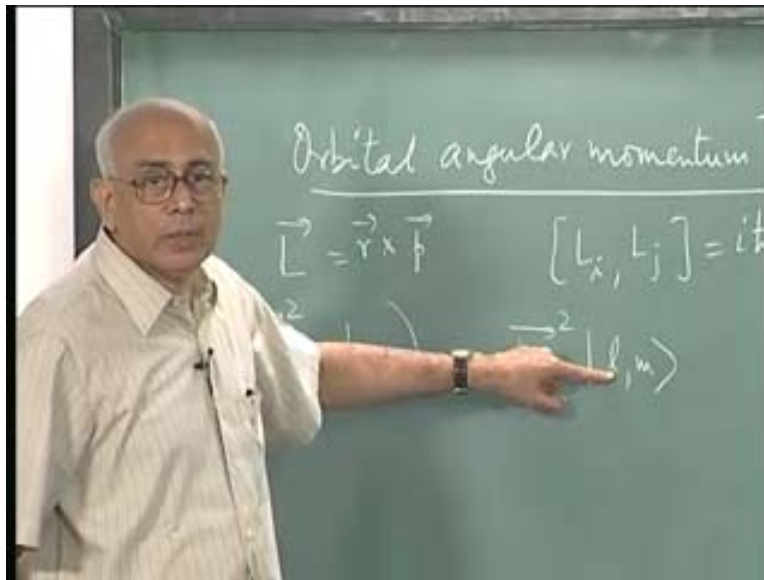


**Quantum Physics**  
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**Lecture no. #20**

Let me start today with the orbital angular momentum and then I will return to this problem of adding 2 angular momenta which is what we had started and I had promised I would show you what the rule for adding quantum mechanical angular momenta is like and why it differs from the classical case because of the non commutativity of various operators. But let's go back a little bit and talk about orbital angular momentum.

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I have in mind the quantum mechanical particle of mass  $m$ , moving in space in 3 dimensions and then we know the orbital angular momentum about the origin is defined as  $L = r \text{ cross } p$ . That's our definition and there is no problem with ordering; whether  $r$  should be on the left or  $p$  should be on the right or vice versa. There is no problem of ordering here because this cross product involves if I resolve it into Cartesian components a given Cartesian component of the position and some other Cartesian component of the momentum which are not conjugate pairs and therefore there is no problem with moving them about either way.

So this is the definition and of course once you write this operator acting on a position space wave function, recall that  $p$  should be replaced by  $-i\hbar \text{ cross } \text{del}$  when acting on position space wave functions. That's our rule for quantum mechanics. Now what sort of wave functions would correspond to eigenstates of the angular momentum? This is what we would like to answer. And of course we know that there are commutation relations  $[L_i, L_j] = i\hbar \text{ cross } \epsilon_{ijk} L_k$ . We already know this that there exist these angular momentum commutation relations.

We also know from our general study of angular momentum that the operator  $L^2$  which is  $L_x^2 + L_y^2 + L_z^2$  commutes with each of the generators. It commutes with all components of the angular momentum and in fact  $L^2$  and any component of  $L$ , let's say  $L_z$ , they can be simultaneously diagonalized and the eigenstates of the system of the orbital angular momentum could be written in terms of 2 quantum numbers.

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The image shows three equations written on a chalkboard:

$$[L_i, L_j] = i\hbar \epsilon_{ijk} L_k$$

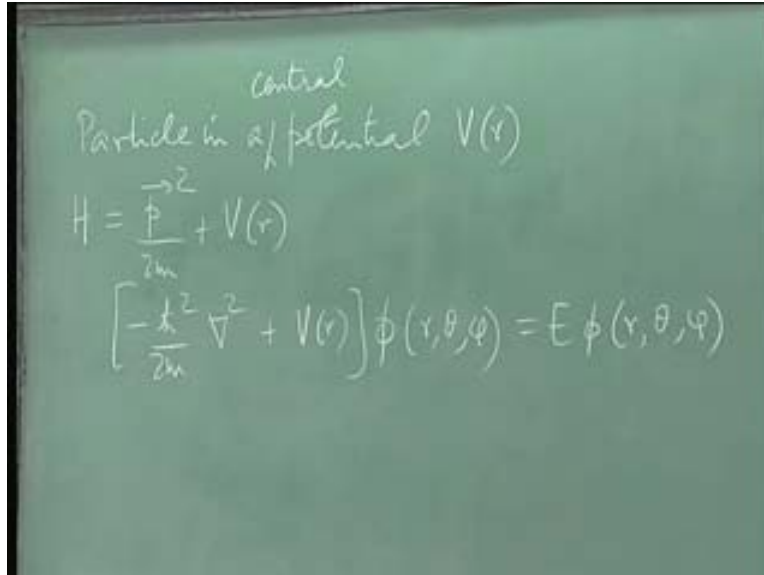
$$L^2 |l, m\rangle = l(l+1)\hbar^2 |l, m\rangle$$

$$L_z |l, m\rangle = m\hbar |l, m\rangle$$

So we have  $L^2$  acting on these eigenstates which are labeled by 2 quantum numbers  $l$  and  $m$ . I will use this notation instead of little  $j$  because I am not talking about orbital angular momentum and this is the standard notation. This is  $l$  times  $l+1$   $\hbar^2$  on  $|l, m\rangle$  and  $L_z$  on  $|l, m\rangle$  is  $m\hbar$  on  $|l, m\rangle$ . Now from a general theory of angular momentum all we know is that this little  $l$  can only take on the values  $0, \frac{1}{2}, 1, \frac{3}{2}$ , and so on but if it's orbital angular momentum, I mentioned that  $l$  can only take on integer values not  $1/2$  odd integer values.

And the reason is buried in the single valuedness of wave functions. Because after all, if I now talk about this angular momentum as the orbital angular momentum of a particle moving in some potential, then the wave function of this potential as a function of position coordinates must be unique. At every point you must have a unique wave function. This automatically will imply as we will see shortly that  $l$  must be an integer. Now let's go back and write this Schrödinger equation. Then we will come back to this and ask what sort of wave functions you would have.

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So this is a particle moving in a potential and I would like to exhibit spherical symmetry in this problem only then is the total angular momentum conserved. Otherwise it's not so interesting to resolve things into spherical harmonics. So what condition do you need classically in order that you have angular momentum conservation? What sort of potential should it be? It should be a central potential. So let's look at a central potential,  $V(r)$ .

What's the Schrödinger equation for the system? well the Hamiltonian is  $p$  squared over  $2m + V$ , which is a function of little  $r$  alone and when it acts on position space wave functions, when the eigen functions or the stationary states of the system would obey something like  $-\hbar^2$  cross squared over  $2m$  del squared  $+ V(r)$  acting on  $\phi$ . That's my symbol for the stationary state wave functions. And this would be a function of  $(r, \theta$  and  $\phi)$  because I would like to use spherical polar coordinates. It's most convenient to do so. This is  $= E \phi(r, \theta, \phi)$ . That's my time independent Schrödinger equation for the stationary state wave functions in the position basis. now what we need to do is to resolve this del squared in spherical polar coordinates and then see if we can solve this problem using the fact that  $V(r)$  is a function of little  $r$  alone. So what is del squared in spherical polar coordinates?

