

# Rest of semester

- **Investigate hydrogen atom (Wednesday 4/15 and Friday 4/17)**
- Learn about intrinsic angular momentum (spin) of particles like electrons (Monday 4/20)
- Take a peak at multielectron atoms including the Pauli Exclusion Principle (Wednesday 4/22)
- Describe some of the fundamentals of quantum mechanics (expectation values, eigenstates, superpositions of states, measurements, wave function collapse, etc.) (Friday 4/24 and Monday 4/27)
- Review of semester (Wednesday 4/29 and Friday 5/1)
- Final exam: Saturday 5/2 from 1:30pm-4:00pm in G125 (this room)

# The radial component of $\psi$

For any central force potential we can write the wave function as

$$\psi(r, \theta, \phi) = R(r)\Theta_{\ell m}(\theta)e^{im\phi}$$
$$\psi(r, \theta, \phi) = R(r)Y_{\ell m}(\theta, \phi)$$

The radial part of the time independent Schrödinger equation can be written as

$$-\frac{\hbar^2}{2m_e} \frac{d^2(rR)}{dr^2} + \left[ V(r) + \frac{\ell(\ell+1)}{2m_e r^2} \right] (rR) = E(rR)$$

This is how we are going to get the energy  $E$  and the  $r$  dependence of the wave function

Note that  $m$  does not appear. This makes sense because it just contains information on the *direction* of the angular momentum.

The total angular momentum is relevant so  $\ell$  shows up.

To solve this equation we need to know the potential  $V(r)$ .

For the hydrogen atom  $V(r) = -\frac{ke^2}{r}$

# The three quantum numbers

Applying boundary conditions to the radial equation gives us yet another quantum number which we have already used:  $n$

In order to work,  $n$  must be an integer which is  $> \ell$

Putting it all together, our wave function is

$$\psi(r, \theta, \phi) = R_{nl}(r)\Theta_{\ell m}(\theta)e^{im\phi} \quad \text{or} \quad \psi(r, \theta, \phi) = R_{nl}(r)Y_{\ell m}(\theta, \phi)$$

The quantum numbers are:

$n = 1, 2, 3, \dots$  is the principal quantum number

$\ell = 0, 1, 2, \dots n-1$  is the angular momentum quantum number

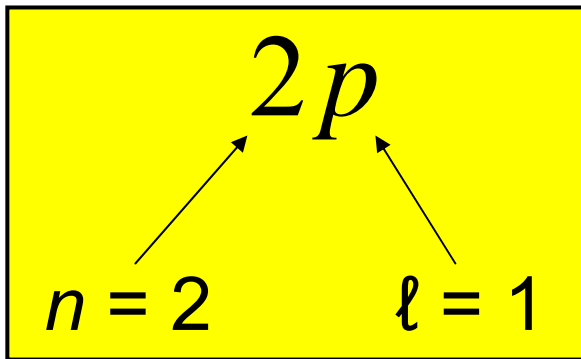
$m = 0, \pm 1, \pm 2, \dots \pm \ell$  is the z-component angular momentum quantum number

# The three quantum numbers

For hydrogenic atoms (one electron), energy levels only depend on  $n$  and we find the same formula as Bohr:  $E_n = -Z^2 E_R / n^2$

For multielectron atoms the energy also depends on  $\ell$ .

There is a shorthand for giving the  $n$  and  $\ell$  values.



Different letters correspond to different values of  $\ell$

	<i>s</i>	<i>p</i>	<i>d</i>	<i>f</i>	<i>g</i>	<i>h ...</i>
$\ell =$	0	1	2	3	4	5

# Hydrogen ground state

The hydrogen ground state has a principal quantum number  $n = 1$

Since  $\ell < n$ , this means that  $\ell = 0$  and therefore the ground state has no angular momentum.

Since  $|m| \leq \ell$ , this means that  $m = 0$  and so the ground state has no z-component of angular momentum (makes sense since it has no angular momentum at all).

Note that Bohr predicted the ground state to have angular momentum of  $\hbar$  which is wrong. Experiments have found that the ground state has angular momentum 0 which is what quantum mechanics predicts.

# Clicker question 1

Set frequency to DA

$n = 1, 2, 3, \dots$  = Principal Quantum Number

$$E_n = -Z^2 E_R / n^2$$

$\ell = 0, 1, 2, \dots, n-1$  = angular momentum quantum number  
= s, p, d, f, ...

