5.111 Principles of Chemical Science
Fall 2008

5.111 Lecture Summary #6

Readings for today: Section 1.9 (1.8 in 3rd *ed*) – Atomic Orbitals.
Read for Lecture #7: Section 1.10 (1.9 in 3rd *ed*) – Electron Spin, Section 1.11 (1.10 in 3rd *ed*) – The Electronic Structure of Hydrogen.

Topics: **Hydrogen Atom Wavefunctions**
I. Wavefunctions (orbitals) for the hydrogen atom ($H\underline{\Psi} = E\underline{\Psi}$)
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 λ, using $E = h\nu$ or $\lambda = c/\nu$) of light emitted or absorbed by any 1-electron atom or ion.

$$\nu = \frac{Z^2 R_H}{h}\left(\frac{1}{n_f^2} - \frac{1}{n_i^2}\right) \qquad \nu = \frac{Z^2 R_H}{h}\left(\frac{1}{n_i^2} - \frac{1}{n_f^2}\right)$$

for $n_i > n_f$ 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_n 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
   $n = 1, 2, 3 \ldots \ldots \infty$
   determines binding energy

2. $l \equiv$ angular momentum quantum number

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

3. m ≡ magnetic quantum number

m = ______________________________________

m is related to *l*
largest value is +*l*, smallest is –*l*
determines behavior of atom in magnetic field

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 ________________ .
Using the terminology of chemists, the Ψ_{100} orbital is instead called the "___" orbital.

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

ℓ = 0 ⇒ ___ orbital **ℓ = 1** ⇒ ___ orbital **ℓ = 2** ⇒ ___ orbital **ℓ = 3** ⇒ ___ orbital

for ℓ = 1: m = 0 _____ orbital, m = ±1 states combine to give ____ and ____ orbitals

	State label	wavefunction	orbital	E_n	E_n[J]
n = 1 ℓ = 0 m = 0		ψ_{100}		$-R_H/1^2$	-2.18×10^{-18}J
n = 2 ℓ = 0 m = 0					-5.45×10^{-19}J
n = 2 ℓ = 1 m = +1					-5.45×10^{-19}J
n = 2 ℓ = 1 m = 0	210	ψ_{210}		$-R_H/2^2$	-5.45×10^{-19}J
n = 2 ℓ = 1 m = -1	21-1	ψ_{21-1}		$-R_H/2^2$	-5.45×10^{-19}J

For a ____________, orbitals with the same n value have the same energy: $E = -R_H/n^2$.

- **Degenerate** ≡ having the same energy
- For any principle quantum number, n, there are _______ degenerate orbitals in hydrogen (or any other 1 electron atom).

Energy Level Diagram

9 degenerate states at second excited energy level

E [J]									
-0.242×10^{-18}	$n = 3$ $\ell = 0$ $m = 0$	3 $\ell = 1$ $m=\pm1$	3 $\ell = 1$ $m=0$	3 $\ell = 1$ $m=\pm1$	3 $\ell = 2$ $\pm1, \pm2$	3 $\ell = 2$ $\pm1, \pm2$	3 $\ell = 2$ $m = 0$	3 $\ell = 2$ $\pm1, \pm2$	3 $\ell = 2$ $\pm1, \pm2$
-0.545×10^{-18}	$n = 2$ $\ell = 0$ $m = 0$	2 $\ell = 1$ $m=\pm1$	2 $\ell = 1$ $m=0$	2 $\ell = 1$ $m=\pm1$					
-2.18×10^{-18}	$n = 1$ $\ell = 0$ $m = 0$								

4 degenerate states at first excited energy level

1 state at ground energy level
1s state described by ψ_{100} 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.

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

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 $Y_{lm}(\theta,\phi)$

$$\Psi_{nlm}(r,\theta,\phi)] = \underline{\hspace{3em}} \times \underline{\hspace{3em}}$$

