Atomic Structure and Chemical Bonding
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Lecture – 23
Hydrogen Atom: The Hamiltonian in Spherical Polar Coordinates

In this group of lectures consisting of several parts, I shall describe the quantum mechanics associated with the Hydrogen Atom, the solution of the Schrodinger equation. I will give you the results of the solution of the Schrodinger equation has its first major achievement in arriving at the spectra of the hydrogen atom, which were known for many decades before that and it is a spectra of the hydrogen atom which prompted Niels Bohr to came up with this first model of quantizing energy and quantizing the angular momentum of an atom. Schrodinger equation of course does this using his prescription and the wave function and we shall see some of the details in the calculation of the energies and in the calculation of probabilities of the electrons and so on.

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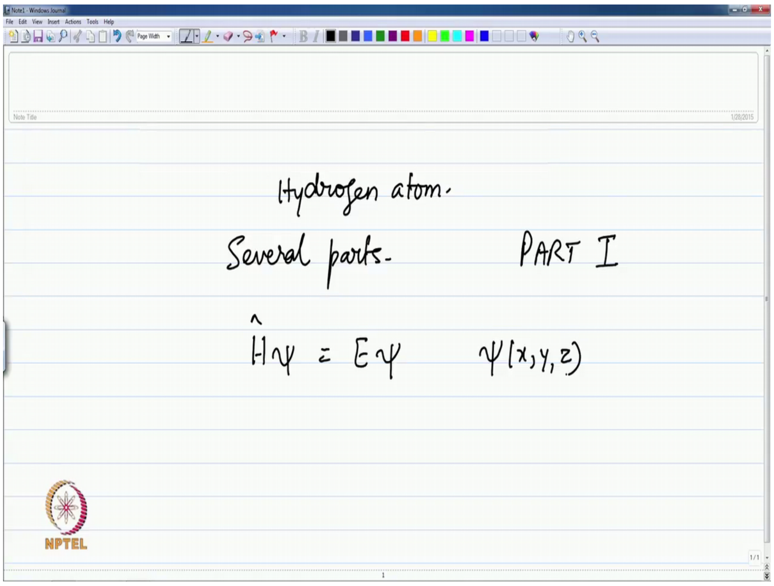

Hydrogen atom.

Several parts. PART I

$\hat{H}\psi = E\psi \qquad \psi(x,y,z)$

So, this is part 1 of the quantum mechanics of hydrogen atom and in the solution of this equation H psi is equal to E psi, where now psi is 3 dimensional Cartesian coordinate.

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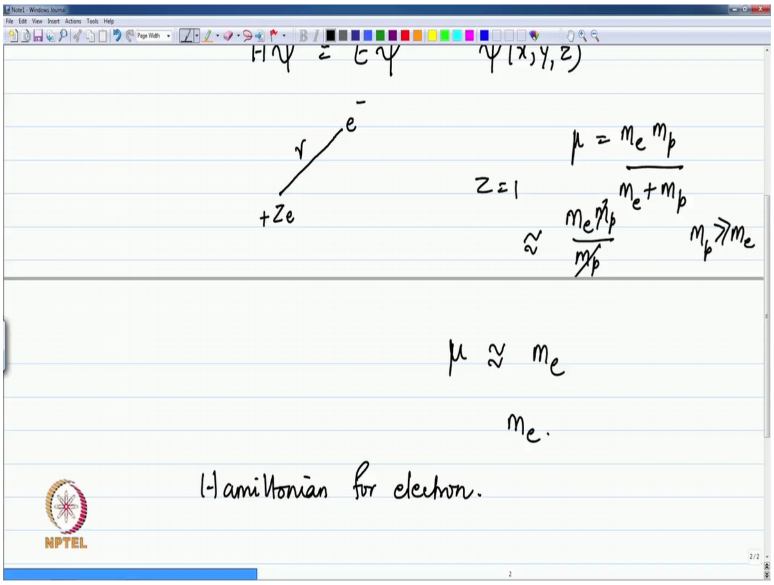

$H\Psi = E\Psi \qquad \Psi(x,y,z)$

$Z = 1$

$$\mu = \frac{m_e m_p}{m_e + m_p} \approx \frac{m_e \cancel{m_p}}{\cancel{m_p}} \qquad m_p \gg m_e$$

$$\mu \approx m_e$$

m_e.

Hamiltonian for electron.

