

# 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 이루어져 있지만 매우 다른 성질(property)를 가졌다.  
왜? 그럴까?



# Why do we study atomic structure?

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- Some of the following properties

- 1) Chemical (화학)
- 2) Electrical (전기)
- 3) Thermal (열)
- 4) Optical (광학)

are determined by the **electronic structure** in atom



# Objectives

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- 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 = 양성자 (혹은 양자라고도 간혹 불림; proton) + 중성자 (neutron)

## □ 원자를 구성하는 입자의 성질

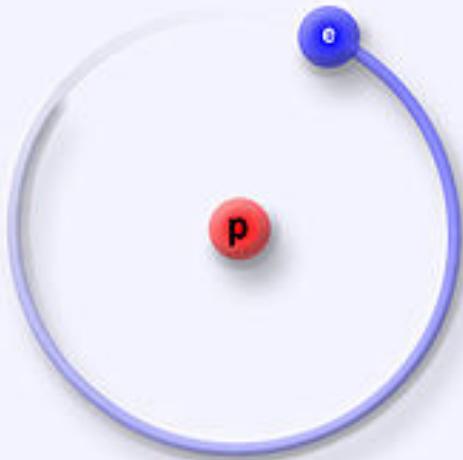
- 전하 (electric charge)를 띤 입자는: 전자와 양성자
- 양성자와 중성자는 비슷한 질량 (약  $1.67 \times 10^{-27}$ kg); 전자는 더욱 작은 질량 ( $9.11 \times 10^{-31}$ kg)

## □ 화학 원소는 원자번호 (atomic number, 기호 Z로 표현되기도)에 따라 분류되기도.

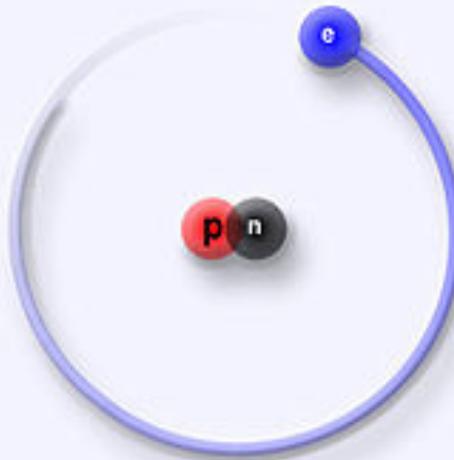
- 원자 번호는 '양성자의 수'와 동일.
- 자연상에 존재하는 원자는 원자번호 1인 수소(Hydrogen)부터 92인 우라늄(Uranium)까지.
- 동일한 원소중에 양성자수는 같아도 중성자가 다를 수 있다 - 동위원소 isotope



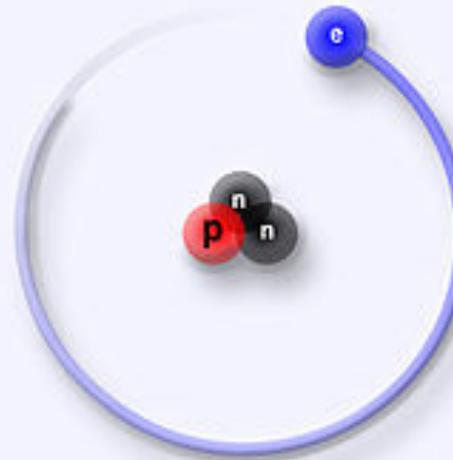
# Isotope: Hydrogen



**Protium**



**Deuterium**



**Tritium**

99.985%

0.015%

the balance



# 기본 개념

## □ 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.
- $1 \text{ amu} = \text{탄소의 원자량}/12 = \text{탄소 동위원소의 평균 질량}/12$

## □ 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

$$\text{amu/atom} = \text{g/mol}$$



# 예제 2.1

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

➤ $^{136}\text{Ce}$	135.907 amu / atom	0.185%
➤ $^{138}\text{Ce}$	137.906 amu / atom	0.251%
➤ $^{140}\text{Ce}$	139.905 amu / atom	88.450%
➤ $^{142}\text{Ce}$	141.909 amu / atom	11.114%

- 세륨의 원자량 ( $\bar{A}$ )은 자연계에 존재하는 동위원소의 ‘평균’ 질량 (weighted average):

$$\text{➤ } \bar{A} = \sum_i f_i A_i$$

- 따라서 세륨의 원자량은?

$$\text{➤ } \bar{A} = 135.907 \times 0.00185 + 137.906 \times 0.00251 + 139.905 \times 0.8845 + 141.909 \times 0.11114$$



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## Atomic models



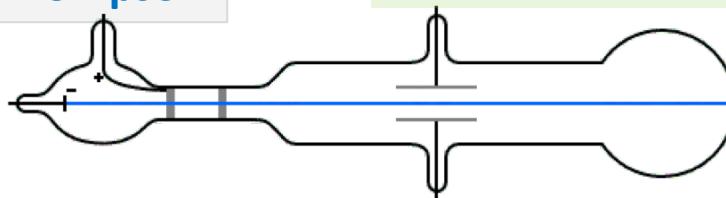
# Historical development of atomic model



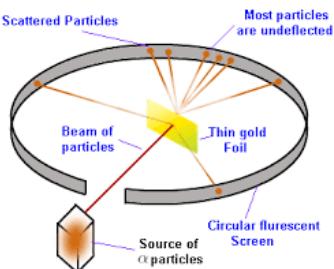
Dalton: All matters are made of atoms



J. J. Thompson



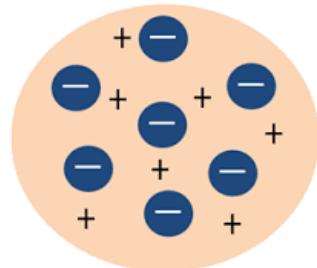
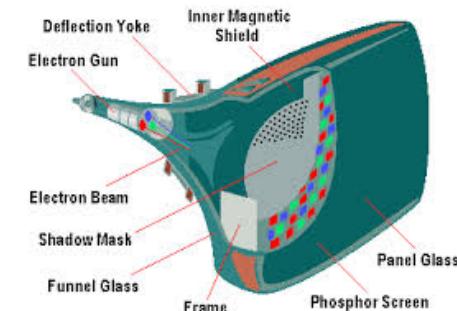
E. Rutherford



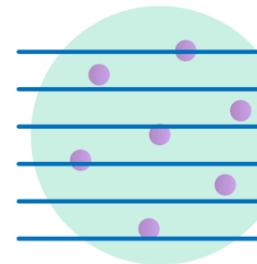
- a) Mostly penetrated.  
b) Some reflected.  
Conclusion?



Niels Bohr: Discrete energy levels (next slide)



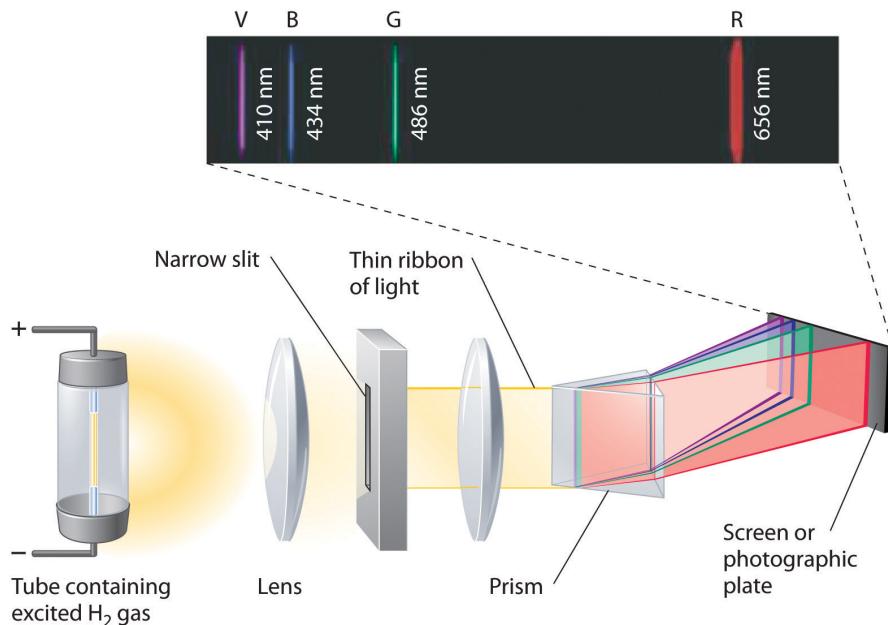
THOMSON MODEL



RUTHERFORD MODEL



# Experimental support on Bohr's model: Atomic Spectral lines



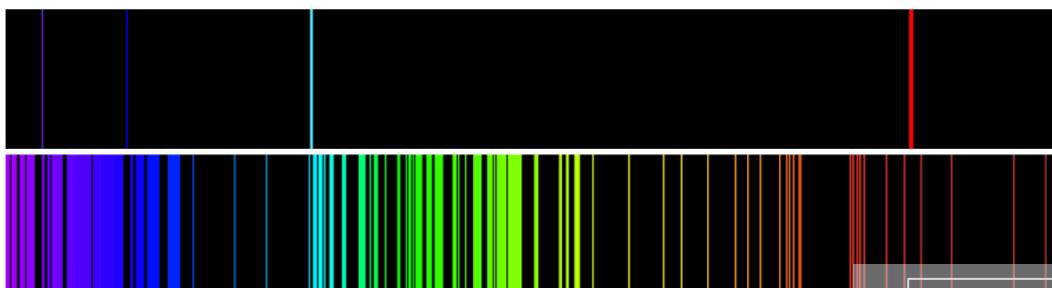
Continuous Spectrum



Emission Lines



Absorption Lines



Hydrogen (H)

Iron (Fe)

WHY?

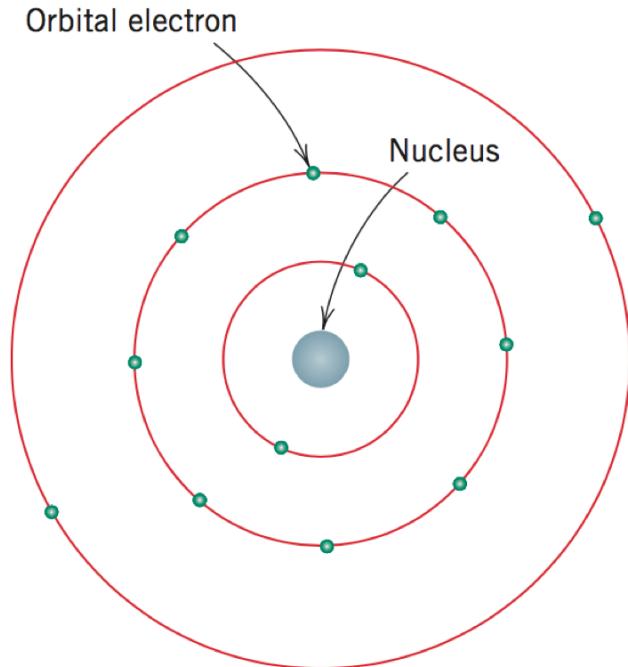
Electrons have discrete levels of energy states



# 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)

- 전자의 에너지가 양자화 (quantized) 되어 있다.
  - 전자는 오직 ‘특정한’ 에너지 값만 가질 수 있다.
  - 전자의 에너지는 변화 가능, 하지만, 오직 허용된 에너지 준위 (state, level)만 가능하다 (양자화)
  - 낮은 에너지상태나 높은 에너지 상태로 ‘도약’(jump; leap) 가능
  - 에너지가 ‘불연속’ 적이다. – 앞서 energy spectrum 결과를 참조.