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

$m = 0, \pm 1, \pm 2, \dots, \pm \ell$  is the z-component of angular momentum

$$L_z = m\hbar$$

A hydrogen atom electron is excited to an energy of  $-13.6/4$  eV. How many different quantum states could the electron be in? That is, how many wave functions  $\psi_{n\ell m}$  have this energy?

A. 1

$$E = -13.6/4 \text{ eV means } n^2 = 4 \text{ so } n = 2$$

B. 2

$$\text{For } n = 2, \ell = 0 \text{ or } \ell = 1.$$

C. 3

**D. 4**

$$\text{For } \ell = 0, m = 0.$$

$$\text{For } \ell = 1, m = -1, 0, \text{ or } 1$$

E. more than 4

1

2-4

# Degeneracy

When multiple combinations of quantum numbers give rise to the same energy, this is called degeneracy.

Ground state:  $n = 1, \ell = 0, m = 0$     1s state    no degeneracy  
 $E_1 = -Z^2 E_R$

1<sup>st</sup> excited state:  $E_2 = -Z^2 E_R / 4$

$n = 2, \ell = 0, m = 0$	2s state	} 4 states (fourfold degenerate)
$n = 2, \ell = 1, m = -1$	} 2p states	
$n = 2, \ell = 1, m = 0$		
$n = 2, \ell = 1, m = 1$		

2<sup>nd</sup> excited state:  $E_3 = -Z^2 E_R / 9$

$n = 3, \ell = 0, m = 0$	3s state	} 9 states (ninefold degenerate)
$n = 3, \ell = 1, m = -1$	} 3p states	
$n = 3, \ell = 1, m = 0$		
$n = 3, \ell = 1, m = 1$		
$n = 3, \ell = 2, m = -2$	} 3d states	
$n = 3, \ell = 2, m = -1$		
$n = 3, \ell = 2, m = 0$		
$n = 3, \ell = 2, m = 1$		
$n = 3, \ell = 2, m = 2$		

# Hydrogen energy levels

$\ell = 0$        $\ell = 1$        $\ell = 2$   
(s)          (p)          (d)

$n = 3$      $\overline{3s}$      $\overline{3p}$      $\overline{3d}$      $E_3 = -E_R / 3^2 = -1.5 \text{ eV}$

$n = 2$      $\overline{2s}$      $\overline{2p}$      $E_2 = -E_R / 2^2 = -3.4 \text{ eV}$

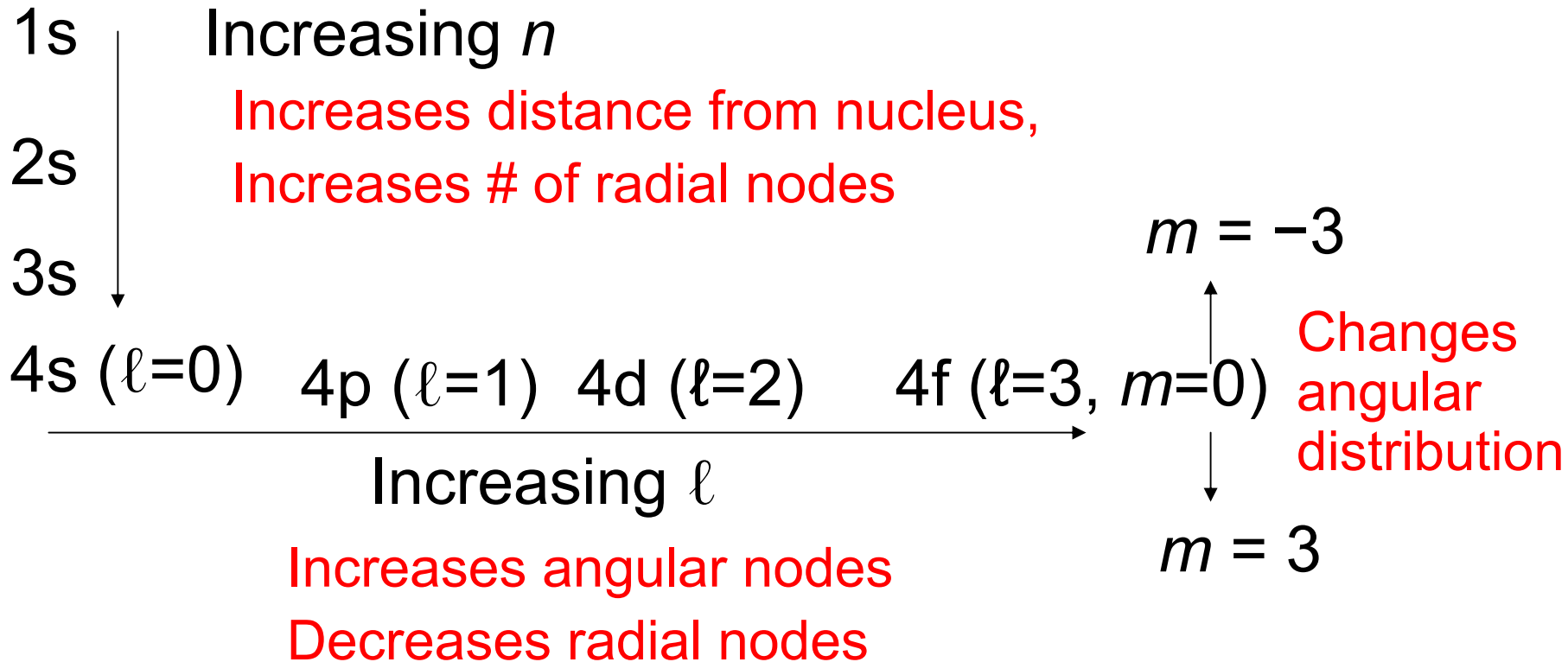
$n = 1$      $\overline{1s}$      $E_1 = -E_R = -13.6 \text{ eV}$

