

# PART 4 – Molecular Orbital Method of Chemical Bonding, and Molecular Interactions

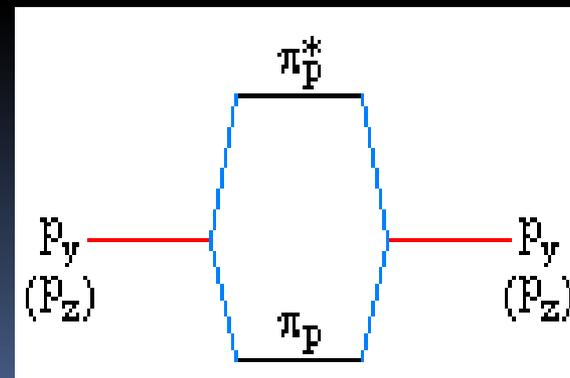
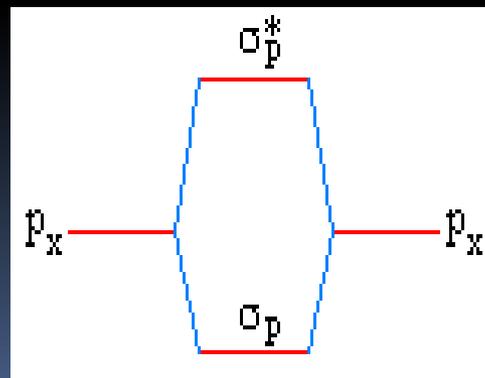
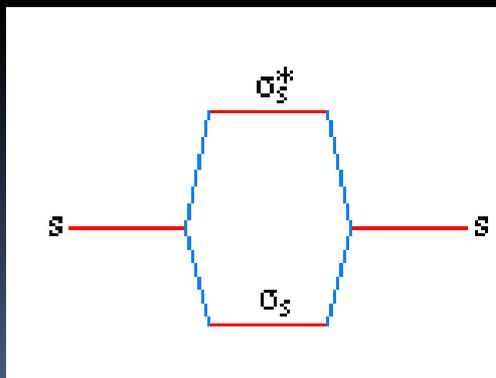
Reference: Chapter 10 in textbook

# Molecular Orbital (MO) Method

- MO method
  - Molecular orbitals are formed by combination of atomic orbitals of bonding atoms;
  - # of total MOs = # of total atomic orbitals;
  - All e's belong to the molecule, not original atoms.
  - Electrons are filled based on the same criteria as in atomic orbitals: (i) Pauli exclusion principle; (ii) Filled from the lowest energy first, (Ground State).

# Molecular Orbital (MO) Method

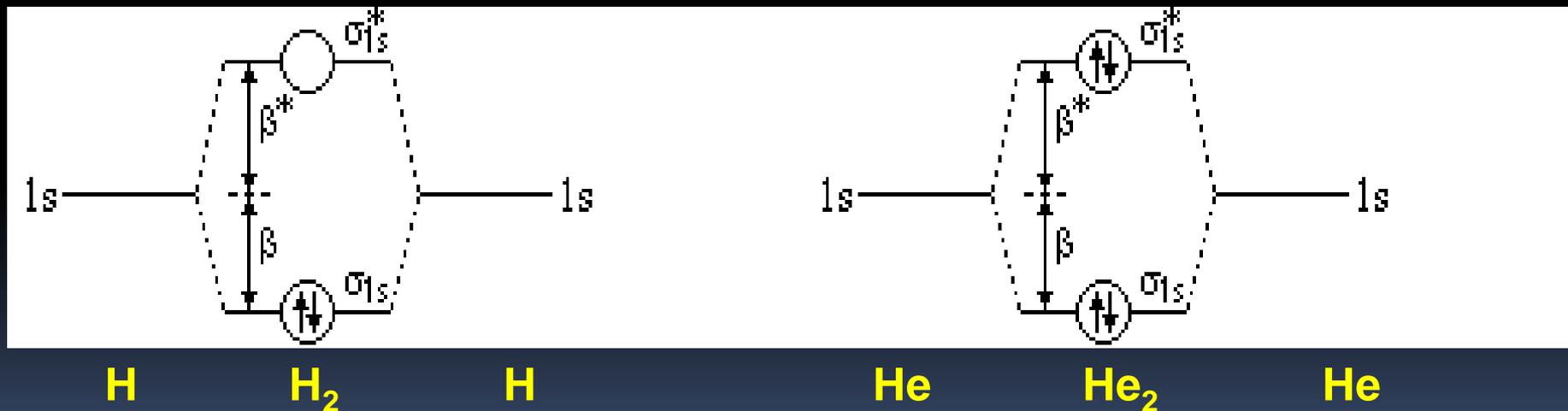
- Bonding, Antibonding, Nonbonding MOs
  - Bonding MO: w/ energy lower than original AO;
  - Antibonding MO: w/ energy higher than original AO;
  - Nonbonding MO: w/ energy equal to original AO;
  - # of bonding MO = # of antibonding MO.



# Homonuclear Diatomic Molecules

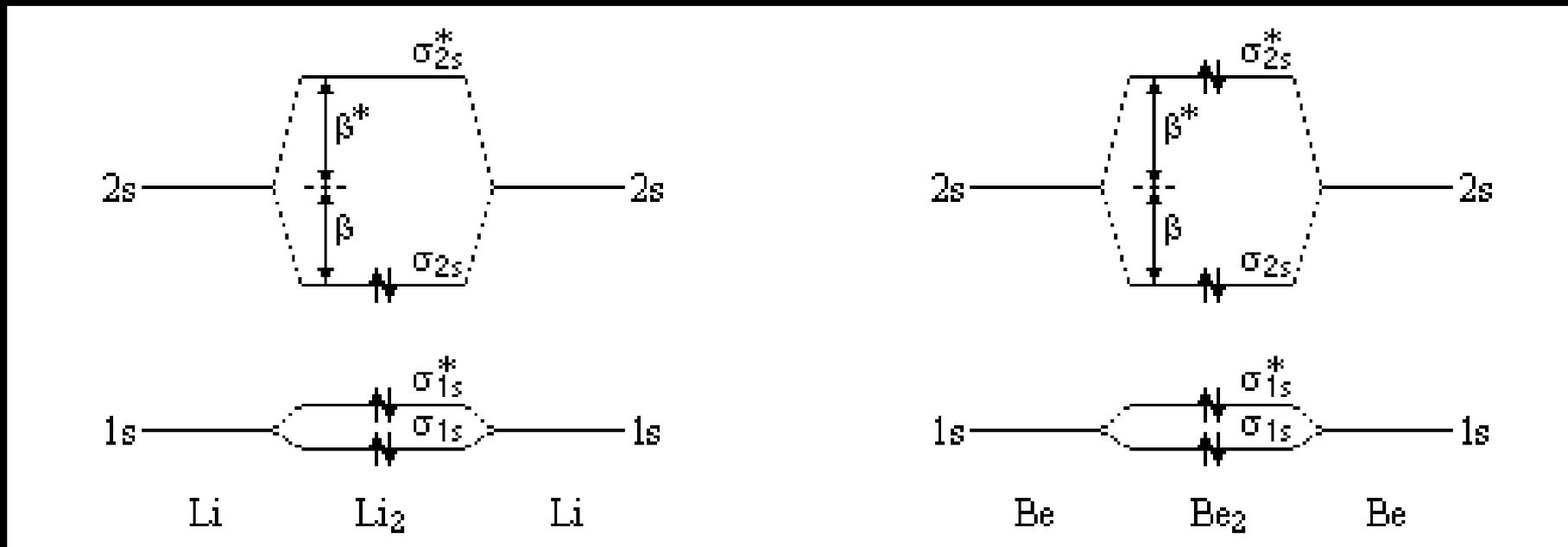
- Bond Order =  $0.5 * (\# \text{ bonding e} - \# \text{ antibonding e})$ 
  - Larger bond order  $\leftrightarrow$  More stable molecule
  - When bond order = 0, it means this molecule cannot exist.

## Example: 1<sup>st</sup> period elements



- Q: Explain (1) why  $H_2^-$ ,  $He_2^+$  ions can exist? (2) What is the bond order of these ions?

