Atomic Structure and Chemical Bonding

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Lecture – 19
Particle on a Ring: The Quantum Model

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 through 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 you have to study the rotational motion of a molecular system, it is important to see how the angular moment are quantized.

And particle in the ring model illustrates that in very simple terms. So, it is a one-dimensional motion. And when I say potential free how 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, when it moving on a ring or motion around a point, obviously there is a central force, which keeps that motion contained to that ring, and therefore there is a potential energy. What we would 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 or a sorry moving in a circle with radius r.

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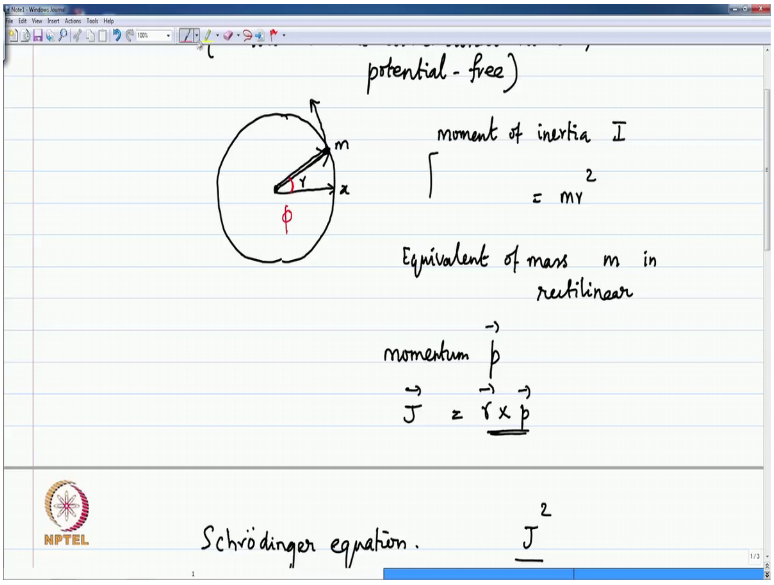

If you have to draw a simple circle around, and the particle is moving on the circle with the radius r, and its mass is m and its non relativistic motion. Then we talk about the moment of inertia I and that is given by m r square. The moment of inertia is essentially the equivalent of the mass in rectilinear motion m in rectilinear that is motion in your frame in which there is no external potential.

The Newton's first law says that a an object which is at rest will remain at rest, and an object which is moving at a certain velocity will continue to move with the 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 the case of circular 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 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 (Refer Time: 04:00) that is in a plane perpendicular, but the vector is facing you towards you. And r cross p this angular momentum is quantized.

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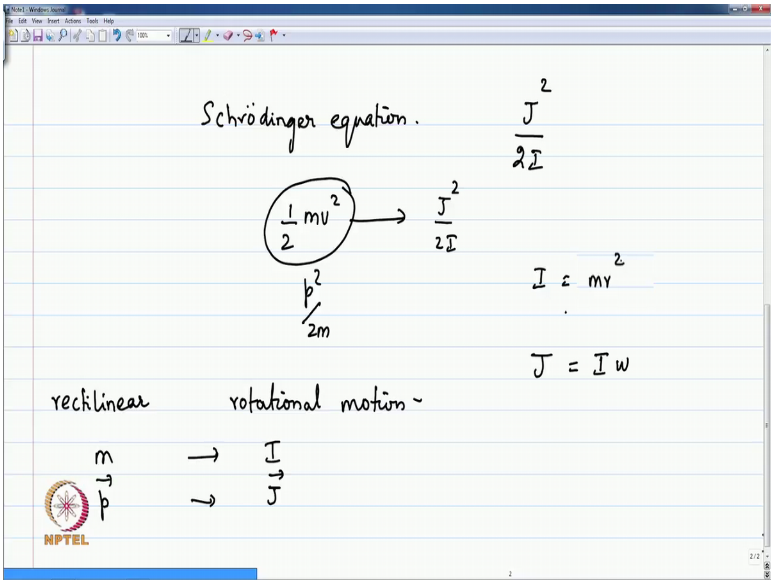

When you use Schrodinger equation for studying the circular for studying the motion about a point you remember the kinetic energy is, of course in classical terms for a particle, it is the angular momentum square divided by 2 I or if you use the standard kinetic energy form that half m v square, you remember that transfers to J square by 2 I, because this goes to p square by 2 m. 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 2 I is a equivalent to p square by 2 m.

Therefore, in rotational motion and if you say rectilinear Cartesian x y a 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 J.

