Introductory Quantum Chemistry

Prof. K. L. Sebastian
Department of Inorganic and Physical Chemistry
Indian Institute of Science, Bangalore

Lecture - 35
Angular Momentum – Continued and Spin

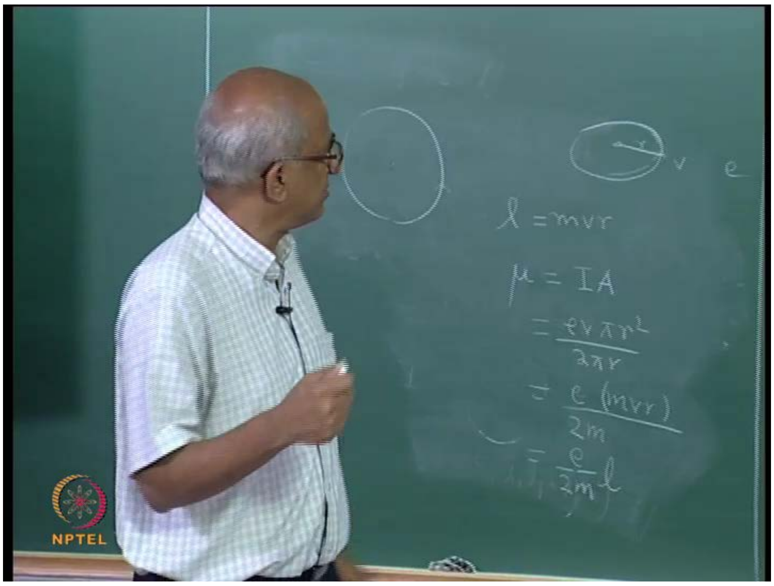
We were talking about space quantization and we said that the angular momentum vector can have only certain values and then of course, it can have only certain orientations. In fact, in the case were l equal to 1, you show that there are only three possible orientations they have different values for the z components of the angular momentum vector. Then you say many of times this can give you only confused what is so special about the z axis there is nothing special about the z axis. If you want you can take z axis the way you want which about direction you want. So, actually the wave you have solve the Schrodinger equation, the solution that we are obtained where such that z is a component the answers that obtained by where such that the z component of the angular momentum had certain values that is what happened.

Now actually, if you remember you see my definition of polar coordinates the z-axis was kind of special, it was special in sense that we measure theta from the z axis. But suppose, I decide to see I will measure, I define a new polar coordinate such that theta is measured from the x axis then the solutions that I would obtained would have had the x component of angular momentum having quantized values like m h cross. So, therefore, the do not be under the impression that the z-axis has anything special. It just the way we did the things z-axis was special, so the solutions were like that, that is the first thing.

Second things, is it is nice to say of arise all this quantization, but what is the proof I am ultimately. You should never believe what a theoretician I am a theoretician. So, you should never believe what a theoretician tells you unless you have experimental evidence without experimental evidence you do not believe anything, anything that any theory has to agree with experiments. So, therefore, it should be possible for me to demonstrate you that this quantization actually exist not enough just say that the quantization is there.

So, let me give you an experiment, which can in principle be used. Though in practice what happen is that the answers that we get will necessitate the modifying of the theory which will the experiment when performed will required that the theory that had be talking you should be modified. We will see. Again, whenever we think of new things also we will ask what will happen in, if the system of a classical mechanics and then compare to quantum mechanics.

(Refer Slide Time: 03:19)



So, imagine you have this electron which is going around the nucleus in perfect circular orbit, in the bar theory as I told you this is a planer orbit, it is plot in one plane, and it will be moving with a velocity v, along a circle of radius r. And if you remember your bar theory, what will happen is that the theory will tell you that the region angular momentum whose magnitude actually equal to mass into velocity into r; not I note that I have written only l, not vector, because I am only concerned with the magnitude at the moment. And now you see the electron is a charge particle, so this is actually charge particle going in a circle that actually is a current right, and so you have a current going in a closed loop and if that happens there will always be a magnetic moment.

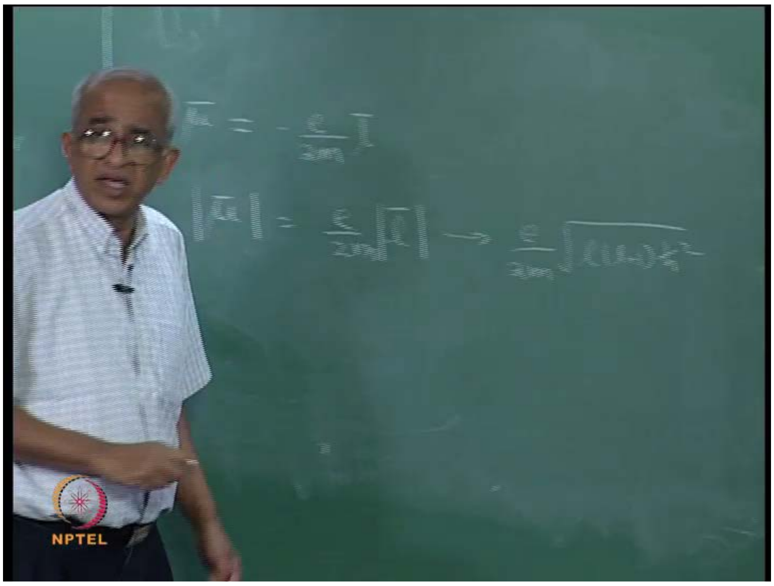
So, if I want to calculate the magnitude of the magnetic moment, I can use a formula, the magnitude of the magnetic moment will be nothing but the current multiplied by area of the loop. If I have a circular loop and then there is a steady current going around its magnitude of current is I and the area of the this loop is equal to a then the magnetic moment that the system would have is I into a. So, what is the area even for this kind of circular orbit, area will be pi r square correct. And I want to calculate the current. So, you have the electron, it is moving with a velocity v, so how many times will the electron go around in the unit time. Well for a circular orbit of course, the perimeter or the circumference is 2 pi r. So, therefore, if the electron is moving with a velocity v, then it will go around the orbit some many times in one seconds right velocity is the distance that it will do cover in one in unit time and 2 pi r is the is the sorry circumference.