# Bohr's model의 한계

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.

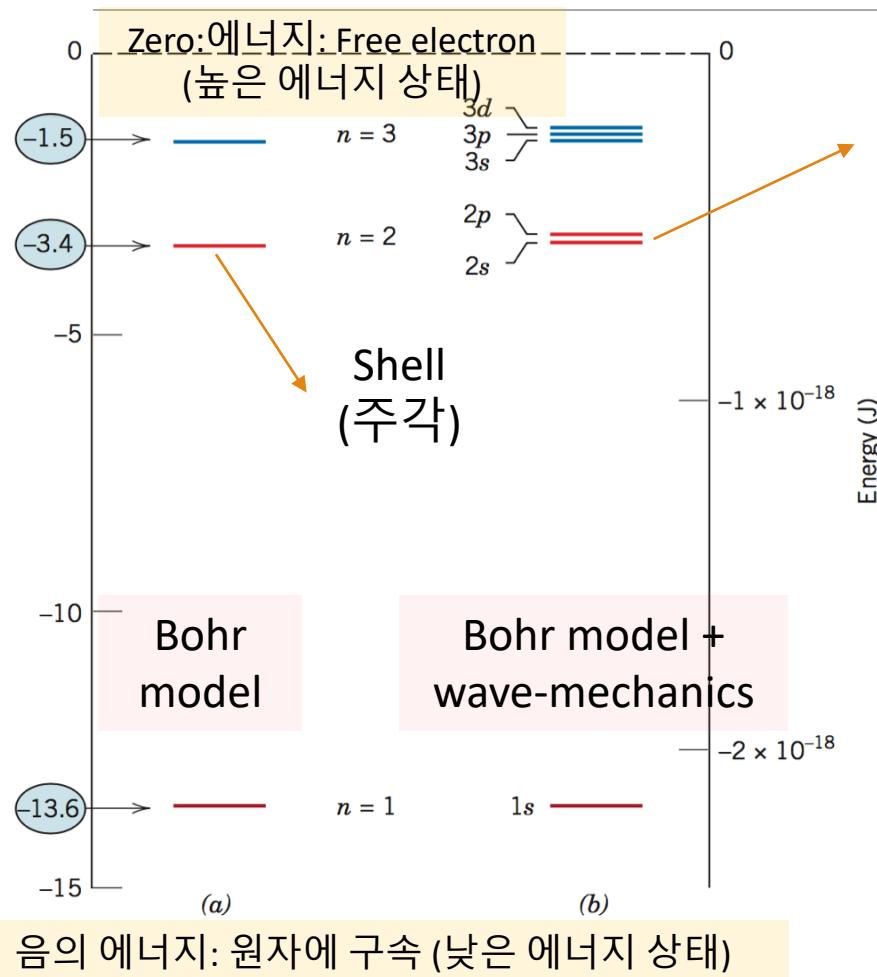
Conclusion: Physicists needed a better model

고전 역학으로 설명안됨

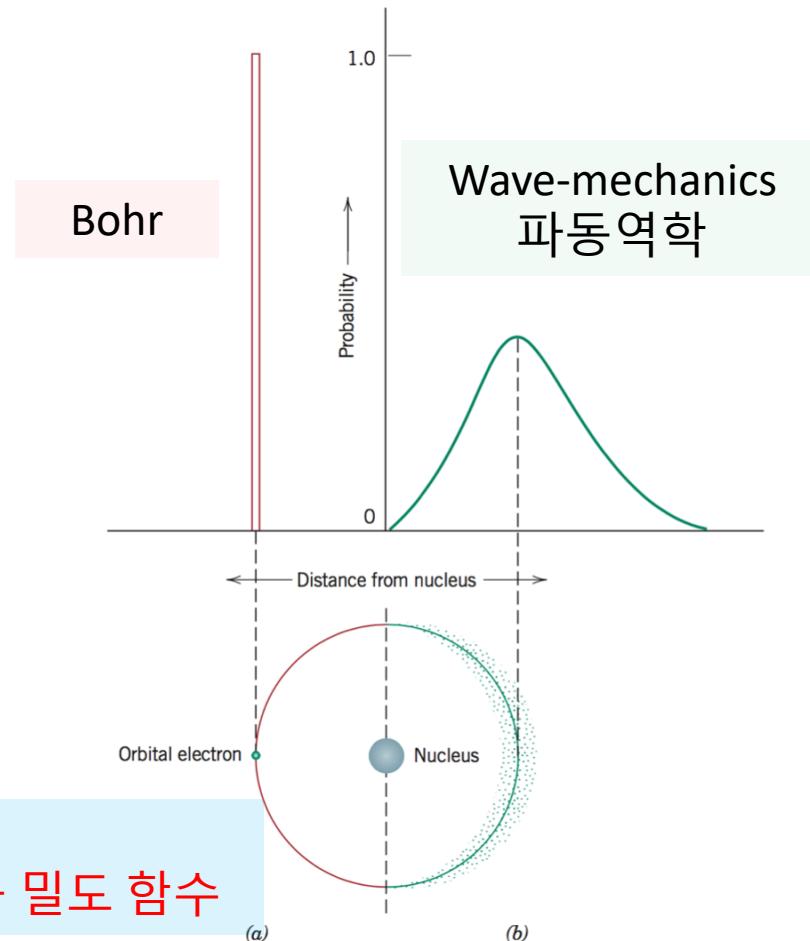
양자역학의 도래



# Bohr's model and Wave-mechanical (파동역학) model



Each shell may consist of subshells (부각)



Orbit과 orbital 차이?

명확한 궤도,  
확률로 표현되는 위치; 확률 밀도 함수



# Electronic Structure

- Electrons have both **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**.
- 네 종류의 양자수 (quantum number)로 전자 확률 밀도가 결정된다 – (양자역학)

Q) Orbit and Orbital?  
- Probability distribution

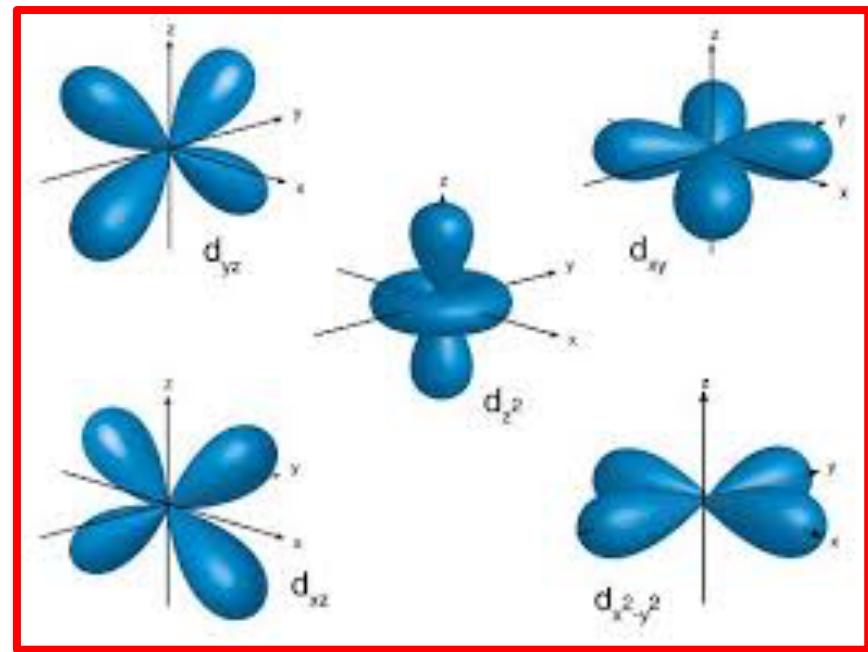
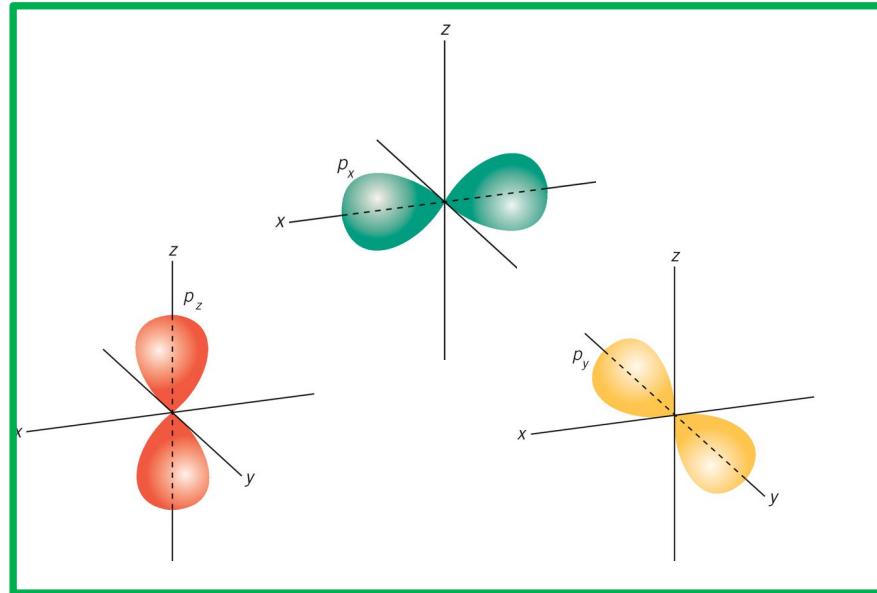
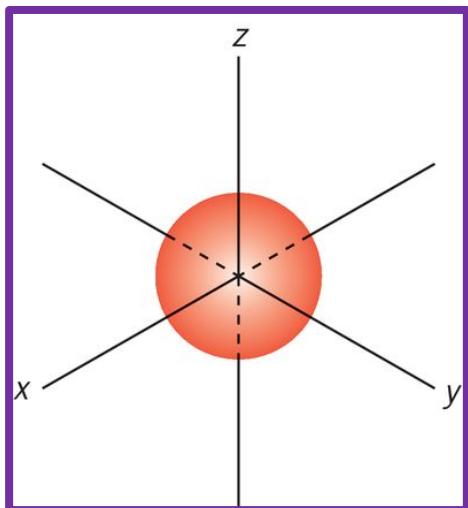


# 파동역학에서의 전자: 양자수에 의해 정의

- 파동역학에서의 전자 위치 (orbital)은 전자 확률 밀도에 따름
- 전자 확률 밀도의 크기, 형태, 방향은 양자수(quantum number)에 의해 특징지어진다 (characterized).
- 보어 모형에 따르면 (전자의) 에너지 수준은:
  - 주각 (shell) 으로 표현.
  - 파동역학에 따르면 각 부각에 세부적으로 부각(subshell)이 존재.
- 각 양자수는
  - 주각은 ‘주양자수’ (principal quantum number,  $n$ )
  - 두번째 양자수는  $l$  (엘)로 표기하며 orbital의 ‘모양’을 결정
  - 세번째 양자수  $m_l$ 은 부각내의 전자궤도수를 결정
  - 네번째 양자수  $m_s$  는 전자의 스핀 모멘트 (spin moment) 결정



