Concepts of Chemistry for Engineering

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Lecture No. 08

Spherical polar coordinates & angular momentum

Before starting our discussion of hydrogen atom, it is important that we prepare ourselves a little bit. Keeping that in mind, today we are going to discuss different coordinate system from the Cartesian coordinate, that is spherical polar coordinate.

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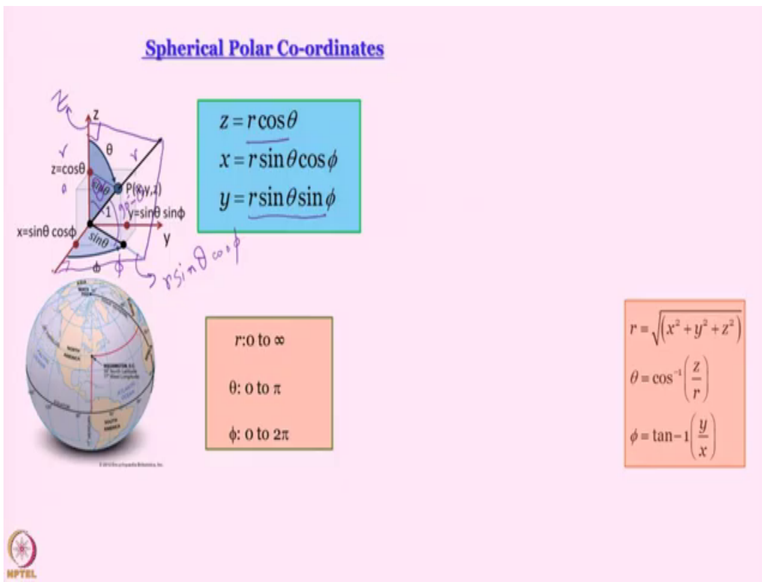

And also, we are going to talk a little bit about this rather important quantity that we must have studied in physics, that is angular momentum. So, the question is, why is it that we need to talk about spherical polar coordinates, why must we work in spherical polar coordinates, if we want to build a quantum mechanical description in angular momentum, that is what we will learn in this lecture.

And why at all talk about angular momentum, that will become clear when we start talking, discussing Schrodinger equation for hydrogen atom. So, spherical polar coordinates I hope are not completely new to most of us, the same point in space that we conventionally described by coordinates x, y and z, can also be described by r, θ and ϕ, where r is the distance from the origin 000 point, the angle θ is the angle between the z axis and the position vector you can call, position vector is a vector joining the origin to the point in question.

So, the angle between z axis and that position vector is called theta. And then, if you drop a perpendicular on the xy plane, let us say, we drop a perpendicular on the xy plane, then the arrow, this blue arrow that we get this is called the projection. Actually, it makes sense for me to join the two tips of the arrow. If you drop a perpendicular from the tip of this arrow to the xy plane, then this arrow that we now get in the xy plane, that is the projection of the position vector that we are working with originally.

The angle between the x axis and the projection vector. This is called ϕ. It is almost hidden by the globe unfortunately, so I will write again, this is called ϕ. Range of r is from 0 to infinity. Remember, r cannot go from - infinity to plus infinity, 0 to infinity, theta goes from 0 to π, 180 degrees, you can ask why is it that does not go to 360 degrees because it is not necessary, we are allowing one of the angles ϕ to go from 0 to 2π.

So, the moment that happens, there is no need for us to talk about θ more than 180 degrees. That is why so, of course, I mean, one can think that theta should range from 0 to 2π and ϕ should range from 0 to π. But this is the convention that is used everywhere. And we should not build our own convention unless it is absolutely necessary, we go with whatever is the existing convention. So, remember, range of theta is from 0 to π, range of phi is from 0 to 2π.

The relationships are very simple $z= r \cos \theta$, quite simple, because if you draw a perpendicular from this point to the z axis, something like this, this is perpendicular, what will be the length of the arrow on the z axis, that is a z-component, that is set and what is this angle, θ. So, it is not very difficult to see that $z= r \cos\theta$, r is missing here for some reason, but here it is written, r is the hypotenuse, z is the side adjacent side. So, $z= r \cos\theta$.

What is x? So, this length is r, so, and this angle is θ, this angle is $90^0-\theta$. So, I hope it is not very difficult to understand that the length of this arrow the projection, that is r multiplied by $\sin\theta$, r multiplied by $\cos (90^0-\theta)$ that is r multiplied by $\sin\theta$. Now, when we look at this triangle here, drop a perpendicular from the tip of the arrow on the xy plane to the x axis this is perpendicular.

