Atomic Energy Structure

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Introduction: why do we study atomic bonding?

- We talked about properties
- What determines the properties?
- Atomic bonding is the first aspect we want to know
  - Later we will learn structures in a larger scale than atomic one.

흑연과 다이아몬드는 모두 탄소로 이루어져 있다.
- 같은 원자로 이루어져있지만 매우 다른 성질(property)를 가졌다.
왜? 그럴까?

Why do we study atomic structure?

- Some of the following properties
  1) Chemical (화학)
  2) Electrical (전기)
  3) Thermal (열)
  4) Optical (광학)

  are determined by electronic structure

Objectives

- Name the a few atomic models and understand the differences (원자 모형/모델)
- Understand quantum mechanical principles (양자역학원리)
- How does an atom bond with its neighboring one? (원자가 주위 원자들과 결합하는 방법)
  a) Force
  b) Energy
  c) Equilibrium condition (평형 상태)
- Types of bonds (원자 결합 종류)
  a) Ionic
  b) Covalent
  c) Metallic
  d) Hydrogen
  e) van der Waals
- Correlate the types of material with their bonds (재료의 종류에 따라 다른 원자 결합 이해)

기본 개념

❑원자의 기본 구성

- 원자 = 원자핵 (nuclei) + 전자 (electron)
- 원자핵 = 양자 (혹은 양성자; proton)+ 중성자 (neutron)

❑원자를 구성하는 입자의 성질

- 전하 (electric charge)를 띈 입자는: 전자와 양성자
- 양성자와 중성자는 비슷한 질량 (약 1.67×10^{-27}kg); 전자는 더욱 작은 질량 (9.11×10^{-31}kg)

❑화학 원소는 원자번호(atomic number, 기호 **Z**로 표현되기도)에 따라 분류되기도.

- 원자 번호는 '양자의 수'와 동일.
- 자연상에 존재하는 원자는 원자번호 1인 수소(Hydrogen)부터 92인 우라늄(Uranium)까지.
- <u>동일한 원소중에 양자수는 같아도 중성자가 다를 수 있다</u> – 동위원소 isotope

기본개념

❑원자량

- ➢자연상에 존재하는 동위원소의 원자 질량을 평균내어 '원자량'(atomic weight)
- ➢일반적으로 원자량의 단위는 SI (즉 kg, g 등)이 아닌 amu (Atomic Mass Unit) 사용한다.
- ➢1 amu = 탄소의 원자량/12 = 탄소 동위원소의 평균 질량/12

❑원자량/분자량 표기?

- ➢원자량 표기
  - ❖즉, *"탄소의 원자량은 탄소 원자 하나가 xxx amu를 가진다."* 라고 표현
  - ❖혹은 *"탄소의 원자량은 xxx amu/atom 이다."* 라고 표현
- ➢분자량 표기?
  - ❖"물(H_2O)의 원자량은 한 몰(mol)당 xxx g (gram) 이다", 라고 표현
  - ❖혹은 "물의 원자량은 xxx g/mol 이다."라고 표현.
- ➢사실 이 두 단위는 동일하다. 즉
  - ❖amu/atom = g/mol

예제 2.1

- 세륨 원자량 계산?
- Cerium은 4개의 동위 원소(isotope)을 가지고 있다.
- 동위원소 / 각 동위원소 질량(A) / 각 동위원소의 분율(fraction)?

동위원소	각 동위원소 질량(A)	각 동위원소의 분율(fraction)?
^{136}Ce	135.907 amu / atom	0.185%
^{138}Ce	137.906 amu / atom	0.251%
^{140}Ce	139.905 amu / atom	88.450%
^{142}Ce	141.909 amu / atom	11.114%

- 세륨의 원자량 ($\bar{A}$)은 자연계에 존재하는 동위원소의 '평균' 질량 (weighted average):
  - $\bar{A} = \sum_i f_i A_i$
- 따라서 세륨의 원자량은?
  - $\bar{A} = 135.907 \times 0.00185 + 137.906 \times 0.00251 + 139.905 \times 0.8845 + 141.909 \times 0.11114$

Atomic models

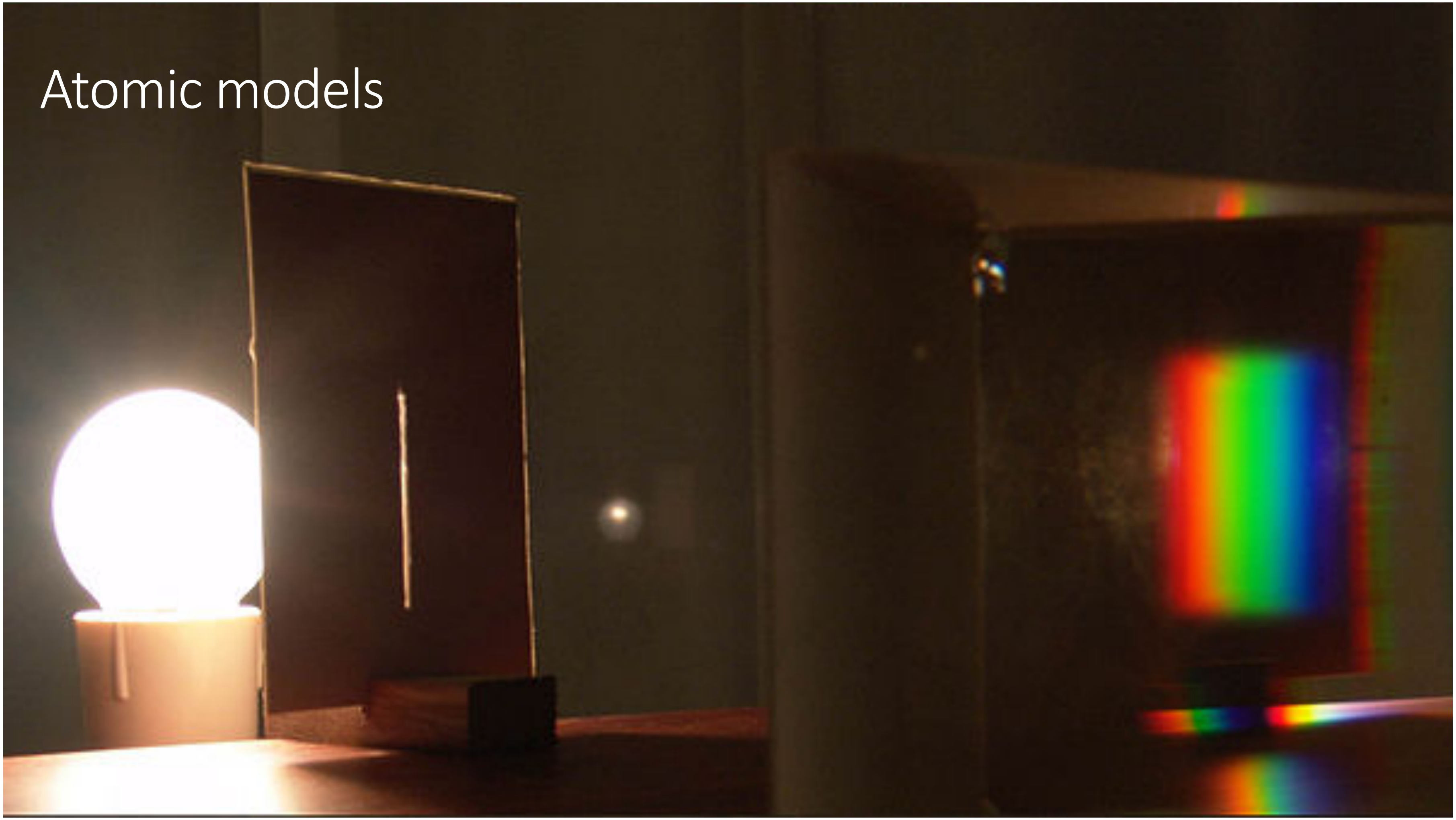
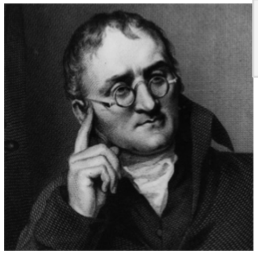
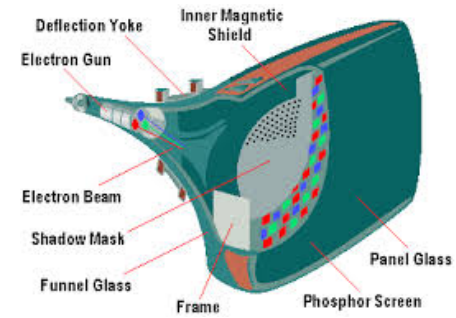


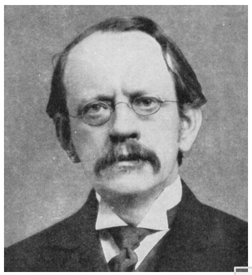
Image from https://en.wikipedia.org/wiki/Spectral_line