We do use a classical starting point of the nucleus with an electron somewhere and the nucleus having a positive charge plus z e. Z is 1 and the electron with a minus charge and the distance of r. I shall not describe this as a two body problem even though that is the right way of doing it the two body problem and then, remove the center of mass from the two body problem and study only the relative motion of the two particle system. Which in this case, the relative mass for or the reduce mass for the two particle system is the mass of the electron times, the mass of the proton divided by the mass of the electron plus that of the proton which is approximately the mass of the electron divided by the times mass of the proton divided by the mass of the proton. Since m p is much much greater than m e and therefore, mu turns out to be approximately m e when you cancel the m p.

So, we shall worry about making that approximation and write the mass as nothing, but the mass of the electron. Therefore, we needed the Hamiltonian for the electron. So, let us assume that the nucleus is stationary does not contribute to the overall kinetic energy of the atom. That is already there in the center of mass which is not considered here.

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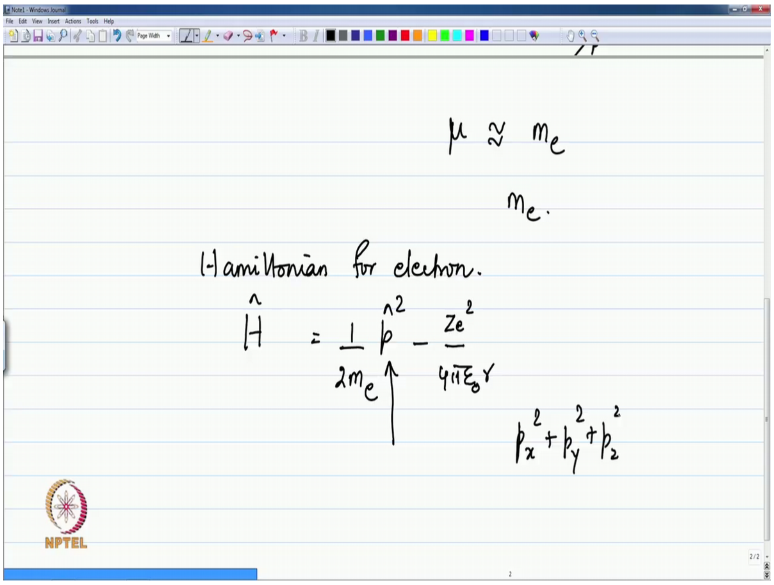

$$\mu \simeq m_e$$

$$m_e.$$

Hamiltonian for electron.

$$\hat{H} = \frac{1}{2m_e}\hat{p}^2 - \frac{Ze^2}{4\pi\varepsilon_0 r}$$

$$p_x^2 + p_y^2 + p_z^2$$

Therefore, if you write to the kinetic energy and the potential energy operator for the hydrogen atom, it will be in terms of the operators, it will be p square 1 by 2 m e minus z e square by 4 pi epsilon naught r, which is the classical columbic energy of interaction between the positive and the negative charge. And this p square which is an operator is given by p x square plus p y square plus p z square.

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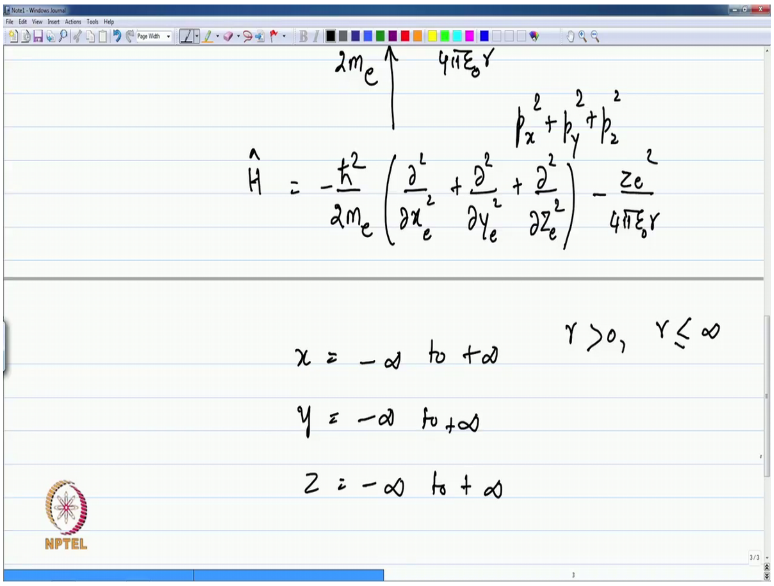

$$2m_e \qquad 4\pi\varepsilon_0 r$$

$$p_x^2 + p_y^2 + p_z^2$$

$$\hat{H} = -\frac{\hbar^2}{2m_e}\left(\frac{\partial^2}{\partial x_e^2} + \frac{\partial^2}{\partial y_e^2} + \frac{\partial^2}{\partial z_e^2}\right) - \frac{Ze^2}{4\pi\varepsilon_0 r}$$