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The image shows a chalkboard with the following handwritten equations:

$$\nabla^2 = \frac{1}{r^2} \frac{\partial}{\partial r} \left( r^2 \frac{\partial}{\partial r} \right) + \frac{1}{r^2 \sin^2 \theta} \frac{\partial^2}{\partial \phi^2} + \frac{1}{r^2 \sin \theta} \frac{\partial}{\partial \theta} \left( \sin \theta \frac{\partial}{\partial \theta} \right)$$

$$+ V(r) \quad \hat{p} \rightarrow -i\hbar \nabla, \quad \hat{p}^2 = -\hbar^2 \nabla^2$$

$$\hat{p}_r^2 = -\hbar^2 \frac{\partial}{\partial r} \left( r^2 \frac{\partial}{\partial r} \right)$$

$$\hat{L}^2 = -\hbar^2 \left[ \frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \left( \sin \theta \frac{\partial}{\partial \theta} \right) + \frac{1}{\sin^2 \theta} \frac{\partial^2}{\partial \phi^2} \right]$$

This is  $\frac{1}{r^2} \frac{\partial}{\partial r} \left( r^2 \frac{\partial}{\partial r} \right) + \frac{1}{r^2 \sin^2 \theta} \frac{\partial^2}{\partial \phi^2} + \frac{1}{r^2 \sin \theta} \frac{\partial}{\partial \theta} \left( \sin \theta \frac{\partial}{\partial \theta} \right)$  of standard formula  $\nabla^2$  written in spherical polar coordinates. This is a standard expansion of  $\nabla^2$  in spherical polar coordinates here. We call that it is also the same as saying that this  $\hat{p}^2$  (Refer Slide Time: 07:59) could also be written as  $\hat{p}_r^2 + \frac{\hat{L}^2}{2m r^2} + V(r)$ . You can resolve the square of the total momentum as the radial part squared + the angular momentum part squared. Notice it's  $\frac{1}{2m}$  here and  $\frac{1}{2m r^2}$  so dimensionally this is right. Now of course we can identify what  $\hat{p}_r^2$  is. This portion comes from  $\hat{p}_r^2$ .

So it's quite clear that since  $\hat{p}$  goes to  $-i\hbar \nabla$  of  $\hat{p}^2 = -\hbar^2 \nabla^2$ . It's immediately cleared by definition it follows that  $\hat{p}_r^2$  is  $-\hbar^2 \frac{\partial}{\partial r} \left( r^2 \frac{\partial}{\partial r} \right)$ . That's the position space differential operator representing the square of the radial momentum. And the rest of it is the angular momentum apart from this factor here because that's already sitting here. So it's clear that  $\hat{L}^2$  has the representation  $-\hbar^2 \left[ \frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \left( \sin \theta \frac{\partial}{\partial \theta} \right) + \frac{1}{\sin^2 \theta} \frac{\partial^2}{\partial \phi^2} \right]$ . There is also a very important.  $\hat{L}$  has dimensions of a Planck's constant.

So  $\hat{L}^2$  is dimensions Planck's constant squared. So this is the way you arrive at the so called radial Schrödinger equation which you must have studied in quantum chemistry when you studied the hydrogen atom. It arose by saying that this system has some energy Eigen states and the wave function is of this (Refer Slide Time: 10:37) form and then for  $\nabla^2$  you simply resolve it in spherical polar coordinates and you got this. Now what's the next step the next step is to try to solve this partial differential equation by this simple method of separation of variables and this is going to work in this present instance because  $V(r)$  is not a function of  $\theta$  and  $\phi$ . So the radial equation will separate out

from the angular equation. Right now we are interested in the angular part. So the next step is to say let  $\psi(r, \theta, \phi) = R(r)$  multiplied by some function  $F(\theta, \phi)$ . I would like to keep  $\theta$  and  $\phi$  together, the 2 angular variables together because the equation that I have, this portion (Refer slide Time: 11:47) has both  $\theta$  and  $\phi$ . It is sort of mixed up in time whereas this is clean this (Refer Slide Time: 11:51) is just separated out.

So therefore the movement I would like to keep it in this fashion this function may further factor into a function of  $\phi$  and the function of  $\theta$  but at the moment I just keep them together in this fashion. then if I apply this operator on it, its immediately clear that in the position basis, these states  $|l, m\rangle$ , because I know that whatever it is, the eigen states of the square of this orbital angular momentum must be labeled by the quantum number  $l$  and the number  $m$  and these are the eigen states. And I know the properties of the states. I know what  $l_+$  does on it and  $l_-$  does on it and so on. So I use this fact here and what does that tell me there? It says that this function  $F(\theta, \phi)$  must satisfy the equation if I plug it in, if I put it in here.  $L^2$  acting on that term must give you  $L(L+1)$  on the other side.

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$$F(\theta, \phi) = \langle \hat{n} | l, m \rangle$$

$$-\hbar^2 \left[ \frac{1}{\sin^2 \theta} \frac{\partial^2}{\partial \phi^2} + \frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \left( \sin \theta \frac{\partial}{\partial \theta} \right) \right] F(\theta, \phi) = l(l+1)\hbar^2 F(\theta, \phi)$$

$F(\theta, \phi)$  you will readily identify is simply taking the orbital angular momentum state  $l, m$  in the position basis. So that's all it is. So I should really put  $\mathbf{R}$  vector here, the bra vector here but it doesn't depend on the radial coordinate at all. It only depends on the angular coordinates. Let's say in spherical polar coordinates, this (Refer Slide Time: 13:38) is  $r$  and this unit vector is  $\hat{n}$  and that's an arbitrary point. So an arbitrary point in space is labeled by radial coordinate  $r$  and 2 angles  $\theta$  and  $\phi$ . And let me call those 2 angles the unit vector  $\hat{n}$  because that specifies the direction. It's just a little bit of saving of notation instead of writing  $\theta$  and  $\phi$ , I write unit vector. So this (Refer Slide Time: 14:05) stands for  $\theta$  and  $\phi$ . What kind of equation should they satisfy? it says  $L^2$  acting on that will give you  $\hbar^2 l(l+1)$

$\frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \left( \sin \theta \frac{\partial}{\partial \theta} + 1 \right) \frac{\partial}{\partial \phi} \left( \frac{\partial}{\partial \phi} + 1 \right)$  acting on this function of  $\theta$  and  $\phi$  for  $f$  of  $n$  if you like and that must be  $= l(l+1) \hbar^2$  on  $F(\theta, \phi)$  because this has an eigenvalue when I take the bra here, an inner product with the unit vector  $\hat{n}$ , this is all and the  $\hbar^2$  cancels on both sides and you can bring this over here and change signs completely. So what's the equation satisfied by this quantity  $F$ . it's  $l(l+1)$ .