Historical development of atomic model



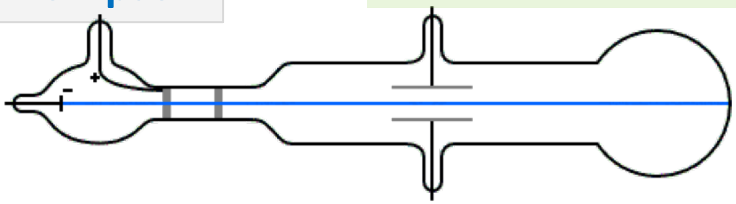
Dalton: All matters are made of atoms

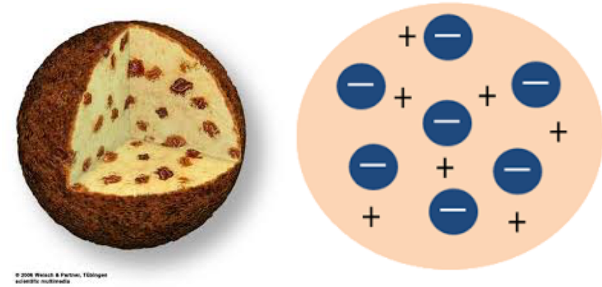


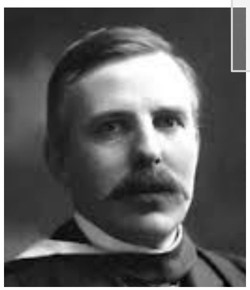


J. J. Thompson

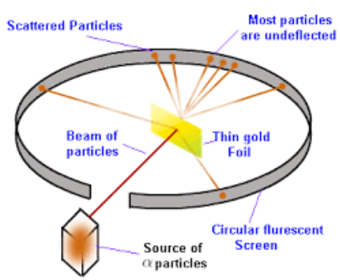
Cathode Ray Tube



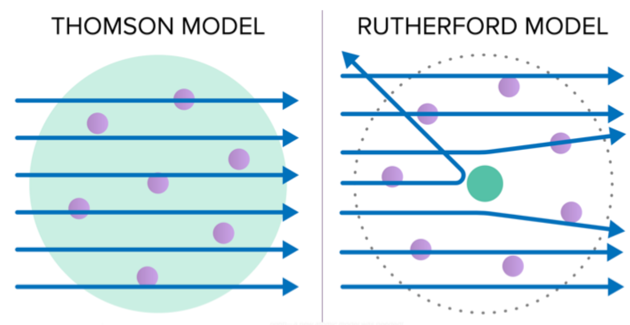




E. Rutherford

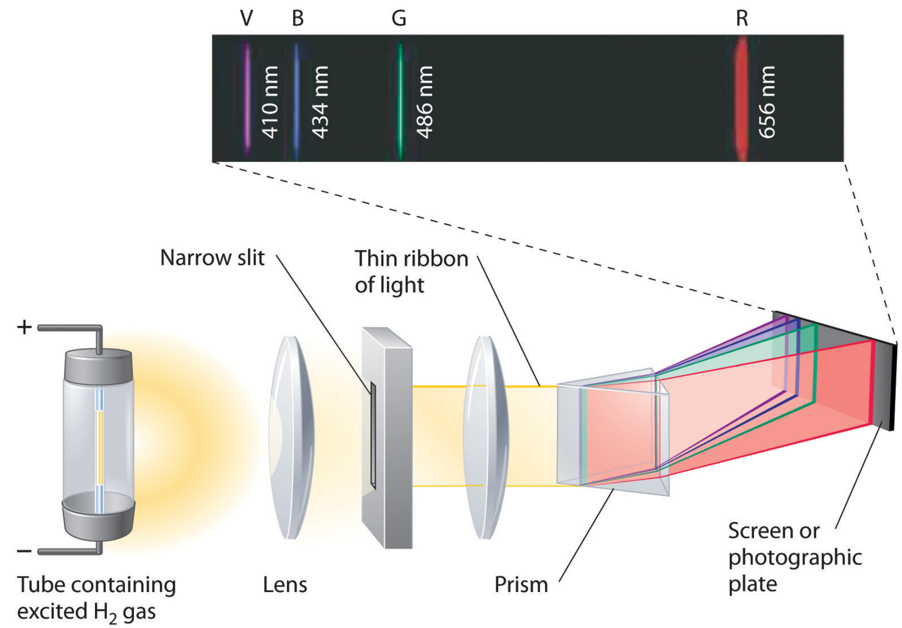


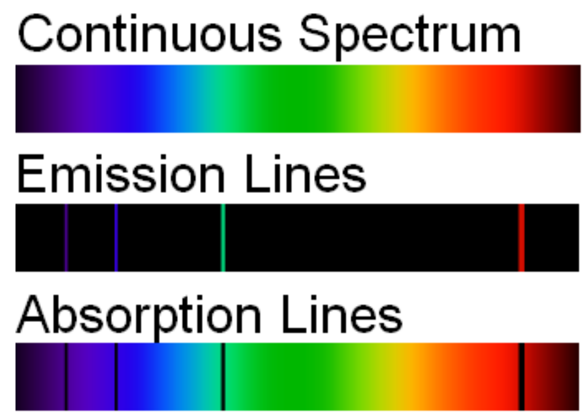
a) Mostly penetrated.
b) Some reflected.
Conclusion?

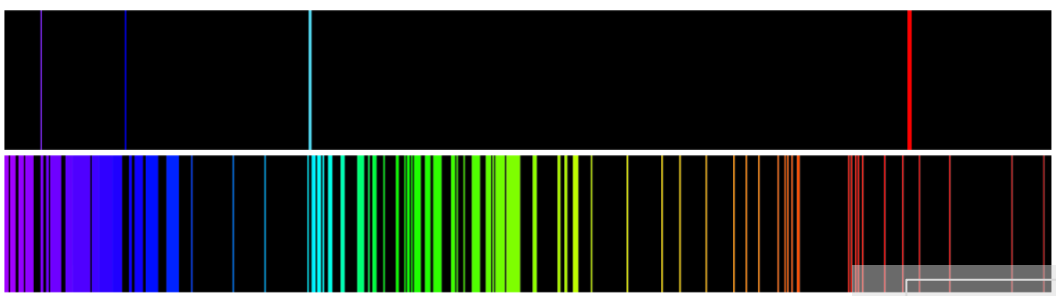


Niels Bohr: Discrete energy levels (next slide)

Experimental support on Bohr’s model: Atomic Spectral lines







Hydrogen (H)

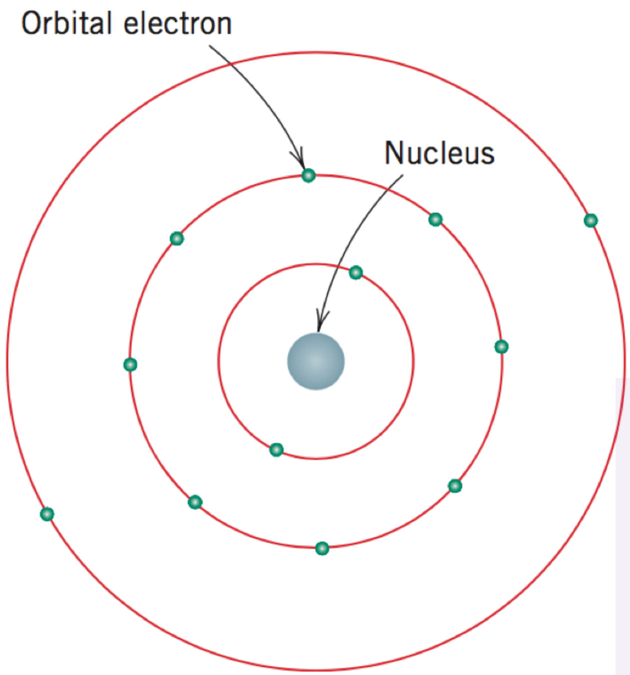
Iron (Fe)

WHY?

Electrons have discrete levels of energy states

Bohr's atom model
(Explain how electrons have discontinuous energy levels)

Think about the "planet model"

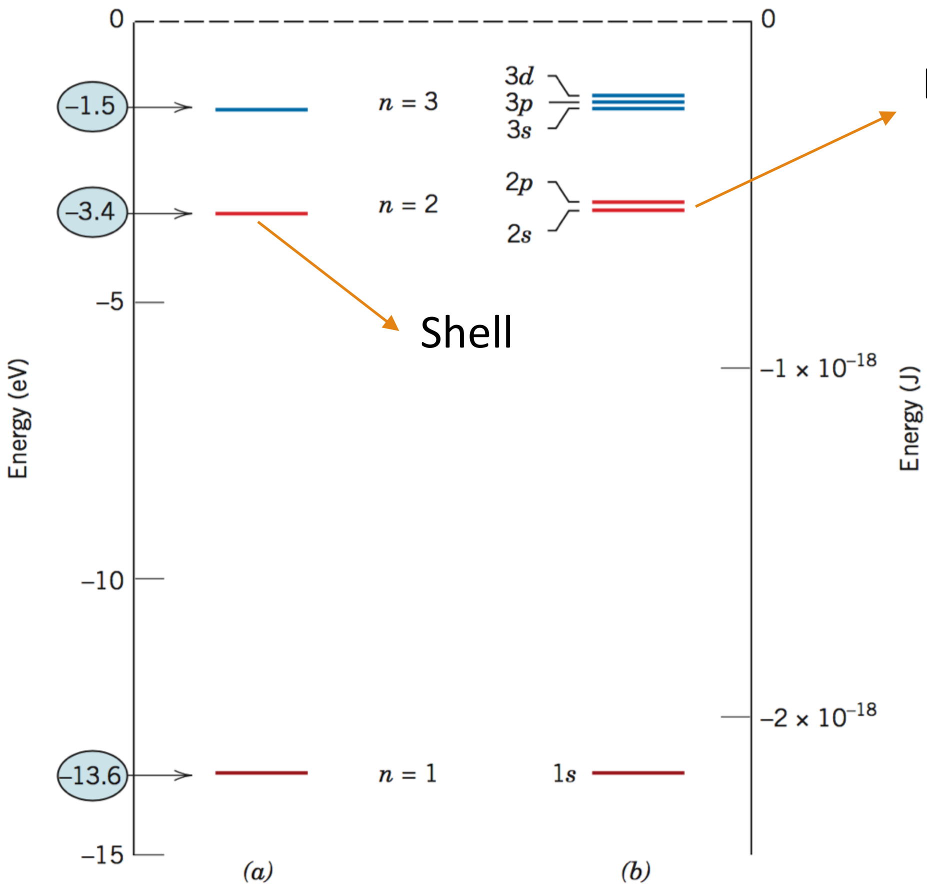


Electrons revolve around the nucleus at a particular distance from nucleus (3 Dimensionally equidistant: shell)

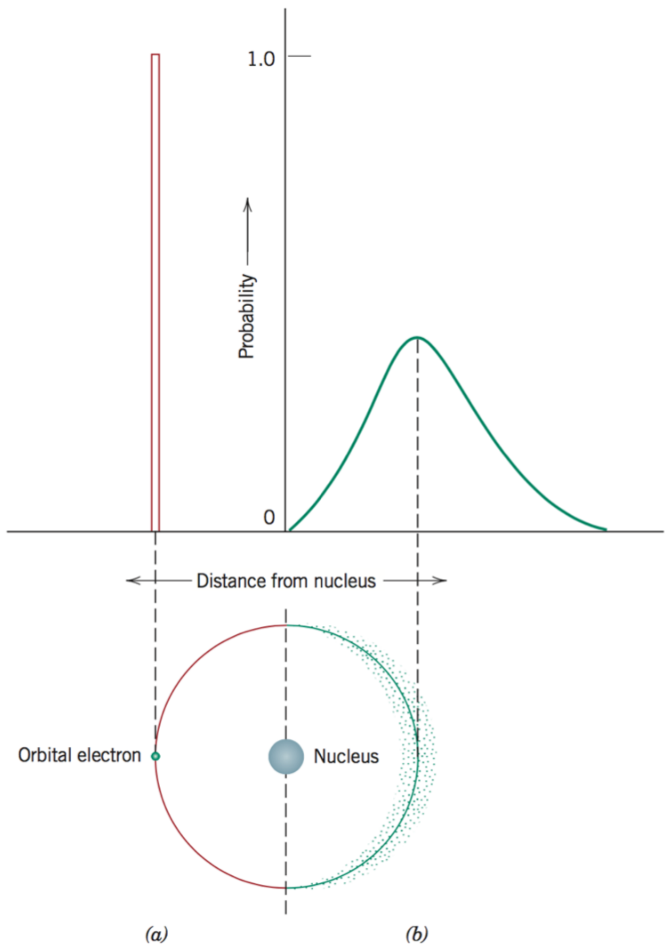
Eventually people found some limitations in Bohr's model. Historically, a) **de Broglie** (1923) discovered that electrons have a dual nature, i.e., it has properties pertaining to both particles and waves. b) **Heisenberg** (1927) proposed the principle of indeterminacy – you cannot know both the position and velocity of a particle at the same time. c) **Schrödinger** (1930) viewed electrons as continuous clouds and introduced 'wave-mechanics' as a mathematical model of atom.

Conclusion: Physicists needed a better model

Bohr's model in comparison with Wave-mechanical model



Each shell may consist of subshells



Electronic Structure

- Electrons have wavelike and particulate properties. (de Broglie - 물질파)
- Two of the wavelike characteristics are
  - electrons are in orbitals defined by a probability.
  - each orbital at **discrete energy level** (불연속성) is determined by quantum numbers.
  - There are four types of quantum numbers:

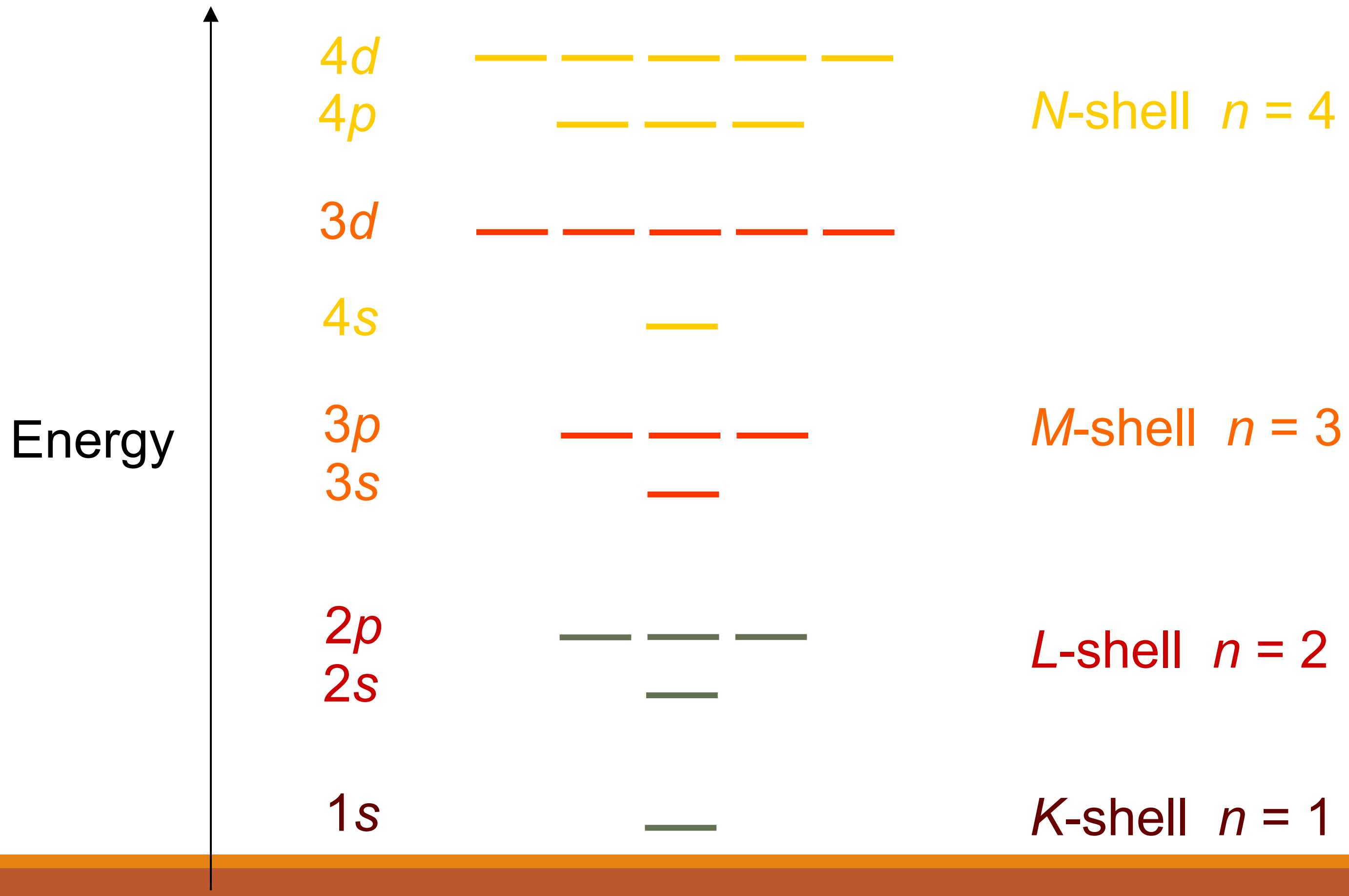
Quantum #	Designation
n = principal (energy level-shell)	K, L, M, N, O (1, 2, 3, etc.)
ℓ = subsidiary (orbitals)	s, p, d, f (0, 1, 2, 3,…, n-1)
m_l = magnetic	1, 3, 5, 7 ($-\ell$ to $+\ell$)
m_s = spin	½, -½

Q) Orbit and Orbital?
- Probability distribution

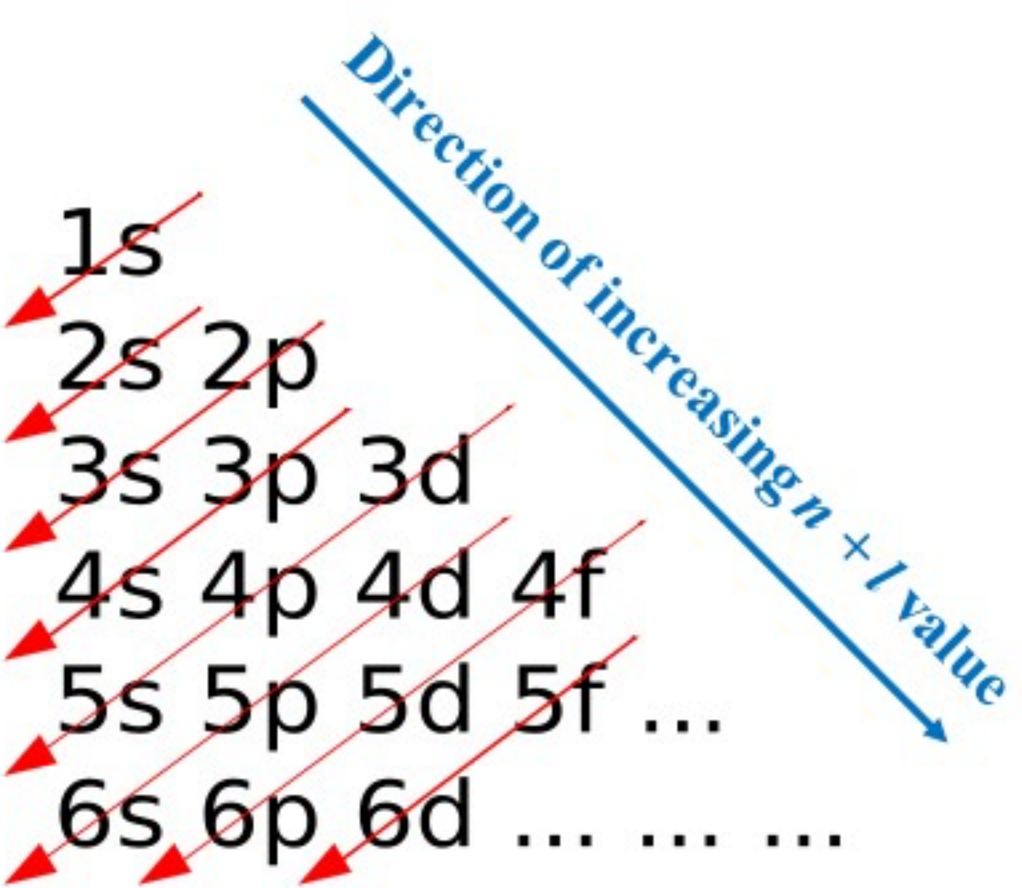
Electron Energy States

Electrons...

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



Aufbau principle (building-up principle)

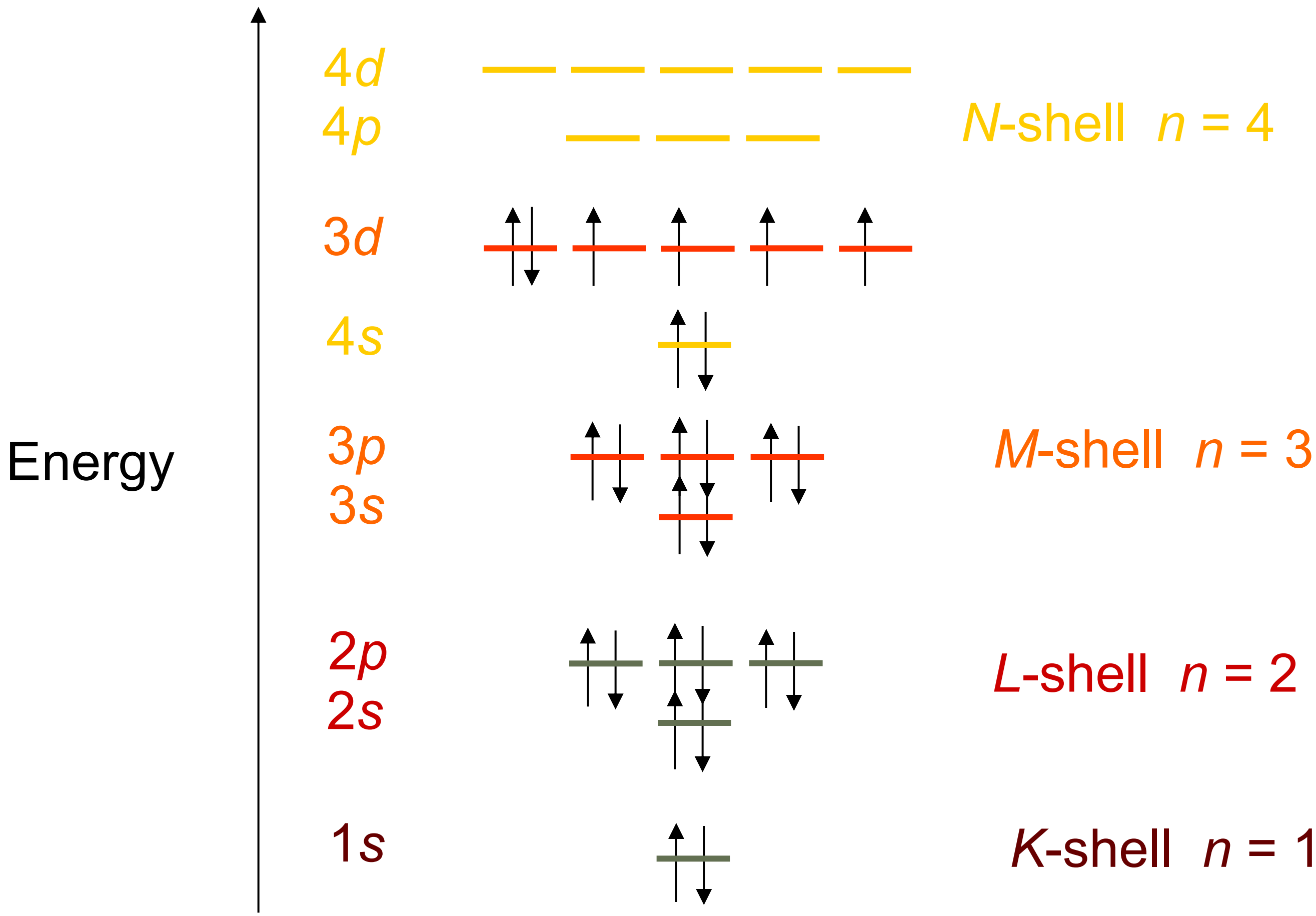


Electronic Configurations

ex: Fe - atomic # = 26

$1s^2 \;\; 2s^2\, 2p^6 \;\; 3s^2\, 3p^6 \;\; \boxed{3d^6 \;\; 4s^2}$

Valence electrons
원자가 전자



원자가 전자: 원자의 바깥껍질에 위치하며 화학 반응에 참여할 가능성이 높은 전자

Atomic Structure

- atom – electrons – 9.11×10^{-31} kg
  protons
  neutrons } 1.67×10^{-27} kg (유효숫자에 유의)

- atomic number = # of protons in nucleus of atom
  = # of electrons in neutral species

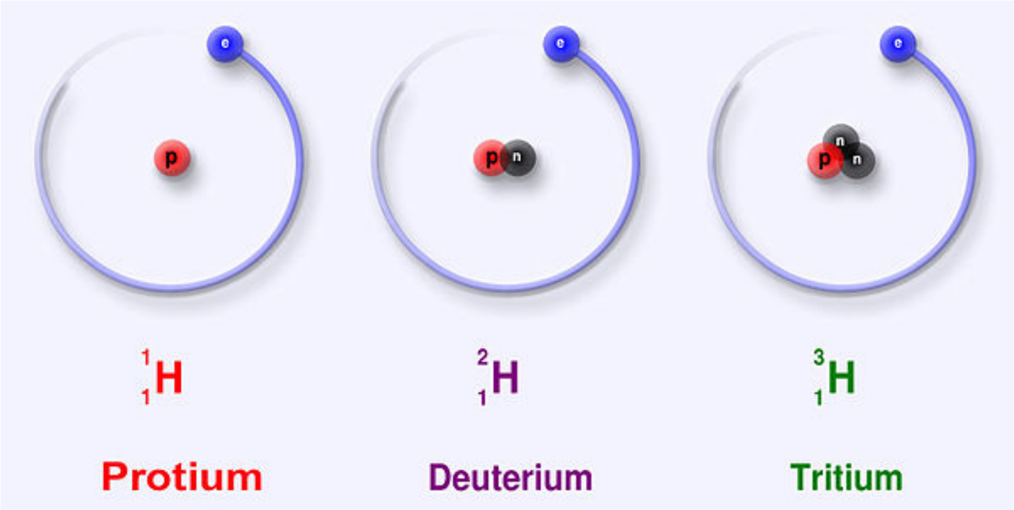
- A [=] atomic mass unit = amu = 1/12 mass of ^{12}C

Atomic wt = wt of 6.022×10^{23} molecules or atoms

1 amu/atom = 1 g/mol

C 12.011 [amu]
H 1.008 [amu]

Isotope and atomic weight example: Hydrogen



99.985% 0.015% the balance

Q) Atomic weight (원자량): average of isotopes in nature

Atomic weight of Hydrogen = 0.99985 x **P** + 0.00015 x (**P**+**N**) + (1-0.99985-0.00015) x (**P**+2**N**) where p and n are masses of **P**roton and **N**eutron, respectively.

