

Basic Quantum Mechanics
Prof. Ajoy Ghatak
Department of Physics
Indian Institute of Technology, Delhi

Module No. # 05
The Angular Momentum – I
Lecture No. # 02
The Angular Momentum Problem (Contd.)

In the previous lecture, we had, we was we were discussing the solution of the Legendre's equation; so we will continue our discussion on the Angular Momentum Problem.

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$$(1-x^2) \frac{d^2 F}{dx^2} - 2x \frac{dF}{dx} + \lambda F(x) = 0$$

$$F(x) = [a_0 + a_2 x^2 + \dots] + [a_1 x + a_3 x^3 + a_5 x^5 + \dots]$$

$$\frac{a_{r+2}}{a_r} = \frac{r(r+1) - \lambda}{(r+2)(r+1)} \rightarrow 1$$

$$\lambda = l(l+1) \quad l = 0, 1, 2, 3, \dots$$

$$\lambda = 6 \quad (l=2)$$

$$\frac{a_{r+2}}{a_r} = \frac{r(r+1) - 6}{(r+2)(r+1)}; \quad \frac{a_2}{a_0} = \frac{-6}{2} = -3$$

$$\frac{a_4}{a_2} = 0$$

$$P_2(x) = a_0 [1 - 3x^2]$$

So, in my last lecture, we had started, we had considered the solution of the differential equation $d^2 F$ by dx^2 minus $2x$ dF by dx plus λF of x , where λ is the Eigen value. We solved this by a power series method and we showed that the solution of the above differential equation can be written as, it can be split into two series a_0 plus $a_2 x^2$ plus $a_4 x^4$ plus $a_1 x$ plus $a_3 x^3$ plus $a_5 x^5$ and so on. And

that a $r+2$ divided by a r was equal to r into $r+1$ minus λ divided by $r+2$ into $r+1$, this is the recurrence relation that we had discussed last time.

Now, since this tends to 1 as r tends to infinity, so if the series remains an infinite series it will diverge at x equal to plus minus 1, we cannot let that happen, because the wave function has to be always finite. And so therefore, we must terminate the series or make it into a polynomial. Either the series will become a polynomial, only when λ is equal to $l(l+1)$, where l can be 0, 1, 2, 3, etcetera. And we will show just now, that when l is 0, 2, 4, etcetera the even series will become a polynomial and the odd series will be an infinite series.

So, there are always for a second order differential equation, there are always two solutions. And we will show that for these values of l one of the solutions is a polynomial. In general both solutions are divergent at x is equal to plus minus 1 only for certain specific values of λ will one of the solutions be well behaved and will be a polynomial. And the other series will again be ill behaved at x equal to plus minus 1 and when l is 1, 3, 5, etcetera then, this series will become a polynomial the odd series will become a polynomial, the even series will remain an infinite series and therefore, a 0 we must put it equal to 0.

So, in my last lecture I had assumed l is equal to 2, so λ was 6 and if λ was 6 then a $r+2$ divided by a r will be r into $r+1$ minus 6 divided by $r+2$ multiplied by $r+1$ and we had obtained that a 2 by a 0, that is $r=0$, so this is equal to minus 6 by 2 that is equal to minus 3 and a 4 by a 2; so $r=2$ into 3 is 6, so this is equal to 0.

So, my polynomial solution becomes which is given by.

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l is 2, so we write it as $P_2(x)$, because this implies λ equal to 6 implies l is equal to 2, so $P_2(x)$ this is equal to $a_0 + a_1x + a_2x^2$, we now choose the coefficient a_0 , such that the $P_2(1)$ is 1.

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$\lambda = 6$
 $P_2(1) = 1$
 $a_0 = -\frac{1}{2}$
 $a_1 = 0$
 $\ell = 3$ $\lambda = 1$ when $\lambda = 6$

$$\frac{a_{r+2}}{a_r} = \frac{r(r+1)-6}{(r+2)(r+1)}$$
 The odd series will be an infinite series
 $a_1 = 0$
 $\frac{a_3}{a_1} = \frac{2-6}{6} = -\frac{4}{6}$
 $\frac{a_5}{a_3} = \frac{+6}{5 \times 4}$ $\frac{a_7}{a_5} = \frac{24}{\dots}$

And therefore, we write P_2 of x will become half 3 x square minus 1 that is a $((0))$ to satisfy this condition we must choose a_0 is equal to minus half. So, this is the polynomial solution and we must choose a_1 equal to 0, so that the odd series is not there therefore, for λ is equal to 6 for λ is equal to 6 this is the P_2 of x is the well behaved solution of this.

Now, let me consider another example, say we take ℓ is equal to 3 ℓ is equal to 3, so then λ will become 12 sorry before that I must I must show that, if I take λ is equal to 6 I again use the recurrence relation a_{r+2} divided by a_r is equal to $r(r+1)-6$ divided by $(r+2)(r+1)$ and we will show that the odd series remains an infinite series.

Let us, see this way just look at as look at the numerator, so a_3 by a_1 , so r is 1, so 1 into 1 plus 1 is 2 2 minus 6 that is 2 minus 6 and this becomes 3 into 2 that is 6, so this is minus 4 by 6 a 5 by a 3 this becomes r is 3. So, 3 into 4 is 12 minus 6 that is 12 minus 6 is plus 6 divided by r is 3 3 plus 2 is 5 5 into 4, whatever it is you see it has changed sign minus to plus, then if I calculate a_7 by a_5 that will be also positive a 's, so r is 5, so 30 minus 6 30 minus 6 will be 24 divided by something.

So, none of the coefficients will become 0, so therefore, when when λ is 6 the odd series the odd series will be an infinite series infinite series and hence we must choose a

1 equal to 0 therefore, P this is the well behaved solution corresponding to lambda equal to 6.