# What do the wave functions look like?

$n = 1, 2, 3, \dots$

$\ell$  (restricted to  $0, 1, 2 \dots n-1$ )

$m$  (restricted to  $-\ell$  to  $\ell$ )



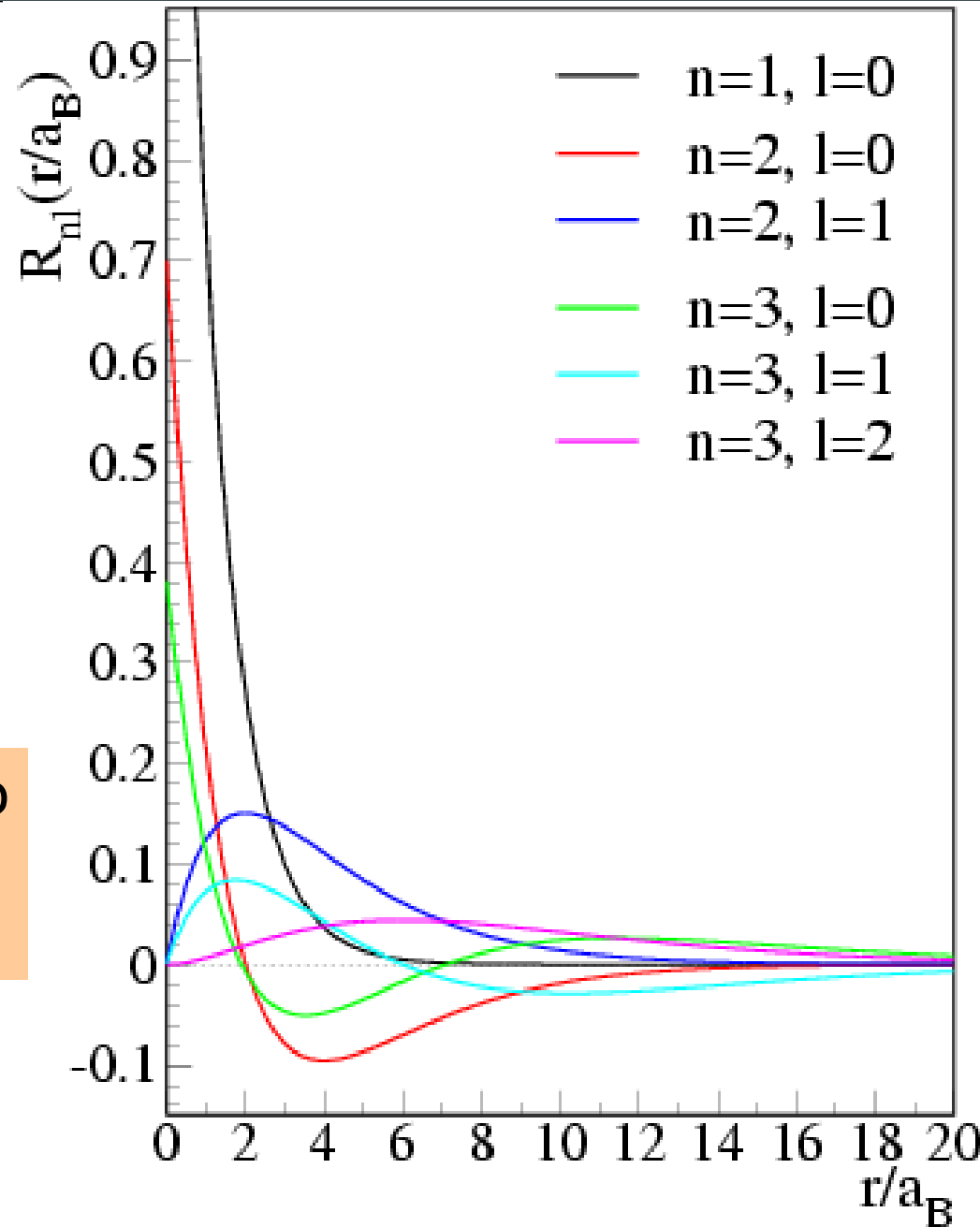
# Radial part of hydrogen wave function $R_{nl}(r)$