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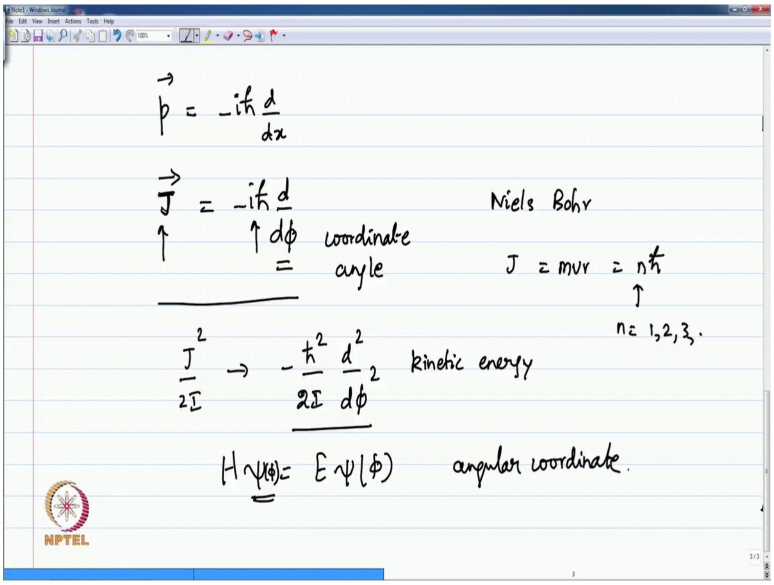

And the kinetic energy half m v square goes over to J square by 2 I. The one-dimensional motion you remember the momentum was replaced in quantum mechanics by the derivative operator minus i h bar d by d x, where p is obviously, sorry if you put the vector arrow, you should not put the subscript here, because that is a component of the momentum. If you put the vector arrow this is gradient operator that for this is also a vector, so the momentum p 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 is the coordinate associated with the angular momentum operator that is essentially with reference to an axis called the x-axis. That is essentially the angle phi, so let me just write that that is the angle phi ok. 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 i h bar d by d phi. So, this is the coordinate which is an angle referenced to a an axis system called 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 of 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 its 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 the discovery on the hydrogen atom.

He said that the angular momentum J is m v r, which is quantized by n h bar, where n is the quantum number 1, 2, 3 etcetera, because as long as the particle circulates I mean its rotates in a circular motion its angular momentum is non-zero. Therefore, the quantum number n has to be 1, 2, 3 for that point. 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 stationary, but we cannot find out where it is you will see those things in a few minutes.

This is the angular momentum operator and, J square by 2 I becomes the operator minus h bar square by 2 I 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 do not be worry about the potentially 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 all over the circle ok. 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 and over this kind of feeling what is a wave function associated in the particle. We are always going to talk about the wave functions 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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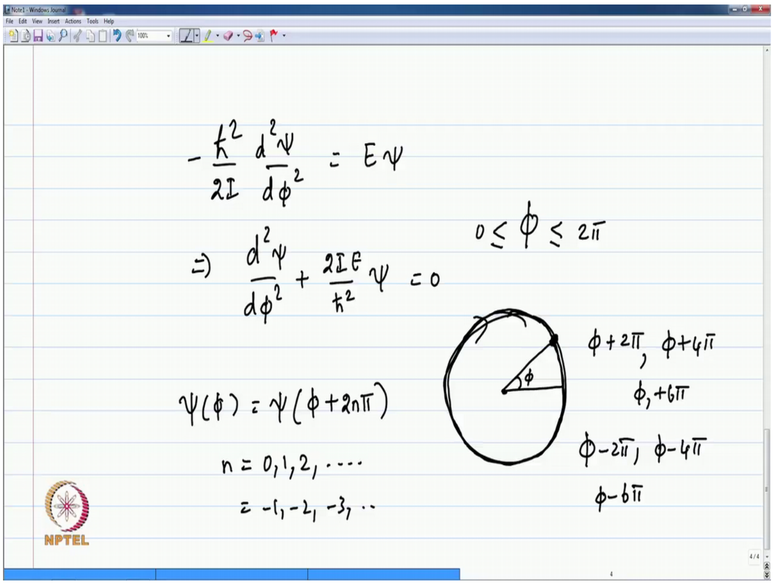

And therefore the solution that you have to worry about is the solution of the equation minus h bar square by 2 I d square psi by d phi square is equal to E psi, which is if you write that d square psi by d phi square plus 2 I E by h bar square psi is equal to 0 but there is one additional requirement, 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 particles 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 phi or phi plus 4 phi or phi plus 6 pi. And what about going around this way, if you go around the opposite direction, that is 5 minus 2 pi, pi minus 4 pi, 5 minus 6 5 does not matter. All these things are referred to this point. Therefore, if the wave function is unique for the particles position or they the systems 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 2 n 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 a cyclic condition.

