5.111 Lecture Summary #6   Monday, September 15, 2014

Readings for today: Section 1.9 – Atomic Orbitals. Section 1.10 – Electron Spin, Section 1.11 – The Electronic Structure of Hydrogen. (Same sections in *4th ed*.)
Read for Lecture #7: Section 1.12 – Orbital Energies (of many-electron atoms), Section 1.13 – The Building-Up Principle. (Same sections in 4th and 5th ed.)

Topics: **I.** Wavefunctions (Orbitals) for the Hydrogen Atom
                II. Shape and Size of S and P Orbitals
                III. Electron Spin and the Pauli Exclusion Principle

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I. WAVEFUNCTIONS (ORBITALS) FOR THE HYDROGEN ATOM
Solving the Schrödinger Equation provides values for E_n and $\Psi(r,\theta,\phi)$.

A total of 3 quantum numbers are needed to describe a wavefunction in 3D.

1.   n ≡ principal quantum number
       n = _____
       determines binding energy (energy level or shell)

2. l ≡ angular momentum quantum number
       l = _____
       l is related to n, determines angular momentum, describes subshell, shape of orbital
            largest value of l = n − 1

3.   m ≡ magnetic quantum number
       m = _____
       m is related to l, determines behavior in magnetic field, describes the specific orbital

To 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.
       n   designates the **shell** or **energy** level   (1,2,3…)
       l designates the **subshell** (**shape** of orbital)   (s, p, d, f…)
       m   designates **orbital orientation** (**specific** orbital)   (p_x, p_y, p_z…)

$\ell = 0 \Rightarrow$ ___ orbital $\ell = 1 \Rightarrow$ ___ orbital $\ell = 2 \Rightarrow$ ___ orbital $\ell = 3 \Rightarrow$ ___ orbital

for $\ell = 1$:   m = 0 is $\mathbf{p_z}$ orbital,   m = ±1 are the $\mathbf{p_x}$ and $\mathbf{p_y}$ orbitals

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	State label	wavefunction	orbital	H atom E_n	H atom E_n[J]
n = 1 $\ell = 0$ m = 0		ψ_{100}			-2.18×10^{-18}J
n = 2 $\ell = 0$ m = 0		ψ_{200}			-5.45×10^{-19}J
n = 2 $\ell = 1$ m = +1		ψ_{211}			-5.45×10^{-19}J
n = 2 $\ell = 1$ m = 0	210	ψ_{210}		$-R_H/2^2$	-5.45×10^{-19}J
n = 2 $\ell = 1$ m = -1	21-1	$\psi_{21\text{-}1}$		$-R_H/2^2$	-5.45×10^{-19}J

What is the corresponding orbital for a 5,1,0 state?

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


_____ ≡ having the same energy

For any principle quantum number, n, there are _____ degenerate orbitals in hydrogen (or any other 1 electron atom).
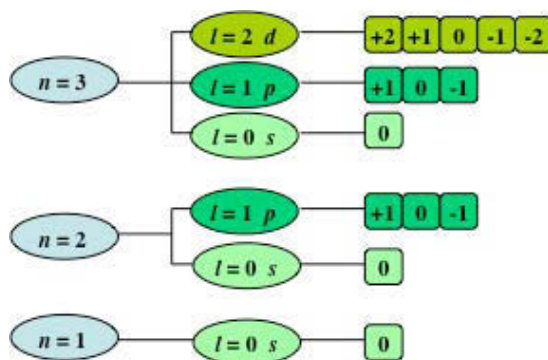
IN THEIR OWN WORDS

MIT graduate student Benjamin Ofori-Okai discusses how energy levels relate to research in nanoscale MRI (magnetic resonance imaging), a technique that allows 3-D imaging of biological molecules, such as proteins, and viruses.
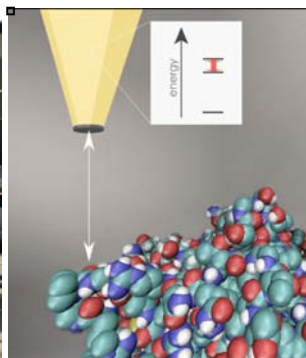
THE PHYSICAL INTERPRETATION OF A WAVEFUNCTION

