Atomic and Molecular Physics
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Lecture -35
Quantum mechanical treatment of Hydrogen like atom (Contd.)

So, we are discussing about the wave function, basically we found the Eigen function solving the Schrodinger equation for hydrogen like atom.

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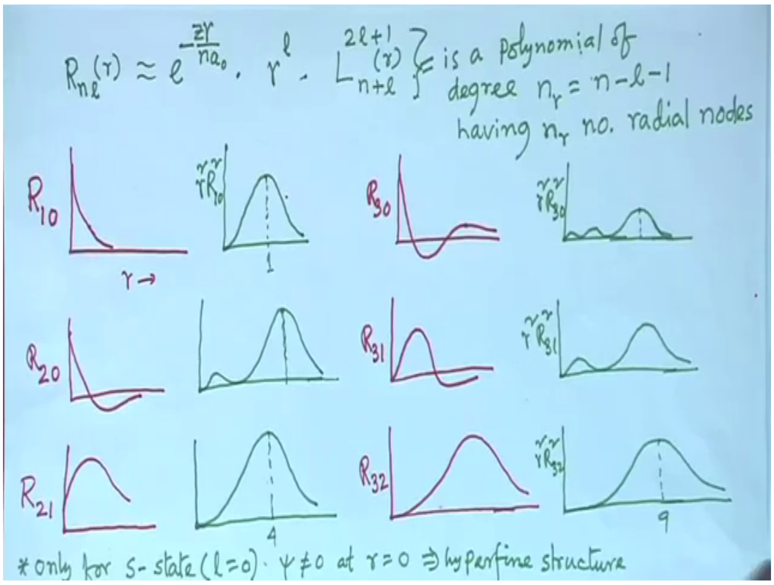

$R_{n\ell}(r) \approx e^{-\frac{Zr}{na_0}} \cdot r^{\ell} \cdot L^{2\ell+1}_{n+\ell}(r)$ } is a polynomial of degree $n_r = n-\ell-1$ having n_r no. radial nodes

* only for s-state ($\ell=0$). $\psi \neq 0$ at $r=0$ ⇒ hyperfine structure

So, we have seen this from wave function; how the radial, how this radial part of the wave function varies and corresponding radial density probability.

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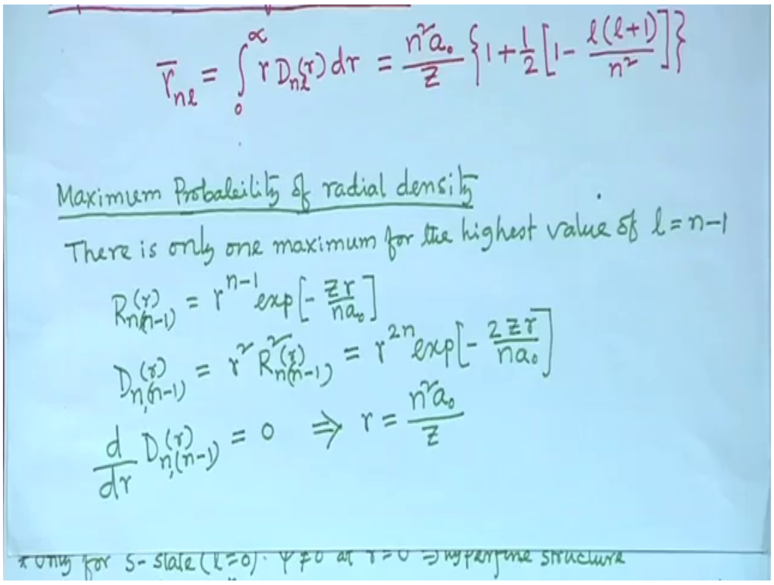

$$\bar{r}_{nl} = \int_0^\infty r D_{nl}(r)\, dr = \frac{n^2 a_0}{Z}\left\{1+\frac{1}{2}\left[1-\frac{l(l+1)}{n^2}\right]\right\}$$

Maximum Probability of radial density

There is only one maximum for the highest value of $l = n-1$

$$R_{n(n-1)}(r) = r^{n-1}\exp\left[-\frac{Zr}{na_0}\right]$$

$$D_{n,(n-1)}(r) = r^2 R^2_{n(n-1)}(r) = r^{2n}\exp\left[-\frac{2Zr}{na_0}\right]$$

$$\frac{d}{dr} D_{n,(n-1)}(r) = 0 \Rightarrow r = \frac{n^2 a_0}{Z}$$

* only for S-state ($l=0$) $\psi \neq 0$ at $r=0$ ⇒ hyperfine structure

So, and also I have shown that this the maximum probability for the for the electron density, electron radial density for the highest value of l n minus 1, that is exactly the Bohr radius which you got from the expression from the Bohr model. So, basically for n equal to 1, it is a 0, n equal to 2 it is 4 a 0, n equal to 3 it is 9 a 0. So, that is why here I have marked this 1 and that is equal to Bohr radius first orbit and then here this l equal to n minus 1, l equal to n minus 1.

So, here this 4 is 4 a 0, 4 times of Bohr radius and this is also l equal to n minus 1 so, this here this 9. So, these are basically exactly the Bohr orbit radius of orbit got from the Bohr model and from wave function also one can predict that one and of course, something more one can find from the wave function. So, this second part, I was discussing the angular distribution angular probability density.