# Orbital: areas where electrons are ‘detected’

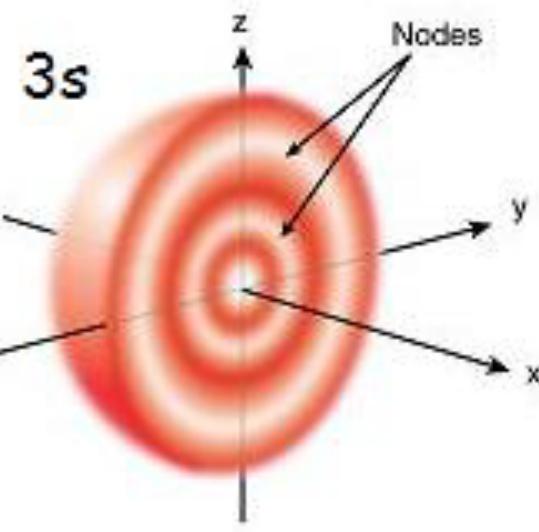
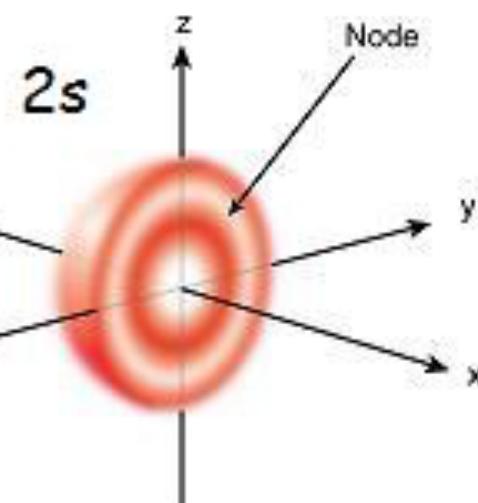
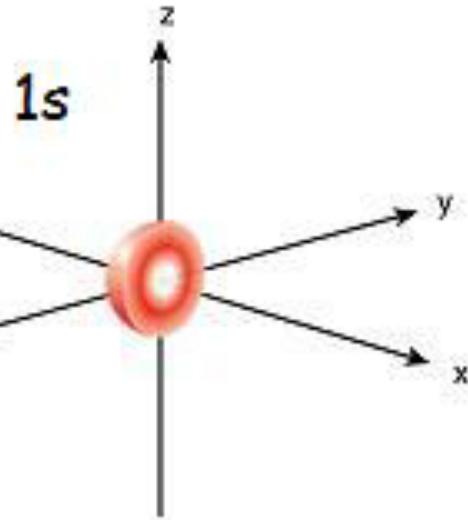


There is a high probability of finding the electron in this direction.

There is very low probability of finding the electron in this direction.

There is very low probability of finding the electron in this direction.

There is a high probability of finding the electron in this direction.



# 양자수 Quantum Numbers

**$n, l, m_l, m_s$**

Quantum # (양자수)

$n$  = principal (energy level-shell)

$\ell$  = subsidiary (orbitals)

$m_l$  = magnetic

$m_s$  = spin

Designation

$K, L, M, N, O$  (1, 2, 3, etc.)

$s, p, d, f$  (0, 1, 2, 3, ...,  $n-1$ )

1, 3, 5, 7 (- $\ell$  to + $\ell$ )

$\frac{1}{2}, -\frac{1}{2}$

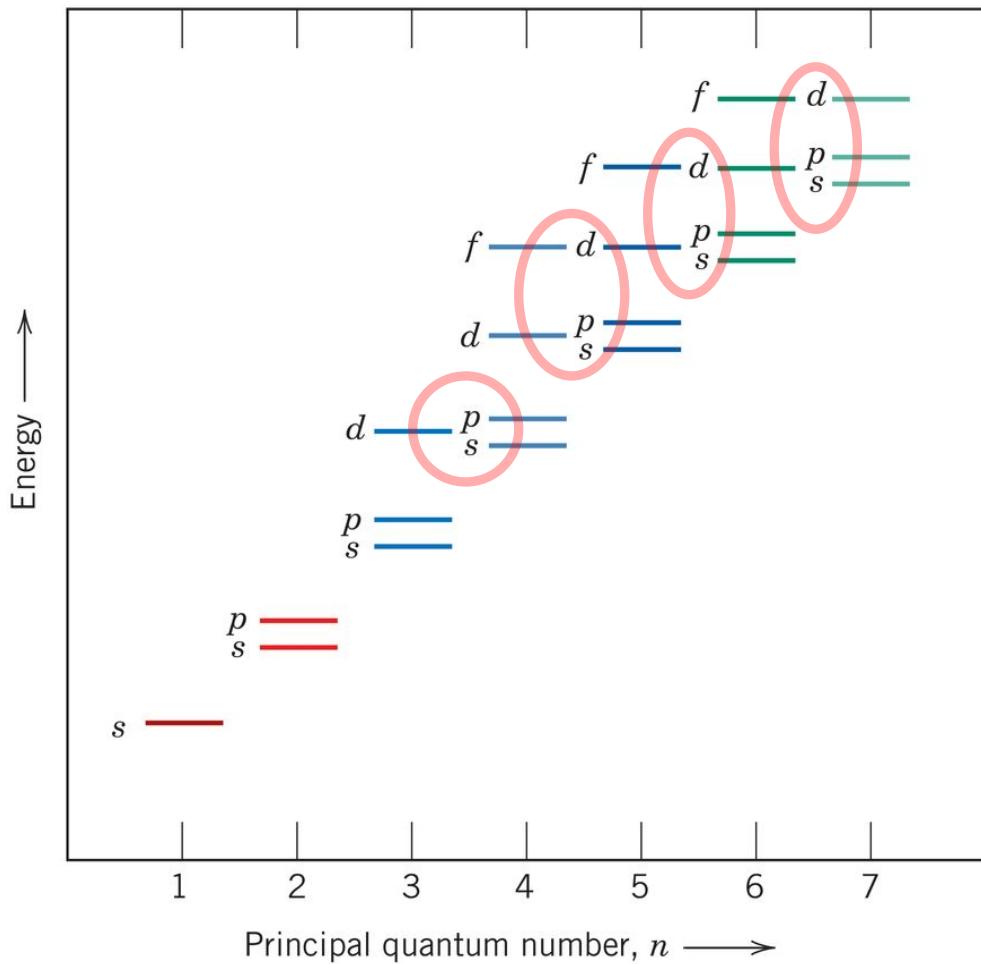
**Table 2.1** Summary of the Relationships among the Quantum Numbers  $n$ ,  $l$ ,  $m_l$ , and Numbers of Orbitals and Electrons

<i>Value of n</i>	<i>Value of l</i>	<i>Values of <math>m_l</math></i>	<i>Subshell</i>	<i>Number of Orbitals</i>	<i>Number of Electrons</i>
1	0	0	1s	1	2
2	0	0	2s	1	2
	1	-1, 0, +1	2p	3	6
	0	0	3s	1	2
3	1	-1, 0, +1	3p	3	6
	2	-2, -1, 0, +1, +2	3d	5	10
	0	0	4s	1	2
4	1	-1, 0, +1	4p	3	6
	2	-2, -1, 0, +1, +2	4d	5	10
	3	-3, -2, -1, 0, +1, +2, +3	4f	7	14

Source: From J. E. Brady and F. Senese, *Chemistry: Matter and Its Changes*, 4th edition. Reprinted with permission of John Wiley & Sons, Inc.



# 주/부각의 상대 전자 에너지 개략도



- 주값이 커질수록 에너지 증가.
- 같은 주각내에서  $l$  값이 커질수록 에너지 증가( $s < p < d$ )
- 주각사이의 에너지 준위가 겹치는 경우가 발생.

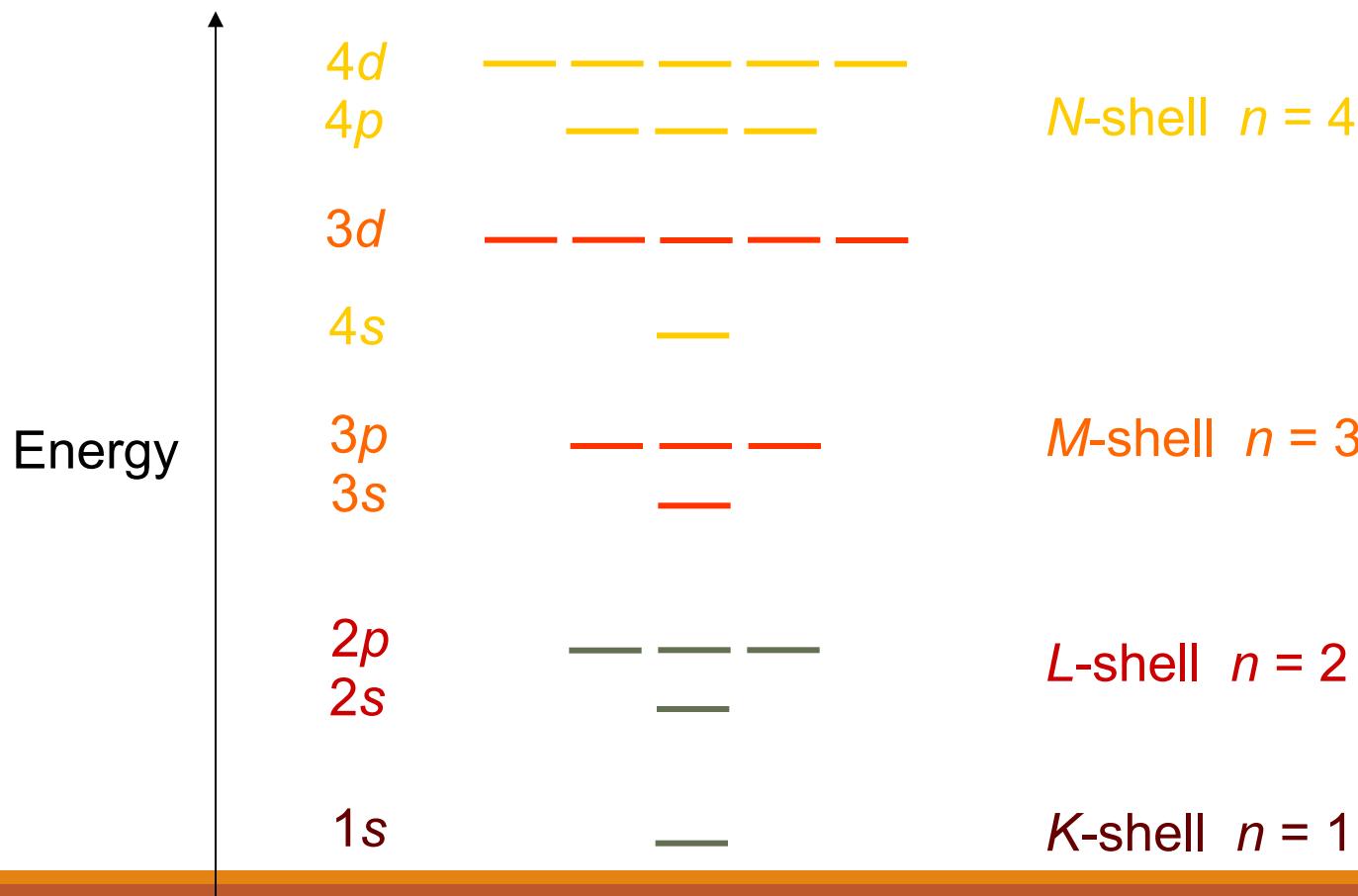
From K. M. Ralls, T. H. Courtney, and J. Wulff, Introduction to Materials Science and Engineering, p. 22. Copyright © 1976 by John Wiley & Sons, New York. Reprinted by permission of John Wiley & Sons, Inc.