So, therefore, the some many number of time the electron is going to go around and the electron as a charge right they mobile let may write just an e, but of course, it is negative I will come to that I will modify these e and put minus right. So, therefore, this how many times the electron is going around it and therefore, the current actually is. So, much current is charge going per unit time right. So, therefore, current is. So, much and the area is. So, much. So, therefore, what is be the magnitude of magnetic moment actually you will have e into v divided by 2 pi r how is that r and r going to cancel pi and pi are going to cancel.

So, I will be left with e will may put a there is a 2 here let me put an m in the denominators which means that I will have to put an m is the nominator. So, I will get m v r correct why do why should I have m v r well we want m v r because that is the angular momentum that is why included that m and therefore, the magnitude of the magnetic moment is nothing, but e divided by 2 m into l where l is magnitude of the angular momentum these is of course, classical right now if I was going to think about it quantum mechanically. What will happen I can say over I mean let me before I go into quantum mechanics I want to modify these because you say this thing mu as well as l or vectors.

So, therefore, what will happen I will have mu equal to value see if you had a charge which is going in this direction like that or maybe like to be very clear let me say I have the circular orbit a charge is going around its for the moment, imagine it is positive. Then if it is going around it then what will happen is that the angular momentum is a vector pointing towards you, if it following that orbit in the direction that I am showing in with my hand. And the magnetic moment also will be in the same direction, but now I say the charge is actually, because I am saying of the electron, the charge is negative then what will happen, the angular moment vector will be still in this direction, but the magnetic moment will be in the opposite direction, because the charge is negative.

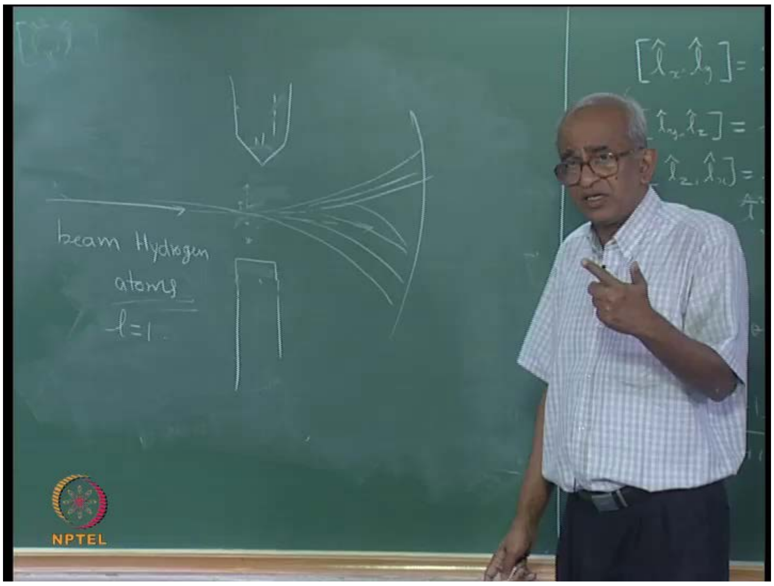
(Refer Slide Time: 08:06)



When therefore, what is the expression that I would have I would have mu equal to minus e divided by 2 m and vector l. So, these is the precise relationship between angular momentum and magnetic moment of the electron. So, therefore, I mean why do we thing of this the answer is that if you had the electron say thing in in these any of this stationary state it is like that it will have a magnetic moment, because the magnetic moment is related to the angular momentum vector. For example, if you think of the s orbital what did you except, for the s orbital, the magnitude of the angular moment vector I did not discuss this simply because it was 0. The the quantum number l is 0 therefore, magnitude of the angular moment vector is zero. So, the it has no angular momentum vector, actually it is 0 and therefore, the magnitude moment also is 0.

But if had l equal to one what will happen l equal to 1 mean the magnetic moment, if you calculate the the magnitude of magnetic moment, you know the precisely how much it is it is going to be mu magnitude and that will be equal to e divided by 2 m magnitude of l. And that actually is going to be e divided by 2 m square root of l into l plus one h cross square these is going to happen if you think of the magnitude of magnetic moment, but because l has 3 different orientations, now the magnitude moment also has three different orientations. Now can I do an experiment which actually will demonstrate this three orientations only if I can do that should I believe in all this stuff that quantum mechanics is telling may, I have to be able to verify this experimentally. So, how I verify this experimentally is the question that I am going to ask.