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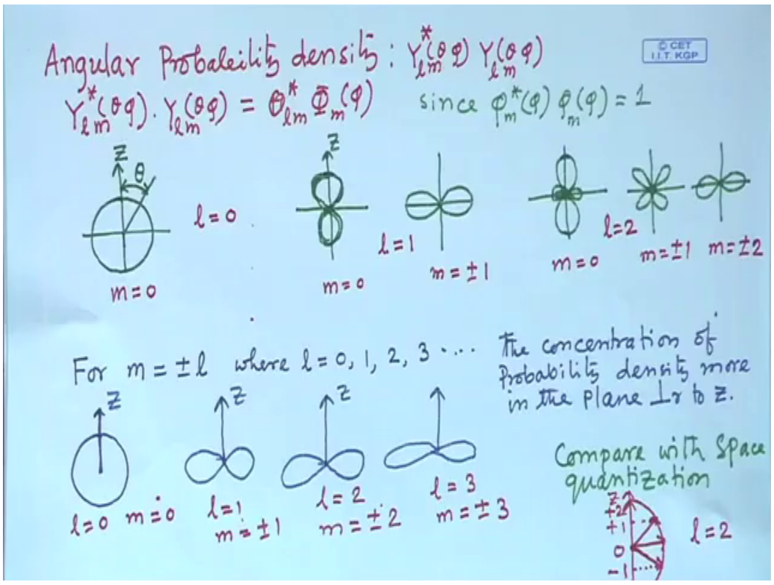

Angular Probability density : $Y^{*}_{lm}(\theta\varphi)\, Y_{lm}(\theta\varphi)$

$Y^{*}_{lm}(\theta\varphi) \cdot Y_{lm}(\theta\varphi) = \Theta^{*}_{lm}\, \Phi_{m}(\varphi)$ since $\varphi^{*}_{m}(\varphi)\, \varphi_{m}(\varphi) = 1$

For $m = \pm l$ where $l = 0, 1, 2, 3 \ldots$

The concentration of probability density more in the plane ⊥r to z.

Compare with Space quantization

And I have shown that this how angular probability density varies for different value of l and m ok so, that I have I have discussed. So, this is the so, this is the directionality of the electron density in atom and these are very useful for in chemistry basically for bonding. So, if you when this atom different atom forms molecule how they form bond and these are this variation of angular variation of probability density. It is basically explained the formation of bonding molecules and also this from here also this is the this is basically, it is comparable with the space quantization in case of Bohr Sommerfeld model whatever we have seen.

This same result basically, we are getting from hydrogen from solving the Schrodinger equation so, that also. So, from whatever from Bohr Sommerfeld model or the atomic structure based on old quantum theory introducing many postulates on in atom basis so, but it can it explains everything about the atomic structure, solving the Schrodinger equation also we are getting we are getting the similar concept or same concept. But it has come in naturally as many times I am telling this after complicated calculation same thing we are getting, but things are has come in natural way. So, that is the difference and also something more we are getting from solving the Schrodinger equation ok.

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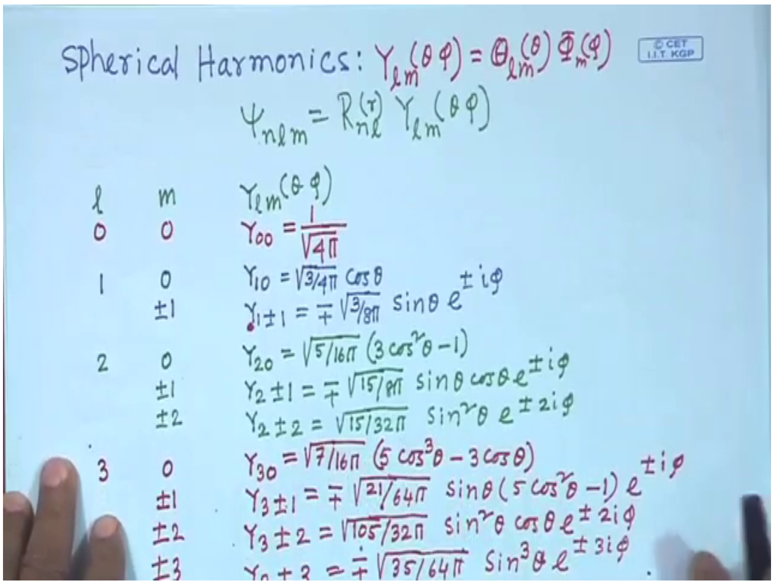

