Here's what happened yesterday!

$$V(r) = -\frac{Ze^2}{4\pi\epsilon_0 r}$$

$$\frac{-\hbar^2}{2M}\left[\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial\psi}{\partial r}\right)+\frac{1}{r^2\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial\psi}{\partial\theta}\right)+\frac{1}{r^2\sin^2\theta}\frac{\partial^2\psi}{\partial\phi^2}\right]$$

$$-\frac{Ze^2}{4\pi\epsilon_0 r}\psi = E\psi$$

choose

$$\psi(r,\theta,\phi) = R(r)T(\theta)P(\phi)$$

$$\frac{\sin^2\theta}{R}\frac{d}{dr}\left(r^2\frac{dR}{dr}\right)+\frac{\sin\theta}{T}\frac{d}{d\theta}\left(\sin\theta\frac{dT}{d\theta}\right)+\frac{1}{P}\frac{d^2P}{d\phi^2}$$

$$+\frac{2Mr^2\sin^2\theta}{\hbar^2}\left(\frac{Ze^2}{4\pi\epsilon_0 r}+E\right)=0$$

Buried inside are 3 differential equations for

$R(r)$ $T(\theta)$ $P(\phi)$

The techniques for 2 of them involve series solutions → sets of polynomials always result.

AFTER THE DUST SETTLES...

WAVE FUNCTIONS

$$\underbrace{\psi_{n\ell m_\ell}}_{\text{3 integer labels}}(r,\theta,\phi) = R_{\underbrace{n\ell}}(r)\,\underbrace{Y_{\underbrace{\ell m_\ell}}(\theta,\varphi)}$$

3 integer labels

famous functions in physics and engineering:
Spherical Harmonics

"EIGENVALUES"

$$E_n = \frac{e^4}{(4\pi\epsilon_0)^2}\frac{M}{\hbar^2 2n^2}$$

The radial wave function $R(r)$ for a given value of the radial (or total) quantum number n and the orbital quantum number l is the product of (1) a normalization constant, (2) $e^{-\alpha r/2}$, where $\alpha = 2Z/na_B$ (a_B is the Bohr radius), and (3) a polynomial in αr. The complete wave function $\psi(r,\theta,\varphi)$ is accordingly given by $\psi_{nlm}(r,\theta,\varphi) = N_{nl}e^{-\alpha r/2}$ (polynomial in αr) (polynomial in cos θ) $e^{im_l\varphi}$, where N_{nl} is the normalization constant such that $\int\int\int\psi^*\psi\, d\mathcal{V} = 1$ ($d\mathcal{V}$ is a volume element).

As examples, the following relations give the wave functions for the states of lowest energy in terms of the Bohr radius a_B ($= 4\pi\epsilon_0\hbar^2/m_re^2$):

$$\psi_{100} = \frac{1}{\sqrt{\pi}}\left(\frac{Z}{a_B}\right)^{3/2} e^{-Zr/a_B} \qquad n = 1,\; l = 0,\; m_l = 0$$

$$\psi_{200} = \frac{1}{2\sqrt{2\pi}}\left(\frac{Z}{a_B}\right)^{3/2}\left(1 - \frac{Zr}{2a_B}\right) e^{-Zr/2a_B} \qquad n = 2,\; l = 0,\; m_l = 0$$

$$\psi_{210} = \frac{1}{2\sqrt{2\pi}}\left(\frac{Z}{a_B}\right)^{3/2}\frac{Zr}{2a_B} e^{-Zr/2a_B}\cos\theta \qquad l = 1,\; m_l = 0$$

$$\psi_{211} = \frac{1}{4\sqrt{\pi}}\left(\frac{Z}{a_B}\right)^{3/2}\frac{Zr}{2a_B} e^{-Zr/2a_B}\sin\theta\, e^{\pm i\varphi} \qquad m_l = \pm 1$$

$$\psi_{300} = \frac{1}{9\sqrt{3\pi}}\left(\frac{Z}{a_B}\right)^{3/2}\left[3 - 6\frac{Zr}{3a_B} + 2\left(\frac{Zr}{3a_B}\right)^2\right] e^{-Zr/3a_B} \qquad n = 3,\; l = 0,\; m_l = 0 \tag{14.11}$$