The probability of finding a particle (the electron!) in a defined region is proportional to the square of the wavefunction.

$$[\Psi_{nlm}(r,\theta,\phi)]^2 = \text{PROBABLITY DENSITY} = \underline{\hspace{3cm}}$$

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

IIA. SHAPE OF S ORBITAL

To consider the shapes of orbitals, we can rewrite the wavefunction Ψ_{nlm} as the product of a radial wavefunction, $R_{nl}(r)$, and an angular wavefunction $Y_{lm}(\theta,\phi)$

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

radial x angular wavefunctions

(a) radial wave functions			(b) angular wave functions		
n	l	$R_{nl}(r)$	l	m_l	$Y_{l,ml}(\theta, \phi)$
1	0	$2\left(\dfrac{Z}{a_0}\right)^{\frac{3}{2}} e^{-Zr/a_0}$	0	0	$\left(\dfrac{1}{4\pi}\right)^{1/2}$
2	0	$\dfrac{1}{2\sqrt{2}}\left(\dfrac{Z}{a_0}\right)^{\frac{3}{2}}\left(2-\dfrac{Zr}{a_0}\right)e^{-\frac{Zr}{2a_0}}$	1	x	$\left(\dfrac{3}{4\pi}\right)^{1/2}\sin\theta\cos\phi$
	1	$\dfrac{1}{2\sqrt{6}}\left(\dfrac{Z}{a_0}\right)^{\frac{3}{2}}\left(\dfrac{Zr}{a_0}\right)e^{-\frac{Zr}{2a_0}}$		y	$\left(\dfrac{3}{4\pi}\right)^{1/2}\sin\theta\sin\phi$
3	0	$\dfrac{2}{9\sqrt{3}}\left(\dfrac{Z}{a_0}\right)^{\frac{3}{2}}\left(3-\dfrac{2Zr}{a_0}-2\dfrac{Z^2r^2}{9a_0^2}\right)e^{-\frac{Zr}{3a_0}}$		z	$\left(\dfrac{3}{4\pi}\right)^{1/2}\cos\theta$

where $a_0 = \underline{\hspace{5cm}}$ (a constant) = 52.9 pm

for a ground state H-atom:

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

$$\underbrace{\qquad}_{R(r)} \quad \underbrace{\qquad}_{Y(\theta,\phi)}$$

For all s orbitals (1s, 2s, 3s, etc.), the angular wavefunction, Y, is a $\underline{\hspace{3cm}}$.

s orbitals are **spherically symmetrical** – independent of $\underline{\hspace{1.5cm}}$ and $\underline{\hspace{1.5cm}}$.

There are three common plots used to help us visualize an s orbital: (1) Probability density Ψ^2 plot of s orbitals in which density of dots represents probability density; (2) Wavefunction plotted again r (distance from nucleus); (3) Radial probability distribution as a function of radius.

