LECTURE # 13, Mon., 10-31

Final example: "free" particle, confined in box of length L. Solutions exist only for

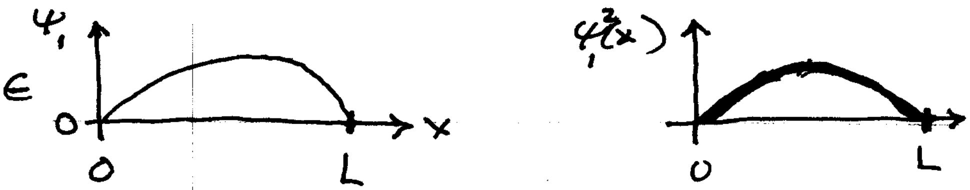
$$E = E_n^b = \frac{h^2}{8mL^2} n^2, \quad n = 1, 2, \ldots$$

→ FUNDAMENTAL INTERPRETATION OF WAVEFUNCTION $\psi(x)$:

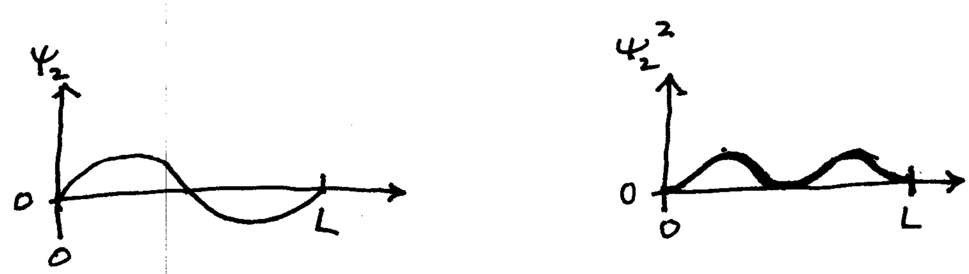
probability of finding particle "at x", i.e., between x and x+dx $= (\psi(x))^2 dx$

E.g., particle-in-a-box $\psi(x)$'s:

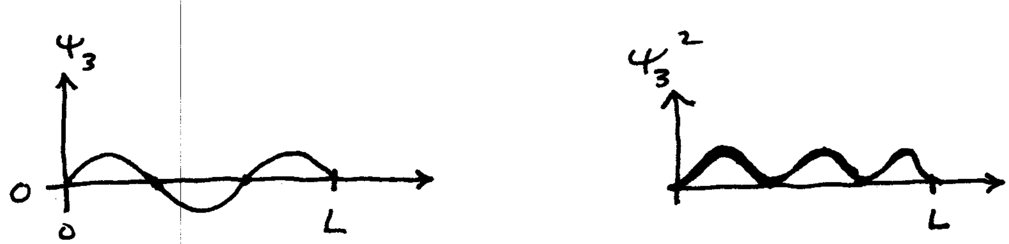
$E_1 = \frac{h^2}{8mL^2} \equiv \epsilon$



$E_2 = 4\epsilon$



$E_3 = 9\epsilon$



$$E_n = n^2 \epsilon, \quad \psi_n(x) = \sqrt{\frac{2}{L}} \sin\left(\frac{n\pi}{L} x\right), \quad n = 1, 2, \ldots$$

NOTE: $n = 0$ would imply $E = E_0 = 0$

But this would correspond to

$$\psi_0(x) = \sqrt{\frac{2}{L}}\,\sin\left(\cancelto{0}{\frac{0\cdot\pi}{L}x}\right) = 0 \quad !$$

i.e., $\psi_0^2 = 0$ everywhere

$\hookrightarrow$ NO PARTICLE IN BOX !

$\hookrightarrow$ NO POSSIBILITY OF ZERO ENERGY !

[zero energy would imply zero KE, i.e., $p=0 \Leftrightarrow \Delta p = 0$]

*) UNCERTAINTY PRINCIPLE

$\rightarrow$ wavefunction/probability ($\psi(x)/\psi^2(x)$) description $\Rightarrow$ uncertainty in position, Δx

$\rightarrow$ it turns out that there is also, necessarily, uncertainty in momentum, Δp

Suppose we want to measure/locate the position of a particle: we must scatter light (λ) off it, $\Rightarrow$'ing $\Delta x \gtrsim \lambda$

But light momentum of h/λ $\Rightarrow$ momentum of particle will be changed by this amount, $\Rightarrow$'ing $\Delta p \approx \frac{h}{\lambda}$

$$\therefore \quad \Delta x\,\Delta p \gtrsim h$$

($\leftrightarrow$ Δx and Δp are inversely proportional to one another !)

