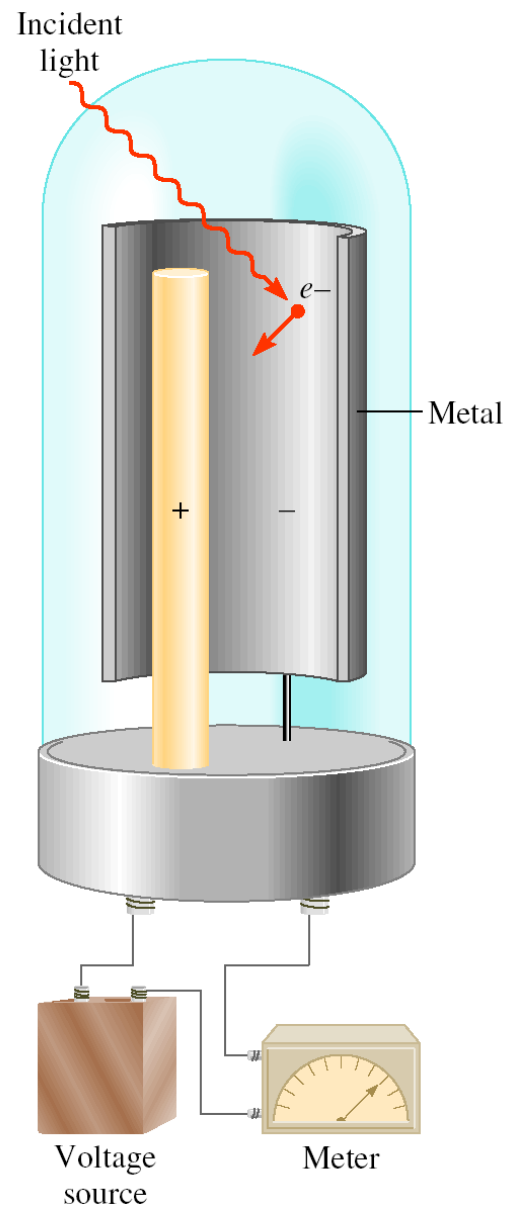
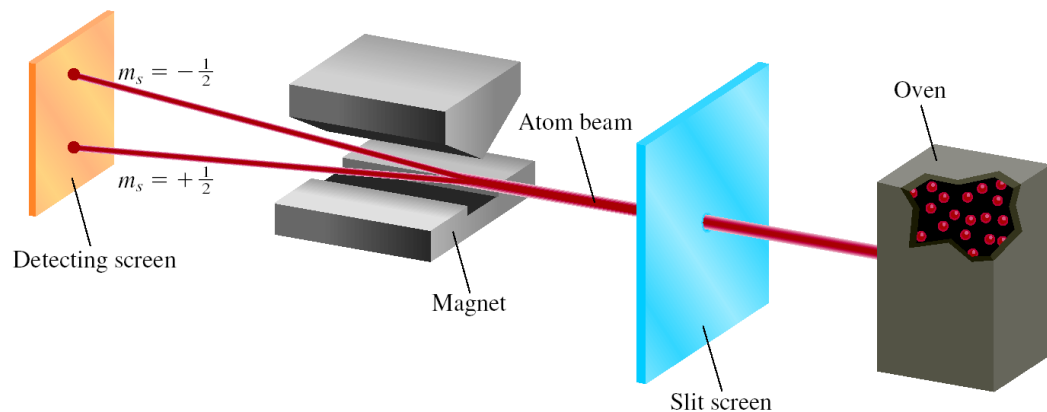


*Please pick up  
either a slide or pair  
of glasses from the back  
of lecture hall!*

# Electronic Structure of Atoms

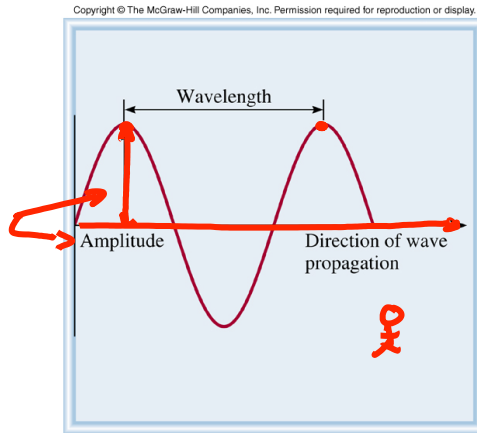
## Chapter 7

### Chemistry E-1a



## Understanding Waves: What are they, What can they do?

- We just finished talking about energy and its transformations. Waves are disturbances that can transmit energy. Let's define some terms which we use to describe waves.



(a)

Wavelength: distance between two crests

$$\lambda = [\text{m}] \text{ meters}$$

$$1 \text{ nm} = 1 \times 10^{-9} \text{ m} \quad (1 \text{ nanometer})$$

frequency  $[\text{s}^{-2}] = \text{waves/time}$

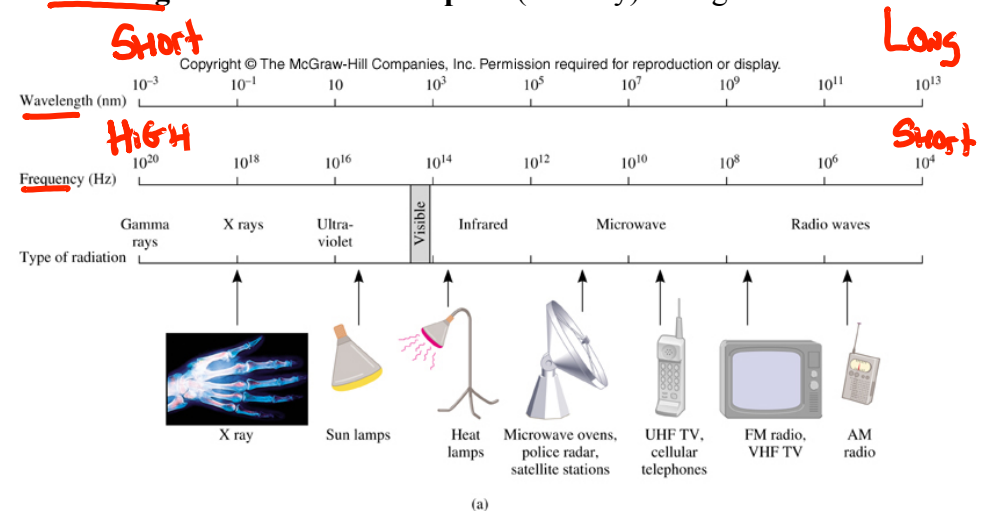
$$\nu \leftarrow \text{"nu"}$$

- What is the relationship between the frequency of a wave, the wavelength of a wave and its speed (velocity) for light waves?