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$l = 3 \quad \lambda = l(l+1) = 12$

$$\frac{a_{r+2}}{a_r} = \frac{r(r+1) - 12}{(r+2)(r+1)}$$

Even series will remain an ∞ series & $a_0 = 0$

$$\frac{a_2}{a_0} = \frac{-12}{2} = -6$$

$$\frac{a_4}{a_2} = \frac{-6}{4 \times 3}$$

$$\frac{a_6}{a_4} = \frac{+8}{6 \times 5}$$

$$\frac{a_3}{a_1} = \frac{-10}{3 \times 2} = -\frac{5}{3}$$

$$\frac{a_5}{a_3} = 0$$

$$a_7 = a_9 = \dots = 0$$

$$F(x) = a_1 \left(x - \frac{5}{3}x^3\right) \quad a_1 F(1) = 1$$

Let this take another example and let me say, let me assume l is equal to 3 then lambda is equal to l into l plus 1, so that is equal to 12 once again let me do this a_{r+2} divided by a_r this becomes r into r plus 1 minus 12 divided by r plus 2 into r plus 1. Now let me take the even series first, so let me write it write down a_2 by a_0 so r is 0, so this is minus 12 multiplied by 2; so this is minus 6. a_4 by a_2 , so r is 2 2 into 3 is 6 that is minus 6 divided by 2 plus 2 is 4 into 3 whatever that number is it is a negative number.

And then a_6 by a_4 r is 4, so this because 4 into 5 that is 20 minus 12 that is plus 8 and therefore, this is 6 into 5; so this has changed sign and therefore, for lambda equal to 12 the even series will remain an infinite series an infinite series and therefore, we must choose a_0 equal to 0.

Now let me choose, let me consider the odd series let me consider the odd series let me write down a_3 by a_1 , so r is 1 so this becomes 1 into 2 that is 2 minus 12 is minus 10 1 plus 2 is 3 1 plus 1 is 2; so 3 into 2 is 6, so this becomes minus 5 by 3 and then a_5 by a_3 . So, r is 3 so this becomes 3 into 4 12 minus 12, so that is 0 and therefore, a_7 equal to a_9 they all will be equal to 0.

So, you will have if the polynomial solution will be F of x is equal to a $1x$ plus a 3 by a 1 that is minus 5 by $3x$ cubed, I choose the coefficient a 1 such that F of 1 is 1 and therefore, we will obtain the Legendre polynomial.

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$$P_5(x) = \frac{1}{2} (5x^3 - 3x) \quad a_1 = -\frac{1}{2}$$

$$P_5(1) = 1$$

$$(1-x^2) \frac{d^2 F}{dx^2} - 2x \frac{dF}{dx} + \lambda F(x) = 0$$

$$\lambda = \ell(\ell+1)$$

$$= 0, 2, 6, 12, 20, \dots$$

$$P_0(x) = 1 \quad ; \quad P_1(x) = x$$

$$P_2(x) = \frac{1}{2}(3x^2 - 1) \quad ; \quad P_3(x) = \frac{1}{2}(5x^3 - 3x)$$

$$P_4(x) = \dots \quad P_5(x) = x^5 \dots$$

So, if I choose the coefficient a 1 such that it is 1 therefore, P_5 by of x becomes $5x$ cubed minus $3x$ divided by 2 , so **I** I should chose a 1 is equal to minus a half then you can see that P_5 of 1 is 1 .

So therefore, **therefore**, to summarize we have found that the **the** Legendre's equation 1 minus x square $d^2 F$ by dx^2 minus $2x$ dF by dx plus λF of x is equal to 0 , it always has two solutions. But, in general both solutions diverge at x equal to plus minus 1 , only when λ is equal to 1 into 1 plus 1 that is λ is equal to 0 , if it is 1 and 2 1 is 2 then it is 6 , 1 is 3 it is 12 , 1 is 4 it is 20 , only when λ is takes these of the values, then one of the series becomes a polynomial and the polynomial solution is the polynomials is known as the Legendre polynomials.

And you have when ℓ is 0 you have P_0 of x which is 1 P_1 of x which is just x , we have determined P_2 of x from first principles and that is half $3x$ square minus 1 and P_3 of x we have just now determined equal to half $5x$ cube minus $3x$. Similarly, we can calculate P_4 of x which will be an even series with highest power of x as x to the power of 4 and P_5 of x the highest power will be x to the power of 5 and so on.

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$$(1-x^2) \frac{d^2 F}{dx^2} - 2x \frac{dF}{dx} + \ell(\ell+1)F(x) = 0 \quad \ell = 0, 1, 2, \dots$$

$$P_\ell(x) \int_{-1}^{+1} P_\ell(x) P_{\ell'}(x) dx = 0 \quad \ell \neq \ell'$$

$$= \frac{2}{2\ell+1} \delta_{\ell\ell'}$$

$$\delta_{\ell\ell'} = 1 \quad \ell = \ell'$$

$$\delta_{\ell\ell'} = 0 \quad \ell \neq \ell'$$

$$\psi_\ell(x) = \sqrt{\frac{2\ell+1}{2}} P_\ell(x)$$

$$\int_{-1}^{+1} \psi_\ell(x) \psi_{\ell'}(x) dx = \delta_{\ell\ell'}$$

$$-1 \leq x \leq +1 \quad f(x) = \sum_{\ell=0,1,2,\dots}^{\infty} c_\ell \psi_\ell(x)$$

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So, alternately we will have **even** even polynomial and the odd polynomial, these are the polynomial solutions of the Legendre's equation; so therefore, the Legendre's equation is I write it down once again $1 - x^2 \frac{d^2 F}{dx^2} - 2x \frac{dF}{dx} + \ell(\ell+1)F(x) = 0$ I write this down directly ℓ into $\ell+1$ $F(x)$ these are the Eigen values, so ℓ takes 0, 1, 2, etcetera and **and** I leave as an exercise for you to find out the when ℓ is 0 then this term is 0.

