Introductory Quantum Mechanics and Spectroscopy
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Lecture – 5
Part I
The Quantum Mechanics of Hydrogen Atom

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 theta coordinate of the angular part and the phi coordinate of the angular part as well. The phi coordinate solution will be identified immediately with the solutions of the particle in a ring, and the theta 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 exist. Surprisingly, that is it; beyond this point, all solutions become approximate.

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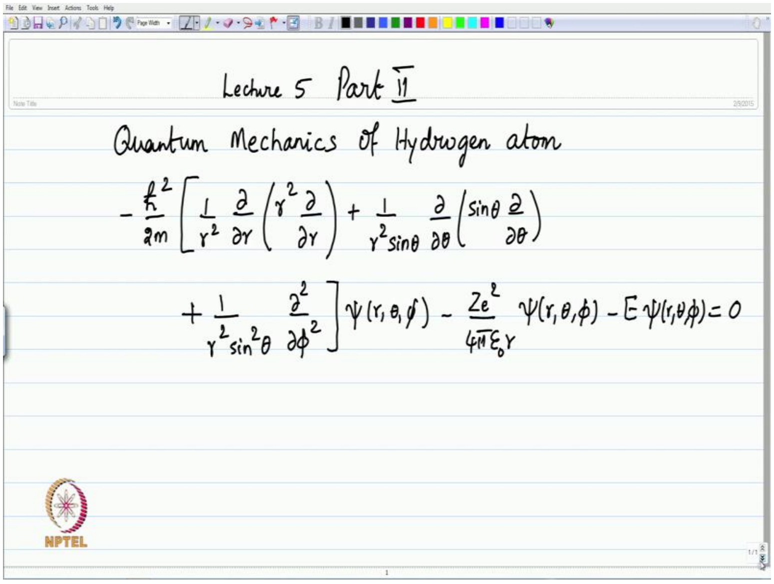

So, let us recap the equation; the overall equation is displayed here from the last lecture. This was the last part of the last lecture. Now, you see that there is the redial derivative; then there is the angular derivative and the phi derivative.

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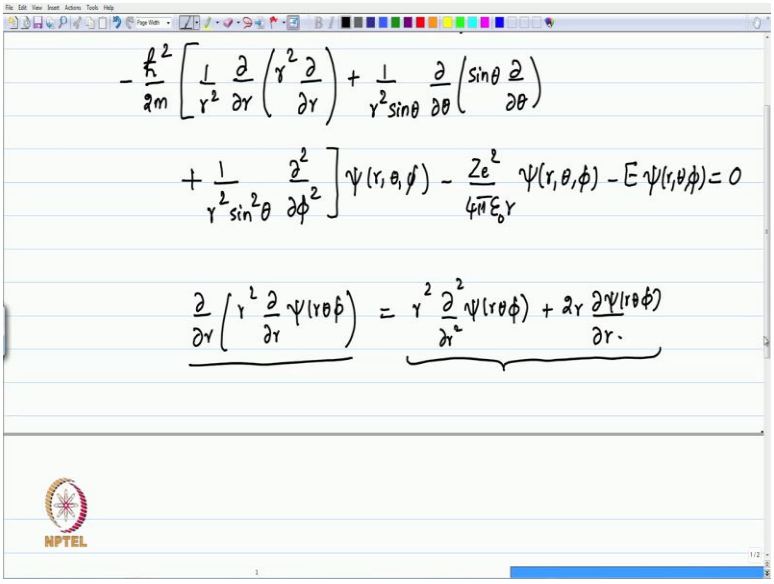

First, let me clarify a couple of notations here. When you write dou by dou r r square dou by dou r psi; r theta phi; what it means is a sum of two terms namely, derivative with respect to r and derivative with respect to the first derivative. Therefore, you have r square dou square by dou r square psi – the partial derivative of psi with respect to r and then the other term namely, 2 r dou psi r theta phi by dou r; that is what is meant by writing in a compact notation like this.

