Chapter 2. Atomic structure and Interatomic Bonding

- Atomic Structure
  - Electrons, protons and neutrons in atoms (Bohr and QM models)
  - The periodic table
- Atomic Bonding
  - Bonding forces and energies
  - Primary interatomic bonds
  - Secondary bonding
  - Molecules

Why Study Atomic Structure and interatomic Bonding?

- An extremely large number of microscopically small hairs on each of their toe pads
- Weak forces of attraction (i.e., van der Waals forces) are established between hair molecules and molecules on the surface
- Self-cleaning: dirt particles don't stick to these toe pads
- Synthetic self-cleaning adhesives???

Some of the important properties of solid materials depends on geometrical atomic arrangements and also the interactions that exist among constituent atoms or molecules.

Atomic Structure
fundamental concepts

- atom – electrons – 9.11 x 10^{-31} kg
  nucleus {protons, neutrons} } 1.67 x 10^{-27} kg
- atomic number Z = # of protons in nucleus of atom
  = # of electrons of neutral species
- atomic mass A
- atomic mass unit= amu = 1/12 mass of ^{12}C
  (A=12.00000 for ^{12}C)
  Isotopes?

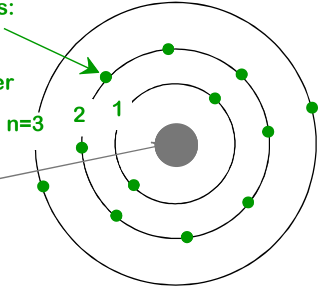
$$A \cong Z + N$$

- Atomic wt = wt of 6.023 x 10^{23} molecules or atoms

1 amu/atom = 1g/mol

Electrons In Atoms- Bohr Atomic Model

Electron orbitals & quantized energy levels



orbital electrons:
n = principal
quantum number

Adapted from Fig. 2.1, *Callister 6e.*

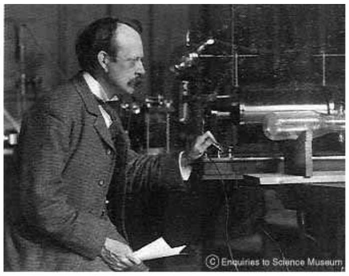
Nucleus: Z = # protons
N = # neutrons
Atomic mass A ≈ Z + N

! **Bohr atomic model:** Electrons are assumed to revolve around the atomic nucleus in discrete orbitals, and the position of any particular electron is more or less well defined in terms of its orbital.

! Quantum-mechanical principle: the energies of electrons are quantized---electrons are permitted to have only specific values of energy. Energy levels or states are separated by finite energies.

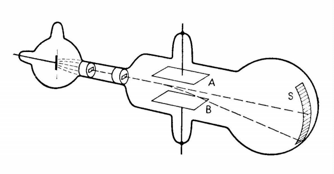
Electron

- In 1897, J.J.Thomson discovered “corpuscles”, small particles with a charge/mass ratio more than 1000 times greater than that of protons, swarming in a see of positive charge (“plum pudding model”).



Sir Joseph John Thomson
(1856-1940)
Nobel prize 1906

Discovery of the ELECTRON



Thomson’s 2nd Cathode ray experiment

Particle & Wave

- In 1924, Louis de Broglie first theorized that the electron had wave-like characteristics. Application of the idea of particle – wave dualism (only known for photons up to then) for any kind of matter. (first person to receive a Nobel Prize on a PhD thesis)

Louis Victor de Broglie (1892-1987)
Nobel prize 1929

Electron=Particle & Wave

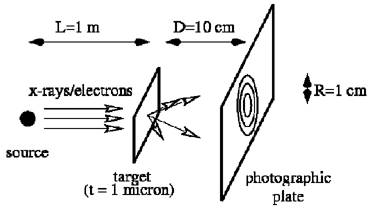
$$\lambda = \frac{h}{p} = \frac{h}{mv}$$

