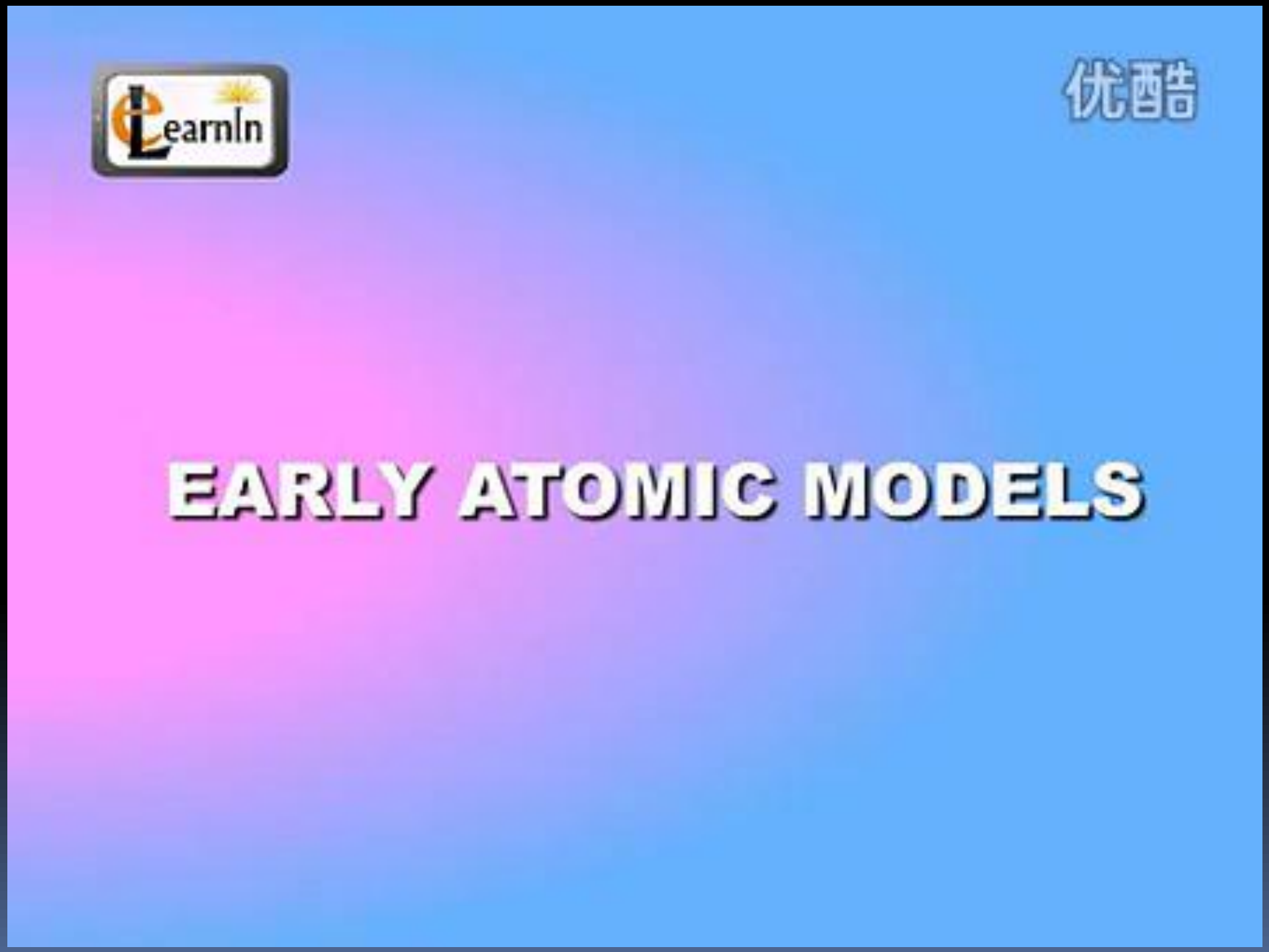
PART 2 – Electronic Structure and the Periodic Table

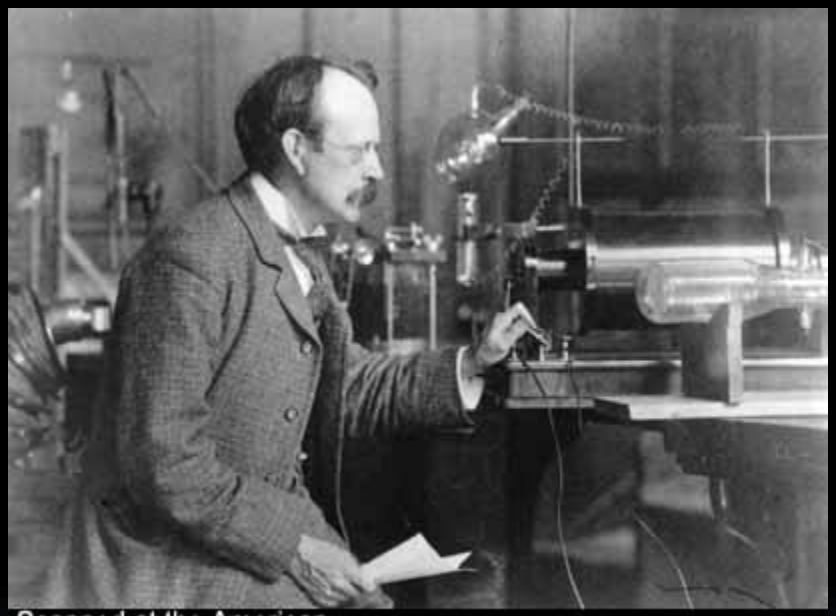
Reference: Chapter 7—8 in textbook

Early Atomic Models



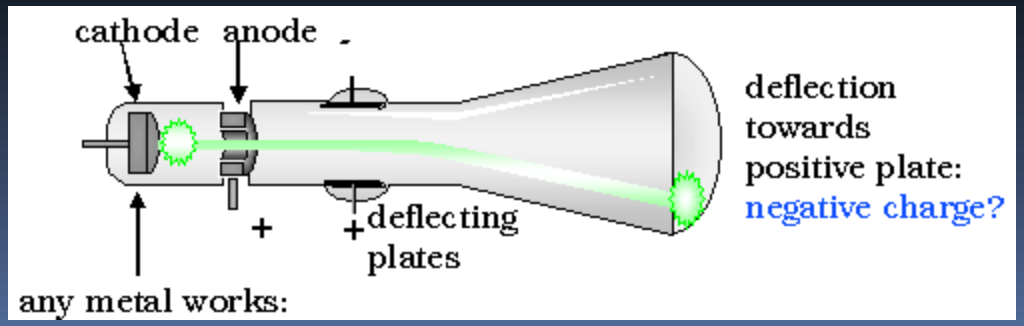
Thomson's 1904 Model of the Atom

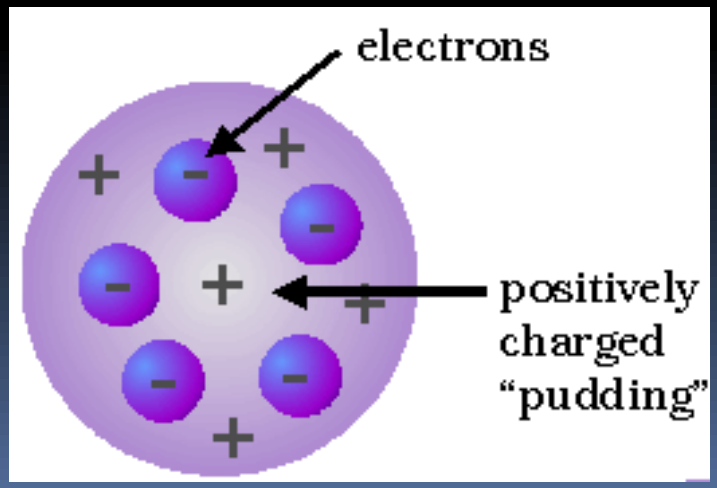
- Plumb Pudding Model



Scanned at the American Institute of Physics

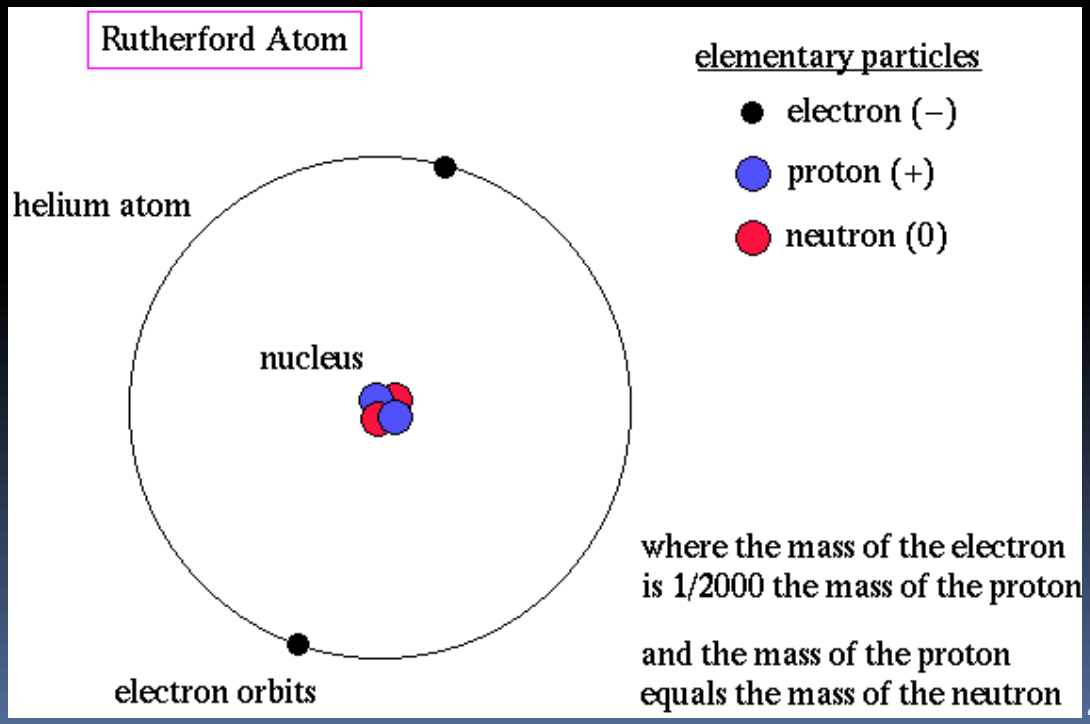
He discovered the electron, a discovery for which he was awarded the Nobel Prize in physics in 1906.



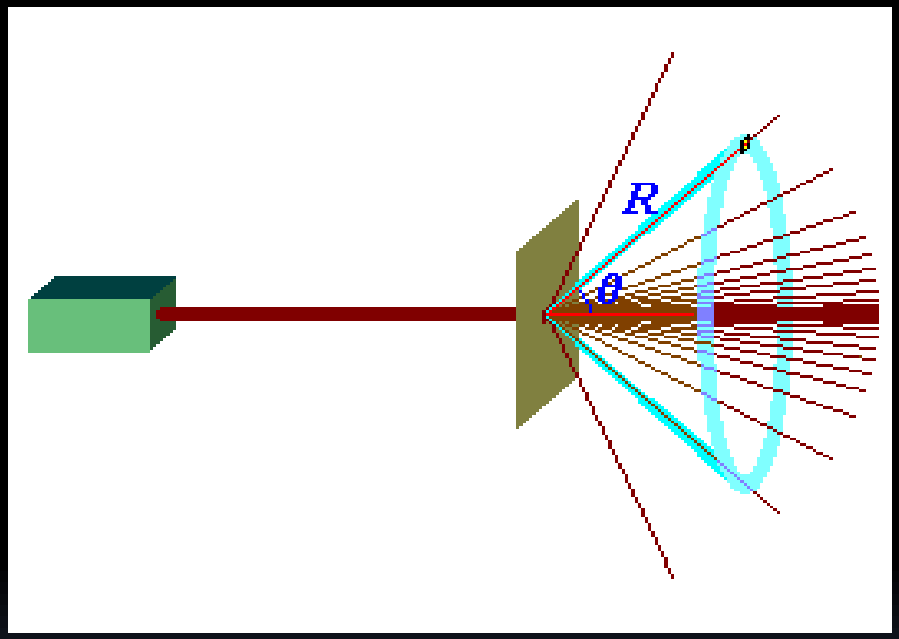


Ernest Rutherford Atom

- Ernest Rutherford is considered the father of nuclear physics. Particles named and characterized by him include the **α** particle, **β** particle and **proton**. Rutherford overturned Thomson's atom model in 1911 with his well-known **gold foil experiment** in which he demonstrated that the atom has a tiny, massive **nucleus**.