$$\lambda \nu = c$$

Speed of Light  $3 \times 10^8 \text{ m/s}$

$$\lambda = \frac{c}{\nu}$$



(a)



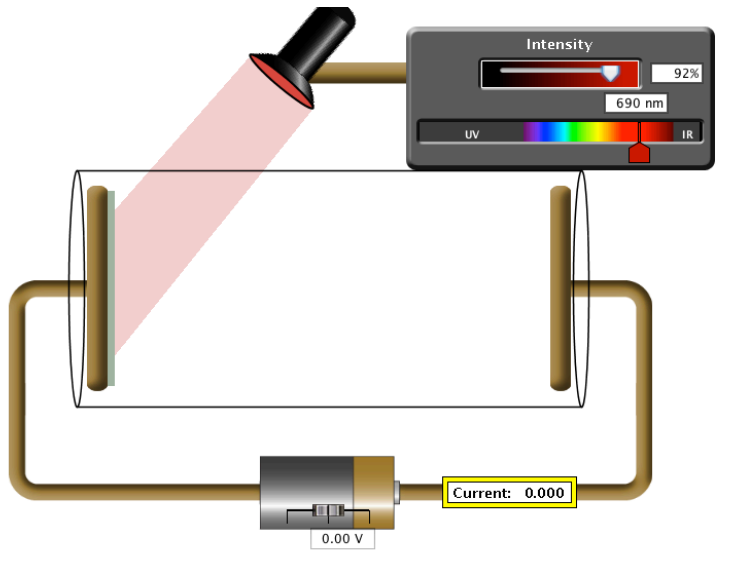
(b)

# Light is a Form of Energy That Can be Used to Remove Electrons From a Metal Surface

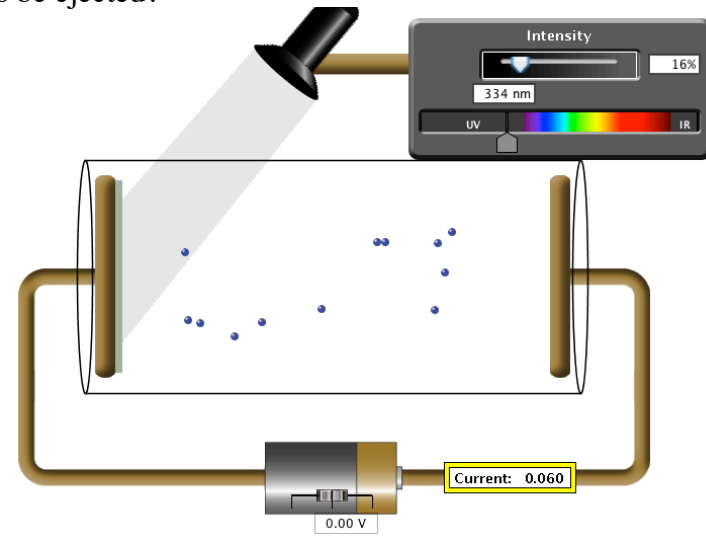
- **Photoelectric Effect:** When light lands on the surface of a metal electrons are ejected from the metal. Lets look at a simulation of photoelectric experiments where we shine light of different wavelengths on a metal surface to see if electrons are emitted.

- In this simulation, electrons ejected from the metal surface are represented as small blue spheres.

a) If we shine visible light on a metal surface, will electrons be ejected?



b) If we shine ultraviolet light on a metal surface, will electrons be ejected?



• **Conclusion:** Light composed of particles called photons

Energy of single photon  $\rightarrow E = h\nu$

$\nwarrow$   $\nwarrow$   $\nwarrow$

Frequency of Light  
Planck's constant  $6.626 \times 10^{-34} \text{ J}\cdot\text{s}$

## Light, Electrons, Waves or Particles

- Light has both wave and particle properties. The wave properties are **wavelength** [ $\lambda$ ] and **frequency** [ $\nu$ ]. When you multiply the wavelength and frequency of light together you get the speed of light ( $c$ ) which is a constant.

$$\boxed{\lambda = \frac{c}{\nu}} \text{ Light}$$

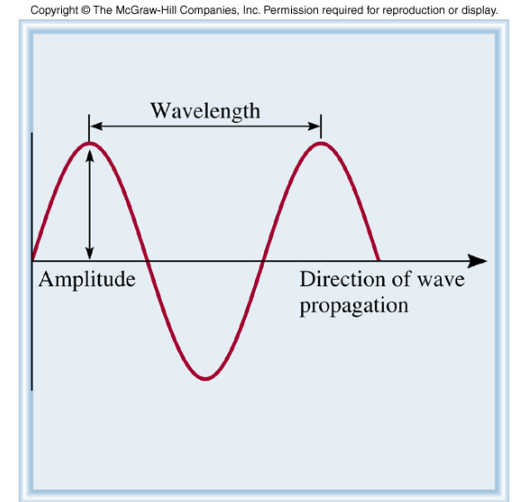
$$\lambda \nu = c \quad (\text{speed of light is } 3 \times 10^8 \text{ m/s})$$

- But Louis deBroglie suggested that, just as light (which is a wave) exhibits particle-like behavior, perhaps matter such as electrons could behave like waves. He suggested that the wavelength of matter should be related to its momentum,  $mu$ .

$$\lambda = \frac{h}{mu}$$

$h$  ← Planck's constant  $6.626 \times 10^{-34} \text{ J}\cdot\text{s}$   
 $u$  ← speed of particle  
 $m$  ← mass of particle ( $k_g$ )

Wavelength of a particle of matter.



