Atomic Energy Structure

메카트로닉스 재료개론 (MFA9008)

창원대학교 신소재공학부
정영웅

yjeong@changwon.ac.kr
https://youngung.github.io
https://github.com/youngung

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 the electronic structure in atom

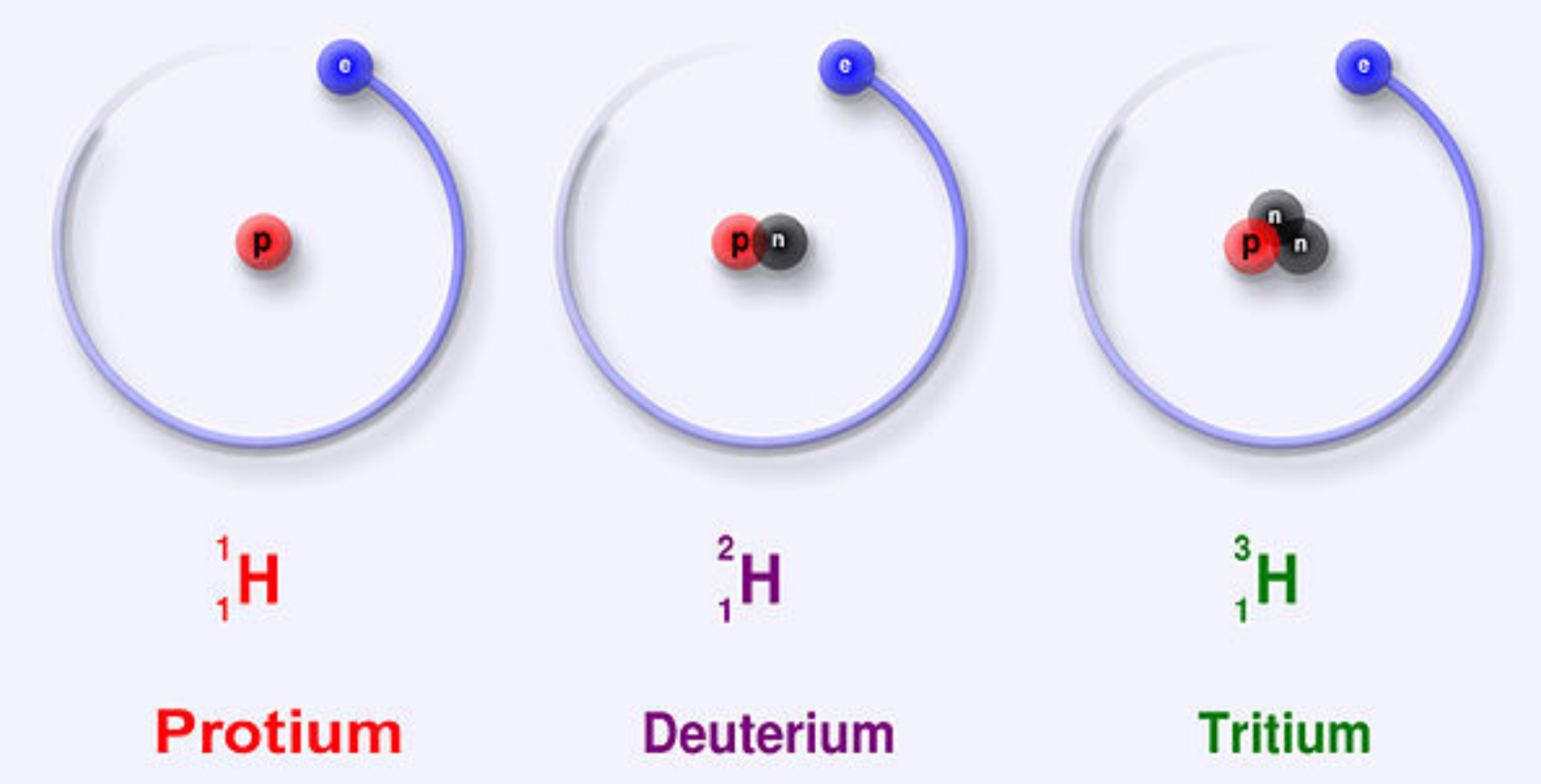
Objectives

- 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 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 '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



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 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)?
  - ^{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

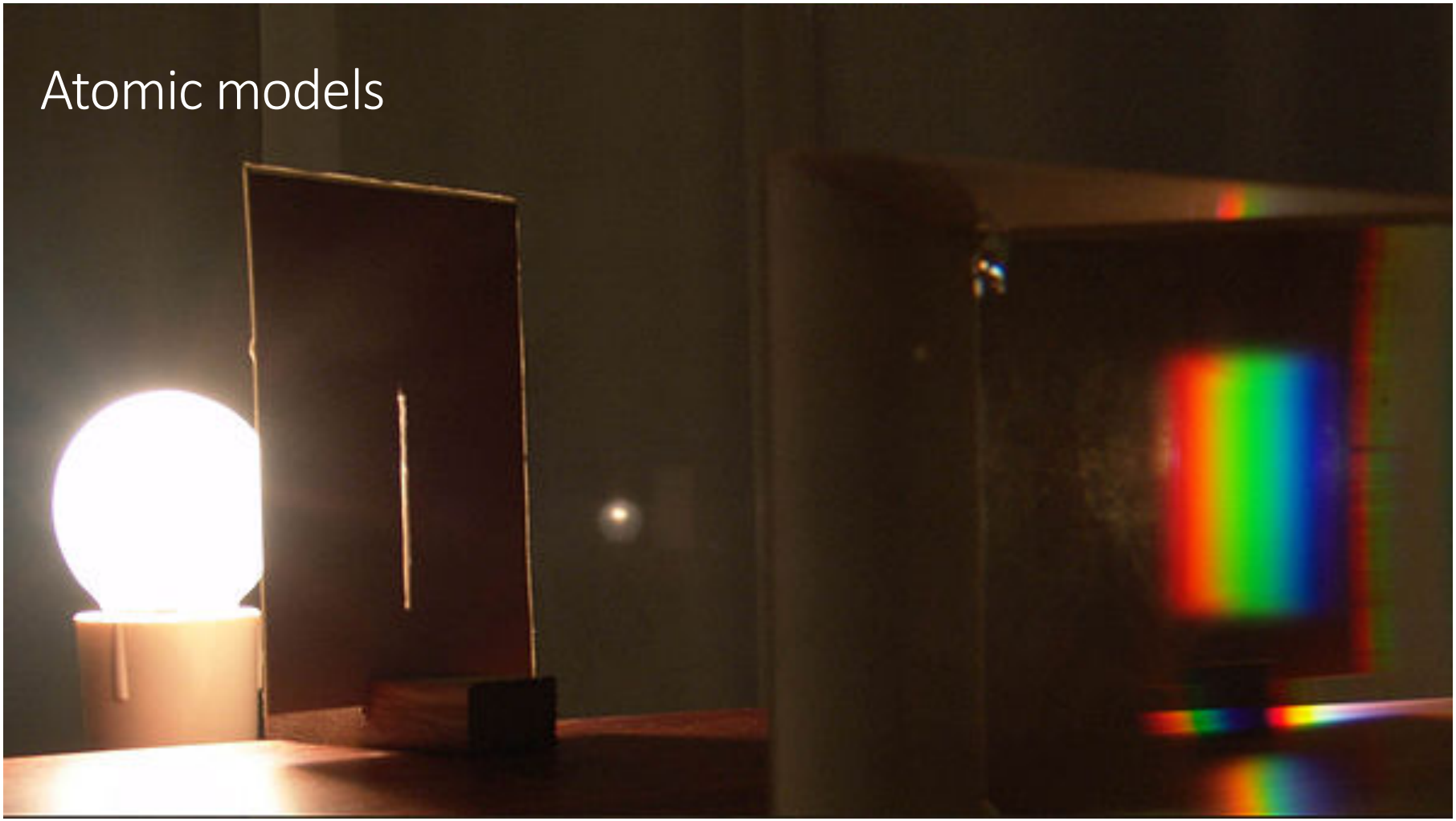
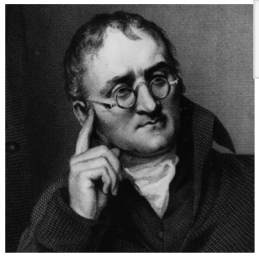
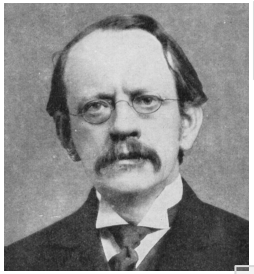


Image from https://en.wikipedia.org/wiki/Spectral_line

Historical development of atomic model

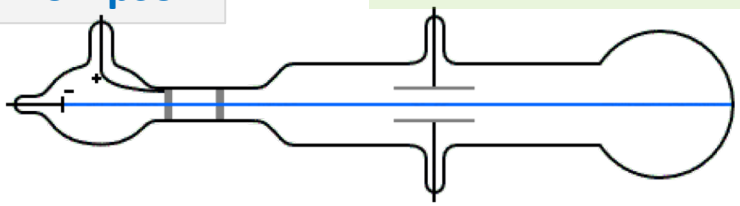


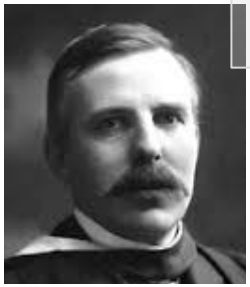
Dalton: All matters are made of atoms



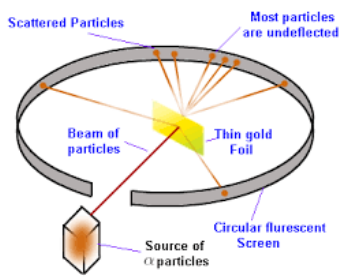
J. J. Thompson

Cathode Ray Tube



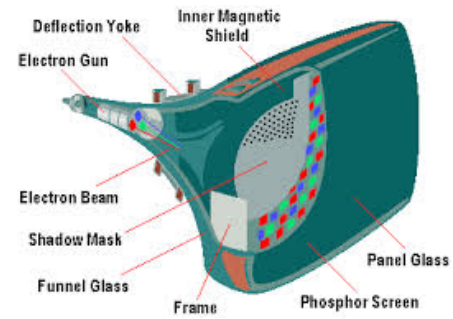


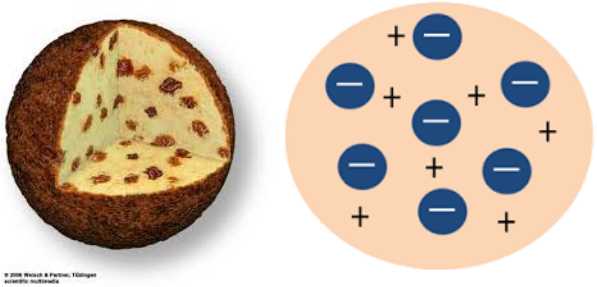
E. Rutherford

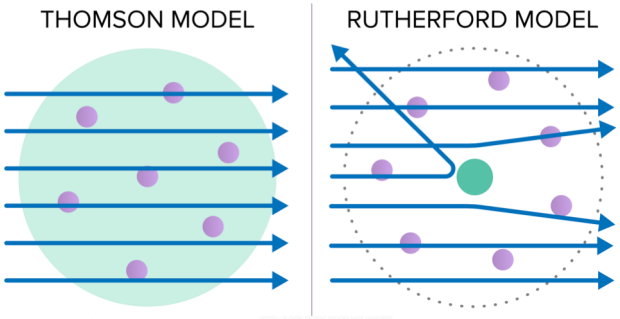


a) Mostly penetrated.
b) Some reflected.
Conclusion?

