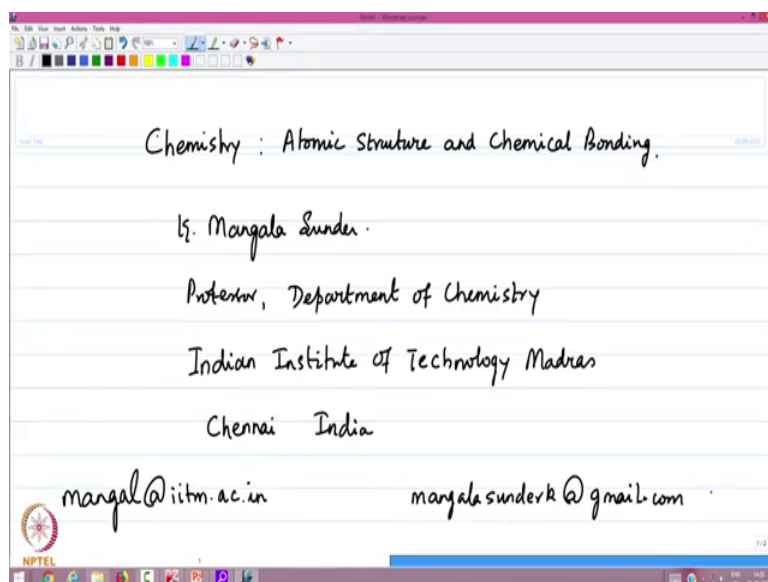


Chemistry Atomic Structure and Chemical Bonding
Prof. K. Mangala Sunder
Department of Chemistry
Indian Institute of Technology, Madras

Lecture – 36
Video Tutorial for Hermite Polynomials and Hydrogen Atom
Part 1

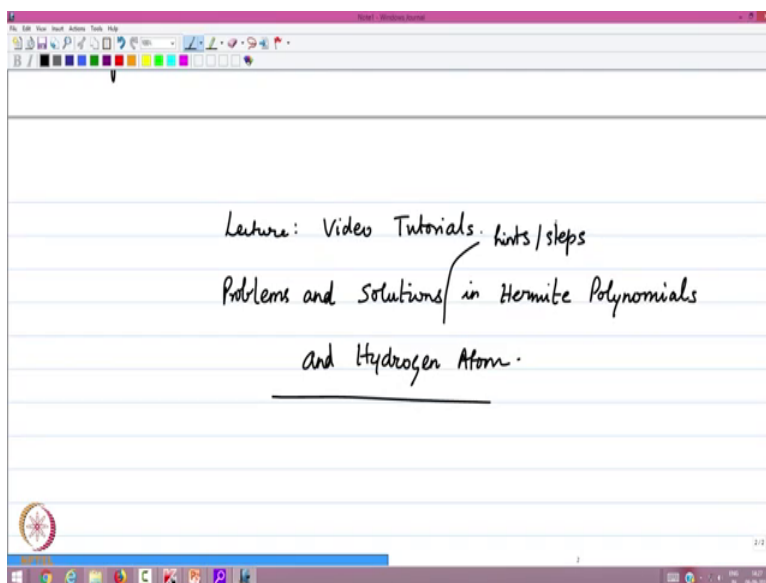
Welcome back to the lectures in Chemistry on the Atomic Structure and Chemical Bonding. My name is Mangala Sunder and I am in the Department of Chemistry in the Indian Institute of Technology Madras.

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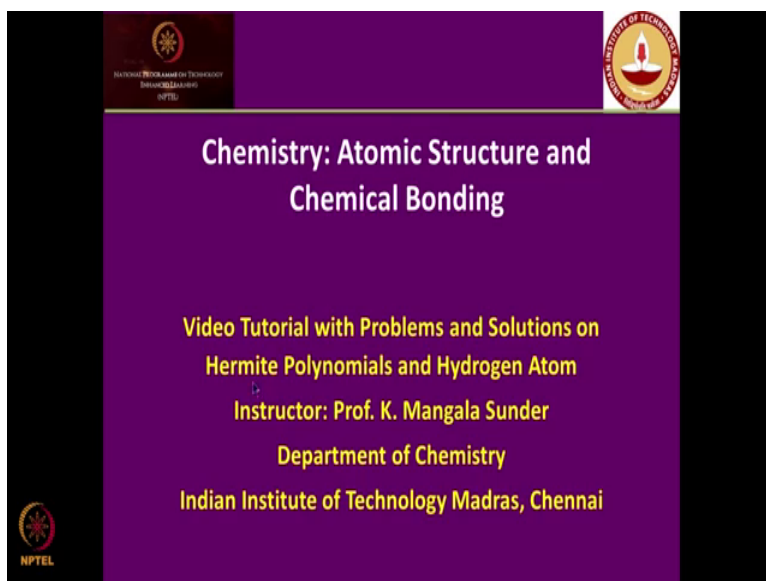
And you have my email addresses in this page. So, please feel free to contact. Now, this lecture is a tutorial lecture.

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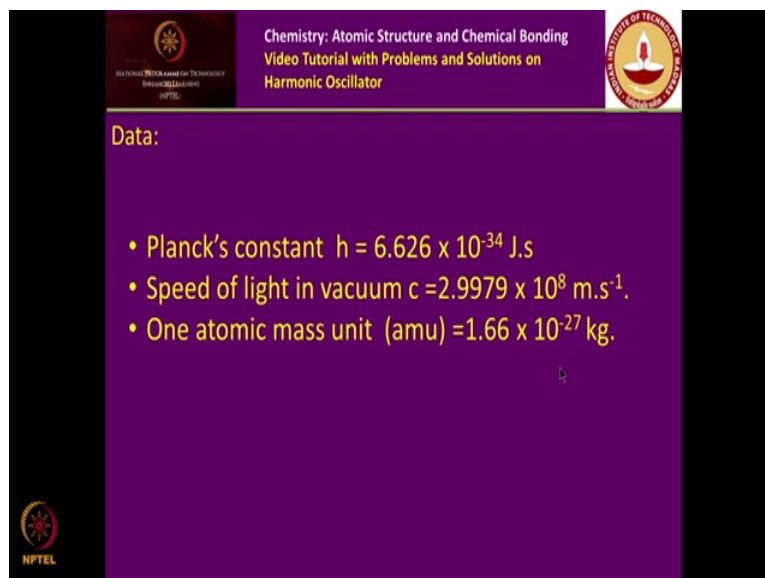
This covers some of the lecture materials of the past 2 weeks on the problems and solutions related to Hermite polynomials and hydrogen atom. Like what I have done with the previous tutorials, let me give you the problem statement first and then take you through the solutions. Very often the solutions will be also not necessarily solutions, but hints or steps. Complete solution to the last detail, I do not think I need to give you because I think you should be able to do the rest of what I leave it as fairly obvious right. So, let me start with the problem sets.

