CHEM F111 : General Chemistry
Semester II: AY 2017-18
Lecture-09, 31-01-2018

Hydrogen atom wavefunction:

$$\Psi_{n,\,l,\,m_l}(r,\theta,\varphi) = N\,R_{n,l}(r)\,\Theta_{l,\,m_l}(\theta)\,\Phi_{m_l}(\varphi)$$

Orbital	n	l	$R_{n,l}$
1s	1	0	$2\left(\dfrac{Z}{a_0}\right)^{3/2} e^{-\rho/2}$
2s	2	0	$\dfrac{1}{2(2)^{1/2}}\left(\dfrac{Z}{a_0}\right)^{3/2}\left(2-\dfrac{1}{2}\rho\right)e^{-\rho/4}$
2p	2	1	$\dfrac{1}{4(6)^{1/2}}\left(\dfrac{Z}{a_0}\right)^{3/2}\rho e^{-\rho/4}$

l	m_l	Y_{l,m_l}
0	0	$\left(\dfrac{1}{4\pi}\right)^{1/2}$
1	0	$\left(\dfrac{3}{4\pi}\right)^{1/2}\cos\theta$
	± 1	$\mp\left(\dfrac{3}{8\pi}\right)^{1/2}\sin\theta\, e^{\pm i\phi}$

$\rho = 2Zr/a_0$

H-atom/Hydrogen like atom

- Consider an electron in an energy state represented by n and orbital angular momentum l.
- An atom is a centrally symmetric system.
- Three spatial coordinates are expressed in: r, θ, Φ.
- The θ and Φ angular dependence is represented by $Y_l^{m_l}$
- The spatial part of the wave function is represented by

$$\boldsymbol{\Psi}_{\boldsymbol{n,\,l,\,m_l}}(\boldsymbol{r},\boldsymbol{\theta},\boldsymbol{\varphi}) = \boldsymbol{N\,R}_{\boldsymbol{n,l}}(\boldsymbol{r})\,\boldsymbol{Y}_{\boldsymbol{l}}^{\boldsymbol{m_l}}(\boldsymbol{\theta},\boldsymbol{\varphi})$$

$\boldsymbol{\Psi}_{\boldsymbol{n,\,l,\,m_l}}(r,\boldsymbol{\theta},\boldsymbol{\varphi})$ simultaneous eigen functions of $\hat{H}, \hat{L}^2, and\ \hat{L}_z$