Niels Bohr: Discrete energy levels (next slide)

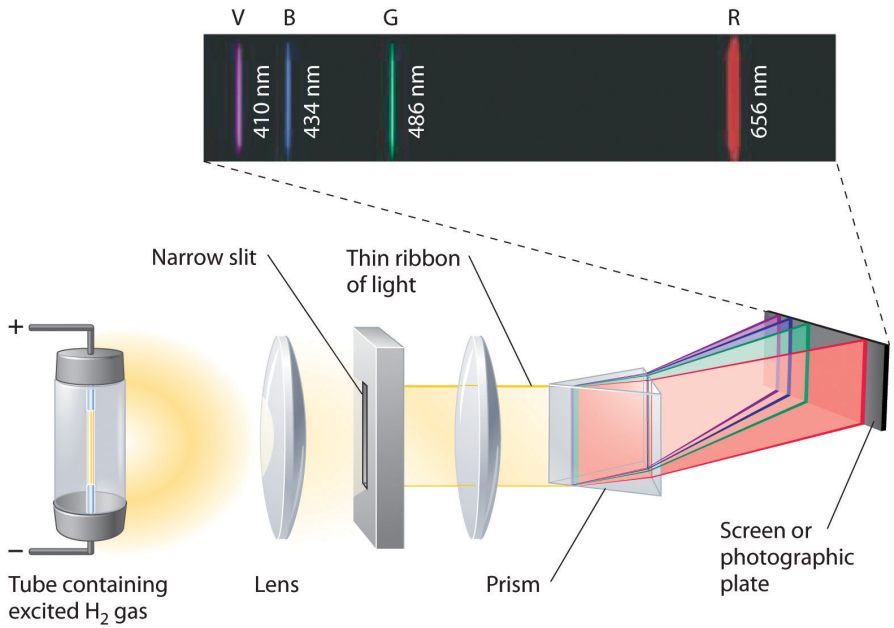


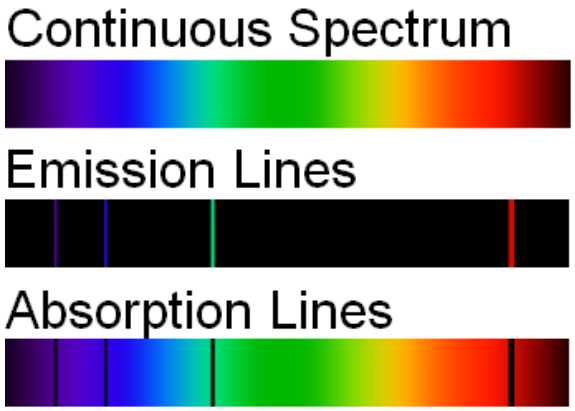


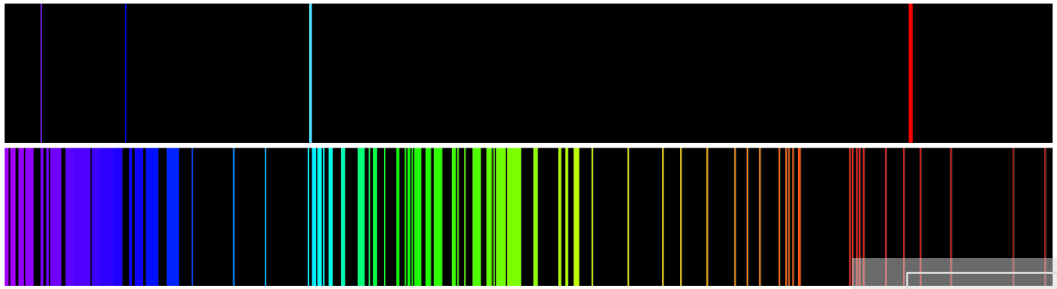


Images from http://www.nobelprize.org http://www.wikipedia.org

Experimental support on Bohr's model: Atomic Spectral lines







Hydrogen (H)

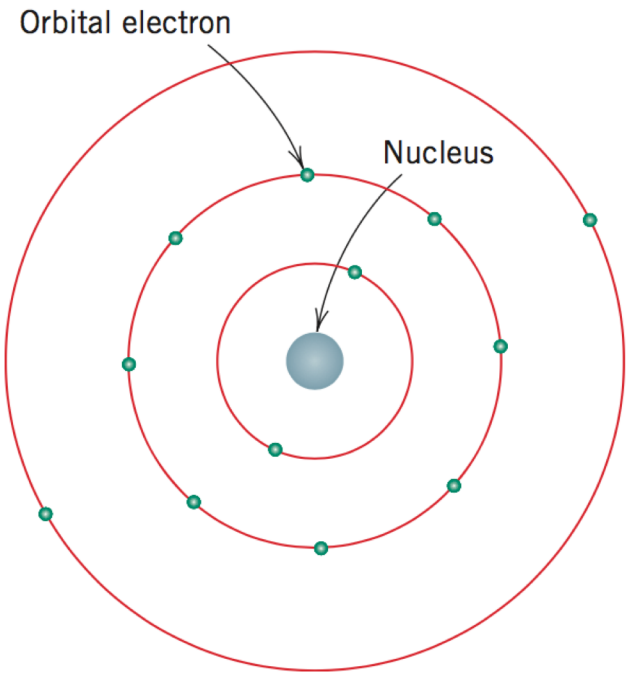
Iron (Fe)

WHY?

Electrons have discrete levels of energy states

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

Think about the "planet model"



- 전자의 에너지가 양자화 (quantized) 되어있다.
  - 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

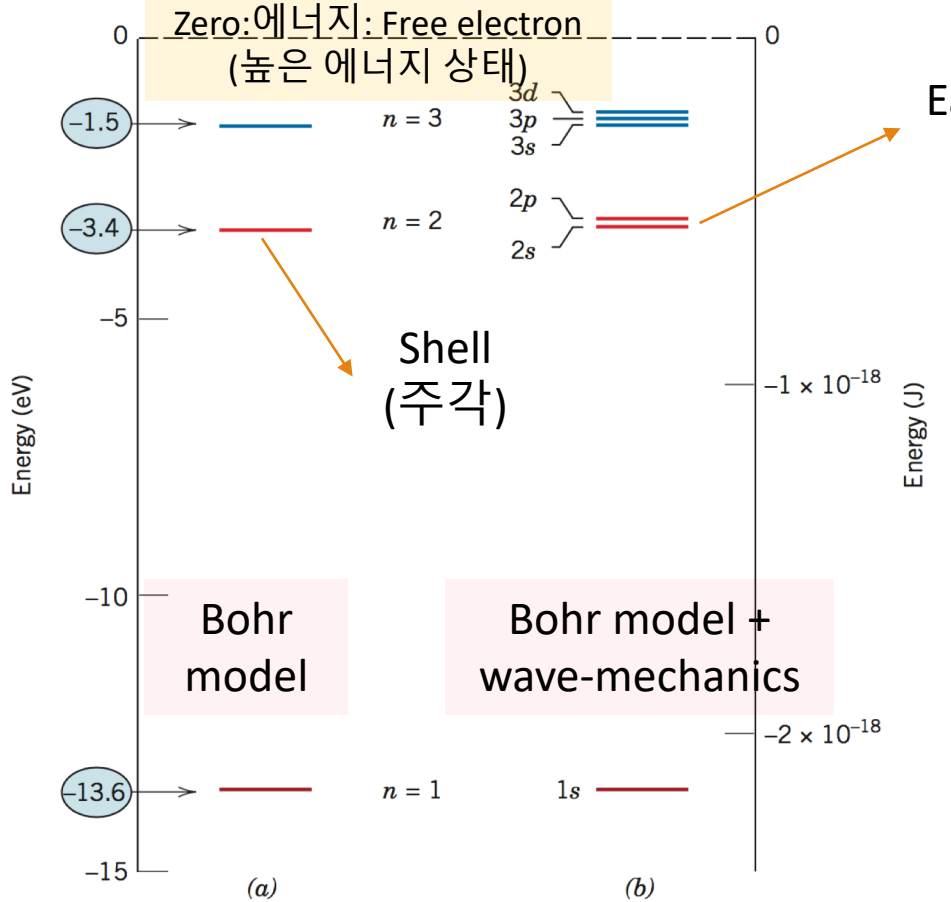
Eventually people found some limitations in Bohr's model.
Historically, a) **de Broglie** (1923) discovered that electrons have a dual nature, i.e., it has properties pertaining to both particles and waves. b) **Heisenberg** (1927) proposed the principle of indeterminacy – you cannot know both the position 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

Zero:에너지: Free electron
(높은 에너지 상태)



Shell
(주각)

Bohr
model

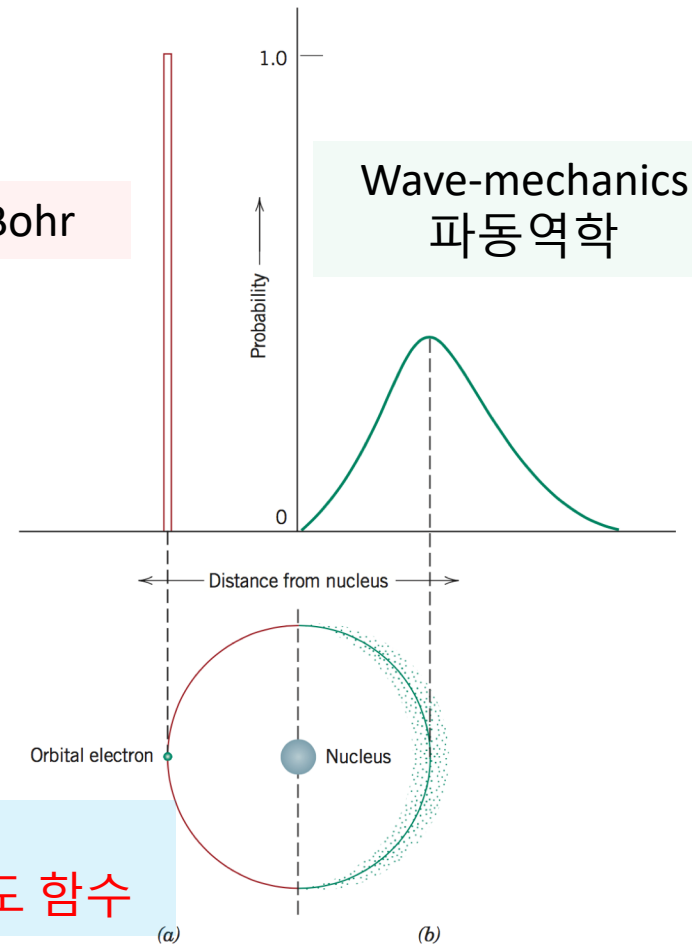
Bohr model +
wave-mechanics

음의 에너지: 원자에 구속 (낮은 에너지 상태)

Each shell may consist of
subshells (부각)

Bohr

Wave-mechanics
파동역학



Orbit과 orbital 차이?

명확한 궤도,
확률로 표현되는 위치; 확률 밀도 함수

Images from W. Calister's textbook

Electronic Structure

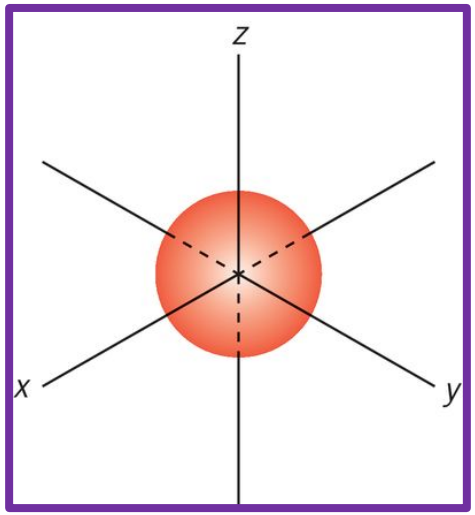
- Electrons have both wavelike and particulate properties. (de Broglie - 물질파)
- Two of the wavelike characteristics are
  - electrons are in orbitals defined by a probability.
  - each orbital at **discrete energy level** (불연속성) is determined by quantum numbers.
- 네 종류의 양자수 (quantum number)로 전자 확률 밀도가 결정된다 – (양자역학)