Electron=Wave

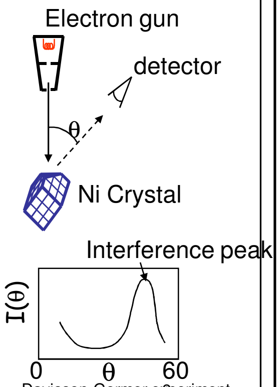
- In 1927, Davisson and Germer, Thomson and Reid, independently carried out their classic electron diffraction experiments (demonstration of wave nature of electrons)

Sir George Paget Thomson
(1892 – 1975)
Nobel Prize: 1937
(shared with C.J. Davison)

Electron=Wave



GP Thomson Experimental Apparatus and Results



Davisson-Germer experiment

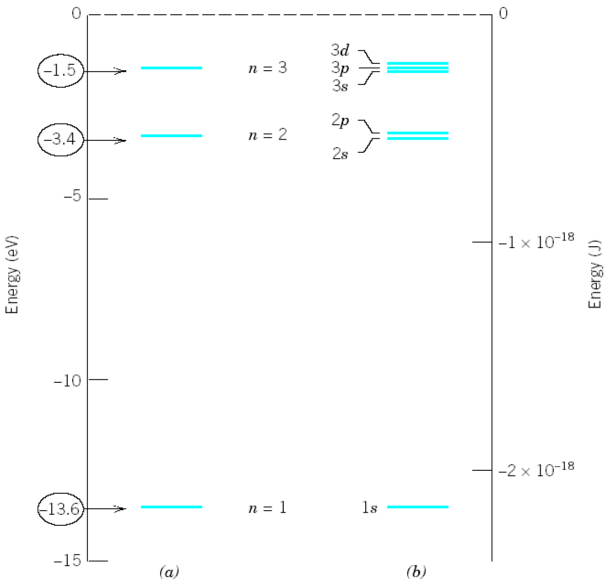
Electrons In Atoms
Wave-mechanical model

- Electron is considered to exhibit both wave-like and particle-like characteristics.

- The electron is no longer treated as a particle moving in a discrete orbital; rather, positions considered to be the probability of an electron’s being at various locations around the nucleus.

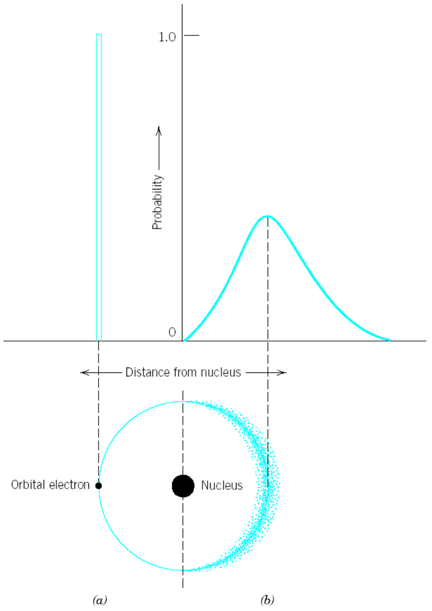
Quantum Mechanics:
Wave or matrix mechanics
→ Probability.

