Quantum Mechanics
Prof. P. Ramadevi
Department of Physics
Indian Institute of Technology- Bombay

Lecture – 39
Hydrogen Atom & Wave Functions, Angular Momentum Operators, Identical Particles II

Okay, so far we have done in a very elaborate fashion, the hydrogen atom problem in spherical polar coordinates doing separation of variables and we tried to solve it elaborately and looking at differential equation how it looks like the familiar special functions equation. Now, we want to slightly go into a way which is applicable to all the central force problems, what is the central force problem?

The potential energy is; potential energy is dependent only on the radial coordinate so suppose, your potential energy is dependent only on the radial coordinate, what happens under rotations that is why it is called central force problems, they are rotationally invariant systems right, so whenever we have a rotationally invariant systems, you can start seeing what is the corresponding operation like translation.

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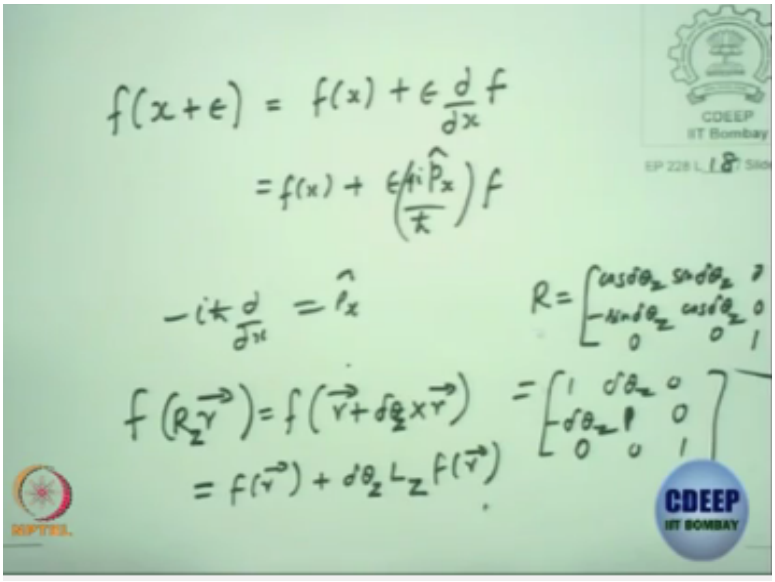

Translationally, invariant system mean, what is the corresponding operator, suppose you want to take a function f of x + epsilon, this is translation, I can write as a Taylor series, right, is that correct an infinite symbol translation can be written for any function this way but now, I can rewrite this as f of x + epsilon; del/ del x, I will try to write it as a Px operator okay, what do you have to do? – i/ h cross can I put; for an infinite symbol 1.

If it is not infinite symbol, you can continue the series, there is no minus okay, yeah, - ih cross del/ del x is Px, so if you want to write del/ del x, then you can do this, good, so for an infinite symbol, translation you have the corresponding differential operation is del/ del x, which can be interpreted as if it is the momentum operator. So, now I will ask you the next question, if I take a r vector and do an infinite symbol rotation, a rotation operator, what is the rotation operator?

Let us take the rotation to be rotation by a small angle about z axis, what will that be; is cos delta theta let me call, sin delta theta - sin delta theta cos delta theta, 0 0 0 0 1, can I do this for an infinite symbol. So, what is the R; for delta theta small, keeping only linear term in delta theta, this can be written as some 1; 1 delta theta 0 - delta theta 0, sorry 1, 0 0 0 1, right, can I do this?

So, what is this; it is f of r vector + this half diagonal matrix, so you could perhaps write it as some delta theta cross r vector, check it out, I am doing this for a rotation about z axis, just for, so let us keep this rotation about z axis and put this theta also with about z axis, you understand what I am; if you do a Taylor series expansion, the first term will be f of r, the second term can be written as; this I want you to do yourself but just you can yourself try and fiddle around and see what the second operation can be written as.

And you will see there will be a angular momentum operator, okay, you will see that it will be like f of r + delta theta z Lz for f of r, leave it you to check, not going to do it right now but so, basically I am trying to drive the point that a translation can be for the wave functions also, a way by infinite symbol translation, if you want to achieve, you need a linear momentum, if you need an infinite symbol rotation, you need an angular momentum.