Atomic weights are usually irrational. People like simpler systems than complex one. The masses of P and N are difficult to comprehend (1.67x10^-27 kg or 9.11x10^-31kg). Let's make it simple by using a reference (i.e., amu) – 다음장에서 계속

amu (Atomic mass unit)

Atomic weights have units that are not familiar to us. Remember people like simple systems rather than complex ones. The masses of **P** and **N** in SI unit are quite difficult to comprehend (1.67x10^-27 kg or 9.11x10^-31kg). Let's make it simpler by using a reference value (i.e., amu).

The reference case is an isotope of carbon.

Carbon has 15 different isotopes, among which only 3 are naturally occurring: ^{12}C, ^{13}C, and ^{14}C. The most common isotope is ^{12}C.

^{12}C has 6 protons and 6 neutrons. **The value of amu is 'defined' as 1/12 of ^{12}C (6 protons + 6 neutrons) atomic weight.**

Orbit (Bohr) and Orbital (Quantum Mechanics)

How to detect the position of electron?

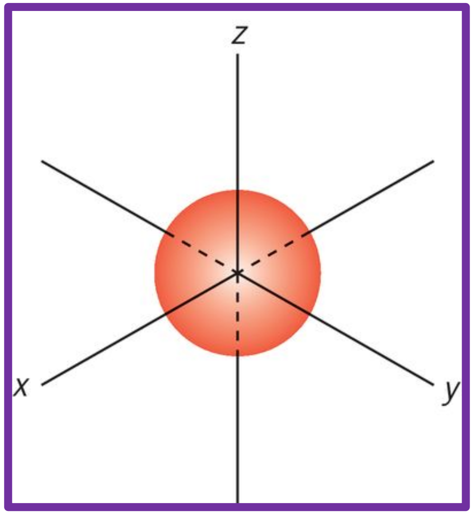
Uncertainty principle (Heisenberg)

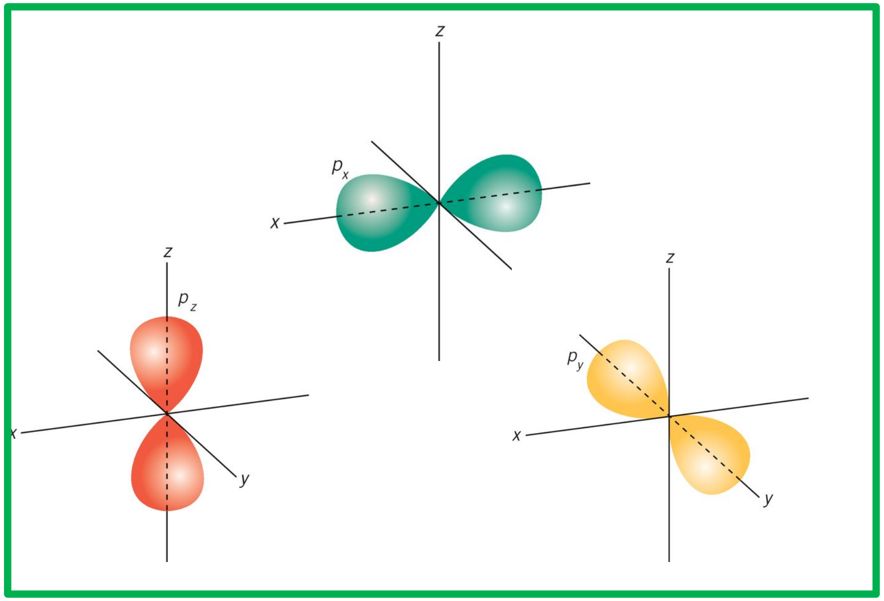
$$\boxed{\sigma_x \sigma_p \geq \frac{\hbar}{2}}$$

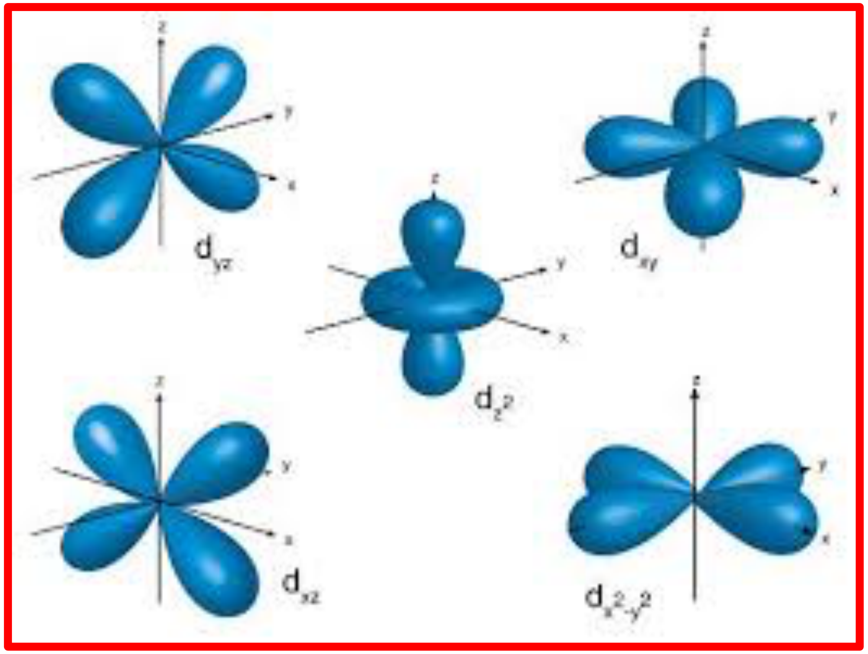
The standard deviation of momentum (σ_p) and the standard deviation of position (σ_x) is inverse proportional to each other, where $\hbar$ is the reduced Planck constant

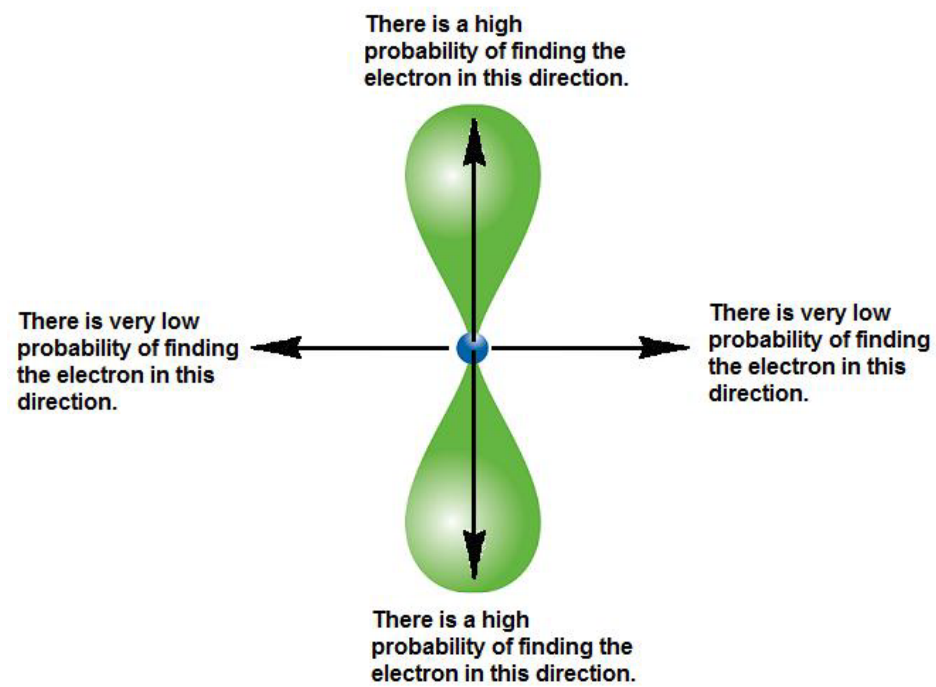
공간상에 전자가 발견될 확률로써 전자의 orbital 설명 (orbit과 orbital의 차이)

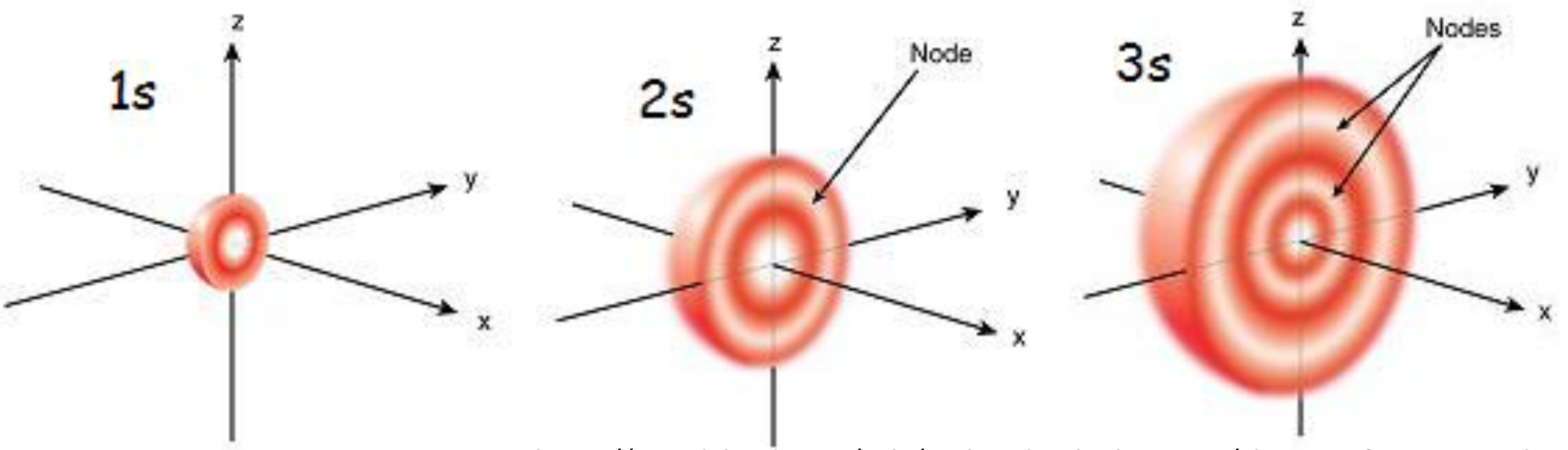
Orbital: areas where electrons are ‘detected’









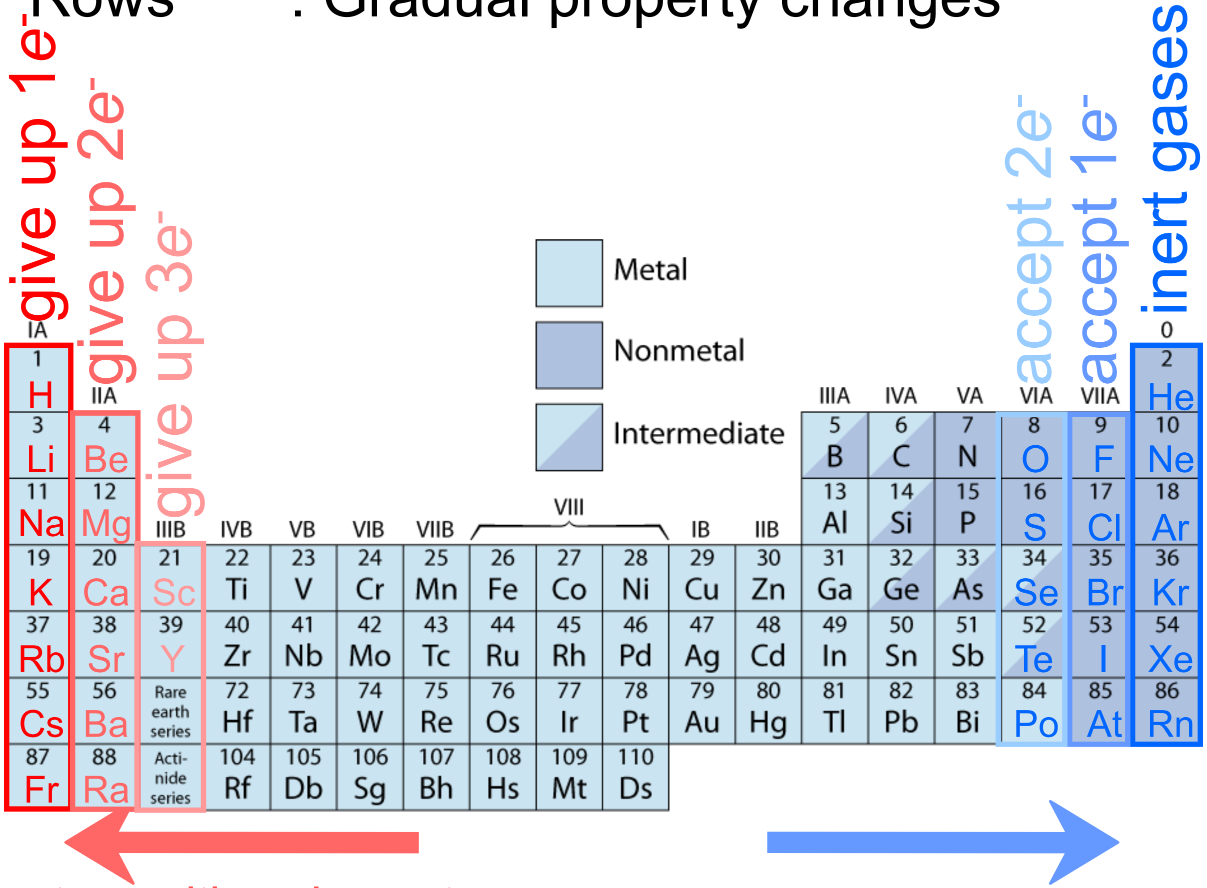


https://en.wikibooks.org/wiki/High_School_Chemistry/Shapes_of_Atomic_Orbitals

The Periodic Table (주기율표)