Comparison of Bohr and QM models

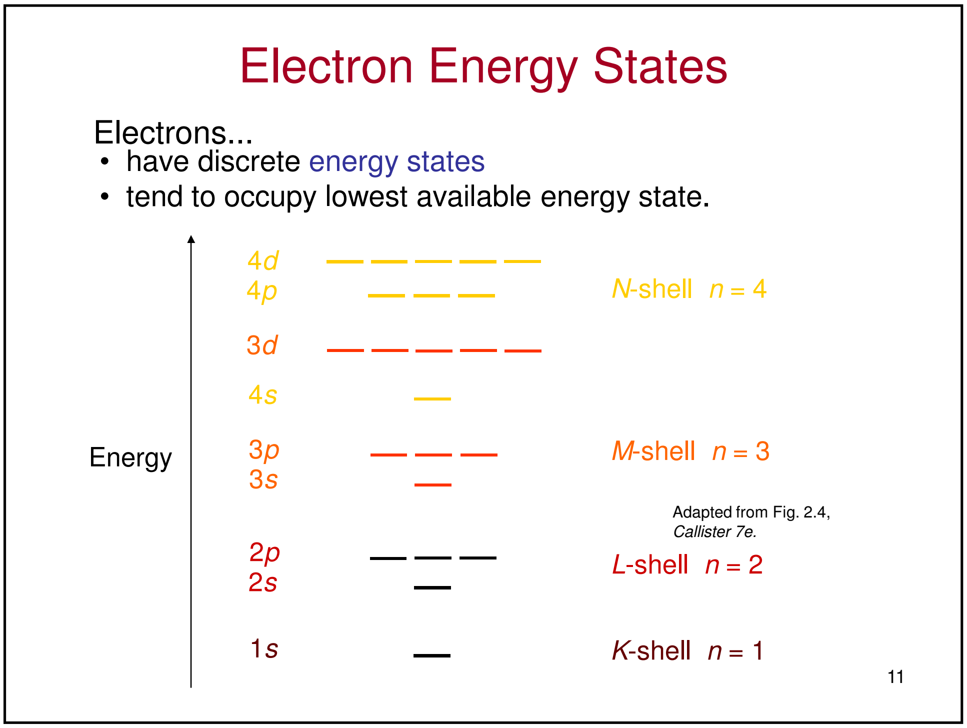


Figs. 2.2

Comparison of Bohr and QM models



Figs. 2.3 from Callister



Electron Energy States

Electrons...

- have discrete energy states
- tend to occupy lowest available energy state.

Energy

4d

4p — *N*-shell *n* = 4

3d

4s

3p — *M*-shell *n* = 3

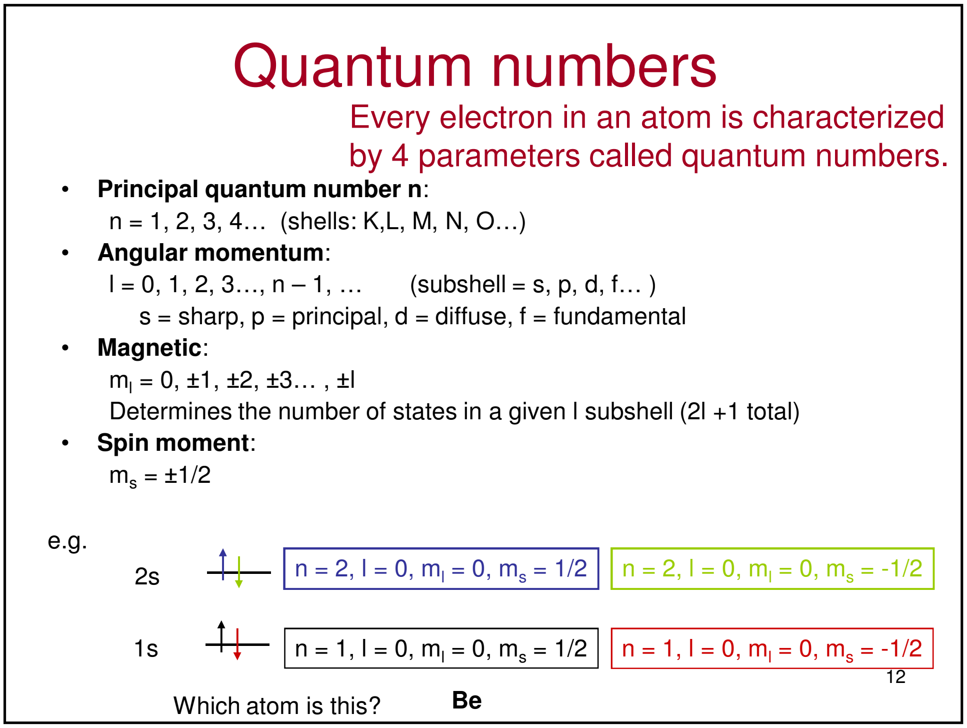
3s

2p — *L*-shell *n* = 2

2s

1s — *K*-shell *n* = 1

Adapted from Fig. 2.4, *Callister 7e.*



Quantum numbers

Every electron in an atom is characterized by 4 parameters called quantum numbers.

