Chemistry I
Introduction to Quantum Chemistry and Molecular Spectroscopy
Lecture 15
The quantum mechanics of Hydrogen atom – Part II

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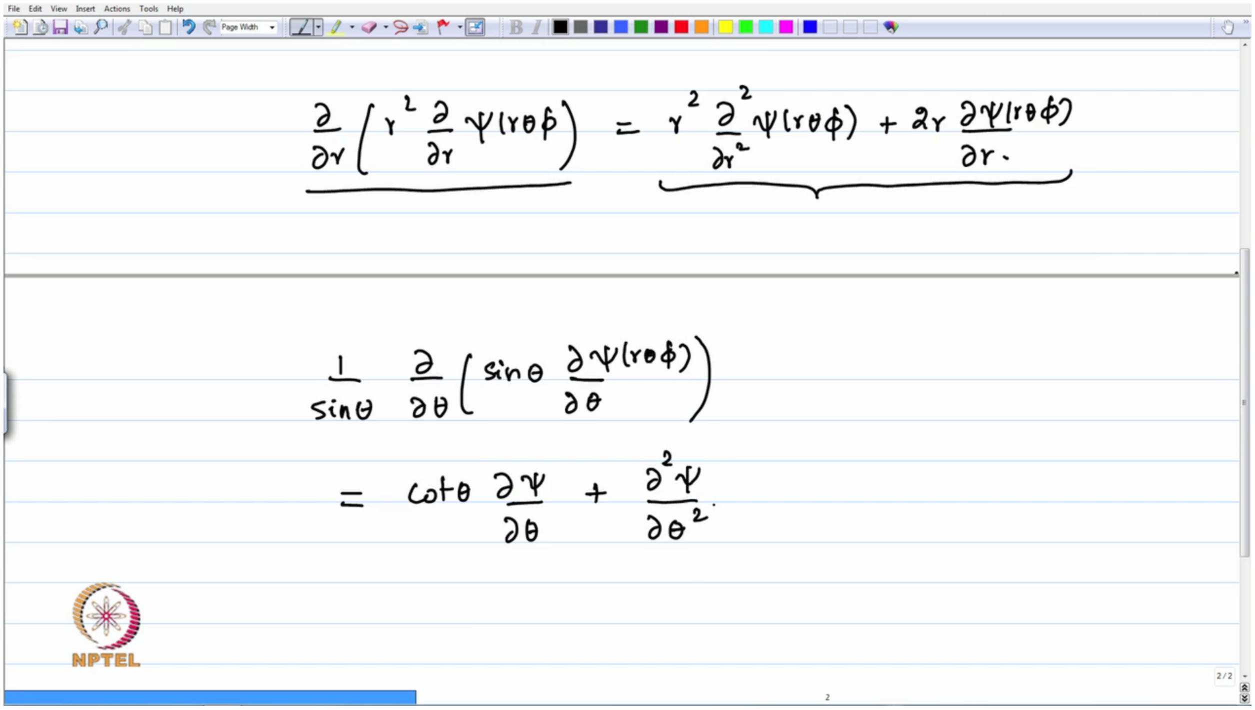
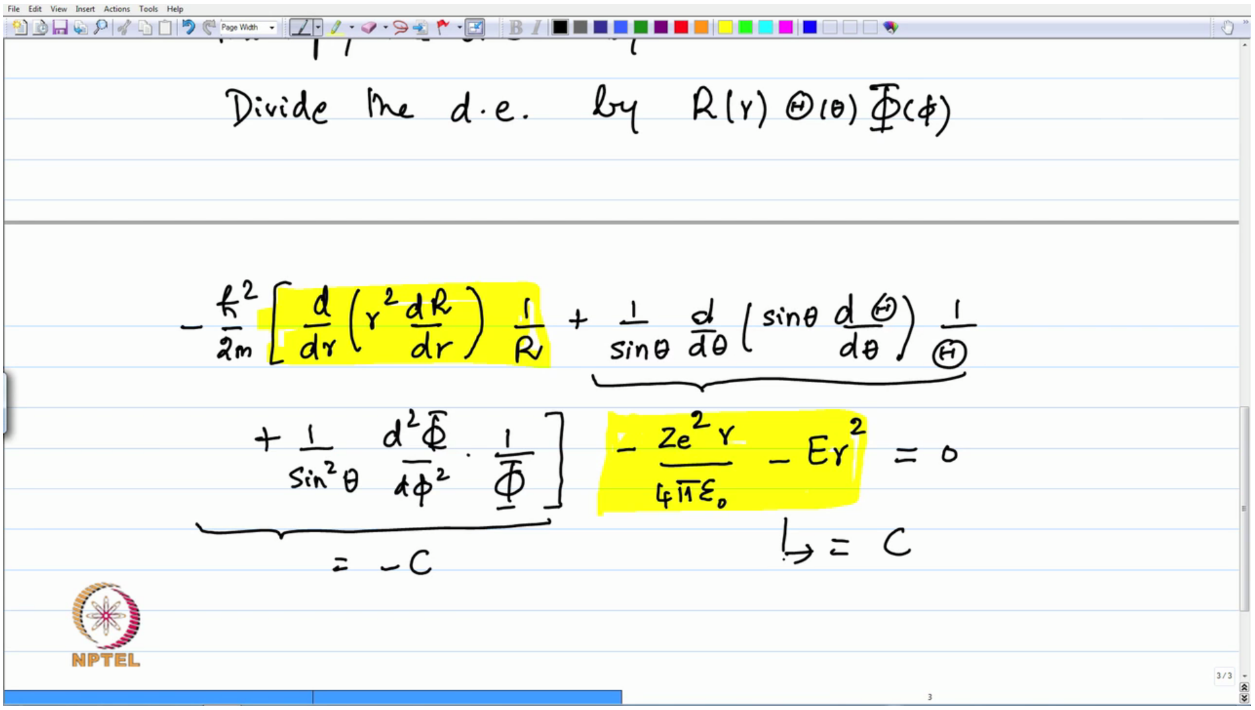
Prof. Mangala Sunder Krishnan: Welcome back to the lecture on the Hydrogen Atom. In the last lecture, we left at the point of the Schrodinger equation being written down using spherical polar coordinates for the hydrogen atom. In this brief segment, I shall tell you how the equation is separated into three component equations for the three variables that we proposed, the radial coordinate, the Θ coordinate of the angular part, and the Φ coordinate of the angular part as well. The Φ coordinate solution will be identified immediately with the solutions of the particle in a ring and the Θ coordinate will become the solutions earlier known in mathematics literature as due to Associated Legendre polynomials.