Now, what we get is this here r sinθ, this is your hypotenuse, and this is adjacent side. So, you get r sinθcosϕ. Similarly, y turns out to be r sinθ, r sinθ is same in both because r sinθ is the length of the projection here, so r sinθsinϕ, quite simple. You can work out the inverse relation here, x, y, z, the Cartesian coordinates are subjects of formula, you can turn it around and make r theta and phi the subject of formula, I will not do that, you can do it yourself, what we get is $r = \sqrt{x^2 + y^2 + z^2}$, of course very obvious.

This is sort of the body diagonal r and the lengths of the three sides of the cuboid are x, y and z. So, of course, $r^2 = x^2 + y^2 + z^2$or $r = \sqrt{x^2 + y^2 + z^2}$. What is θ? Actually, what is θ comes from the first relationship anyway cosθ = z/r, so θ of course is $cos^{-1}\frac{z}{r}$, what is ϕ?

The easiest relationship is that what is $\frac{\sin\phi}{\cos\phi}$? That will be y/x. So, that is tan ϕ. So, ϕ = $tan^{-1}\frac{y}{x}$. I said you do it, I will not. But then I ended up doing it. Because it is so simple anyway. So, these are the relationships. And well, I think by enlarge, you can remember it. But if required, you can always derive it, it is not such a big deal.

The point I want to make is that spherical polar coordinates are things that we are sort of introduced to very early in our lives when we were in school. If you think of a globe, we have all studied geography at some level. And we know about latitude and longitude. What is latitude? What is longitude? Are they related to θ and ϕ? r of course is constant for the earth, that is the surface of the earth. But what about θ, what about ϕ?

θ is not exactly latitude. It is 90 degrees - latitude. Because latitude, remember, is defined from the equator. So, what we call theta = 90 degrees in our system is written 0 degrees as far as latitude is concerned. And there the range is plus 90 to - 90. So, theta is related to latitude, and phi is actually longitude. Phi goes around like this in the equatorial plane. So, phi is exactly longitude.

Now, we have been already introduced to this $d\tau$ business, we know that $\Psi\Psi^* d\tau$ is the probability of finding the particle at some point r, within a small volume element. And we have said that if you work in Cartesian coordinates, x, y z, then $d\tau$ is simply dx, dy, dz. When we work in spherical polar coordinates, it becomes a little different. And this is something that we will use. So, we better learn.

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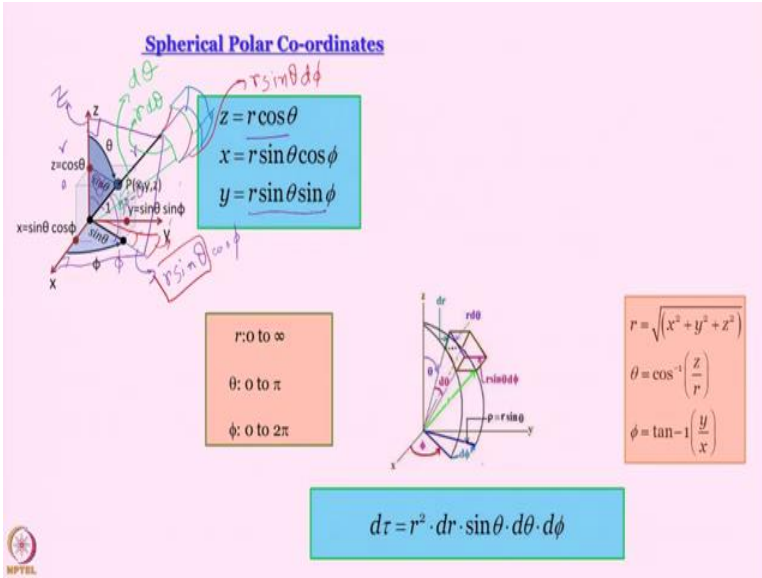

So, here the diagram is drawn already, but I will still try to draw it so that we understand little better. So, let us, let me draw here maybe. So, suppose I want to define a volume element at this point, what do I do? I increase all the coordinates a little. So, I can increase r by an amount dr. Of course, the way I have drawn it, this is a large amount, actually dr is very, very small compared to the length of r. Here, I am exaggerating, so that we see better.

