Last Time

① Schrödinger Eq. in 2D

notation $\Psi(x,y,t)$ is function of time

$$\left[\frac{P_x^2}{2m} + \frac{P_y^2}{2m} + V(x,y)\right]\Psi(x,y,t) = E\,\Psi(x,y,t)$$

or

$$\left[-\frac{\hbar^2}{2m}\left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2}\right) + V(x,y)\right]\Psi(x,y,t) = +i\hbar\frac{\partial}{\partial t}\Psi(x,y,t)$$

For 3D replace:

$$\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} \longrightarrow \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}$$

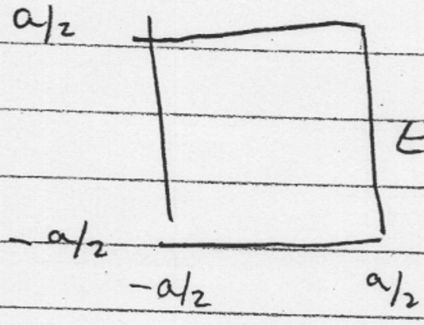
Now we looked for stationary states

$$\Psi(x,y,t) = \psi(x,y)\,e^{-iEt/\hbar}$$

Then found the 2D time indep Schrödinger eq

$$\left[-\frac{\hbar^2}{2m}\left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2}\right) + V(x,y)\right]\psi(x,y) = E\,\psi(x,y)$$

Then example: Particle in 2D box



$\psi = 0$ out side box:

Continuity: $\psi = 0$ at edges of box

Then in side box: $V = 0$

$$(*) \qquad -\frac{1}{\psi}\frac{\hbar^2}{2m}\left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2}\right)\psi = E$$

So try a solution:

$$(**) \qquad \psi(x,y) = X(x)\,Y(y)$$

Boundary conditions $\psi = 0$ at edges:

$$X\Big|_{x=\pm a/2} = 0 \qquad\qquad Y\Big|_{y=\pm a/2} = 0$$

Find plugging ** into *

$$\underbrace{\frac{1}{X}\frac{-\hbar^2}{2m}\frac{\partial^2 X}{\partial x^2}}_{\mathcal{E}_n = \text{const}} + \underbrace{\frac{1}{Y}\frac{-\hbar^2}{2m}\frac{\partial^2 Y}{\partial y^2}}_{\mathcal{E}_m = \text{const}} = E$$

Now have a particle in box in two direction (See handout)

$$\psi_{nm} = X_n(x)\, Y_m(y)$$

$$X_n(x) = \begin{cases} \sqrt{2/a}\,\cos(n\pi x/a) & n = 1, 3, 5 \\ \quad \cdots\ \sin\ \cdots & n = 2, 4, 6 \end{cases}$$

$$Y_m(y) = \begin{cases} \sqrt{2/a}\,\cos(m\pi y/a) & m = 1, 3, 5 \\ \quad - - - - - - & \end{cases}$$

The energies

$$E_{nm} = \varepsilon_n + \varepsilon_m$$

$$E_{nm} = \frac{\hbar^2\pi^2}{2ma^2}(n^2 + m^2)$$

Then we have

$$E_{11} = \frac{\hbar^2\pi^2(1^2+1^2)}{2ma^2}$$

$$E_{12} = E_{21} = \frac{\hbar^2\pi^2}{2ma^2}(1^2+2^2) \Leftarrow \text{degeneracy}$$

$$E_{22} = \frac{\hbar^2\pi^2}{2ma^2}(2^2+2^2)$$

2D Particle in (Square) Box

1. For the particle in the two dimensional box the potential is

$$V = \begin{cases} 0 & \text{inside box } -L/2 < x, y < L/2 \\ \infty & \text{outside box} \end{cases} \tag{1}$$

We solved the Schrödinger equation

$$\left[\frac{-\hbar^2}{2m}\left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2}\right) + V(x,y)\right]\Psi(x,y) = E\Psi(x,y) \tag{2}$$