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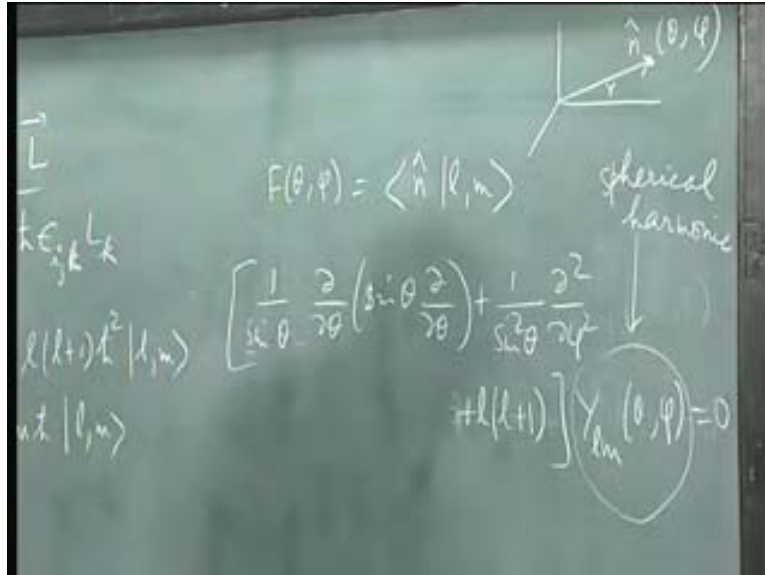
The chalkboard shows the following equations:

$$F(\theta, \phi) = \langle \hat{n} | l, m \rangle$$

$$\left[ \frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \left( \sin \theta \frac{\partial}{\partial \theta} \right) + \frac{1}{\sin^2 \theta} \frac{\partial^2}{\partial \phi^2} + l(l+1) \right] F(\theta, \phi) = 0$$

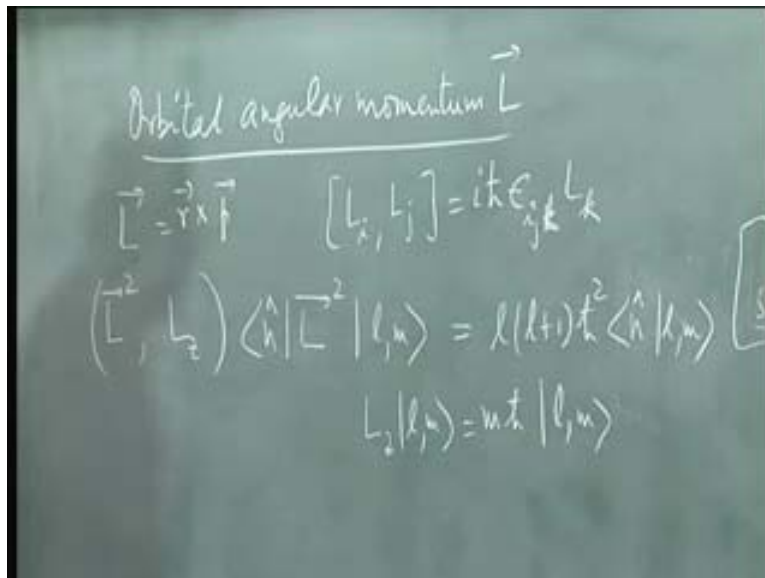
So let me write this down  $+ l(l+1)$  this whole thing acting on  $F(\theta, \phi)$  must be  $= 0$ . so that's the partial differential equation obeyed by  $F(\theta, \phi)$  any angular dependence on the wave function must obey that equation. But its clear that this operator here depends on  $l$ . and for each one, there are many values of  $m$  possible. so its very likely that this function here depends on both  $l$  and  $m$ . just as in the 1 dimensional particle in a box problem, when you solved the equation for this stationary states, we found out that the energy eigen states  $\psi$  were actually labeled by subscript  $n$  quantum number  $n$  and the solution was  $\sin n \pi x / l$  for different values of  $n$ . so let's put that label  $n$ .

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$Y_{lm}(\theta, \varphi) = 0$ . (Refer Slide Time: 16:46) this function is called as spherical harmonics. It's a solution of a homogeneous equation which involves theta and phi and some function labeled by 2 quantities l and m.

(Refer Slide Time: 00:17:15 min)



So this becomes  $\langle n | l, m \rangle$  but in the position bases, the action of  $L^2$  is given by the action of this differential operator because  $\mathbf{p}$  is replaced by  $-i\hbar \nabla$ . So that automatically said  $\nabla^2$ , the angular part is simply that operator. So this is the same as saying that differential operator acting on  $\langle n | l, m \rangle$  which gave you this differential equation and the solutions are called spherical harmonics and we can simplify



this. This is in our standard problem in ordinary differential equations. if we assume that  $Y_{lm}$ , trial solution would be a product of a function of  $\phi$  times a function of  $\theta$  and then it turns out that these  $Y_{lm}$ 's ( $\theta, \phi$ ) are in fact of the form  $e^{im\phi}$  times some constant times  $P_{lm}(\theta)$ , where this is a normalization constant. this quantity here is called the associated Legendre polynomial Legendre of order  $l$ . there are actually  $2l + 1$  of them for each value of  $l$ , this  $m$  runs from  $-l$  to  $+l$ . Student – Why have you set  $F(\theta, \phi)$  as  $\langle n|l,m\rangle$ ? Professor - well the actual wave function  $\psi(r, \theta, \phi)$  is actually short hand for  $r$  vector with the abstract state,  $\psi$ .

(Refer Slide Time: 00:19:00 min)

$$\psi(r, \theta, \phi) = \langle r, \theta, \phi | \psi \rangle$$

$$F(\theta, \phi) =$$

That's what the wave function stands for. But now i am saying this  $r$  is labeled by  $(r, \theta, \phi)$  and if i assume that this function is a product of function of  $r$  and a function of  $\phi$  and  $\theta$ , then clearly only the angular momentum part is affected  $l$  and  $m$  and that's exactly what has happened here. So the actual state vector would really think of a hydrogen atom problem. The angular they actual state vector would be labeled by  $n, l, m$  with the principle quantum number as well and this guy here is what i  $\psi$  of  $r \theta \phi$  but this becomes a product of a radial function times  $Y_{lm}$  of  $\theta \phi$ . So I simply said that as far as the orbital angular momentum part is concerned, this doesn't play any role. It's only  $l$  and  $m$  and instead of  $r$ , i replace it with  $\theta$  and  $\phi$  or the unit vector  $\hat{n}$ .  $m$  doesn't appear explicitly here. So the whole point is this equation has many solutions. For a given value of  $l$ , it has  $2l + 1$  independent solutions.

And of course in quantum mechanics, the general state was always a linear superposition of all the independent solutions. So you have to take that into account. Just as in the particle in a box problem when you solve the eigenvalue problem, you follow a very simple eigenvalue problem. there you discovered however that the solutions were of the form  $\sin n \pi x$  over  $l$ . so you have to label the solutions by this quantum number  $n$  and then make the statement that if these formed a complete set, a general solution is a linear superposition of all independent solutions and the same thing happens here (Refer Slide



Time: 21:40). If I have written down 1 angular solution, if I am going to write down the actual wave function, then I would have to sum this over all allowed values of  $m$  in general, for a general state and then fix all the constants depending on my initial state or boundary conditions and so on.

This is how the Legendre's equation makes its appearance. It simply separates out the angular part. You still have to now deal with this question of what does the radial equation look like. What is the equation satisfied by this? I will come to that in a minute but the angular part looks like this and the reason why spherical harmonics are important is because this is going to be the angular part of the wave function for any central potential because independent of what  $V(r)$  is, what its functional form is, this is going to always be the angular part. So it's a standard thing and therefore one should first solve it and write it down.