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So, this is for my polynomials and hydrogen atom ok.

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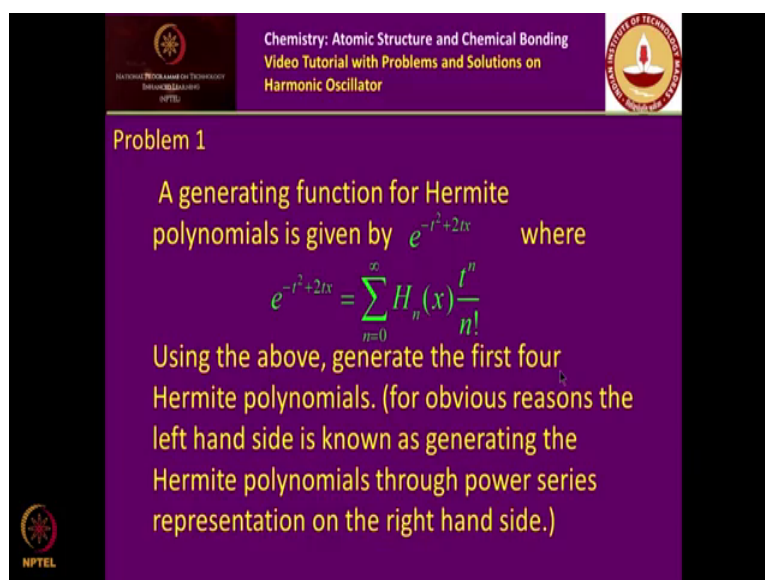
Chemistry: Atomic Structure and Chemical Bonding
Video Tutorial with Problems and Solutions on
Harmonic Oscillator

Data:

- Planck's constant $h = 6.626 \times 10^{-34}$ J.s
- Speed of light in vacuum $c = 2.9979 \times 10^8$ m.s⁻¹.
- One atomic mass unit (amu) $= 1.66 \times 10^{-27}$ kg.

So, these constants are you might use them I think in these this particular problems that I am not probably giving any numerical problem. Therefore, you may not need these things, but keep this in mind.

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Chemistry: Atomic Structure and Chemical Bonding
Video Tutorial with Problems and Solutions on
Harmonic Oscillator

Problem 1

A generating function for Hermite polynomials is given by e^{-t^2+2tx} where

$$e^{-t^2+2tx} = \sum_{n=0}^{\infty} H_n(x) \frac{t^n}{n!}$$

Using the above, generate the first four Hermite polynomials. (for obvious reasons the left hand side is known as generating the Hermite polynomials through power series representation on the right hand side.)

The very first problem is on Hermite polynomial. Now, these are all mathematical tools and I am hoping that some of you will actually do this mathematics fairly on your own and be able to derive simple expressions and become more comfortable with the

technique. Therefore, this whole tutorial may look like its nothing, but mathematics of differential equations and simply substituting in differential equations various things or calculating integrals. But, a certain amount of drudgery is really required in order for you to understand to the nitty gritty details of how to calculate things in quantum mechanics.

Therefore, in quantum chemistry particularly where you have a lot of numerical inputs that we will come later if you were to become an expert quantum chemist. So, details are given here, attention is all in the details as they always said and I have also said this many times the devil is in the details. Therefore, it is important for you to go through these carefully and understand for yourself that problems of this kind or fundamental to your stepping's I mean they are stepping stones for you are more difficult the problems in the research, in the area of research in various things.

First problem is on representing the Hermite polynomial through a generating function ok. The generating function that you see on the left hand side is an exponential minus t^2 plus $2tx$. This is an exponential function in t and the x and if you expand the left hand side in a power series, you would see it is a function of x as well as a function of t . And, this is expanded as a power series in t t raised to n by n factorial with the coefficients which are functions of x and those coefficients turn out to be the Hermite polynomials of various orders n from 0 to infinity.

So, the problem is to verify using the above use this equality and generate the first four Hermite polynomials. And, I have just given some words namely for obvious reasons the left hand side is known as generating the Hermite polynomials through a power series representation on the right hand side; that is the coefficients of the power series of Hermite polynomials ok. Now, how do we go about ok? There are two two ways of doing it: one is a Brute-force method, the other is a slightly more involved and fundamental method of Taylor series ok.

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Brute-force

$$e^{-t^2 + 2tx} = \sum_{n=0}^{\infty} H_n(x) \frac{t^n}{n!} \quad \left. \frac{d^n}{dt^n} \right|_{t=0}$$

Power series

$$e^{-x} = 1 - x + \frac{x^2}{2!} - \frac{x^3}{3!} + \frac{x^4}{4!} - \dots$$

$$e^{-(t^2 - 2tx)} = 1 - (t^2 - 2tx) + \frac{(t^2 - 2tx)^2}{2} - \frac{(t^2 - 2tx)^3}{3!} + \dots$$

$$= H_0(x) + H_1(x)t + H_2(x)\frac{t^2}{2!} + H_3(x)\frac{t^3}{3!} + \dots$$

$$H_0(x) = 1$$

First one let us do the Brute-force method and I will leave the steps in between, I am not going to fill up every gap. Please if you are solving this problem you are only getting the help to do things by yourself, $e^{-t^2 + 2tx}$ is given to you as the series. $H_n(x) t^n / n!$. Quite obviously, if you expand this as a power series right it is like you remember exponential minus x is $1 - x + x^2 / 2 - x^3 / 3! + x^4 / 4! - \dots$, that is exactly what we will do.

Therefore, this term is equal to 1 let me write that here $e^{-t^2 + 2tx}$ ok. Then it is $1 - t^2 + 2tx + (t^2 - 2tx)^2 / 2 - (t^2 - 2tx)^3 / 3! + \dots$. Let us do that for the first 2 or 3 polynomials so, that you know what is being done ok.