$$\widehat{L^2} = \widehat{L_x^2} + \widehat{L_y^2} + \widehat{L_z^2}$$
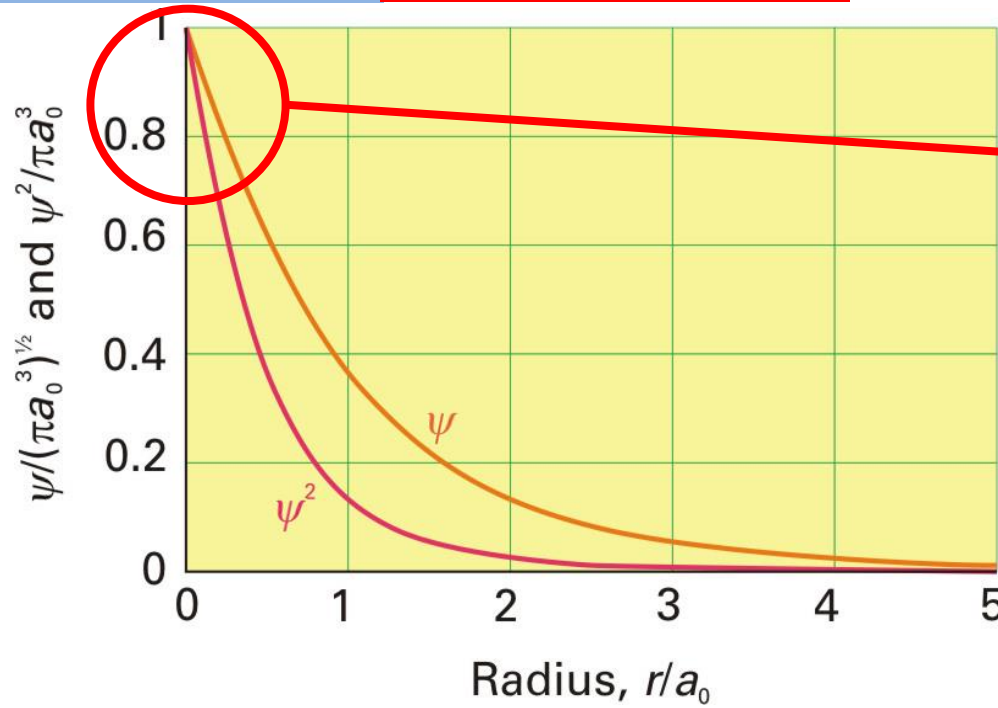
Work out: Determine the (i) energy, (ii) angular momentum, and (iii) Z-component of angular momentum for an in H-atom having the following wave function {a_0 is the Bohr Radius}:
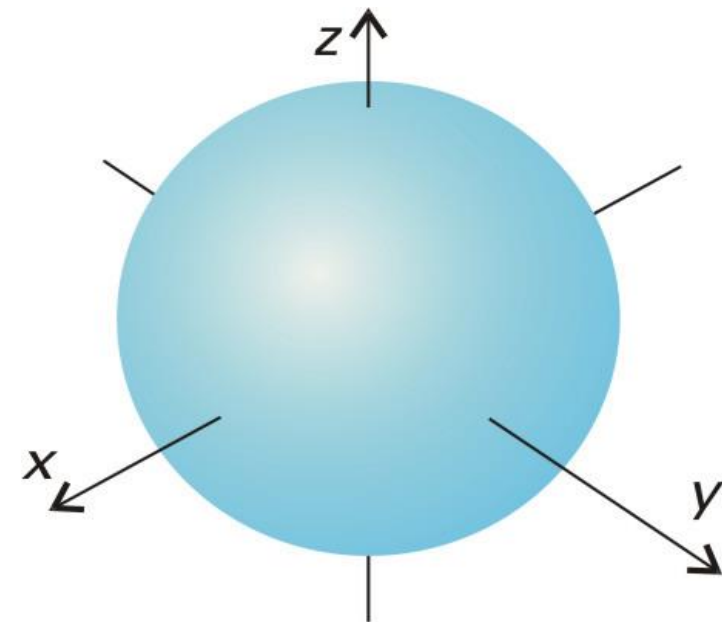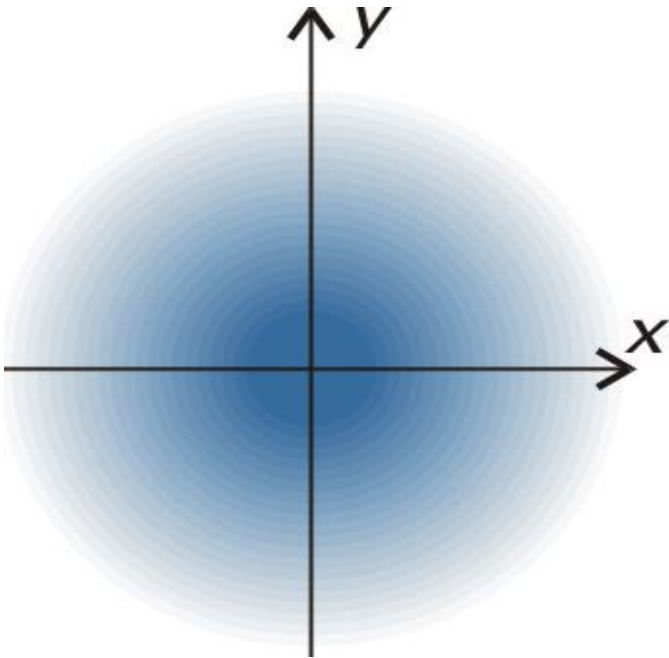
$$\Psi_{n,\,l,\,m}(r,\theta,\varphi) = \frac{1}{\sqrt{32\pi}}\left(\frac{Z}{a_0}\right)^{3/2}\left(\frac{Zr}{a_0}\right)e^{-Zr/2a_0}\cos\theta$$

Work out: Calculate the probability at the nucleus for an electron with n=1, l=0, and m_l=0.

1s wave function and probability density

????

1s – radial distribution function

$|\psi|^2 \Rrightarrow |\Psi_{n,l,m_l}(r,\theta,\varphi)|^2 \Rrightarrow$ Probability of finding an electron in any region

$|\psi|^2 \Rrightarrow$ Dimensions: 1/volume

$|\psi|^2$ multiplied by infinitesimal volume element $\Rrightarrow$ dimensionless, probability

Consider H-atom 1s orbital: $\qquad \Psi_{1,0,0}(r,\theta,\varphi) = \frac{1}{\sqrt{\pi}}\left(\frac{Z}{a_0}\right)^{3/2} e^{-Zr/a_0}$

