CHAPTER 2:
BONDING AND PROPERTIES

ISSUES TO ADDRESS...

- What promotes bonding?
- What types of bonds are there?
- What properties are inferred from bonding?

Atomic Structure (Chemistry Review)

- atom – - electrons – 9.11×10^{-31} kg
  + protons, neutrons } 1.67×10^{-27} kg
- atomic number = # of protons in nucleus of atom
  = # of electrons of neutral species
- A [=] atomic mass unit = amu = 1/12 mass of ^{12}C

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

  1 amu/atom = 1g/mol

  C 12.011
  H 1.008 etc.

Average Atomic Weight (Mass)

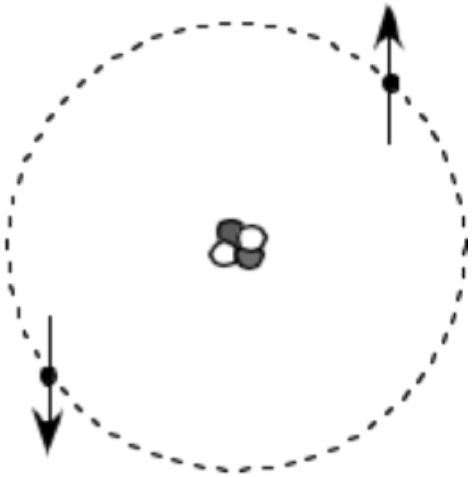
$$\bar{A}_M = \sum_i f_{i_M} A_{i_M}$$

Cerium has four naturally occuring isotopes:
0.185% of ^{136}Ce, with atomic weight of 135.907 amu,
0.251% of ^{138}Ce, with atomic weight of 137.906 amu,
88.450% of ^{140}Ce, with atomic weight of 139.905 amu, and
11.114% of ^{142}Ce, with atomic weight of 141.909 amu.
Calculate the average atomic weight of Ce.

$$\bar{A}_M = \frac{0.185}{100}(135.907) + \frac{0.251}{100}(137.906) + \frac{88.450}{100}(139.905) + \frac{11.114}{100}(141.909)$$

=140.115 amu

Idealized structure of an atom



Atoms have a dense, massive nucleus with neutral neutrons and positively charged protons. The number of protons in the nucleus determines the atomic number Z. The negatively-charged electrons are much lighter and orbit around the nucleus. Any given orbital can have two electrons, one with spin “up” and the other spin “down”.

Atomic Structure

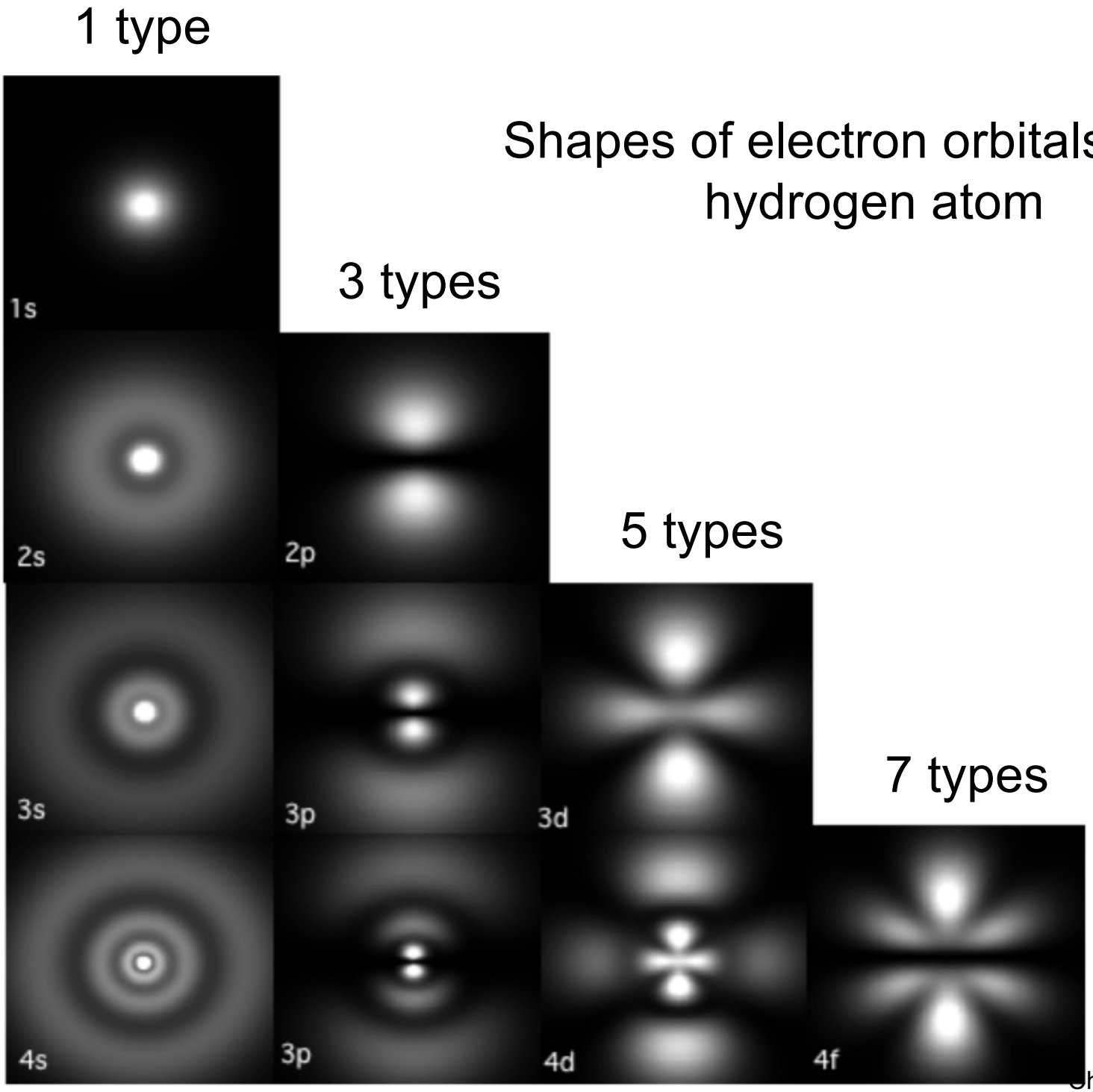
- Valence electrons determine all of the following properties
    1) Chemical
    2) Electrical
    3) Thermal
    4) Optical

Electronic Structure

- Electrons have wave-like and particle-like properties.
  - This means that electrons are in specific orbitals defined by a probability.
  - Each orbital at discrete energy level determined by quantum numbers.

Quantum #	Designation
n = principal (energy level, shell)	*K*, *L*, *M*, *N*, *O* (1, 2, 3, …)
l = subsidiary (orbitals, shape)	*s*, *p*, *d*, *f* (0, 1, 2, 3,…, n-1)
m_l = magnetic	1, 3, 5, 7 (-l to +l)
m_s = spin	½, -½

