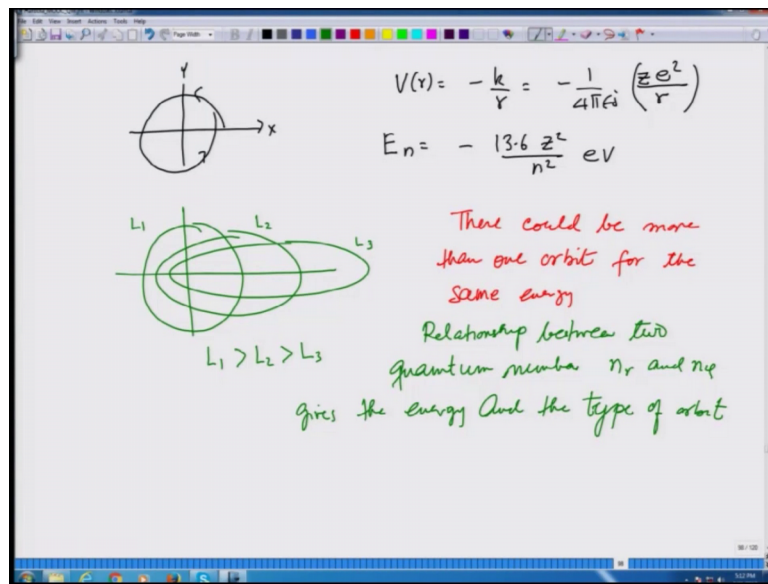


**Introduction to Quantum Mechanics**  
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**Lecture – 03**

**Wilson-Sommerfeld quantum condition III - Particle moving in Coulomb potential in 3d and related quantum numbers**

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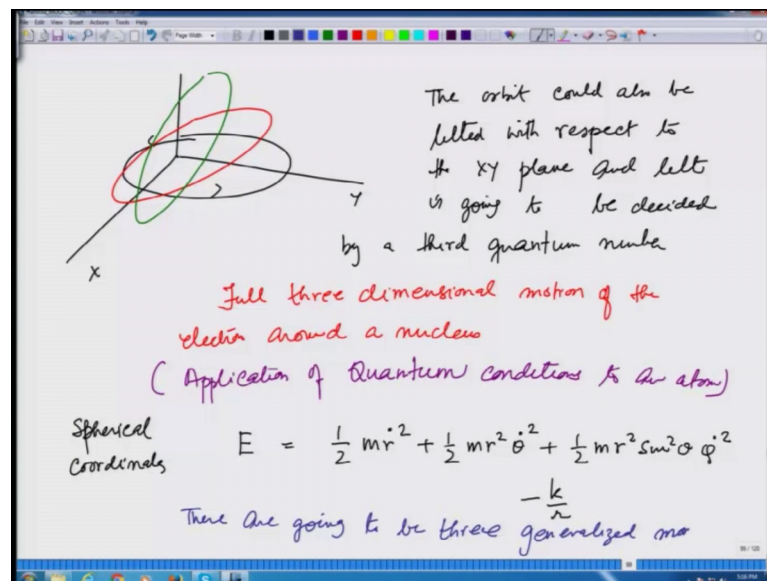
In the previous lecture we considered an electron moving in a plane in the potential  $v$   $r$  equals minus  $k$   $r$ , which is minus  $1$  over  $4 \pi \epsilon_0 z e$  square over  $r$ . And found that the energy is came out to be precisely the same as that in the bohr model. However, what was new in this was that for the same energy values we also obtained orbits which could be of different values.

So, for example, suppose these 3 orbits have all the same energies and have angular momentum  $L_1$   $L_2$  and  $L_3$ . We found that  $L_1$  is greater than  $L_2$  is greater than  $L_3$ , because the different angular momentums are different. And the energies are the same. So, we included the possibility through quantum numbers right. That orbits could be a different kinds. So, what we saw was there could be more than one orbit for the same energy. And the relationship between 2 quantum numbers namely  $n_r$  and  $n_\phi$  gives the energy and the type of orbit. So, this was a kind of quantum mechanics being developed still the old quantum theory, but why I am doing all this is what you will see is that the

ideas that later the true quantum mechanics gave the answers that the true quantum mechanics gave was ideas were already setting in through older quantum theory. That is why I am doing this the previous lecture and this lecture devoted to old quantum theory.