- Columns: Similar Valence Structure – similar chemical property
- Rows   : Gradual property changes

비슷한 화학적
물성이 ‘주기성’을 보이며,
그것이 valence electron과
관련이 있다.

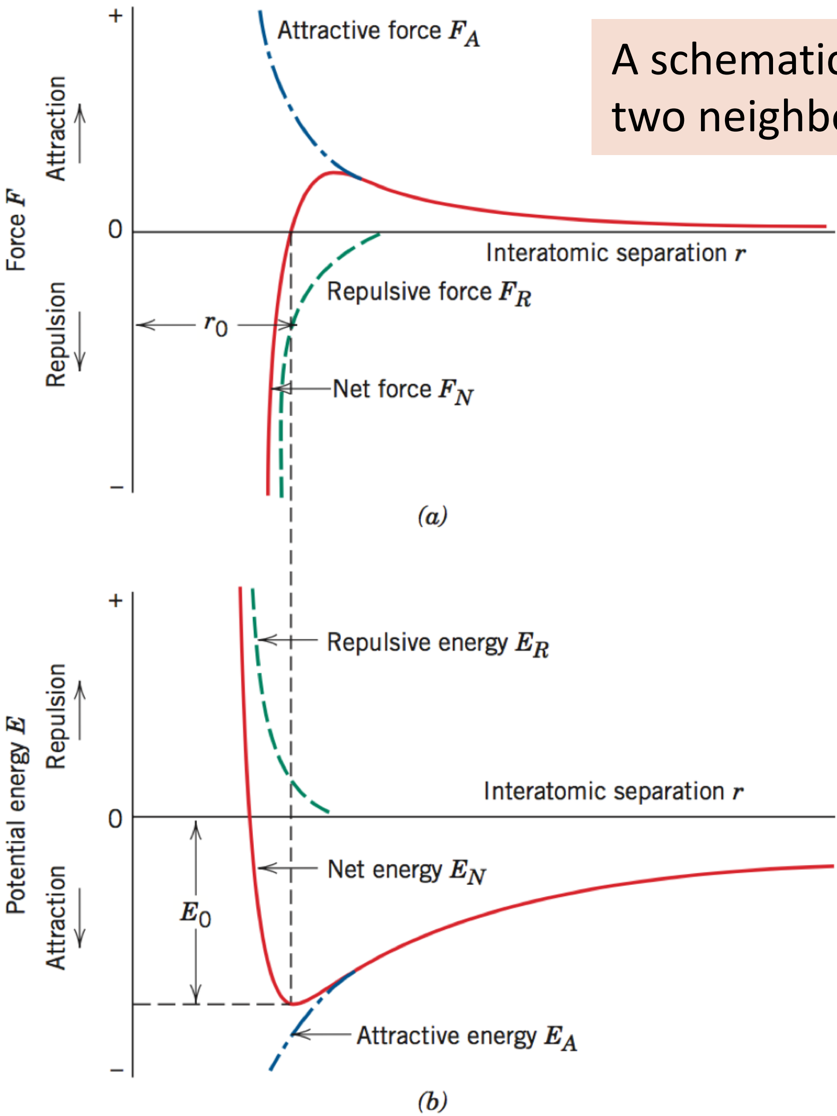


Adapted from Fig. 2.8, *Callister & Rethwisch 9e.*

Electropositive elements:
쉽게 전자를 포기(기부)하고
양이온(+, cation)이 되려함

Electronegative elements:
쉽게 전자를 얻어 음이온(-, anion)이 되려함

Bonding forces and energy



A schematic illustration that help you understand the bonding of two neighboring atoms

힘의 평형점?
The interatomic distance at which the potential energy is minimum

Simple explanation using Coulombic forces – attraction between the electrons and nuclei (protons) and attraction between electrons and between nuclei. Also, note that the electrons are located in the outer region so that when atoms are getting closer, electrons are the ones that dominate the bonding forces –Coulombic force: $\mathrm{F} \propto \frac{1}{r^2}$

$$E^{\text{potential}} = \int_r^\infty F^{\text{attraction}}(\mathrm{r})\, dr + \int_r^\infty F^{\text{repulsion}}(\mathrm{r})\, d$$

E_0: bonding energy

Material properties and bonding?

Examples:

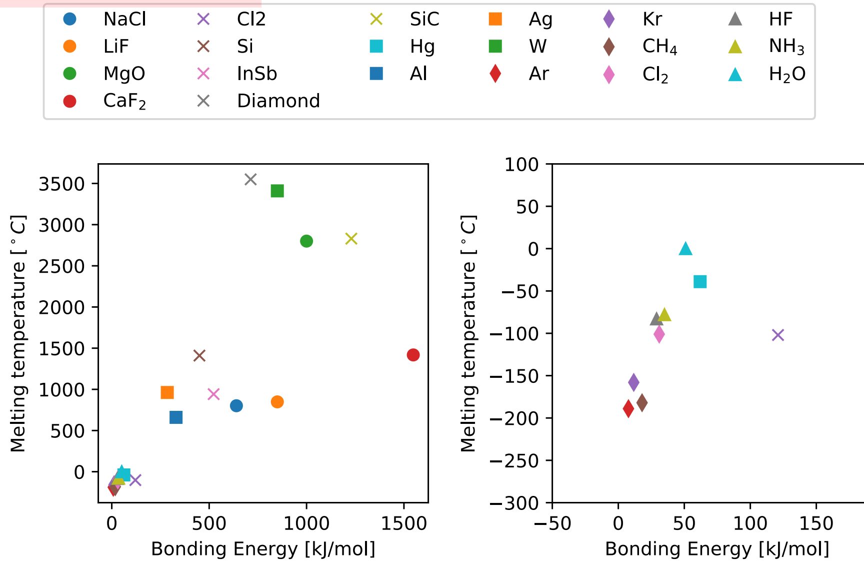
- Melting temperature T_m determines the state of materials at a certain temperature such as room temp.

E_0	Preferred state in room temperature	T_m
High	Solid	High
Intermediate	Liquid	Intermediate
Low	Gas	Low

- Stiffness, thermal coefficients are also closely related with the atomic bonding behavior

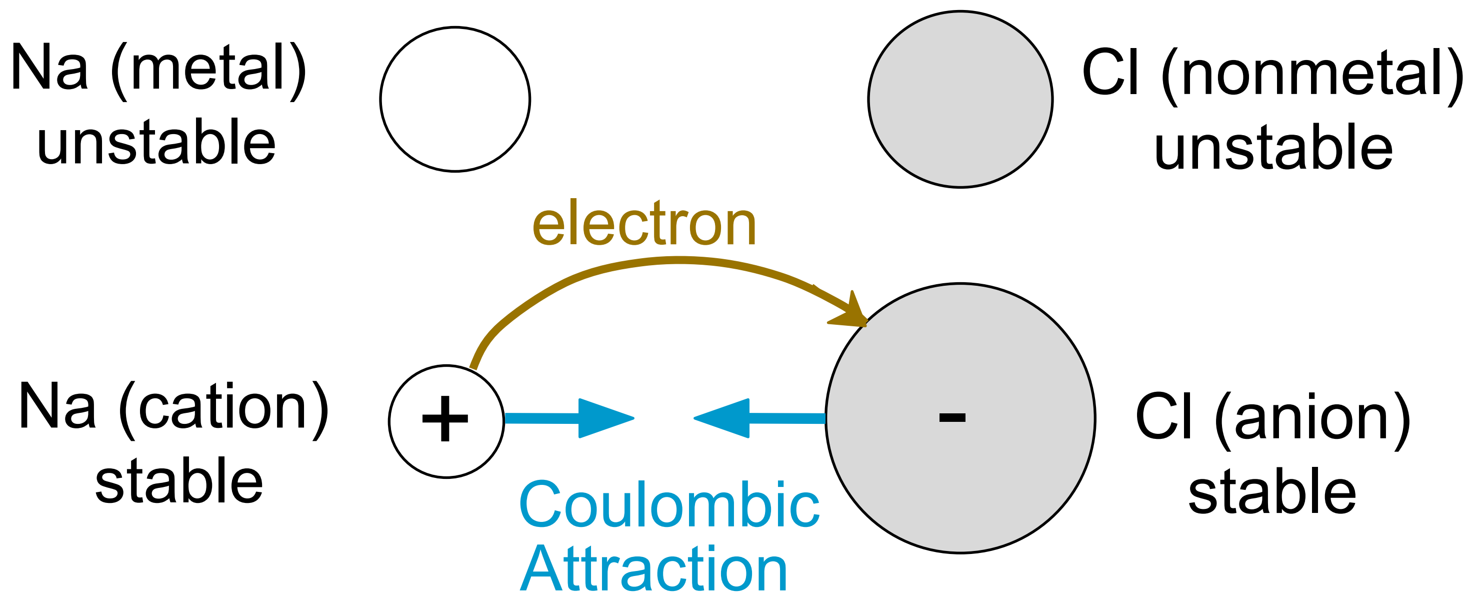
- Primary bonding (relatively strong) – chemical bond
  - Ionic (Valence electrons are transferred) - circles
  - Covalent (Valence electrons are shared, directional) - crosses
  - Metallic (Valence electrons are delocalized) - squares

- Secondary bonding (relatively weaker) – physical bond
  - Dipole-Dipole
  - Polar module-induced dipole
  - H-bonds (triangles)
  - Fluctuating dipole (weakest)



Ionic Bonding: Introduction

- Occurs between + and - ions.
- Requires electron transfer (전자의 교환 – donor and acceptor)
- Large difference in electronegativity required (next slide)
- Example: NaCl



Electron configuration of a participant becomes that of the corresponding inert gas.
In the above example, Na and Cl have the configuration of He and Ar, respectively.

