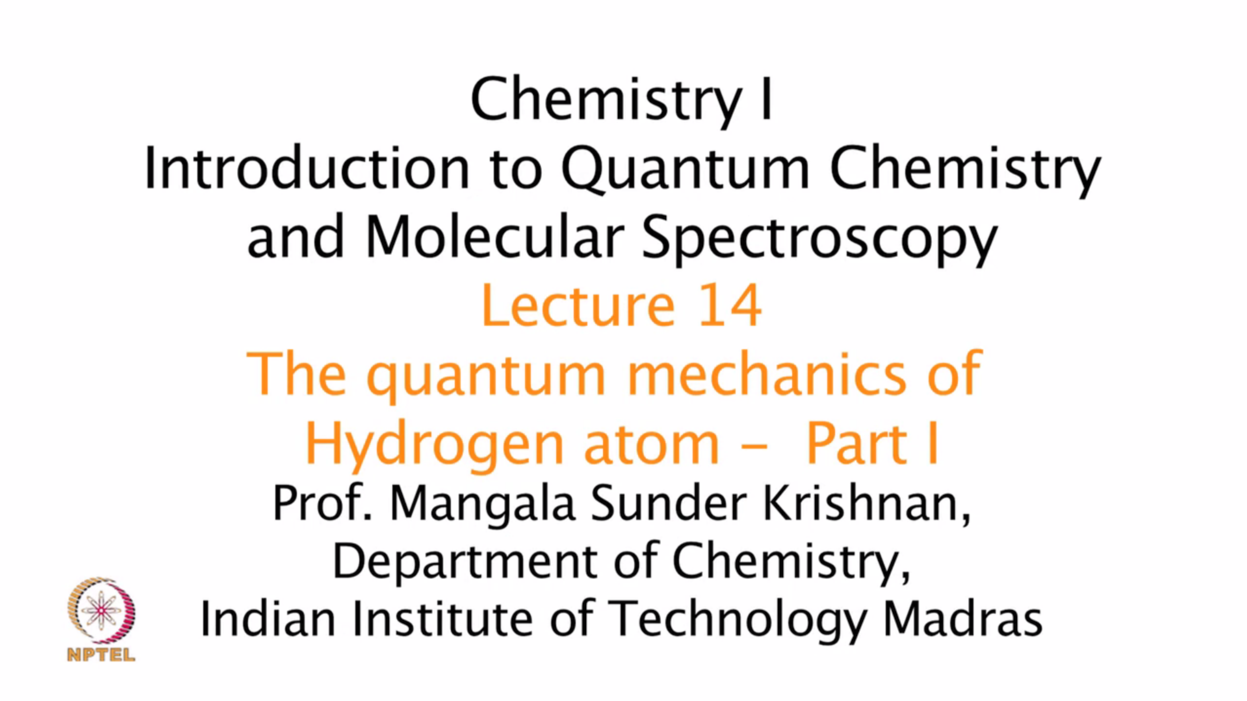

Chemistry I
Introduction to Quantum Chemistry and Molecular Spectroscopy
Lecture 14
The quantum mechanics of Hydrogen atom – Part I
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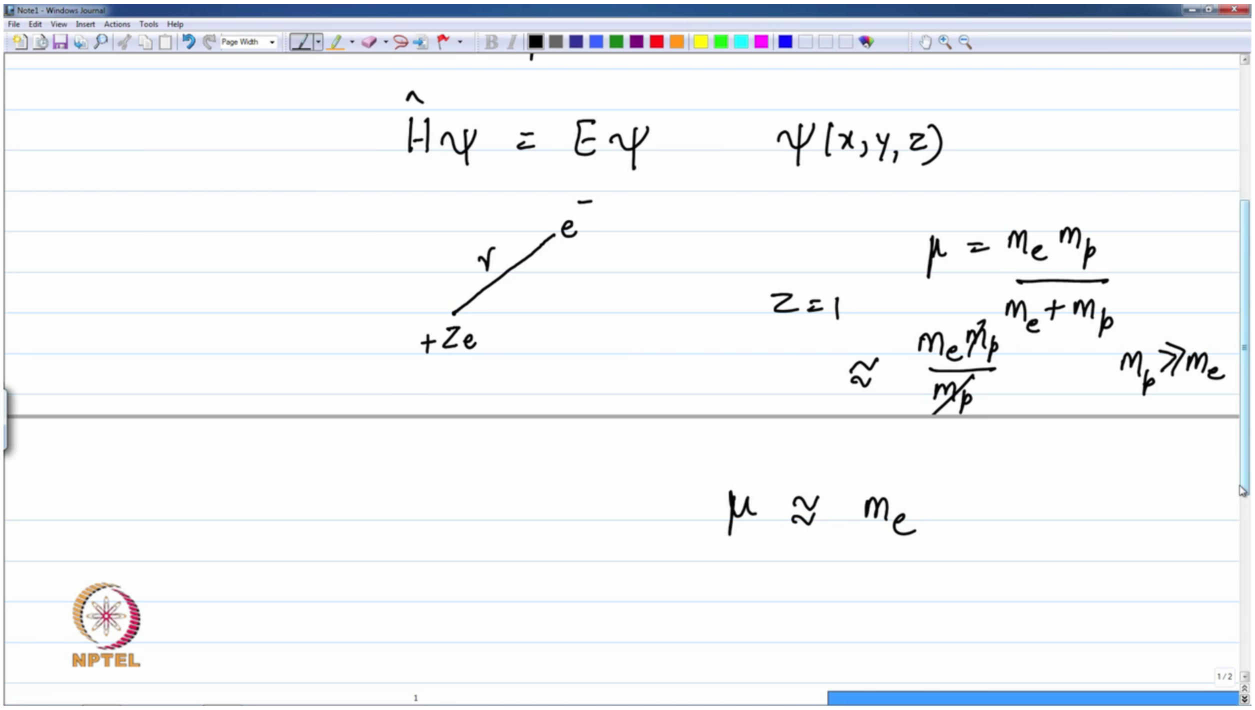
NPTEL

Prof. Mangala Sunder Krishnan: Welcome back to the lectures on CY1001 or Introductory Chemistry. 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. 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's the spectra of the hydrogen atom, which prompted Niels Bohr to come up the first model of quantizing the 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.