The radial part will be identified with Laguerre polynomials and the hydrogen atom is a very good example of taking the mathematics to a slightly more rigorous level and showing that the analytic solutions for this particular real problem exists. Surprisingly, that's it. Beyond this point all solutions become approximate.



So let's recap the equation. The overall equation is displayed here from the last lecture this was the last part of the last lecture. Now you see that that is the radial derivative, then there is the angular derivative, and the Φ derivative. First, let me clarify a couple of notations here. When you write ∂/∂r (r^2 ∂/∂r ψ(r,θ,φ), what it means is a sum of two terms, namely derivative with respect to r and derivative with respect to the first derivative. Therefore, you have r^2 $\partial^2/\partial r^2$ ψ, the partial derivative of Ψ with respect to r and then the other term namely 2r ∂ψrθφ/dr. That's what is meant by writing in a compact notation like this, okay and second when you write 1/sinθ in a similar way, ∂/∂θ (sinθ ∂ψ/∂θ (r, θ,φ). This again means two terms, namely the sine θ derivative being a cotθ, because it's cosθ by sinθ, then you have ∂ψ/∂θ + sinθ cancels when you don’t take the derivative, it is $\partial^2\psi/\partial\theta^2$, okay. So one must keep in mind that this is what is meant by writing derivatives in bracket form, okay.