Next going to consider is 3 dimensional case. And in the 3 dimensional case what happens this orbit need not be confined to only x y plane.

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There is a possibility that the orbit could be tilted it could be even more tilted. So, these tilt is going to bring in new quantum number, and additional third quantum number. So, the possibility we are considering is that the orbit could also be tilted with respect to the xy plane. And that tilt is going to be decided by a third quantum number. So, for that we now consider a full 3 dimensional motion of the electron around a nucleolus which also can be called the application of quantum conditions to an atom.

This is the full glorified 3 dimensional view. So, in this case the energy I am going to use this spherical coordinates and the energy e is going to given by 1 half m r dot square plus 1 half m r square theta dot square plus 1 half m r square sin square theta pi dot square minus k by r. So now, there are going to be 3, to be 3 generalized momenta and what are these?

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$$p_r = \frac{\partial E}{\partial \dot{r}} = m \dot{r} \leftrightarrow \text{connected to motion along } r \text{ (linear momentum)}$$

$$p_\theta = \frac{\partial E}{\partial \dot{\theta}} = m r^2 \dot{\theta} \leftrightarrow \text{dimension of angular momentum}$$

$$p_\phi = \frac{\partial E}{\partial \dot{\phi}} = m r^2 \sin^2 \theta \dot{\phi} \leftrightarrow \text{dimension of angular momentum}$$

$$\vec{L} = \vec{r} \times m \vec{v} = m r \hat{r} \times (\dot{r} \hat{r} + r \dot{\theta} \hat{\theta} + r \sin \theta \dot{\phi} \hat{\phi})$$

$$= m r^2 \dot{\theta} (\hat{r} \times \hat{\theta}) + m r^2 \sin \theta \dot{\phi} \hat{r} \times \hat{\phi}$$

$$= m r^2 \dot{\theta} \hat{\phi} - m r^2 \sin \theta \dot{\phi} \hat{\theta}$$

$$\hat{\phi} = -\hat{x} \sin \phi + \hat{y} \cos \phi \quad \hat{\theta} = \hat{x} \cos \theta \cos \phi + \hat{y} \cos \theta \sin \phi - \hat{z} \sin \theta$$

$$\vec{L} = m r^2 \dot{\theta} (-\hat{x} \sin \phi + \hat{y} \cos \phi) - m r^2 \sin \theta \dot{\phi} \hat{\theta}$$

These are  $p_r$  which is partial E over partial  $\dot{r}$ , which is  $m \dot{r}$  this is  $p_\theta$  which is partial E over partial  $\dot{\theta}$ , which is  $m r^2 \dot{\theta}$ . And this is  $p_\phi$  which is equal to  $\partial E / \partial \dot{\phi}$  which is  $m r^2 \sin^2 \theta \dot{\phi}$ , and what are these?

This you can see is connected to motion along  $r$  has a dimension of linear momentum. The second one is the dimension of angular momentum. And so, does the third one and what are the interpretations?

So, let us see what angular momentum of a particle moving in 3 dimension is this is  $\vec{r} \times m \vec{v}$  which I can write as  $m r \hat{r} \times (\dot{r} \hat{r} + r \dot{\theta} \hat{\theta} + r \sin \theta \dot{\phi} \hat{\phi})$ . And you take this cross product this comes up to be  $m r^2 \dot{\theta} \hat{r} \times \hat{\theta} + m r^2 \sin \theta \dot{\phi} \hat{r} \times \hat{\phi}$ . And you know  $\hat{r} \times \hat{\theta} = \hat{\phi}$  and  $\hat{r} \times \hat{\phi} = -\hat{\theta}$ . So it becomes  $m r^2 \dot{\theta} \hat{\phi} - m r^2 \sin \theta \dot{\phi} \hat{\theta}$ .