(Refer Slide Time: 11:22)

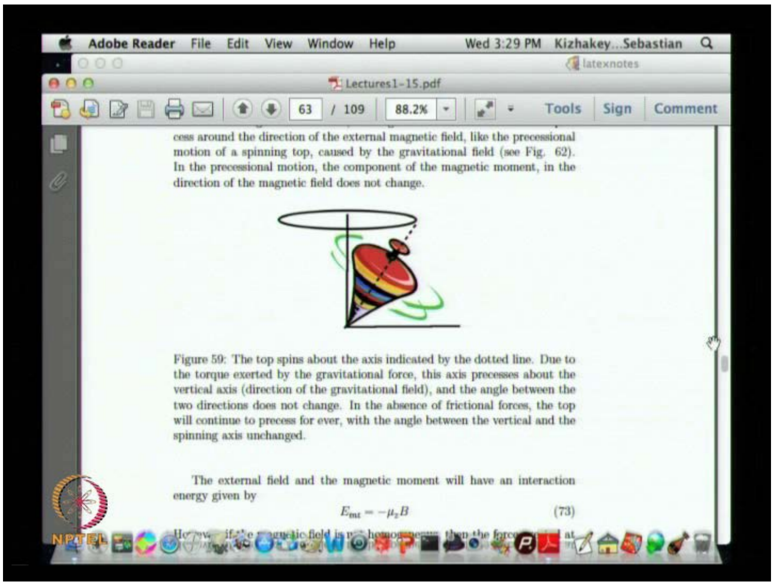


So, let me imagine, I have here a beam of hydrogen atoms, a beam of hydrogen atoms. I should tell you that this is a very very difficult experiment. And in fact, I do not know whether this particular experiment as ever been done, may be it is done I mean because these days people have done almost everything that can be done this kind of experiment. I was originally done with silver atoms. We will come to that in a in a few minutes, but let us imagine that I have beam of hydrogen atoms, and I will prepare then in the state with l equal to one. Suppose I can prepare them in the state with l equal to one that actually mean I mean because you would be have a little bit of familiarity with the spectroscopic, what is do is you take hydrogen atom expose to radiation of correct frequency, so that the hydrogen atom makes a transaction from the 1 s orbital to the 2 p orbit that is all or it is not necessary that should 2 p it may be it 3 p you can take a transaction that is that also you needs to do in principle.

So, suppose I have made this hydrogen atom in the l equal to one stage, so what will happen you see the are all having a non 0 value for angular momentum vector that means they all would I mean I would except all of them to have a tiny magnetic moment So, there are all tiny magnets, and the magnates are not having random orientation in space. Suppose suppose I now say I have going to apply a magnetic fields the by having these two poles of a magnet then what will happen these hydrogen atom, there are actually tiny magnets I can perhaps represent the one hydrogen atom magnetic moment by this. This is north and that is the south and so what will happen this is magnetic moment that it would have. Not only the magnetic moment, it would also have right an angular momentum because l is equal to one and both actually are in the same direction right in that direction.

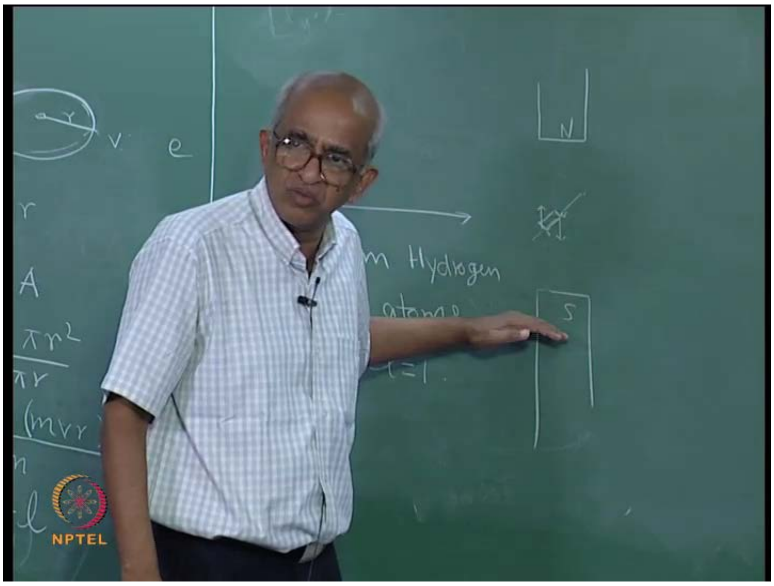
Of course, you see magnetic moment if it is in this direction, the angular momentum will be in the opposite direction. So, if you say that there is a magnetic moment for this atom, what will happen in these magnetic field is going to act upon the magnet, you see I mean the they have a tiny magnet and it is put in a magnetic field. So, what will try to do it in I mean we all know we all have all played with magnets, if experiencing the earth's magnetic field it will actually try to tilt. But the system has an angular momentum, and if the system as an angular momentum actually this is very interesting it is like a spinning top if the system experiences say torque what do I mean by a torque you see there is force acting at this end may be trying to move within direction, there is a force acting on this other end in the opposite direction. So, therefore, that what I referred as torque that actually should tilt it in this fashion, but because this system as an angular momentum, it does not actually tilt, but instead it undergoes what is refer to as a precessional motion you should be familiar with this.

(Refer Slide Time: 15:18)



I have it on my computer. So, here is the precessional of a spinning top. So, what will happen let me repeat. Here is my magnet the region angular momentum associated with this magnet, and then you applied torque trying to tilt direction of the magnet. But with the magnet actually it does not tilt, but instead it undergoes precessional motion right that is what it does.