# Electron Energy States

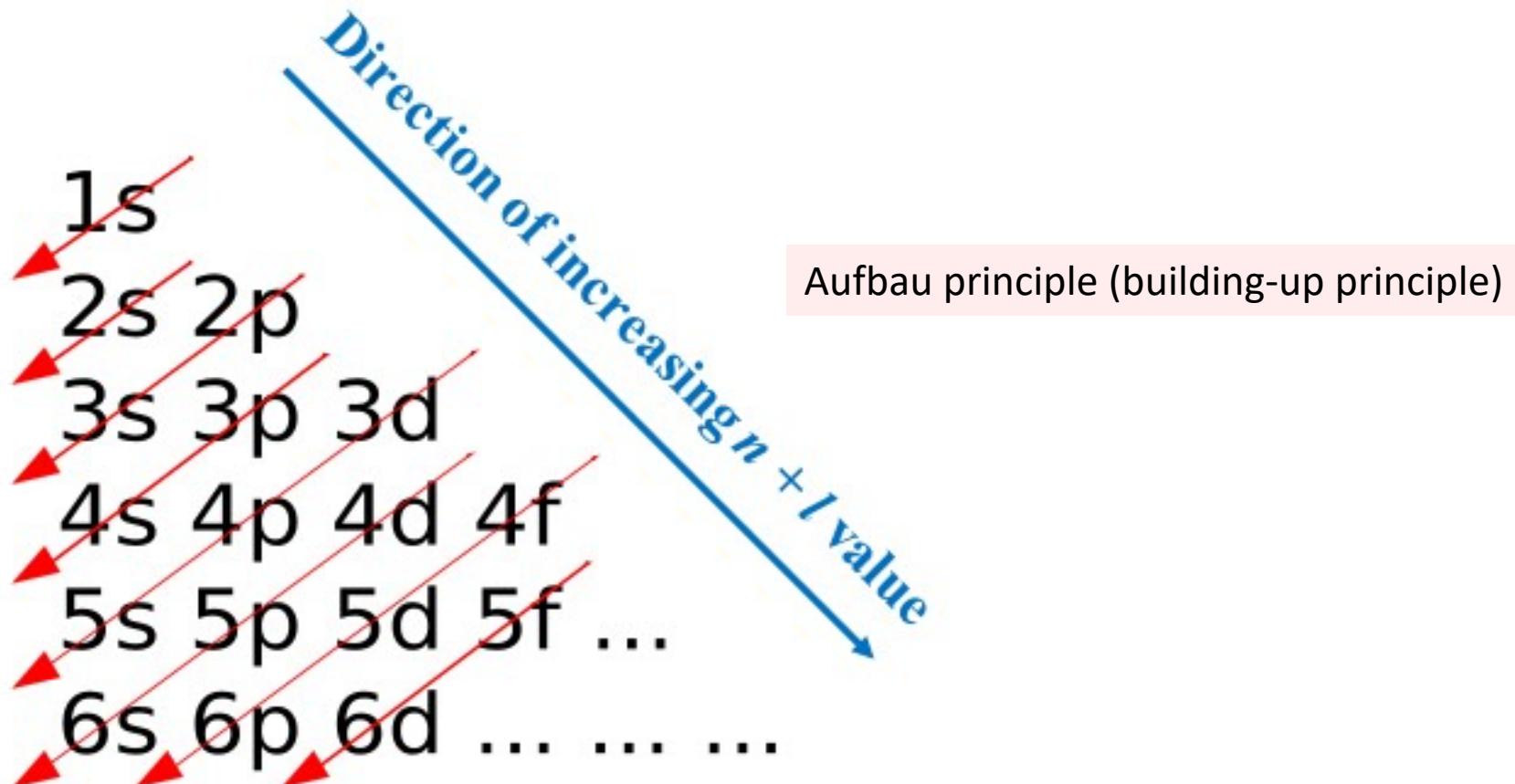
Electrons...

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



# 전자 배위 (전자 구조)

- 전자 배위 (혹은 전자 구조; electron configuration); 원자에 전자가 채워지는 방식;
- 파울리의 배타원리(Pauli exclusion principle): 하나의 준위에는 최대 스핀 방향이 각각 다른 2개의 이하의 전자까지만 채워질 수 있다. (그 이상은 불가능)

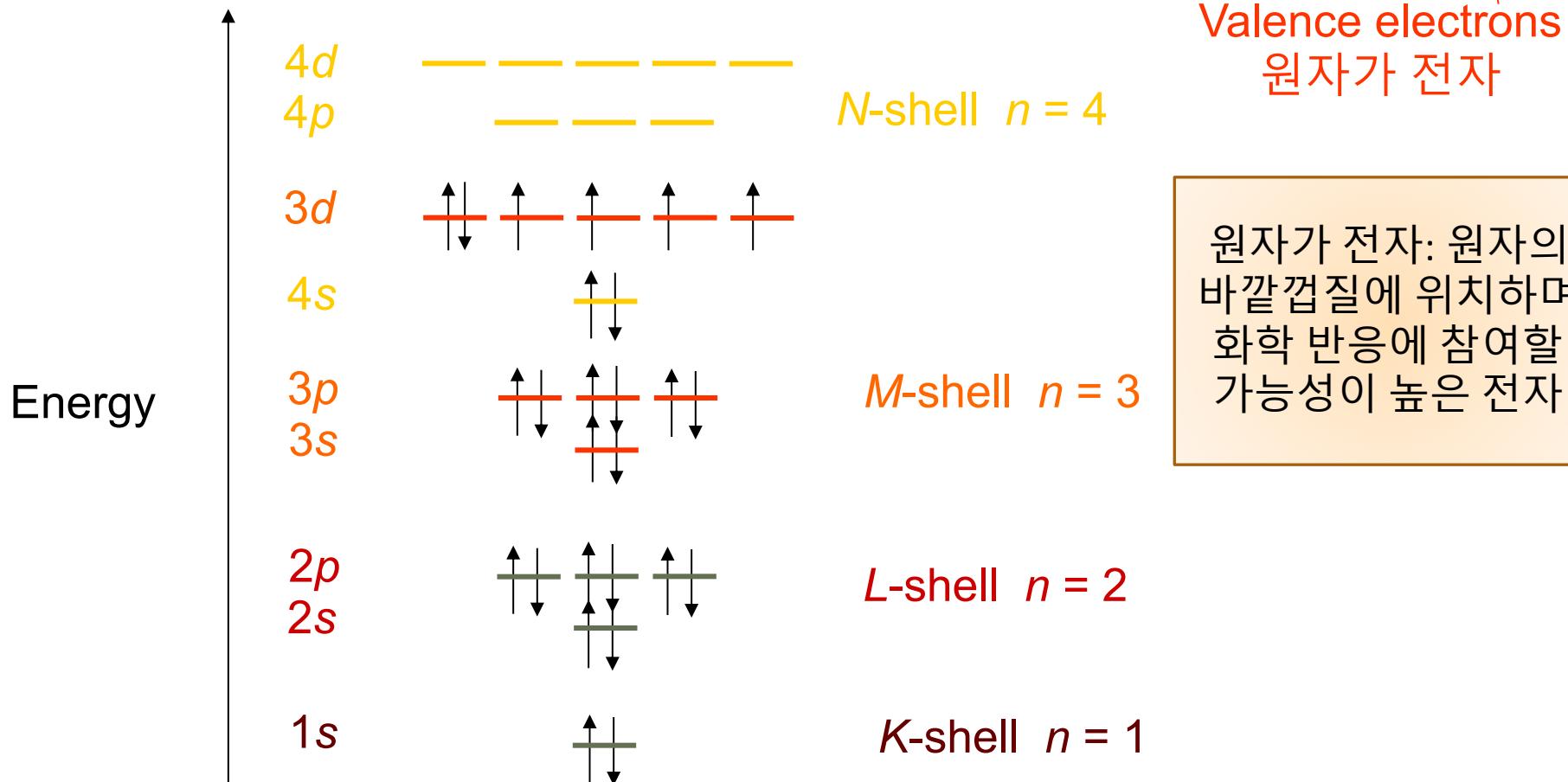


# Electronic Configurations

ex: Fe - atomic # = 26

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

$3d^6 \quad 4s^2$



# Valence electron (원자가 전자)

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## □ 원자가 전자 (valence electron)

- 일반적으로 최외각에 채워진 전자를 일컬으며, 이러한 전자들은 속해있는 원자가 결합할 때 '참여'한다.
- 따라서, 원자가 전자는 '결합 방식', 형태 등에 영향을 미친다.
- 유념할 것은, 원자의 '결합 방식'은 해당 결합으로 만들어진 '재료'의 성질에 매우 큰 영향을 끼친다!

## □ Valence electron의 영향?

- 예를 들어, 안정된 전자 배위(즉, 최외각의 에너지 준위가 '가득'찬 경우)를 가진 원소들은 남들과 잘 결합하려 하지 않는다 – 불활성 기체(inert gas) – Neon, Argon, Krypton, Helium.
- 이온결합, 공유 결합 ... 등의 결합 방식을 구분하는 요인이 된다.



# The Periodic Table (주기율표)

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

The periodic table illustrates the following trends:

- Electron Gain:** Elements in groups 13-17 (III A to VII A) are labeled "give up 1e<sup>-</sup>", "give up 2e<sup>-</sup>", and "give up 3e<sup>-</sup>".
- Electron Loss:** Elements in groups 1-2 (IA and IIA) are labeled "accept 1e<sup>-</sup>", "accept 2e<sup>-</sup>", and "accept 3e<sup>-</sup>".
- Inert Gases:** Helium (He) and the noble gases (Ne, Ar, Kr, Xe, Rn) are labeled "inert gases".
- Metallicity:** Metals are represented by light blue squares, while nonmetals are represented by dark blue squares.
- Nonmetallicity:** Nonmetals are represented by dark blue squares, while metals are represented by light blue squares.
- Intermediate:** Elements in group 18 (VIIIA) are labeled "Intermediate".
- Actinide Series:** Elements 57 through 71 are part of the actinide series.
- Rare Earth Series:** Elements 58 through 72 are part of the lanthanide series.

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

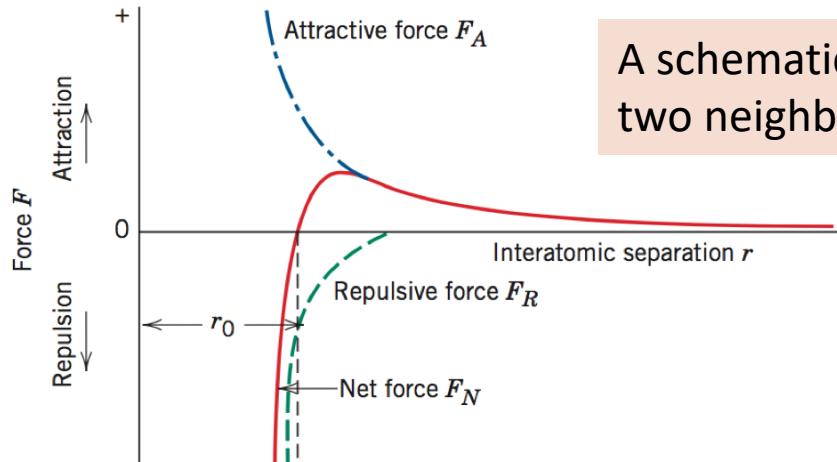
Adapted  
from Fig. 2.8,  
*Callister &  
Rethwisch*  
9e.