$$\psi_{310} = \frac{\sqrt{2}}{9\sqrt{\pi}}\left(\frac{Z}{a_B}\right)^{3/2}\frac{Zr}{3a_B}\left(2 - \frac{Zr}{3a_B}\right) e^{-Zr/3a_B}\cos\theta \qquad l = 1,\; m_l = 0$$

$$\psi_{311} = \frac{1}{9\sqrt{\pi}}\left(\frac{Z}{a_B}\right)^{3/2}\frac{Zr}{3a_B}\left(2 - \frac{Zr}{3a_B}\right) e^{-Zr/3a_B}\sin\theta\, e^{\pm i\varphi} \qquad m_l = \pm 1$$

$$\psi_{320} = \frac{1}{9\sqrt{6\pi}}\left(\frac{Z}{a_B}\right)^{3/2}\left(\frac{Zr}{3a_B}\right)^2 e^{-Zr/3a_B}(3\cos^2\theta - 1) \qquad l = 2,\; m_l = 0$$

$$\psi_{321} = \frac{1}{9\sqrt{\pi}}\left(\frac{Z}{a_B}\right)^{3/2}\left(\frac{Zr}{3a_B}\right)^2 e^{-Zr/3a_B}\sin\theta\cos\theta\, e^{\pm i\varphi} \qquad m_l = \pm 1$$

$$\psi_{322} = \frac{1}{18\sqrt{\pi}}\left(\frac{Z}{a_B}\right)^{3/2}\left(\frac{Zr}{3a_B}\right)^2 e^{-Zr/3a_B}\sin^2\theta\, e^{\pm 2i\varphi} \qquad m_l = \pm 2$$

14.4 Probability Density and Charge-cloud Density

The probability density corresponding to one of the wave functions $\psi_{nlm_l}(r,\theta,\varphi)$ is given by $\psi^*\psi$. The quantity $|\psi|^2\, d\mathcal{V}$ represents the probability that if the electron could be located experimentally at any instant, it would be found in the volume element $d\mathcal{V}$. It is not possible, however, to follow the electron in an orbital motion around the nucleus by means of a succession of such observations as the astronomers follow the planets around the sun; for one observation with a γ-ray microscope of sufficient revolving power would suffice, because of the Compton effect, to eject the electron from the atom.

There is no suggestion here of orbital motion, but often it is convenient to imagine the electronic charge to be distributed in space as sort of a charge cloud with a density

$$\eta = e\psi^*\psi$$

Many effects of the atom on its surroundings are approximately the same as if the atom actually contained a distribution of charge of density η. Rather than following a fixed orbit, an electron is said to occupy an atomic *orbital* determined by ψ_{nlm_l}.

Since φ appears in ψ as $e^{im_l\varphi}$, it is clear that $\psi^*\psi$ is not a function of φ. Consequently, when the electron is in one of its quantum states, the probability density (or charge-cloud density) has cylindrical symmetry about the chosen polar axis and $|\psi|^2 = R^2\Theta^2$. Polar graphs of the function $\Theta^2_{lm_l}$ (Fig. 14.1) reveal that the variation with θ, although symmetrical relative to the plane $\theta = \pi/2$, is large unless $l = 0$. The latter leads to a spherical distribution. The angular variation of charge density is of great interest when one approaches the problem of binding between atoms in terms of atomic orbitals.

For discussing the average radial variation in charge density let $\mathcal{P}_r\, dr$ denote the total probability (and $\eta\, dr$ the numerical amount of charge) contained between two spheres of radii r and $r + dr$ drawn about the nucleus as a center. The volume between the two spheres is propor-

QUANTUM NUMBERS of the Quantum Central Force Prob.

n & l figure into the radial and polar equations...

$\boxed{n:}$ principle quantum number

$n = 1, 2, 3 \ldots \infty$ in this "well"

$\boxed{l:}$ orbital angular momentum quantum number

$l = 0, 1, 2 \ldots (n-1)$ $\qquad 0 \le l \le n$

connected to value of n

$\boxed{m_l:}$ magnetic quantum number

$m_l = -l, -l+1, \ldots -1, 0, 1, \ldots, l-1, l$

$-l \le m_l \le l$

$2l+1$ total values

Why l related to angular momentum?