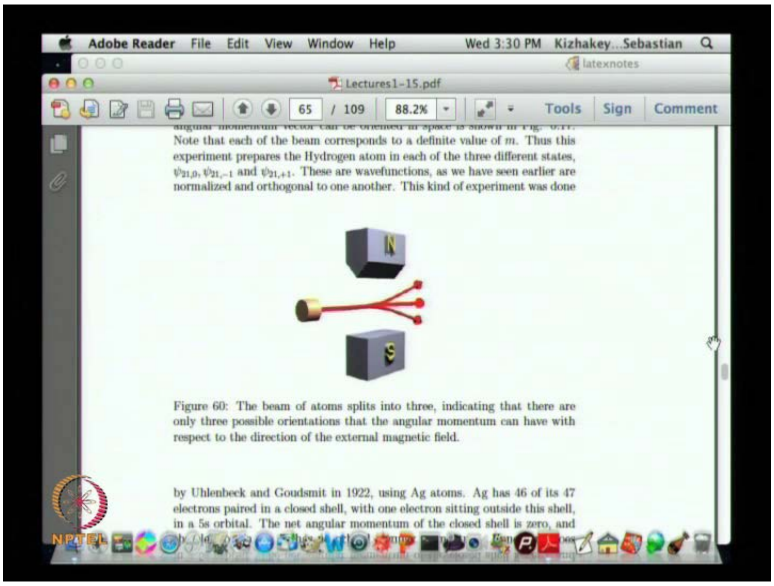
(Refer Slide Time: 15:49)



And further the the there is a force acting on this let me say in this direction, the another force acting on this in that direction the two forces are actually equal, but opposite in direction. So, that the net force acting on the magnet trying to moving it from this position is 0 it only trying to tilt it it is not actually causing the center of mass of the magnet to move because this force and that force actually are exactly equal. So, if I short of a beam of hydrogen atoms what will happen they will actually simply pass through, they will simply pass through because you see they may get they may undergo this precessional motion for some time and then come out that is all. That is the case if the magnetic field is uniform everywhere.

But suppose the magnetic field was not uniform, how can I make it non uniform the answer is your you will see you have and a special kinds of magnets maybe something like that, that think I have a pictures. You can see that they are the top of pole of the magnet is construct differently and why we do that the answer is that that if you had such a such a shape, the magnetic field is not uniform everywhere, it is going to be varying from point to point.

(Refer Slide Time: 17:04)



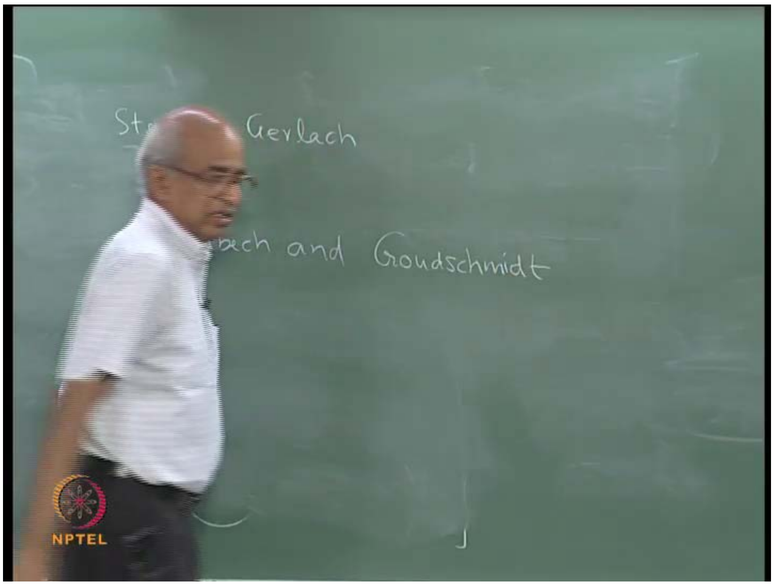
And if it is varying from point to point, what will happen the force that is exhaled at this end and the force that is exhaled at the other end are not going to be the same. And therefore, there will be net force and that will cause a displacement of this magnet may be in the upward direction or maybe in the downward direction depending upon how the magnet is orientated, depending upon how the magnet is orientated it may be displaced in the upward direction are in the downward direction.

And now imagine, you see, I am going to have a large number of this magnets, their orientations in space or are in different directions. If I short then and applied these in homogeneous magnetic field, what will happen, some of them will go down, some of them will go up, and say many of them, it simply depends upon the orientation that the magnet. They tiny magnets have and therefore, what you would expect is that if I had detective here I would find it, arriving at 3 different locations along my screen. But if the orientation that that this magnet can have, is special what will happen. In fact, we have seen that because of the angular moment vector, there are only three possible orientations when l equal to one.

So, therefore, there are only 3 possible ways, they magnet can be oriented with respect to the z direction. This is now my z direction notice that I have made sub directions special by putting a magnetic field in that direction. So, therefore, what I as what would happen is that my tiny magnets can have only 3 kinds orientations with respect to that direction proved l equal to one. And so what would you except your beam of hydrogen atoms which go through the magnetic field they will be split up into three right that is what shown in this picture. So, this is what would would except and therefore, this is actually a very clear experimental verification of the space quantization that I was talk about. You can imagining doing same experiment with l equal to 2, you will find that the beam will split up into five.

So, all everything seem to be nice, but unfortunately this experiment if you did it this way, let us say I will do with with hydrogen atoms in the ground stage, the electron are in the all in one as a atomic orbital what would you expect happen if it is in the one s, angular momentum vector is zero. So, you do not except the beam to be a splitted, but if you did the experiment, you will find that this split up into two. As I said this kind of experiment is extremely difficult, if you do with the hydrogen atom, because you see hydrogen atom they do not excess free it is difficult make them. You have it start with hydrogen molecules dissociated then accelerate the whole thing do something to get hydrogen atom, but silver atom are very easy; just I evaporate silver they will come out.