If you do a rotation about z axis, you need the z component of the angular momentum, so angular momentum is conserved in rotationally invariant system is what you have all learnt in classical mechanics, right how did you check that the angle of momentum is conserved in rotational invariant system, take Kepler problem or anything Kepler system central force potentials.

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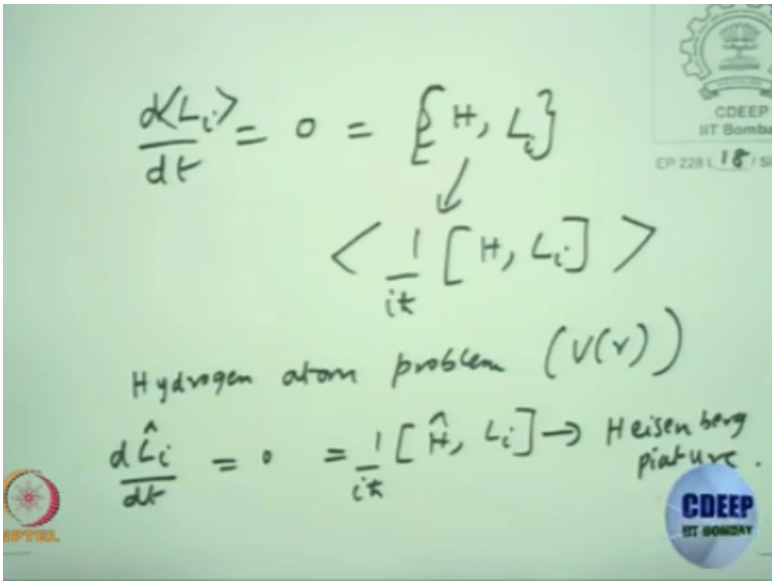

How do you show that dL/ dt is 0, the Heisenberg's equations of motion which you do which shows that the Hamiltonian, Poisson bracket, right, Poisson bracket of any component was that 0 for rotationally invariant system or central force but economically, what you have to do, this will become 1/ih cross, is that right? so hydrogen atom problem is a central force problem which is rotationally invariant and we expect the left hand side to be 0.

And that is possible if Hamiltonian commutes with angular momentum, right, they are compatible operators, so this means hydrogen atom problem, all central force includes all V of r potentials, need not be this hydrogen atom, rotationally invariant systems, angular momentum is conserved in classical mechanics, (()) (07:37) theorem says that the rate of change of expectation value of angular momentum is conserved and using your Heisenberg's picture equations for motion or Schrodinger picture on the expectation values.

So, this is not a right thing, so I need to put an expectation value here okay, if you say that the states do not evolve in time in Heisenberg picture, I can remove that expectation value, it is not required, I can write an operator here, everybody is familiar with this, right, so this then I am looking at Schrodinger picture but I could write it in the Heisenberg picture as an operator, this is Heisenberg picture.

So, all central force problems, angular momentum commutes with Hamilton, how do we see this in the hydrogen atom problem, we have done the psi nlm but we never looked at it from this point of view and that is why I was bringing in this angular momentum operator, okay, so I

let me just briefly tell you the angular momentum operator and how angular momentum operator commutes with the hydrogen atom Hamilton.

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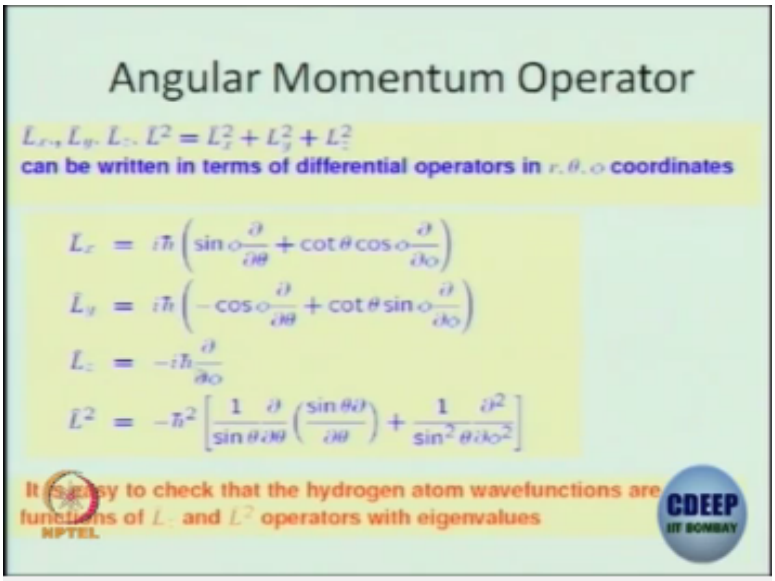