$|\Psi_{1,0,0}(r,\theta,\varphi)|^2 \; \alpha \; e^{-2Zr/a_0}$

- Imagine an electron probe with infinitesimal small volume $d\tau$ (dx dy dz)
- Gives the greatest reading at the nucleus.
- Reading decreases along any radius vector.
- Reading is constant if the probe is moved on a circle of constant radius.
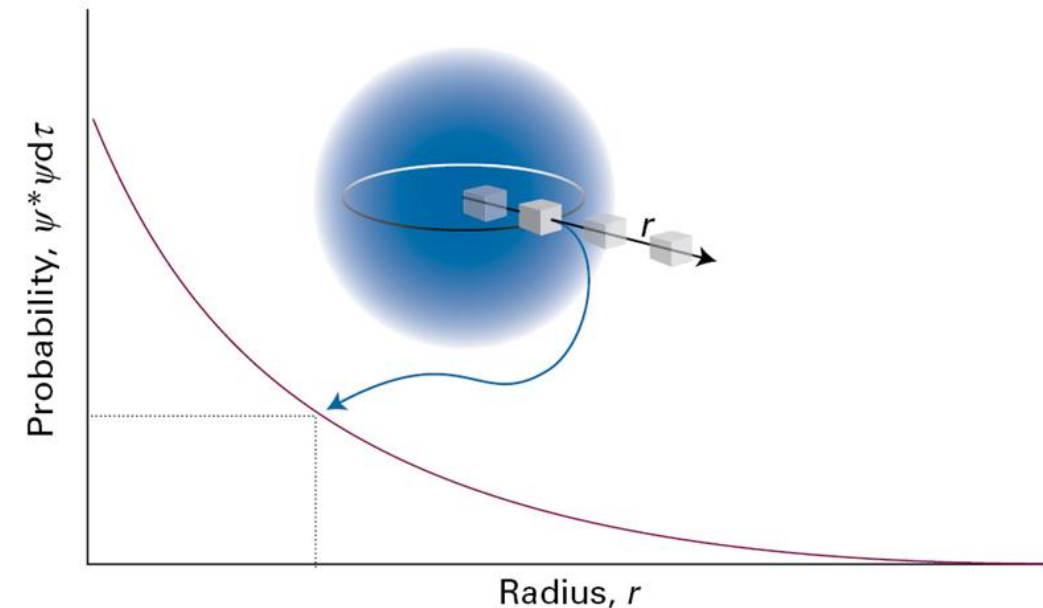
1s – radial distribution function

How do we measure the probability of finding the electron anywhere between the two walls of a spherical shell of thickness dr at radius r?
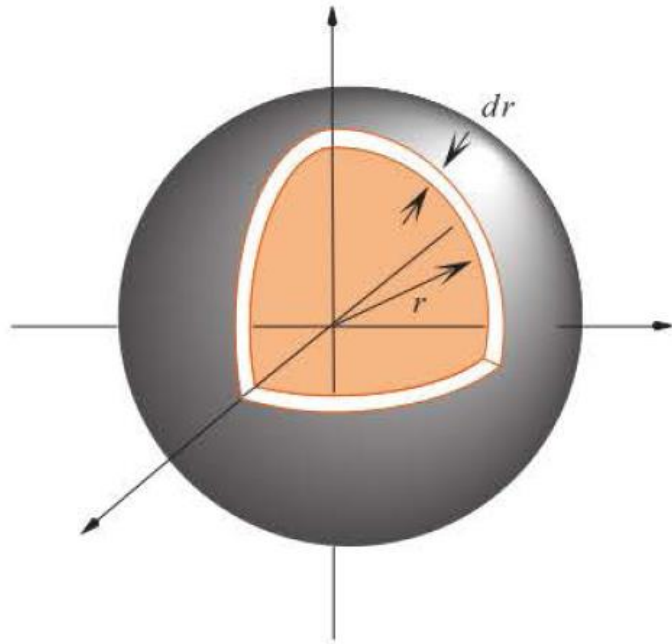
The sensitive volume of the probe: $4\pi r^2 dr$

Probability:

$$|\psi|^2 \times 4\pi r^2 dr = P(r)\, dr$$

$$P(r) = 4\pi r^2\, |\psi|^2$$

P(r) is called the radial distribution function – when P(r) is multiplied by the dr, it gives the probability of finding the electron anywhere between the two walls of a spherical shell of thickness dr at radius r
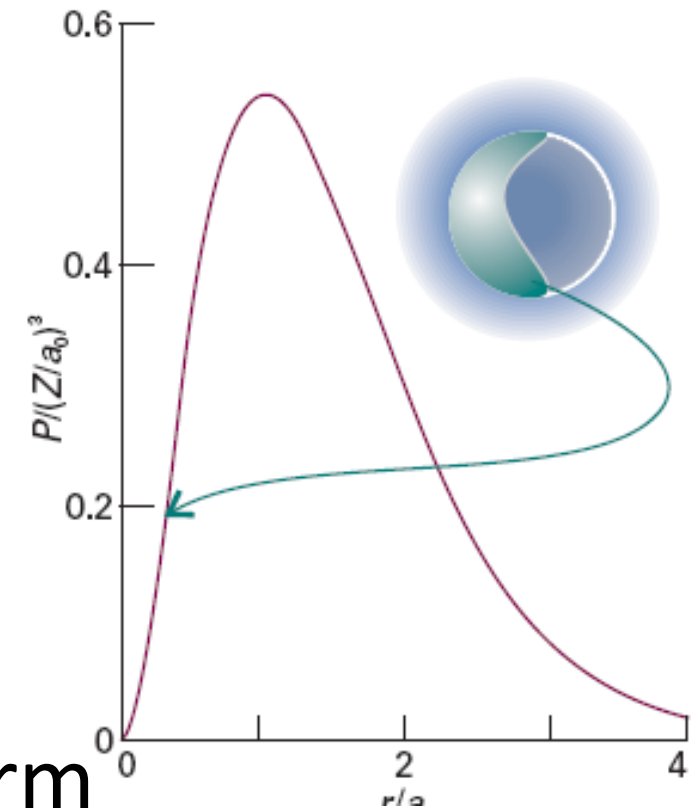
1s – radial distribution function