Spherical Harmonics: $Y_{lm}(\theta\varphi) = \Theta_{lm}(\theta)\,\Phi_m(\varphi)$

$$\Psi_{nlm} = R_{nl}(r)\,Y_{lm}(\theta\varphi)$$

l	m	$Y_{lm}(\theta\varphi)$
0	0	$Y_{00} = \frac{1}{\sqrt{4\pi}}$
1	0	$Y_{10} = \sqrt{3/4\pi}\cos\theta$
	±1	$Y_{1\pm1} = \mp\sqrt{3/8\pi}\sin\theta\, e^{\pm i\varphi}$
2	0	$Y_{20} = \sqrt{5/16\pi}\,(3\cos^2\theta - 1)$
	±1	$Y_{2\pm1} = \mp\sqrt{15/8\pi}\sin\theta\cos\theta\, e^{\pm i\varphi}$
	±2	$Y_{2\pm2} = \sqrt{15/32\pi}\sin^2\theta\, e^{\pm 2i\varphi}$
3	0	$Y_{30} = \sqrt{7/16\pi}\,(5\cos^3\theta - 3\cos\theta)$
	±1	$Y_{3\pm1} = \mp\sqrt{21/64\pi}\sin\theta\,(5\cos^2\theta - 1)\, e^{\pm i\varphi}$
	±2	$Y_{3\pm2} = \sqrt{105/32\pi}\sin^2\theta\cos\theta\, e^{\pm 2i\varphi}$
	±3	$Y_{3\pm3} = \mp\sqrt{35/64\pi}\sin^3\theta\, e^{\pm 3i\varphi}$

So, basically spherical harmonics as I showed you and plot it polar graph so, this Y l m we tell it is spherical harmonics and it has two up to for theta and phi dependent. So, overall this Eigen function for hydrogen like atom whatever we after solving Schrodinger equation we got that has two part, one is radial part and another is angular part so, angular part is spherical called spherical harmonics and this spherical harmonics I have shown this expression for few demo of l and m and we have plotted also.

Now, this spherical harmonics in real form is basically it is a complex number are there right e to the power i phi 2 i phi etcetera ok.

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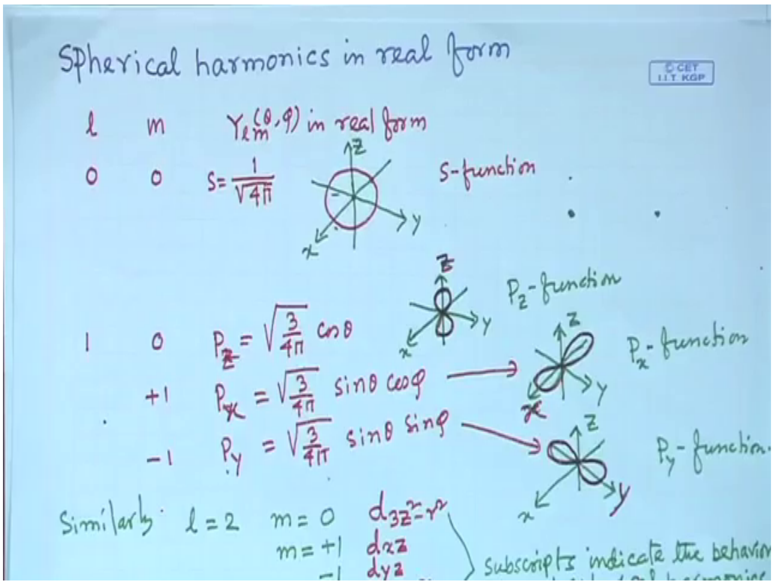

Spherical harmonics in real form

l	m	$Y_{lm}(\theta,\phi)$ in real form	
0	0	$S = \frac{1}{\sqrt{4\pi}}$	S-function
1	0	$P_z = \sqrt{\frac{3}{4\pi}} \cos\theta$	P_z-function
	+1	$P_x = \sqrt{\frac{3}{4\pi}} \sin\theta \cos\phi$	P_x-function
	−1	$P_y = \sqrt{\frac{3}{4\pi}} \sin\theta \sin\phi$	P_y-function

Similarly $l = 2$ $m = 0$ $d_{3z^2-r^2}$
$m = +1$ d_{xz}
-1 d_{yz}

subscripts indicate the behavior

So, in real form spherical harmonics the real form one can write like this ok this l equal to 0, m equal to 0. So, S equal to 1 by square root of 4 pi and it is it is graph is like this distribution is spherical distribution, circular distribution and when you rotate about the z axis when you rotate it so, it will be sphere. So, this is called S function right so, in real form on in reality whatever we are terms, we are reading this basically it is l equal to 0 and m equal to 0, whatever the n value does not matter. So, you tell this S orbit or this the S function similarly, P function that is for l equal to 1 and m equal to 0 plus minus 1. So, this basically P function. Now generally we use as a in Cartesian coordinate basically using Cartesian coordinate we use P x, P y, P z.

So, here this is P value basically just real part we have taken, here you can see that for l equal to 1, m equal to 0 plus minus 1 so, it is cos theta so, it is cos theta is there P z term and P x plus 1 and minus 1. We are telling that is plus 1 this P x and this minus 1 is P y. So, here it is sin theta e to the power plus minus i phi so, e to the power plus minus i phi it is basically cos theta plus minus i sin theta. So, only real part if we take so, this for one we have taken cos phi another part is sin phi real for to be so, that is so, we are telling this spherical harmonics in real form.

So, why it is called like this P z, P x, P y it is named nomenclature has come because of the distribution of this distribution along the x axis, y axis, z axis. So, P z, it is basically this distribution it is along the z axis it is P x distribution along the x axis and other one P y it is distribution along the y axis ok so, that is why.