L dot L is what we call it as Lx square + Ly square + Lz square, in order to study spherically symmetric systems, we use this r, theta, phi and you can make a change of variable and rewrite all these Cartesian components in terms of spherical coordinates, what is Lz in spherical coordinates and you can show that Lx; please check this just a change of variable, write this as R cross P x component, rewrite it in terms of theta phi similarly, Ly.

And Lz will be a - ih cross del/ del phi, so it is just del/ del phi, it is going to operate on which part of the wave function, only the phi dependent P, which is like e to the im L phi, L squared is also formally you can try to write Lx square + Ly square + Lz square, you combine this and I leave it you to verify this okay, why am I doing this? My aim is to show that the Hamiltonian commutes with let us say Lz, Hamiltonian commutes with L dot L.

If it commutes with Lz it is; it better commute with L dot L also, each Li it is going to commute.

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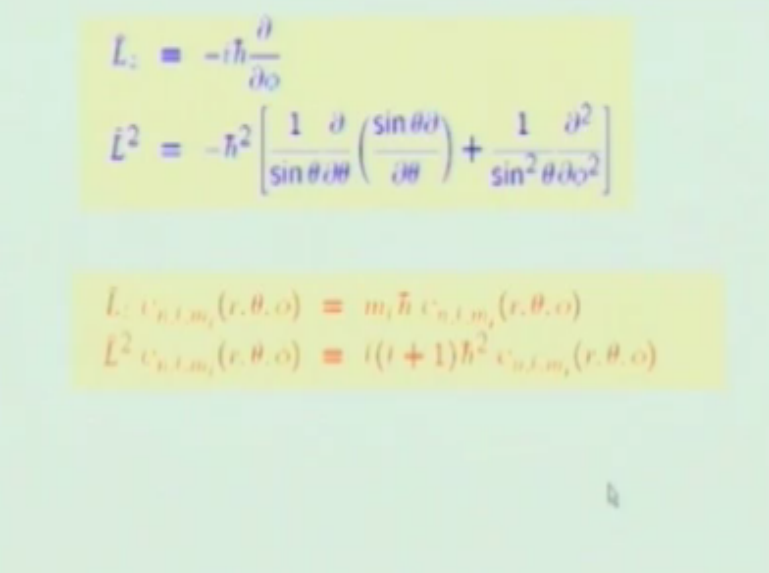

So, how do we do this, so this is the differential operator position representation for the angular momentum z component and the L dot L now, it is for you to check to take Lz on the hydrogen atom wave function, I already pointed out that it is going to be on the 5 dependent piece of the wave function which is roughly e to the i ml5, so it will give you del/ del phi, there is an ih cross here, so you will get ml h cross.

So, what do we see; we find that hydrogen atom wave function is an Eigen function of the Lz operator is that expected, compatible operators if you have should be the wave function solutions, if you have 2 operators; a and b, the Eigen functions of a and b will be simultaneous Eigen functions, these were Eigen functions of the Hamiltonian, we explicitly see that I do not know whether you all see the thrill that rotationally invariant system Hamiltonian has to commute with angular momentum components.

That means, if it commutes you can write a simultaneous Eigen basis for both the Hamiltonian and Lz and it is happening, this is an eigenvalue equation, what is the Eigen value; Eigen value is ml h cross, what about L dot L; this also you can see that this will be the operator form for the your theta phi part of the wave function. Please go back and look at the theta phi part of the wave function and you can see that you can pull out an eigenvalue which is not L square.