Experiment to Discover Atom Structure



α -particle :

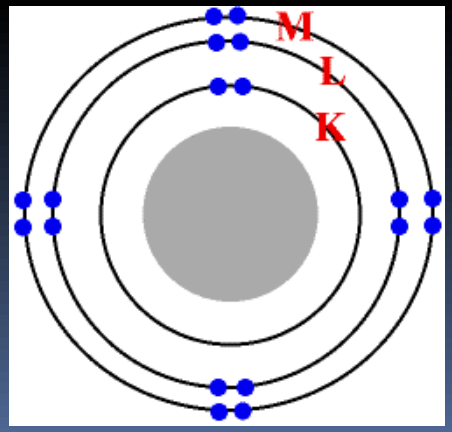
He^{2+}

mass number = 4

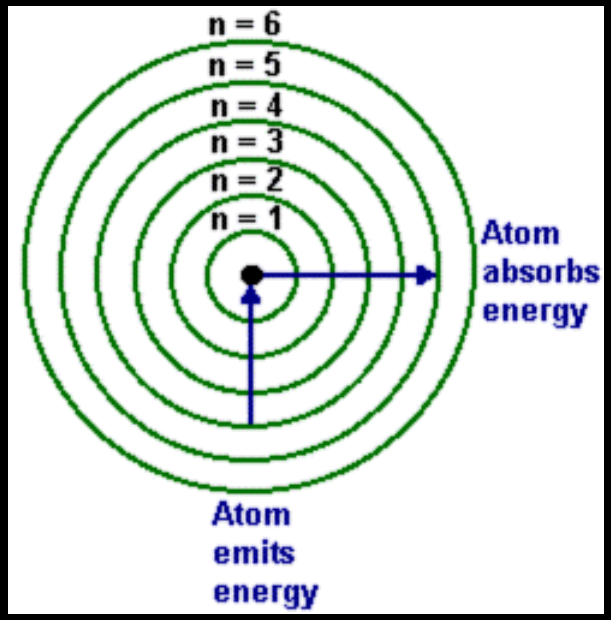
Nucleus and Electron Model

Atomic Structure

- Nucleus – protons and neutrons
  - Proton: 1 unit atomic mass,1 unit positive charge
  - Neutron: 1 unit atomic mass, Neutral (no charge)
- Electrons
  - Electron: little mass, 1 unit negative charge
- Atom and Ion
  - Atom: # protons = # of electrons
  - Ion: Atom gains/loses electron(s)

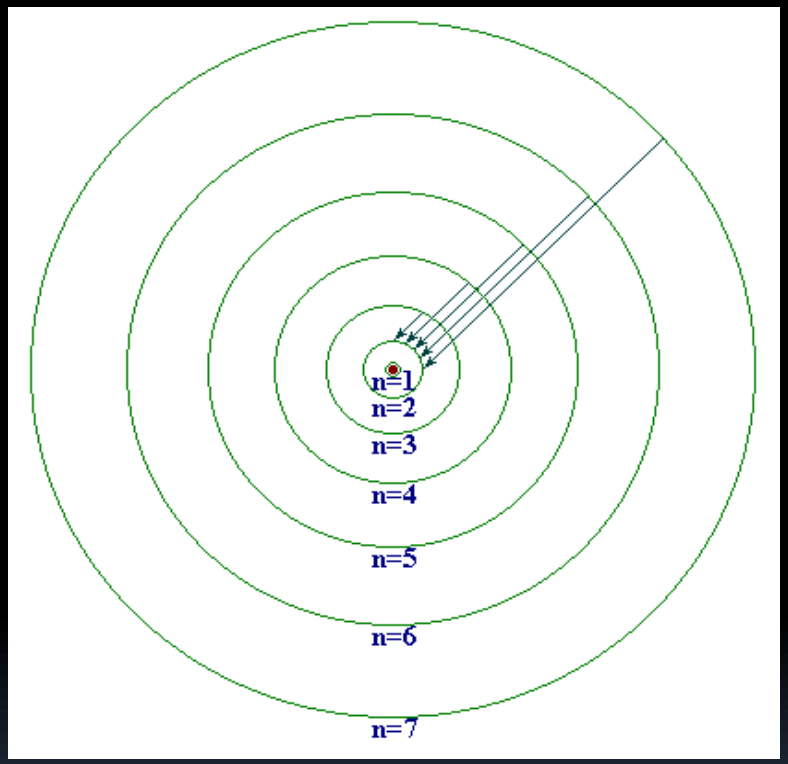


Bohr's Model of Atoms – Incorrect

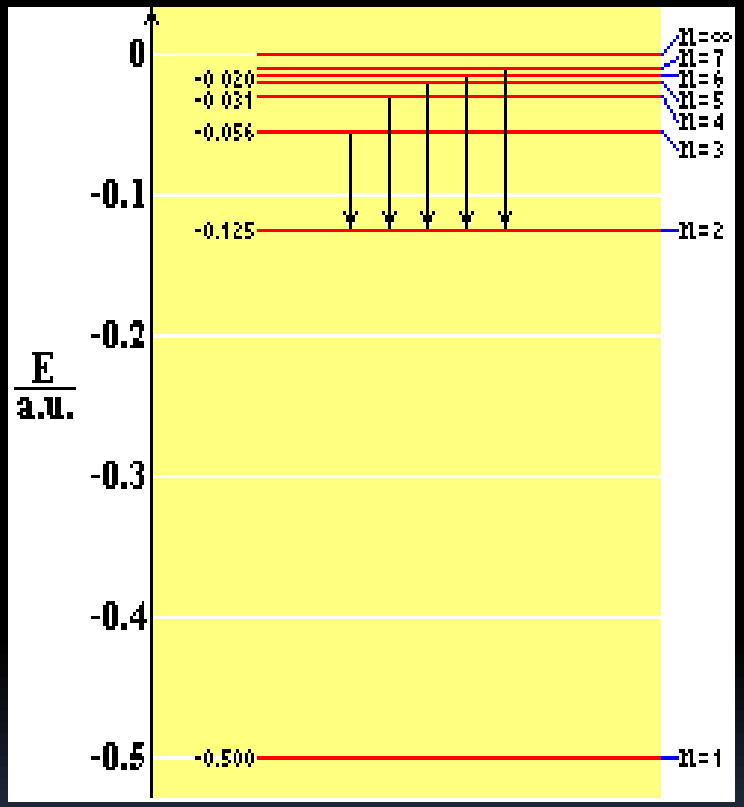


- Bohr's assumptions for e- orbital in an atom:
  - x Electrons are circling around the nucleus.
  - ✓ Electrons only stay in specific orbitals, and need absorb or emit energy when transiting onto another orbital.

Orbitals & Energy States for Hydrogen



Orbital



Energy States

For H-atom, the orbital energy: $E_1 = -13.6$ eV, $E_n = E_1 / n^2$

Periodic Table of Elements

Atomic # / Symbol / Name / Atomic Mass

C Solid
Hg Liquid
H Gas
Rf Unknown

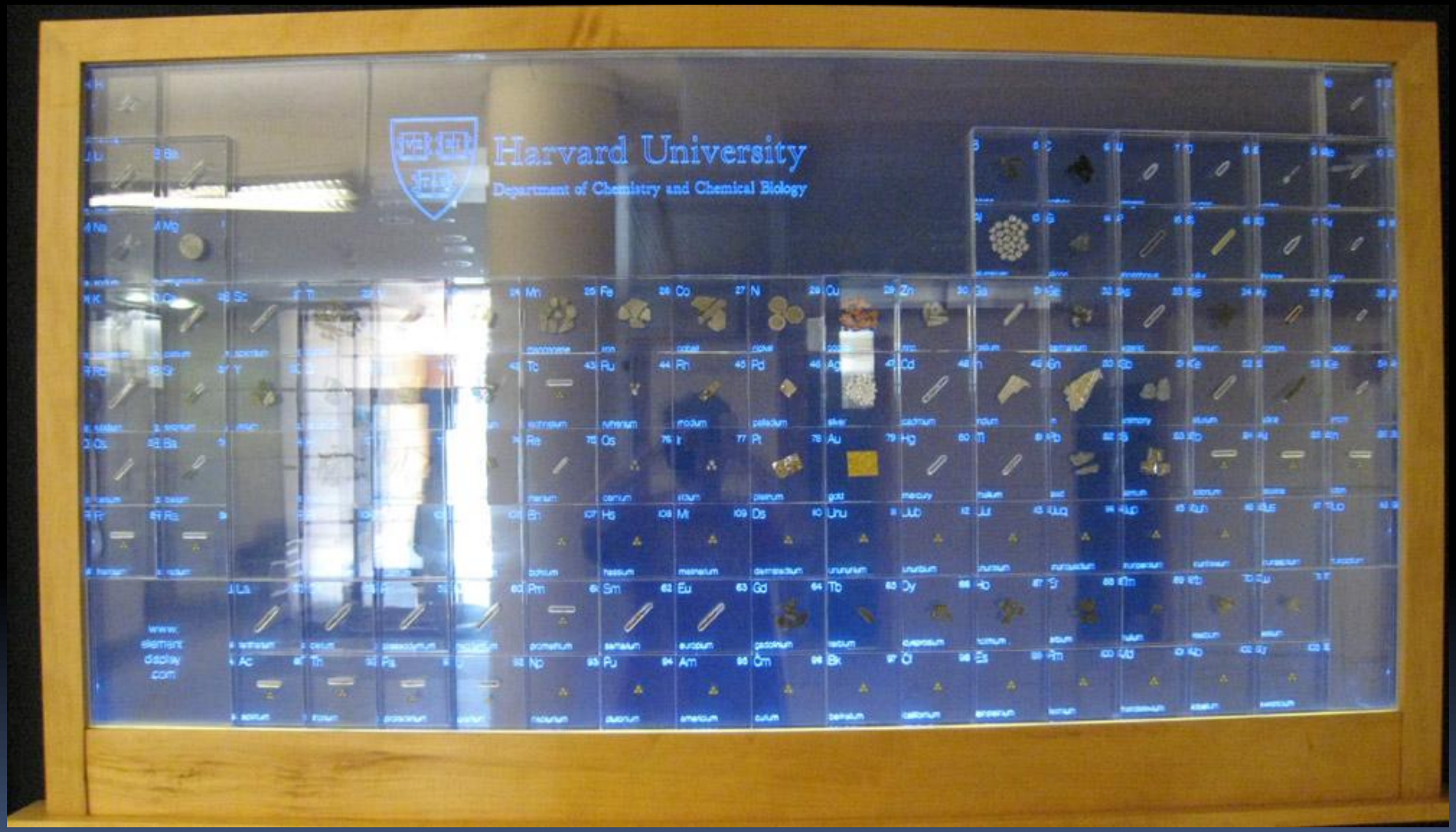
Metals: Alkali metals, Alkaline earth metals, Lanthanoids, Actinoids, Transition metals, Poor metals
Nonmetals: Other nonmetals, Noble gases

	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
1	1 H Hydrogen 1.00794																	2 He Helium 4.002602
2	3 Li Lithium 6.941	4 Be Beryllium 9.012182											5 B Boron 10.811	6 C Carbon 12.0107	7 N Nitrogen 14.0067	8 O Oxygen 15.9994	9 F Fluorine 18.9984032	10 Ne Neon 20.1797
3	11 Na Sodium 22.98976928	12 Mg Magnesium 24.3050											13 Al Aluminium 26.9815386	14 Si Silicon 28.0855	15 P Phosphorus 30.973762	16 S Sulfur 32.065	17 Cl Chlorine 35.453	18 Ar Argon 39.948
4	19 K Potassium 39.0983	20 Ca Calcium 40.078	21 Sc Scandium 44.955912	22 Ti Titanium 47.867	23 V Vanadium 50.9415	24 Cr Chromium 51.9961	25 Mn Manganese 54.938045	26 Fe Iron 55.845	27 Co Cobalt 58.933195	28 Ni Nickel 58.6934	29 Cu Copper 63.546	30 Zn Zinc 65.38	31 Ga Gallium 69.723	32 Ge Germanium 72.64	33 As Arsenic 74.92160	34 Se Selenium 78.96	35 Br Bromine 79.904	36 Kr Krypton 83.798
5	37 Rb Rubidium 85.4678	38 Sr Strontium 87.62	39 Y Yttrium 88.90585	40 Zr Zirconium 91.224	41 Nb Niobium 92.90638	42 Mo Molybdenum 95.96	43 Tc Technetium (97.9072)	44 Ru Ruthenium 101.07	45 Rh Rhodium 102.90550	46 Pd Palladium 106.42	47 Ag Silver 107.8682	48 Cd Cadmium 112.411	49 In Indium 114.818	50 Sn Tin 118.710	51 Sb Antimony 121.760	52 Te Tellurium 127.60	53 I Iodine 126.90447	54 Xe Xenon 131.293
6	55 Cs Caesium 132.9054519	56 Ba Barium 137.327	57–71	72 Hf Hafnium 178.49	73 Ta Tantalum 180.94788	74 W Tungsten 183.84	75 Re Rhenium 186.207	76 Os Osmium 190.23	77 Ir Iridium 192.217	78 Pt Platinum 195.084	79 Au Gold 196.966569	80 Hg Mercury 200.59	81 Tl Thallium 204.3833	82 Pb Lead 207.2	83 Bi Bismuth 208.98040	84 Po Polonium (208.9824)	85 At Astatine (209.9871)	86 Rn Radon (222.0176)
7	87 Fr Francium (223)	88 Ra Radium (226)	89–103	104 Rf Rutherfordium (261)	105 Db Dubnium (262)	106 Sg Seaborgium (266)	107 Bh Bohrium (264)	108 Hs Hassium (277)	109 Mt Meitnerium (268)	110 Ds Darmstadtium (271)	111 Rg Roentgenium (272)	112 Uub Ununbium (285)	113 Uut Ununtrium (284)	114 Uuq Ununquadium (289)	115 Uup Ununpentium (288)	116 Uuh Ununhexium (292)	117 Uus Ununseptium	118 Uuo Ununoctium (294)

For elements with no stable isotopes, the mass number of the isotope with the longest half-life is in parentheses.