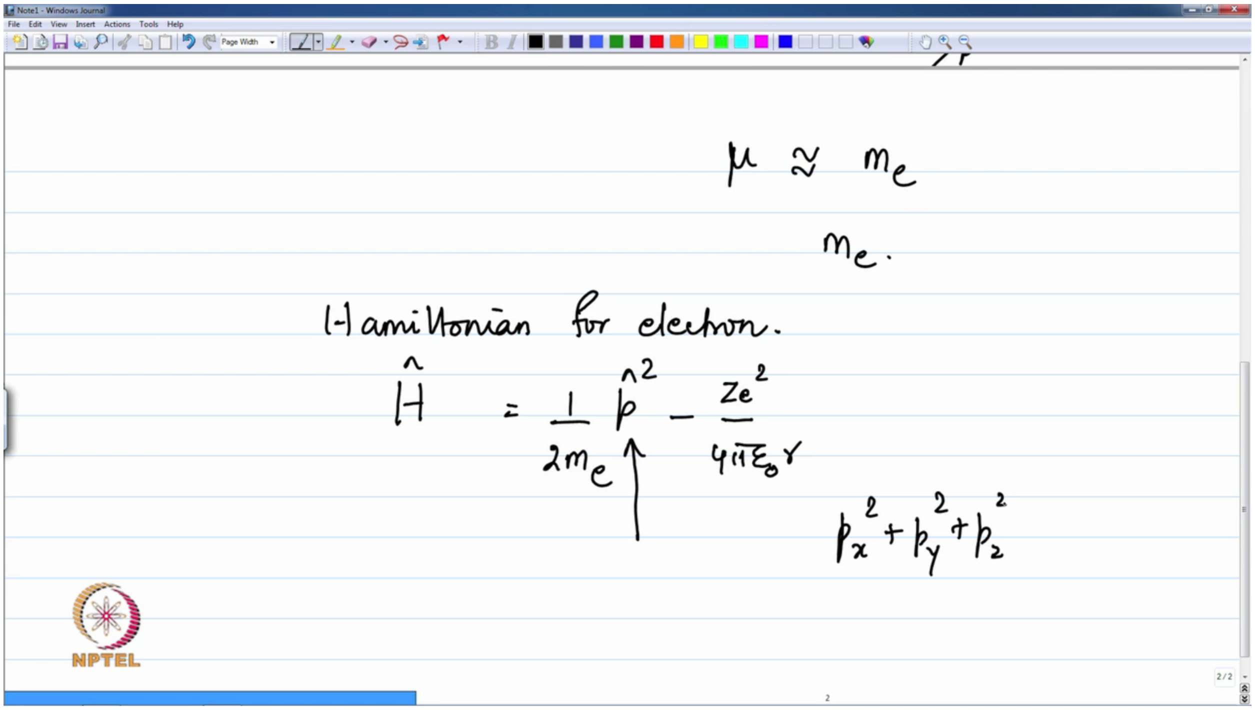
$$\hat{H}\psi = E\psi \qquad \psi(x,y,z)$$

$$Z=1$$

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

$$\mu \approx m_e$$

So this is part 1 of the Quantum Mechanics of Hydrogen Atom, and in the solution of this equation $\hat{H}\psi = E\psi$ where now ψ is three-dimensional $\psi(x,y,z)$ Cartesian coordinates, we do use a classical starting point of the nucleus with an electron somewhere and the nucleus having a positive charge $+Ze$, $Z=1$ and the electron with the minus charge and the distance of r. I shall not describe this as a two-body problem, even though that's right we are doing it, the two body problem and then remove the center 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 the or the reduced 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. We shall variables making that approximation and write the mass as nothing but the mass of the electron. Therefore, we needed the Hamiltonian for the electron.