And this is nothing but  $m r^2 \dot{\theta} \hat{\phi} - m r^2 \sin \theta \dot{\phi} \hat{\theta}$ .  $\hat{r} \times \hat{\phi}$  is minus  $\hat{\theta}$  unit vector, so minus  $m r^2 \sin \theta \dot{\phi} \hat{\theta}$ . Let me remind you from the previous process that  $\hat{\phi}$  unit vector is nothing but  $\hat{x} \sin \phi + \hat{y} \cos \phi$  with a minus sign plus  $\hat{y}$  unit vector cosine of  $\phi$ . And the  $\hat{\theta}$  unit vector is nothing but  $\hat{x} \cos \theta \cos \phi + \hat{y} \cos \theta \sin \phi - \hat{z} \sin \theta$ .

So, if I substitute these in let us do that then the angular momentum vector  $L$  comes out to be  $m r^2 \dot{\theta} \hat{\phi} - m r^2 \sin \theta \dot{\phi} \hat{\theta}$  minus  $x \sin \phi$  plus  $y \cos \phi$  minus  $m r^2 \sin \theta \phi \dot{\theta}$  unit vector.

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The whiteboard shows the following derivation:

$$\vec{L} = m r^2 \dot{\theta} \hat{\phi} - m r^2 \sin \theta \dot{\phi} \hat{\theta}$$

$$p_{\phi} = L_z, \quad L^2 = p_{\theta}^2 + \frac{p_{\phi}^2}{\sin^2 \theta}$$

$$L_z = 0 - m r^2 \sin \theta \dot{\phi} (-\sin \theta \hat{z})$$

$$= (m r^2 \sin^2 \theta \dot{\phi}) \hat{z}$$

The term  $m r^2 \sin^2 \theta \dot{\phi}$  is circled and labeled  $p_{\phi} = L_z$ .

$$\vec{L} = m r^2 \dot{\theta} \hat{\phi} - m r^2 \sin \theta \dot{\phi} \hat{\theta}$$

$$= p_{\theta} \hat{\theta} - \frac{p_{\phi}}{\sin \theta} \hat{\theta} \Rightarrow L^2 = p_{\theta}^2 + \frac{p_{\phi}^2}{\sin^2 \theta}$$

So, starting from the expression  $L$  is equal to  $m r^2 \dot{\theta} \hat{\phi} - m r^2 \sin \theta \dot{\phi} \hat{\theta}$  minus  $m r^2 \sin \theta \phi \dot{\theta}$  unit vector. I am now going to show you that  $p_{\phi}$  is equal to nothing but the  $z$  component of  $L$ . And  $L^2$  is nothing but  $p_{\theta}^2$  plus  $p_{\phi}^2$  over  $\sin^2 \theta$ .

So, let us do that if I take the  $z$  component of  $L$ , it is 0 from  $\hat{\phi} \cdot \hat{z}$  gives you 0 contribution from for the  $z$  component, minus  $m r^2 \sin \theta \dot{\phi}$  and  $\hat{\theta} \cdot \hat{z}$  component of  $\hat{\theta}$  is  $-\sin \theta$ . So, this comes out to be  $m r^2 \sin^2 \theta \dot{\phi}$ . And this is nothing but  $p_{\phi}$ . So, what I have shown is  $p_{\phi}$  is nothing but  $L_z$ , and from the expression for  $L$  which is  $m r^2 \dot{\theta} \hat{\phi} - m r^2 \sin \theta \dot{\phi} \hat{\theta}$ , I can write this as  $p_{\theta} \hat{\theta} - \frac{p_{\phi}}{\sin \theta} \hat{\theta}$ .  $\hat{\theta}$  and  $\hat{\phi}$  are perpendicular to each other. So, this immediately implies that  $L^2$  is  $p_{\theta}^2$  plus  $p_{\phi}^2$  over  $\sin^2 \theta$ .