Its association with E_n ... $\Rightarrow$ also r & p

Remember $\vec{L} = \vec{r} \times \vec{p}$ classically.

$L_x = y p_z - z p_y$; $L_y = z p_x - x p_z$; $L_z = x p_y - y p_x$

$\downarrow$ QM $\Rightarrow$ operators

$$L_x = -i\hbar\left(y\frac{\partial}{\partial z} - z\frac{\partial}{\partial y}\right); \quad L_y = -i\hbar\left(z\frac{\partial}{\partial x} - x\frac{\partial}{\partial z}\right); \quad L_z = -i\hbar\left(x\frac{\partial}{\partial y} - y\frac{\partial}{\partial x}\right)$$

So, $\hat{L}$ is an operator

If one forms $L^2 = L_x^2 + L_y^2 + L_z^2$

and

goes to spherical coordinates...

$$L^2 = -\hbar^2 \left(\frac{\partial^2}{\partial \theta^2} + \cot\theta \frac{\partial}{\partial \theta} + \frac{1}{\sin^2\theta} \frac{\partial}{\partial \varphi^2} \right)$$

the same as the angular part of the Sch. Eq... for which the $Y_{\ell m}(\theta,\varphi)$ are solutions

$$L^2 Y_{\ell m}(\theta,\varphi) = \lambda Y_{\ell m}(\theta,\varphi) = \hbar^2 \ell(\ell+1) Y_{\ell m}(\theta,\varphi)$$

~~Yours~~ your book writes this relationship as.

$$L^2 = \hbar^2 \ell(\ell+1) \quad \text{or}$$

$$\boxed{L = \hbar\sqrt{\ell(\ell+1)}}$$

Remember Bohr's angular momentum condition

$L = n\hbar$ here $L = \hbar\sqrt{\ell(\ell+1)}$

$= 0 \quad n=0$ $\qquad = 0 \quad \ell = 0 \ldots n = 0$

$= \hbar \quad n=1$ $\qquad = \hbar\sqrt{n^2+n} \quad \ell = n$

$= 2\hbar \quad n=2$ $\qquad = \hbar\sqrt{2} \quad n = 1 = \ell$

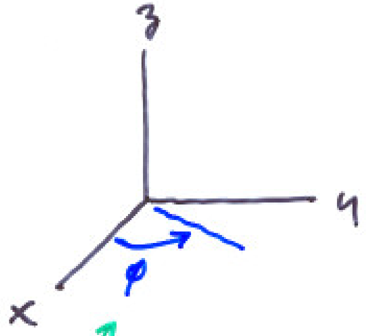
$= \hbar\sqrt{6} \quad n = 2 = \ell$

→ the Bohr idea of a fixed orbit planetary electron is no-good

the strange $L = \hbar \underbrace{\sqrt{\ell(\ell+1)}}$

comes from wave-like solutions

$\vec{L}$ is a vector... ℓ determines the magnitude not the direction.



determines the rotation about z

⇒ related to the z component of the $\vec{L}$ vector

$$\boxed{L_z = m_\ell \hbar}$$

So, $|\vec{L}|$ and L_z are quantized

only certain orientations in space are allowed

-- determined by L_z's quantization.

"space quantization"

What about L_x and L_y?