Ionic Bonding: Electronegativity (전기음성도)

- Ranges from 0.9 to 4.1,
- Large values: tendency to acquire electrons.
  (높을 수록 전자를 더 많이 받으려는 성향 증가)

IA	IIA	IIIB	IVB	VB	VIB	VIIB	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 3.1	O 3.5	F 4.1	Ne –
Na 1.0	Mg 1.3											Al 1.5	Si 1.8	P 2.1	S 2.4	Cl 2.9	Ar –
K 0.9	Ca 1.1	Sc 1.2	Ti 1.3	V 1.5	Cr 1.6	Mn 1.6	Fe 1.7	Co 1.7	Ni 1.8	Cu 1.8	Zn 1.7	Ga 1.8	Ge 2.0	As 2.2	Se 2.5	Br 2.8	Kr –
Rb 0.9	Sr 1.0	Y 1.1	Zr 1.2	Nb 1.3	Mo 1.3	Tc 1.4	Ru 1.4	Rh 1.5	Pd 1.4	Ag 1.4	Cd 1.5	In 1.5	Sn 1.7	Sb 1.8	Te 2.0	I 2.2	Xe –
Cs 0.9	Ba 0.9	La 1.1	Hf 1.2	Ta 1.4	W 1.4	Re 1.5	Os 1.5	Ir 1.6	Pt 1.5	Au 1.4	Hg 1.5	Tl 1.5	Pb 1.6	Bi 1.7	Po 1.8	At 2.0	Rn –
Fr 0.9	Ra 0.9	Ac 1.0															

Lanthanides: 1.0-1.2
Actinides: 1.0-1.2

Smaller electronegativity
전자를 별로 안 필요

Larger electronegativity
전자 매우 원함

Ionic Bonding: electron transfer

Ionic bond: metal + nonmetal

- Between 'donor' and 'acceptor'
- Forms inert gas configurations (i.e., filling the shell completely, thus stable electron configuration)
- The atoms become ions and render the **columbic** attraction.

Dissimilar electronegativities

ex) MgO: Mg $\underbrace{1s^2\ 2s^2\ 2p^6}_{[Ne]}\ \underbrace{3s^2}_{3s^2}$ O $1s^2\ 2s^2\ 2p^4$

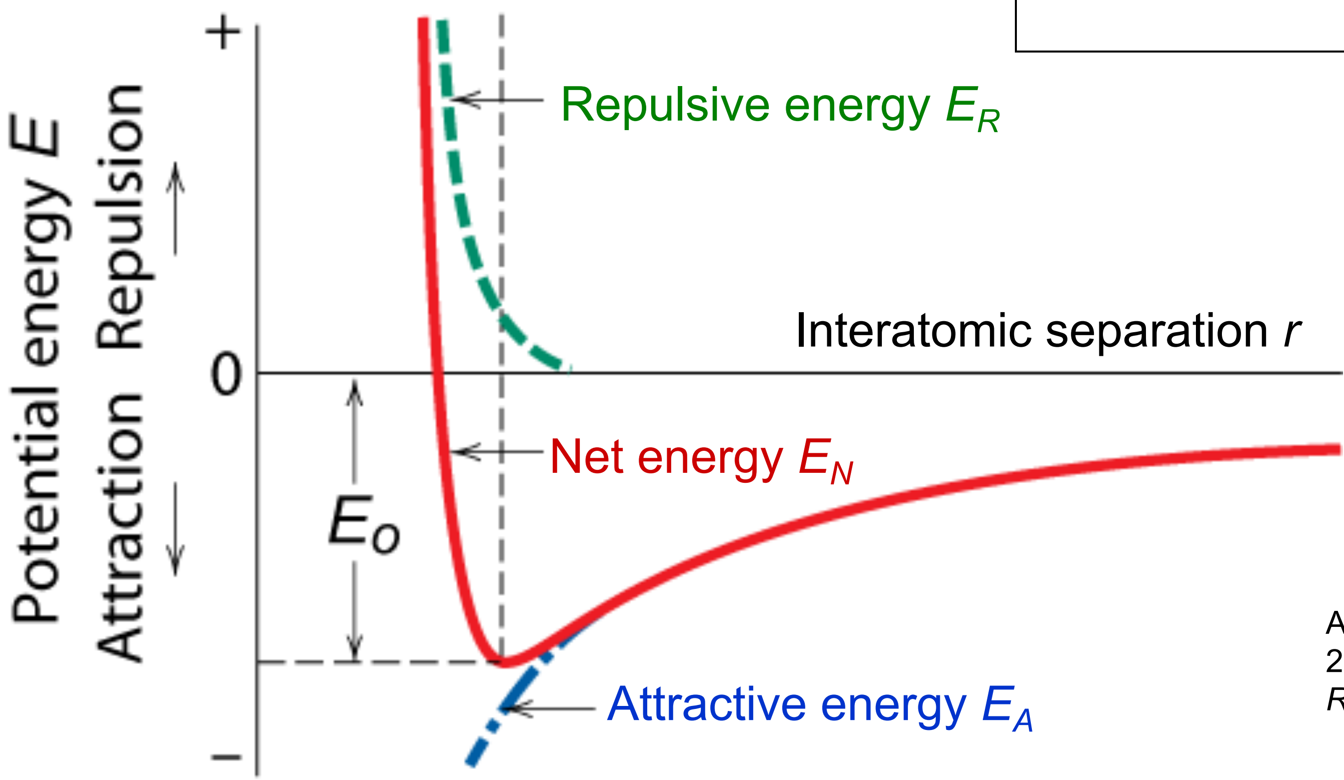
Mg^{2+} $\underbrace{1s^2\ 2s^2\ 2p^6}_{[Ne]}$ O^{2-} $\underbrace{1s^2\ 2s^2\ 2p^6}_{[Ne]}$

Ionic Bonding: Bonding forces and energy

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

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

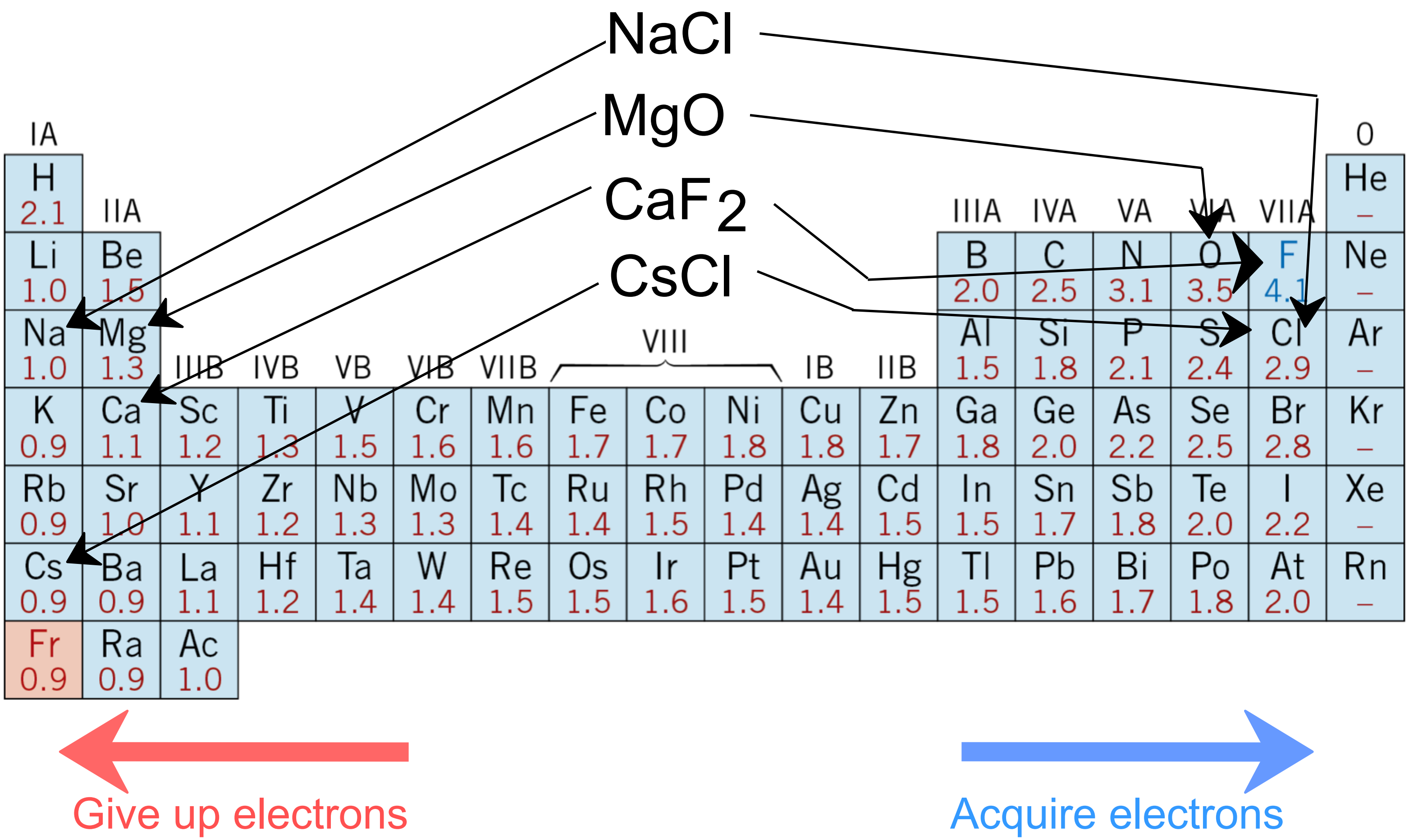
예제 2.2



Adapted from Fig. 2.10(b), *Callister & Rethwisch 9e.*

Ionic Bonding: examples

- Predominant bonding in Ceramics

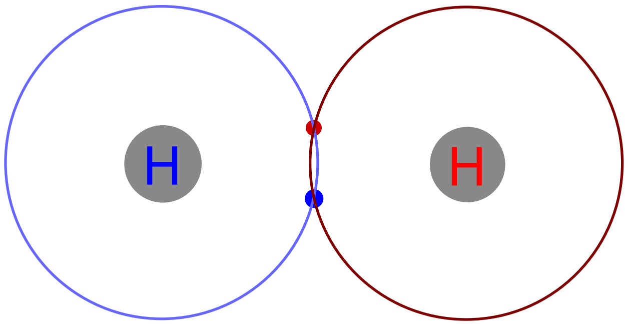


Covalent Bonding

- similar electronegativity ∴ share electrons
- bonds determined by valence – *s* & *p* orbitals dominant
- Example: H_2

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

H_2



- shared 1*s* electron from 1st hydrogen atom
- shared 1*s* electron from 2nd hydrogen atom

The same H atoms are bonded: The participants have the same electronegativities.

Fig. 2.12, *Callister & Rethwisch 9e.*

Hybridization (hybrid orbitals)

Mixing orbitals into a new orbitals (with different energy levels and shapes).