**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?

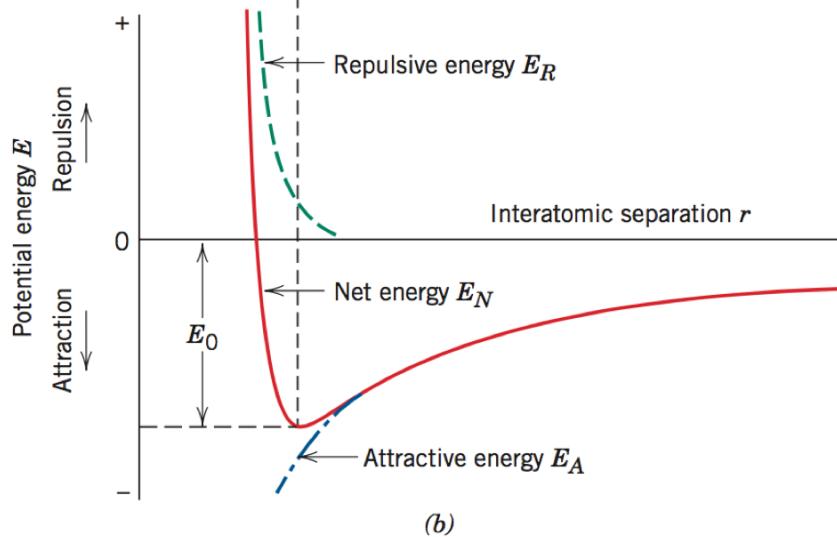
The interatomic distance at which the potential energy is minimum

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:

$$F \propto \frac{1}{r^2}$$

$$E_{\text{potential}} = \int_r^\infty F_{\text{attraction}}(r) dr + \int_r^\infty F_{\text{repulsion}}(r) dr$$

$E_0$ : bonding energy



# Material properties and bonding?

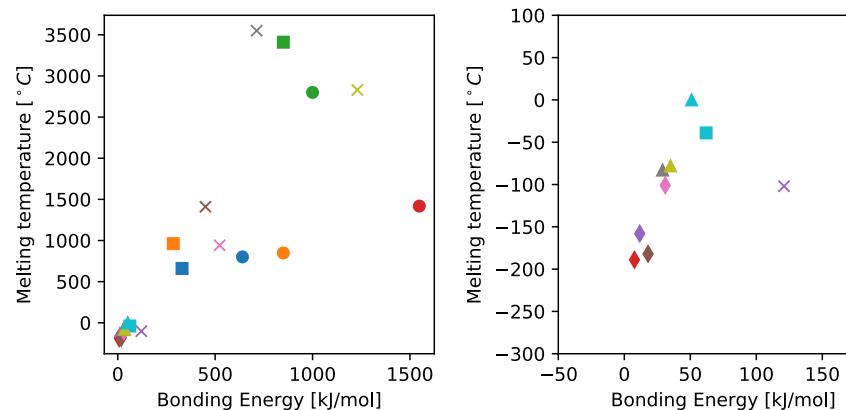
Examples:

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

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

● NaCl	×	Cl <sub>2</sub>	×	SiC	■	Ag	◊	Kr	▲	HF
● LiF	×	Si	■	Hg	■	W	◆	CH <sub>4</sub>	▲	NH <sub>3</sub>
● MgO	×	InSb	■	Al	◆	Ar	◆	Cl <sub>2</sub>	▲	H <sub>2</sub> O
● CaF <sub>2</sub>	×	Diamond	■							

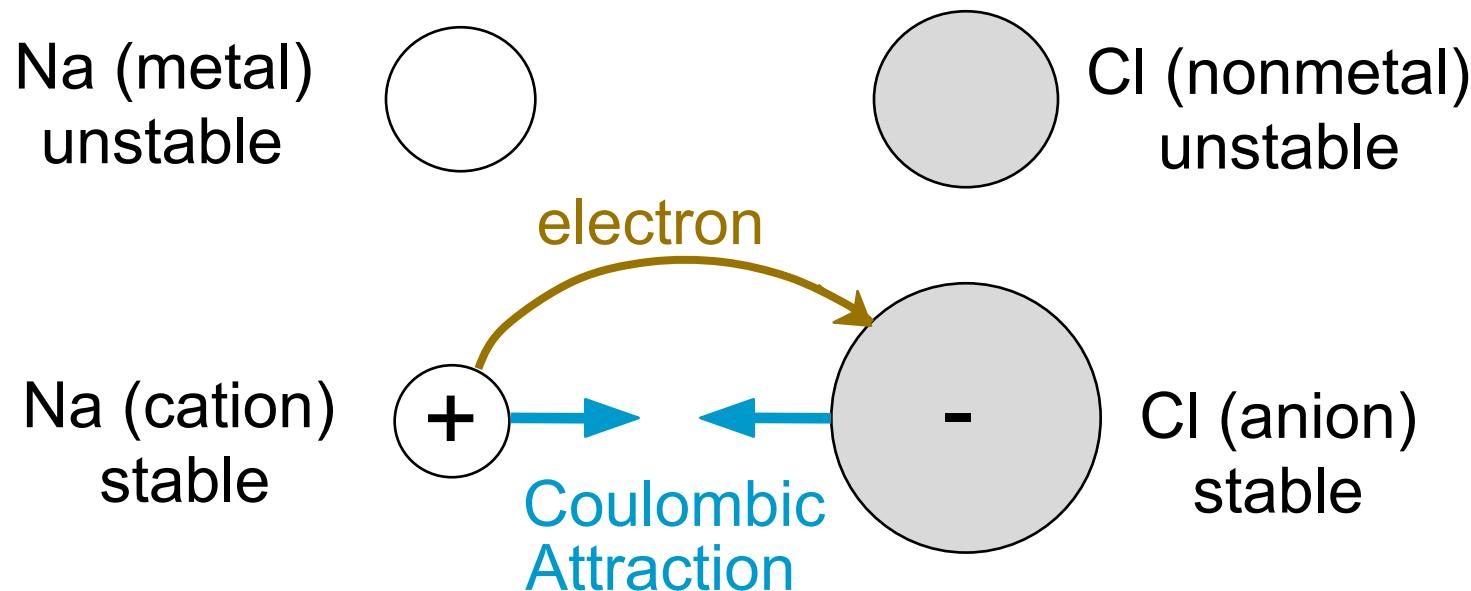


- Secondary bonding (relatively weaker) – physical bond
  - Dipole-Dipole
  - Polar module-induced dipole
  - H-bonds (triangles)
  - Fluctuating dipole (weakest)



# 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												0	He —				
H 2.1		IIA		VIII					IB		IIB			He —			
Li 1.0	Be 1.5	Na 1.0	Mg 1.3	IIIB	IVB	VB	VIB	VIIB	VIII		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

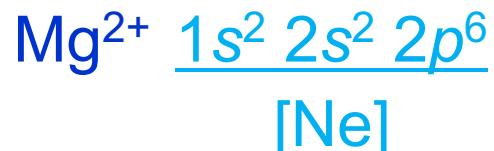
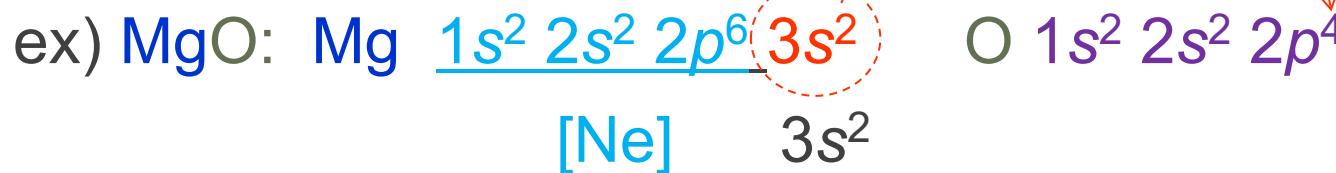


# Ionic Bonding: electron transfer

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.