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The whiteboard contains the following handwritten text:

$$E = \frac{1}{2} m \dot{r}^2 + \frac{1}{2} m r^2 \dot{\theta}^2 + \frac{1}{2} m r^2 \sin^2 \theta \dot{\phi}^2 - \frac{k}{r}$$
$$p_r = m \dot{r} \quad p_\theta = m r^2 \dot{\theta} \quad p_\phi = m r^2 \sin^2 \theta \dot{\phi} = L_z$$

(Angular momentum)  $L^2 = \left( p_\theta^2 + \frac{p_\phi^2}{\sin^2 \theta} \right)$

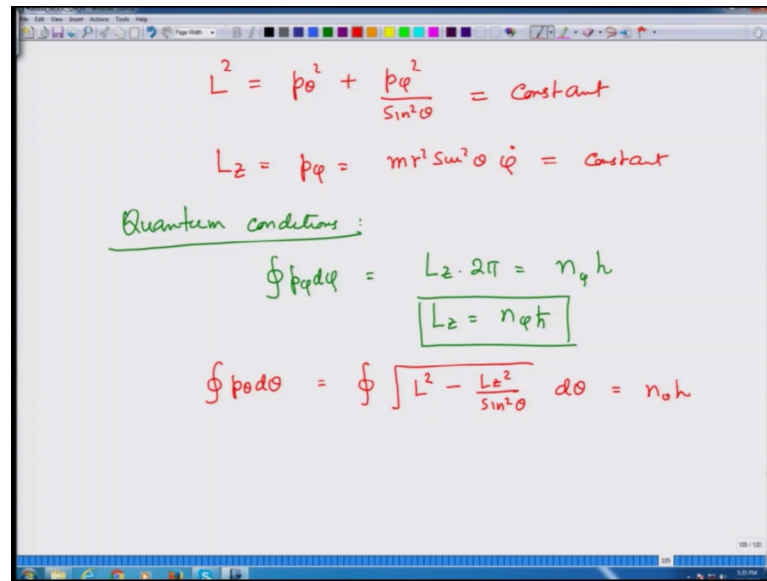
For central field motion ( $V \propto \frac{1}{r}$ )

$\vec{L}$  is conserved  $\Rightarrow$  All components of  $\vec{L}$  are conserved

So, let us see what we have found we found that energy for 3 dimensional motion of an electron around nucleus is going to be given as 1 half  $\dot{r}$  square plus 1 half  $m r$  square  $\dot{\theta}$  square plus 1 half  $m r$  square  $\sin$  square  $\theta$   $\dot{\phi}$  square minus  $k$  over  $r$ . And  $p_r$  is  $m \dot{r}$ ,  $p_\theta$  is  $m r$  square  $\dot{\theta}$  and  $p_\phi$  is  $m r$  square  $\sin$  square  $\theta$   $\dot{\phi}$ . And this is nothing but  $L_z$ . And  $p_\theta$  is such that  $L^2$  that is the angular momentum I am using  $L$  for angular momentum  $L^2$  is  $p_\theta^2$  plus  $p_\phi^2$  over  $\sin^2 \theta$ . As we have found this so far.

Now, for central feel motion mainly when  $v$  is of form  $1$  over  $r$ . The force is central  $L$  is conserved and this means all components of  $L$  are conserved right.

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The image shows a whiteboard with handwritten mathematical equations. At the top, the total angular momentum squared is given as  $L^2 = p_\theta^2 + \frac{p_\phi^2}{\sin^2\theta} = \text{Constant}$ . Below this, the z-component of angular momentum is given as  $L_z = p_\phi = m r^2 \sin^2\theta \dot{\phi} = \text{Constant}$ . A section titled "Quantum conditions:" follows. The first condition is  $\oint p_\phi d\phi = L_z \cdot 2\pi = n_\phi h$ , which is boxed to yield  $L_z = n_\phi h$ . The second condition is  $\oint p_\theta d\theta = \oint \sqrt{L^2 - \frac{L_z^2}{\sin^2\theta}} d\theta = n_\theta h$ .

So, what that means is,  $L^2$  which is equal to  $p_\theta^2$  plus  $p_\phi^2$  over  $\sin^2\theta$  is a constant, throughout the motion. And  $L_z$  which is  $p_\phi$  which is  $m r^2 \sin^2\theta \dot{\phi}$  is also a constant.

