Chemistry I-CY1001 (IIT Madras)
Introductory Quantum Mechanics and Spectroscopy

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Lecture – 7
Part 1
Particle on a Ring

Welcome back to the lectures in Chemistry. We shall deal with one more model namely, the model of a particle on a ring before we close the lecture sets 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 was not necessary until now. But, if we have to study the rotational motion of a molecular system, it is important to see how the angular momenta are quantized. And, particle on a ring model illustrates that in very simple terms. So, it is a one-dimensional motion. And, when I say potential free, you have to take this with a bit of assault, because any accelerator motion is not independent of potential. Therefore, if you talk about a particle moving on a ring or motion around a point; obviously, there is a central force, which keeps at motion contained to that ring. Therefore, that is a potential energy. What we would do is to neglect that component and only look at the particle with its rotational kinetic energy.

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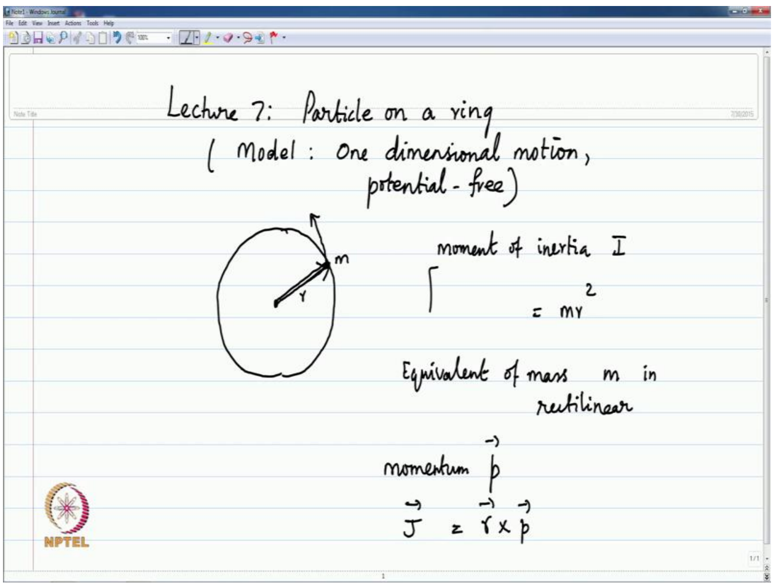

And, the rotational kinetic energy of a very simple mass of say m moving in a circle with radius r; if you have to draw a simple circle around; and, the particle is moving on the circle with the radius r, and its mass is m, and its non realistic motion; then, we talk about the moment of inertia I. And, that is given by m r 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, the object, which is moving at the set velocity will continue to move with constant velocity as long as no forces act on them and so on. So, that is the inertia; the concept of inertia came from that.

And, in a case of circlular motion, it is 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 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 – r cross p. And, in this case, of course, you know r and 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.

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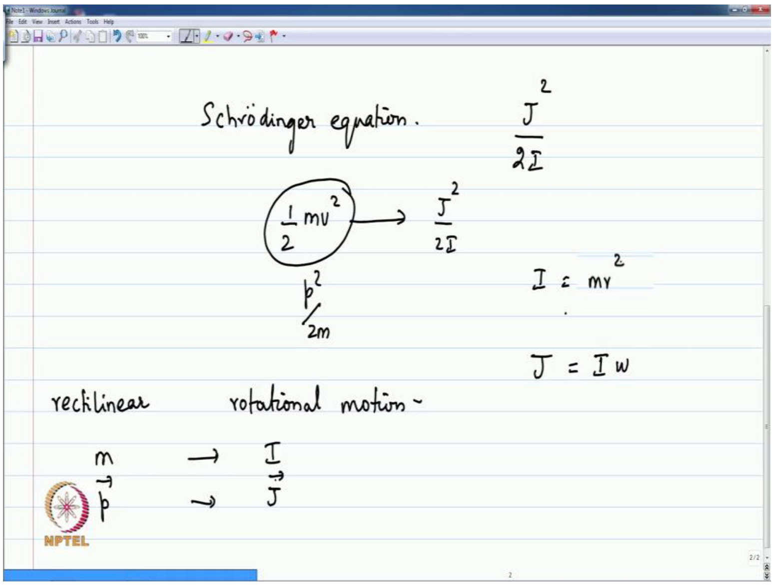

