Materials Science and Engineering I

Ch. 2 Atomic structure and bonding

Smith and Hashemi, "Foundations of Materials Science and Engineering", 6th Ed., McGraw-Hill 2019

Materials Science and Engineering
National Tsing Hua University

Outline

- Atomic structure
  - Atom and subatomic particles
  - Atomic models
  - Energy states
  - Trends of atomic size, ionization energy and electron affinity in the periodic table
- Chemical bonding
  - Primary bonds
  - Secondary bonds

Cathode ray tube

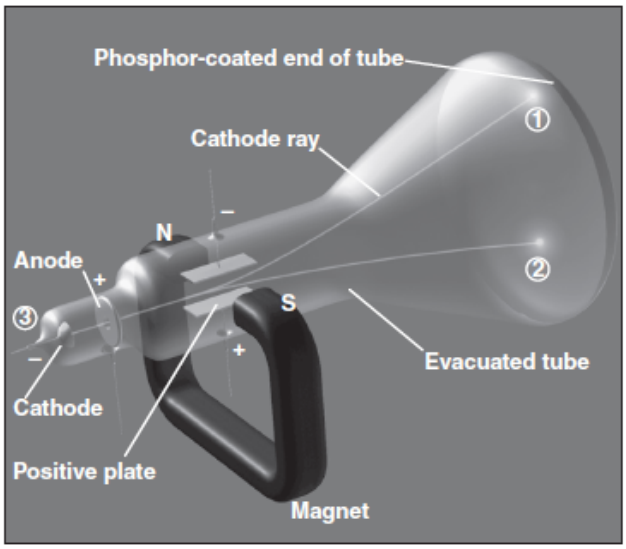
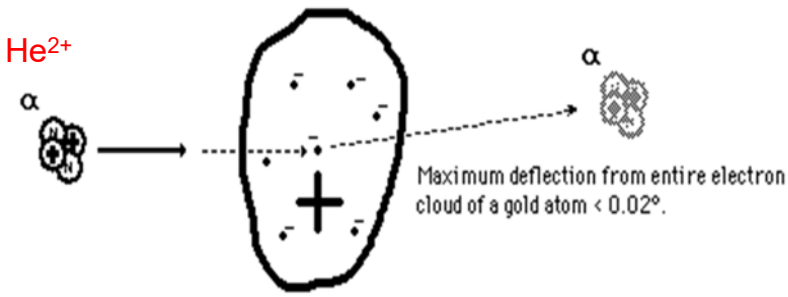


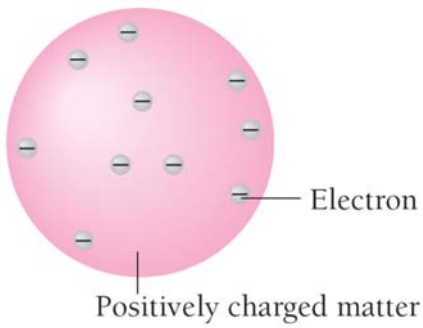
Figure 2.1
A cathode ray tube, consisting of a glass tube, cathode, anode, deflecting plates, and a flourescence screen.

Atoms must be made up of smaller constituents or subatomic particles

Thomson atomic model (1897)

➢ An atom was a positively charged blob with sprinkled negatively charged electrons in it. — **"raisin pudding"** model

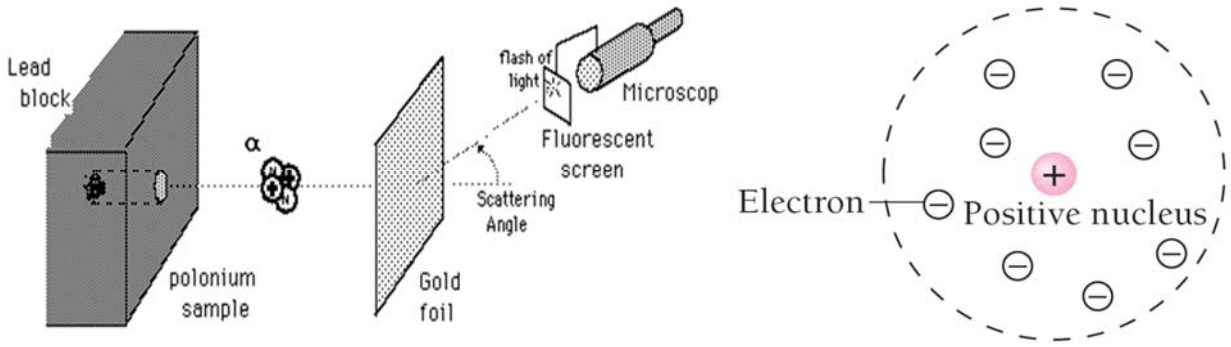




The conservation of momentum and energy for an elastic collision dictate that the angle must be less than 90 degrees if the projectile is more massive than the target.

Rutherford atomic model (1910-1911)

α-particles from a radioactive source were directed to strike a thin gold foil. α–particles produce a tiny, but visible flash of light when they strike a fluorescent screen. Surprisingly, α–particles were found at large deflection angles and some were even found to be back-scattered.



The positive matter in atoms was concentrated in a very small volume - **nuclei**.

Rutherford's Experiment

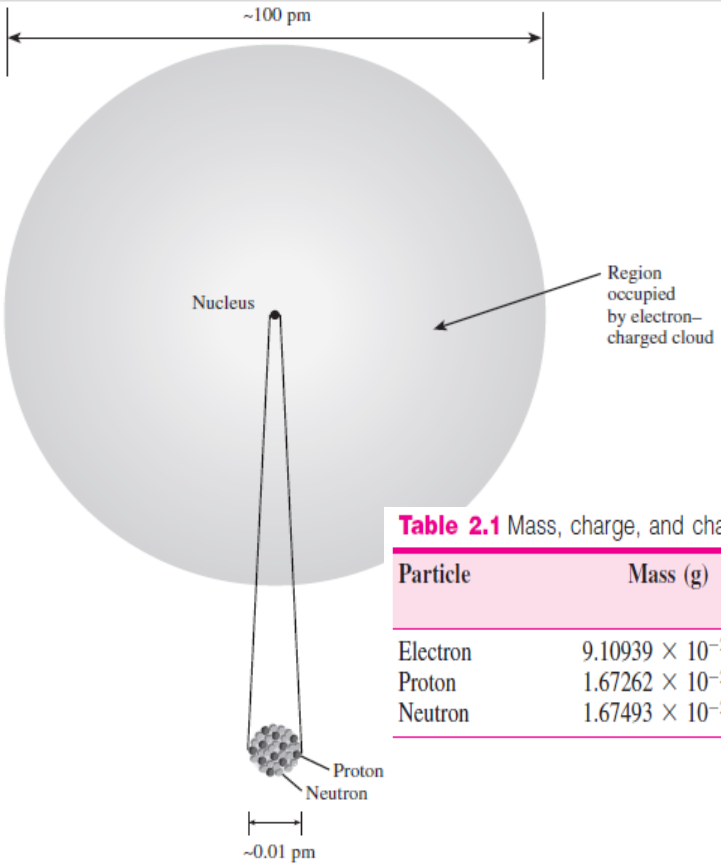


Table 2.1 Mass, charge, and charge unit of protons, neutrons, and electrons

Particle	Mass (g)	Charge	
		Coulomb (C)	Charge unit
Electron	9.10939×10^{-28}	-1.06022×10^{-19}	−1
Proton	1.67262×10^{-24}	$+1.06022 \times 10^{-19}$	+1
Neutron	1.67493×10^{-24}	0	0

Atomic Number and Atomic Mass

- **Atomic Number = Number of Protons in the nucleus**
- **Unique to an element**
  - **Example : Hydrogen = 1, Uranium = 92**
- **Relative atomic mass = Mass in grams of 6.023 x 10^{23} (*Avagadro Number*) Atoms.**
  - **Example : Carbon has 6 Protons and 6 Neutrons. Atomic Mass = 12.**
- **One atomic mass unit (amu) is 1/12th of mass of carbon atom.**
- **One gram mole = Gram atomic mass of an element.**
  - **Example :**

One gram mole of Carbon ⟷ 12 grams of Carbon ⟷ 6.023 x 10^{23} Carbon atoms

Periodic Table

Periodic Table of the Elements

Metals (main-group)
Metals (transition)
Metals (inner transition)
Metalloids
Nonmetals

Period	MAIN-GROUP ELEMENTS IA (1)	IIA (2)	TRANSITION ELEMENTS IIIB (3)	IVB (4)	VB (5)	VIB (6)	VIIB (7)	VIIIB (8)	VIIIB (9)	VIIIB (10)	IB (11)	IIB (12)	MAIN-GROUP ELEMENTS IIIA (13)	IVA (14)	VA (15)	VIA (16)	VIIA (17)	VIIIA (18)
1	1 H 1.008																	2 He 4.003
2	3 Li 6.941	4 Be 9.012											5 B 10.81	6 C 12.01	7 N 14.01	8 O 16.00	9 F 19.00	10 Ne 20.18
3	11 Na 22.99	12 Mg 24.31											13 Al 26.98	14 Si 28.09	15 P 30.97	16 S 32.07	17 Cl 35.45	18 Ar 39.95
4	19 K 39.10	20 Ca 40.08	21 Sc 44.96	22 Ti 47.88	23 V 50.94	24 Cr 52.00	25 Mn 54.94	26 Fe 55.85	27 Co 58.93	28 Ni 58.69	29 Cu 63.55	30 Zn 65.39	31 Ga 69.72	32 Ge 72.61	33 As 74.92	34 Se 78.96	35 Br 79.90	36 Kr 83.80
5	37 Rb 85.47	38 Sr 87.62	39 Y 88.91	40 Zr 91.22	41 Nb 92.91	42 Mo 95.94	43 Tc (98)	44 Ru 101.1	45 Rh 102.9	46 Pd 106.4	47 Ag 107.9	48 Cd 112.4	49 In 114.8	50 Sn 118.7	51 Sb 121.8	52 Te 127.6	53 I 126.9	54 Xe 131.3
6	55 Cs 132.9	56 Ba 137.3	57 La 138.9	72 Hf 178.5	73 Ta 180.9	74 W 183.9	75 Re 186.2	76 Os 190.2	77 Ir 192.2	78 Pt 195.1	79 Au 197.0	80 Hg 200.6	81 Tl 204.4	82 Pb 207.2	83 Bi 209.0	84 Po (209)	85 At (210)	86 Rn (222)
7	87 Fr (223)	88 Ra (226)	89 Ac (227)	104 Rf (261)	105 Db (262)	106 Sg (266)	107 Bh (262)	108 Hs (265)	109 Mt (266)	110 Uun (269)	111 Uuu (272)	112 Uub (277)	113	114 Uug (285)	115	116 Uuh (289)	117	118 Uuo

INNER TRANSITION ELEMENTS

6	Lanthanides	58 Ce 140.1	59 Pr 140.9	60 Nd 144.2	61 Pm (145)	62 Sm 150.4	63 Eu 152.0	64 Gd 157.3	65 Tb 158.9	66 Dy 162.5	67 Ho 164.9	68 Er 167.3	69 Tm 168.9	70 Yb 173.0	71 Lu 175.0
7	Actinides	90 Th 232.0	91 Pa (231)	92 U 238.0	93 Np (237)	94 Pu (242)	95 Am (243)	96 Cm (247)	97 Bk (247)	98 Cf (251)	99 Es (252)	100 Fm (257)	101 Md (258)	102 No (259)	103 Lr (260)

Source: Davis, M. and Davis, R., Fundamentals of Chemical Reaction Engineering, McGraw-Hill, 2003.