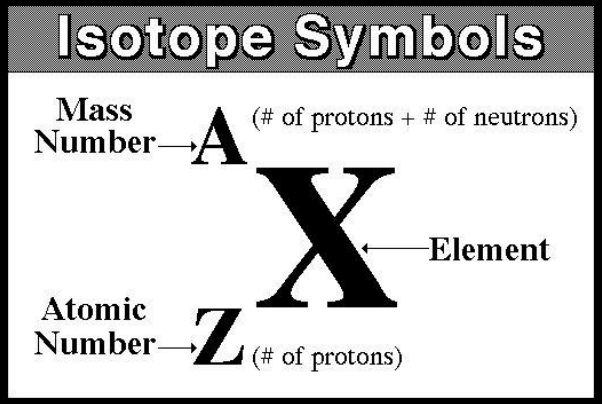
57 La Lanthanum 138.90547	58 Ce Cerium 140.116	59 Pr Praseodymium 140.90765	60 Nd Neodymium 144.242	61 Pm Promethium (145)	62 Sm Samarium 150.36	63 Eu Europium 151.964	64 Gd Gadolinium 157.25	65 Tb Terbium 158.92535	66 Dy Dysprosium 162.500	67 Ho Holmium 164.93032	68 Er Erbium 167.259	69 Tm Thulium 168.93421	70 Yb Ytterbium 173.054	71 Lu Lutetium 174.9668
89 Ac Actinium (227)	90 Th Thorium 232.03806	91 Pa Protactinium 231.03588	92 U Uranium 238.02891	93 Np Neptunium (237)	94 Pu Plutonium (244)	95 Am Americium (243)	96 Cm Curium (247)	97 Bk Berkelium (247)	98 Cf Californium (251)	99 Es Einsteinium (252)	100 Fm Fermium (257)	101 Md Mendelevium (258)	102 No Nobelium (259)	103 Lr Lawrencium (262)

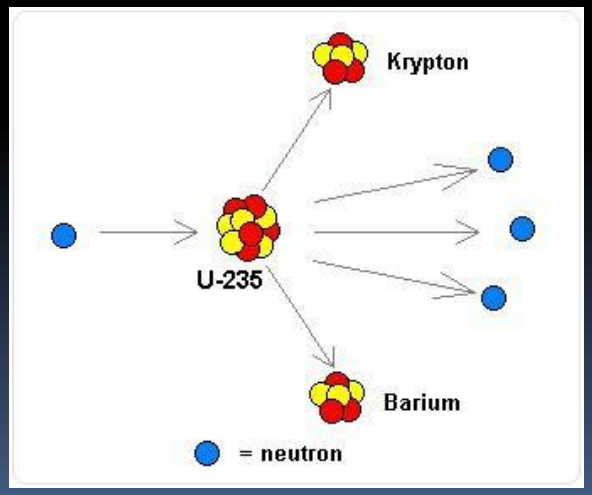
A “real” Periodic Table



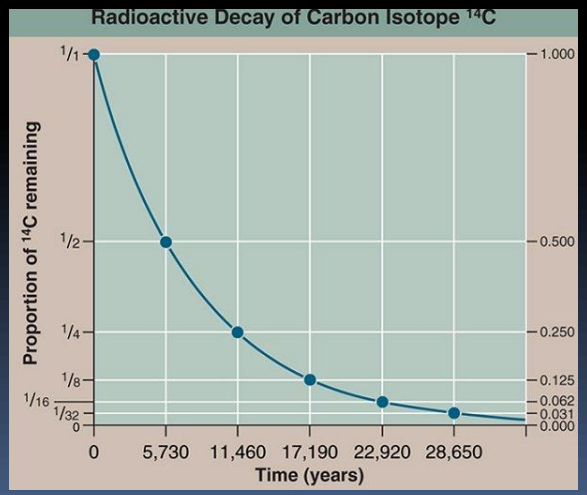
Isotope

- Isotope
  - same protons, different neutrons
  - Q: ^{3}H, ^{14}C, ^{31}P, ^{238}U
  - the use of isotopes in science/technology





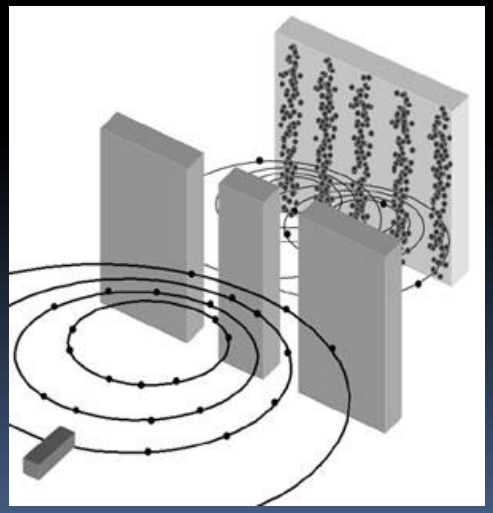
Nuclear power plant

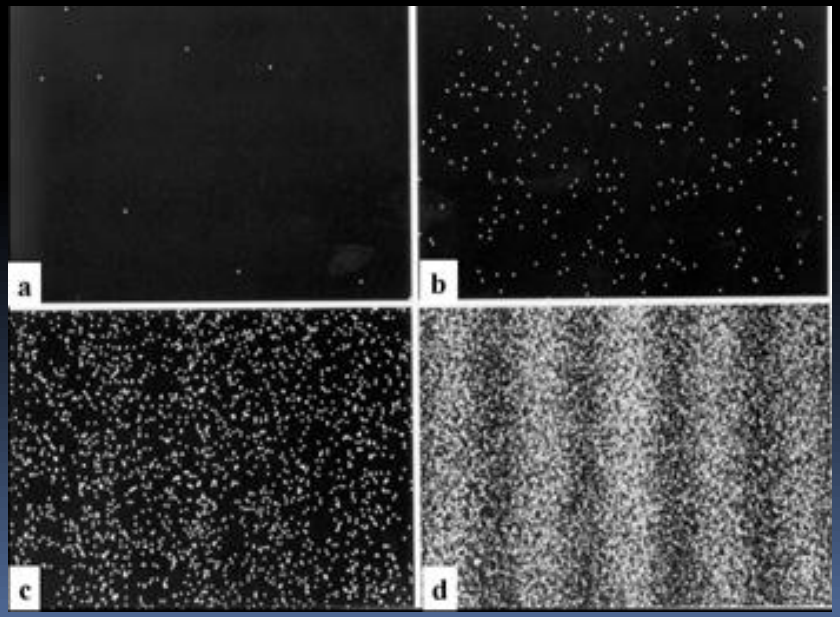


Archaeology

Wave-Particle Duality

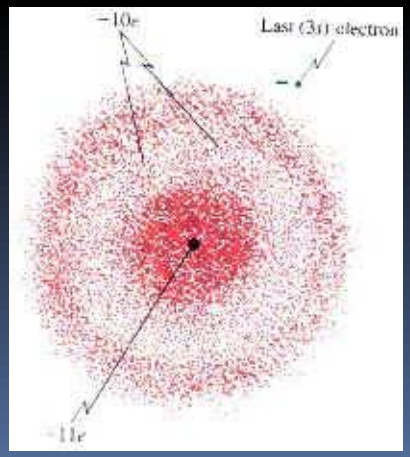
- Any material (e.g. light, electron) is both a particle and a wave.
- Wave function (ψ), and probability density
- Energy of a wave



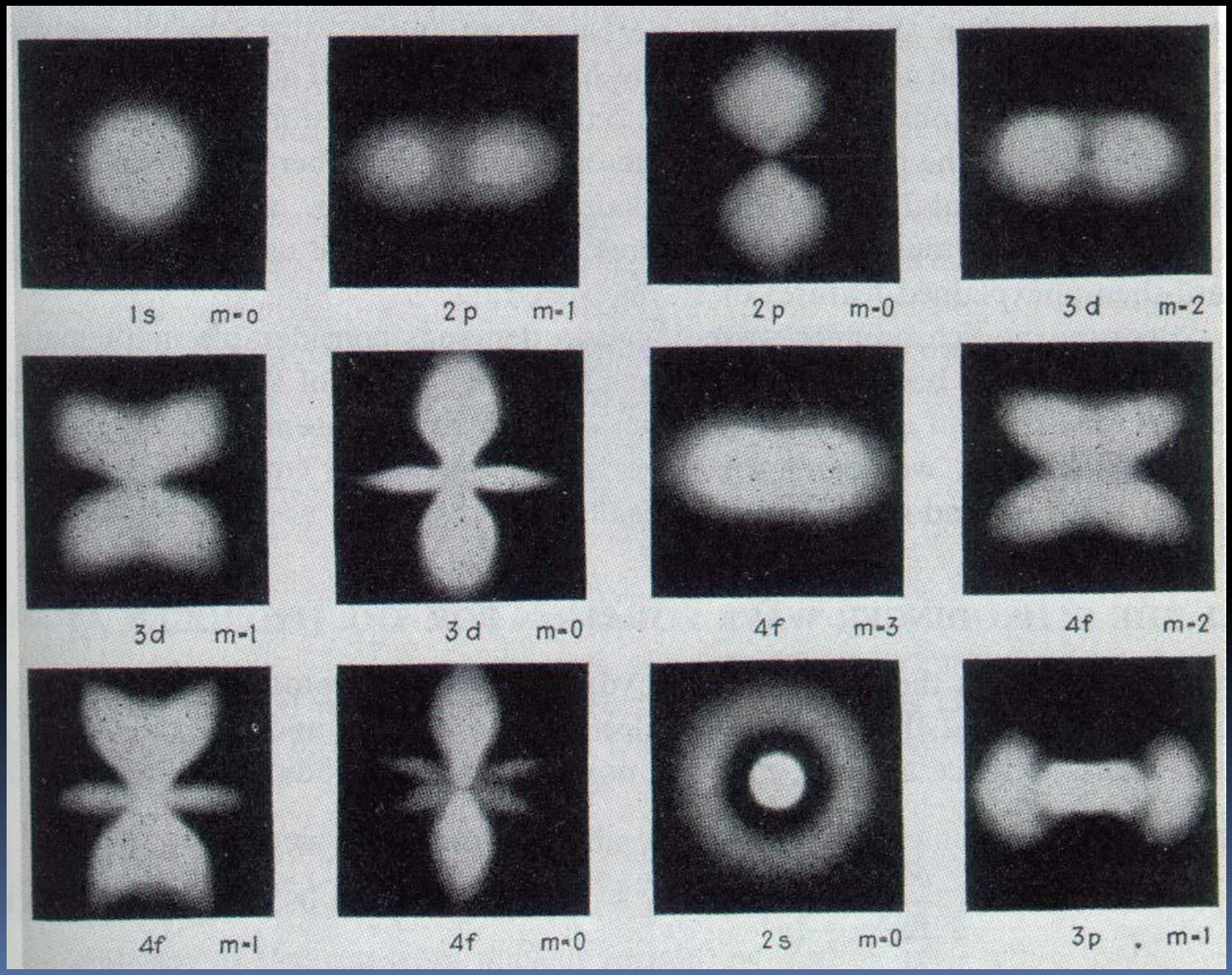


Electron Cloud

- Electron cloud
  - The uncertainty principle: $\Delta x * \Delta p > h/2\pi$
    - Example: why position and momentum cannot be accurately measured?
  - Electron cloud: a region where electrons are likely to be found.
- Atomic orbital



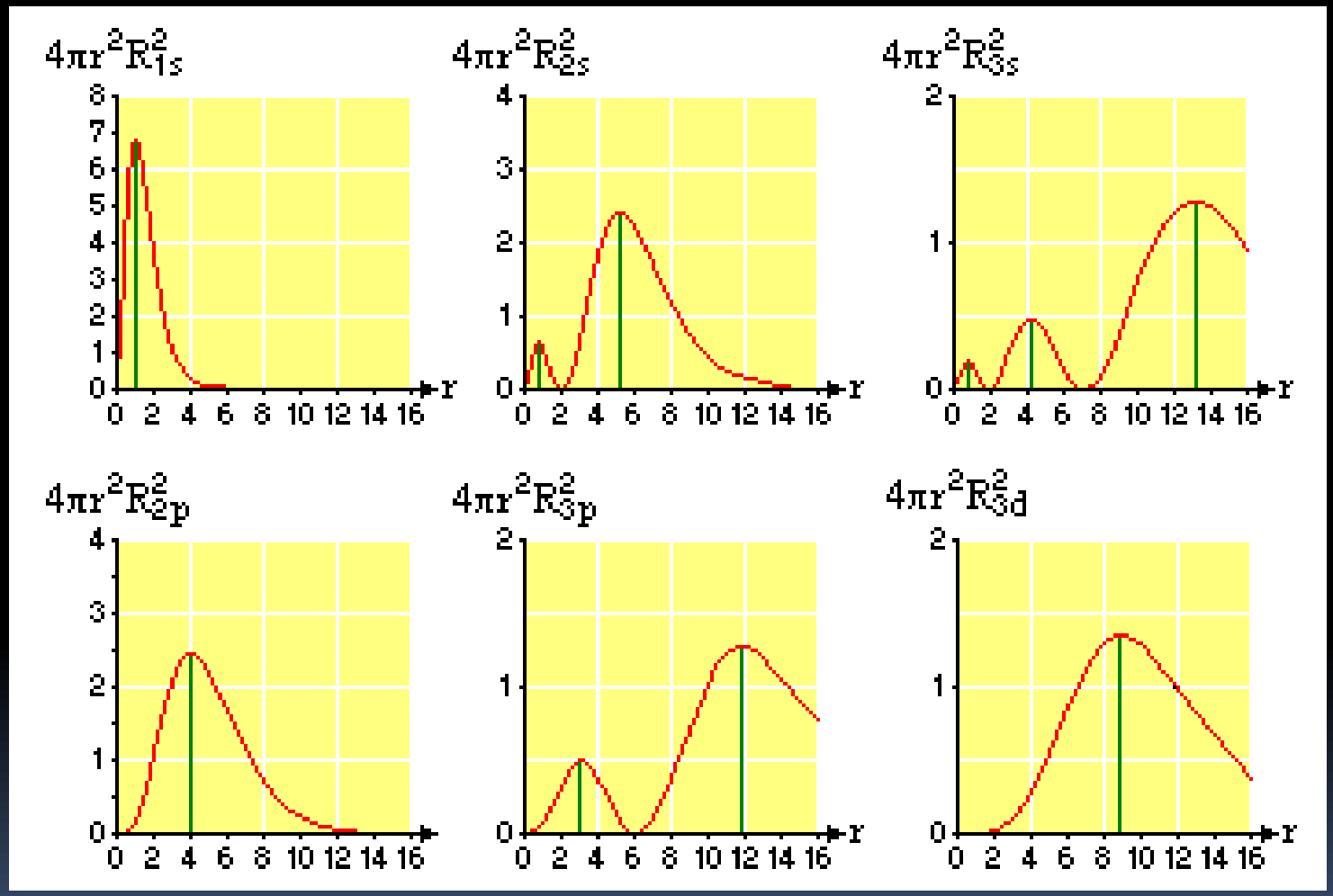
Atomic Orbitals



Electron Configuration

- Atomic orbitals
  - the probability of an electron's position and energy
- 4 Quantum numbers
  - n (Principal): 1, 2, 3, 4, …
  - l (Angular momentum): 0, 1, 2, 3, …, n-1
    - s (l = 0), p (l = 1), d (l = 2), f (l = 3), …
  - m (Magnetic): 0, ± 1, ± 2, …, $\pm l$
  - m_s (Spin): $\pm 1/2$