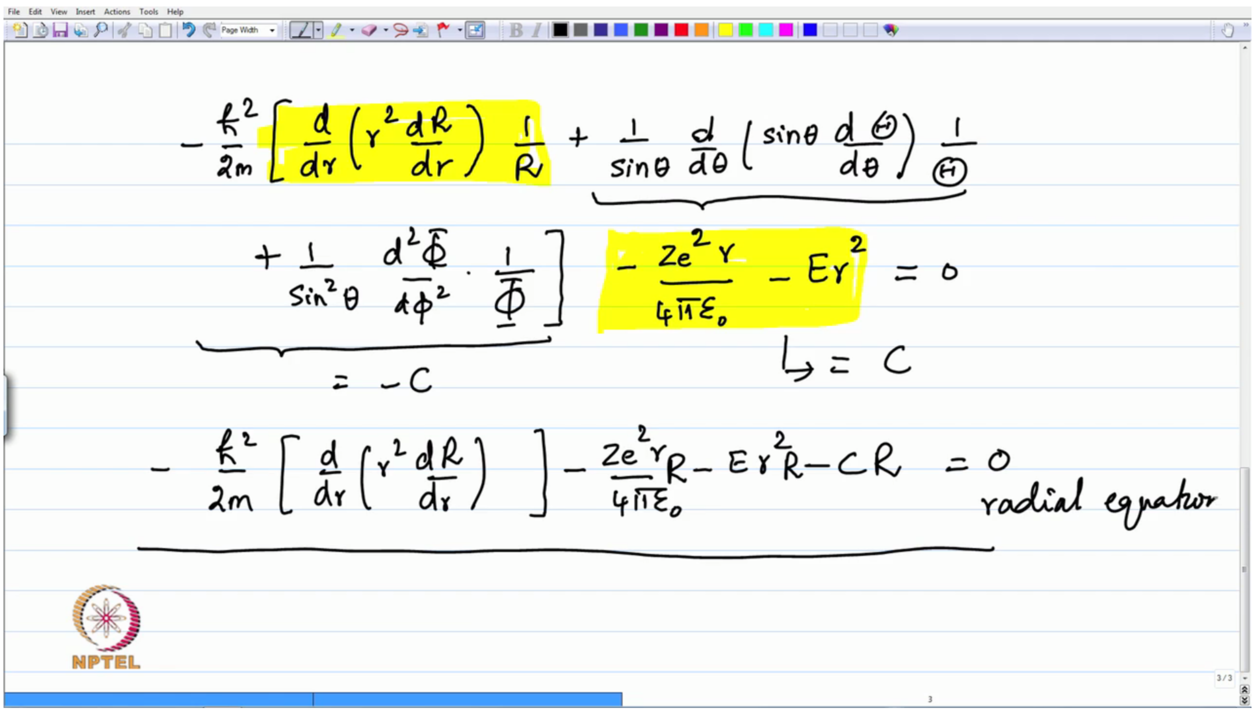


Now given this particular form of ψ or θφ and given the form of the differential equation, our purpose was to solve this equation by separating the ψs into independent coordinate dependent functions, namely writing ψ(r,θ,φ) function as the product of three functions, a function of radial part only, a function of θ coordinate only, and a function of φ coordinate only. This separation is possible because of the particular form of the hydrogen atom equation, namely that the potential energy is only dependent on the radial coordinate, and therefore, if you look at this particular equation here, the radial terms that you have here, the radial terms, this and this and this, will be separated out when you multiply the whole equation by r2, you would see that these are the only terms, which will depend on r and the other term will have the r2 removed, so they will depend on θ and φ. Therefore, you will have a differential equation in which one part of the equation depends only on one coordinate, the other part depends only on the other two coordinates, and then you can immediately realize that these two independent quantities must be separately equal to a constant, which will cancel each other.