And the determination of the solution is extremely simple I would like all of you to find out the two independent solution of this particular equation, so the **two** one of the independent solutions will diverge and the other solution is the Legendre polynomials P_ℓ of x , which are alternately involved odds powers of x and even powers of x . These Legendre polynomials in the domain plus and minus 1, they satisfy the following normality, orthogonality condition that is minus 1 to plus 1 $P_\ell(x)$ and multiplied by $P_{\ell'}(x) dx$ is equal to 0, if ℓ is not equal to ℓ' and if ℓ is equal to ℓ' , then this becomes $\frac{2}{2\ell+1}$.

So, I can write this down as $\delta_{\ell\ell'}$, but $\delta_{\ell\ell'}$ is the kronecker delta symbol, which is equal to 1 if ℓ is equal to ℓ' is 0 if ℓ is not equal to ℓ' . And therefore, we can define the normalized wave function $\psi_\ell(x)$ as $\sqrt{\frac{2\ell+1}{2}} P_\ell(x)$, they form a complete set of orthonormal functions in the domain x lying between plus 1 and minus 1 the orthonormality condition is minus 1 to plus 1 $\psi_\ell(x)$ and $\psi_{\ell'}(x)$ is equal to $\delta_{\ell\ell'}$.

of x , actually if I take the complex conjugate it is the same function, so ψ_l of x dx is equal to $\delta_{ll'}$.

And any arbitrary well behaved function, say f of x can be expanded in the domain $-1 < x < 1$ as $\sum c_n \psi_l$ of x this is something like as Fourier series where l goes from $0, 1, 2, 3$ to infinity; any well behaved function can be expanded and the coefficient c 's of n can be determined by using the orthonormality condition of the Legendre polynomials.

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$$L^2 Y = \lambda \hbar^2 Y(\theta, \phi) \quad \ell = 0, 1, 2, \dots$$

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

$$L_z = -i\hbar \frac{\partial}{\partial \phi} \quad m = 0$$

$$\Phi(\phi) = \frac{1}{\sqrt{2\pi}} e^{im\phi} \quad m = 0, \pm 1, \pm 2, \dots$$

$$\lambda = \ell(\ell+1)$$

$$L^2 Y_{\ell, m}(\theta, \phi) = \ell(\ell+1) \hbar^2 Y_{\ell, m}(\theta, \phi)$$

$$L_z Y_{\ell, m}(\theta, \phi) = m \hbar Y_{\ell, m}(\theta, \phi) \quad m = -\ell, \dots, +\ell$$

So therefore, we had solve the problem, we **we** started out by trying to find out the Eigen values and Eigen functions of L^2 , we said that first **first** we said that we wrote down this is equal to $\lambda \hbar^2 Y(\theta, \phi)$. We first showed that the, to summarize $Y(\theta, \phi)$, the ϕ dependence the θ dependence if I write as F of θ , then the ϕ dependence will be Φ of ϕ . And Φ of ϕ is the normalized function was $1/\sqrt{2\pi} e^{im\phi}$, m equal to 0 plus minus 1 plus minus 2 .

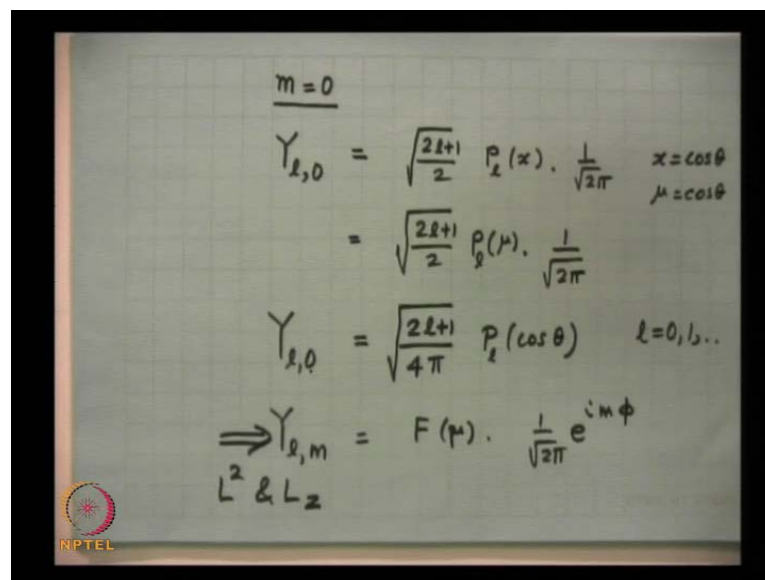
Then we consider the m equal to 0 case and we converted this equation **into a** into the Legendre equation and we found that for m equal to 0 , λ was equal to $l(l+1)$. Actually if one solves this equation directly and we will do that slightly later after about ten lectures, we will do that **that** the Eigen values of L^2 is always $l(l+1)$, so the Eigen functions are denoted by $Y_{lm}(\theta, \phi)$ these are known as the spherical

harmonics the expressions for which we will derive little later l into $l + 1$ \hbar cross's square $Y_{lm}(\theta, \phi)$.