Radial part of the wave function for  $n=1$ ,  $n=2$ ,  $n=3$ .

x-axis is in units of the Bohr radius  $a_B$ .

Number of radial nodes ( $R(r)$  crosses x-axis or  $|R(r)|^2$  goes to 0) is equal to  $n-l-1$

Quantum number  $m$  has no affect on the radial part of the wave function.



$$|R_{nl}(r)|^2$$

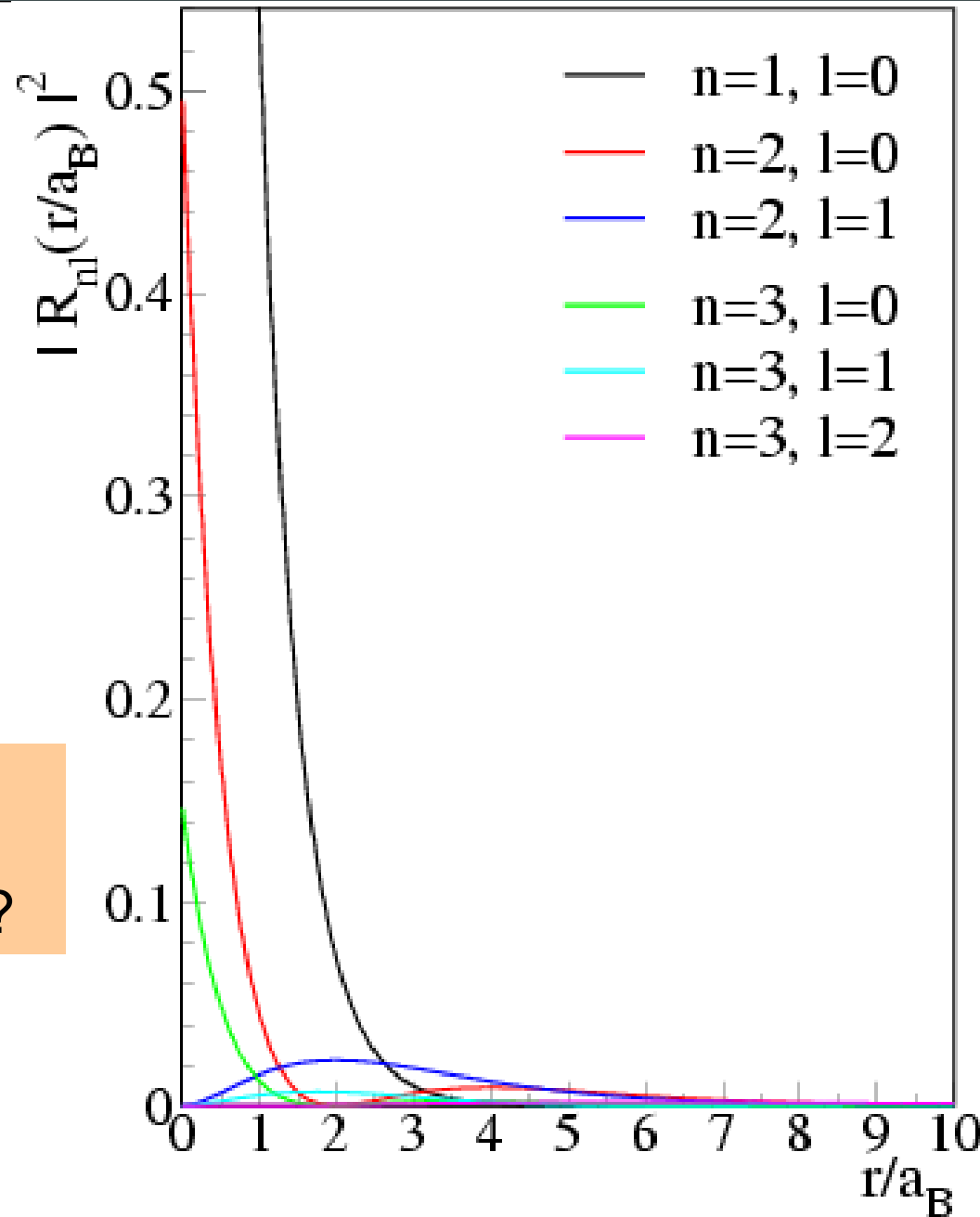
The radial part of the wave function squared

