Chemistry II: Introduction to Molecular Spectroscopy
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Lecture – 07
Introduction to quantum mechanics II

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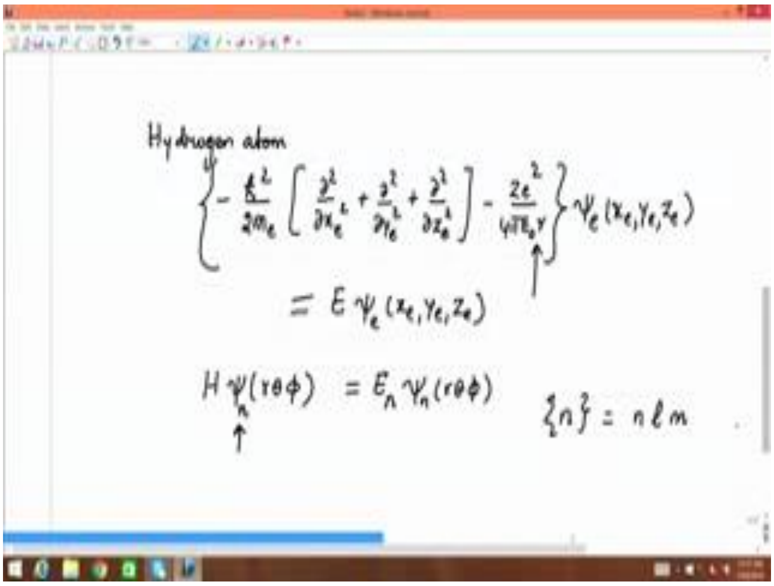

Hydrogen atom

$$\left\{-\frac{\hbar^2}{2m_e}\left[\frac{\partial^2}{\partial x_e^2}+\frac{\partial^2}{\partial y_e^2}+\frac{\partial^2}{\partial z_e^2}\right]-\frac{Ze^2}{4\pi\epsilon_0 r}\right\}\psi_e(x_e,y_e,z_e)$$

$$= E\,\psi_e(x_e,y_e,z_e)$$

$$H\psi_n(r\theta\phi) = E_n\psi_n(r\theta\phi) \qquad \{n\} = n\,l\,m$$

Welcome back to the lecture on Chemistry and the Introduction to Molecular Spectroscopy. So, the lecture will continue on the quantum mechanics that I introduced a little bit in the previous lecture the summary of quantum results that we need to use. We started with the description on the hydrogen atom and wrote down the Schrodinger equation as all of this representing the total energy of the electron acting on the wave functions psi e, which is a function of the three coordinates y e, z e. So, this is the h psi is equal to E psi e x e, y e, z e.

Now, hydrogen atom due to the specific property of the potential energy between the electron and the nucleus being spherically symmetric that is it has same value on a sphere of radius r on any part on the surface of the sphere. The standard method for solving the hydrogen atom problem is to use the spherical polar coordinate system. So, one writes the wave function in terms of the three polar coordinates r, theta, phi and obtains solutions n. Now, remember this n, when we complete this equation E n psi n r theta phi; n stands for a set of three quantum numbers namely a principle quantum number n, and Azimuthal quantum number l, and magnetic quantum number m - three quantum numbers are there.

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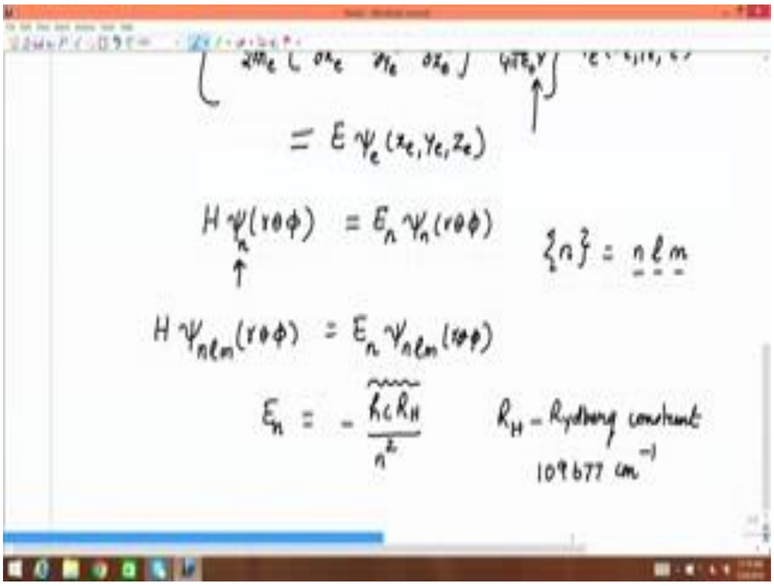

$$= E\psi_e(x_e, y_e, z_e)$$

$$H\psi_n(r\theta\phi) = E_n\psi_n(r\theta\phi) \qquad \{n\} = \underline{n}\,\underline{l}\,\underline{m}$$