For, H-atom 1s orbital:

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

Interpretation:

1. $r^2 = 0$ at the nucleus, P(0) = 0
2. As $r \rightarrow \infty$, P(r) $\rightarrow$ 0 due to exponential term
3. P(r) passes through a maxima.

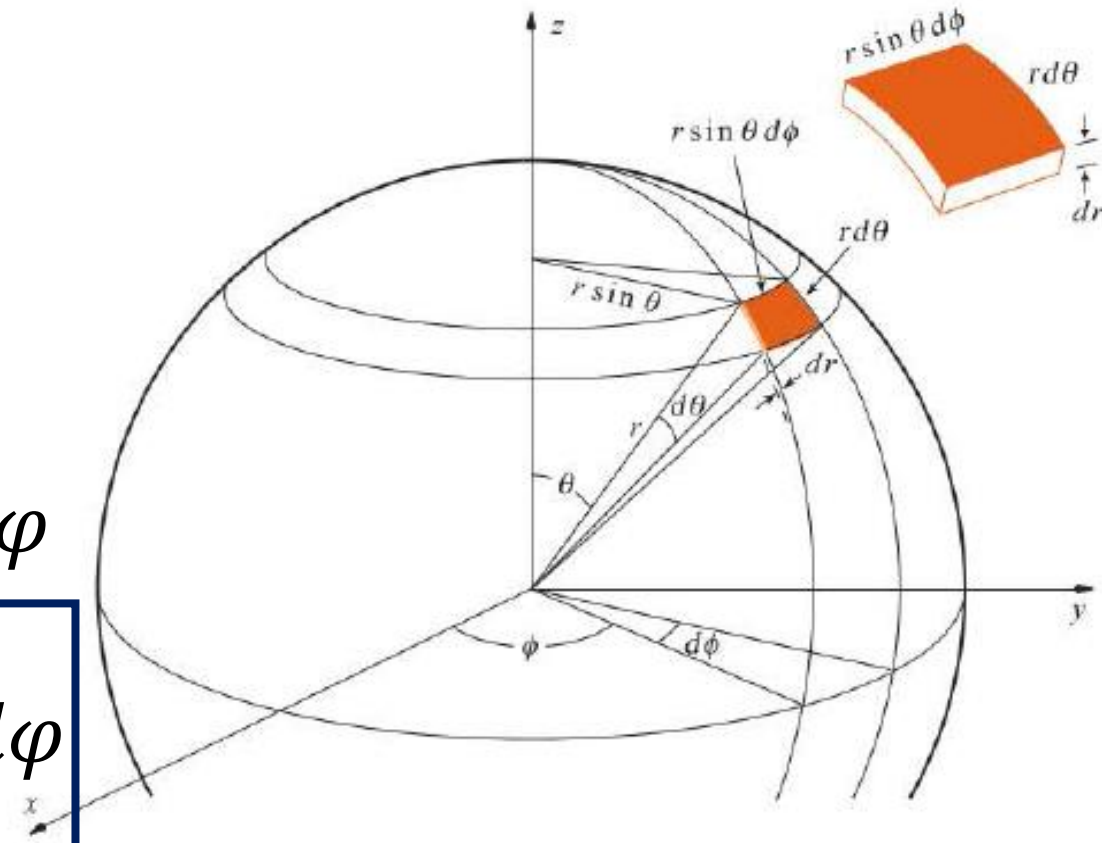**All orbitals are not spherically symmetric!!**
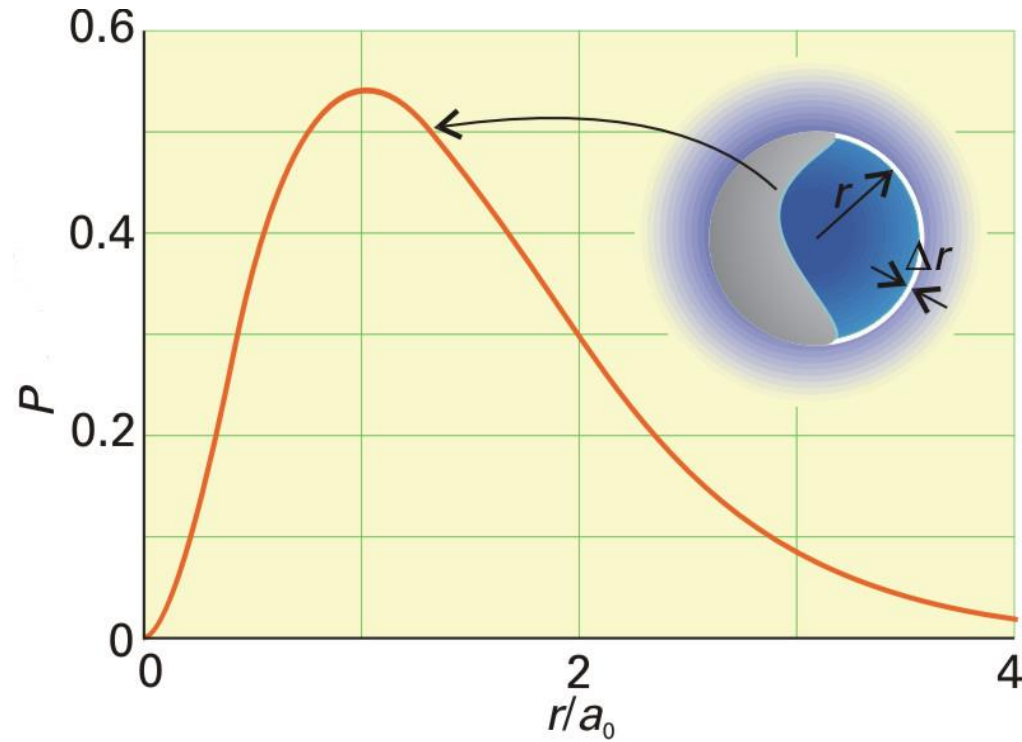
Radial distribution function – general form