# MO of Li<sub>2</sub> and Be<sub>2</sub>



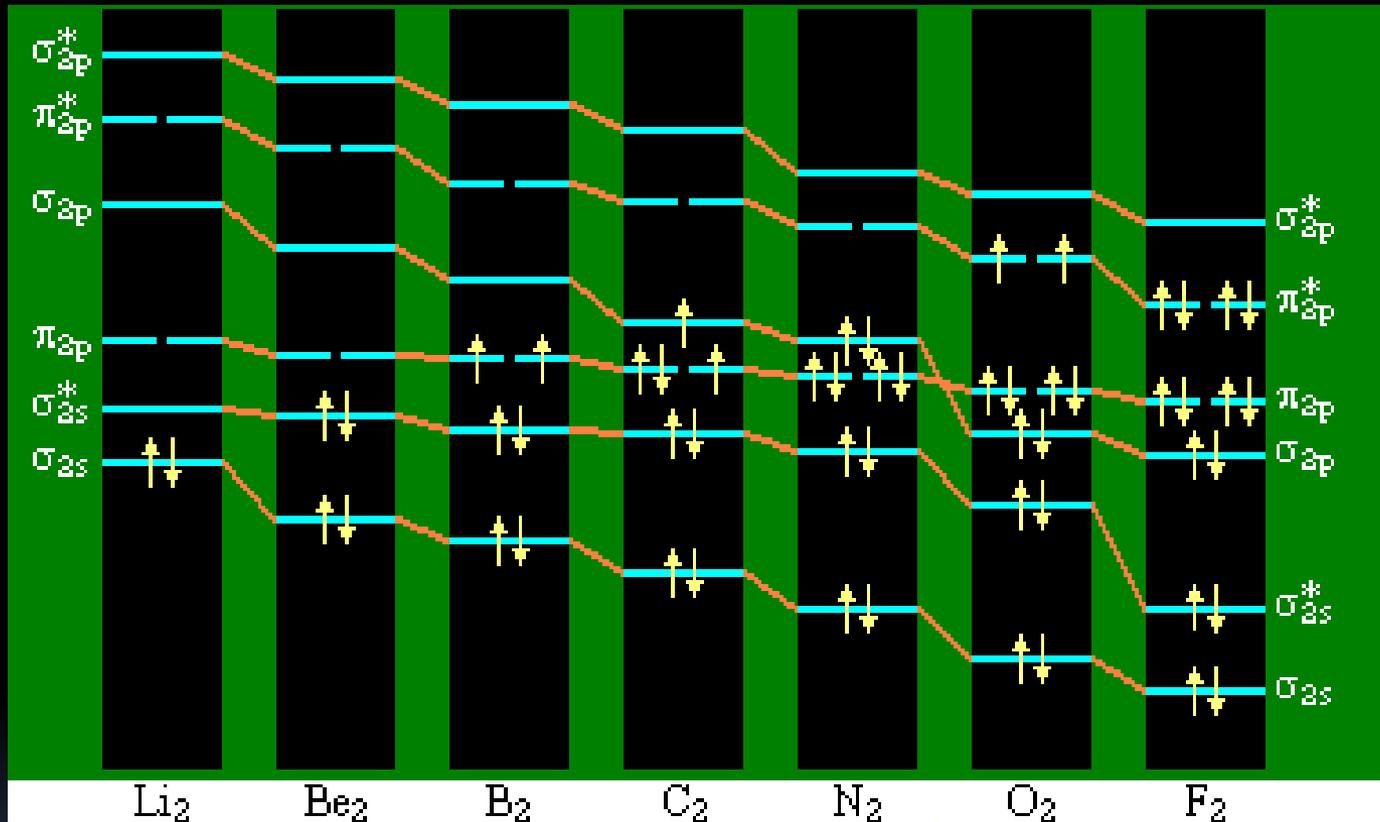
## Ground State Electron Configuration in MO



# 2<sup>nd</sup> Period Homonuclear Molecules

Molecules	Electron configuration	Bond order	Bond length (pm)	Bond energy (kJ·mol <sup>-1</sup> )
Li <sub>2</sub>	KK (σ <sub>2s</sub> ) <sup>2</sup>	1	267	108
Be <sub>2</sub>	KK (σ <sub>2s</sub> ) <sup>2</sup> (σ <sub>2s</sub> <sup>*</sup> ) <sup>2</sup>	0	245	9
B <sub>2</sub>	KK (σ <sub>2s</sub> ) <sup>2</sup> (σ <sub>2s</sub> <sup>*</sup> ) <sup>2</sup> (π <sub>2p</sub> ) <sup>2</sup>	1	159	289
C <sub>2</sub>	KK (σ <sub>2s</sub> ) <sup>2</sup> (σ <sub>2s</sub> <sup>*</sup> ) <sup>2</sup> (π <sub>2p</sub> ) <sup>4</sup>	2	124	599
N <sub>2</sub>	KK (σ <sub>2s</sub> ) <sup>2</sup> (σ <sub>2s</sub> <sup>*</sup> ) <sup>2</sup> (π <sub>2p</sub> ) <sup>4</sup> (σ <sub>2p</sub> ) <sup>2</sup>	3	110	942
O <sub>2</sub>	KK (σ <sub>2s</sub> ) <sup>2</sup> (σ <sub>2s</sub> <sup>*</sup> ) <sup>2</sup> (σ <sub>2p</sub> ) <sup>2</sup> (π <sub>2p</sub> ) <sup>4</sup> (π <sub>2p</sub> <sup>*</sup> ) <sup>2</sup>	2	121	494
F <sub>2</sub>	KK (σ <sub>2s</sub> ) <sup>2</sup> (σ <sub>2s</sub> <sup>*</sup> ) <sup>2</sup> (σ <sub>2p</sub> ) <sup>2</sup> (π <sub>2p</sub> ) <sup>4</sup> (π <sub>2p</sub> <sup>*</sup> ) <sup>4</sup>	1	141	154

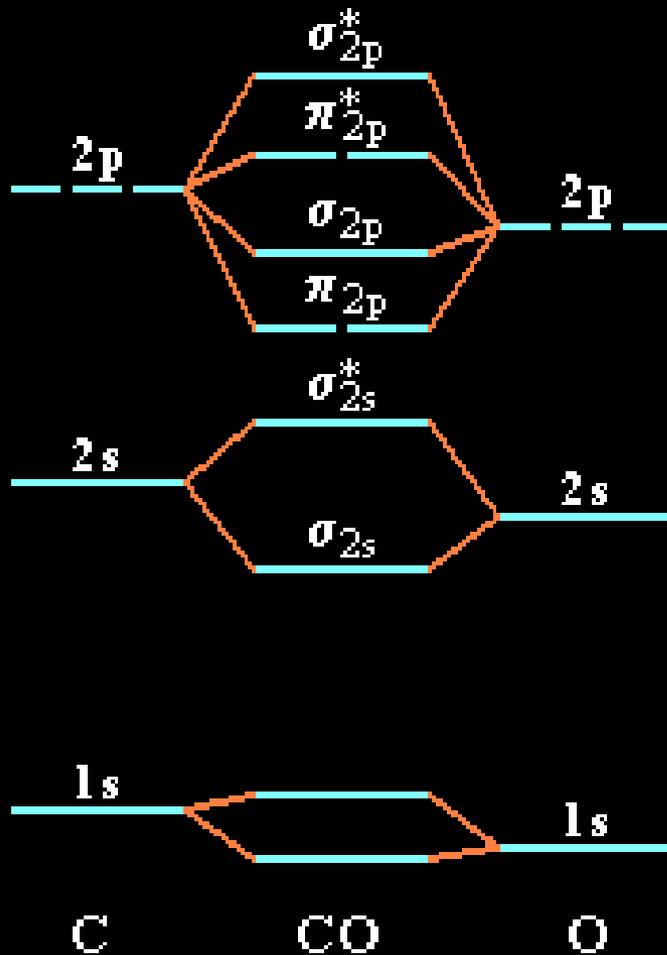
# MO Energy



Energy crossing between  $\sigma_{2p}$  and  $\pi_{2p}$  MOs

- Q: Among the molecules above, (1) Which one is the most stable? (2) Which ones have paramagnetism?

