

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?

- 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

- 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

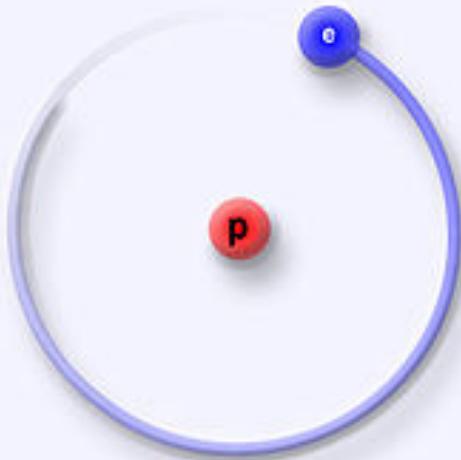
- 전하 (electric charge)를 띤 입자는: 전자와 양성자
- 양성자와 중성자는 비슷한 질량 (약 1.67×10^{-27} kg); 전자는 더욱 작은 질량 (9.11×10^{-31} kg)

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

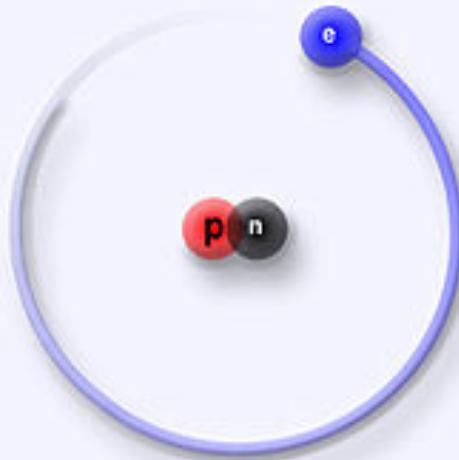
- 원자 번호는 '양성자의 수'와 동일.
- 자연상에 존재하는 원자는 원자번호 1인 수소(Hydrogen)부터 92인 우라늄(Uranium)까지.
- 동일한 원소중에 양성자수는 같아도 중성자가 다를 수 있다 - 동위원소 isotope



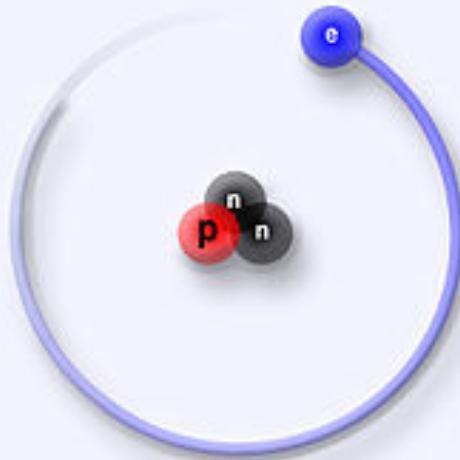
Isotope: Hydrogen



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 $xxx \text{ amu}/\text{atom}$ 이다.”라고 표현

➤ 분자량 표기?

- ❖ “물(H_2O)의 원자량은 한 몰(mol)당 xxx g (gram) 이다.”라고 표현
- ❖ 혹은 “물의 원자량은 $xxx \text{ g/mol}$ 이다.”라고 표현.

➤ 사실 이 두 단위는 동일하다. 즉

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



예제 2.1

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

➤ ^{136}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

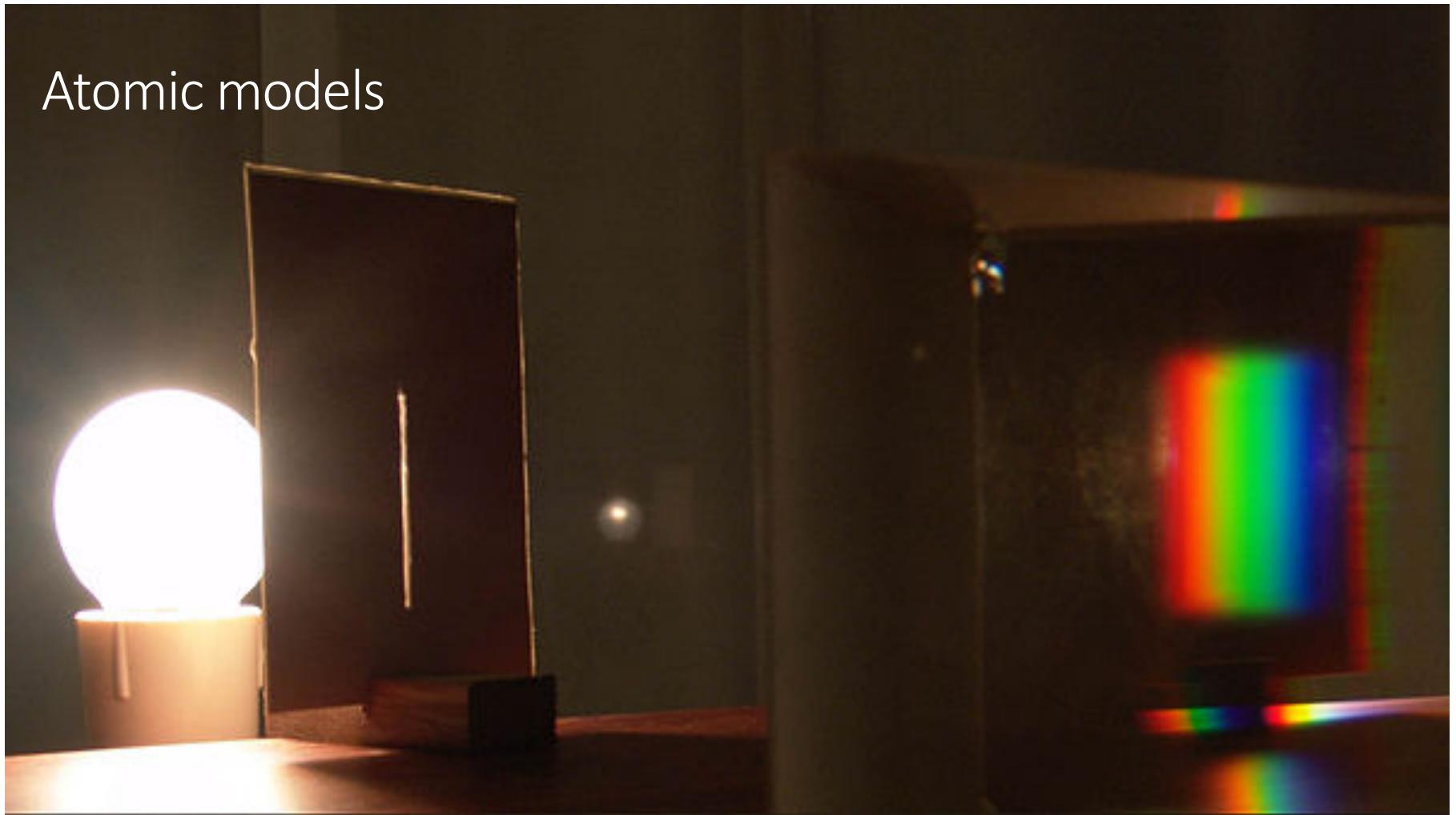


Image from https://en.wikipedia.org/wiki/Spectral_line



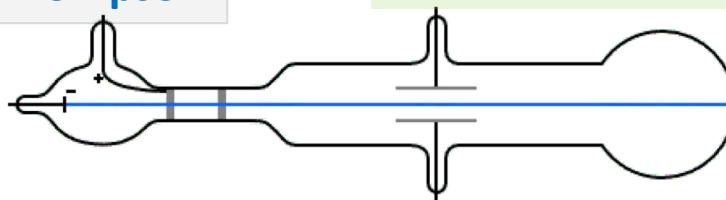
Historical development of atomic model



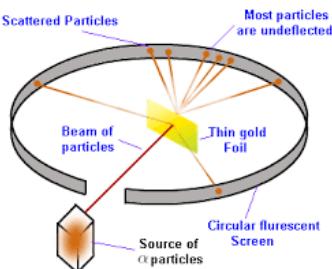
Dalton: All matters are made of atoms



J. J. Thompson



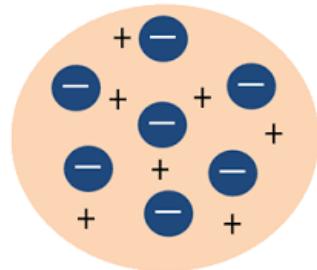
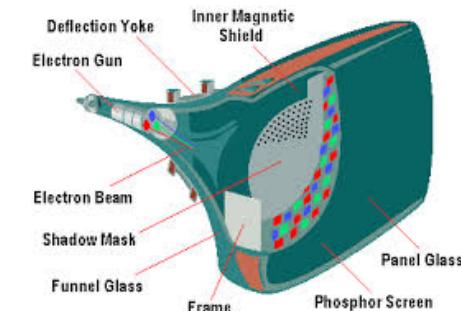
E. Rutherford



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

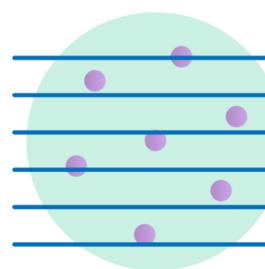


Niels Bohr: Discrete energy levels (next slide)

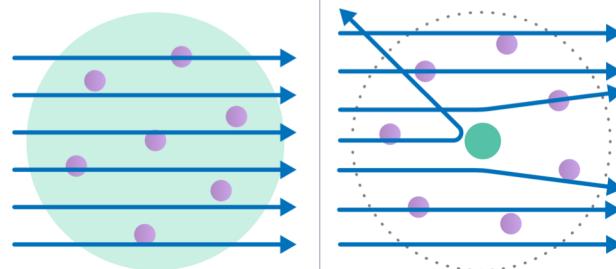


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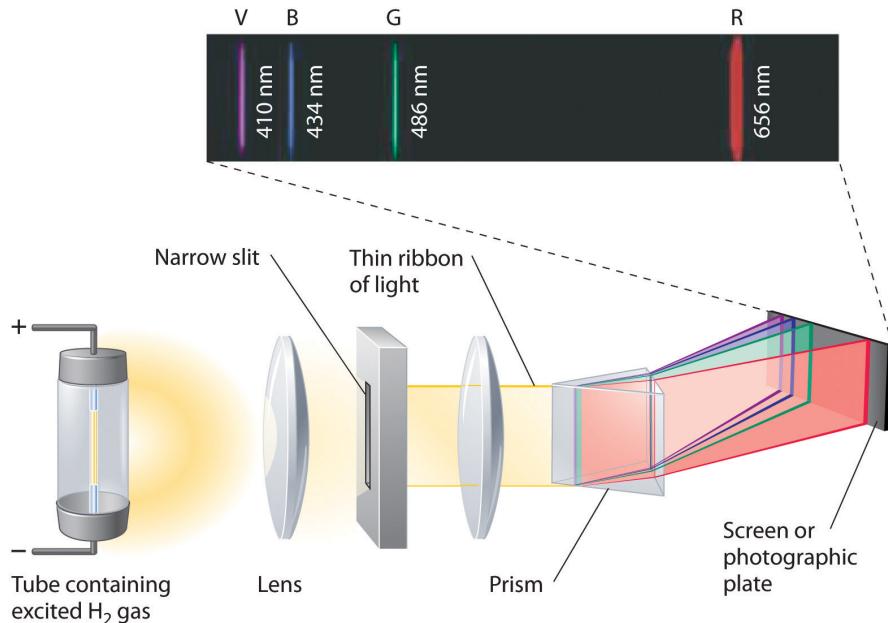
THOMSON MODEL



RUTHERFORD MODEL



Experimental support on Bohr's model: Atomic Spectral lines



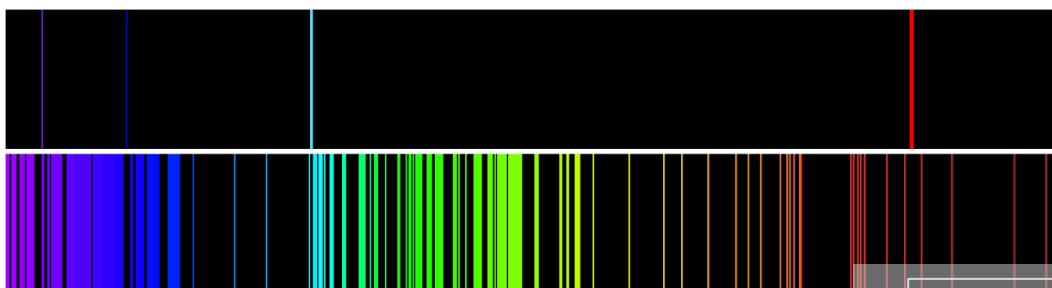
Continuous Spectrum



Emission Lines



Absorption Lines



Hydrogen (H)

Iron (Fe)

WHY?