So now let us apply quantum conditions. What does these give? The easiest to apply is  $\oint p_\phi d\phi$  which is nothing but this constant  $L_z$  times  $2\pi$  should be equal to  $n_\phi h$  or  $L_z$  is equal to  $n_\phi h$ . That is one quantum condition for  $p_\theta$  is going to be  $\oint p_\theta d\theta$ . And we will see what the limits of this are going to be, which is equal to  $\oint \sqrt{L^2 - \frac{L_z^2}{\sin^2\theta}} d\theta$  over this period is going to be equal to  $n_\theta h$ .

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$$L^2 = p_\theta^2 + \frac{p_\phi^2}{\sin^2\theta} = \text{Constant}$$

$$L_z = p_\phi = m r^2 \sin^2\theta \dot{\phi} = \text{Constant}$$

Quantum conditions:

$$\oint p_\phi d\phi = L_z \cdot 2\pi = n_\phi h$$

$$L_z = n_\phi \hbar$$

$$\oint p_\theta d\theta = \oint \sqrt{L^2 - \frac{L_z^2}{\sin^2\theta}} d\theta = n_\theta h$$

$L_z$  is z component of  $\vec{L}$   
 $|L_z| \leq L$

And now  $L_z$  is z component of  $L$  angular momentum. Since  $L_z$  is z component of  $L$  it means that modulus  $L_z$  has to be less than or equal to  $L$ .

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$$\int \sqrt{L^2 - \frac{L_z^2}{\sin^2\theta}} d\theta$$

to be real

Then  $L^2 - \frac{L_z^2}{\sin^2\theta} \geq 0$

$$\sin^2\theta \geq \frac{L_z^2}{L^2}$$

$$-\frac{|L_z|}{L} \leq \sin\theta \leq \frac{|L_z|}{L}$$

$$\theta = \sin^{-1}\left(\frac{|L_z|}{L}\right)$$

$$\theta = \sin^{-1}\left(\frac{|L_z|}{L}\right)$$

$$\int \sqrt{L^2 - \frac{L_z^2}{\sin^2\theta}} d\theta = 2\pi (L - |L_z|)$$

Now, let us look at the integral square root of  $L$  square minus  $L_z$  square over  $\sin$  square  $\theta$   $d\theta$ . Now if you want  $L$  square minus  $L_z$  square over  $\sin$  square  $\theta$  square root to be real, then  $L$  square minus  $L_z$  square over  $\sin$  square  $\theta$  is greater than or equal to 0. And  $\sin$  square  $\theta$  has to be greater than or equal to  $L_z$  square over  $L$  square and  $\sin \theta$ , is then limited to minus  $L_z$  by  $L$  modulus to modulus  $L_z$  by  $L$ . And

therefore, this integral from here becomes integral sin inverse mode L z over L to sin inverse theta equals theta equals sin inverse mode L z over L, square root of L square minus L z square over sin square theta d theta.

Again we are not going into how these integral is calculated, but it is value comes out to be after you perform the integral with comes out to be 2 pi L minus mod L z.

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The image shows a whiteboard with the following handwritten equations and text:

$$\oint p_{\phi} d\phi = n_{\phi} h \Rightarrow L_z = n_{\phi} h$$

$$\oint p_{\theta} d\theta = 2\pi (L - |L_z|) = n_{\theta} h$$

$$L - |L_z| = n_{\theta} h$$

$$L = |L_z| + n_{\theta} h$$

$$= (|n_{\phi}| + n_{\theta}) h$$

$z$  Component of angular momentum =  $n_{\phi} h$   
 $n_{\phi} = 0, \text{ positive or negative integers}$

$$L = (n_{\theta} + |n_{\phi}|) h \quad n_{\theta} = 1, 2, \dots \quad (n_{\theta} + |n_{\phi}| \text{ total Ang. mom})$$

So, what we have found is integral p phi d phi is equal to n phi h gives you L z equals n phi h cross. And integral p theta d theta gives you 2 pi L minus mod L z equals n theta h or L minus mod L z is equal to n theta h cross, or L equals mod L z plus n theta h cross, which is n phi plus n theta modulus h cross. So, what we have found is that the angular momentum z component of angular momentum is equal to n phi h cross.