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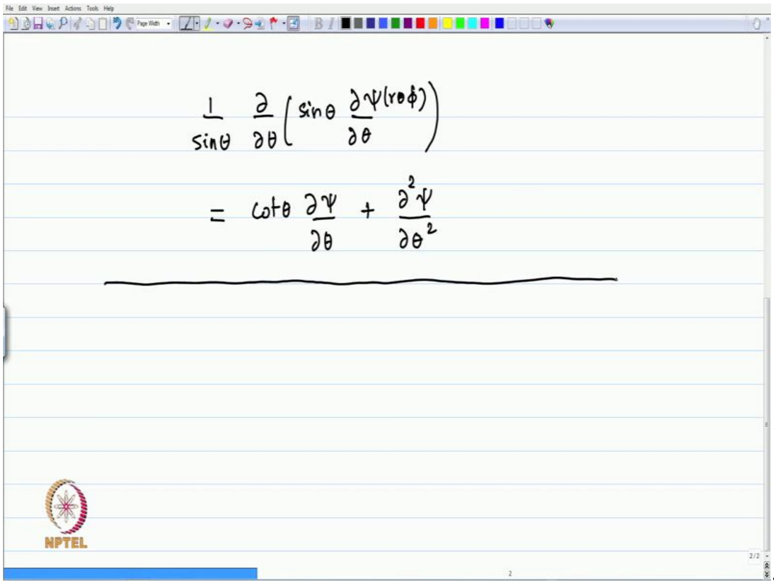

And second when you write 1 by sin theta in a similar way; dou by dou theta of sin theta dou psi – dou theta of r theta and phi. This again names two terms namely, a sin theta derivative being a cot theta here, because it is cos theta by sin theta. Then you have dou psi by dou theta plus sin theta cancels when you do not take the derivative; it is dou square psi by dou theta square. So, one must keep in mind that this is what is meant by writing derivatives in bracket form.

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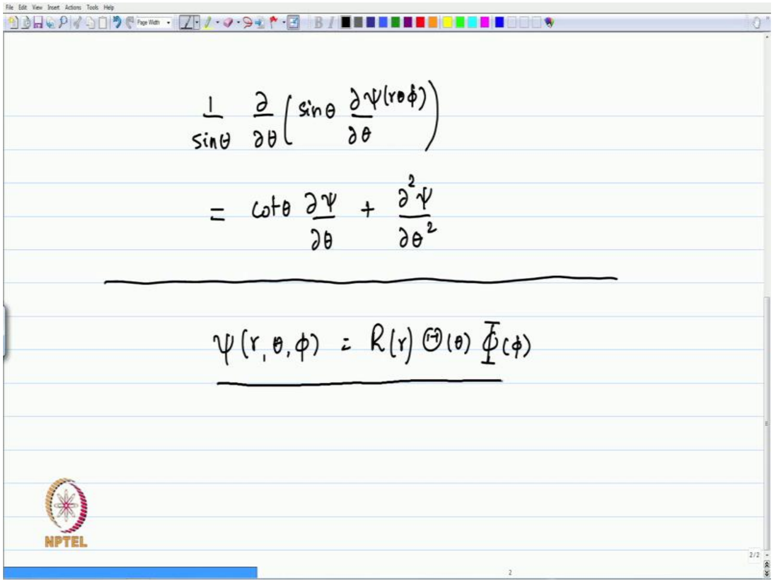

Now, given this particular form of psi or theta phi and given the form of the differential equation, our purpose was to solve this equation by separating the size into independent coordinate dependent functions namely, writing psi theta phi function as the product of three functions, a function of radial part only – a function of theta coordinate only and a function of phi 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 coordinates.

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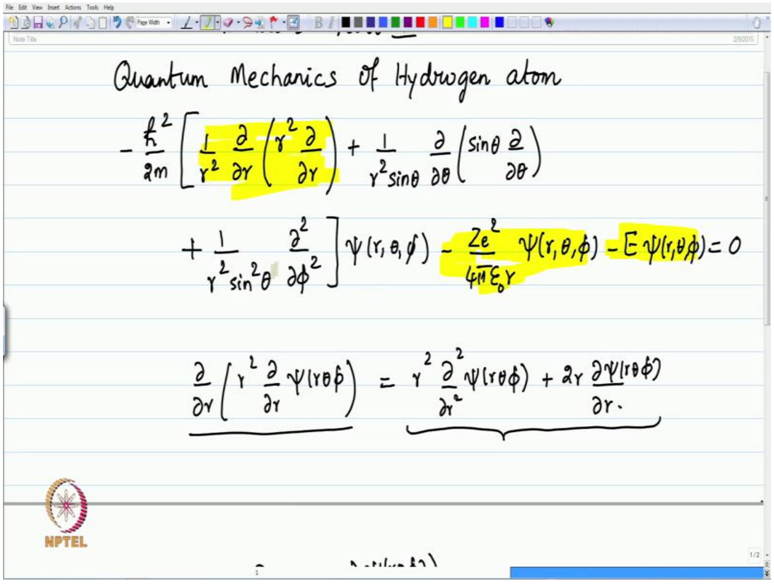