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RADIAL PROBABILITY DISTRIBUTION (RPD) reports on the probability of finding an electron in a spherical shell of thickness dr at a distance r from origin. Maximum probability or most probable value of r is denoted _____ .
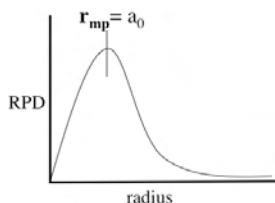
r_{mp} for a 1s H atom = a_0 = 52.9 pm = 0.529 x 10^{-10} m = 0.529Å
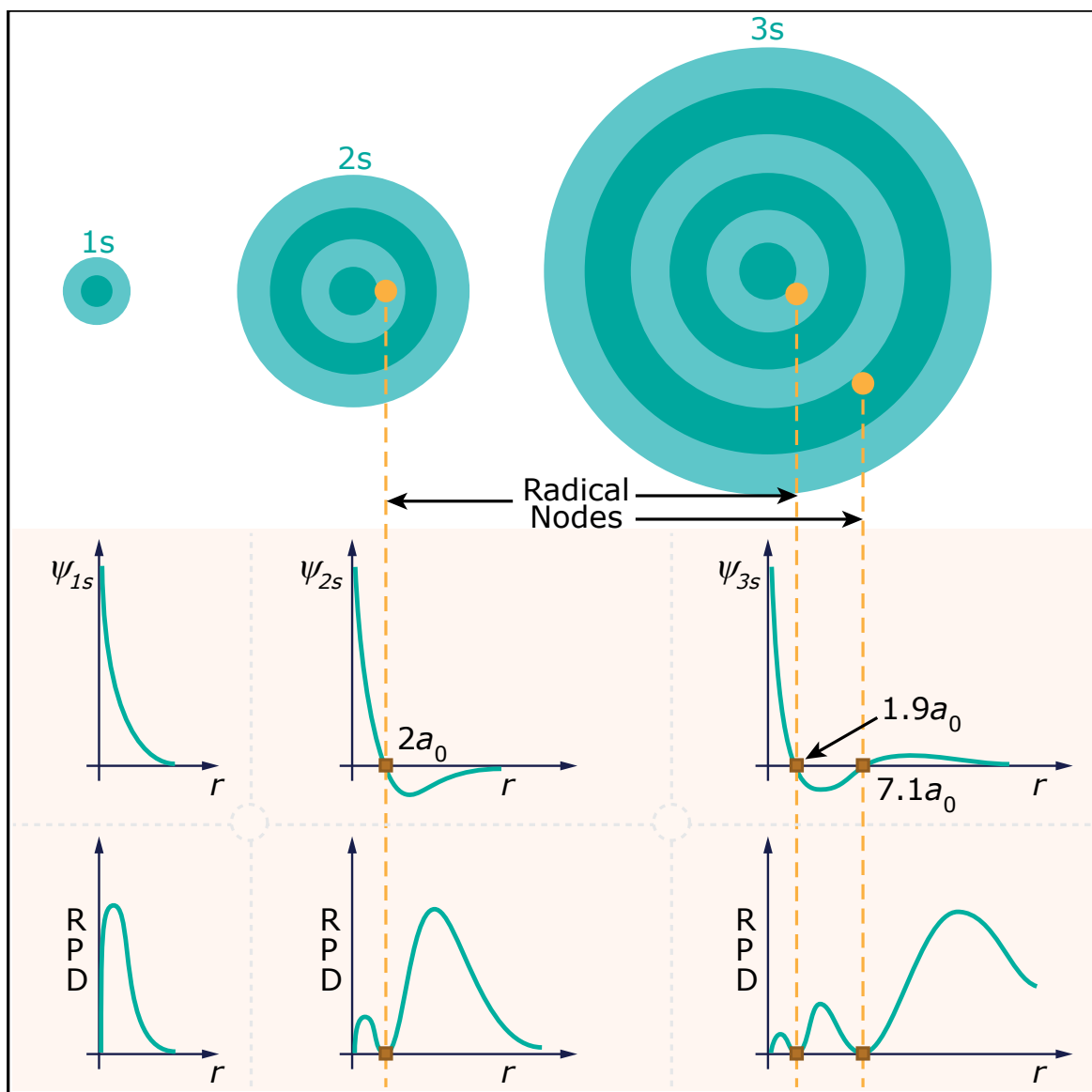
a_0 ≡ Bohr radius

Image by MIT OpenCourseWare.
Adapted from Oxtoby, D., et al. Principles of Modern Chemistry, fifth edition.
Thomson Brooks/Cole, 2002. ISBN: 9780030353734.

NODE: A value for r, θ, or φ for which Ψ (and Ψ^2) = _____ .

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.