$x = -\infty$ to $+\infty$

$y = -\infty$ to $+\infty$

$z = -\infty$ to $+\infty$

$r > 0, \; r \leq \infty$

The 3 components of the momentum in a coordinate system which is probably fixed in the nucleus itself for arguments and then, of course p x is replaced by the derivative operators, so that the Hamiltonian becomes minus h bar square by 2 m e dou square by dou x e square plus dou square by dou y e square plus dou square by dou z e square, where these are the coordinates of the electron with respect to that origin and then, you have the potential energy minus z e square by 4 pi epsilon naught r and r is in principle greater than 0 and less than or equal to infinity. At infinity of course the coulombic interaction is 0, therefore here the boundary includes the entire three dimensional world, the whole universe.

So, the boundaries are explicitly accessed from minus infinity to plus infinity, y is from minus infinity to plus infinity and also z is from minus infinity to plus infinity.

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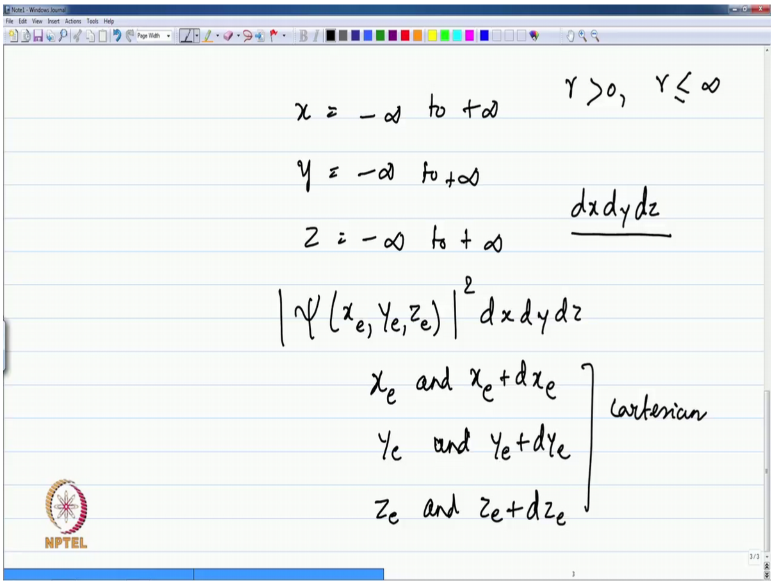

$x = -\infty$ to $+\infty$ $\quad r > 0,\ r \leq \infty$

$y = -\infty$ to $+\infty$

$z = -\infty$ to $+\infty$ $\quad \underline{dx\,dy\,dz}$

$$\left|\psi(x_e, y_e, z_e)\right|^2 dx\,dy\,dz$$

$$\left.\begin{array}{l} x_e \text{ and } x_e + dx_e \\ y_e \text{ and } y_e + dy_e \\ z_e \text{ and } z_e + dz_e \end{array}\right] \text{Cartesian}$$

So, this is the three dimensional region and the volume element that we talked about for the particle for the electron probability is psi is the volume element is dx dy dz and then, the probability is psi x e, y e, z e absolute square dx dy dz as the probability of finding the electron in the region or in the cube between x e and x e plus d x e y e and y e plus d y e and z e and z e plus d z e. This is the three dimensional Cartesian coordinate representation for the hydrogen electron problem, the nucleus electron problem.

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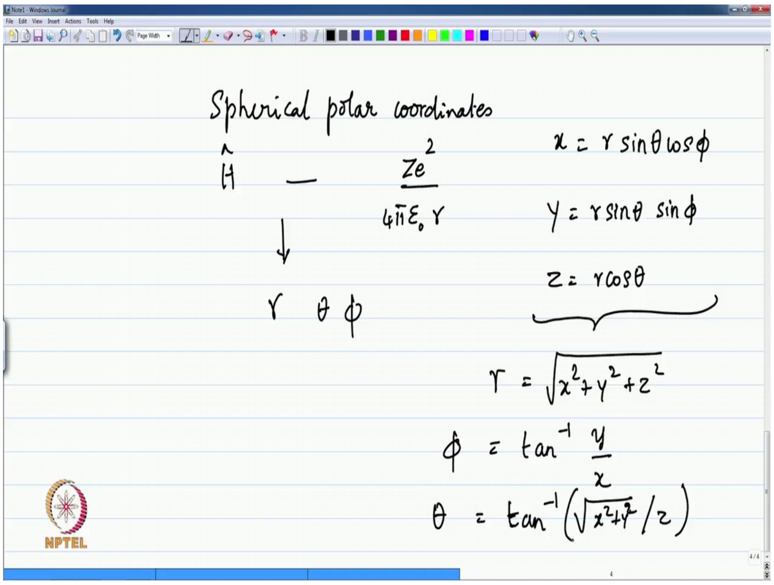