So, P x is nothing, but l equal to 1, m equal to 0, P sorry l equal to 0 it is P z, l equal to plus 1 for l equal to 1 of course, so, plus 1 this P x and minus 1 this P y. So, it is as per the nomenclature as for the distribution of the angular distribution of the of the charge or electrons electronic charge. So, similarly for l equal to 2 and m equal to will be 0 plus minus 1 plus minus 2.

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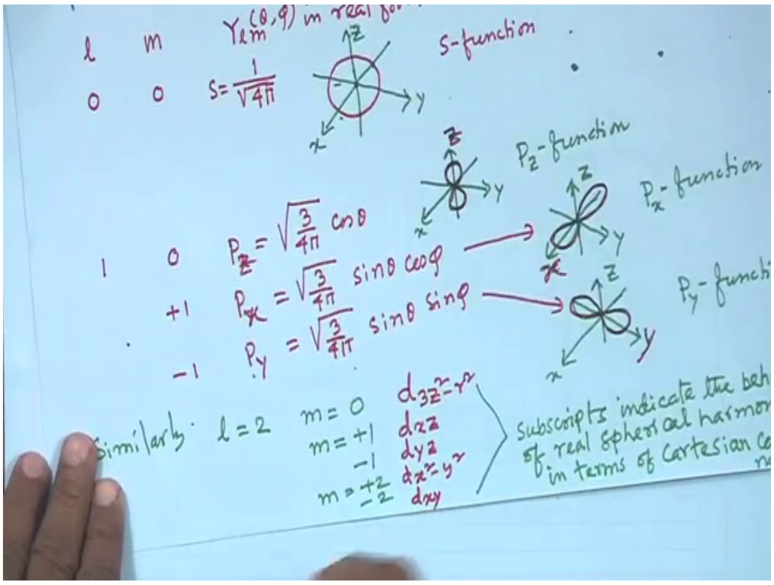

So, it’s nomenclature is like this t m equal to 0, this d 3 z square minus r square, m equal to plus 1 d x y minus 1 d y z, m equal to plus 2 d x square minus y square this. So, this subscript is basically this has come as we have seen according to the distribution of the electron in Cartesian coordinate.

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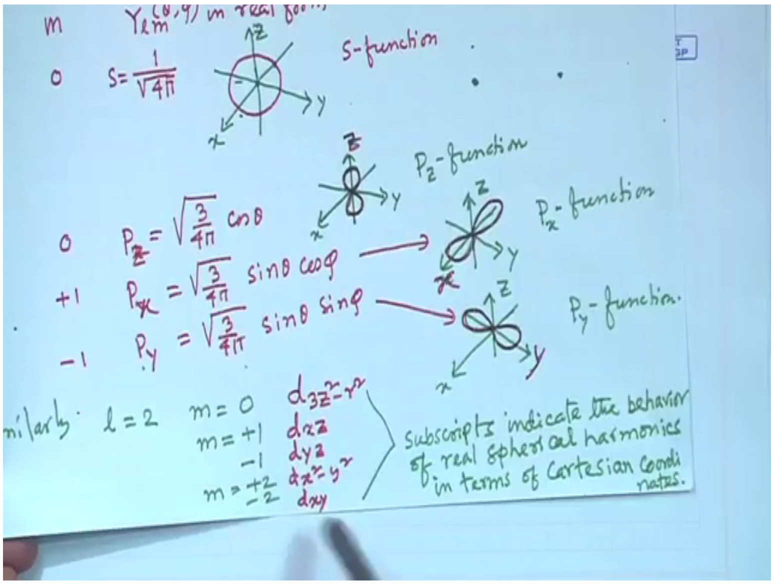

m $Y_{lm}(\theta,\varphi)$ in real

0 $S = \frac{1}{\sqrt{4\pi}}$

0 $P_z = \sqrt{\frac{3}{4\pi}} \cos\theta$

+1 $P_x = \sqrt{\frac{3}{4\pi}} \sin\theta \cos\varphi$

−1 $P_y = \sqrt{\frac{3}{4\pi}} \sin\theta \sin\varphi$

milarly: $l = 2$ $m = 0$ $d_{3z^2-r^2}$

$m = +1$ d_{xz}

-1 d_{yz}

$m = +2$ $d_{x^2-y^2}$

-2 d_{xy}

Subscripts indicate the behavior of real spherical harmonics in terms of Cartesian coordinates.

So, here also this has come as for this distribution of the charge in Cartesian coordinate so, this I am not describing or showing this plots. So, this, but these are the we are familiar with P x, P y, P z d 3 z square minus r square d. So, the d has 5 orbital’s right and yes and P has 3 orbital’s right and S has only 1 orbital’s so, these 3 and 5 again P x, P y, P z the here other case d 3 z square minus r square, etcetera. So, this nomenclature has come because of the distribution of spherical harmonics in terms of Cartesian coordinate.

So, now, I would like to discuss about the orbital angular momentum operator and commutator because it is very useful. So, what we have seen that we have solved the Schrodinger equation so, we got the Eigenvalue equation means if we got this Eigen function that is high n l and now if you operate Hamiltonian energy operator on these wave function Eigen wave function, then we get Eigenvalue equation h psi n l equal to e n psi n l. So, that is Eigenvalue equation and we get the Eigenvalue e n, but this psi n l m it is the Eigen function of Eigen function of Hamiltonian h.