And, r cross p – this angular momentum is quantized when you use Schrodinger equation for studying the motion about a point. You remember the kinetic energy is of course, in classical transfer, a particle; it is the angular momentum square divided by 2I; or, if you use the standard kinetic energy form that, half m v square; you remember that transfers to J square by 2I, because this goes to p square by 2m. And, you know that, I is m r square. And also, with 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 – a motion in one direction, the mass – the analogous quantity is I for the particle – the moment of inertia. The linear momentum – the analogous quantity is the angular momentum J.

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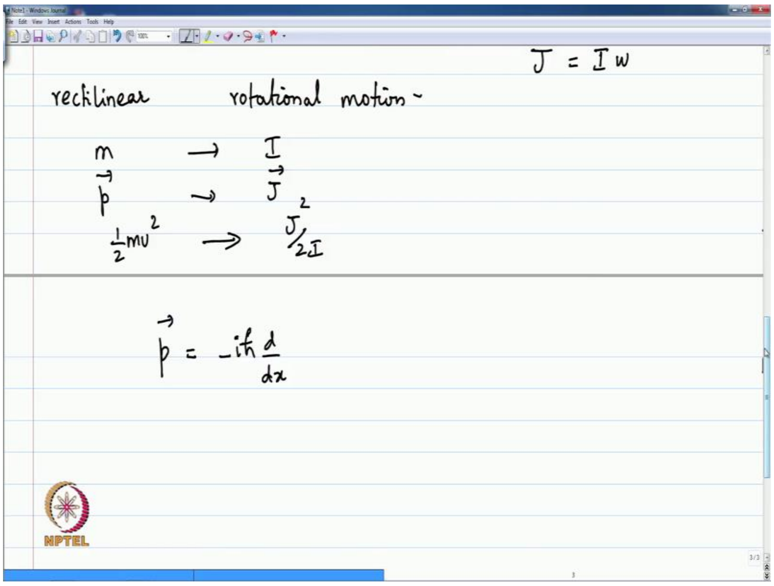

And, the kinetic energy half m v square goes over to J square by 2I. The one-dimensional motion; you remember the momentum was replaced in quantum mechanics by the derivative operator minus ih bar d by dx, where p is obviously… If you put the vector arrow, you should not put the subscript here, because that is a component of the momentum. If you put the vector arrow, this is gradient operator. Therefore, this is also a vector. So, the momentum p is associated with the coordinate x.

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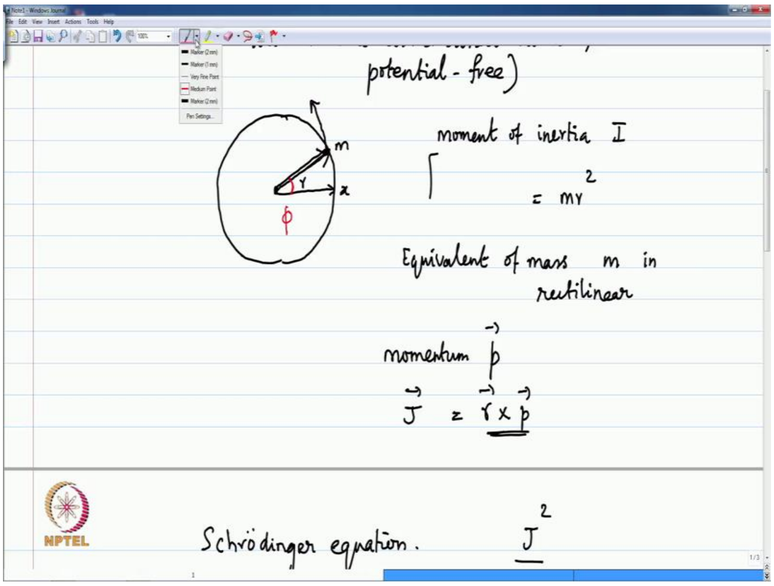

In a similar way, if you look at the angular momentum for the particle in circular motion as we will start with that as a simple example; what is the coordinate associated with the angular momentum operator that is essentially with reference to an axis called x-axis;

that is essentially the angle phi. So, let me just right that; that is the angle phi.