Like, $$\Psi_{2,\,1,\,0}(r, \theta, \varphi) = \frac{1}{\sqrt{32\pi}} \left(\frac{Z}{a_0}\right)^{3/2} \left(\frac{Zr}{a_0}\right) e^{-Zr/2a_0} \cos\theta$$

Wave function: $R(r)\, Y_l^{m_l}$
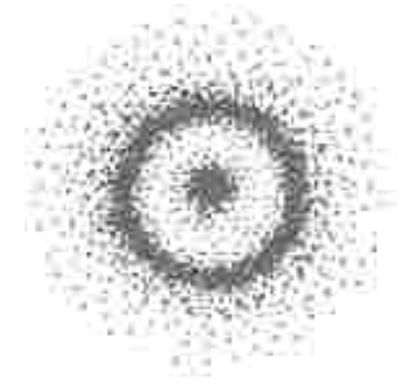
$$d\tau = r^2\, dr\, \sin\theta\, d\theta\, d\varphi$$

$$P(r)\, dr$$

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

$$= r^2\, |R(r)|^2 dr \boxed{\int_0^\pi \int_0^{2\pi} |Y_l^{m_l}|^2\, \sin\theta\, d\theta\, d\varphi}$$

$$= r^2\, |R(r)|^2 dr$$

Most probable radius

1s

2s

$$\frac{dP(r)}{dr} = 0$$

How do we calculate the most probable radius?

The maximum of P(r) marks the most probable radius at the electron will be found!!
For a 1s orbital in hydrogen, P(r) is maximum at r = a_o (Bohr radius)

Most probable radius

Calculate the most probable radius, r*, at which an electron will be found when it occupies a 1s orbital of a hydrogenic atom of atomic number Z (H to Ne^{9+})

	H	He^+	Li^{2+}	Be^{3+}	B^{4+}	C^{5+}	N^{6+}	O^{7+}	F^{8+}	Ne^{9+}
r*/pm	52.9	26.5	17.6	13.2	10.6	8.82	7.56	6.61	5.88	5.29