And therefore, if you look at this particular equation here, the radial terms that you have here – the radial terms this, and this, and this – will be separated out. When you multiply the whole equation by r square, you would see that, these are the only terms, which will depend r, and the other term will have the r square removed – r squared removed. So, they will depend on theta and phi. 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 is possible to separate this equation into independent coordinates.

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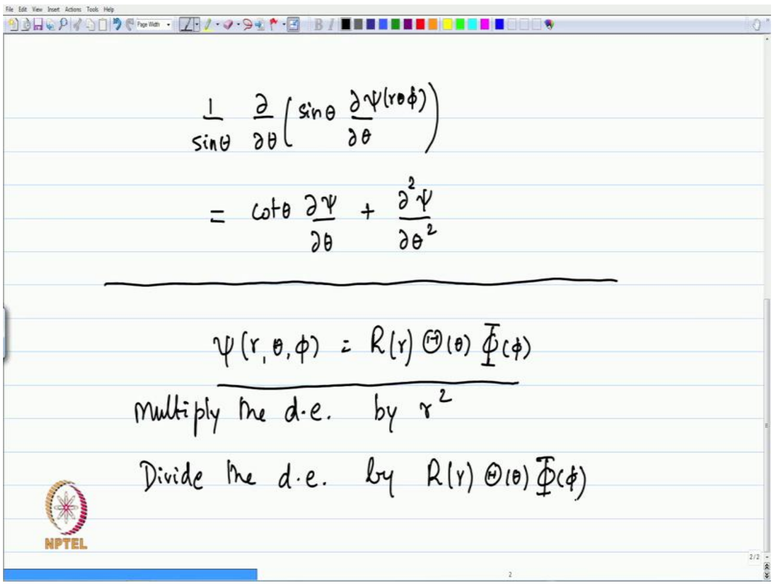

So, let us multiply the differential equation by r – r square – d.e. by r square; and also divide the d.e. by R of r theta of theta and phi of phi.

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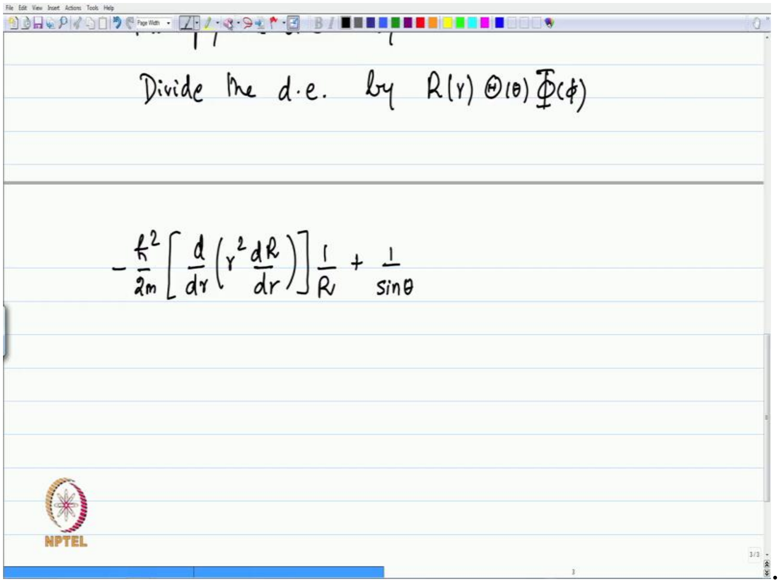

When you do that the resulting equation for the radial part and the angular path take this form – minus h bar square by 2m d by dr of r square dR by dr. And since we have divided everything by the wave function itself, you will have 1 by R, because the theta phi will be canceled; likewise you have 1 by sin theta. So, let me do the following.