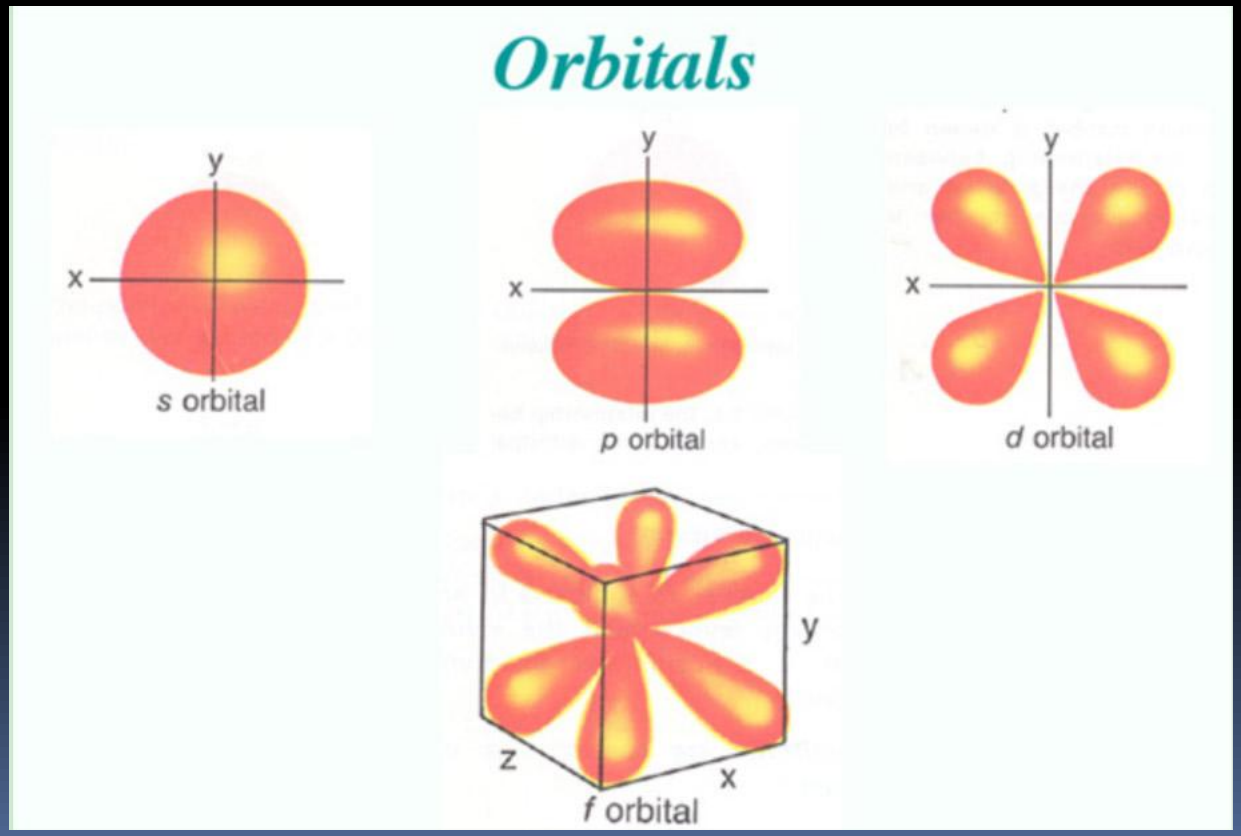
Atomic Orbitals: Radial Distribution



The radial distribution of an atomic orbital represents the probability of finding an electron in a certain distance from the nucleus.

Atomic Orbitals: Angular Distribution

- Shape of an orbital represents the probability of finding electrons:



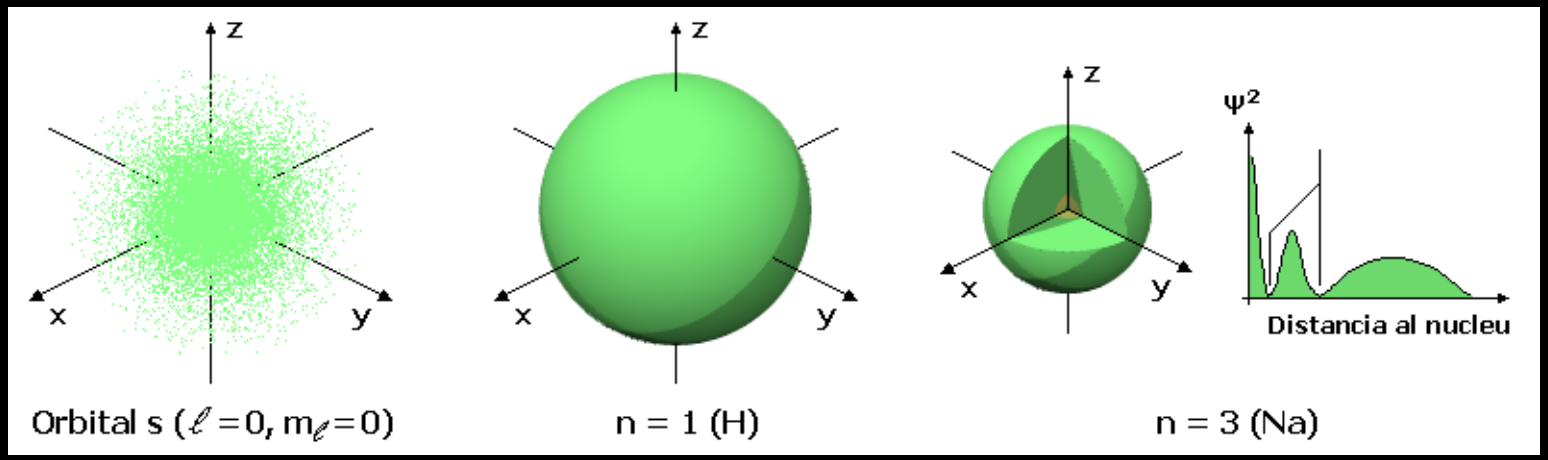
Electron Configuration – contl'd

- Total # of orbitals is n^2, (for principal quantum number of n).
  - n = 1 → l = 0 (1 s orbital): 1s
  - n = 2 → l = 0 (1 s orbital), 1 (3 p orbitals): 2s, $2p_x$, $2p_y$, $2p_z$
  - n = 3 → l = 0 (1 s orbital), 1 (3 p orbitals), 2 (5 d oribitals): 3s, $3p_x$, $3p_y$, $3p_z$, $3d_{xy}$, $3d_{xz}$, $3d_{yz}$, $3d_{x2-y2}$, $3d_{z2}$

n	*l*	m_l	*orbital*	*# of orbitals in subshell*	*Total # of orbitals*
1	0	0	1s	1	1
2	0	0	2s	1	4
	1	1,0,-1	2p	3	
3	0	0	3s	1	9
	1	1,0,-1	3p	3	
	2	2,1,0,-1,-2	3d	5	
4	0	0	4s	1	16
	1	1,0,-1	4p	3	
	2	2,1,0,-1,-2	4d	5	
	3	3,2,1,0,-1,-2,-3	4f	7	

s- Orbital

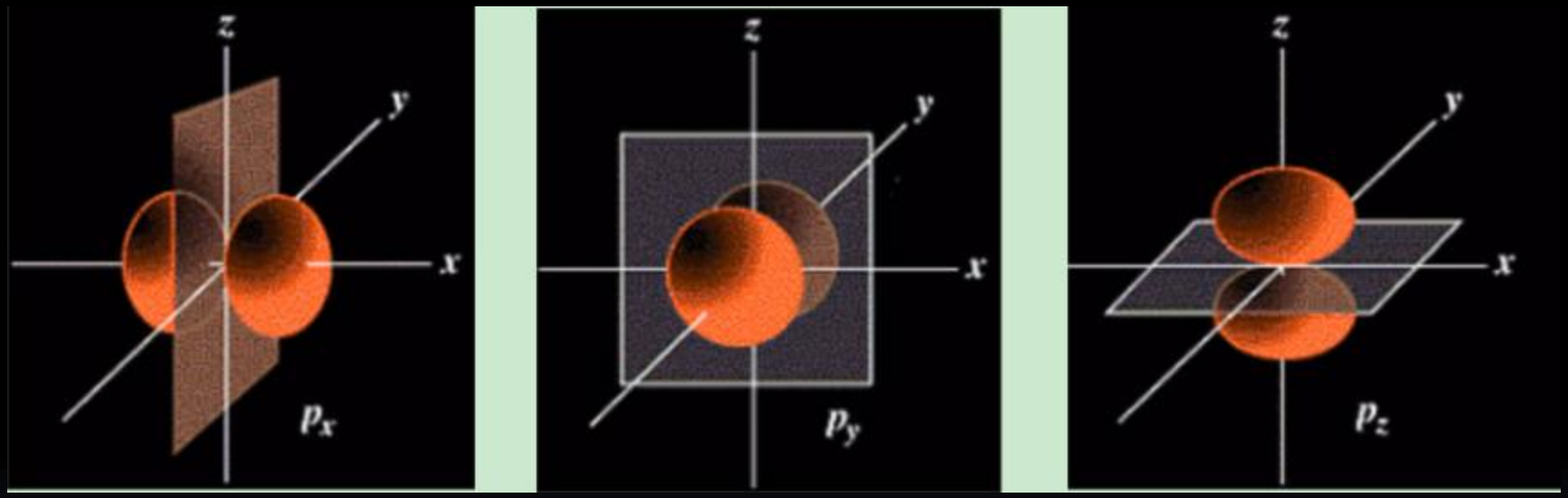
- s-orbital: center symmetric



  - Number of “node” (zero-electron-density region) = ?

p- Orbital

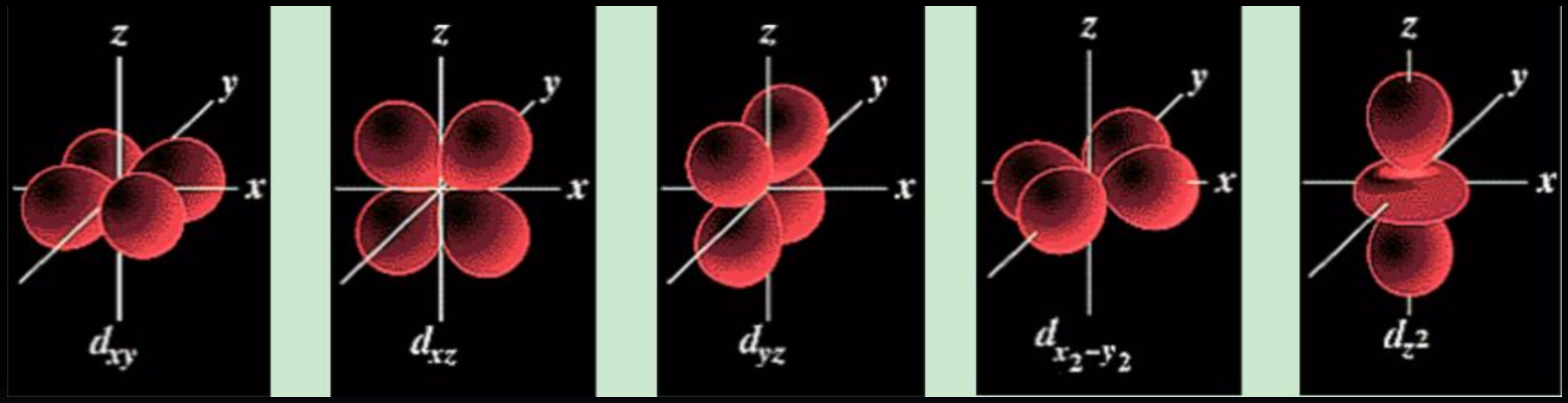
- p-orbital: axial symmetric



  - Which axis is the symmetric axis?
  - Number of “node” = ?
  - Which axis has node?