1s orbital is drawn towards the nucleus as the nuclear charge increases

Most probable radius

FIG. 6·2. Probability distribution in hydrogen.
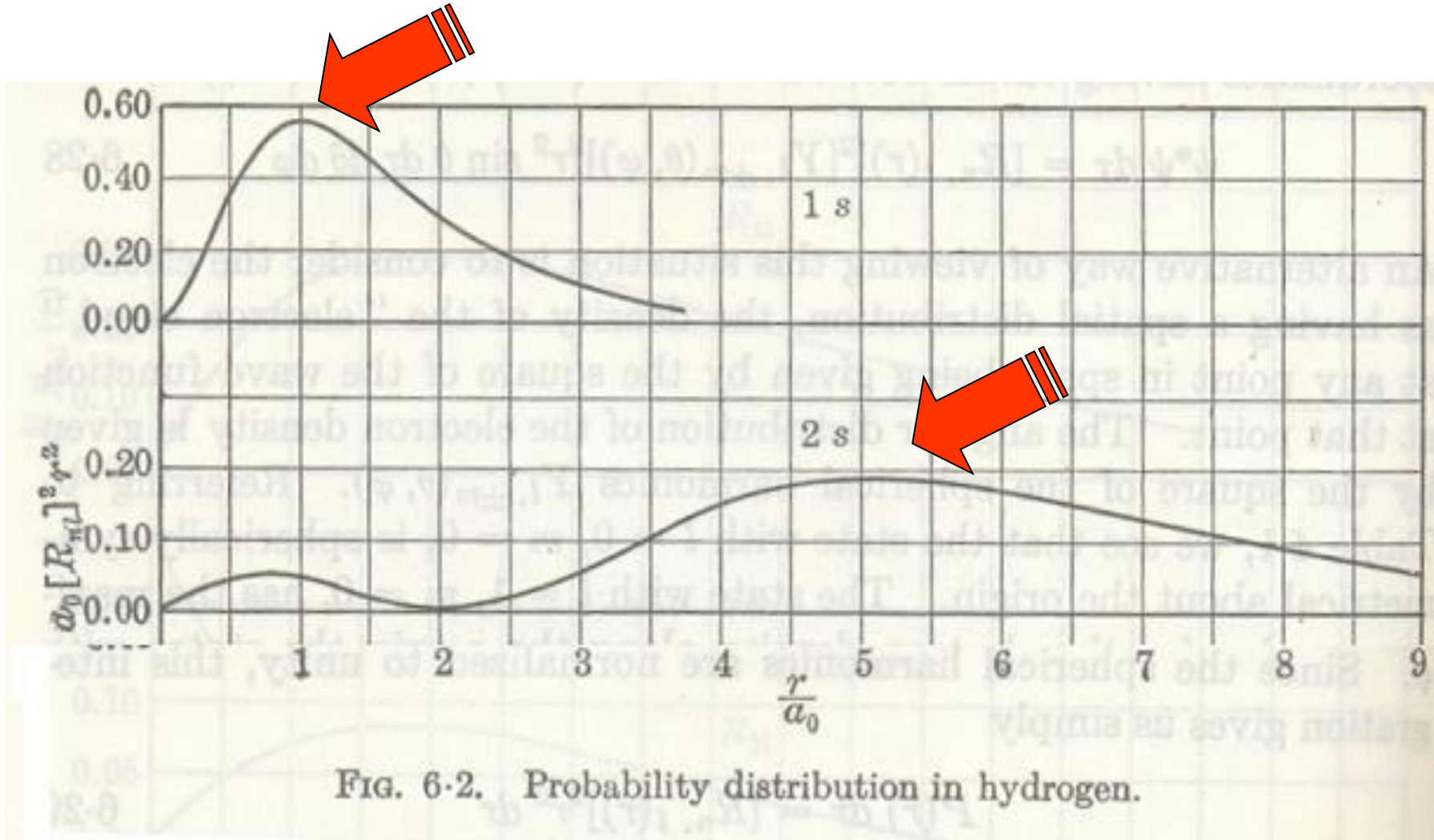
For 2s orbital: Most probable radius is 5.2 a_0 = 275 pm

Hydrogen atom wave function for n = 2

n = 2 state $\Rightarrow l = 0 , 1; for\ l = 1, m_l = 0\ and\ 1,\ 0\ ,\ -1$

$$\Psi_{2,0,0}(r,\theta,\varphi) = \frac{1}{\sqrt{32\pi}} \left(\frac{Z}{a_0}\right)^{3/2} \left(2 - \frac{Zr}{2a_0}\right) e^{-Zr/2a_0}$$

$$\Psi_{2,1,0}(r,\theta,\varphi) = \frac{1}{\sqrt{32\pi}} \left(\frac{Z}{a_0}\right)^{3/2} \left(\frac{Zr}{a_0}\right) e^{-Zr/2a_0} \cos\theta$$

$$\Psi_{2,1,\pm 1}(r,\theta,\varphi) = \frac{1}{\sqrt{64\pi}} \left(\frac{Z}{a_0}\right)^{3/2} \left(\frac{Zr}{a_0}\right) e^{-Zr/2a_0} \sin\theta\ \boxed{e^{\pm i\varphi}}$$
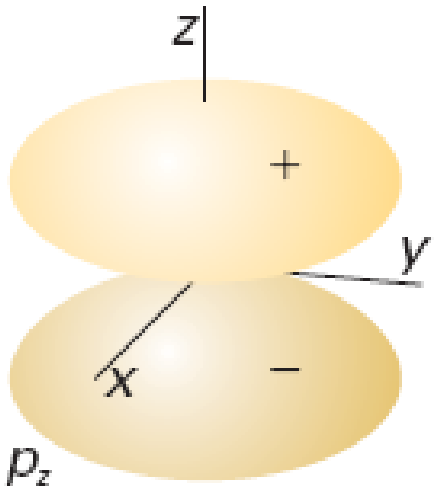
2s orbital