And since this is z component it could take negative or positive values both. So, I will do not say n phi could be 0 or positive or negative integers. They are integers, but take positive and negative values, L which is the magnitude of angular momentum is going to be equal to n theta plus modulus n phi h cross and you can see that, n theta should take values of 1 2 and so on. So, that even if n phi is 0 there is a possibility of n theta having the angular momentum being finite we are excluding 0 angular momentum.



So, this is now we have got 2 quantum numbers,  $n_\theta$  and  $n_\phi$ .  $n_\theta$  is related to the  $n_\theta$  plus  $n_\phi$  is related to the total angular momentum. And  $n_\phi$  is related to the z component of the angular momentum.

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$$L_z = p_\phi = n_\phi \hbar \quad n_\phi = 0, \pm 1, \pm 2 \dots$$

$$L = \text{magnitude of angular momentum}$$

$$= (n_\phi + n_\theta) \hbar$$

$$= k \hbar \quad k = 1, 2, 3 \dots$$

$$|L_z| \leq L \Rightarrow |n_\phi| \hbar \leq k \hbar$$

$$\text{or } \boxed{-k \leq n_\phi \leq k}$$

Below the equations are several diagrams illustrating the possible orientations of the angular momentum vector  $L$  relative to the z-axis. Each diagram shows a vertical z-axis and a vector  $L$  of magnitude  $k\hbar$ . The diagrams show the z-component  $L_z$  for different values of  $n_\phi$ :
 

- $L_z = k\hbar$  (vector along z)
- $L_z = (k-1)\hbar$  (vector at an angle)
- $L_z = (k-2)\hbar$  (vector at a larger angle)
- $L_z = (k-3)\hbar$  (vector at an even larger angle)
- $L_z = -k\hbar$  (vector opposite to z)
- $L_z = -(k-1)\hbar$  (vector at an angle in opposite direction)
- $L_z = -(k-2)\hbar$  (vector at a larger angle in opposite direction)

So, let us just again summarize  $L_z$  which is  $p_\phi$  is equal to  $n_\phi \hbar$ , and  $n_\phi$  is 0 and plus minus 1 plus minus 2 and so on.  $L$  which is the magnitude of total angular momentum is going to be  $n_\phi$  modulus plus  $n_\theta \hbar$ . So, this is equal to let us call it  $k \hbar$   $k$  equals 1 2 3 and so on.

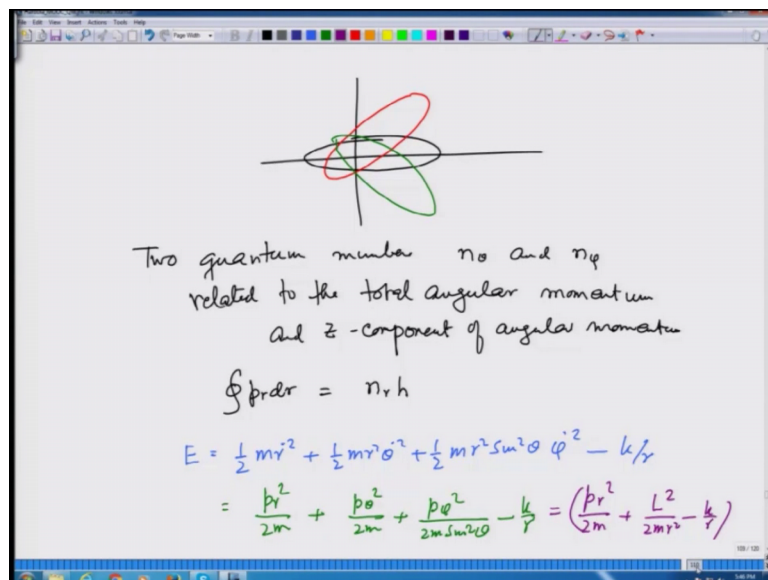
Since we found that  $|L_z| \leq L$ , this necessarily implies that  $n_\phi \hbar$  is less than equal to  $k \hbar$ . Or  $n_\phi$  is confined between minus  $k$  and  $k$ . What that means, is that you could have a net angular momentum  $k \hbar$  and it could be in a direction which is in the z direction. Next it could be, So this will be  $k \hbar$  or it will be  $(k-1) \hbar$  So that the angular momentum is pointing in certain direction it cannot be any arbitrary direction. The projection has to be  $(k-1) \hbar$ . Third I could have this  $k \hbar$  and the z component would be  $(k-2) \hbar$ . I am just drawing these symbolically these angles are not written to be precise. In fact,  $(k-2) \hbar$  if I would show it will be like this, and the angular momentum would be at an angle larger than (Refer Time: 22:03).

