Quantum Mechanics
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Lecture - 38
Hydrogen Atom & Wave Functions, Angular Momentum Operators, Identical Particles - I

So last lecture, I went on till the radial component of the hydrogen atom wave function and I said they are given by the Laguerre special function, right. So I do not want you to memorize I was saying in the beginning of the class, nothing I want you to memorize; whatever data is required I will be giving it. You should be able to decide for what that data is and put it in your accordingly in your answers, okay.

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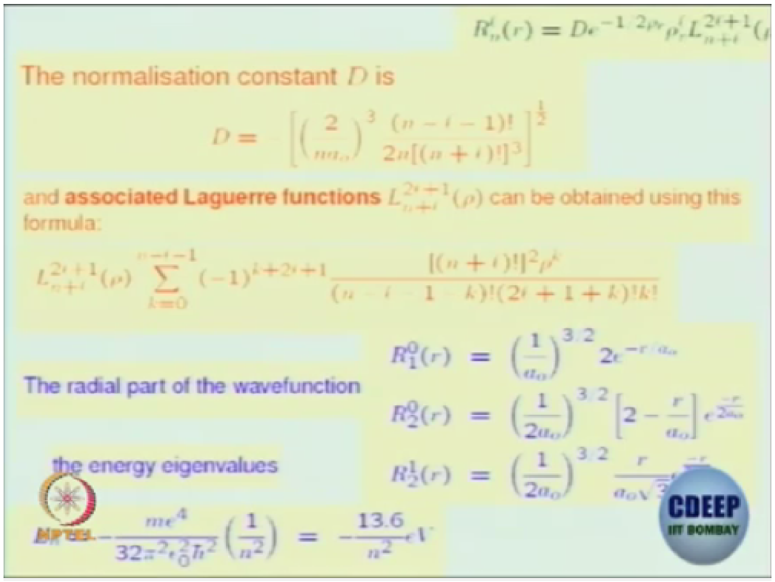

$R^l_n(r) = D e^{-1/2\rho_r} \rho_r^l L^{2l+1}_{n+l}($

The normalisation constant D is

$$D = \left[\left(\frac{2}{na_0}\right)^3 \frac{(n-l-1)!}{2n[(n+l)!]^3}\right]^{\frac{1}{2}}$$

and **associated Laguerre functions** $L^{2l+1}_{n+l}(\rho)$ can be obtained using this formula:

$$L^{2l+1}_{n+l}(\rho) \sum_{k=0}^{n-l-1} (-1)^{k+2l+1} \frac{[(n+l)!]^2\rho^k}{(n-l-1-k)!(2l+1+k)!k!}$$

The radial part of the wavefunction

$$R^0_1(r) = \left(\frac{1}{a_0}\right)^{3/2} 2e^{-r/a_0}$$

$$R^0_2(r) = \left(\frac{1}{2a_0}\right)^{3/2} \left[2 - \frac{r}{a_0}\right] e^{\frac{-r}{2a_0}}$$

$$R^1_2(r) = \left(\frac{1}{2a_0}\right)^{3/2} \frac{r}{a_0\sqrt{3}}$$

the energy eigenvalues

$$E_n = -\frac{me^4}{32\pi^2\epsilon_0^2\hbar^2}\left(\frac{1}{n^2}\right) = -\frac{13.6}{n^2} eV$$

So just to recall I called Rn, capital Rn and then there was the Azimuthal quantum number L so this wave function for the radial component is constrained by the principal quantum number as well as a Azimuthal quantum number and that is incorporated in your Laguerre, associated Laguerre function. So these normalizations are worked out already so for simple cases maybe for n=1 or l=1 you can verify what is happening n=2 and l = 1 we could verify, okay.

So there is an = sign which is missing here. So this is the new summation formula for the Laguerre associated Laguerre function. And you can write to substitute here and verify. So there is an = sign here you can try to verify that you get R1 0 to be this R2 0, please check it out, okay.

So this is the radial part of the wave function for the hydrogen atom problem. And the energy eigenvalues also will be from this solution to that equation you can read off what the energy is and that is nothing.