d- Orbital

- d-orbital: center symmetric



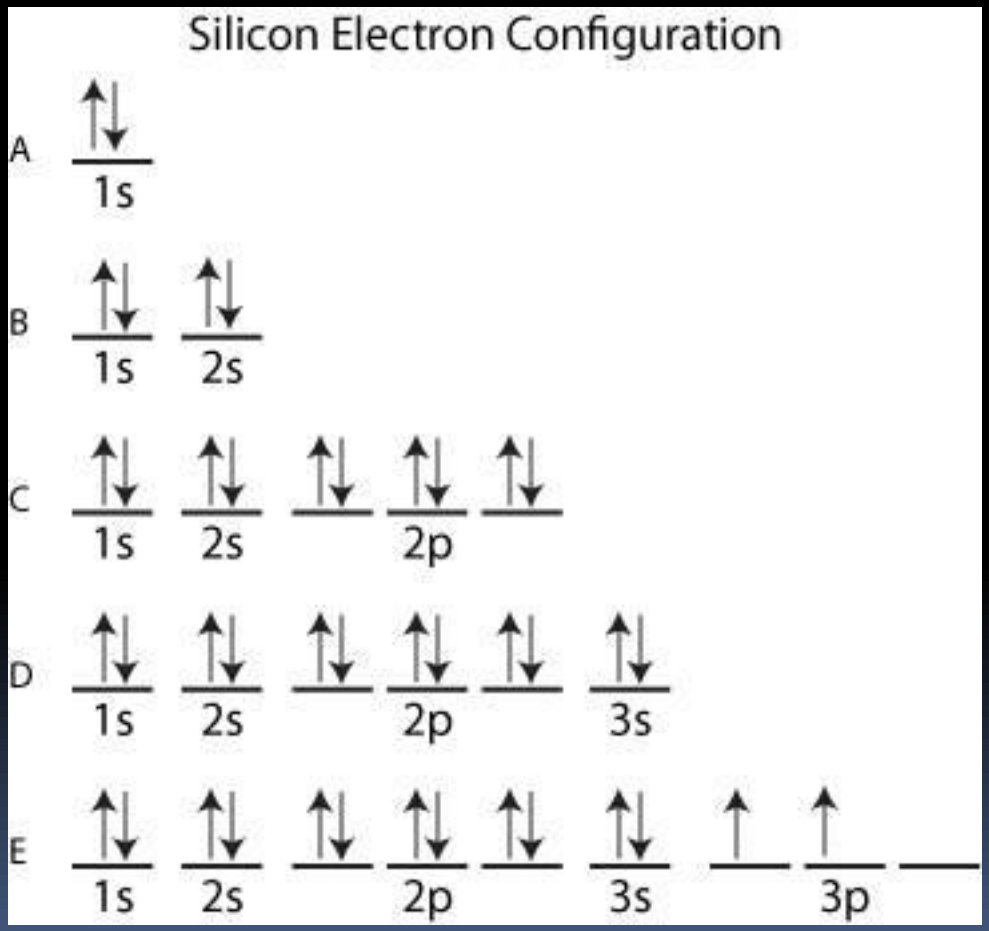
  - Which axis is the symmetric axis?
  - Number of “node” = ?

Electron Configuration – contl'd

- Pauli exclusion principle
  - in each orbital, one electron spins up, and the other spins down.
- Electrons are filled from low energy orbital (state) to high energy orbital (state).
  - the higher n and l → the higher energy (<u>NOT always true !!</u>)
- Full shell and Half-full shell are normally stable

How to Fill in Electrons in Orbitals

- Use the Periodic table as a guide (Pg. 271):
  - Add e to ns orbital when in IA and IIA;
  - Add e to np orbital when in IIIA and IIIB;
  - Add e to (n-1)d orbital when in IIIB – IIB.



Examples

Electron Configurations of Several Lighter Elements

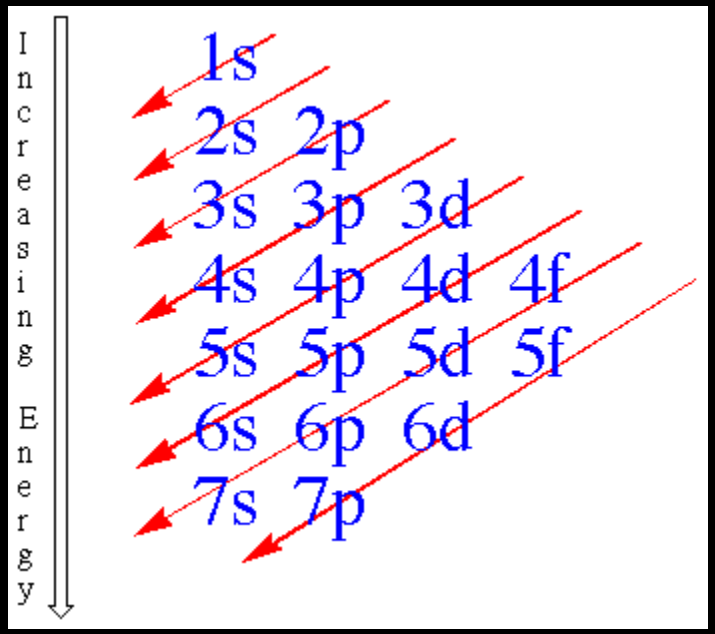
Element	Total Electrons	Obital Diagram 1s	2s	2p			3s	Electron Configuration
Li	3	↑↓	↑					$1s^2 2s^1$
Be	4	↑↓	↑↓					$1s^2 2s^2$
B	5	↑↓	↑↓	↑				$1s^2 2s^2 2p^1$
C	6	↑↓	↑↓	↑	↑			$1s^2 2s^2 2p^2$
N	7	↑↓	↑↓	↑	↑	↑		$1s^2 2s^2 2p^3$
NE	10	↑↓	↑↓	↑↓	↑↓	↑↓		$1s^2 2s^2 2p^6$
Na	11	↑↓	↑↓	↑↓	↑↓	↑↓	↑	$1s^2 2s^2 2p^6 3s^1$

Ne (10 e) → $1s^2\ 2s^2\ 2p_x^2\ 2p_y^2\ 2p_z^2$, (or $1s^2\ 2s^2\ 2p^6$)

P (15 e) → $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p_x^1\ 3p_y^1\ 3p_z^1$

K (19 e) → $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^1$ (NOT: $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^1$)

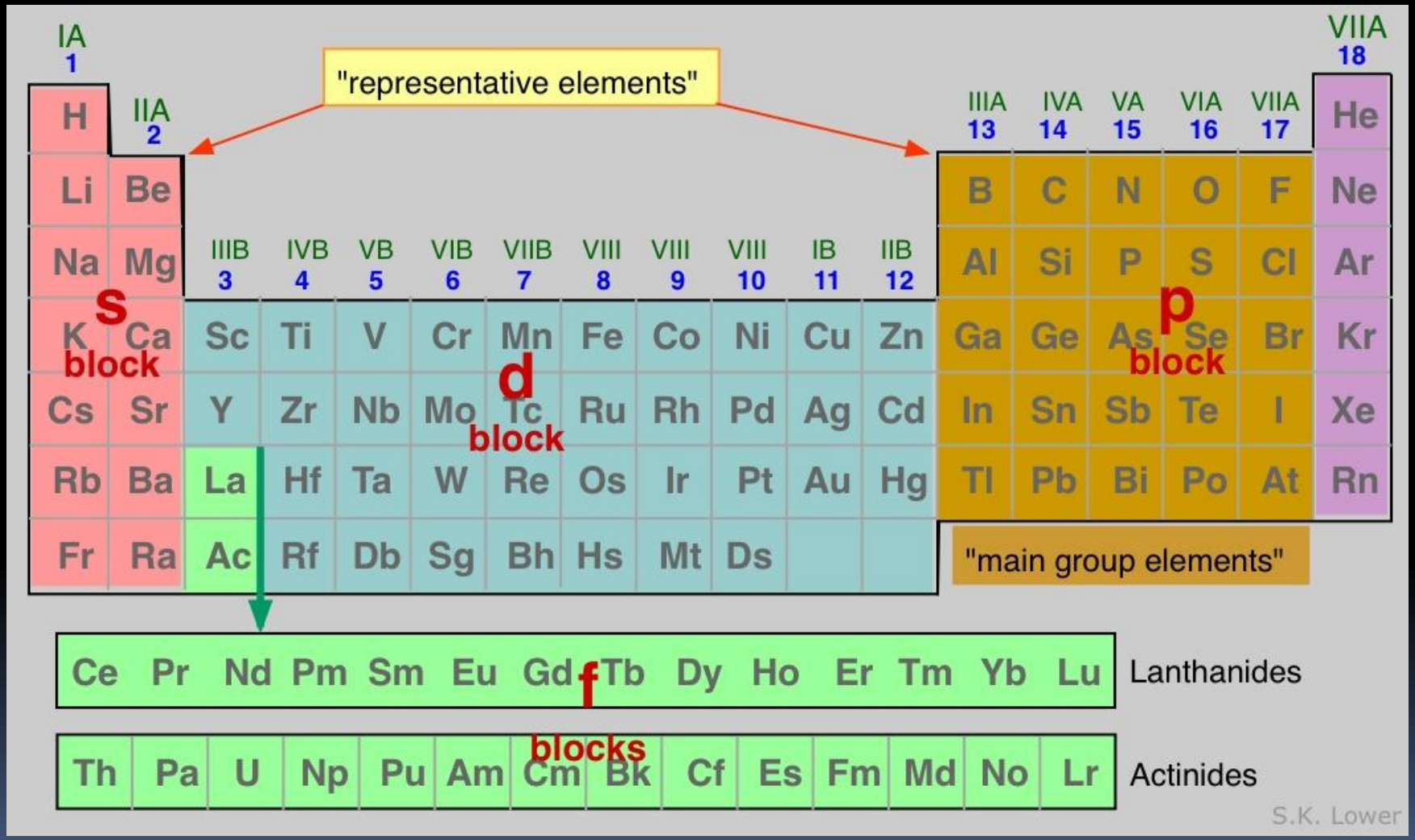
Another Helpful Diagram



- Use this diagram as a guide for writing orbitals (from lower energy to higher energy)

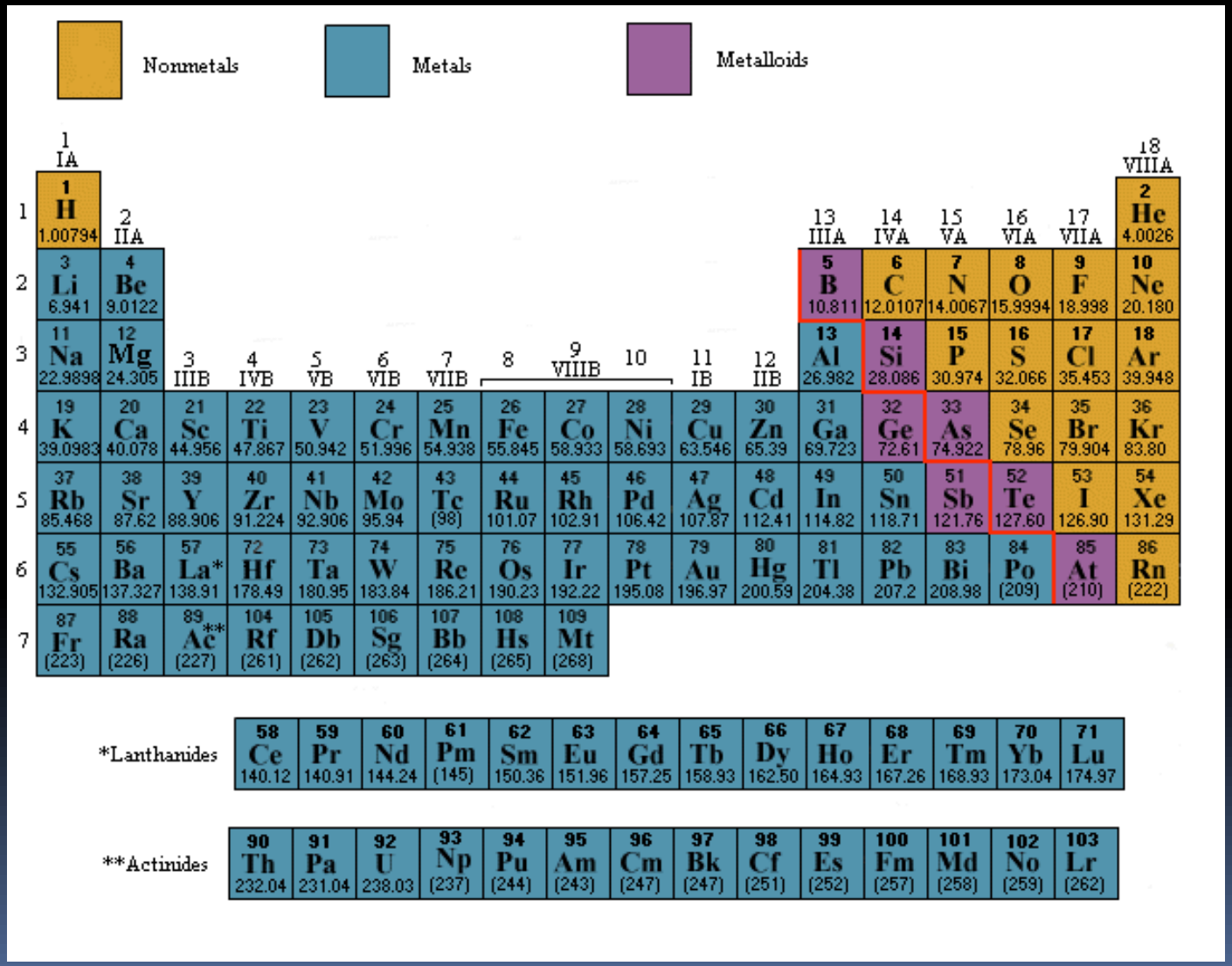
- K:
- Ca:
- Sc (21e):

Electron Configuration in Periodic Table



Different "blocks" represent where the last electron is filled in.