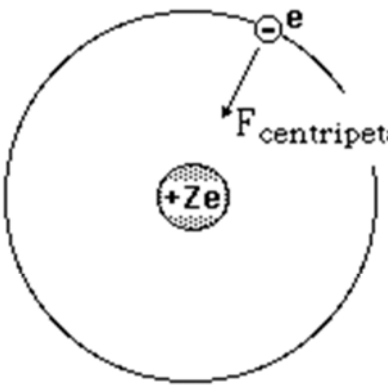
Example problem (wt% → at.%)

- A 100 gram alloy of nickel and copper consists of 75 wt% Cu and 25 wt% Ni. What are percentage of Cu and Ni Atoms in this alloy?

  Given: 75g Cu Atomic Weight 63.54
  25g Ni Atomic Weight 58.69

- Number of gram moles of Cu = $\frac{75\ g}{63.54\ g/mol} = 1.1803\ mol$
- Number of gram moles of Ni = $\frac{25\ g}{58.69\ g/mol} = 0.4260\ mol$
- Atomic Percentage of Cu = $\frac{1.1803}{(1.1803+0.4260)} \times 100 = 73.5\%$
- Atomic Percentage of Ni = $\frac{0.4260}{(1.1803+0.4260)} \times 100 = 25.5\%$

Classical electron orbital theory



Newton's Second Law

$$F_{centripetal} = \frac{mv^2}{r} = \frac{Ze^2}{4\pi\varepsilon_0 r^2}$$

so

Kinetic Energy T

$$T = \frac{mv^2}{2} = \frac{Ze^2}{8\pi\varepsilon_0 r}$$

Potential Energy

$$U = \frac{-Ze^2}{4\pi\varepsilon_0 r}$$

Total Energy

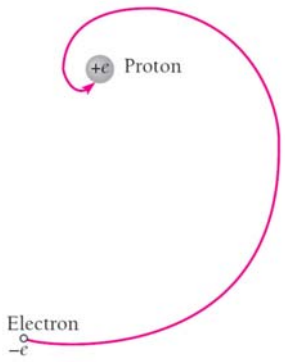
$$T + U = \frac{-Ze^2}{8\pi\varepsilon_0 r}$$

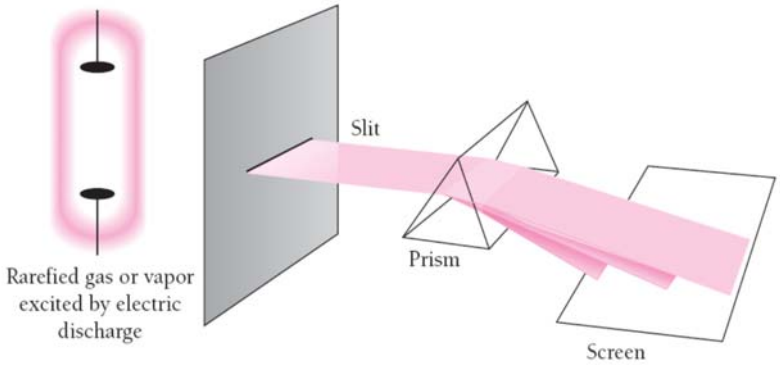
The orbit energy is negative because this is a bound state.

This is the energy of a single electron in orbit around a bare nucleus

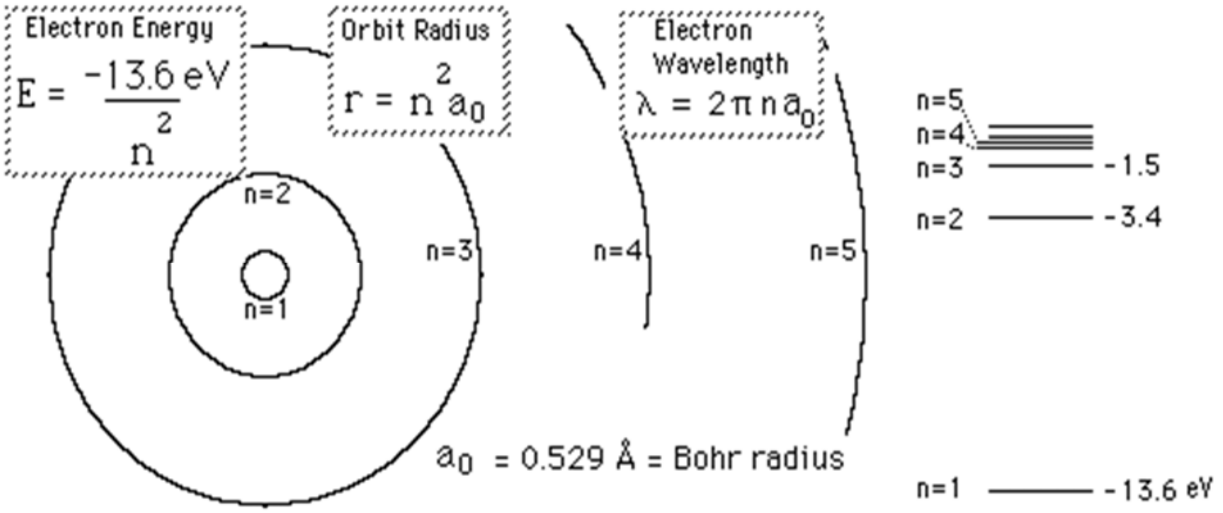
Failure of classical electron orbital theory

- Electrons circulating around the nucleus will emit EM wave and lose its energy. They will spiral into the nucleus and crash into the nucleus in a fraction of a second.
- The atomic spectra can not be explained by classical electron orbital theory either.

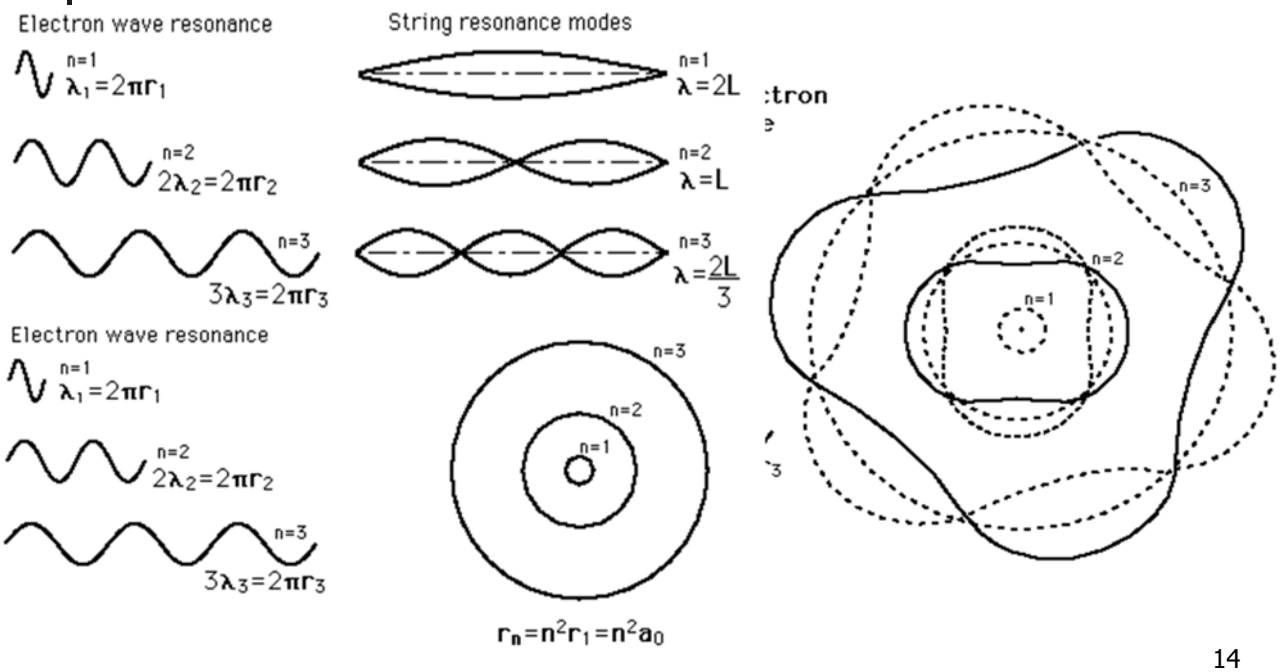




Bohr atomic model



Bohr atomic model- resonance



Energy in Hydrogen Atom

- Hydrogen atom has one proton and one electron
- Energy of hydrogen atoms for different energy levels is given by $E = -\frac{13.6}{n^2} ev$ (n=1,2…..) *principal quantum numbers*
- Example: If an electron undergoes transition from n=3 state to n=2 state, the energy of photon emitted is

$$\Delta E = -\frac{13.6}{3^2} - \frac{13.6}{2^2} = 1.89 ev = 3.02 \times 10^{-19} J$$

- Energy required to completely remove an electron from hydrogen atom is known as *ionization energy*

A hydrogen atom exists with its electron in the $n = 3$ state. The electron undergoes a transition to $n = 2$ state. Calculate (a) the energy of the corresponding photon, (b) its frequency, and (c) its wavelength. (d) Is the energy absorbed or emitted, and (e) which series does it belong to and what specific type of emission does it represent?

Solution

a. Energy of the photon emitted is

$$E = \frac{-13.6 \text{ eV}}{n^2} \quad (2.3)$$

$$\Delta E = E_3 - E_2$$

$$= \frac{-13.6}{3^2} - \frac{-13.6}{2^2} = 1.89 \text{ eV} \blacktriangleleft$$

$$= 1.89 \text{ eV} \times \frac{1.60 \times 10^{-19} \text{ J}}{\text{eV}} = 3.02 \times 10^{-19} \text{ J} \blacktriangleleft$$

b. The frequency of the photon is

$$\Delta E = h\nu$$

$$\nu = \frac{\Delta E}{h} = \frac{3.02 \times 10^{-19} \text{ J}}{6.63 \times 10^{-34} \text{ J} \cdot \text{s}}$$

$$= 4.55 \times 10^{14} \text{ s}^{-1} = 4.55 \times 10^{14} \text{ Hz} \blacktriangleleft$$

c. The wavelength of the photon is

$$\Delta E = \frac{hc}{\lambda}$$

or

$$\lambda = \frac{hc}{\Delta E} = \frac{(6.63 \times 10^{-34} \text{ J} \cdot \text{s})(3.00 \times 10^8 \text{ m/s})}{3.02 \times 10^{-19} \text{ J}}$$

$$= 6.59 \times 10^{-7} \text{ m}$$

$$= 6.59 \times 10^{-7} \text{ m} \times \frac{1 \text{ nm}}{10^{-9} \text{ m}} = 659 \text{ nm} \blacktriangleleft$$

d. Energy is released as its quantity is positive, and the electron is transitioning from a higher orbit to a lower orbit.

e. The emission belongs to the Blamer series (Fig. 2.6) and corresponds to the visible red light (Fig. 2.4).