$$\Psi_{2,0,0}(r,\theta,\varphi) = \frac{1}{\sqrt{32\pi}} \left(\frac{Z}{a_0}\right)^{3/2} \left(2 - \frac{Zr}{2a_0}\right) e^{-Zr/2a_0} = f(r)$$

$$\Psi_{2,1,0}(r,\theta,\varphi) = \frac{1}{\sqrt{32\pi}} \left(\frac{Z}{a_0}\right)^{3/2} \left(\frac{Zr}{a_0}\right) e^{-Zr/2a_0} \cos\theta$$

$$= r\cos\theta\, f(r) = z\, f(r) \qquad \boxed{\Psi_{p_z} = z\, f(r)}$$
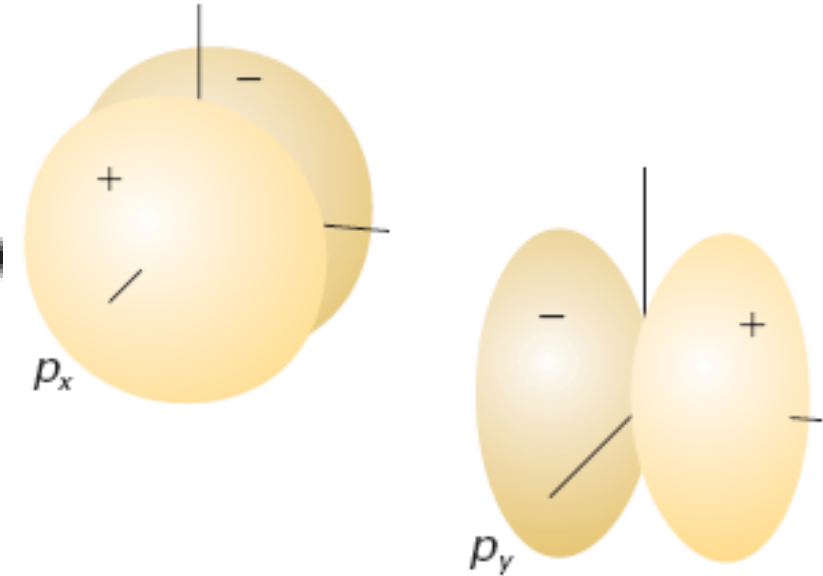
XY plane is nodal plane – angular node is one

$$\Psi_{2,\,1,\,\pm 1}(r,\theta,\varphi) = \frac{1}{\sqrt{64\pi}} \left(\frac{Z}{a_0}\right)^{3/2} \left(\frac{Zr}{a_0}\right) e^{-Zr/2a_0} \sin\theta\; \boxed{e^{\pm i\varphi}}$$

What is your idea about p-orbitals?

$$\psi_{p_x} = -\frac{1}{2^{1/2}}(p_{+1} - p_{-1}) = r\sin\theta\cos\phi\, f(r) = xf(r)$$

$$\psi_{p_y} = \frac{i}{2^{1/2}}(p_{+1} + p_{-1}) = r\sin\theta\sin\phi\, f(r) = yf(r)$$

Also an energy eigen function with same energy and eigen function of the angular momentum operator

Orthonormal wave functions

$$\int \psi_m^* \, \psi_n \, d\tau = \delta_{mn}$$

$\delta_{mn} = 1$ if m = n
$\phantom{\delta_{mn}} = 0$ if m $\neq n$

❖ Show that hydrogenlike atomic wave function $\Psi_{2\,1\,0}$ is normalized and it is orthogonal to $\Psi_{2\,0\,0}$.

❖ Show that the PIB wave functions satisfy the relation: $\int_0^a \psi_n^*(x) \, \psi_m(x) dx = 0 \; for \; m \neq n$

This concept would be used in bonding

What do we learn?

Do consider an experimental set-up in which you can populate 2p$_x$ state of H-atom. Now, try to measure the following parameters:
1) Energy
2) Total angular momentum
3) Z-component of angular momentum
What would be the outcome?