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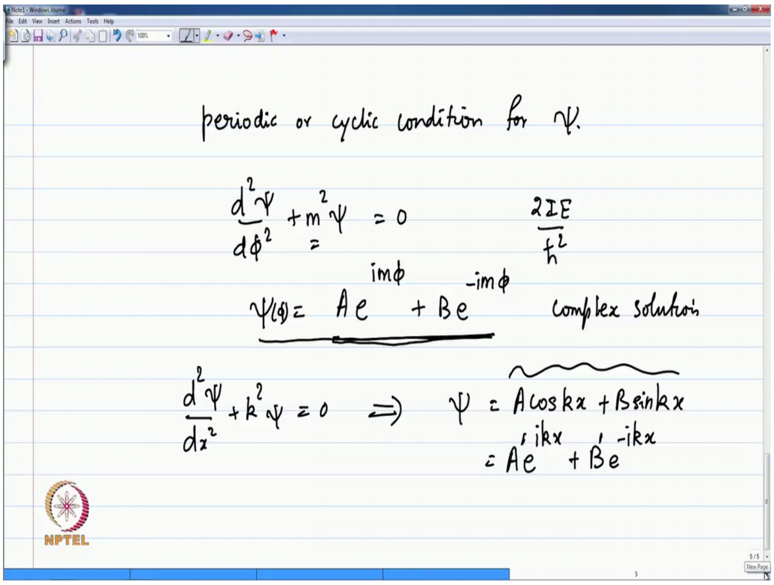

Periodic or cyclic condition for the psi psi therefore, if you write this particular quantity d square psi by d phi square with some value m square psi is equal to 0, because we know that this kind of equation this is a positive value, because it is 2 I E by h bar square. And the particle having any 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 that psi is equal to A cos k x plus B sin k x. We did not use the general complex solutions here.

We could have written that this is also A e to the i k x plus B e to the minus i k x. We could have written A prime B prime some other constants, because after all the exponential i k x can be written as cos k x plus i sine k x exponential minus i k x also can be written that way with a minus sign. And it is possible for you to get this solution. We use to that solution from 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 e 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 being 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 the skips 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 I h bar d by d phi I have 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 ok. Now, psi phi is given by this general quantity A exponential i m phi plus B e exponential minus I m phi.

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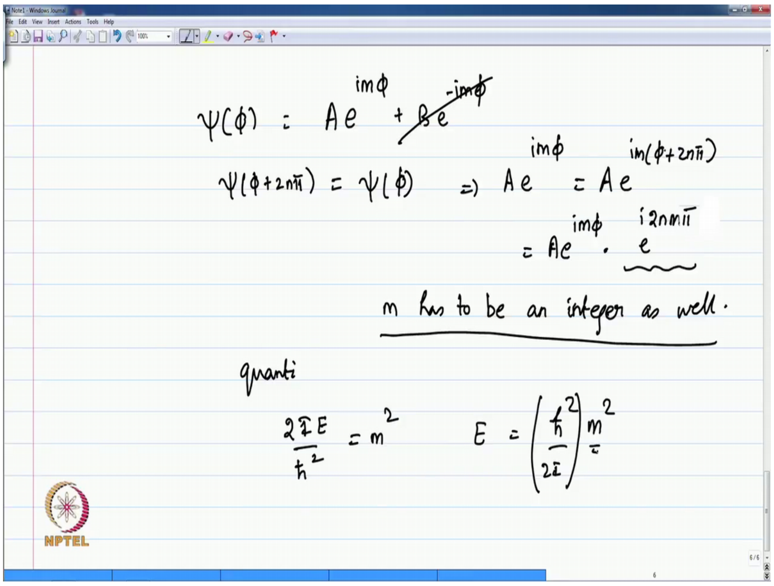

Let us for the time being let us worry about motion, in one directional sense therefore let us not consider that. Please remember psi of phi plus 2 n pi must be psi of phi, because the wave function is unique. It does not matter as long as the n is integral integer 0, 1, 2, 3 etcetera. This condition 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 or plus no minus plus 2 n pi.

Therefore, what is this A exponential i m phi times A exponential 2 n m i phi sorry, 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 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 ok. 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 is should be should not be considered as a quantum number. Now, the m being a quantum number is a requirement for the wave functioned 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 2 I E by h bar square as m squared. Therefore, what happens to m and if this is an integer then the energy is h bar square m square by 2 I ok. 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 sign of the integer is the energy is always positive as long as the particle is having finite kinetic energy in a circular motion.

And it is the unit for that is now h bar square by 2 i 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. This remember m l 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. There is a 4 pi here 4 pi square here and there is a 2, so you have 8 pi square i which is nothing other than m l square ok. Therefore, particle in a one-dimensional motion and particle in a circular motion with only kinetic energy being considered or I 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 i m phi to generate this quantum number m as integer what about minus i m. It is the same thing except that the sense of the motion which is either what is called the clock anti clockwise or clockwise. Whether the angular momentum operator associated to that whether its 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 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 ok. 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 is equally important in a more nuclear magnetic resonance spectroscopy when microwave motion actually couples in the form of some of the interactions, there is the spin rotation interactions and so on. Therefore, particle in a one-dimensional motion on a ring, it is 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 phi that is the rotational coordinates. We will continue this in the next part.

Until then thank you.