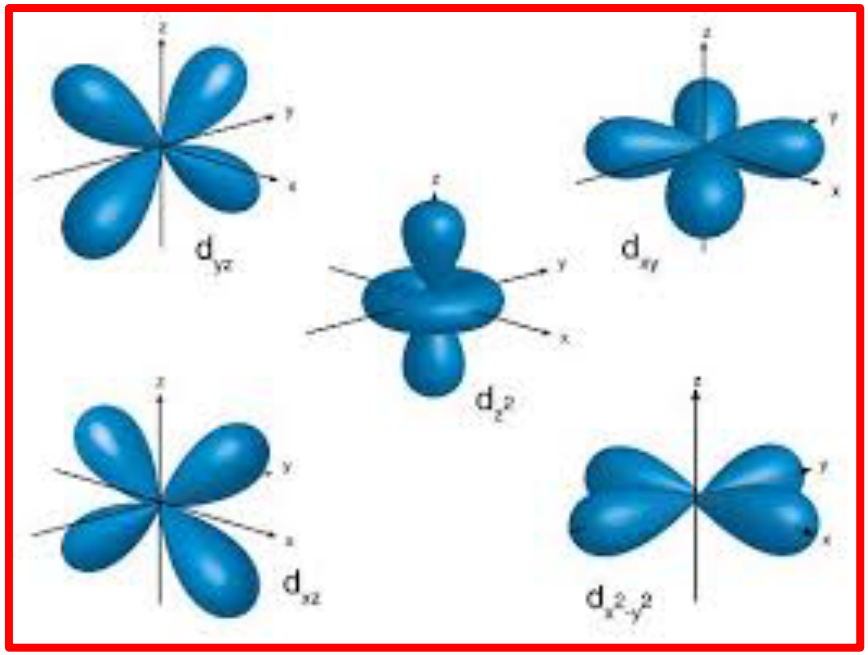
Q) Orbit and Orbital?
- Probability distribution

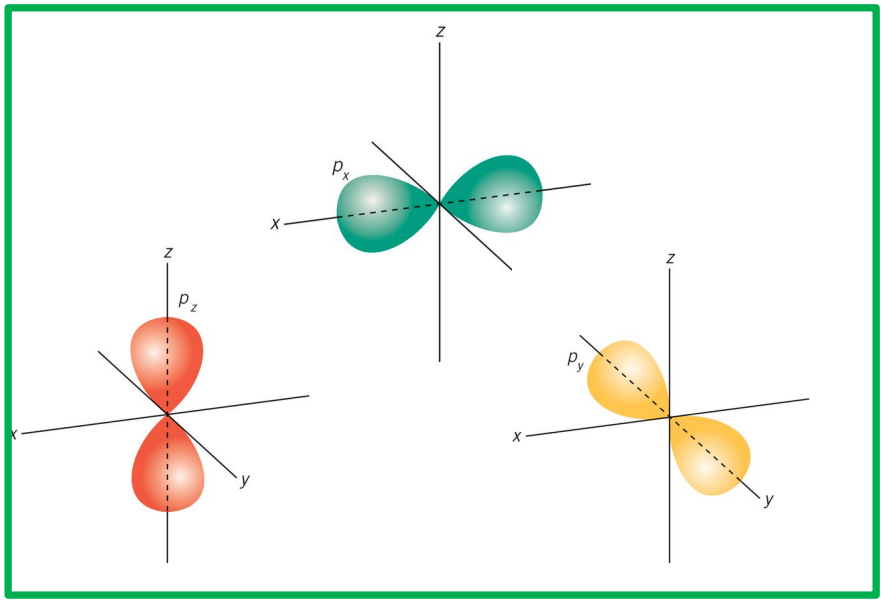
파동역학에서의 전자: 양자수에 의해 정의

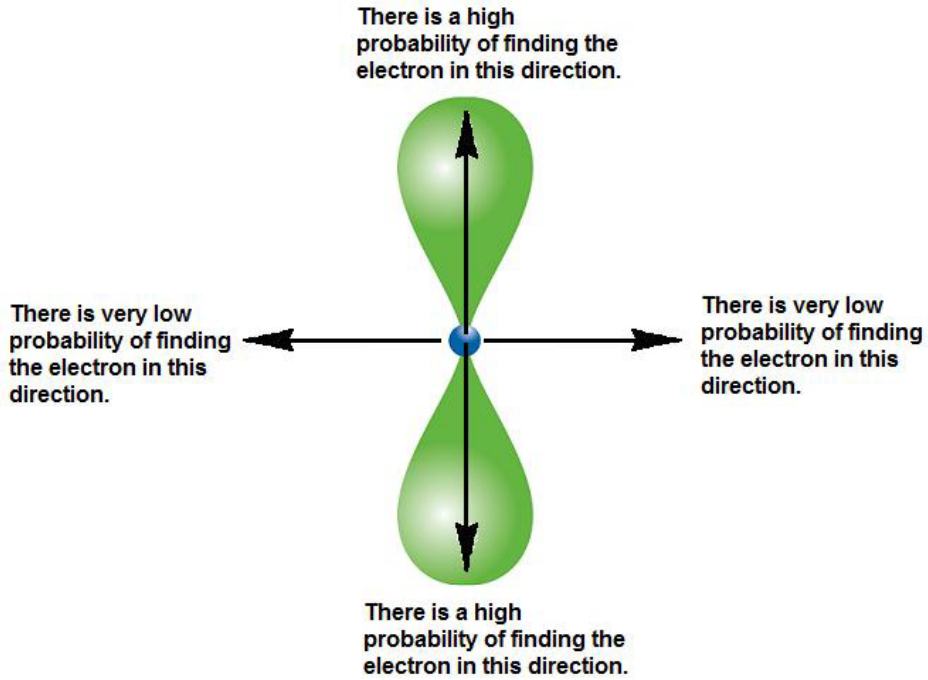
- 파동역학에서의 전자 위치 (orbital)은 전자 확률 밀도에 따름
- 전자 확률 밀도의 크기, 형태, 방향은 양자수(quantum number)에 의해 특징지어진다 (characterized).
- 보어 모형에 따르면 (전자의) 에너지 수준은:
  - 주각 (shell) 으로 표현.
  - 파동역학에 따르면 각 부각에 세부적으로 부각(subshell)이 존재.
- 각 양자수는
  - 주각은 '주양자수' (principal quantum number, **n**)
  - 두번째 양자수는 l (엘)로 표기하며 orbital의 '모양'을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

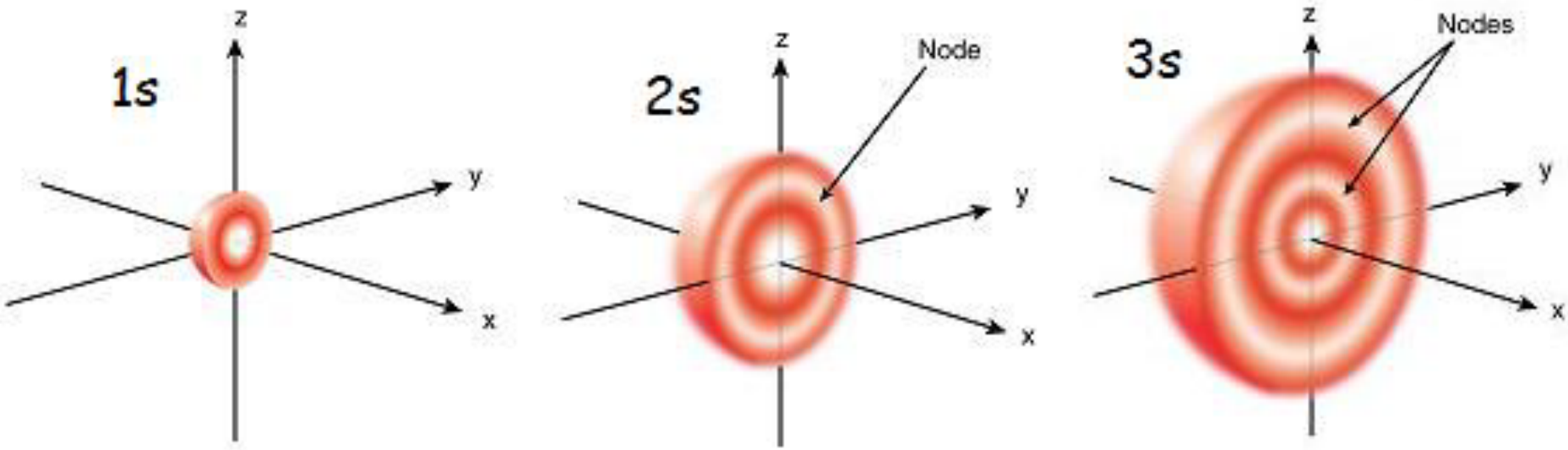
Orbital: areas where electrons are ‘detected’











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

양자수 Quantum Numbers

n, l, m_l, m_s

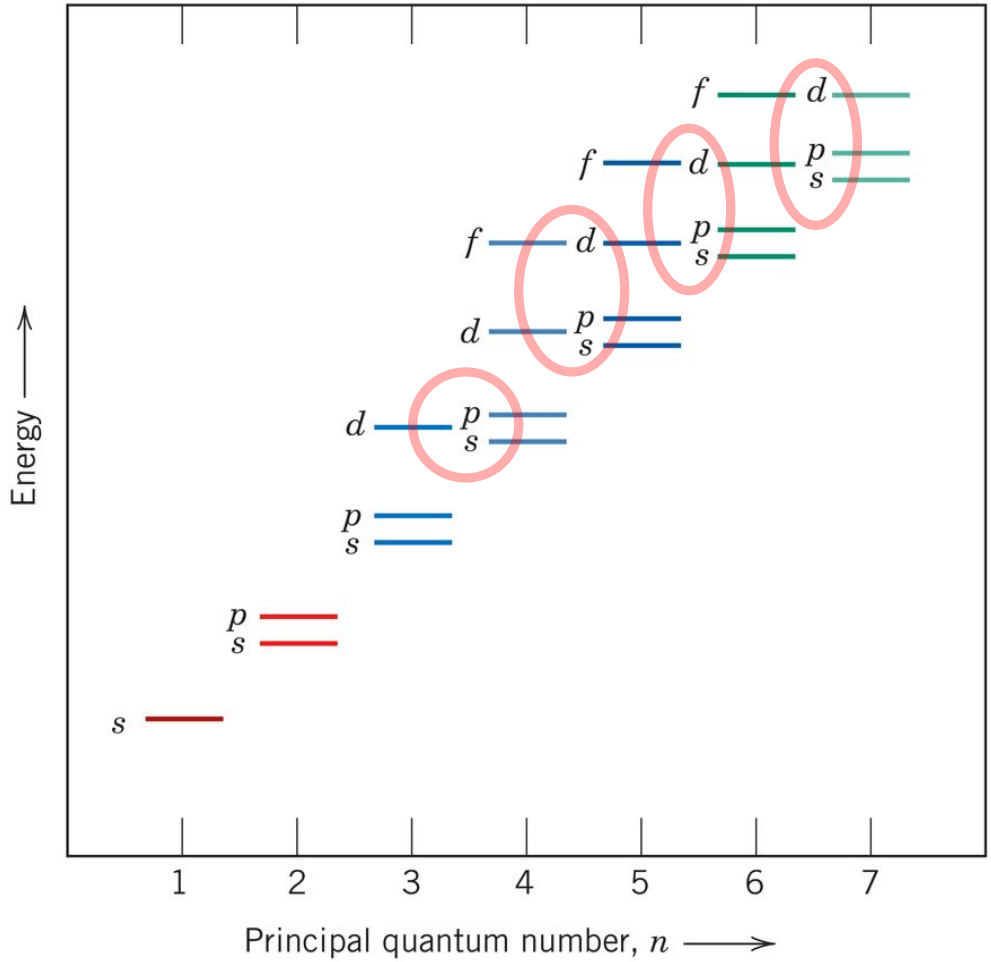
Quantum # (양자수)	Designation
n = principal (energy level-shell)	K, L, M, N, O (1, 2, 3, etc.)
ℓ = subsidiary (orbitals)	s, p, d, f (0, 1, 2, 3,…, n-1)
m_l = magnetic	1, 3, 5, 7 ($-\ell$ to $+\ell$)
m_s = spin	½, -½

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

Value of n	*Value of l*	*Values of m_l*	*Subshell*	*Number of Orbitals*	*Number of Electrons*
1	0	0	1*s*	1	2
2	0	0	2*s*	1	2
	1	−1, 0, +1	2*p*	3	6
3	0	0	3*s*	1	2
	1	−1, 0, +1	3*p*	3	6
	2	−2, −1, 0, +1, +2	3*d*	5	10
4	0	0	4*s*	1	2
	1	−1, 0, +1	4*p*	3	6
	2	−2, −1, 0, +1, +2	4*d*	5	10
	3	−3, −2, −1, 0, +1, +2, +3	4*f*	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