Spherical polar coordinates

$$\hat{H} \quad - \quad \frac{Ze^2}{4\pi\varepsilon_0 r}$$

$$\downarrow$$

$$r \quad \theta \quad \phi$$

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

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

$$\underbrace{z = r\cos\theta}$$

$$r = \sqrt{x^2+y^2+z^2}$$

$$\phi = \tan^{-1}\frac{y}{x}$$

$$\theta = \tan^{-1}\left(\sqrt{x^2+y^2}/z\right)$$

Instead of Cartesian coordinates in the case of hydrogen atoms, one uses spherical polar coordinates and the reason for that is that if you look at the hydrogen atom, the potential energy is spherically symmetric. Therefore, the important contribution to the stability of the hydrogen atom which is the binding energy between the coulombic charges being spherically symmetrical, the system is better described using the spherical polar coordinates which if you recall have 3 variables, the radius of the sphere and then, the polar angles, theta and phi on the sphere.

The standard relations for these are x is equal to r sin theta cos phi and y is r sin theta sin phi and z is r cos theta. These are the equations for the transformation between polar and Cartesian coordinates and the inverse transformation is of course r is square root of x square plus y square plus z square. And if you take the ratio of x by y r sin theta cancels off and you have cot phi or phi is tan inverse y by x and the last relation is theta which is given in terms of tan inverse square root of x square plus y square divided by z, ok.

So, the coordinate transformation allows you to either use the spherical or the Cartesian coordinate by using the relationship between them. And this one animation gives you the relation or the visualization of the spherical polar coordinate system and the values let me play the animation.

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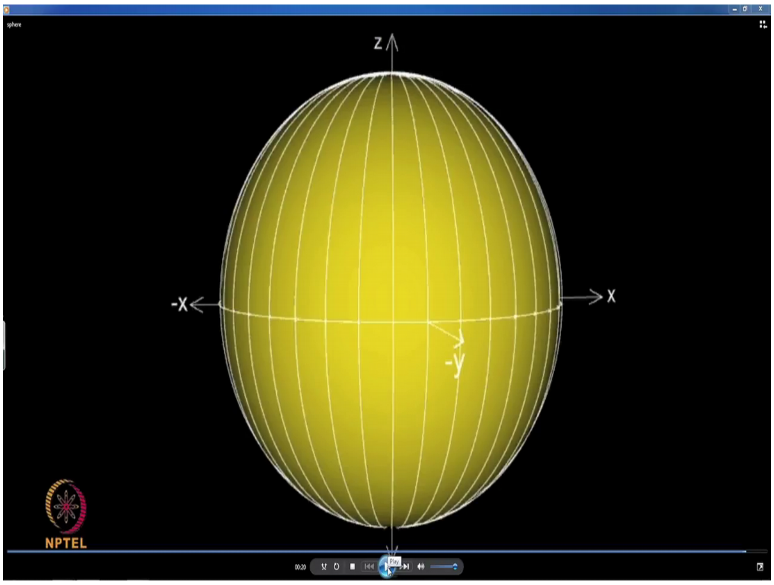

Here the relation between the Cartesian and the spherical system is given for a given one value of r, the radius of a sphere and you can see that if you fix your polar axis called z axis, then the polar angle theta is the angle theta varying from 0 to pi as shown by these different radii. So, that is a variation of theta and theta varies from 0 to pi only and the other angle is of course the azimuthal angle phi which is perpendicular in a plane perpendicular to this and if you rotate to this arc semi arc by 2 pi, you generate the surface of the sphere.

So, that is the azimuthal angle phi with respect to your chosen x axis, ok. So, that is a spherical coordinate system in which you can see the variation in theta given by these very different arcs and the value of phi corresponding to each one of these arcs starting from the x axis here at some arbitrary point and then, going around the x axis to the plus y to the minus x to the minus y and back you have 2 pi.