- **Principal quantum number n**:
  n = 1, 2, 3, 4… (shells: K,L, M, N, O…)
- **Angular momentum**:
  l = 0, 1, 2, 3…, n – 1, … (subshell = s, p, d, f…)
  s = sharp, p = principal, d = diffuse, f = fundamental
- **Magnetic**:
  $m_l = 0, \pm1, \pm2, \pm3\ldots, \pm l$
  Determines the number of states in a given l subshell (2l +1 total)
- **Spin moment**:
  $m_s = \pm1/2$

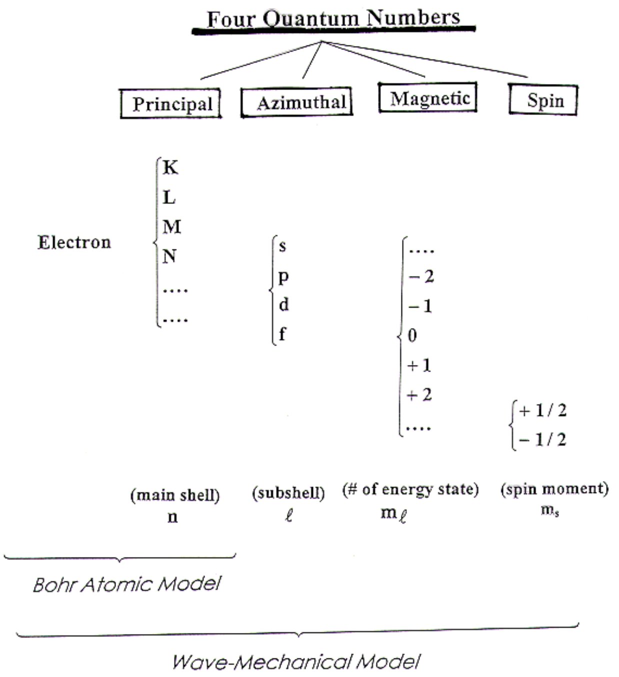
e.g.

2s: $n = 2, l = 0, m_l = 0, m_s = 1/2$ | $n = 2, l = 0, m_l = 0, m_s = -1/2$

1s: $n = 1, l = 0, m_l = 0, m_s = 1/2$ | $n = 1, l = 0, m_l = 0, m_s = -1/2$

Which atom is this? **Be**

Four Quantum Numbers



Principal **Azimuthal** **Magnetic** **Spin**

Electron

K
L
M
N
....
....

s
p
d
f

....
-2
-1
0
$+1$
$+2$
....

