Chapter Seven

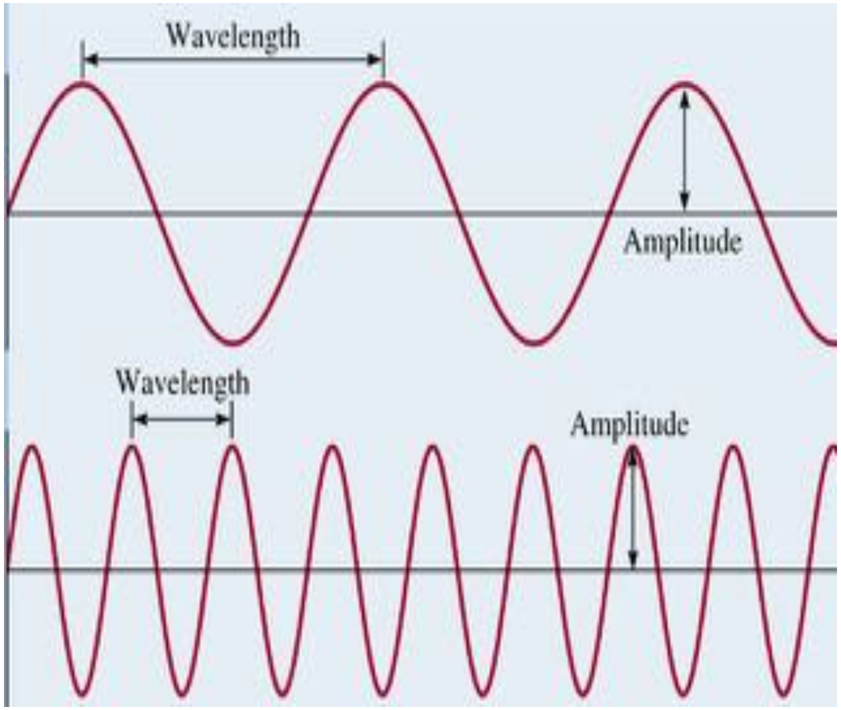
The Electronic Structure of Atoms

Wave Theory

Wave

- Repeating disturbance spreading out from a defined origin
- Characterized by wavelength, frequency and amplitude

Wavelength (λ)



- Distance between identical pts
- Units some form of meters

Frequency (ν)

- Number of waves that pass through a point in 1 second
- Units of cycles/sec or Hz

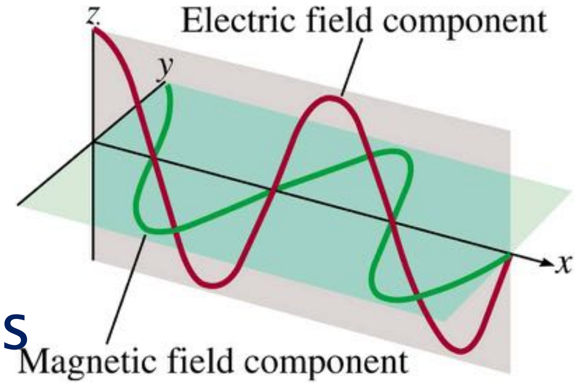
Amplitude

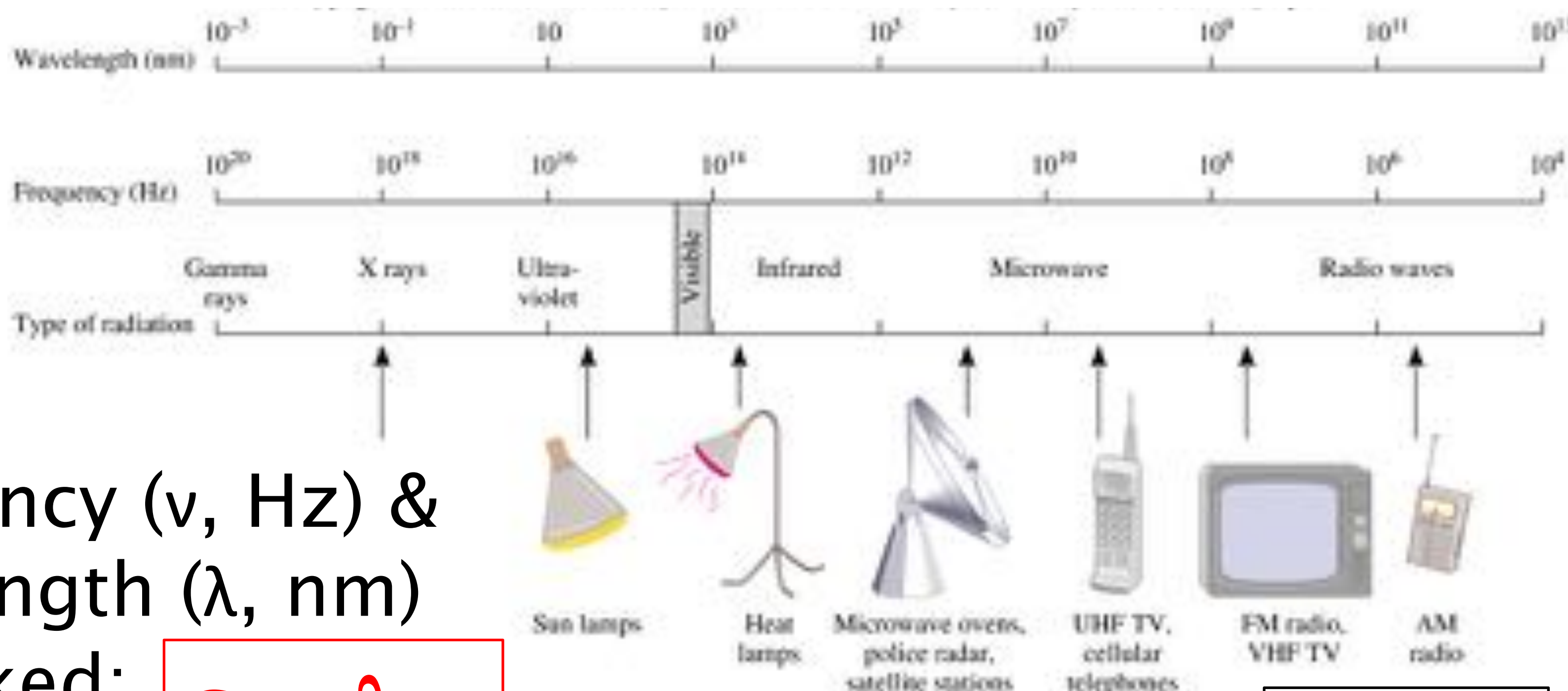
- Height of wave from center point
- Intensity of wave

Electromagnetic Radiation

Electromagnetic Radiation

- Emission/transmission of energy
- In form of waves
- Has electrical & magnetic components
- Travels at the speed of light (c= 3.00 x 10^8 m/s)





Frequency (ν, Hz) & wavelength (λ, nm) are linked: $\boxed{c = \lambda\nu}$

$\boxed{Hz = s^{-1}}$

Using the relationship $c = \lambda\nu$:

What is the wavelength of an FM-radiowave with a 94.9 MHz frequency?

A: 3.16 m

Max Planck's Quantum Theory

Studied energy emitted by objects

- Amount of energy emitted was directly related to wavelength at which energy was emitted

Theory: Energy must be in discrete amounts.