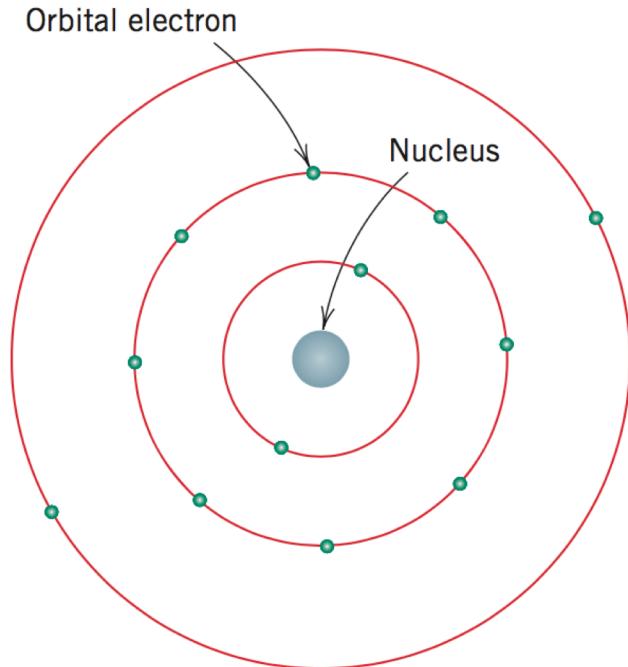
Electrons have discrete levels of energy states



Bohr's atom model

(Explain how electrons have discontinuous energy levels)

Think about the “planet model”



- 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.

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



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.

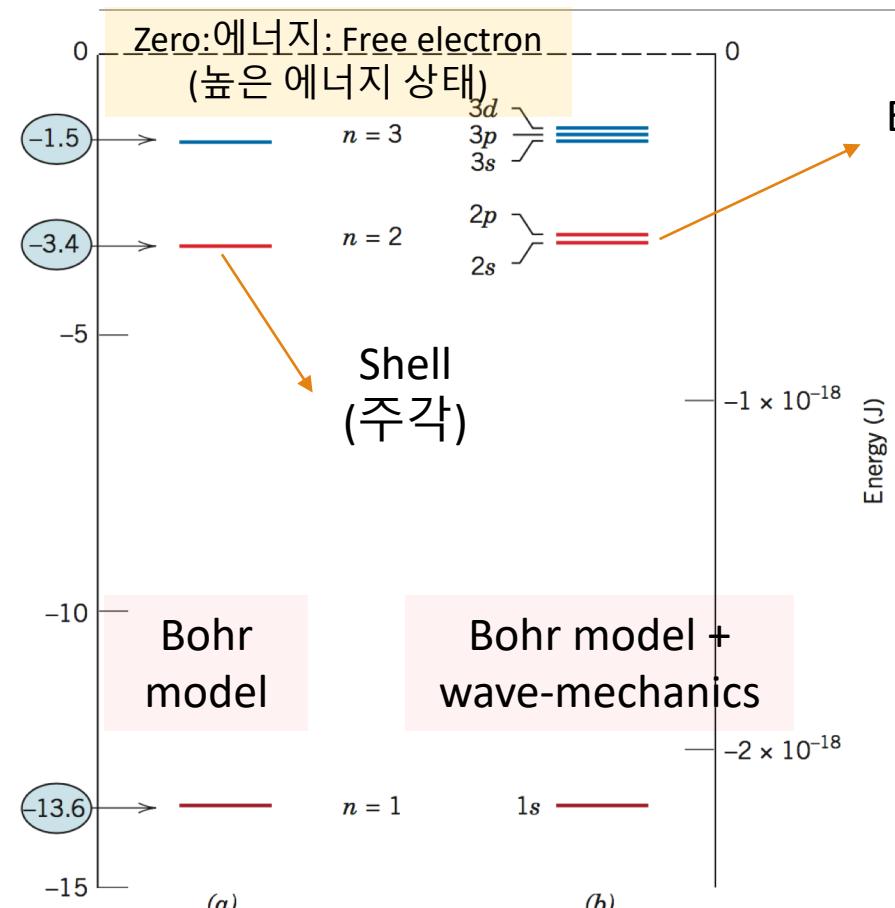
Conclusion: Physicists needed a better model

고전 역학으로 설명안됨

양자역학의 도래



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



음의 에너지: 원자에 구속 (낮은 에너지 상태)

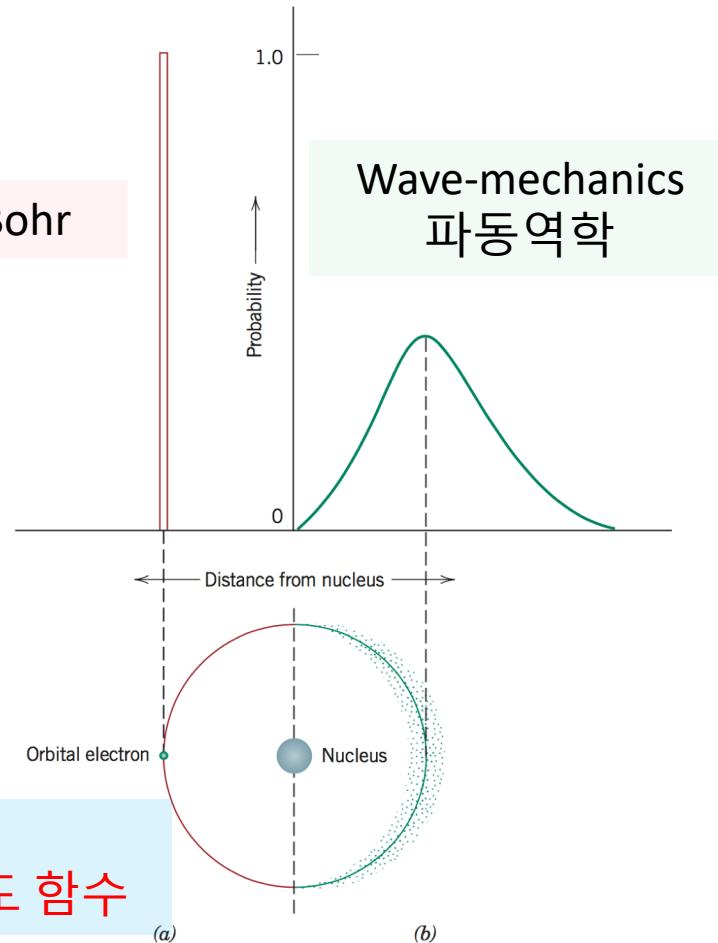
Orbit과 orbital 차이?

명확한 궤도,
확률로 표현되는 위치; 확률 밀도 함수

Each shell may consist of
subshells (부각)

Bohr

Wave-mechanics
파동역학



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

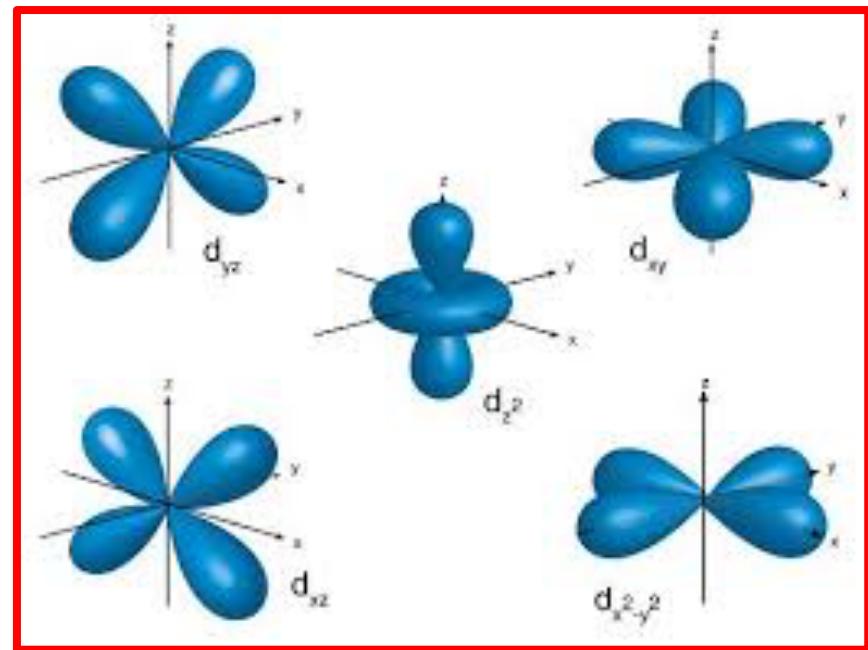
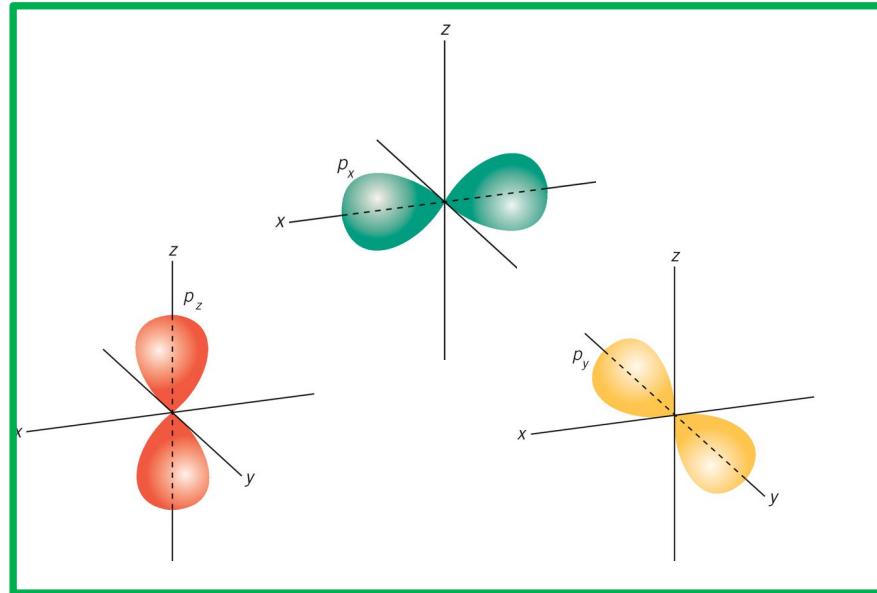
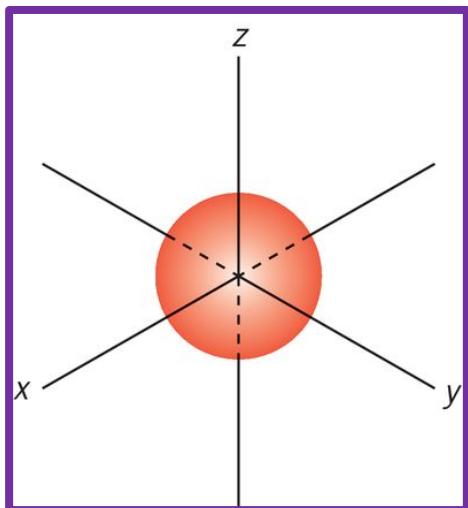


파동역학에서의 전자: 양자수에 의해 정의

- 파동역학에서의 전자 위치 (orbital)은 전자 확률 밀도에 따른
- 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’