But L * L + 1 times H cross, will you go and look at that theta part of the wave function, so you will see that.

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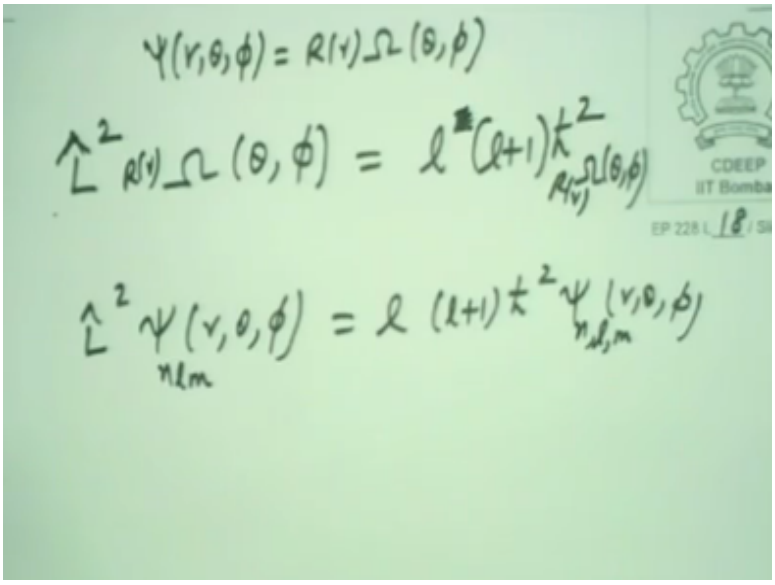

So, L squared operator on your omega of theta phi, so this operator is exactly like the differential operator which was in front of this omega of theta phi and you can show that it is C, which was l * l + 1 times h cross on omega of theta, why only theta and phi are affected; angular momentum, when you write the differential operator position basis you see it is only on theta phi; the theta phi.

So, your wave function when you write psi r theta phi, you could write it as R of r omega of theta phi and then when you try to write the differential operators, a differential operators nothing but your L dot L operator, you can check that out, we wrote that differential operator explicitly there but please you can go and check that the differential operator which we have which involves the sin theta del/ del theta.

So that operator can be written in a compact fashion as L dot L operator and this one was from the differential equation that we compared it to the spherical harmonics and we found that the solution is l * l + 1, okay, there is a h cross square coming up here because of the definition of the L square, so please check this, l * l + 1, so what is this? This is also an Eigen value equation putting a R of r does not matter, does it matter?

So, L squared on psi r theta phi is nlm is l * l + 1 h cross squared psi nlm r theta phi, so the Eigen value of the energy Eigen functions for the L square operator is going to be l * l + 1 H cross square that is what at least we see from the hydrogen atom, okay.

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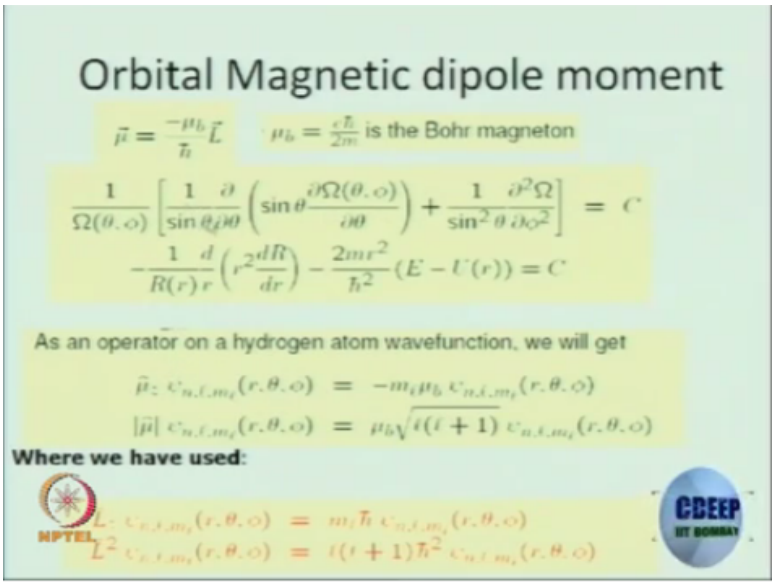

With this data, couple of things which you can start attempting is orbital magnetic dipole moment, sure you all know this, right Bohr magneton multiplied by the orbital angular momentum is the magnetic moment, right, this is the Bohr magneton, L is angular momentum suppose, I take the z component of this magnetic dipole moment operator act on this wave function; be an Eigen state or not an Eigen state; going to be an Eigen state, going to give you H cross cancels, you have a minus ml Mu v.