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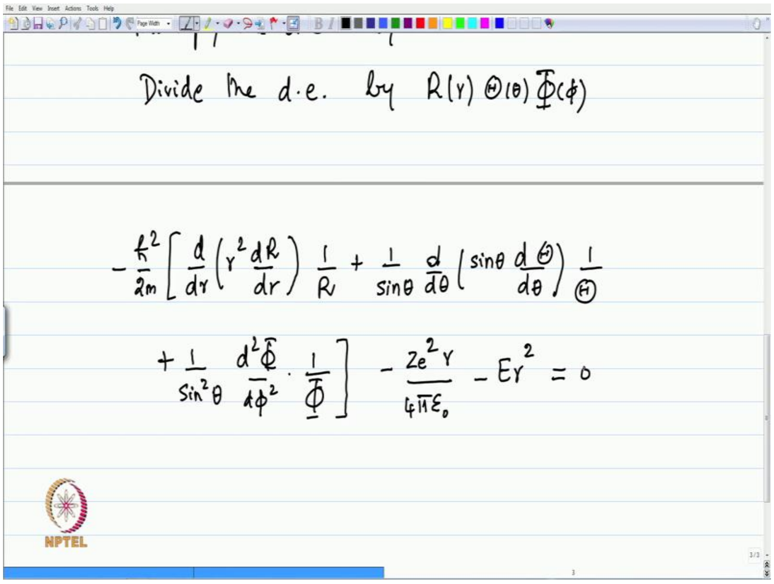

It is not… And minus h bar square by 2m is common to both. So, you have 1 by sin theta d by d theta of sin theta d theta by d theta. And again, this term will be divided by 1 by of this theta function. Then you have the last term for the kinetic energy – 1 by sin square theta d squared phi by d phi square times 1 by phi. So, this will be the radial part, angular part of the kinetic energy term. And then the remaining namely, minus z e square r because we have multiplied everything by r square by 4 pi epsilon naught; and will not have any function here because that has been divided out. And also, what is left over is the E r square is equal to 0. So, this is the form after doing the separation, the division; and then we are moving the parts independently.

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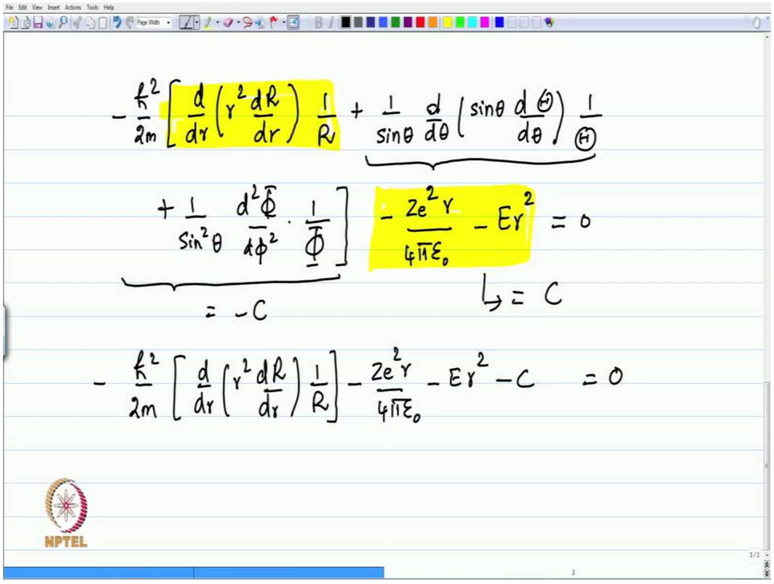

So, what you have here are the radial part given by this term and these terms. And everything else does not depend on radius – the coordinate r; that depends only on the theta and phi. Therefore, it is straight forward for you to write this as equal to some constant C in which case the remaining term – this and this will be equal to minus C, so that the sum of this is 0. So, we have two equations: one for the radial equation – minus h bar square by 2m d by dr r squared d capital R by d small r divided by R plus… So, that is a kinetic energy term. And then you have the potential energy contribution minus Ze square r by 4 pi epsilon naught minus E r square – minus C is equal to 0, because this whole thing is C.