It can be simultaneous Eigen function of other operator also, operator is basically it is the objective is if we if we operate operator operate operator on the wave function then it gives it gives this some Eigen value. So, that Eigen value is basically we are interested for that and that is that is the observable.

So, if I want to know about the energy so, we apply h Hamiltonian if we want to know the angular momentum so, we have to operate l. So, now, we want to see whether this psi n l m whether it is simultaneous wave function of l angular momentum or not so, for that we have to know about the operator and commutator. So, if two operator to operator commutes then we tell that these two operators; May will have or May have the simultaneous wave function.

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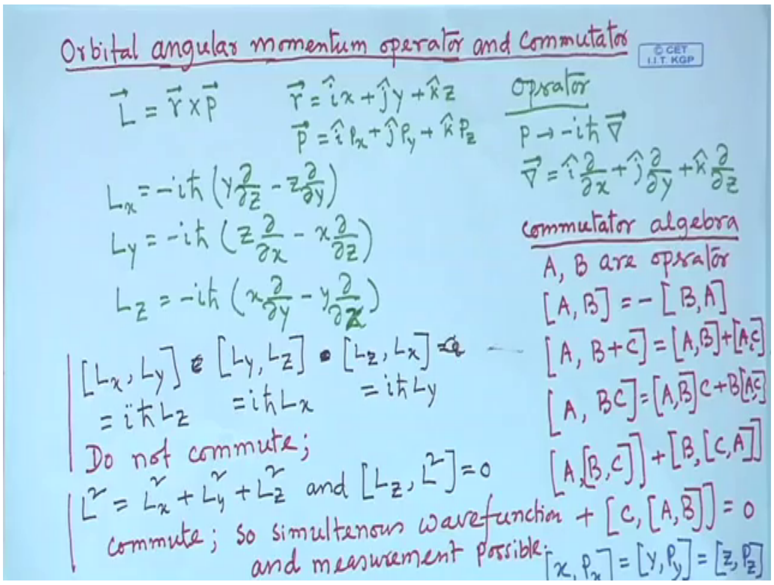

Orbital angular momentum operator and Commutator

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

$\vec{r} = \hat{i}x + \hat{j}y + \hat{k}z$

$\vec{p} = \hat{i}P_x + \hat{j}P_y + \hat{k}P_z$

Oprator

$P \to -i\hbar\vec{\nabla}$

$\vec{\nabla} = \hat{i}\frac{\partial}{\partial x} + \hat{j}\frac{\partial}{\partial y} + \hat{k}\frac{\partial}{\partial z}$

$L_x = -i\hbar\left(y\frac{\partial}{\partial z} - z\frac{\partial}{\partial y}\right)$

$L_y = -i\hbar\left(z\frac{\partial}{\partial x} - x\frac{\partial}{\partial z}\right)$

$L_z = -i\hbar\left(x\frac{\partial}{\partial y} - y\frac{\partial}{\partial x}\right)$

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

Do not commute;

$L^2 = L_x^2 + L_y^2 + L_z^2$ and $[L_z, L^2] = 0$

commute; So simultenous wavefunction and measurement possible.

commutator algebra

A, B are oprator

$[A, B] = -[B, A]$

$[A, B+C] = [A, B] + [A, C]$

$[A, BC] = [A, B]C + B[A, C]$

$[A, [B, C]] + [B, [C, A]] + [C, [A, B]] = 0$

$[x, P_x] = [y, P_y] = [z, P_z]$

So, this orbital angular momentum operator if we if I tell from the basics of angular momentum you know in classical mechanics it is the r cross p, r is position position and p is linear momentum. So, r is it has three component I along the x direction y direction z direction i j k at the unit vector. Similarly, P x, P y, P z this three component along x y and z direction so, in form of operator P is in quantum mechanics so, that already you know I told you. So, P basically it is in operator from minus i h cross del, del is nothing, but this.

So, then operator it follows it follows commutators algebra ok, some relation it follows. So, this if a and b are operator it can be energy operator it can be momentum operator whatever so, this they follows this commutator algebra commutator A B equal to minus B A if you just exchange. So, these are the commutator algebra it follows.

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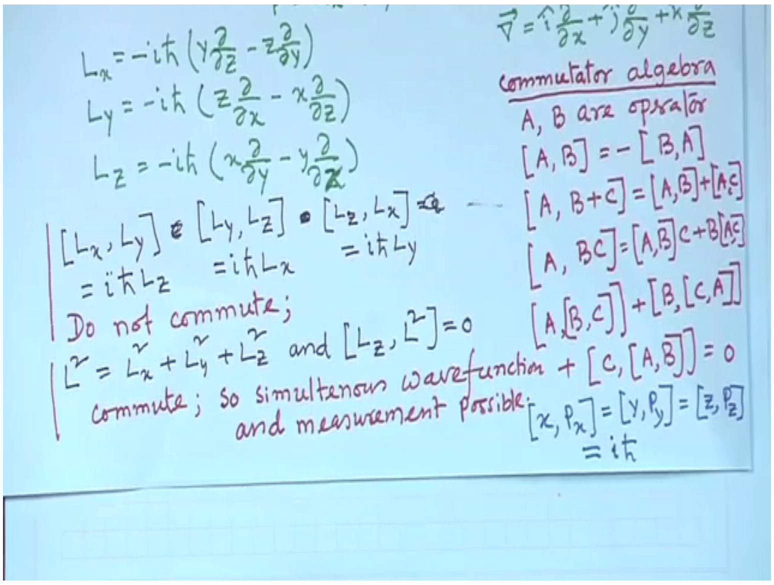