And similarly, the magnitude of the Mu vector, you can do Mu dot Mu, if you do Mu dot Mu, it will be L dot L; L dot L on the state is l * l + 1 h cross square, if you want the magnitude, it is not just L, it is a square root of l * l + 1 suppose, you have a function of this L; all operator they will also be Eigen states that is all I am trying to say, so where we have used L is; is this and l squared is l * l + 1 h cross square.

And also you could remember that this is what I was saying, this operator which I have is your L squared operator on omega and C was l * l + 1.

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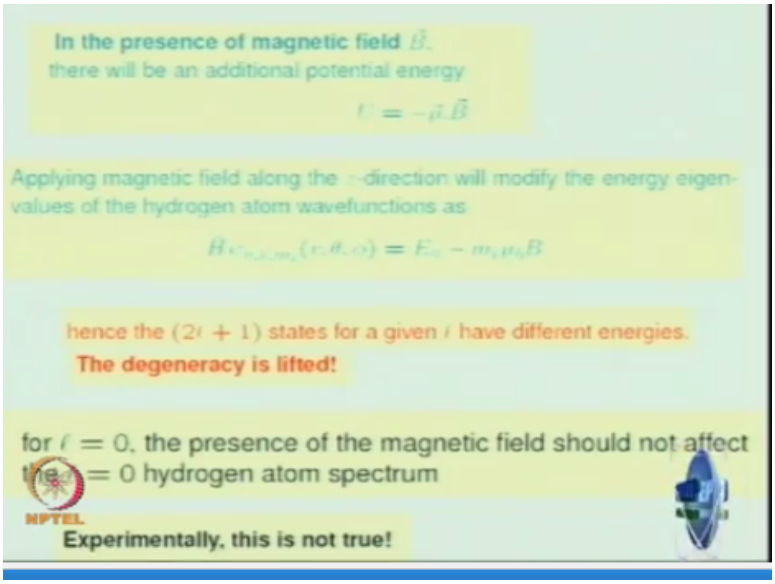

So, why am I slowly going into this typically, you will have interacting with the magnetic field, what is that effect called? Zeeman Effect, so what will be the term in the potential energy you have to add; Mu dot v, if you turn on a magnetic field and if the object has magnetic moment; orbital magnetic moment there will be a Mu dot v, so what is our aim? If we add this term, what happens experimentally, you all know what happens; what happens?

This is a splitting right, they start seeing that some of the levels which you are degenerate, they separate right, this is what they saw, can we see these some equations, okay so we try and operate this operator, Hamiltonian will be; let us take Mu dot v or the hydrogen atom Hamiltonian, add it with a - Mu dot v, when we turn on the magnetic field on a central potential, you had the hydrogen atoms Hamiltonian and then a - Mu dot v added to it.

So, we know that the hydrogen atom will give you a En energy but this interaction term or this potential energy due to the magnetic field, we have done this, what is Mu z do? If suppose, you take the magnetic field to be along the z direction, Mu z will give you a ml time; - ml times Mu b right, you seen this, sorry I should have put a multiplying that wave function which I have not done, so please put that wave function.

So, it is an eigenvalue equation again but initially, the energies of those wave functions were En, they will still be En only for ml = 0 but ml != 0 it starts showing whether it is + or - L or it goes from - L to + L, there will be distinct levels with different energies and that shift will be Bohr magneton times the magnetic field is the way of using eigenvalue equations simultaneous Eigen functions of commuting operators, everything comes into picture, right.

So, this is one thing which you should see but what exactly you have initially, there was degeneracy but now, 2l + l states for a given L have different energies.