Next, what do I have to do? I have to work with theta. How do I work with θ? Change theta a little bit so, make it θ+dθ. So, now I can draw another line, where this small angle here was smaller than what it seems in this diagram is dθ. So now see, what will be the length of this r? Since dθ is a small angle, this length is going to be r dθ. So, two sides of the volume element are defined already. One side is dr. The other side is r dθ.

What about the third side? How do I define the third side? So, drop this. Now, I will increase ϕ a little bit like this. So, now our projection will go somewhere here. I can think this arc, this will be the third side of the volume element, just draw a perpendicular like this, this arc is the volume element, what will be the length?

Remember, this length here, we already said is r sinθ. And I have, increased angle by dϕ. So, this is going to be r sinθ dϕ. I am not writing in a nice place, this is going to be, we will write here, r sinθ dϕ. So, the three sides of the volume element are defined now, just to see whether we understand it or not, I will draw the other sides of the arc as well.

Let us hope I have not forgotten which color I used. This is one and now I will draw r, this is r, again we have to increase this as well. And just because I am a little bored of changing colors, I will complete the volume element with the same color anyway. So, I hope you see the volume element here, the volume element is not exactly a cuboid, it has a curved side, but the curved sides are almost linear, because they are small segments of a large sphere you can think.

And in case you have had trouble understanding my poorly drawn diagram, here you have a little better diagram, here also you see the sides are dr, r dθ and r sinθdϕ. So, the volume element, volume of the volume element is going to be r^2 dr sinθ dθ dϕ. This is very important and we are going to use this later on in our discussion. Now, let us talk about angular momentum. As you will see, when we discuss hydrogen atom, angular momentum is going to be a very important property that we will worry about.

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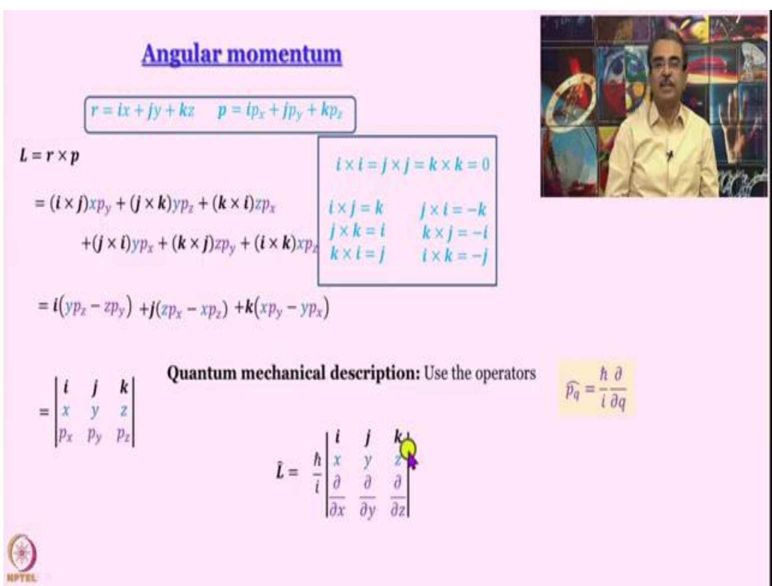

I think once again, we all know that angular momentum is defined as a X product of r and p, rXp. What is the meaning of X product, r is a vector, p is a vector, L is also a vector. So, L is the vector product of r and p. What is the magnitude of L then? Magnitude of L= rp sinθ. And what will be the direction? Direction will be perpendicular to the plane of r and p, r and p will always be in some plane, so direction of L is going to be perpendicular to that.

Now, let us work out what this is. And while doing that, it makes sense if you work with x, y and z components to begin our discussion. So, we will write r like this $r = i_x + j_y + k_z,$ i, j, k are the unit vectors along x, y and z respectively, and x, y and z are the scalar values of well x, y and z respectively. So, r vector is given by $i_x + j_y + k_z$ and p vector is given by $p = ip_x + jp_y + kp_z$

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We want to work out what is L=rXp. And when we do that, this is what we get. First of all, why do we have six terms and not nine terms, we should have got something like (i X i) xp_x also. Well, the thing is, we need to remember this, i X i, j X j, k X k, everything is = 0. Because remember what the magnitude is going to be, it is going to be sin θ, i square sin theta, that kind of thing would have happened, the angle between i and i, j and j and k and k, this angle is 0, sin θ is 0. So, X product of the same vector with itself is 0. We do not have to worry about that.