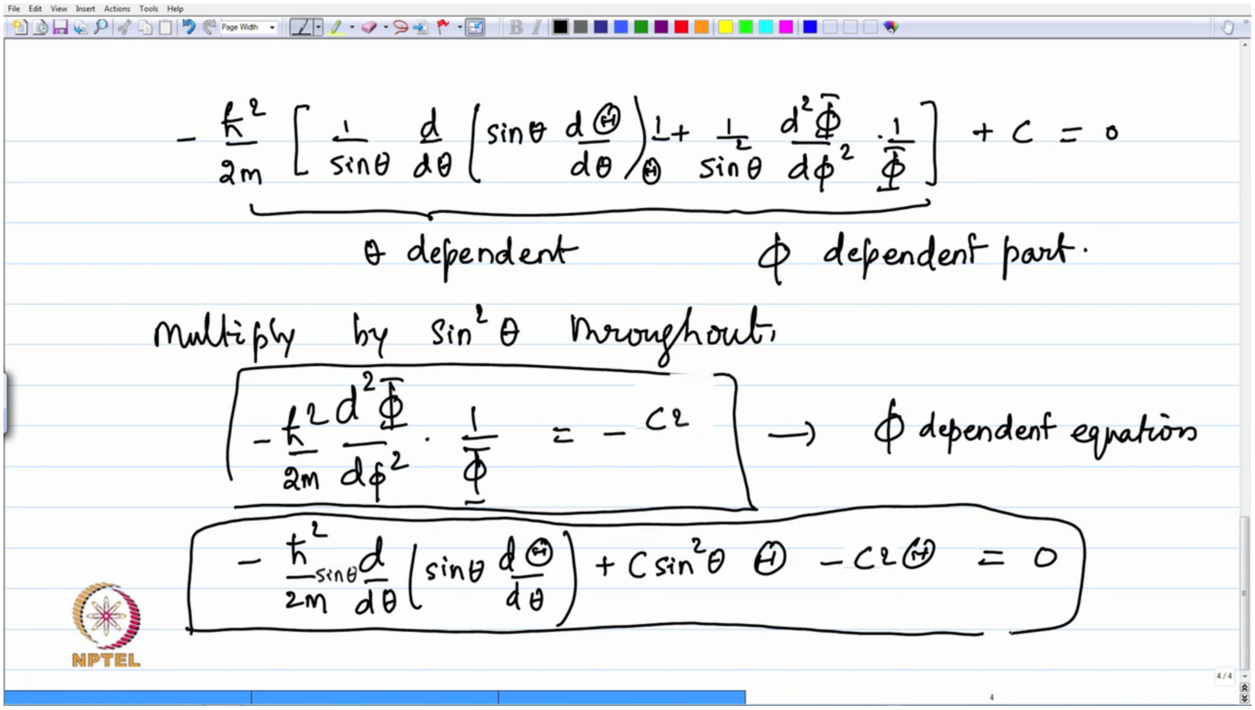
Therefore it's possible to separate this equation into independent coordinates. So let's multiply the differential equation by r^2, d.e. by r^2, and divide the d.e. by R(r) Θ(θ) and Φ(φ). When you do that, the resulting equation for the radial part and the angular part take this form, $-\hbar^2/2m$ [d/dr(r^2 dR/dr) and since we have divided everything by the wave function itself, you will have 1/r, because the θφ will be cancelled. Likewise you have 1/sinθ -- sorry, let me do the following. It is not -- -ħ/2m is common to both, so you have 1/sinθ d/dθ (sinθ dΘ/dθ) and again this term will be multiplied by 1/Θ and then you have the last term for the kinetic energy, 1/sin2θ d2Θ/dφ2 .