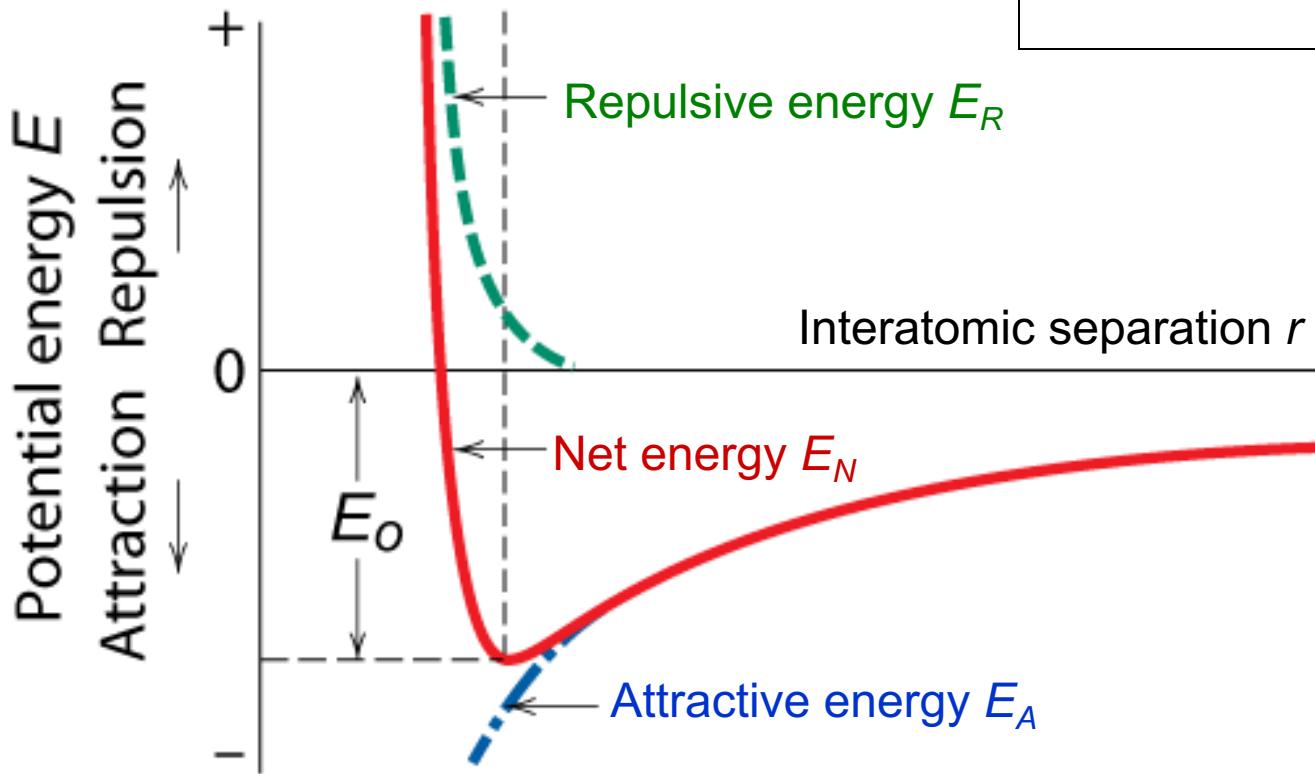
Dissimilar electronegativities



# Ionic Bonding: Bonding forces and energy

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

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



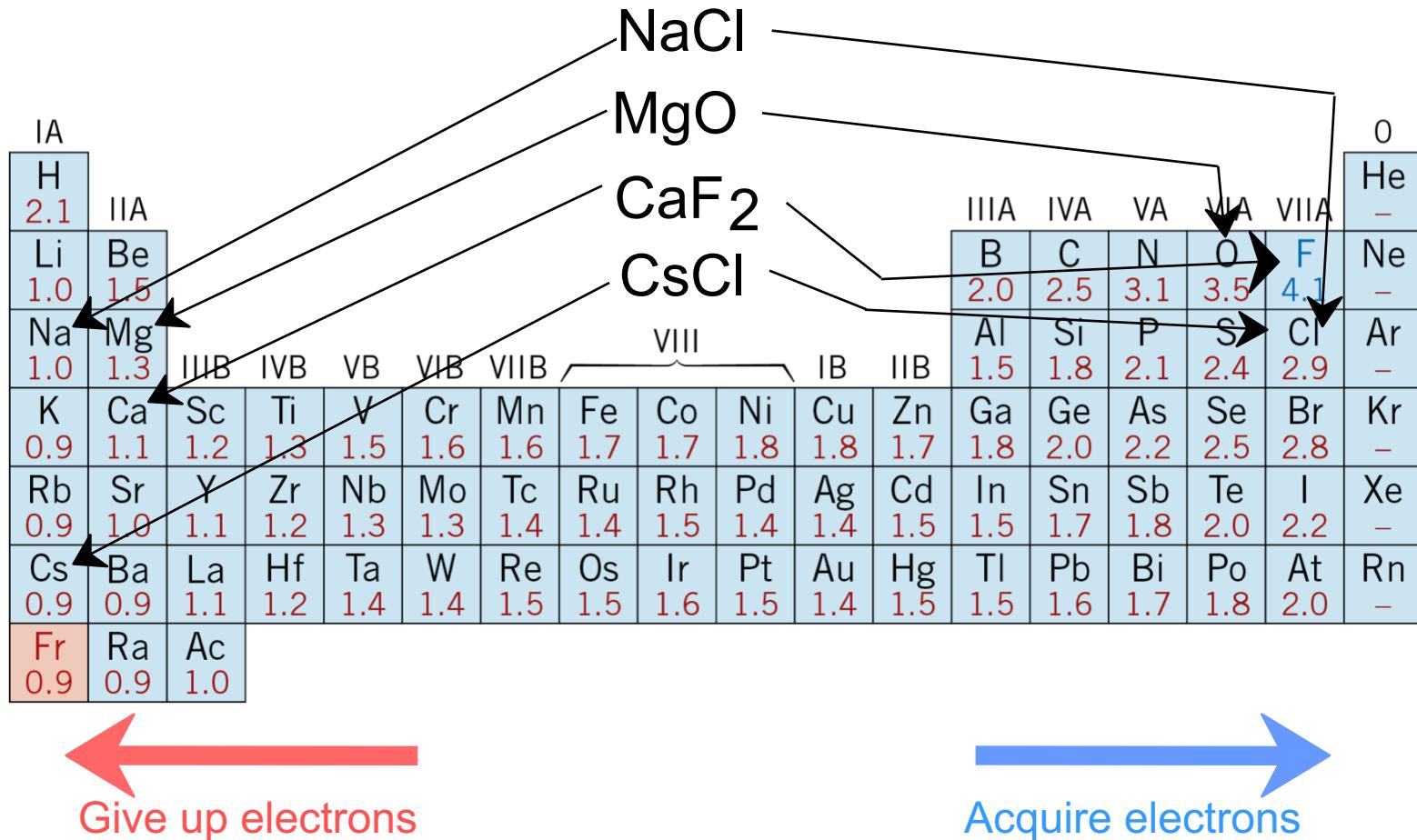
예제 2.2

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:  $\text{H}_2$

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

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

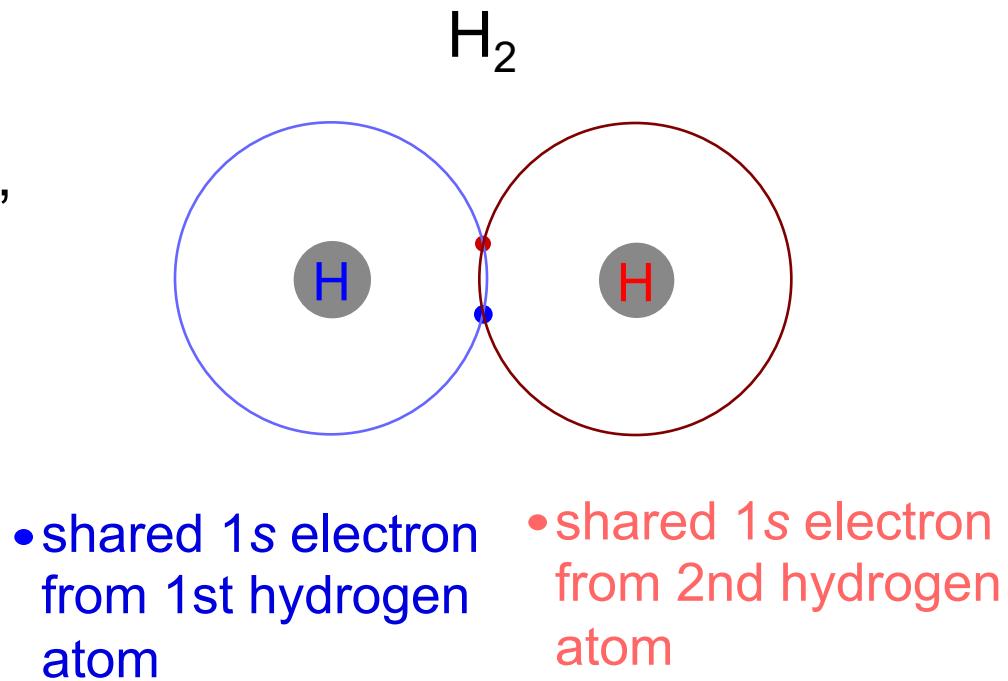
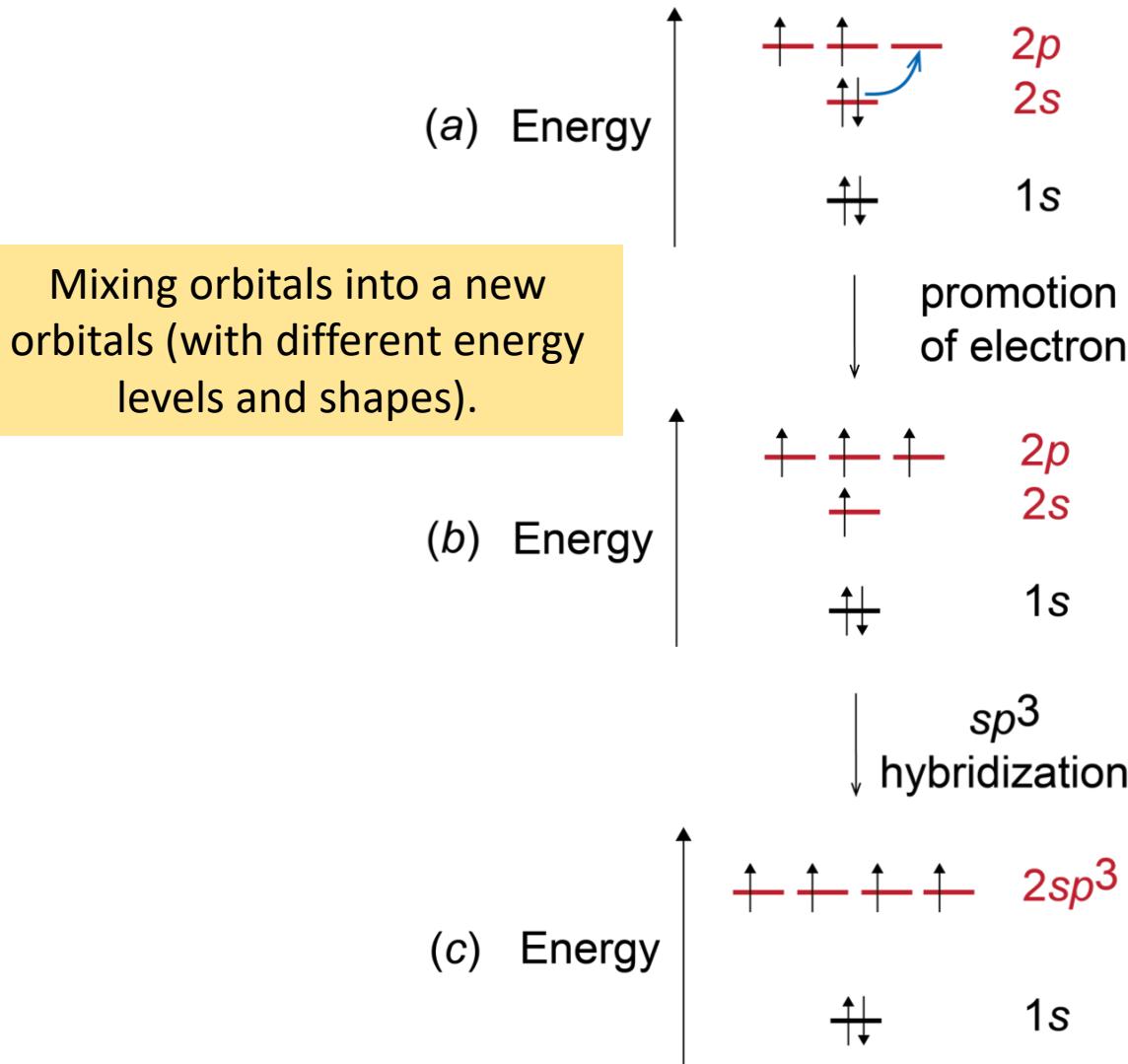


Fig. 2.12, Callister & Rethwisch 9e.



# Hybridization (hybrid orbitals)



Carbon can form  $sp^3$  hybrid orbitals

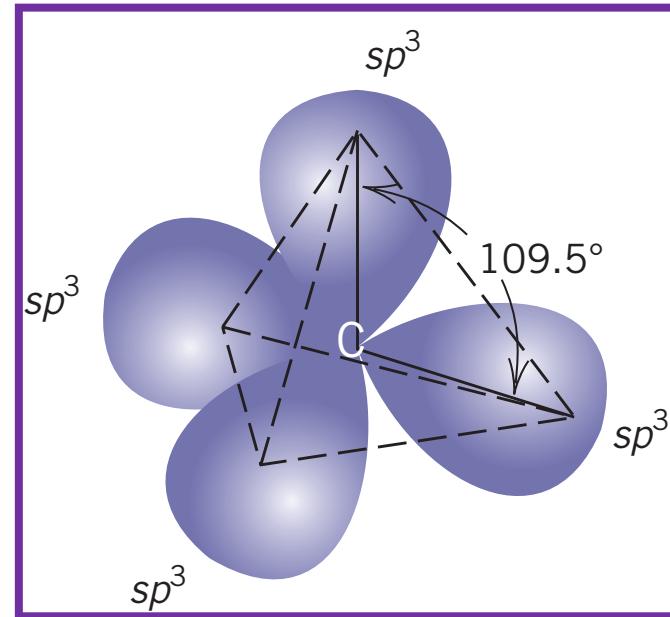


Fig. 2.14, Callister & Rethwisch 9e.  
(Adapted from J.E. Brady and F. Senese, *Chemistry: Matter and Its Changes*, 4<sup>th</sup> edition. Reprinted with permission of John Wiley and Sons, Inc.)

