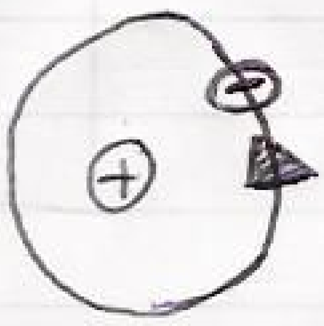
Nov, 22, 2010

probability density functions {Pictures of $|\psi|^2$ in hydrogen}

$n=1$  $n=2$  $n=2$ 

Bohr model | Modern Quantum Mechanics



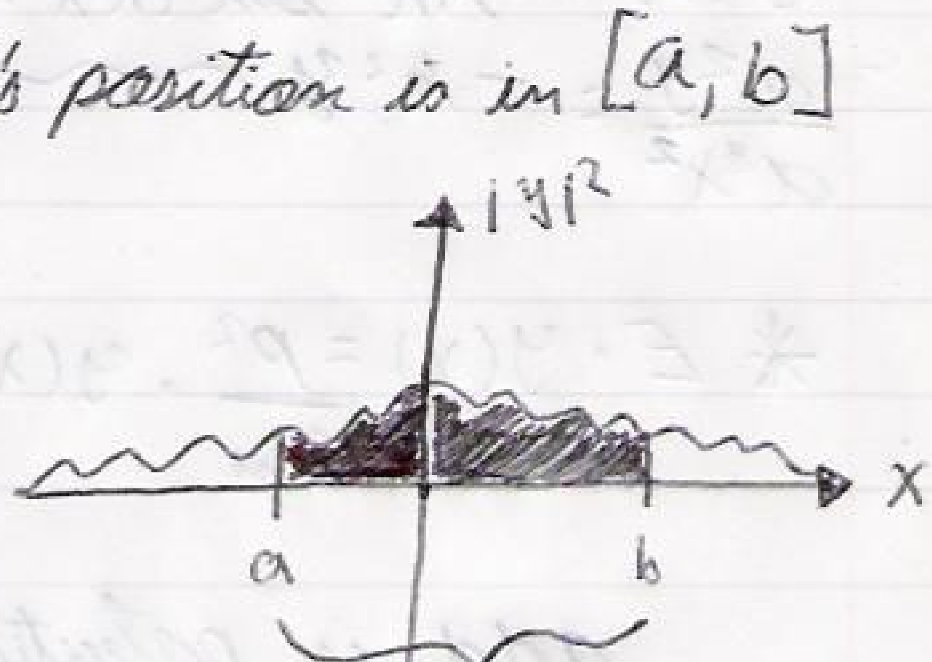
electron cloud

$|\psi(\vec{x})|^2$ = probability density of electron being found at position x

$\int_a^b |\psi|^2 dx$ = probability that the particle's position is in $[a, b]$

$\psi(\vec{x})$ is called the <u>wavefunction</u>.

It can be positive or negative (or even complex).



area = probability particle will be found in $[a, b]$

Require $\int_{-\infty}^{\infty} |\psi|^2 dx = 1$

$\frac{h}{\lambda} = p =$ momentum $\Rightarrow \lambda = \frac{h}{p}$

Think of a particle as a very simple wave:

$$y(x) = A \sin(kx + \phi)$$

$k =$ "wave number" $= \frac{\text{radians}}{\text{lenghts}}$

$$\lambda = \frac{2\pi}{k} = \frac{\text{radians/cycle}}{\text{radians/lenght}} = \frac{\text{lenght}}{\text{cycle}} = \text{wavelenght}$$

$$E = \frac{1}{2} m v^2 = \frac{1}{2} m \left(\frac{p}{m}\right)^2 = \frac{p^2}{2m} \longrightarrow {}^{*}E \cdot y(x) = \frac{p^2}{2m} \cdot y(x)^{*}$$

Assume $U = 0$ & $v \ll c$

reduced Planck constant

$$\hbar = \frac{h}{2\pi}$$

"h-bar"

