

# Lecture #5

Reading:

## 1.9-Atomic Orbitals

**Topics:** Hydrogen Atom Wavefunctions  
I. Wavefunctions (orbitals) for the hydrogen atom ( $H\Psi = E\Psi$ )  
II. Shapes of H-atom wavefunctions: s orbitals  
III. Radial probability distributions

### ENERGY LEVELS (continued from Lecture #5)

The Rydberg formula can be used to calculate the frequency (and also the  $E$  or  $\lambda$ , using  $E = h\nu$  or  $\lambda = c/\nu$ ) of light emitted or absorbed by any 1-electron atom or ion.

$$v = \frac{Z^2 R_H}{h} \left( \frac{1}{n_f^2} - \frac{1}{n_i^2} \right) \quad \text{for } n_i > n_f \qquad v = \frac{Z^2 R_H}{h} \left( \frac{1}{n_i^2} - \frac{1}{n_f^2} \right) \quad \text{for } n_f > n_i$$

$n_f > n_i$  in \_\_\_\_\_. Electrons absorb energy causing them to go from a lower to a higher E level.

$n_i > n_f$  in \_\_\_\_\_. Electrons emit energy causing them to go from a higher to a lower E level.

## I. WAVEFUNCTIONS (ORBITALS) FOR THE HYDROGEN ATOM

When solving  $H\Psi = E\Psi$ , the solutions are  $E_{\ell}$  and  $\Psi(r, \theta, \phi)$ .

$\Psi(r, \theta, \phi) \equiv$  stationary state wavefunction: time-independent

In solutions for  $\Psi(r, \theta, \phi)$ , two new quantum numbers appear! A total of 3 quantum numbers are needed to describe a wavefunction in 3D.

1.  $n \equiv$  principal quantum number  
 $n = 1, 2, 3 \dots \infty$   
determines binding energy
2.  $l \equiv$  angular momentum quantum number  
 $l = 0, 1, 2, 3, \dots, n-1$   

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 $l$  is related to  $n$   
largest value of  $l = n - 1$   
determines angular momentum

3.  $m \equiv$  magnetic quantum number

$$m = \frac{-l, \dots, 0, \dots, l}{\begin{array}{l} m \text{ is related to } l \\ \text{largest value is } +l, \text{ smallest is } -l \\ \text{determines behavior of atom in magnetic field} \end{array}}$$

To completely describe an orbital, we need to use all three quantum numbers:

$$\Psi_{nlm}(r, \theta, \phi)$$

The wavefunction describing the ground state is  $\Psi_{100}(r, \theta, \phi)$ .

Using the terminology of chemists, the  $\Psi_{100}$  orbital is instead called the "1s" orbital.

An orbital is (the spatial part) of a wavefunction;  $n$ (shell)  $l$ (subshell)  $m$ (orbital)

$l = 0 \Rightarrow$  s orbital  $l = 1 \Rightarrow$  p orbital  $l = 2 \Rightarrow$  d orbital  $l = 3 \Rightarrow$  f orbital

for  $l = 1$ :  $m = 0$   $p_z$  orbital,  $m = \pm 1$  states combine to give  $p_x$  and  $p_y$  orbitals

	State label	wavefunction	orbital	$E_n$	$E_n[\text{J}]$
$n = 1$ $l = 0$ $m = 0$	100	$\Psi_{100}$	1s	$-R_H/1^2$	$-2.18 \times 10^{-18} \text{J}$
$n = 2$ $l = 0$ $m = 0$	200	200	2s		$-5.45 \times 10^{-19} \text{J}$
$n = 2$ $l = 1$ $m = +1$	211	211	$2B_c$		$-5.45 \times 10^{-19} \text{J}$
$n = 2$ $l = 1$ $m = 0$	210	$\Psi_{210}$	$2P_z$	$-R_H/2^2$	$-5.45 \times 10^{-19} \text{J}$
$n = 2$ $l = 1$ $m = -1$	21-1	$\Psi_{21-1}$	$2P_-$	$-R_H/2^2$	$-5.45 \times 10^{-19} \text{J}$

For a H-atom( ) orbitals with the same  $n$  value have the same energy:  $E = -R_H/n^2$ .

- Degenerate  $\equiv$  having the same energy
- For any principle quantum number,  $n$ , there are  $n^2$  degenerate orbitals in hydrogen (or any other 1 electron atom).