What about the others? i X j is = k. Remember, these are all perpendicular to each other. So, k is basically along z axis is perpendicular to the xy plane. And j X i is -k that is important to understand. So, if you change the order in this vector product, the direction is going to change even the magnitude will remain the same. And this is very easy to remember also, i X j = k, j X k = i, kXi = j, in alphabetical order, go in alphabetical order, if you are going in alphabetical order, you are going to get positive.

And if you go in anti-alphabetical order j X i, that will be - k, k X j - i, i X k is - j, it is as simple as that, if you just want to remember it, of course, you can work it out and see what it is. So, let us see, in this expansion that we have performed, let us collect the terms in i. Remember i is obtained by taking cross product of j and k that is i and cross product of k and j is - i. So, (j X k)yp_z, this becomes i yp_z and we have (k X j) zp_y that becomes - i zp_y. So, if I call the terms in i, I get i(yp_z – zp_y), this very nice symmetric expression.

And the other two terms also turn out to be like this j(zp_x – xp_z) , k(xp_y – yp_z). So, see what is (yp_z – zp_y) that is the x component of the angular momentum, because it is multiplying the unit vector along the x direction What is $(zp_x – xp_z)$? It is the y component of angular momentum. And what is $(xp_y – yp_z)$? That is the z component of angular momentum.

This is conveniently written in the form of a determinant, $i(yp_z – zp_y)$, - $j(xp_z – zp_x)$, which boils down to $+j(zp_x – xp_z)$, $+k(xp_y – yp_z)$,. It is a very simple determinantal form in which we can write this. So, this is the classical description.

Now, let us think, how we are going to write the same expressions in the language of quantum mechanics. Remember, in quantum mechanics, we have an operator for every physical observable, operator for x, y and z are just position multiplying the wave function. Operator for something like p_x would be $\frac{\hbar}{i}\frac{\partial}{\partial x}$, operator for p_y would be $\frac{\hbar}{i}\frac{\partial}{\partial y}$, for p_z the operator is $\frac{\hbar}{i}\frac{\partial}{\partial z}$.

So, all we have to do is in this determinant, we have to substitute x, y and z by $\hat{x}, \hat{y}, \hat{z}$ respectively, and we have to substitute $\widehat{p_x}$ by $\frac{\hbar}{i}\frac{\partial}{\partial x}$ and so on and so forth. When we do that, this is the angular momentum operator that we generate, if you know position and momentum operator, you can virtually generate all operators that we require. So, $\hat{L}=\frac{\hbar}{i}\begin{vmatrix} i & j & k \\ x & y & z \\ \frac{\partial}{\partial x} & \frac{\partial}{\partial y} & \frac{\partial}{\partial z} \end{vmatrix}$

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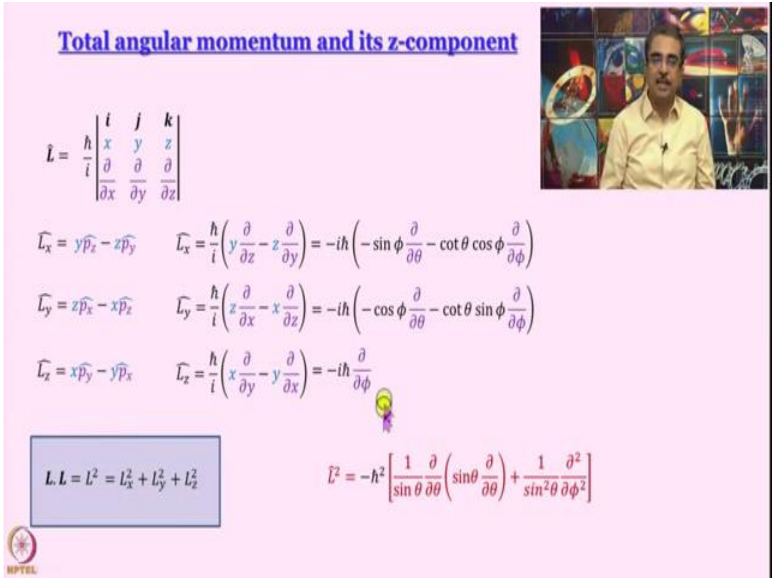

This is what it is. Now, we will have something to say about the total angular momentum and z component of angular momentum starting from here, basically, we want to write down the operators for total angular momentum and z component of angular momentum in terms of spherical polar coordinates, you will see why, the problem actually becomes simple.