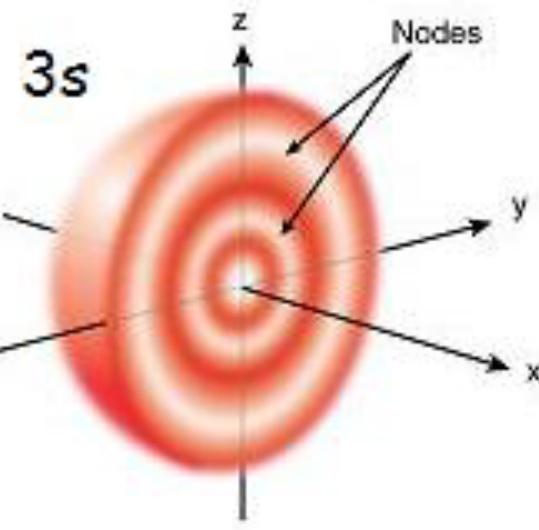
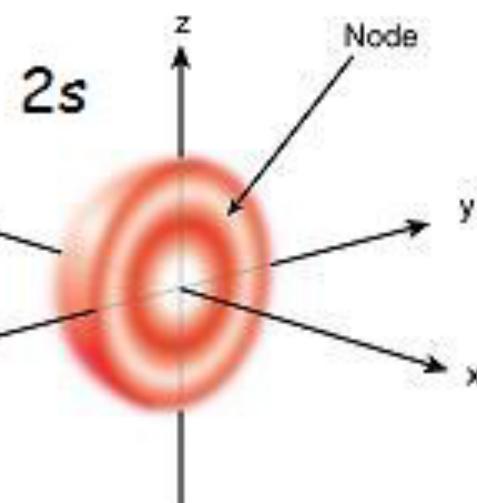
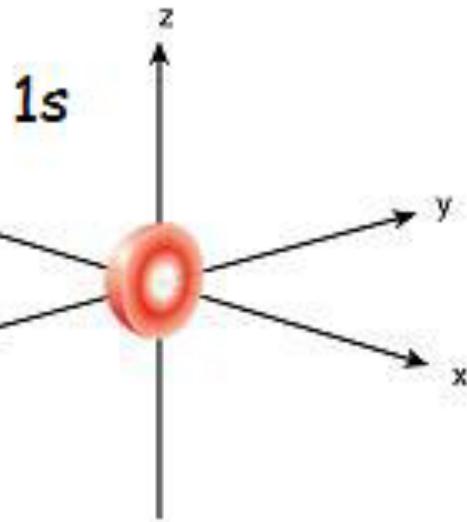


There is a high probability of finding the electron in this direction.

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)

l = 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 (- l to + l)

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

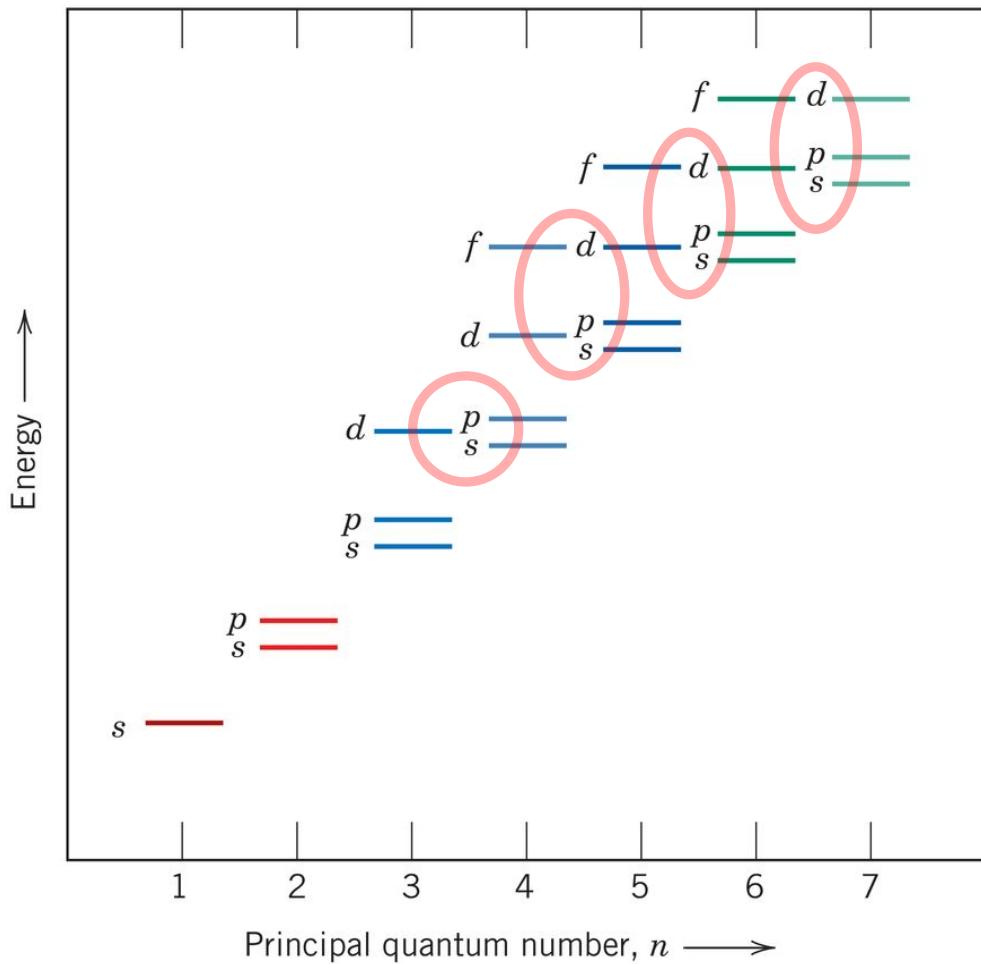
Table 2.1 Summary of the Relationships among the Quantum Numbers n , l , m_l , and Numbers of Orbitals and Electrons

<i>Value of n</i>	<i>Value of l</i>	<i>Values of m_l</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.

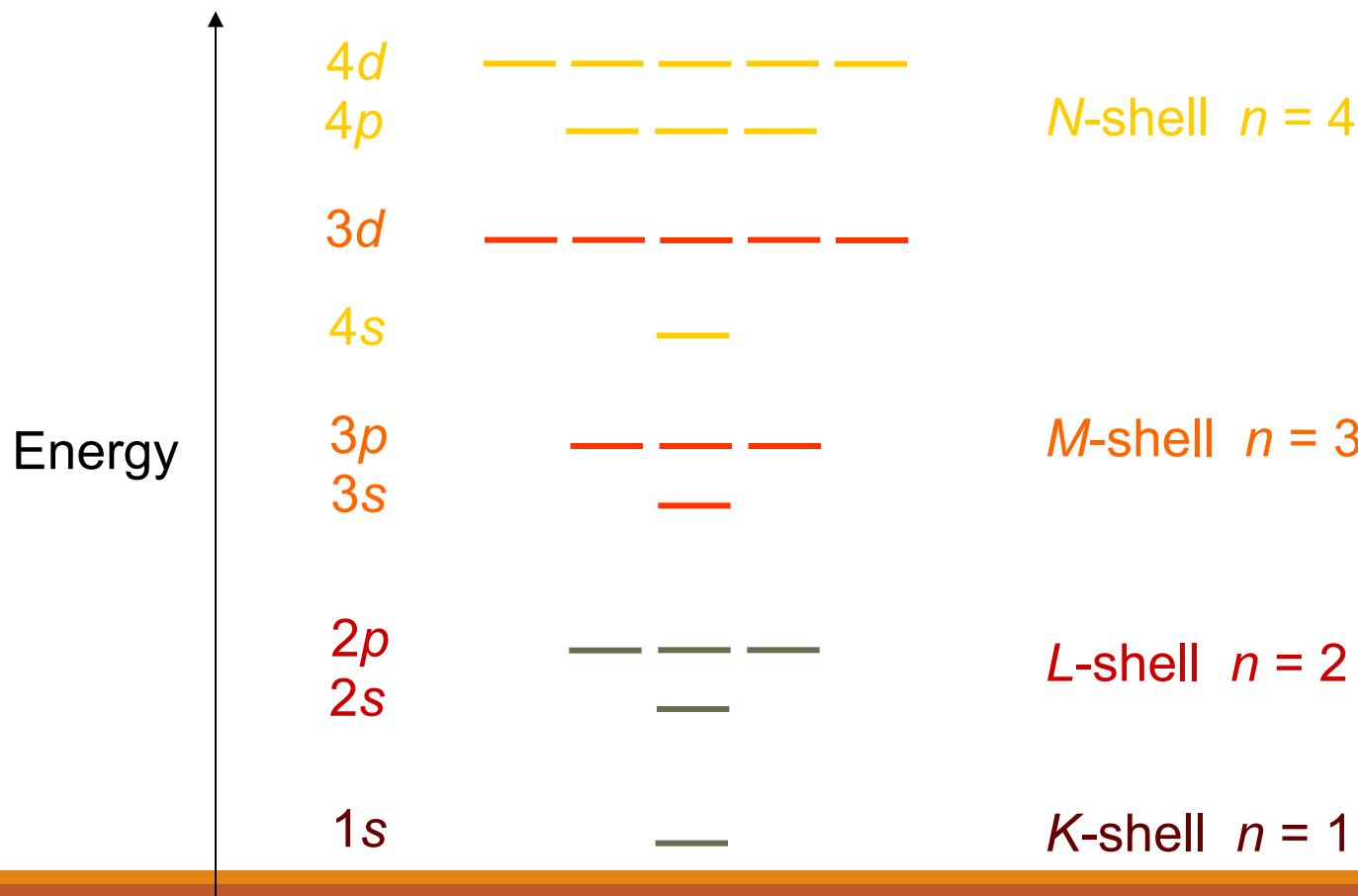
From K. M. Ralls, T. H. Courtney, and J. Wulff, Introduction to Materials Science and Engineering, p. 22. Copyright © 1976 by John Wiley & Sons, New York. Reprinted by permission of John Wiley & Sons, Inc.



Electron Energy States

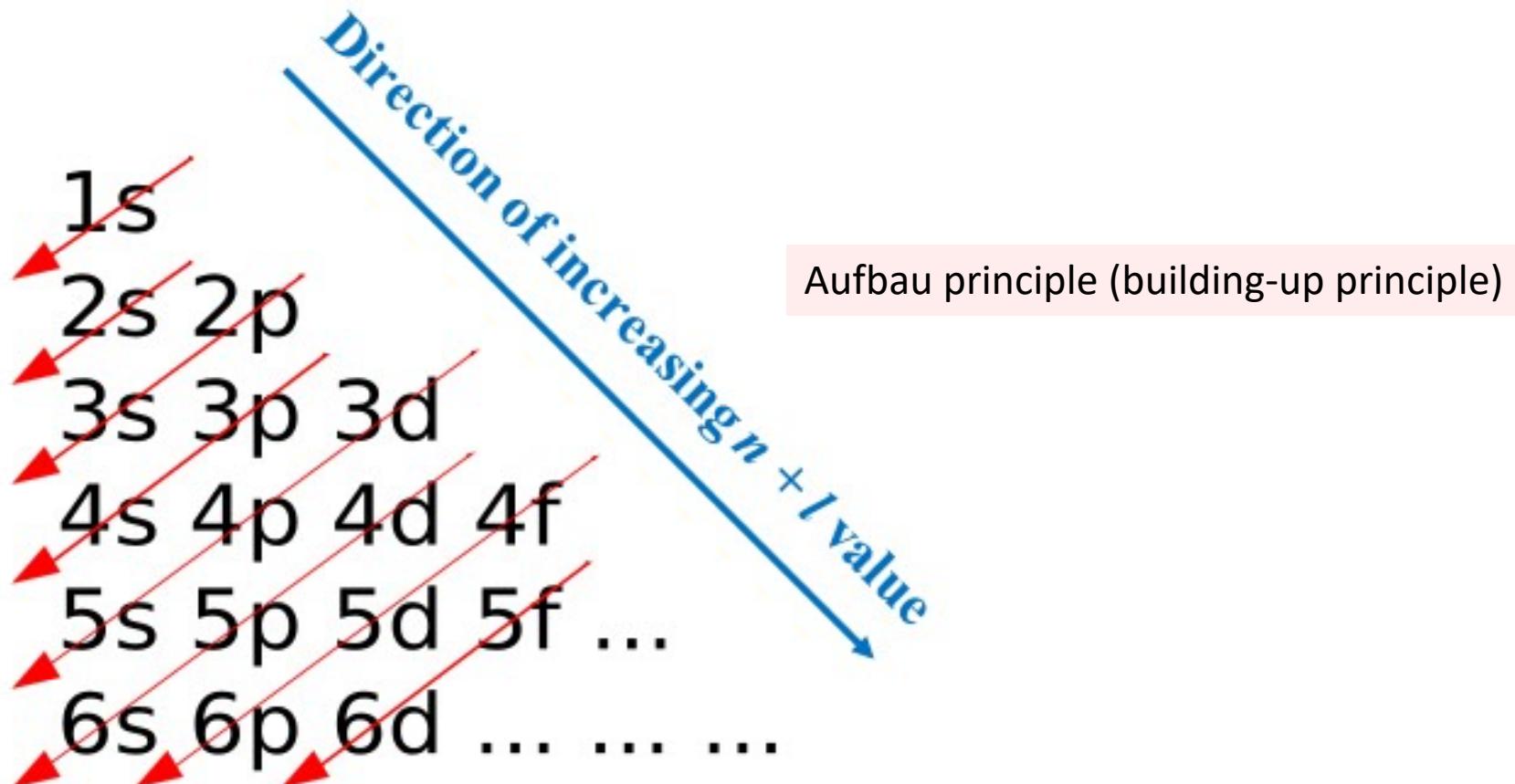
Electrons...