Energy Level Diagram						9 degenerate states at second excited energy level			
E [J]	3s	3p <sub>z</sub>	3p <sub>x</sub>	3p <sub>y</sub>	3d <sub>xy</sub>	3d <sub>yz</sub>			
-0.242 × 10 <sup>-18</sup>	<div>n = 3</div> <div>ℓ = 0</div> <div>m = 0</div>	<div>3</div> <div>ℓ = 1</div> <div>m = ±1</div>	<div>3</div> <div>ℓ = 1</div> <div>m = 0</div>	<div>3</div> <div>ℓ = 1</div> <div>m = ±1</div>	<div>3</div> <div>ℓ = 2</div> <div>±1, ±2</div>	<div>3</div> <div>ℓ = 2</div> <div>±1, ±2</div>	<div>3</div> <div>ℓ = 2</div> <div>m = 0</div>	<div>3</div> <div>ℓ = 2</div> <div>±1, ±2</div>	<div>3</div> <div>ℓ = 2</div> <div>±1, ±2</div>
-0.545 × 10 <sup>-18</sup>	<div>2s</div> <div>n = 2</div> <div>ℓ = 0</div> <div>m = 0</div>	<div>2p<sub>z</sub></div> <div>2</div> <div>ℓ = 1</div> <div>m = ±1</div>	<div>2p<sub>x</sub></div> <div>2</div> <div>ℓ = 1</div> <div>m = 0</div>	<div>2p<sub>y</sub></div> <div>2</div> <div>ℓ = 1</div> <div>m = ±1</div>	4 degenerate states at first excited energy level				
-2.18 × 10 <sup>-18</sup>	<div>1s</div> <div>n = 1</div> <div>ℓ = 0</div> <div>m = 0</div>	1 state at ground energy level 1s state described by ψ <sub>100</sub> or 1s							

## II. SHAPES OF H-ATOM WAVEFUNCTIONS: S ORBITALS

### THE PHYSICAL INTERPRETATION OF A WAVEFUNCTION

Max Born (German physicist, 1882-1970). The probability of finding a particle (the electron!) in a defined region is proportional to the square of the wavefunction.

$$[\Psi_{nlm}(r, \theta, \phi)]^2 = \text{PROBABILITY DENSITY}$$

probability of finding an electron per unit volume at r, θ, φ

To consider the shapes of orbitals, let's first rewrite the wavefunction as the product of a radial wavefunction,  $R_{nl}(r)$ , and an angular wavefunction  $Y_{lm}(\theta, \phi)$

$$\Psi_{nlm}(r, \theta, \phi) = \frac{R_{nl}(r)}{r} \times \frac{Y_{lm}(\theta, \phi)}{r^2}$$

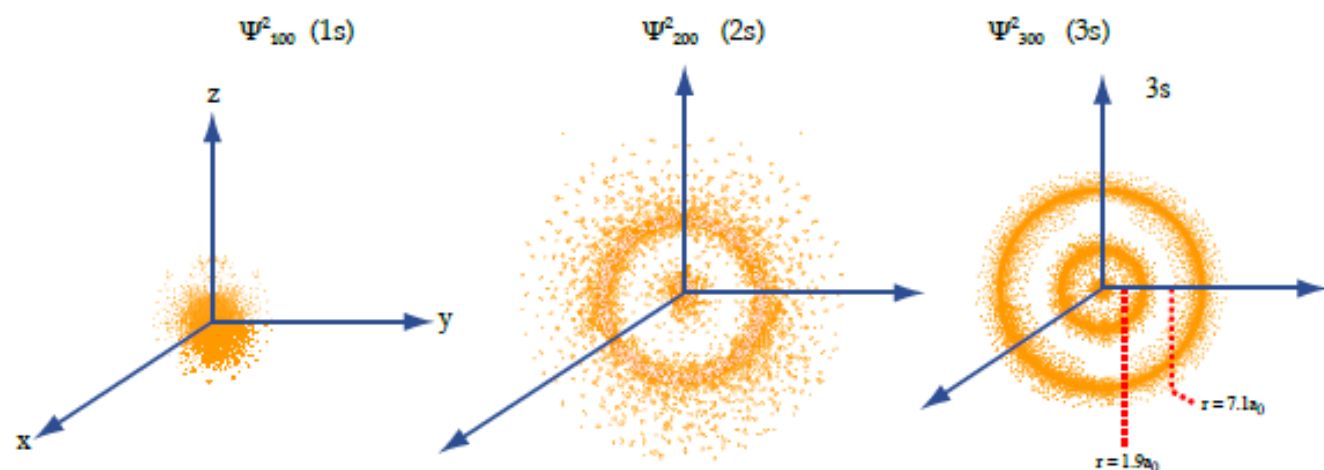
for a ground state H-atom:

$$\Psi_{100}(r, \theta, \phi) = \underbrace{\frac{2e^{-r/a_0}}{a_0^{3/2}}}_{R(r)} \times \underbrace{\left(\frac{1}{4\pi}\right)^{1/2}}_{Y(\theta, \phi)} = \frac{e^{-r/a_0}}{(\pi a_0^3)^{1/2}}$$