- Amounts were defined by λ (& ν – they are related!)

$$E = h\nu = hc/\lambda$$

- Can have multiples of these discrete amounts

$$E = h\nu,\ \ E = 2h\nu,\ \ E = 3h\nu\ \ldots$$

- **h = Plank's constant = 6.626 x 10^{-34} J s**

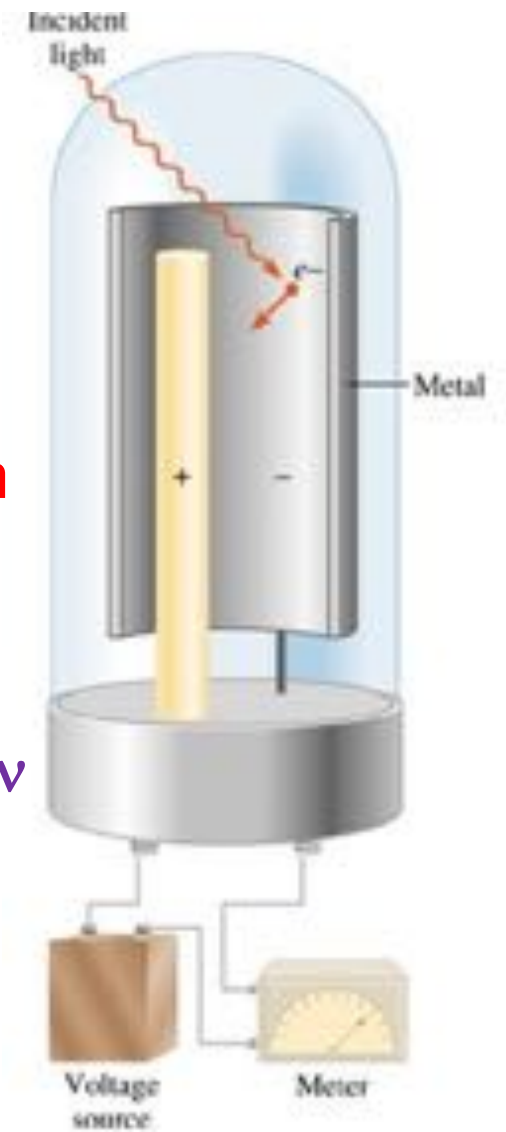
Called the smallest amount of energy a Quantum.

Didn't know why, but math worked over entire spectrum

Einstein and the Photoelectric Effect

Experiment to prove why E= hν

- Full spectrum of light hits metal surface
- Energy transferred to electrons in metal
- Electrons break free and escape to anode
- Flow of electrons recorded with voltmeter
- Light energy must be at or above a certain frequency to dislodge electrons



Conclusions:

- **Light energy has wave properties: E = hν**

&

- **Light energy has particle properties**

Particles of light were later called "photons"

Using E = hν (h = 6.626 x 10^{-34} Js)

What is the energy of a radiowave with a frequency of 94.9 MHz? A: 6.29 x 10^{-26} J

What wavelength has an energy of 1.00 x 10^{-20}J?

A: 1.99 x 10^{-5} m
Or 19.9 μm

Using $E = h\nu$ ($h = 6.626 \times 10^{-34}$ Js)

What is the energy per photon and per mole of photons of violet light, with a wavelength of 415 nm?

A: 4.79×10^{-19} J/photon
A: 2.88×10^{5} J/mol

Continuous vs. Line Spectra

Continuous spectrum:

- Occurs when all visible light is present: white light

Line Spectrum

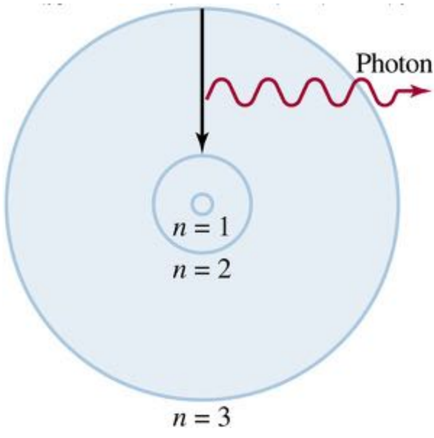
- Occurs when light is produced through an element
- Pattern of lines is characteristic of the element
- Can be used for identification of elements

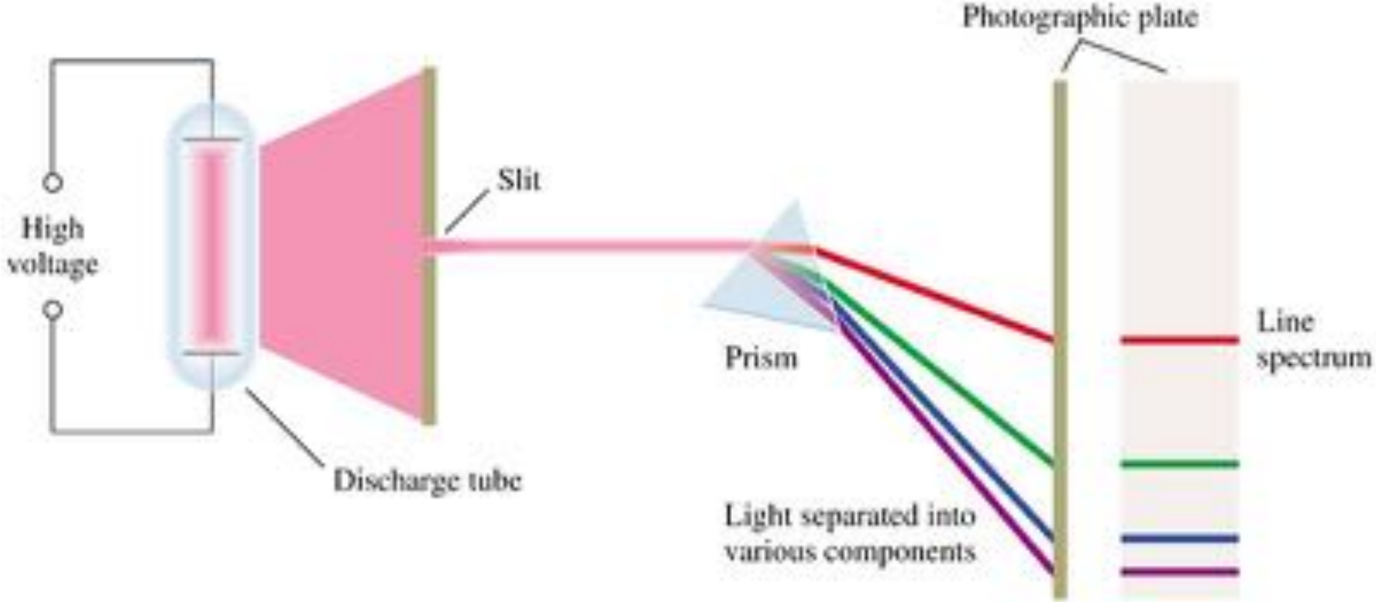
Bohr's Theory of the Hydrogen Atom

Emission Spectra: Pattern of radiation that is emitted when photons are removed from a substance.

