UNIT: IV
Quantum Theory of Hydrogen

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The hydrogen atom is the simplest physical system *containing interaction potentials* (i.e., not just an isolated particle).

Simple: one proton, one electron, and the electrostatic (Coulomb) potential that holds them together.

The potential energy in this case is just

$$V = -\frac{e^2}{4\pi\varepsilon_0 r}$$

(the attractive potential between charges of +e and –e, separated by a distance r).

This is a stationary state potential (no time dependence). We could just plug it in to Schrödinger's equation to get

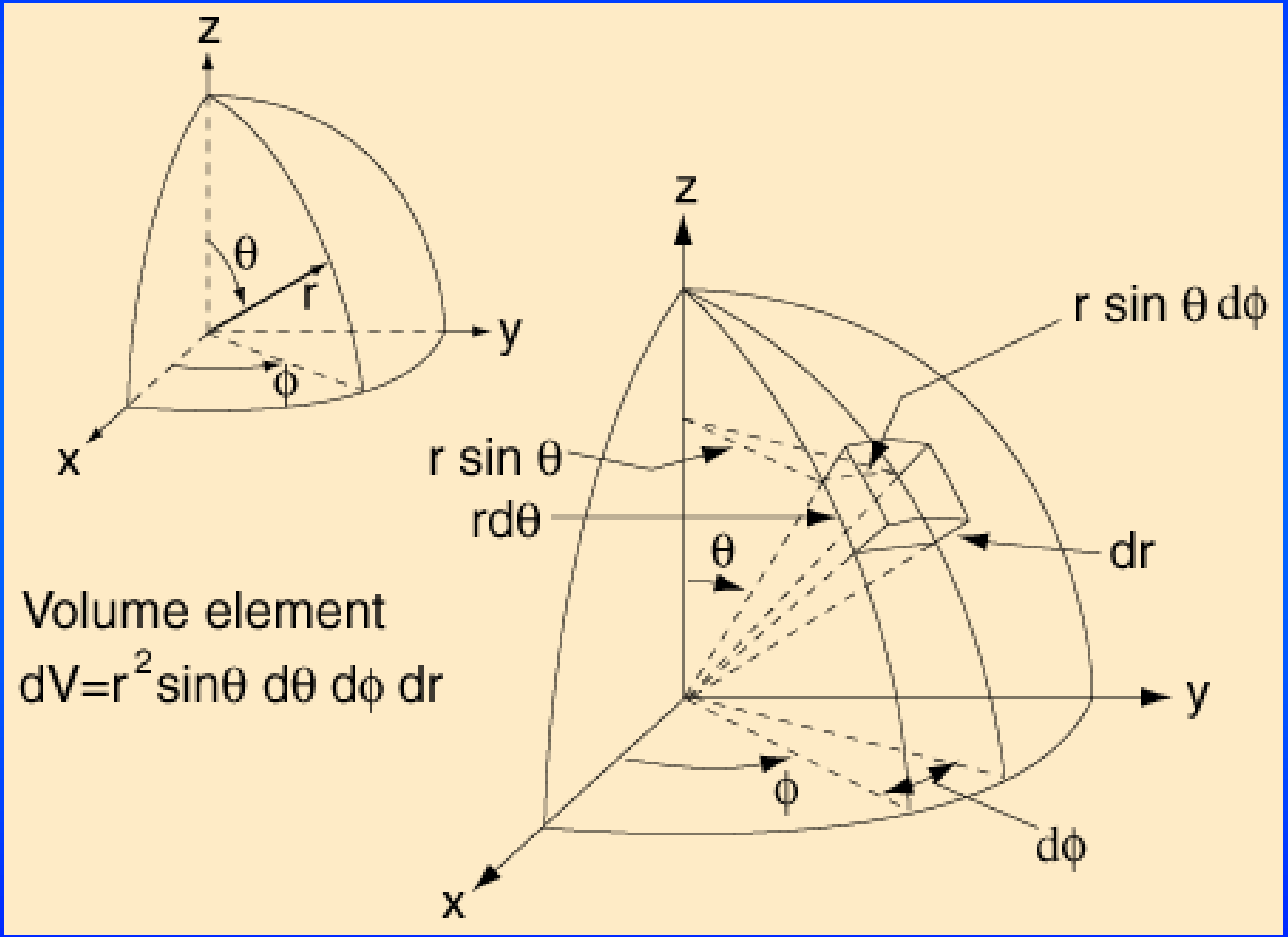
$$\frac{\partial^2\psi}{\partial x^2} + \frac{2m}{\hbar^2}\left[E - \left(-\frac{e^2}{4\pi\varepsilon_0 r}\right)\right]\psi = 0$$