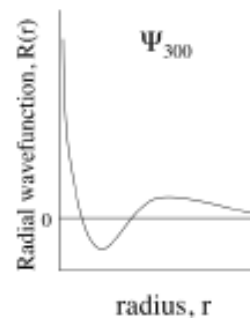
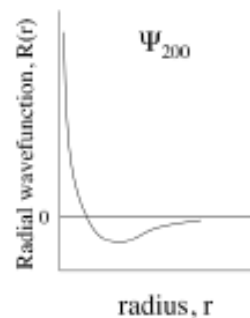
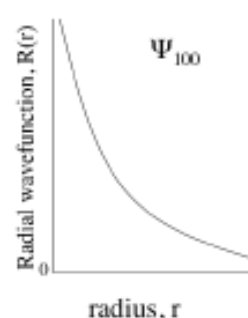
where  $a_0 =$  Bohr radius (a constant) = 52.9 pm ( )

- For all s orbitals (1s, 2s, 3s, etc.), the angular wavefunction, Y, is a constant.
- s-orbitals are spherically symmetrical – independent of \_\_\_\_\_ and \_\_\_\_\_.

Probability density plot of s orbitals: density of dots represent probability density



Figures by MIT OpenCourseWare.



**NODE:** A value for  $r$ ,  $\theta$ , or  $\phi$  for which  $\Psi$  (and  $\Psi^2$ ) = 0. In general, an orbital has  $n-1$  nodes.

**RADIAL NODE:** A value for  $r$  for which  $\Psi$  (and  $\Psi^2$ ) = 0. In other words, a radial node is a distance from the radius for which there is no probability of finding an electron.

In general, an orbital has  $n - 1 - l$  radial nodes.

1s:  $1 - 1 - 0 = 0$  radial nodes

2s:  $\frac{2}{2} - \frac{1}{1} - \frac{0}{0} = 1$  radial nodes

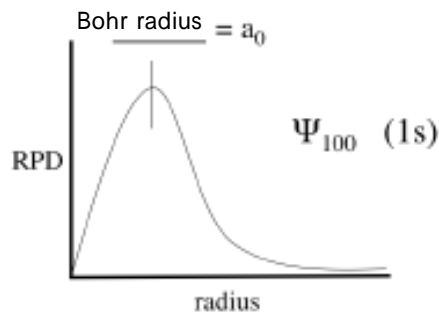
3s:  $\frac{3}{2} - \frac{1}{1} - \frac{0}{0} = 2$  radial nodes

### III. RADIAL PROBABILITY DISTRIBUTION

Probability of finding an electron in a spherical shell of thickness  $dr$  at a distance  $r$  from origin.

Radial Probability Distribution (for s orbitals ONLY) =  $4\pi r^2 \Psi^2 dr$

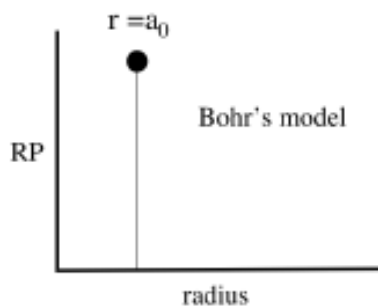
We can plot the radial probability distribution as a function of radius.  
Radial probability distribution for a hydrogen 1s orbital:



Maximum probability or most probable value of  $r$  is denoted  $r_{mp}$ .

$$r_{mp} \text{ for a 1s H atom} = a_0 = 0.529 \times 10^{-10} \text{ m} = 0.529 \text{ \AA} \quad a_0 \equiv \text{BOHR radius}$$

1913 Niels Bohr (Danish scientist) predicted quantized levels for H atom prior to

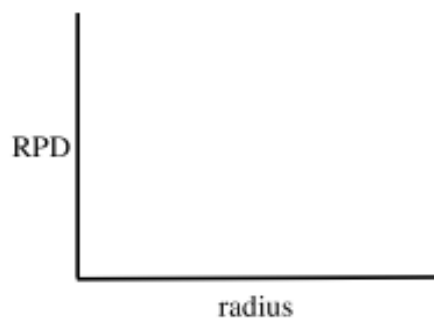


QM development, with the electron in well-defined circular orbits.

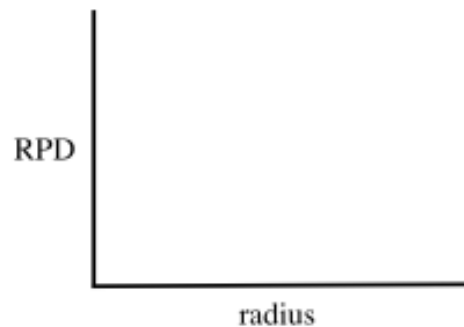
This was still a purely particle picture of the  $e^-$ .

But, an electron does not have well-defined orbits! The best we can do is to find the probability of finding  $e^-$  at some position  $r$ .

Knowing only probability is one of main consequences of Quantum Mechanics. Unlike CM, QM is non-deterministic. The uncertainty principle forbids us from knowing  $r$  exactly.



$\Psi_{200}$  (2s)



$\Psi_{300}$  (3s)