You must remember, these formulae and Y_{lm} are such that its ϕ dependence is of this form and therefore, these are also Eigen functions of the operator L_z as we had discussed earlier, $Y_{lm}(\theta, \phi)$ is equal to $m \hbar$ cross $Y_{lm}(\theta, \phi)$, you may recall that the operator representation of L_z was equal to minus \hbar cross $\frac{\partial}{\partial \phi}$ we had derived this and since the ϕ dependences of this form therefore, L_z operating on $Y_{lm}(\theta, \phi)$ is equal to $m \hbar$ cross. Further we will also show that for a given value of l , m lies between minus l to plus l so when l is 2, so when l is 2 m will be minus 2, minus 1, 0, plus 1, plus 2 and we will discuss this in greater detail after about 4, 5 lectures.

So, these are known as spherical harmonics, **these are known as spherical harmonics** and they are simultaneous Eigen functions of the operator L^2 and L_z , the Eigen values of L^2 is $l(l+1) \hbar^2$, where l takes the values 0, 1, 2, 3, etcetera and the Eigen values of L_z are $m \hbar$.

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The image shows a handwritten derivation on a grid background. At the top, it says $m=0$. Below that, the spherical harmonic $Y_{l,0}$ is expressed as a Legendre polynomial $P_l(x)$ multiplied by a normalization factor $\frac{1}{\sqrt{2\pi}}$. It then shows the substitution $x = \cos \theta$ and $\mu = \cos \theta$. The final result for $Y_{l,0}$ is given as $\sqrt{\frac{2l+1}{4\pi}} P_l(\cos \theta)$ for $l=0, 1, 2, \dots$. Below this, it states $\Rightarrow Y_{l,m} = F(\mu) \cdot \frac{1}{\sqrt{2\pi}} e^{im\phi}$ for L^2 and L_z . An NPTEL logo is visible in the bottom left corner.

$$\begin{aligned}
 m=0 \\
 Y_{l,0} &= \sqrt{\frac{2l+1}{2}} P_l(x) \cdot \frac{1}{\sqrt{2\pi}} \quad x = \cos \theta \\
 & \quad \mu = \cos \theta \\
 &= \sqrt{\frac{2l+1}{2}} P_l(\mu) \cdot \frac{1}{\sqrt{2\pi}} \\
 Y_{l,0} &= \sqrt{\frac{2l+1}{4\pi}} P_l(\cos \theta) \quad l=0, 1, 2, \dots \\
 \Rightarrow Y_{l,m} &= F(\mu) \cdot \frac{1}{\sqrt{2\pi}} e^{im\phi} \\
 & \quad L^2 \text{ \& } L_z
 \end{aligned}$$

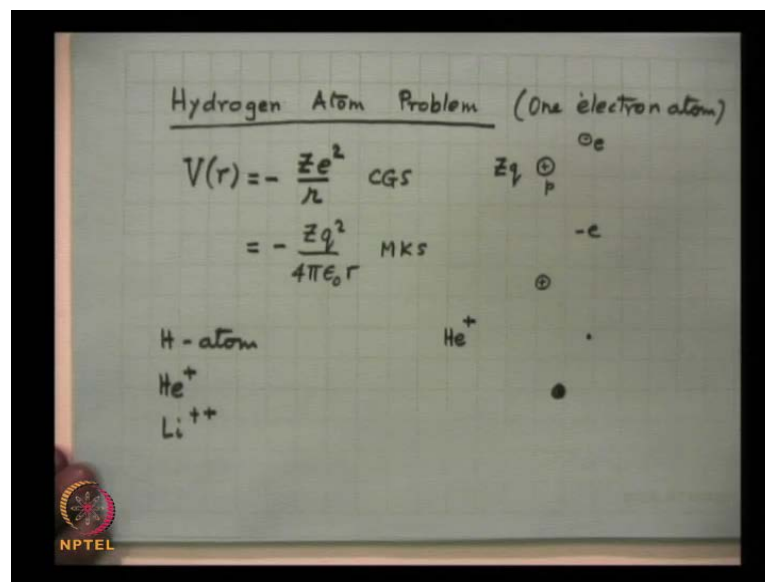
So, what we have already determined if for m equal to 0 **m equal to 0** for that $Y_{l,0}$ when m is 0, then we have shown that these are the **these are the** Legendre polynomials so we have the normalized Legendre polynomials are $\sqrt{\frac{2l+1}{2}} P_l(x)$; remember that x here is not the x, y, z coordinate but, it is $x = \cos \theta$, in fact I think it is better to write $\mu = \cos \theta$, so that not to confuse within the x coordinate.

So, Y_{10} we will write as $2l + 1$ by $2P_l$ of $\cos \theta$, that is μ multiplied by the when m is 0 then the ϕ part is just 2π ; and the θ part is just 2π , so this will become this is a the spherical harmonic $2l + 1$ by $4\pi P_l$ of $\cos \theta$.

So, there are two formulae that we have found out, one that l is 1 at l equal to 0 Y_{10} are this we have derived from first principles l is 0, 1, 2, 3, etcetera l is equal to 0 1 2 3 etcetera we have also shown that Y_{lm} is equal to $F \times F$ of θ or μ multiplied by 1 over $\sqrt{2\pi}$ $e^{im\phi}$ and these are simultaneous Eigen function of L^2 operator and L_z .

So, that completes the angular momentum problem, we will once we introduce the bra and ket algebra, we will find out the complete solution to the problem and will give you a recipe for calculating almost any spherical harmony. But, at the moment we have just solved for the m equal to 0, case but, we will do the general case little later may be about 5, 7 lectures later, so with this understanding of the angular momentum problem we now go ahead to solve the hydrogen atom problem.