$$H\psi_{nlm}(r\theta\phi) = E_n\psi_{nlm}(r\theta\phi)$$

$$E_n = -\frac{\widetilde{hcR_H}}{n^2} \qquad R_H - \text{Rydberg constant}$$

$$109677\ \text{cm}^{-1}$$

Therefore the wave function for the hydrogen atom is given by psi n l m r theta phi. And the Eigen value for this for the electron of course, it is only on the principle quantum number. Therefore, we have degeneracy for the wave function psi n l m r theta and phi. The standard practice is to solve the Schrodinger equation using method of separation of variables and the energies are obtained in the process as the familiar expression that Niels-Bohr also showed earlier using the Rydberg constant-R H is the Rydberg constant. And in terms of numbers experimentally as well as theoretically the number is 109677 centimeter inverse. Please remember this is h c nu bar.

If you recall the first lecture it is R h is a wave number and the energy is inversely proportional to the square of the quantum number. Particle in a box the energies proportional to m square; harmonic oscillator the energy is proportional to n; the hydrogen atom energy proportional to 1 by n square. So, quantum number dependences are different for different models.

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E_n $n=1,$ $= -hcR_H$ -13.6 eV

$n=2$ $-\frac{13.6}{4}$

$n=3$ $-\frac{13.6}{9}$ etc.

$n \to \infty \Rightarrow 0$

.

The wave functions themselves are written as a product of a radial and an angular orbital anyway. First, E n then n is 1 the energy corresponds to minus h c Rydberg constant and that is in the electron volt familiar electron volt, it is minus 13.6 electron volts for n equal to 1. Obviously, for n equal to 2, it is minus 13.6 divided by 4; and for n equal to 3, it is minus 13.6 divided by 9 etcetera until n goes to infinity, this energy level is 0.

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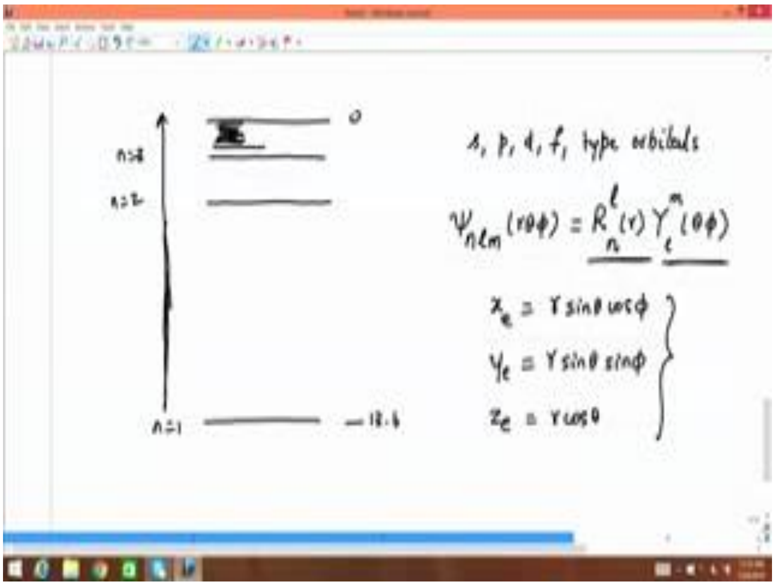

s, p, d, f, type orbitals

$$\Psi_{nlm}(r\theta\phi) = \underline{R_n^l(r)}\,\underline{Y_l^m(\theta\phi)}$$

$$\left.\begin{aligned} x_e &= r\sin\theta\cos\phi \\ y_e &= r\sin\theta\sin\phi \\ z_e &= r\cos\theta \end{aligned}\right\}$$

.

So, if you look at these spectrum of the hydrogen atom in an energy scale, if you do that and if you write this as the 0, and this as the minus 13.6 then the next energy this is for n equal to 1, the next energy is one-fourth of this, so roughly somewhere this is about half. So, roughly here n equal to 2, sorry it is one-fourth, therefore it is somewhere here, n equal to 2. And the next one is one-ninth of this, so somewhere here n equal to 3. And you can see that the energy levels become very, very dense as you go long and the state of 0 is for infinitely large quantum numbers and when the electron is completely free from the nucleus.

So, this is the energy level picture. And what about the wave function picture the wave function picture leads to the familiar description in terms of the s, p, d, f type orbitals. In chemistry so far we have not needed the g orbitals; we have not discovered elements with sufficiently large atomic number which warrants g orbitals. And the wave functions psi n l m r theta phi is expressed in terms of a radial function, which depends on the quantum number l and n and it is a function of radial coordinate r, and an angular function which is a function of the quantum numbers l and m and it is dependent on the angles theta and phi. And these are polar coordinates you recall that x e is r sin theta cos phi on the spherical system; y e is r sin theta sin phi, and z e is r cos theta. So, these are the theta phi or theta phi dependences of the coordinates, therefore the wave function is expressed using that. And you see that the radial part you see that these are radial part and then there is a angular part.