(a)

$$J = kg \frac{m^2}{s^2}$$

$$m_e = 9.11 \times 10^{-31} k_g$$

$k_{\text{electron}}$

- Lets collect all of our equations that deal with the energy and wavelength of light and the energy and wavelength of matter (like electrons)

	Light	Matter
Energy	$E = h\nu$	$KE = \frac{1}{2} m u^2$
Wavelength	$\lambda = c/\nu$	$\lambda = \frac{h}{mu}$

## The Photoelectric Effect: Conservation of Energy

- How can we explain the photoelectric effect in terms of conservation of energy. The energy of the incoming photons of light striking the surface of the metal. Any energy left over goes into

$$E_{\text{photon}} = E_{\text{binding}} + KE_{\text{ejected electron}}$$

$$E_p = E_b + \frac{1}{2} m u^2$$

$$h\nu = h\nu_0 + \frac{1}{2} m u^2$$

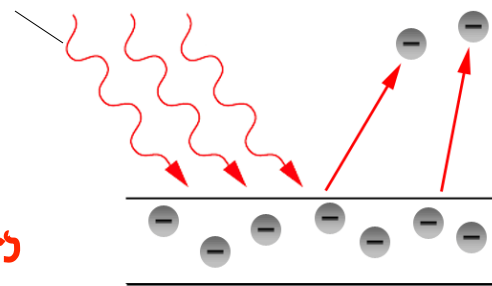
$\nu_0$  = threshold frequency

$$\boxed{h \frac{c}{\lambda} = h\nu} = \phi + \frac{1}{2} m u^2$$

Work function is the binding energy

$$\nu = c/\lambda$$

These 'squiggly' lines represent incoming photons of light striking the surface of the metal:



ejected electrons  
photoelectrons

These electrons are still bound to the metal surface. The energy to required to remove these electrons is called the **binding energy** or **threshold frequency**.

Metal	Binding Energy
Al	$6.53 \times 10^{-19} \text{ J}$
Cs	$3.04 \times 10^{-19} \text{ J}$
Cu	$8.01 \times 10^{-19} \text{ J}$
Pb	$7.21 \times 10^{-19} \text{ J}$

- The minimum frequency of light (threshold frequency) which can cause the photoelectric effect in cesium is  $4.6 \times 10^{14} \text{ s}^{-1}$ . If light with a wavelength of  $4.40 \times 10^{-7} \text{ m}$  strikes a cesium surface, calculate the minimum deBroglie wavelength of the emitted photoelectrons. A **photoelectron** is an electron discharged from an atom or metal by a photon of light.

$$\lambda = \frac{h}{m_e v_e}$$

## The Photoelectric Effect: Conservation of Energy (cont)

• (This is the same question from the previous page.) The minimum frequency of light (threshold frequency) which can cause the photoelectric effect in cesium is  $4.6 \times 10^{14} \text{ s}^{-1}$ . If light with a wavelength of  $4.40 \times 10^{-7} \text{ m}$  strikes a cesium surface, calculate the minimum deBroglie wavelength of the emitted photoelectrons. A photoelectron is an electron discharged from an atom or metal a photon of light.  $m_e = 9.11 \times 10^{-31} \text{ kg}$

a) Calculate the energy of light with threshold frequency of cesium:.

$$E = h\nu = (6.626 \times 10^{-34} \text{ J} \cdot \text{s}) (4.6 \times 10^{14} \text{ s}^{-1})$$

$$E_b = 3.048 \times 10^{-19} \text{ J}$$

b) Calculate the energy of the incoming light that strikes the surface of the cesium:

$$E = h\nu = h \cdot \frac{c}{\lambda} = (6.626 \times 10^{-34} \text{ J} \cdot \text{s}) \left( \frac{3 \times 10^8 \text{ m/s}}{4.40 \times 10^{-7} \text{ m}} \right)$$

$$E_p = 4.518 \times 10^{-19} \text{ J}$$

c) Does the incoming photon have enough energy to liberate the electron from the metal surface? If it does, will there be any energy left over? Where does the energy go?

yes yes KE ejected electron

d) Determine the DeBroglie wavelength of the ejected photoelectron.

$$\lambda_e = \frac{h}{m_e v_e}$$

$\lambda$        $v$  speed

$$E_p = E_b + \frac{1}{2} m v^2$$

$$4.518 \times 10^{-19} \text{ J} = 3.048 \times 10^{-19} \text{ J} + \frac{1}{2} (9.11 \times 10^{-31} \text{ kg}) (v_e^2)$$

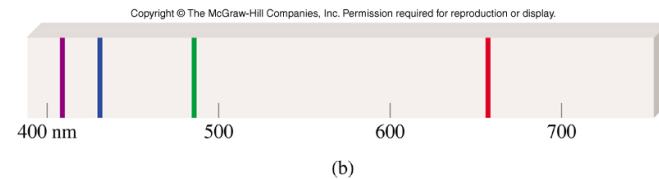
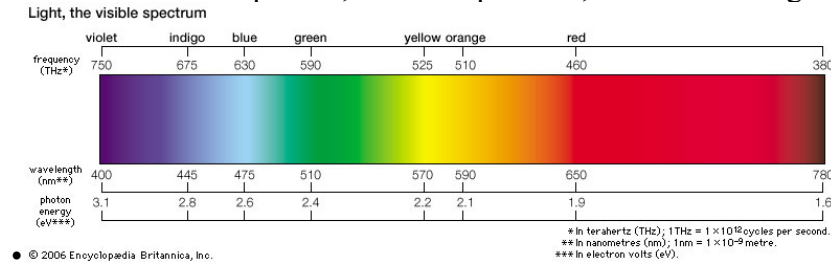
$$5.55 \times 10^{-5} \frac{\text{m}}{\text{s}} = v_e \leftarrow \text{Speed of ejected electron}$$

$$\lambda_e = \frac{(6.626 \times 10^{-34} \text{ J} \cdot \text{s})}{(9.11 \times 10^{-31} \text{ kg}) (5.55 \times 10^{-5} \text{ m/s})}$$

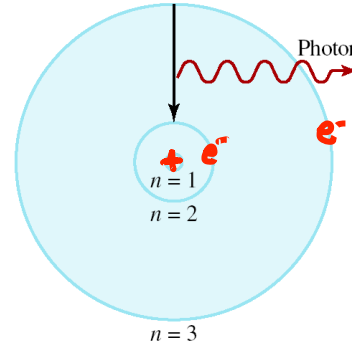
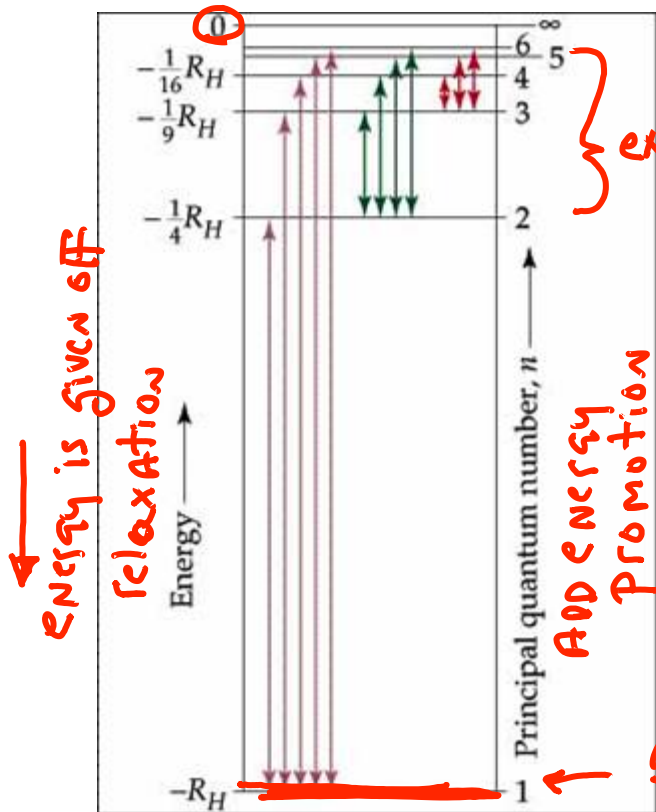
$$\lambda_e = 1.31 \times 10^{-9} \text{ m}$$