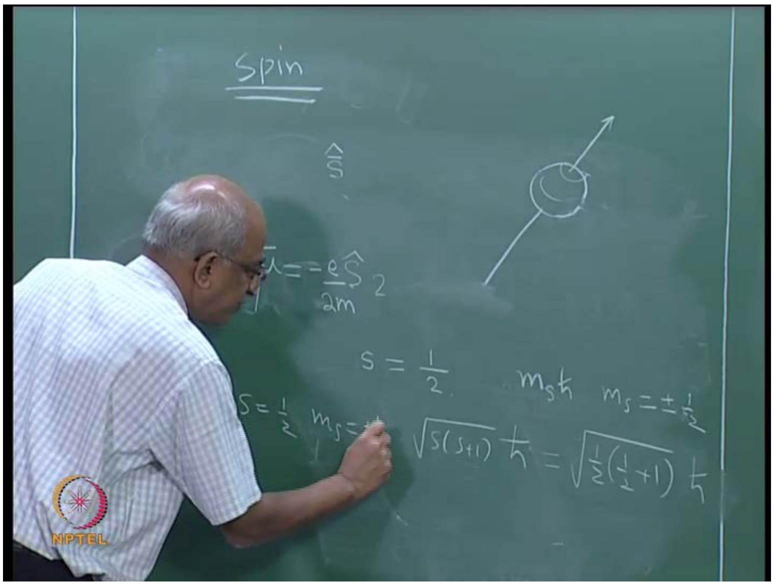
(Refer Slide Time: 21:06)



It is actually done by Stern and Gerlach long ago and they use a beam of silver atoms and it has found that the beams split into two. And they had no explanation for this, and explanation was actually given by Uhlenbeck and Goudschemidt. The ways silver atoms is you see you have a close to shell and with one electron sitting outside and that electron sitting in s orbit. If the close shell as no angular moment net angular moment is 0, the electron that is sitting outside you do except it that they have an angular moment, because it sitting in an s orbit.

And when they did this experiment with silver atoms they did not have they do know quantum mechanics that then because quantum mechanics was get to developed. They did this experiment and found that the beam actually splits up into two. And therefore, there is something that we have not yet discussed, and what leads this answer is that in electron in hydrogen atom sitting in a one s orbital, it has a magnetic moment even though. We did not expect one give to its orbital motion it was going around the nucleus, but that there was no angular moment, but electron does have an angular momentum and not only that when I say how do I know it is angular momentum, I say that because I have found that there is a magnetic moment, but this experiment only show you that there is magnetic moment.

(Refer Slide Time: 23:20)



So, therefore, I there is a angular momentum and that angular momentum and that angular momentum can have two orientations in space and to explain these the idea of spin was suggested. So, if you like you can imagine at least in those days this is what people did that first. We imagine that the electron is something like a sphere this is not a correct picture, before I even introduce that is the picture I want to say that this is not the way one has to think of spin, but this is helpful. Imagine it is a sphere having a finite size and imagine that it is spinning about such an axis. So, the electron as a negative charge. So, if it is a spinning that actually means the charge is actually going around; that means, it is where is angular momentum there is also a magnetic moment.

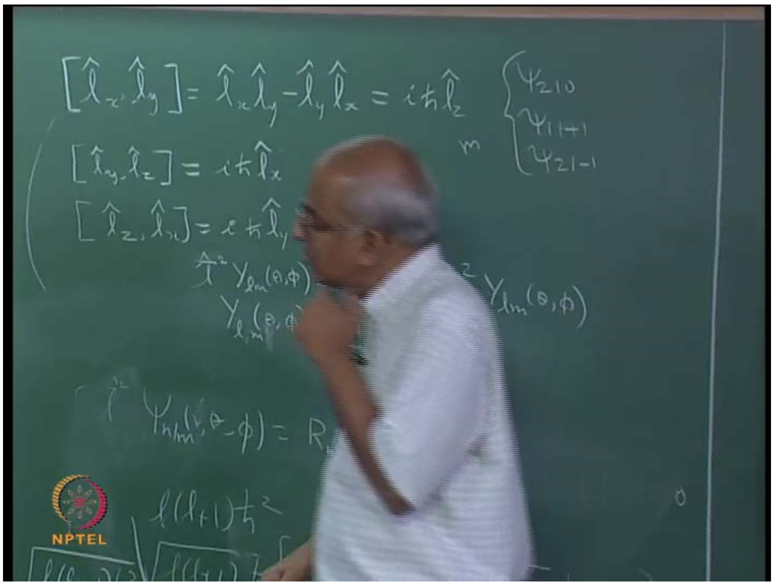
And the angular momentum associate with these we will call it spin angular moment and we will denoted by the symbol S with a line on top of it, but as it usual in quantum mechanics you see whenever you say you have a quantity we have thing of the operator. So, for we will have spin operator which is a vector operator just like your angular moment operator is that obtained. When I say that angular moment operator those of operator they are repeat as orbit angular momentum operators because they were concerned with orbital motion. Now I am think spinning motion where you can imagine you have a ball, which is just spinning and I am sure you are all familiar with spinning of balls you all play cricket definitely. So, therefore, spinning and the spinning leads to an angular momentum and because the electron is charge it also leads to a magnetic moment, and you can expect that the spin angular momentum is related to the magnetic moment, this is what happened with orbital angular momentum.

So, what would you expect if I use the same expression as earlier why would have obtained minus e by 2 m times, yes, this is what happened with orbit angular momentum, but interestingly this formula is not correct for electron. You have to multiply this cyclic by the factor which is two almost actually two point naught naught naught someone eight are something; let us not worry about that it is equal to 2 for our purposes. And further what is happening that this is spin has only two possible orientations right. So, what does that mean, it means that following you see at look at an angular momentum vector having at an l quantum number having an azimuthal quantum number equal to l then the magnitude of the angular momentum vector is square root of l into l plus one into h cross square that is what the magnitude is. And then the this as how many different orientations, the different orientations correspond to m being 0 plus or minus one plus or minus 2 plus or minus 3 etcetera until plus or minus l.