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The image shows a handwritten derivation in a software window. The top part shows the expansion of $e^{-(t^2-2tx)}$ as a power series: $e^{-(t^2-2tx)} = 1 - (t^2-2tx) + \frac{(t^2-2tx)^2}{2} - \frac{(t^2-2tx)^3}{3!} + \dots$. This is then equated to $H_0(x) + H_1(x)t + H_2(x)\frac{t^2}{2!} + H_3(x)\frac{t^3}{3!} + \dots$. Below this, $H_0(x) = 1$ is written. The next part identifies $H_1(x)$ as the coefficient of t , which is $2x$. Then $H_2(x)$ is identified as the coefficient of t^2 , which is $-1 + \frac{4x^2}{2} = \frac{4x^2 - 2}{2}$.

So, now we collect the this is; obviously, H_0 of x plus H_1 of x times t plus H_2 of x times t square by 2 factorial plus H_3 of x times t cube by 3 factorial plus so on that is what is given. Therefore, right away you can write H_0 of x is equal to 1 always trivial results are the first one every teacher is happy to give and as know he solves the problem really nicely. This is trivial ok; H_1 of x is the coefficient of t ok. On this side the coefficient of t , if you remember if you recall this is t square and there is no powers of t here. Because, when you expand this the smallest power of t that you will have is t square and then you will have t cube and t to the 4 and so on.

So, there is only one term namely minus of minus $2tx$ which is $2x$. So, this is H_1 H_2 of x is the coefficient of t square and now you have the coefficient of t square from the first term namely minus 1. And, you have the coefficient of t square from here which is the the term is $4tx^2$ that is what you would get. What is do t square by 2 that is what we need, is it not it? Coefficient of t square by 2. So, if you do that this 2 goes away so, what we have is plus $4x^2$ by 2 and the expression is $4x^2$ minus 2 divided by 2 ok. And, you can see that this 2 is 2 you know need them therefore; the coefficient of this term H_2 of x is $4x^2$ minus 2.

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$$H_1(x) \rightarrow \text{coeff of } t = 2x \quad \checkmark$$

$$H_2(x) = \frac{t^2}{2!} = -1 + \frac{4x^2}{2} = \frac{4x^2 - 2}{2} \quad \checkmark$$

$$H_3(x) = \frac{t^3}{3!} = \frac{-4x}{2} + \frac{8x^3}{6} = \frac{8x^3 - 12x}{6} = H_3(x)$$

$$e^{-t^2+2tx} \Rightarrow \text{Taylor Series around } t=0$$

$$f(t) = f(0) + \frac{df}{dt}\bigg|_{t=0} t + \frac{d^2f}{dt^2}\bigg|_{t=0} \frac{t^2}{2} + \frac{d^3f}{dt^3}\bigg|_{t=0} \frac{t^3}{3!} + \dots$$

$H_3(x)$ is the coefficient of t cube by 3 factorial and that if you look at here carefully there is an a minus b whole square. So, the a b here the 2 a b term will contain a t and a t square so, that is a t cube. So, what you have is minus 2 into 2 minus 4 x divided by 2. So, minus 4 x divided by 2 that is one term and the other t cube term that you can get is this 1 a minus b whole cube this term a minus b whole cube equivalent. So, there is a minus b cube which will give you and also a there is a minus sign here. So, this will give you 8 x cube by 3 factorial plus 8 x cube by 6 which will be essentially minus 8 x cube minus 12 x by 6. And therefore, you can see that the coefficient is 8 x cube minus 12 x and that is H_3 of x . So, this is a Brute-force way.

There is another nice way which is a function if it is a power series you can see this e to the minus t square by plus 2 t x ok. The function if this is treat this as a Taylor series, expand this using a Taylor series at t is equal to 0. So, if you expand any function of t as a Taylor series with around t is equal to 0 or not at around t is equal to 0, then you will have the solution $f(0)$ plus $d f$ by $d t$ evaluated at t is equal to 0 times t plus d square f by $d t$ square. Evaluated again a t is equal to 0 t square by 2 plus d cube f by $d t$ cube at t is equal to 0 divided multiplied by t cube by 3 factorial and so on.

Because, the Taylor series of any function around a point or near a point is given by the value of the function at that point and all the analytic all the derivatives which we hope or analytic and continue is whatever that is they are all they all exist. This is what is

given and now if you think of the exponential minus t square plus 2 t x as a function of t. Then when you put t is equal to 0, you will get what is left over is the function of x and that function of x is essentially the H n of x here this one ok. So, this is essentially a Taylor series where H n of x is the d of this function divided by dt, whatever is the order nth order derivative evaluated at t is equal to 0. So, then it is easy for you integrate exactly the same result namely e to the minus t square plus 2 t x.

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$$e^{-t^2+2tx} : f(0) = 1$$

$$\frac{df}{dt} \Big|_{t=0} = \left[e^{-t^2+2tx} \times (2x-2t) \right] \Big|_{t=0} = 2x = H_1(x)$$

$$\frac{d^2f}{dt^2} \Big|_{t=0} \Rightarrow \frac{d}{dt} \left[e^{-t^2+2tx} (2x-2t) \right] = \left[(2x-2t)^2 e^{-t^2+2tx} + e^{-t^2+2tx} (-2) \right] \Big|_{t=0}$$

$$= 4x^2 - 2 = H_2(x)$$

If you evaluate f of 0 that is 1 because, the exponential of 0 then d f by dt is going to give you e to the minus t square plus 2 t x times 2 x minus 2 t ok, 2 x minus 2 t. And, if you want to evaluate this at 0 then this whole function is evaluated at t is equal to 0. This becomes 1 and this becomes 2 dx. Therefore, the df by dt evaluated at t is equal to 0 is 2 x and that is the first term H 1 of x. Now, d square f by dt square we will take the derivative from this point namely d by dt of this function e to the minus t square plus 2 t x times 2 x minus 2 t because, that is already the first derivative.

And so, this will give you again 2 x minus 2 t whole square e to the minus t square plus 2 t x. And, then you have the derivative of this term which is e to the minus t square plus 2 t x times minus 2. So, this has to be evaluated at t is equal to 0 and do not evaluate at t is equal to 0 these all function. So, if you do that you know you get 2 x square which is 4 x square and you get a minus 2 everything else becomes 1 or 0. Therefore, this gives you 4 x square minus 2 and that is equal to H 2 of x.

So, now you can obviously, do this by taking the derivative successive derivatives of this function as a function of t. And, if you said that t equal to 0 whatever is the coefficient that is left over is this one. These are essentially d raise to f d to the power yeah d n f dt n evaluated at t is equal to 0 (Refer Time: 14:15) right. So, this is the other method ok, as you learn more and more you try to be more and more efficient and quick in doing Brute-force is the last thing that you do. If you know no other method yes go ahead, use the Brute-force method. Now, let us go to the second problem.