$L_x = -i\hbar\left(y\frac{\partial}{\partial z} - z\frac{\partial}{\partial y}\right)$

$L_y = -i\hbar\left(z\frac{\partial}{\partial x} - x\frac{\partial}{\partial z}\right)$

$L_z = -i\hbar\left(x\frac{\partial}{\partial y} - y\frac{\partial}{\partial x}\right)$

$[L_x, L_y] = i\hbar L_z \quad [L_y, L_z] = i\hbar L_x \quad [L_z, L_x] = i\hbar L_y$

Do not commute;

$L^2 = L_x^2 + L_y^2 + L_z^2$ and $[L_z, L^2] = 0$

commute; So simultenous wavefunction and measurement possible.

$\vec{\nabla} = \hat{i}\frac{\partial}{\partial x} + \hat{j}\frac{\partial}{\partial y} + \hat{k}\frac{\partial}{\partial z}$

commutator algebra

A, B are oprator

$[A, B] = -[B, A]$

$[A, B+C] = [A, B] + [A, C]$

$[A, BC] = [A, B]C + B[A, C]$

$[A, [B, C]] + [B, [C, A]] + [C, [A, B]] = 0$

$[x, P_x] = [y, P_y] = [z, P_z] = i\hbar$

And also position and momentum linear momentum the their commutation relation is x P x equal to y P y equal to z P z equal to i h cross so; that means, they do not commute position and momentum the linear momentum they does not commute, if they commute then this should be equal to 0. So, they does not commute; that means, they will not have simultaneous wave function or also they cannot be measured simultaneously if you measure one accurately other one uncertain will be infinity ok.

So, that is the rules in quantum mechanics so, now, using this commutator algebra and this relation position momentum relation so, one can one can one can find out one can easily prove that L x because we are interested for orbital angular momentum. So, orbital angular momentum here you can write three component L x, L y, L z so, these are the this so, you can write. So, one can find out easily these are the three components.

Now, they will their commutation relation is like this that can be proved whatever here I have given so, that can be proof easily. So, this L x so, these three components basically they do not commute with each other L x L y is equal to i h cross L z, L y L z equal to i h cross L x, L z L y equal to i h cross L y. So, they does not commute means they do not have simultaneous wave function. We cannot have simultaneous wave function for them, but L square is basically L x square plus L y square plus L z square and L square and L z they commute with each other L z than L square, they commute with each other so, that equal to 0 ok.

So; that means, this L z and L square will have the simultaneous wave function and also it can be measured there is their object this, these are operator and then correspond if we apply so, they are corresponding z component of angular momentum and there is square of that angular momentum or this angular momentum can be measured accurately.

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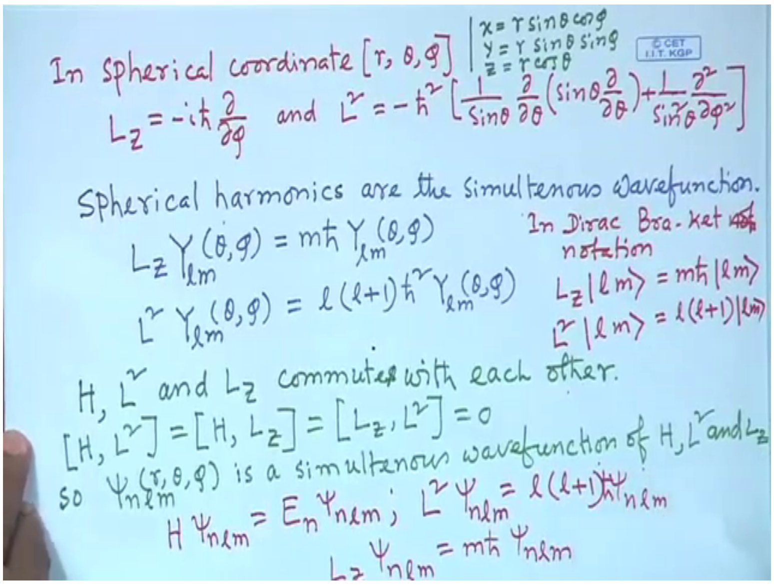

In spherical coordinate $[r, \theta, \varphi]$

$x = r\sin\theta\cos\varphi$
$y = r\sin\theta\sin\varphi$
$z = r\cos\theta$

$L_z = -i\hbar\frac{\partial}{\partial\varphi}$ and $L^2 = -\hbar^2\left[\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right) + \frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\varphi^2}\right]$

Spherical harmonics are the simultenous wavefunction.