1/Θ. So will be the radial part, angular part of the kinetic energy term. And then the remaining, namely -ze2r, because we have multiplied everything by r^2 by $4\pi\varepsilon_0$, and we will not have any function here because that has been divided out and also one is left over is the $Er^2 = 0$, okay.

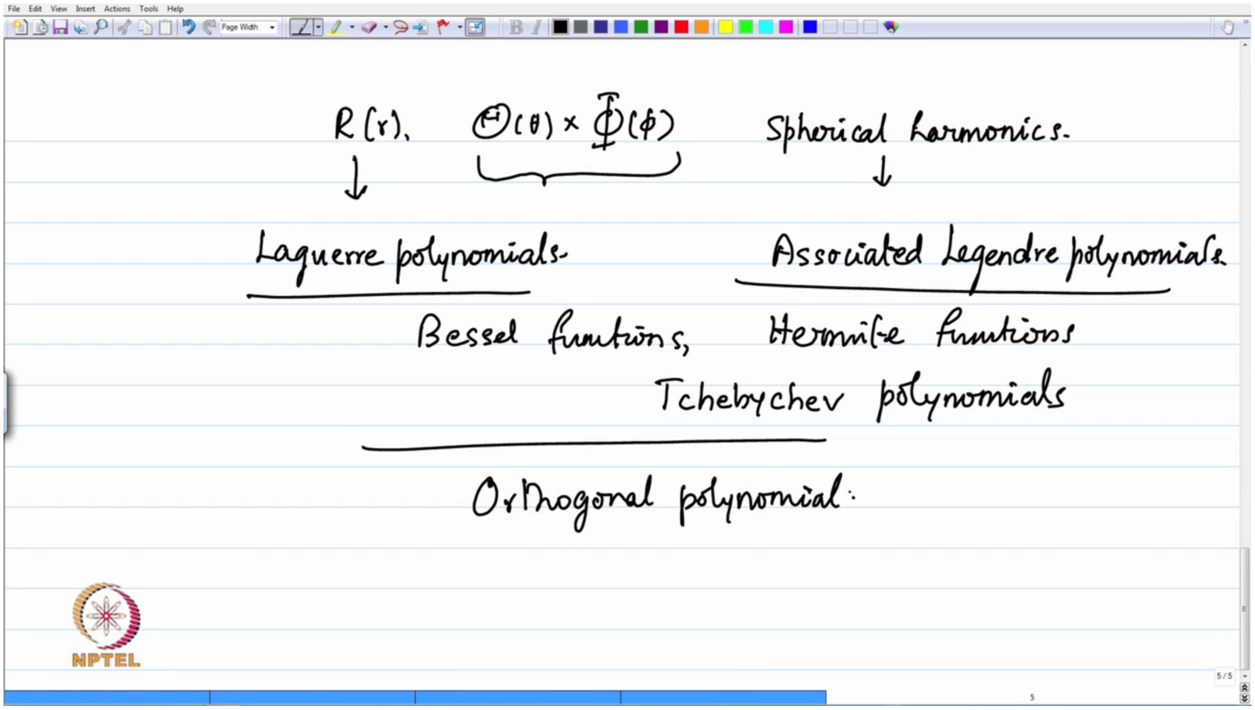
So this is the form after doing the separation, the division and then removing the parts independently. So what you have here are the radial part given by this term and these terms, and everything else does not depend on radius, the coordinate r, but depends only on the θ and φ. Therefore, it's straightforward for you to write this as equal to sum constant C in which case the remaining term, this and this, will be equal to -C, so that the sum of this is 0, okay.



So we have two equations, one for the radial equation $-\hbar^2/2m\ [d/dr\ (r^2\ dR/dr)$ $1/R$ + so that's a kinetic energy term, and then you have the potential energy contribution $-ze^2$ or by $4\pi\varepsilon_0$ - Er^2 - C = 0, because the whole thing is C, and if you write it in the standard form, you can now get rid of this R and multiply everything by the R, so you have the R here. See this is the radial equation.