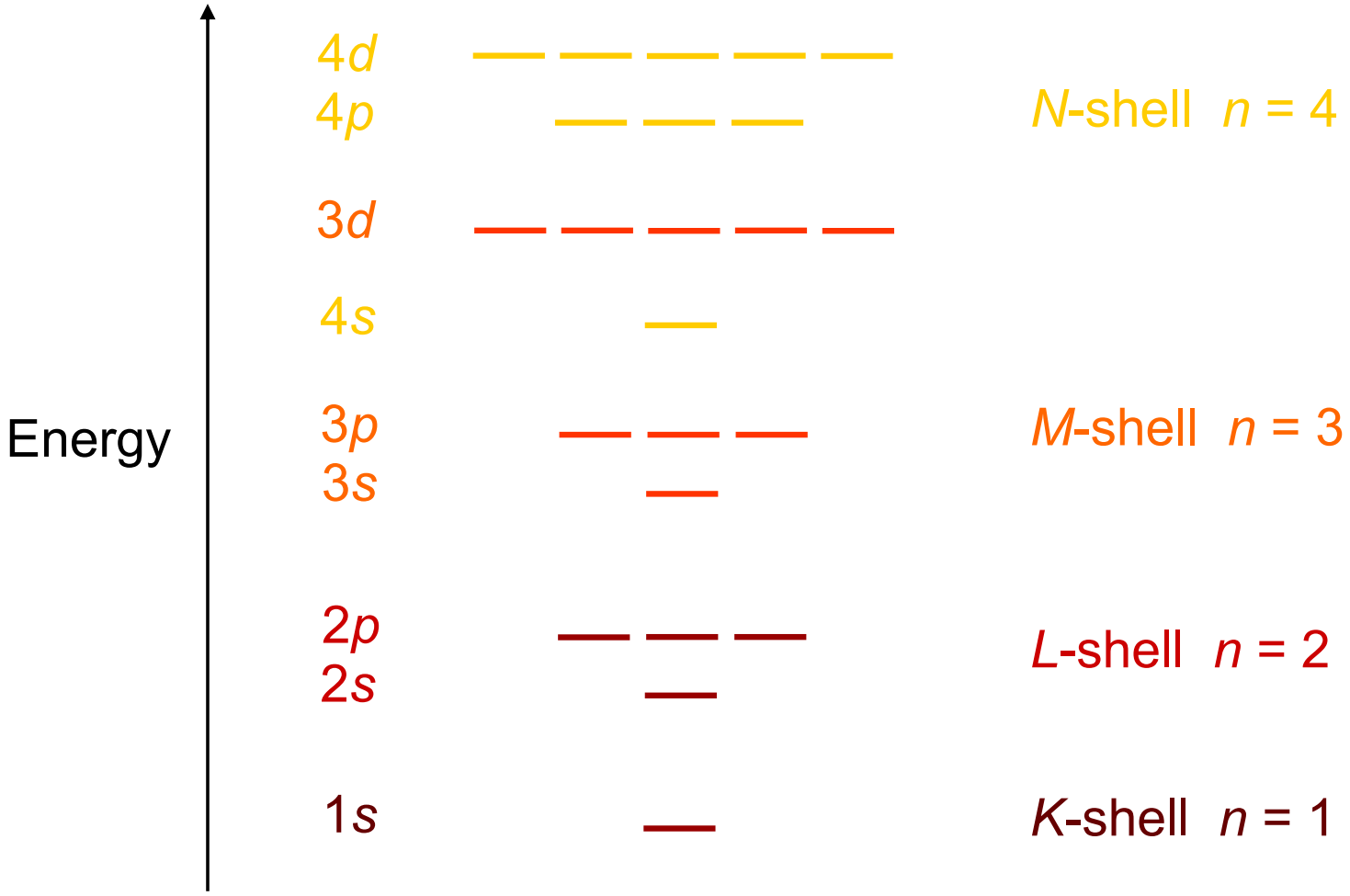
Shapes of electron orbitals in the hydrogen atom



Electron Energy States

Electrons...

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



SURVEY OF ELEMENTS

- Most elements: Electron configuration not stable.

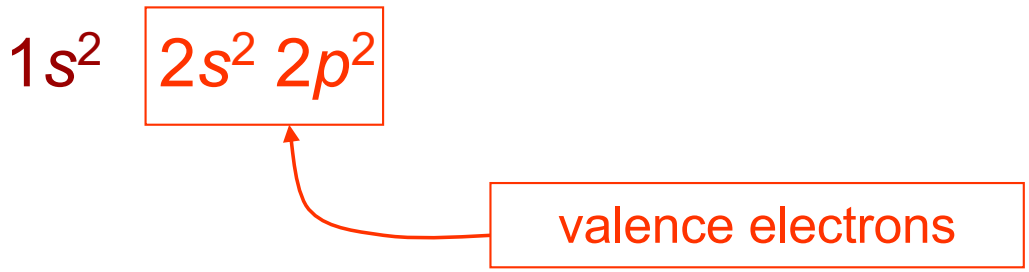
Element	Atomic #	Electron configuration	
Hydrogen	1	$1s^1$	
Helium	2	$1s^2$	(stable)
Lithium	3	$1s^2 2s^1$	
Beryllium	4	$1s^2 2s^2$	
Boron	5	$1s^2 2s^2 2p^1$	
Carbon	6	$1s^2 2s^2 2p^2$	
...		...	
Neon	10	$1s^2 2s^2 2p^6$	(stable)
Sodium	11	$1s^2 2s^2 2p^6 3s^1$	
Magnesium	12	$1s^2 2s^2 2p^6 3s^2$	
Aluminum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

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

Electron Configurations

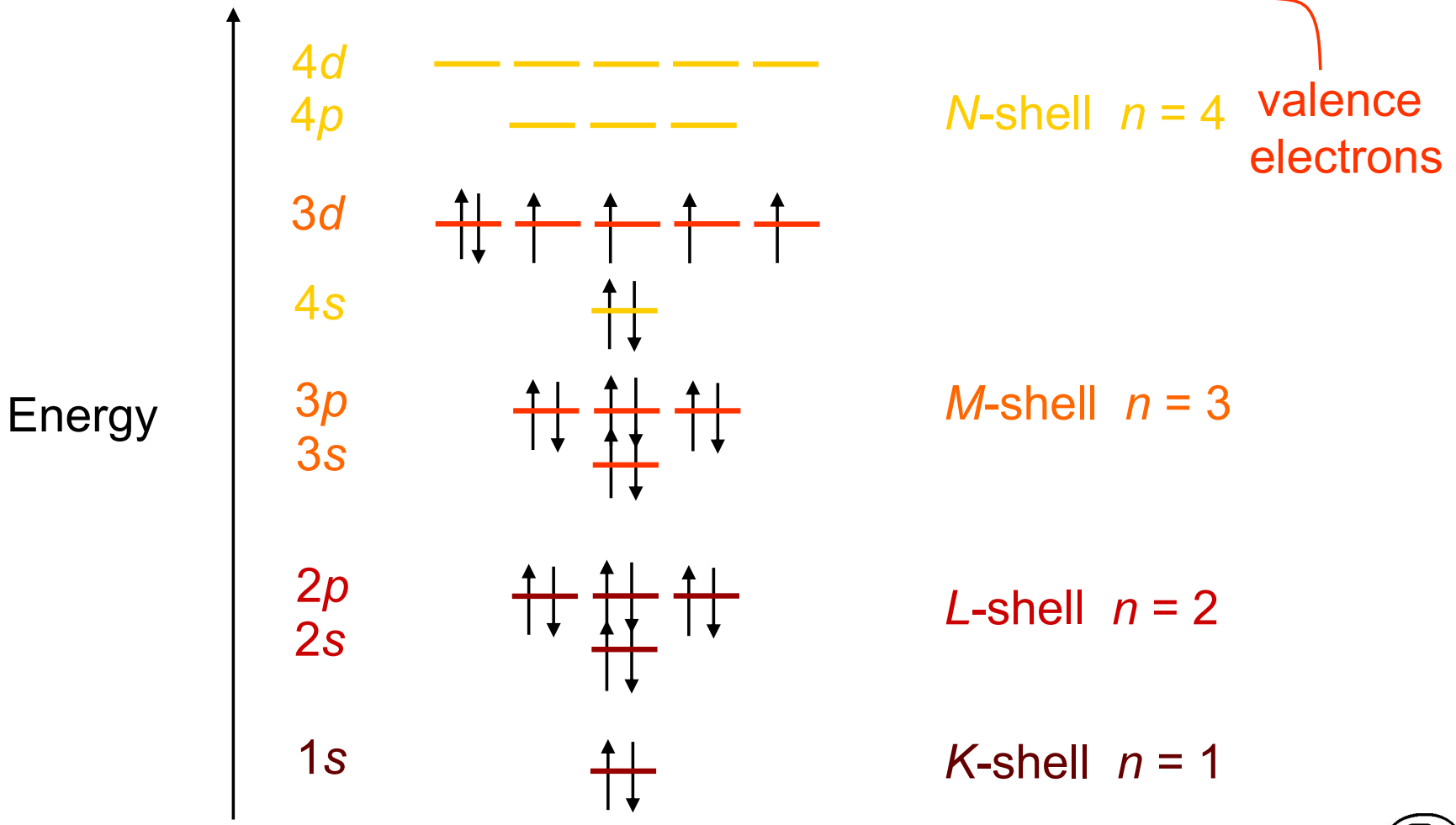
- Valence electrons – those in unfilled shells
- Filled shells more stable
- Valence electrons are most available for bonding and tend to control the chemical properties