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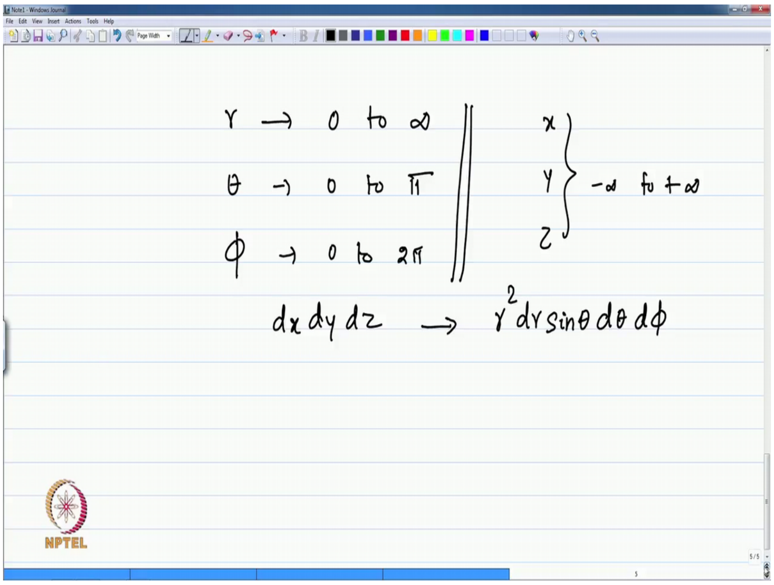

$r \rightarrow 0 \text{ to } \infty$

$\theta \rightarrow 0 \text{ to } \pi$

$\phi \rightarrow 0 \text{ to } 2\pi$

$\left.\begin{matrix} x \\ y \\ z \end{matrix}\right\} -\infty \text{ to } +\infty$

$dx\,dy\,dz \rightarrow r^2 dr \sin\theta \, d\theta \, d\phi$

Therefore, if we recall our lecture component or varies from 0 to infinity being the radius of the sphere, the sphere is from 0 radius to all over the universe and theta varies from 0 to pi.

As the polar angle varying from 0 to pi as you have seen with respect to the z axis and the phi which goes around the circle in 2 pi, pi is 0 to 2 pi and these are relations in parallel to the x y z all going from minus infinity to plus infinity in the Cartesian axis in taking care of the whole universal space. Therefore, these are the limits and dx dy dz which is a volume element in Cartesian coordinate space will have to be expressed in terms of the volume elements in spherical polar coordinate system and that is given by r square dr sin theta d theta d phi.

Those of you who are not familiar with this transformation must go back and look at the coordinate transformation and the simple differentials expressed from one coordinate to the other. And the relations are given by what is known as the Jacobian, the magnitude of the Jacobian.

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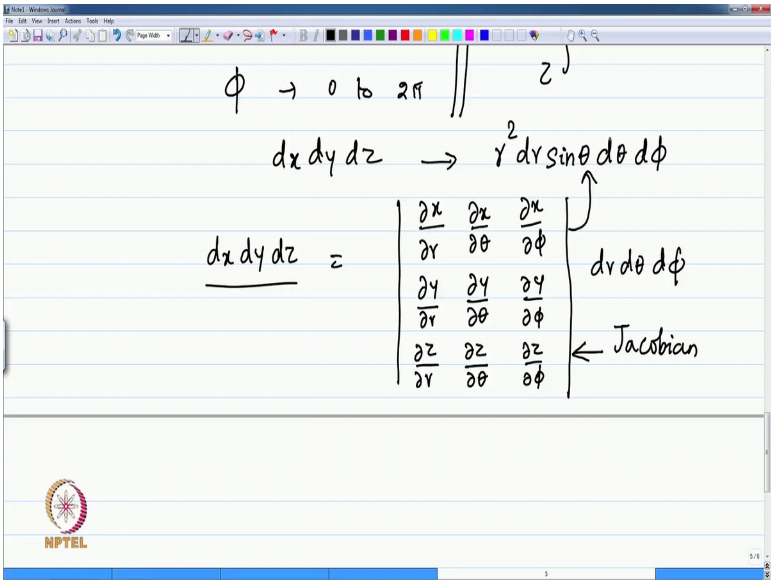

$\phi \rightarrow 0$ to 2π || z)

$$dx\,dy\,dz \longrightarrow r^2\,dr\,\sin\theta\,d\theta\,d\phi$$

$$\underline{dx\,dy\,dz} = \begin{vmatrix} \frac{\partial x}{\partial r} & \frac{\partial x}{\partial \theta} & \frac{\partial x}{\partial \phi} \\ \frac{\partial y}{\partial r} & \frac{\partial y}{\partial \theta} & \frac{\partial y}{\partial \phi} \\ \frac{\partial z}{\partial r} & \frac{\partial z}{\partial \theta} & \frac{\partial z}{\partial \phi} \end{vmatrix} dr\,d\theta\,d\phi$$

← Jacobian

The Jacobian being the partial derivative of x with respect to r, x with respect to theta and x, with respect to phi and the partial derivative of y, with respect to r, with respect to theta and with respect to phi and likewise the partial derivative with respect to z with of z with respect to r and with respect to theta, with respect to phi. The determinant of this multiplied by dr d theta d phi is this is called the Jacobian and this is in elementary transformation matrix that transforms volume elements from one coordinate system, another coordinate system and this Jacobian with the magnitude has r square sin theta with the drb theta d phi. Therefore, when you calculate the volume elements and when you calculate the probability is using spherical polar coordinate system.