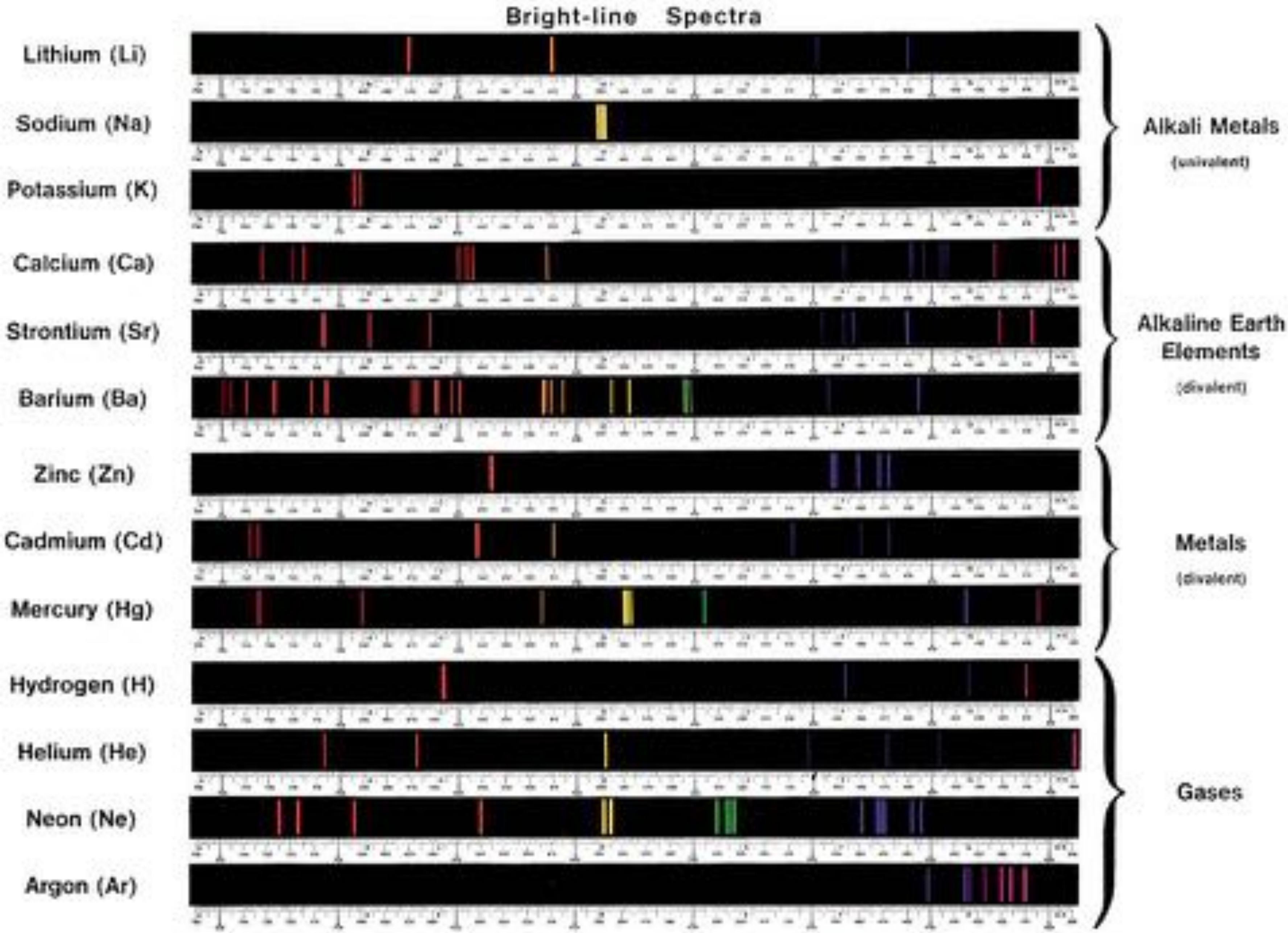
Procedure

- Add energy to a substance
- Photons are emitted as a beam of light
- Separate wavelengths through a prism
- Record pattern on a photographic plate



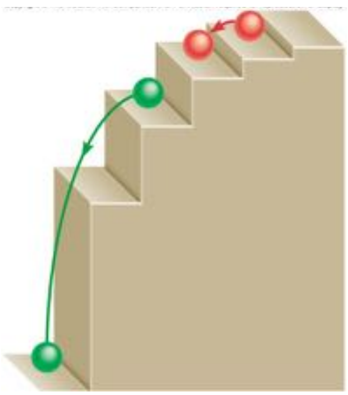


Elemental Line Spectra



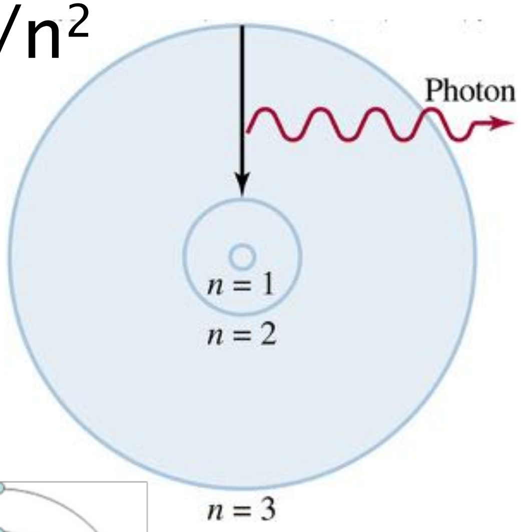
Bohr's Hydrogen Atom

Niels Bohr (1913): Electron energy (E_n) was quantized



- Only certain specified values allowed
- Stable levels called <u>energy levels</u>
- Photon absorbed/released when electron moves from 1 level to another

The energy of each stable orbit: $E_n = -R_H/n^2$

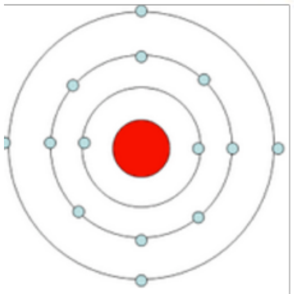


- *n* is the quantum number of the level
- *n* is always an integer, 1,2,3,...etc.

Proportionality constant R_H

- Rydberg constant
- **$R_H = 2.18 \times 10^{-18}$ J**

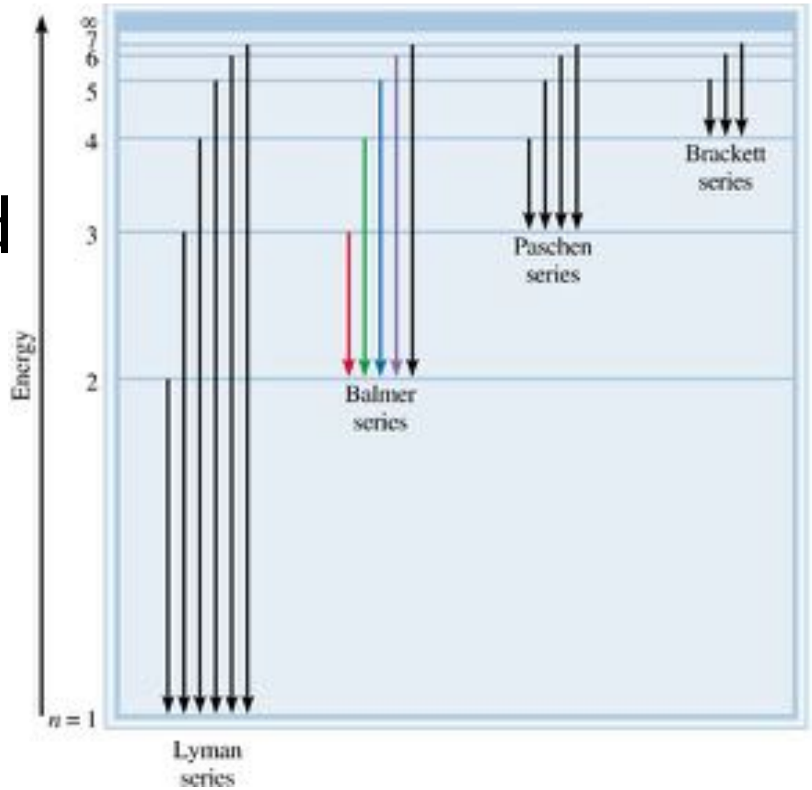
Leads to orbit description of atoms



Energy Level Calculations

All calculations done by comparing energy levels

- Electron moves between levels
- $E = -R_H (1/n_f^2 - 1/n_i^2)$



Energy emitted or absorbed

- <u>High to low level:</u>
  - energy released (-)
- <u>Low to high level:</u>
  - energy absorbed (+)

Ground state: An e^-'s lowest possible energy level

Excited state: All other levels

Calculate the wavelength of the electron shift from n = 4 to n =2. Is light emitted or absorbed?