So, if the quantum number is l then there are 2 l plus 1 different orientations right for example, if l equal to 1, there are 3 different orientations; if l equal to 2, there are five different orientations. Now here what we are finding is that externally we are finding that two only, two orientations. So, how can we bring that into the same kind of frame work right, the answer is to say that there is they say quantum number similar to these l, but somewhat different. I will tell you why it is different, I am going to denote that quantum number by S that the quantum number l could take any value from 0, 1, 2, 3 etcetera up to infinite there, but this S quantum number, I am going to say that it can have only the value half, hence not only that it can be orientated such that is that component is m s times h cross with m s being plus half or minus half these are only two possibilities. Why do I say that because that is the what the experiment says, because if the experiment shows that there are only two possible orientations right.

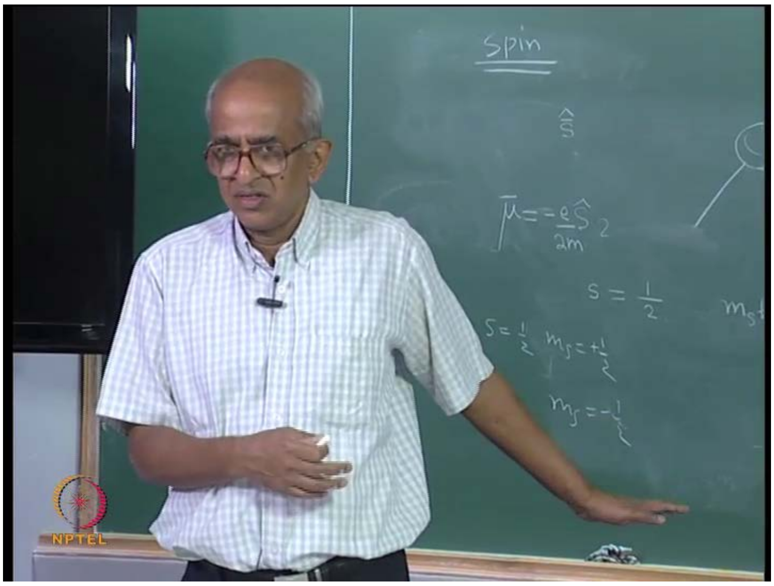
So, therefore, I will say that there are only two possible orientation, see if you had a general value for l number of orientations would be 2 l plus one. So, if you put instead of 1, if you put half there then you would the realized there two possible orientations only. So, it is as if this quantum number l is taking the value half and we do not call it l anymore, because we are we are not concerned with orbital motion, but we are concerned with spin motion, so we call it S. Therefore, the the way we are going to work now is to say that this experiment demonstrate that there is something like this spin with it has angular momentum associated with it, and it has a quantum number s equal to half this will specify the magnitude of the angular momentum vector which will be equal to square root of s into s plus one h cross.

(Refer Slide Time: 30:15)



Just like what you have there, the only thing instead of l, you will have to put s, but their l will take values different values you know 1, 2, 3 etcetera, but you are s concerned it can only 1 value equal to half. And hence the magnitude of the angle of the spinning angular momentum will be square root of half into half plus 1 h cross. And there are two possible orientations. And again if you look at look at these case the angular momentum case. You have functions like psi 2 1 0, psi 2 1 plus 1 psi 2 1 minus 1, they have different values for m, this functions have different value for m, but the values of l are the same right.

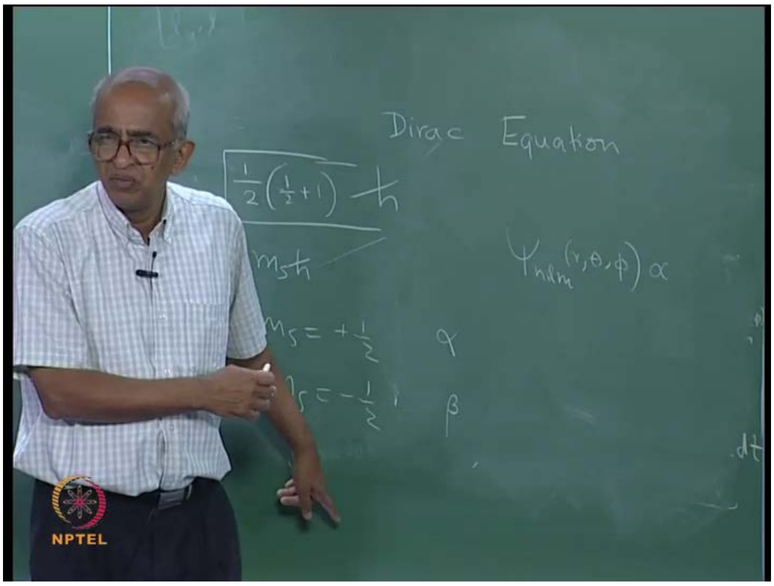
(Refer Slide Time: 30:42)



So, similarly you can say what I should imagine is that I have a straight where s is equal to half and m s is equal to plus half these is one possible straight in which spin of the electron can be. The spin of the electron oriented in such a fashion that the z component of the spin angular momentum is plus half time h cross that is one possible state of the electron. And there is another possible state of the electron in which this spin is oriented in a different fashion and that state would have m s equal to minus half. I said this are all just written down using induction to explain the experiments well this is definitely is unsatisfactory if you are a pure theoretician, because you see I mean you want to understand this this this the thing not just assume something.