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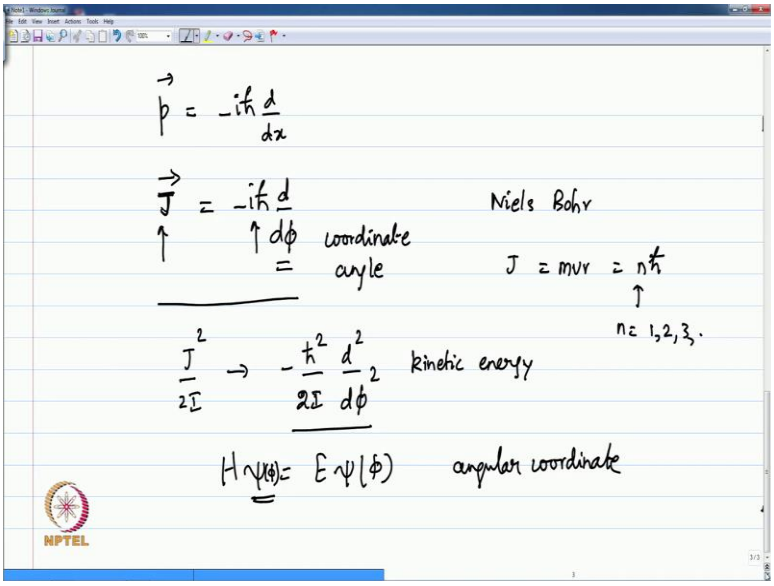

Therefore, with respect to the angle phi, if we have to write correspondingly the angular momentum operator J, we have to write that. The angular momentum operator is given by ih bar d by d phi. So, this is the coordinate, which is an angle referenced to an axis system call the x-axis or whatever; that you start as a 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 phi. And, you notice that, the dimension of the angular momentum J is captured in the dimension of the h bar, because phi is dimensionless; it is 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 mentioned in his discovery on the hydrogen atom; he said that, the angular momentum J is mvr, which is quantized by nh bar, where n is the quantum number – 1, 2, 3, etcetera because as long as the particle circulates, I mean it rotates in a circular motion, it is angular momentum is nonzero. Therefore, the quantum number n has to be 1, 2, 3 for that part. However, we will see that, n can actually take a value of 0; which means that, the particle does not have any angular momentum; it is a stationary, but we cannot 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 d square by d phi 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 does not change. Let us assume that; because if that is fixed; then the potential energy due to that radius is a constant and we 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 psi is equal to E psi; the psi is now a function of the angle phi. It is a wave function, which is actually represented by the value of psi at every given angle phi as it goes around 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 got over this kind of feeling what is a wave function associated with 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 angle coordinate – angular coordinate phi.

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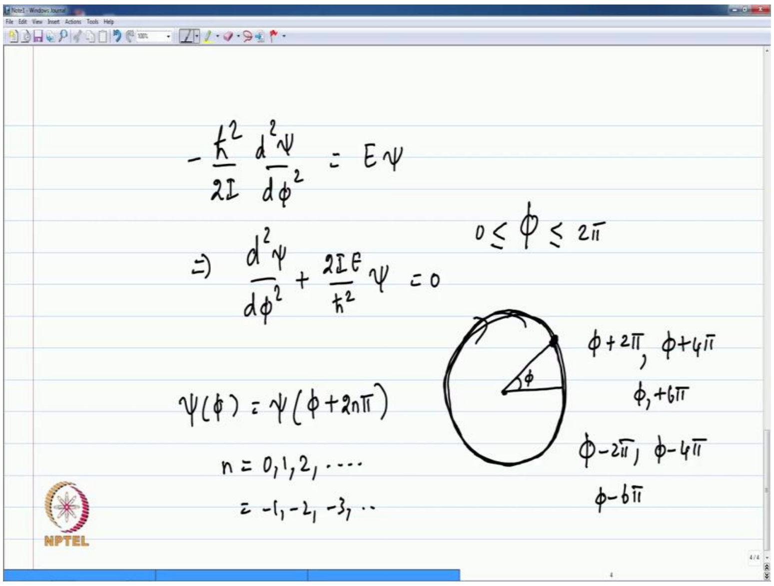