But proportional to 1/n squared in electron volts, you can write it as 13.6 electron volts; negative sign because it is a bounce state.

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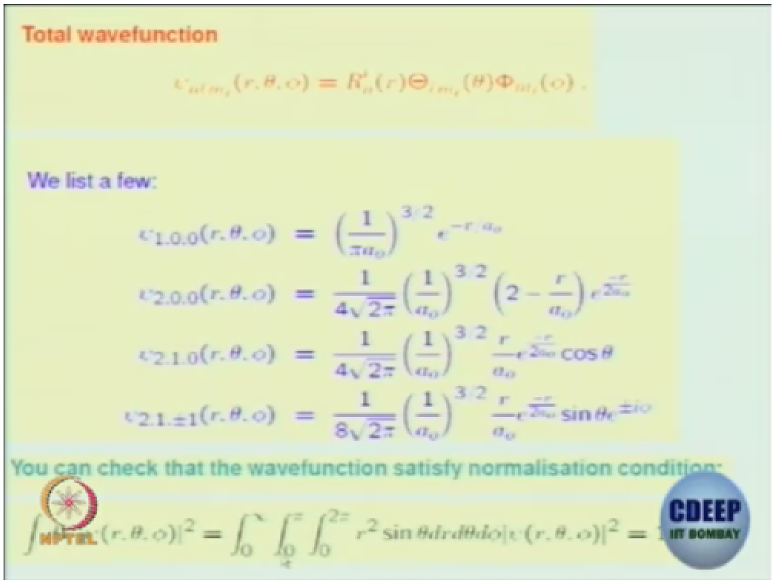

Total wavefunction

$$\psi_{nlm_l}(r,\theta,\phi) = R_n^l(r)\Theta_{lm_l}(\theta)\Phi_{m_l}(\phi).$$

We list a few:

$$\psi_{1,0,0}(r,\theta,\phi) = \left(\frac{1}{\pi a_0}\right)^{3/2} e^{-r/a_0}$$

$$\psi_{2,0,0}(r,\theta,\phi) = \frac{1}{4\sqrt{2\pi}}\left(\frac{1}{a_0}\right)^{3/2}\left(2-\frac{r}{a_0}\right)e^{\frac{-r}{2a_0}}$$

$$\psi_{2,1,0}(r,\theta,\phi) = \frac{1}{4\sqrt{2\pi}}\left(\frac{1}{a_0}\right)^{3/2}\frac{r}{a_0}e^{\frac{-r}{2a_0}}\cos\theta$$

$$\psi_{2,1,\pm1}(r,\theta,\phi) = \frac{1}{8\sqrt{2\pi}}\left(\frac{1}{a_0}\right)^{3/2}\frac{r}{a_0}e^{\frac{-r}{2a_0}}\sin\theta e^{\pm i\phi}$$

You can check that the wavefunction satisfy normalisation condition:

$$\int |\psi(r,\theta,\phi)|^2 = \int_0^\infty \int_0^\pi \int_0^{2\pi} r^2 \sin\theta dr d\theta d\phi |\psi(r,\theta,\phi)|^2 = 1$$

So formally hydrogen atom wave function can be written as now with three quantum numbers ML from the Phi variable differential equation. And then L and ML together it was going to be showing up in though theta part of the wave function and then we have this principal quantum number and the Azimuthal quantum number showing up in the radial part of the wave function. So you can list a few of them, the ground state wave function.

We know what this is; this is 1 and this M=0 so these two are 1 and then there is a normalization and you can also check the normalization. What is the normalization condition this also is stressed last time? It is an integral over DV and DV should be written in the spherical polar coordinates which will have an R squared sine theta d Phi d theta, so that integral has to be done; you cannot blindly do d theta, d Phi and dr and write the normalization. Okay. It is a volume integral.

And if it is different coordinate if it is Cartesian coordinate it would having dx, dy, dz but because it is spherical coordinates there will be a Jacobian factor you cannot forget the Jacobian factor. So similarly, so you can check the first and the second just for the get a feel on the wave function; you do not need to memorize any of these things but check the normalization whether you are able reproduce. And check whether plugging in those general associated Laguerre functions you can write this wave function and so on, just please check, okay.