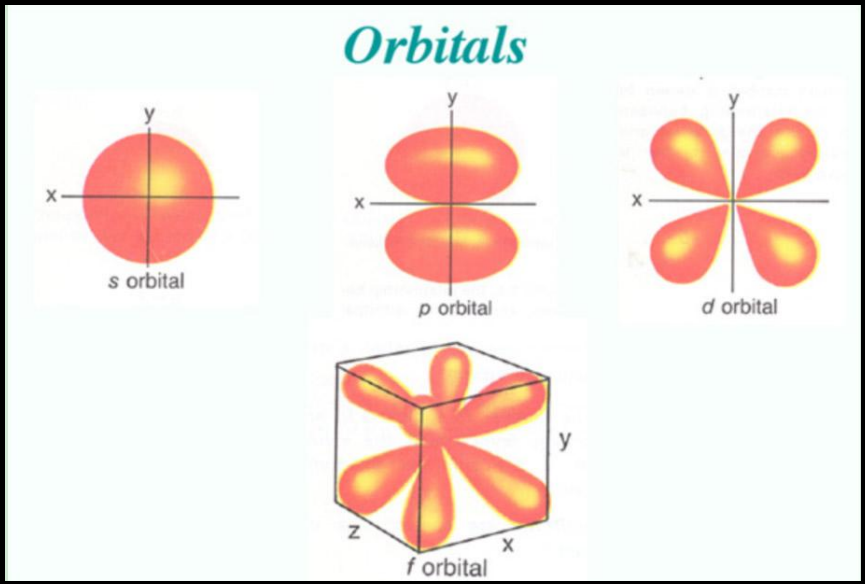
Main Groups, Metals & Non-metals



Main Groups in Periodic Table

- Main group: designated as Group IA, IIA, IIIA, …, VIA, VIIA, and VIIIA (0).
  - The number represents how many electrons are in the outmost shell.
  - IA and IIA are active metals; VIA and VIIA are active non-metals; IIIA, IVA, VA are continuously changing from metal to non-metal.

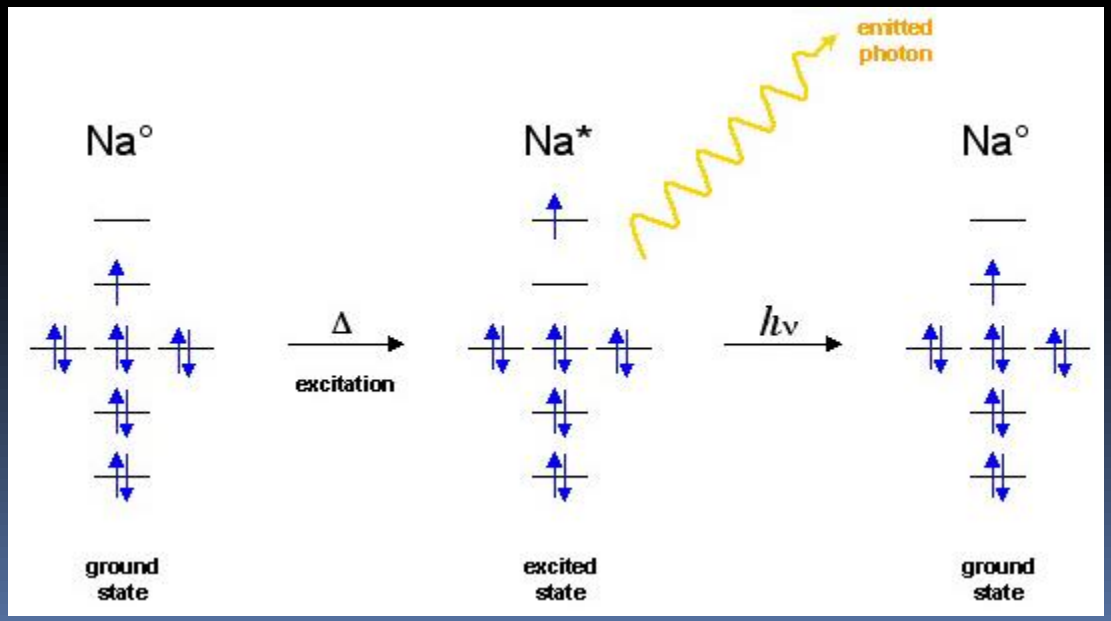
Picture of the Atomic Orbitals



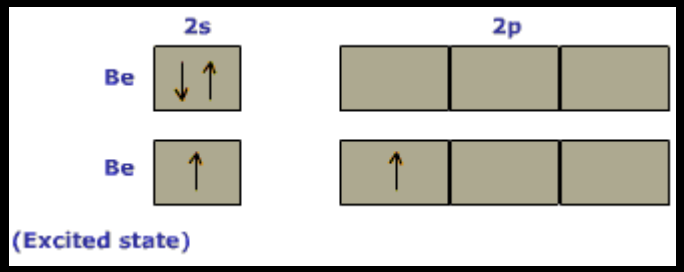
- In each “Shell” – principal quantum number n, there are different sets of orbitals, which have different shape, symmetry, and energy.
- Electrons need to absorb energy (e.g. from a photon) to transit from a lower energy state to a higher one, or emit energy (by emitting a photon) to transit from a higher energy state to a lower one.

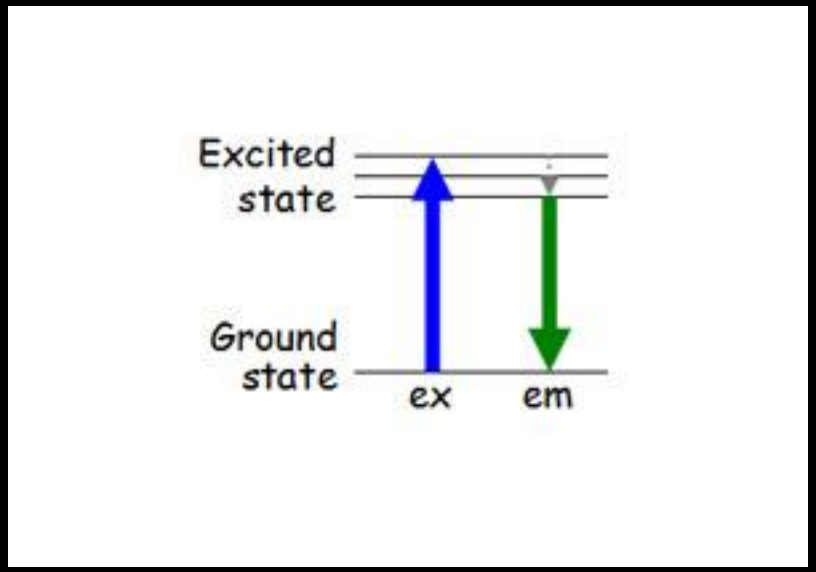
Electron's States

- Electron's states: sets of electron configurations, related to different energy.
- Ground State – a set w/ the lowest energy configuration.
- Excited State(s) – sets of higher energy.



Simplified Drawing – only last e^-

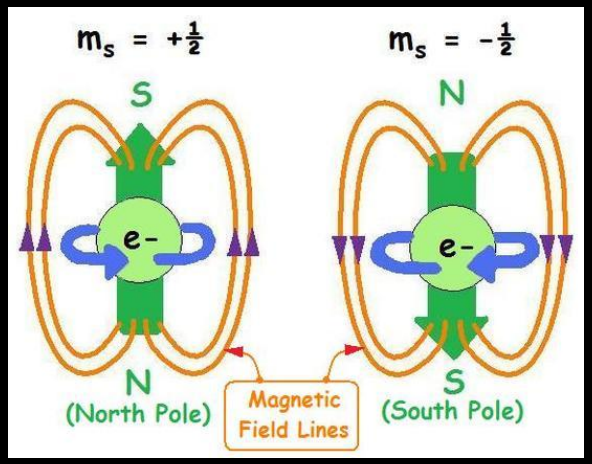




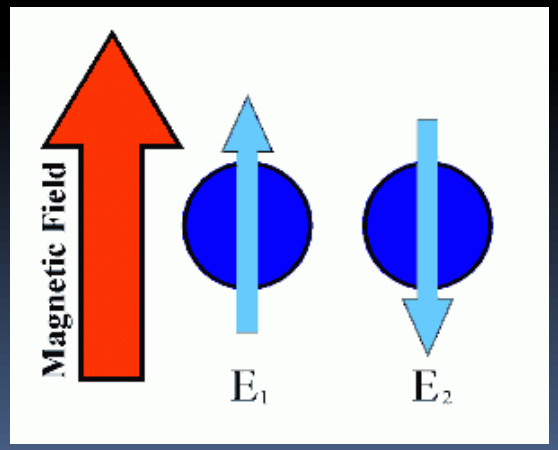
- For the first a few excited states, we only need to pay attention to the last electron (the one in the highest energy orbital).

Magnetic Quantum Number and Spin

- Magnetic Quantum Number
  - For electrons, m_s (Spin): $\pm 1/2$



- Electron spin
  - Equal energy when **M-**field is off.
  - Magnetism of materials.

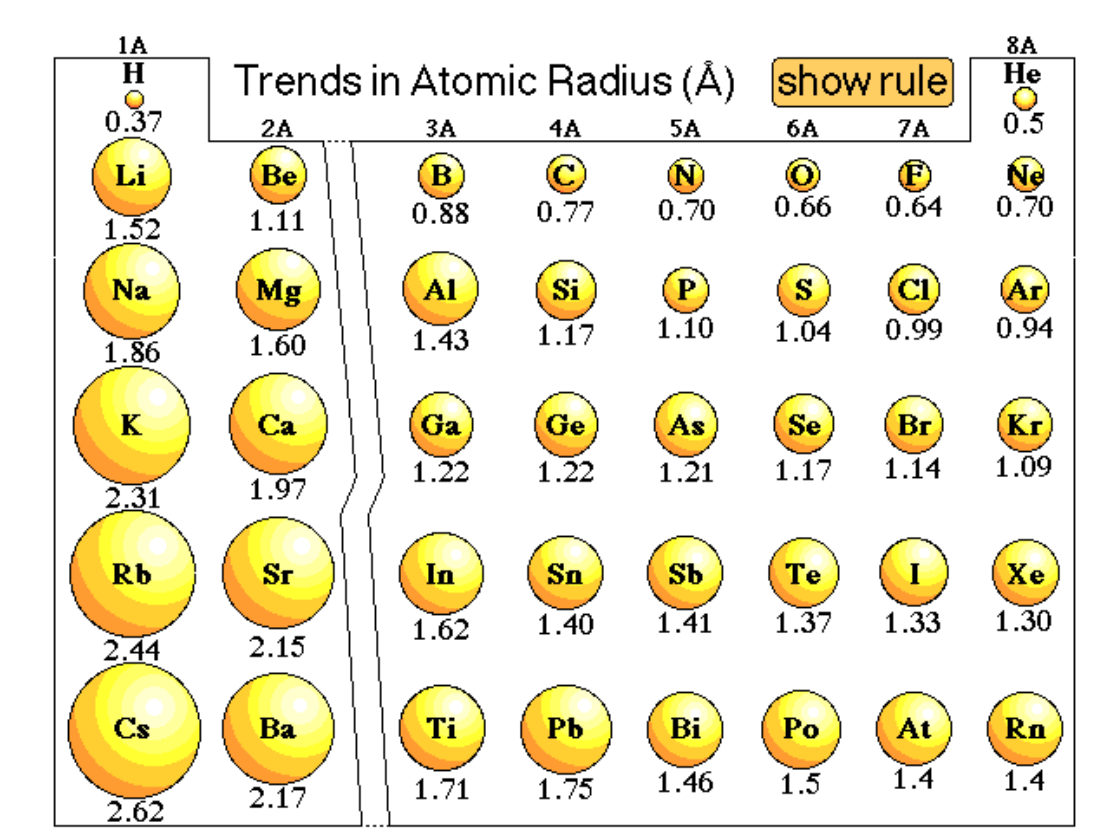


Unpaired Electrons and Magnetism

- Unpaired electron in atom
  - Q: Which of the following atom(s) has unpaired electron(s): (a) C; (b) O; (c) Mg; (d) K.
  - Atoms with unpaired electrons will respond to the external magnetic field
- Paramagnetic
  - Molecules or atoms that have unpaired electrons
- Diamagetic
  - Molecules or atoms that do not have unpaired electrons

Atomic Radii

- Atomic radius



  - From left to right, atomic radius decreases.
  - From up to down, atomic radius increase.