So, this is  $(k-2) \hbar$   $k \hbar$ . Not only that it could be in the opposite direction. So, if I would draw to the scale even the first one would not be like this, instead it will be

that  $\mathbf{k} \times \mathbf{h}$  is right along  $\mathbf{k}$ . It could also be in the opposite direction the net angular momentum could be the other direction. And magnitude remains  $kh$  and the  $z$  component could be minus  $\mathbf{k} \times \mathbf{h}$ , I could also have  $\mathbf{k} \cdot \mathbf{h}$  with the minus sign. And the angular momentum point in this way  $\mathbf{k} \times \mathbf{h}$ . I could also have the angular momentum  $\mathbf{k} \cdot \mathbf{h}$  in the negative direction and the net angular momentum point in this way.

So, what this showing is some sort of space quantization That the orbits are such that they could be either in the  $x-y$  plane or they could be tilted, but they cannot be tilted arbitrarily they would be tilted such that the  $z$  component is still an integer multiple of  $\mathbf{k} \times \mathbf{h}$  and the total angular momentum remains the same.

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So, we have found 2 quantum numbers  $n_\theta$  and  $n_\phi$  related to the total momentum and  $z$  of angular momentum. I am still to do  $p_r dr$  to be equal to  $n_r h$  let us do that now.

So, remember energy was equal to  $\frac{1}{2} m \dot{r}^2$  plus  $\frac{1}{2} m r^2 \dot{\theta}^2$  plus  $\frac{1}{2} m r^2 \sin^2 \theta \dot{\phi}^2$  minus  $k/r$ . And quickly I can write this as  $p_r^2 / 2m$  plus  $p_\theta^2 / 2m$  plus  $p_\phi^2 / 2m \sin^2 \theta$  minus  $k/r$ . And you can see from what we derived earlier this is nothing but  $p$  equal to  $p_r^2 / 2m$  plus  $L^2 / 2m r^2$  minus  $k/r$ .

So, I have the energy given as  $\frac{pr^2}{2m}$  plus  $\frac{L^2}{2mr^2}$  minus  $\frac{k}{r}$  over  $r$ .

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The whiteboard contains the following handwritten content:

$$E = \frac{pr^2}{2m} + \frac{L^2}{2mr^2} - \frac{k}{r}$$

$$pr = \sqrt{2mE - \frac{L^2}{r^2} + \frac{2mk}{r}}$$

This is exactly the same expression that we had obtained in two-d case (in the previous lecture)

$$\oint pr dr = n_r h$$

$$E_n = -\frac{mk^2}{2n^2 \hbar^2} = -\frac{m(z^2 e^4)}{32\pi^2 \epsilon_0^2 \hbar^2 a^2}$$