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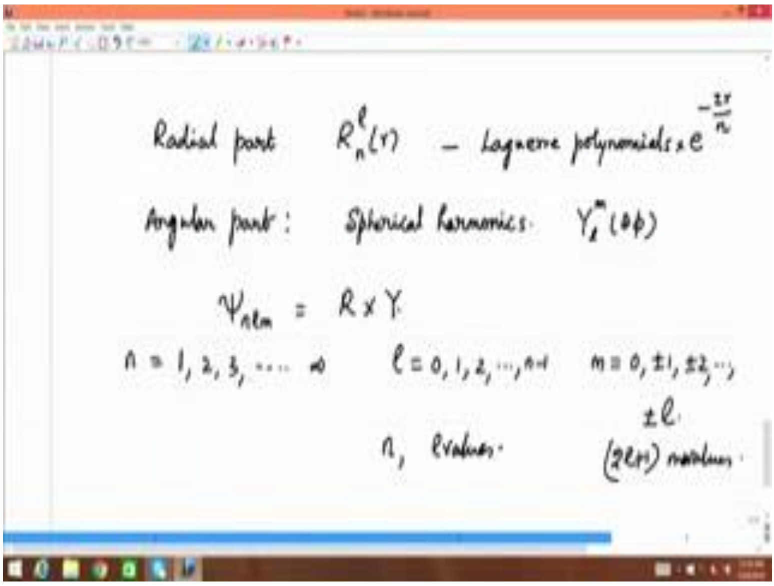

Radial part $R_n^l(r)$ – Laguerre polynomials $\times e^{-\frac{2r}{n}}$

Angular part : Spherical harmonics. $Y_l^m(\theta\phi)$

$\psi_{nlm} = R \times Y.$

$n = 1, 2, 3, \dots \infty$ $l = 0, 1, 2, \dots, n-1$ $m = 0, \pm 1, \pm 2, \dots, \pm l.$

$n,$ l values. $(2l+1)$ m values.

.

The radial part R l n of r is multiplied is expressed using Laguerre polynomials and times an exponential of minus z r by n, where n is the principle quantum number. And the angular part is described by spherical harmonics Y l m theta phi therefore, psi n l m is the product of the two R times Y. What are the values for n, the mathematics tells us that the n has the allowed values 1, 2, 3 all the way to infinity, l has the allowed value 0, 1, 2 up to n minus 1 for any given n; and the m has the values 0 plus minus 1, plus minus 2 until plus minus l. So, there are 2 l plus 1 m values, there are n l values and n of course, can go from 1, 2, 3 to infinity.

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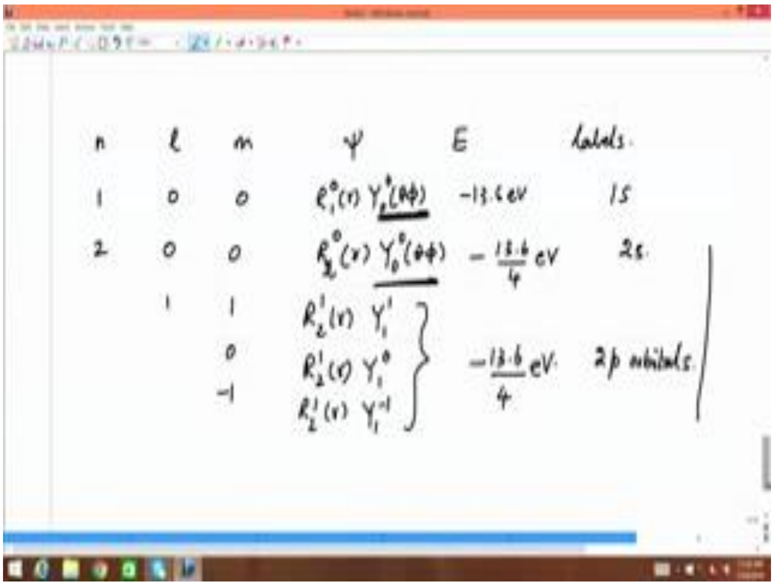

n	l	m	ψ	E	labels
1	0	0	$R_1^0(r)\, \underline{Y_0^0(\theta\phi)}$	-13.6 eV	1s
2	0	0	$R_2^0(r)\, \underline{Y_0^0(\theta\phi)}$	$-\frac{13.6}{4}$ eV	2s
	1	1	$R_2^1(r)\ Y_1^1$	$-\frac{13.6}{4}$ eV	2p orbitals
		0	$R_2^1(r)\ Y_1^0$		
		-1	$R_2^1(r)\ Y_1^{-1}$		

So, the typical wave function picture that comes out of this is when n l m and psi, if we write and the energies and the labels we have then n is 1, l is 0, m is 0. This is R 1 0 of r Y 0 0 of theta phi and the energy is minus 13.6 e v, this is the 1 s orbital. And then n is 2, you have l is equal to 0, and l equal to 1; for l equal to 0, m is equal to 0 is the only allowed value R 2 0 of r Y 0 0 theta phi this is the l m, and this is minus 13.6 by 4 e v this is the 2 s orbital. It is actually angled independent 0 0 is square root of 1 by square root of 4 pi that is a number. So, it is independent of theta phi. So, all those things which are angled independent.