Ionic Radii

- Ionic radius
  - Cations are smaller than their original atoms;
    - e.g. $Na^{+} < Na$, $Ca^{2+} < Ca$
  - Anions are larger than their original atoms;
    - e.g. $O^{2-} > O$, $Cl^{-} > Cl$
  - For isoelectronic, the higher the nuclear charge, the smaller the radius.
    - e.g. $O^{2-} > F^{-} > Ne > Na^{+} > Mg^{2+} > Al^{3+}$

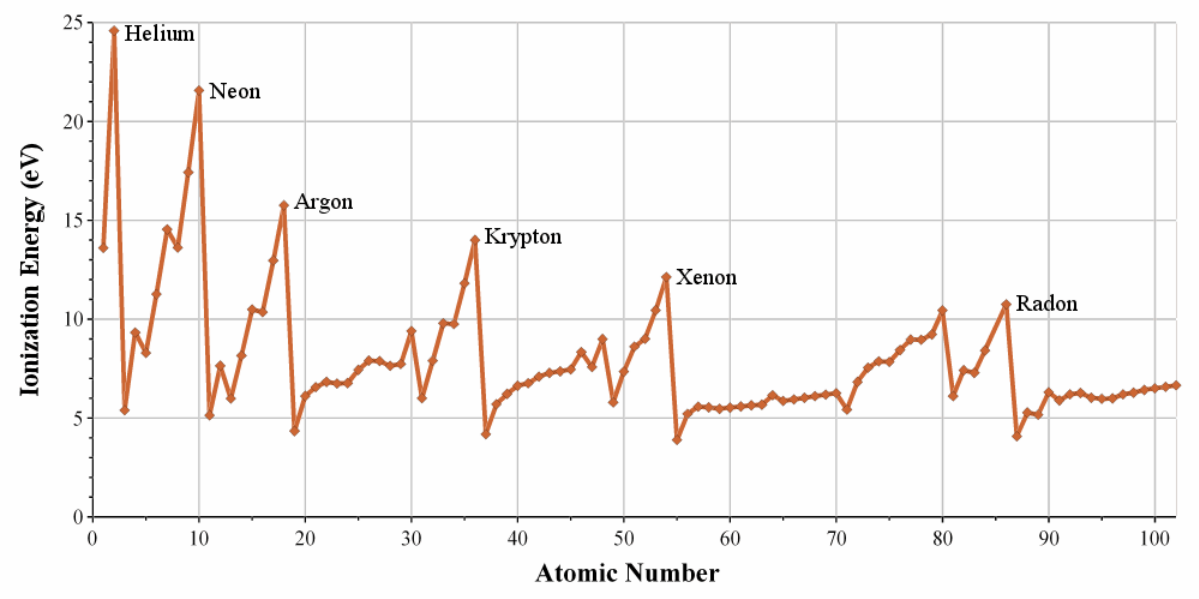
Question

- (1) Place the following ions in order of increasing ionic radius: S^{2-}, Cl^{-}, P^{3-}.

- (2) Which ion of each set has larger radius: (a) Ca^{2+}, Ba^{2+}; (b) As^{3-}, Se^{2-}; (c) Sn^{2+}, Sn^{4+}.

Ionization Energy

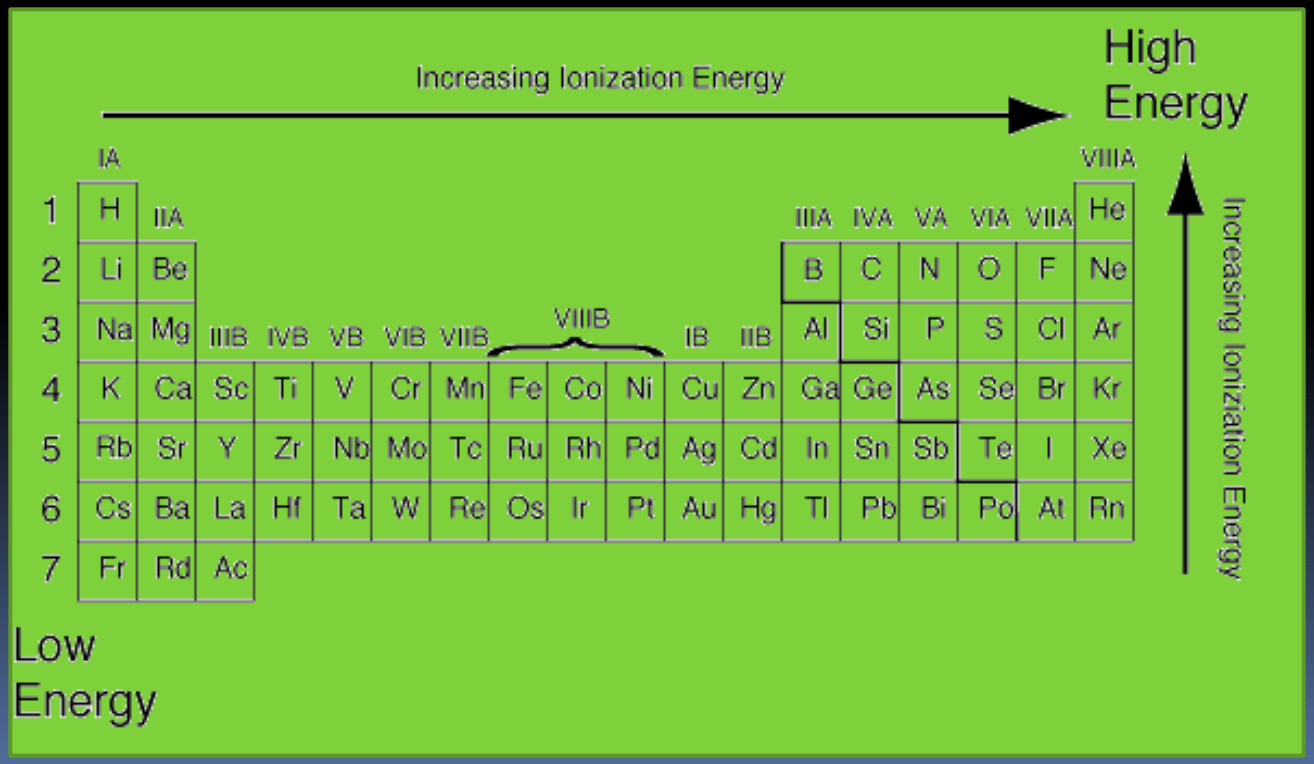
- First Ionization Energy (IE_1):
  - energy required to remove the outermost e^- in an atom



- Successive Ionization Energy
  - Getting higher, and further ionize a full shell is hard.

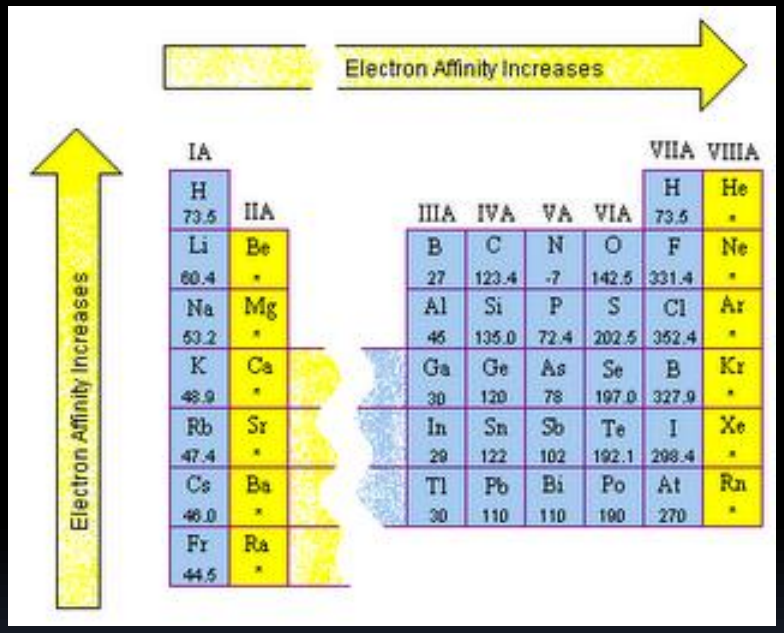
Ionization Energy

- IE_1 Changing trend:
  - Increase from left to right;
  - Decrease from up to down.



Electron Affinity

- Definition: the energy change when an electron is added to the neutral species to form a negative ion.

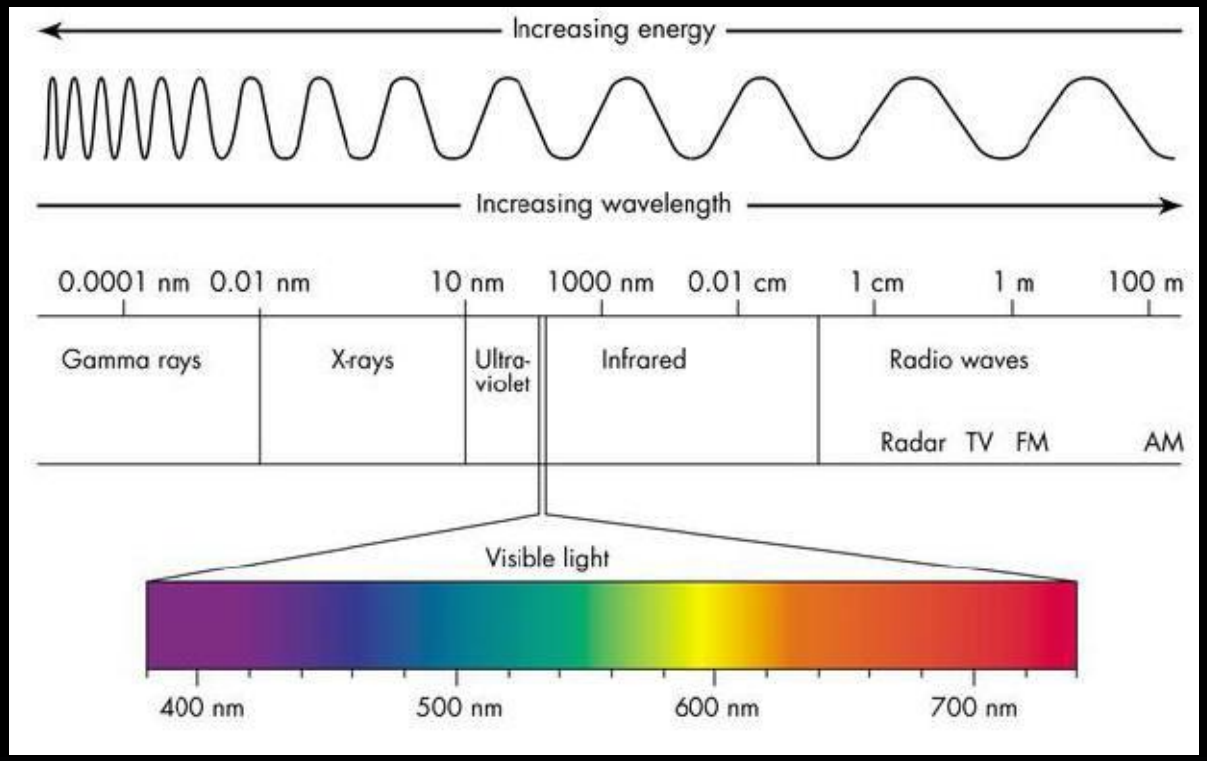


- Exothermic (give off heat) and Endothermic (Absorb heat)
  - cation + anion is exothermic; anion + anion is endothermic.

Questions

- (1) Place the following ions in order of increasing ionic radius: S^{2-}, Cl^{-}, P^{3-}.
- (2) Which ion of each set has larger radius: (a) Ca^{2+}, Ba^{2+}; (b) As^{3-}, Se^{2-}; (c) Sn^{2+}, Sn^{4+}.
- (3) Arrange the species of each set in increasing of IE_1: (a) Al, P, Si; (b) Ca, Be, Mg; (c) Fe, Fe^{2+}, Fe^{3+}.
- (4) Arrange the species of each set in increasing electron affinity: (a) P, S, Si; (b) Cl, Br, F, (c) H, H^{+}, H^{-}.
- (5) Predict whether each change will be exothermic or endothermic: (a) $Ca^{2+} + e^{-} \rightarrow Ca^{+}$; (b) $S^{-} + e^{-} \rightarrow S^{2-}$.
- (6) What is the frequency in Hertz of photons that have energy of $3.5*10^{3}$ <u>kJ/mol</u>? (Note: This unit suggests there are 1 mol of photons.)

Energy of "Light", (Electromagnetic Wave)



- Energy of a photon: $E = h\nu = hc/\lambda$;
  - ν: frequency of light, unit: Hz;
  - λ: wavelength of light, unit: nm;
  - c: speed of light, $3*10^8$ m/s; h: Planck's constant, $6.63*10^{-34}$ J·s
  - n photons: total energy = n*E = n hv.

Spectrum

- Energy is associated with electron transition from one orbital (energy state) to another.
  - Absorption spectrum: e- from a lower energy state to a higher energy state → Absorb energy;
  - Emission spectrum: e- from a higher energy state to a lower energy state → Give off energy.

Question

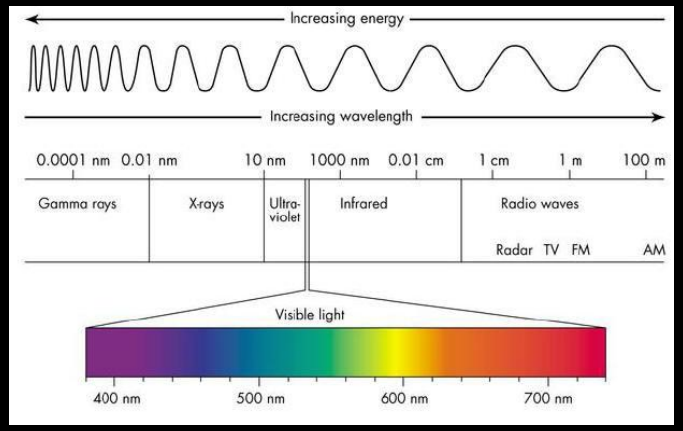
- Q1: (a) Convert a wavelength of 546 nm to meter; (b) Convert a frequency of 300 GHz to Hz; (c) Which types of electromagnetic waves are in (a) and (b)?