(Refer Slide Time: 14:37)

The slide is titled "Chemistry: Atomic Structure and Chemical Bonding" and "Video Tutorial with Problems and Solutions on Harmonic Oscillator". It features the NPTEL logo and the IIT Bombay logo. The main content is as follows:

Problem 2
 A generating function for Laguerre polynomial is given by (where l is zero)

$$L_n(x) = \frac{e^x}{n!} \frac{d^n}{dx^n} (x^n e^{-x}), \quad n = 1, 2, 3, \dots$$

a. Generate the first four Laguerre polynomials.
 b. Using the results and the identity

$$L_n^l(x) = (-1)^l \frac{d^l}{dx^l} (L_{n+1}(x)), \quad l = 1, 2, 3, \dots, n-1$$

Generate the first few radial functions, 2p, 3s, 3p and 3d.

Second problem is now on Laguerre polynomials which was which were provided to you as a solution to the radial part of the hydrogen atom. I have circulated in the lecture notes, a fairly elaborate set of notes on the hydrogen atom. And, somewhere in the middle of the lecture set of 30-35 pages you can see the Laguerre polynomials being given.

Now, we have a simple mathematical tool for calculating the Laguerre polynomials or evaluating them. And, this is a generating function that I have given here for the Laguerre polynomial. But, now we assume that you remember in the case of hydrogen atom the Laguerre polynomial has to indices n and L . Here we have the Laguerre polynomial with L equal to 0, the first expression it is again repeated derivative of a function. And, this use this to generate the first three or four polynomials. Why do we

need that? We need that to calculate the actual hydrogen atom Laguerre polynomials, that we have obtained in the earlier lecture notes.

The $L_{n,l}$ in our case n is the principal quantum number from the hydrogen atom, L is the asymmetry orbital angular the angular momentum quantum number and l can take a maximum value of n minus 1 and the minimum value of 0. Therefore, the Laguerre polynomials for any n we have n Laguerre polynomials. So, if n is 1 n is 2 there are 2, if n is 3 there are 3 that is given by this expression. So, and that uses the L_{n+1} of x which calc is calculated from the previous step again it is purely algebraic resolved ok, let us look at that.

(Refer Slide Time: 16:27)

The image shows a screenshot of a software window with a white background and a blue border. The window title is "MS Paint". The content is handwritten in black ink on a grid background. It starts with "Problem 2" followed by the general formula for the Laguerre polynomial: $L_n(x) = \frac{e^x}{n!} \frac{d^n}{dx^n} (x^n e^{-x})$. Below this, it shows the calculation for $L_0(x) = 1$. Then for $L_1(x)$, it shows $L_1(x) = \frac{e^x}{1!} \frac{d}{dx} (x e^{-x}) = e^x [e^{-x} - x e^{-x}] = (1-x)$. Finally, it shows the formula for $L_2(x) = \frac{e^x}{2!} \frac{d^2}{dx^2} (x^2 e^{-x})$. The window has a standard Windows taskbar at the bottom with various application icons and a system tray on the right.

Problem 2, let us first calculate the 3 or 4 L_n of x and L_n of x is the exponential x divided by n factorial times d^n derivative with respect to x of the function x raise to n e to the minus x . So, L_0 of x so, derivative is identity 1 $n=0$ therefore, this is x raise to n n is 0. Therefore, L_0 of x gives you 1 L_1 of x is the first derivative, but of this function e raise to x by 1 factorial n is 1 d by dx and $x e$ to the minus x which will give you e to the $x e$ to the minus x minus x times e to the minus x . So, that of course, the exponential cancels out so, it is $1 - x$. L_2 of x will be e raise to x divided by 2 factorial d^2 by dx^2 of the function $x^2 e$ to the minus x . Therefore, we will take the derivative 2 derivatives.

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$$= \frac{e^x}{2} \frac{d}{dx} [2xe^{-x} - x^2 e^{-x}] = \frac{e^x}{2} [2e^{-x} - 2xe^{-x} + x^2 e^{-x} - 2xe^{-x}]$$

$$= \frac{1}{2} [2 - 4x + x^2]$$

$$L_3(x) = \frac{1}{6} [6 - 18x + 9x^2 - x^3]$$

L_1, L_2, L_3

$$L_n^l(x) \quad n=1, l=0$$

So, it is e^x times $\frac{d}{dx}$ of $2xe^{-x} - x^2e^{-x}$. So, if we take this one more derivative $\frac{d}{dx}$ of $2e^{-x} - 2xe^{-x} + x^2e^{-x} - 2xe^{-x}$ that is all from here. And, then you have 2 derivative two terms from this one minus plus x^2e^{-x} minus $2xe^{-x}$ raise to minus x .

So, this will give you this is a minus $2x$ here minus $2x$ here. So, it is minus $4x$ and that is a 2 there is an x^2 . So, what you have is $\frac{1}{2} [2 - 4x + x^2]$ exponential x and minus x cancel out. These are $2 - 4x + x^2$ this is L_2 , one more derivative L_3 of x I would leave it to you to actually get the form. And, let me write down the final answer L_3 of x is given by $\frac{1}{6} [6 - 18x + 9x^2 - x^3]$.

Basically, you have to take the derivative of $n!$ $\frac{d^3}{dx^3} x^3 e^{-x}$ that is what we have to do. So, it is a repeated application of differentiation ok. Use these L_1, L_2 and L_3 to get the next function L_{n+1} of x . So, if $n=1$ in our case $l=0$. Therefore, if we have to use the L_{n+1} expression recall that the expression for L_{n+1} of x is $(-1)^{n+1} \frac{d^{n+1}}{dx^{n+1}} x^{n+1} e^{-x}$.

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$$L_n^l(x) = (-1)^l \frac{d^l}{dx^l} L_{n+l}^l(x) \quad l=0 \quad n=1$$

$$L_1^0(x) = L_1(x) = 1-x$$

$$L_2^0 \quad L_2^1 \quad l=0, 1$$

$$l=0 \quad L_2^0 = L_2(x)$$

$$L_2^1 = (-1) \frac{d}{dx} L_3(x) = (-1) [-18 + 18x - 3x^2]$$

$$L_2^1 = 18 - 18x + 3x^2$$

So, if l is 0 and n is 1 then you have L_1 of x ok, I do not even want write L_0 of x because L_0 is the raise there is no L anyway. So, the first one for which L is can be mentioned is the n equal to 1. So, that will be when l is 0 this is 1 and this is there is no derivative. And therefore, L_1 of x 0 is L_1 ok. And L_1 is what? 1 minus x , which is 1 minus x ok. If you do n L_2 then there are two functions, L_2 of 0 and L_2 of 1.