If you are using Cartesian coordinates transformed, the relation from Cartesian to the polar and these are the mathematical formulas already well known and derived from elementary differential value calculus. Keep this in mind.

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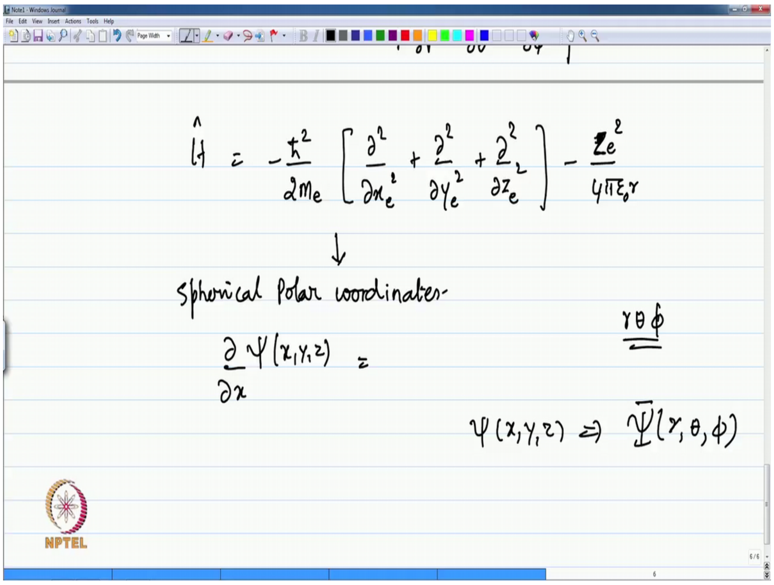

$$\hat{H} = -\frac{\hbar^2}{2m_e}\left[\frac{\partial^2}{\partial x_e^2} + \frac{\partial^2}{\partial y_e^2} + \frac{\partial^2}{\partial z_e^2}\right] - \frac{Ze^2}{4\pi\varepsilon_0 r}$$

$$\downarrow$$

Spherical Polar coordinates

$\underline{\underline{r\theta\phi}}$

$$\frac{\partial}{\partial x}\psi(x,y,z) =$$

$$\psi(x,y,z) \Rightarrow \bar{\Psi}(r,\theta,\phi)$$

Therefore, now we have this Hamiltonian expressed in terms of minus h bar square by 2 m e dou square by dou x e square plus dou square by dou y e square plus dou square by dou z e square minus h z e square by 4 pi epsilon naught r. This needs to be changed to polar coordinates, spherical polar coordinates. That is not a trivial exercise, but it is not a very hard exercise. The derivatives for example dou by dou x of any function of xyz are expressed in another coordinate system like r theta phi. If we have to x plus phi in terms of r theta pi, the derivatives are expressed using the partial derivatives of the coordinates with respect to the new coordinates.

So, for example dou by dou x of psi if you wanted to write the appropriate wave function in the polar coordinate, namely psi xyz is replaced by the corresponding substitution of the x and y and z using r theta pi using this function.

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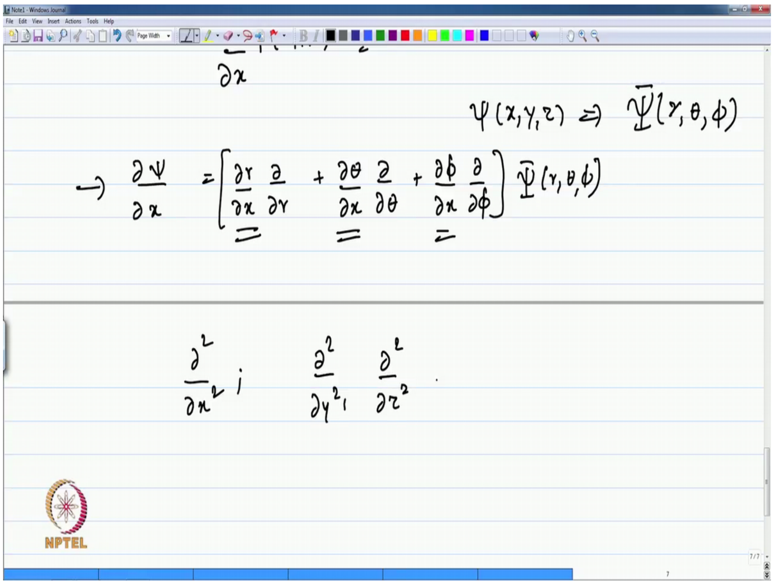