# The Hydrogen Atom: Niels Bohr

- We have two different sources of light in the front of the classroom: one will look white, the other pinkish. Let's look at each source through a diffraction grating. Diffraction gratings separate the light into the different wavelengths of light that make up the source. Below we have a picture, called a spectrum, of what each light 'looks like' through a diffraction grating.



- What do the lines from the Hydrogen spectrum (above right) tell us about the locations of electrons in a hydrogen atom.



$n \uparrow, E \uparrow$

$$E_n = -R_H \left( \frac{1}{n^2} \right)$$

$n = \infty$   
Ionization

$n$  = principal quantum number

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

For the equation above:  $R_H$  is the Rydberg constant ( $2.18 \times 10^{-18}$  J),  $n$  is the principal quantum number and can be any integer from 1 up to infinity

The equation below is for **transitions** (movement) of an electron between two different quantum numbers.

Note:  $n_i$  is the initial location of the electron,  $n_f$  is the final location of the electron.  $\Delta E$  is the **change in energy** from the movement of the electron from one energy level to another. Energy can be given off or absorbed in the form of light energy  $h\nu$ :

ground state  $\Delta E < 0$  given off  
 $\Delta E > 0$  absorbed

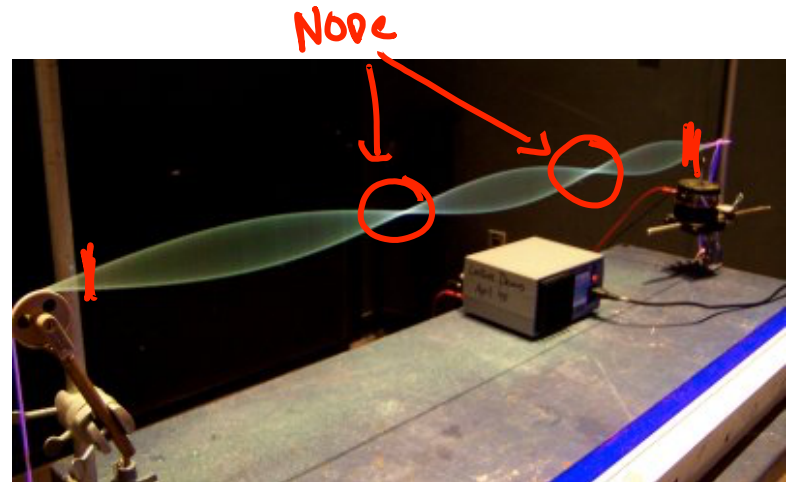
$$\Delta E = h\nu = R_H \left( \frac{1}{n_i^2} - \frac{1}{n_f^2} \right)$$

## Wave Mechanics and “Quantization”

- The Bohr model of an electron in an atom that treated the electron like a particle. This model of the atom said that the electron's location and energy were quantized. **Quantization** means that the electron in the atom can only have **certain energies**. Contrast this with a bike that can have any speed and hence any kinetic energy depending on how fast you can pedal.
- **DeBroglie discovered the wave properties of electrons** in atoms, let's try to understand the wave properties of electrons in atoms by understanding the properties of waves. We are going to postulate that the electrons in atoms have some of the same properties of standing waves. Why can we do this? Well, the ends of a standing wave are tethered between two fixed points. Electrons are ‘tethered’ to the atom because of the attractive forces from the protons in the nucleus.

- Standing waves are confined to a limited region in space and they can adopt only **certain stable frequencies**. This is a property of all standing waves and it tells us that the **frequency of standing waves is quantized**. Is this also a property of an electron in an atom?

- Look at the picture on the right where a standing wave is being produced by a vibrating string. The places where there is no displacement of the string we call **a nodes**. **Node = no wave**



- a) How many nodes do you see in this wave? Can an electron in an atom have a node?

↳ ges → 2

- a) Look at the demonstration of these standing waves. What is the relationship between frequency and the number of nodes present in the wave?

↳ ↑ $\nu$ , ↑Nodes

- c) Recall our discussion of light, what is the equation that can be used to determine the energy of light? What is the relationship between energy and frequency?

↳  $E = h\nu$

- d) What is the relationship between the number of nodes and energy of the wave?

↑ $E$ , ↑Nodes



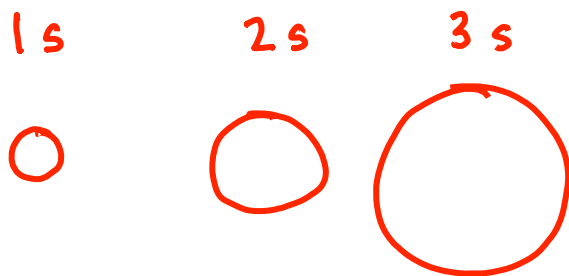
# Orbitals and Quantum Numbers

- Erwin Schrodinger realized that an electron confined to an atom might behave like a wave confined to a string. He was able to derive the wavefunction  $\psi$ , that describes the behavior of an electron in an atom. Each possible solution of his wave equation corresponds to a standing wave, and is referred to as an orbital. An orbital is a three-dimensional region of space which defines where electrons can be found.
- Each solution to the Schrodinger equation contains three quantum numbers.  
What are these quantum numbers, what do they mean, what are the valid integers, and what do they represent?