So here whenever L is 0 and Phi is 0 you know the quantum numbers corresponding to that there will not be a theta phi dependence. But if suppose the L becomes 1 then there will be a cos theta; if it becomes ml = +1 or -1 you can have it e to the power of + or -. Im Phi where M is +1 or -1, okay. So you see that everything coming up from the Legendre, Associated Legendre and so on. we called it as a spherical harmonics. So please verify this.

I will put the file today in the Moodle and you can very also verify the normalization condition which is integral of DV which is r squared sine theta dr, d theta, d phi and limits are also theta from 0 to Pi, Phi from 0 to 2pi and RS comes 0 to infinity.

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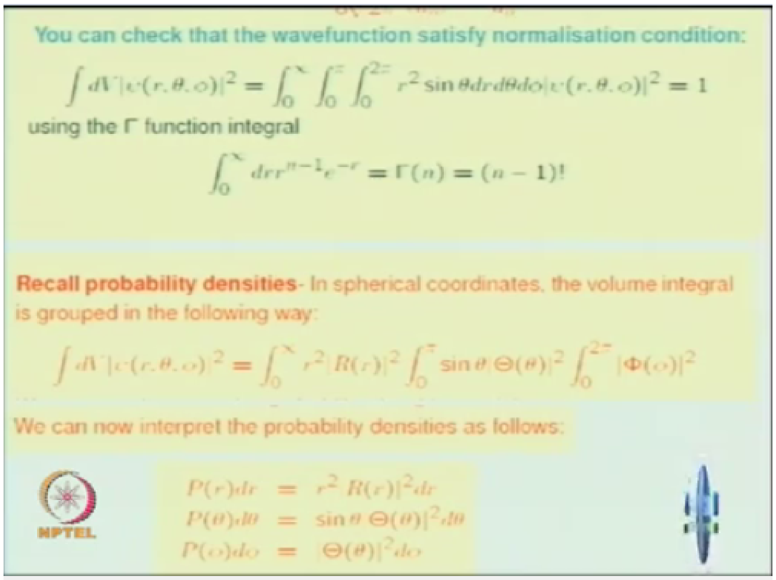

You can check that the wavefunction satisfy normalisation condition:

$$\int dV |\psi(r,\theta,\phi)|^2 = \int_0^\infty \int_0^\pi \int_0^{2\pi} r^2 \sin\theta dr d\theta d\phi |\psi(r,\theta,\phi)|^2 = 1$$

using the Γ function integral

$$\int_0^\infty dr r^{n-1} e^{-r} = \Gamma(n) = (n-1)!$$

Recall probability densities- In spherical coordinates, the volume integral is grouped in the following way:

$$\int dV |\psi(r,\theta,\phi)|^2 = \int_0^\infty r^2 |R(r)|^2 \int_0^\pi \sin\theta |\Theta(\theta)|^2 \int_0^{2\pi} |\Phi(\phi)|^2$$

We can now interpret the probability densities as follows:

$$\begin{aligned} P(r)dr &= r^2 |R(r)|^2 dr \\ P(\theta)d\theta &= \sin\theta |\Theta(\theta)|^2 d\theta \\ P(\phi)d\phi &= |\Theta(\theta)|^2 d\phi \end{aligned}$$

And you can also use this gamma function integrals, this data and all will be given in the question paper if it is required so this is the gamma function where n is an integer and you can write this as n-1 factorial. So you can also; this is something which I mentioned last time that you can split that integral into three integrals the dr integral with r squared factor and then sine theta with the d theta integral part and Phi has nothing.

So each one you could try to normalize when you do this integration and you can interpret them as probability of finding the particle between r and r+dR radial coordinate is this; theta and theta + d theta is this; and Phi and Phi+ d Phi something wrong here. What is wrong? This has to be a capital Phi or r, I need to correct all these Phi, but I am announcing it so please correct it right away and when the Phi comes it is still not corrected but just remember.