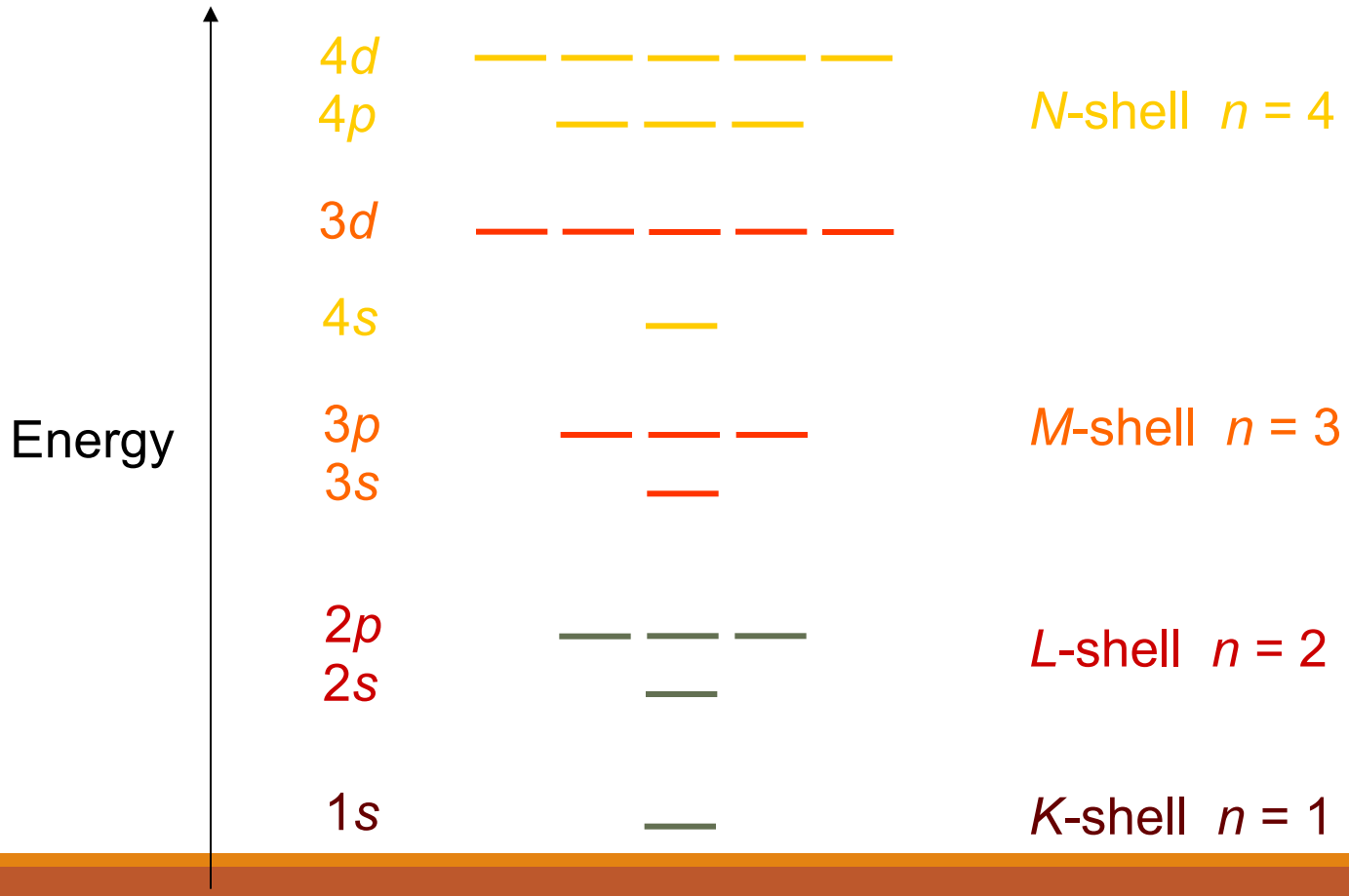
From K. M. Ralls, T. H. Courtney, and J. Wulff, Introduction to Materials Science and Engineering, p. 22. Copyright © 1976 by John Wiley & Sons, New York. Reprinted by permission of John Wiley & Sons, Inc.

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

Electron Energy States

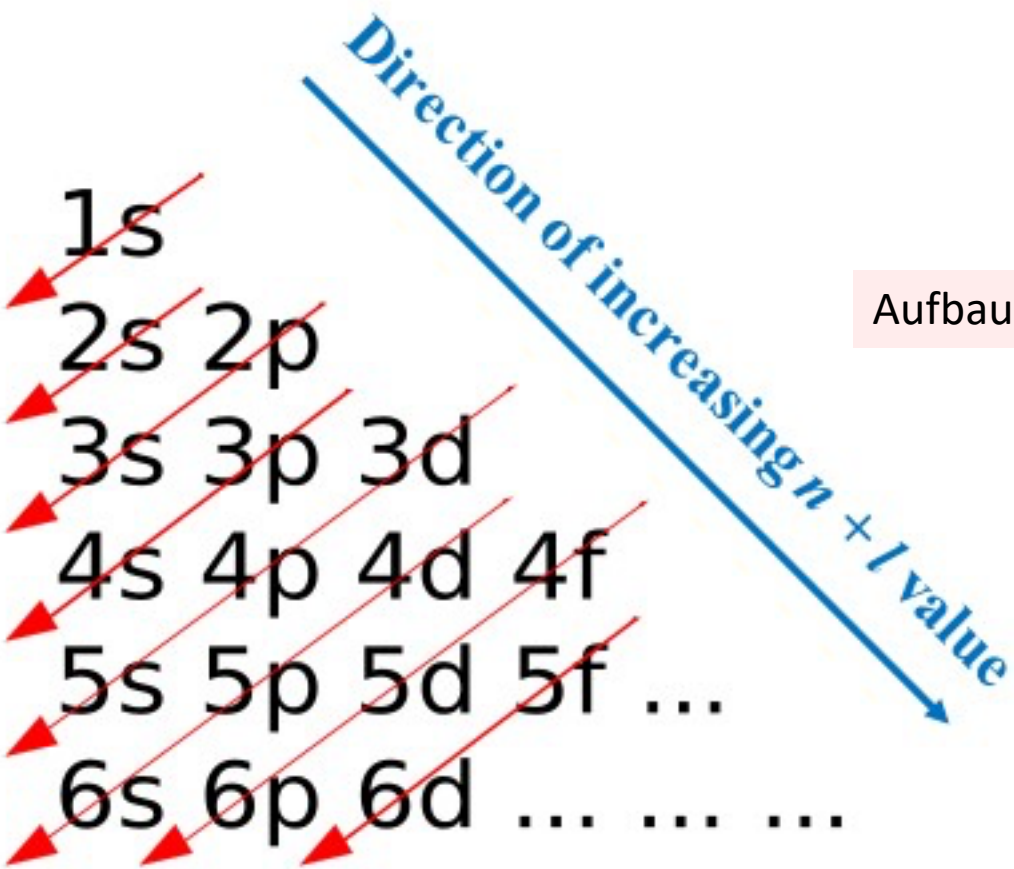
Electrons...

- 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)



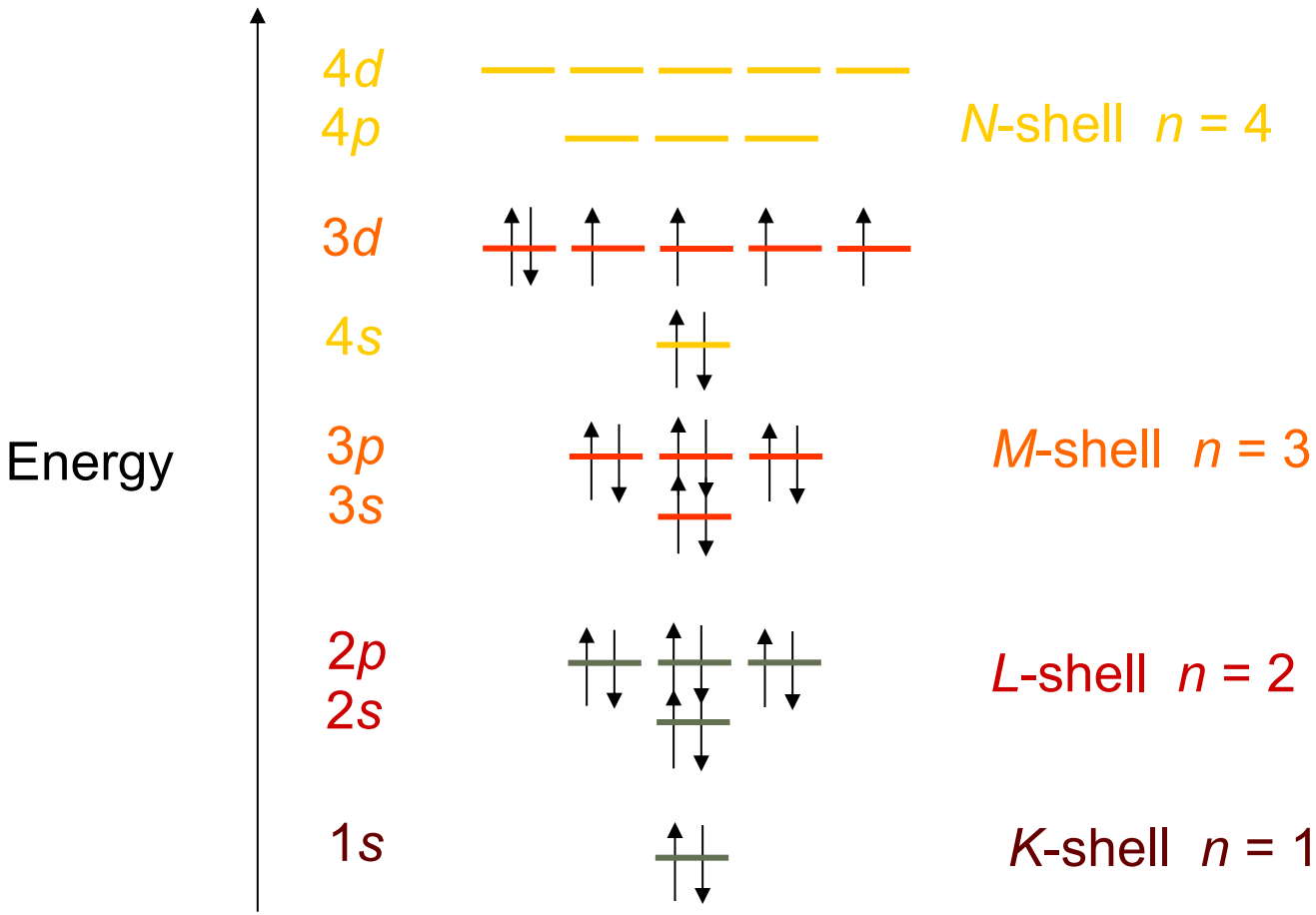
Aufbau principle (building-up principle)