Now these things here I presume you are familiar with properties of Legendre polynomials. I will write them down in the problem set. They are  $P_l(\cos \theta)$ . So that's standard notation,  $Y_{lm}(\theta, \phi) = \sqrt{\frac{2l+1}{4\pi}} P_l(\cos \theta) P_m(\sin \theta \cos \phi)$ , that's the normalization factor,  $P_l(\cos \theta)$ . So remember again that  $P_{lm}$  or  $Y_{lm}$  is really short hand for  $P_l(\cos \theta) P_m(\sin \theta \cos \phi)$  where  $m$  runs for  $-l$  to  $+l$  and in the special case when  $m$  is 0, it just reduces to the original Legendre polynomial. Otherwise it's called the associated Legendre polynomial. So it's some derivatives of the original polynomial.

So we actually have our eigenfunctions explicitly in the position basis  $Y_{lm}$ . So we could write this whole thing out in the position basis and it turns out then that the  $L^2$  acting on  $Y_{lm}$  gives you this constant times  $Y_{lm}$  and  $L_z$  acting on this  $Y_{lm}$  gives you  $m \hbar$  times  $Y_{lm}$ . Now you could ask what happens to  $L_x$  and  $L_y$ . What do they look like in spherical polar coordinates? That's just an exercise in polar coordinates conversion from Cartesian to spherical polar coordinates. So let me write those expressions down.

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Handwritten equations on a chalkboard showing the angular momentum operators in spherical coordinates:

$$\vec{L} = \vec{r} \times \vec{p} \quad (\vec{p} = -i\hbar \vec{\nabla})$$

$$L_x = y p_z - z p_y \rightarrow -i\hbar \left[ -\sin\theta \frac{\partial}{\partial \phi} - \cot\theta \cos\phi \frac{\partial}{\partial \phi} \right]$$

$$L_y = z p_x - x p_z \rightarrow -i\hbar \left[ \cos\phi \frac{\partial}{\partial \theta} - \cot\theta \sin\phi \frac{\partial}{\partial \phi} \right]$$

$$L_z = x p_y - y p_x \rightarrow -i\hbar \frac{\partial}{\partial \phi}$$

Remember that  $L$  is  $r$  cross  $p$ . so  $L_x = y p_z - z p_y$ . These 2 commute between themselves so it doesn't matter which order i write it in.  $L_y = z p_x - x p_z$  and  $L_z = x p_y - y p_x$ . Now you could ask what do these look like in the position basis. Suppose i am going to act on functions of  $r$  theta phi what do these look like in spherical polar coordinates? This goes over n2 again the root is by saying  $p$  is  $= -i \hbar$  cross  $\text{del}$  that's all you have to do.  $p$  is represented by  $-i \hbar$  cross  $\text{del}$  then, this  $p_z$  is  $\frac{\partial}{\partial z}$  with a  $-i \hbar$  cross etc. but now i have to convert from Cartesian coordinates to spherical polar coordinates and when i do that, the answer turns out to be  $-i \hbar$  cross  $\frac{\partial}{\partial y}$  but  $L_x$  and  $L_y$  turn out to be little mess here. Why we insist on quantization in the  $z$  direction is, you notice I wrote  $\sigma_3$  as a diagonal matrix and not  $\sigma_1$  or  $\sigma_2$  by convention.

The reason is it arose from here, the original problem that was solved were solved like the hydrogen atom in the spherical polar coordinates and in spherical polar coordinates, and you give a special status to the polar axis which conventionally is taken to be the  $z$  axis. So that's how the  $z$  axis got singled out. And not surprisingly  $L_z$  just turns out to have an extremely simple form here but not  $L_x$  and  $L_y$ , these turn out to be more complicated.  $L_x$  is  $-i \hbar \sin \phi \frac{\partial}{\partial \theta} - \cot \theta \cos \phi \frac{\partial}{\partial \phi}$  and  $L_y$  is  $-i \hbar \cos \phi \frac{\partial}{\partial \theta} + \cot \theta \sin \phi \frac{\partial}{\partial \phi}$ . Of course,  $L^2$  is this. So if i take those operators and do  $L_x^2 + L_y^2 + L_z^2$  and simplify, i should get this (Refer Slide Time: 27:32). So as you can see, the transverse components of the angular momentum are quite messy. They mix up theta and phi.

This (Refer Slide Time: 27:45) is cotangent where as  $L_z$  is very simple. So now you can also see where you got the  $e^{im\phi}$  from. Because it's clear that you must have  $L_z$  acting on  $|l, m\rangle$  must be  $= m \hbar$  cross on  $|l, m\rangle$ . therefore  $L_z$  acting on  $e^{im\phi}$  in the position basis, so that's  $-i \hbar$  cross  $\frac{\partial}{\partial \phi}$  of this here must be  $= m \hbar$  cross  $\langle n | l, m \rangle$ . And it's obvious that the solution to this is  $e^{im\phi}$ .

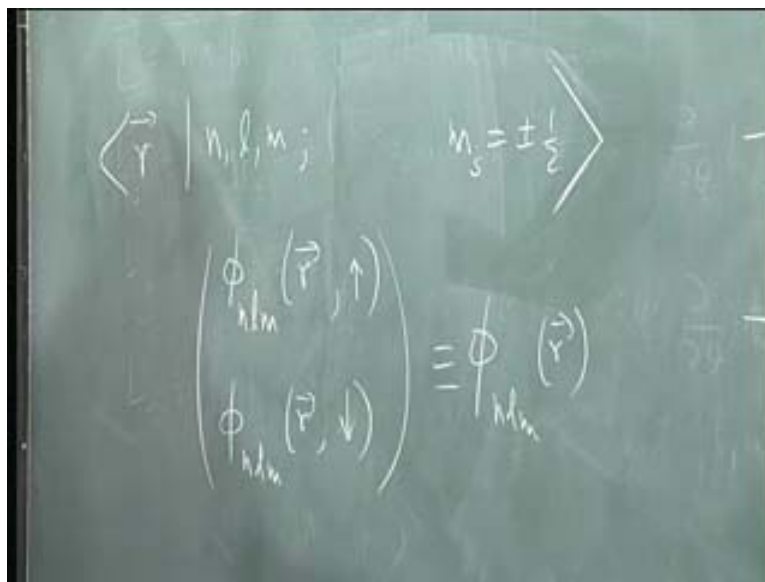
So that's how the azimuthal part that depends on phi just stand out to be a phase factor  $e^{im\phi}$  but of course the full  $\text{del}^2$  involves  $L_x^2$  and  $L_y^2$  which is messy. Therefore you got these nontrivial Legendre polynomials. Now why should  $L$  be an integer? The answer is why  $l, m$  of theta phi must comeback to itself if phi increases  $2\pi$ . So about any arbitrary axis, if you rotate by a  $2\pi$ , you should get right back to original wave function. That turns out that requirement makes  $L$  an integer because of the single valuedness of the position space wave function. So that's the requirement. There are other reasons which one can give if you start with  $r$  cross  $p$ . Then it's automatic immediately.

But if i start with an abstract angular momentum, then little  $l$  is a quantum number for the square of the total angular momentum. It could be integer or 1/2 odd integer but this single valuedness forces it. we start with  $r$  cross  $p$  then by definition when i solve these differential equations, this differential equation  $L^2$  acting on some function of theta and phi  $= l(l+1)$ . And there is a the theory of second order differential equation which tells you that the solutions have to be single valued, unique, etc. so the uniqueness

theorem for the so called stone believable problem which is what this reduces to, imposes already that  $l$  must be an integer.

Please notice that the  $1/2$  order integer values of  $l$  don't come about from any differential equation. We didn't any differential equation for those cases. We just said this is an abstract state vector in angular momentum states. We never wrote down differential equations, so they do not come from such differential equation they not position basis representations at all. so that's an extra input. The spin degree of freedom of an electron has nothing to do its special wave dependence. It has nothing do with its dependence on  $r$ ,  $\theta$  &  $\phi$ .