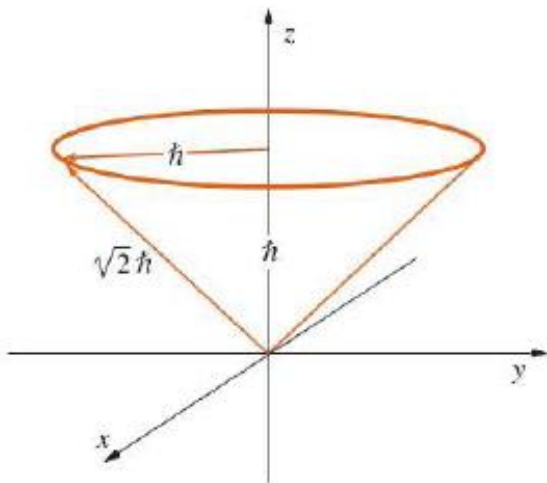$$\psi_{p_x} = -\frac{1}{2^{1/2}}(p_{+1} - p_{-1}) = r\sin\theta\cos\phi\, f(r) = xf(r)$$
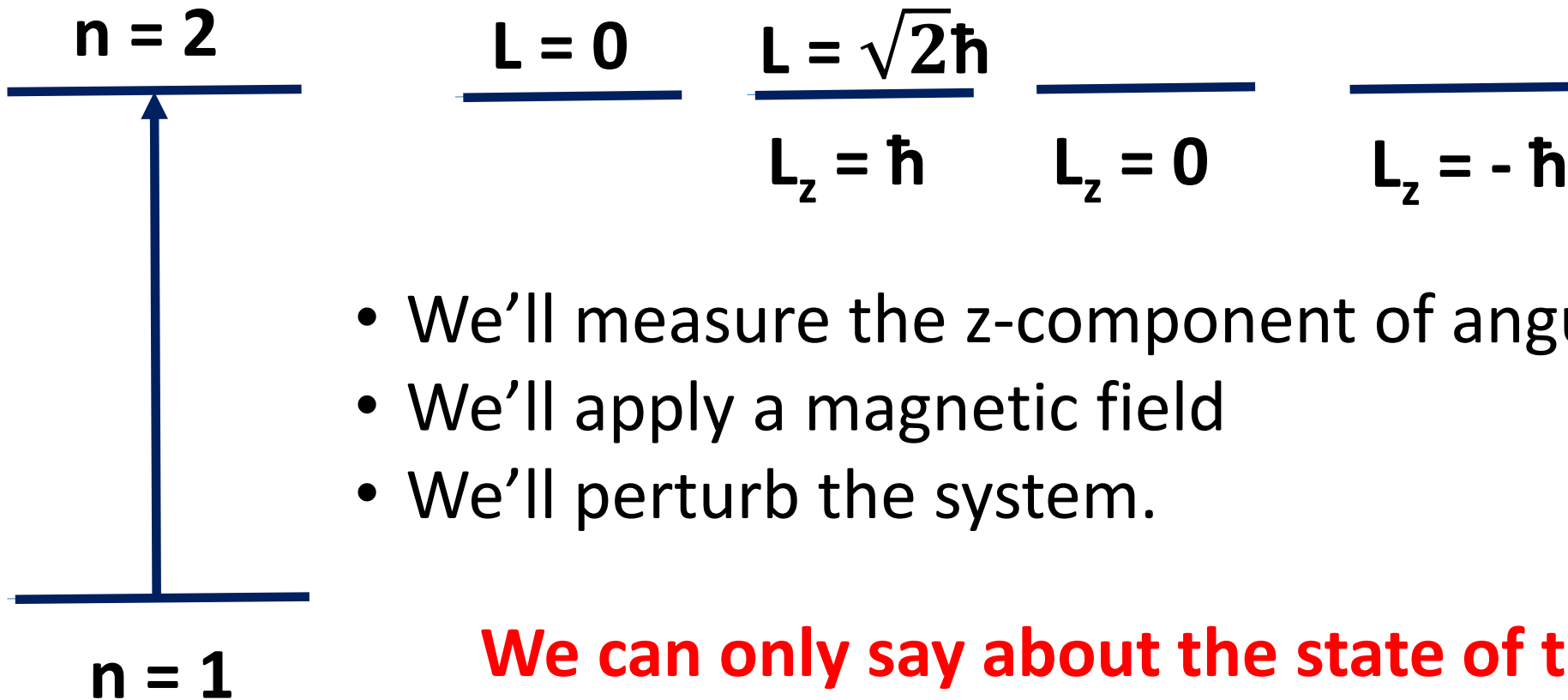
What do we learn?

- Atomic states
- Energy: 2s and 2p are having same energy
- Angular momentum: We can differentiate 2s and 2p
- There are three states in 2p??
- One of the component of angular momentum – Z-component

We can measure total angular momentum and any one of the components: L_x, L_y, or L_z

A thought experiment

n = 2

L = 0   **L = $\sqrt{2}\hbar$**

L$_z$ = $\hbar$ **L$_z$ = 0**   **L$_z$ = - $\hbar$**

- We'll measure the z-component of angular momentum
- We'll apply a magnetic field
- We'll perturb the system.

n = 1

We can only say about the state of the system when we are trying to measure