And why are you worrying only about z component, we will say that as well even though it might be taking things a little too far for this particular course. So, in case you find that discussion to be too much, you can just skip that part, it depends on whatever is being done in your college.

So, $\widehat{L_x} = y\widehat{p_z} - z\,\widehat{p_y}$, $\widehat{L_y} = z\widehat{p_x} - x\,\widehat{p_z}$, $\widehat{L_z} = x\widehat{p_y} - y\,\widehat{p_x}$. So, and then when we write the expressions for the $\widehat{p_q}$ kind of operators, where q can be x or y or z, this is the expression that we get $\widehat{L_x}$= $\frac{\hbar}{i}\,(y\frac{\partial}{\partial z} - z\frac{\partial}{\partial y})$, $\widehat{L_y}$= $\frac{\hbar}{i}\,(z\frac{\partial}{\partial x} - x\frac{\partial}{\partial z})$, $\widehat{L_z}$= $\frac{\hbar}{i}\,(x\frac{\partial}{\partial y} - y\frac{\partial}{\partial x})$. Now, you know the relationship between r, θ, ϕ and x, y, z, using these relationships it is possible to convert from this $\frac{\partial}{\partial z}, \frac{\partial}{\partial y}$ to things like $\frac{\partial}{\partial r}, \frac{\partial}{\partial \phi}, \frac{\partial}{\partial \theta}$. It is a little longish so we are not going to do it here. If your interested it is not difficult, it is just a little too long, you can do it yourself.

So, it turns out that in spherical polar coordinates $\widehat{L_x} = -i\hbar(-sin\phi\,\frac{\partial}{\partial\theta} - cot\theta\;cos\phi\,\frac{\partial}{\partial\phi})$, For $\widehat{L_y}$, the operator looks very very similar, $\widehat{L_y} = -i\hbar(-cos\phi\,\frac{\partial}{\partial\theta} - cot\theta\;sin\phi\,\frac{\partial}{\partial\phi})$. The only difference is wherever you have sin ϕ for L_x you have cosϕ for L_y, Lz hat is the best of them all $\widehat{L_z} = -i\hbar\frac{\partial}{\partial\phi}$. Very, very convenient that is what we are going to work with.

And the other operator that is very important is not L, we generally do not work with L, we work with square of angular momentum. And that operator is obtained by taking $\widehat{L^2}$ = $\widehat{L_x^2}$+$\widehat{L_y^2}$+$\widehat{L_z^2}$. And to cut a long story short, this is the form of the operator $\widehat{L^2}$ = -$\hbar^2$[$\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}(\sin\theta\frac{\partial}{\partial\theta}) + \frac{1}{sin^2\theta}\frac{\partial^2}{\partial\phi^2}$]. This is something that will keep on coming back in our discussion later on.

Do you have to remember this? For God's sake, no, we should provide this whenever it is required. There is no need to remember too much here, if you remember $-i\hbar\frac{\partial}{\partial\phi}$ I am very happy, L square please do not try to remember it will be provided in our discussions whenever required. So, these are the two operators that we are going to work with $\widehat{L_z}$ and $\widehat{L^2}$.

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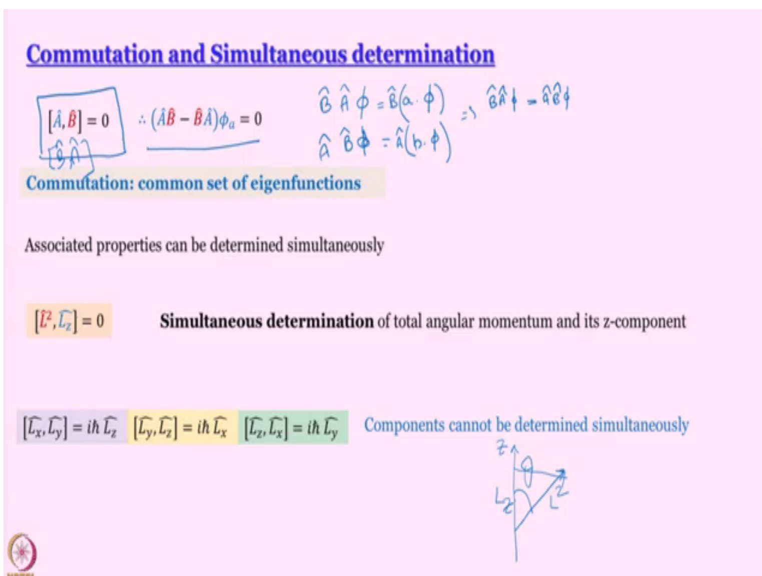