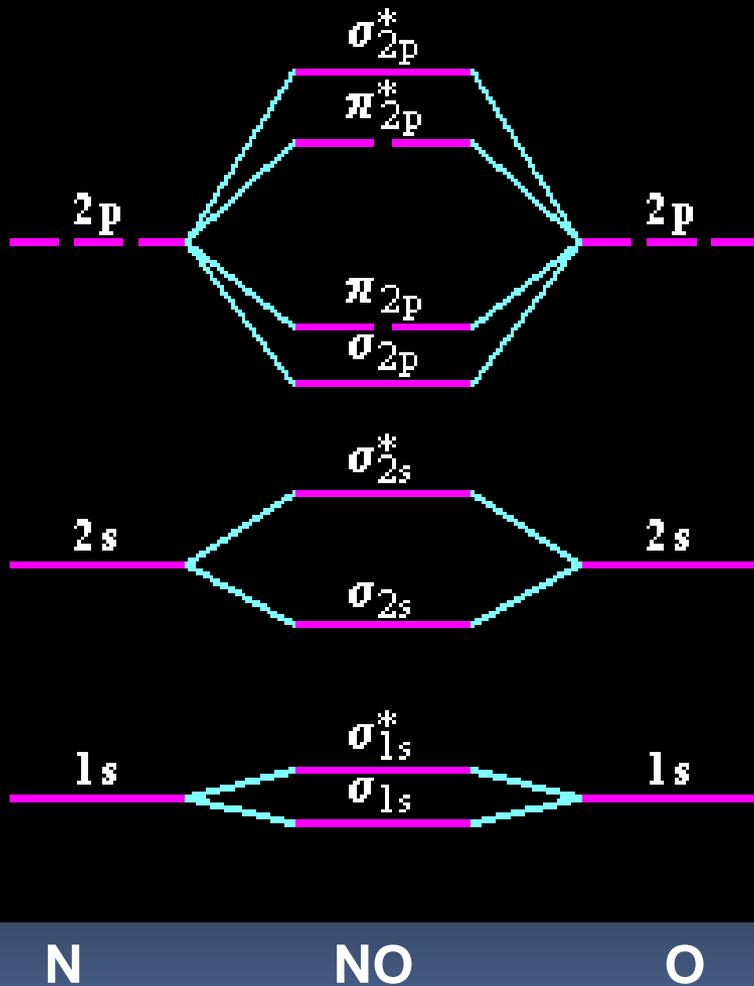
# Heteronuclear Diatomic Molecules



**CO (ground state):**



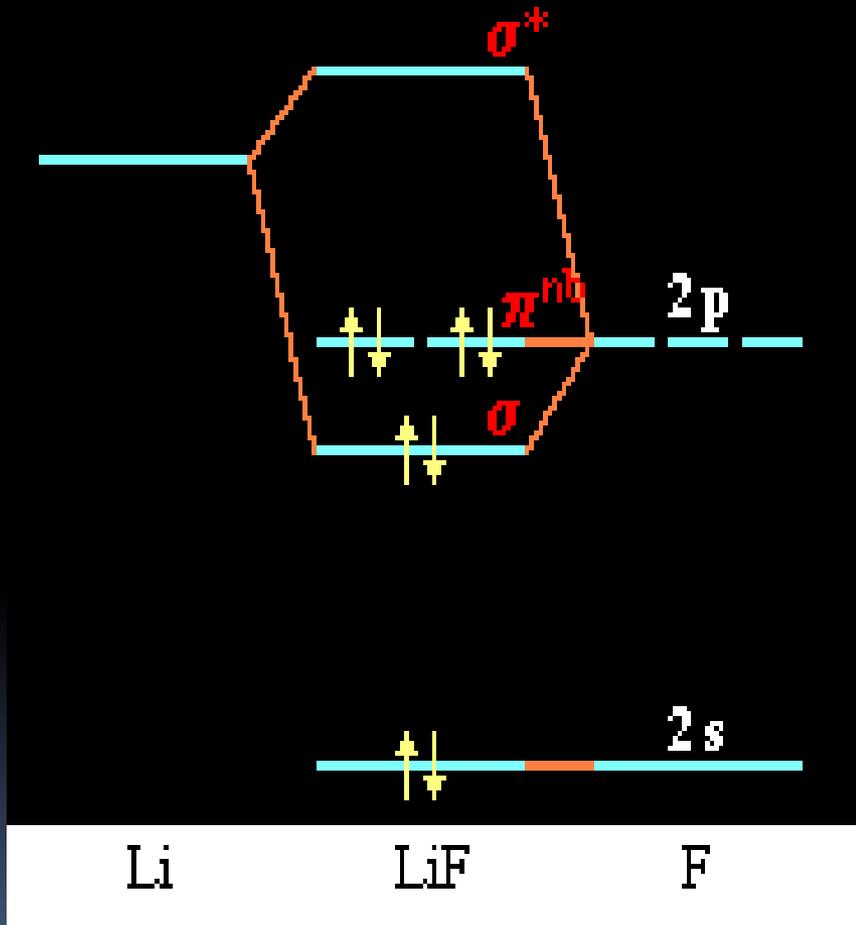
# Heteronuclear Diatomic Molecules



**NO (ground state):**



# Heteronuclear Diatomic Molecules

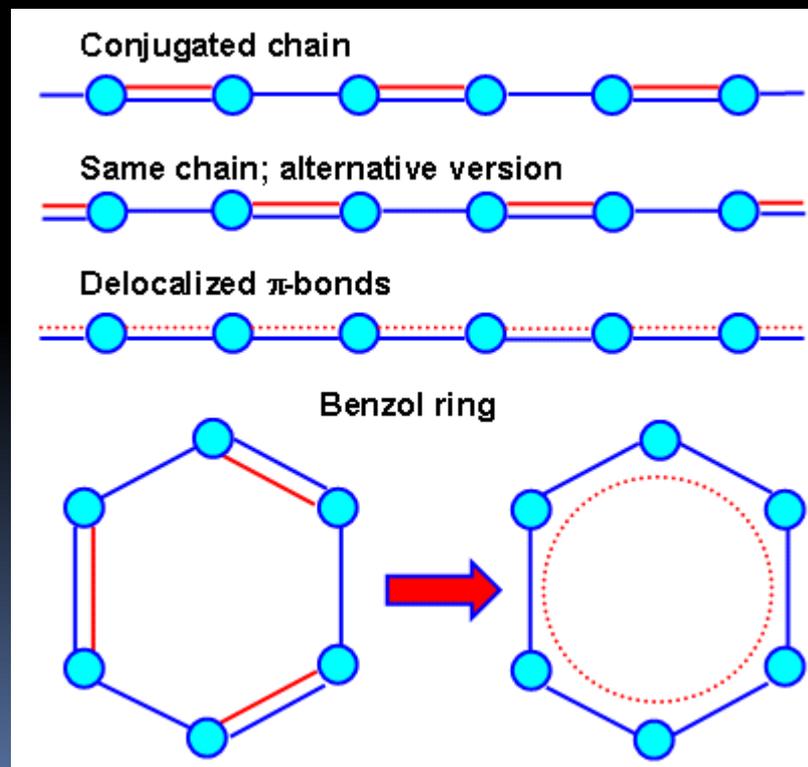


# Delocalization of Electrons

- Conjugated double bond: switching between single-bond and double bond.
- $\pi$ -bond electrons in the conjugated system are delocalized.

- Example:

- $C_6H_6$  (benzene)
- $CH_2=CH-CH=CH_2$



# Conjugated $\pi$ Bond

- Conjugated  $\pi$  bond molecules/ions:
  - All conjugated atoms are in a same plane, each giving a p-orbital to form the conjugated  $\pi$  bond;
  - Total  $\pi$  electron numbers  $< 2 * \text{p-orbitals}$
- $\Pi_n^m$  (formed by  $n$  p-orbitals and  $m$  p-electrons)
  - $m=n$ : Most of the organic conjugated molecules;
  - $m>n$ : double bond next to an atom with lone pair e (e.g. N, O, Cl, S)
  - $m<n$ : cations, e.g.  $(\text{CH}_2=\text{CH}-\text{CH}_3)^+$ ,  $(\text{C}_6\text{H}_5)_3\text{C}^+$

# Molecular Orbital Method

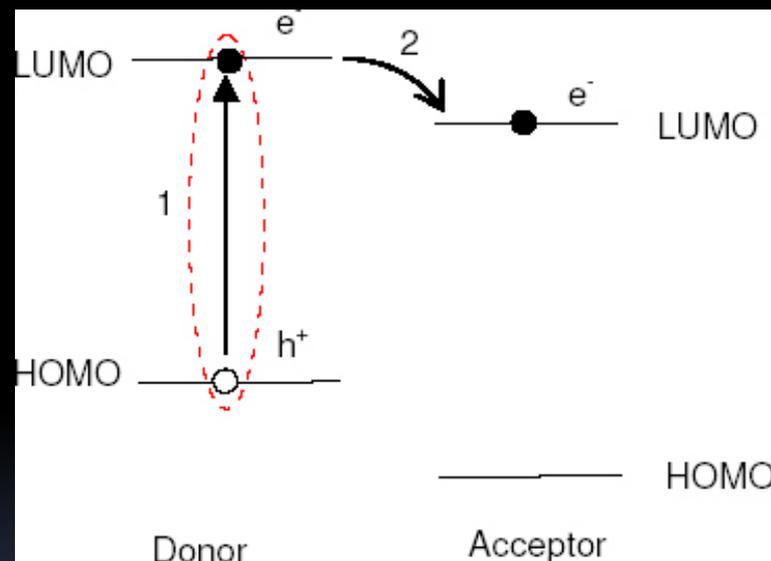
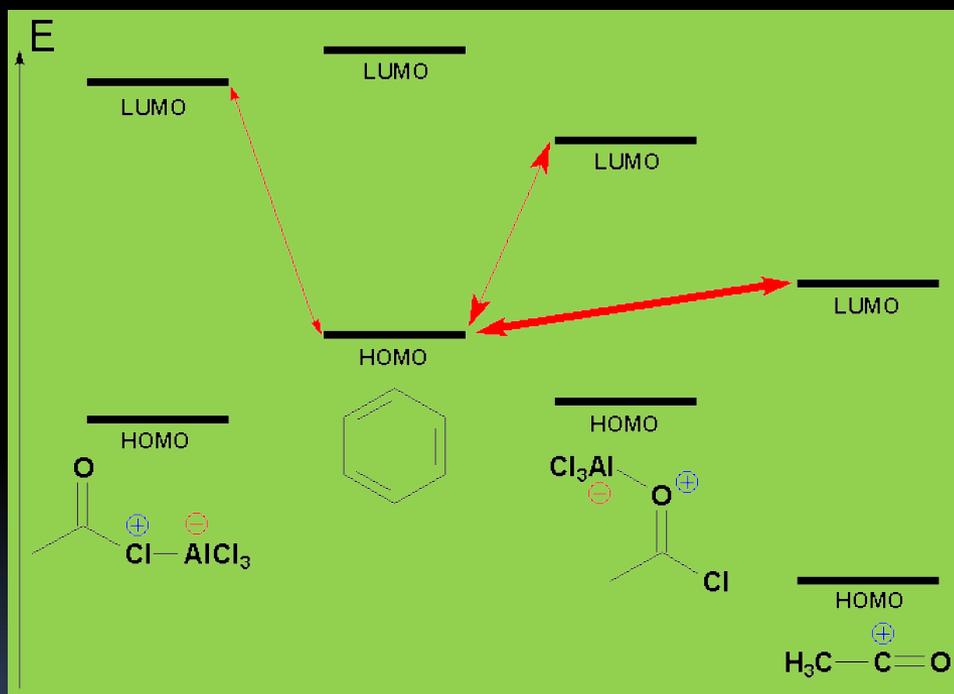
**Textbook, page 386, 10.90:**

For the compound  $\text{H}_2\text{C}=\text{CHCOOCH}_3$ ,

- (a) draw a complete structure;
- (b) How many pi-bonds and how many sigma bonds are in this molecule?
- (c) What hybridizations are applied for each carbon?
- (d) How many electrons are de-localized?
- (e) How many atoms lie in the same plane?
- (f) What are the bond angles between each bond?

# HOMO and LUMO

- HOMO: Highest Occupied Molecular Orbital
- LUMO: Lowest Unoccupied Molecular Orbital



- HOMO & LOMO are very useful in predicting chemical reactivity, optical/electrical properties.

# Band Theory of Bonding in Solids

- Changing from “Bond” to “Band”
  - In solid where huge number of atoms exist (& closely pack), discrete MOs become continuous bands.

