Atomic Structure and Chemical Bonding
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Lecture - 24
Hydrogen Atom: Separation of the Schrödinger Equation

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 2 component equations for the 3 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 exists. Surprisingly that is it beyond this point all solutions become approximate.

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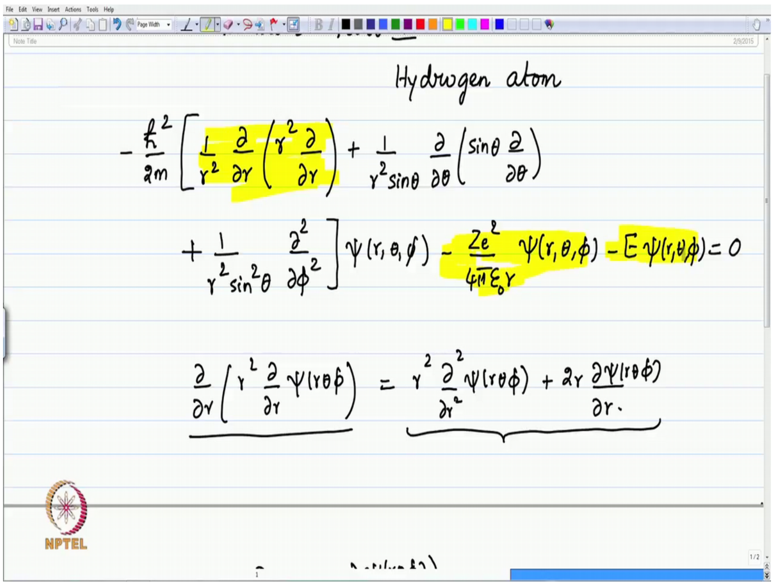

So, let us recap the equation. The overall equation is displayed here from the last lecture. This was the last part of the last lecture. Now, you see that there is the radial derivative, then there is the angular derivative and the phi derivative. First let me clarify a couple of notations here. When you write dou by dou r r square dou by dou r psi or theta pi, 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, ok.

Second when you write 1 by sine theta in a similar way dou by dou theta of sine theta dou psi dou theta of r theta and pi, this again means 2 terms namely the sine theta derivative being a cot theta here because it is cos theta by sine theta. Then you have dou psi by dou theta plus sine 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 pause.

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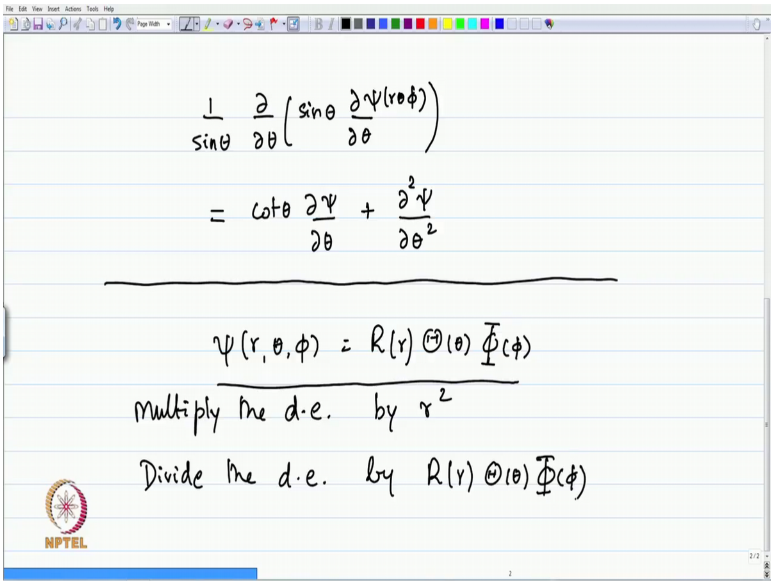

Now, given this particular form of psi or theta pi and given the form of the differential equation, our purpose was to solve this equation by separating the size into independent coordinate dependent functions namely writing psi theta pi function as the product of 3 functions; a function of radial part 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. 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 on r and the other term will have the r square removed or square removed.

So, they will depend on theta and pi. 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 in two independent coordinates. So, let us multiply the differential equation by r r square d e by r square and also divide the d by R of r theta of theta and phi of phi.