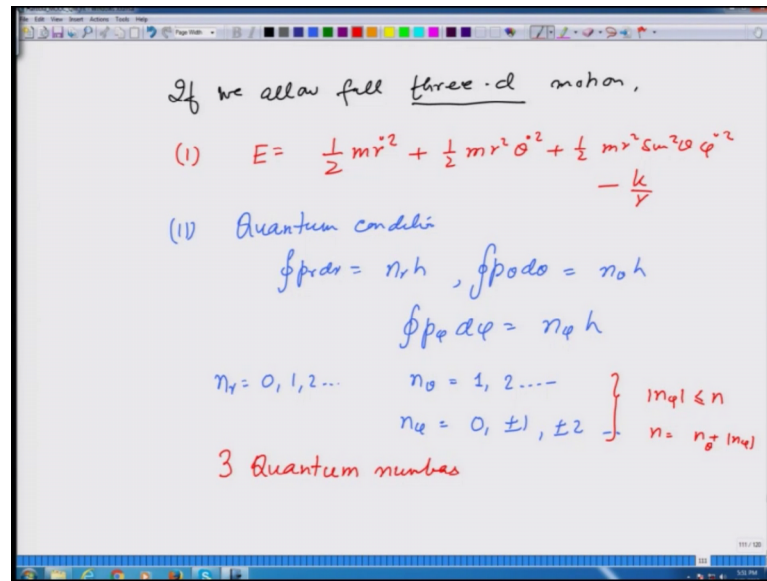
$$n = (n_r + n_\theta + |n_\phi|)$$

$$n_r = 0, 1, 2, \dots$$

So,  $pr$  is given as square root of  $2 m e$  minus  $L$  square over  $r$  square plus  $2 m k$  over  $r$ . Which is exactly the same expression as I have obtained in 2 dimensional case. So, this is exactly the same expression that we had obtained in 2 d case. Let me write in the previous lecture.

So, it will give me exactly the same answer if I do integral  $pr dr$  equals  $n_r h$  I will urge to back to that lecture and get exactly the same answer  $E_n$  equals minus  $m k$  square over  $2 n$  square  $h$  cross square which is same as minus  $m z$  square  $e$  raise to 4 over  $30 2 \pi$  square  $\epsilon_0$  square  $h$  cross square  $n$  square; where  $n$  now is going to be  $n_r$  plus  $n_\theta$  plus  $n_\phi$ . That is the value of  $n$ , and  $n_r$  because  $n$  minimum is one could be 0 1 2 and so on. So, what I have shown through you through this lecture In this is that if we allow full 3 d motion, what happens?

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One, E is given as 1 half m r dot square plus 1 half m r square theta dot square plus 1 half m r square sin square theta phi dot square minus k over r. And the quantum conditions are pr dr is equal to nr h p theta d theta is equal to n theta h and p phi d phi is equal to n phi h. And we have found that nr will be 0 1 2 and so on. N theta would be equal to 1 2 and so on, n phi will be 0 plus minus 1 plus minus 2 and so on.

More importantly what we have are now 3 quantum numbers. Through this we also found that mod of n phi was less than or equal t n, where n is equal to n plus n theta plus mod n phi, because z component has to be less than or equal to the total angular momentum.

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(iii)  $E_n = -\frac{13.6 z^2}{n^2} \text{ eV}$

Possibility of an orbit having energy  $E_n$  being unique is GONE

(iv) Different orbits with different quantum numbers  $n_r$ ,  $n_\theta$  and  $n_\phi$  could have the same energy  $E_n$  depending on  $(n_r + n_\theta + |n_\phi|)$

An orbit has 3 quantum numbers  $n$ ,  $k$ ,  $n_\phi$   
 $|n_\phi| \leq k$

So, we found 3 quantum numbers third the energy  $E_n$  comes out to be exactly the same as bohr model e v, but now the possibility of an orbit having energy  $E_n$  being unique is gone. What we could instead have is that different orbits with different quantum numbers  $n_r$ ,  $n_\theta$  and  $n_\phi$  could have the same energy  $E_n$  depending on  $n_r$  plus  $n_\theta$  plus  $\text{mod } n_\phi$ .

So, this gives that an orbit has 3 numbers, which I could write as  $n$  which is same as  $n_r$  plus  $n_\theta$  plus  $n_\phi$  k. Which gives the total angular momentum and  $n_\phi$ ,  $\text{mod } n_\phi$  being less than or equal to  $k$ . So, these are ideas I am just doing it to introduce to the ideas, how the idea of quantum numbers arose from these quantum conditions and these are going to lead us to understand the quantum nature better and better. Calculations I am going to give you some simple calculations based on Wilson sommerfeld quantum, conditions which are in use today also. And what you will see later when the full quantum mechanics comes into being when we start solving problems with that that how close to 2 quantum mechanics these ideas came.

What is important and what I am going to cover in the next lecture is having these 3 quantum numbers now people try to explain the spectrum of different atoms and also the periodic table and came up with the concept of electron spin.