So, you have l values equal to 0 and 1. So, let us do the case l equal to 0 which is L_2 of 0, you know immediately that this is going to give you nothing other than the original L_2 of x . So, also there you can see there because, if this l is 0 this l is also 0. So, what you have is L_n 0 is the same as L_n x ok. Now, L_2 of 1 is minus 1 d by dx of since, n is 2 and l is 1 this is L_3 of x . So, L_3 of x we have calculated already take the derivative of this and you will get minus 18 plus 18 x , you get minus 1 times minus 18 plus 18 x and then you have minus 3 x square c 2 plus 3 x square. So, what you have is L_2 of 1 gives you 18 minus 18 x plus 3 square.

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Chemistry: Atomic Structure and Chemical Bonding
Video Tutorial with Problems and Solutions on
Harmonic Oscillator

Problem 3
Verify for the first few polynomials, the identity

$$\left(2x - \frac{d}{dx}\right)^n 1 = H_n(x)$$

The next problem is the follows is again on the Hermite polynomial, were now you write the Hermite polynomial using the operation of this power with the differential inside on identity 1 ok. This will give you $H_n(x)$; again it is only to be verified by a simple application of the algebraic calculations.

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$$\left(2x - \frac{d}{dx}\right)^n 1 = H_n(x)$$

$$H_1(x): \left(2x - \frac{d}{dx}\right) 1 = 2x = H_1(x)$$

$$H_2(x) = \left[2x - \frac{d}{dx}\right] \left[2x - \frac{d}{dx}\right] 1 \quad \left[2x - \frac{d}{dx}\right] 2x = 4x^2 - 2 = H_2(x)$$

$$H_3(x) = \left[2x - \frac{d}{dx}\right] \left[2x - \frac{d}{dx}\right] \left[2x - \frac{d}{dx}\right] 1 \Rightarrow \left[2x - \frac{d}{dx}\right] (4x^2 - 2)$$

$$= 8x^3 - 4x - 8x = 8x^3 - 12x = H_3(x)$$

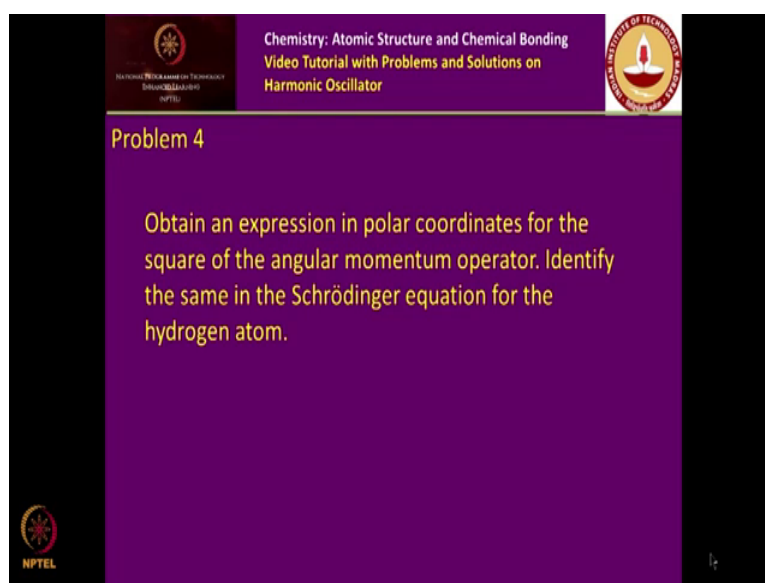
So, let us do that the $2x - \frac{d}{dx}$ raised to n acting on 1 is $H_n(x)$. So, when n is 0 of course, H_0 is 1. So, let us not consider $H_1(x)$ of x $H_1(x)$ is $2x - \frac{d}{dx}$ on 1 which will give you of course, $\frac{d}{dx}$ on 1 is 0. So, it gives you $2x$ and therefore, that

is H_1 of x . H_2 of x is basically $2x$ minus d by dx operating on $2x$ minus d by dx on 1 ; remember n is 2 . Therefore, when you have operators like this with the raise to power it means essentially operating them one after the other.

So, here you know that this will give you $2x$ from the previous result. Therefore, now you have $2x$ minus d by dx acting on $2x$ gives you $4x$ square minus 2 and that is equal to $H_2 x$. So, now it is quite clear what you should do for H_3 and others is basically repeated application of this derivative $2x$ minus d by dx $2x$ minus d by dx and $2x$ minus d by dx on 1 .

So, I think you have seen this it is already $4x$ square minus 2 therefore, you have $2x$ minus d by dx on $4x$ square minus 2 . It gives you $8x$ cube 2 gives you $2x$ on $4x$ square gives you $8x$ cube, $2x$ on minus 2 gives you minus $4x$ and the d by dx 1 minus $4x$ square gives you another $8x$. So, that it gives you $8x$ cube minus $12x$ and that is H_3 of x . So, likewise you can carry this calculation for higher order polynomials.

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The image shows a slide from a video tutorial. At the top, there are logos for NPTEL (National Programme on Technology Enhanced Learning) and IIT Bombay. The text on the slide reads: "Chemistry: Atomic Structure and Chemical Bonding Video Tutorial with Problems and Solutions on Harmonic Oscillator". Below this, the slide is titled "Problem 4" and contains the text: "Obtain an expression in polar coordinates for the square of the angular momentum operator. Identify the same in the Schrödinger equation for the hydrogen atom." The slide has a purple background with white and yellow text.

Problem 4, this is a fairly involved problem. I think it is important that we use spherical polar coordinates for the hydrogen atom, but now the circle polar coordinates should be used to get the angular momentum, the orbital angular momentum operator in the case of hydrogen. Obtain an expression in polar coordinates for the square of the angular momentum operator. Identify the same in the Schrodinger equation for the hydrogen atom. There are second step is very important.

In fact, precisely the angular term is nothing, but L^2 where L is the moment of inertia for the electron in the hydrogen atom. And, that L^2 operator is what we are going to get through this problem ok. Now, is this somewhat long. So, let us try and do this slowly, but the algebraic steps are again fairly clear if you know differentiation and integration and you have been following the lectures.