  – example: C (atomic number = 6)



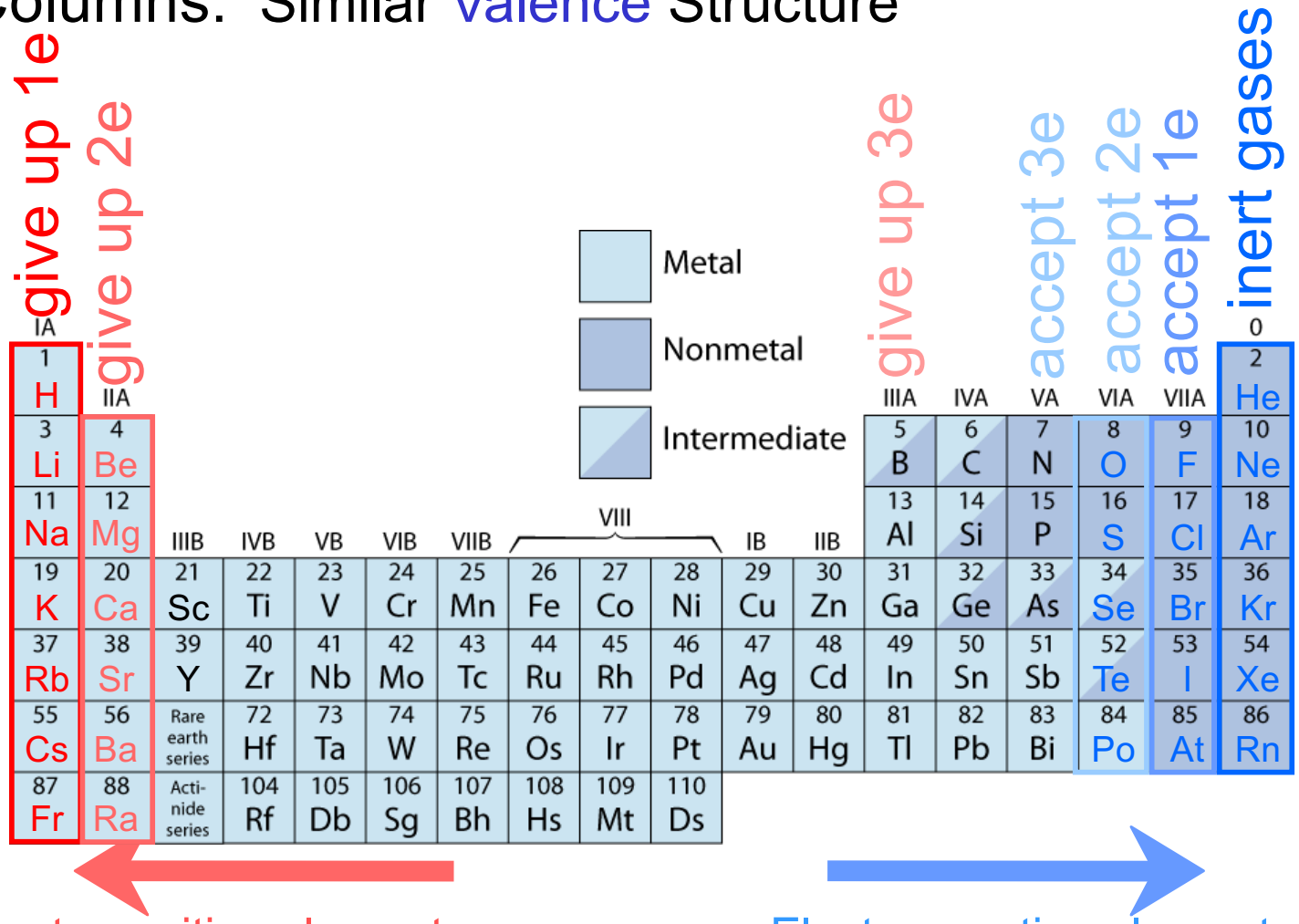
Electronic Configurations

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



The Periodic Table

- Columns: Similar Valence Structure



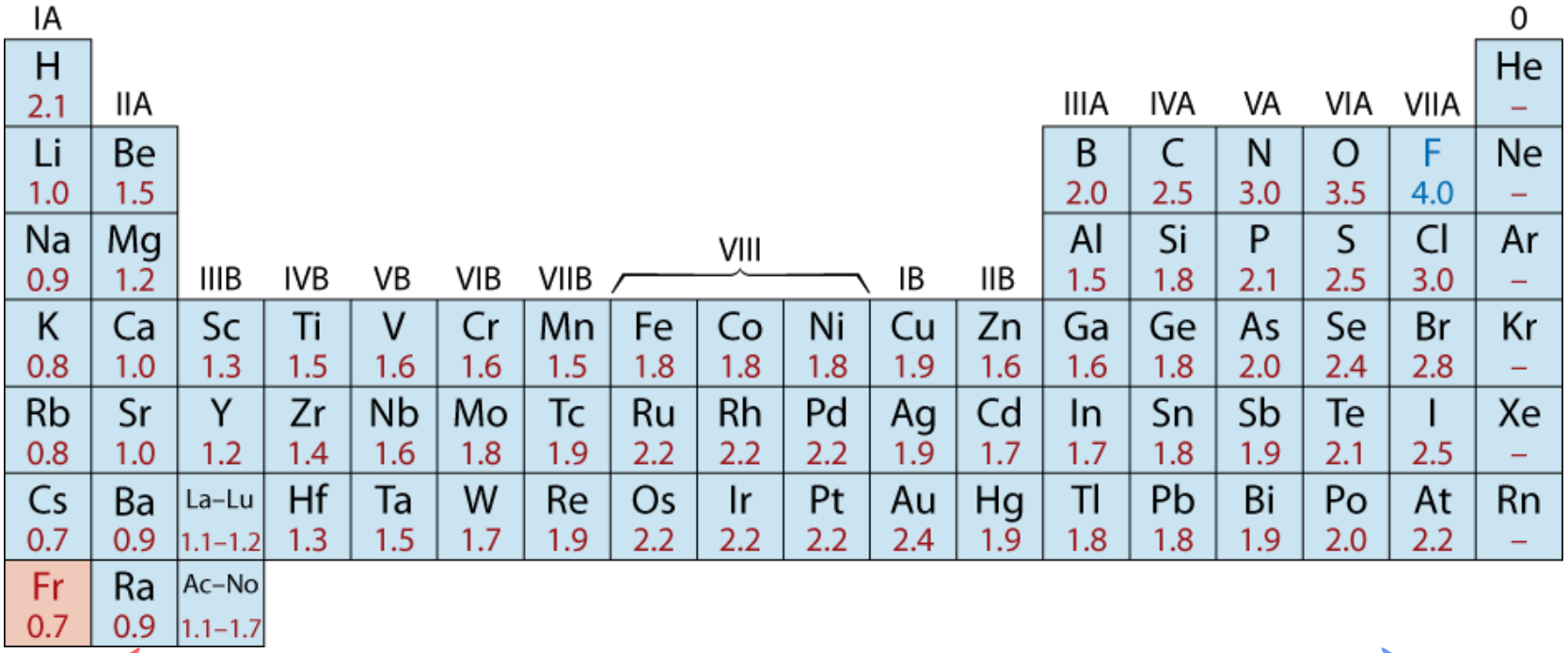
Adapted from Fig. 2.6, *Callister 7e.*

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
  Small values: tendency to give up electrons