2. The wave functions are described by two quantum numbers n_x, n_y and are

$$\Psi_{n_x,n_y}(x,y) = \mathsf{X}_{n_x}(x)\mathsf{Y}_{\mathsf{n_y}}(\mathsf{y}) \tag{3}$$

with

$$n_x = 1, 2, 3, \ldots \qquad \text{and} \qquad n_y = 1, 2, 3, \ldots \tag{4}$$

Where

$$\mathsf{X}_{n_x}(x) = \begin{cases} \sqrt{\frac{2}{L}}\cos\left(\frac{n_x \pi x}{L}\right) & n_x = 1, 3, 5, \ldots \\ \sqrt{\frac{2}{L}}\sin\left(\frac{n_x \pi x}{L}\right) & n_x = 2, 4, 6, \ldots \end{cases} \tag{5}$$

and similarly

$$\mathsf{Y}_{n_y}(y) = \begin{cases} \sqrt{\frac{2}{L}}\cos\left(\frac{n_y \pi y}{L}\right) & n_y = 1, 3, 5, \ldots \\ \sqrt{\frac{2}{L}}\sin\left(\frac{n_y \pi y}{L}\right) & n_y = 2, 4, 6, \ldots \end{cases} \tag{6}$$

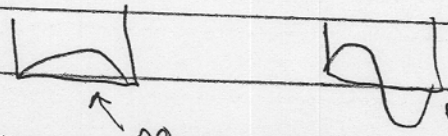
3. The Energies are a sum of the energies

$$E_{n_x,n_y} = \epsilon_x + \epsilon_y \tag{7}$$

$$= \frac{\hbar^2\pi^2}{2ML^2}n_x^2 + \frac{\hbar^2\pi^2}{2ML^2}n_y^2 \tag{8}$$

Comments and Vocabulary (see pictures)

- $n_x - 1 \equiv$ " ~~number~~ # of excitations in x-direction "



no excitations

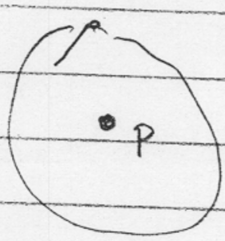
one excitation

- $n_y - 1 =$ " ~~S~~# of excitations in y-direction

- $E_{12} = E_{21}$ = same energy or degeneracy

$$= \frac{\hbar^2 \pi^2}{2ma^2}(1^2 + 2^2)$$

Today Motion In 3D



$$V(r) = \frac{-e^2}{4\pi\varepsilon_0}\frac{1}{r}$$

$$\vec{F}(r) = -\frac{\partial V}{\partial r}\hat{r} = -\frac{e^2}{4\pi\varepsilon_0}\frac{1}{r^2}\hat{r}$$

force

Want to solve for standing waves

(*) $$\left[\frac{-\hbar^2}{2m}\nabla^2 + V(r)\right]\psi(r,\theta,\varphi) = E\,\psi(r,\theta,\varphi)$$

$$\nabla^2 = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial y^2}$$

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

Try separation of variables

(**) $$\psi(r,\theta,\varphi) = R(r)\,\Theta(\theta)\,\Phi(\varphi)$$

Substitute (**) into (*) and find an kind of Schrödinger equation for R Θ Φ separately, but its a little complicated because of the Spherical Geometry a little

Wave fcns are characterized by three quantum numbers

$$\psi_{n\ell m} = R_{n\ell}(r)\, \Theta_{\ell m}(\theta)\, \Phi_m(\varphi)$$

Wave fcns have radial and angular excitations in θ and φ

(1) $n \equiv$ principle quantum #

$n-1$ = "total number of excitations" angular or radial

$n = 1, 2, 3, 4, 5 \ldots$

$E_{n\ell} = \dfrac{-13.6\,\text{eV}}{n^2}$ ← This is specific to $1/r$ potential

in general E depends on ℓ

(2) $\ell \equiv$ angular quantum number

= "total # of angular excitations"

$= 0, 1, 2, 3 \ldots n-1$

$= s, p, d, f \ldots n-1$

$\ell = 0, 1, 2$ are also known as s, p, d

"sharp, principle, diffuse"

a) ~~#~~ number of radial excitations $= n-1-\ell$

b) $\overline{L^2}$ = average angular momentum squared

$= \overline{L_x^2 + L_y^2 + L_z^2}$

$\overline{L^2} = \ell(\ell+1)\hbar^2$ ← we will show later

③ $m \equiv$ magnetic quantum #

$|m| = \pm$ "# of angular excitations around z-axis"

$= 0, \pm 1, \pm 2, \pm \ldots \pm \ell$

↑

sign indicates wether angular excitation is spinning clockwise or counter clockwise

a) $\overline{L_z} = m\hbar$ ← we will show later

Wave functions Hydrogen

- We will solve the Shrödinger equation for the Coulomb potential

$$V(r) = -\frac{e^2}{4\pi\epsilon_o}\frac{1}{r} \qquad r = \sqrt{x^2+y^2+z^2} \tag{9}$$

- The wave functions are

$$\psi_{nlm}(r,\theta,\varphi) = R_{nl}(r)\Theta_{lm}(\theta)\Phi_m(\varphi) \tag{10}$$

Here th labels n, l and m are the quantum numbers. One for each dimension r, θ, φ.