- 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)

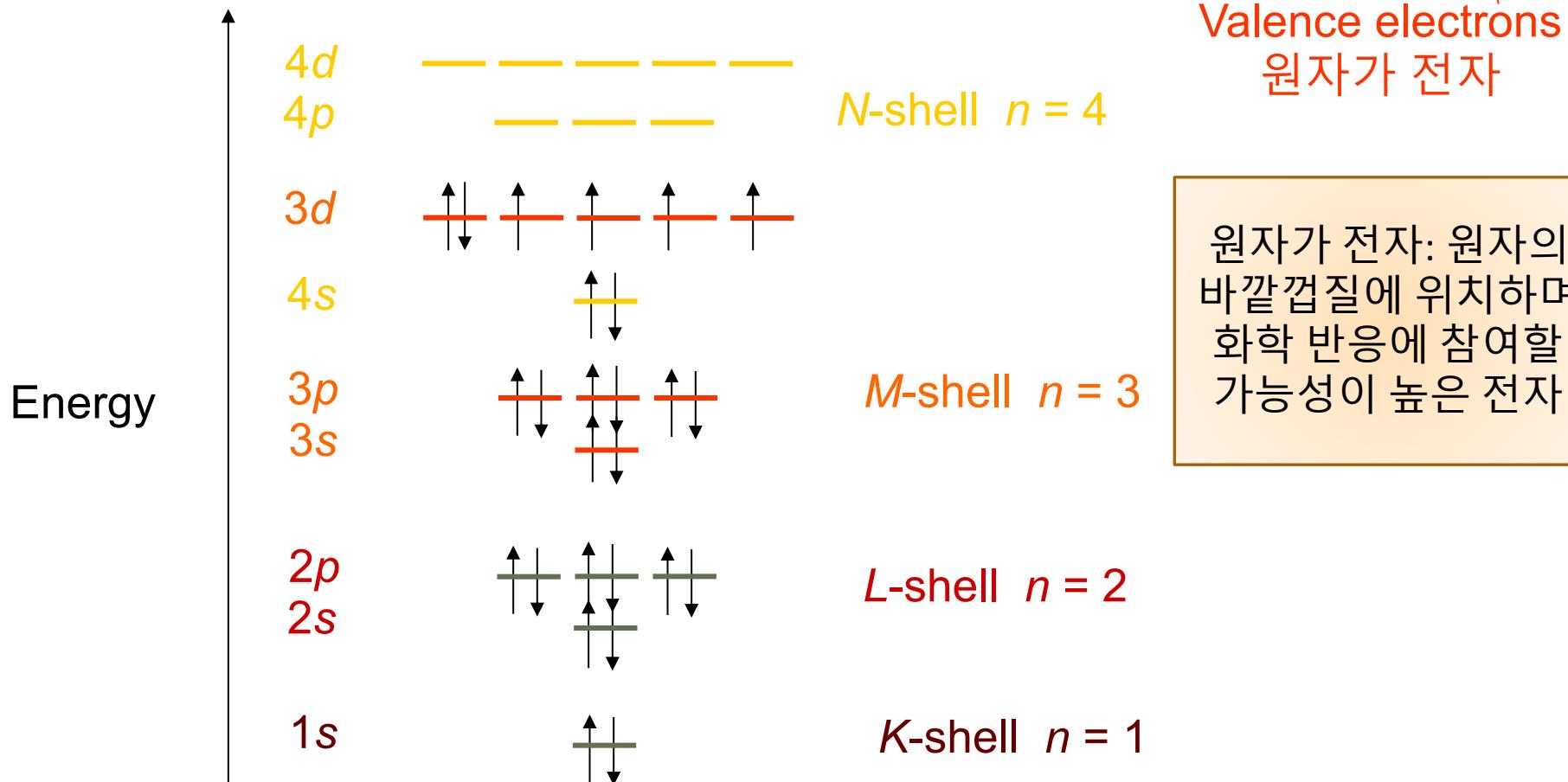


Electronic Configurations

ex: Fe - atomic # = 26

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

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



Valence electrons
원자가 전자

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



Valence electron (원자가 전자)

□ 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/physical property
- Rows : Gradual property changes

The periodic table illustrates several trends:

- Electron Gain:** Elements in groups 1, 2, and 3 are highlighted in red and labeled "give up 1e⁻", "give up 2e⁻", and "give up 3e⁻" respectively, indicating they tend to lose electrons.
- Electron Loss:** Elements in groups 17, 16, 15, and 14 are highlighted in blue and labeled "accept 1e⁻", "accept 2e⁻", and "accept 3e⁻" respectively, indicating they tend to gain electrons.
- Inert Gases:** Helium (He) and the noble gases (Ne, Ar, Kr, Xe, Rn) are highlighted in light blue and labeled "inert gases", showing they are relatively unreactive.
- Metallicity:** A legend indicates that light blue represents "Metal".
- Nonmetallicity:** A legend indicates that dark blue represents "Nonmetal".
- Intermediate:** A legend indicates that medium blue represents "Intermediate".
- Periodic Trends:** The table shows the periodic nature of properties like atomic radius, ionization energy, and electronegativity across groups and periods.

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

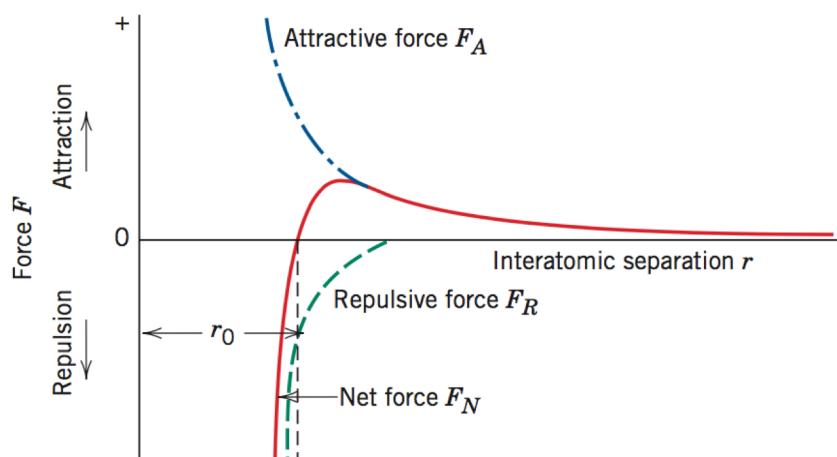
Adapted
from Fig. 2.8,
*Callister &
Rethwisch*
9e.

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?

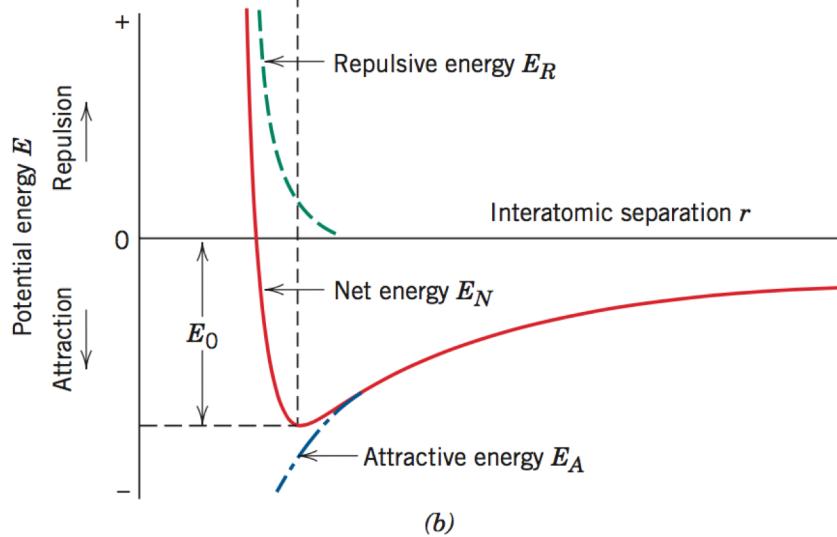
The interatomic distance at which the potential energy is minimum

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:

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

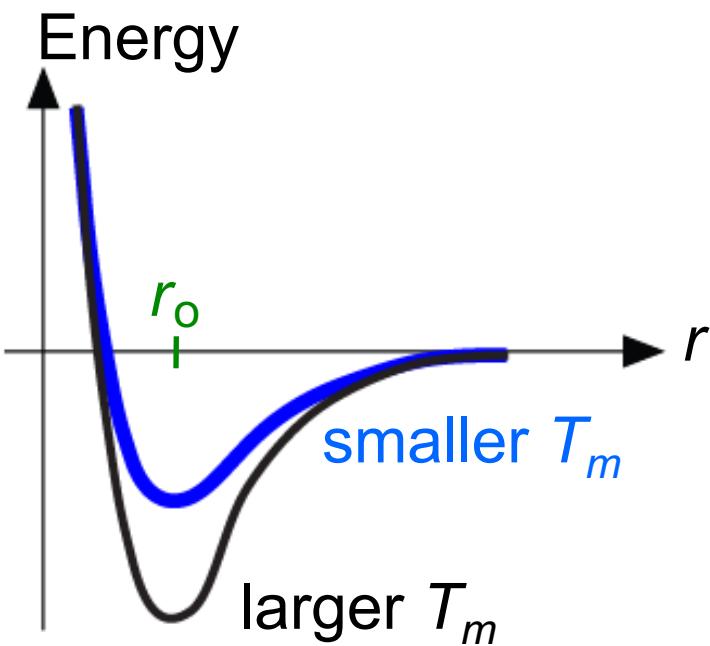
$$E^{\text{potential}} = \int_r^\infty F^{\text{attraction}}(r) dr + \int_r^\infty F^{\text{repulsion}}(r) dr$$

E_0 : bonding energy



Properties From Bonding: Ex) T_m

- Melting Temperature, T_m



T_m is larger if E_o is larger.



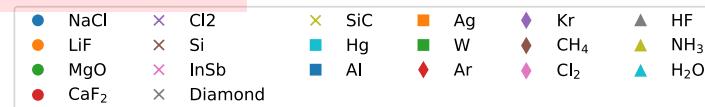
Material properties and bonding?