Electronic Configurations

ex: Fe - atomic # = 26

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

Valence electrons
원자가 전자



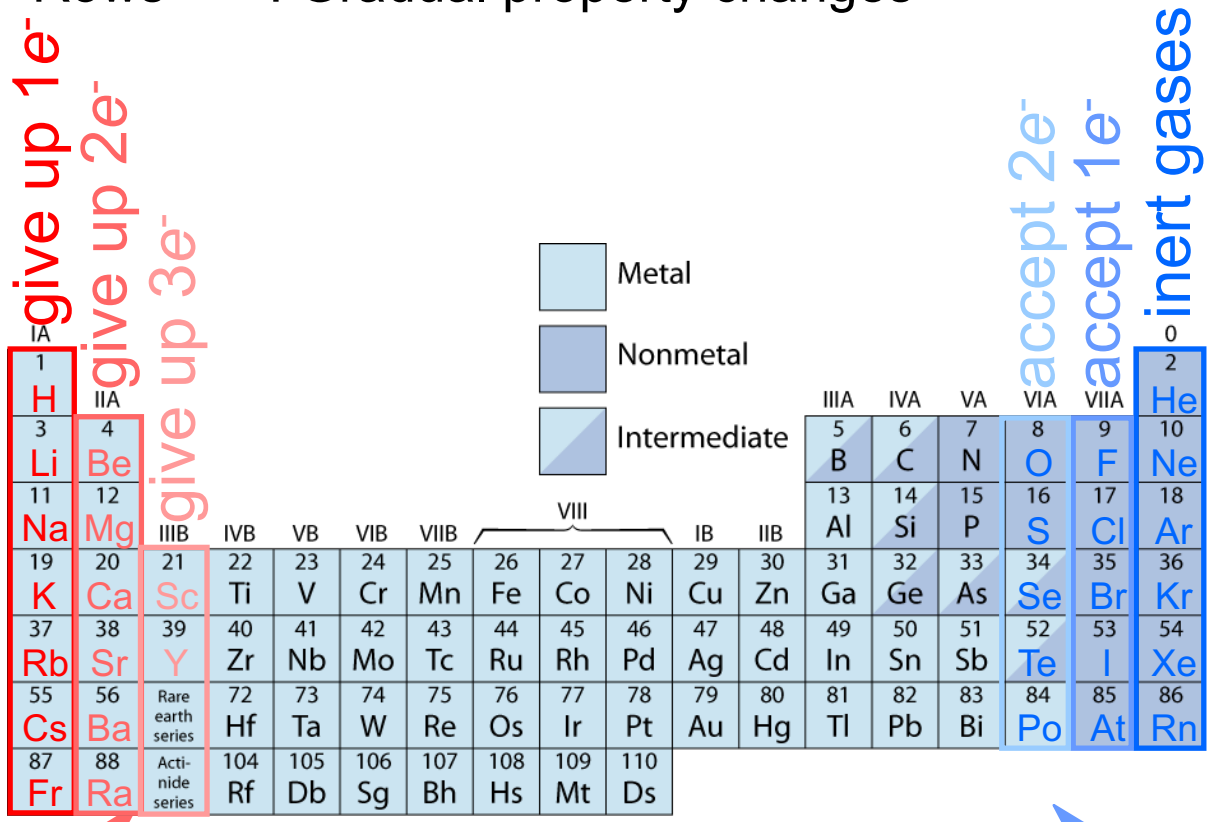
원자가 전자: 원자의 바깥껍질에 위치하며 화학 반응에 참여할 가능성이 높은 전자

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



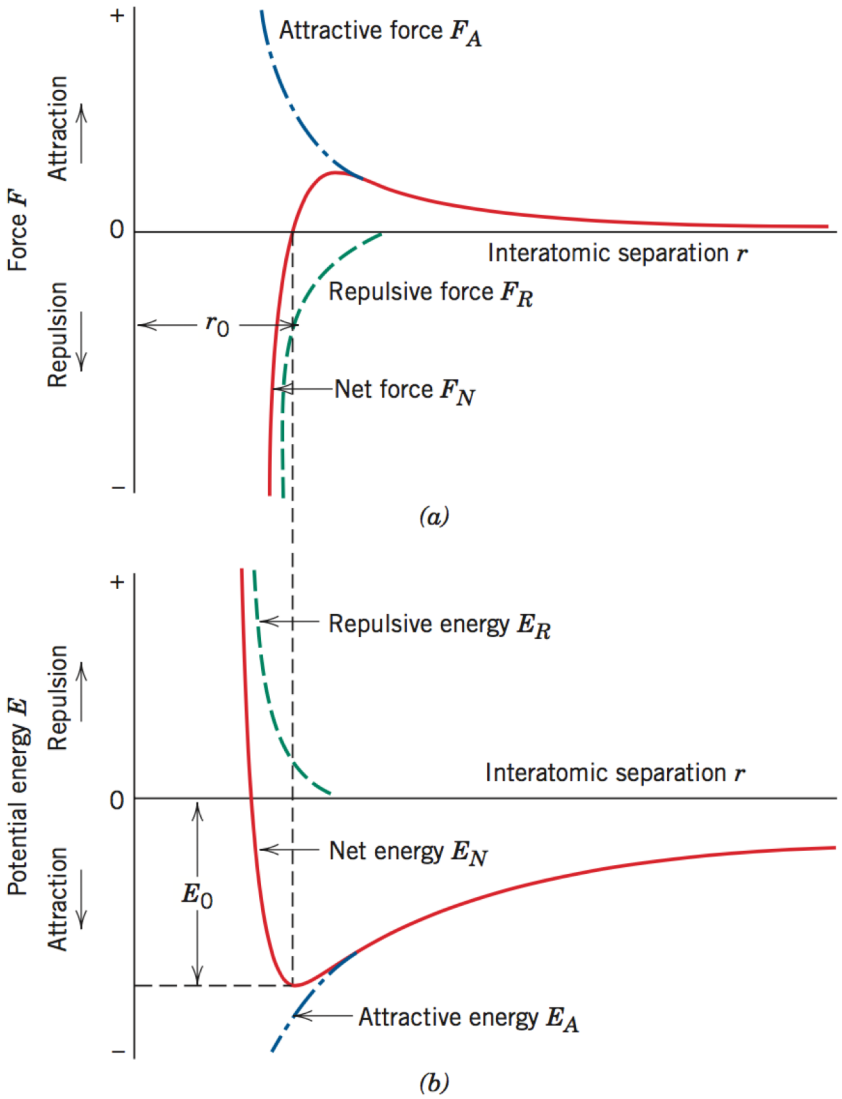
비슷한 화학적 물성이 '주기성'을 보이며, 그것이 valence electron과 관련이 있다.

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

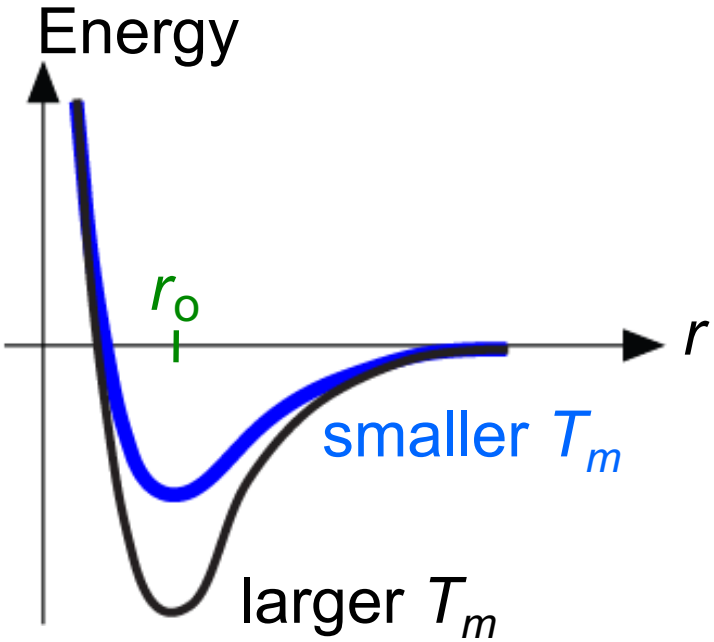
Simple explanation using Coulombic forces – attraction between the electrons and nuclei (protons) and attraction between electrons and between nuclei. Also, note that the electrons are located in the outer region so that when atoms are getting closer, electrons are the ones that dominate the bonding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

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

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:

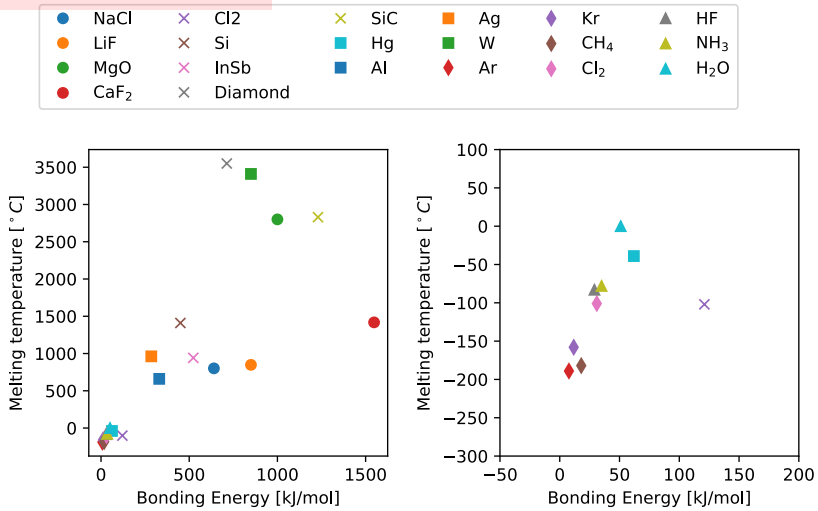
- Melting temperature T_m determines the state of materials at a certain temperature such as room temp.

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

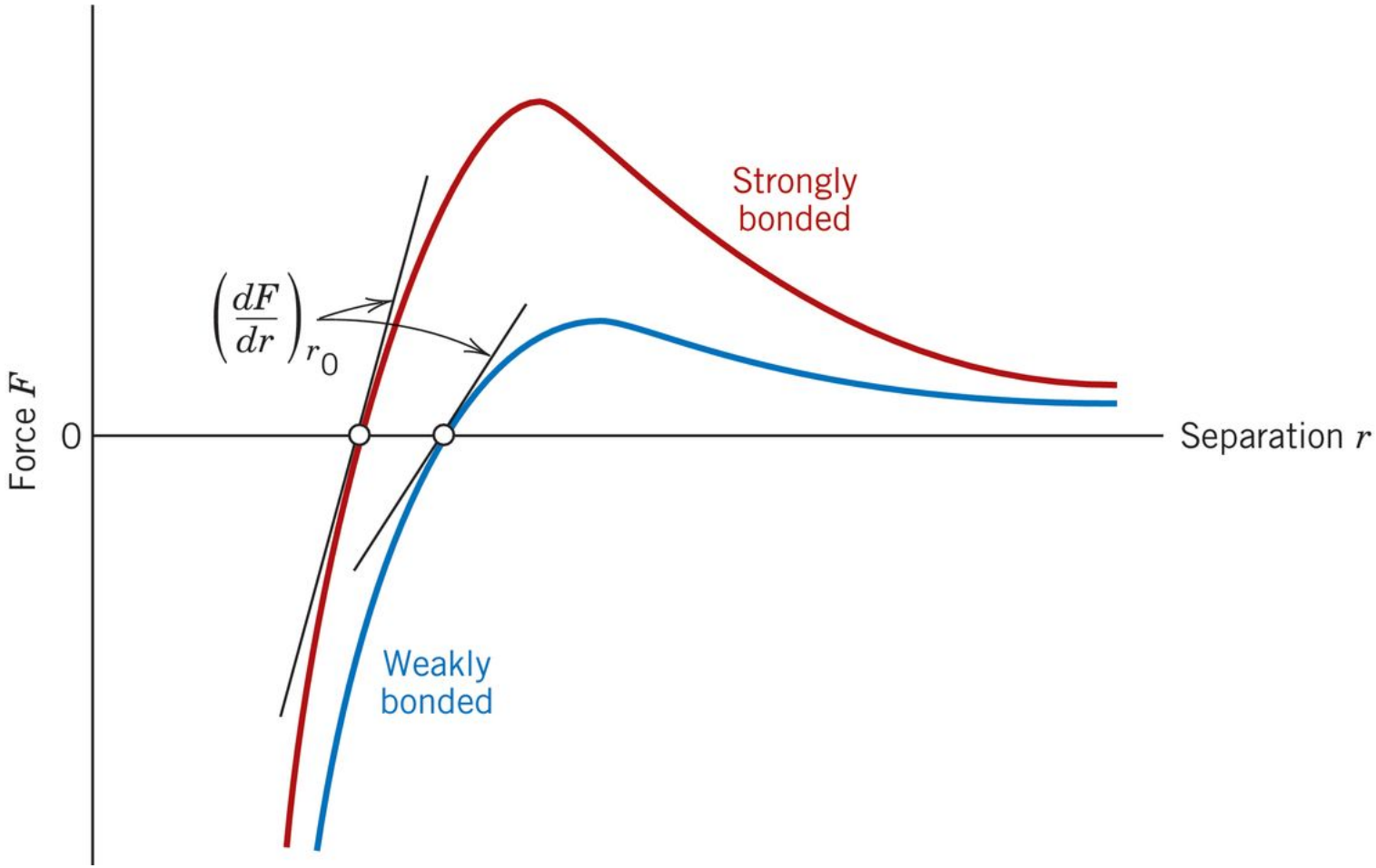
- Stiffness, thermal coefficients are also closely related with the atomic bonding behavior

- 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)