$\mu \approx m_e$

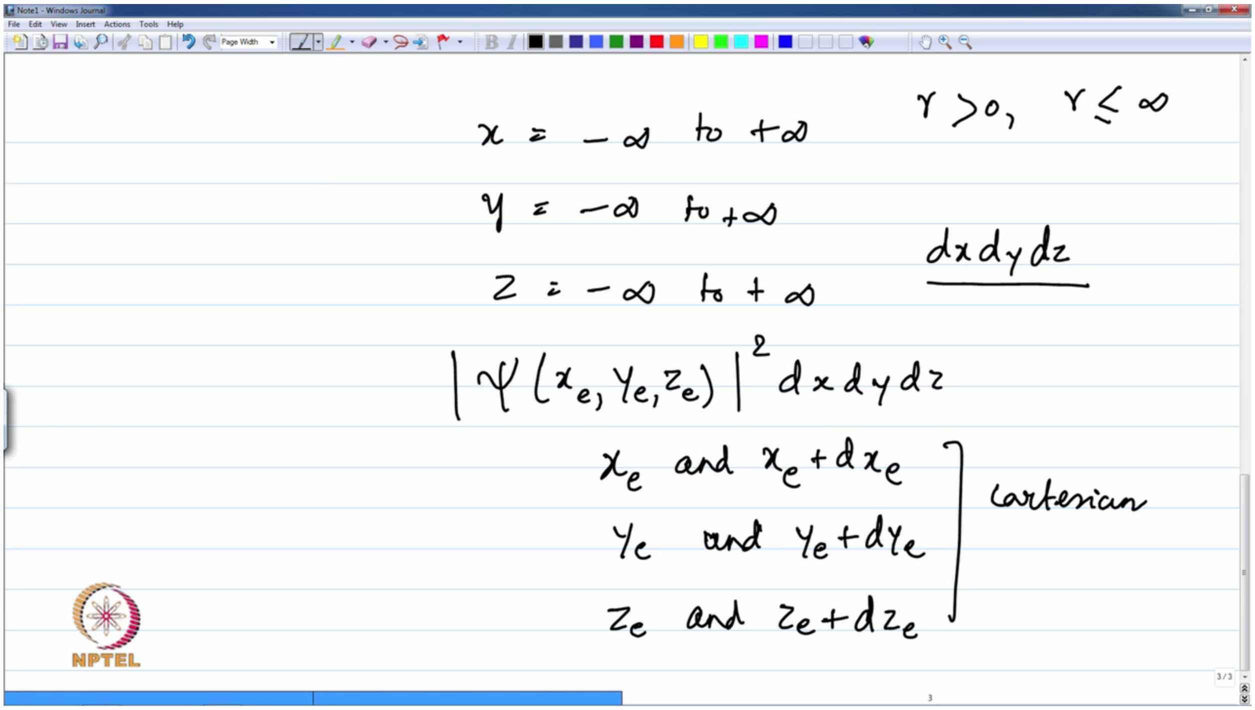
m_e.

Hamiltonian for electron.

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

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

So let's assume that the nucleus is stationary, does not contribute to the overall kinetic energy of the atom. That's already there in the center mass which is not considered here. 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^2 $1/2m_e$ - $Z_e^2/4\pi\varepsilon_0 r$, which is the classical columbic energy of interaction between the positive and the negative charge, and this P^2, which is an operator is given by $P_x^2+P_y^2+P_z^2$, the three components of the momentum in a coordinate system which is probably fixed in the nucleus itself for arguments.



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

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

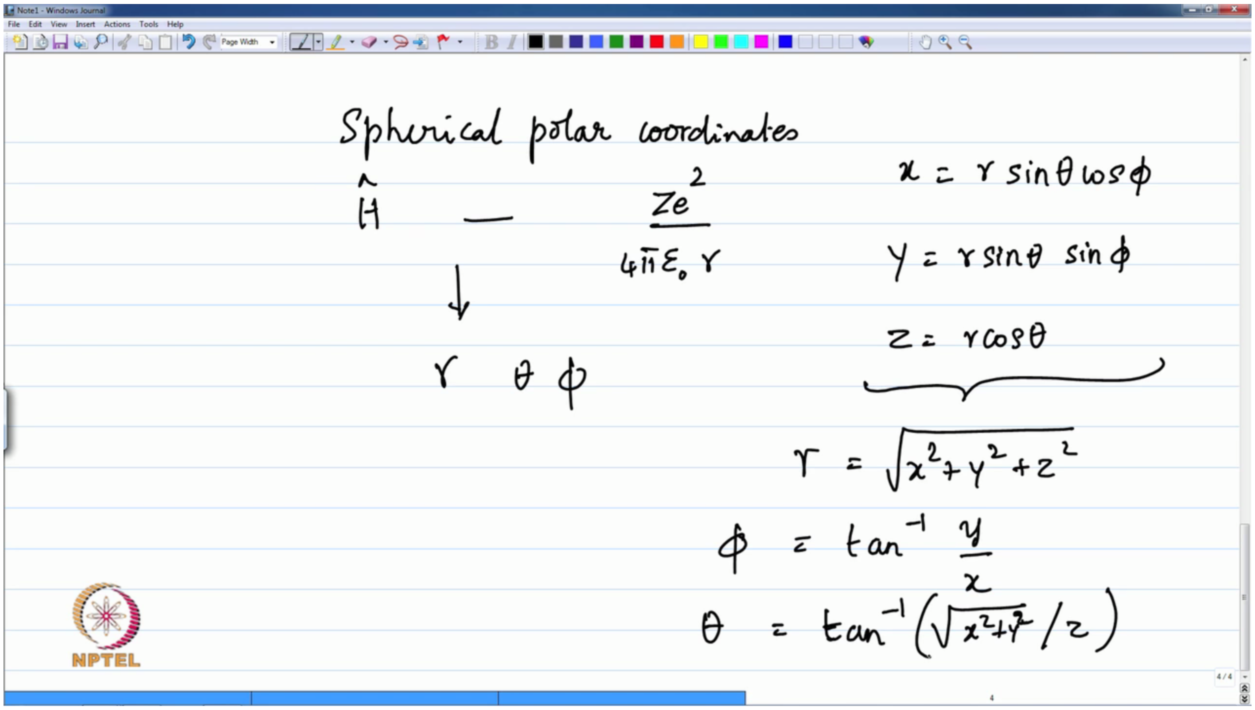
$z = -\infty$ to $+\infty$ $\quad \underline{dx\,dy\,dz}$

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

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

And then of course Px is replaced by the derivative operators so that the Ĥ becomes -hcross^2/2m$_e$ ($\partial^2/\partial x_e^2 + \partial^2/\partial y_e^2 + \partial^2/\partial z_e^2$), and these are the coordinates of the electron with respect to that origin and then you have the potential energy - ze^2/4πε$_0$r and r is in principle >0 and ≤∞, at infinity of course the coulombic interaction is zero.