Fig. 2.13, Callister & Rethwisch 9e.



# Hybridization (hybrid orbitals): carbon $sp^3$

- **Example:  $\text{CH}_4$  (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.

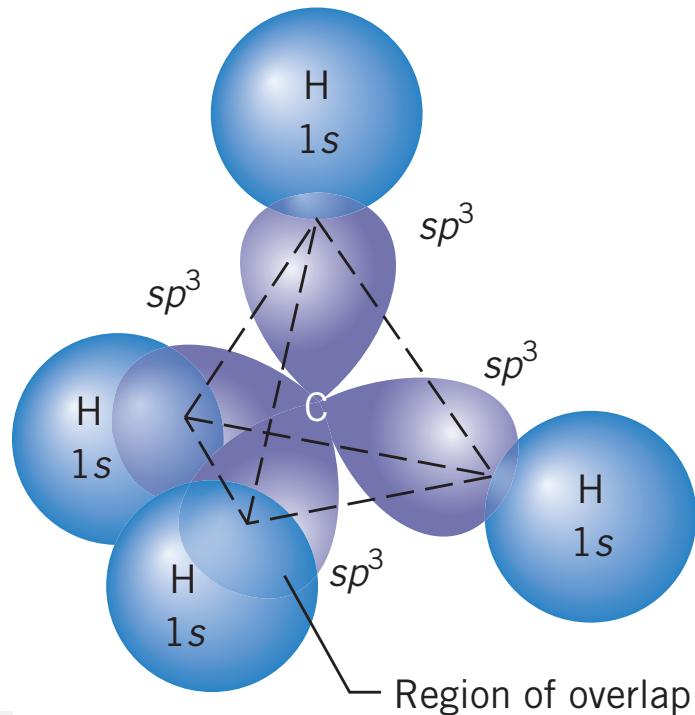
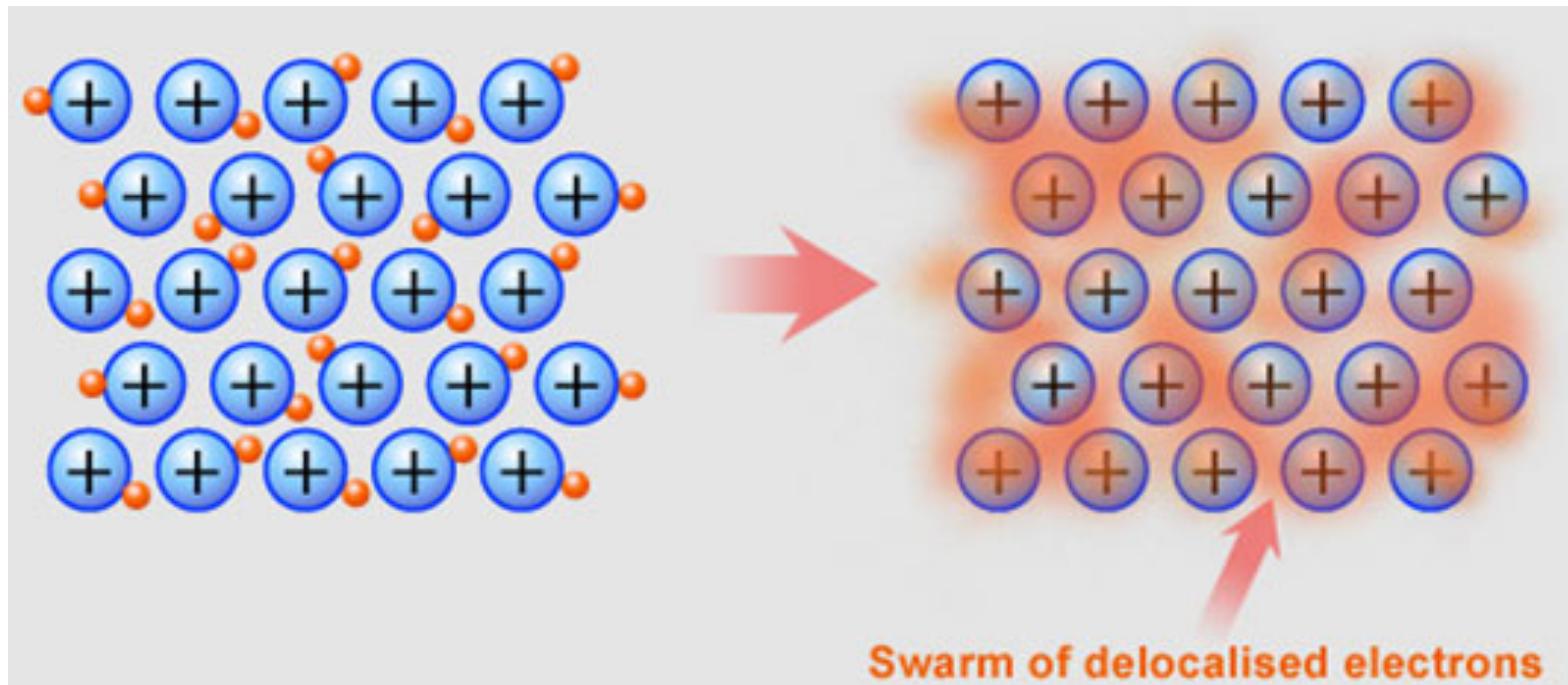


Fig. 2.15, Callister & Rethwisch 9e.  
(Adapted from J.E. Brady and F. Senese, *Chemistry: Matter and Its Changes*, 4<sup>th</sup> edition. Reprinted with permission of John Wiley and Sons, Inc.)

# Metallic bonding

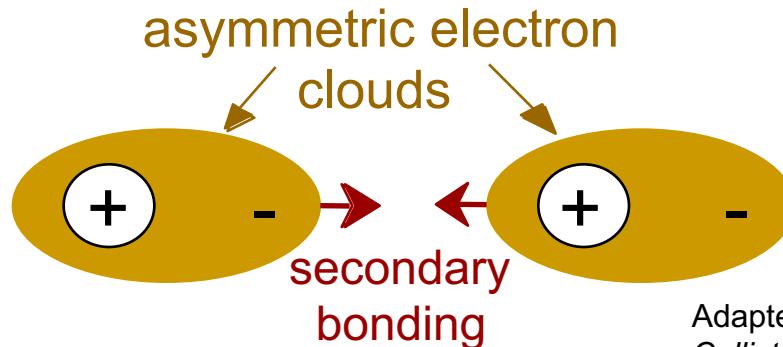
- ❑ The most outer electrons are not ‘localized’ and can freely move around.
- ❑ Electron cloud (sea).
- ❑ Electron adhesives
- ❑ Delocalized electron cloud is the origin of good electrical and thermal conductivities



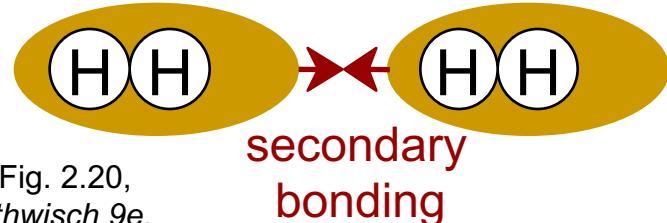
# Secondary Bonding

Arises from interaction between **dipoles** (atom or molecule)

- Fluctuating **dipoles**



ex: liquid H<sub>2</sub>  
H<sub>2</sub> → ← H<sub>2</sub>



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

- Permanent **dipoles**-molecule induced

Originally symmetric but gets asymmetric by neighboring

-general case:

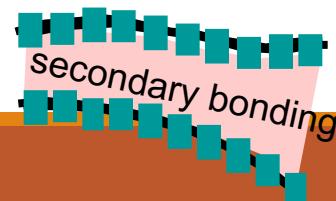


Adapted from Fig. 2.22,  
*Callister & Rethwisch 9e.*

-ex: liquid HCl



-ex: polymer



secondary bonding



# A special case of secondary bonding: Hydrogen bonding

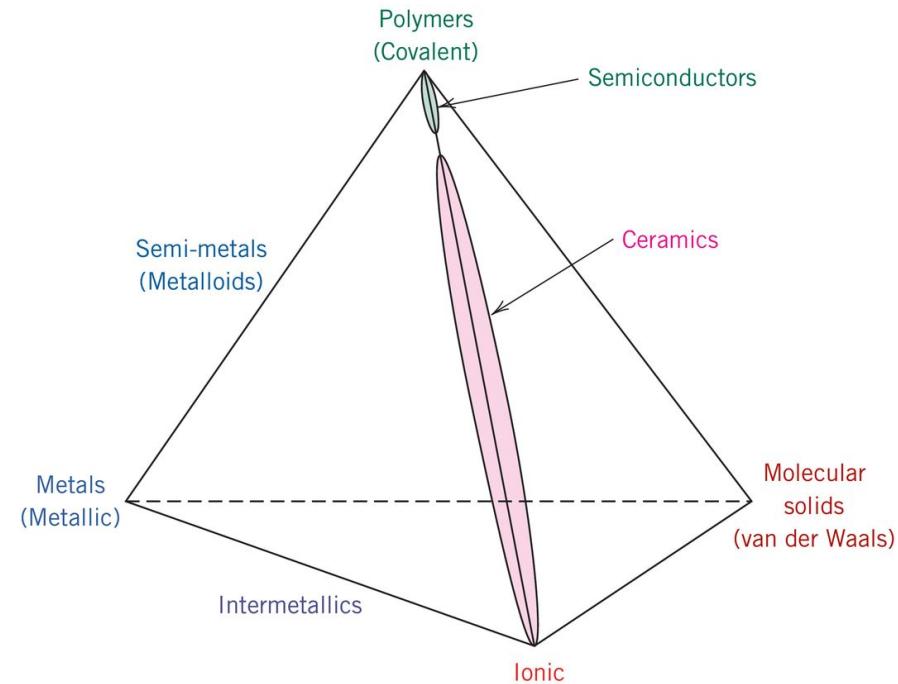
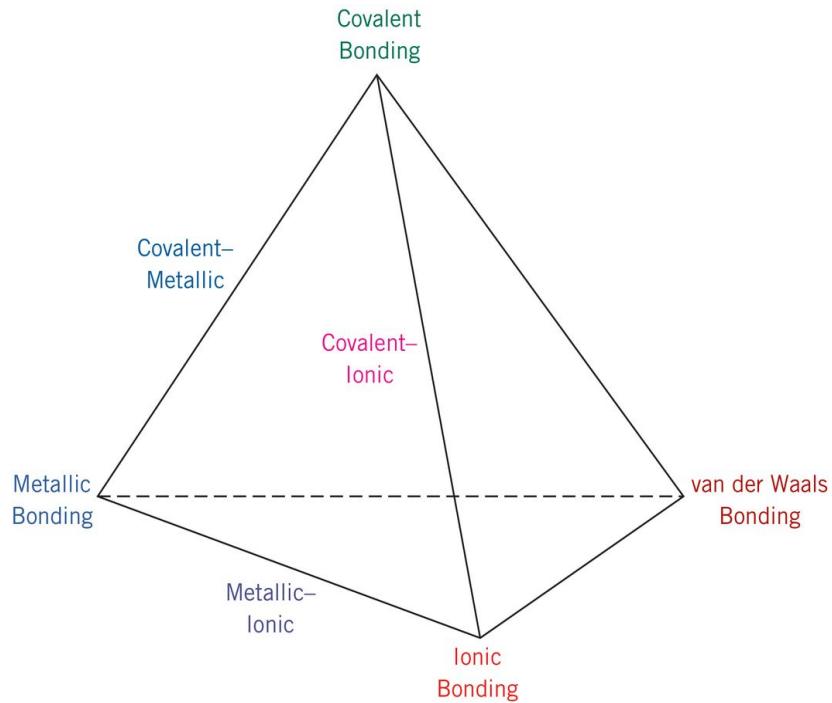
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- ❑ A special case of secondary bonding
- ❑ What makes hydrogen bonding strong?