$+1/2$
$-1/2$

(main shell) n

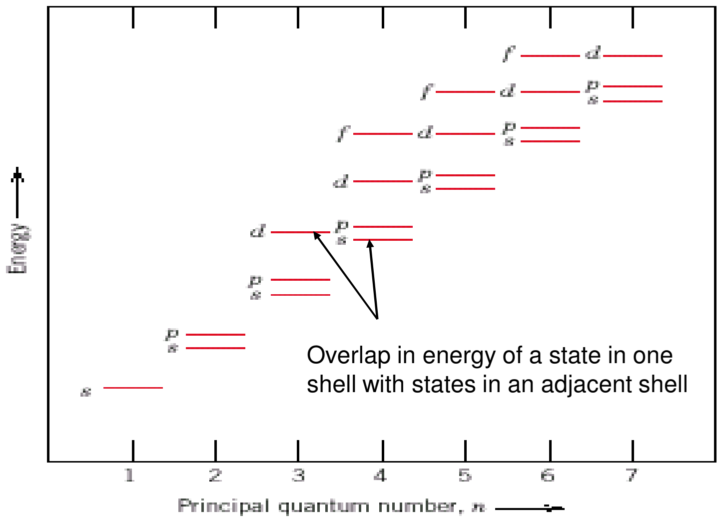
(subshell) ℓ

(# of energy state) m_ℓ

(spin moment) m_s

Bohr Atomic Model

Wave-Mechanical Model



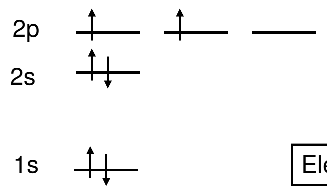
Overlap in energy of a state in one shell with states in an adjacent shell

Relative energies of the electrons for the various shells and subshells

Electron Configuration

- Shorthand notation to represent which states electrons occupy in an atom (without specifying electron spin).

e.g. Carbon

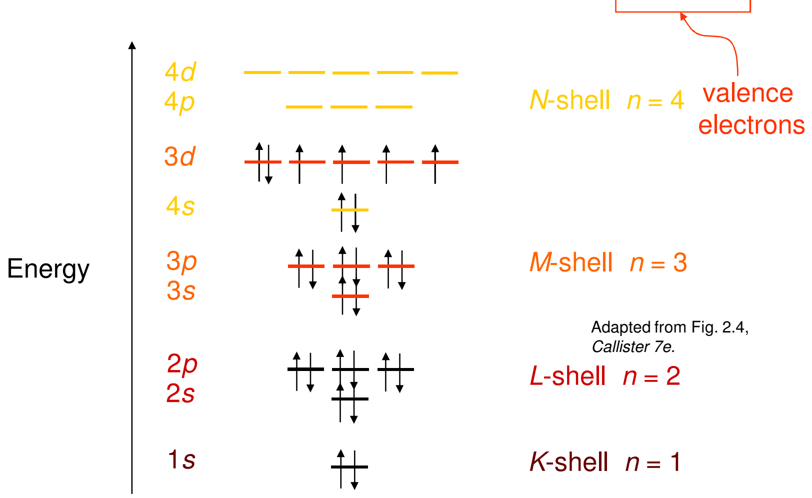


Electron configuration: $1s^2 2s^2 2p^2$

Note
- each energy level can only hold no more than two electrons of opposite spin **(Pauli exclusion principle).**
-for degenerate levels (e.g. 2p-orbitals), each orbital is filled with one electron before electrons are paired up.
- Valence electrons are those that occupy the outermost shell.

Electron Configuration

ex: Fe - atomic # = 26 $1s^2\ 2s^2 2p^6\ 3s^2 3p^6\ \boxed{3d^6\ 4s^2}$



Adapted from Fig. 2.4, *Callister 7e.*

Electron Configuration

1 electron in the s-orbital: **Alkali metals**
Li, Na, K, Rb…

2 electrons in the s-orbital: **Alkaline earths**
Be, Mg, Ca…

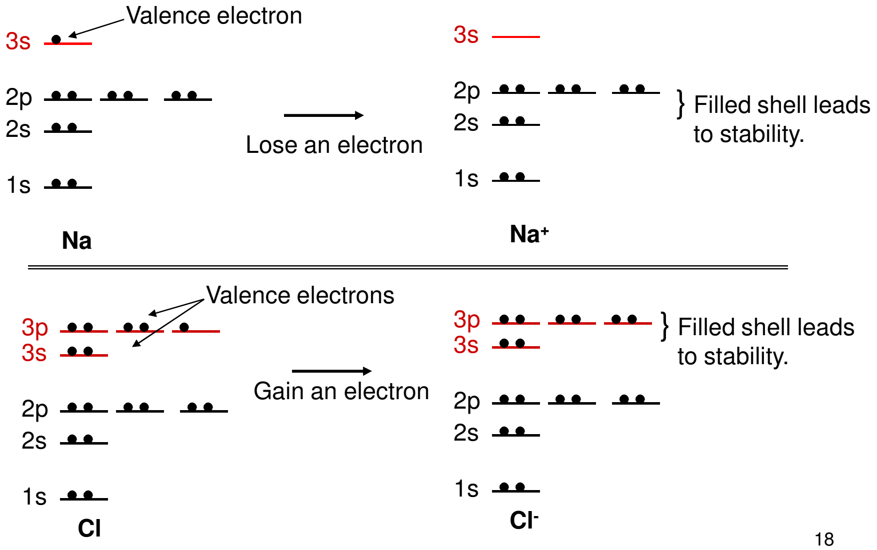
Filled s-orbital and 4 electrons in p-orbital: **Chalcogens**
O, S, Se…