And the angular equation will be whatever is left over, namely $-\hbar 2/2m$ [$1/\sin\theta$ $d/d\theta$ what you have here is ($\sin\theta\, d\Theta/d\theta$) $1/\Theta$ + $1/\sin^2\theta$, $d2\Phi/d\varphi 2$. $1/\Phi$] all of this is equal to -C, therefore, +C = 0, okay. Now this equation again can be separated into θ dependent part only and φ dependent part only. If you multiply by sin2θ the whole equation, you will get C sin2θ, and then the first term will contain all the θ dependence term. The second one will not have the θ dependent form, it will be only φ dependent part. Therefore, when you multiply this by sin2θ throughout and equate the term $d^2\Phi/d\varphi 2$. $1/\Phi$ to some constant which by recognition of the particular in a ring problem, we would equate that to a constant, then the other term will depend on $+m^2$, will be equal to $+m^2$. So this is the φ dependent equation and what you will have is for the θ dependent form -- on there is also a $-\hbar 2/2m$ here, okay, and then you have the θ dependent form, which is $-\hbar^2/2m\ \sin\theta\ d/d\theta\ (\sin\theta\ d\Theta/d\theta)$ and if we do the algebra carefully, it will be $+C \sin^2\theta\ .\ \Theta - C^2\Theta = 0$, okay. So that would be $C \sin^2\theta - m^2\theta = 0$. So this would be the θ dependent equation and this would be the φ dependent equation, okay.



So we are in a position to solve each one of them separately and obtain the formal answer, the analytic solutions for these three quantities. So what you do is when you solve these equations, which I will not describe here, when you solve this equation, you will get a radial function, you will get an angular function, and you will get a φ, which is also and part of an angular function. The product of the two together is known in not only hydrogen atom but in general for such equations it's known as spherical -- the solutions are known as spherical harmonics. The radial function will contain what are known as the Laguerre polynomials. Spherical harmonics are constructed using the five functions and polynomials known as Associated Legendre polynomials. All these things Laguerre, Associated Legendre polynomial, Bessel functions, Hermite functions which we will see in the solution of the harmonic oscillator, Hermite function or Hermite polynomials, then Tchebyshev polynomial, there are many ways by which the Tchebyshev is written, Tchebyshev polynomials and so on. They all form a group of polynomials well known in mathematics as Orthogonal polynomials, and these are important in the differential equation representation or a coordinate representation of the wave function in a suitable coordinate system, and these polynomials have been known for more than 200 years.

Schrodinger saw that his equation mapped into the differential equations that were already known, and therefore, he immediately put forward the solutions from those differential equations and obtained the conditions. Let me summarize or let me conclude with the following statement that the radial function will depend on two coordinates, two quantum numbers n and l. The product of the two together will be called the spherical harmonics will depend on two quantum numbers l and m. The l will be the same for both the radial and angular function for a given energy, and therefore, the overall solution will be the product of the two and that's equal to ψ with the three quantum numbers nlm or (r,θ,φ).

I am not going to describe how to obtain this radial and the angular parts, but in the next part of this lecture, I shall describe the forms of the radial parts and the forms of the angular part and we will see some pictures for the angular parts, which are popularly known as the representations of the atomic orbitals. You would have seen them in textbooks, both in the high school and in college textbooks with the P orbital having two lobes in the z direction, in the x direction and the y direction, and the D orbitals having some other representation. All these things are functional representations of the real and imaginary parts of the spherical harmonics on a spherical system, on a coordinate system given by spherical polar coordinates, the spherical surface. We will see some of that and that will give us a clear picture on what the solutions mean. Not necessarily how to obtain. That's part of the next level of mathematics course or next level of physics our chemistry course that you might take. It's not part of this series of lectures. You might them elsewhere. We will continue with this in the next part. Until then thank you.