# Mixed bonds

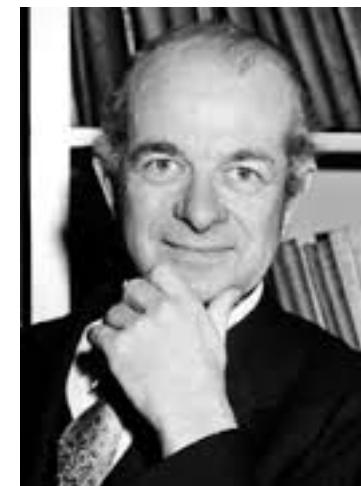
Not all bondings are ‘pure’.



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

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



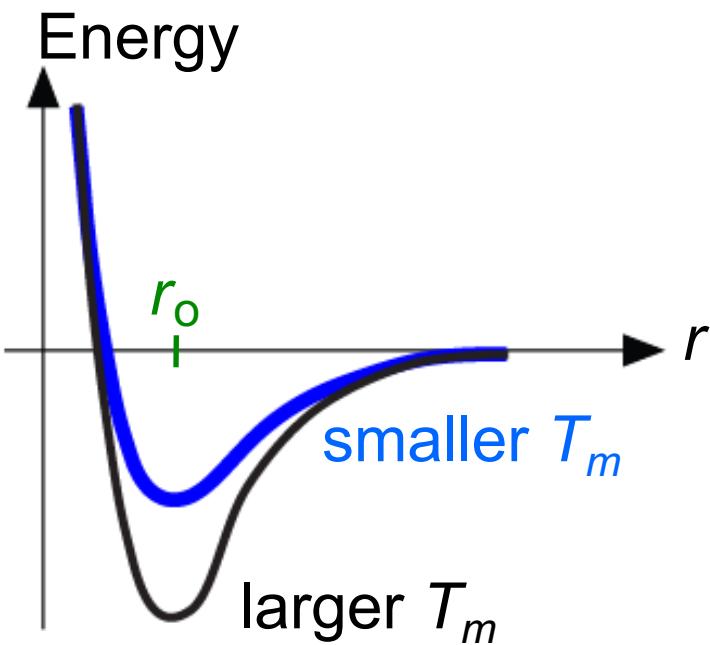
Linus Pauling

Consult with the electronegativity table to determine the bonding nature



# Properties From Bonding: Ex) $T_m$

- Melting Temperature,  $T_m$

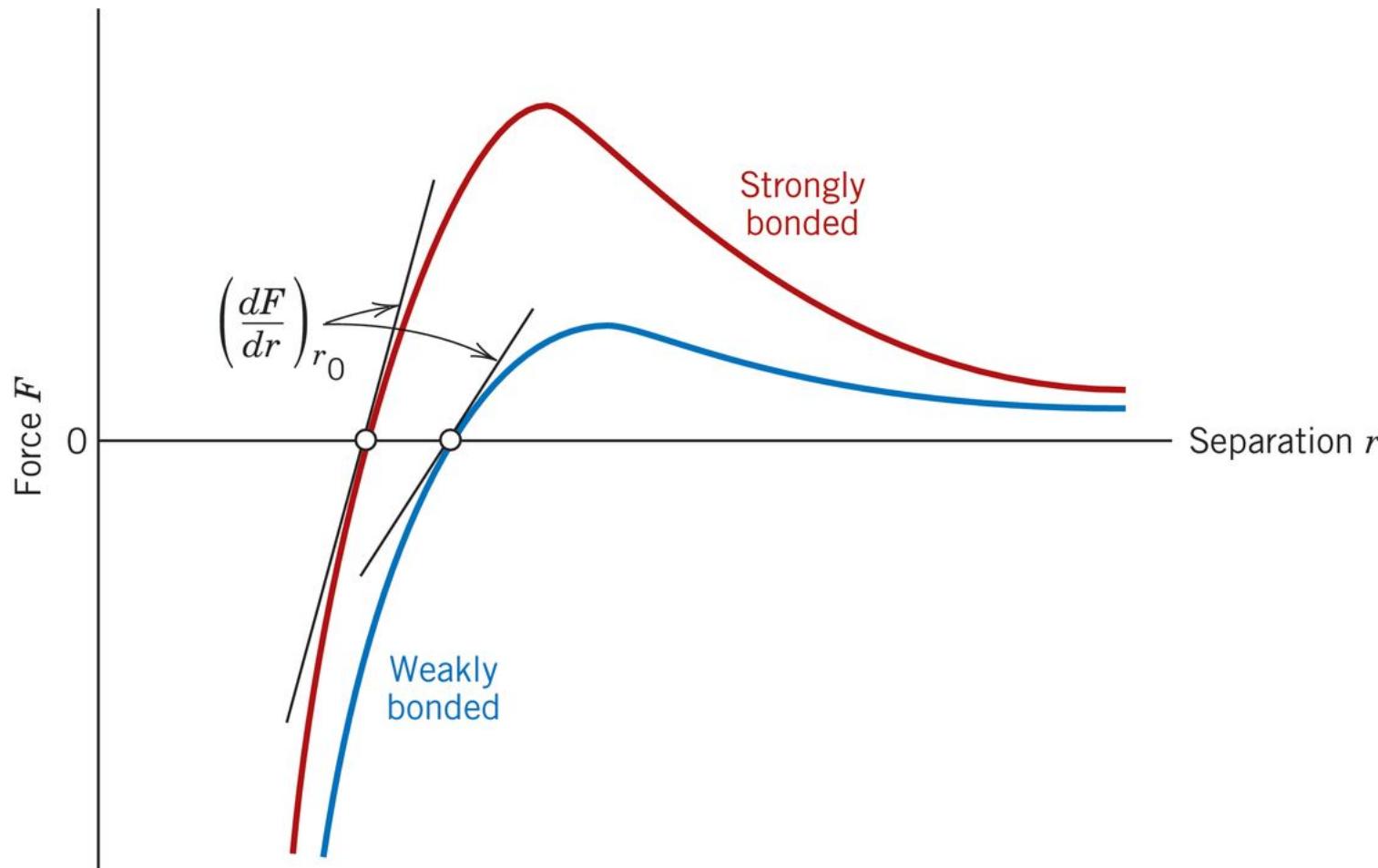


$T_m$  is larger if  $E_o$  is larger.



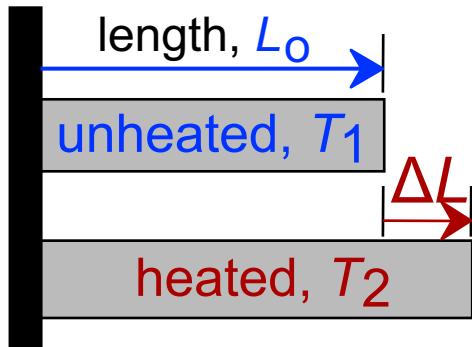
# Properties From Bonding: Ex) Stiffness

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# Properties From Bonding: Ex) Thermal expansion

- Coefficient of thermal expansion,  $\alpha$



coeff. thermal expansion

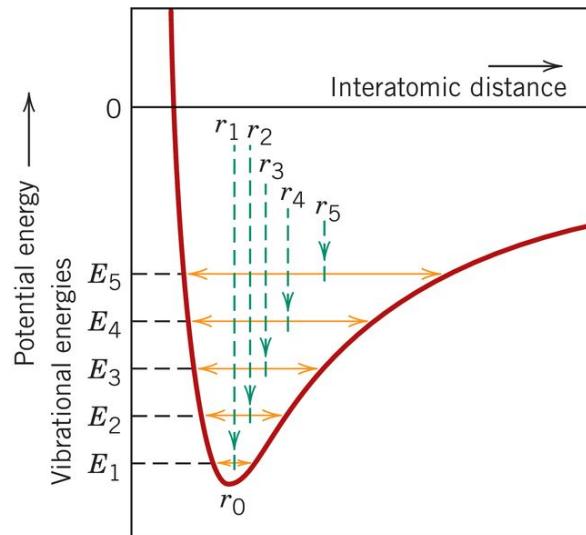
$$\frac{\Delta L}{L_0} = \alpha (T_2 - T_1)$$

Asymmetric

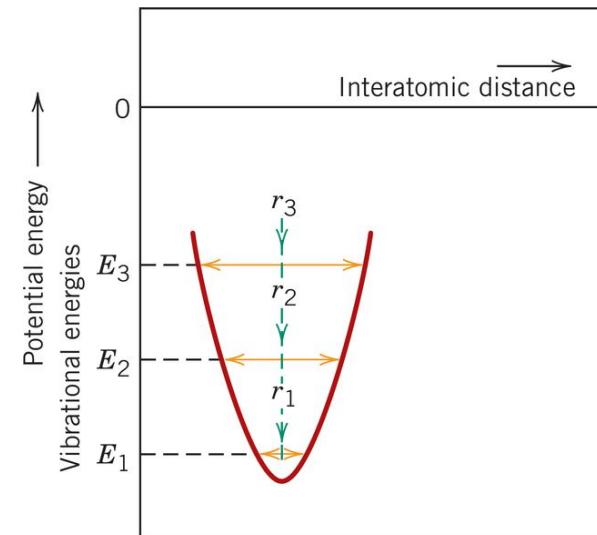
Symmetric

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

Temperature increase induces vibration of atoms



(a)



(b)

# Summary: Primary Bonds

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## Ceramics

(Ionic & covalent bonding):

### Large bond energy

large  $T_m$   
large  $E$   
small  $\alpha$

## Metals

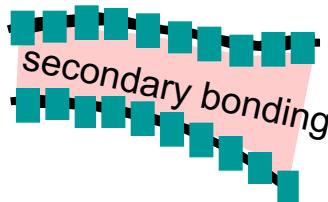
(Metallic bonding):

### Variable bond energy

moderate  $T_m$   
moderate  $E$   
moderate  $\alpha$

## Polymers

(Covalent & Secondary):



### Directional Properties

Secondary bonding dominates

small  $T_m$   
small  $E$   
large  $\alpha$



# 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