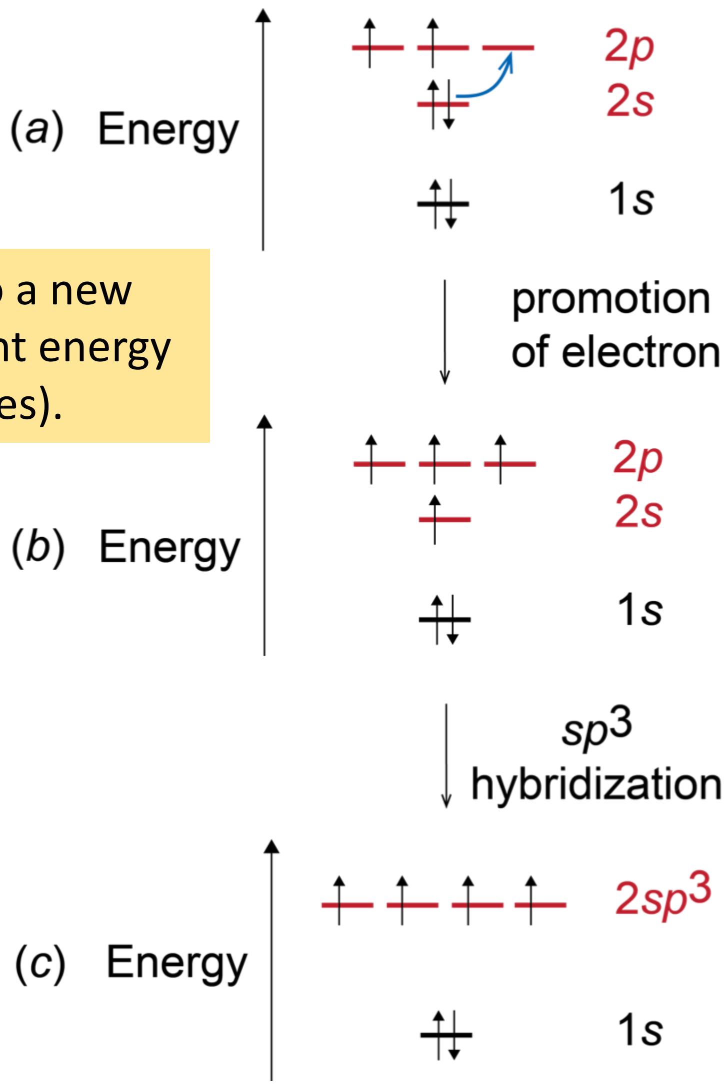


Fig. 2.13, *Callister & Rethwisch 9e.*

Carbon can form sp^3 hybrid orbitals

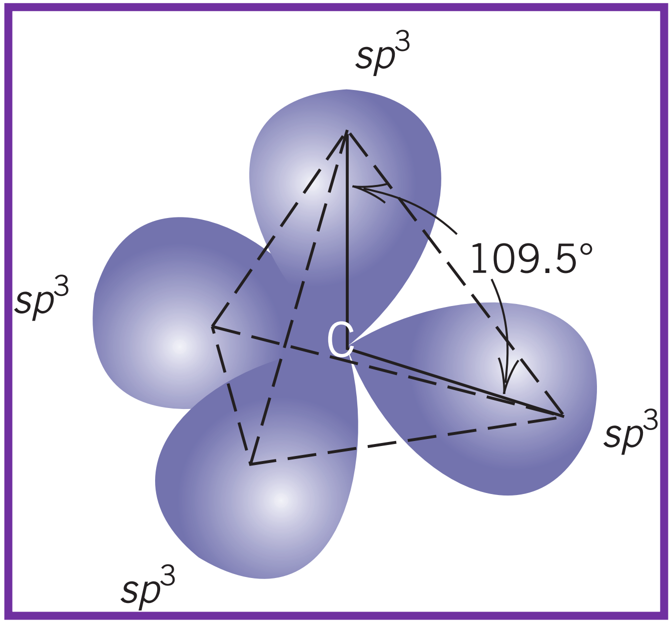


Fig. 2.14, *Callister & Rethwisch 9e.*
(Adapted from J.E. Brady and F. Senese, *Chemistry: Matter and Its Changes*, 4th edition. Reprinted with permission of John Wiley and Sons, Inc.)

Hybridization (hybrid orbitals): carbon sp^3

- **Example: CH_4 (Methane)**

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

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

Electronegativities of C and H are comparable, so electrons are shared in covalent bonds.

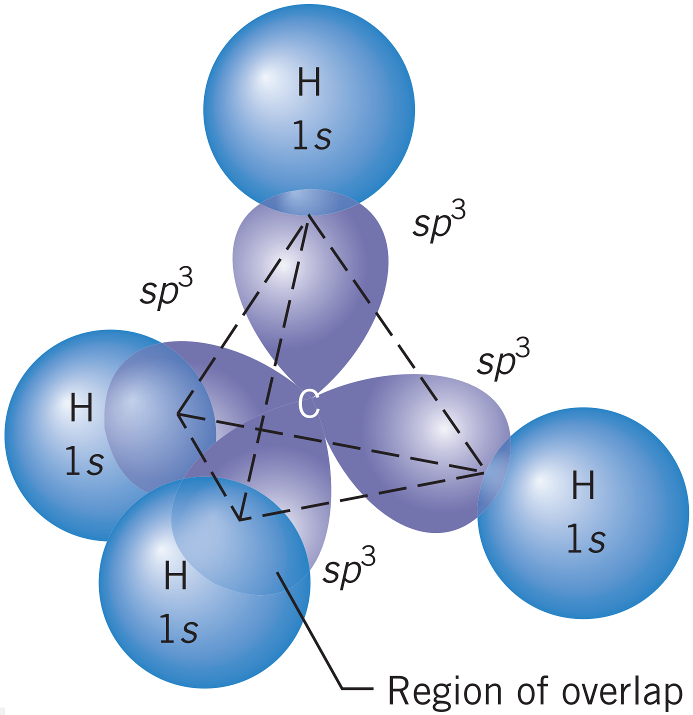
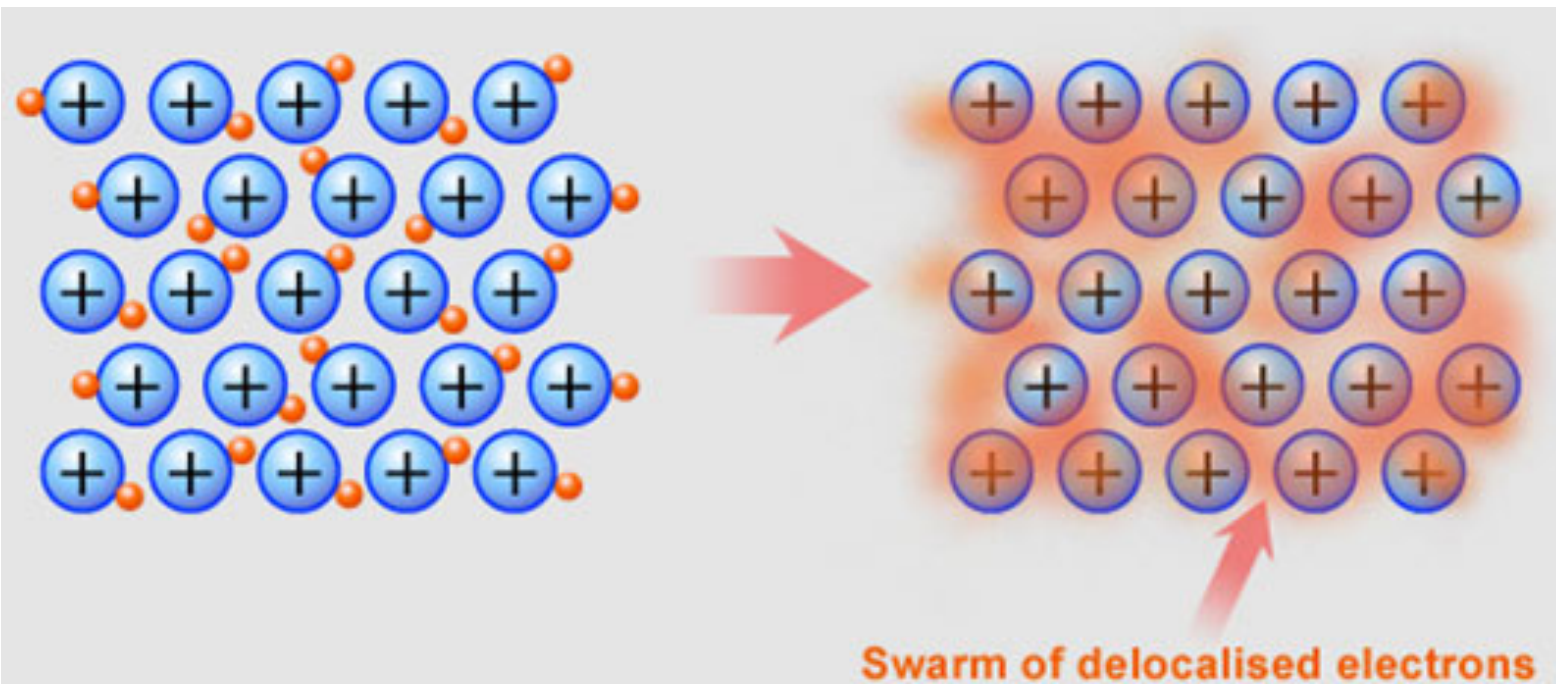


Fig. 2.15, *Callister & Rethwisch 9e.*
(Adapted from J.E. Brady and F. Senese, *Chemistry: Matter and Its Changes*, 4th edition. Reprinted with permission of John Wiley and Sons, Inc.)

Metallic bonding

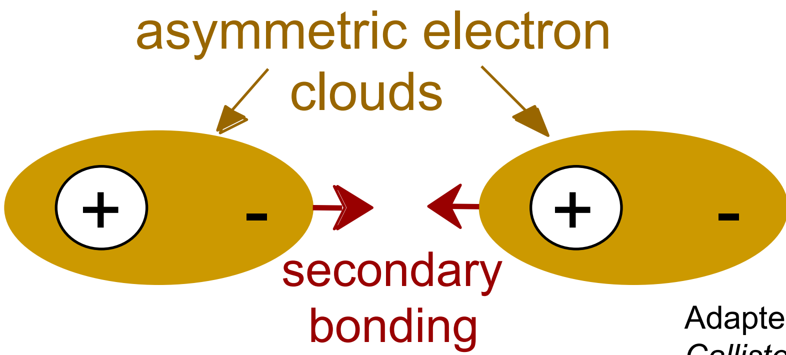
- The most outer electrons are not ‘localized’ and can freely move around.
- Electron cloud (sea).
- Electron adhesives
- Delocalized electron cloud is the origin of good electrical and thermal conductivities



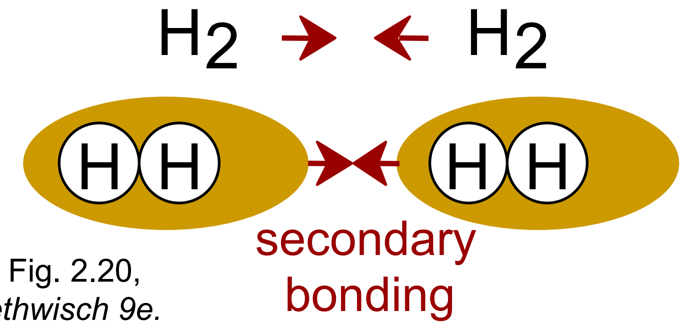
Secondary Bonding

Arises from interaction between dipoles (atom or molecule)

- Fluctuating dipoles



ex: liquid H_2



Adapted from Fig. 2.20, *Callister & Rethwisch 9e.*

- Permanent dipoles-molecule induced

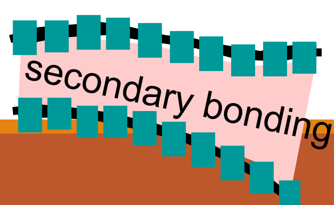
  Originally symmetric but gets asymmetric by neighboring

-general case:

Adapted from Fig. 2.22, *Callister & Rethwisch 9e.*

-ex: liquid HCl

-ex: polymer



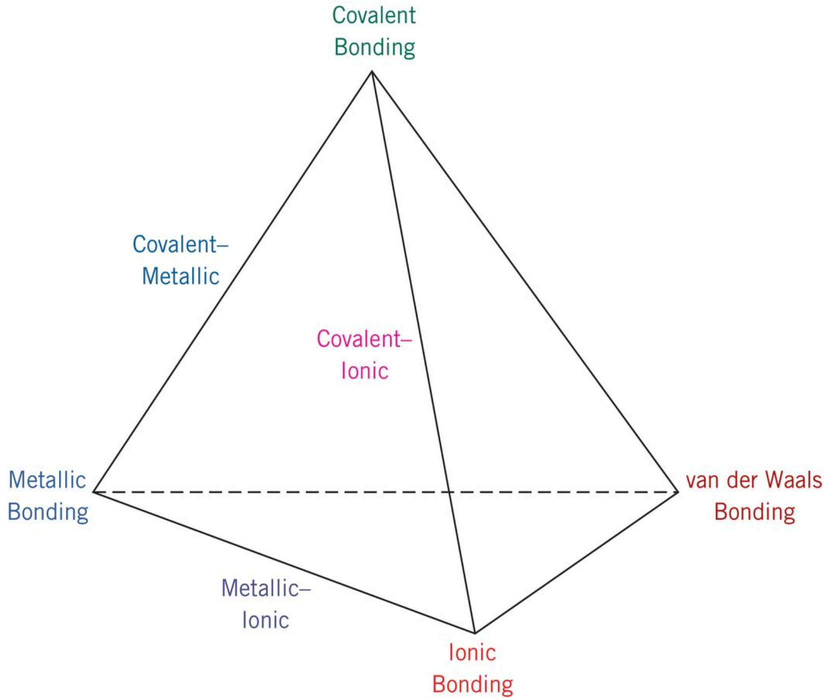
secondary bonding

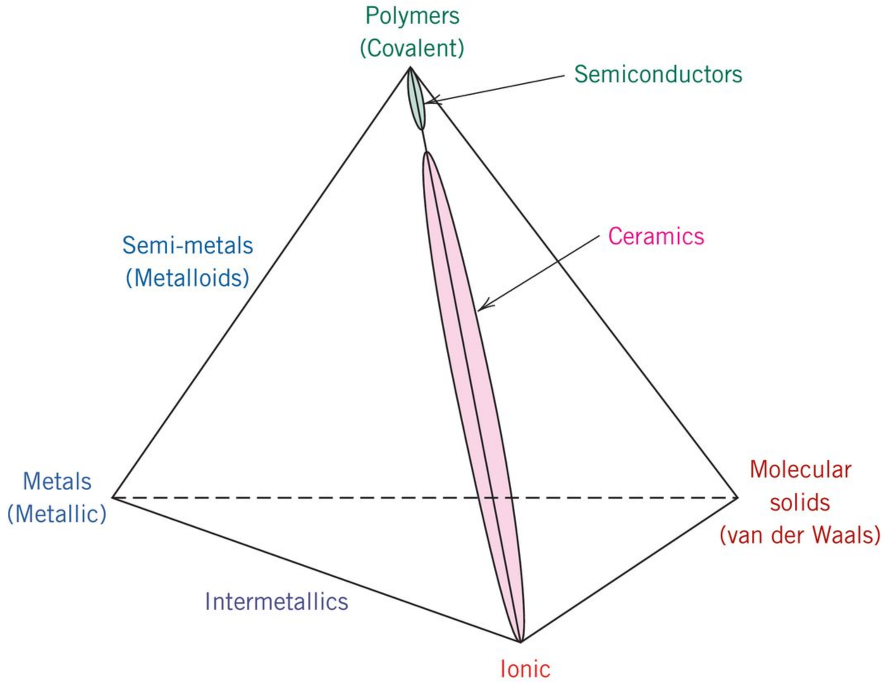
A special case of secondary bonding: Hydrogen bonding