The potential looks quite simple, but it is a function of r, not x or (xyz). What can we do about that?

$$x^2 + y^2 + z^2 = r^2 \Rightarrow r = \sqrt{\left(x^2 + y^2 + z^2\right)}$$

$$\frac{\partial^2\psi}{\partial x^2} + \frac{2m}{\hbar^2}\left[E - \left(- \frac{e^2}{4\pi\varepsilon_0\sqrt{\left(x^2+y^2+z^2\right)}}\right)\right]\psi = 0$$

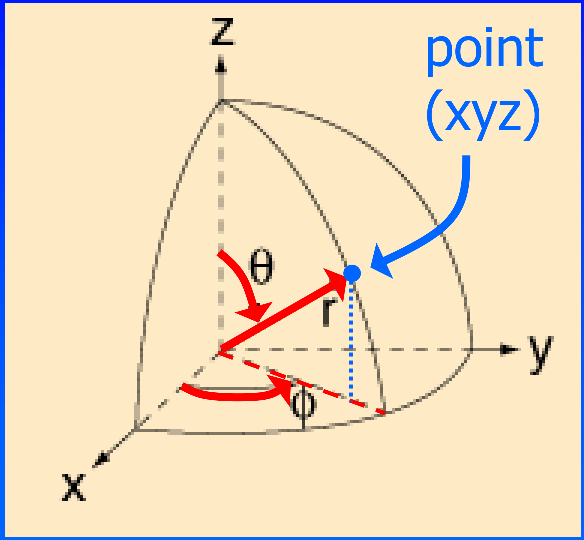
The spherically symmetric potential "tells" us to use spherical polar coordinates!



http://hyperphysics.phy-astr.gsu.edu/hbase/sphc.html

In spherical polar coordinates, r is the length of the radius vector from the origin to a point (xyz)

$$r = \sqrt{\left(x^2 + y^2 + z^2\right)},$$



θ is the angle between the radius vector and the +z axis

$$\theta = \cos^{-1}\left(\frac{z}{\sqrt{\left(x^2 + y^2 + z^2\right)}}\right),$$

and φ is the angle between the projection of the radius vector onto the xy plane and the +x axis

$$\phi = \tan^{-1}\left(\frac{y}{x}\right).$$

The equations on the previous slide tell us how to express $(r\theta\phi)$ in terms of (xyz). We can also express (xyz) in terms of $(r\theta\phi)$:

$$x = r\sin(\theta)\cos(\phi),\ y = r\sin(\theta)\sin(\phi),\ z = r\cos(\theta).$$

Now we can re-write the 3D Schrödinger equation

$$\frac{\partial^2\psi}{\partial x^2} + \frac{\partial^2\psi}{\partial y^2} + \frac{\partial^2\psi}{\partial z^2} + \frac{2m}{\hbar^2}(E - V)\psi = 0$$

In three dimensions, and in spherical polar coordinates, as

$$\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial\psi}{\partial r}\right) + \frac{1}{r^2\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial\psi}{\partial\theta}\right) + \frac{1}{r^2\sin^2\theta}\frac{\partial^2\psi}{\partial\phi^2} + \frac{2m}{\hbar^2}(E - V)\psi = 0.$$

$$\sin^2\theta \frac{\partial}{\partial r}\left(r^2 \frac{\partial \psi}{\partial r}\right) + \sin\theta \frac{\partial}{\partial \theta}\left(\sin\theta \frac{\partial \psi}{\partial \theta}\right) + \frac{\partial^2 \psi}{\partial \phi^2} + \frac{2mr^2 \sin^2\theta}{\hbar^2}\left(\frac{e^2}{4\pi\varepsilon_0 r} + E\right)\psi = 0.$$

This equation gives us the wave function ψ for the electron in the hydrogen atom. If we can solve for ψ, in principle we know "everything" there is to know about the hydrogen atom.

Separation of Variables

A differential equation for each variable

Schordinger's equation in spherical polar coordinates for hydrogen atom can be separated into three independent equations involving each single coordinate only

$\psi(r, \theta, \phi)$ has a form of product of three different functions R(r) , Θ (θ), Φ (ϕ)

Hydrogen Atom Wavefunction: $\psi(r, \theta, \varphi) = R(r)\,\Theta(\theta)\,\Phi(\varphi)$

The function R(r) describes how the wave function ψ of electron varies along radius vector from nucleus with θ, And ϕ constant

The function Θ (θ) describes how the wave function ψ of electron varies with zenith angle θ along a meridian on a sphere centered at the nucleus with r And ϕ constant