$\frac{\text{lenght}}{\text{cycle}} =$ wavelenghts $\Rightarrow p = \frac{h}{\lambda} = \frac{h}{2\pi/k} = \frac{hk}{2\pi} = \hbar k$

$$\Downarrow$$

$$\frac{p^2}{2m} = \frac{\hbar^2 k^2}{2m} = -\frac{\hbar^2}{2m} \cdot \frac{d^2}{dx^2} \Rightarrow \boxed{p = i\hbar \frac{d}{dx}}$$

Momentum operator

- derivatives
- $y'(x) = Ak \cos(kx + \phi)$
- $y''(x) = -Ak^2 \sin(kx + \phi)$
- $\frac{d^2 y}{dx^2} = -k^2 y \rightsquigarrow \frac{d^2}{dx^2} = -k^2$

$$* \; E \cdot y(x) = \frac{p^2}{2m} \cdot y(x)^{*} \rightarrow \boxed{E y = \frac{-\hbar^2}{2m} \frac{d^2 y}{dx^2}}$$

add in potential energy:
schrödinger Equation (time-independent)

$$\boxed{E y = \frac{-\hbar^2}{2m} \frac{d^2 y}{dx^2} + U y}$$

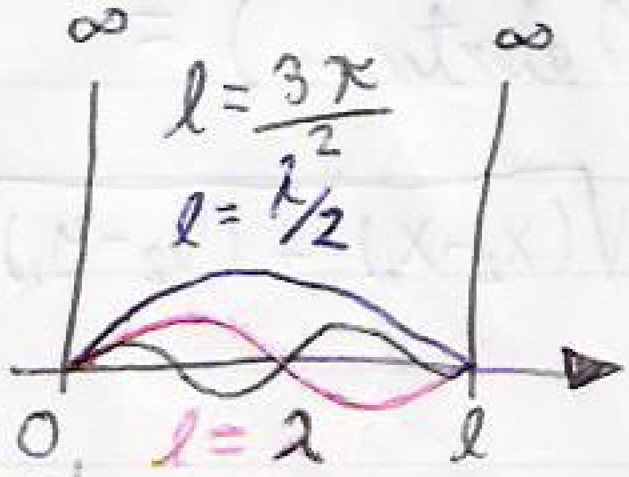
because $E = \frac{p^2}{2m} + U$

$$\Downarrow$$

$$E y = \left(\frac{p^2}{2m} + U\right) y$$

Particle in a box

$$U(x)\begin{cases}\infty : x \le 0 \\ 0 : 0 < x < l \\ \infty : l \le x\end{cases}$$



Solutions:

$$E = \frac{n^2 h^2}{8 m l^2} : n = 1, 2, 3, 4, \ldots$$

$$E\psi = \frac{-\hbar^2}{2m}\frac{d^2\psi}{dx^2} \text{ for } 0 < x < l$$

$$k = \frac{n\pi}{l} \qquad \lambda = \frac{2\pi}{k} \Rightarrow l = \frac{n\lambda}{2}$$

$\psi(x) = 0$ if $x \le 0$

$\psi(x) = 0$ if $x \ge l$

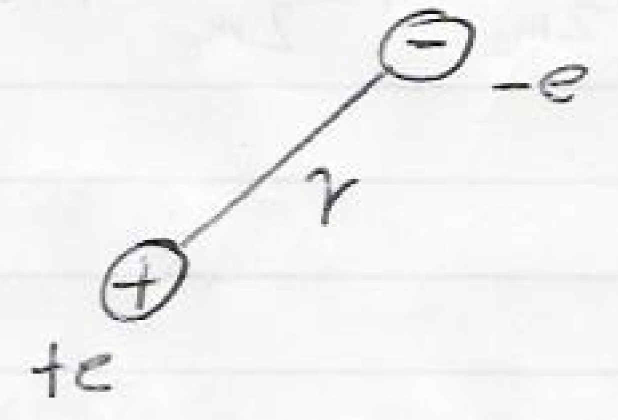
$$\int_0^l |\psi|^2 dx = 1$$

$$\psi(x)\begin{cases}0 : x \le 0 \\ A\sin(kx) : 0 < x < l \\ 0 : x \ge l\end{cases}$$

$$A = \sqrt{\frac{2}{l}}$$

$$= \sqrt{\frac{2}{l}}\sin\left(\frac{n\pi x}{l}\right) \quad n = 1, 2, 3, 4 \ldots$$