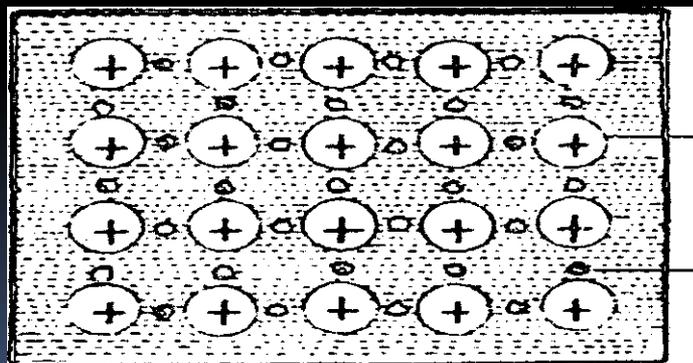
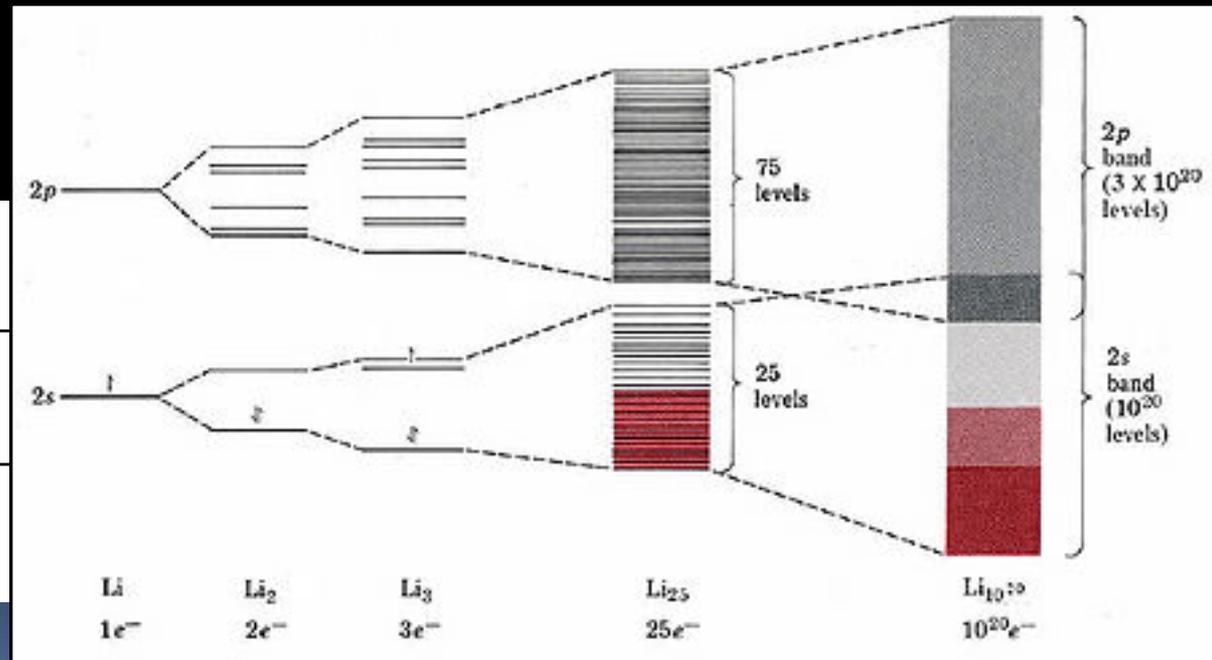
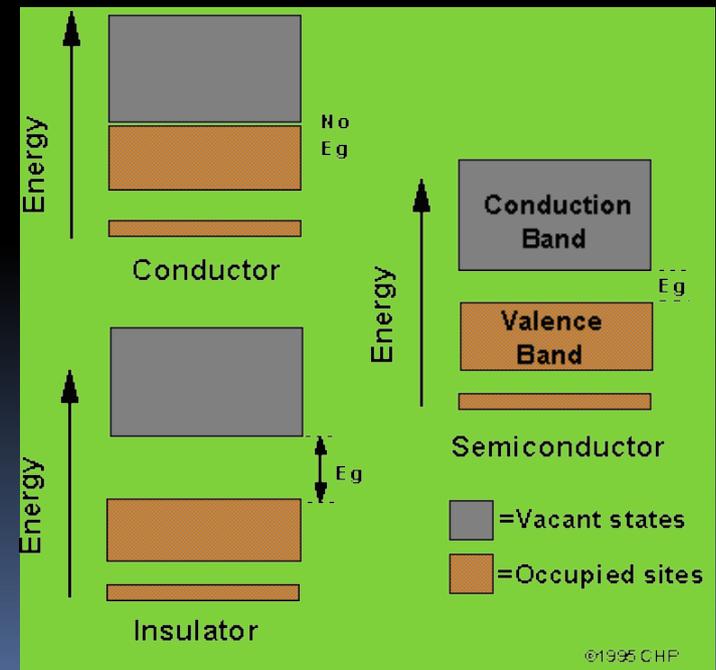
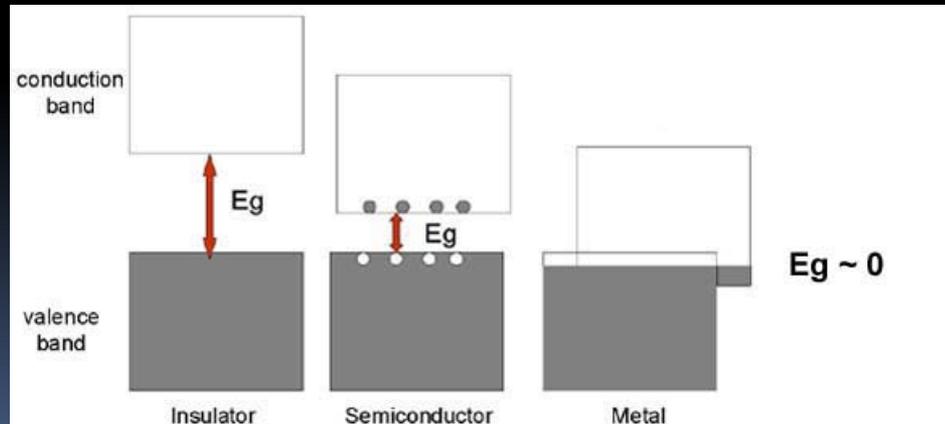


Fig. 6.9 Electron sea model for metals.



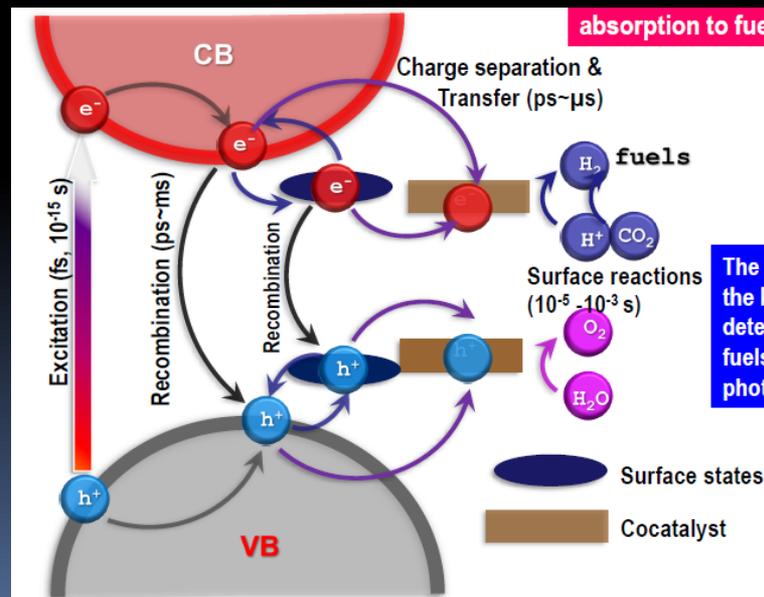
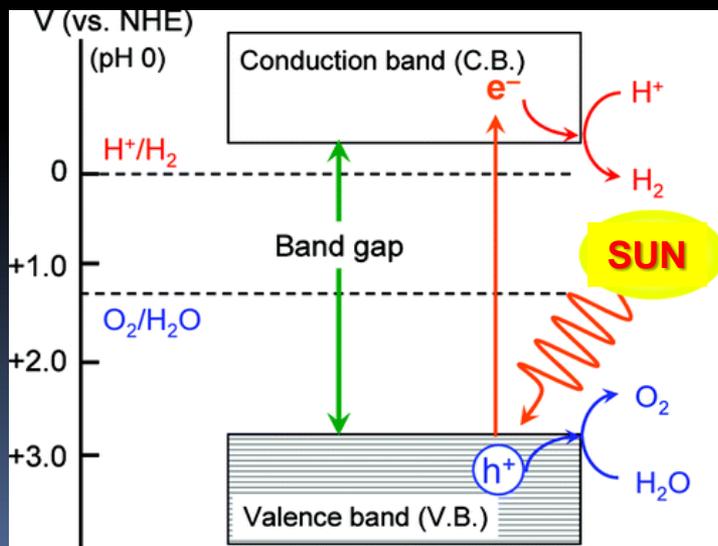
# Band Structures

- Valence Band (Bonding orbitals in MO)
- Conduction Band (Nonbonding orbitals in MO)
- Band gap ( $E_g$ )
- Fermi energy (in metal)



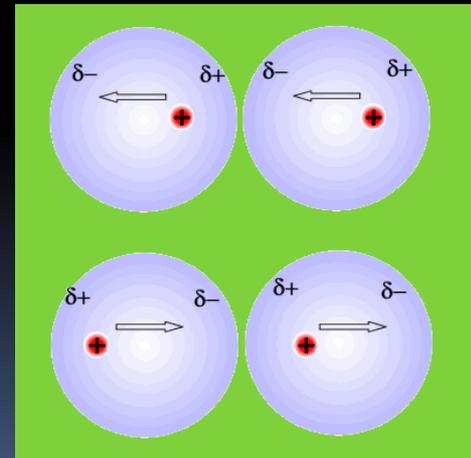
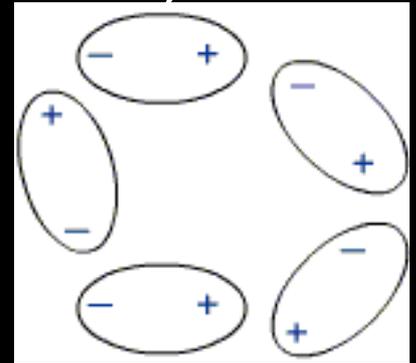
# Photoelectrochemical Water Splitting

- Photoelectrochemical (PEC) cells are solar cells which generate electrical energy from light. Each cell consists of a semiconducting photoanode and a metal counter electrode immersed in an electrolyte.
- These semiconductors can drive the hydrogen and oxygen evolution using electrons/holes generated under solar illumination.