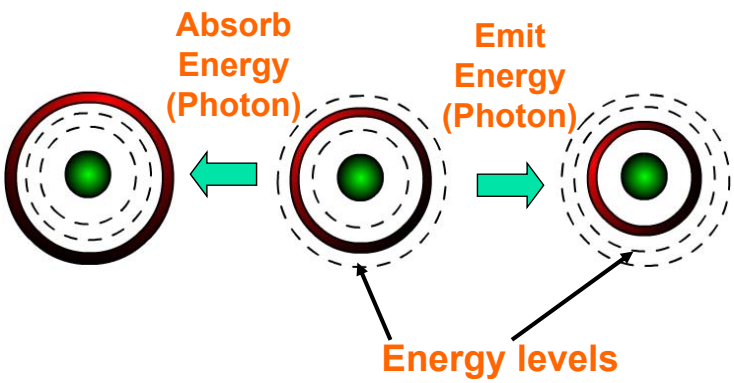
Energy states

- Electron rotates at definite energy levels.
- Energy is absorbed to move to higher energy level.
- Energy is emitted during transition to lower level.
- Energy change due to transition = ΔE = $\frac{hc}{\lambda}$

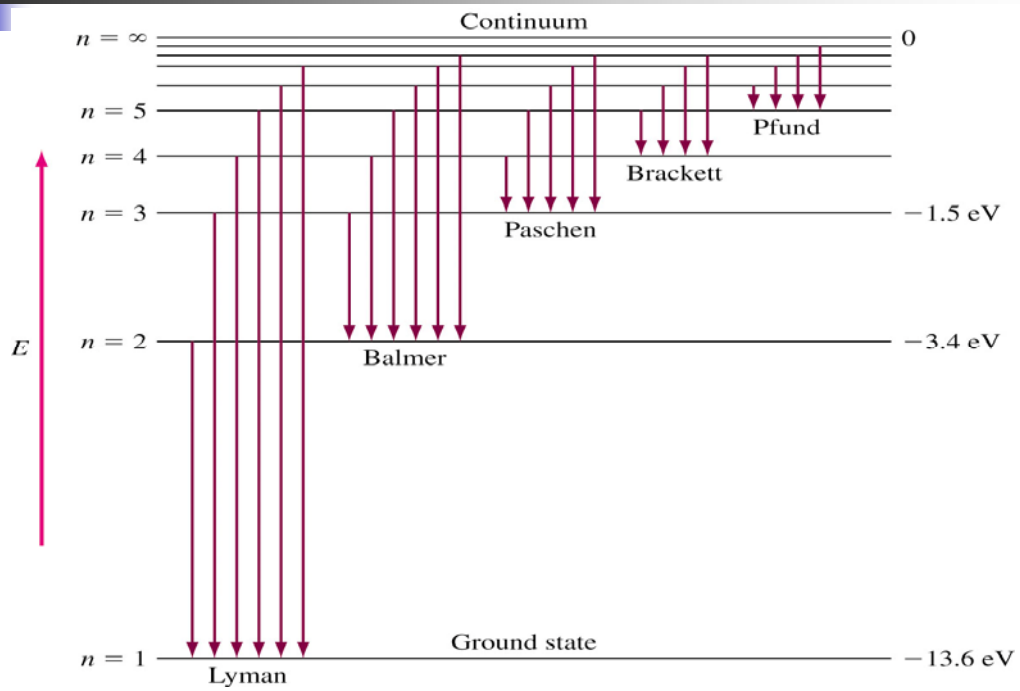
h=Planks Constant = 6.63 x 10^{-34} J.s

c= Speed of light

λ = Wavelength of light



Energy-level diagram for the line spectrum of hydrogen



Source: F. M. Miller, Chemistry: Structure and Dynamics, McGraw-Hill, 1984, p.141

Wave-Particle Duality

- De Broglie proposed in 1923 that a moving particle of momentum ***p*** behaves like a wave with a characteristic wavelength ***λ=h/p***

$\longrightarrow$ v = 40 m/s = 90 mi/hr

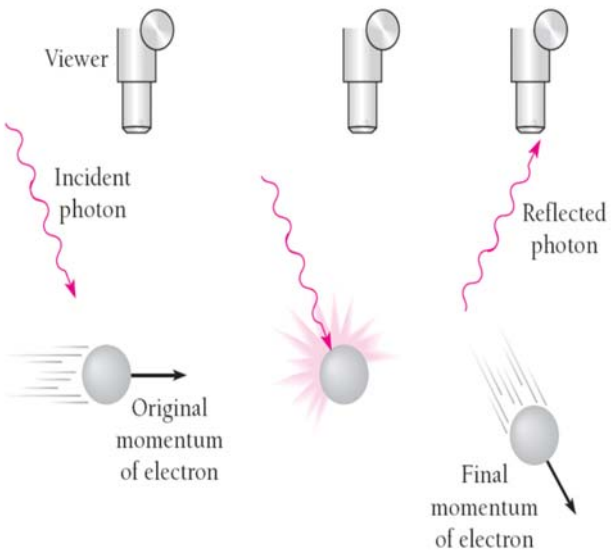
m=0.15 kg

$$\lambda = \frac{h}{mv} = \frac{6.626 \times 10^{-34}\ \text{J s}}{(0.15\ \text{kg})(40\ \text{m/s})} = 1.1 \times 10^{-34}\ \text{m}$$

For an electron accelerated through 100 Volts: $v = 5.9 \times 10^{6}$ m/s

$$\lambda = \frac{6.626 \times 10^{-34}\ \text{Js}}{(9.11 \times 10^{-31}\ \text{kg})(5.9 \times 10^{6}\ \text{m/s})} = 1.2 \times 10^{-10} = 0.12\ \text{nm}$$

Uncertainty principle



- The original particle information (position, velocity) is disturbed by the incident photon.
- The amount of momentum change Δp is in the same order of the photon momentum $\Delta p \approx h/\lambda$
- An estimate of position uncertainty is $\Delta x \geq \lambda$ $\Rightarrow \Delta x \cdot \Delta p \geq h/4\pi$

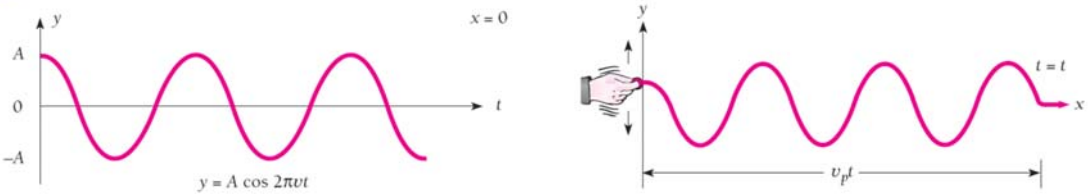
How to describe particle by "wave"?

- **Schrodinger's attempt** — Consider the particle as an assembly of waves that fulfills some kind of wave equation. The solution of the wave equation is called ***wave function*** that contains the all physical information of the particle such as velocity, momentum, kinetic energy, …
- The **wave function** represents the probability amplitude for finding a particle at a given point in space at a given time.

Ψ(x,y,z,t)= Amplitude of probability wave

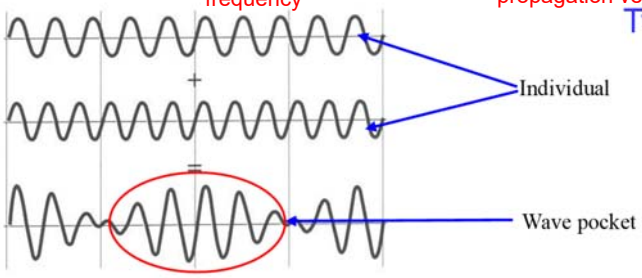
Ψ*Ψ= Probability density

Wave Propagation



$$y = A\cos 2\pi\nu(t - x/v_p) = A\cos 2\pi(\nu t - x/\lambda) = A\cos(\omega t - kx)$$

frequency propagation velocity angular frequency wave vector



Two propagating waves superimposed:

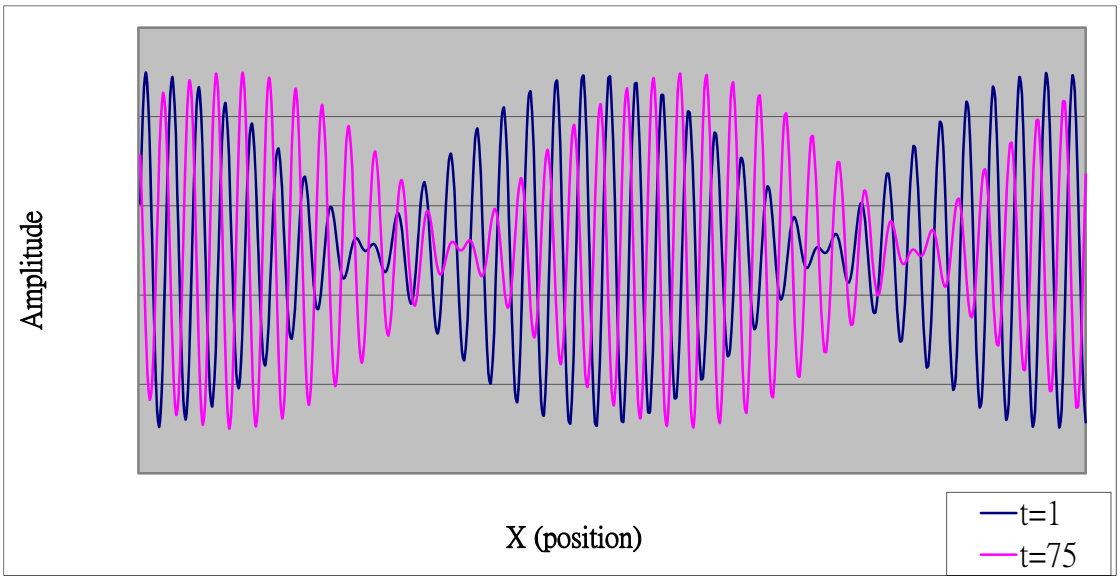
$$y_1 = A\cos(\omega t - kx)$$

$$y_2 = A\cos[(\omega + \Delta\omega)t - (k + \Delta k)x]$$

$$y = y_1 + y_2 = 2A\cos\tfrac{1}{2}[(2\omega + \Delta\omega)t - (2k + \Delta k)x]\cos\tfrac{1}{2}(\Delta\omega t - \Delta kx)$$

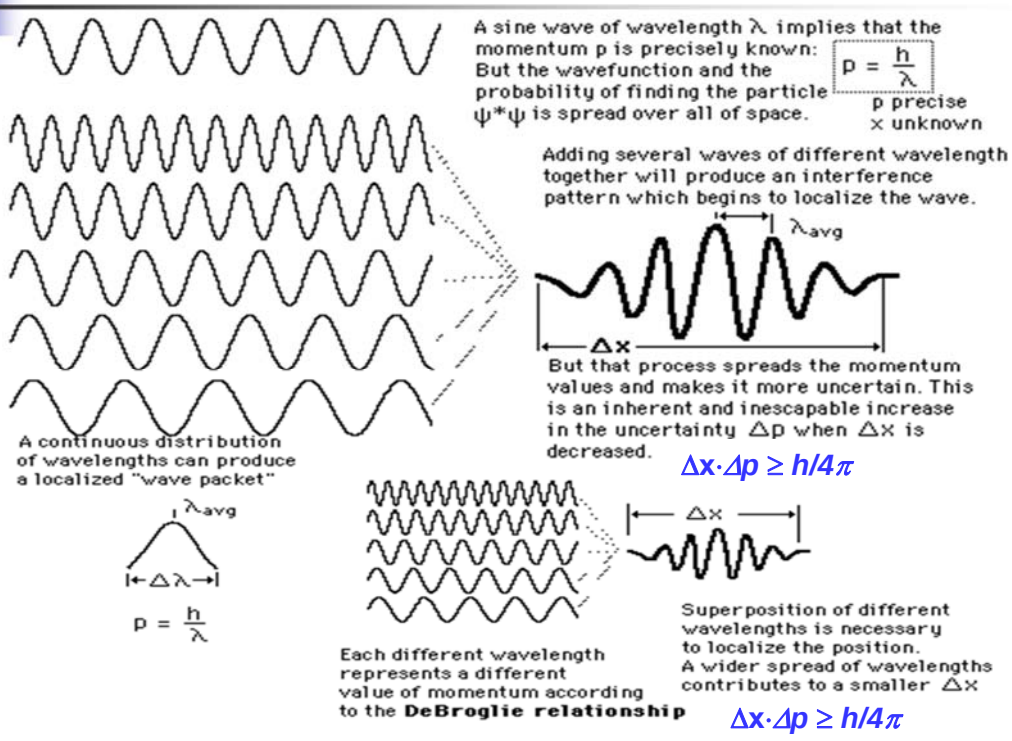
Superposition of two COS waves

$$y = 2A\cos(\omega t - kx)\cos\tfrac{1}{2}(\Delta\omega t - \Delta kx)$$



k=50, w=100, Δk=3, Δw=1

Uncertainty principle



Matter wave and electron density

- de Broglie's proposition: $\lambda = h/p = h/(mv)$
- Heisenberg rejected Bohr's concept of an "orbit" of fixed radius for an electron. $\Delta x \cdot \Delta p \geq h/4\pi$
- Schrodinger used the wave equation to explain the behavior of electrons. The solution of the wave equation is called wave function ψ (x,y,z,t). *$\psi^2 = \psi^* \psi$ represents the probability of finding an electron of a given energy level in a given region of space.*
- The probability is called electron density. For the ground state electron, there is 90% chance of finding an electron within a sphere of radius 100 pm.