$L_z Y_{\ell m}(\theta,\varphi) = m\hbar Y_{\ell m}(\theta,\varphi)$

$L^2 Y_{\ell m}(\theta,\varphi) = \ell(\ell+1)\hbar^2 Y_{\ell m}(\theta,\varphi)$

In Dirac Bra-ket notation

$L_z|\ell m\rangle = m\hbar|\ell m\rangle$

$L^2|\ell m\rangle = \ell(\ell+1)|\ell m\rangle$

H, L^2 and L_z commutes with each other.

$[H, L^2] = [H, L_z] = [L_z, L^2] = 0$

so $\psi_{n\ell m}(r,\theta,\varphi)$ is a simultenous wavefunction of H, L^2 and L_z

$H\psi_{n\ell m} = E_n\psi_{n\ell m}$; $L^2\psi_{n\ell m} = \ell(\ell+1)\hbar^2\psi_{n\ell m}$

$L_z\psi_{n\ell m} = m\hbar\psi_{n\ell m}$

So, now, in spherical coordinate in spherical coordinate this L z is equal to minus i h cross del by del phi and L square equal to minus h cross square 1 by sin theta del by del theta sin theta del by del theta plus 1 by sin square theta del square by del phi square. So, these basically we have seen this basically you have seen when we are solving the Schrodinger equation in spherical coordinate so, this part was there basically ok.

So, these are the form of L z and L square in spherical coordinate and they commute with each other so, they will have simultaneous wave function. So, basically the spherical harmonics whatever we have seen Y l m function of theta and phi so, this is the wave function for L z as well as for L square. So, if we apply L z on this so, it is it is follows the Eigenvalue equation and gives the Eigenvalue this m h cross. Similarly, for L square if we apply on this so, you will get the Eigen value l l plus 1.

So, this also it can be shown that this and this spherical harmonic is the part of the of the psi n l m so, this complete wave function complete wave function for hydrogen like atom psi n l. So, it has two part one radial part are n l and Y l m so; that means, if you apply this L z and L square on psi n l m so, you will get this same result. So; that means, we can tell this L z and L square have simultaneous wave function that is psi n l m so and also h so, also this psi n l m is the wave function of h Hamiltonian.

So; that means, H L square and L z commutes, should communes with each other. Then only it will have the simultaneous wave function and that happens and that happens H L square this commutator if equal to 0 H, L z this commutation commutator it is equal to 0 L z, L square of course, we have seen that is equal to 0 ok.

So, other way if there is if two operator have simultaneous wave function then they must commute or if two operator commutes with each other then they will have the simultaneous wave function. So, finally, we can tell that psi n l m r theta phi is a simultaneous wave function of H, L square and L z and so; that means, just if you operate H on the psi n l, we are we will get Eigen value n. Similarly, for L square will get l l plus 1 and L z we applied. So, this is m h cross.

So, here you can see this we have a function and we have showed that it has it is the wave function of simultaneous wave function of H, L square and L z. So, here we are getting energy we are getting angular momentum. So, basically so, is if probably remember that we earlier we have written l equal to l h cross right so, but Eigen value basically l h cross, but here just it is slightly different it is it will be square root of square root of l l plus 1. So, instead of l in from quantum mechanics this angular momentum this Eigen value we are getting square root of l l plus 1. Similarly, z component that is basically the space quantization so, we are getting n Eigen value that is m h cross ok.

So, these are the information is very important and this whatever here at the end I told you so, that is that has come in natural wave from quantum mechanics, which also we have seen in case of old quantum theory and that is basically similar result so, or same result we got from the quantum mechanics also.

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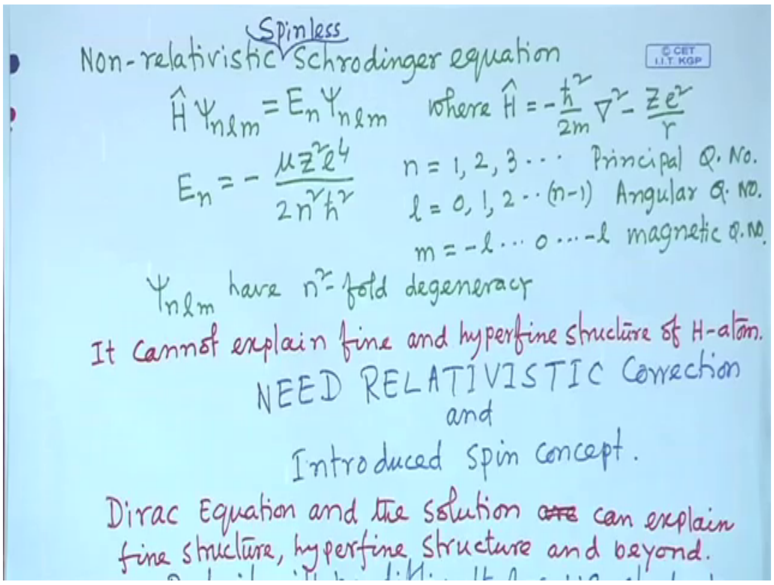

Non-relativistic Spinless Schrodinger equation

$\hat{H}\Psi_{nlm} = E_n\Psi_{nlm}$ where $\hat{H} = -\frac{\hbar^2}{2m}\nabla^2 - \frac{Ze^2}{r}$

$E_n = -\frac{\mu Z^2 e^4}{2n^2\hbar^2}$

n = 1, 2, 3 ··· Principal Q. No.
l = 0, 1, 2 ·· (n-1) Angular Q. No.
m = -l ··· 0 ···· -l magnetic Q. No.