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So, we will solve the hydrogen atom problem the simplest atomic problem and also we will solve the deuteron problem which consists of a neutron and a proton, as we all know that the hydrogen atom actually consists of two particles, one is the negatively charged particle and the other is this is the electron and this is the proton. But, the force between the the potential energy between this two depends only on the magnitude of the distance

between the two. In this case if we use the CGS system of units, so then this is $z e$ square by r , if you are using MKS system of units then this is $z e$ is the charge of the proton, charge of the nucleus, so in the case of **in the case of** hydrogen atoms z is 1, so you have $z q$ square by $4 \pi \epsilon_0 r$.

So, this in the MKS units, this in the CGS units where we are considering the hydrogen like atom problem, so we have either one proton and one electron or we can have z protons and only one electron; something like helium ionized helium **helium** ion **ion** so we have a nucleus which consists of **which consists of** two protons and two neutrons and only one electron. So, we are actually considering a **one electron problem** one electron atom, so that is the hydrogen atom or the singly ionized helium atom or doubly ionized lithium atom or something, whichever has one electron circulating it.

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The image shows a handwritten derivation on a piece of paper. At the top, the Hamiltonian is given as $H = \frac{p_1^2}{2m_1} + \frac{p_2^2}{2m_2} + V(|\vec{r}_1 - \vec{r}_2|)$. Below this, the Schrödinger equation is written as $H\Psi(\vec{r}_1, \vec{r}_2) = E\Psi(\vec{r}_1, \vec{r}_2)$. The positions \vec{r}_1 and \vec{r}_2 are defined as (x_1, y_1, z_1) and (x_2, y_2, z_2) respectively. The derivation then shows the expansion of the Laplacian operator in Cartesian coordinates, leading to the equation $-\frac{\hbar^2}{2m_1} \left[\frac{\partial^2}{\partial x_1^2} + \frac{\partial^2}{\partial y_1^2} + \frac{\partial^2}{\partial z_1^2} \right] \Psi - \frac{\hbar^2}{2m_2} \left[\frac{\partial^2}{\partial x_2^2} + \frac{\partial^2}{\partial y_2^2} + \frac{\partial^2}{\partial z_2^2} \right] \Psi + V\Psi = E\Psi$. Finally, the wave function is separated into the product of two single-particle wave functions: $\Psi(\vec{r}_1, \vec{r}_2) = \psi_1(\vec{r}_1) \psi_2(\vec{r}_2)$.

Now, since we have two particles it is really a two body problem **it is a two body problem**, so we write down the Hamiltonian the total energy is p^2 square by $2m$ this is the kinetic energy of the electron, this is the kinetic energy of the proton or of the nucleus plus the potential energy. Now, we assume which is true in the case of the hydrogen atom, but the potential energy depends only on the magnitude of the distance between the two particles this is known as a central force model.

That is here is the proton and here is the electron, the potential energy depends only on the magnitude of the distance between these two, so if the proton I write down the

coordinates as x_1, y_1, z_1 this is the \mathbf{r}_1 vector, whose coordinates are x_1, y_1, z_1 and the electron has the coordinate say \mathbf{r}_2 vector whose coordinates are x_2, y_2 and z_2 ; then the potential energy depends only on the magnitude of the distance between these two as it is indeed the case for the coulomb potential.

So, our objective, what is our objective? Objective is to solve the Schrödinger equation, now it is a function of 6 coordinates, so I abbreviate this and write this as \mathbf{r}_1 , \mathbf{r}_2 this is equal to e times ψ of \mathbf{r}_1 , \mathbf{r}_2 ; where \mathbf{r}_1 vector is an abbreviation for x_1, y_1, z_1 and \mathbf{r}_2 vector is an abbreviation for x_2, y_2, z_2 . So, we are really considering 6 coordinates 3 of the electron and 3 of the proton, how to solve this?

[illegible]

Now, I leave this as an exercise for you to prove that if I try to separate the variables like this $\psi(r_1, r_2)$ like this say $\psi_1(r_1)$ and $\psi_2(r_2)$ if I assume the separation of variables like this and if I substitute it with this equation, because the potential energy function depends only on the magnitude of the distance. The variables will not separate out **the variables will not separate out** and therefore, the method of separation of variables will not work **the method of separation of variables will not work.**

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$$\vec{r} = \vec{r}_1 - \vec{r}_2 \Rightarrow \begin{aligned} x &= x_1 - x_2 \\ y &= y_1 - y_2 \\ z &= z_1 - z_2 \end{aligned}$$

COM coordinates

$$\vec{R} = \frac{m_1 \vec{r}_1 + m_2 \vec{r}_2}{m_1 + m_2}; \quad X = \frac{m_1 x_1 + m_2 x_2}{m_1 + m_2}$$

$$Y = \dots$$

$$Z = \dots$$

$$\frac{\partial^2 \Psi}{\partial x_1^2}; \quad \frac{\partial \Psi}{\partial x_1} = \frac{\partial \Psi}{\partial x} \cdot \frac{\partial x}{\partial x_1} + \frac{\partial \Psi}{\partial x} \cdot \frac{\partial x}{\partial x_1}$$

$$= \frac{\partial \Psi}{\partial x} + \frac{m_1}{m_1 + m_2} \frac{\partial \Psi}{\partial x}$$

And therefore, in order to solve this equation, we have to introduce the relative coordinate **the relative coordinate** is represented by r which is $r_1 - r_2$ this means that we introduce the relative coordinate x as $x_1 - x_2$ y as $y_1 - y_2$ and z as $z_1 - z_2$, small z these are known as the relative coordinates. And then we also introduce the center of mass coordinates **the center of mass coordinates** and this I reply write as R is equal to $m_1 r_1 + m_2 r_2$ divided by $m_1 + m_2$, so therefore, the x coordinate of that which I denote by capital X , that will be $m_1 x_1 + m_2 x_2$ divided by $m_1 + m_2$ and similarly, y and similarly, z .