- A special case of secondary bonding
- What makes hydrogen bonding strong?

Mixed bonds

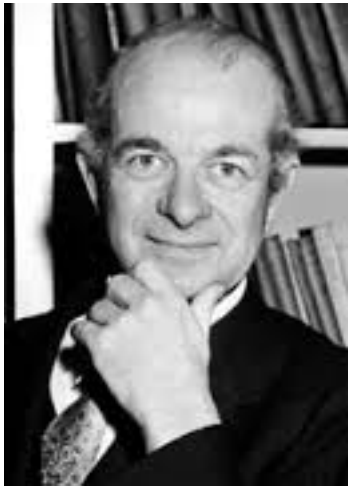
Not all bondings are ‘pure’.





Mixed bonds: example (Eq. 2.16 & 예제 2.3)

$$\%IC = \{1 - \exp[-0.25(X_A - X_B)^2]\} \times 100$$

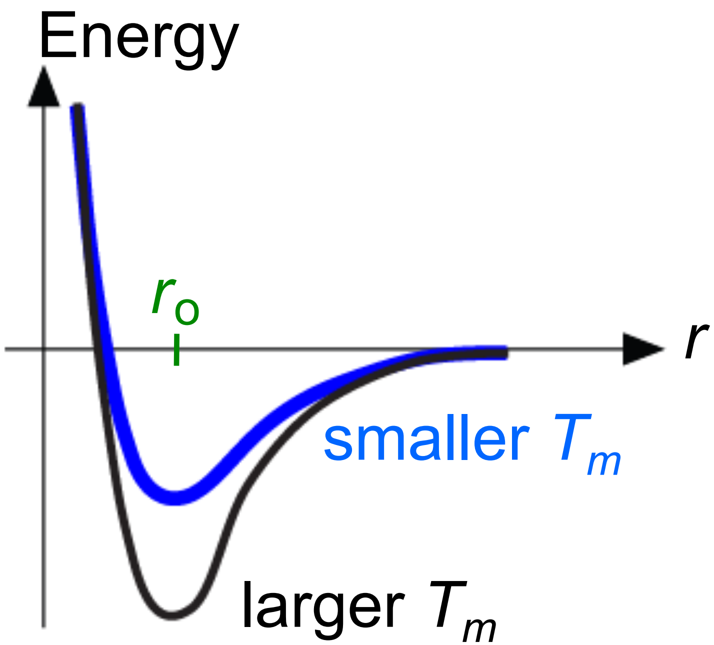


Linus Pauling

Consult with the electronegativity table to determine the bonding nature

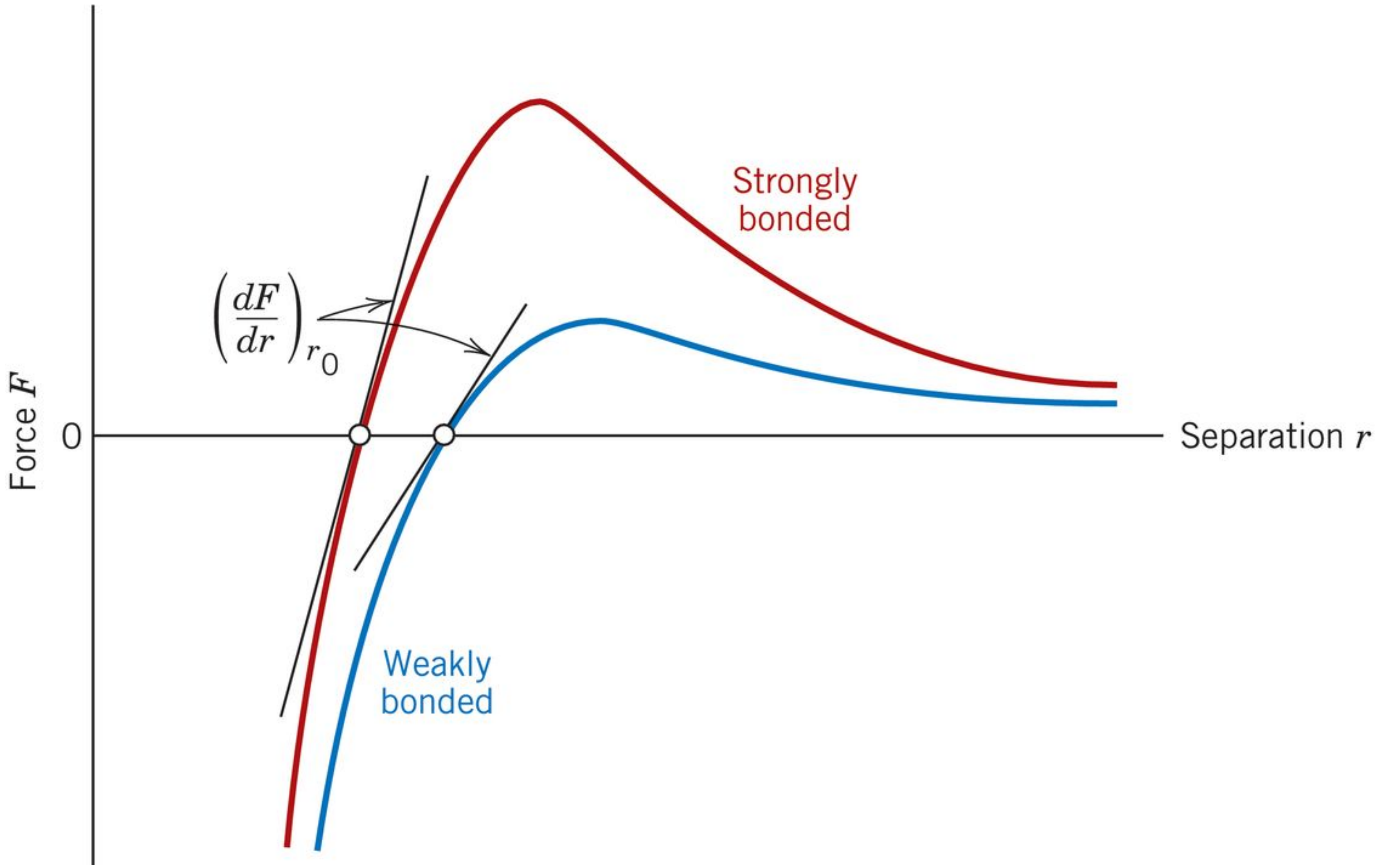
Properties From Bonding: Ex) T_m

- Melting Temperature, T_m



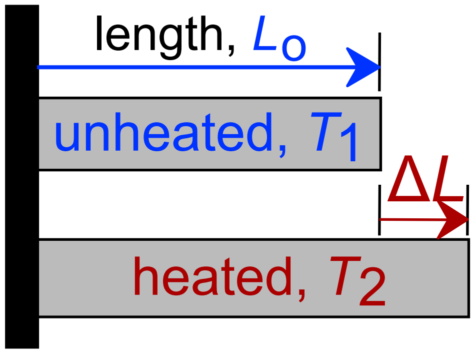
T_m is larger if E_o is larger.

Properties From Bonding: Ex) Stiffness



Properties From Bonding: Ex) Thermal expansion

- Coefficient of thermal expansion, α



coeff. thermal expansion

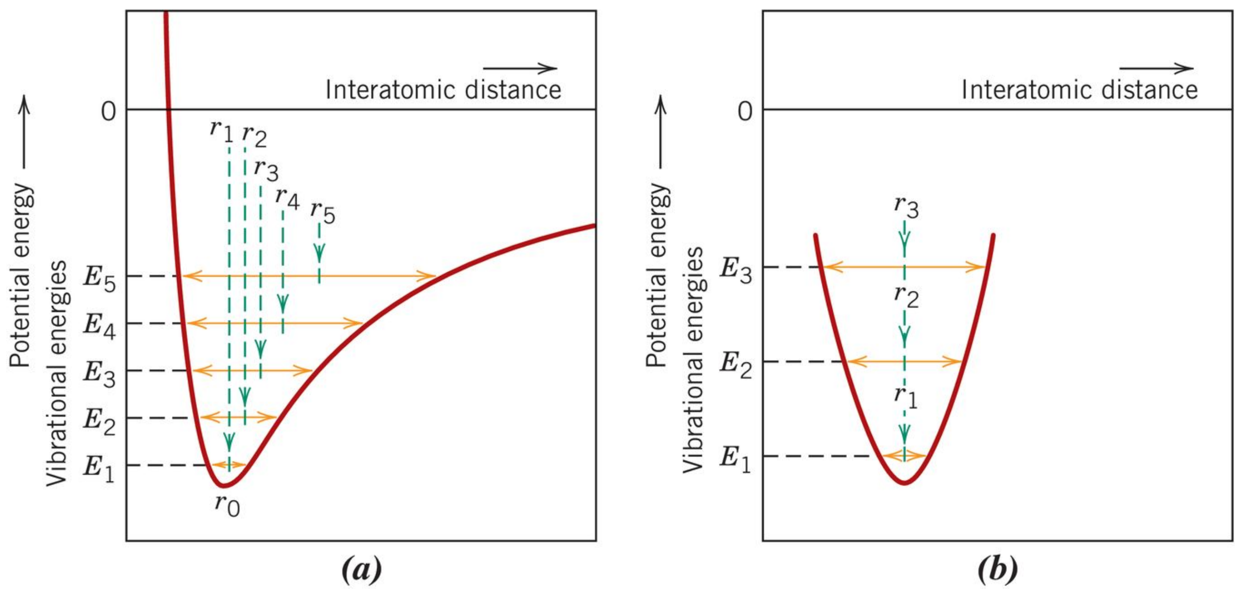
$$\frac{\Delta L}{L_o} = \alpha \, (T_2 - T_1)$$

Thermal expansion can be viewed as increase of average interatomic distance.

Temperature increase induces vibration of atoms

Asymmetric

Symmetric



Summary: Primary Bonds

Ceramics

(Ionic & covalent bonding):

Large bond energy

large T_m

large E

small α

Metals

(Metallic bonding):

Variable bond energy

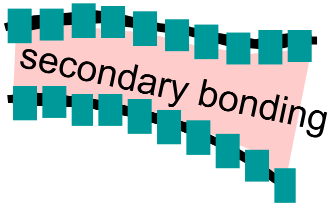
moderate T_m

moderate E

moderate α

Polymers

(Covalent & Secondary):



Directional Properties

Secondary bonding dominates

small T_m

small E

large α

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