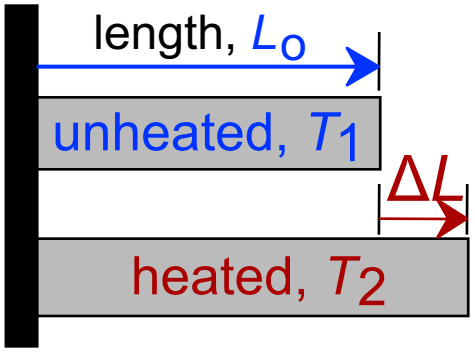


Properties From Bonding: Ex) Stiffness



Properties From Bonding: Ex) Thermal expansion

- Coefficient of thermal expansion, α

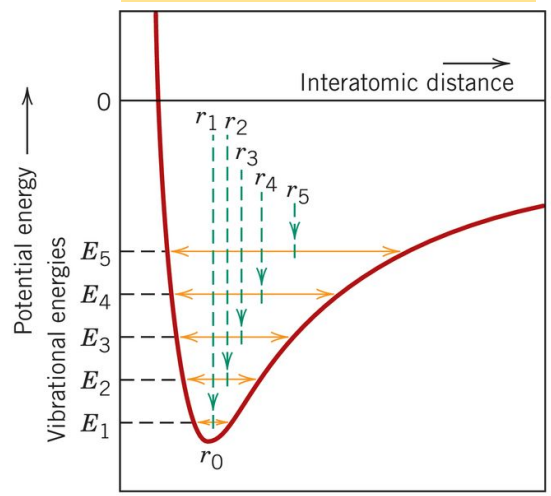


coeff. thermal expansion

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

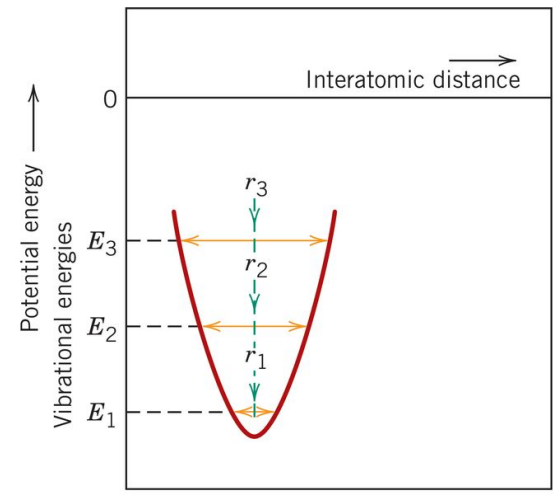
- Thermal expansion can be viewed as increase of ***average*** interatomic distance.
- Temperature increase induces vibration of atoms

Asymmetric



(a)

Symmetric



(b)

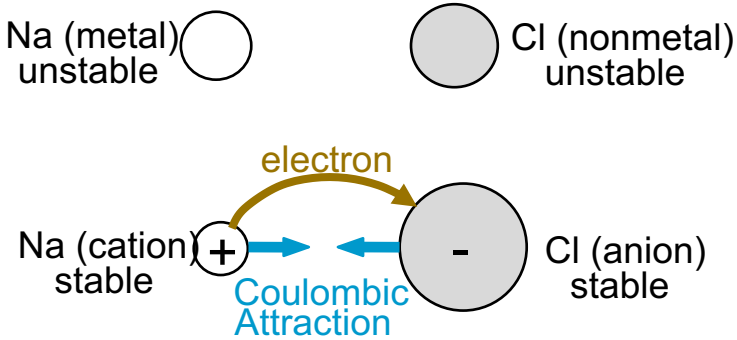
Adapted from R. M. Rose, L. A. Shepard, and J. Wulff, The Structure and Properties of Materials, Vol. 4, Electronic Properties. Copyright © 1966 by John Wiley & Sons, New York. Reprinted by permission of

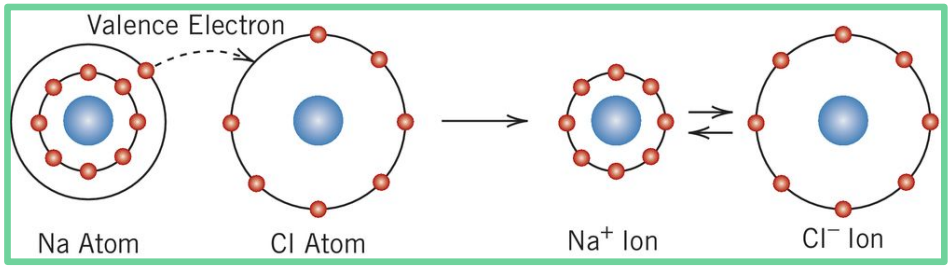
원자결합 종류

- Primary bonds
  - 이온결합 (ionic)
  - 공유결합 (covalent)
  - 금속결합 (metallic)
- Secondary bonds, van der Waals bonding

Ionic Bonding: Introduction

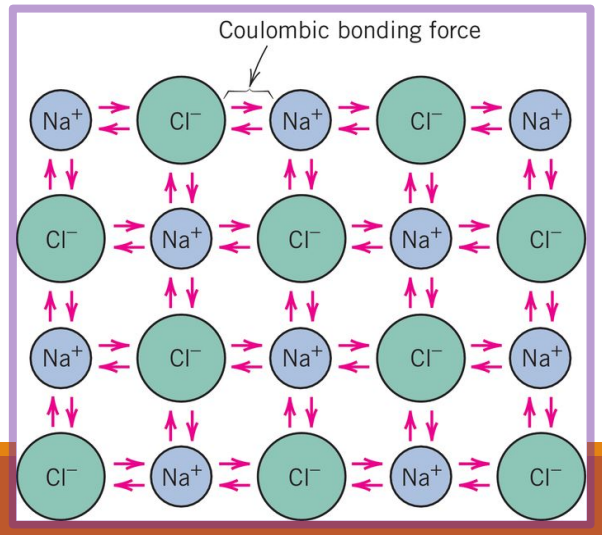
- Occurs between + and - ions.
- Requires electron transfer (전자의 교환 – donor and acceptor)
- Large difference in electronegativity required (next slide)
- Example: NaCl





[Ne] [Ar]

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	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 $\underline{1s^2\ 2s^2\ 2p^6}\ 3s^2$ O $1s^2\ 2s^2\ 2p^4$

[Ne] $3s^2$

Mg^{2+} $\underline{1s^2\ 2s^2\ 2p^6}$ O^{2-} $\underline{1s^2\ 2s^2\ 2p^6}$

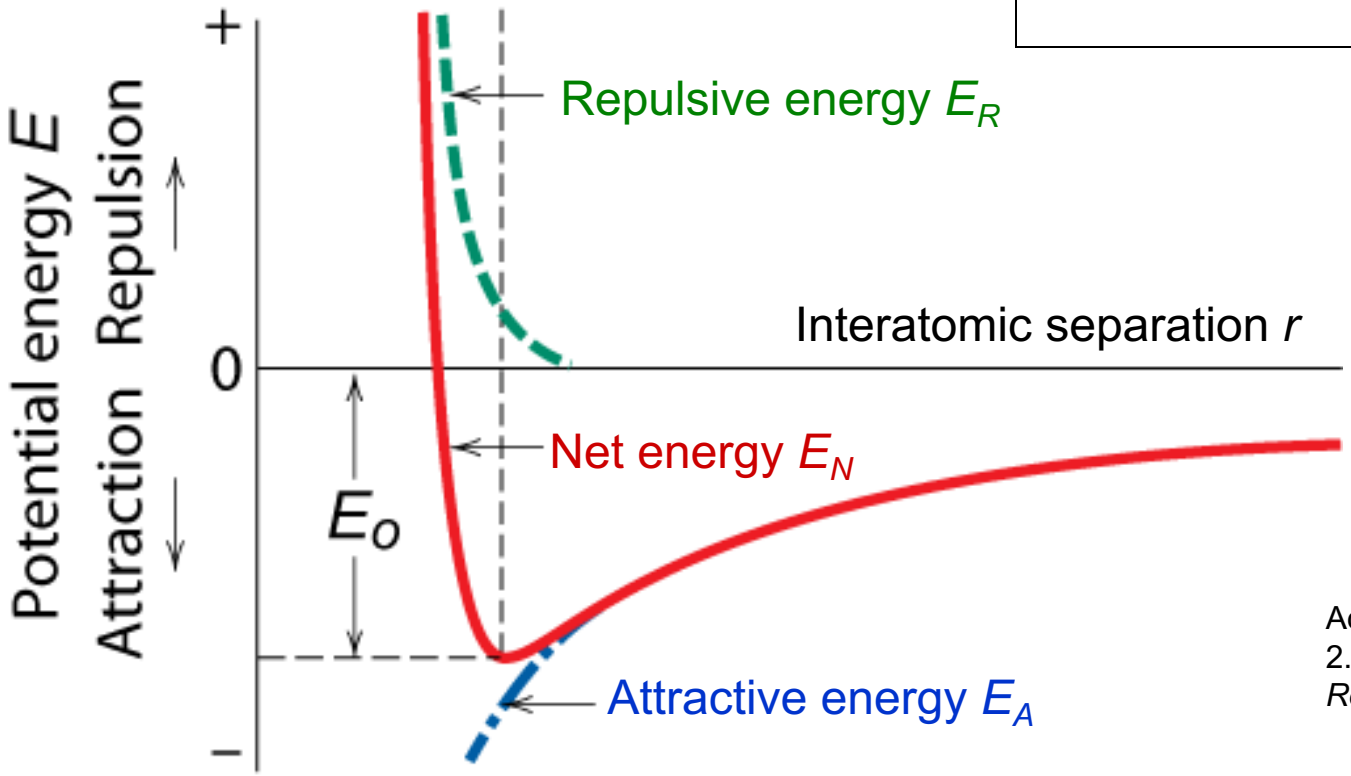
[Ne] [Ne]

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.*

** Tips

- 우리 교재 갖은 전공 용어들이 사용된다.
- 전공 용어들에 대해 속히 '친숙함'을 가지는 것이 매우 중요.
- 교재 뒷부분 "용어해설"을 참고하길.

Ionic Bonding: examples

- Predominant bonding in Ceramics

NaCl

MgO

CaF_2

CsCl

IA	IIA	IIIB	IVB	VB	VIB	VIB	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															

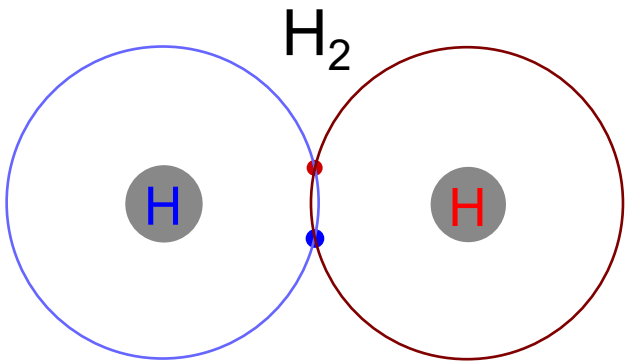
Give up electrons

Acquire electrons

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 1*s* electron from 1st hydrogen atom
- shared 1*s* 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)