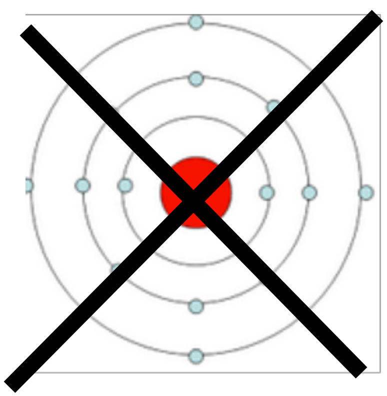
$$E = -R_H \left(\frac{1}{n_f^2} - \frac{1}{n_i^2} \right)$$

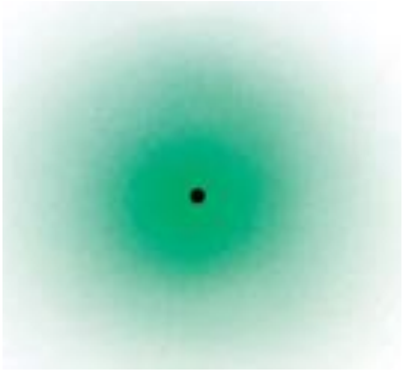
$R_H = 2.18 \times 10^{-18}$ J

A: λ = 486 nm Visible blue green light is emitted (neg E value)

Modern View of the Atom: Quantum Mechanics – a very brief intro

- (Nucleus in center, protons & neutrons in nucleus)
- Electrons outside nucleus
  - located in "cloud" surrounding the nucleus
  - likely location based on probability functions
  - quantum numbers used to describe probable location





$$i\hbar\frac{\partial\Psi}{\partial t} = -\frac{\hbar^2}{2m}\nabla^2\Psi + [V_1(x) + iV_2(x)]\Psi$$

Quantum Numbers and Atomic Orbitals

Atomic orbital

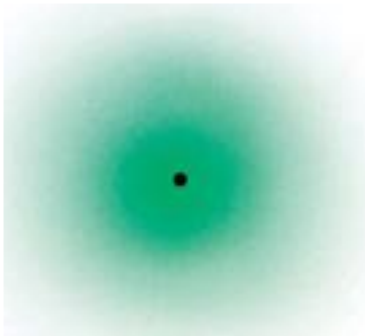
- A region in space with a high probability of finding an electron.
- Identified by 4 quantum numbers.

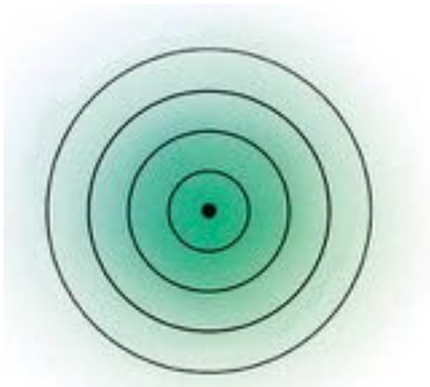
4 Quantum Numbers (think of it as a dorm address)

1. Principal quantum number (n):	Building
2. Angular momentum quantum number (*l*)	Floor
3. Magnetic quantum number (m_l)	Room #
4. Electron spin quantum number (m_s)	Bed

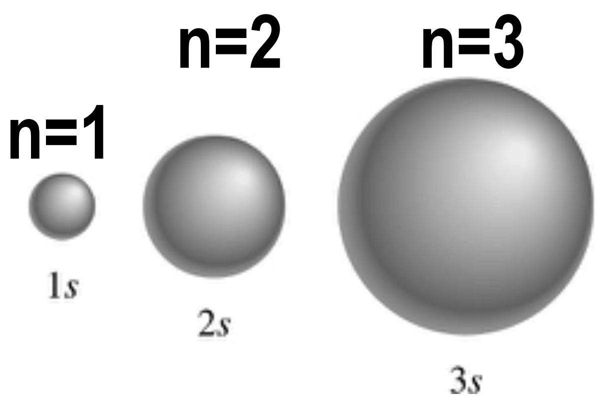
The Principal Quantum Number (n)

- Restricted to the positive integers: 1, 2, 3, 4, 5, 6, 7
- The shell or <u>energy level</u> of the orbital





- Indicates the size of the orbital
  - max distance e^- can travel from nucleus
- Integers correspond to <u>row numbers</u> in Periodic Table
  - row an element is in tells you the highest energy level in the ground state



The Angular Momentum Quantum Number (ℓ)

- Indicates orbital shape
  - Designation: s, p, d or f

*l*evel	0	1	2	3
Name	s	p	d	f

- Designates the subshell
  - Values range from 0 to n-1
  - 0-6 theoretically, but realistically 0-3
  - Give rise to "Blocks" in periodic table

Energy Level (n)	Math	Allowed ℓ values	Orbitals
1	1-1 = 0	0	s only
2	2-1 = 1	0, 1	s & p
3	3-1 = 2	0, 1, 2	s, p, & d

The Magnetic Quantum Number (m_ℓ):

Determines the orientation in space of the orbitals

- "orientation" refers to proximity to axes (x, y, z)
- Integers from $-\ell$ to $+\ell$

Determines the <u>number</u> of orbitals in a subshell

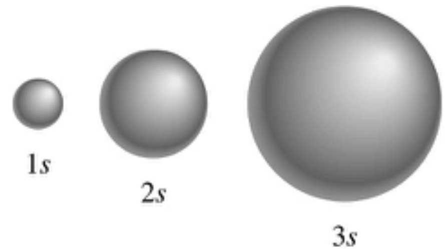
- The number of possible values for $m_\ell = 2\ell + 1$

Orbital	ℓ value	Allowed m_ℓ values	Number of Orbitals per Energy Level
s	0	0	1
p	1	-1, 0, 1	3
d	2	-2, -1, 0, 1, 2	5
f	3	-3, -2, -1, 0, 1, 2, 3	7

Orbital Shapes = ℓ quantum number

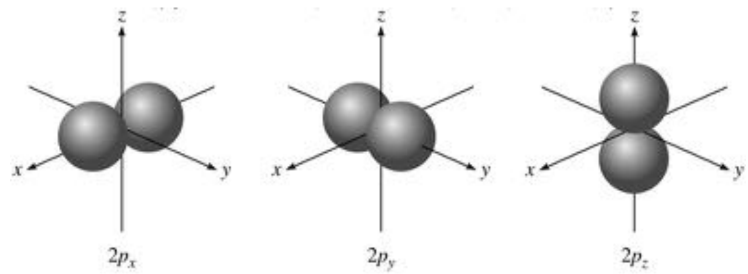
ℓ = 0: s orbitals

- Spherical
- **One** per energy level



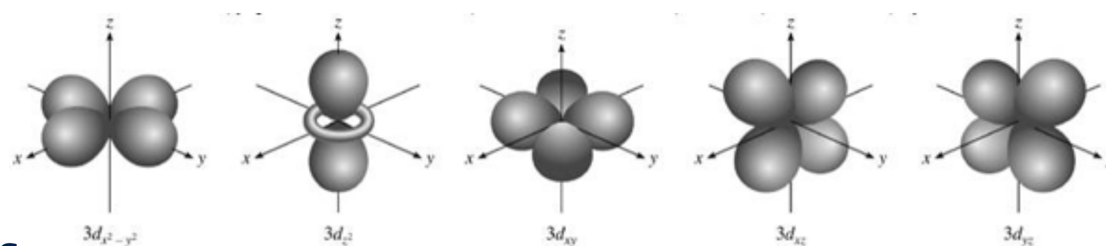
ℓ = 1: p orbitals

- 2 teardrops joined at center
- **Three** per energy level



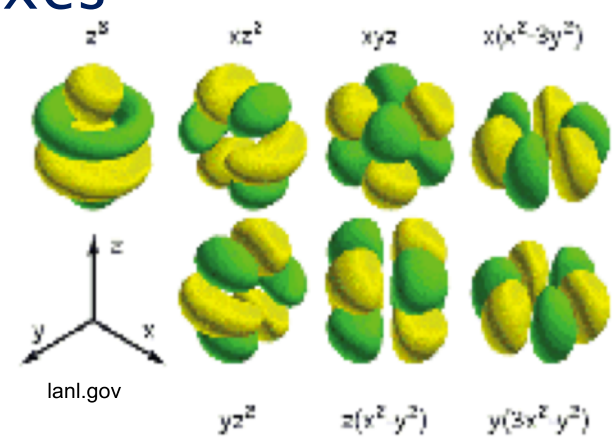
ℓ = 2: d orbitals

- Most are like two p orbitals along different axes
- **5** per energy level



ℓ = 3: f orbitals.