Therefore, here the boundary includes the entire three-dimensional world, the whole universe. So the boundaries are explicitly x = -∞ to +∞, y = -∞ to +∞, and also z = -∞ to +∞. So this is the three-dimensional region and the volume element that we talk about for the particle for the electron probability is the ψ -- the volume element is dx dy dz and then the probability is ψ(x_e,y_e,z_e)|2 dx dy dz as the probability of finding the electron in the region or in the cube between x_e and x_e+dx_e, y_e and y_e+dy_e and z_e and z_e=dz_e. This is the three-dimensional Cartesian coordinate representation for the hydrogen electron problem, the nucleus electron problem.



Spherical polar coordinates

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

$$\downarrow$$

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

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

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

$$z = r\cos\theta$$

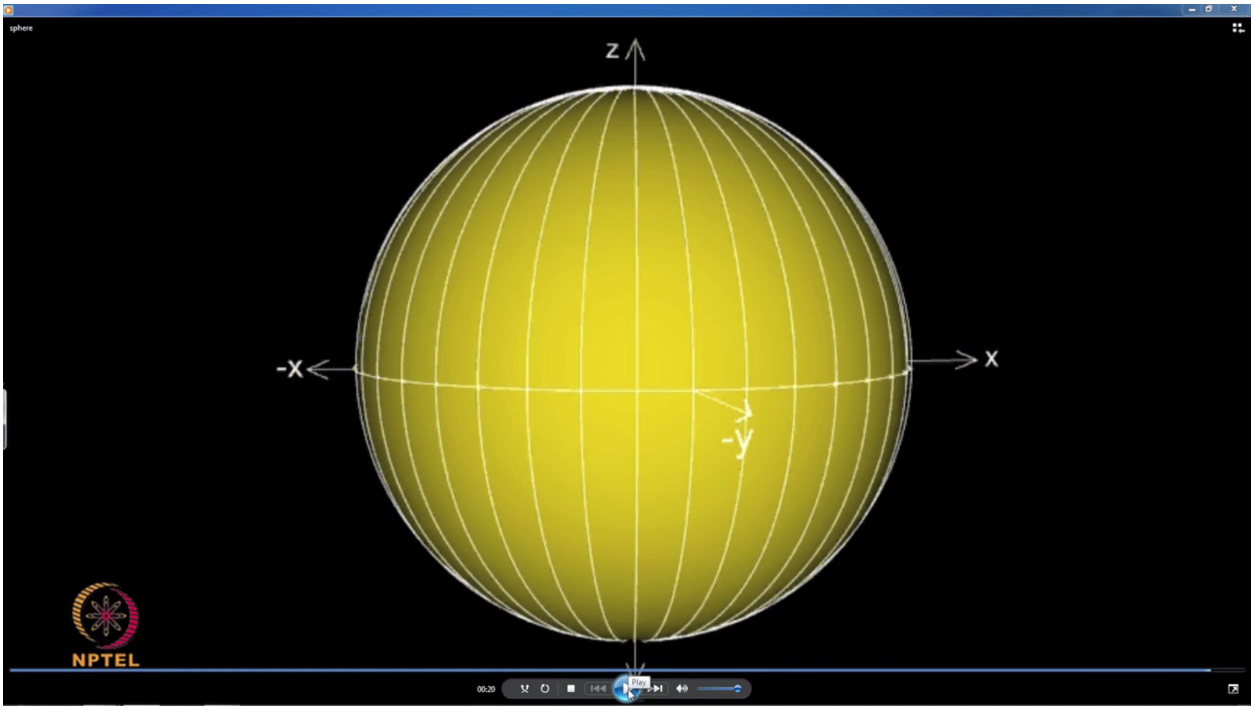
$$\underbrace{\qquad\qquad\qquad}$$

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

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

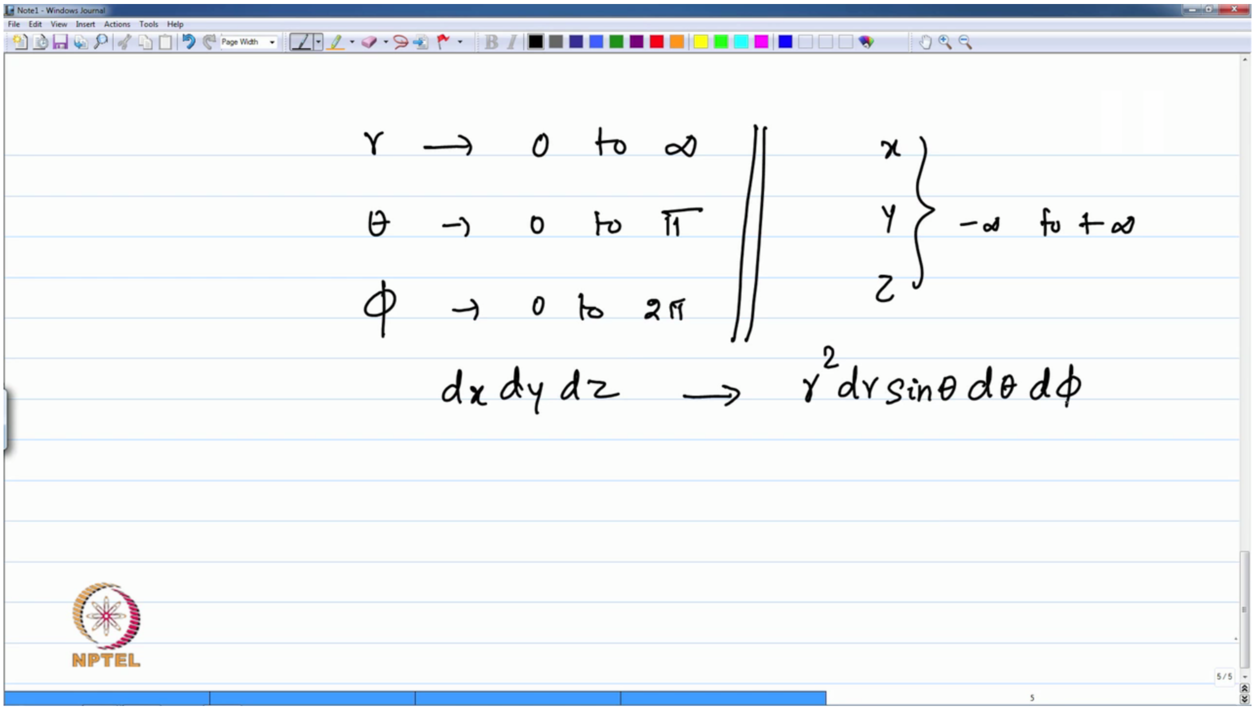
$$\theta = \tan^{-1}\left(\sqrt{x^2+y^2}/z\right)$$