To calculate the number of radical nodes $n - 1 - l$

Ψ^2_{100} Ψ^2_{200} Ψ^2_{300}

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

2s: _____ radial nodes
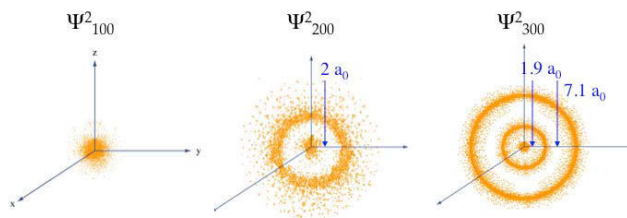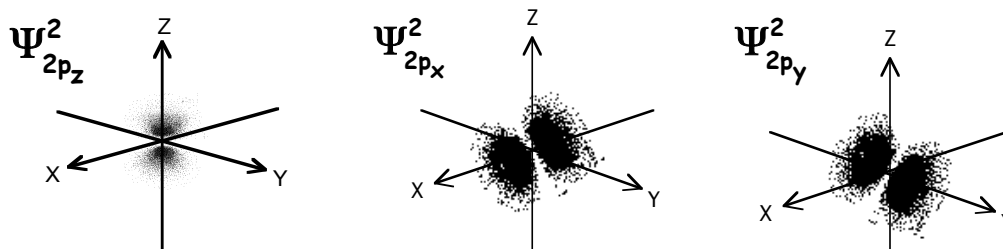
3s: _____ radial nodes

4p: _____ radial nodes

Figure by MIT OpenCourseWare.

IIB. THE SHAPE OF P ORBITALS

- Unlike s orbitals, p orbitals have θ, ϕ dependence.
- P orbitals _____ spherically symmetrical.
- P orbitals consist of two lobes (of opposite sign) separated by a _____ plane on which $\Psi = 0$ (and $\Psi^2 = 0$).
- There is zero probability of finding a p-electron in a nodal plane. Thus, there is _____ probability of finding a p-electron at the nucleus.

Probability density maps of p orbitals:

$\Psi^2_{2p_z}$ $\Psi^2_{2p_x}$ $\Psi^2_{2p_y}$

Nodal planes: xy   yz   xz

Nodal planes (planes that have no electron density) arise from angular nodes in the wavefunction.

ANGULAR NODE: A value for _____ at which Ψ (and Ψ^2) = 0.