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That tells us that really when we describe an electron in addition to the quantum numbers  $n$ ,  $l$  and  $m$  which come from the  $r$ ,  $\theta$ ,  $\phi$  degrees of freedom if you like, for instance in the hydrogen atom. In addition to these there is there is this spin quantum number and that implies that  $S$  is  $1/2$  and there is in corresponding  $L_z$  component or  $z$  component here which is also denoted by  $m_s$  and this is  $= +$  or  $- 1/2$ . So in addition the states of the electron are described by this extra quantum number, the spin quantum number which has nothing to do its positional dependence as far as the wave function is concerned. So what does that mean? It says that really these are the states of the electron and since we know the spin is  $1/2$  for every electron, we don't write this.

We just write this. So you have really four quantum numbers to describe the electron and hydrogen atom for instance, the principle quantum number, orbital angular momentum quantum number, the magnetic which tells you the eigenvalue of  $L_z$  and the spin. Whether  $m_s$  is  $+ 1/2$   $\hbar$  cross or  $- 1/2$   $\hbar$  cross. Therefore, when I take the position space representative of this, I really have 2 wave functions. I really have  $\phi$  and they are labeled by this  $nlm$  and they are functions of  $r$  but you should also say whether the spin is  $+ 1/2$   $\hbar$  cross or  $- 1/2$   $\hbar$  cross. You have to add that.

So what one does is to say  $r$  and spin up for instance, i should put  $\phi_{nlm}$   $r$  and spin down. And very often, it's convenient since, clearly what's happening is the position space wave function is a member of  $L_2$ , square integrable functions of the space coordinates,  $r$  theta phi. But there are 2 such wave functions. One corresponding to  $S_z = + 1/2 \hbar$  cross eigenstate and the other to  $- 1/2$ . so its convenient to combine both of them and put them as a column vector because the spin space is 2 dimensional. So you will write them as a column vector here. And then you would write this whole thing as  $\phi_{nlm}(r)$  by definition. so this phi here is the square integrable function as far as  $r$  is concerned but it is really a column matrix with 2 elements, each of which is square integrable and these are the wave functions corresponding to the 2 spin states.

So it immediately becomes clear that if you are describing the wave function in position space or momentum space for that matter of a spin  $s$  particle, you really need  $2s + 1$  wave functions, each of which is square integrable. So you get a multi component wave function. And each component would obey the position space Schrödinger equation and this spin degree of freedom is independent. This is how in the hydrogen atom, you get this 2 wave functions always. And you have to include both of them in a complete description of the hydrogen atom.

So i hope this makes it clear to you that the spin degree of freedom has nothing to do with any mechanical motion. It has nothing to do with the  $r$  , $p$  or anything like that. It's an internal degree of freedom of the system. You should treat it mentally on the same footing that you treat the rest mass of the electron or the charge of the electron. These are internal properties of the system. And they do not arise due to any spatial dependence of the wave function. This is also the reason why we dealt with just the up state or the down separately. And now let's talk about addition of angular of momenta to look at the total angular momentum of a particle which is now in some potential and therefore has some orbital angular momentum about the origin and has a spin degree of freedom as well.

(Refer Slide Time: 00:36:29 min)

The image shows a chalkboard with the following mathematical derivations:

$$\nabla^2 = \frac{1}{r^2} \frac{\partial}{\partial r} \left( r^2 \frac{\partial}{\partial r} \right) + \frac{1}{r^2 \sin^2 \theta} \frac{\partial^2}{\partial \theta^2} + \frac{1}{r^2 \sin^2 \theta} \frac{\partial^2}{\partial \phi^2}$$

$$H = -\frac{\hbar^2}{2m} \nabla^2 + V(r) \quad \vec{p} \rightarrow -i\hbar \nabla, \quad \text{or } \vec{p}^2 = -\hbar^2 \nabla^2$$

$$L^2 = -\hbar^2 \left[ \frac{1}{\sin^2 \theta} \frac{\partial^2}{\partial \theta^2} + \frac{1}{\sin^2 \theta} \frac{\partial^2}{\partial \phi^2} \right]$$

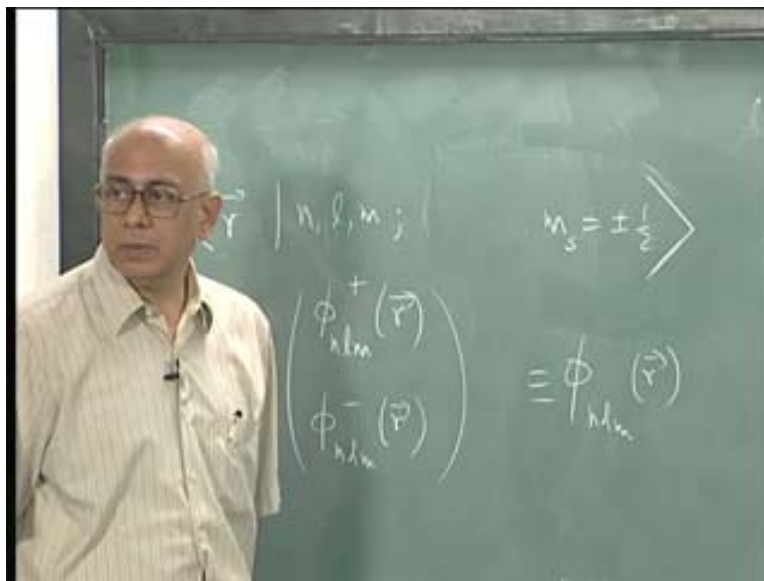
$$L^2 F(\theta, \phi) = -\hbar^2 l(l+1) F(\theta, \phi)$$

I didn't work this out fully but I said that if you use this differential equation  $L^2$  on the wave function it will be  $L^2$  acting on the wave function  $F(\theta, \phi) = -\hbar^2 l(l+1) F(\theta, \phi)$ . This is the second order differential equation and  $\theta$  runs from 0 to  $\pi$  and  $\phi$  runs from 0 to  $2\pi$ . And that differential equation one can show that it must have solutions which are unique for every  $\theta$  and  $\phi$  in the physical region. That imposes the requirement that this single valuedness of this  $F(\theta, \phi)$  can only be satisfied if  $l$  is an integer.

Now this comes from this the area of differential equation which I haven't gone into but the fact that you have this second order differential equation automatically imposes this. But you can ask where did this come from (Refer Slide Time: 37:30). This came from saying  $p$  is represented by  $-i\hbar \nabla$ . It came by saying that  $L$  is  $r \times p$ . I put in the fact that the orbital angular momentum is special. It's not just the general angular momentum. It is representable in terms of the dynamical variables of the system; the position and the linear momentum. That has led finally to the fact that the wave function must be single valued. The orbital part of the wave function must be single valued in turn that puts a condition on  $l$ . We will do this if time permits when you solve the hydrogen atom problem, the requirement that the square integrable wave function automatically quantizes the energy of the system. So it constraints the possible set of solutions. In exactly the same way this imposes a single valuedness. Student – Are the coefficients equal?

Professor - what would the physical significance of this (Refer Slide Time: 38:45) be? let me use a little bit of short hand notation. let's just call this  $+$  and  $-$  (Refer Slide Time: 38:57) so that I write this out more easily.