Examples:

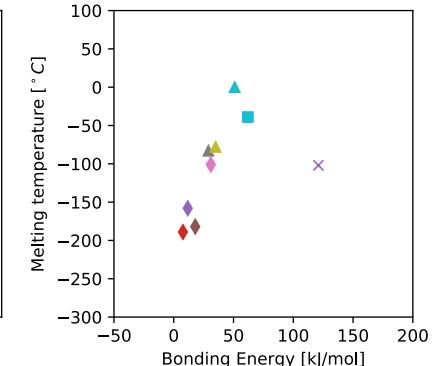
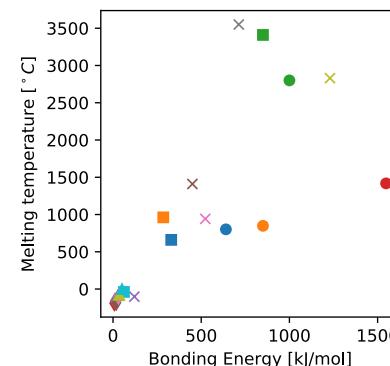
- Melting temperature T_m determines the state of materials at a certain temperature such as room temp.
- Stiffness, thermal coefficients are also closely related with the atomic bonding behavior

- 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

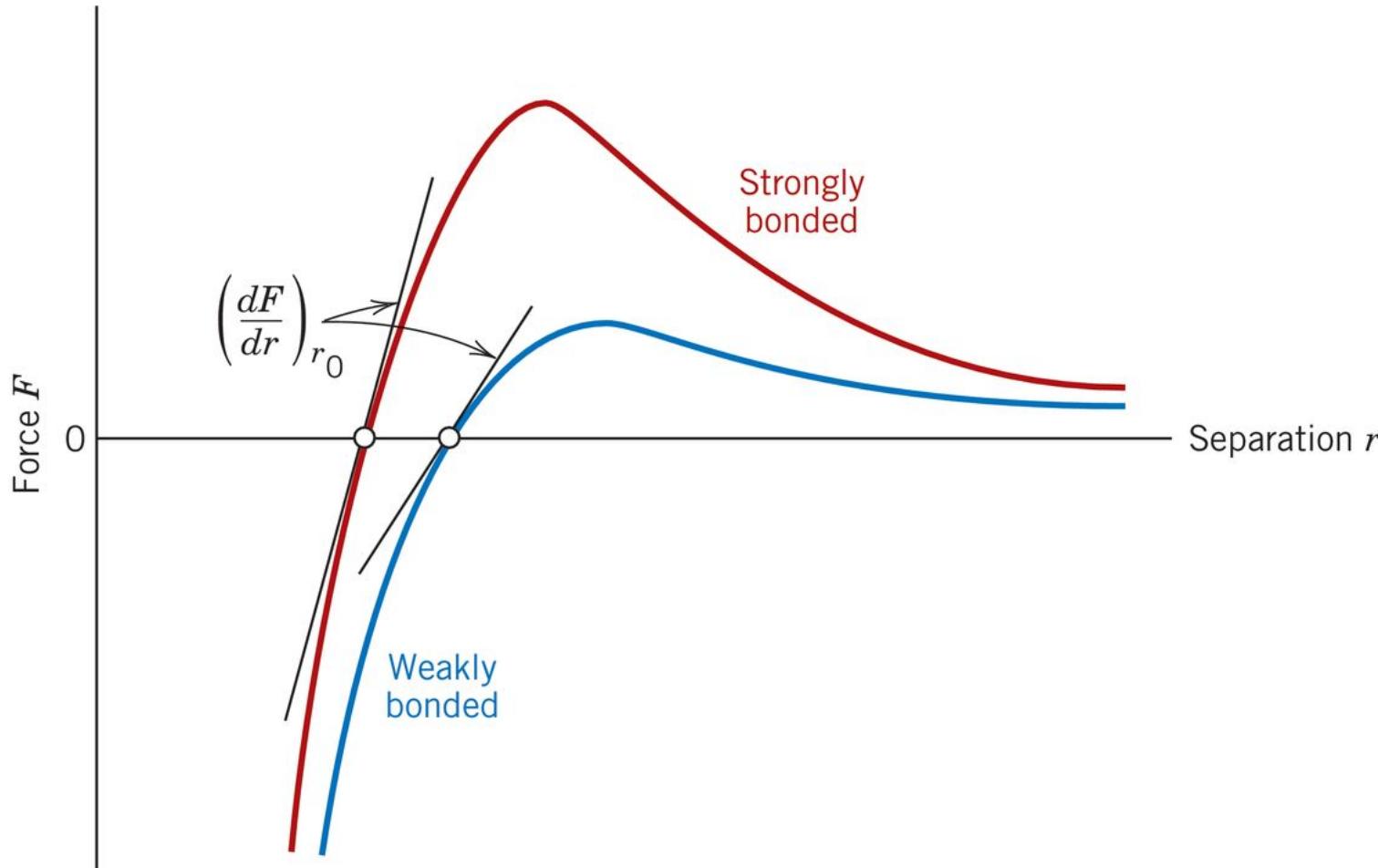
E_0 (결합에너지)	Preferred state in room temperature	T_m
High	Solid	High
Intermediate	Liquid	Intermediate
Low	Gas	Low



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

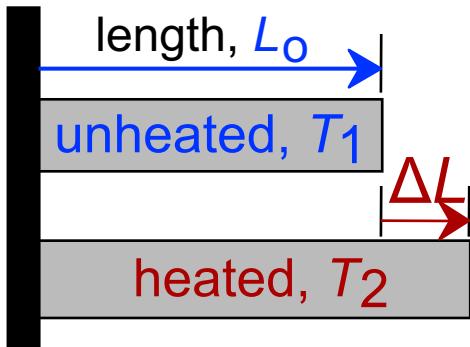


Properties From Bonding: Ex) Stiffness



Properties From Bonding: Ex) Thermal expansion

- Coefficient of thermal expansion, α

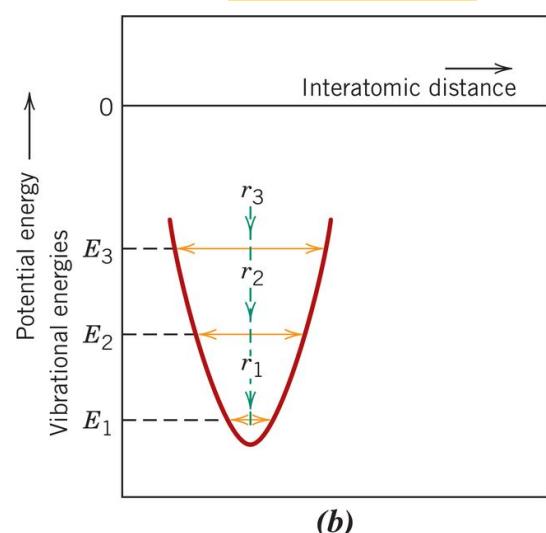
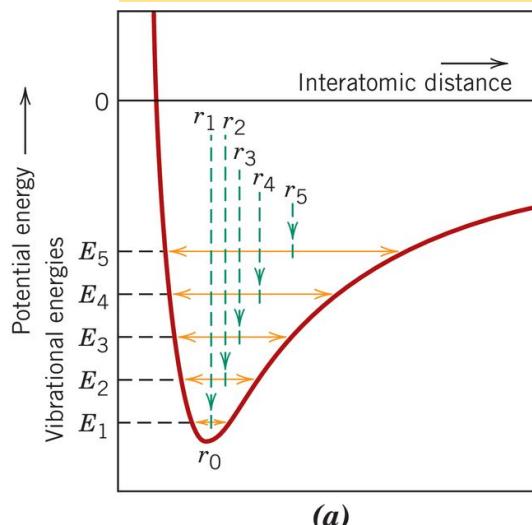


coeff. thermal expansion

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

Asymmetric

Symmetric



Adapted from R. M. Rose, L. A. Shepard, and J. Wulff, The Structure and Properties of Materials, Vol. 4, Electronic Properties. Copyright © 1966 by John Wiley & Sons, New York. Reprinted by permission of



원자결합 종류

□ Primary bonds

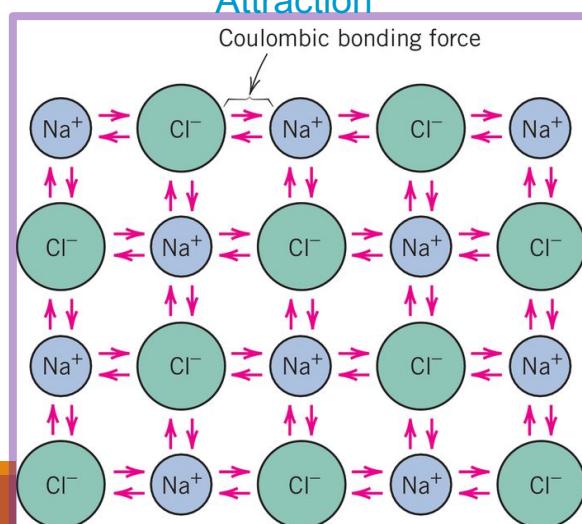
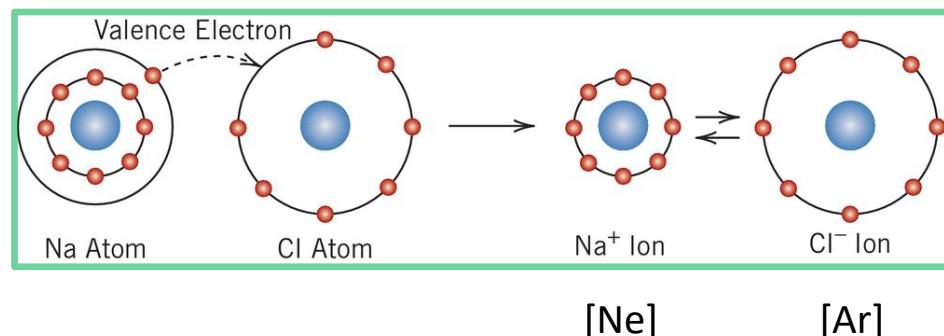
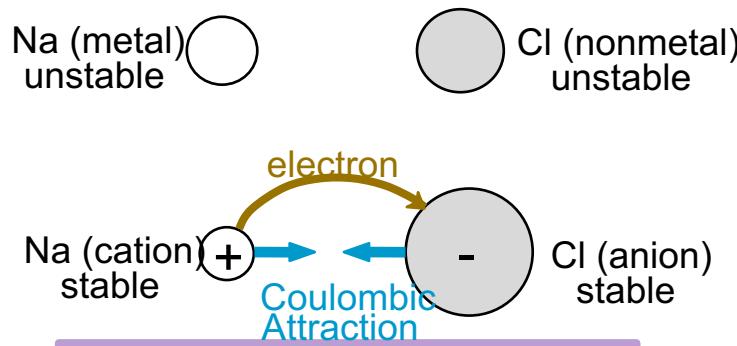
- 이온결합 (ionic)
- 공유결합 (covalent)
- 금속결합 (metallic)

□ Secondary bonds, van der Waals bonding



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.

이온결합은 방향성(directionality)이 없다.