Smaller electronegativity

Larger electronegativity

Ionic bond – metal + nonmetal

donates electrons

accepts electrons

Dissimilar electronegativities

ex: MgO

Mg $1s^2\ 2s^2\ 2p^6\ 3s^2$ or [Ne] $3s^2$

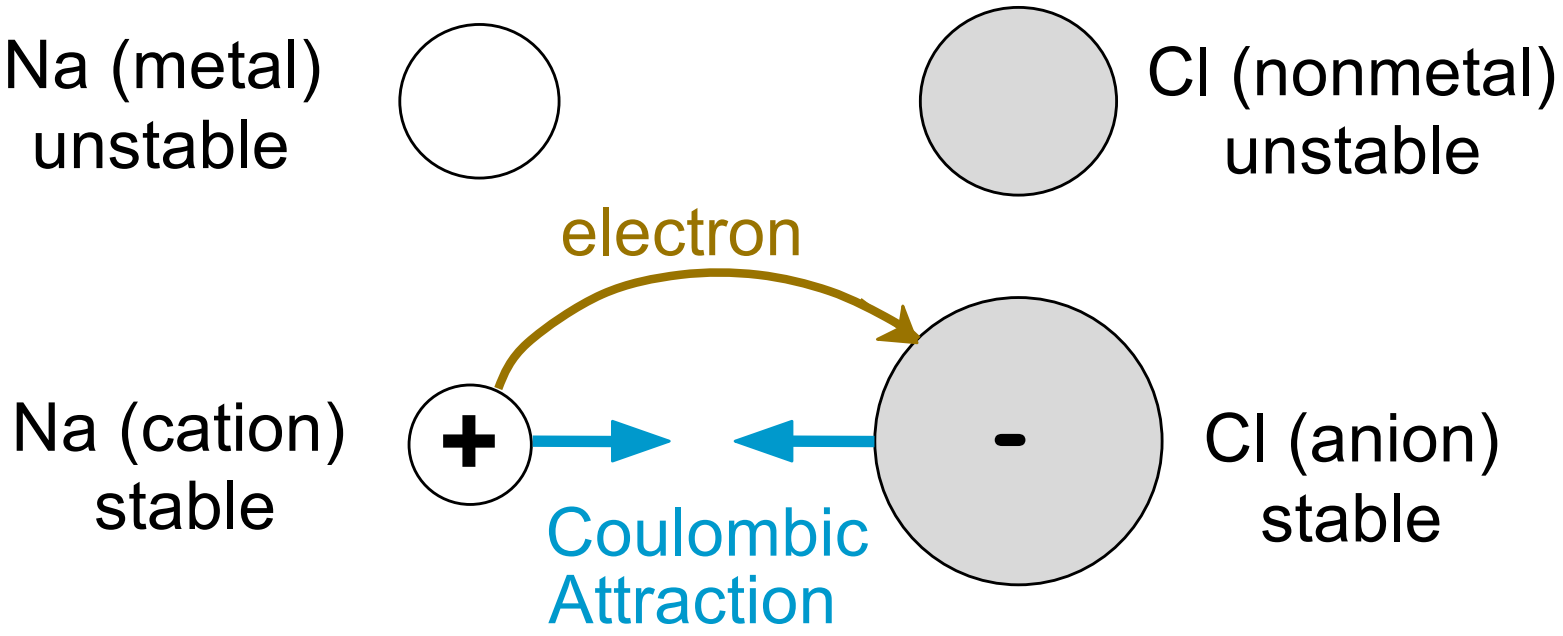
O $1s^2\ 2s^2\ 2p^4$

Mg^{2+} $1s^2\ 2s^2\ 2p^6$ or [Ne]

O^{2-} $1s^2\ 2s^2\ 2p^6$ or [Ne]

Ionic Bonding

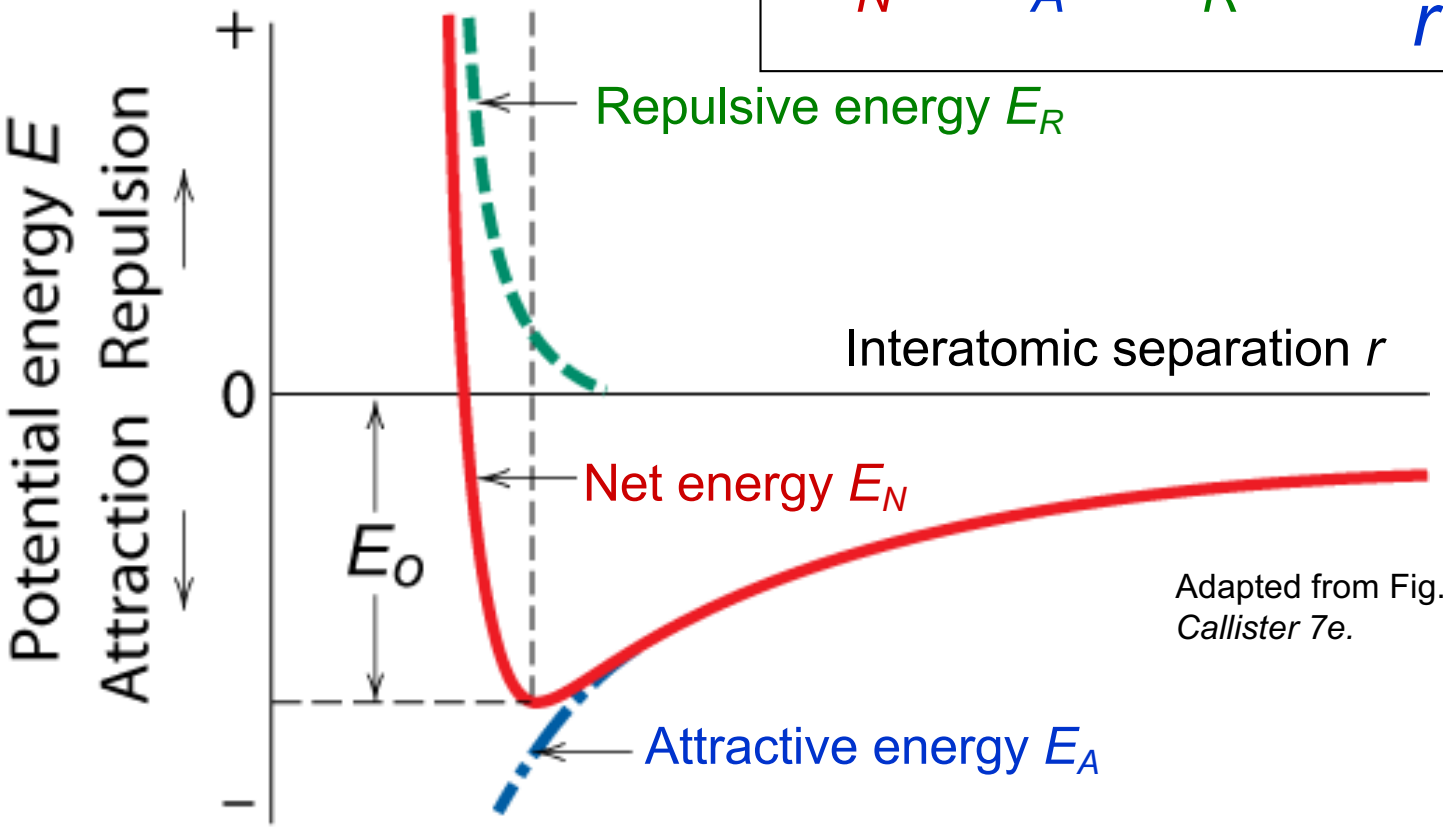
- Occurs between + and - ions.
- Requires electron transfer.
- Large difference in electronegativity required.
- Example: NaCl



Ionic Bonding

- Energy – minimum energy most stable
  - Energy balance of attractive and repulsive terms