(Refer Slide Time: 00:38:55 min)



This  $+$  corresponds to  $+\frac{1}{2}\hbar$  cross and  $-$  corresponds to  $-\frac{1}{2}\hbar$  cross. then the physical meaning of  $\phi_{nlm}^+$  or  $\phi_{nlm}^-$  whole squared would be the probability density of the

particle at the spatial point  $r$  when the system is in the quantum state described by  $n l m$  and this spin state has  $+1/2 \hbar$  cross and similarly for the  $-$ . Now there is no requirement that in general without further information that these 2 coefficients should be equal at all. They are just 2 probability densities. And if you do things to this electron to polarize it in one direction or the other or you let it evolve, this can certainly change with time. But they are the 2 independent amplitudes for the 2 spin states.

And you can't reduce it any further. They may satisfy a total normalization condition but they are actually independent. Now look at what happens to the total angular momentum. There is no Schrödinger equation for the spin. Why has that happened? The reason is I didn't put anything into the Hamiltonian which should distinguish between the 2 spin states of the system. But suppose I put a magnetic field, and then it's a different story. Now let's see what happens if I take this hydrogen atom or this central potential problem and put a constant uniform magnetic field say. then this Hamiltonian has an extra term  $+$  and we saw if it's an electron, it's  $\mu_B$  Bohr magneton times  $B$  times  $\sigma \cdot \hat{n}$  where  $\hat{n}$  was the direction of the magnetic field.

Now of course it's very clear that you have coupled to a spin degree of freedom but that  $\sigma$  acts on either the top or the bottom of this column vector. And then now you have to differentiate all together. It's immediately clear that in general, the differential equations for the up and the down states would actually be mixed up and coupled to each other. Because, this  $\sigma$  and when it acts on the upstate, there will be the portion from the down state and vice versa. If this thing is in some arbitrary direction, this can certainly have. so not only is this part it will going to be moving in this potential but it can also undergo spin flip transition. And then of course you have a different problem all together. So that's the good point. The reason I didn't show up here was because I didn't put anything in the Hamiltonian which would coupled to this spin. Remove it I put it in then it's a different story. Otherwise I would say the system is unpolarized, and then their probabilities should be the same. Nothing is going to happen. Now what is the total angular momentum?

(Refer Slide Time: 00:42:09 min)

The image shows a chalkboard with the following handwritten equations:

$$[\vec{L}_i, \vec{S}_j] = 0$$
$$\vec{J} = \vec{L} + \vec{S}$$
$$\vec{J}^2 = (\vec{L} + \vec{S})^2 = \vec{L}^2 + \vec{S}^2 + 2\vec{L} \cdot \vec{S}$$
$$= \vec{L}^2 + S(S+1)\hbar^2 + 2\vec{L} \cdot \vec{S}$$

The total angular momentum  $\vec{J}$  is  $\vec{L} + \vec{S}$ . but you see the components of  $\vec{L}$  and the components of  $\vec{S}$  commute with each other completely. Therefore  $\vec{J}^2$  is  $\vec{L}^2 + \vec{S}^2 + 2\vec{L} \cdot \vec{S}$ . the whole squared which can be written as  $\vec{L}^2 + \vec{S}^2 + \vec{L} \cdot \vec{S}$  or  $\vec{S} \cdot \vec{L}$  or both. it doesn't matter in this case. So you write this as  $+2\vec{L} \cdot \vec{S}$  because the various components  $L_i S_j = 0$ . So  $\vec{J}^2$  is given by this (Refer Slide Time: 43:00). But you see if i am talking about an electron  $\vec{S}^2$ , no matter what state of the system, you are always in an eigenstate of  $\vec{S}^2$  with eigenvalue  $S(S+1)\hbar^2$ . So this (Refer Slide Time: 43:20) portion of it become redundant.

I mean it's just a constant. So this is  $\vec{L}^2 + S(S+1)\hbar^2 + 2\vec{L} \cdot \vec{S}$ . we know what happens here. This (Refer Slide Time: 43:42) will be labeled by little  $l$  and this is first order in  $L$ . so all the 3 components would contribute. And you can quantize along any axis. So the addition theorem in this case becomes rather simple because these 2 commute with each other and there is no problem etcetera. This is always for an electron. This is  $3/4\hbar^2$  but we would like to do this in general and see what happens if i add 2 angular momenta  $J_1$  and  $J_2$ . They come from different origins and i add these 2. I would like to know what's the resultant here. So let's face that problem. Let us see whether we can add 2 arbitrary angular momenta.



(Refer Slide Time: 00:44:30 min)

Handwritten equations on a chalkboard:

$$\vec{J}_1 : [J_{1i}, J_{1j}] = i\hbar \epsilon_{ijk} J_{1k}$$

$$\vec{J}_2 : [J_{2i}, J_{2j}] = i\hbar \epsilon_{ijk} J_{2k}$$

I start with an angular momentum  $J_1$ , this has components  $J_1 x$ ,  $J_1 y$ ,  $J_1 z$  etcetera and this satisfies the commutation relations  $J_1 i J_1 j = i \hbar$  cross epsilon  $\epsilon_{ijk} J_{1k}$ . where  $i j k$  are the Cartesian components  $i$  have another angular momentum  $J_2$  and that satisfies exactly the same sort of relation with 2 replacing 1. and these are independent of each other. So  $J_1 i J_2 k = 0$ . So my physical system has a total angular momentum  $J$  which is made up of 2 mutually commuting quantum mechanical angular momenta  $J_1$  and  $J_2$  And I would like to know what are the angular momentum eigenstates of my system. I can't do naive vector addition;  $J_1 + J_2$  because of the following problem.

(Refer Slide Time: 00:45:49 min)

Handwritten equations on a chalkboard:

$$J_1^2 |j_1, m_1\rangle = j_1(j_1+1)\hbar^2 |j_1, m_1\rangle$$

$$J_2^2 |j_2, m_2\rangle = j_2(j_2+1)\hbar^2 |j_2, m_2\rangle$$

$$|j_1, m_1\rangle \otimes |j_2, m_2\rangle$$

$$\left( \begin{matrix} \hbar^2 j_1(j_1+1) & \hbar^2 j_2(j_2+1) \\ \hbar^2 j_1 & \hbar^2 j_2 \end{matrix} \right)$$

This is characterized by a quantum number little  $j_1$ , say then the states of the system are given by  $j_1$  and  $m_1$  where little  $j_1$  is a quantum number which is 0,  $\frac{1}{2}$ , 1, etc. and  $j_1$  squared would have eigenvalues little  $j_1$  little  $j_1 + 1$  times  $\hbar$  cross squared and  $m_1$  is a corresponding eigen state of  $J_1 z$ . so  $j_1$  squared is  $j_1$  into  $j_1 + 1$   $\hbar$  cross squared, the same state you want  $m_1$  and  $J_1 z$  on  $j_1 m_1$  is  $\hbar$  cross  $m_1$ . And i assume that little  $j_1$  is given to me, similarly for  $J_2$ . Now what's the maximum set of mutually commuting operators so that i can start writing these states down?