- Complicated shapes
- **7** per energy level



Orbitals with same n & ℓ values are "degenerate"

degenerate = same energy

(Note: In some cases there are slight energy differences)

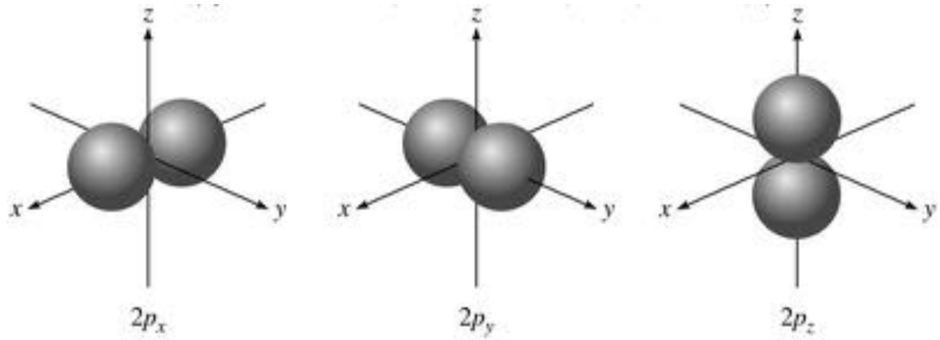
Possible quantum numbers for an electron in a 3p orbital:

n = 3

ℓ can be 0 to 3-1 (0, 1, 2) BUT if it is a p orbital $\ell = 1$

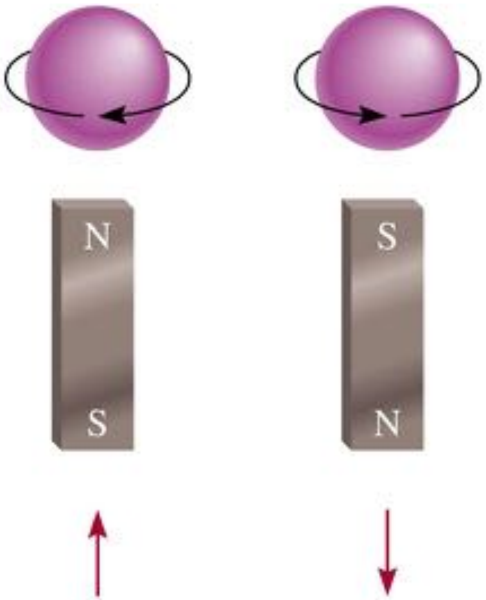
m_ℓ can be $+\ell$ to $-\ell$ = -1, 0, +1

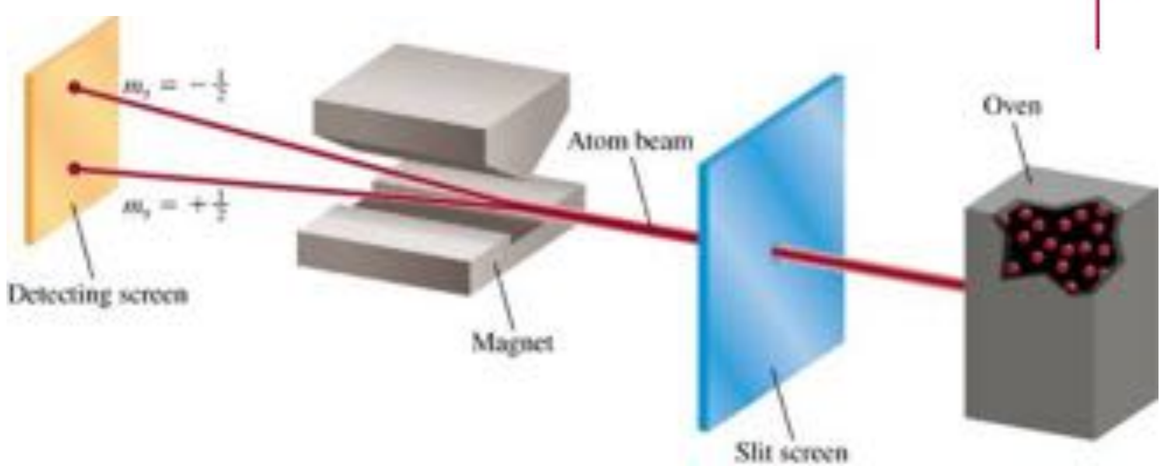
Since the 3p orbitals are degenerate, any of the three m_ℓ values could be correct



Electron Spin Quantum Number (m_s)

- A magnetic field is induced by the moving electric charge of an electron as it spins
  - Opposite spins cancel one another
  - No net magnetic field for the pair
  - Allows 2 electrons to occupy 1 orbital
  - Unpaired e^- lead to magnetism
- Two possible values: **+1/2 and −1/2**





Quantum Numbers Summary

TABLE 7.2 Relation Between Quantum Numbers and Atomic Orbitals

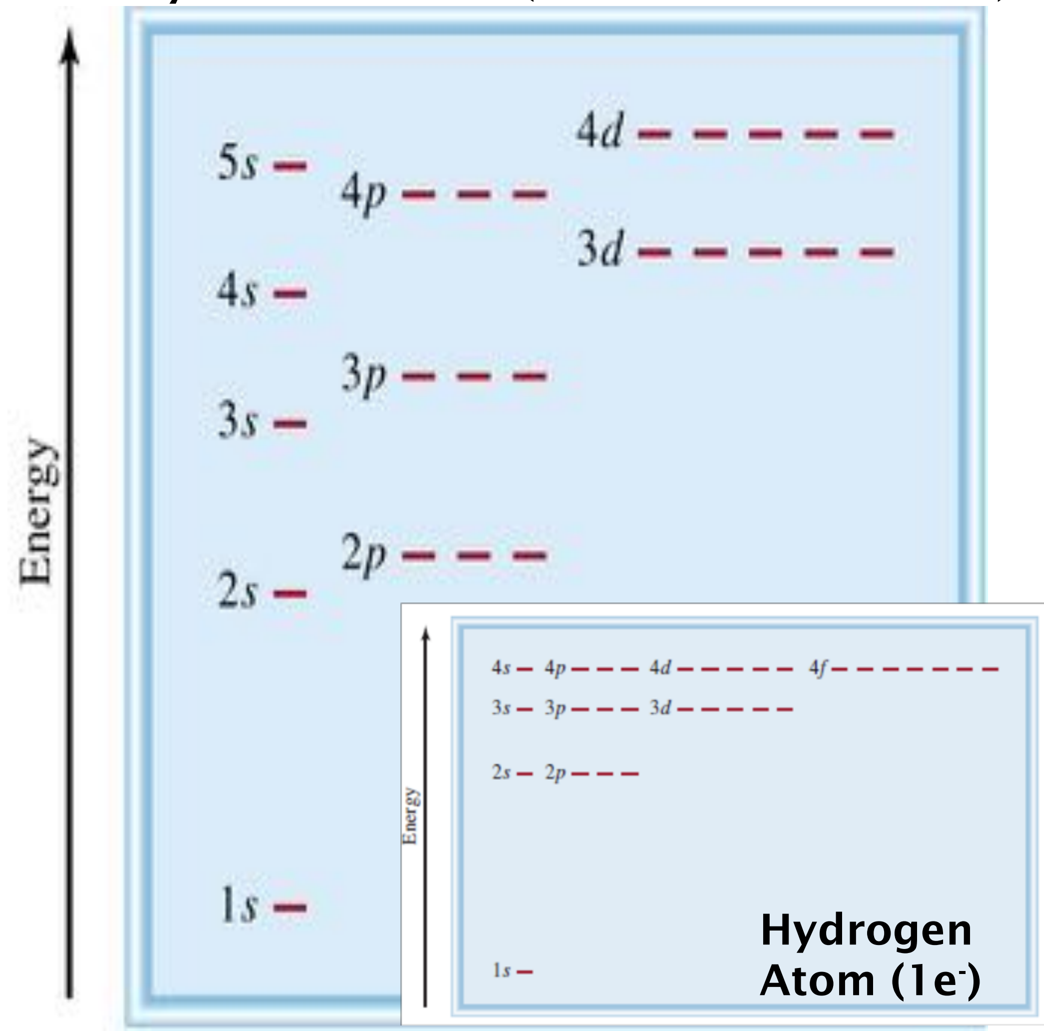
n	ℓ	m_ℓ	Number of Orbitals	Atomic Orbital Designations
1	0	0	1	$1s$
2	0	0	1	$2s$
	1	$-1, 0, 1$	3	$2p_x, 2p_y, 2p_z$
3	0	0	1	$3s$
	1	$-1, 0, 1$	3	$3p_x, 3p_y, 3p_z$
	2	$-2, -1, 0, 1, 2$	5	$3d_{xy}, 3d_{yz}, 3d_{xz}, 3d_{x^2-y^2}, 3d_{z^2}$
⋮	⋮	⋮	⋮	⋮