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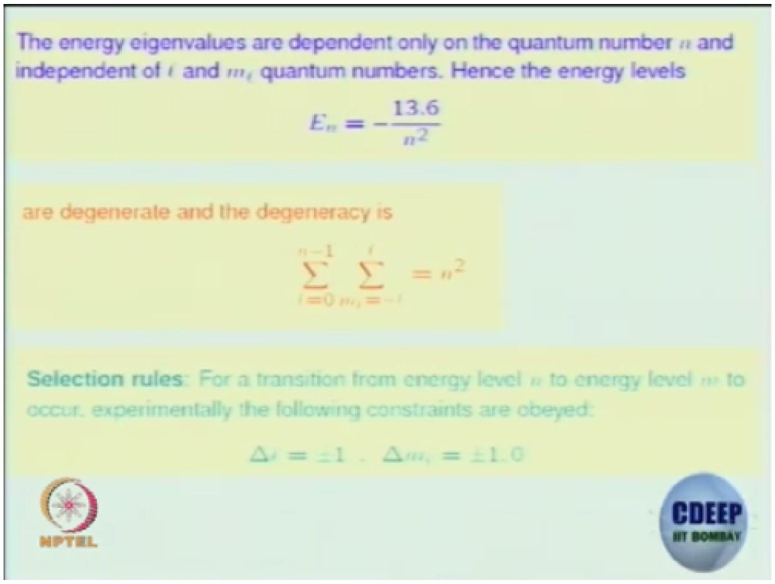

The energy eigenvalues are dependent only on the quantum number n and independent of ℓ and m_ℓ quantum numbers. Hence the energy levels

$$E_n = -\frac{13.6}{n^2}$$

are degenerate and the degeneracy is

$$\sum_{\ell=0}^{n-1} \sum_{m_\ell=-\ell}^{\ell} = n^2$$

Selection rules: For a transition from energy level n to energy level m to occur, experimentally the following constraints are obeyed:

$$\Delta\ell = \pm 1 \;,\; \Delta m_\ell = \pm 1, 0$$

So clearly the energy eigenvalues are independent of the Azimuthal quantum number and Magnetic quantum, right just like we did Landau levels. It tells you that this was also degenerate but it is not infinitely degenerate; there is a restriction. Given an n the differential equations put some restriction on L, L has to be N-1, you can take values from 0 to L-1 and ML has to be some for every L it is constrained to –L to +L so these things comes from the differential equation, so that we cannot.

So there you can actually tell water the degeneracy for every principle quantum number. I am sure you have done it in chemistry. What is a degeneracy? It is just n squared, if you do not include the spin quantum number okay but if you way include the spin quantum number you will have a 2n squared. So there is another thing which I felt you should know is that is that typically when we do transitions in the lab the lab person.

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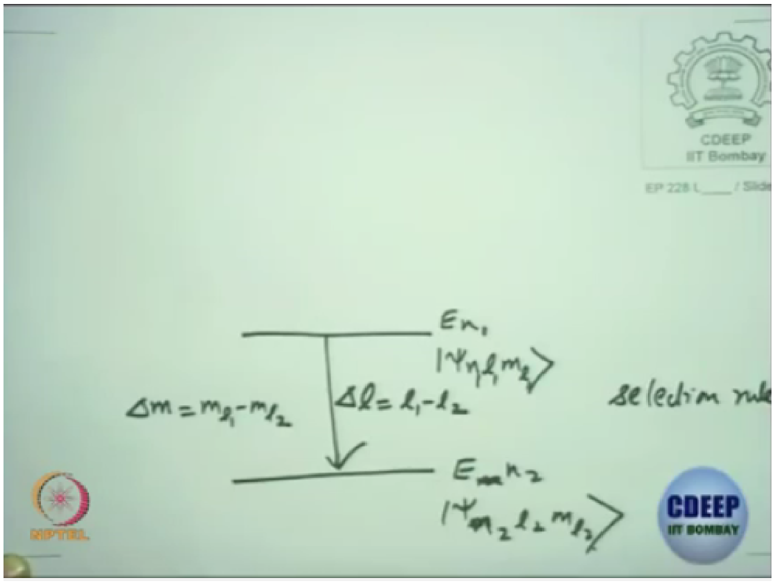

Suppose he is looking at update which is with energy En, l Psi nlml Okay. So the En state has 2n squared degeneracy if you include spin quantum number if do not include it is n squared degeneracy. I am taking a specific state. The question is whether this atom can, you not do a transaction to any excited state or from the excited state to a lower energies. Suppose I take another lower energy state Em with Psi m sorry the; probably this is not a very good notation.