(Refer Slide Time: 26:03)

The image shows a handwritten note on a digital whiteboard. At the top, it defines the angular momentum vector \vec{L} as the cross product of the position vector \vec{r} and the momentum vector \vec{p} . Below this, the three Cartesian components are given: $L_x = -i\hbar(y\frac{\partial}{\partial z} - z\frac{\partial}{\partial y})$, $L_y = -i\hbar(z\frac{\partial}{\partial x} - x\frac{\partial}{\partial z})$, and $L_z = -i\hbar(x\frac{\partial}{\partial y} - y\frac{\partial}{\partial x})$. A bracket on the right side of these three equations is labeled "Cyclical".

$$\vec{L} = \hat{x}L_x + \hat{y}L_y + \hat{z}L_z \quad \vec{r} \times \vec{p}$$

$$L_x = -i\hbar \left(y \frac{\partial}{\partial z} - z \frac{\partial}{\partial y} \right)$$

$$L_y = -i\hbar \left(z \frac{\partial}{\partial x} - x \frac{\partial}{\partial z} \right)$$

$$L_z = -i\hbar \left(x \frac{\partial}{\partial y} - y \frac{\partial}{\partial x} \right)$$

Cyclical

So, the angular momentum is obviously, given in Cartesian coordinates as the x component angular momentum L_x plus L_y plus L_z and it is $\vec{r} \times \vec{p}$ in the classical definition. And, you can write up therefore, L_x is minus $i\hbar$ when \vec{p} is replaced by you have minus $i\hbar$ $\frac{d}{dx} \frac{d}{dy} \frac{d}{dz}$. Then L_x will be $y \frac{d}{dz} - z \frac{d}{dy}$ and L_y is minus $i\hbar$ $z \frac{d}{dx} - x \frac{d}{dz}$.

Then the L_z is minus $i\hbar$ $x \frac{d}{dy} - y \frac{d}{dx}$. It is easy to remember, this is cyclical $yzzxxyzyxzyx$ and ok. Now, you should remember from recall from the lecture notes and also the previous lectures that the derivative $\frac{d}{dx}$ in spherical polar coordinates is given by this expression $\sin\theta \cos\phi \frac{d}{dr} + \cos\theta \cos\phi \frac{1}{r} \frac{d}{d\theta} - \sin\phi \frac{1}{r \sin\theta} \frac{d}{d\phi}$.

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The image shows a handwritten derivation on a digital notepad. It contains the following equations:

$$\frac{\partial}{\partial x} = \sin\theta \cos\phi \frac{\partial}{\partial r} + \frac{\cos\theta \cos\phi}{r} \frac{\partial}{\partial \theta} - \frac{\sin\phi}{r \sin\theta} \frac{\partial}{\partial \phi}$$

$$\frac{\partial}{\partial y} = \sin\theta \sin\phi \frac{\partial}{\partial r} + \frac{\cos\theta \sin\phi}{r} \frac{\partial}{\partial \theta} + \frac{\cos\phi}{r \sin\theta} \frac{\partial}{\partial \phi}$$

$$\frac{\partial}{\partial z} = \cos\theta \frac{\partial}{\partial r} - \frac{\sin\theta}{r} \frac{\partial}{\partial \theta}$$

$$L_x = -i\hbar \left(y \frac{\partial}{\partial z} - z \frac{\partial}{\partial y} \right)$$

Below these equations, the Cartesian coordinates are defined in terms of spherical coordinates:

$$x = r \sin\theta \cos\phi$$

$$y = r \sin\theta \sin\phi$$

$$z = r \cos\theta$$

And, likewise for the operators $\frac{\partial}{\partial y}$ is $\sin\theta \sin\phi \frac{\partial}{\partial r} + \frac{\cos\theta \sin\phi}{r} \frac{\partial}{\partial \theta} + \frac{\cos\phi}{r \sin\theta} \frac{\partial}{\partial \phi}$. And, the last one $\frac{\partial}{\partial z}$ is $\cos\theta \frac{\partial}{\partial r} - \frac{\sin\theta}{r} \frac{\partial}{\partial \theta}$. So, these are expressions which were derived and they are given in the lecture notes, in accompanying this course and we will use this to write the L_z for example, which is $-i\hbar \left(y \frac{\partial}{\partial z} - z \frac{\partial}{\partial y} \right)$.

Now, let me not to L_z L_z is slightly longer and the final result is extremely simple. So, $2 L_x$ I think L_x is simpler $-i\hbar \left(y \frac{\partial}{\partial z} - z \frac{\partial}{\partial y} \right)$. And, remember in polar coordinates x is $r \sin\theta \cos\phi$, y is $r \sin\theta \sin\phi$ and z is $r \cos\theta$ that is the polar coordinate expression.

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$$\begin{aligned}
 & -i\hbar \left[r \sin\theta \sin\phi \left(\cos\theta \frac{\partial}{\partial r} - \frac{\sin\theta}{r} \frac{\partial}{\partial \theta} \right) \right. \\
 & \quad \left. - r \cos\theta \left(\sin\theta \sin\phi \frac{\partial}{\partial r} + \frac{\cos\theta \sin\phi}{r} \frac{\partial}{\partial \theta} + \frac{\cos\phi}{r \sin\theta} \frac{\partial}{\partial \phi} \right) \right] \\
 & = -i\hbar \left(-\sin\phi \frac{\partial}{\partial \theta} - \cot\theta \cos\phi \frac{\partial}{\partial \phi} \right) \\
 L_y & = -i\hbar \left(\cos\phi \frac{\partial}{\partial \theta} - \cot\theta \sin\phi \frac{\partial}{\partial \phi} \right) \\
 L_z & = -i\hbar \frac{\partial}{\partial \phi} \quad \left(x \frac{\partial}{\partial y} - y \frac{\partial}{\partial x} \right)
 \end{aligned}$$

Therefore, you simply have to multiply the x y derivative terms. So, the first term is minus i h bar r sin theta sin phi it is y dou by dou z sin phi sins cos theta dou by dou r minus sin theta by r dou by dou theta minus y by. So, the other one is z d by dy therefore, minus r cos theta times sin theta sin phi dou by dou r plus cos theta sin phi by r dou by dou theta. And, plus cos phi by r sin theta dou by dou theta and dou by dou phi ok, this is what it is.

You can simplify it and cancel the terms for example, it is gets cancelled and then that is also a sin square term this is sin square theta term r sin phi r cancels out. So, it is sin phi sin square theta and this sin phi cos square theta with a both the domain are same therefore, they add up to give you 1. So, the final result is minus i h bar minus sin phi by dou by dou theta times minus cot theta cos phi dou by dou phi right just do this algebra.