Filled s-orbital and 5 electrons in p-orbital: **Halogens**
F, Cl, Br…

Partially filled d-orbital: **Transition metals**
e.g. Mn, Fe, Co…

→ Note: **valence electrons** determine which group atoms belong to.

Valence Electrons



Valence electron

Lose an electron

} Filled shell leads to stability.

Valence electrons

Gain an electron

} Filled shell leads to stability.

- Most elements: Electron configuration not stable.

Element	Atomic #	Electron configuration
Hydrogen	1	$1s^1$
Helium	2	$1s^2$ (stable)
Lithium	3	$1s^2 2s^1$
Beryllium	4	$1s^2 2s^2$
Boron	5	$1s^2 2s^2 2p^1$
Carbon	6	$1s^2 2s^2 2p^2$
...		...
Neon	10	$1s^2 2s^2 2p^6$ (stable)
Sodium	11	$1s^2 2s^2 2p^6 3s^1$
Magnesium	12	$1s^2 2s^2 2p^6 3s^2$
Aluminum	13	$1s^2 2s^2 2p^6 3s^2 3p^1$
...		...
Argon	18	$1s^2 2s^2 2p^6 3s^2 3p^6$ (stable)
...	...	...
Krypton	36	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6$ (stable)

Adapted from Table 2.2, *Callister 7e.*

- Why? Valence (outer) shell usually not filled completely.

Stable Configuration

Stable electron configurations...

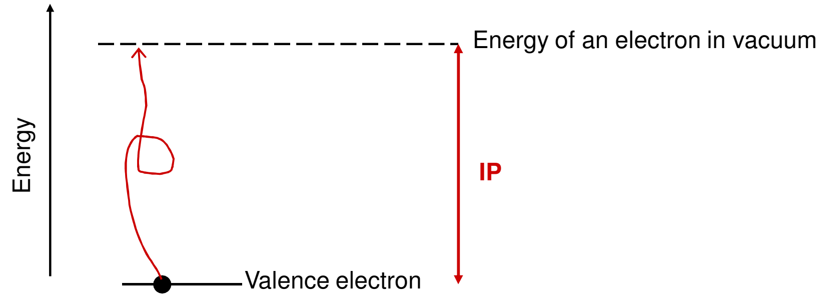
- **have complete s and p subshells**
- **tend to be inert.**

Z	**Element**	**Configuration**
2	**He**	$1s^2$
10	**Ne**	$1s^2 2s^2 2p^6$
18	**Ar**	$1s^2 2s^2 2p^6 3s^2 3p^6$
36	**Kr**	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6$

Adapted from Table 2.2, *Callister 6e.*

Noble gases

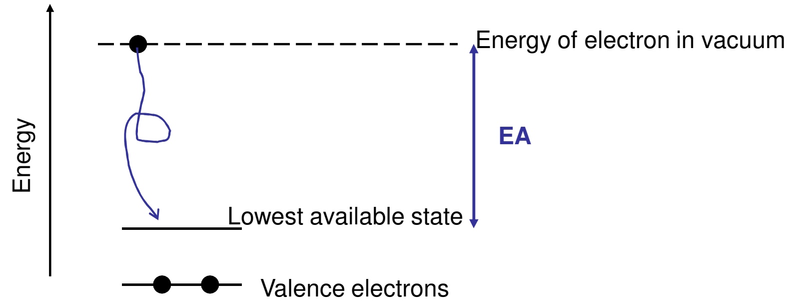
How much energy does it require to take an electron out of an atom?