Electron Configuration:
Finding a home for each electron

The energy of an electron is defined by both n & ℓ

- Principle shells (size)
  - n = 1,2, 3, 4 or 5
- Subshells (shape)
  - ℓ = 0, 1, 2, or 3
  - n determines number of subshells
  - s, p, d, f orbitals
  - <u>Shielding</u> impacts relative energies

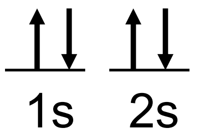
Many-electron atom (f subshell not shown)



Rules & Principles Governing e⁻ Configurations

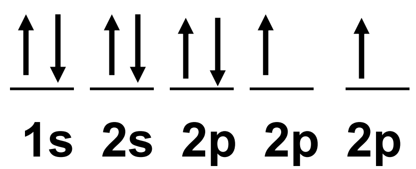
Pauli Exclusion Principle:

- No 2 e^- in an atom can have the same set of 4 quantum #s
  - If in the same orbital, e^- must have opposite spins



Hund's rule:

- Electrons in the same subshell occupy degenerate orbitals singly, before pairing
  - Degenerate = same energy



Ex: Oxygen, O Z = 8

The Aufbau Principle:

- In general, each successive electron added to an atom occupies the lowest energy orbital available
  - There are some exceptions

(Z = 1) H $1s^1$

(Z = 2) He $1s^2$

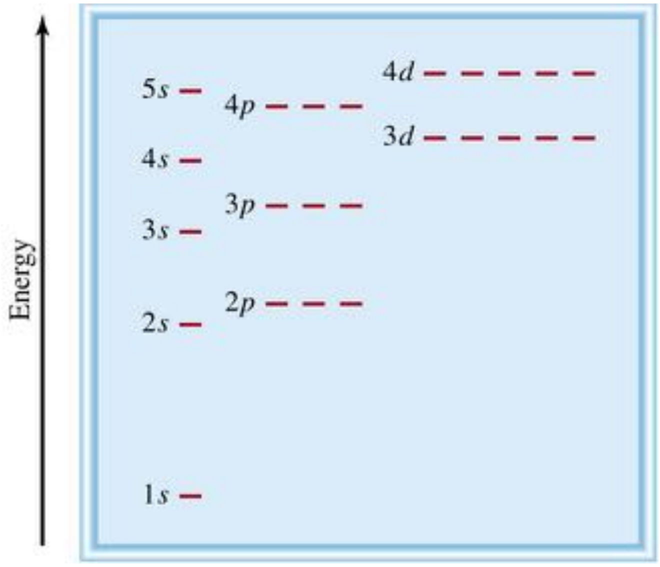
(Z = 3) Li $1s^2 2s^1$

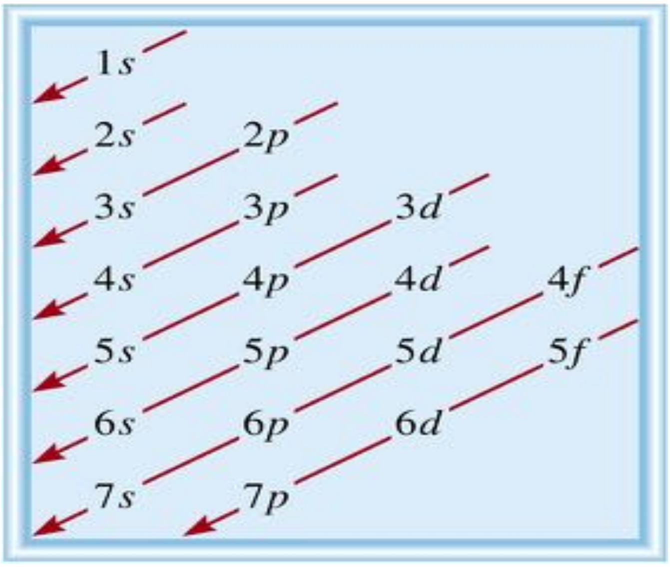
Orbital Filling in Multi-electron Atoms

- Fill low to high energy
- 2 electrons per orbital
- Shielding impacts the energy of orbitals
- Use chart to account for overlap of n values

1s < 2s < 2p < 3s < 3p < 4s < 3d < 4p < 5s < 4d < 5p < 6s

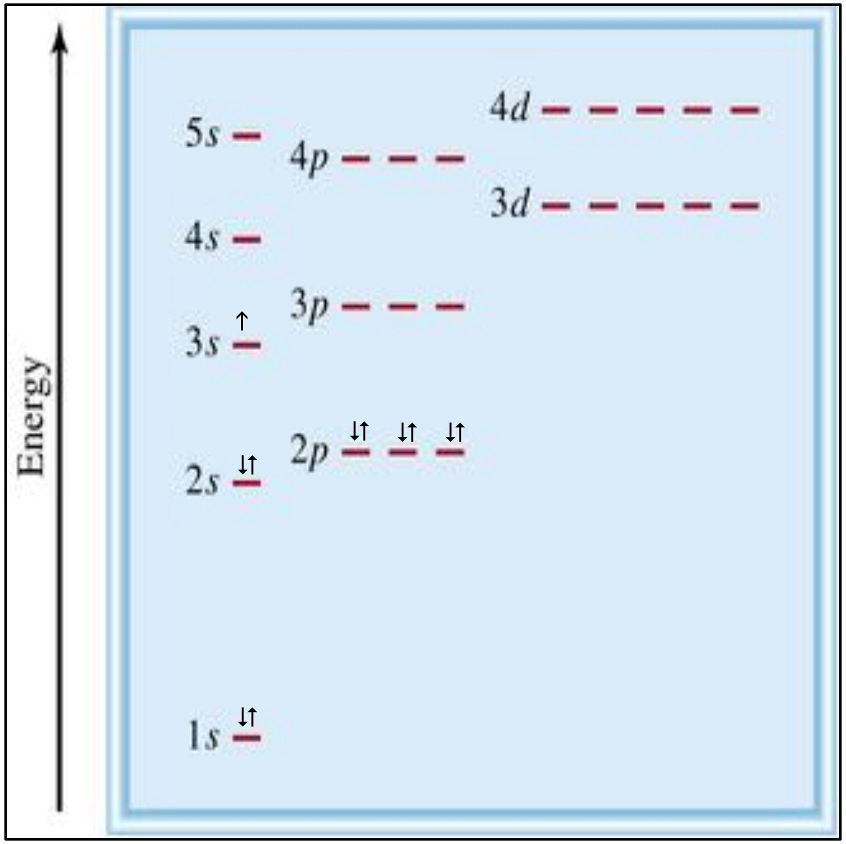
- Format: spdf or orbital notation
- Ends when a home is found for each electron





Electron Configuration con't

- Defines the orbital ("home") for each electron
- # electrons = atomic number (Z) of atom (if neutral)
- Max 2 electrons per orbital



Orbital Diagrams

- Energy increases from bottom to top
  - Higher energy levels at top
- Boxes or lines represent orbitals
  - # lines at one level = # degenerate orbitals
- Arrows (⇂↾) represent e^-
- 2 e^- allowed per orbital
  - one arrow up & one down to show the different spins