– Hydrogen atom –



$$U = \frac{1}{4\pi\varepsilon_0}\cdot\frac{(+e)(-e)}{r}$$

In 3D: $U = \dfrac{-e^2}{4\pi\epsilon\sqrt{(x^2+y^2+z^2)}}$

Schrödingers equation:

$$p^2 = p^2_x + p^2_y + p^2_z = -\hbar^2\left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}\right) = \hbar^2\nabla^2$$

$$E = \frac{p^2}{2m} + U \Rightarrow E\psi = \frac{p^2}{2m}\psi + U\psi$$

$$E\psi = \frac{-\hbar^2}{2m}\nabla^2\psi + \left(\frac{-e^2}{4\pi\epsilon_0\sqrt{x^2+y^2+z^2}}\right)\psi$$

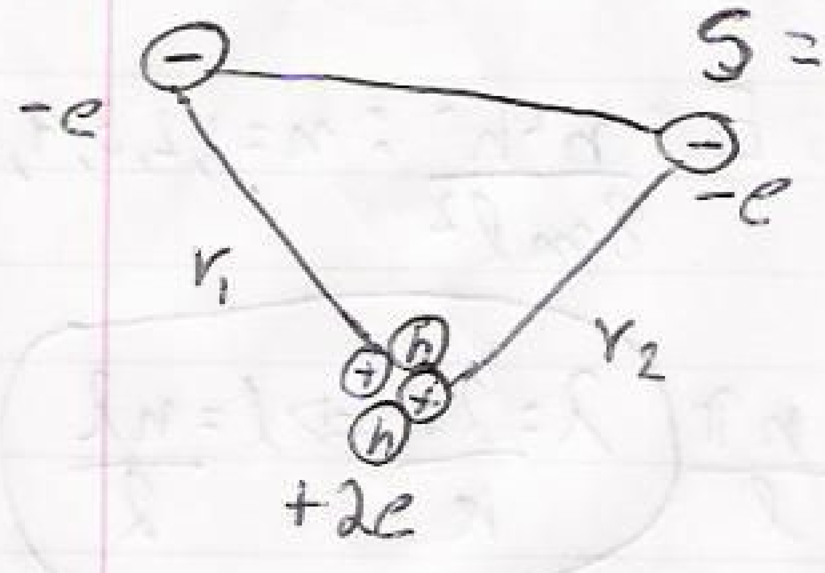
$\psi = \psi(x, y, z)$

Requires

Get same values for E as in Bohr model

$$\int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\int_{-\infty}^{\infty} |\psi|^2\, dx\, dy\, dz = 1$$

= Helium Atom (2 electrons) =



$$s = \sqrt{(x_2-x_1)^2+(y_2-y_1)^2+(z_2-z_1)^2}$$

$$U(x_1, y_1, z_1, x_2, y_2, z_2$$

$$\Downarrow$$

$$\frac{1}{4\pi\varepsilon_0}\left(\frac{-2e^2}{r_1}+\frac{-2e^2}{r_2}+\frac{e^2}{s}\right.$$

$$\cancel{p^2 = |\vec{p}_1+\vec{p}_2|^2 = p_1^2 + 2\vec{p}_1\cdot\vec{p}_2 + p_2^2}$$

$$\cancel{p^2 = -\hbar^2(\nabla_1^2 + 2\vec{\nabla}_1\cdot\vec{\nabla}_2 + \nabla_2^2)}$$

$$r_1 = \sqrt{x_1^2+y_1^2+z_1^2}$$

$$\vec{p}_1 = i\hbar\left(\frac{\partial}{\partial x_1}, \frac{\partial}{\partial y_1}, \frac{\partial}{\partial z_1}\right) = \underline{i\hbar\vec{\nabla}_1}$$

$$\psi(x_1, y_1, z_1, x_2, y_2, z_2)$$

$$\boxed{\cancel{E\psi = \left(\frac{p^2}{2m}+U\right)\psi}}$$

Actually, it should be: $E = \frac{p_1^2}{2m_e} + \frac{p_2^2}{2m_e} + U$

$$\Rightarrow E\psi = \left(\frac{-\hbar^2}{2m_e}(\nabla_1^2+\nabla_2^2) + U\right)\psi.$$