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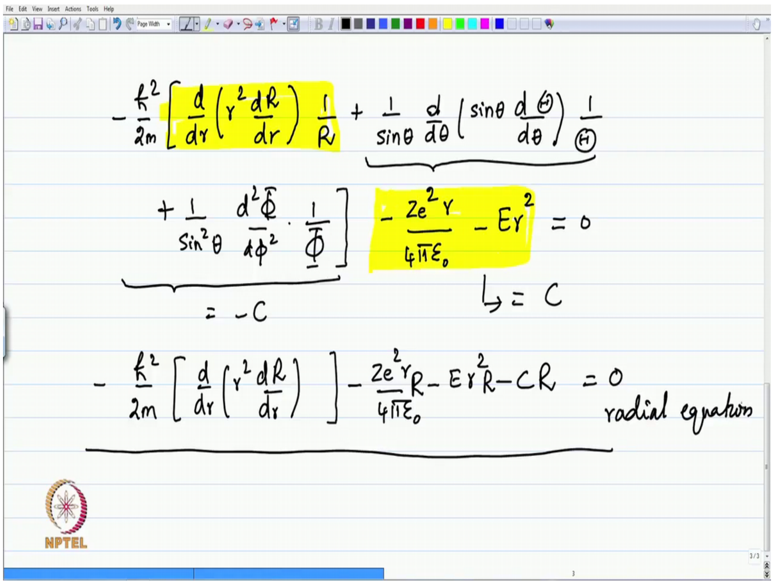

When you do that the resulting equation for the radial part and the angular part take this form; minus h bar square by 2 m d by dr of r square dR by dr and since we have divided everything by the wave function itself, you will have 1 by R because the theta pi will be cancelled likewise you have 1 by sine theta, sorry.

So, let me do the following. Sorry it is not and minus h bar square by 2 m is common to both. So, you have 1 by sine theta d by d theta of sine theta d theta by d theta and again this term will be much divided by 1 by of theta function, then you have the last term for the kinetic energy 1 by sine square theta d square phi by d phi square times 1 by phi, ok. 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 are 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 E r square is equal to 0.

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 theta and phi. Therefore, it is straightforward 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, ok.

So, we have two equations; one for the radial equation minus h bar square by 2 m d by dr r square d capital R by d small r divided by r plus. So, that is the kinetic energy term and then, you have the potential energy contribution minus d square r by 4 phi epsilon naught minus e r square minus C is equal to 0 because this whole thing is C and if you write it in the standard form, you can now get rid of this or and multiply everything by R.

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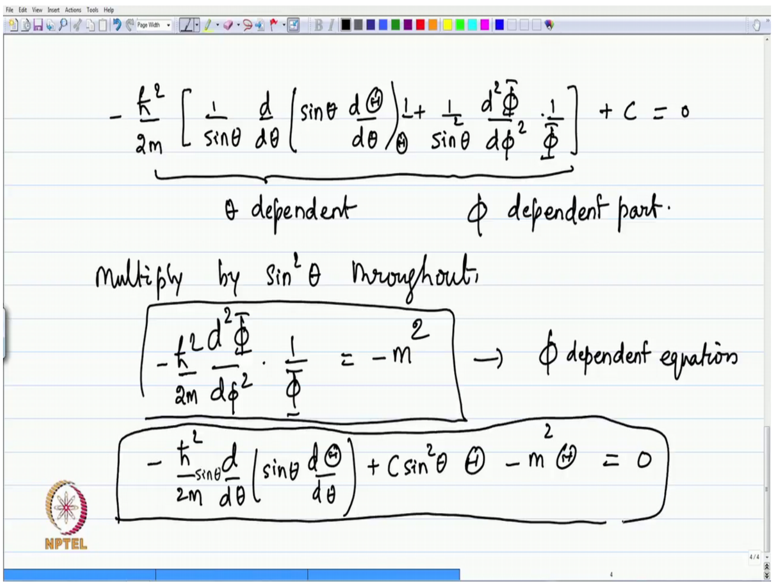

So, you have R here and C R. This is the radial equation and the angular equation will be whatever is left over, namely minus h bar square by 2 m sine theta 1 by sine theta, sorry what did I write. Yes 1 by sine theta d by d theta. What you have here is, sine theta d theta by d theta plus 1 by sine square theta, ok. That is also 1 by capital of theta here 1 by sine square theta d square 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, ok. Now, this equation again can be separated into theta dependent part only and phi dependent part only. If you multiply by sine squared theta, the whole equation you will get c sine square theta and then, the first term will contain all the theta dependents term.

The 2nd one will not have the theta dependent form. It will be only phi dependent part. Therefore, then you multiply this by sine 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 the 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 dependent form or there is also a minus h bar square by 2 m here, and then, you have the theta dependent form which is minus h bar square by 2 m, sine theta d by d theta of sine theta d theta by d theta and if we do the algebra carefully, it will be plus C sine square theta times theta.