Let me put En1 En2 n1 l1 ml1 so n2 l2 ml2 and this undergo transaction is the question. So then there are some selection rules, not all of them there are these orthogonality condition which will come in mathematics but experimental will try to look for a transaction which corresponds to going from this set of quantum numbers to this set of quantum numbers whether the transaction is possible. So this is what is called is selection rule.

So when it is possible? Delta l which is l1-l2, what condition on it when this will be allowed? Similarly, delta m, ml1-ml2 what are the conditions under which it will happen the transition will happen. This is what is called as a selection rule. Okay. So let me tell you first what is the data which experimental is tells us and then we will see from math or quantum mechanics so that we can reproduce that information.

So right now that delta l constraint is given to be experimentally they find delta l must be + or – 1 and delta ml has to be either 0 or + or -1 is what they say. How do we verify, this where the similar problem can help?

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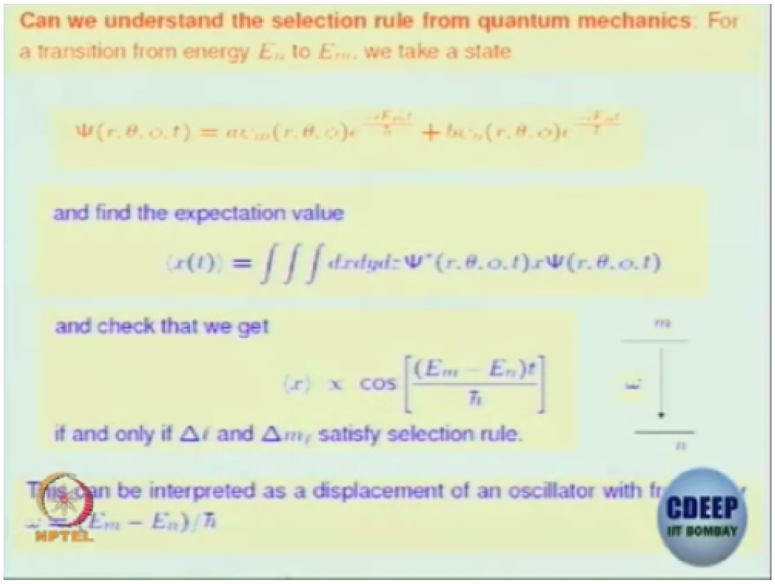

Can we understand the selection rule from quantum mechanics: For a transition from energy E_n to E_m, we take a state

$$\Psi(r,\theta,\phi,t) = a\psi_m(r,\theta,\phi)e^{\frac{-iE_m t}{\hbar}} + b\psi_n(r,\theta,\phi)e^{\frac{-iE_n t}{\hbar}}$$

and find the expectation value

$$\langle x(t)\rangle = \int\int\int dx dy dz \Psi^*(r,\theta,\phi,t) x \Psi(r,\theta,\phi,t)$$

and check that we get

$$\langle x\rangle \propto \cos\left[\frac{(E_m - E_n)t}{\hbar}\right]$$

if and only if Δl and Δm_l satisfy selection rule.

This can be interpreted as a displacement of an oscillator with fr

$\omega = (E_m - E_n)/\hbar$

So how do we understand the experimental data on the selection rule? To understand that try to write in arbitrary state; I told you that this toggling cannot happen unless you write a superpose state. If it is in the stationary state it will remain in the stationary state. Okay. There is no way you can undergo transition. To undergo a transition or to understand transition you need to take a superpose state where these are the stationary states and this state superpose state is it a eigen state of Hamiltonian. Yes, or no? No, it cannot. Okay.

So this superpose state is what you formally I am not trying to put all the quantum numbers I am calling the energy level m and energy level n. And to understand this transition you take a superpose it. And find in this state you find an expectation value of x of t, we can do that. So this is Psi* in the position place you can try to write, formally you could take r vector or r of t and do this, in one dimension you can take x because this is not a right way of writing.