- Q2: What is the energy in Joules for a photon that has a wavelength of Q1 above?

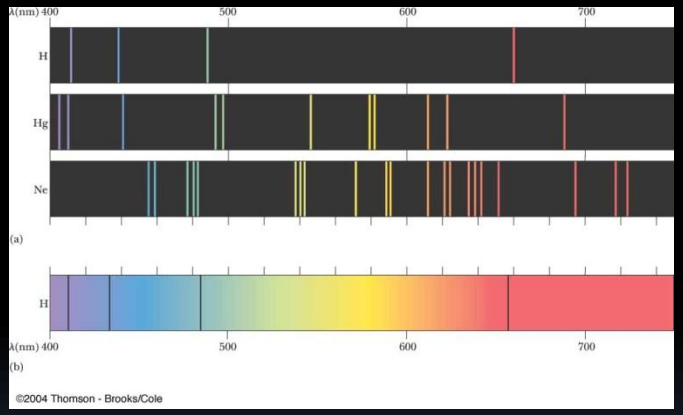
- Q3: What is the frequency in Hertz of photons that have energy of $3.5*10^3$ kJ/mol.

Spectrum

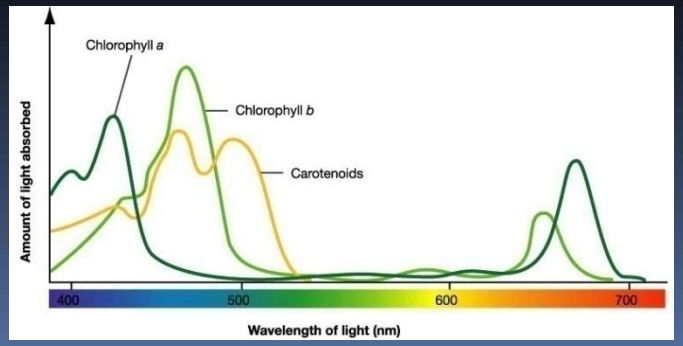
- Full spectrum



- Atomic spectrum

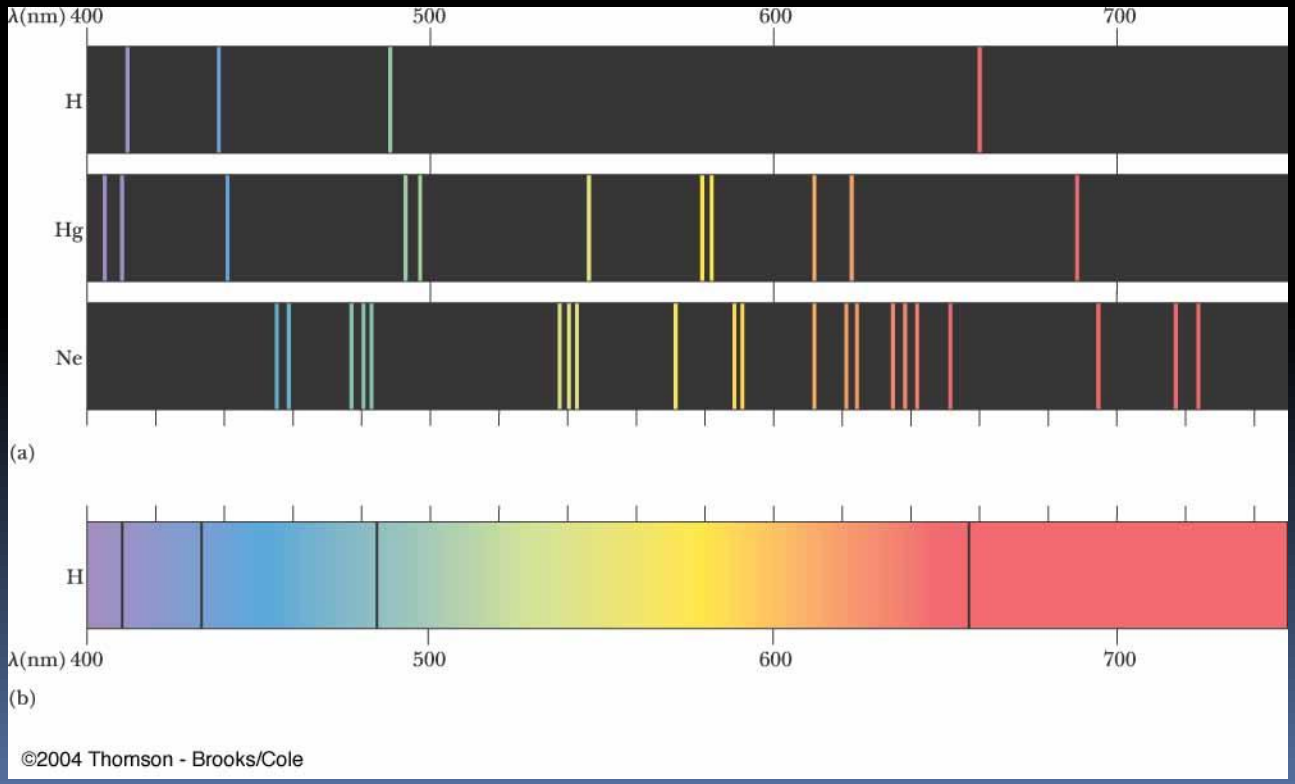


- Molecular spectrum



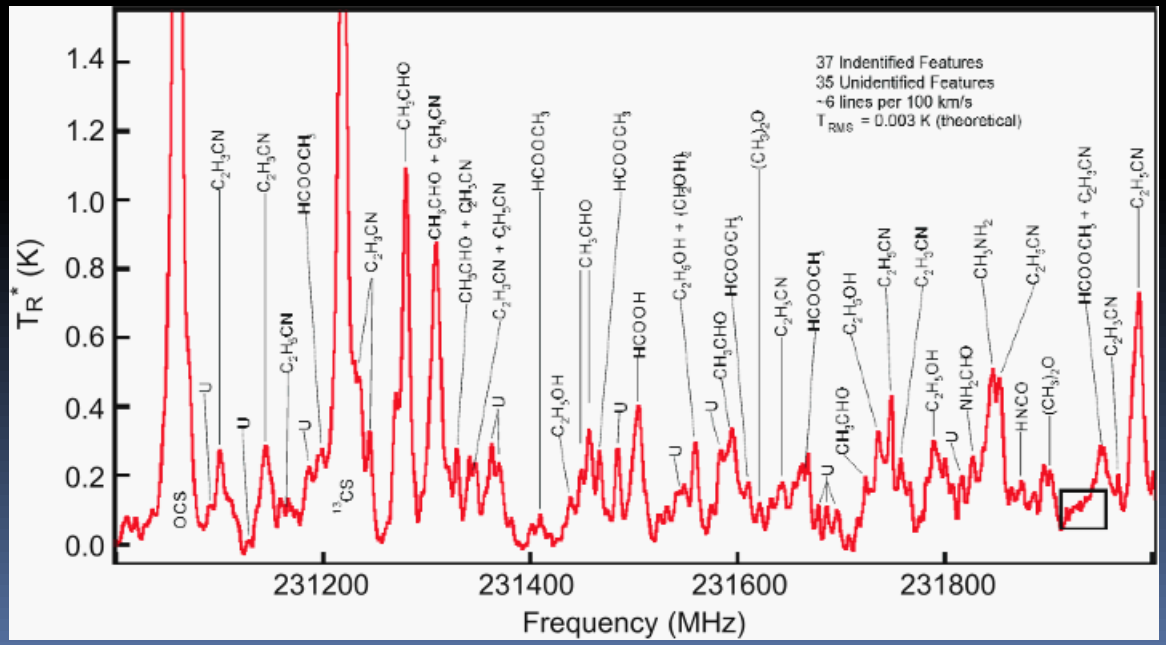
Absorption Spectra

- Atomic spectrum
  - Sharp, narrow lines indicating energy difference between different orbitals (energy state).



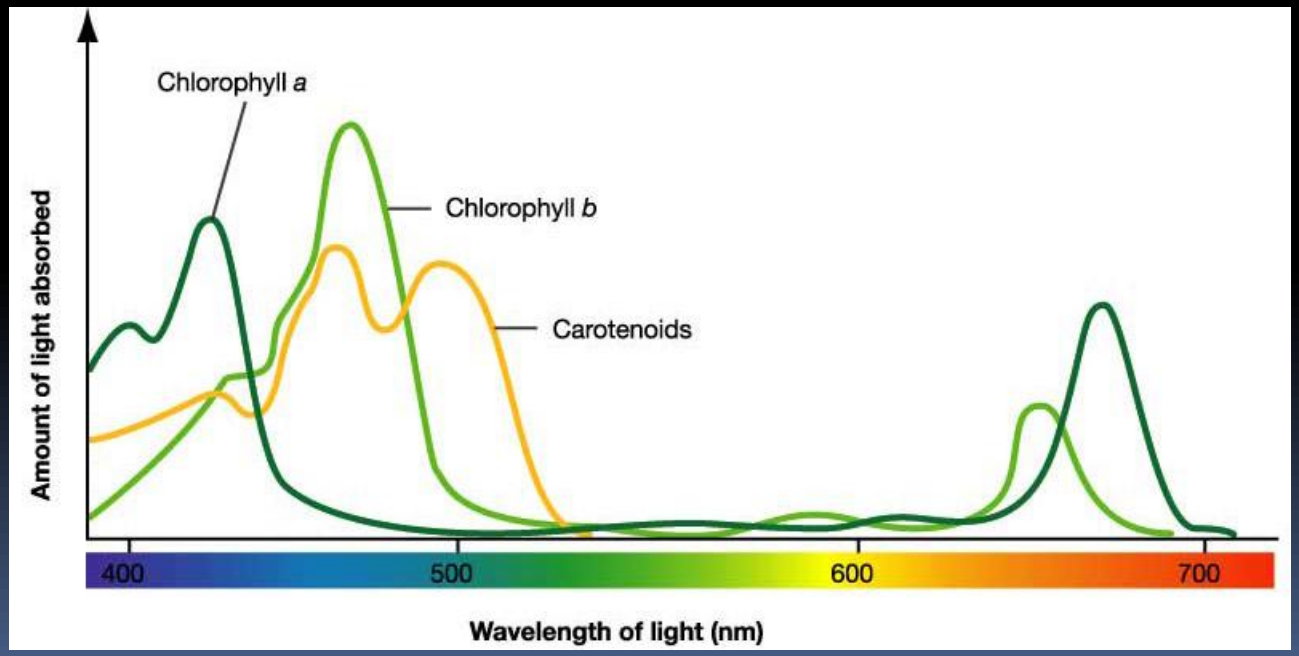
Absorption Spectra

- Molecular spectrum
  - Relatively wide bands (instead of narrow lines) indicating energy difference between orbitals.
  - Line widening is due to molecule's flexibility and its interaction with environment.



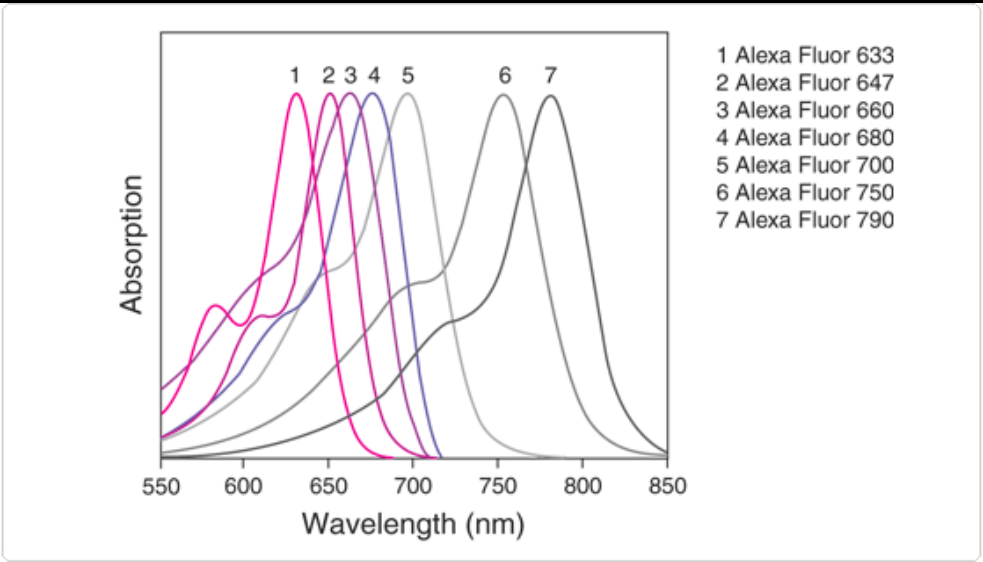
Use Spectrum to Analyze Molecule

- The positions of line adsorption provides qualitative information of molecule types;
- Can also be quantitative.



Other Important Concepts of Spectra

- Red Shift
  - Absorb lower energy (longer wavelength)
- Blue Shift
  - Absorb higher energy (shorter wavelength)
- Absorbed color and materials' color is complementary – check the "color wheel".



Question

- Q1: Below is the absorption graph of a DNA solution. (a) What is the central absorption peak position (i.e. wavelength)? (b) What is the energy corresponding to this absorption? (c) If this is the only peak of this DNA solution, what is the color of this solution?