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

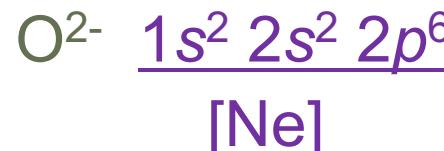
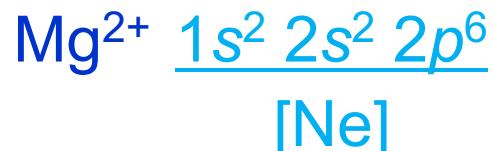
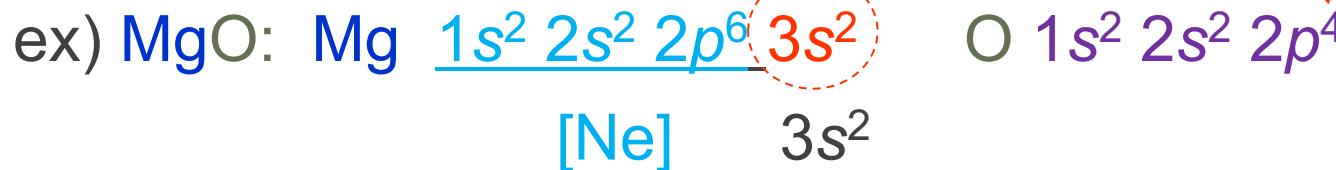


Ionic Bonding: electron transfer

Ionic bond: metal + nonmetal

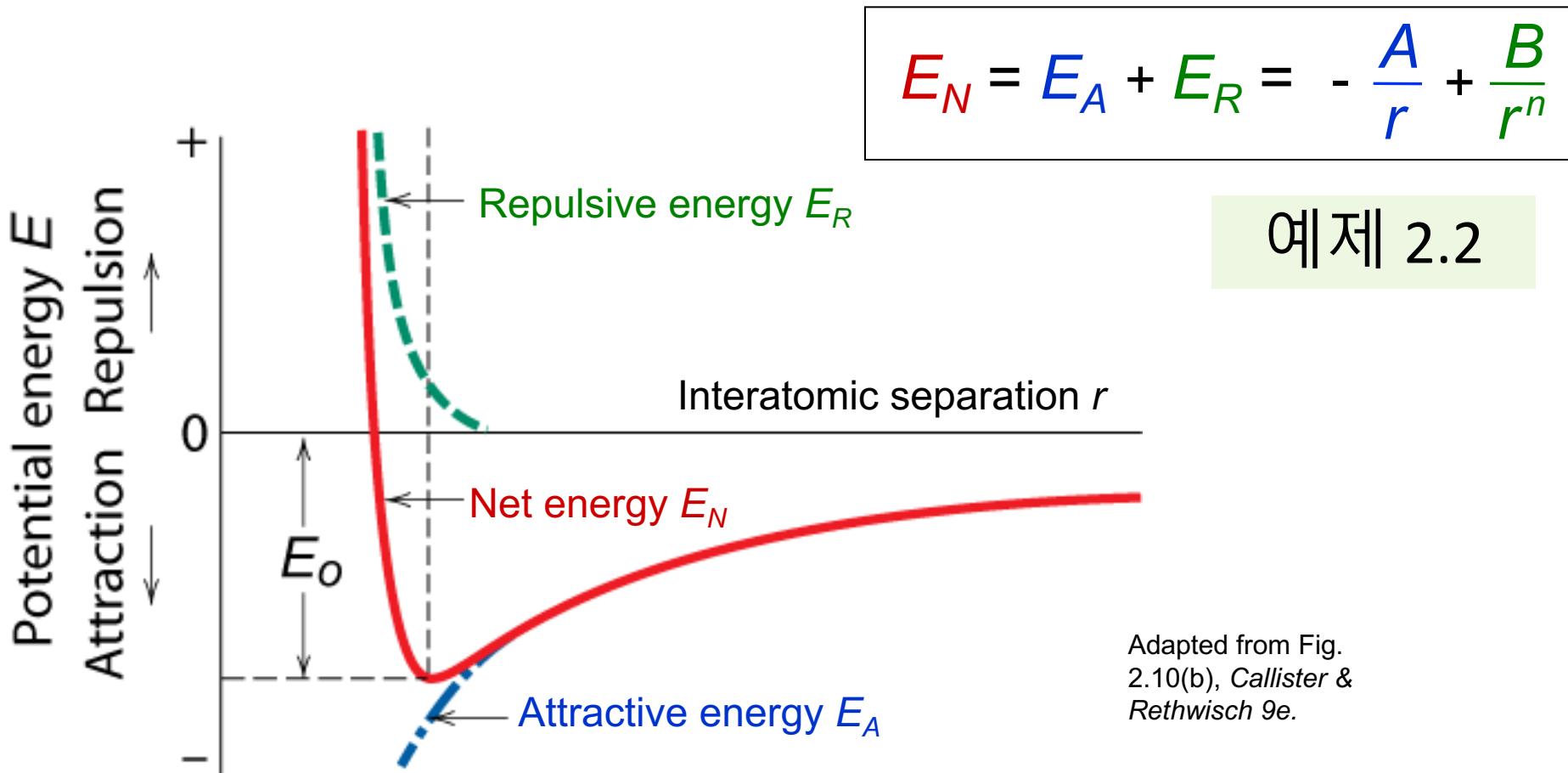
- Between ‘donor’ and ‘acceptor’
- Forms inert gas configurations (i.e., filling the shell completely, thus stable electron configuration)
- The atoms become ions and render the **columbic** attraction.

Dissimilar electronegativities



Ionic Bonding: Bonding forces and energy

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



결합에너지와 용융온도

Table 2.3
Bonding Energies and
Melting Temperatures
for Various Substances

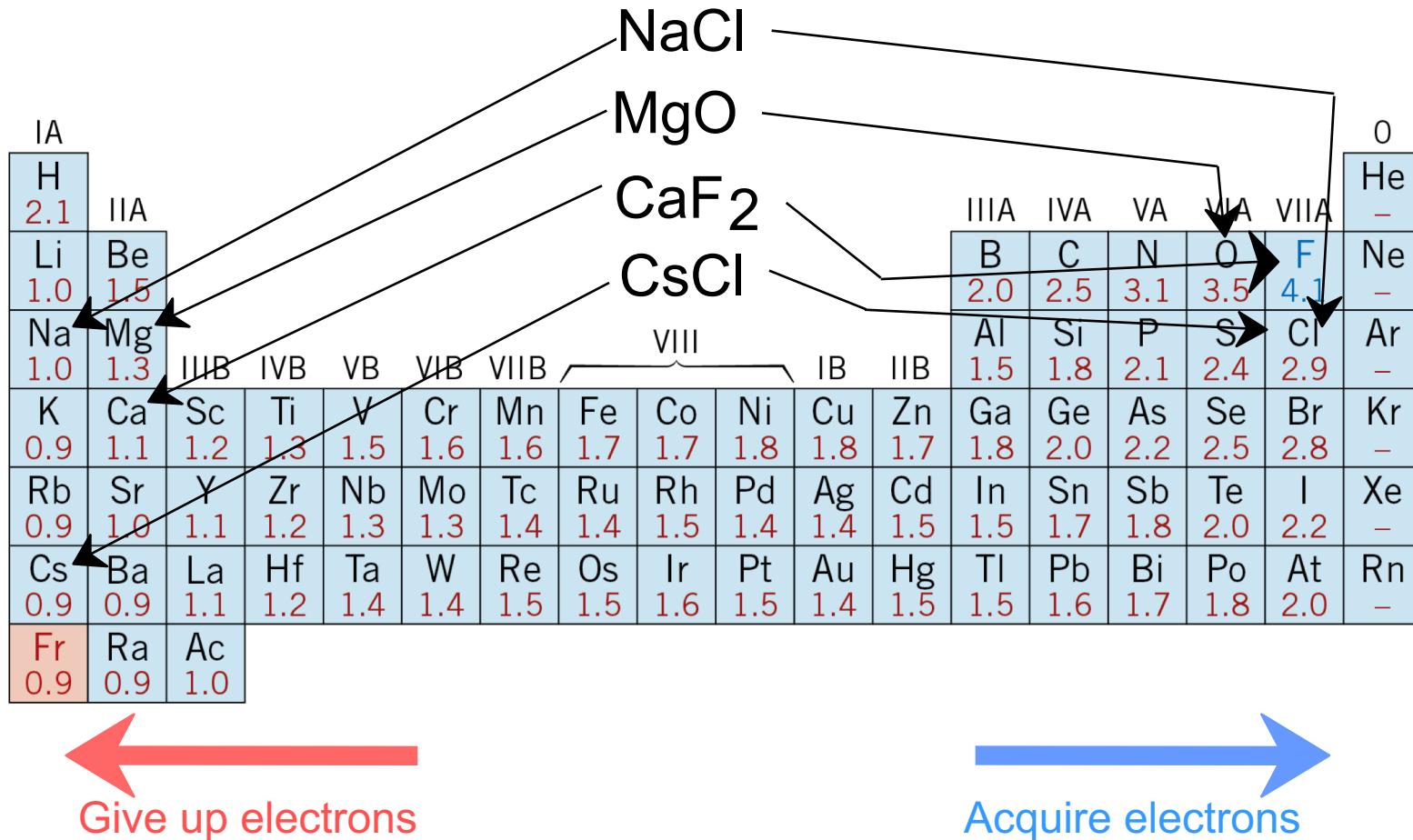
Substance	Bonding Energy (kJ/mol)	Melting Temperature (°C)
Ionic		
NaCl	640	801
LiF	850	848
MgO	1000	2800
CaF ₂	1548	1418
Covalent		
Cl ₂	121	-102
Si	450	1410
InSb	523	942
C (diamond)	713	>3550
SiC	1230	2830
Metallic		
Hg	62	-39
Al	330	660
Ag	285	962
W	850	3414
van der Waals^a		
Ar	7.7	-189 (@ 69 kPa)
Kr	11.7	-158 (@ 73.2 kPa)
CH ₄	18	-182
Cl ₂	31	-101
Hydrogen^a		
HF	29	-83
NH ₃	35	-78
H ₂ O	51	0

^aValues for van der Waals and hydrogen bonds are energies *between* molecules or atoms (*intermolecular*), not between atoms within a molecule (*intramolecular*).



Ionic Bonding: examples

- Predominant bonding in Ceramics

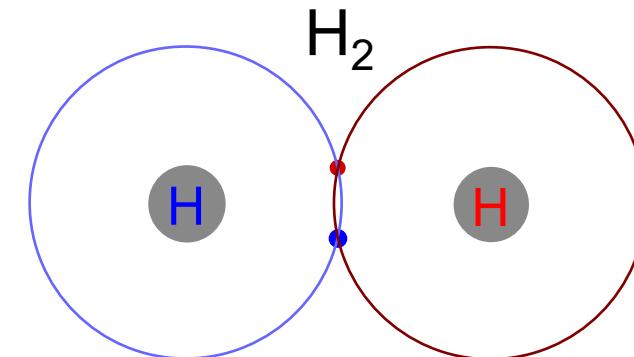


Covalent Bonding

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

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

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



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

공유결합은 매우 단단한 결합인 다이아몬드부터 낮은 결합력을 가진 비스무트(Bi)까지 다양하다. 전자는 원자와 단단히 결합되어, 전기적으로 부도체 혹은 반도체이다.