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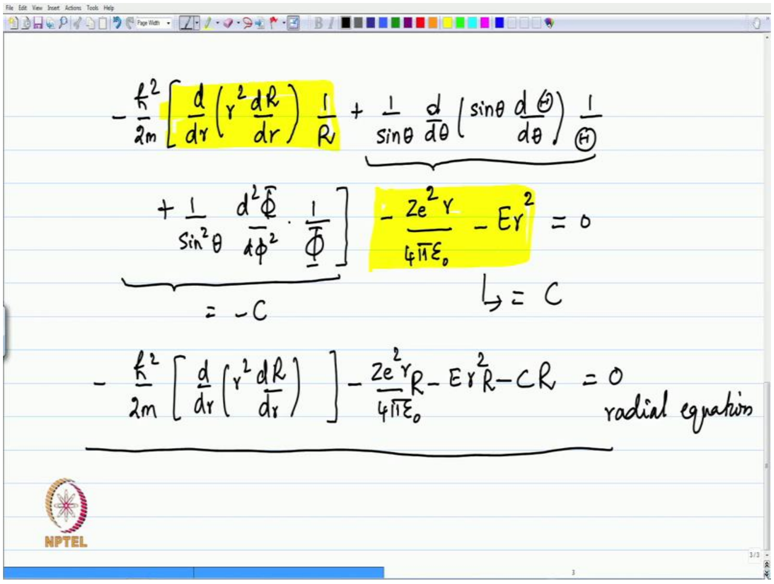

And if you write it in this standard form; you can now get rid of this R and multiply everything by R. So, you have the R here and CR. This is the radial equation.

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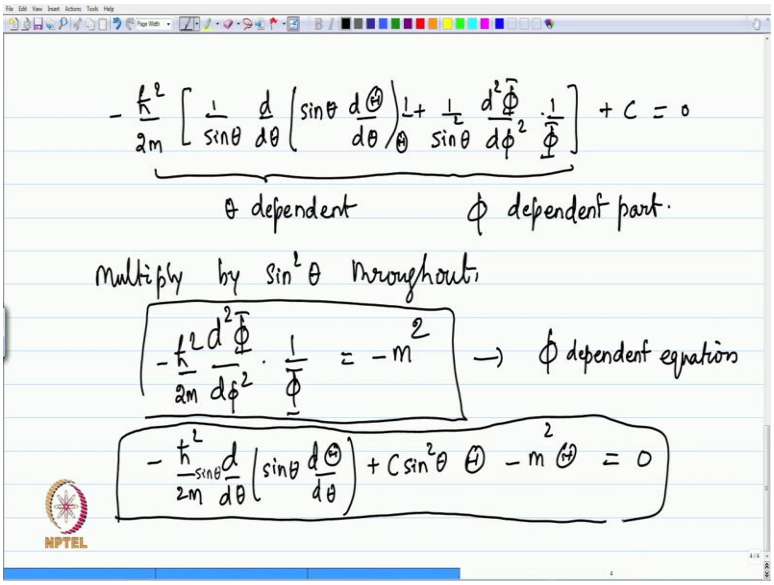

And the angular equation will be whatever is left over namely, minus h bar square by 2m, 1 by sin theta; what did I write? Yes, 1 by sin theta – d by d theta. What you have here is sin theta d theta by d theta plus 1 by sin square theta. That is also 1 by capital of theta here, 1 by sin square theta d squared phi by d phi square multiplied by 1 by phi. All of this is equal to minus C; therefore, plus C is equal to 0. Now, this equation again can be separated into theta-dependent part only and phi-dependent part only. If you multiply by sin square theta the whole equation, you will get C sin square theta. And then the first term will contain all the theta dependents term. The second one will not have the theta depend form; it will be only phi dependent part. Therefore, when you multiply this by sin square theta throughout and equate the term d square phi by d phi square times 1 by phi to some constant, which by recognition of the particle in a ring problem, we would equate that to a constant; then the other term will depend on plus m square will be equal to plus m square. So, this is the phi-dependent equation.

And what you will have is for the theta depend form, there is also a minus h bar square by 2m here. And then you have the theta depend form, which is minus h bar square by 2m sin theta d by d theta of sin theta d theta by d theta. And if we do the algebra carefully, it will be plus C sin square theta times theta… So, that would be the C sin square theta minus m square theta is equal to 0. So, this would be the theta-dependent equation and this would be the phi-dependent equation. So, we are in a position to solve each one of them separately and obtain the formal answer – the analytical solution for these three quantities.