So, the way one can actually derive this things, this as follows. See till now we were discussing what is referred as schrodinger equation. The schrodinger equation has to be defect that it does not worry about relativity theory at all. But you have to actually to include relativity theory if you want to describe the natural world in correct fashion, and if you included relativity theory actually what you will have to do is you will have to formulate an equation which has originally formulated by Dirac.

(Refer Slide Time: 32:15)

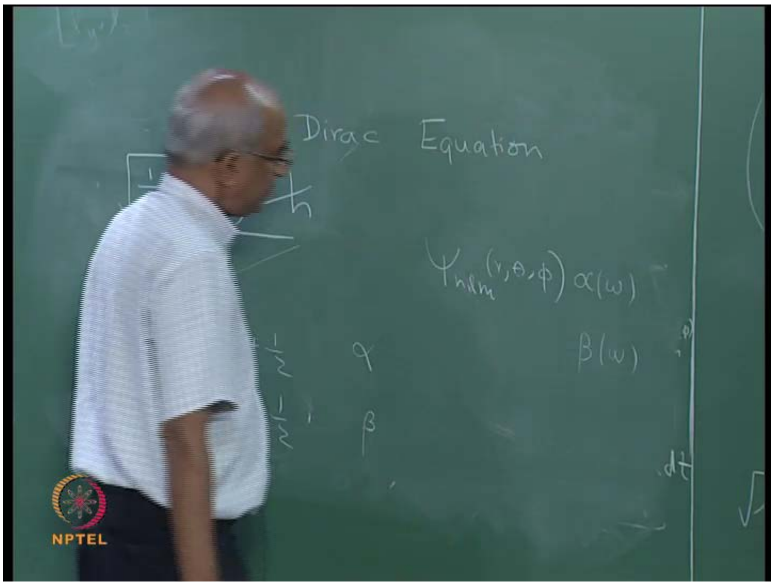


This properly takes relativity theory into account. And if you sold the Dirac equation this spin will automatically come out of the solution. We are handling the non-relative stick equation known as Schrödinger equation and by solving that what happens we got only 3 quantum numbers, we did not get the fourth quantum number. If you want to get the fourth quantum number, you have to do a very detailed derivation using an equation which is referred to the Dirac equation, and we will not do that because you see that chemist are not terribly interested in the Dirac equation of course, they are interested in the spin. So, therefore, what is normally done is to introduce a spin as a an assumption this is what chemists would normally do and that is all that we are going to do. We are not go into go into Dirac equation.

So, therefore, we now have this I mean if you say you can say this is an additional postulate of quantum mechanics of chemist, the additional postulate being that the electron has spin associated with which it has a spin angular momentum, this spin angular momentum has only a certain magnitude. The magnitude is actually may let me write it down I may have not kept it in down anywhere. Magnitude is actually square root of half into half plus one h cross is the magnitude of the spin angular momentum vector. And the spin has two orientation characterized by different values of m s; m s being is there plus half or minus. And corresponding to different values of the magnetic quantum number m for this functions, you had each one had a different wave function. So, similarly you will have to say that these two different states of the spin should have some spin wave function.

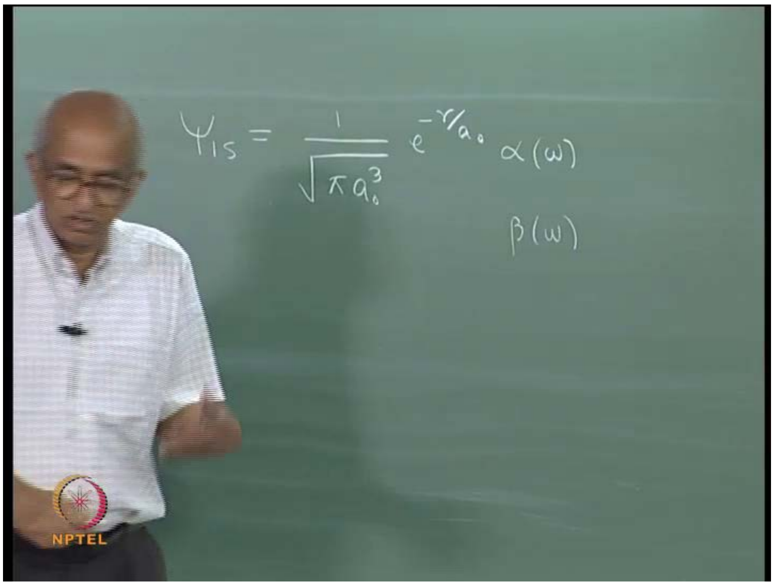
Again that has to be assume what we will do is we will say that if m s is equal to plus half, there must be a wave function characterizing that state, and that I will denote as alpha. So, here the spin is oriented in a direction which is upward such that the z component of the spin angular momentum is plus half h square. So, we normally say that the spin is pointing up, so that state we will denote by a simple alpha. And if ms is equal to minus half you will say that the state is going to be denoted as beta.

(Refer Slide Time: 35:28)



So we will say that the wave function or the statement, the let me not say state function, the wave function for an electron will have an additional part up to now we had only psi n l m r theta pi this was obtained from the Schrodinger equation. But now I am going to say that in additional to this wave function has another part which I will denote by the symbol may be alpha, this is actually the over may be beta, but this things are actually this this function is a function of r theta pi and. So, this is natural that this may be may be thought of function of something. You can say after that something because this is all postulates that something is something that is not very clear, but we will say that is our spin coordinate and denoted by the symbol omega if you like, which you can say it is actually some coordinate with which is connected with you orientation of spin. And similarly the other functions what will happen is that you will have beta of omega.