Electron density in a hydrogen atom

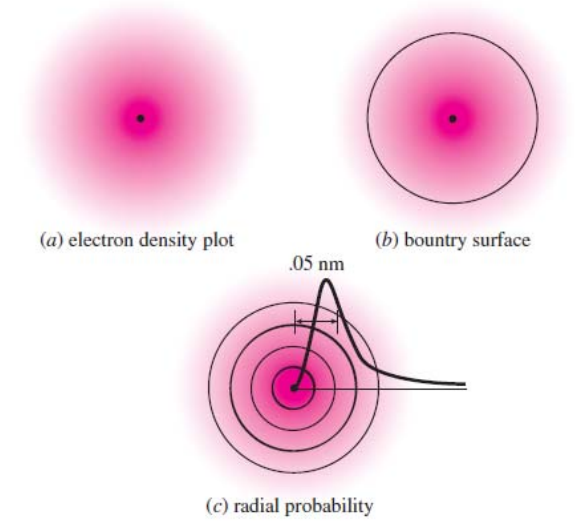
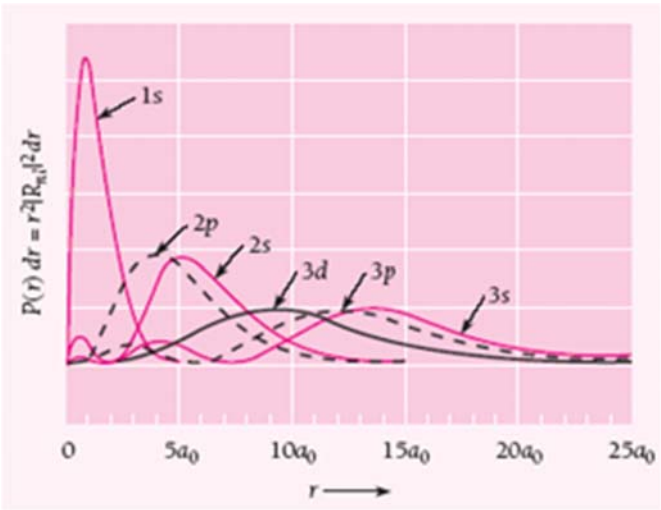
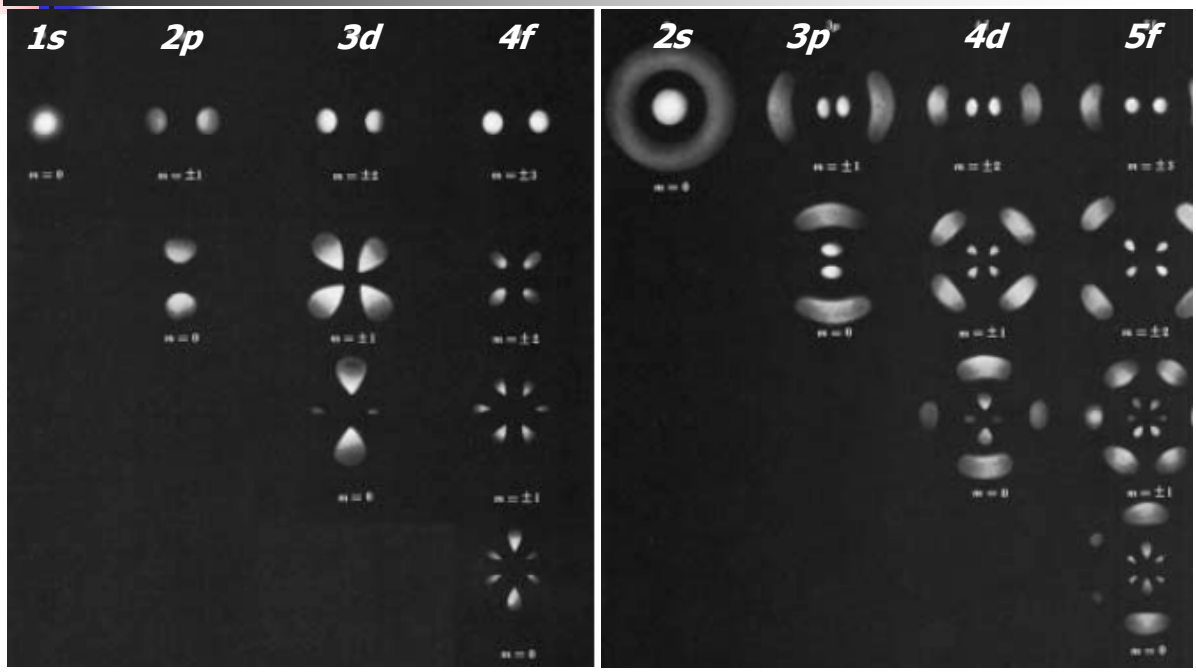


Figure 2.7



"Concepts of Modern Physics", 6th ed, Arthur Beiser, p.213

Electron distribution for different orbital quantum numbers



Source: Concepts of Modern Physics", 6th ed, Arthur Beiser, p.216-217

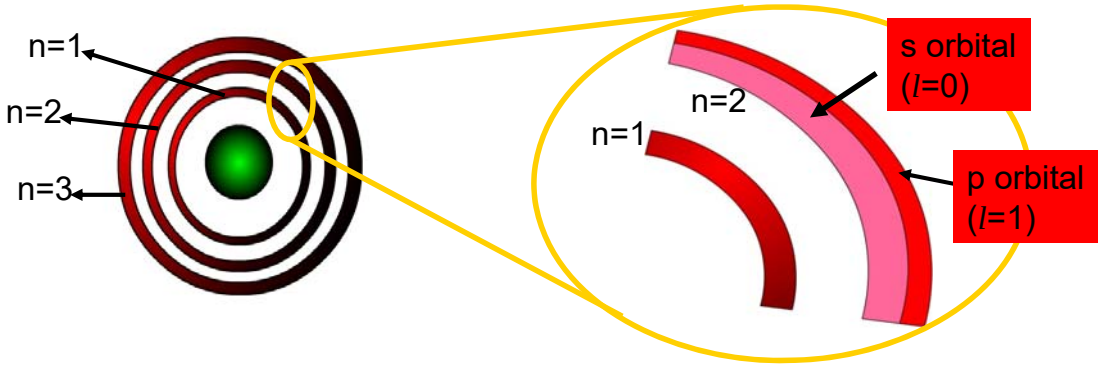
Quantum Numbers of Electrons of Atoms

Principal Quantum Number (n)

- Represents main energy levels.
- Range 1 to 7.
- Larger the 'n' higher the energy.

Subsidiary (orbital) Quantum Number *l*

- Represents sub energy levels (orbital).
- Range 0…n-1.
- Represented by letters s,p,d and f.



Quantum numbers of electrons in atoms

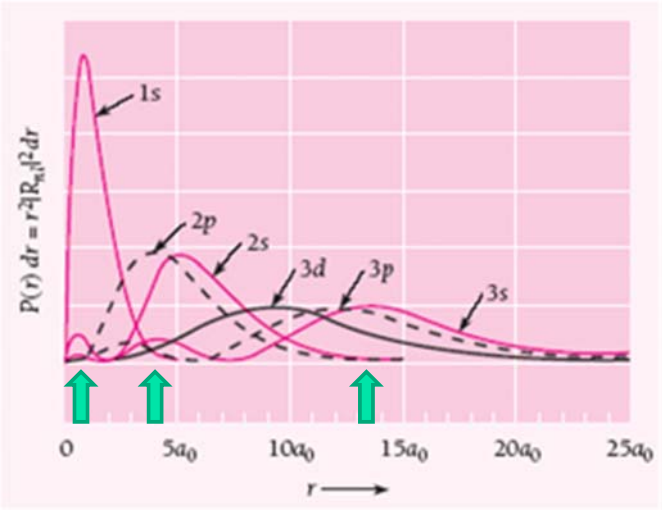
Magnetic Quantum Number m_l.

- Represents spatial orientation of single atomic orbital.
- Permissible values are $-l$ to $+l$.
  - Example:- if l=1, m_l = -1,0,+1. i.e. $2l$+1 allowed values.
- No effect on energy.

Electron spin quantum number m_s.

- Specifies two directions of electron spin.
- Directions are clockwise or anticlockwise.
- Values are +1/2 or –1/2.
- Two electrons on same orbital have opposite spins.
- No effect on energy.

Energy state of multielectron atoms



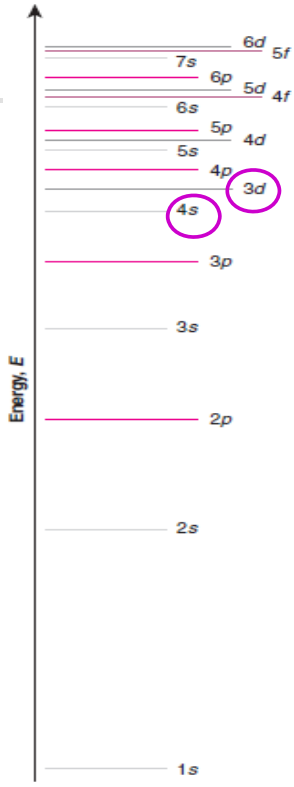


Figure 2.9

Electron Structure of Multielectron Atom

- Maximum number of electrons in each atomic shell is given by $2n^2$.
- Atomic size (radius) increases with addition of shells.
- Electron Configuration lists the arrangement of electrons in orbitals.
  - Example :-

Orbital letters

Number of Electrons

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

Principal Quantum Numbers

  - For Iron, (Z=26), Electronic configuration is

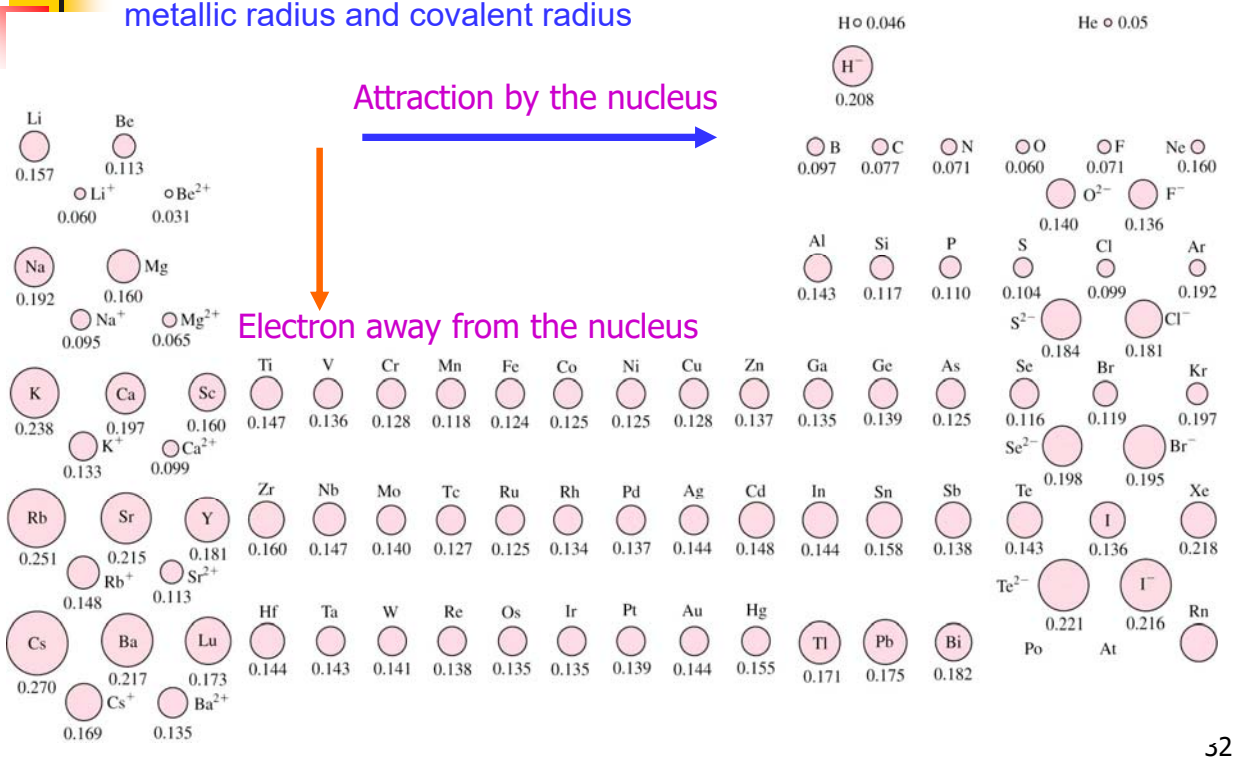
$$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^6\ 4s^2$$

Trends in atomic size

Half of the distance between the nuclei of 2 adjacent atoms: metallic radius and covalent radius

Attraction by the nucleus

Electron away from the nucleus



Ionization energy (IE)

The energy required to remove an electron from its atom.