Now, why is it that we are not interested in L_x and L_y? Because, again, we are not going to do the derivation. If you are interested in the derivation, I recommend that you see my lectures that are available on YouTube for a more elaborate quantum chemistry course, you have to write an Anindya Dutta quantum and search within YouTube you will see 68 lectures and they are named. So, you go and see and go through the angular momentum lectures you will get answers to whatever questions you might have at this point.

For now, let us take it axiomatically that in quantum mechanics, if two operators commute, what is the meaning of commute? Meaning you take a wave function, make $\hat{A}$ operate on it first and then make $\hat{B}$ operate on it, you get something. Then you reverse the sequence of operation, make $\hat{B}$ operate on it first and then make $\hat{A}$ operate on it, you get the same answer.

So, another way of writing it would be this, what I am saying is you have some wave function ϕ I will just write ϕ here, make $\hat{A}$ operate on it, you get something let us say $\hat{A}\ \phi$. Now, make $\hat{B}$ operate on it. So, basically $\hat{B}$ is operating on $\widehat{A\ \phi}$. So, this is what you get, $\hat{B}\widehat{(A\ \phi)}$

The other sequence let $\hat{B}$ operate on ϕ, you get let us say $\hat{B}\phi$. Now, let $\hat{A}$ operate on this $\hat{B}\phi$, then you get $\hat{A}(\hat{B}\phi)$. It can be proved we are not going to prove here that $\hat{B}\widehat{(A\ \phi)}$= $\hat{A}(\hat{B}\phi)$. or you can write like this, $(\hat{A}\hat{B}$-$\hat{B}\hat{A})\phi$ = 0**,** that in the convenient notation that we write, we write like this, $[\hat{A},\hat{B}]$=0 within third bracket means commutator. A hat B hat - B hat A hat.

$\hat{B}\hat{A}$, what is $\hat{B}\hat{A}$? $\hat{B},\hat{A}$ the sequence of operation is just opposite. Of course, in this case it will be same, but the crux of the matter is that if the commutator is 0, then they have a common set of wave functions and properties associated with A hat and B hat can be determined simultaneously.

It turns out again, we are not going to prove it here. It is there in those angular momentum lectures. It can be shown that $\widehat{L^2}$ and $\widehat{L_z}$ commute. That means, you can determine the square of total angular momentum and the z component of angular momentum simultaneously for a system.

However, $\widehat{\boldsymbol{L_x}}$ and $\widehat{\boldsymbol{L_y}}$, $\widehat{\boldsymbol{L_y}}$ and $\widehat{\boldsymbol{L_z}}$, $\widehat{\boldsymbol{L_z}}$ and $\widehat{\boldsymbol{L_x}}$ do not commute. They do not commute. So, Lx and Ly, Ly and Lz, Lz and Lx they cannot be determined together. So, the only hope you have is to determine the total angular momentum and its component along one direction that we call z direction.

Here students usually have this question what is z direction, I am talking about hydrogen atom let us say. How does the atom know what is z, atom does not know. Remember wave function collapse, remember that everything in your system is in an entangled state before you make the measurement, only when you make the measurement, the wave function collapses into something.

Suppose, I want to measure the z component of angular momentum. How do I see it experimentally? I apply a magnetic field Zeeman effect. So, the direction of the magnetic field becomes the z direction. What we are saying is if we have an angular momentum, we have an angular momentum like this, when we apply a magnetic field. Now, this z direction is defined. So, theta is defined with respect to the direction of the magnetic field.

Now, we can determine the length of this arrow which is the angular momentum itself actually, we can determine square of it, we cannot really determine whether it is pointing up or down, just like, just from here, $\boldsymbol{L^2}$ is what we can determine. And the other thing that we can determine is the z component. So, from here you get $\boldsymbol{L^2}$. From here you get Lz. Combining the two you can say whether the arrow is pointing up or down of course, this is what we are going to discuss in a little more detail when we talk about hydrogen atom.