$$\psi(x,y,z) \Rightarrow \Psi(r,\theta,\phi)$$

$$\rightarrow \frac{\partial\psi}{\partial x} = \left[\underline{\underline{\frac{\partial r}{\partial x}}}\frac{\partial}{\partial r} + \underline{\underline{\frac{\partial \theta}{\partial x}}}\frac{\partial}{\partial \theta} + \underline{\underline{\frac{\partial \phi}{\partial x}}}\frac{\partial}{\partial \phi}\right]\Psi(r,\theta,\phi)$$

$$\frac{\partial^2}{\partial x^2}; \quad \frac{\partial^2}{\partial y^2}, \quad \frac{\partial^2}{\partial z^2}.$$

Then, there is a very simple partial derivative chain rule which tells you how to calculate dou psi by dou x as nothing other than dou by dou r, with dou r by dou x derivative plus dou theta by dou x dou by dou theta plus dou phi by dou x dou by dou phi acting on the wave function psi r theta pi. So, this is the transformation of the derivative form of the cartesian coordinate into the corresponding polar coordinates. And of course, you can calculate dou r by dou x dou theta by dou x and dou phi by dou x from the inverse relations that you already have that, ok.

From this you can calculate the derivative of r with respect to x y and z the derivative of phi with respect to x y and z and the derivative of theta with respect to x y and z. Therefore, the partial derivatives that you need to calculate for expressing the kinetic energy in spherical polar coordinate system involves 3 such quantities namely dou square by dou x square which is operating this once more. But be careful that the terms contain already r theta and v and therefore, the partial derivatives have to be taken carefully and you have to do the same thing for dou square by dou y square and dou square by dou z square.

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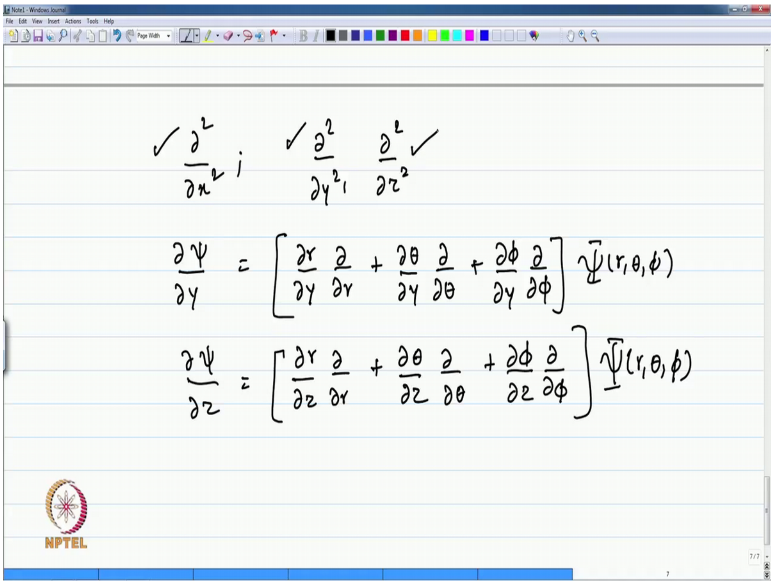

$$✓\ \frac{\partial^2}{\partial x^2}\ ; \quad ✓\ \frac{\partial^2}{\partial y^2}, \quad \frac{\partial^2}{\partial z^2}\ ✓$$

$$\frac{\partial \psi}{\partial y} = \left[\frac{\partial r}{\partial y}\frac{\partial}{\partial r} + \frac{\partial \theta}{\partial y}\frac{\partial}{\partial \theta} + \frac{\partial \phi}{\partial y}\frac{\partial}{\partial \phi}\right]\psi(r,\theta,\phi)$$

$$\frac{\partial \psi}{\partial z} = \left[\frac{\partial r}{\partial z}\frac{\partial}{\partial r} + \frac{\partial \theta}{\partial z}\frac{\partial}{\partial \theta} + \frac{\partial \phi}{\partial z}\frac{\partial}{\partial \phi}\right]\psi(r,\theta,\phi)$$

Therefore, let me summarize this particular part of the lecture with the corresponding expressions, namely dou psi by dou y as dou r by dou y dou by dou r plus dou theta by dou y dou by dou theta plus dou phi by dou y dou by dou phi acting on the wave function psi of r theta and pi. And similarly, dou psi by dou z as dou r by dou z dou by dou r plus dou theta by dou z dou by dou theta plus dou phi by dou z dou by dou phi acting on the corresponding wave functions i or theta pi.