So, theta phi independent they are called the s orbitals. When l is 1, m can be 1, 0 or minus 1. And these are obviously, written as R 2 1 Y 1 1, R 2 1 Y 1 0, R 2 1 Y 1 minus 1. And these are usually called the 2 p orbitals, both the 2 s and 2 p orbitals of the same energy because, the energy depends only on the principle quantum number, and therefore, you have 4 orbitals for n equal to 2.

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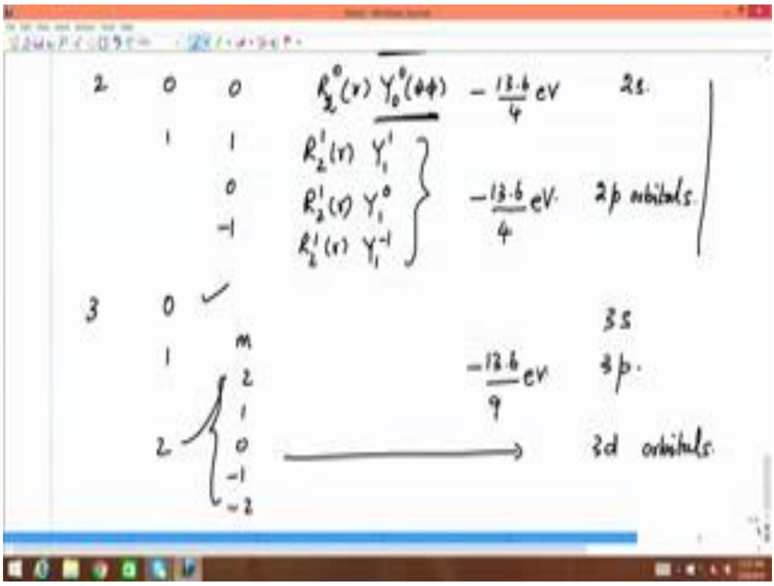

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And likewise when you do n equal to 3, you got 0 1 and 2; 0 is same as what is called the 3 s orbital, 1 is what is called the 3 p orbital and then l is 2 you have got five quantum numbers namely 2 1 0 minus 1 minus 2 for the m. And there are five wave functions all of which both 0, 1 and I mean all the 3 9 functions together will have the same energy minus 13.6 by 9 e v. And these five functions are called the 3 d orbitals, and the labels of 3 d orbitals come from the specific features that you are familiar with this spherical harmonics.

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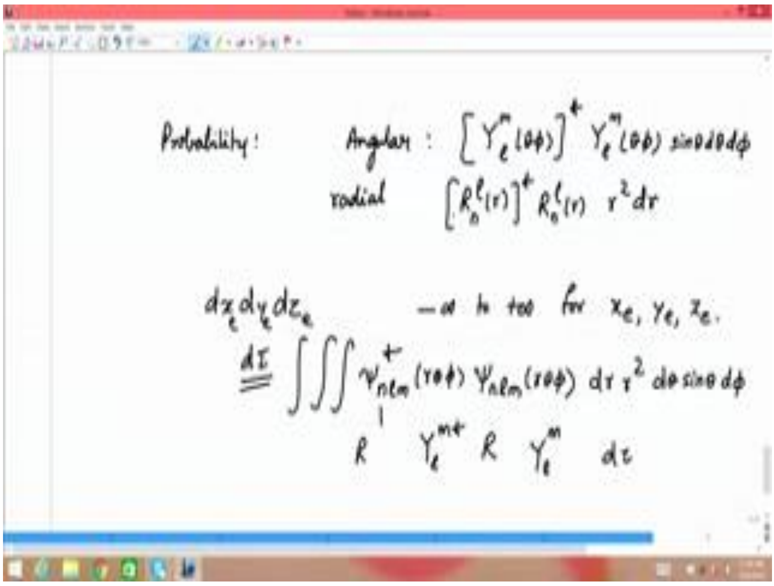

Probability: Angular : $\left[Y_l^m(\theta\phi)\right]^* Y_l^m(\theta\phi) \sin\theta\, d\theta\, d\phi$

radial $\left[R_n^l(r)\right]^* R_n^l(r)\ r^2 dr$

$dx_e\, dy_e\, dz_e$ $-\infty$ to ∞ for x_e, y_e, z_e.