So, that would be C sine 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, ok. So, we are in a position to solve each one of them separately and obtain the formal answer, the analytic solutions for these 3 quantities. So, what you do is when you solve these equations, which I will not describe here.

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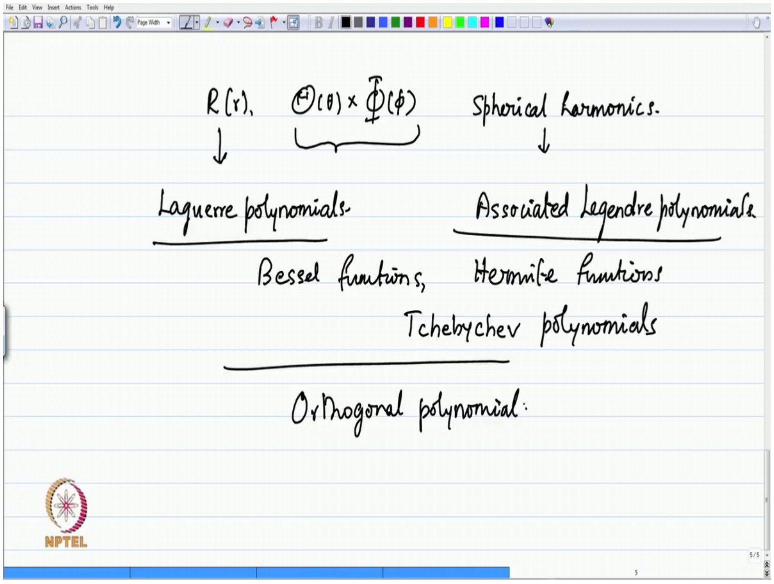

When you solve this equation, you will get a radial function, you will get an angular function and you will get a phi which is also a part of the angular function. The product of the two together is known in not only hydrogen atom, but in general for such equations it is known as spherical, the solutions are known as spherical harmonics. The radial function will contain what are known as the Laguerre polynomials. Spherical harmonics are constructed using the phi functions and polynomials known as associated Legendre polynomials. All these things Legendre associated Legendre Polynomial, Bessel functions, Hermite functions which we will see in the solution of the harmonic oscillator, Hermite function or Hermite polynomials, then Chebyshev's polynomial. There are many ways by which this Chebyshev is written Chebyshev 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 that were already known and therefore, he immediately put forward the solutions from those differential equations and obtain the conditions.

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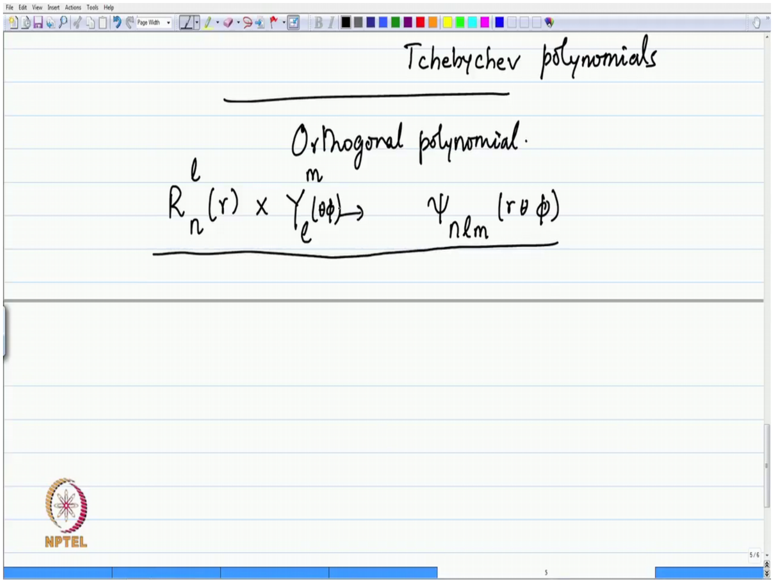

Let me summarize or let me conclude with the following statement that the radial function will depend on 2 coordinates, 2 quantum numbers n and l. The product of the two together will be called the spherical harmonics will depend on 2 quantum numbers l and m. The l will be the same for both the radial 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 3 quantum numbers n, l, m or theta and pi.

I am not going to describe 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 in you would have seen them in textbooks, both in the high school and in college textbooks with the p r between having 2 lobes in the z direction, in the x direction and 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.

Basically 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.

Until then thank you.