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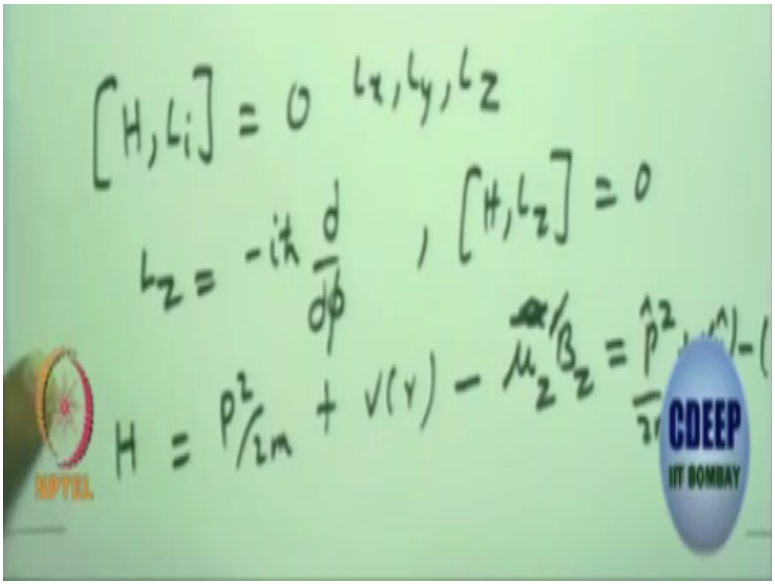

So, I said that the Hamiltonian commutes with Li = 0, where Li could be lx, Ly, Lz but for convenience Lz operator was - ih cross del/ del phi and we found that H and Lz is 0, this is fine, suppose, you take the Hamiltonian which is P squared over 2m + v of r and then I want to also add a Mu dot B and I take the Mu to be along z direction, so then what happens here; it is P squared over 2m + v of r and then this will be a Bohr magneton times Lz quantum number times Bz okay.

So, let me not write those factors, it depends on Lz operator now, the question you are asking is whether this new Hamiltonian, this is a new Hamilton, whether it commutes with Lz; it does not commute with Lx and Ly, the old Hamiltonian commuted with Lx and Ly also but the new Hamiltonian commutes still with Lz, is that obvious from here, adding a term proportional to Lz, if I take the commutator with Lz, this term anyway commutes.

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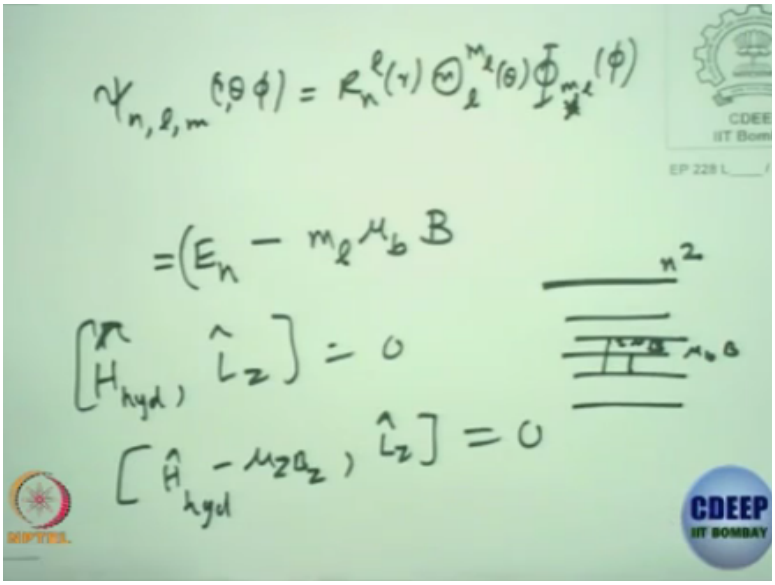

And this will also commute; trivial, so it is a simultaneous Eigen state of Lz and Hamiltonian, so if you go and write your wave function, write it this way, you will see that that shift will shift the energy by an overall ml factor and that keeps adding to your energy eigenvalue, so whatever you found En, will get an ml Mu that is what will happen, I am arguing from a different point of view that the Hamiltonian; initial Hamiltonian of hydrogen atom commutes with Lz.