$$\underline{\underline{d\tau}} \iiint \psi_{nlm}^*(r\theta\phi)\, \psi_{nlm}(r\theta\phi)\, dr\, r^2\, d\theta \sin\theta\, d\phi$$

$$R \quad Y_l^{m*} \quad R \quad Y_l^m \quad d\tau$$

The probability distributions for the hydrogen atom are the last thing that I would like to write before we move onto the angular momentum. The probability issues are angular distribution is due to the Y l m theta phi star Y l m theta phi multiplied by sin theta d theta d phi. This is like the psi star psi d x. In the case of angles, you have sin theta d theta d phi come in as the angular element. And in the case of radial probability, the rest of it namely R n l of r star R n l of r r square d r; remember that in the Cartesian space the coordinate, x e y e and z e for the electron can have values going from minus infinity to plus infinity for all three of them x e ye and z e. Therefore, this is the volume element that you must have d tau for the probability distribution and normalizing the wave function when you write psi n l m r theta phi psi star n l m and psi n l m r theta phi.

The corresponding thing in the radial the in the spherical polar coordinate system not volume element d tau is given by d r r square and then you have d theta sin theta and d phi. So, this is obviously broken into a radial part and an angular part star and an angular part and you see that the integrally separable it is a three poled triple integral. And the triple integral is easily separated into an angular distribution and radial distribution. So, these are some of the basic elements that you need to know in the model problems of quantum mechanics, which will keep coming again and again in the spectroscopy and every other area of theoretical chemistry. Now, the last thing that I want to do for this particular course relevant and something that needs to be recapped is angular momentum.

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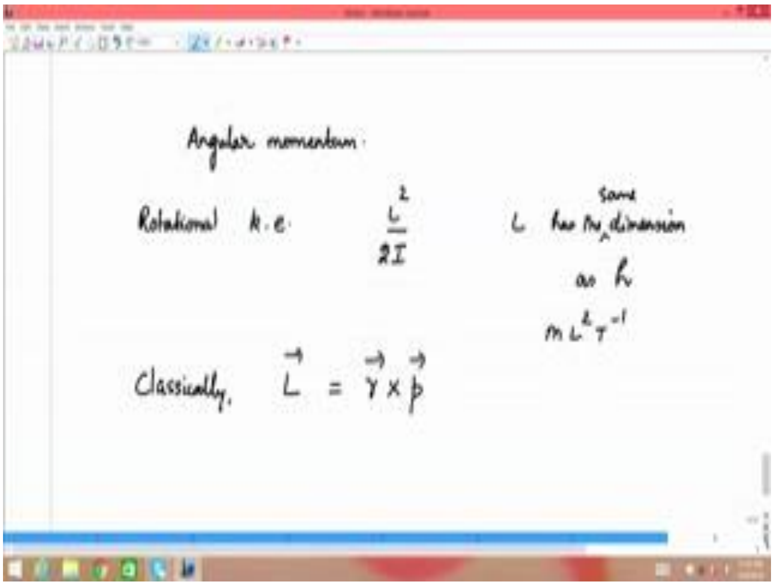

Angular momentum.

Rotational k.e. $\frac{L^2}{2I}$

L has the same dimension as $\hbar$

$m L^2 T^{-1}$

Classically, $\vec{L} = \vec{r} \times \vec{p}$

In fact, we have already touched upon angular momentum and we discussed this spherical harmonics, I mean I did not tell you so but we will see that in a minute. The rotational kinetic energy of a system moving around the point is given by the square of the angular momentum divided by it is moment of inertia. And L - angular momentum has the same dimension as h bar has the same dimension as h mass length square T to the minus 1. Classically, the angular momentum is the position vector r of the particle times p the momentum cross p r cross p is the vector product and L is directed L is the access for the L is perpendicular to the plain containing r n p is a vector cross product. Therefore, that is a classical definition.

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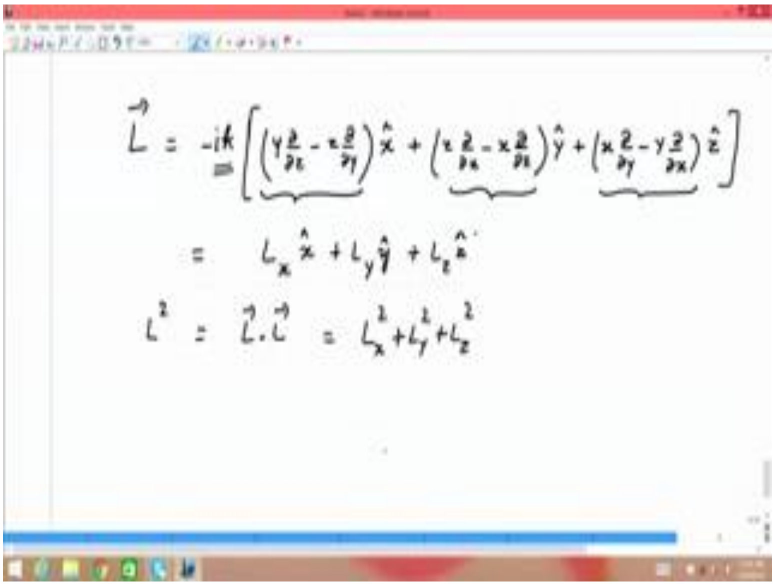