And therefore, the solution that you have to worry about is the solution of the equation – minus h bar square by 2I d square psi by d phi square is equal to E psi; which is if you write that, d square psi by d phi square plus 2IE by h bar square psi is equal to 0. But, there is one additional requirement namely that, the value of phi is between 0 and 2 pi. If it is more than 2 pi, what is it? It does not matter. When you say if this angle is phi 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 phi by 2 pi? The wave function is unique to that value of phi or phi plus 2 pi or phi plus 4 pi or phi plus 6 pi. And, what about going around this way – if you go around the opposite direction, that is, phi minus 2 pi, phi minus 4 pi, phi minus 6 pi? Does not matter; all these things are referred 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 phi, it should be the same for all values. Therefore, we simply write psi of phi is the same thing as psi of phi plus 2n pi; where, n is 0, 1, 2, 3, etcetera. If you want that in the positive direction, n can also be minus 1, minus 2, minus 3, etcetera. So, the wave function now satisfies not a boundary condition, but what is called a periodic or a cyclic boundary condition. It is called the cyclic condition.

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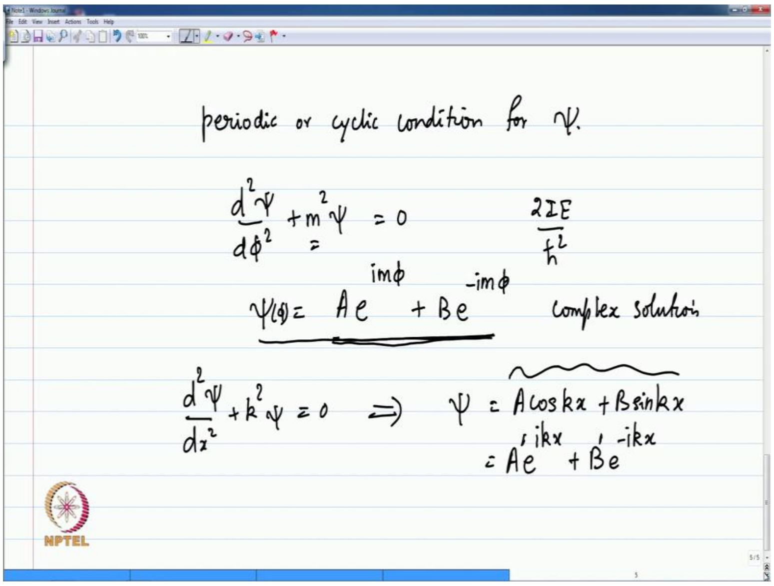

Periodic or cyclic condition for the psi; therefore, if you write this particular quantity d square psi by d phi square with some value m square psi is equal to 0, because we know that, this kind of equation; this is a positive value, because it is 2I E by h bar square. And, the particle having any kinetic 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 psi is equal to A e to the i m phi plus B e to the minus i m phi. Now, I am using imaginary, that is, complex solutions. You also remember that, a similar equation for the particle in a one-dimensional box d square psi by dx square plus k square psi is equal to 0 was given as a solution with psi is equal to A cos kx plus B sin kx. We did not use the general complex solutions here. We could have written that. This is also A e to the ikx plus B e 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 cos kx plus i sin kx; exponential minus ik also can be written that way with the minus sign. And, it is 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 psi of phi – if we use this as a general solution that, the exponential i m phi and the exponential minus i m phi. It is 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 a one-dimensional box. So, I mean 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 will jump this ((Refer Slide Time: 16:07)). I am 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 d by d phi; I have skipped quite a number of the steps. Some of these things would be more obvious when you do a little more elaborate mathematics in the next course.