- In general the wave functions are characterized by the three quantum numers

1. The *principle* quantum number

$$n = 1, 2, 3, 4 \ldots \tag{11}$$

$(n-1)$ is the "total number of excitations in either the radial or angular directions".

$$E_n = -\frac{\hbar^2}{2ma_0^2}\frac{1}{n^2} = -\frac{13.6\,\text{eV}}{n^2} \tag{12}$$

2. The *angular* quantum number is the total number of angular excitations which should be less than or equal to the total number of excitations, $(n-1)$:

$$\ell = 0, 1, \ldots n-1 \tag{13}$$

$(n-1)-\ell$ is the number of radial excitations. ℓ labels the total angular momentum of this wave functions:

$$\overline{\mathbb{L}^2} = \ell(\ell+1)\hbar^2. \tag{14}$$

For $\ell = 0, 1, 2, 3, 4 \ldots$ these wave-fcns also called by the names

$$\ell = s, p, d, f, g \tag{15}$$

i.e. an "s-wave" is another name for the $\ell = 0$ wave function.

3. And a "magnetic" quantum number which labels the z component of the angular momentum

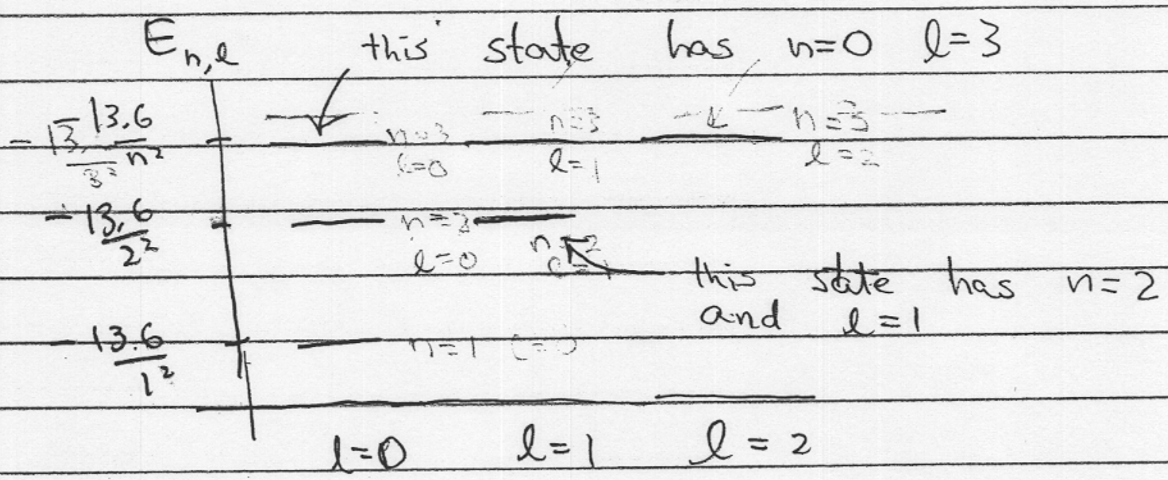
$$\overline{\mathbb{L}_z} = m\hbar \tag{16}$$

with

$$m = -\ell, -\ell+1, \ldots, \ell-1, \ell \tag{17}$$

n ℓ m		$\Phi_m(\varphi)$	$\Theta_{lm}(\theta)$	$R_{nl}(r)$	Ψ_{nlm}
1 0 0	$1s$	1	1	$\frac{1}{\sqrt{\pi a_o^3}}e^{-r/a_o}$	$\frac{1}{\sqrt{\pi a_o^3}}e^{-r/a_o}$
2 0 0	$2s$	1	1	$\frac{1}{\sqrt{32\pi a_o^3}}\left(2-\frac{r}{a_o}\right)e^{-r/2a_o}$	$\frac{1}{\sqrt{32\pi a_o^3}}\left(2-\frac{r}{a_o}\right)e^{-r/2a_o}$
2 1 0	$2p$	1	$\sqrt{3}\cos(\theta)$	$\frac{1}{\sqrt{96\pi a_o^3}}\frac{r}{a_o}e^{-r/2a_o}$	$\frac{1}{\sqrt{32\pi a_o^3}}\frac{r}{a_o}e^{-r/2a_o}\cos(\theta)$
2 1 ±1	$2p$	$e^{\pm i\varphi}$	$\sqrt{\frac{3}{2}}\sin(\theta)$	$\frac{1}{\sqrt{96\pi a_o^3}}\frac{r}{a_o}e^{-r/2a_o}$	$\frac{1}{\sqrt{64\pi a_o^3}}\frac{r}{a_o}e^{-r/2a_o}\sin(\theta)e^{\pm i\varphi}$