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

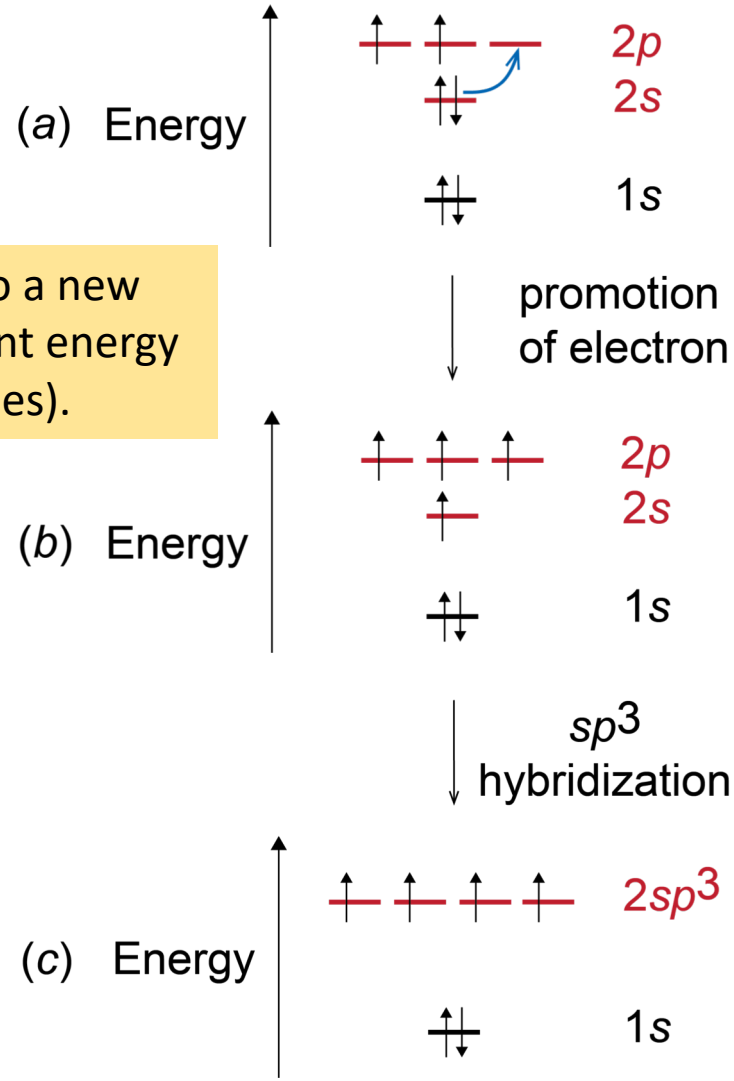


Fig. 2.13, *Callister & Rethwisch 9e.*

Carbon can form sp^3 hybrid orbitals

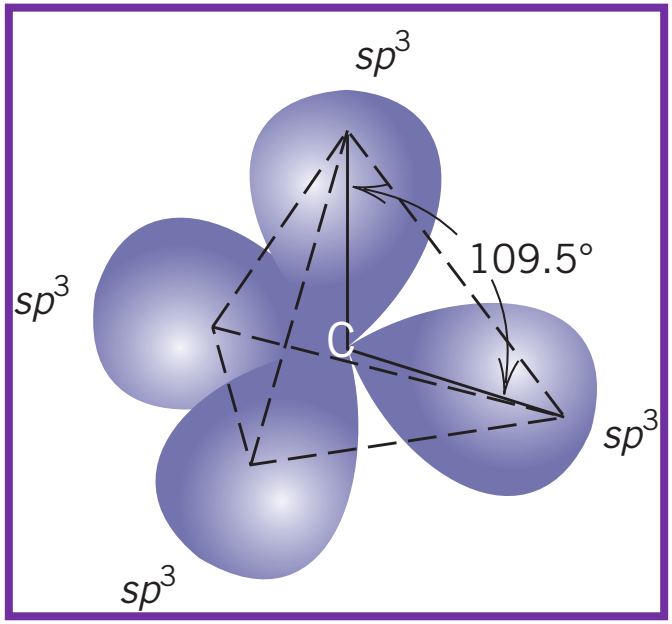


Fig. 2.14, *Callister & Rethwisch 9e.*
(Adapted from J.E. Brady and F. Senese, *Chemistr Matter and Its Changes*, 4th edition. Reprinted with permission of John Wiley and Sons, Inc.)

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

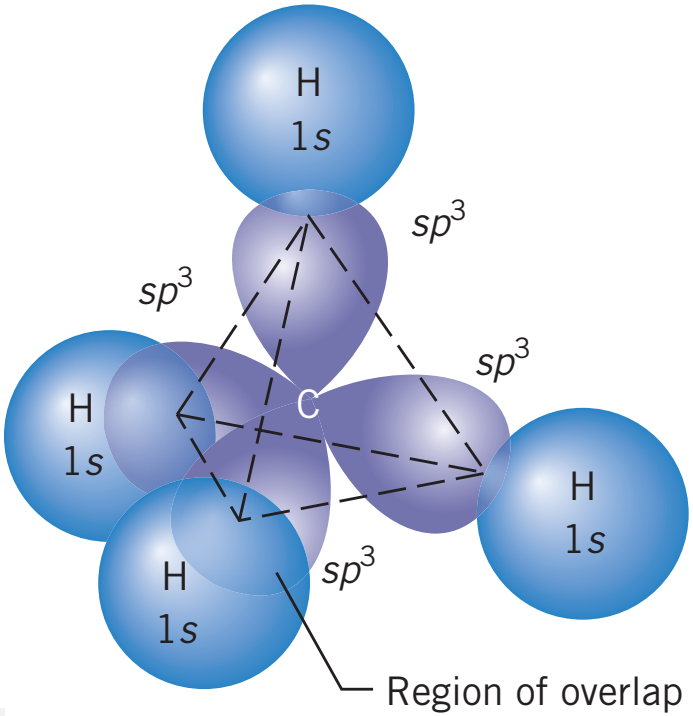


Fig. 2.15, *Callister & Rethwisch 9e.*
(Adapted from J.E. Brady and F. Senese, *Chemistry: Matter and Its Changes*, 4th edition. Reprinted with permission of John Wiley and Sons, Inc.)

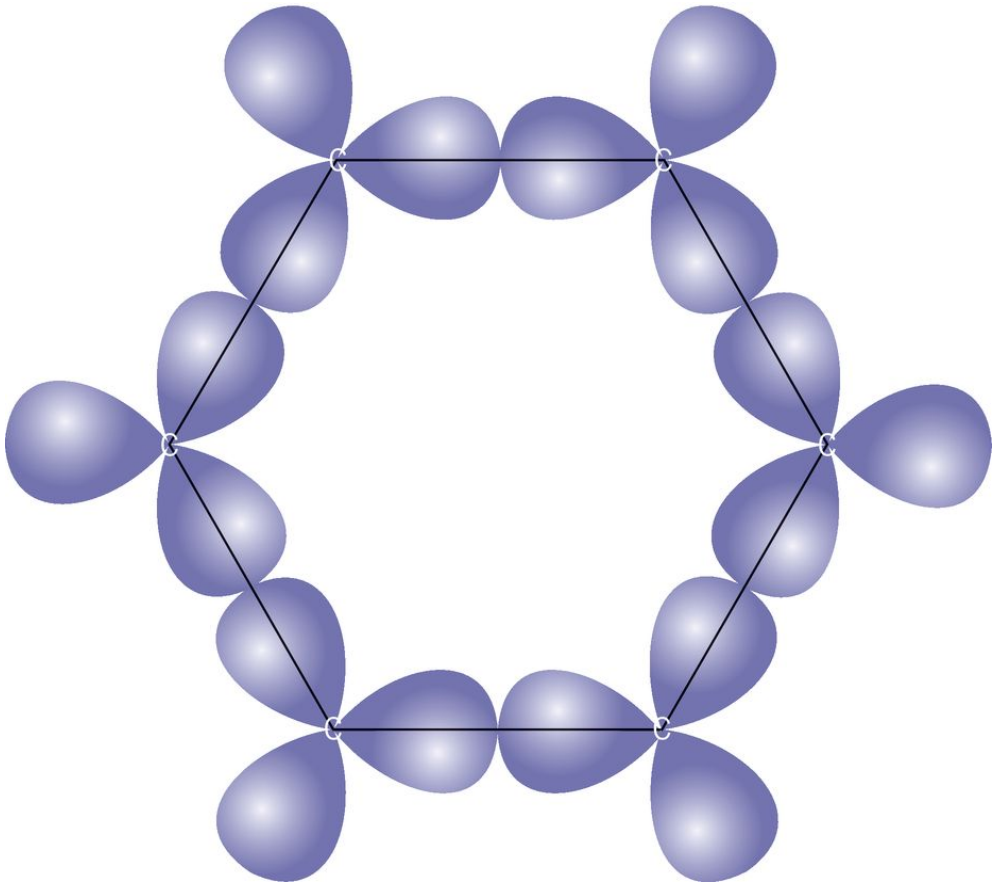
Electronegativities of C and H are comparable, so electrons are shared in covalent bonds.

C: 2.5

H: 2.1

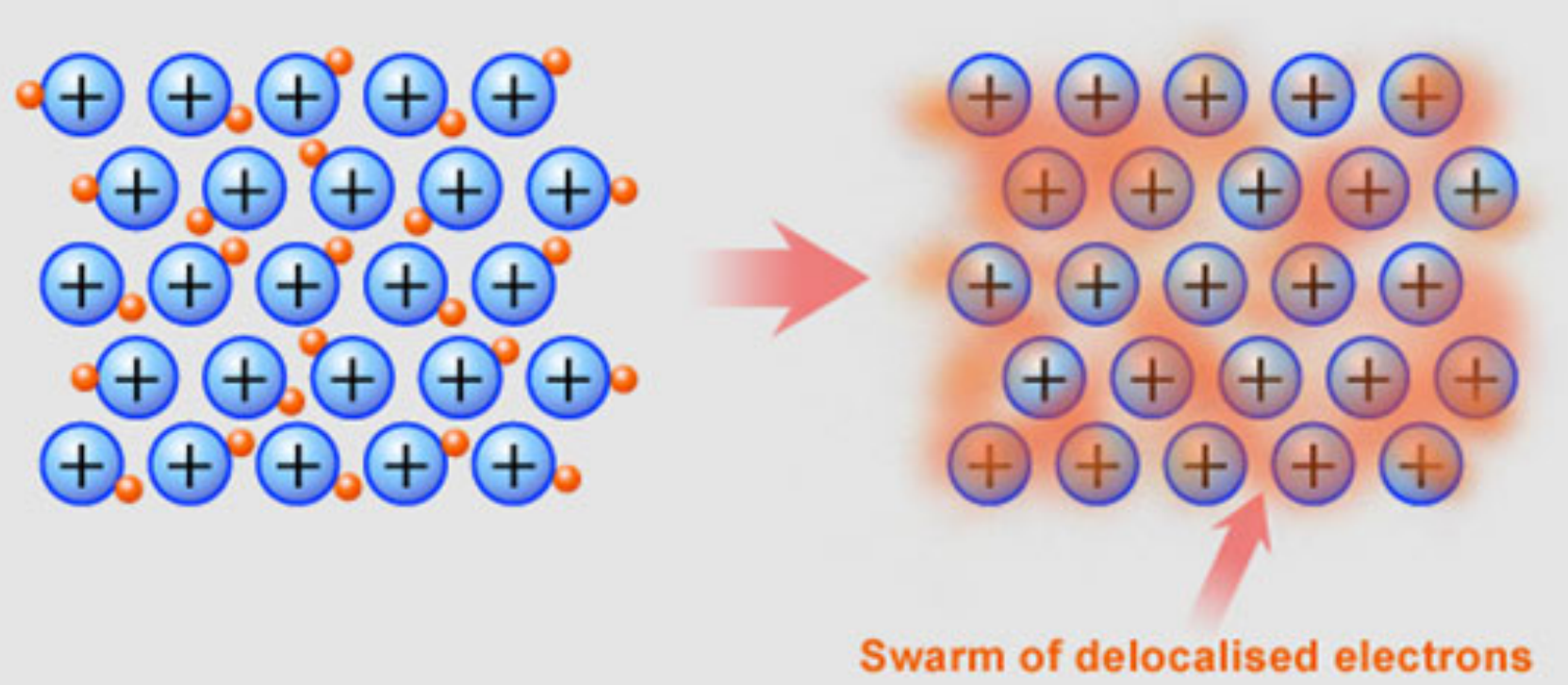
sp^2 Hybridization

- 탄소에서 나타나는 sp^2 혼성결합



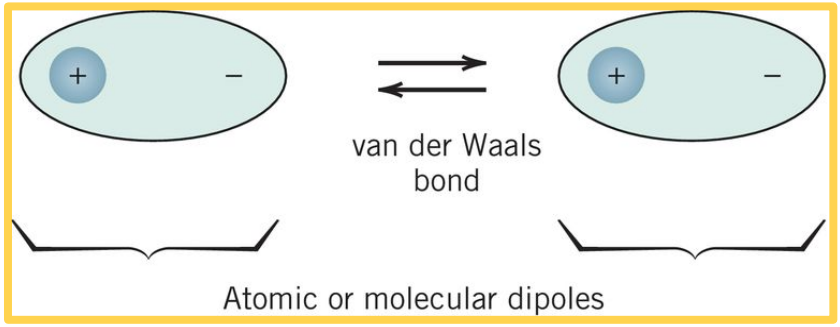
Metallic bonding

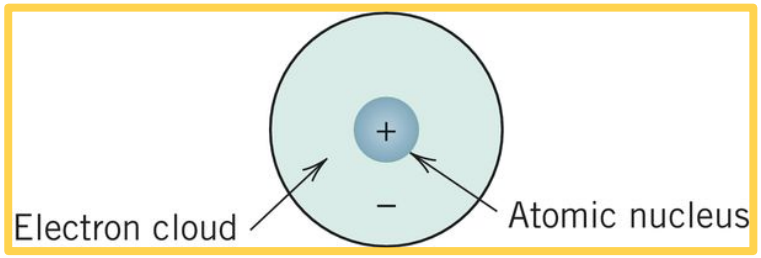
- The most outer electrons are not ‘localized’ and can freely move around.
- Electron cloud (sea)
- Electron adhesives
- Delocalized electron cloud is the origin of good electrical and thermal conductivities