So, instead of the coordinates $x_1, y_1, z_1, x_2, y_2, z_2$, these are 6 coordinates we write down we **we** try to transform the equation in terms of the these 6 coordinates small x small y small z and capital X , capital Y , capital Z and please see small x and capital X involve only x_1 and x_2 , small y and capital Y only involve y_1 and y_2 and small z and capital Z only involve z_1 and z_2 , so that makes life much simpler and let me **let me** do a little bit of algebra.

So, we have to calculate something like $\frac{\partial^2 \Psi}{\partial x_1^2}$, so first we must calculate what is $\frac{\partial \Psi}{\partial x_1}$, so if I transform this, so I will get $\frac{\partial \Psi}{\partial x_1}$ by $\frac{\partial \Psi}{\partial x} \times \frac{\partial x}{\partial x_1} + \frac{\partial \Psi}{\partial x} \times \frac{\partial x}{\partial x_1}$ by $\frac{\partial x}{\partial x_1}$. Now I need not consider $\frac{\partial \Psi}{\partial y}$, because $\frac{\partial \Psi}{\partial y}$ by $\frac{\partial x}{\partial x_1}$ will be 0, because x only x and x depend only on x_1 and x_2 , so what is $\frac{\partial x}{\partial x_1}$

so that is 1, so we will have delta psi by delta x plus delta x by x 1 is m 1 divided by m 1 plus m 2 divided delta psi by delta x. Now, I want to I want to obtain this, so you will you had to differentiate this once again, so let me do this carefully, so we will have, let me do this carefully.

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$$\begin{aligned} \frac{\partial^2 \Psi}{\partial x_1^2} &= \frac{\partial}{\partial x} \left(\frac{\partial \Psi}{\partial x} \right) + \frac{\partial}{\partial x} \left(\frac{\partial \Psi}{\partial x} \right) \frac{m_1}{m_1 + m_2} \\ &+ \frac{m_1}{m_1 + m_2} \left[\frac{\partial}{\partial x} \left(\frac{\partial \Psi}{\partial x} \right) \frac{\partial x}{\partial x_1} + \frac{\partial^2 \Psi}{\partial x^2} \cdot \frac{m_1}{m_1 + m_2} \right] \\ &= \frac{\partial^2 \Psi}{\partial x^2} + \frac{\partial^2 \Psi}{\partial x \partial x} \cdot \frac{2m_1}{m_1 + m_2} + \left(\frac{m_1}{m_1 + m_2} \right)^2 \frac{\partial^2 \Psi}{\partial x^2} \\ \cancel{\frac{m_1}{m_1 + m_2}} \frac{\partial^2 \Psi}{\partial x_1^2} &= \frac{\partial^2 \Psi}{\partial x^2} + \frac{\partial^2 \Psi}{\partial x \partial x} \frac{2m_1}{m_1 + m_2} + \left(\frac{m_1}{m_1 + m_2} \right)^2 \frac{\partial^2 \Psi}{\partial x^2} \end{aligned}$$

So, delta 2 psi by delta x 1 square, will be now if I differentiate this, so you will have delta by delta x times delta psi by delta x delta x by delta x 1 which was 1 plus delta by delta x of delta psi you have to do it little patiently, multiplied by delta x capital X by x 1 and that we have just now found to be m 1 by m 1 plus m 2 plus the second term.

So, you will have m 1 by m 1 plus m 2, first I differentiate this term with respect to x, so again delta by delta x of delta psi by delta x times small delta of x divided by delta x 1 this is 1, this is unity plus delta by delta x 2 psi by delta x square and then delta x by delta x 1 that is m 1 by m 1 plus m 2, little cumbersome but, very straightforward.

So, you write this as this is equal to delta 2 psi by delta x square plus delta 2 psi by delta x x delta x times 2 m 1 by this term and this term will add up and 1 plus m 2; and then this will be m 1 by m 1 plus m 2 whole square, so m 1 by m 1 plus m 2 whole square delta 2 psi by delta capital X square.

Now, as you have seen that I must multiply this by minus h cross's square by 2 m 1, so if I multiply this by minus h cross's square by 2 m 1, so I will obtain minus h cross's

square by $2m_1 \Delta^2 \psi$. Let me **let me** write down **let me write down** first this equation that $\Delta^2 \psi$ by Δx^2 square if I, so we will obtain the same expression excepting there will be a minus sign here. So, $\Delta^2 \psi$ by Δx^2 square plus I instead of plus sign here we will have a minus sign, that is because Δx by Δx^2 is minus 1. So, this equation tells us that Δx by Δx^2 is 1 but, Δx by Δx^2 is minus 1 (Refer slide time: 39:39), because of that you will have a minus sign here, $\Delta^2 \psi$ by Δx^2 square $2m_2$ by m_1 plus m_2 plus m_2 by m_1 plus m_2 whole square and the same term $\Delta^2 \psi$ by Δx^2 square.

So therefore, the now, I multiply the first equation by minus \hbar^2 cross square by $2m_1$ and the second equation by minus \hbar^2 cross's square by $2m_2$, if I do that the you will get the following result.