IN GENERAL (AS SHOWN BY HEISENBERG)

$$\Delta x\,\Delta p \geq \frac{h}{4\pi}$$

*) BACK TO WAVEFUNCTIONS AND PROBABILITIES

→ $(\psi(x))^2$ is a <u>probability density</u>

$(\psi(x))^2 dx$ is a <u>probability</u>, i.e.,

the probability of finding the particle between x and $x + dx$

($\leftrightarrow$ in the interval length dx at x)

NOTE: $(\psi(x))^2$ has dimensions (units) of

$$\frac{1}{\text{length}} \quad \left(\frac{1}{m}\right)$$

For example, wavefunctions for particle in a box are $\sqrt{\frac{2}{L}} \sin\left(\frac{n\pi}{L} x\right)$, so that

$$(\psi_n(x))^2 = \left(\frac{2}{L}\right) \sin^2\left(\frac{n\pi}{L} x\right), \qquad n = 1, 2, \ldots$$

→ BUT ALL OF ABOVE REFERS TO PARTICLE MOVING IN ONE DIMENSION (confined to a line!)

→ WHAT ABOUT THE ELECTRON IN THE HYDROGEN ATOM?

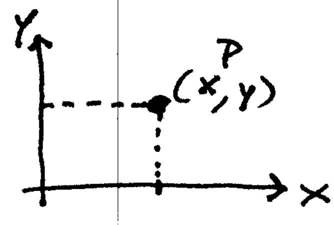
$$(\psi(x))^2 dx \longrightarrow (\psi(x,y,z))^2 \underbrace{dx\,dy\,dz}_{d\tau}$$

= probability of finding particle in small volume $d\tau$ at the point x, y, z

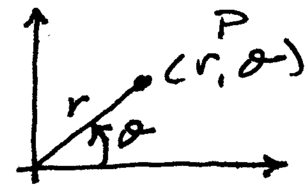
→ For H-atom, there are more convenient coordinates than x, y, z for specifying the position of the electron:

SPHERICAL (vs CARTESIAN) COORDINATES

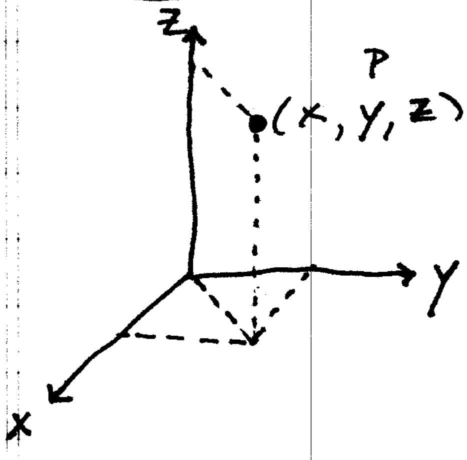
* First, recall <u>polar</u> <u>coordinates</u> for positions in the plane (TWO DIMENSIONS)



$\longrightarrow$ $x = r\cos\theta$, $y = r\sin\theta$



* SPHERICAL COORDINATES

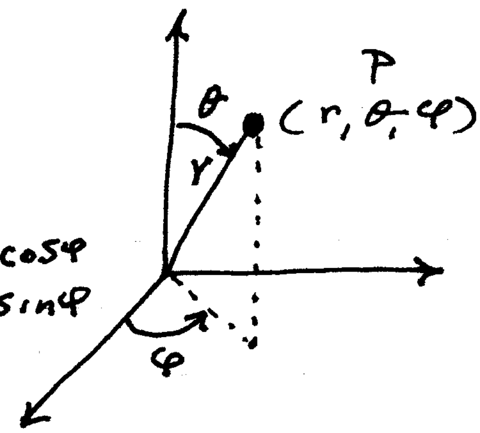


$\longrightarrow$

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

$y = r\sin\theta\sin\varphi$

$z = r\cos\theta$



So, ..., what are H-atom wavefunctions?

$$E_{n=1} = -\frac{R}{1^2} = R \qquad \psi_1(r,\theta,\varphi) = \left(\frac{1}{4\pi}\right)^{1/2} 2\left(\frac{1}{a_0}\right)^{3/2} e^{-r/a_0}$$

$\boxed{\text{independent of } \theta \,\&\, \varphi}$

$$\left(\psi_1(r,\theta,\varphi)\right)^2 d\tau = \frac{1}{\pi}\frac{1}{a_0^3}\, e^{-2r/a_0}\; d\tau$$

= same probability for all positions r, θ, φ in a spherical shell of radius r and thickness dr

$\frac{1}{a_0^3} \leftrightarrow \frac{1}{V}$

$d\tau \leftrightarrow V$