$n$ : principal quantum number

Possible values:  $n = 1, 2, 3, \dots$

Represents: size



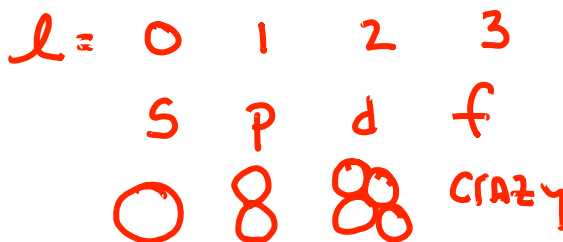
$l$ : angular momentum quantum number

Possible values: can be any value from 0 to  $n-1$

(NOTE: how value depends upon  $n$ )

"The Chemist's Code":

Represents: shape



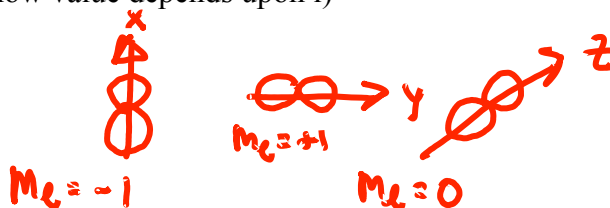
$m_l$ : magnetic quantum number

Possible values: can be any value from  $-l$  to  $+l$

(NOTE: how value depends upon  $l$ )

Represents: orientation in space

Includes zero  
 $l=1, m_l = -1, 0, +1$



## Orbitals and Quantum Numbers

- Each combination of  $n$ ,  $l$  and  $m_l$ , describes one orbital. Each orbital can hold two electrons.

a) How many orbitals have  $n = 3$  and  $l = 2$ ? List all of the orbitals that can possess these two quantum numbers.

$$m_l = -l \text{ to } +l$$
$$-2, -1, 0, +1, +2$$

$$n=3, l=2, m_l=-2$$

$$n=3, l=2, m_l=-1$$

$$n=3, l=2, m_l=0$$

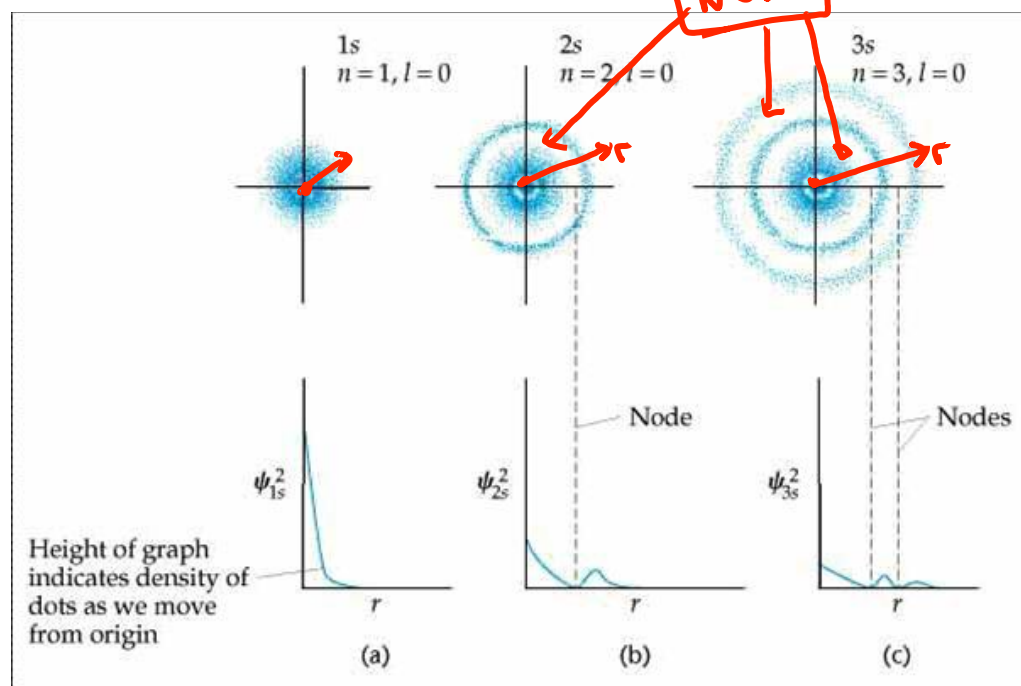
$$n=3, l=2, m_l=+1$$

$$n=3, l=2, m_l=+2$$

d orbitals  
Five

## Orbitals: Where are the electrons?

- We want to know two things about electrons in atoms: location and energy. However, because electrons have wave properties (the shape and energy of an orbital are the result of these properties), we can't know exactly where the electron is at any given moment (uncertainty principle). However, we can determine the *probability* of finding an electron in a given location.
- Plotting the square of the **wavefunction**  $\psi^2$  gives us a map of the probability of finding an electron in an atom.



**Nodes** signify areas where there is no electron density, meaning there is no probability of finding an electron in this area.

### RADIAL NODE

What kind of nodes are found in the s-orbital?

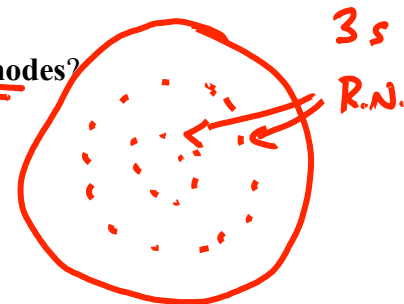
**RADIAL NODE:** is at some radius from the nucleus there is an area of no electron density

What is the relationship between energy (principal quantum number **n**) and the number of radial nodes?

$$R.N. = n - l - 1$$
  
 # OF RADIAL NODES

$$R.N. 1s = 1 - 0 - 1 = 0$$

$$R.N. 3s = 3 - 0 - 1 = 2$$



KNOW how to draw/represent orbitals and their nodes.

## The p orbitals

- The **p orbitals** are shaped somewhat like a peanut. (p = peanut?)

How many p orbitals for a given principal quantum number  $n$ ? **3** A 2p orbital should have one node; is it a radial node?

$n=2, l=1$   
 $n-l-1 = 2-1-1 = 0$   
 $\hookrightarrow R.N. = 0$

Why do we call this an **angular node**?