$$\vec{L} = -i\hbar\left[\underbrace{\left(y\frac{\partial}{\partial z} - z\frac{\partial}{\partial y}\right)}\hat{x} + \underbrace{\left(z\frac{\partial}{\partial x} - x\frac{\partial}{\partial z}\right)}\hat{y} + \underbrace{\left(x\frac{\partial}{\partial y} - y\frac{\partial}{\partial x}\right)}\hat{z}\right]$$

$$= L_x\hat{x} + L_y\hat{y} + L_z\hat{z}$$

$$L^2 = \vec{L}\cdot\vec{L} = L_x^2 + L_y^2 + L_z^2$$

.

And in quantum mechanics when you replace the momentum by the corresponding derivative operator L becomes minus i h bar y dou by dou z minus z dou by dou y x unit vector plus z dou by dou x minus x dou by dou z y unit vector plus x dou by dou y minus y dou by dou x z unit vector, and L is a vector. So, what you have is essentially L x x component of the angular momentum, the y component L y of the angular momentum times y, the z component of the angular momentum times L z. And the square of the angular momentum L square is L dotted with itself and that is given by the quantity L x square plus L y square plus L z square. The components of the angular momentum L x r given by minus i h bar times that L y by minus i h bar times that and L z with the minus i h bar times that. So, these are operator representation for the angular momentum in quantum mechanics.

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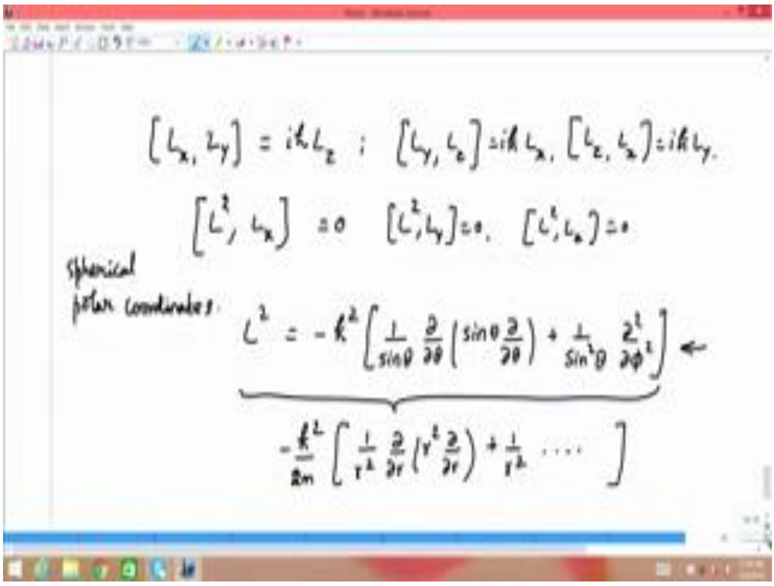

$$[L_x, L_y] = i\hbar L_z \; ; \; [L_y, L_z] = i\hbar L_x, \; [L_z, L_x] = i\hbar L_y.$$

$$[L^2, L_x] = 0 \quad [L^2, L_y] = 0, \quad [L^2, L_z] = 0$$

spherical polar coordinates.

$$\underbrace{L^2 = -\hbar^2\left[\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right) + \frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\phi^2}\right]}_{-\frac{\hbar^2}{2m}\left[\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right) + \frac{1}{r^2}\cdots\right]} \leftarrow$$

.

And they have this property namely L x does not commute with L y and the commutation of L x and L y is given by i h bar L z. And likewise for cyclic permutations namely L y L z is i h bar L x L z L x is i h bar L y. The square of the angular momentum operator and this if you take them and any of these components, if you take the square of the angular momentum operator L square and it is commutation with L x, the answer is 0. L square commutes with all the three components L square L y is 0; L square L z is 0. And in the spherical polar coordinates, in spherical polar coordinates, the square of the angular momentum is given by minus h bar square 1 by sin theta dou by dou theta acting on sin theta dou by dou theta plus 1 by sin square theta dou square by dou phi square.

And this is used in the solution of the hydrogen atom when you transform the hydrogen atom kinetic energy, you would see that this term comes with a minus h bar square by 2 m with one term preceding that namely 1 by r square dou by dou r r square dou by dou r and then you have 1 by r square times everything the minus h bar square is outside. Therefore, you have 1 by r square sin theta dou by dou theta multiplied by this derivative and then you have 1 by r square sin square theta multiplied by that. Therefore, this comes straight from the spherical polar coordinate representation of the angular momentum and the operator for the angular momentum L square.