If I write the volume integral as dx dy dz I should write Psi* or I should right d volume in r theta Phi coordinate and then I can put a radial coordinate expectation value, okay. X you take a radial coordinate is what I am saying here right now. Take the radial coordinate and try and work it out. The expectation value of the radial coordinate in your wave function which is a superpose wave function. Please do this yourself and see what you get. Let us now even do this.

You do a one-dimensional particle in the box just for a simplest case. Let us take a one-dimensional particle in a box take a super position of ground state and first excited state and then workout what is the expectation value of x as a function of time. X will be independent of time if the state was a stationary state, expectation value. Is that right? If expectation value is going to be dependent on time that time dependence is going to be a function of oscillatory functions of the difference between the energy levels.

This kind of tells you something. It is like some kind of a harmonic oscillator position in classical harmonic oscillator, right. You have a cos Omega t. So in sense you see that this is similar to your harmonic oscillator frequency with frequency being Em-En/h cross. Even in a one-dimensional problem. If you do it in the three-dimensional hydrogen atom problem this formally you have to write n1 l1 ml1.

And this one should be n2 l2 ml2 and then do the integration over the volume to find the radial coordinate expectation value that you can do it sitting in a hospital room you know, calmly and you can do this. Just a straightforward exercise, and basically it will depend on a cos Omega t or cos between their energy difference between those two levels. And it will be nonzero in the case of hydrogen atom problem. If delta l is + or -1 and if delta ml is 0 or + or -1.

This I want you to verify. So will you try to check? Take this ground state, so what is the ground state is 1 0 0, right. So take this ground state.

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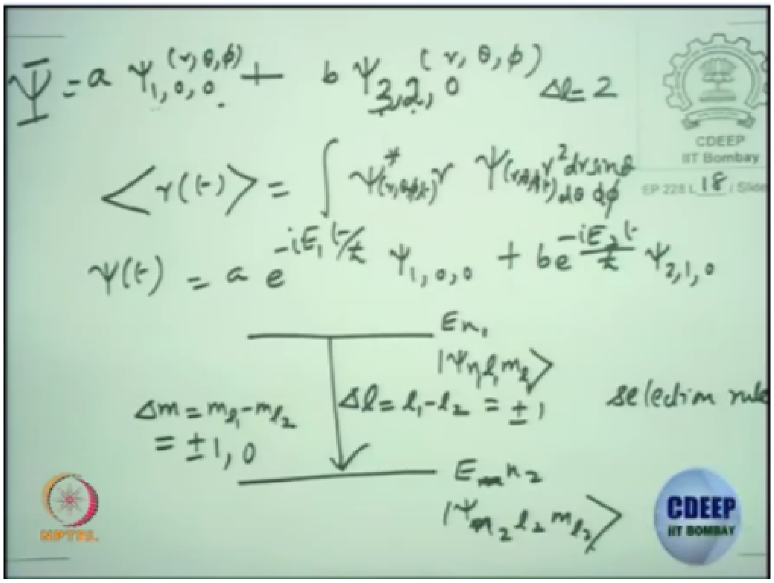

$$\Psi = a\,\psi_{1,0,0}^{(r,\theta,\phi)} + b\,\psi_{3,2,0}^{(r,\theta,\phi)} \quad \Delta l = 2$$

$$\langle r(t)\rangle = \int \psi^*_{(r,\theta,\phi,t)}\, r\, \psi_{(r,\theta,\phi,t)}\, r^2\, dr\, \sin\theta\, d\theta\, d\phi$$

$$\psi(t) = a\, e^{-iE_1 t/\hbar}\, \psi_{1,0,0} + b\, e^{-iE_2 t/\hbar}\, \psi_{2,1,0}$$

E_{n_1}

$|\psi_{n_1 l_1 m_{l_1}}\rangle$

$\Delta l = l_1 - l_2 = \pm 1$ selection rul

$\Delta m = m_{l_1} - m_{l_2} = \pm 1, 0$

E_{n_2}

$|\psi_{n_2 l_2 m_{l_2}}\rangle$

And then and take b times; take; okay which is r theta phi; r theta phi and do the expectation value of r of p which is nothing but someone call this as the superpose wave function capital Psi. Psi* r Psi then the volume will be there r square dr sine theta d theta d phi, oaky. I want to do it at t, I want to do it at r theta phi at t. What do you have to do there? You have to try to write Psi at t will be a e power –iE1 t over h cross Psi 1 0 0 + b e power –iE2 t over h cross Psi 2 1 0, is that right?