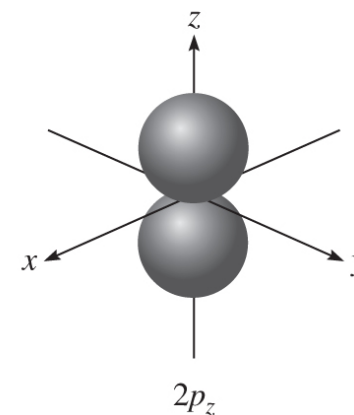
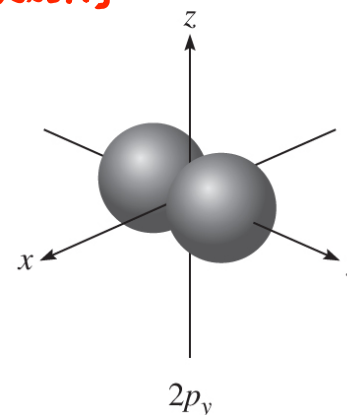
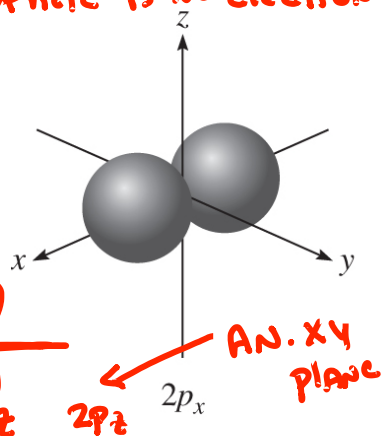
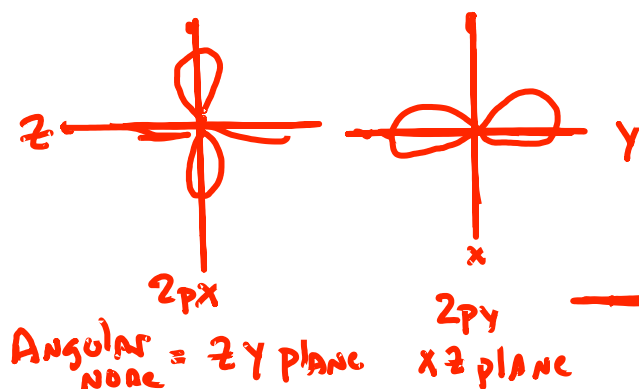
AT SOME ANGLE TO THE ORBITAL THERE EXISTS

$R.N. 3p = 3-1-1 = 1$

What is the relationship between the quantum number  $l$  and the number of angular nodes?

A PLANE OR A CONE WHERE THERE IS NO ELECTRON DENSITY

$l = \# \text{ Angular nodes}$



Steps for drawing two dimensional representations of s and p-orbitals:

1. Identify and draw orbital shape given by  $l$  (angular momentum qn).

✓ For an **s orbital**, shape is just a **sphere** (or a circle for a 2-D slice).

There are no angular nodes.

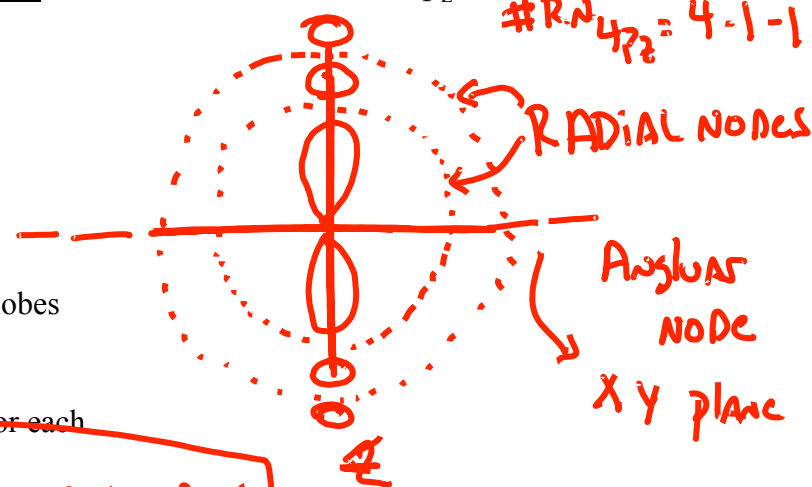
✓ For a **p orbital**, the orbital “points” along the specified axis and has an angular node perpendicular to the axis. For instance, a  $p_x$  orbital has two lobes aligned along the x-axis, and a node in the  $yz$ -plane.

✓ 2. Determine the number of **radial nodes** ( $n-l-1$ ). Add an additional lobe for each radial node.

3. Label radial and angular nodes on sketch.

b) Draw the  $4p_z$  orbital.

$\# R.N. 4p_z = 4-1-1 = 2$

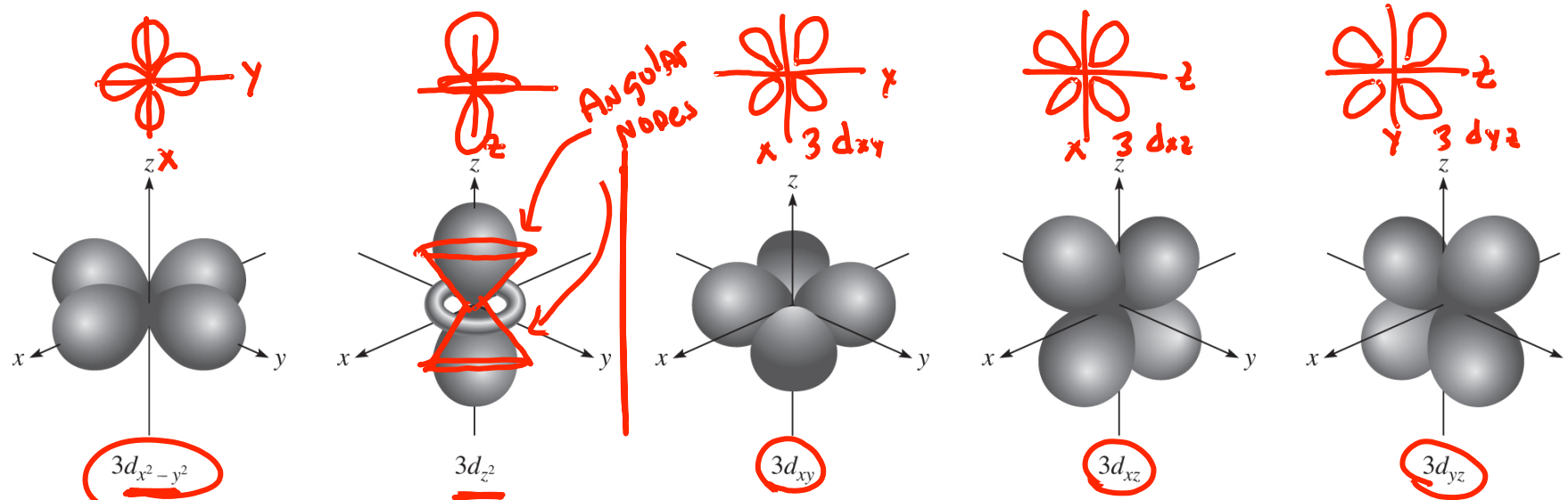


**TOTAL # OF NODES =  $n-1$**

## The d orbitals

- The **d orbitals** have two different shapes. How many d orbitals for a given principal quantum number  $n$ ?

A **d** orbital should have  $l=2, 2 \text{ AN.}$  *two angular nodes*, can you find them?