Instead of Cartesian coordinates, in the case of hydrogen atom 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 columbic charges being spherically symmetrical the system is better described using the spherical polar coordinate which, if you recall, have three variables, the radius of the sphere, and then the polar angle, θ and φ on the sphere. The standard relations for these are x = r sinθ cosφn and y = r sinθ sinφn and z = r cosθ. These are the equations for the transformation between polar and Cartesian coordinates and the inverse transformation is of course r = rootx^{2}+y^{2}+z^{2}, and if you take the ratio of x/y or sinθ cancels of and you have cot φ or φ = tan-1 y/x, and the last relation is θ, which is given in terms of tan^{-1} (rootx^{2}+y^{2}/z). 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. Here the relation between the Cartesian and the spherical system is given one value of r, the radius of the sphere, and you can see that if you fix a polar axis called the z axis, then the polar angle θ is the angle θ varying from 0 to π as shown by these different radii. So that's a variation of θ, and θ varies from 0 to π only, and the other angle is of course the azimuthal angle φ, which is perpendicular, in a plain perpendicular to this, and if you rotate this arc, semi arc, by 2 π, you will generate the surface of the sphere. So that's the azimuthal angle φ with respect to your chosen x axis.

So that’s a spherical coordinate system in which you can see the variation in θ given by these different arcs and the value of φ 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 +y to the -x to the -y and back.



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

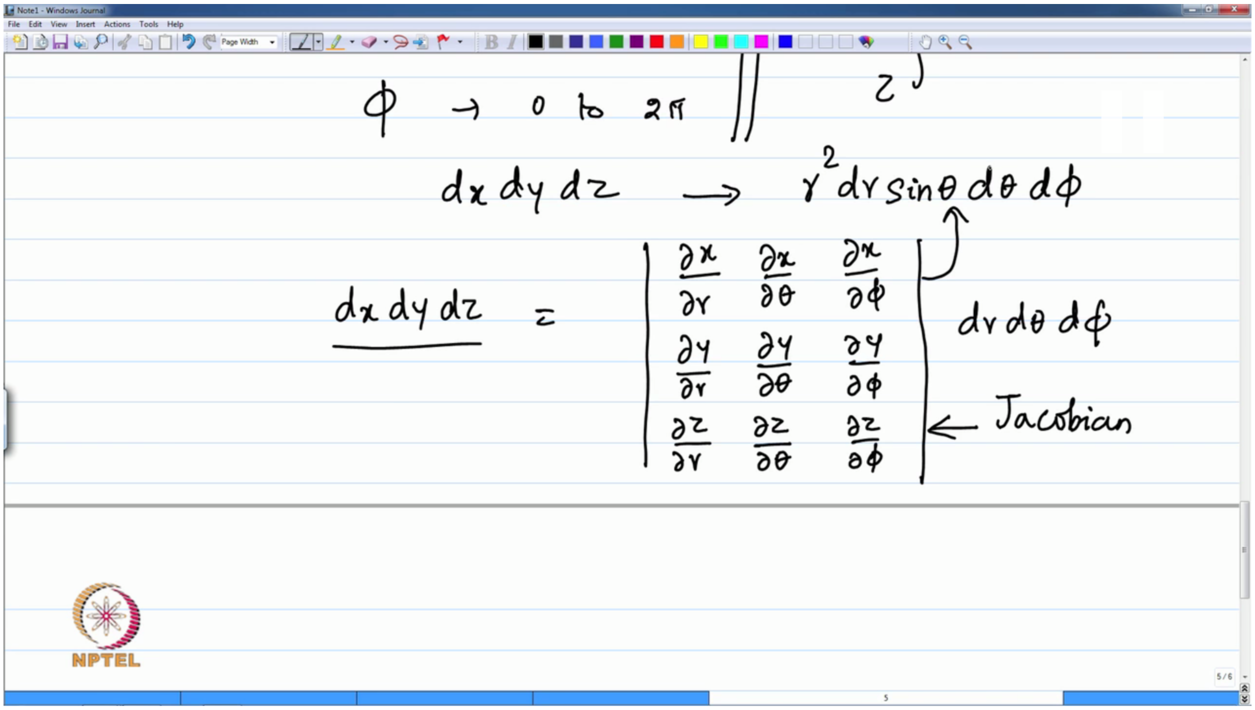
$$\theta \rightarrow 0 \text{ to } \pi$$

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

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

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

Therefore, if we recall our lecture component r varies from 0 to ∞ being the radius of the sphere the sphere is from 0 radius to all over the universe, and θ varies from 0 to π as the polar angle varying from 0 to π as you have seen with respect to the z axis and the φ which goes around the circle in 2π, φ = 0 to π, and these are relations in parallel to the x, y, z all going from -∞ to ∞ 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's given by r2dr sinθ dθ dφ.