The function Φ (ϕ) describes how the wave function ψ of electron varies with azimuth angle ϕ along a parallel on a sphere centered at the nucleus with r And θ constant

Simply

$$\psi = R \Theta \Phi$$

Thus the partial derivatives in Schrödinger's equation become

$$\frac{\partial \psi}{\partial r} = \Theta \, \Phi \frac{\partial R}{\partial r} = \Theta \, \Phi \frac{dR}{dr}$$

$$\frac{\partial \psi}{\partial \theta} = R \, \Phi \frac{\partial \Theta}{\partial \theta} = R \, \Phi \frac{d\Theta}{d\theta}$$

$$\frac{\partial^2 \psi}{\partial \phi^2} = R \, \Theta \frac{\partial^2 \Phi}{\partial \phi^2} = R \, \Theta \frac{\partial^2 \Phi}{\partial \phi^2}$$

The partial derivatives become full derivatives because R, Θ, and Φ depend on r, θ, and ϕ only.

Schrodinger's equation for H atom

$$\sin^2\theta \frac{\partial}{\partial r}\left(r^2 \frac{\partial \psi}{\partial r}\right) + \sin\theta \frac{\partial}{\partial \theta}\left(\sin\theta \frac{\partial \psi}{\partial \theta}\right) + \frac{\partial^2 \psi}{\partial \phi^2} + \frac{2mr^2 \sin^2\theta}{\hbar^2}\left(\frac{e^2}{4\pi\varepsilon_0 r} + E\right) \psi = 0 .$$

Substituting $\psi = R\Theta\Phi$ into Schrödinger's equation and divide by $R\Theta\Phi$. The result is

$$\frac{\sin^2\theta}{R} \frac{d}{dr}\left(r^2 \frac{dR}{dr}\right) + \frac{\sin\theta}{\Theta} \frac{d}{d\theta}\left(\sin\theta \frac{d\Theta}{d\theta}\right) + \frac{1}{\Phi} \frac{\partial^2 \Phi}{\partial \phi^2} + \frac{2mr^2 \sin^2\theta}{\hbar^2}\left(\frac{e^2}{4\pi\varepsilon_0 r} + E\right) = 0 .$$

Third term of above eq. is function of azimuth angle ,Rearranging above equation

$$\frac{\sin^2\theta}{R}\frac{d}{dr}\left(r^2\frac{dR}{dr}\right)+\frac{\sin\theta}{\Theta}\frac{d}{d\theta}\left(\sin\theta\frac{d\Theta}{d\theta}\right)+\frac{2mr^2\sin^2\theta}{\hbar^2}\left(\frac{e^2}{4\pi\varepsilon_0 r}+E\right)=-\frac{1}{\Phi}\frac{\partial^2\Phi}{\partial\phi^2}.$$

Differential eq. for function ϕ is

$$\frac{1}{\Phi}\frac{\partial^2\Phi}{\partial\phi^2}=m_l^2$$

Dividing above eq. by $\sin^2\theta$ and rearranging

$$\frac{1}{R}\frac{d}{dr}\left(r^2\frac{dR}{dr}\right) + \frac{2mr^2}{\hbar^2}\left(\frac{e^2}{4\pi\varepsilon_0 r} + E\right) = \frac{m_l^2}{\sin^2\theta} - \frac{1}{\Theta\,\sin\theta}\frac{d}{d\theta}\left(\sin\theta\frac{d\Theta}{d\theta}\right)$$

.

The equation for function Θ and R are

$$\frac{m_l^2}{\sin^2\theta} - \frac{1}{\Theta\,\sin\theta}\frac{d}{d\theta}\left(\sin\theta\frac{d\Theta}{d\theta}\right) = l(l+1)$$

$$\frac{1}{R}\frac{d}{dr}\left(r^2\frac{dR}{dr}\right) + \frac{2mr^2}{\hbar^2}\left(\frac{e^2}{4\pi\varepsilon_0 r} + E\right) = l(l+1)$$

Equation for Φ

$$\frac{\partial^2 \Phi}{\partial \phi^2} = m_l^2 \Phi$$

Equation for Θ

$$\frac{1}{\Theta \, sin\theta} \frac{d}{d\theta}\left(\sin\theta \frac{d\Theta}{d\theta}\right) + \left[l(l+1) - \frac{m_l^2}{sin^2\theta}\right]\Theta = 0$$

Equation for Φ

$$\frac{1}{r^2}\frac{d}{dr}\left(r^2 \frac{dR}{dr}\right) + \left[\frac{2m}{\hbar^2}\left(\frac{e^2}{4\pi\varepsilon_0 r} + E\right) - \frac{\ell(\ell+1)}{r^2}\right]R = 0$$