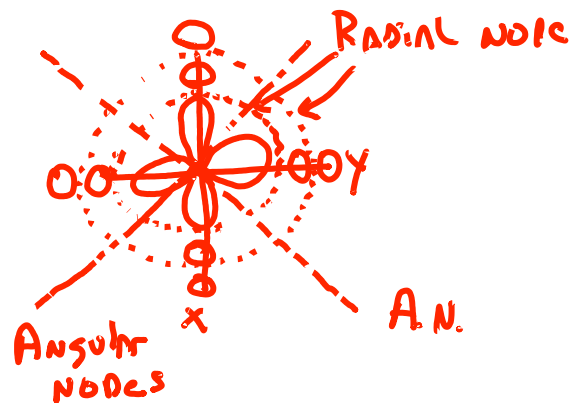


### Steps for drawing two dimensional representations of d-orbitals:

- Identify and draw orbital using the guide below:
  - The  $d_{xy}$ ,  $d_{xz}$ ,  $d_{yz}$  orbitals all have lobes bisecting the two specified axes.
  - The  $d_{x^2-y^2}$  and  $d_{z^2}$  have lobes aligned with the specified axes. The  $d_{z^2}$  has an additional ring of electron density around the z-axis.
- Determine the number of **radial nodes** ( $n-l-1$ ) and add an additional lobe for each radial node ~~present~~.
- Label radial and angular nodes in sketch. Each orbital will have two angular nodes and the angular nodes on the  $d_{z^2}$  orbital are two cones originating at the origin of the coordinate axes.

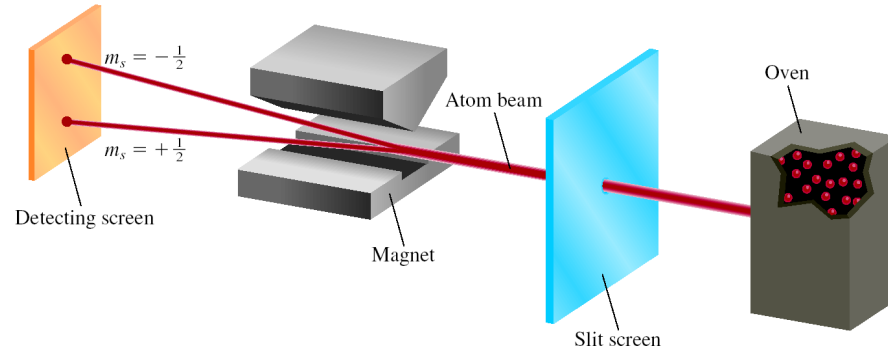
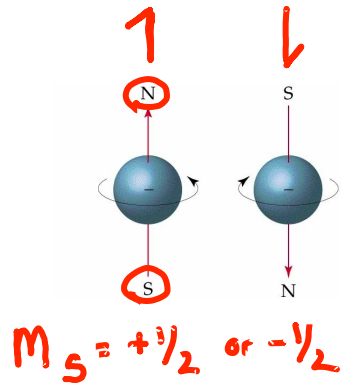
a) Draw the 5  $d_{x^2-y^2}$  orbital.

$$5d = 5 - 2 - 1 = 2 \text{ \# R.N.}$$



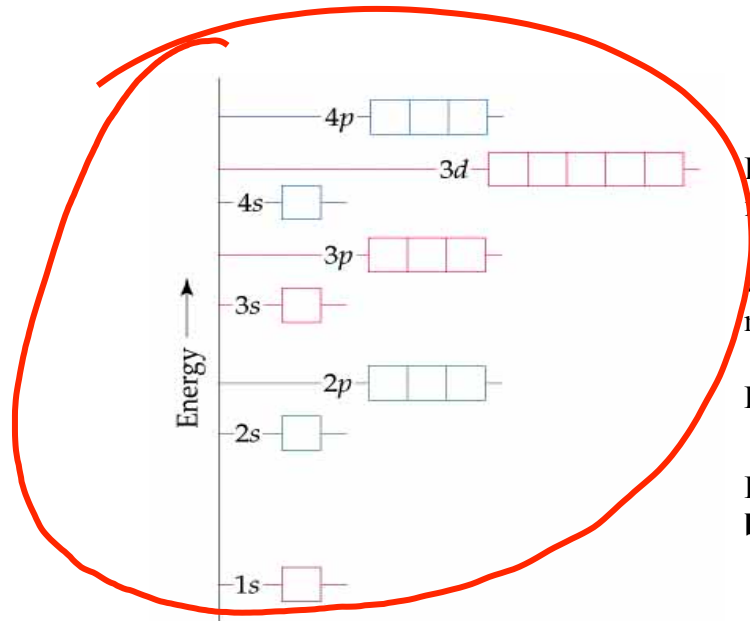
## Orbitals and Quantum Numbers

- The *Pauli Exclusion Principle* states that no two electrons can have identical sets of quantum numbers.
- There is another quantum number,  $m_s$ , for electron spin, allowing for **each orbital to contain up to two electrons**.  
What do we mean by electron spin? How does this allow two electrons per orbital?



**How can we put electrons into orbitals of a multi-electron atom?**

Start at the bottom! Why do the orbitals have the energy levels they do?



Each principle quantum number can contain a number of orbitals that vary in angular momentum quantum numbers.

Orbitals with that share a principle quantum number but have different angular momentum quantum numbers are called **subshells**.

For example: the  $n = 3$  level has three different subshells: 3s, 3p, and 3d.

**Know that, except for hydrogen, the energy of an orbital depends upon both  $n$  and  $l$ . For hydrogen the energy depends only on  $n$ .**

## Electron Configurations: Hydrogen to Neon

- Let's fill in the electrons for the elements H, He, Li, Be and B, then for C, N, O, F and Ne.

NOTE: If a substance has any unpaired electrons, it is said to be **paramagnetic**. If all of its electrons are *paired*, it is said to be **diamagnetic**. We will return to these items again in our discussions on bonding. Paramagnetic atoms act like magnets with a north and south end.