Formats for Electron Configurations

spdf Notation

- Front number = energy level
- Letter = type of orbital (s, p, d, or f)
  - Degenerate orbitals are combined together
- Superscript = # electrons in that type of orbital
  - Degenerate orbitals are combined, so the superscript can be more than 2 if it is a p, d, or f orbital (p max 6, d max 10, f max 14)

Examples:

Ne: Z = 10

$1s^2 2s^2 2p^6$

Na: Z = 11

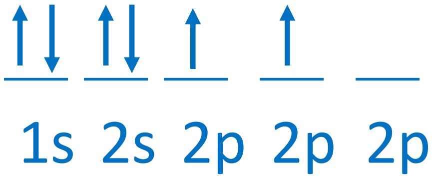
$1s^2 2s^2 2p^6 3s^1$

Orbital Notation

- Number = energy level
- Letter = type of orbital
  - Degenerate orbitals are NOT combined
- Arrows = electrons
  - Put one e^- in each degenerate orbital before pairing
  - If 2 e^- in one orbital, one arrow must be up, the other down

Example:

C: Z = 6



Writing Electron Configurations

Sulfur:

Vanadium:

Writing Electron Configurations for Ions

Remove Electrons from Highest Energy Level First

Magnesium ion (Mg^{2+}):

Fluorine ion (F^{-}):

Manganese (II) ion (Mn^{2+}):

Noble Gas Configuration

- Abbreviation of Electron Configuration (ex: Na: [Ne]$3s^1$)
- Noble gas symbol replaces the portion of the e^- config. that is identical to the e^- config. of the noble gas.
- Always use the largest noble gas that is smaller than the element
- Can use for either spdf or orbital notation
- ex: Arsenic

  regular configuration: $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10} 4p^3$

- ex: Strontium

  regular configuration: $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10} 4p^6 5s^2$

Exceptions To The Aufbau Principle

Half filled & filled subshells provide additional stability

Cr and Cu ½ fill/fill their 3d shell before the 4s shell.

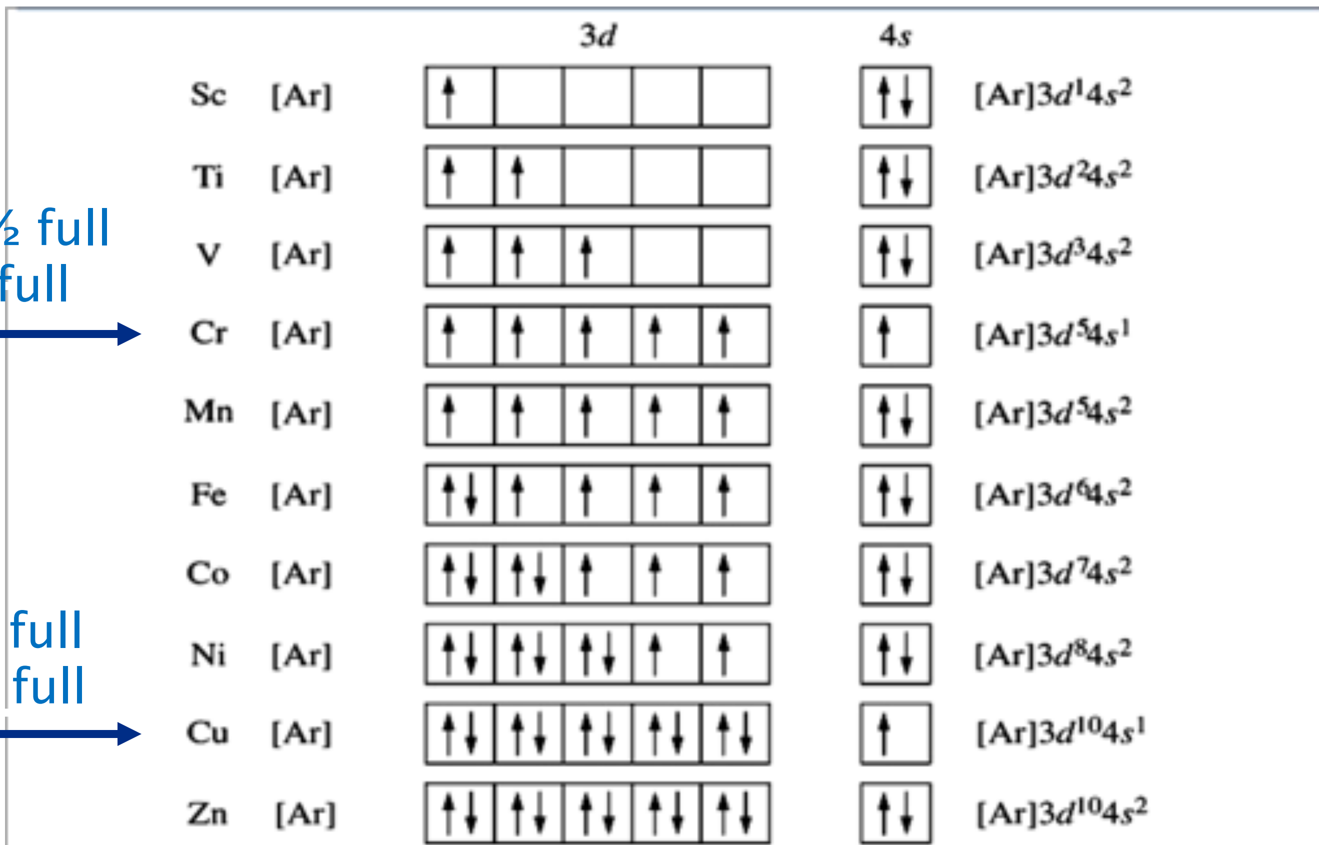
Elements in same columns as Cr & Cu behave in same way.

Similar behavior seen in p block.

Cr & Cu are the only exceptions you need to know.

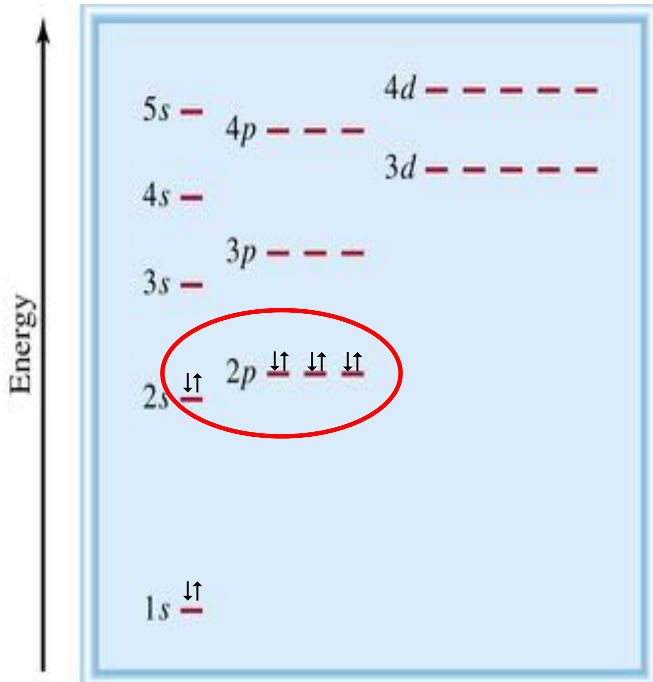
Cr: 3d ½ full
& 4s ½ full

Cu: 3d full
& 4s ½ full



Magnetism in Multi-electron Atoms

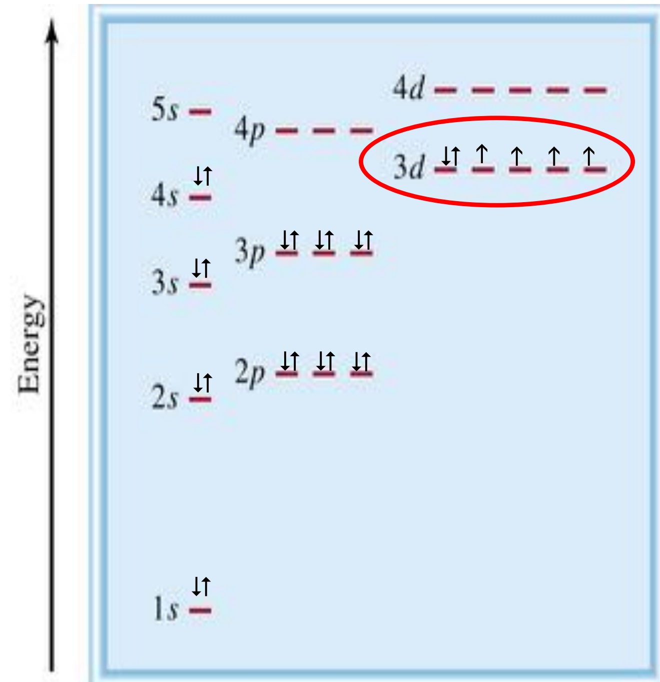
- +1/2 & -1/2 spins will cancel if electrons paired
- No magnetic properties without spin present
  - # unpaired electrons proportional to magnetic properties