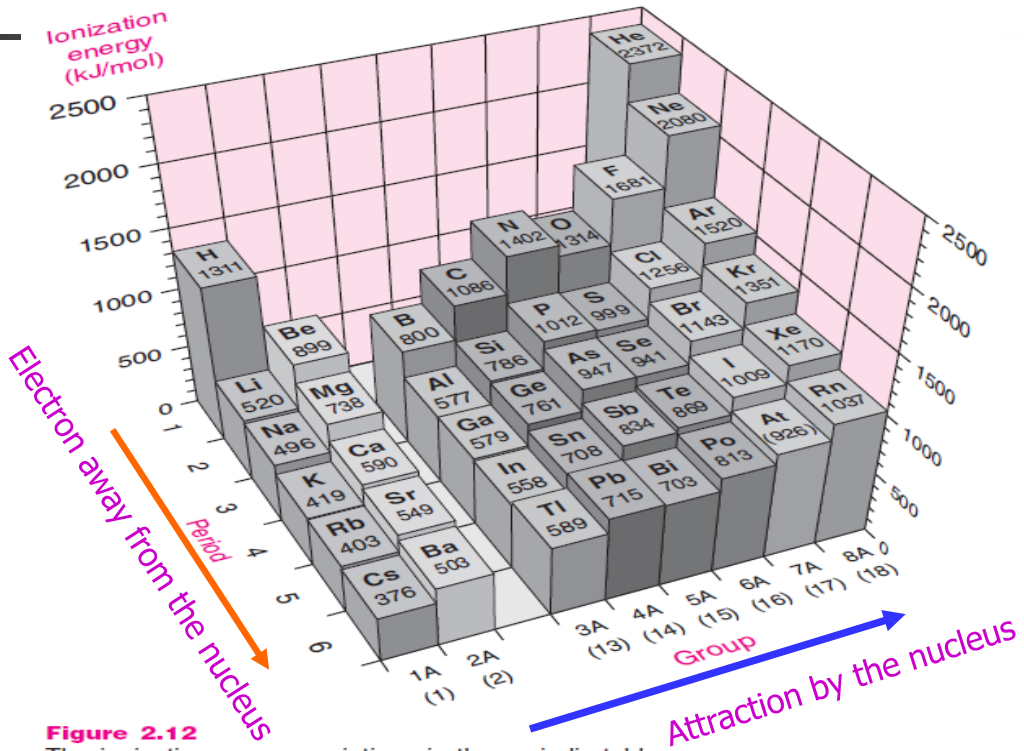
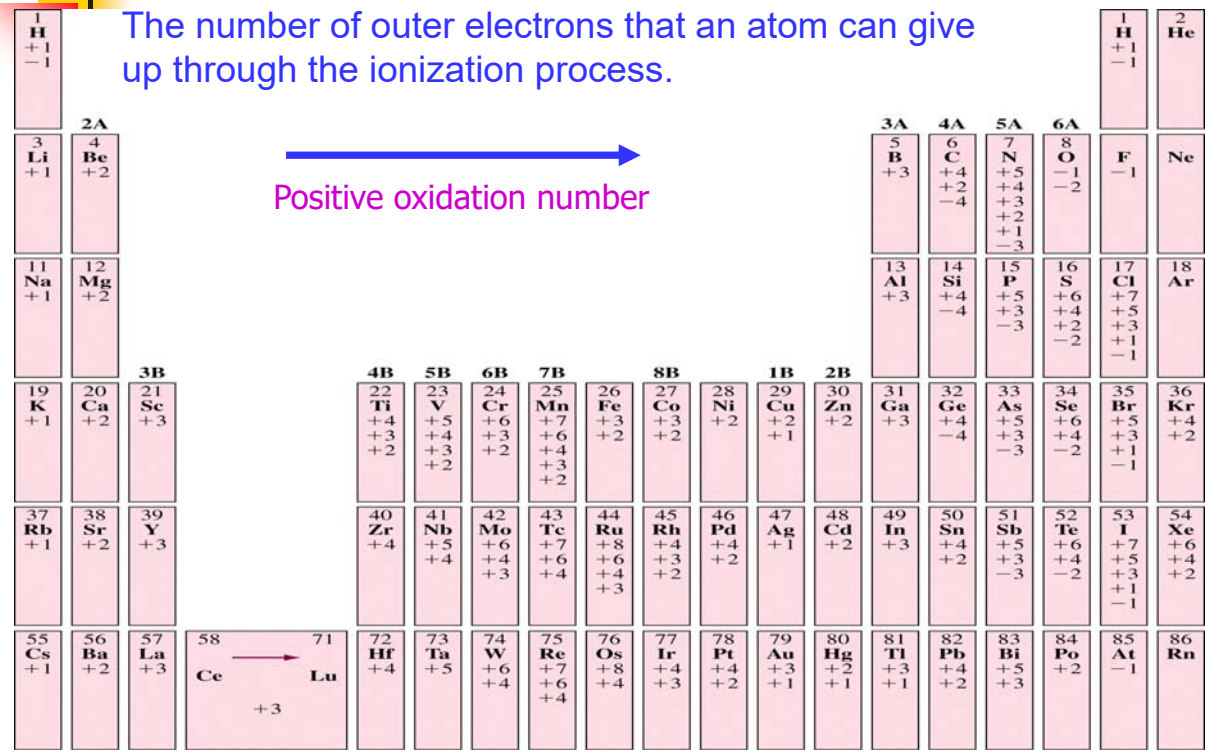


Figure 2.12
The ionization energy variations in the periodic table.

Oxidation number

The number of outer electrons that an atom can give up through the ionization process.

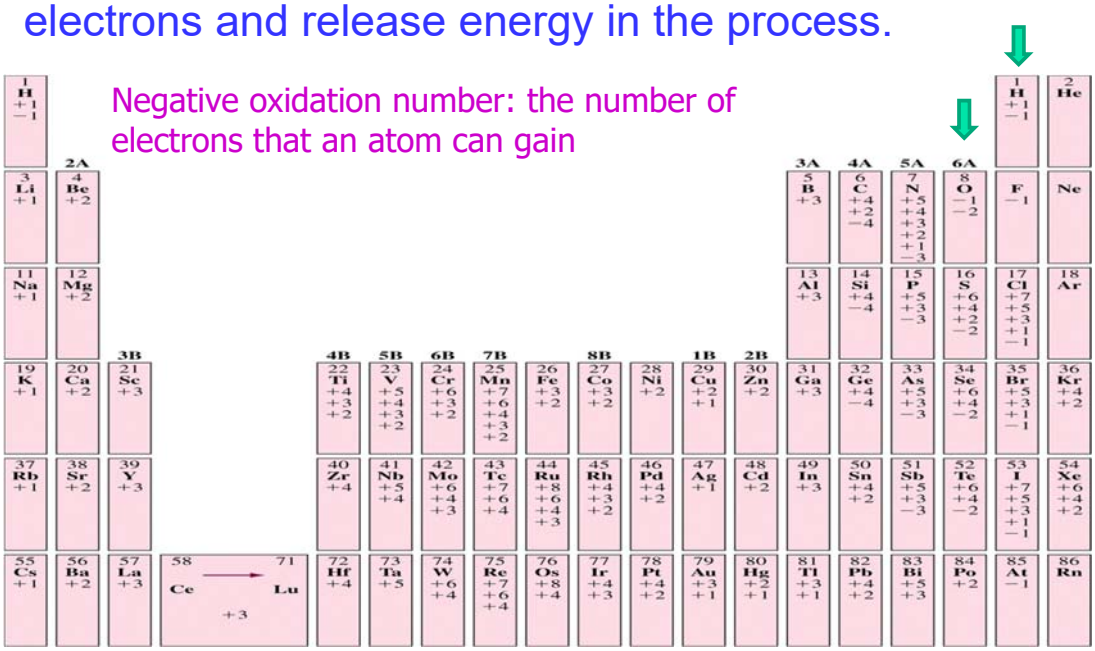
Positive oxidation number



Electron affinity (EA)

- Electron affinity: The tendency to accept one or more electrons and release energy in the process.

Negative oxidation number: the number of electrons that an atom can gain



Electron Structure and Chemical Activity

- **Except Helium, most *noble gasses* (Ne, Ar, Kr, Xe, Rn) are chemically very stable (high ionization energy and no electron affinity)**
  - **All have s^2 p^6 configuration for outermost shell.**
  - **Helium has $1s^2$ configuration**
- **Electropositive elements give electrons during chemical reactions to form *cations*.**
  - **Cations are indicated by positive oxidation numbers**
  - **Example:**

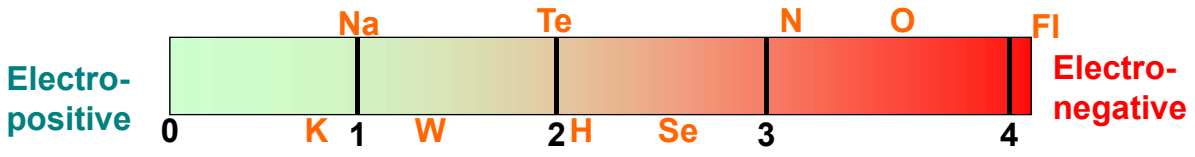
$$Fe : 1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^6\ 4s^2$$

$$Fe^{2+} : 1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^6$$

$$Fe^{3+} : 1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^5$$

Electron Structure and Chemical Activity

- **Electronegative elements accept electrons during chemical reaction.**
- **Some elements behave as both electronegative and electropositive.**
- **Electronegativity is the degree to which the atom attracts electrons to itself**
  - **Measured on a scale of 0 to 4.1**
  - **Example : Electronegativity of Fluorine is 4.1**
    Electronegativity of Sodium is 1.