# van der Waals Interaction

- Weak interaction: 10-100 times lower energy than chemical bonds (2-20 kJ/mol)
  - Dipole-dipole interaction
  - Dipole-induced dipole interaction
  - Induced dipole-induced dipole
    - Higher MW (or larger molecule) → higher induced-induced interaction



# van der Waals Interaction

	<b>Polar</b>	<b>Polar &amp; Nonpolar</b>	<b>Nonpolar</b>
<b>Dipole-Dipole</b>	✓	×	×
<b>Dipole-Induced</b>	✓	✓	×
<b>Induced-Induced</b>	✓	✓	✓

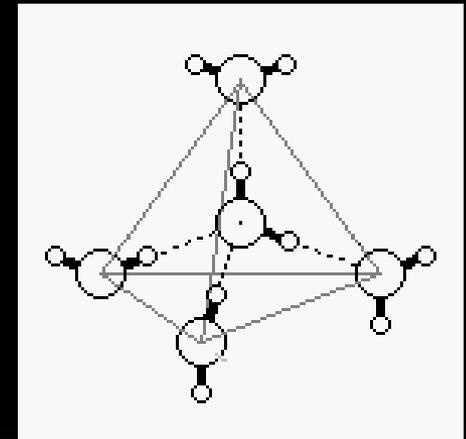
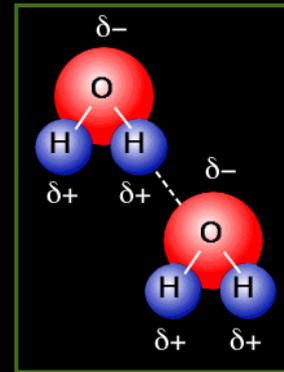
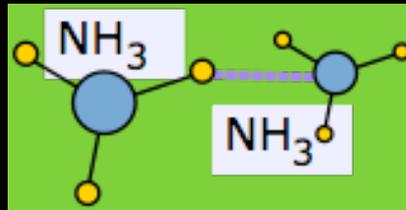
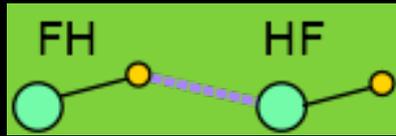
- Energy: Dipole-dipole > Dipole-Induced > Induced-Induced

# Hydrogen Bond

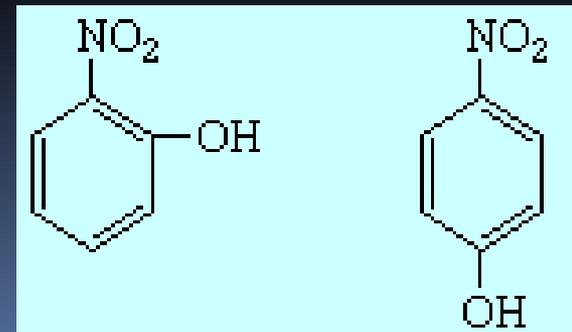
- Hydrogen Bond
  - consisting of a hydrogen atom between two high electronegative atoms (e.g., N, O, F), with one side being a covalent bond and the other being an electronic interaction
  - Bond energy:
    - Chemical bond (100—600 kJ/mol)
    - Hydrogen bond (20—40 kJ/mol)
    - van der Waals interaction (2-20 kJ/mol)

# Hydrogen Bond

- Examples:
  - Intermolecule Hydrogen bond
    - e.g.  $\text{H}_2\text{O}$ ,  $\text{NH}_3$ ,  $\text{HF}$ ,



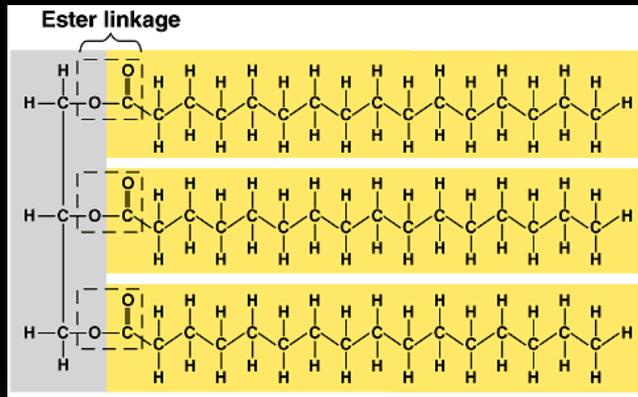
- Intramolecule Hydrogen bond
  - e.g. DNA, proteins



# Hydrophobic & Hydrophilic Groups

- Hydrophobic (oil-like)

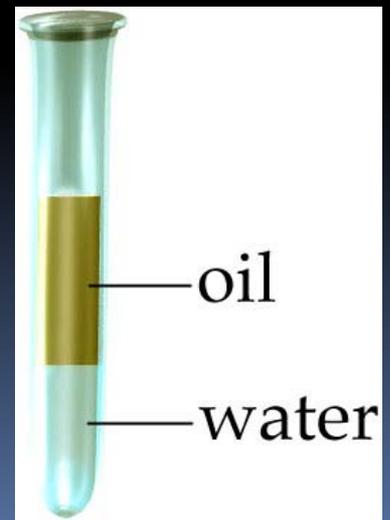
- Only containing non-polar or weakly polar groups, e.g. nonpolar molecules, CH chains/rings, ...



**fat molecule**

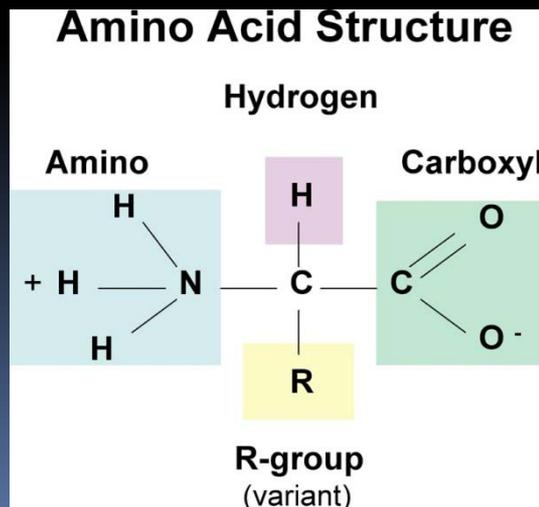
- Hydrophilic (water-like)

- Containing highly polar group(s), e.g.  $-\text{OH}$ ,  $-\text{NH}_2$ ,  $-\text{COOH}$ ,  $-\text{X}$  ( $\text{X} = \text{F}, \text{Cl}, \text{Br}, \text{I}$ ),  $-\text{SH}$ , ...



# Protein Structure – Amino Acids

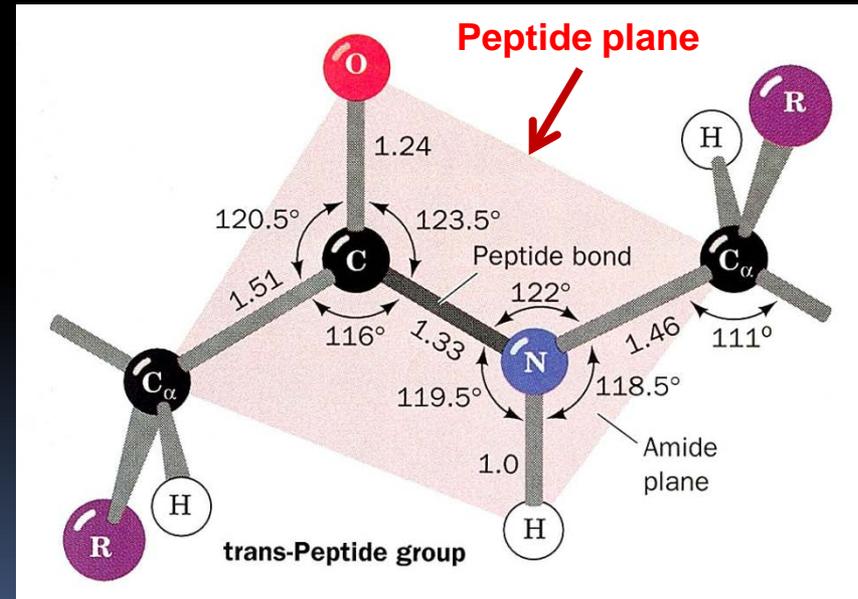
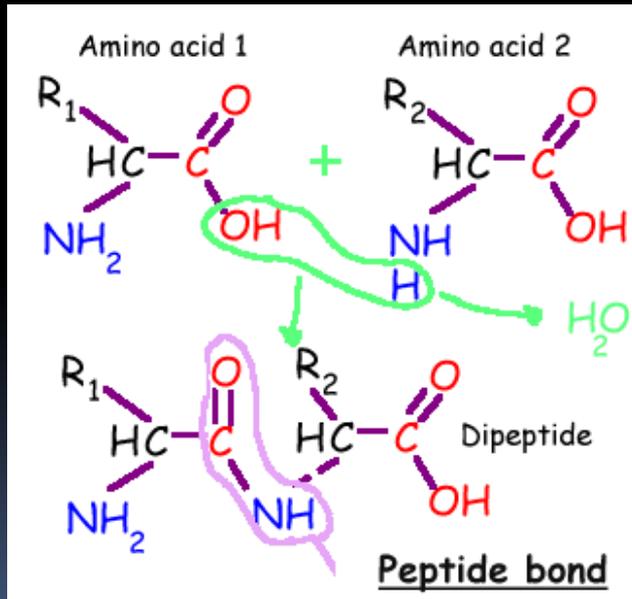
- Amino Acids
  - Amino acids have a –COOH and a –NH<sub>2</sub> in the same C atom;
  - Isoelectric point (pI)