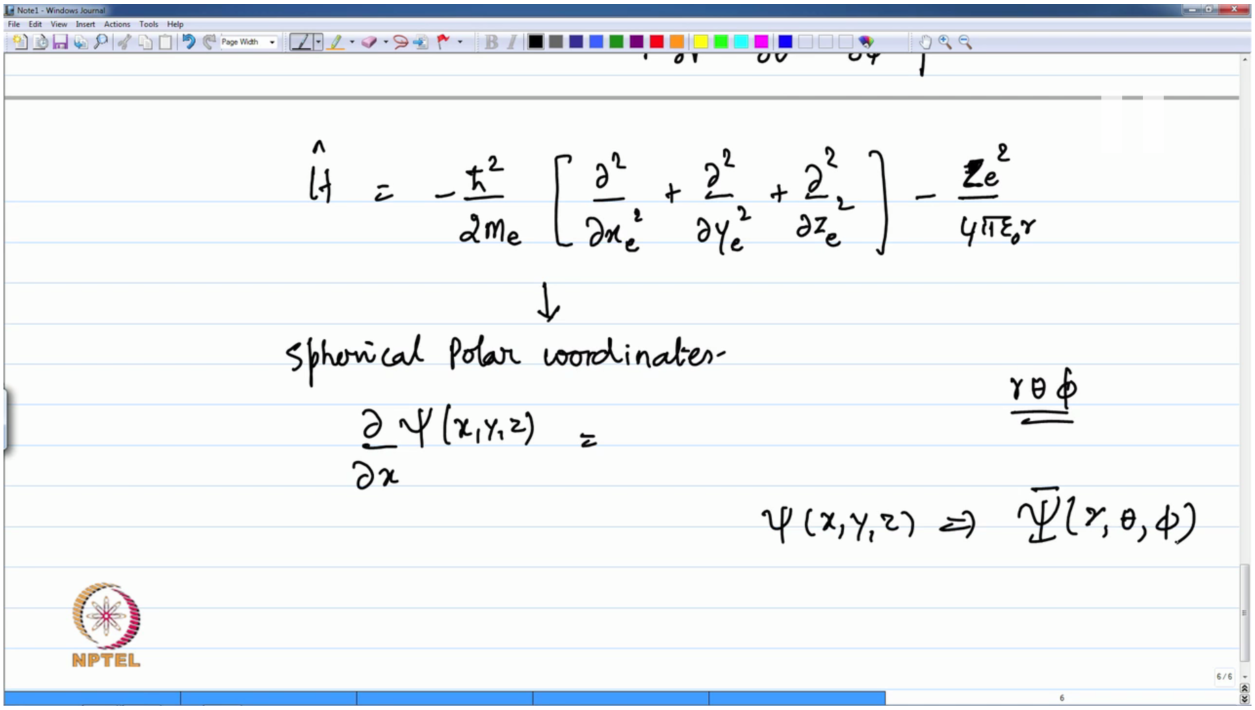
$$\phi \rightarrow 0 \text{ to } 2\pi \qquad z)$$

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

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

Those of you who are not familiar with this transformation must go back and look at the coordinate transformation and the simple differential expressed from one coordinate to the other, and the relations are given by what is known as the Jacobian, the magnitude of the Jacobian, the Jacobian being partial derivative of x with respect to r, x with respect to θ, and x with respect to φ, and likewise the partial derivative with respect to Z with respect to r and with respect to θ and with respect to φ. The determinant of this multiplied by drdθdφ is this is called the Jacobian and this is an elementary transformation matrix that transforms volume elements from one coordinate system to another coordinate system and this Jacobian that the magnitude has to be r2 sinθ with the drdθdφ.

Therefore, when you calculate the volume elements and when you calculate the probability using spherical polar coordinate system, if you are using Cartesian coordinates, transform the relation from Cartesian to the polar and these are the mathematical formulas already well-known and derived from elementary differential calculus. Keep this in mind.