In general, an orbital has: $n - 1$ total nodes

                              _____ angular nodes

                              _____ radial nodes

2s: _____ total nodes, _____ angular nodes, _____ radial nodes

2p: _____ total nodes, _____ angular nodes, _____ radial nodes

3d: _____ total nodes, _____ angular nodes, _____ radial nodes

IIC. ORBITAL SIZE

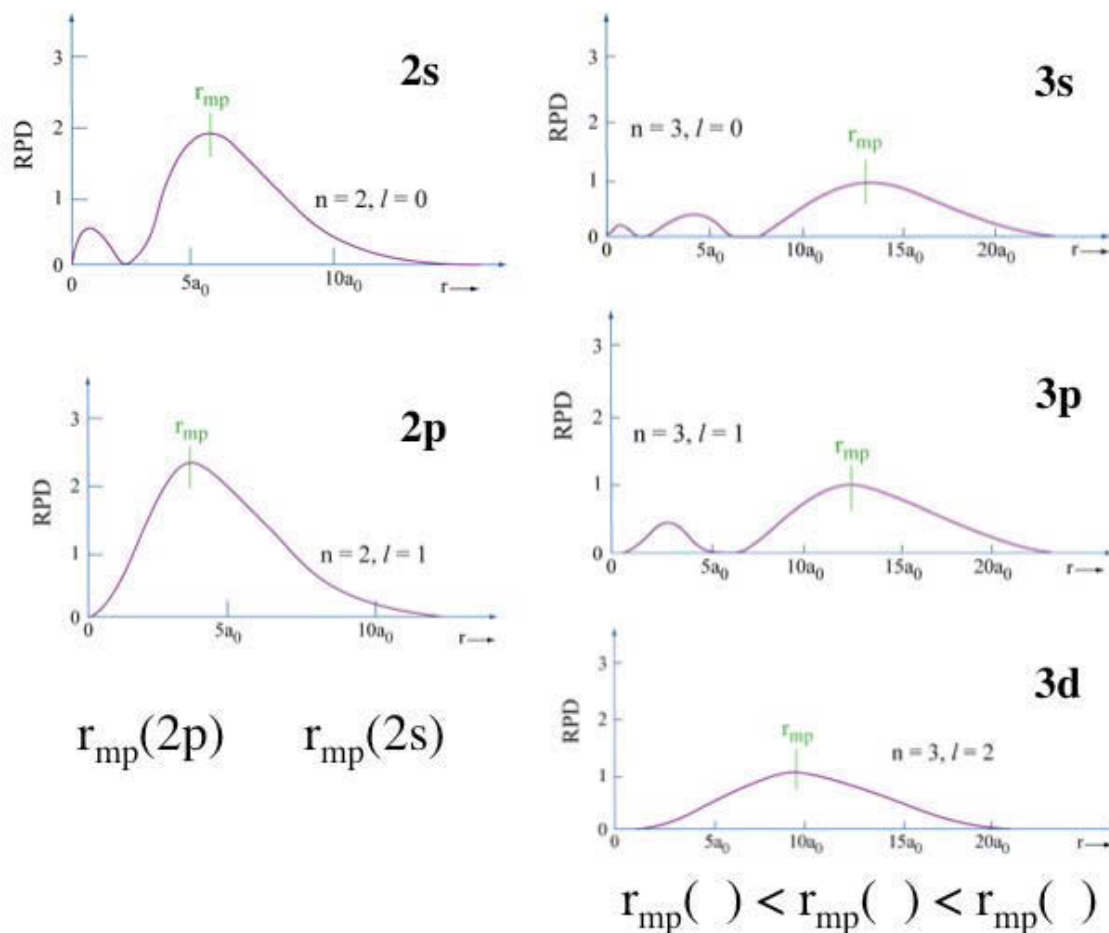$$r_{mp}(\ ) < r_{mp}(\ ) < r_{mp}(\ )$$

Figure by MIT OpenCourseWare.

As n increases (from 1 to 2 to 3), the orbital r_{mp} "size" _____ .

As l increases (from s to p to d) for a given n, the orbital r_{mp} "size" _____ .

Only electrons in s states have a substantial probability of being very close to nucleus. This means that although the "size" (also called the boundry surface) of s orbitals is larger than p or d orbitals, s-electrons are the _____ shielded.

III. ELECTRON SPIN: THE FOURTH QUANTUM NUMBER

A fourth quantum number describes the spin of an electron within an orbital: the spin

magnetic quantum number, _____

There is no classical analogy to spin.
- An electron can have two spin states:

$$m_s = \text{_____ (spin up)} \quad or \quad m_s = \text{_____ (spin down).}$$

- m_s completes the description of an _____ and is NOT dependent on the orbital.

So we can describe a given orbital using three quantum numbers (n, l, m_l) and a given electron using 4 quantum numbers (n, l, m_l, m_s).

$$\Psi_{nlm_l} \qquad\qquad\qquad \Psi_{nlm_lm_s}$$

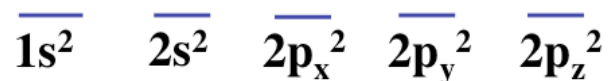describes an _____   describes an _____

PAULI EXCLUSION PRINCIPLE

No two electrons can be in the same orbital and have the same spin.

No two electrons in the same atom can have the same _____ quantum numbers.

Ne

$$\overline{\underline{}}\quad \overline{\underline{}}\quad \overline{\underline{}}\quad \overline{\underline{}}\quad \overline{\underline{}}$$

1s²   2s²   2p$_x$²   2p$_y$²   2p$_z$²

Within each orbital, electrons are paired (one spin up and one spin down).

One orbital can hold no more than two electrons.

5.111 Principles of Chemical Science
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