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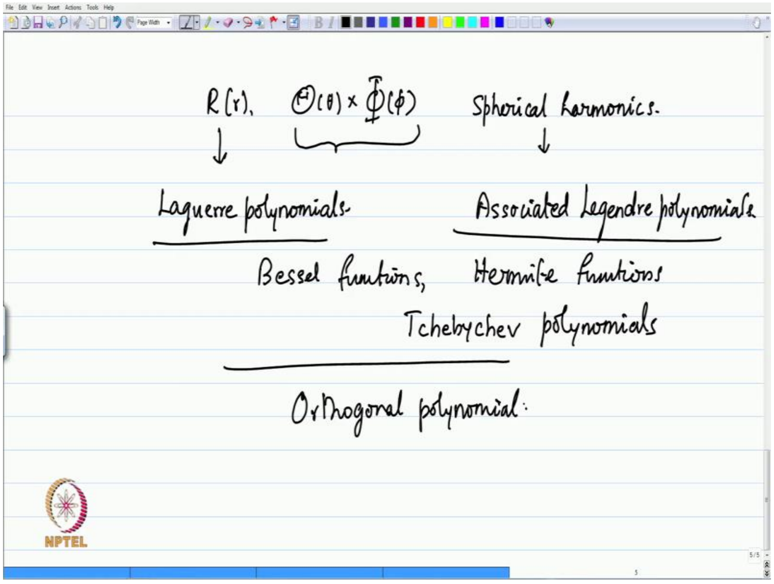

So, what you do is when you solve these equations, which I will now describe here. When you solve this equation, you will get a radial function, you will get an angular equation and you will get a phi, which is also a part of the angular function. The product of the two together is known in not only hydrogen atom, but in general, for such equation, it is known as spherical… The solutions are known as the spherical harmonics. The radial function will contain what are known as the Laguerre polynomials. Spherical harmonics are constructed using the phi functions and the polynomials known as associated Lengendre 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 Tchebychev polynomial – there are many ways by which the Tchebychev is written – Tchebychev 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 are well known for more than 200 years. Schrodinger saw that his equation mapped into the differential equations ((Refer Time: 16:32)) are already known. And therefore, he immediately put forward the solutions from those differential equations and obtain the conditions.

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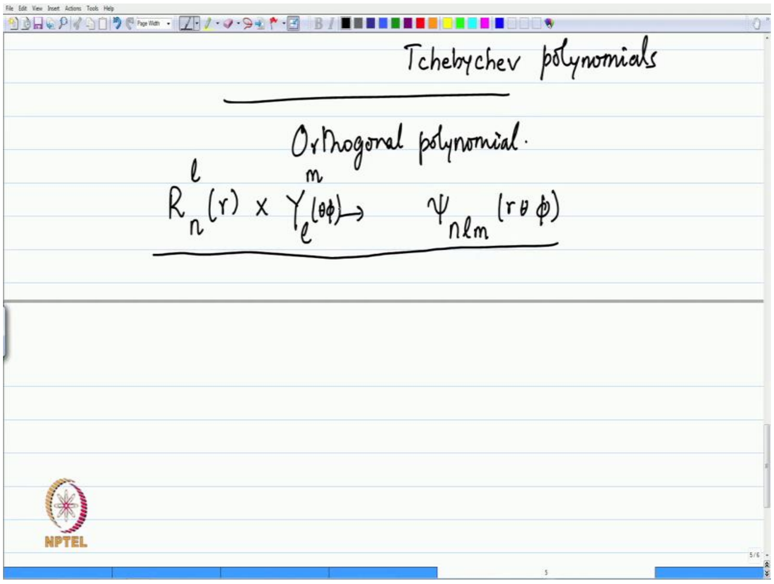

Let me summarize or let me conclude with the following statement, that the radial function will depend on two coordinate, two quantum numbers – n and l. The product of the two together will be called the spherical harmonics – will depend on two quantum numbers l and m; the l will be the same for both the radial and angular function for a given energy. And therefore, the overall solution will be the product of the two; and that is equal to psi with the three quantum numbers n, l, m – r, theta and phi. 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 text books both in the high school and in college text books with the p-orbital having two lobes in the z direction, in the x direction, and in the y direction; and the d orbitals having some other representation. All these things are functional representations of the real and imaginary parts of this 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 them; that is part of the next level of mathematics course or next level of physics or chemistry course that you might take. It is not part of this series of lectures; you might find them elsewhere. We will continue with this in the next part.

Thank you.