	NONPOLAR, HYDROPHOBIC	R GROUPS	POLAR, UNCHARGED	
Alanine Ala A MW = 89	$\begin{matrix} ^- \text{OOC} \\   \\ \text{H}_3\text{N}^+ - \text{CH} - \text{CH}_3 \end{matrix}$		$\begin{matrix} \text{H} - \text{CH} - \text{COO}^- \\   \\ \text{N} \text{H}_3^+ \end{matrix}$	Glycine Gly G MW = 75
Valine Val V MW = 117	$\begin{matrix} ^- \text{OOC} \\   \\ \text{H}_3\text{N}^+ - \text{CH} - \text{CH} \begin{matrix} / \text{CH}_3 \\ \backslash \text{CH}_3 \end{matrix} \end{matrix}$		$\begin{matrix} \text{HO} - \text{CH}_2 - \text{CH} - \text{COO}^- \\   \\ \text{N} \text{H}_3^+ \end{matrix}$	Serine Ser S MW = 105
Leucine Leu L MW = 131	$\begin{matrix} ^- \text{OOC} \\   \\ \text{H}_3\text{N}^+ - \text{CH} - \text{CH}_2 - \text{CH} \begin{matrix} / \text{CH}_3 \\ \backslash \text{CH}_3 \end{matrix} \end{matrix}$		$\begin{matrix} \text{OH} \\   \\ \text{CH} - \text{CH} - \text{COO}^- \\   \\ \text{CH}_3 \quad \text{N} \text{H}_3^+ \end{matrix}$	Threonine Thr T MW = 119
Isoleucine Ile I MW = 131	$\begin{matrix} ^- \text{OOC} \\   \\ \text{H}_3\text{N}^+ - \text{CH} - \text{CH} \begin{matrix} / \text{CH}_3 \\ \backslash \text{CH}_2 - \text{CH}_3 \end{matrix} \end{matrix}$		$\begin{matrix} \text{HS} - \text{CH}_2 - \text{CH} - \text{COO}^- \\   \\ \text{N} \text{H}_3^+ \end{matrix}$	Cysteine Cys C MW = 121
Phenylalanine Phe F MW = 131	$\begin{matrix} ^- \text{OOC} \\   \\ \text{H}_3\text{N}^+ - \text{CH} - \text{CH}_2 - \text{C}_6\text{H}_5 \end{matrix}$		$\begin{matrix} \text{HO} - \text{C}_6\text{H}_4 - \text{CH}_2 - \text{CH} - \text{COO}^- \\   \\ \text{N} \text{H}_3^+ \end{matrix}$	Tyrosine Tyr Y MW = 181
Tryptophan Trp W MW = 204	$\begin{matrix} ^- \text{OOC} \\   \\ \text{H}_3\text{N}^+ - \text{CH} - \text{CH}_2 - \text{C}_8\text{H}_6\text{N}_2 \end{matrix}$		$\begin{matrix} \text{NH}_2 \\   \\ \text{C} = \text{O} - \text{CH}_2 - \text{CH} - \text{COO}^- \\   \\ \text{N} \text{H}_3^+ \end{matrix}$	Asparagine Asn N MW = 132
Methionine Met M MW = 149	$\begin{matrix} ^- \text{OOC} \\   \\ \text{H}_3\text{N}^+ - \text{CH} - \text{CH}_2 - \text{CH}_2 - \text{S} - \text{CH}_3 \end{matrix}$		$\begin{matrix} \text{NH}_2 \\   \\ \text{C} = \text{O} - \text{CH}_2 - \text{CH}_2 - \text{CH} - \text{COO}^- \\   \\ \text{N} \text{H}_3^+ \end{matrix}$	Glutamine Gln Q MW = 146
Proline Pro P MW = 115	$\begin{matrix} ^- \text{OOC} \\   \\ \text{H}_3\text{N}^+ - \text{CH} - \text{CH}_2 - \text{CH}_2 \end{matrix}$		<b>POLAR BASIC</b> $\begin{matrix} + \text{NH}_3 - \text{CH}_2 - (\text{CH}_2)_3 - \text{CH} - \text{COO}^- \\   \\ \text{N} \text{H}_3^+ \end{matrix}$	Lysine Lys K MW = 146
Aspartic acid Asp D MW = 133	<b>POLAR ACIDIC</b> $\begin{matrix} ^- \text{OOC} \\   \\ \text{H}_3\text{N}^+ - \text{CH} - \text{CH}_2 - \text{C}(=\text{O})\text{O}^- \end{matrix}$		$\begin{matrix} \text{NH}_2 \\   \\ \text{C} = \text{N} - \text{H} - (\text{CH}_2)_3 - \text{CH} - \text{COO}^- \\   \\ \text{N} \text{H}_3^+ \end{matrix}$	Arginine Arg R MW = 174
Glutamic acid Glu E MW = 147	$\begin{matrix} ^- \text{OOC} \\   \\ \text{H}_3\text{N}^+ - \text{CH} - \text{CH}_2 - \text{CH}_2 - \text{C}(=\text{O})\text{O}^- \end{matrix}$		$\begin{matrix} \text{HN} \text{C}(\text{NH}_2) \text{CH}_2 - \text{CH} - \text{COO}^- \\   \\ \text{N} \text{H}_3^+ \end{matrix}$	Histidine His H MW = 155

# Protein Structure – Peptides

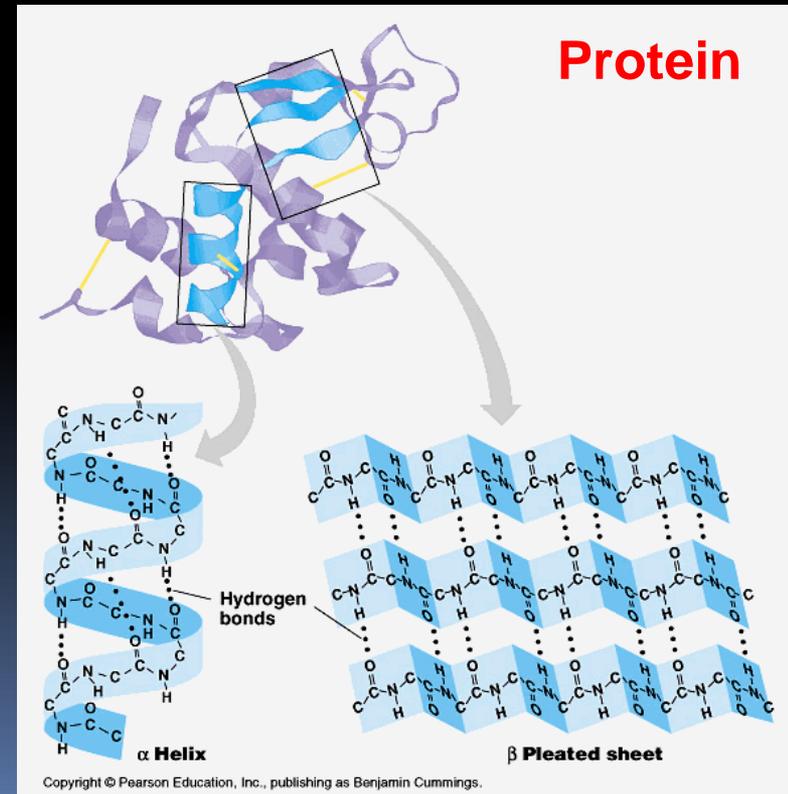
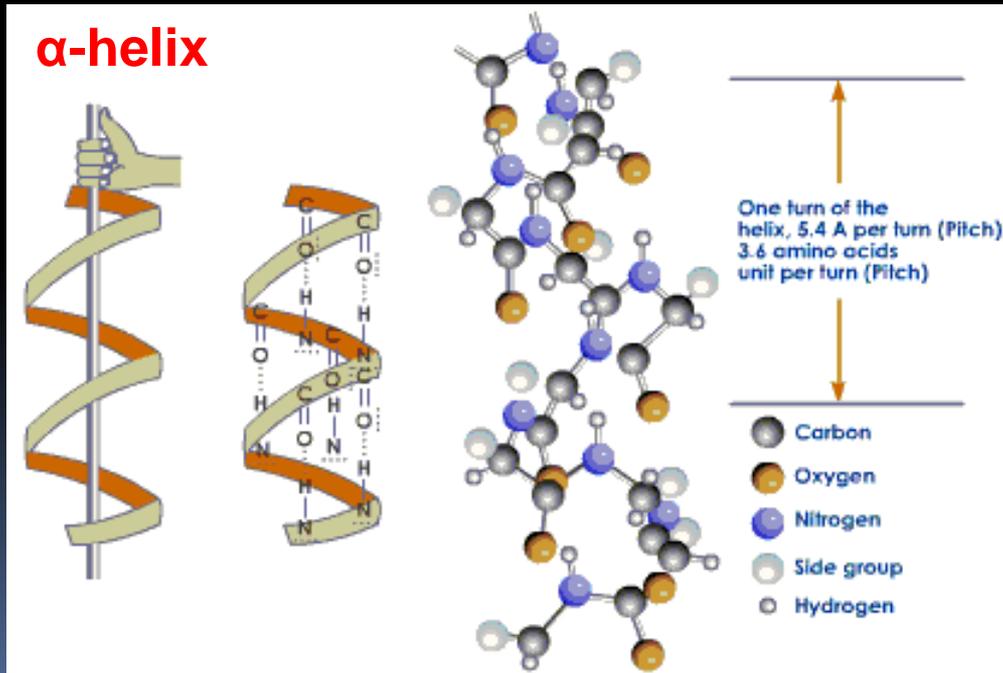
- Amino Acids → Peptides
  - A peptide bond is formed by linked a  $\text{-COOH}$  in one amino acid and a  $\text{-NH}_2$  in another amino acid.