- **Ionization potential (IP):** Energy required to pull out a valence electron (in vacuum).

By convention, IP is positive (i.e. need to put in energy to pull out the electron).

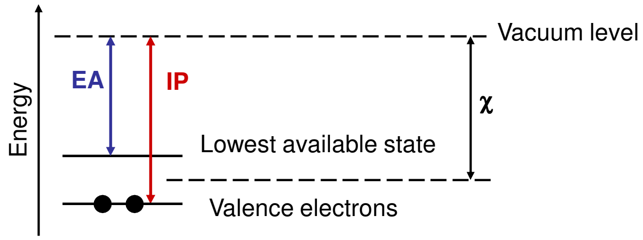
How much energy does it require to place an electron in an atom?



- **Electron Affinity (EA):** Energy gained by putting an electron in (from vacuum).

By convention, EA is negative (i.e. electron goes from higher energy state in vacuum to lower energy state in atom).

How do we determine when an atom will accept an electron or give one up?



- **Electronegativity (χ):** a measure of how likely an atom will take up or give up an electron

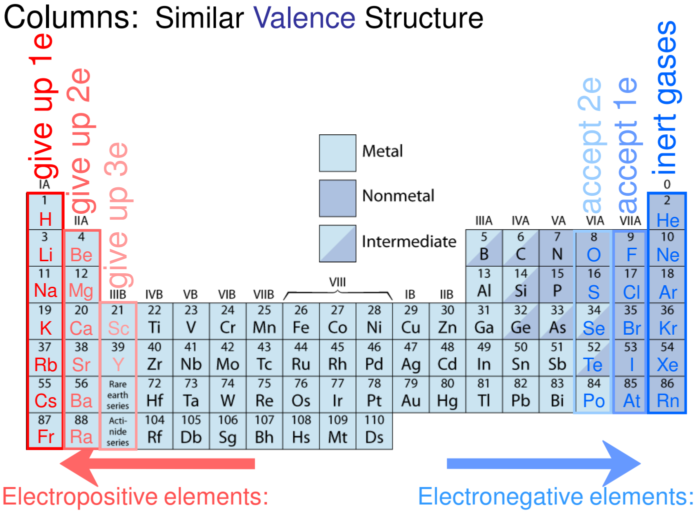
A simple (and intuitive) definition: $\chi \sim \frac{IP+EA}{2}$

-When two atoms are brought together, the atom with larger χ will have higher electron density around its nucleus.

-Larger Δχ ⟶ more ionic bond.

The Periodic Table

- Columns: Similar Valence Structure



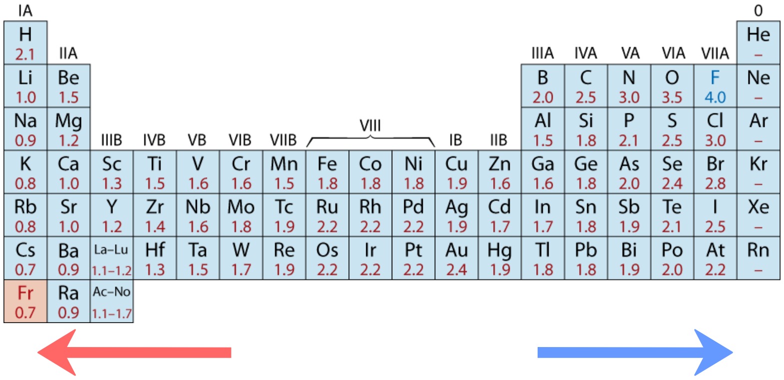
Adapted from Fig. 2.6, *Callister 7e.*

Electropositive elements:
Readily give up electrons
to become + ions.

Electronegative elements:
Readily acquire electrons
to become - ions.