Electronegativity

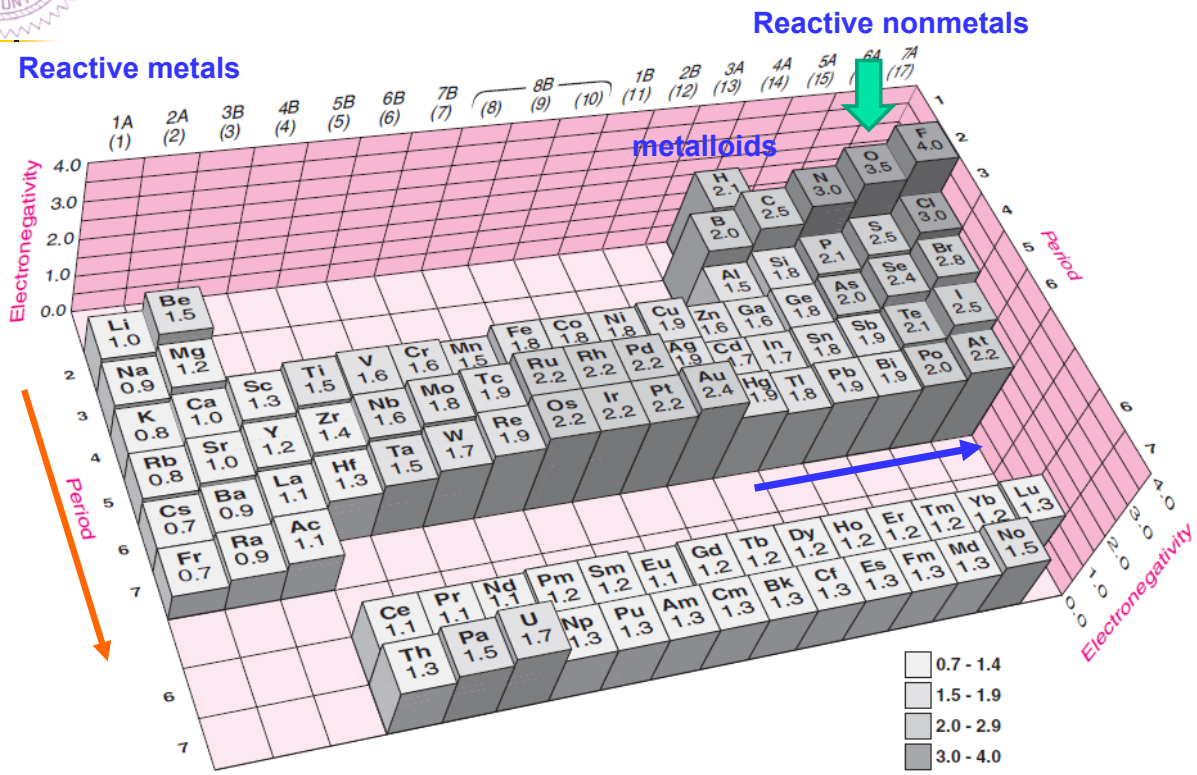


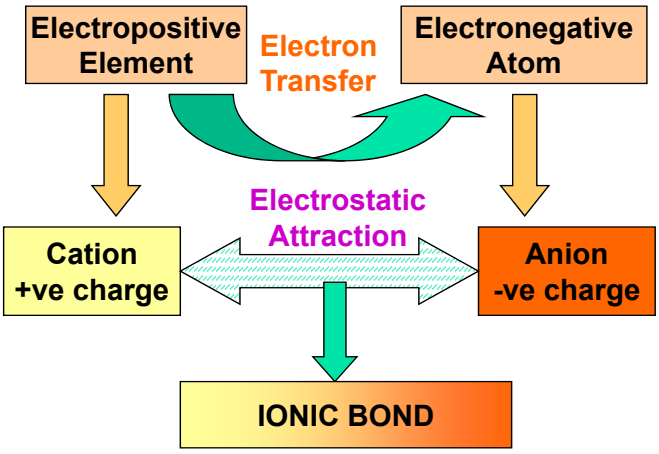
Figure 2.14
The electronegativity variations in the periodic table.

Atomic and Molecular Bonds

- **Ionic bonds: Strong atomic bonds due to transfer of electrons**
- **Covalent bonds: Large interactive force due to sharing of electrons**
- **Metallic bonds: Non-directional bonds formed by sharing of electrons**
- **Permanent Dipole bonds: Weak intermolecular bonds due to attraction between the ends of permanent dipoles.**
- **Fluctuating Dipole bonds: Very weak electric dipole bonds due to asymmetric distribution of electron densities.**

Ionic Bonding

- **Ionic bonding is due to electrostatic force of attraction between cations and anions.**
- **It can form between metallic and nonmetallic elements.**
- **Electrons are transferred from electropositive to electronegative atoms**



Ionic Bonding – NaCl

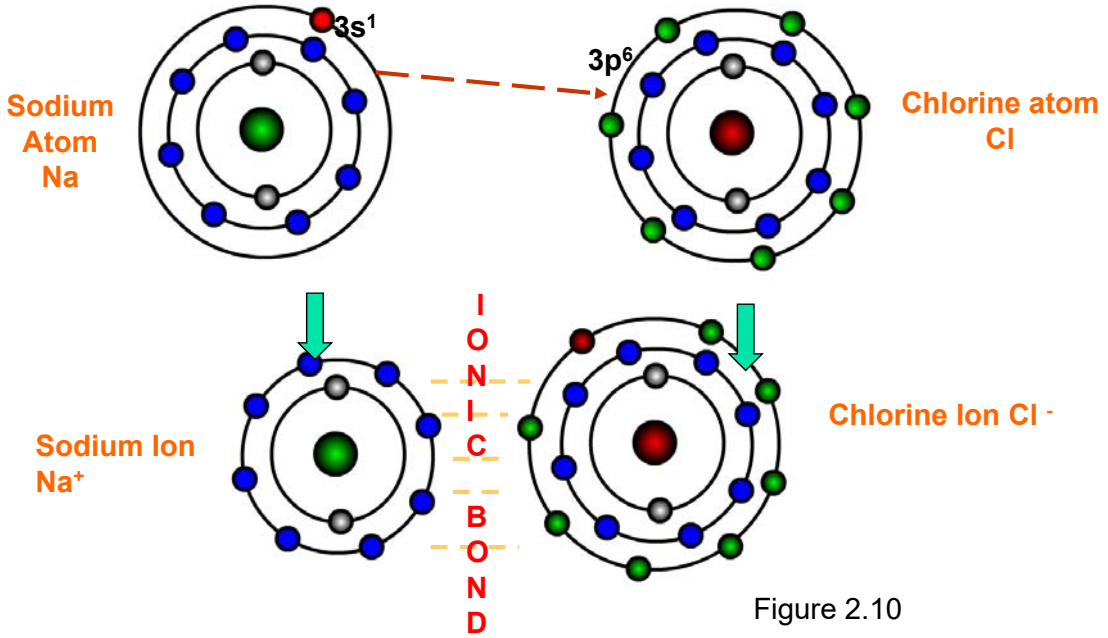


Figure 2.10

Ionic force for an ion pair

- Nucleus of one ion attracts electron of another ion.
- The electron clouds of ions repulse each other when they are sufficiently close.

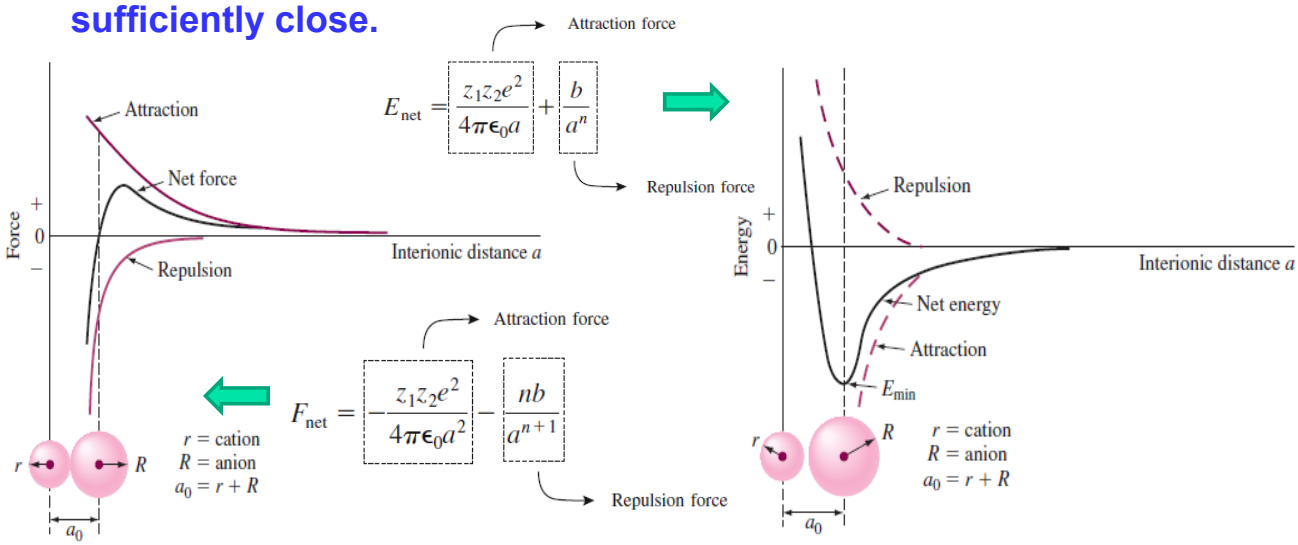


Figure 2.16

Figure 2.17

Ion Force for Ion Pair

$$F_{attractive} = -\frac{(Z_1 e)(Z_2 e)}{(4\pi \varepsilon_0 a^2)} = -\frac{Z_1 Z_2 e^2}{(4\pi \varepsilon_0 a^2)}$$

Z_1, Z_2 = number of electrons removed or added during ion formation
e = electron charge
a = interionic separation distance
ε_0 = permeability of free space ($8.85 \times 10^{-12} c^2/Nm^2$)

$$F_{repulsive} = -\frac{nb}{a^{n+1}}$$

(n and b are constants)

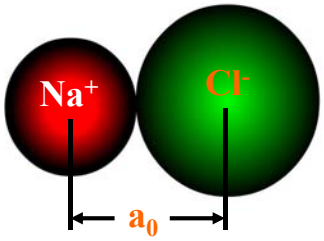
$$F_{net} = -\frac{Z_1 Z_2 e^2}{(4\pi \varepsilon_0 a^2)} - \frac{nb}{a^{n+1}}$$

n: 7~10, experimentally determined

Interionic Force - Example

- **Force of attraction between Na+ and Cl^- ions**

Z_1 = +1 for Na^+, Z_2 = -1 for Cl^-
e = 1.60×10^{-19} C , $\varepsilon_0 = 8.85 \times 10^{-12}$ C^2/Nm^2
a_0 = sum of radii of Na^+ and Cl^- ions
= 0.095 nm + 0.181 nm = 2.76×10^{-10} m



$$F_{attraction} = -\frac{Z_1 Z_2 e^2}{(4\pi \varepsilon_0 a^2)} = \frac{(+1)(-1)(1.60 \times 10^{-19} C)^2}{4\pi (8.85 \times 10^{-12}\ C^2/Nm^2)(2.76 \times 10^{-10}\ m)} = +3.02 \times 10^{-9} N$$

Interionic energies for ion pairs

- **Net potential energy for a pair of oppositely charged ions**

$$E_{net} = \underbrace{\frac{Z_1 Z_2 e^2}{(4\pi\varepsilon_0 a)}}_{\text{Attraction Energy}} + \underbrace{\frac{b}{a^n}}_{\text{Repulsion Energy}}$$

Attraction Energy → Energy Released

Repulsion Energy → Energy Absorbed

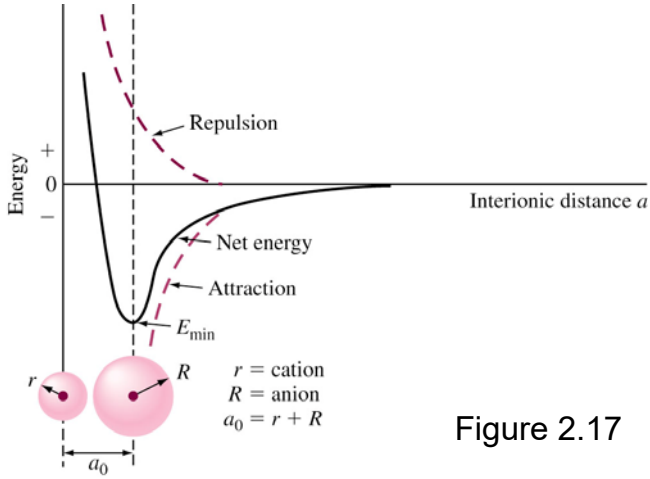


Figure 2.17

- **E_{net} is minimum when ions are at equilibrium separation distance a_0**

If the attractive force between Mg^{2+} and S^{2-} ions at equilibrium is 1.49×10^{-9} N, calculate (a) the corresponding interionic distance. If S^{2-} ion has a radius of 0.184 nm, calculate (b) the ionic radius for Mg^{2+} and (c) the repulsion force between the two ions at this position.

