. Periodic or cyclic condition for the Ψ. Therefore if you write this particular quantity d square Ψ by d φ square with some value m square Ψ is equal to 0 because we know that this kind of equation this is a positive value because it's 2IE by h bar square and the particle having any kinetic energy in a circular motion obviously has a positive energy, moment of inertia is positive h bar square h bar is positive therefore this is a positive quantity and this of course has a solution Ψ is equal to a Ae to the im φ plus Be to the minus im φ. Now I am using imaginary that is complex solutions.

You also remember that a similar equation for the particle in the one dimensional box d square Ψ by dx square plus k square Ψ is equal to 0 was given as a solution that Ψ is equal to Acoskx plus Bsinkx we did not use the general complex solutions here. We could have written that. This is also Ae to the ikx plus Be to the minus ikx we could have written A prime, B prime, some other constants because after all the exponential ikx can be written as coskx plus isinkx exponential minus ikx also can be written that way with a minus sign and it's possible for you to get this solution. We used that solution for the particle in a one dimensional box because that was convenient to illustrate the boundary conditions very quickly. Here in the circular motion the Ψ of φ if we use this as a general solution that the exponential im φ and the exponential minus im φ it's more convenient to describe the angular momentum of the particle. Therefore, this is the solution that we employ and then we try and see what this means for the particle in the one dimensional box.



So I have been rather very quick in taking this through because I believe that you have gone through the four lectures and therefore you are comfortable with the level of mathematics that has been introduced so far. Therefore I'll jump the steps. I'm not even suggesting to you how to derive the kinetic energy in the form or how to write the angular momentum as minus ih bar by d φ. I've skipped quite a number of these steps. Some of these things would be more obvious when you do a little more elaborate mathematics in the next course.

Now Ψ of φ is given by this general quantity Ae im φ plus Be – im φ let's for the time being let's worry about motion in one directional sense. Therefore let's not consider that. Please remember Ψ of φ plus 2n π be Ψ of φ because the wave function is unique it does not matter as long as the n is integral integer 0, 1, 2, 3, etc. this condition has to be satisfied. Therefore you remember Ae to the im φ should also be equal to Ae to the im φ plus or plus 2n π. Therefore what is this Ae im φ times Ae 2nmi φ sorry there is no A. A is already there. If the wave function has to be the same for all such values of repeating φ φ, φ plus 2 π, φ plus 4 π, φ plus 6 π and so on then the only possible value for that is that m has to be an integer as well. That's the quantization. Please remember the n is not a quantization. N is a boundary requirement cyclic requirement. It's a periodic boundary requirement for the particle sustained in a circle or in a circular motion. That comes out naturally from the way we have defined the angle φ. That comes naturally by the definition of the angular φ. Therefore n there should not be considered as a quantum number. Now the m being a quantum number is a requirement for the wave function to satisfy in order for that wave function to be unique and you immediately see that if m is an integer you remember you put 2IE by h bar square as m square. Therefore what happens to m and if this is an integer then the energy is h bar squared m square by 2I.



Now this is the unit for the energy and this is the quantum number and now the energy is given by the square of an integer. So irrespective of what the value of the sin of the integer is the energy is always positive as long as the particle is having a finite kinetic energy in a circular motion and it's the unit for that is now h bar square by 2I in a similar way that you had for a particle in a one dimensional box it was h square by 8 m l square that you had. Please remember m l square. Dimensionally that's the same thing as imr square here the l is the equivalent of the radius of the circle r, h bar square by h square by 8 m l square is almost I mean it's identical to h square there is a 4 π here, 4 π square here and there's a 2 so you have 8 π square I which is nothing other than m l square.

Therefore, particle in the one-dimensional motion and particle in a circular motion with only kinetic energy being considered are I mean have been very close to each other but there is a subtle difference. The subtle difference is that the particular motion we have taken e to the im φ to generate this quantum number m as integer. What about minus im? It's the same thing except that the sense of the motion which is either what is anti clockwise or clockwise whether the angular momentum operator associated to that whether it's pointing upwards with respect to the plane of the motion or whether it is pointing downwards or inverse with respect to the plane of motion that's what comes out of it and therefore what's meant by this linear combination we don't know anything about the value of the angular momentum. It's very interesting. So this is the initial mathematical consequences.

In the next part of this lecture what I would do is to illustrate some of these things and also calculate the value of angular momentum and these are extremely important in studying rigid body rotations in quantum mechanics as well as molecular rotations in microwave and even infrared spectroscopy where rotations and vibrations happen together. Therefore, for chemists this is also extremely important and in a sense it's equally important in the NMR, Nuclear Magnetic Resonance spectroscopy when microwave motion actually couples in the form of some of the interactions there's spin rotation interactions and so on. Therefore particle in a one-dimensional motion on a ring it's one-dimensional because we have kept the two – the second dimensional component the radius as a constant and the one dimension refers to the one variable fee that is the rotational quadrant. We will continue this in the next part; until then thank you.