(Refer Slide Time: 40:44)

$$-\frac{\hbar^2}{2m_1} \frac{\partial^2 \psi}{\partial x_1^2} - \frac{\hbar^2}{2m_2} \frac{\partial^2 \psi}{\partial x_2^2}$$

$$= -\frac{\hbar^2}{2} \left(\frac{1}{m_1} + \frac{1}{m_2} \right) \frac{\partial^2 \psi}{\partial x^2}$$

$$\frac{1}{\mu} = \frac{1}{m_1} + \frac{1}{m_2}$$

$$= -\frac{\hbar^2}{2\mu} \frac{\partial^2 \psi}{\partial x^2} = -\frac{\hbar^2}{2M} \frac{\partial^2 \psi}{\partial x^2}$$

So, you will obtain **you will obtain** minus \hbar^2 cross's square by $2m_1 \Delta^2 \psi$ by Δx^2 square plus minus \hbar^2 cross's square by $2m_2 \Delta^2 \psi$ by Δx^2 square has to be little careful. So, the first two terms add, so you get minus \hbar^2 cross's square by $2 \left(\frac{1}{m_1} + \frac{1}{m_2} \right)$ and you see I divide by m_1 here and I divide by m_2 here and this minus this will become 0, so this term the cross term will cancel out and the second term will therefore, be if I divide by m_1 .

So, it will be minus m_1 and from this it will be m_2 , so m_1 plus m_2 divided by m_1 plus m_2 whole square $\Delta^2 \psi$ by Δx square capital **i'm sorry** this I forgot to write here $\Delta^2 \psi$ by Δx square.

So, if I add these two terms then I will finally, obtain this the reduced mass of two particles is defined by $1/\mu$ is defined to be equal to $1/m_1$ plus $1/m_2$. So therefore, this equation becomes minus \hbar cross's square by 2μ $\Delta^2 \psi$ by Δx square and this becomes minus, I forgot to, so minus \hbar cross's square by 2 capital M $\Delta^2 \psi$ by Δx square.

Similarly, for the y dependent term and the z dependent term and therefore, we finally, obtain, so the second so to this we must add $\Delta^2 \psi$ by Δy square $\Delta^2 \psi$ by Δz square and here we must add $\Delta^2 \psi$ by Δy square plus $\Delta^2 \psi$ by Δz square.

(Refer Slide Time: 43:37)

The image shows a handwritten derivation of the Schrodinger equation for two particles. The equations are written on a grid background:

$$H\Psi = E\Psi$$

$$-\frac{\hbar^2}{2m_1} \left(\frac{\partial^2}{\partial x_1^2} + \frac{\partial^2}{\partial y_1^2} + \dots \right) - \frac{\hbar^2}{2m_2} \left(\frac{\partial^2}{\partial x_2^2} + \dots \right) + V\Psi = E\Psi$$

$$-\frac{\hbar^2}{2\mu} \left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} \right) \Psi - \frac{\hbar^2}{2M} \left(\frac{\partial^2}{\partial X^2} + \dots \right) \Psi + V\Psi = E\Psi(\vec{r}, \vec{R})$$

$\uparrow V(r)$

Method of Separation of Variables

$$\Psi(\vec{r}, \vec{R}) = \psi(\vec{r}) \Phi(\vec{R})$$

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Therefore, the Schrodinger equation **schrodinger equation** which was \hbar psi is equal to E psi and if you remember this was minus \hbar cross's square by $2m_1$ **2 m 1** Δ^2 by Δx 1 square plus Δ^2 by Δy 1 square plus Δ^2 by Δz 1 square minus \hbar cross's square by $2m_2$ Δ^2 by Δx 2 square plus Δ^2 by Δy 2 square plus Δ^2 by Δz 2 square plus V into psi is equal to E psi.

Now, we had shown we had we have just, now calculated this and we have found that these **these** 6 terms become from here minus \hbar^2 cross's square by 2μ Δ^2 by Δx square, this is the relative coordinate Δ^2 by Δy square plus Δ^2 by Δz square ψ minus \hbar^2 cross's by $2m$ Δ^2 by ΔX square plus Δ^2 by ΔY square plus Δ^2 by ΔZ 's square ψ plus $V\psi$ is equal to $E\psi$. Now this V depends only on r and what is r^2 x^2 plus y^2 plus z^2 square under the root it does not depend on capital X , capital Y , capital Z .

So, now we assume that the ψ is a function of small r vector and capital R vector and if we now use the method of separation of variables if we now use the method of separation of variables. And assume that ψ of r comma R is equal to ψ of r and say ϕ of R capital and if I substitute it here, because the potential energy function. Now depends only on small r the variables will separate out and that is a major simplification of the problem for any two body problem in which the potential energy function depends only on the distance between the two particles can always be reduced to this; and as we will show just now, one will describe one of the equations will describe the uniform translational motion of the atom as a whole like a free particle and the second term will describe the internal energies of the hydrogen atom.

Now, this will be true even for the electron proton problem which is the simplest problem in nuclear physics, if we assume that the potential energy between the neutron and proton depends only on the distance between the two particles. Then that particular problem which involve the Schrodinger equation involves six coordinates can be transformed to two equations, one describing the internal motion of the deuteron and the second is the uniform translational motion of this of the nucleus as a whole.

So, in the hydrogen atom problem we transform this to two coordinates, one was the relative coordinate and the other was the central mass coordinates, so the hydrogen atom as a whole as a free particle moved as I will show in a minute moves as a whole and then there are internal motions between the electron and the internal motions of the atom which will lead to the discrete states. But, that they are the mass has to be replaced by the reduced mass; in the case of the hydrogen atom problem, since the proton is very much heavier than the electron the reduced mass is almost the mass of the electron but, in neutron proton problem, where the mass of neutron is almost equal to the mass of that

proton, the two the reduced mass is about half of the neutron mass or half of the proton mass, so there it makes a tremendous amount of difference.