Solution

The value of a_0, the sum of the Mg^{2+} and S^{2-} ionic radii, can be calculated from a rearranged form of Coulomb's law.

a.
$$a_0 = \sqrt{\frac{-Z_1 Z_2 e^2}{4\pi\epsilon_0 F_{attraction}}}$$

$$Z_1 = +2 \text{ for } Mg^{2+} \qquad Z_2 = -2 \text{ for } S^{2-}$$
$$|e| = 1.60 \times 10^{-19}\,\text{C} \qquad \epsilon_0 = 8.85 \times 10^{-12}\,\text{C}^2/(\text{N}\cdot\text{m}^2)$$
$$F_{attractive} = 1.49 \times 10^{-9}\,\text{N}$$

Thus,
$$a_0 = \sqrt{\frac{-(2)(-2)(1.60 \times 10^{-19}\,\text{C})^2}{4\pi[8.85 \times 10^{-12}\,\text{C}^2/(\text{N}\cdot\text{m}^2)](1.49 \times 10^{-8}\,\text{N})}}$$
$$= 2.49 \times 10^{-10}\,\text{m} = 0.249\,\text{nm}$$

b.
$$a_0 = r_{Mg^{2+}} + r_{S^{2-}}$$
or
$$0.249\,\text{nm} = r_{Mg^{2+}} + 0.184\,\text{nm}$$
$$r_{Mg^{2+}} = 0.065\,\text{nm} \blacktriangleleft$$

The repulsion force between Na^+ (r = 0.095 nm) and Cl^- (r = 0.181) ions at equilibrium is -3.02×10^{-9} N. Calculate (a) the value of constant b using the repulsive force section of Eq. 2.8, and (b) the bonding energy, E_{min}. Assume $n = 9$.

■ **Solution**

a. To determine the b value for a NaCl ion pair,

$$F = -\frac{nb}{a^{n+1}} \tag{2.6}$$

The repulsive force between a Na^+Cl^- ion pair is -3.02×10^{-9} N.
Thus,

$$-3.02 \times 10^{-9}\,\text{N} = \frac{-9b}{(2.76 \times 10^{-10}\,\text{m})^{10}}$$

$$b = 8.59 \times 10^{-106}\,\text{N} \cdot \text{m}^{10} \blacktriangleleft$$

b. To calculate the potential energy of the Na^+Cl^- ion pair,

$$E_{Na^+Cl^-} = \frac{+Z_1Z_2e^2}{4\pi\epsilon_0 a} + \frac{b}{a^n}$$

$$= \frac{(+1)(-1)(1.60 \times 10^{-19}\,\text{C})^2}{4\pi[8.85 \times 10^{-12}\,\text{C}^2/(\text{N} \cdot \text{m}^2)](2.76 \times 10^{-10}\,\text{m})} + \frac{8.59 \times 10^{-106}\,\text{N} \cdot \text{m}^{10}}{(2.76 \times 10^{-10}\,\text{m})^9}$$

$$= -8.34 \times 10^{-19}\,\text{J}^* + 0.92 \times 10^{-19}\,\text{J}^*$$

$$= -7.42 \times 10^{-19}\,\text{J} \blacktriangleleft$$

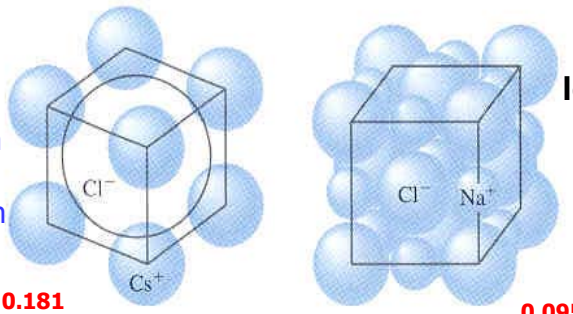
Ion Arrangements in Ionic Solids

- **Ionic bonds are *Non Directional***
- **Geometric arrangements are present in solids to maintain electric neutrality.**
  - **Example:- in NaCl, six Cl- ions pack around central Na+ Ions**

$r(Cl^-)$=0.181 nm

$r(Cs^+)$=0.169 nm

$r(Na^+)$=0.095 nm



Ionic packing efficiency In NaCl and CsCl

Figure 2.18

0.169/0.181 =0.934 **CsCl**

NaCl **0.095/0.181 =0.525**

- **As the ratio of cation to anion radius decreases, fewer anion surround central cation.**

Bonding Energies

- Lattice energies and melting points of ionically bonded solids are high.
- Lattice energy decreases when size of ions increases.
- Multiple bonding electrons increase lattice energy.

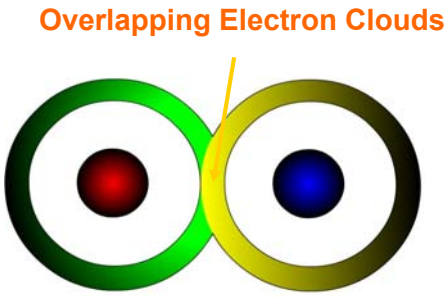
Table 2.5 The lattice energy and melting point values for various ionic solids

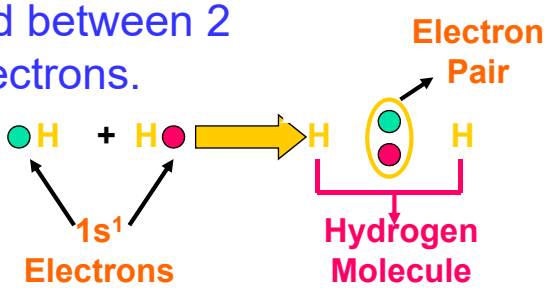
Ionic solid	Lattice energy* kJ/mol	Lattice energy* kcal/mol	Melting point (°C)
LiCl	829	198	613
NaCl	766	183	801
KCl	686	164	776
RbCl	670	160	715
CsCl	649	155	646
MgO	3932	940	2800
CaO	3583	846	2580
SrO	3311	791	2430
BaO	3127	747	1923

*All values are negative for bond formation (energy is released).

Covalent Bonding

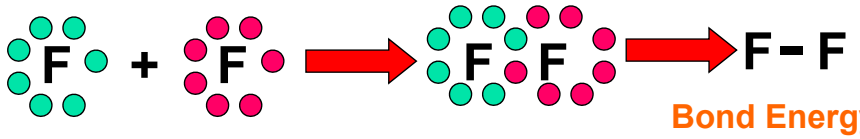
- In covalent bonding, outer s and p electrons are shared between two atoms to obtain noble gas configuration.(full occupancy of the outer electron shell)
- Take place between elements with small differences in *electronegativity* and close by in periodic table.
- In hydrogen, a bond is formed between 2 atoms by sharing their $1s^1$ electrons.





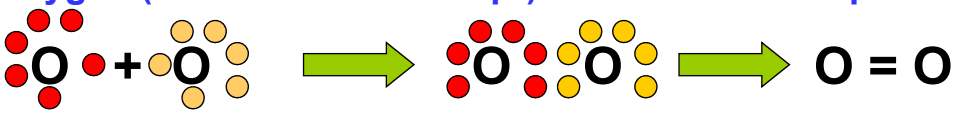
Covalent Bonding - Examples

- In case of F_2, O_2 and N_2, covalent bonding is formed by sharing p electrons
- Fluorine gas (Outer orbital – $2s^2\ 2p^5$) share one p electron to attain noble gas configuration.



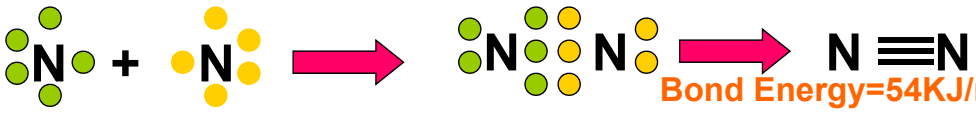
Bond Energy=160KJ/mol

- Oxygen (Outer orbital - $2s^2\ 2p^4$) atoms share two p electrons



Bond Energy=28KJ/mol

- Nitrogen (Outer orbital - $2s^2\ 2p^3$) atoms share three p electrons

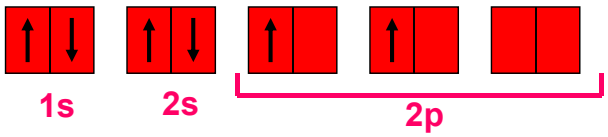


Bond Energy=54KJ/mol

Covalent Bonding in Carbon

- Carbon has electronic configuration $1s^2\ 2s^2\ 2p^2$

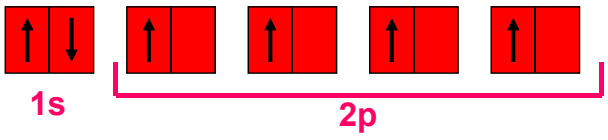
Ground State arrangement



Two ½ filled 2p orbitals

Indicates carbon Forms two Covalent bonds

- *Hybridization* causes one of the 2s orbitals promoted to 2p orbital. Result → four sp^3 orbitals.



Four ½ filled sp^3 orbitals

Indicates four covalent bonds are formed

Bond energy and bond length

Bond	Bond energy* kcal/mol	Bond energy* kJ/mol	Bond length (nm)
C—C	88	370	0.154
C═C	162	680	0.13
C≡C	213	890	0.12
C—H	104	435	0.11
C—N	73	305	0.15
C—O	86	360	0.14
C═O	128	535	0.12
C—F	108	450	0.14
C—Cl	81	340	0.18
O—H	119	500	0.10
O—O	52	220	0.15
O—Si	90	375	0.16
N—O	60	250	0.12
N—H	103	430	0.10
F—F	38	160	0.14
H—H	104	435	0.074

*Approximate values since environment changes energy. All values are negative for bond formation (energy is released).

Source: L. H. Van Vlack, "Elements of Materials Science," 4th ed., Addison-Wesley, 1980.