Diamagnetic

All electrons paired

Ne: $1s^2 2s^2 2p^6$



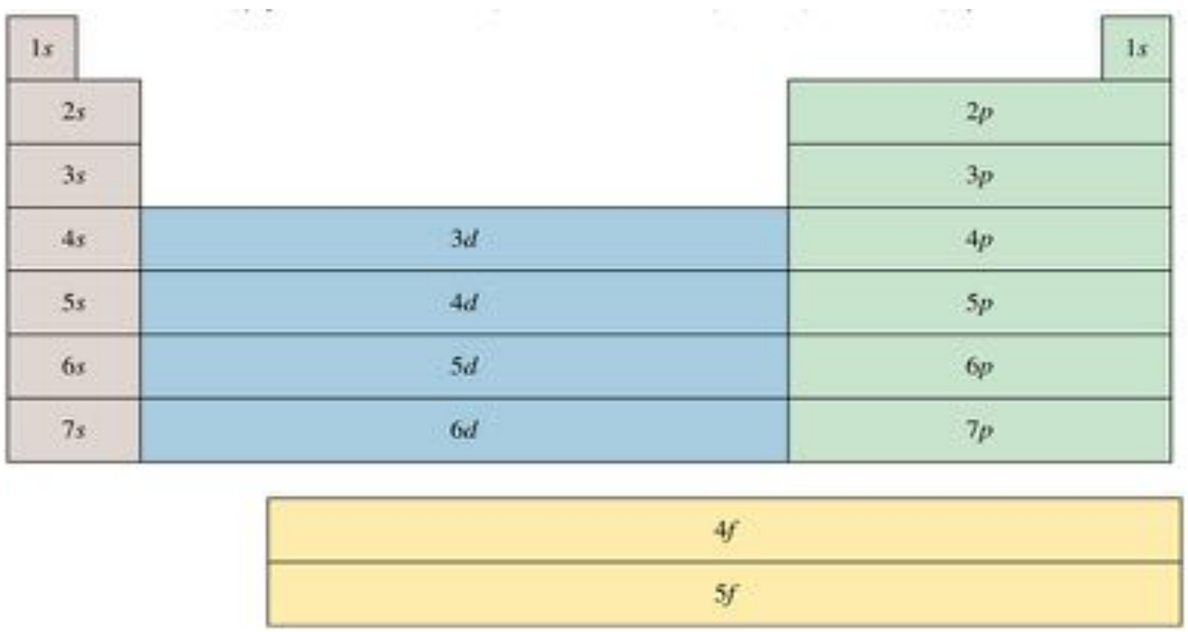
Paramagnetic

At least 1 unpaired electron

Fe: $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^6$

Quantum Numbers, Electron Configuration, & the Periodic Table

- **Principle quantum number, n**
  - Row number of periodic table, values of 1-7
- **Angular momentum quantum number, ℓ**
  - Specific area of periodic table, spdf "blocks"
- **Can follow the periodic table to fill e^- configuration**
- **Can use location on Periodic Table to determine where e^- configuration will end**



A possible set of quantum numbers for the last electron added to complete an atom of selenium would be:

n:

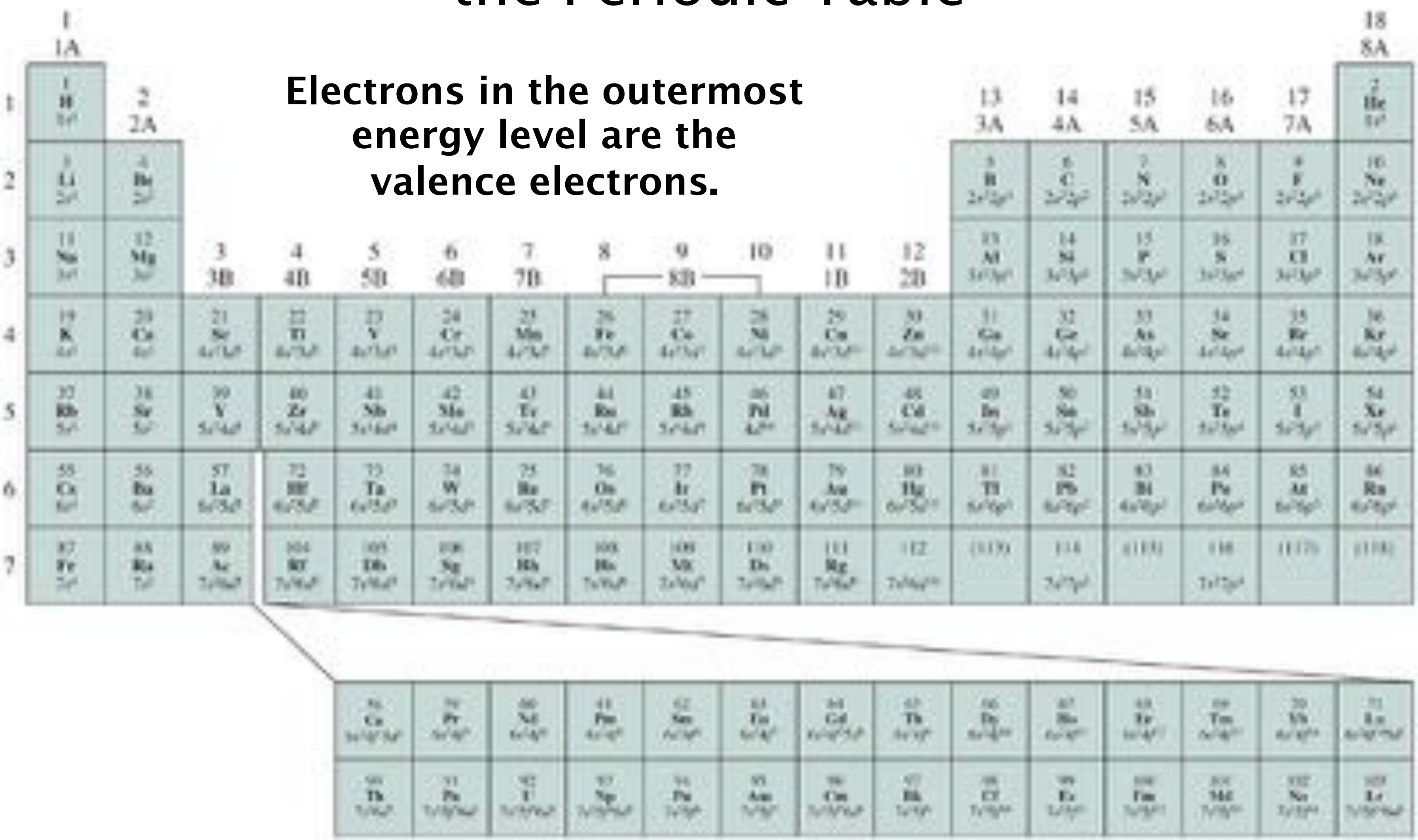
l:

m_l:

m_s:

Electronic Configurations and the Periodic Table

Add 1 electron for each square (ie element) in the Periodic Table



Electrons in the outermost energy level are the valence electrons.