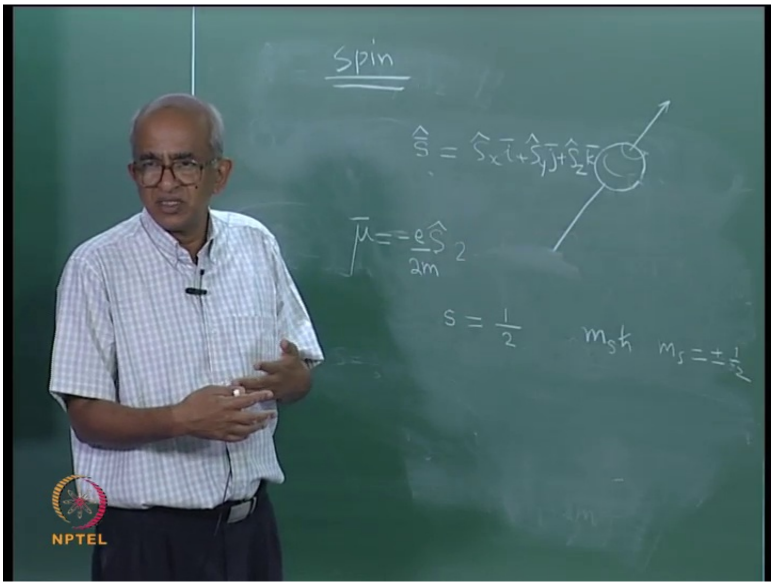
(Refer Slide Time: 36:42)



So, if you think of the ground state wave function for hydrogen atom, the wave function would look like psi 1 s equal to 1 by square root of pi a 0 cube e to the power of minus r by r by a 0. And this wave function does not contain spin, now if we added spin also to this function, what will happen is that you will have either alpha of omega; alpha is the spin wave function, omega is the spin coordinate over we have the other possibility of having beta of omega. So, there are two possible states, two possible spin states being represented by the wave functions alpha omega and beta omega. So, there are two possible states for the electron.

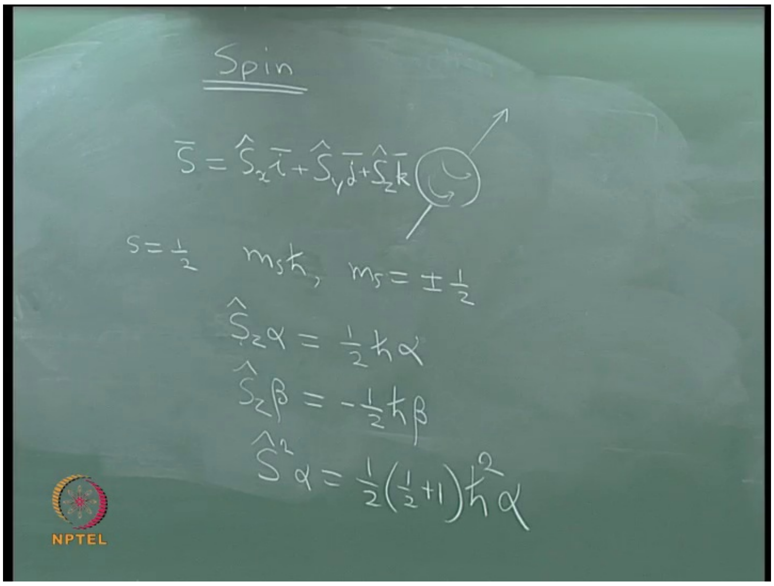
See until now I said that the ground state actually a ground state of the hydrogen atom is non degenerate, but when I take this into accounts, spin into account, it is no longer degenerate because the electron has a spin, the spin function can be either alpha or beta. So, therefore, there are two possible state now, it is doubly degenerate.

(Refer Slide Time: 38:12)



And not only that you can also introduce see if you say that s is a vector you can actually introduce operators corresponding to x component, y component and z components. You can introduce them also and then what you will do you have to follow analogy with with orbital angular momentum, because whenever you have an operator you will need to know what are the committed relationships. So, you will say that s x committed with s y should be equal to how much it has to be equal to i h cross S z.

(Refer Slide Time: 38:44)



And similarly, you will have other commutation relationship and that is the way it is what will happen you will find that s square can be defined, s square will commute with s x s y, and s z s x s y is z among themselves, they would not commute. And therefore, you can specify only the value of s square and you like S z. And further S z operating up on alpha, what will it give me. Here you say alpha is the state where the electrons spin is pointing up it is pointing up in such a fashion that z component is plus half times h cross. So, if s z operates up on alpha what I would expect is I would get half h cross times alpha while if S z operated up on beta I will get minus half times h cross and not only that. If s square operated up on alpha here I mean alpha is an Eigen function of s square with an eigen value which will be equal to how much s into s plus one h cross square into alpha and this is actually half into half plus one.

So, this is how we things are, so you would realize that if I wanted to get spin, you have to take relativity theory into account and if you did it properly then of course, spin can be derived from what is refer to as the Dirac equation. So, therefore, is strictly speaking spin is a relative strict phenomenon and this picture that I have drawn here imaging that the electron is a hard spear which is actually rotating spinning about an axis that is not the correct picture, but it is useful picture, if you are going to think about spin. It is useful, but it is not necessary that that will give you the correct result.

I think, I will stop here today.