Ψ_{nlm} have n^2-fold degeneracy

It cannot explain fine and hyperfine structure of H-atom.

NEED RELATIVISTIC Correction
and
Introduced spin concept.

Dirac Equation and the solution ~~are~~ can explain fine structure, hyperfine structure and beyond.

So, if so, this so far whatever we have discussed and solved solving the Schrodinger equation or hydrogen like atom this; what we got the information. So, whatever information we got that is not sufficient to explain the atomic spectra of hydrogen because atomic spectra of hydrogen shows the fine structure as well as it shows the hyperfine structure, that already you have seen.

I have discussed based on the old quantum theory and from Schrodinger equation what we got energy level energy, we got exactly, we also got the concept of orbit radius, we also got the concept of angular momentum space quantization right and here it shows it shows the this energy it shows that the psi n l m it has n square fold degeneracy means there are n square number of these Eigen states or Eigen function, but they will have the same energy well just for n equal to 1, l equal to 0 and m equal to 0 ok.

So, it has so, it is n equal to 1 it has some energy and for that energy we have one wave function n square n equal to 1, for n equal to 2 l equal to so, we will have 0 and 1, two l value and for each value l value, l equal to 0 and m equal to 0, m equal to 0. So, that is 1 and l equal to 1, m equal to 0 and plus minus 1. So, we will have 4 Eigen states or four Eigen function, but for that is for n equal 2 will have these four Eigen functions so, means n square n equal to 4 Eigen functions having the same energy e 2 and so, these are called the degeneracy.

So, this n square fold degeneracy, but actually the degeneracy is not there it is that is that is what we see the fine structure also hyperfine structure and this is Schrodinger equation we have solved. So, basically it cannot explain fine and hyperfine structure why because this Schrodinger equation is non relativistic spin less Schrodinger equation, we have not this Schrodinger equation has not considered spin of the electron. Also it is non relativistic because we have written energy like this p square by 2 m plus v r potential energy ok.

So, these are non-relativistic Hamiltonian and because of this non-relativistic spin less Schrodinger equation it is unable to explain fine and hyperfine structure.

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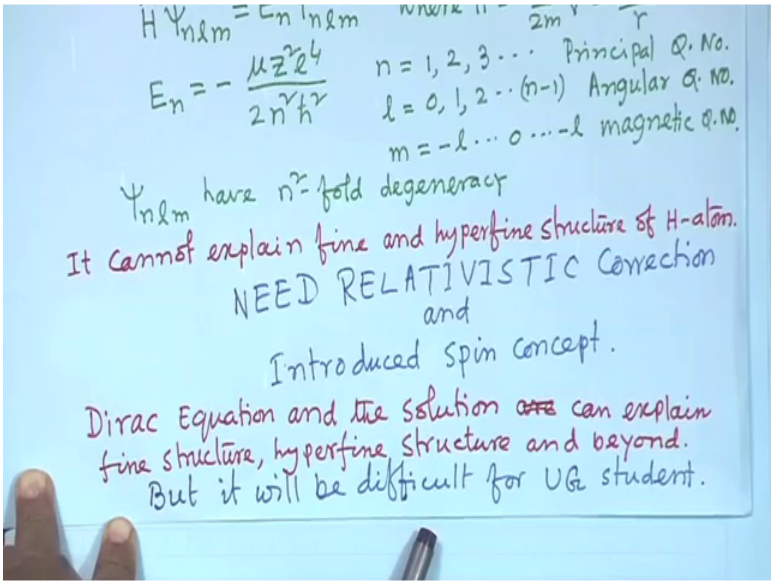

$H\Psi_{nlm} = E_n \Psi_{nlm}$ where

$E_n = -\frac{\mu Z^2 e^4}{2n^2\hbar^2}$

$n = 1, 2, 3 \cdots$ Principal Q. No.

$l = 0, 1, 2 \cdots (n-1)$ Angular Q. NO.

$m = -l \cdots 0 \cdots -l$ magnetic Q. NO.

Ψ_{nlm} have n^2-fold degeneracy

It cannot explain fine and hyperfine structure of H-atom.

NEED RELATIVISTIC Correction

and

Introduced spin concept.

Dirac Equation and the solution ~~are~~ can explain fine structure, hyperfine structure and beyond.

But it will be difficult for UG student.

So, basically we need relativistic correction also we need to introduce spin concept so, that is the basically Dirac equation. So, in Dirac equation everything is included, it is the relativistic Hamiltonian also spin concept is included there. So, basically Dirac equation and the solution and its solution basically can explain everything, can explain fine structure hyperfine structure and beyond that, but it will be difficult for undergraduate student. So, we will not we will not we will not solve this Dirac equation, but briefly I think I will discuss the result comes out as come came out from come out from the Dirac equation in next class. So, I will stop here.

Thank you for your attention.