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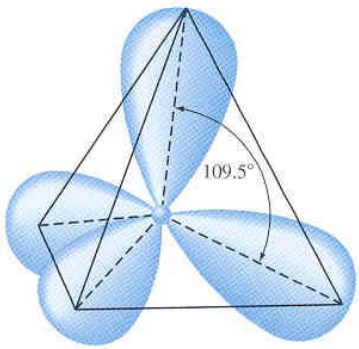
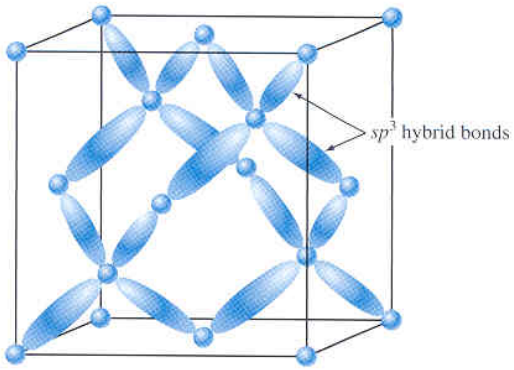
Structure of Diamond

- **Four sp^3 orbitals are directed *symmetrically* toward corners of regular tetrahedron.**
- **This structure gives high hardness, high bonding strength (711KJ/mol) and high melting temperature (3550°C).**



Carbon Atom

Figure 2.18

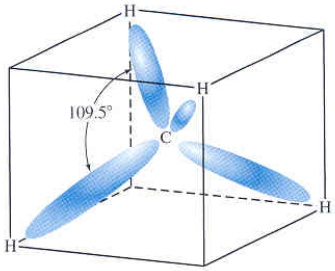


Tetrahedral arrangement in diamond

Figure 2.19

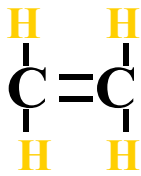
Carbon Containing Molecules

- In Methane, Carbon forms four covalent bonds with Hydrogen.
- Molecules are very weakly bonded together resulting in low melting temperature (-183°C).
- Carbon also forms bonds with itself.
- Molecules with multiple carbon bonds are more reactive.
  - Examples:-



Methane molecule

Figure 2.24

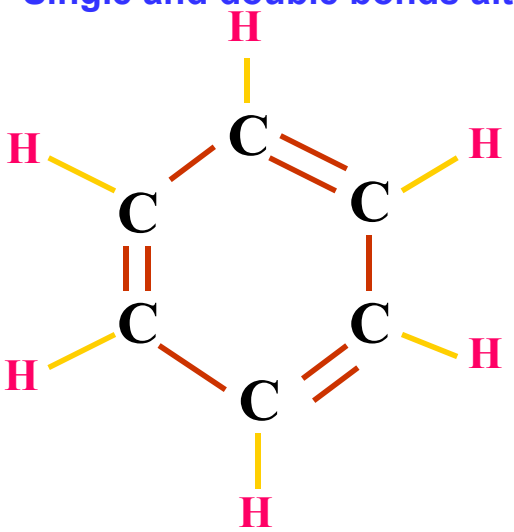


Ethylene

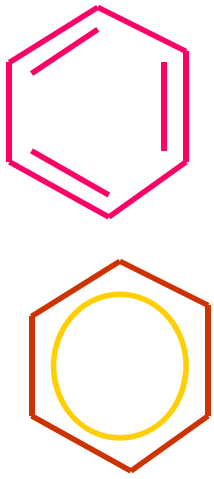
Acetylene

Covalent Bonding in Benzene

- Chemical composition of Benzene is C_6H_6.
- The Carbon atoms are arranged in hexagonal ring.
- Single and double bonds alternate between the atoms.



Structure of Benzene



Simplified Notations

Figure 2.26

Metallic Bonding

- Atoms in metals are closely packed in crystal structure.
- Loosely bounded valence electrons are attracted towards nucleus of other atoms.
- Electrons spread out among atoms forming electron clouds.
- These free electrons are reason for electric conductivity and ductility.
- Since outer electrons are shared by many atoms, metallic bonds are *Non-directional.*

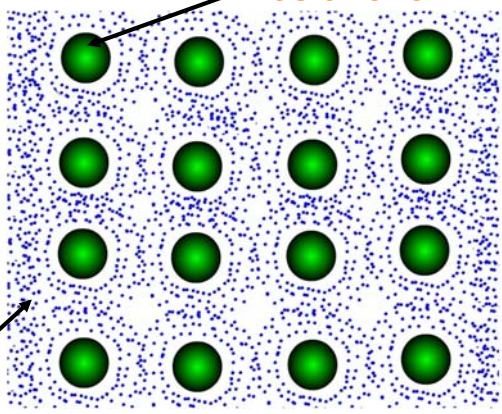


Figure 2.24

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Metallic Bonds (Cont..)

- Overall energy of individual atoms are lowered by metallic bonds
- Minimum energy between atoms exist at equilibrium distance a_0
- Fewer the number of valence electrons involved, more metallic the bond is. (valence e- freer to move)
  - Example:- Na → Bonding energy 108KJ/mol, Melting temperature 97.7°C
- Higher the number of valence electrons involved, higher is the bonding energy.
  - Example:- Ca → Bonding energy 177KJ/mol, Melting temperature 851°C

Ionic-covalent mixed bonding

- Most covalent-bonded molecules have some ionic binding, and vice versa.
- Pauling proposed the following equation to determine the percentage ionic character of bonding in a compound AB:

% ionic character = $(1-\exp(-(1/4)(X_A - X_B)^2)\times 100\%$

X_A and X_B: electronegativities of atom A and B in the compound

GaAs: X_{Ga}=1.8; X_{As}=2.2 ; % ionic character = 4%

ZnSe: X_{Zn}=1.7; X_{Se}=2.5 ; % ionic character = 15%

Metallic-Covalent mixed bonding

- Transition metals have mixed metallic-covalent bonding involving *dsp* hybridized bonding orbitals.
- Mixed metallic-covalent bonding leads to high M.P.
- Group IVA elements transit from pure covalent bonding in C (diamond) to some metallic character in Si and Ge, and to pure metallic bonding in Sn and Pb.

Metallic-ionic mixed bonding

- Large difference in electronegativity for the elements forming a compound.

  → significant amount of electron transfer between the elements

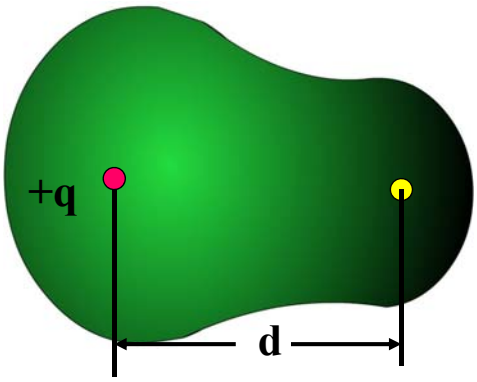
  → ionic binding in the compound
- Intermetallic compounds:

  $NaZn_{13}$ (more ionic character)

  Al_9Co_3 and Fe_5Zn_{21} (less ionic character)

Secondary Bonding

- **Secondary bonds are due to attractions of *electric dipoles* in atoms or molecules.**
- **Dipoles are created when positive and negative charge centers exist.**



Dipole moment=μ =q.d

q= Electric charge
d = separation distance

- **There are two types of bonds → permanent and fluctuating.**

Fluctuating Dipoles

- **Weak secondary bonds in noble gasses.**
- **Dipoles are created due to asymmetrical distribution of electron charges.**
- **Electron cloud charge changes with time.**

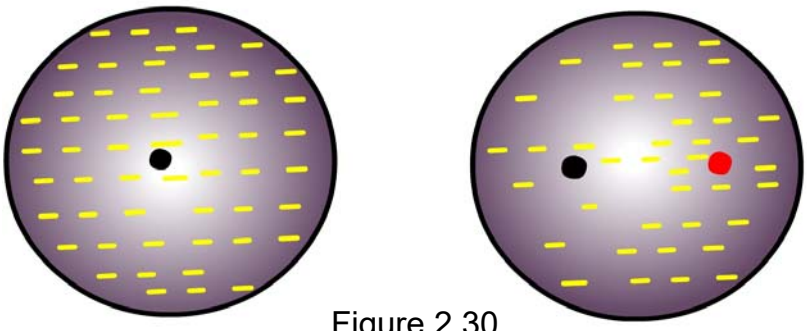


Figure 2.30

Symmetrical distribution of electron charge

Asymmetrical Distribution (Changes with time)

Melting and boiling points of noble gases

Table 2.10 Melting and boiling points of noble gases at atmospheric pressure

Noble gas	Melting point (°C)	Boiling point (°C)
Helium	−272.2	−268.9
Neon	−248.7	−245.9
Argon	−189.2	−185.7
Krypton	−157.0	−152.9
Xenon	−112.0	−107.1
Radon	−71.0	−61.8

- As atomic size of noble gases increases, the M.P. and B.P. increase due to stronger bonding forces since the electrons have more freedom to create stronger dipole moments

Permanent Dipoles

- **Dipoles that do not fluctuate with time are called Permanent dipoles.**

  Examples:

CH_4 → Symmetrical Arrangement Of 4 C-H bonds → No Dipole moment

CH_3Cl → Asymmetrical Tetrahedral arrangement → Creates Dipole

Hydrogen Bonds

- **Hydrogen bonds are *Dipole-Dipole interaction* between polar bonds containing hydrogen atom.**
  - **Example :-**
    - **In water, dipole is created due to asymmetrical arrangement of hydrogen atoms.**
    - **Attraction between positive oxygen pole and negative hydrogen pole.**

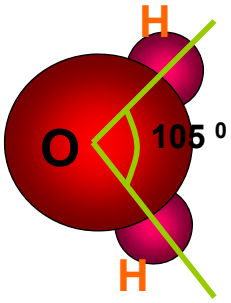
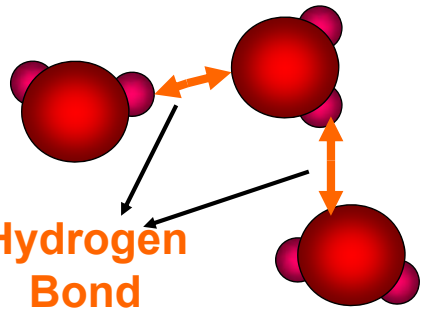


Figure 2.28



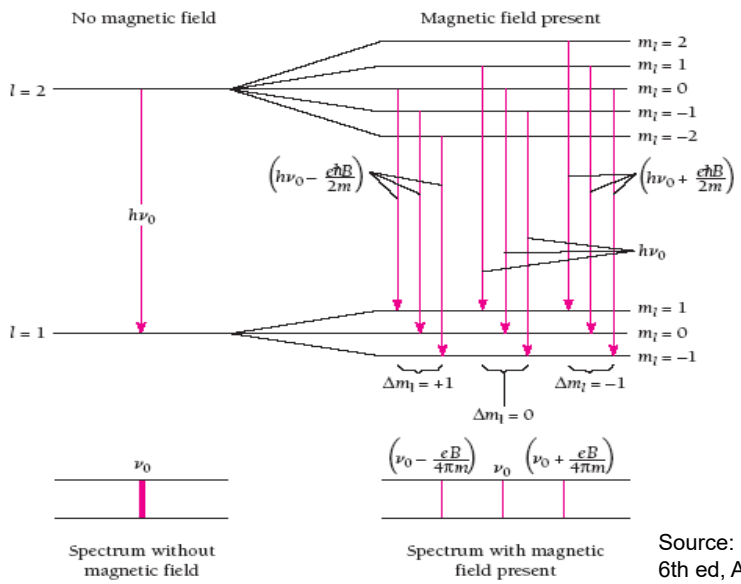
Summary

- Atomic models and their experimental evidences
- Trends of atomic size, ionization energy and electron affinity in the periodic table
- Atomic bonding nature and corresponding physical properties

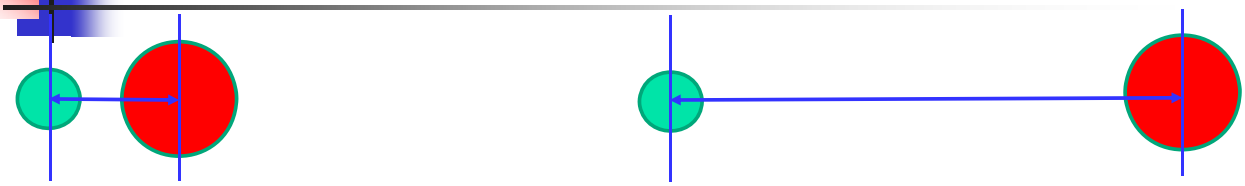
Backup slide

Normal Zeeman effect

There is slight shift in energy levels due to the interaction between the orbital magnetic moment and the external magnetic field. This displacement of the energy levels gives the uniformly spaced splitting of the spectral lines.



Source: Concepts of Modern Physics", 6th ed, Arthur Beiser, p.225



attraction

$$F_a = -\frac{z_1 z_2 e^2}{4\pi\varepsilon_0}\frac{1}{a^2}$$

$$E_{a_0} = -\int_{a_0}^{\infty} F da = \frac{z_1 z_2 e^2}{4\pi\varepsilon_0}\frac{1}{a_0}$$

$$\boxed{E_{a_0} + \int_{a_0}^{\infty} F da = 0}$$

repulsion

$$F_r = -\frac{nb}{a^{n+1}}$$

$$E_{a_0} = -\int_{a_0}^{\infty} F da = \frac{b}{a^n}$$