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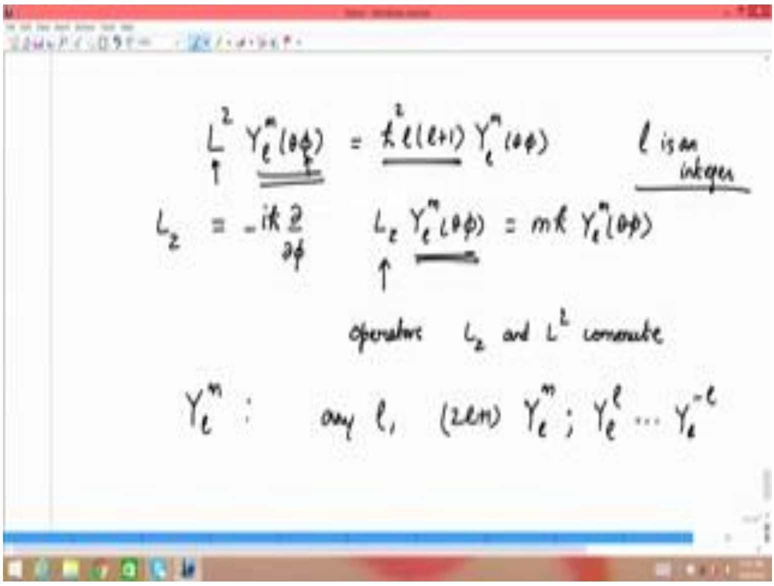

$L^2 \, \underline{Y_l^m(\theta\phi)} = \underline{\hbar^2 l(l+1)} \, Y_l^m(\theta\phi)$ $\quad$ l is an integer

$L_z = -i\hbar \frac{\partial}{\partial\phi}$ $\quad$ $L_z \, \underline{Y_l^m}(\theta\phi) = m\hbar \, Y_l^m(\theta\phi)$

operators L_z and L^2 commute

Y_l^m : any l, $(2l+1)$ Y_l^m ; $Y_l^l \cdots Y_l^{-l}$

Therefore, immediately can be identified to have this Y L m as the Eigen value, L square on Y l m theta phi will give you h bar square L into plus L Y l m theta phi l m theta phi. The operator L z, if you again go through the algebra of the coordinate representation and transformation will come out with this form minus i h bar dou by dou phi, the same as the phi here. And this has L z on Y l m theta phi the Eigen value m h bar Y l m theta phi. And Y l m is simultaneously Eigen function of both L square and L z, because the operators commute, L z and L square commute.

Therefore, mathematics tells us that it is possible to have the same Eigen function for both of them, but with of course, different Eigen values namely m h bar for L z and h bar square L into L plus 1 for the operator L square. And you remember Y l m of course, has limitations in the sense for any L there are 2 L plus 1 Y l m s starting from Y l l to Y l minus l. Therefore, there are 2 L plus 1 such functions Eigen functions for any angular momentum quantum number given by l, l is an integer this is something that you are already familiar with.

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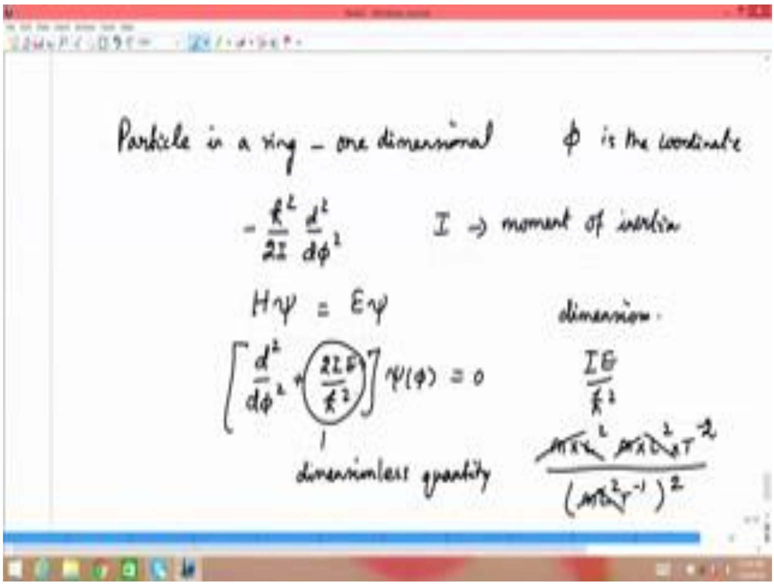

Particle in a ring – one dimensional ϕ is the coordinate

$$-\frac{\hbar^2}{2I}\frac{d^2}{d\phi^2} \qquad I \rightarrow \text{moment of inertia}$$

$$H\psi = E\psi$$

dimension.

$$\left[\frac{d^2}{d\phi^2} + \underbrace{\boxed{\frac{2IE}{\hbar^2}}}_{\text{dimensionless quantity}}\right]\psi(\phi) = 0$$

$$\frac{IE}{\hbar^2}$$

$$\frac{\cancel{M \times L^2}\,\cancel{M \times L^2 \times T^{-2}}}{(ML^2T^{-1})^2}$$

.