Electronegativity

- Ranges from 0.7 to 4.0,
- Large values: tendency to acquire electrons.

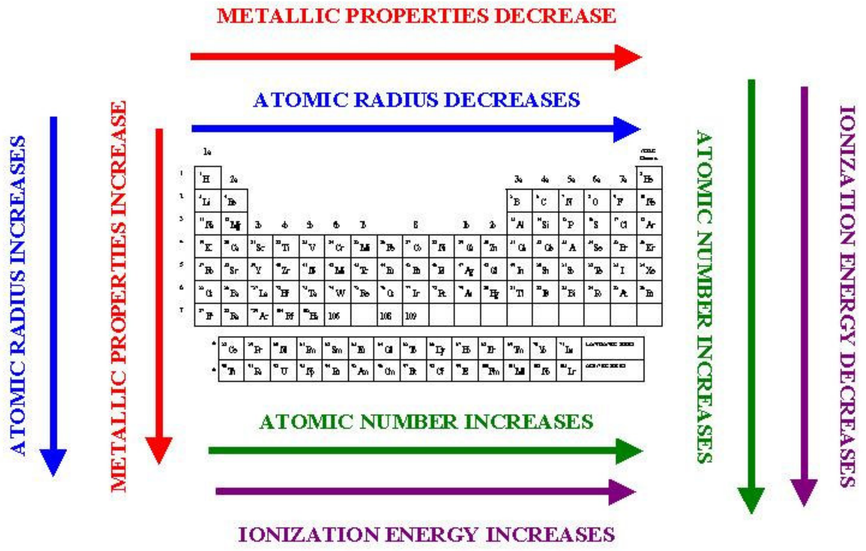


IA	IIA	IIIB	IVB	VB	VIB	VIIB	VIII	VIII	VIII	IB	IIB	IIIA	IVA	VA	VIA	VIIA	0
H 2.1																	He –
Li 1.0	Be 1.5											B 2.0	C 2.5	N 3.0	O 3.5	F 4.0	Ne –
Na 0.9	Mg 1.2											Al 1.5	Si 1.8	P 2.1	S 2.5	Cl 3.0	Ar –
K 0.8	Ca 1.0	Sc 1.3	Ti 1.5	V 1.6	Cr 1.6	Mn 1.5	Fe 1.8	Co 1.8	Ni 1.8	Cu 1.9	Zn 1.6	Ga 1.6	Ge 1.8	As 2.0	Se 2.4	Br 2.8	Kr –
Rb 0.8	Sr 1.0	Y 1.2	Zr 1.4	Nb 1.6	Mo 1.8	Tc 1.9	Ru 2.2	Rh 2.2	Pd 2.2	Ag 1.9	Cd 1.7	In 1.7	Sn 1.8	Sb 1.9	Te 2.1	I 2.5	Xe –
Cs 0.7	Ba 0.9	La–Lu 1.1–1.2	Hf 1.3	Ta 1.5	W 1.7	Re 1.9	Os 2.2	Ir 2.2	Pt 2.2	Au 2.4	Hg 1.9	Tl 1.8	Pb 1.8	Bi 1.9	Po 2.0	At 2.2	Rn –
Fr 0.7	Ra 0.9	Ac–No 1.1–1.7															

Smaller electronegativity

Larger electronegativity

Adapted from Fig. 2.7, *Callister 7e.* (Fig. 2.7 is adapted from Linus Pauling, *The Nature of the Chemical Bond*, 3rd edition, Copyright 1939 and 1940, 3rd edition. Copyright 1960 by Cornell University.



METALLIC PROPERTIES DECREASE

ATOMIC RADIUS DECREASES

ATOMIC RADIUS INCREASES

METALLIC PROPERTIES INCREASE

ATOMIC NUMBER INCREASES

IONIZATION ENERGY DECREASES

ATOMIC NUMBER INCREASES

IONIZATION ENERGY INCREASES

SUMMARY OF TRENDS IN THE PERIODIC TABLE