In a similar way you can get L y to be minus i h bar cos phi dou by dou theta minus cot theta sin phi dou by dou phi. So, this is what I meant when I said L z is very very simple it is minus i h bar dou by dou phi. But the cancellation of the terms will happen when your substitute L z as x dou by dou y minus y dou by dou x do that right, you will get this too.

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The image shows a handwritten derivation on a whiteboard. At the top, it lists the components of angular momentum: $L_x^2 + L_y^2 + L_z^2$ and $(L_x)(L_x) + (L_y)(L_y) + L_z(L_z)$. Below this, the total angular momentum squared is given as $L^2 = -\hbar^2 \left[\frac{1}{\sin\theta} \frac{\partial}{\partial\theta} \left(\sin\theta \frac{\partial}{\partial\theta} \right) + \frac{1}{\sin^2\theta} \frac{\partial^2}{\partial\phi^2} \right]$. The next part is labeled 'Hamiltonian!' and shows
$$-\frac{\hbar^2}{2m_e} \left[\frac{1}{r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial}{\partial r} \right) + \frac{1}{r^2 \sin\theta} \frac{\partial}{\partial\theta} \left(\sin\theta \frac{\partial}{\partial\theta} \right) + \frac{1}{r^2 \sin^2\theta} \frac{\partial^2}{\partial\phi^2} \right] - \frac{Ze^2}{4\pi\epsilon_0 r}$$

So, this is $L_x^2 + L_y^2 + L_z^2$ therefore, to do L^2 you do exactly what was done in the lecture notes again; $L_x^2 + L_y^2 + L_z^2$ has repeated application of L_x on L_x plus L_y on L_y plus L_z on L_z . And, when you do that and add on these terms which takes probably about half an hour to an hour. The answer that you get L^2 is $-\hbar^2 \left[\frac{1}{\sin\theta} \frac{\partial}{\partial\theta} \left(\sin\theta \frac{\partial}{\partial\theta} \right) + \frac{1}{\sin^2\theta} \frac{\partial^2}{\partial\phi^2} \right]$ ok.

Now, this is not something new this is exactly what you have as the angular part. Please remember the hydrogen atom Hamiltonian, we call that there is a radial part and there is an angular part. The radial part is $-\frac{\hbar^2}{2m_e} \left[\frac{1}{r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial}{\partial r} \right) + \frac{1}{r^2 \sin\theta} \frac{\partial}{\partial\theta} \left(\sin\theta \frac{\partial}{\partial\theta} \right) + \frac{1}{r^2 \sin^2\theta} \frac{\partial^2}{\partial\phi^2} \right]$ plus the potential energy term $-\frac{Ze^2}{4\pi\epsilon_0 r}$.

This is all that you have minus you had this potential energy term that $-\frac{Ze^2}{4\pi\epsilon_0 r}$. Now, identify these terms whatever that you calculated so far, the term that you calculated L^2 is $-\hbar^2 \left[\frac{1}{\sin\theta} \frac{\partial}{\partial\theta} \left(\sin\theta \frac{\partial}{\partial\theta} \right) + \frac{1}{\sin^2\theta} \frac{\partial^2}{\partial\phi^2} \right]$ ok. And, that is $-\hbar^2 \left[\frac{1}{\sin\theta} \frac{\partial}{\partial\theta} \left(\sin\theta \frac{\partial}{\partial\theta} \right) + \frac{1}{\sin^2\theta} \frac{\partial^2}{\partial\phi^2} \right]$ plus the $-\frac{Ze^2}{4\pi\epsilon_0 r}$; the only $-\frac{Ze^2}{4\pi\epsilon_0 r}$ is common. In fact, the $-\hbar^2$ is also gone. So, what is left over is $2m_e r$.

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The image shows a handwritten equation for the Hamiltonian H of a hydrogen atom, written in a presentation software window. The equation is:

$$H = -\frac{\hbar^2}{2m_e r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial}{\partial r} \right) + \frac{L^2}{2m_e r^2} - \frac{Ze^2}{4\pi\epsilon_0 r}$$

The term $\frac{L^2}{2m_e r^2}$ is circled in red. Below it, the expression $+\frac{L^2}{2I}$ is written, where I represents the moment of inertia.

So, essentially the term hydrogen atom function contains the Hamiltonian contains a radial R dependent part the derivative. But, its I mean that is like that out minus \hbar square by $2 m_e r$ square dou by dou $r r$ square dou by dou r and then you have minus L square by $2 m_e r$ square. This is nothing, but I the moment of inertia of the electron moving around the nucleus at a radial distance of r and then you have this potential energy is a Ze square by $4 \pi \epsilon_0$ dot r ok.

So, you see that the angular momentum is right here in the angular part of the hydrogen atom. It is L square by minus L square by $2 I$ sorry, it is not minus L squared it is plus this is the minus \hbar square so, it is plus right L square by $2 I$. So, this is the association of the angular momentum with a hydrogen atom. And therefore, you can see that the rotational part as well as the distance in the radial part of the hydrogen atom or both coupled to each other. So, this is the problem number 4 ok. Let us do one more problem before we stop at this tutorial and then continue the same tutorial as part 2 in the next half. So, let us finish the last next one which is also a somewhat involved problem I believe.

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Chemistry: Atomic Structure and Chemical Bonding
Video Tutorial with Problems and Solutions on
Harmonic Oscillator

Problem 5

Verify the relations

$$L^2 Y_l^m(\theta\phi) = \hbar^2 l(l+1) Y_l^m(\theta\phi) \text{ and}$$

$$L_z Y_l^m(\theta\phi) = \hbar m Y_l^m(\theta\phi)$$

for the first few spherical harmonics.

You know it is not involved ok, it is it is very simple it says it verify the relations the L square operator, we just discussed acting on the spherical harmonics $Y_{l m}(\theta, \phi)$ which we already know of a solutions is just a verification that the $Y_{l m}$'s are actually the eigen functions of the L square and the L z operator. And, give you the eigenvalues $\hbar^2 l(l+1)$ from the L square operator and $\hbar m$ for the L z operator ok.