- Recall: What is “peptide plane”? Why it is formed?

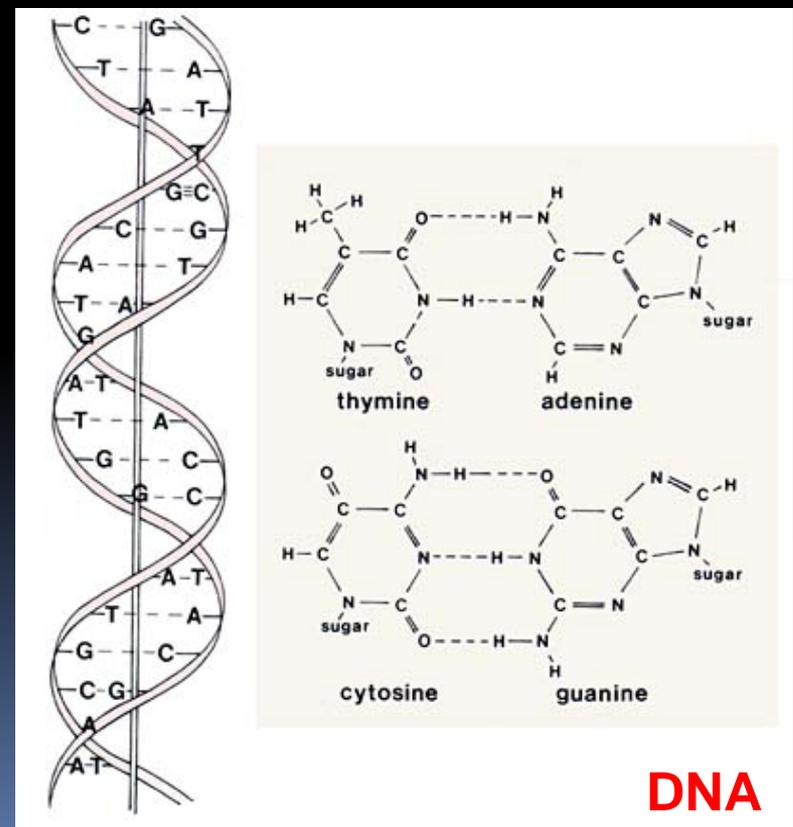
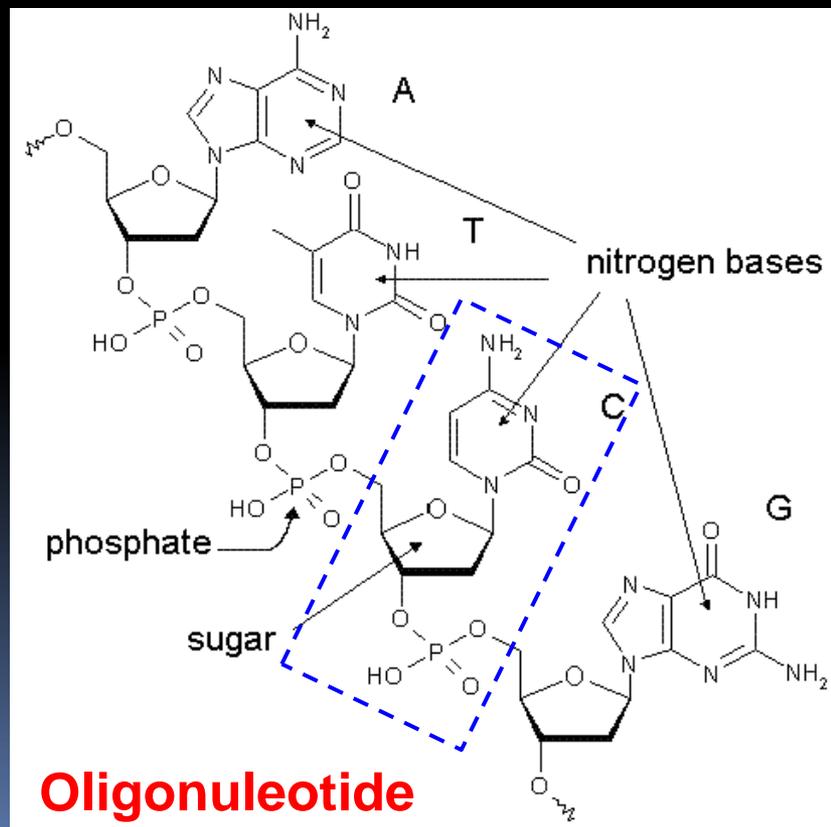
# Introduction of Proteins

- Amino Acids → Peptides → Proteins
  - A protein is formed of multiple peptide chains, via multiple interactions including hydrogen bond, hydrophobicity, etc.



# Oligonucleotide & DNA Structures

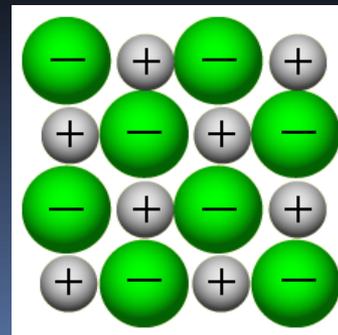
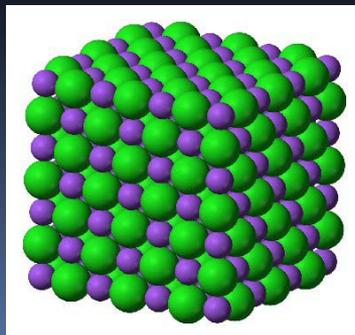
- Oligonucleotide:
  - including: phosphate group + sugar ring + base group
- DNA: formed by oligonucleotide linkage & interaction



# Types of Crystals

- Ionic Crystal

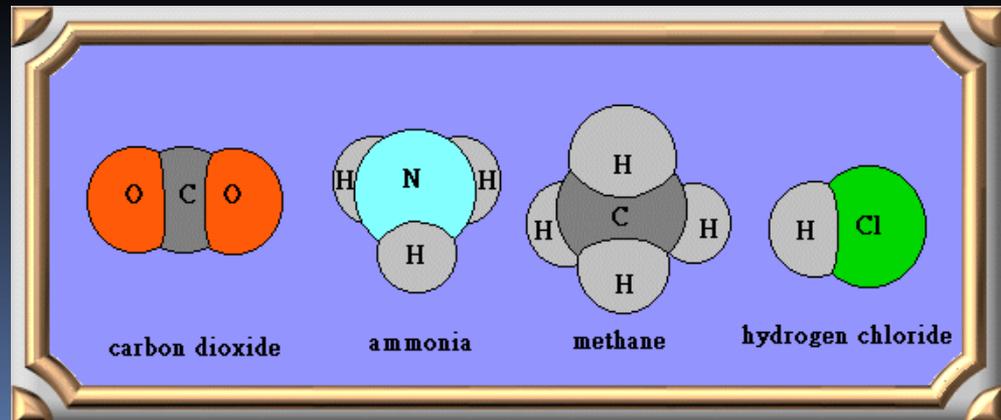
- Formed between an active metal and an active nonmetal elements
- e.g NaCl:  $\text{Na} \rightarrow \text{Na}^+ + \text{e}^-$ ,  $\text{Cl} + \text{e}^- \rightarrow \text{Cl}^-$
- Usually, high melting temperature, high boiling temperature; Hard.



# Types of Crystals

- Molecular Crystal

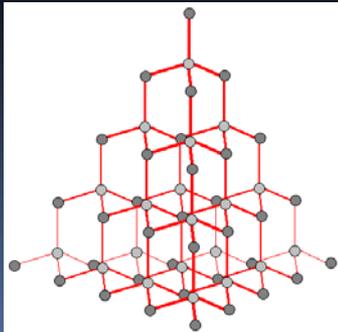
- Formed between one or more nonmetal elements.
- e.g.  $H_2$ ,  $HCl$ ,  $CO_2$ ,  $Ar$ ,  $H_2O$  ...
- Low melting temperature, low boiling temperature; soft.
- Melting, boiling temperatures depend on their intermolecule interaction (e.g. van de Waals' interaction, hydrogen bond)



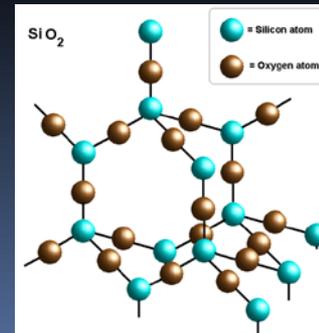
# Types of Crystals

- Atomic Crystal

- Formed between one or more IVA group elements, or with an IVA element and oxygen.
- e.g. C, Si, SiC, SiO<sub>2</sub> ...
- Extremely high melting and boiling temperature; Very hard.