Then we usually draw the energy level diagram



Examples

(1) Thus for $n=2$ states we are referring to:

$n=2, \ l=0 \ m=0$

$n=2, \ l=1 \ m=0, \pm 1$

(2) When we refer to a 3d state we mean

$n=3 \ l=2 \quad m=0, \pm 1, \pm 2$

$$\overline{L}^2 = 2(2+1)\hbar^2$$

$$L_z = 0, \pm\hbar, \pm 2\hbar$$

(3) What is the degeneracy of the $n=3$ level?

Solution:

$n=3 \quad l=0 \qquad\qquad \leftarrow \quad 1 \text{ state} = (2l+1)$

$n=3 \quad l=1 \quad m=0,\pm1 \leftarrow \quad 3 \text{ states} = (2l+1)$

$n=3 \quad l=2 \quad m=0,\pm1,\pm2 \leftarrow \quad 5 \text{ states} = (2l+1)$

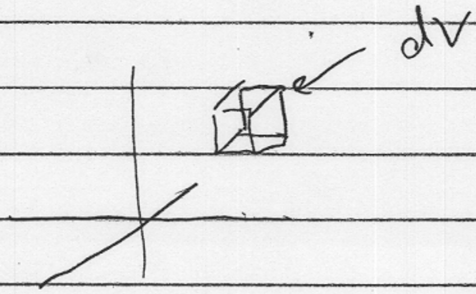
So the total degeracy is

$1+3+5=9 \Rightarrow$ generally $\sum_{l=0}^{n-1}(2l+1) = n^2$

$= 3^2$

Radial Probability density:

(1).



$$dP = |\psi|^2\, dV$$

probability per volum

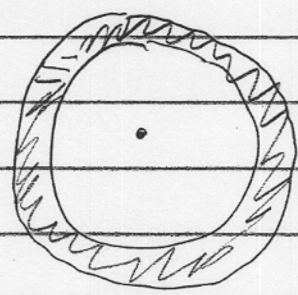
Take $l=0$ $m=0$ waves (no angular dependence or excitations

$$\Theta = 1 \quad \text{and} \quad \Phi = 1$$

Then:

$$\psi = R_{nl}(r)$$

dP -



$$dP = |\psi|^2\, dV = |R_{nl}(r)|^2 \underbrace{4\pi r^2 dr}_{dV} = \text{probability}$$

= probabity to find electron between $r + dr$ at any angle

Actually this works for $l \neq m \neq 0$

$$dP = |\psi|^2 \, dV$$

$$dP = \int_{\text{sphere}} |R|^2 \, |\Theta|^2 \, |\Phi|^2 \, r^2 dr \, d\Omega$$

$$= |R|^2 \, r^2 dr \underbrace{\int d\Omega \, |\Theta|^2 |\Phi|^2}_{\substack{\text{constant:} \\ \text{can choose to be } 4\pi}}$$

$$dP = |R_{nl}|^2 \, 4\pi r^2 dr \equiv \mathcal{P}(r) \, dr$$

$$\mathcal{P}(r) = |R|^2 \, 4\pi r^2$$

← probability per unit r

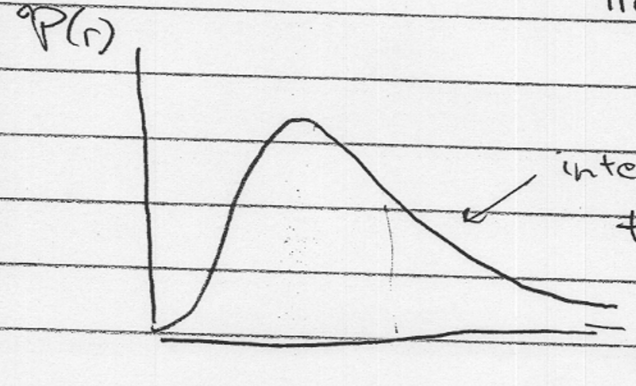
Example: The ground state wave ($n=0$, $l=0$, ...) function of hydrogen is (see table)

$$\psi = \frac{1}{\sqrt{\pi a_0^3}} e^{-r/a_0}$$

① Graph the Probility density $P(r)$

Solution: $R_{nl} = \frac{1}{\sqrt{\pi a_0^3}} e^{-r/a_0}$ $\quad \Phi = \Theta = 1$