Note that all  $\ell=0$  states peak at  $r=0$

Since angular momentum is  $\vec{r} \times \vec{p}$  the electron *cannot* be at  $r=0$  and have angular momentum.

Does this represent the probability of finding the electron near a given radius?

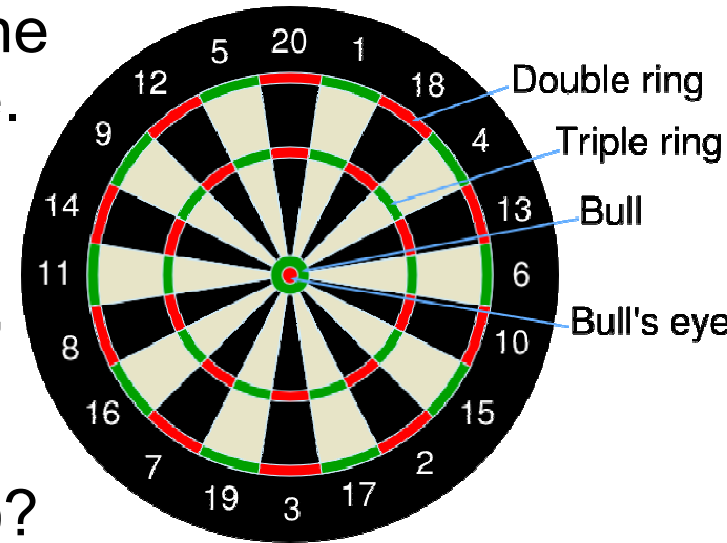
Not quite.



## Clicker question 2

Set frequency to DA

Assume that darts are thrown such that the probability of hitting any point is the same. The double ring is at  $r = 16.5$  cm and the triple ring is at a  $r = 10.0$  cm. Each ring has the same width in  $r$ . For a given dart, what is the probability of hitting a double compared to the probability of hitting a triple? That is, what is  $P(\text{double})/P(\text{triple})$ ?



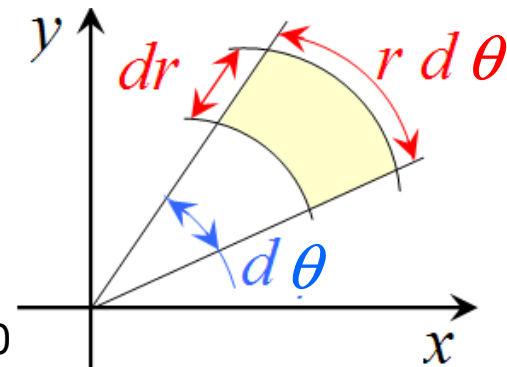
- A. 1
- B. 1.28
- C. 1.65**
- D. 2.72
- E. Some other value

The width in  $r$  is the same ( $dr$ ) so to get the area we multiply this width by the circumference ( $2\pi r$ ).

So probability is proportional to  $r$

$$\frac{P_{\text{double}}}{P_{\text{triple}}} = \frac{r_{\text{double}}}{r_{\text{triple}}} = 1.65$$

Can also consider the differential area in polar coordinates  $dA = r dr d\theta$



# Probability versus radius: $P(r) = |R_{nl}(r)|^2 r^2$

In spherical coordinates, the volume element has an  $r^2$  term so probability increases with  $r^2$ .

Most probable radius for the  $n = 1$  state is at the Bohr radius  $a_B$

Most probable radius for all  $\ell = n - 1$  states (those with only one peak) is at the radius predicted by Bohr ( $n^2 a_B$ ).