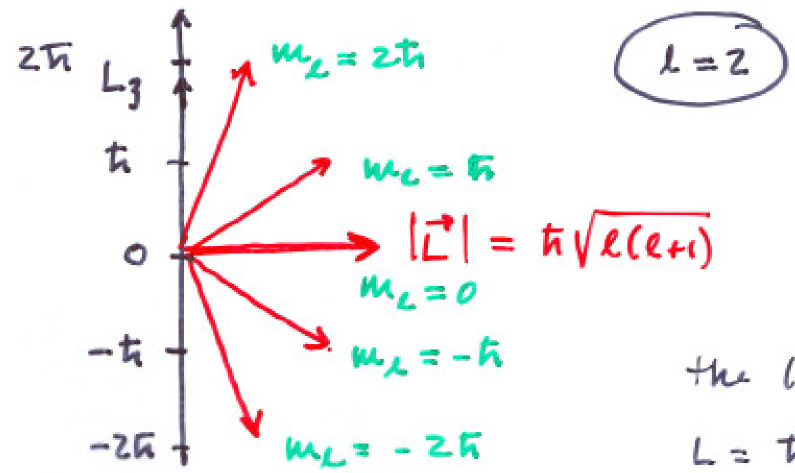
If we knew L_x and L_y -- say by quantizing them -- then

we would know $\vec{L}$

... and know a component of the electron's position as well.

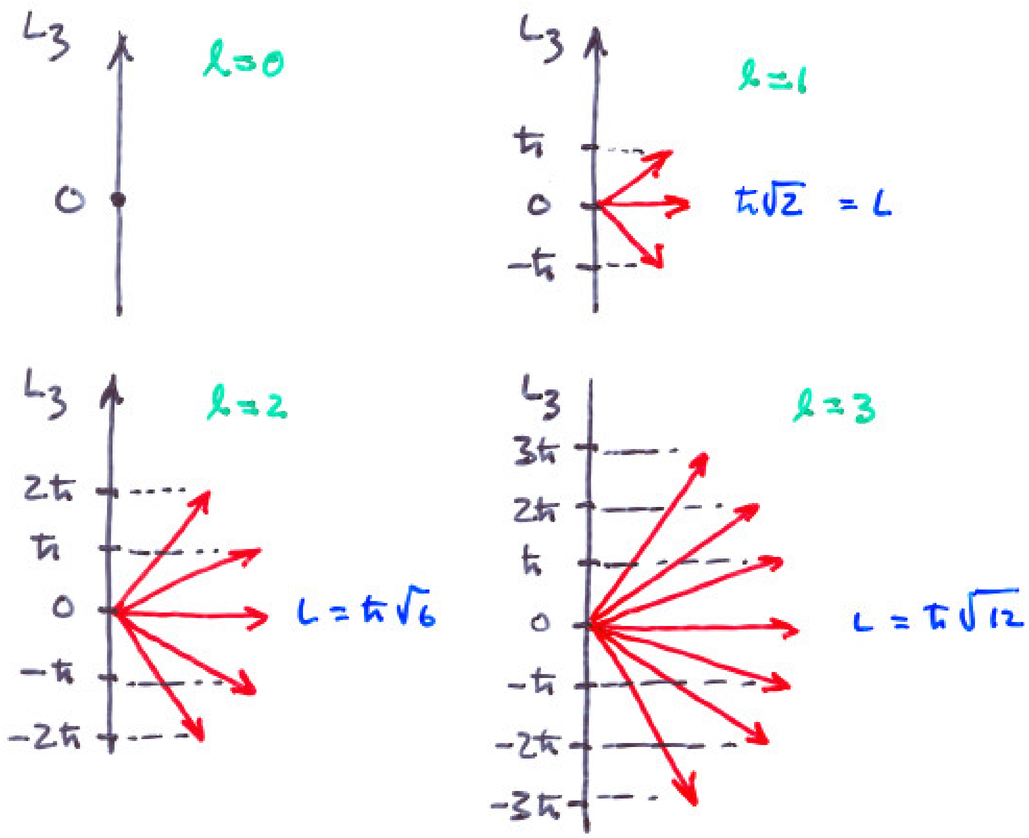
Uncertainty principle says "no"

→ only $|\vec{L}|$ and L_z are quantized.



the length is

$L = \hbar\sqrt{6}$



The old-timey notation

$\ell =$	0	1	2	3	4	5
	"s"	"p"	"d"	"f"	"g"	"h"

Speak like this: "n" is the number

"ℓ" sometimes the letter

$n=3$ & $\ell=1$: "3p state"

WAVEFUNCTIONS ARE NOT THE PHYSICS

→ probability distributions are...