(공유결합에서 나타나는)

Hybridization (hybrid orbitals)

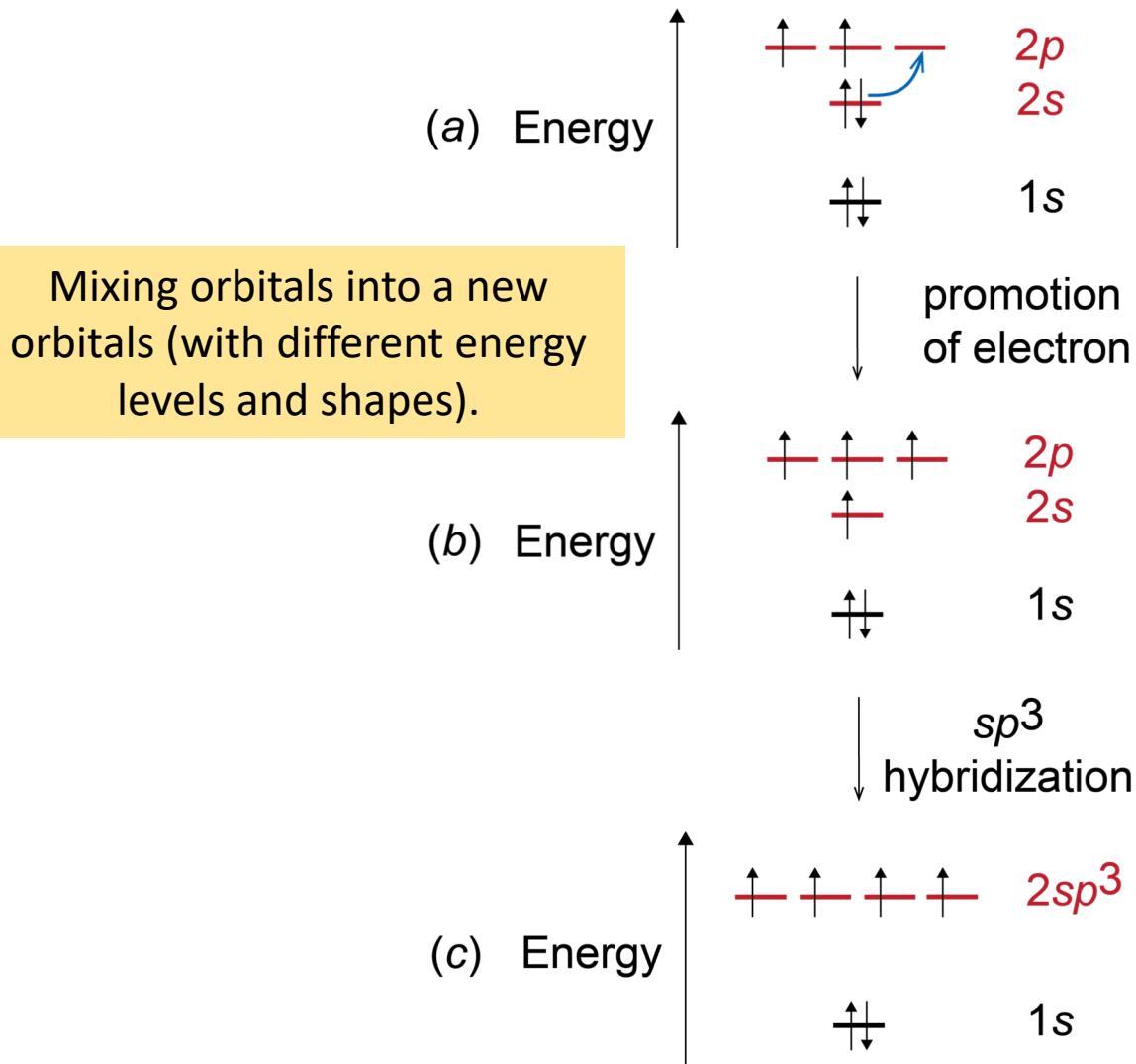


Fig. 2.13, Callister & Rethwisch 9e.

Carbon can form sp^3 hybrid orbitals

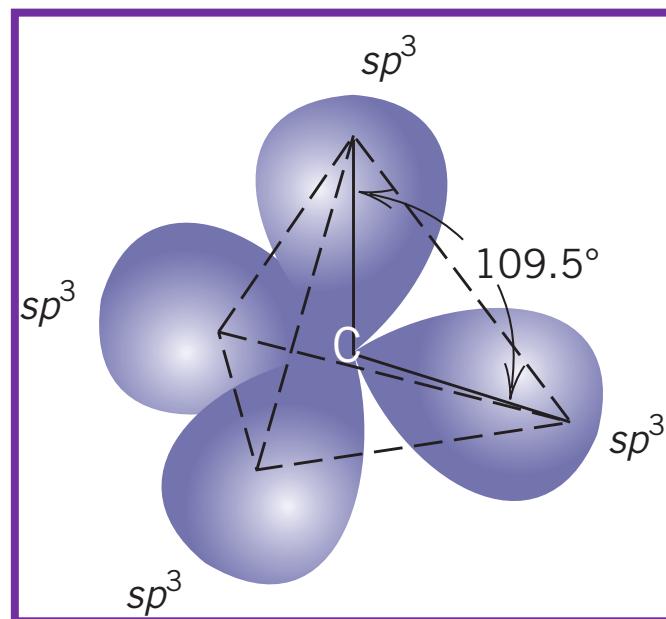


Fig. 2.14, Callister & Rethwisch 9e.
(Adapted from J.E. Brady and F. Senese, *Chemistry: Matter and Its Changes*, 4th edition. Reprinted with permission of John Wiley and Sons, Inc.)



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.

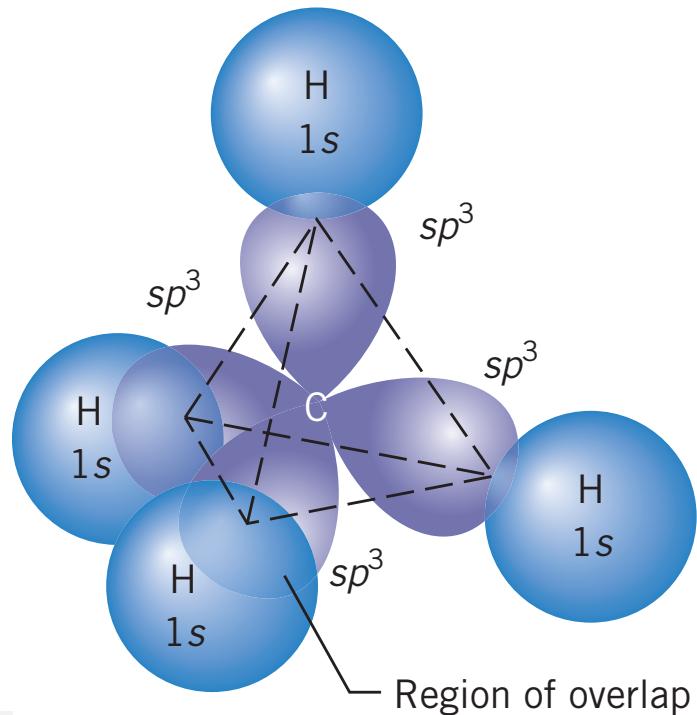
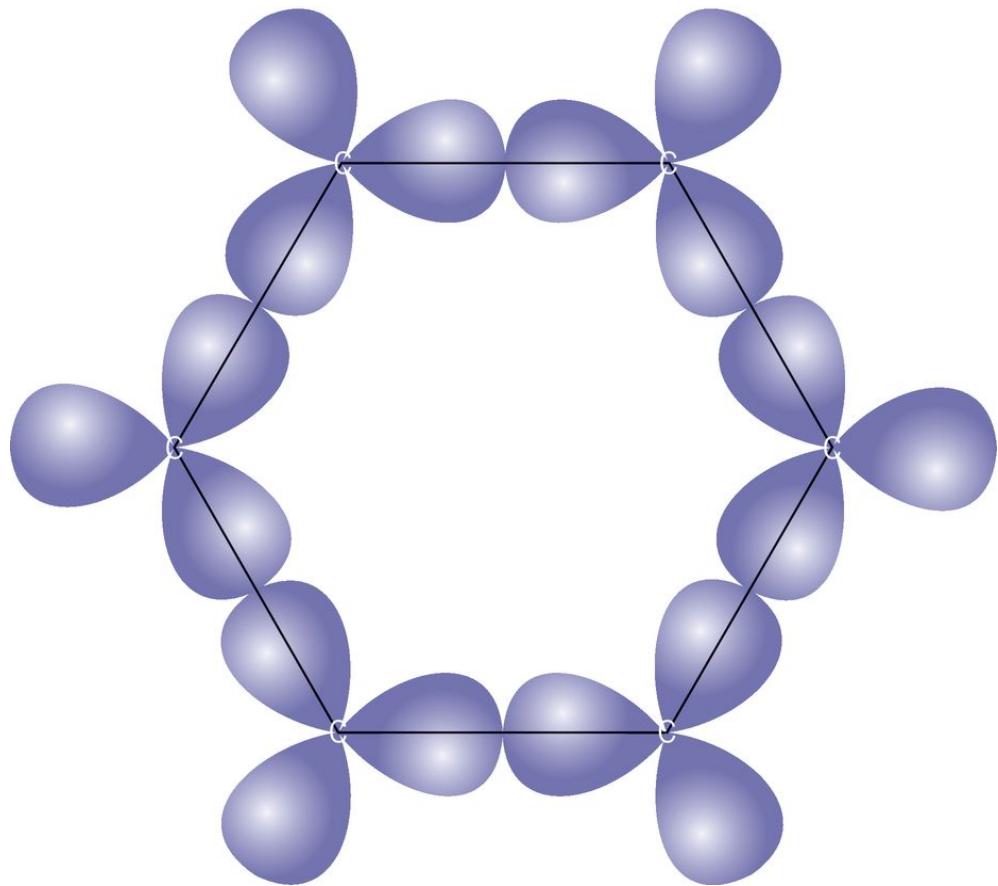


Fig. 2.15, Callister & Rethwisch 9e.
(Adapted from J.E. Brady and F. Senese, *Chemistry: Matter and Its Changes*, 4th edition. Reprinted with permission of John Wiley and Sons, Inc.)

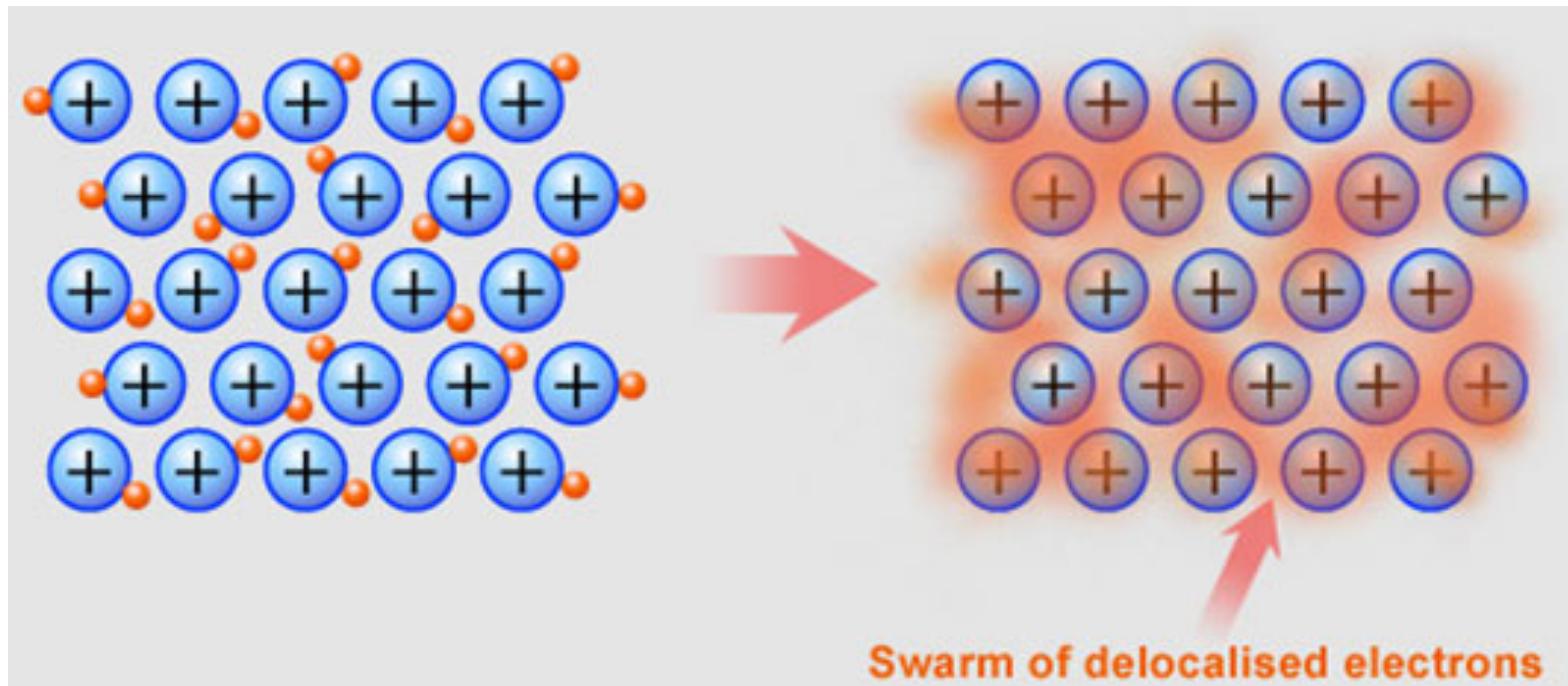
sp² Hybridization

▣ 탄소에서 나타나는 sp² 혼성결합



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

□ 앞서 기술한 이온, 공유, 금속 결합에 비해 매우 낮은 결합력.