You have to substitute this here and use orthogonality everything and see whether this nonzero or 0. Similarly, you put this to be; here I think there are no other possibility, if we are taking 3 then you can check that this is not 0; this is going to be 0. If you get this state you can show that this expectation value will be; if suppose I take the ground state and this is n=3 but 1=2 what is delta l here, delta l is 2. But the selection rules tells me delta l has to be + or -1.

So for the wave function if you try to do the expectation value of the radial coordinate it will turn out to be 0 but for the earlier one which I took that is 2 1 0 it will be nonzero. You get what I am saying. So this one has to be + or -1 or 0 and this one has to be + or -1. Yeah, so it is like a harmonic oscillator position which is toggling as cos Omega t with the frequency being the difference between these two levels.

And if such a thing happens there is a radiation with that frequency which is C. This is the interpretation. Experimentally the experimental is tells us that we see only lines; if the system is prepared and they can be only that specific l n m and the n2 l2 and m2 they say that they can see transition provided l1-l2 is - or -1 and they see transition provided delta m which is + or -1 or 0.

I am asking you to mathematically verify using your orthogonality property that the expectation value of this position operator radial component of the position operator as a function of time which in general behaves like as of it is the harmonic oscillator. This is proportional to cos Omega t that is all. If that coefficient which multiplies cos Omega t is 0 then that is a justification, why such a transition was not seen in lab?

So this is what is called as a kind of stringent selection rule that from one state to another state even though the energy supposed from an excited state to the ground state even though the energy allow that it can decay and go to the ground state there may be some kind of a stringent condition in the system which will not allow it to go to that. If it goes into that state mathematics will also help me to show that expectation value of this position of the radial coordinate of this operator satisfies this condition. It is nonzero.

Okay, this is the way I try to interpret from theory what experimental is. Another way of saying is that the; there are also other conditions like the potential energy is dependent on all over r potential, right in the hydrogen atom. These are central force problems. And you can show that if you do a parity transformation; what is parity? Is to a inversion; take an r vector and make it to -r vector, that is the Hamiltonian (()) (18:48).

It is similar to your symmetric potential problem I was telling b of x = b of –x one-dimensional and what is that reflect in your wave functions that made your wave functions to be either odd functions or even functions. So there will be a similar argument here that l=0 and l=1 sorry both if this is l=0 then it is impossible for such a transition to happen because of this parity constraint. It can be seen independently.

Right now we are not doing that symmetry; I am not bringing in that symmetry but I am just saying mathematically if you an explicit integration turns out to be 0 but you can also argue by that. Okay, we will do these things. We will come to it. We will try it in a direction notation and it is very interesting to see that there are ways in which you can see the selection rules in a beautiful way. You can explicitly do that and check whether it is 0 or not just for the; okay.

So formally even in one-dimensional problem you can try to say that expectation value is proportional to this. But if you do the three-dimensional of hydrogen atom problem for the radial coordinate for a superpose state then you can try to see that there is the time dependence and it will be nonzero only if the delta l land delta ml is satisfies the selection rule. As he was trying to say suppose you take this to be 1 0 0 and 2 0 0 will just be 0 is a question.

And I want you to verify that, okay. Use the orthogonality of your associated Legendre associated Laguerre and make sure that you can verify and see whether it will be 0 or nonzero. You can see it trivially that there is the cos theta there coming up and when you do that integral sine theta cos theta d theta it will be 0, okay that you can do it yourself. Okay so this, this the evaluation can be interpreted as the displacement of an oscillator with frequency Omega.

This is what I have been trying to stress with the difference in energy between the two levels and h cross Omega is this, okay.