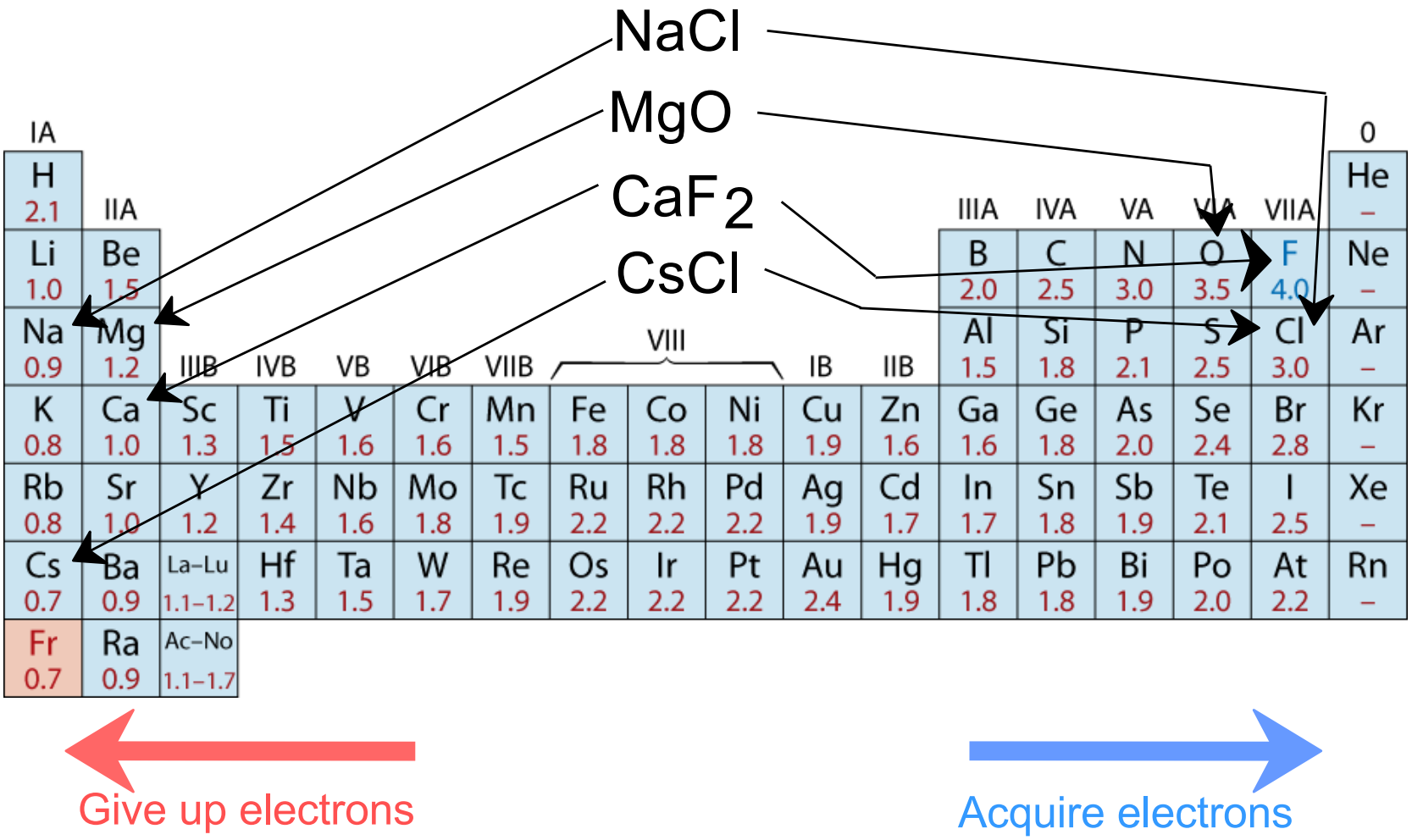
$$E_N = E_A + E_R = -\frac{A}{r} + \frac{B}{r^n}$$



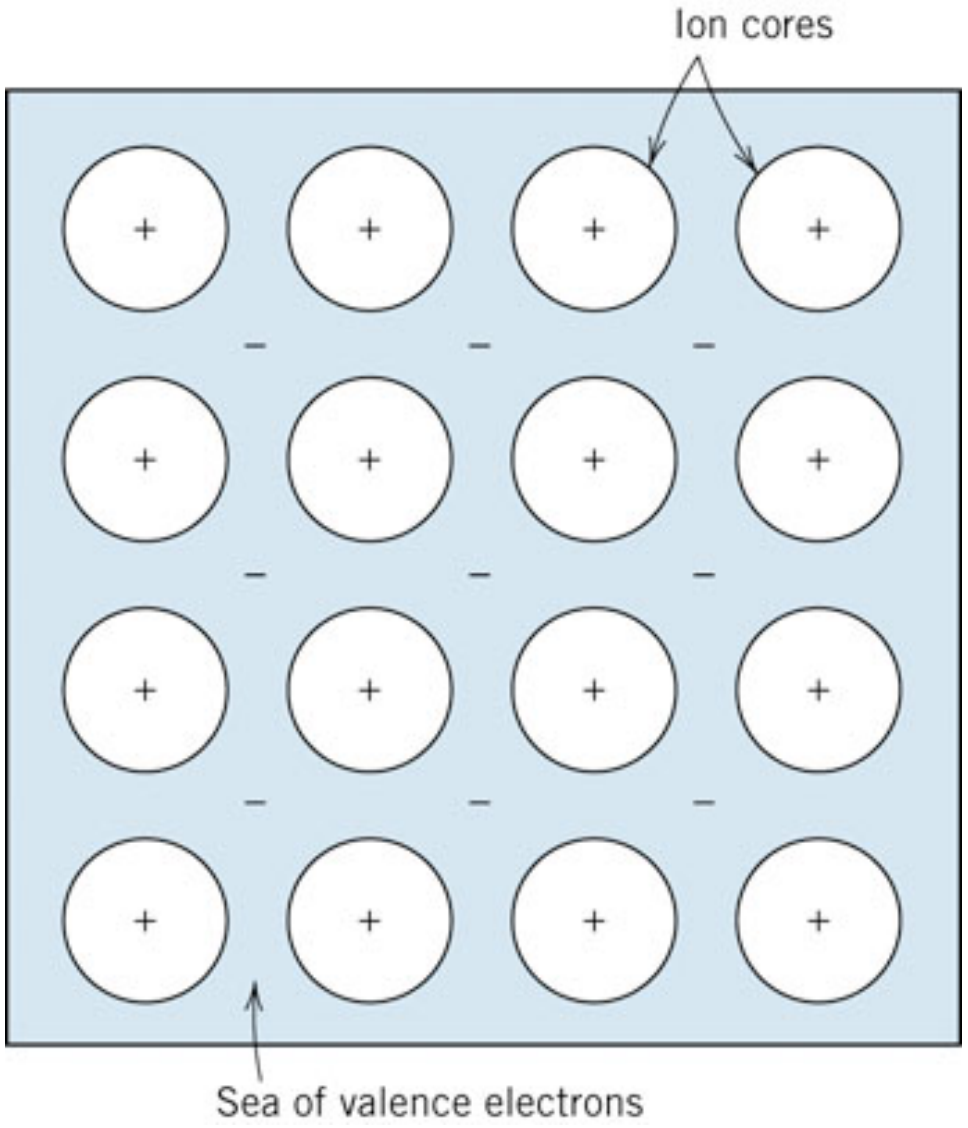
Adapted from Fig. 2.8(b), *Callister 7e.*

Examples: Ionic Bonding

- Predominant bonding in Ceramics



Metallic Bonding



Strong bonds

Non-directional

Electrical conductors
Heat conductors
Optically reflective

Can be quite ductile, depends on crystal structure, perfection

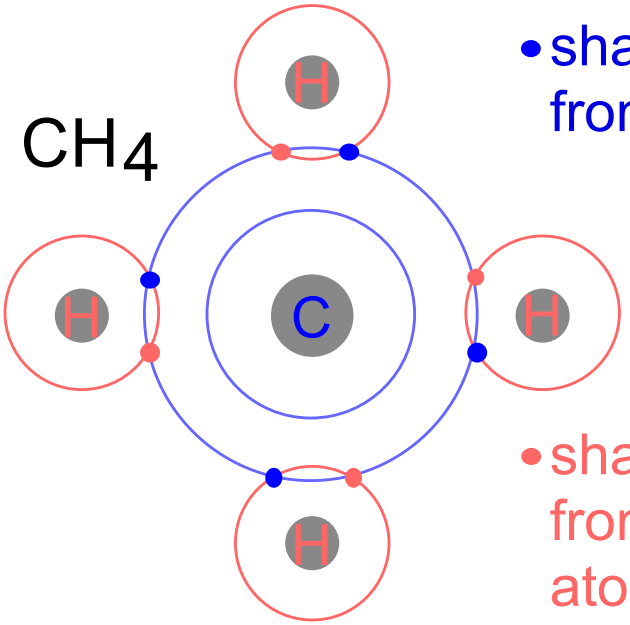
Covalent Bonding

- similar electronegativity ∴ share electrons
- bonds determined by valence – *s* & *p* orbitals dominate bonding
- Example: CH_4