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

$$\downarrow$$

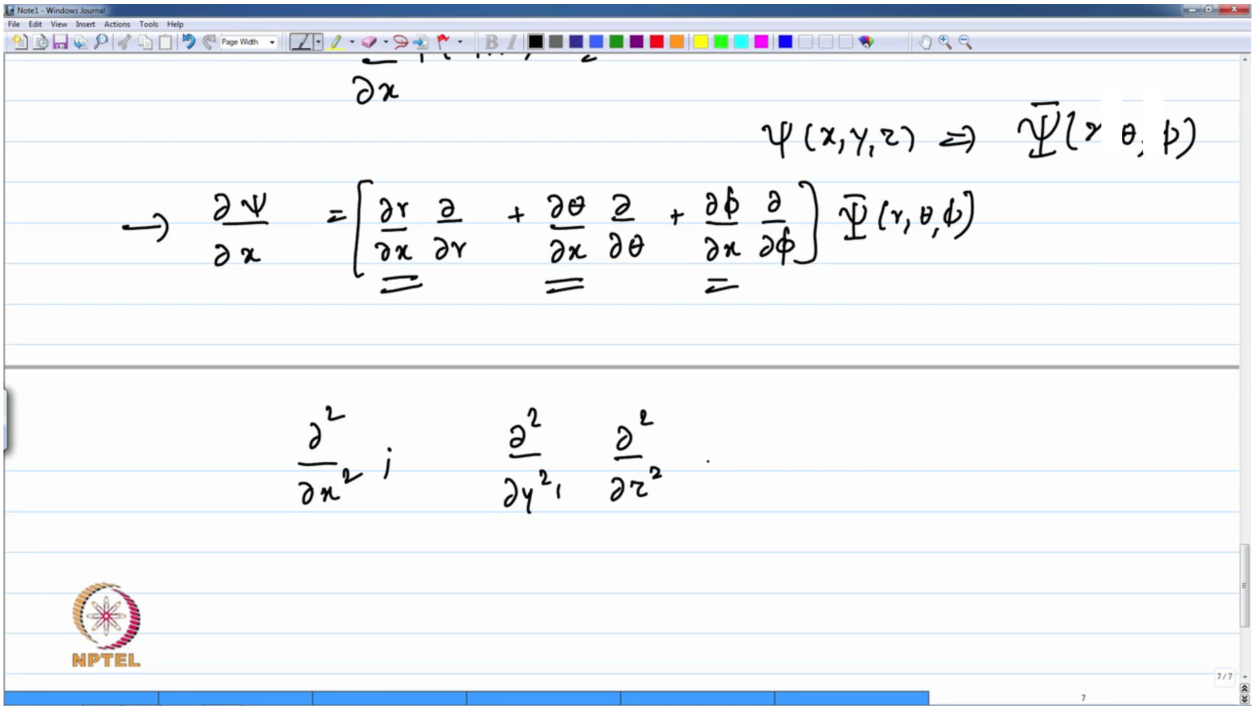
Spherical Polar coordinates

$r\theta\phi$

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

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

Therefore, now we have this Hamiltonian expressed in terms of -hcross2/2m_e $[\partial^2/\partial x_e^2 + \partial^2/\partial y_e^2 + \partial^2/\partial z_e^2]$ $-z_e^2/4\pi\varepsilon_0 r$. This needs to be changed to polar coordinates, spherical polar coordinates. That's not a trivial exercise, but it's not a very hard exercise. The derivatives, for example, $\partial/\partial x$ of any function of (x,y,z) are expressed in another coordinate system like or (r,θ,φ) if you have to express high in terms of (r,θ,φ). The derivatives are expressed using the partial derivatives of the coordinates with respect to the new coordinates. So, for example, $\partial/\partial x(\psi)$ if you wanted to write the appropriate wave function in the polar coordinate, namely $\psi(x,y,z)$ is replaced by the corresponding substitution of the x and y and z using (r,θ,φ), using this function.



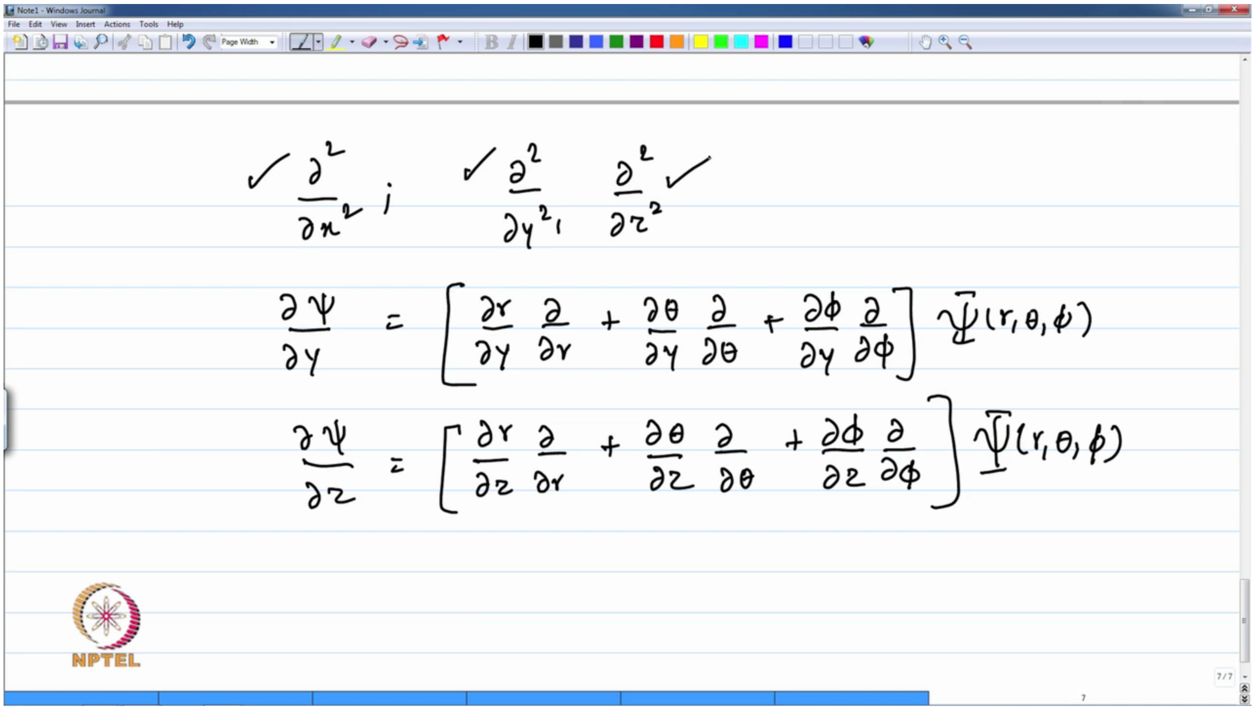
∂x

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

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

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

Then there is a very simple partial derivative chain rule, which tells you how to calculate $\partial\psi/\partial x$ as nothing other than [$\partial/\partial r$ with $\partial r/\partial x$ + $\partial\theta/\partial x$ ∂/dethθ + $\partial\varphi/\partial x$ $\partial/\partial\varphi$] acting on the wave function $\psi(r,\theta,\varphi)$. So this is the transformation of the derivative form of the Cartesian coordinate into the corresponding polar coordinate. And of course you can calculate $\partial r/\partial x$, $\partial\theta/\partial x$ and $\partial\varphi/\partial x$ from the inverse relations that you already have. You already have that, okay. From this you can calculate the derivative of r with respect to x, y and z, the derivative of φ with respect to x, y and z, and the derivative of θ 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 three such quantities, namely ∂^2/deltx^2, which is operating this once more, but being careful that the terms contain already r, θ and φ, and therefore, the partial derivatives have to be taken carefully, and you have to do the same thing for $\partial^2/\partial y^2$ and $\partial^2/\partial z^2$.