Low Energy (orbitals) → Higher energy (orbitals)

	1s	2s	2p	Configuration	Para- or Diamagnetic
H:	<div style="border: 1px solid black; padding: 2px; text-align: center;">↑</div>	<div style="border: 1px solid black; width: 20px; height: 20px;"></div>	<div style="border: 1px solid black; width: 20px; height: 20px;"></div> <div style="border: 1px solid black; width: 20px; height: 20px;"></div> <div style="border: 1px solid black; width: 20px; height: 20px;"></div>	$1s^1$	P
He:	<div style="border: 1px solid black; padding: 2px; text-align: center;">↑↓</div>	<div style="border: 1px solid black; width: 20px; height: 20px;"></div>	<div style="border: 1px solid black; width: 20px; height: 20px;"></div> <div style="border: 1px solid black; width: 20px; height: 20px;"></div> <div style="border: 1px solid black; width: 20px; height: 20px;"></div>	$1s^2$	D
Li:	<div style="border: 1px solid black; padding: 2px; text-align: center;">↑↓</div>	<div style="border: 1px solid black; padding: 2px; text-align: center;">↑</div>	<div style="border: 1px solid black; width: 20px; height: 20px;"></div> <div style="border: 1px solid black; width: 20px; height: 20px;"></div> <div style="border: 1px solid black; width: 20px; height: 20px;"></div>	$1s^2 2s^1$	P
Be:	<div style="border: 1px solid black; padding: 2px; text-align: center;">↑↓</div>	<div style="border: 1px solid black; padding: 2px; text-align: center;">↑↓</div>	<div style="border: 1px solid black; width: 20px; height: 20px;"></div> <div style="border: 1px solid black; width: 20px; height: 20px;"></div> <div style="border: 1px solid black; width: 20px; height: 20px;"></div>	$1s^2 2s^2$	D
B:	<div style="border: 1px solid black; padding: 2px; text-align: center;">↑↓</div>	<div style="border: 1px solid black; padding: 2px; text-align: center;">↑↓</div>	<div style="border: 1px solid black; padding: 2px; text-align: center;">↑</div> <div style="border: 1px solid black; width: 20px; height: 20px;"></div> <div style="border: 1px solid black; width: 20px; height: 20px;"></div>	$1s^2 2s^2 2p^1$	P

Now where does the next electron go for C? **Hund's Rule:** Don't crowd the electrons!

	1s	2s	2p	Configuration	Para- or Diamagnetic
C:	<div style="border: 1px solid black; padding: 2px; text-align: center;">↑↓</div>	<div style="border: 1px solid black; padding: 2px; text-align: center;">↑↓</div>	<div style="border: 1px solid black; padding: 2px; text-align: center;">↑</div> <div style="border: 1px solid black; padding: 2px; text-align: center;">↑</div> <div style="border: 1px solid black; width: 20px; height: 20px;"></div>	$1s^2 2s^2 2p^2$	P
N:	<div style="border: 1px solid black; padding: 2px; text-align: center;">↑↓</div>	<div style="border: 1px solid black; padding: 2px; text-align: center;">↑↓</div>	<div style="border: 1px solid black; padding: 2px; text-align: center;">↑</div> <div style="border: 1px solid black; padding: 2px; text-align: center;">↑</div> <div style="border: 1px solid black; padding: 2px; text-align: center;">↑</div>	$1s^2 2s^2 2p^3$	P
O:	<div style="border: 1px solid black; padding: 2px; text-align: center;">↑↓</div>	<div style="border: 1px solid black; padding: 2px; text-align: center;">↑↓</div>	<div style="border: 1px solid black; padding: 2px; text-align: center;">↑↓</div> <div style="border: 1px solid black; padding: 2px; text-align: center;">↑</div> <div style="border: 1px solid black; width: 20px; height: 20px;"></div>	$1s^2 2s^2 2p^4$	P
F:	<div style="border: 1px solid black; padding: 2px; text-align: center;">↑↓</div>	<div style="border: 1px solid black; padding: 2px; text-align: center;">↑↓</div>	<div style="border: 1px solid black; padding: 2px; text-align: center;">↑↓</div> <div style="border: 1px solid black; padding: 2px; text-align: center;">↑↓</div> <div style="border: 1px solid black; padding: 2px; text-align: center;">↑</div>	$1s^2 2s^2 2p^5$	P

From <http://tinyurl.com/fill-electrons> (the UC Davis Chemistry Wiki)

- Aufbau Principle:** Fill the lowest energy orbitals first, and then move up to higher energy orbitals only after the lower energy orbitals are full.
- Hund's Rule:** Every orbital in a subshell is singly occupied before any orbital is doubly occupied. All of the electrons in singly occupied orbitals have the same spin (to maximize total spin).
- When assigning electrons to orbitals, an electron first seeks to fill all the orbitals with similar energy (also referred to as degenerate orbitals) before pairing with another electron in a half-filled orbital. In visualizing this process, consider how electrons exhibit the same behavior as the same poles on a magnet would if they came into contact; as the negatively charged electrons fill orbitals, they first try to get as far as possible from each other before having to pair up.

## Using the Periodic Table to Write Electron Configurations

### Steps to determine an electron configuration for any element:

1. Find the element of interest on the periodic table, then write the noble gas on the previous period (row) in brackets.
2. Add additional electrons in the following order: (n)s electrons, then (n-1) d electrons, then (n)p electrons until the total number of electrons equals the atomic number of the element of interest.
3. For elements with an atomic number of 73 or greater, the (n-2)f electrons will begin filling after the first (n-1)d electron is filled. The (n-1)d-electrons will continue filling immediately after all (n-2)f-electrons have filled.

(NOTE: n = period (row) number on the periodic table. See table below for illustration.)

Write the electron configuration for **Ne**:

[illegible]



## Using the Periodic Table to Write Electron Configurations: More Practice

Diagram of the periodic table showing subshell filling order. The subshells are labeled:  $(n)s$ ,  $(n-1)d$ ,  $(n)p$ , and  $(n-2)f$ . Red arrows indicate the sequence of filling:  $4s \rightarrow 3d \rightarrow 4p$ . A red arrow also points from the  $6s$  subshell to the  $4f$  subshell in the lanthanide series.

$4s, 4p, 4d$   
Subshell

Write the *abbreviated* electron configurations for:

P:  $[Ne] 3s^2 3p^3$

Rh:  $[Kr] 5s^2 4d^7$

Po:  $[Xe] 6s^2 5d^{10} 4f^{14} 6p^4$

Write the expected electron configuration for Cr:

$[Ar] 4s^2 3d^4$

The actual configuration is  $[Ar] 4s^1 3d^5$ . Why?

$\frac{1}{4s} \quad \frac{1}{3d} \frac{1}{3d} \frac{1}{3d} \frac{1}{3d} \frac{1}{3d}$

$\frac{1}{2}$  Filled Subshell  
Special Stability

Why do you think that Cu has a configuration of  $[Ar] 4s^1 3d^{10}$ ?

$\frac{1}{4s} \quad \frac{1}{3d} \frac{1}{3d} \frac{1}{3d} \frac{1}{3d} \frac{1}{3d} \frac{1}{3d}$

Fully filled Subshell