These are the derivative equivalents and you calculate likewise the dou square terms, the dou square by dou y square terms and the dou square by dou z square terms.

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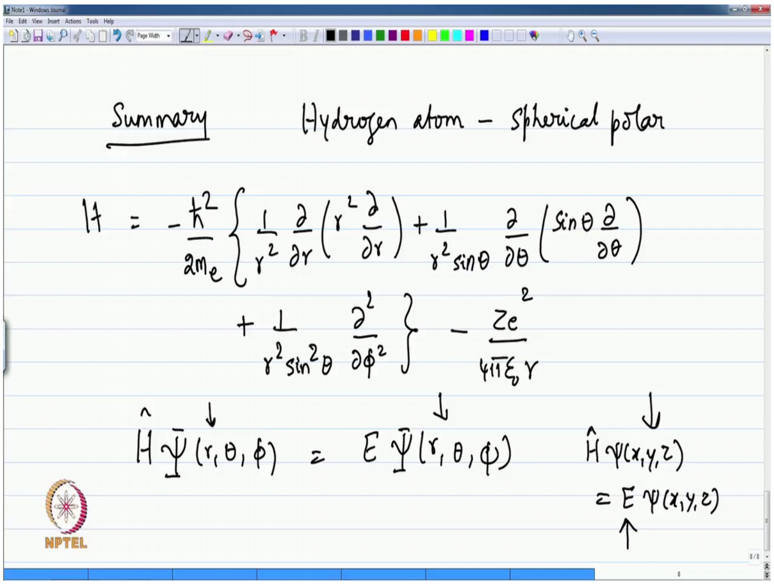

Summary Hydrogen atom – Spherical polar

$$H = -\frac{\hbar^2}{2m_e}\left\{\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right)+\frac{1}{r^2\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right)+\frac{1}{r^2\sin^2\theta}\frac{\partial^2}{\partial\phi^2}\right\}-\frac{Ze^2}{4\pi\varepsilon_0 r}$$

$$\hat{H}\,\overset{\downarrow}{\Psi}(r,\theta,\phi) = E\,\overset{\downarrow}{\Psi}(r,\theta,\phi) \qquad \overset{\downarrow}{\hat{H}\psi(x,y,z)} = \underset{\uparrow}{E}\,\psi(x,y,z)$$

So, the summary of doing that calculation and if you are doing it for the first time about 2 to 3 hours, it is worth the time that you have to give in order to add all these terms and cancel and arrive at the final form. But I will write the final magic form that everybody uses for solving the hydrogen atom Hamiltonian in polar spherical coordinates. The Hamiltonian is minus h bar square by 2 m e 1 by r square dou by dou r of r square dou by dou r plus 1 by r square sin theta dou by dou theta sin theta dou by dou theta plus 1 by r square sin square theta dou square by dou phi square. All of which is the transformation of the derivatives to this spherical polar form and therefore, this is nothing but the kinetic energy term in terms of the spherical polar coordinates with the potential energy minus z e square by 4 pi epsilon naught r and the equation that you are looking for solving is H psi r theta and v is equal to e psi r theta and pi instead of the H psi x y z in terms of e psi x y z, ok.

The wave functions are different in the different polar different coordinate systems, but please remember the energy which is independent of the coordinate representation will not be different between different coordinate system. How you represent your coordinates should not lead to any changes in the eigenvalue for the hydrogen electron and therefore, the traditional method is to use the spherical polar coordinates and that allows the wave function to be separated into r dependent wave function only a theta dependent wave function only, in the phi independent wave function only. If you recall the particle in the two dimensional box where we had x y dependent wave function being separated into x, only the function term and then, y only wave function terms.

We were able to get the energies and the solutions etc, therefore separation of variables is far more detailed here in the case of hydrogen atom and let me stop with this as the focal point for the next part of the lecture on what is called the substitution of the wave function in terms of the 3 radial only, polar theta angle dependent only and azimuthal angle phi dependent only functions and how we separate this into 3 different equations. We will not solve them, but in the 2nd part we will look at the solution and the 3rd part we will see some physical representations of the wave functions themselves, the real and imaginary parts. So, let me stop with part 1 here. We will continue exactly from this in the next part.

Until then thank you.