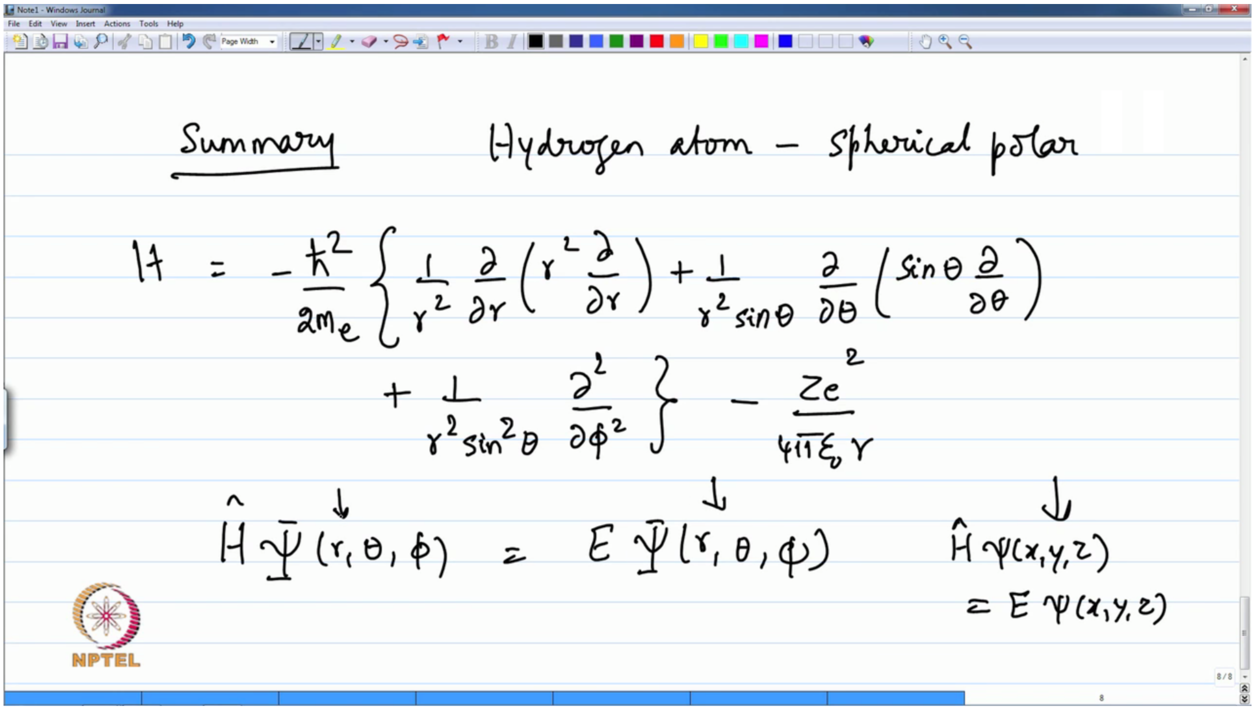


$$\checkmark\ \frac{\partial^2}{\partial x^2};\quad \checkmark\ \frac{\partial^2}{\partial y^2},\quad \frac{\partial^2}{\partial z^2}\ \checkmark$$

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

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

Therefore, let me summarize this particular part of the lecture with the corresponding expressions, namely ∂ψ/∂y = [∂r/∂y ∂/∂r + ∂θ/∂y ∂/∂θ + ∂φ/∂y ∂/∂φ] acting on the wave function ψ (r,θ,φ), and similarly, ∂ψ/∂z = [∂r/∂z ∂/∂r + ∂θ/∂z ∂/∂θ + ∂φ/∂z ∂/∂φ] acting on the corresponding wave function ψ (r,θ,φ). These are the derivative equivalents and you calculate likewise the ∂2 terms the ∂2/∂2 terms and ∂2/∂2 term.



Summary   Hydrogen atom – Spherical polar

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

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

So the summary of doing that calculation, and if you are doing it for the first thing about 2 to 3 hours is what 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 coordinate. $\hat{H} = -\mathrm{hcross}^2/2me \{1/r^2\ \partial/\partial r\ (r^2\ \partial/\partial r) + 1/r^2\sin\theta\ \partial/\partial\theta(\sin\theta\ \partial/\partial\theta) + 1/r^2\sin 2\theta\ \partial^2/\partial\varphi^2\}$ all of which is the transformation of the derivatives to the spherical polar form and for this is nothing with the kinetic energy term in terms of the spherical polar coordinates with the potential energy $-ze2/4\pi\varepsilon_0 r$, and the equation that you are looking for solving is the $\hat{H}\ \psi\ (r,\theta,\varphi) = E\ \psi\ (r,\theta,\varphi)$, instead of the $\hat{H}\ \psi\ (x,y,z) = E\ \psi\ (x,y,z)$, okay.

The wave functions are different in the 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 eigen value 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 an r dependent wave function only, θ dependent wave function only, and the φ dependent wave function only.

If you recall, the particle in the two-dimensional box where we had an xy dependent wave function being separated into x only wave function term and then y only they function term, and they were able to get the energies and the solutions et cetera. 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 pre-radial only polar θ angle dependent only and azimuthal angle φ dependent only functions, and how we separate this into three different equations. We will not solve them but in the second part we will look at the solution, and the third part, we will see some physical representations of the wave functions themselves, the real and imaginary parts.

So let me start with part one here. We will continue exactly from this in the next part. Until then, thank you.