But I can also write hydrogen atom + Mu dot b with the Mu z Bz Lz that is also 0, from here also I can find what is the shift in the energy by using the operator (()) (22:03) even from the wave function formalism you will see that there will be a shift, so what is happening is that this one was having a n square degeneracy now, you will see that will get for a specific L there will be a splitting which is happening and each one will be a; this difference will be a Mu Bb, 2 Mu Bb and so on, you understand what I am saying, right that is a Zeeman's split okay.

So, I am just trying to say that you can formally do this also and check out that the shifts in the energy happens, it is no longer degenerate, there will be a 12 + 1 states for any given L having different energies and so, the degeneracy gets lifted by this Zeeman effect, L = 0, what is expect you, will there be this effect? So, L = 0 in the presence of magnetic field or in the absence of magnetic field, I do not see any difference.

L = 0, is like as if the particle is almost at rest, does not have any, no, it is kind of heavy and stationary or it is rest that you can treat the state to be at L = 0 and the spectrum will not be able to say whether you are in B = 0 or B != 0 experimentally, this is not true, what do they see?

There is this additional thing which we never brought in our Schrodinger equation which is the spin angular momentum.

And we cannot discuss spin angular momentum in non-relativistic Schrodinger equation, non-relativistic because your kinetic energy operator is P squared over 2m, if you want to do relativistic quantum mechanics, what should be the modification, the kinetic energy or the total energy has to be written as P square C square + m0 square C power 4, this is the way you have to write in the square root, right, so that is not what we are doing.

We are always taking the kinetic energy as P squared over 2m which is non-relativistic quantum mechanics and we are studying non relativistic quantum mechanics which is the Schrodinger equation and we cannot see this additional quantum number which is the spin quantum number in non-relativistic quantum mechanics but experimentally, I am not governed by this, they are seeing what they are seeing.

So, they are seeing even for L = 0, they see degeneracy is lifted but mathematically, I see L = 0, there is no distinguishing whether we put a magnetic field or no magnetic field, clear okay.

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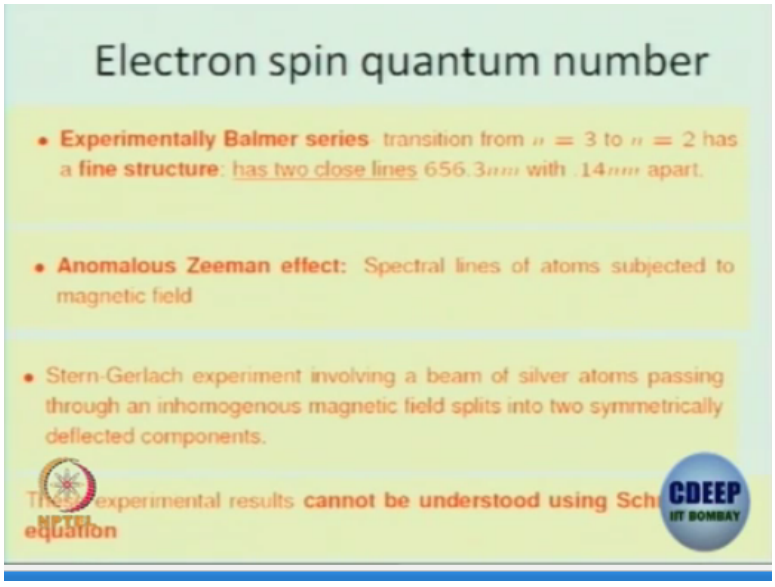

So that brings in the concept by putting by hand electrons spin quantum number in non-relativistic quantum mechanics so experimentally, when they do a transition from n = 3 to n = 2, they do see that there are small closed lines which are 0.1 14 nanometer apart, they cannot account it without introducing the electron spin quantum number and also in the Zeeman effect as I said L = 0, did; they did c2 lines.

They cannot account for it just by Mu dot B term which is where Mu is the orbital magnetic moment and the other convincing thing is the Stern-Gerlach experiment which involves the beam of silver atoms which are produced and it is made to they are taken to be almost at L = 0 and they are made to go through the single homogeneous magnetic field and they see to beams coming out. So, these experimental results cannot be understood using Schrodinger equation, what is the reason?