REMEMBER: (for 1 dimension) we had:

The probability that a particle will be found in the infinitesimal interval between x and $x+dx$ is $P(x)\,dx$....

$$P(x)\,dx = \psi^*(x,t)\,\psi(x,t)\,dx$$

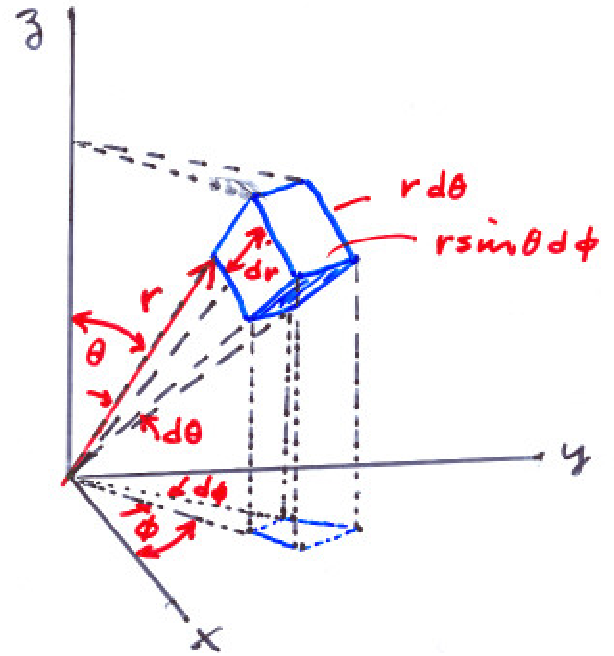
Now ~~we~~ we're in 3 dimensions and the same thing holds for a tiny element of volume dv

$$P(\vec{r})\,dv = \psi^*(r,\theta,\varphi)\,\psi(r,\theta,\varphi)\,dv$$
$$= |\psi|^2\,dv$$

→ there are many possible states, depending on n, l, m_l.

$$\psi_{nlm_l}(r,\theta,\varphi) = R_{nl}(r)\,Y_{lm_l}(\theta,\varphi)$$

need dv:



$$dv = r^2 dr \sin\theta \, d\theta \, d\varphi$$

The wavefunctions defined above are normalized as we want. So,

$$1 = \iiint_{\text{all space}} |R(r)|^2 |Y(\theta,\varphi)|^2 r^2 dr \sin\theta \, d\theta \, d\varphi$$

$$1 = \int_0^\infty |R(r)|^2 r^2 dr \int_0^\pi \int_0^{2\pi} |Y(\theta,\varphi)|^2 \sin\theta \, d\theta \, d\varphi$$

From these we can isolate 2 interesting probability distributions.

$r^2|R(r)|^2 dr$ – probability of finding the particle in a thin shell between r & $r+dr$

$|Y(\theta,\varphi)|^2 \sin\theta\, d\theta\, d\varphi$ – probability of finding the particle within an area bounded by θ and φ to $\theta + d\theta$ and $\varphi + d\varphi$

They were separately normalized each to 1.

Notice $$\int_0^{\pi}\int_0^{2\pi} \sin\theta\, d\theta\, d\varphi = 4\pi$$

$$\parallel$$

$$\iint d(\cos\theta) d\theta\, d\varphi = \int_{-1}^{1} d(\cos\theta) d\theta \int_0^{2\pi} d\varphi$$

$$= 2 \cdot 2\pi \quad \checkmark$$

the area of a whole sphere in angular units is 4π stervadians

Easiest to visualize are the radial distributions.

$\rightarrow$ integrated over all angles.

$$P(r)\,dr = \int_0^{\pi}\int_0^{2\pi} |\psi|^2 r^2 dr \sin\theta\, \underline{d\theta}\, \underline{d\varphi}$$

$$= \underset{\substack{\uparrow \\ \text{radial probability density for any state}}}{|R(r)|^2 r^2 dr} \underbrace{\int_0^{\pi}\int_0^{2\pi} \sin\theta\, d\theta\, d\varphi\, |Y(\theta,\varphi)|^2}_{=\,1}$$