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$$L_z Y_l^m(\theta\phi) \Rightarrow \Phi(\phi) e^{im\phi} f(\theta) \times N_{l,m}$$

$$-i\hbar \frac{\partial}{\partial \phi} Y_l^m(\theta\phi) \Rightarrow -i\hbar \frac{\partial}{\partial \phi} e^{im\phi} = \hbar m e^{im\phi}$$

$$L^2 Y_1^0(\theta) = \hbar^2 2 Y_1^0(\theta) \quad Y_1^0 \sim \cos\theta$$

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

$$= 2\hbar^2 \cos\theta = 2\hbar^2 Y_1^0$$

Now, simple things first L z is the simple thing first, L z operator on $Y_{l m}(\theta, \phi)$ ok. Remember all $Y_{l m}(\theta, \phi)$ in the function the phi dependence is only $e^{im\phi}$,

the rest of it is function of theta and some normalization constants, some normalization constants which depend on l and m . Therefore, the L_z operator being minus $i\hbar$ $\frac{d}{d\phi}$, the only action of this operator on $Y_{l,m}(\theta, \phi)$ will be only to do this minus $i\hbar$ $\frac{d}{d\phi}$ on $e^{im\phi}$.

Because, the other part is theta part not affected by this and this gives you right away minus i into plus i and $\hbar m$ and it gives you $im\phi$. And, that is exactly what you have in the tutorial $\hbar m Y_{l,m}$ this is to right away. But, for its very very elementary and there should not be any confusion about that. What about the L^2 ? I will do it for a simple case, L^2 on say $Y_{1,0}$ because, we will again ignore the theta the the phi part because, anyway it is going to give exactly the same result if you put the phi part in.

This is supposed to give the final result since L is 1 and the m is 0 this is suppose to give $\hbar^2 L(L+1) Y_{1,0}$ and it should give you $Y_{1,0}$. As per this relation l is 1 therefore, L^2 on $Y_{1,0}$ this is not m dependent, it is \hbar^2 into 2 ok. Well, see $Y_{1,0}$ is some constant times $\cos\theta$ the constant appears on both sides so, we do not need to do that. So, we will simply write $Y_{1,0}$ as the $\cos\theta$ ok. Therefore, the operator that you have to worry about is $1 - \frac{d^2}{d\theta^2}$ of $\cos\theta$ that is the $Y_{1,1} - Y_{1,0}$. The other term which is $1 - \frac{d^2}{d\phi^2}$ will not change the $\cos\theta$ there will be 0.

Therefore, we do not need it, this is the only thing and therefore, we can evaluate this immediately as $1 - \frac{d^2}{d\theta^2}$ and this gives you minus $\sin^2\theta$. So, it gives you minus $\sin^2\theta$ and also there is a minus \hbar^2 , oh sorry minus \hbar^2 . So, it gives you a minus \hbar^2 and you can see immediately $\frac{d^2}{d\theta^2} \cos\theta$ gives you a $\sin\theta \cos\theta$ there is a 2. So, it gives you minus into minus plus. So, it is $2\hbar^2 \cos\theta$, the $\sin\theta$ cancels off. And therefore, it is $2\hbar^2 Y_{1,0}$, easy.

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$$\begin{aligned} \sin\theta e^{i\phi} &\sim Y_l^m \\ \mathcal{L}^2 Y_l^m &\sim -\hbar^2 \left[\frac{1}{\sin\theta} \frac{\partial}{\partial\theta} \left(\sin\theta \frac{\partial}{\partial\theta} \right) + \frac{1}{\sin^2\theta} \frac{\partial^2}{\partial\phi^2} \right] \sin\theta e^{i\phi} \\ e^{i\phi} &\left\{ -\hbar^2 \frac{1}{\sin\theta} \frac{\partial}{\partial\theta} (\sin\theta \cos\theta) + \frac{\hbar^2}{\sin\theta} (-1) e^{i\phi} \right\} \\ &= \frac{-\hbar^2}{\sin\theta} (-\sin^2\theta + \cos^2\theta) - \frac{\hbar^2}{\sin\theta} (-1) \\ &= 2\hbar^2 \sin\theta e^{i\phi} = 2\hbar^2 Y_l^m \end{aligned}$$

Same thing you can do for the sin theta e raise to i phi which is Y 1 1 ok. The idea of doing both of them is that because, the derivative will contain both the theta part and phi part. So, if it is L square on Y 1 1, this is the same as minus h bar square 1 by sin theta dou by dou theta of sin theta dou by dou theta plus 1 by sin square theta dou square by dou phi square on this function sin theta e raise to i phi. So, the first term does not contain the e raise to i phi. Therefore, that is unaffected and the rest of it will give you minus h bar square 1 by sin theta dou by dou theta sin theta of this will give you cos theta. So, we have dou by dou theta of sin theta cos theta and the other term we will the sin theta will cancel out.

So, you will have 1 by sin theta and the dou square by dou phi square on it the i phi will give you minus 1 e right; this is what we will get. And, there is a minus h bar square also here as we decided to take it outside; we have we have done it therefore, it is inside. So, now you can simplify this and you will see that this gives you and you simply canceled this off take this derivative this is cos theta is minus sin theta. So, it is minus sin square theta and sin theta gives you cos square theta. So, it gives you plus cos square theta.

So, (Refer Time: 42:10) to be multiplied by minus h bar square by sin theta and you already have a minus h bar square by sin theta times minus 1. So, you can see that 1 minus cos square theta is sin square theta so, you will get 2 sin theta. So, eventually when you do the algebraic simplification this gives you 2 h bar square sin theta e to the i

ϕ which is nothing other than $2\hbar^2 Y_{11}$. So, L^2 on Y_{11} gives you $L(L+1)\hbar^2 Y_{11}$. So, the same thing can be verified for all the spherical harmonics which are listed all over the textbooks. And, also in the Wikipedia you can find out the spherical harmonics given up to l equal to 9 and so on.

In chemistry we do not need to worry so, much about l equal to 9. In the case of atomic orbitals because l equal to 3 is the last we have, f orbitals this is the most we have on the atoms. But, for reaction dynamics and for microwave spectroscopy and various other places you will need a very high value of n . Therefore, spherical harmonics are extremely important and manipulation of spherical harmonics and the simple differential equations integrals all these things, we will give you some comfort and confidence that you can face the formal mathematical tools quite efficiently. The purpose of these tutorials is to basically tell you that there is really nothing hard, you have to just sit down and learn things the way they have to be learned and there is no short circuiting the whole thing.

You have to sit down and do the problems, if you want to understand quantum mechanics. I have tried to help you as much as I can, we will continue this part of the video tutorial in the next set with the remaining 3 or 4 problems. And, until I provide the solutions the video tutorials are available on the website. I would request all of you to actually try that on your own and then later compare your results with what I provided our solutions.

Until then thank you very much.