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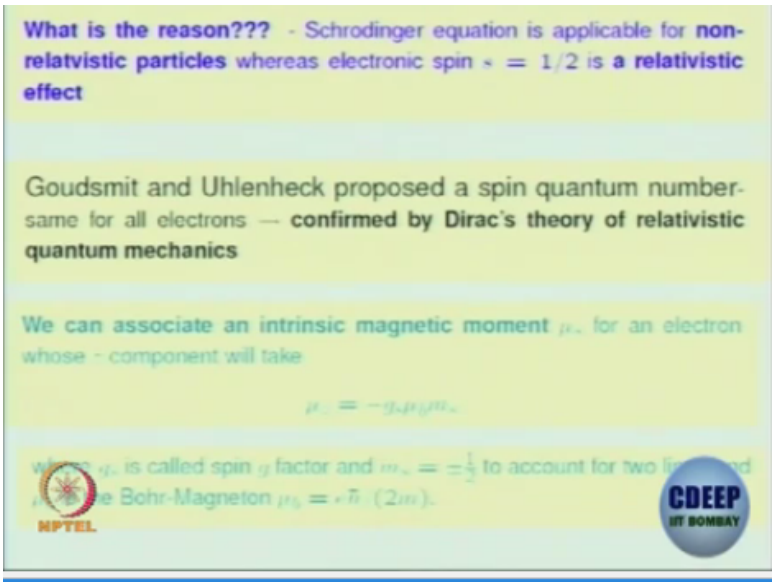

This I have already said Schrodinger equation is applicable for non-relativistic particles whereas, the electron spin is relativistic effect, so for relativistic theory, we need to study Dirac's equation and Goudsmit make these people had proposed a spin quantum numbers which is same for all the electrons. So, what does that tell us in theory? I have to introduce a similar term like the way we introduced the orbital magnetic moment, a spin magnetic moment.

And we also introduce a proportionality factor which is the G factor and MS is taken to be + or – 1/2 if we take this, then we can account for all the experimental data okay.

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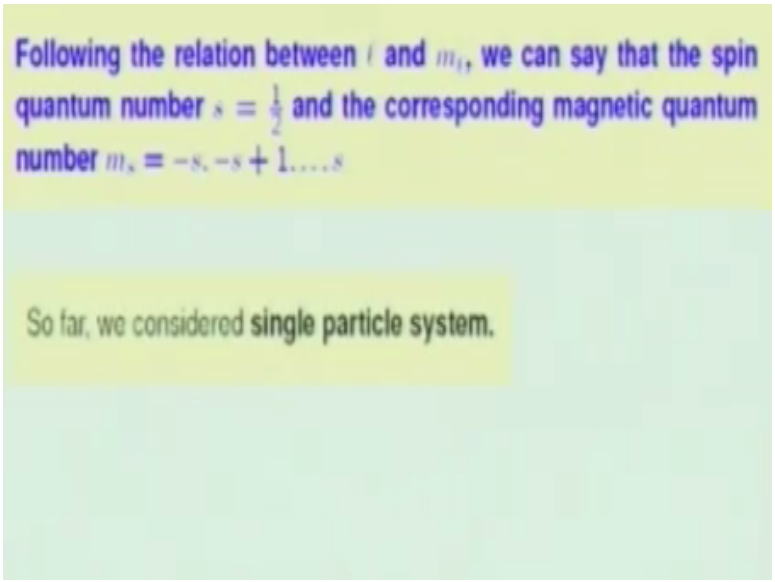

So, just like your orbital angular momentum L and Azimuthal quantum number l and ml, you can have an s; s is always 1/2 for the electrons and you will have an ms which goes from - s to + s, if it is 1/2 then it goes from -1/2 to + 1/2 that is why you see 2 distinct lines which is accounting for the spin angular momentum even though L is 0, even though L is 0, when you turn on a magnetic field, you see 2 distinct lines, 2 splitting's is because of the spin quantum number with s = 1/2 and ms = -1/2 and + 1/2 so, let me stop here.