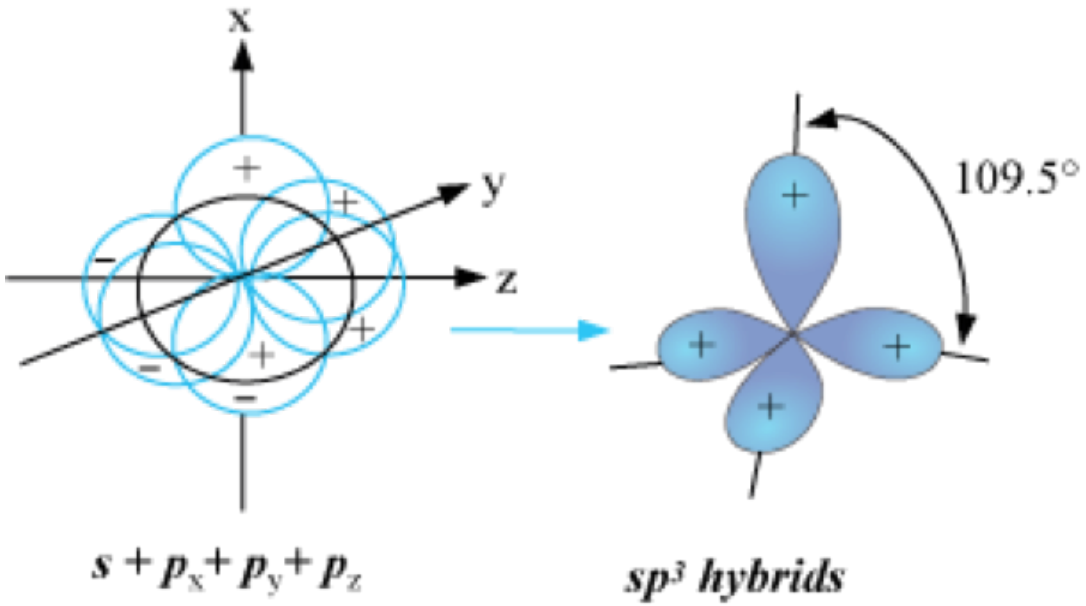
C: has 4 valence e^-, needs 4 more

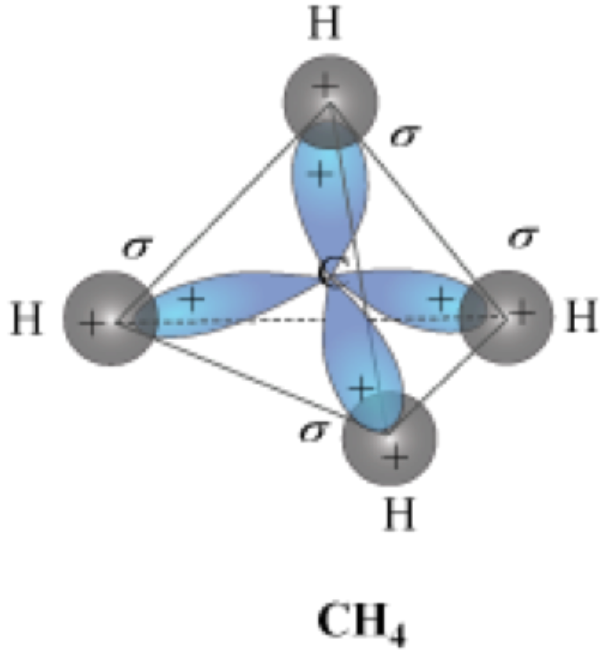
H: has 1 valence e^-, needs 1 more

Electronegativities are comparable.