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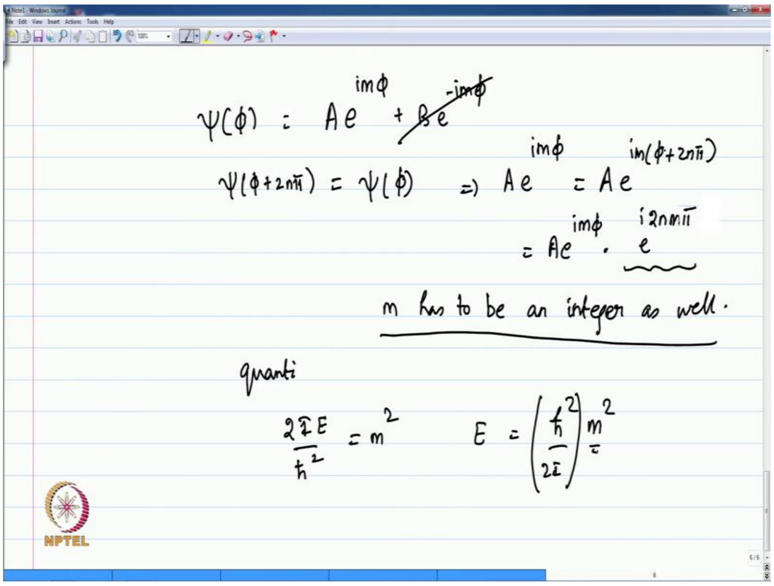

Now, psi of phi is given by this general quantity A exponential i m phi plus B exponential i m phi. Let us… For the time being, let us worry about motion in one-directional sense. Therefore, let us not consider that. Therefore, please remember psi of phi plus 2n pi must be psi of phi, because the wave function is unique. It does not matter as long as n is integer 0, 1, 2, 3, etcetera. This condition has to be satisfied. Therefore, you remember A e to the i m phi should also be equal to A e to the i m phi plus 2n pi. Therefore, what is this? A exponential i m phi times A exponential 2 n m i phi – there is no A; A is already there. If the wave function has to be the same for all such values of repeating phi phi, phi plus 2 pi, phi plus 4 pi, phi plus 6 pi and so on; then, the only possible value for that is that, m has to be an integer as well. That is the quantization. Please remember – the n is not a quantization; the n is a boundary requirement – cyclic requirement. It is a periodic boundary requirement for the particle to stay in a circle or in a circular motion. That comes out naturally from the way we have defined the angle phi. That comes naturally by the definition of the angle phi. 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 square 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 – the sign 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 is the unit for that is now h bar square by 2I in a similar way that you had for the particle in a one-dimensional box. It was h square by 8 ml square that you had. Please remember ml square. Dimensionally, that is the same thing as I or m r 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 is identical to h square, that is, a 4pi here – 4pi square here and there is a 2. So, you have 8 pi square I, which is nothing other than m l square.

Therefore, particle in a one-dimensional motion and particle in a circular motion with only kinetic energy being considered or I mean very close to each other; but, that is a subtle difference. The subtle difference is that, the particular motion… We have taken e to the im phi to generate this quantum number m as an integer. What about minus im? It is the same thing, except that the sense of the motion, which is either what is called anti-clock wise or clock wise. Whether the angular momentum operator associated with that; whether it is pointing upwards with respect to the plane of the motion; or, whether it is pointing downwards or inwards with respect to the plane of motion, that is what comes out of it. And therefore, what is meant by this linear combination? We do not know anything about the value of the angular momentum. It is 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 in spectroscopy, where rotations and vibrations happen together. Therefore, for chemists, this is also extremely important. And, in a sense, it is equally important in a bar nuclear magnetic resonance spectroscopy when microwave motion actually couples in the form of some of the interactions – spin rotation interaction and so on. Therefore, particle in a one-dimensional motion on a ring; it is one-dimensional because we have kept the second dimensional component – the radius as a constant. And, the one dimension refers to the one variable phi, that is, a rotational coordinates. We will continue this in the next part; until then, thank you.