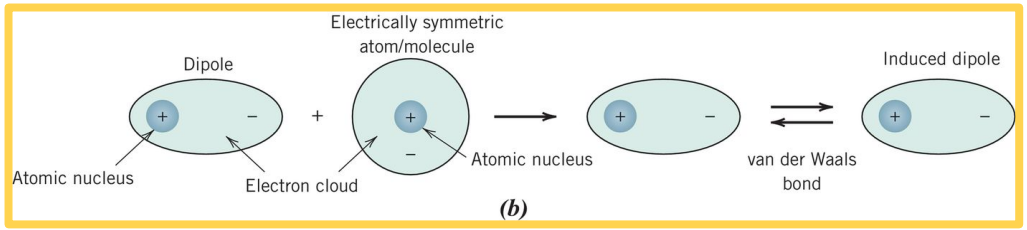


Secondary bonding

- 앞서 기술한 이온,공유, 금속 결합에 비해 매우 낮은 결합력.
  - 따라서, 위 세 결합이 존재할 때, '가려진다'.
- 이차 결합은, 이미 이온,공유,금속 결합등으로 묶인 원자 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 분자 들 사이에서
    - 3. 극성 분자들 사이에서 존재.
  - 수소 결합
- 원자나 분자에서 양전하와 음전하가 근접하게 분리 위치할 때는 언제나 전기적 쌍극자 (electric dipole)가 존재하게 된다.



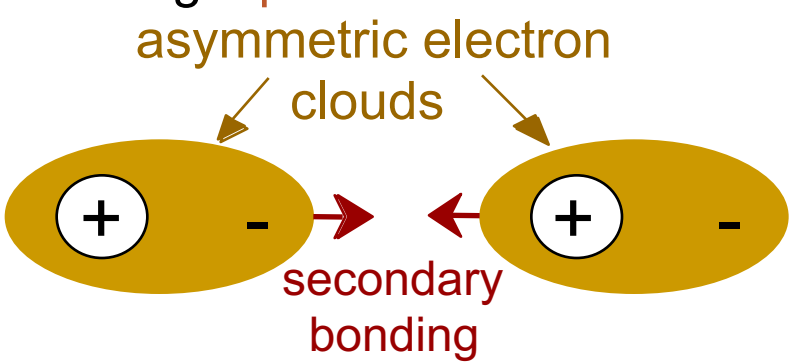




Secondary Bonding

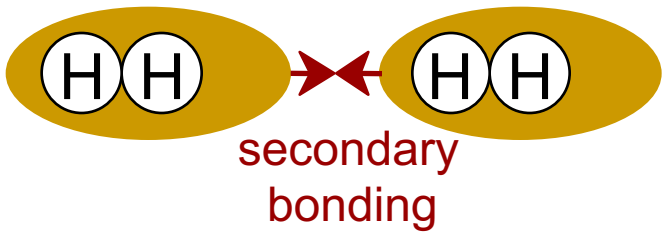
Arises from interaction between dipoles (atom or molecule)

- Fluctuating dipoles



ex: liquid H_2

$H_2 \rightarrow \leftarrow H_2$



- Permanent dipoles-molecule induced

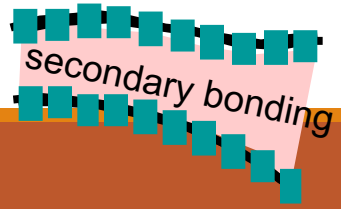
  Originally symmetric but gets asymmetric by neighboring dipoles.

-general case:

-ex: liquid HCl

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

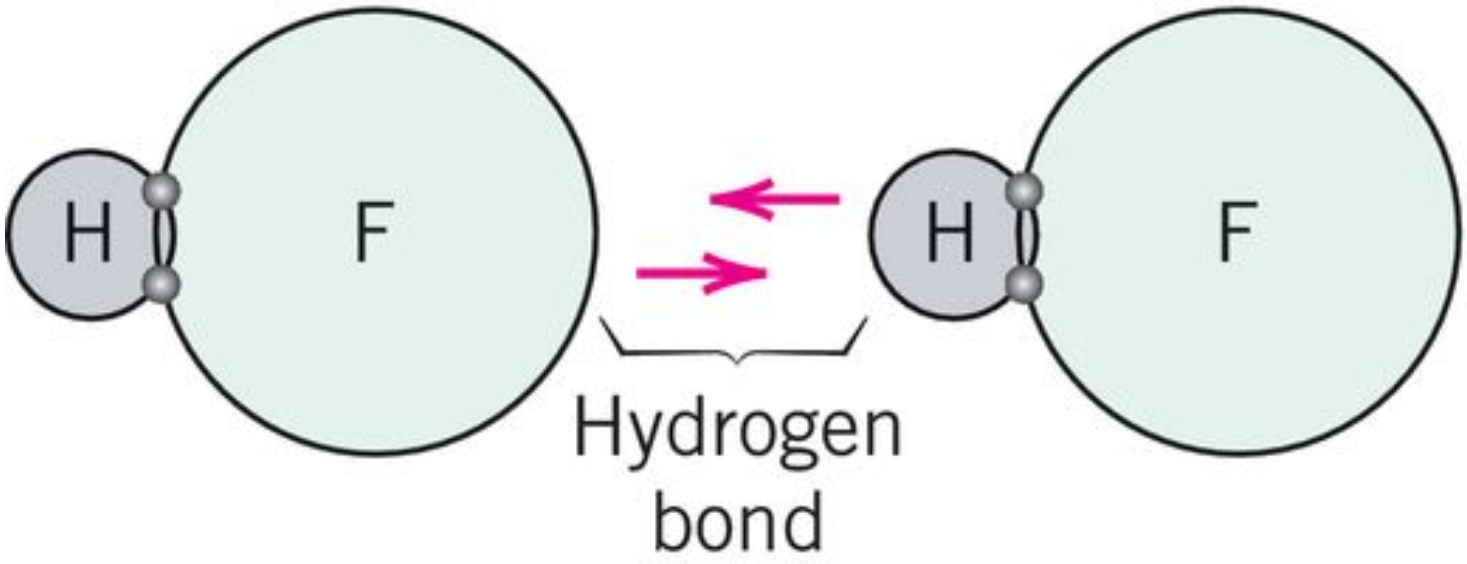
-ex: polymer



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

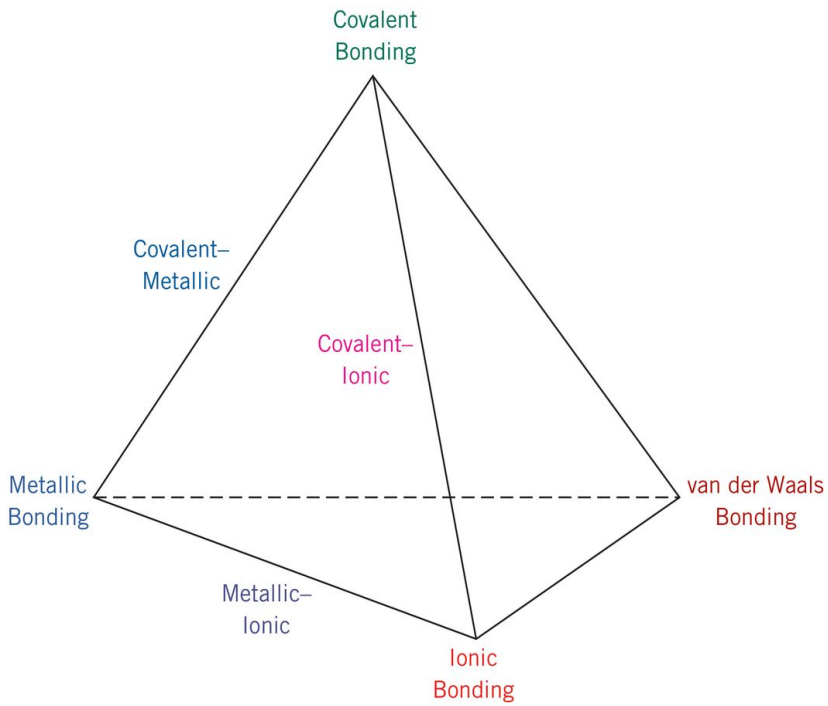
A special case of secondary bonding: Hydrogen bonding

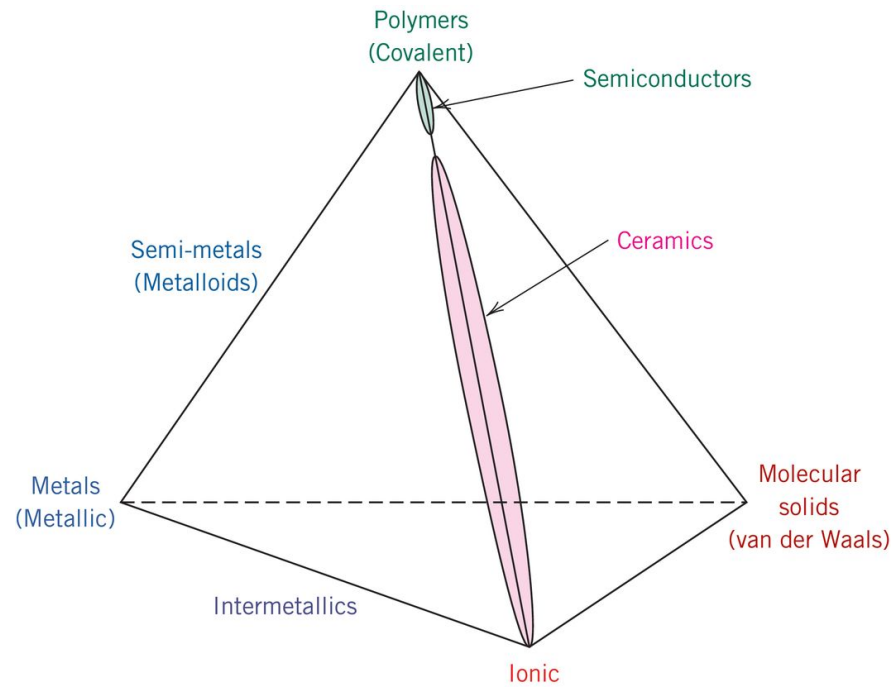
- A special case of secondary bonding
- What makes hydrogen bonding strong?
  - 양성자를 차폐하는 '유일한' 전자가 결합에 참여하면, 매우 강한 Columbic force 작용 가능. 따라서 이차 결합중 수소 결합이 가장 강하다.



Mixed bonds

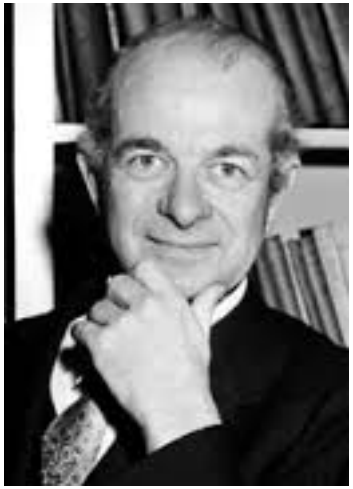
Not all bondings are ‘pure’.





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

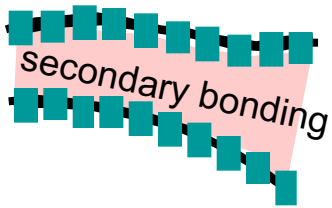
(Metallic bonding):

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