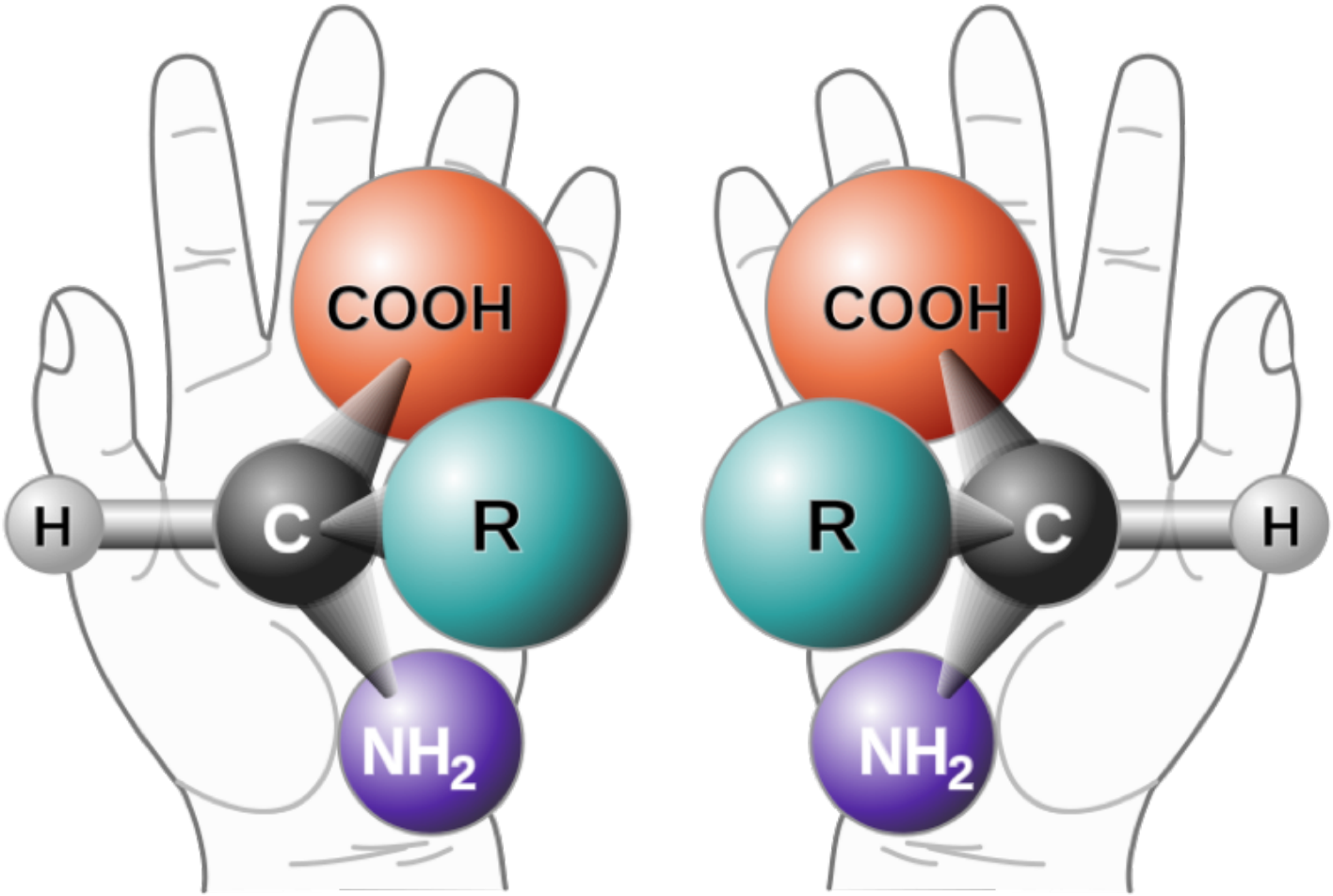
1 s + 3 p = 4 sp^3 hybrid orbitals





methane (natural gas): tetrahedron

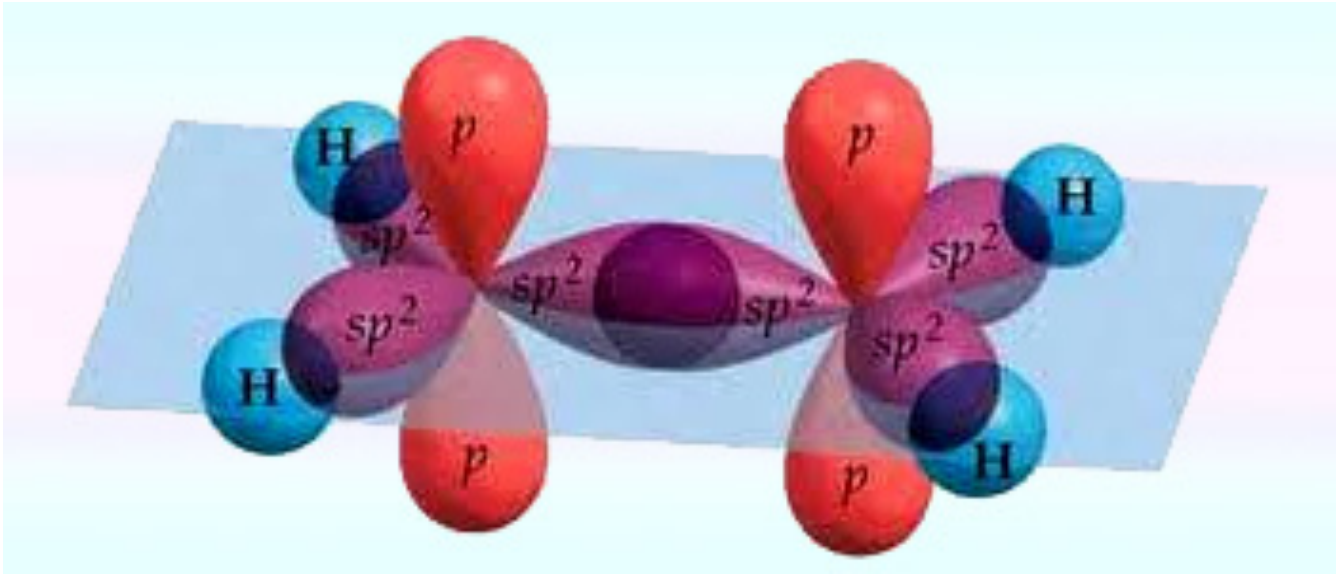
Tetrahedral carbons can be chiral

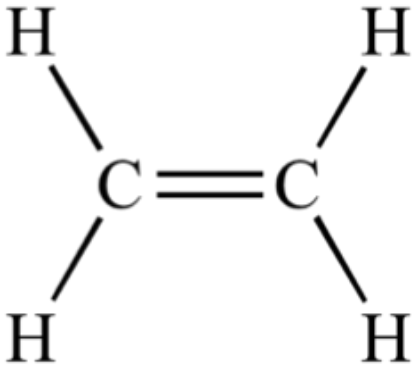


Left handed enantiomer

Right handed enantiomer

1 s + 2 p = 3 sp^2 hybrid orbitals



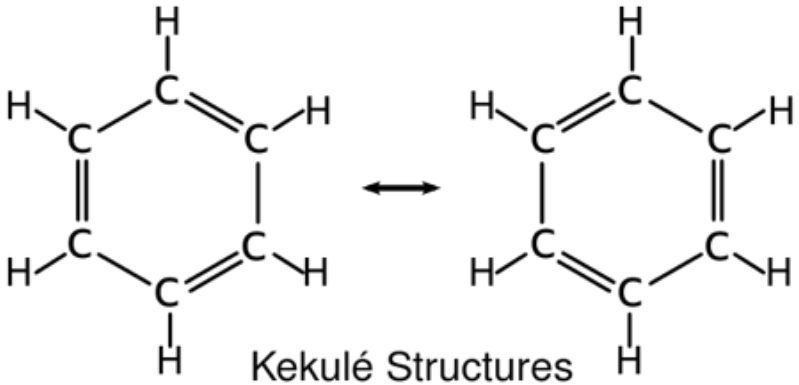


ethene or ethylene
1 sp^2-sp^2 σ bond
1 p-p π bond

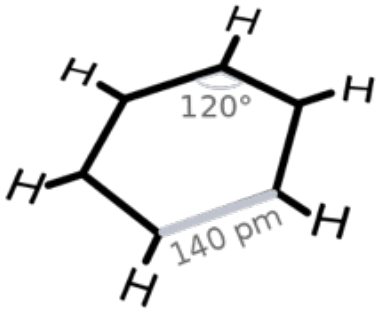
Benzene: alternating single, double bonds

C_6H_6

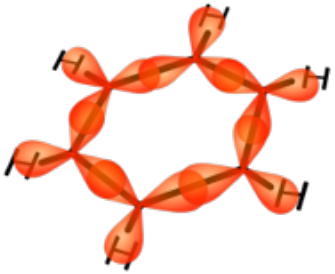
Benzene
Molecular formula



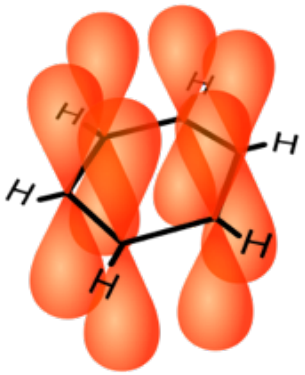
Kekulé Structures
(Isomers)



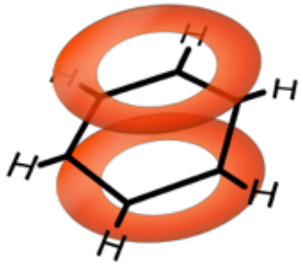
Planar Hexagon
Bond Length 140 pm



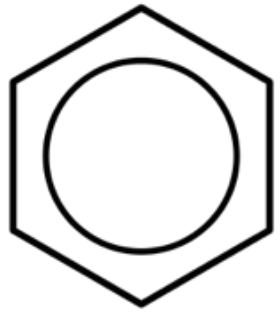
Sigma Bonds
sp^2 Hybridized orbitals



6 p_z orbitals



delocalized pi
system



Benzene ring
Simplified depiction

Primary Bonding

- Metallic Bond -- delocalized as electron cloud

- Ionic-Covalent Mixed Bonding

$$\%\ \text{ionic character} = \left(1 - e^{-\frac{(X_A - X_B)^2}{4}}\right) x\,(100\%)$$

where X_A & X_B are electronegativities

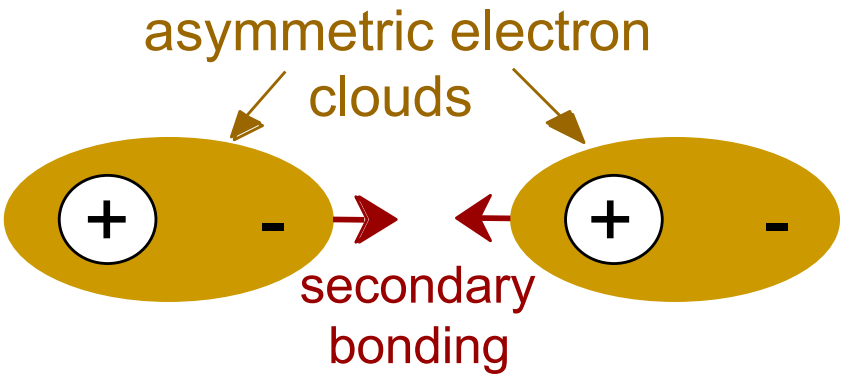
Ex: MgO $\quad X_{Mg} = 1.3$, $X_O = 3.5$

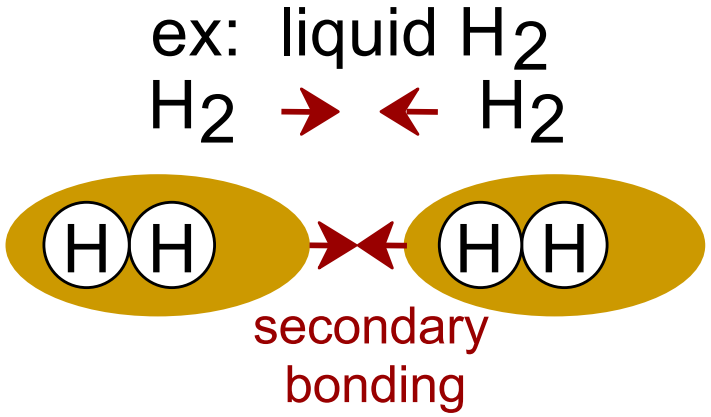
$$\%\ \text{ionic character} = \left(1 - e^{-\frac{(3.5-1.3)^2}{4}}\right) x\,(100\%) = 70.2\%\ \text{ionic}$$