Well if these 2 angular momenta don't talk to each other, then the states of the system must be of the form  $j_1 m_1$  direct product with  $j_2 m_2$ . Those are the angular momentum states of my system and i have to tell you what that  $J_1$  is doing. Then what's  $J_2$  doing. And how many states of this kind are there for a given little  $j_1$ ? There are  $2 j_1 + 1$ . So this is  $2 j_1 + 1$  and that's  $2 j_2 + 1$  and this is the dimensionality of my angular momentum space. So let's take specific examples, spin 1/2 electron and let's say it's in the orbital angular momentum quantum number state  $L = 2$  the d state of the electron. Then little  $j_1$  is  $L$ , that's 2. The dimensionality of your angular momentum space is 10. So what are the mutually commuting observables? In this case they would be  $J_1$  squared  $J_1 z$ ,  $J_2$  squared,  $J_2 z$ . that's my set of mutually commuting observables. And the dimensionality of this Hilbert space is  $2 j_1 + 1$  times  $2 j_2 + 1$ . Every state can be written in this basis as a superposition of these states. so let me give it some short hand notation.

(Refer Slide Time: 00:49:00 min)

Handwritten equations on a chalkboard:

$$J_1^2 |j_1, m_1\rangle = j_1(j_1 + 1) \hbar^2 |j_1, m_1\rangle$$

$$J_2^2 |j_2, m_2\rangle = j_2(j_2 + 1) \hbar^2 |j_2, m_2\rangle$$

$$|j_1, m_1\rangle \otimes |j_2, m_2\rangle \equiv |j_1, j_2, m_1, m_2\rangle$$

Dimensionality:  $(2j_1 + 1) \times (2j_2 + 1)$

Operators:  $(J_1^2, J_1 z, J_2^2, J_2 z)$

I will call this (Refer Slide Time: 49:06)  $j_1 j_2 m_1 m_2$  let me use short hand notations for this just call it  $j_1 j_2 m_1 m_2$ . and for fixed little  $j_1$  and fixed little  $j_2$  essentially its only  $m_1$  and  $m_2$  that change over the different states  $m_1$  takes  $2 j_1 + 1$  values similarly for  $m_2$  and the total number of possible states is this product here. But you see i can do this in a different way. I can find another set of mutually commuting observables which is the following.

(Refer Slide Time: 00:49:38 min)

Handwritten equations on a chalkboard:

$$[J_{1i}, J_{2z}] = 0$$

$$\vec{J} = \vec{J}_1 + \vec{J}_2, \quad J^2 = J_1^2 + J_2^2 + 2\vec{J}_1 \cdot \vec{J}_2$$

If  $J$  is  $J_1 + J_2$ , then  $J^2 = J_1^2 + J_2^2 + 2J_1 \cdot J_2$ . Again because  $J_1$  and  $J_2$  commute with each other, so it doesn't matter what order I write them in. And this total angular momentum squared can be quantized. That too satisfies commutation relations.  $J_i$  with  $J_j$  is  $i\hbar \epsilon_{ijk}$  etc. so I can find another way of doing this.

(Refer Slide Time: 00:50:25 min)

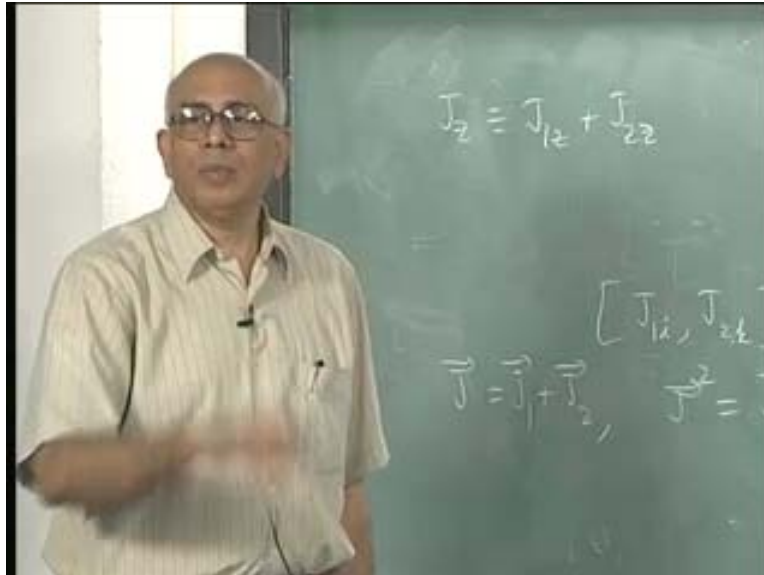
Handwritten equations on a chalkboard:

$$J^2 = (J_{1x}^2 + J_{1y}^2 + J_{1z}^2) + (J_{2x}^2 + J_{2y}^2 + J_{2z}^2) + 2(J_{1x}J_{2x} + J_{1y}J_{2y} + J_{1z}J_{2z})$$

$$J^2 = (J_x^2 + J_y^2 + J_z^2)$$

That is  $J^2 J_z$ , because that commutes with  $J^2$ , and what's the definition of  $J_z$ ?

(Refer Slide Time: 00:50:40 min)



By definition is  $J_1 z + J_2 z$ . That's the whole idea of adding these 2 vectors. You add each component. And what else? I claim there are 2 other operators which you can find from all these terms.  $J_1$  squared and  $J_2$  squared would commute with these operators because look at what happens to  $J_1$  squared commuting, whether it commutes with  $J_z$  or not?  $J_1$  squared is  $J_1 x$  squared +  $y$  squared +  $z$  squared, that commutes with every component of  $J_1$ . So it certainly commutes with this and  $J_1$  has nothing to do with  $J_2$ . So it commutes with this. Therefore this operator commutes with as well as that. It commutes with these too because it certainly commutes with itself. It doesn't have anything to do with this quantity and this is a linear combination of the components of  $J_1$ , each of which this commutes with. So certainly this commutes with this it commutes with this and so does this and they mutually commute (Refer Slide Time: 51:33 to 51:57). So this is another possibility.

I can choose the independent maximally commuting set of observables in 2 different ways in this case. Notice I cannot add  $J_1 z$  to this because the moment I do that, what happens if I add  $J_1 z$  to this,  $J$  squared has this problematic term sitting here. so this must be  $J_1 x J_1 y$  and  $J_1 z$  and that will not commute with  $J_1 z$ . so I am not allowed to add  $J_1 z$  here or  $J_2 z$ . similarly I cannot put anything from here into that. I can't put  $J_z$  into that (Refer Slide Time: 52:13 to 52:43). So these are 2 independent ways of doing things and each of them must give exactly the same answer. If I choose this (Refer Slide Time: 53:08), then my eigenstates are labeled by  $j_1 j_2 m_1 m_2$ . This is what we did earlier. It's just direct product states. But if I choose this what are the eigen states labeled by they labeled by the eigen values of this maximal set of commuting observables. So these are label by little  $j$ , little  $m$  and then  $J_1$  and  $J_2$ . Since  $J_1$  and  $J_2$  are common, let me put that first. That's the standard notation  $j_2$  and then put  $j_1$ . This is the different basis. its like choosing rotated coordinate system 2 different basis but we still have to answer the question of does this form a basis what are the allowed values of  $j$  what are the allowed values of  $m$  we don't know that at the moment. All I am saying is this transforms like the

square of an angular momentum therefore its eigenvalues have to be of the form  $j$  times  $j + 1$ . And that call that  $j$  here and similarly this is  $m$ . I have to find the relation between these 2 basis and I have also to show you that for instance if I have a state of this kind  $m$  must be  $= m_1 + m_2$  must be  $=$  that is any single component that quantum number simply add up. I have to show you that this is the case. So let's do that in the following way. You agree that this (Refer Slide Time: 55:02) is a state in the angular momentum space of the system.