(Refer Slide Time: 49:34)

$$\underbrace{-\frac{\hbar^2}{2\mu} \cdot \frac{1}{\psi} \left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} \right) \psi + V(r)}_{\nabla^2 \psi} = E_r$$

$$\underbrace{-\frac{\hbar^2}{2M} \cdot \frac{1}{\Phi} \left(\frac{\partial^2}{\partial X^2} + \frac{\partial^2}{\partial Y^2} + \dots \right) \Phi}_{E_c} = E_c$$

$$\Psi = \psi(\vec{r}) \Phi(\vec{R})$$

$$E_r + E_c = E$$

$$-\frac{\hbar^2}{2\mu} \cdot \frac{1}{\psi} \nabla^2 \psi + V = E_r$$

$$\boxed{\nabla^2 \psi + \frac{2\mu}{\hbar^2} [E_r - V(\vec{r})] \psi(\vec{r}) = 0}$$

So, you see now we will substitute this here and and if I this will require a little algebra which I will request all of you to do, if I substitute it here and divide by psi times phi then, we will obtain the following equation. Minus h cross's square by 2 mu 1 upon psi delta 2 by delta x square plus delta 2 by delta y square plus delta 2 by delta z square this from now on we will represent by del square del square psi, so this will be one term plus, since we have divided by psi and phi, so this will be just v which depends on r coordinate.

And then there is the second term minus h cross's square by 2 m 1 upon capital phi and so delta 2 by delta capital X's square plus delta 2 by delta y square plus delta 2 by delta z square capital phi; this we will have equal to E, because we have divided by psi we have written psi is equal to small psi which depends only on the r vector multiplied by capital phi which depends only on the R vector and we have divided the whole equation by psi times phi.

So, we now set this is equal to the E the central of mass, so we write this as a, so this is the the energy corresponding to the center of mass, so we write this as E c and this total thing we write it as the relative energy, so E r plus E c is equal to the total energy of the system.

So, let me write down the E_r portion, so minus \hbar^2 cross's square by 2μ 1 over ψ del square ψ plus V is equal to E 's of r , so we will obtain del square ψ plus 2μ by \hbar^2 cross's square E_r minus V of r ψ is equal to 0 . Please see there is a difference this is r vector and this is just r this is the modulus of the r vector, so this gives describes the internal motion of the hydrogen atom and we will solve this.

And the second one will be minus \hbar^2 cross's square let me write it down on a separate page.

(Refer Slide Time: 52:43)

$$-\frac{\hbar^2}{2M} \nabla^2 \Phi = E_c \Phi$$

$$\left[\frac{\partial^2}{\partial x^2} + \dots \right] \Phi + \frac{P^2}{\hbar^2} \Phi = 0$$

$i \vec{P} \cdot \vec{R} / \hbar$

$$\Phi(\vec{R}) = \dots e$$

Center of Mass moves as a free particle

$$\frac{P^2}{2M}$$

$M = m_1 + m_2$

So, this equation will be minus \hbar^2 cross's square by 2 capital M 1 over Φ delta 2 by delta X square capital plus delta 2 by delta y square plus delta 2 by delta z square is equal to the central of mass energy multiplied by Φ .

So, we can write this as delta 2 by delta x square plus delta 2 by delta y square plus delta 2 by delta z square Φ plus $2M E_c$ by \hbar^2 cross's square so P^2 by \hbar^2 cross's square Φ is equal to 0 . So, this is the Schrodinger equation for a free particle, so I can write this term as Φ of R **phi of r** will be equal to sum constant e to the power of $i \vec{P} \cdot \vec{R}$ by \hbar cross all values of P^2 will be allowed. So, it will this is the **the the** center of mass moves as a free particle the whole the center of mass moves as a whole hydrogen atom is moving as a whole and all values of the energy are allowed therefore, the center of mass moves as a free particle **free particle** with energy P^2 by $2M$, M is the total mass that is m_1 plus m_2 where M is the m_1 plus m_2 .

(Refer Slide Time: 55:03)

Handwritten derivation on a whiteboard:

$$-\frac{\hbar^2}{2\mu} \cdot \frac{1}{\psi} \left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} \right) \psi + V(r) \psi = E_r \psi$$

$$-\frac{\hbar^2}{2M} \cdot \frac{1}{\Phi} \left(\frac{\partial^2}{\partial X^2} + \frac{\partial^2}{\partial Y^2} + \dots \right) \Phi = E_c \Phi$$

where $\Psi = \psi(\vec{r}) \Phi(\vec{R})$

$$E_r + E_c = E$$

$$-\frac{\hbar^2}{2\mu} \nabla^2 \psi + V = E_r \psi$$

$$\nabla^2 \psi + \frac{2\mu}{\hbar^2} [E_r - V(r)] \psi = 0$$

$$E_{\text{total}} = E_r + E_c$$

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So, we have this part and then the second part will be the second part will be this particular equation, we will and the total energy of the atom will be the total energy of the atom will be equal to the relative energy which will be we will find to be discrete plus the center of mass energy. And the center of mass itself behaves are like a free particle and what in our next lectures, we will try to solve this particular equation for the hydrogen atom problem.

(Refer Slide Time: 55:34)

Handwritten equation on a whiteboard:

$$\nabla^2 \psi(\vec{r}) + \frac{2\mu}{\hbar^2} [E - V(r)] \psi(\vec{r}) = 0$$

$r = |\vec{r}|$

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So, let me write down what will be the **the the** starting point of the next lecture that $\nabla^2 \psi$ of r this is the relative coordinate plus 2μ by \hbar^2 cross's square I will I will remove the subscript r minus V of r ψ of r is equal to 0, this will be the solution of this equation will determine the energy states of the hydrogen atom. Once again r vector is the relative coordinate and small r is the magnitude of the relative coordinate, because the potential energy function depends only on the distance.

And as I had mentioned this analysis that we have presented is valid for any spherically symmetric potential, any potential energy function for which the potential energy function depends only on the distance it need not be just coulomb only on the distance we will be described by the analysis that we have presented today thank you.