SECONDARY BONDING

Arises from interaction between dipoles

- Fluctuating dipoles





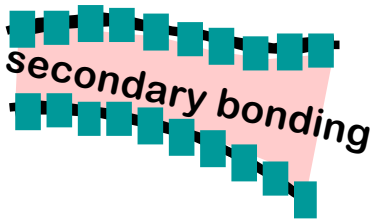
- Permanent dipoles-molecule induced

-general case:

Adapted from Fig. 2.14, *Callister 7e.*

-ex: liquid HCl

-ex: polymer



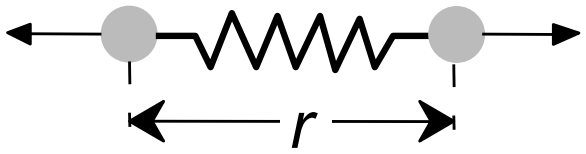
secondary bonding

Summary: Bonding

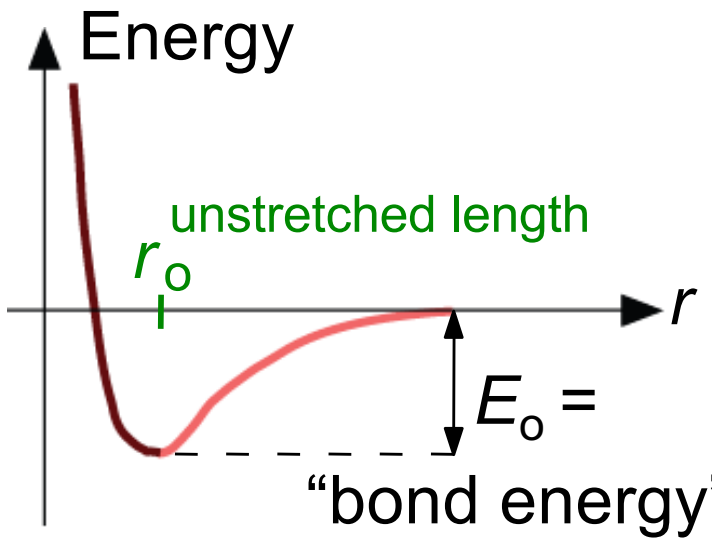
Type	Bond Energy	Comments
Ionic	Large!	Nondirectional (ceramics)
Covalent	Variable large-Diamond small-Bismuth	Directional (semiconductors, ceramics polymer chains)
Metallic	Variable large-Tungsten small-Mercury	Nondirectional (metals)
Secondary	smallest	Directional inter-chain (polymer) inter-molecular

Properties From Bonding: T_m

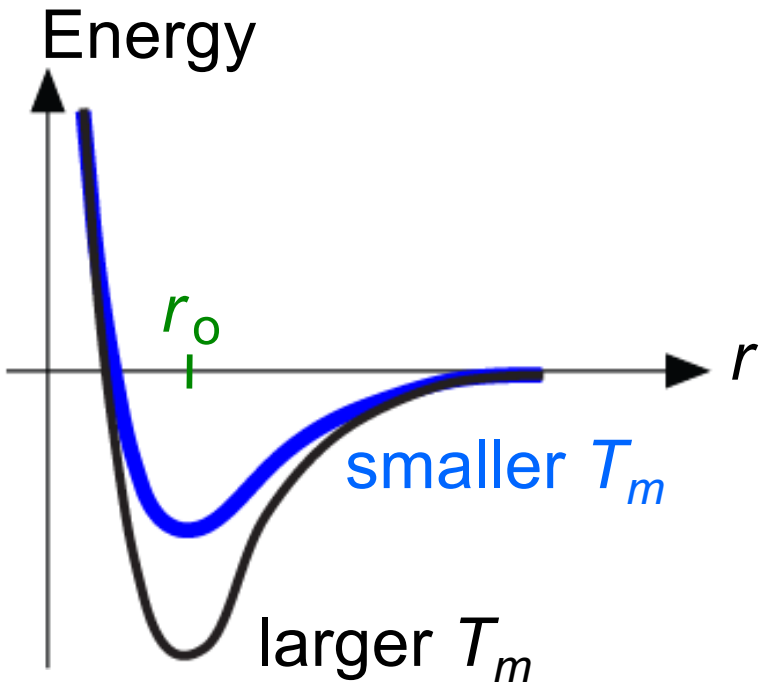
- Bond length, r



- Bond energy, E_o



- Melting Temperature, T_m

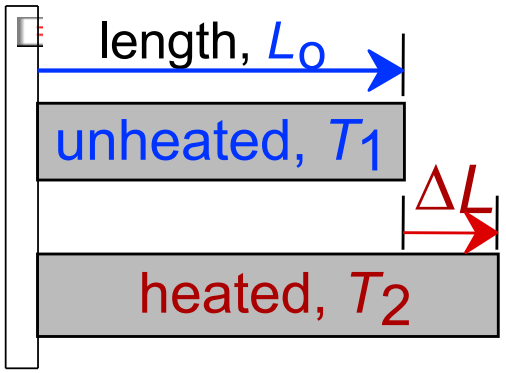


T_m is larger if E_o is larger.

Modulus (E) related to curvature at r_o

Properties From Bonding : α

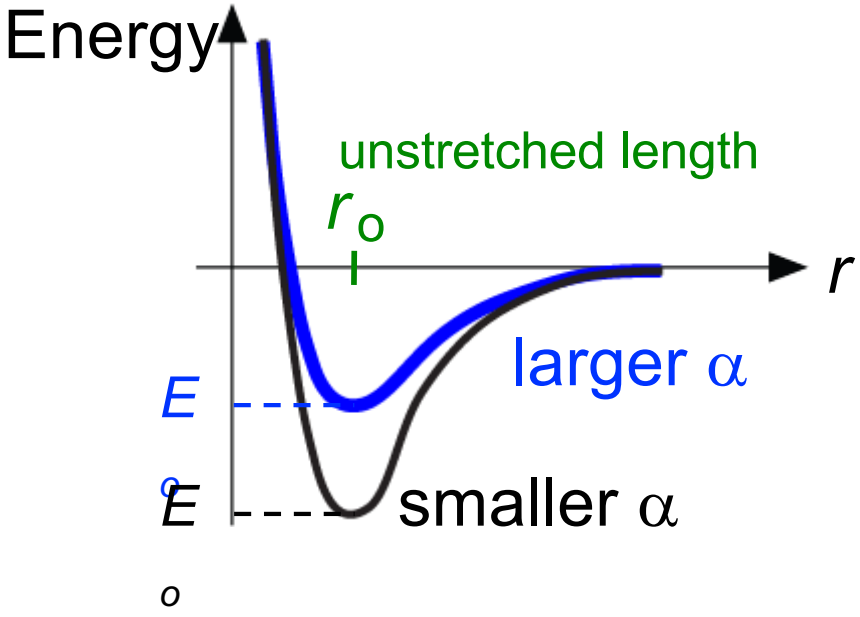
- Coefficient of thermal expansion, α



coeff. thermal expansion

$$\frac{\Delta L}{L_o} = \alpha\,(T_2 - T_1)$$

- α ~ symmetry at r_o



α is larger if E_o is smaller.

Summary: Primary Bonds

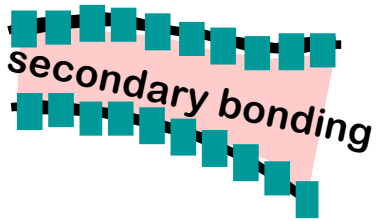
Ceramics
(Ionic & covalent bonding):

Large bond energy
large T_m
large E
small α

Metals
(Metallic bonding):

Variable bond energy
moderate T_m
moderate E
moderate α

Polymers
(Covalent & Secondary):



Directional Properties
Secondary bonding dominates
small T_m
small E
large α