(Refer Slide Time: 00:55:08 min)

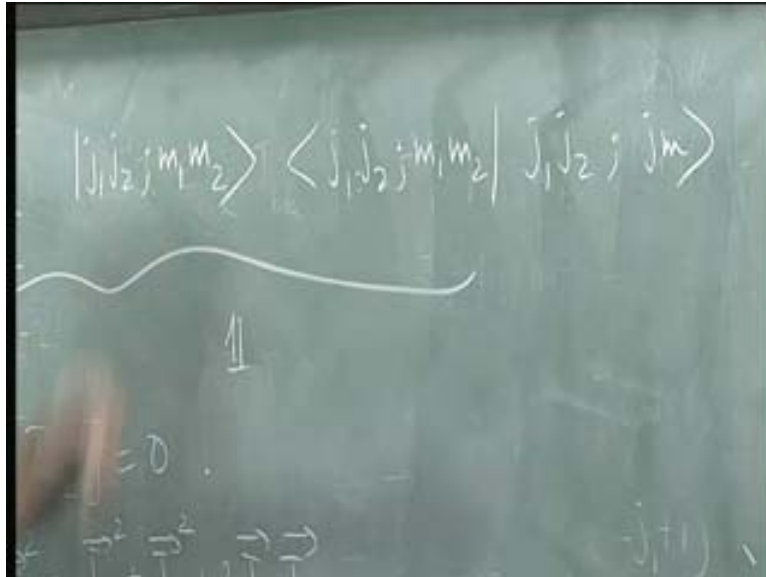
The chalkboard contains the following mathematical expressions:

$$|j_1 j_2 j m\rangle = \sum_{m_1} \sum_{m_2} |j_1 j_2 m_1 m_2\rangle$$

$$[J_{1z}, J_{2z}] = 0$$

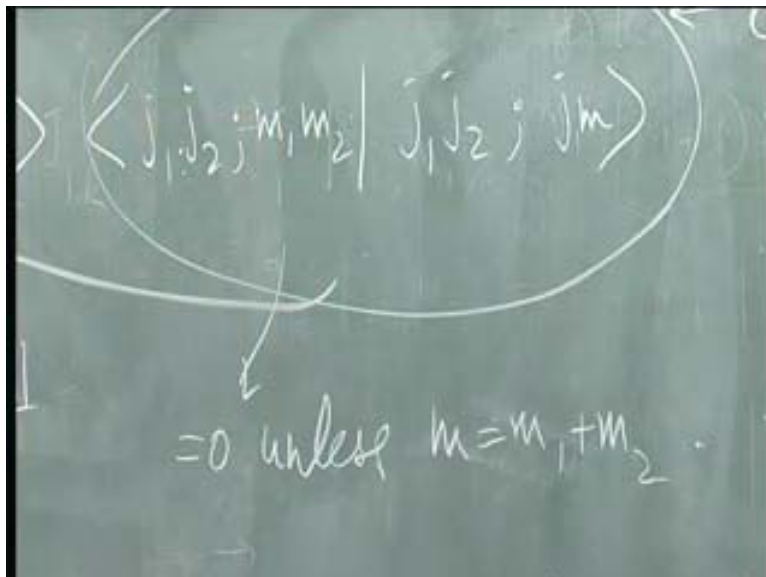
Therefore I should be able to write  $|j_1, j_2, j, m\rangle =$  a summation over all the other possibilities in the basis of states of this kind, some coefficients times  $j_1 j_2 m_1 m_2$ . Since little  $j_1$  little  $j_2$  are fixed, it's a summation over  $m_1$  and  $m_2$ . But actually the way to find the coefficients is to say, this forms a basis and therefore  $\langle j_1 j_2; m_1, m_2 |$  is the unit operator in this base acting on the original state  $|j_1, j_2; j, m\rangle$ . You will see the power of this Dirac notation.

(Refer Slide Time: 00:56:21 min)



I wanted you to recognize clearly that these kets are in the original basis and these kets are in the new basis that I am trying to find (Refer Slide Time: 56:32 to 56:39). This  $m_1 m_2$  has a different status from this  $j, m$  but I don't want to clutter the notation. So you agree that those coefficients are just numbers and these (Refer Slide Time: 57:03) are your basis vectors. This set of coefficients are a set of complex numbers in general and they transform from one angular momentum basis to another. I have still to show that the  $j, m$  basis this is the basis I have not done that yet but their coefficients they are overlaps functions. This (Refer Slide Time: 57:25) set are called Clebsch Gordan coefficients. Our job is to find them for given little  $j_1$  and little  $j_2$ .

(Refer Slide Time: 00:57:59 min)



This is = 0 unless  $m = m_1 + m_2 = 0$  (Refer Slide Time: 58:05). And now you will see the power of this Dirac notation because i prove that almost effortlessly in the following way. Let's take this state  $|j_1 j_2 j m\rangle$  and act on it with one of these suitable operator.

(Refer Slide Time: 00:58:28 min)

$$\langle j_1 j_2, m_1 m_2 | (J_z - J_{1z} - J_{2z}) | j_1 j_2, j m \rangle = 0$$

$$(m - m_1 - m_2) \langle j_1 j_2, m_1 m_2 | j_1 j_2, j m \rangle = 0$$

So let's take  $J_1 J_2 J_m$  i act on it with  $J_z - J_1 z - J_2 z$  and i put this bra here  $\langle j_1 j_2 m_1 m_2$ . This operator and i sandwiched between these states. This state here is an eigenstate of  $J_1 z$  and  $J_2 z$  with eigenvalues  $m_1$  and  $m_2$ . This state is an eigenstate of  $J_z$  with eigenvalue  $m$ . so i cleverly operate this on right but these guys cleverly operate on the left. so that gives me  $m - m_1 - m_2$  on this Clebsch  $J_1 J_2 m_1 m_2 J_1 J_2 J_m$  must be = 0 (Refer Slide Time: 59:00 to 59:44). That can only happen because  $J_z$  is  $J_1 - J_2 z$  by definition. So the right hand side is 0.

So either this is 0 or else that Clebsch vanishes. So this is the power of this notation is unbelievable. So that's why i said any component like the z component just adds up linearly but the angular momentum itself has this quantum rule of addition which is nontrivial. so that's our first statement the next thing i have to show is that this little j actually can take on a large number of values, all the way from  $mod j_1 - j_2$  to  $+ j_1 + j_2$  i have to show that next time. But this is the way we are going to derive the addition rule for angular momentum. Once that rule is set in place, and then the whole thing is finished.

So you can see that addition of angular momenta in quantum mechanics is somewhat nontrivial. You get these Clebsch Gordan coefficients for 2 angular momenta. Now if you add 3 of them, you first you have to add 2 and then the third one and then you add four of them and it gets more complicated. These are called 3J symbols, 6J symbols, 9J symbols and so on. People have gone up to 15J symbols. Volumes have been written and it becomes very nontrivial because the number of symmetries of these coefficients. They are called Racah coefficients. It's is very complex and very intricate and has many



fascinating connections with other branches of mathematics. so what starts out as kind of a practical thing in order to find out how quantum mechanical angular momenta actually leads to a sub branch of mathematics itself. But I will get back to this and will evaluate this Clebsch Gordan coefficients in the simplest cases.