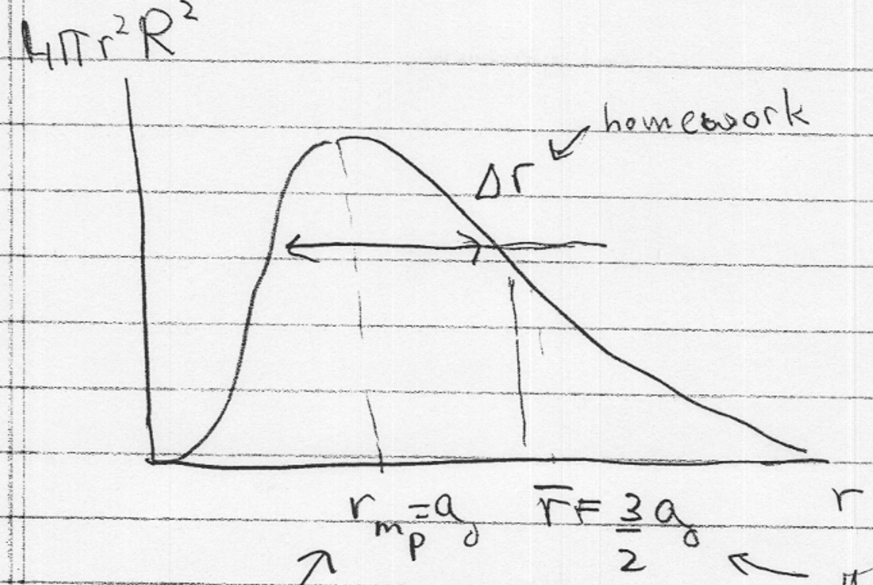
$$P(r) = R^2 \, 4\pi r^2 \, dr = \frac{4\pi}{\pi a_0^3} r^2 e^{-2r/a_0}$$



integral under this curve is one

Kinds of Problems one can now pose

① $1 = \int_0^\infty P(r)\, dr$ ← normalize the wave fcn electron must be somewhere

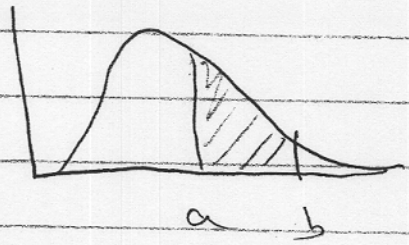


We will show this now

See example 7.3 of book

② P_{ab} = # prob between r_a & r_b

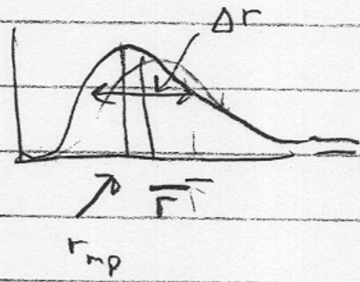
$$= \int_a^b dr\, \mathcal{P}(r)$$



③ $$\overline{r} = \int_0^\infty dr\, \mathcal{P}(r)\, r$$

$$\overline{r^2} = \int_0^\infty dr\, \mathcal{P}(r)\, r^2$$

$$\Delta r^2 = \overline{r^2} - \overline{r}^2$$



$$\overline{PE} = \overline{V} = \int_0^\infty dr\, \mathcal{P}(r)\, \frac{-e^2}{4\pi\varepsilon_0 r}$$

④ most probable $\left.\frac{\partial \mathcal{P}}{\partial r}\right|_{r_{mp}} = 0$

* Bohr model often gives the right order of magnitude for these averages

- Sometimes its exactly right

e.g.

$$\bar{r} = \int_0^\infty dr\, \mathcal{P}(r) \quad r$$

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

$$= 4a_0 \int_0^\infty \frac{dr}{a_0} \quad \left(\frac{r}{a_0}\right)^2 \quad e^{-2r/a_0} \quad \frac{r}{a_0}$$

divide by a_0 and bring ou a_0

$$u = \frac{r}{a_0}$$

$$\bar{r} = 4a_0 \int_0^\infty du \quad u^3 \quad e^{-2u}$$

Note: $\int_0^\infty dx \quad x^n \quad e^{-x} = n!$

So let $x = 2u$

$$\bar{r} = \frac{4a_0}{16} \int_0^\infty dx\, x^3\, e^{-x} \quad = \frac{4 \cdot 3 \cdot 2}{16} a_0 = \frac{3}{2} a_0$$

$$\bar{r} = \frac{3}{2} a_0$$