➤ 따라서, 위 세 결합이 존재할 때, '가려진다'.

□ 이차 결합은, 이미 이온, 공유, 금속 결합 등으로 뿐만 아니라 그룹 간의 결합에서 찾을 수 있다.

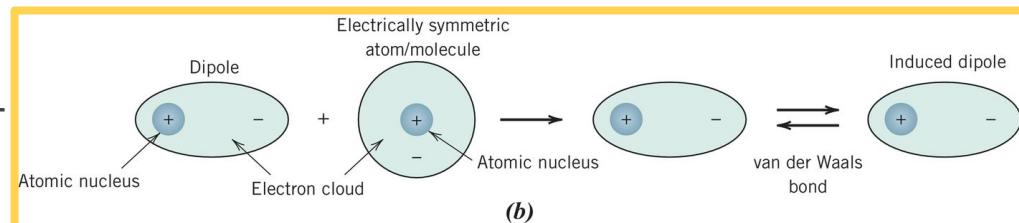
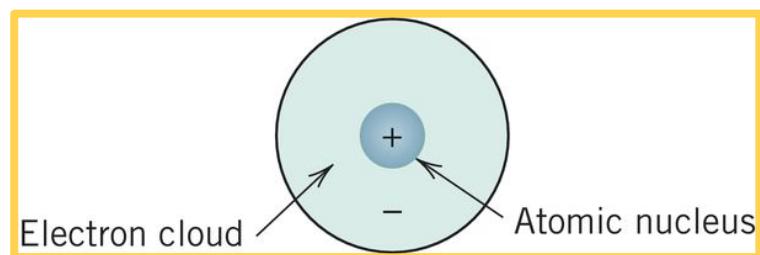
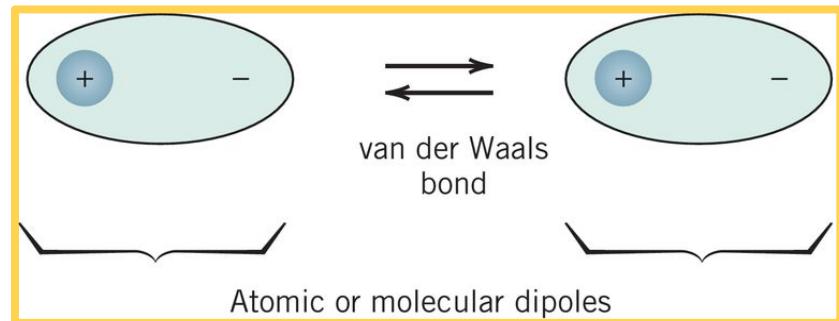
□ 2차 결합력은 원자나 분자의 쌍극자 (dipole)에서 나온다.

➤ 쌍극자(dipole) 간 상호작용은

- ❖ 1. 유도 쌍극자들 사이에
- ❖ 2. 영구 쌍극자와 극성 분자들 사이에서
- ❖ 3. 극성 분자들 사이에서 존재.

➤ 수소 결합

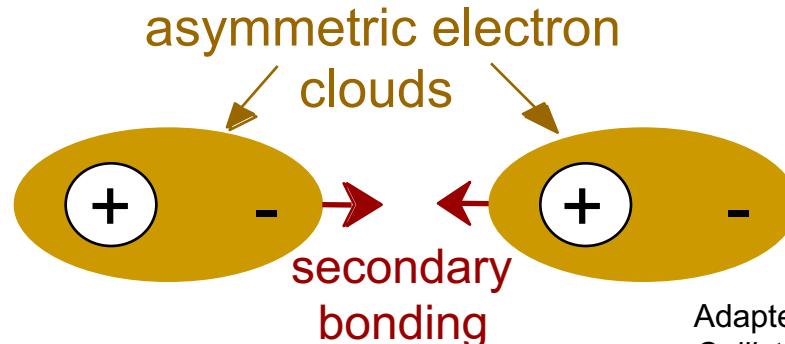
□ 원자나 분자에서 양전하와 음전하가 근접하게 분리 위치할 때는 언제나 전기적 쌍극자 (electric dipole)가 존재하게 된다.



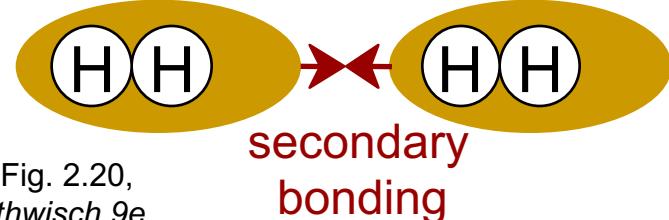
Secondary Bonding

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

- Fluctuating **dipoles**



ex: liquid H₂
H₂ → ← H₂



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

- Permanent **dipoles**-molecule induced

Originally symmetric but gets asymmetric by neighboring dipoles.

-general case:



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

-ex: liquid HCl



-ex: polymer



secondary bonding

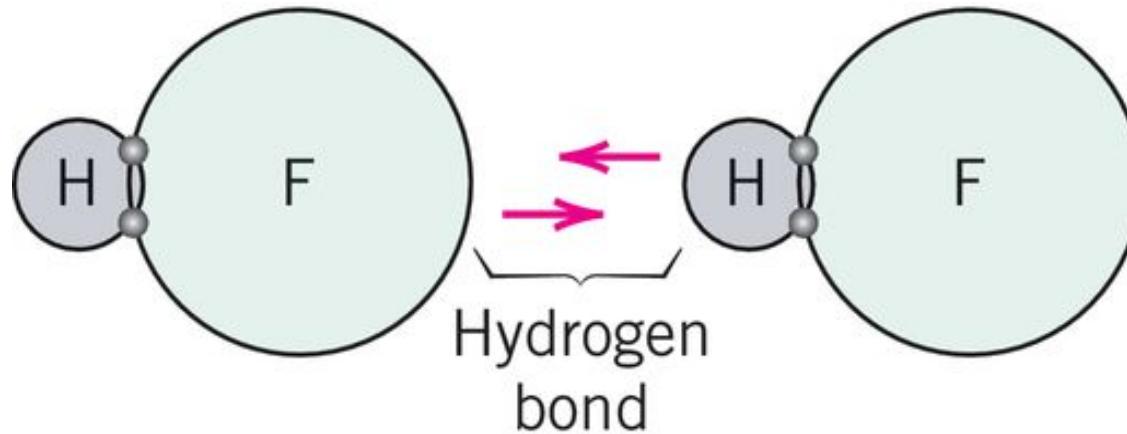


A special case of secondary bonding: Hydrogen bonding

□ A special case of secondary bonding

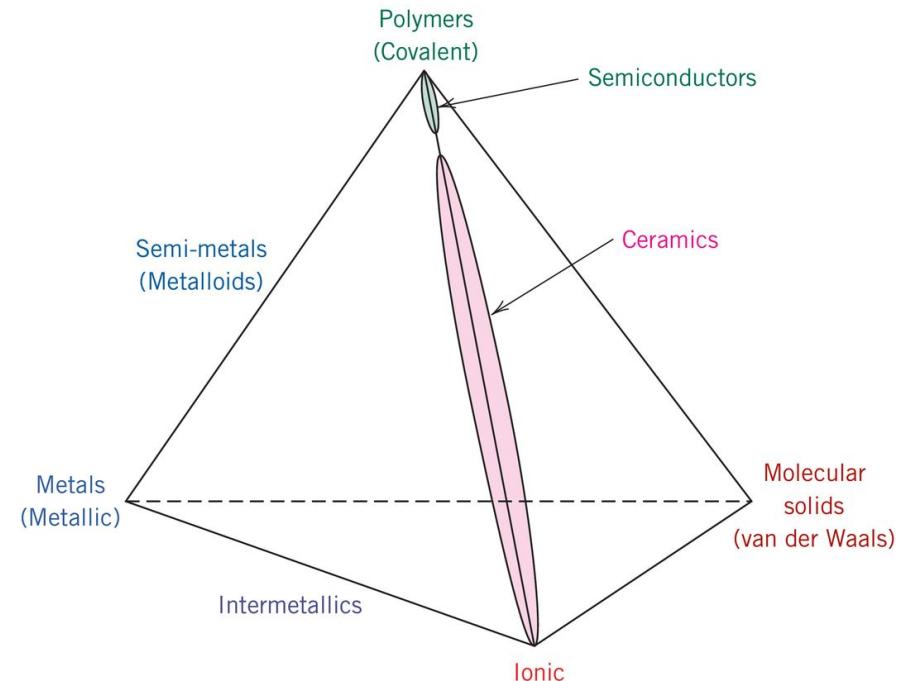
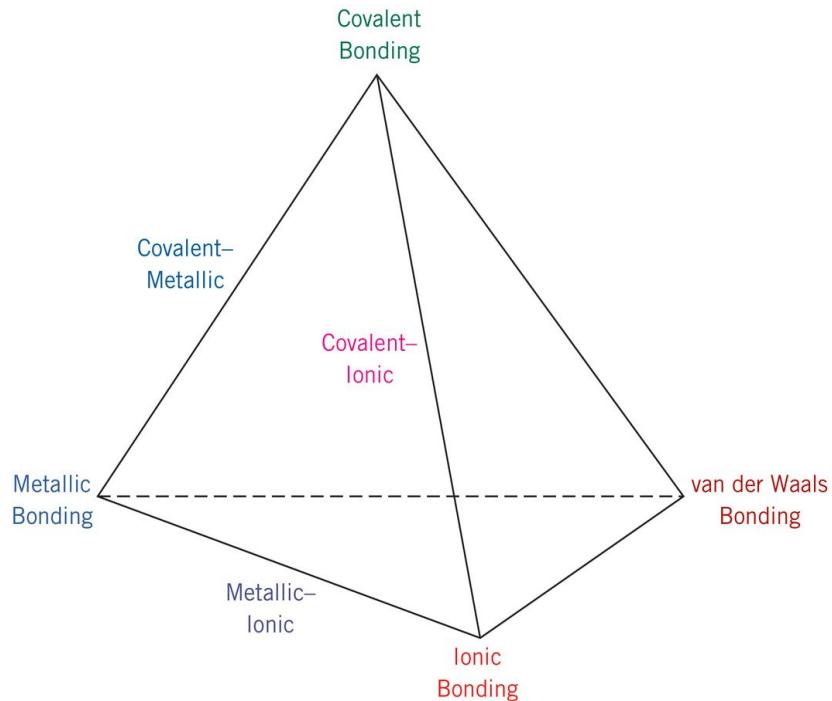
□ What makes hydrogen bonding strong?

➤ 양성자를 차폐하는 '유일한' 전자가 결합에 참여하면, 매우 강한 Columbic force 작용 가능.
따라서 이차 결합중 수소 결합이 가장 강하다.



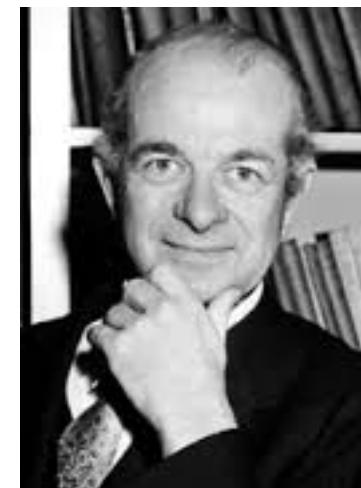
Mixed bonds

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



Summary: Primary Bonds

Ceramics

(Ionic & covalent bonding):

Large bond energy

large T_m
large E
small α

Metals

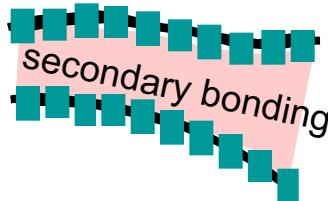
(Metallic bonding):

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