But if you recall the particle in a ring, which is a one-dimensional problem, only phi is the coordinate, and the kinetic energy is given by minus h bar square, by 2 I d square by d phi square. I is the moment of inertia of the particle moving on a ring, moment of inertia. And the equation that one needs to solve for the particle in a ring is H psi is equal to E psi this is the H, therefore the differential equation that you need to solve is d square d phi square plus 2 I E by h bar square psi of phi equal to 0.

And note that the dimension of I E by h bar square dimension. If you look at it, I is the moment of inertia, so it is mass time to length square E is the energy which has the dimension mass in length square into time minus 2. And h bar square, h has the dimension of mass length square time to the minus one and it is square. Therefore, I E by h r square is dimensionless, because you see everything is cancels here m square cancels with this m square L square L square cancels with L 4 and, so does T to the minus 2. Therefore, it is a dimensionless quantum number dimensionless quantity. Of course, phi is a angle, it is dimensionless. Therefore, you can see any derivative involving phi should only be added to another dimensionless quantity.

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$$\left[\frac{d^2}{d\phi^2} + m^2\right]\psi_m(\phi) = 0$$

$m = 0, \pm 1, \pm 2, \dots$

$$E \Rightarrow \frac{2IE}{\hbar^2} = m^2 \Rightarrow E = \frac{\hbar^2 m^2}{2I}$$

$\downarrow$

one dimension.

Three dimensions $$E_l = \frac{\hbar^2 l(l+1)}{2I}$$

So, you need some dimensions are extremely important. Therefore, what you see is that the solution to this equation turns out to be d square by d phi square plus a quantum number m whose square is included and then you have a psi m phi is equal to 0, and m has the values 0, plus minus 1, plus minus 2 and so on. And you can immediately see that the energy which is given by the expression 2 I E by h bar square is equal to m square gives you energy is equal to h bar square m square by 2 I, this is for one dimension.

For three dimensions or more than one dimension, you already have that. This one, for three dimensions, you already have this result. The angular momentum square gives you the Eigen values l into l plus 1. And you see that h bar square l into l plus 1 instead of h bar square m square. Therefore, if you have to do the same problem in three-dimension from 1 to 3, you see that E l is given by h bar square l into l plus 1 by 2 I for the specific router for overall square of the angular momentum.

And this is what we will see as an important quantity later when we study the diatomic molecular spectroscopy rotational spectroscopy. And also when we study the rotational spectroscopy of a spherical top molecule, you will see that the Eigen values for the rotational energies will be a quantum number l into l plus 1 and the units are h bar square by 2 I. I is the moment of inertia for the molecule in that case. And therefore, the relation that we have here should be recalled when we do the microwave spectroscopy and also when we do rho vibrational spectroscopy later.

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$$E \Rightarrow \frac{2IE}{\hbar^2} = m^2 \Rightarrow E = \frac{\hbar^2 m^2}{2I}$$

$$\downarrow$$

one dimension.

Three dimensions $E_l = \frac{\hbar^2 l(l+1)}{2I}$

$$\psi_m = e^{\pm im\phi} \Longleftarrow \frac{d^2}{d\phi^2}\psi_m + m^2\psi_m = 0$$

$$\psi = \underbrace{A_m e^{im\phi} + B_{-m} e^{-im\phi}}$$

.

The Eigen functions for rotational angular momentum are obviously given. In the case of a one dimension, it is easy to write that the Eigen functions psi m r e to the plus or minus i m phi that would be the solution for this equation namely d square by d phi square of psi m plus m square psi m is equal to 0 that would be the solution exponential plus or minus I m phi. And a general solution psi for a particle in a one-dimensional motion can be a linear combination of both namely A m e to the i m phi plus B minus m e to the minus i e m phi.

Just to indicate that there are two different constants and there is a linear combination of both the acceptable solutions. And this is a degenerate solution because the energy depends on the square of m, so it does not matter whether m is plus or minus, the corresponding exponential i m phi will be the solution and both of which are different wave functions. So, for a particle on a ring, you have degeneracy's for every m other than m equal to 0. So, these are important relations for understanding the role of angular momentum in rotations and also the coupling of rotations with molecular vibrations and so on. And therefore, please keep this in mind.

I think I have come to the summary of whatever that minimally quantum mechanics we needed before we move on to understanding elementary microwave and infrared spectroscopy. Therefore, anything else that we need I would provide that that point of time. We will continue this with another important result in electronic spectroscopy for measurement quantitatively using what is known as the Beer Lambert’s law, and then we move on to the first most important topic for spectroscopy the Born-Oppenheimer approximation. This week we will complete both of these, and then we move onto the lectures on the molecular spectroscopic details for rotations and vibrations.

Until then thank you very much.