Look at the lowest state $\psi_{n\ell m_\ell} = \psi_{100}$

$$\psi_{100}(r,\theta,\varphi) = R_{10}(r)\,Y_{00}(\theta,\varphi)$$

$$Y_{00}(\theta,\varphi) = \frac{1}{\sqrt{4\pi}}$$

$$R_{10}(r) = \cancel{\frac{2Z}{\sqrt{a_0^3}} e^{-r/a_0}} = \left(\frac{Z}{a_0}\right)^{3/2} 2\, e^{-Zr/a_0}$$

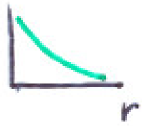
remember $a_0 = \dfrac{\hbar^2 4\pi\epsilon_0}{me^2}$ the Bohr radius

So, the likelihood of the electron being in a radial region between r and $r+dr$ in the 1s state is

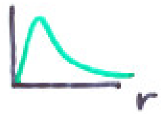
$$P_{10}(r)\,dr = |R_{10}(r)|^2 r^2 dr$$

$$= \left(\left(\frac{Z}{a_0}\right)^{3/2} 2 e^{-Zr/a_0} \right)^2 r^2 dr$$

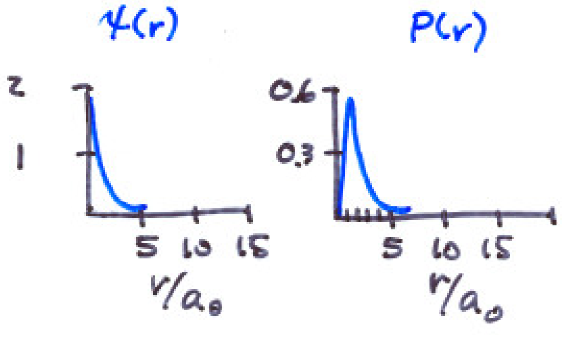
Look at this behavior. ψ goes like e^{-Zr}:



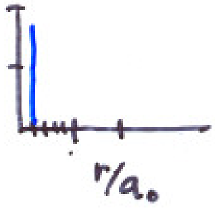
But the probability goes like $r^2 e^{-2r}$:



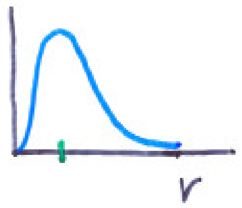
$$P_{10}(r)\,dr = 4 \frac{Z^3}{a_0^3} r^2 e^{-2Zr/a_0} dr$$



What would Bohr have said?



only at $r = a_0$



remember, because Y_{00} = constant

P_{10} is spherically symmetric

a cloud of probability

densest at the peak, least dense at center...

What is the most probable distance in hydrogen?

$$P_{10}(r) = \frac{4}{a_0^3} r^2 e^{-2r/a_0}$$

differentiate...

$$\frac{dP_{10}}{dr} = \frac{4}{a_0^3}\left[2r e^{-2r/a_0} - r^2 \left(\frac{2r}{a_0}\right) e^{-2r/a_0} \right]$$

$$= \frac{4}{a_0^3} e^{-2r/a_0} \left[2r - \frac{2r^2}{a_0} \right] = 0$$ for extremum.

obviously $r = 0$ does this... a minimum

but so does $r = a_0$ -- a maximum!

The most probable distance is the Bohr radius.

that's satisfying

What's the AVERAGE distance?

$$\langle r \rangle = \int_0^\infty r\, P_{10}(r)\, dr$$

$$= \frac{4}{a_0^3} \int_0^\infty r^3 e^{-2r/a_0} dr$$

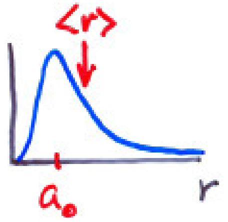
like a class of integrals:

$$\int_0^\infty z^n e^{-z} dz = n!$$

change variables: $z = 2r/a_0$

$$\langle r \rangle = \frac{a_0}{4}(3!)$$

$$\langle r \rangle = 3/2\, a_0$$



Where is the electron? can't ask that, as you know.

The likelihood of finding the electron between some $r = a$ and $r = b$ will be

$$P_{10}(ab) = \int_a^b P_{10}(r)\, dr$$