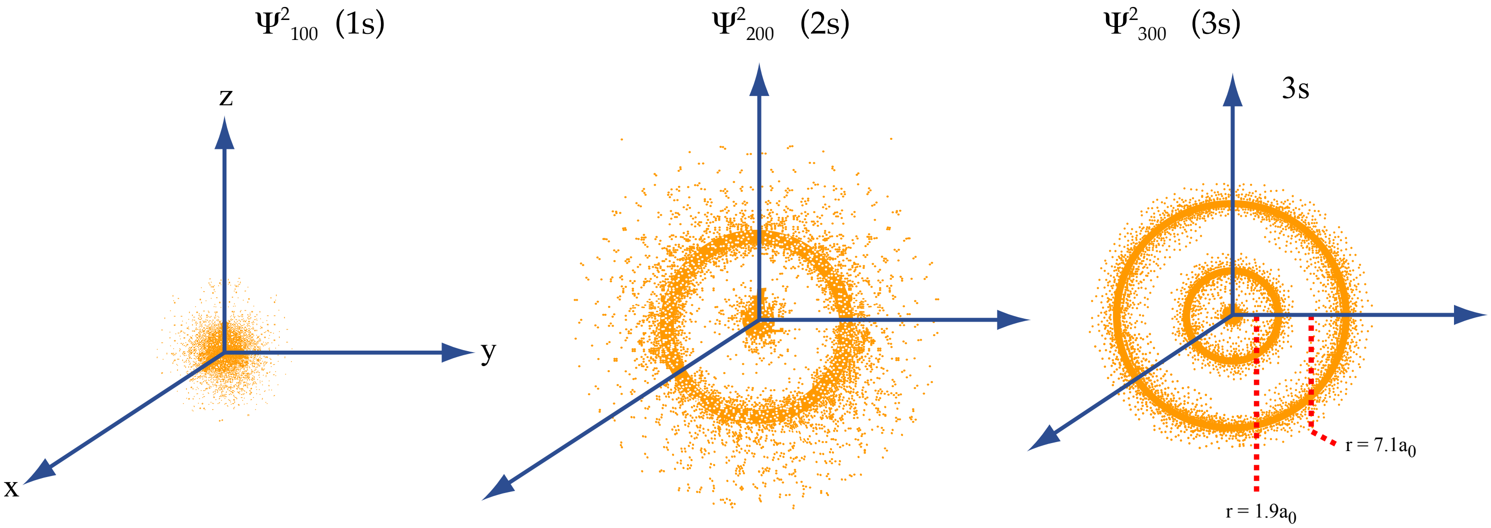
for a ground state H-atom:

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

where a_0 = ______________________________ (a constant) = 52.9 pm

- For all s orbitals (1s, 2s, 3s, etc.), the angular wavefunction, Y, is a ______________.
- s-orbitals are **spherically symmetrical** – independent of _____ and_____.

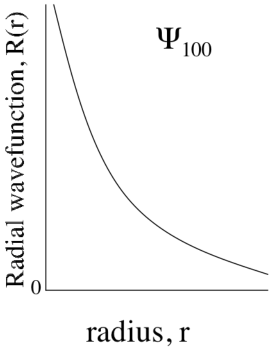
Probability density plot of s orbitals: density of dots represent probability density

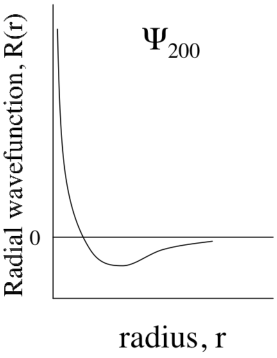

Ψ^2_{100} (1s)

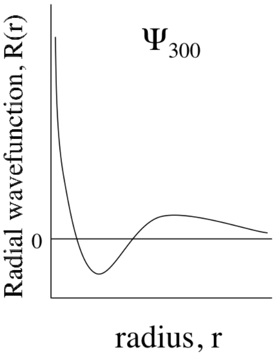
Ψ^2_{200} (2s)

Ψ^2_{300} (3s)

Figures by MIT OpenCourseWare.







NODE: A value for r, θ, or ϕ for which Ψ (and Ψ^2) = ______. In general, an orbital has n -1 nodes.

RADIAL NODE: A value for ______ for which Ψ (and Ψ^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: ____ – ____ – ____ = ____ radial nodes

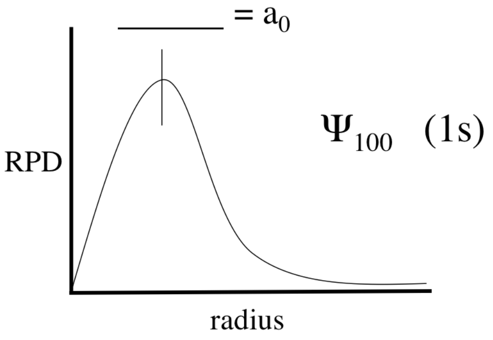
3s: ____ – ____ – ____ = ____ radial nodes

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:

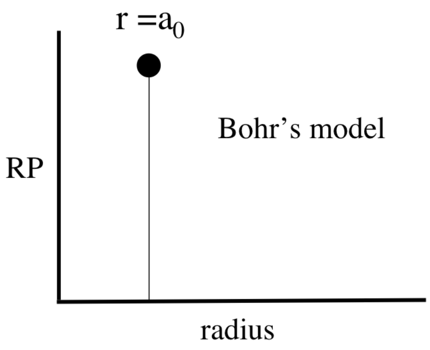


Maximum probability or most probable value of r is denoted r_{mp}.

r_{mp} for a 1s H atom = a_0 = 0.529×10^{-10} m = 0.529Å $a_0 \equiv$ 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.