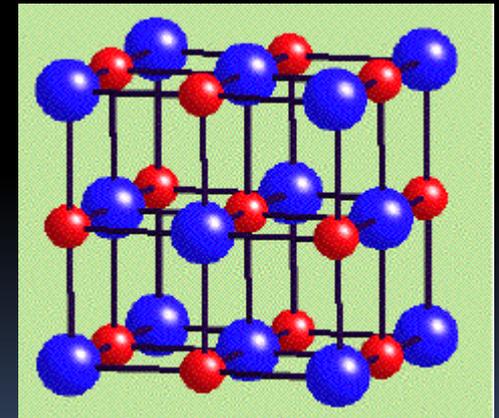
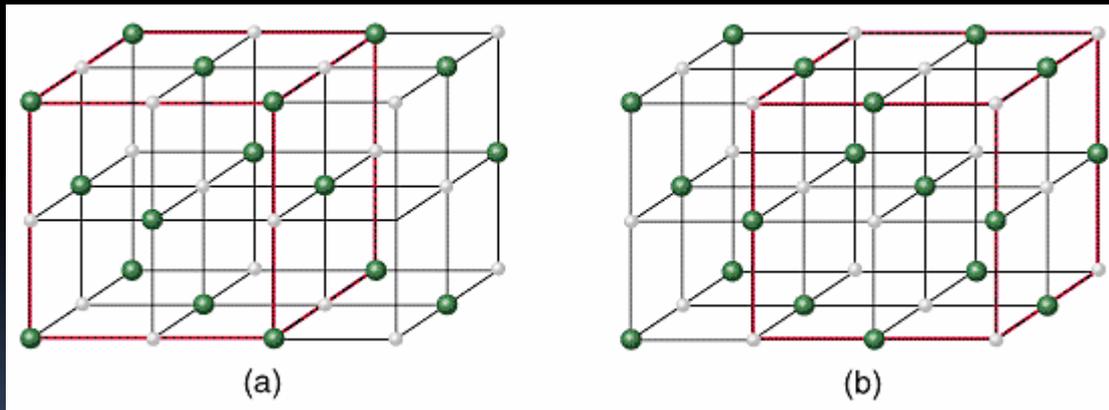
**Diamond (C)**



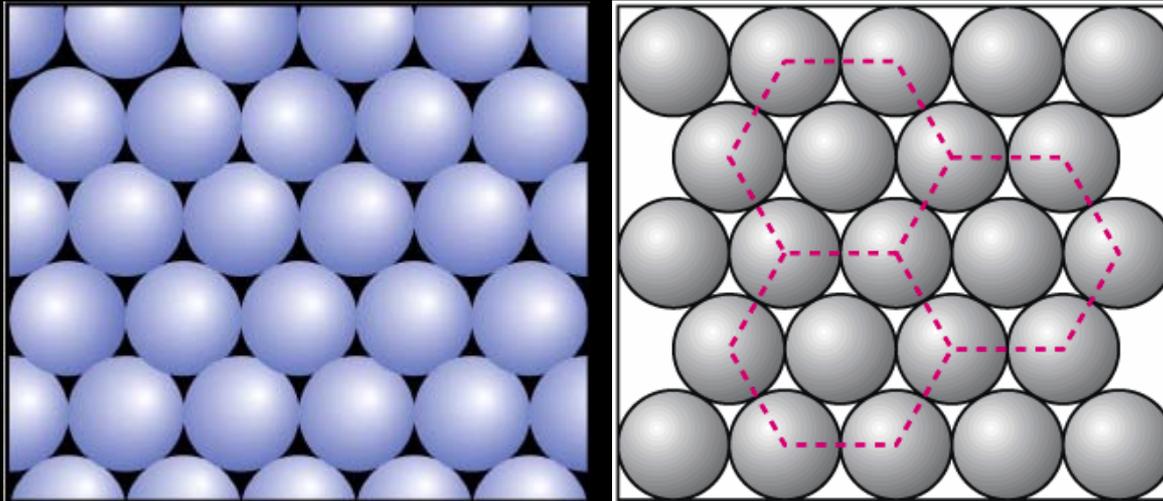
**Silicon dioxide**

# Unit Cell

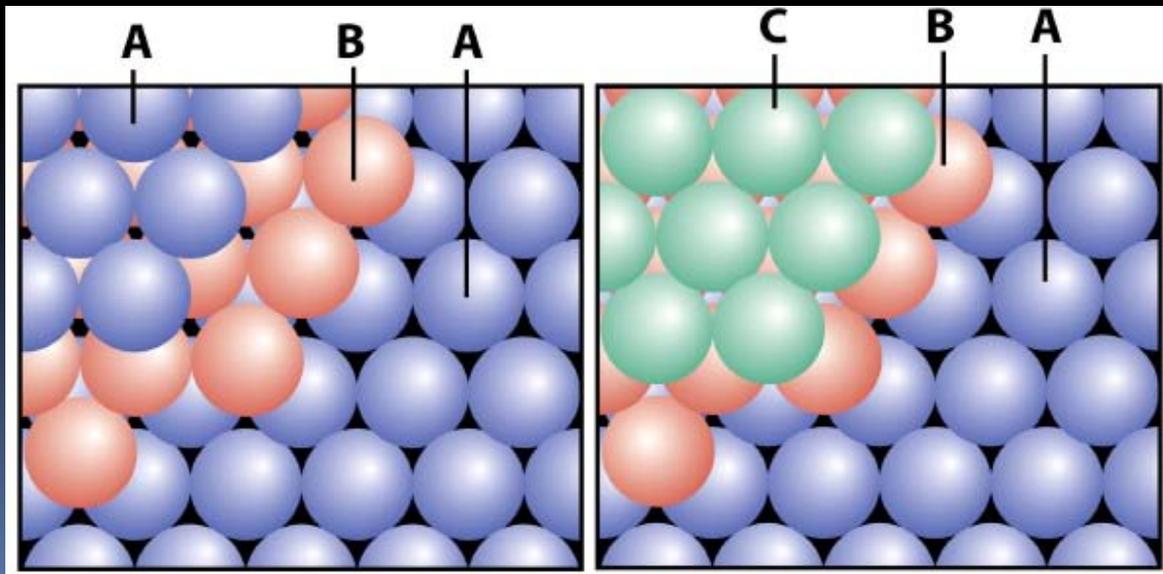
- An important concept in describing crystal structures.
- Reproduces the whole when stacked together repeatedly



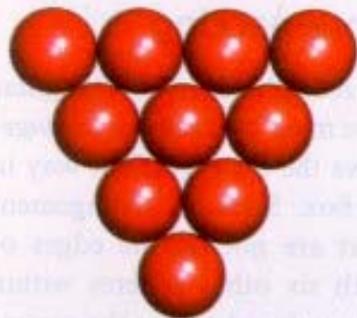
# The Close Packing of Spheres



## Two Major Types of Close Packing

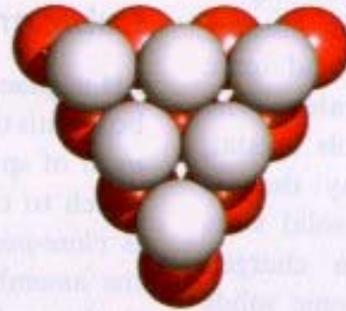


# Two Major Types of Close Packing



(a)

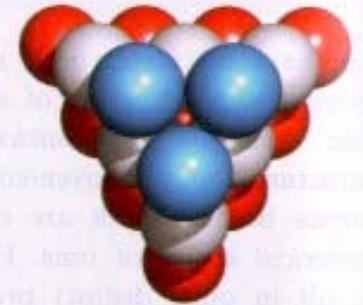
Place one sphere  
over every other  
hollow in layer A



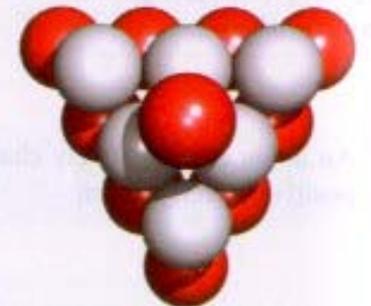
Layer B contains two  
different types of  
hollow (see text)

By placing spheres in  
one or other of these  
different hollows, two  
new layers of spheres  
can be produced.

(b)



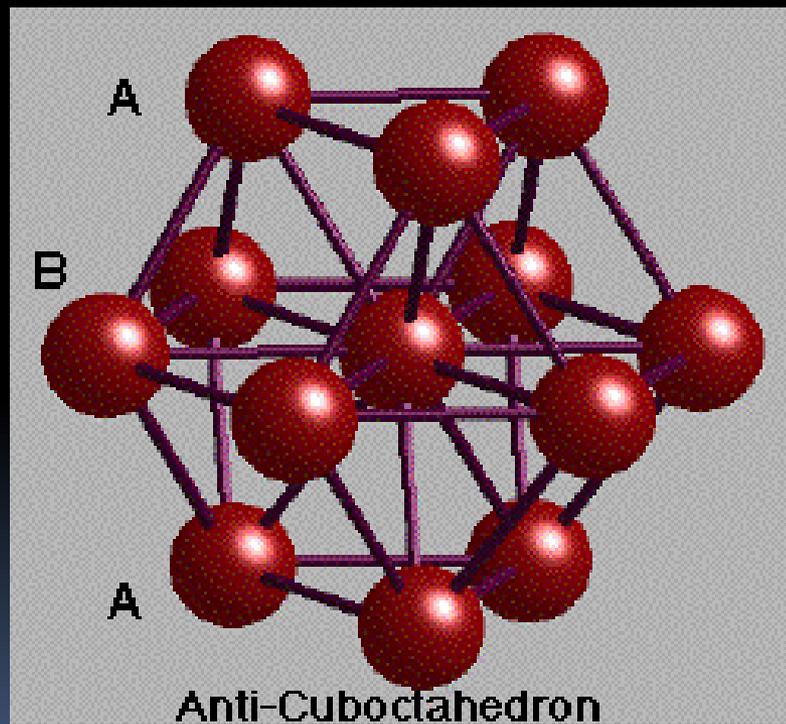
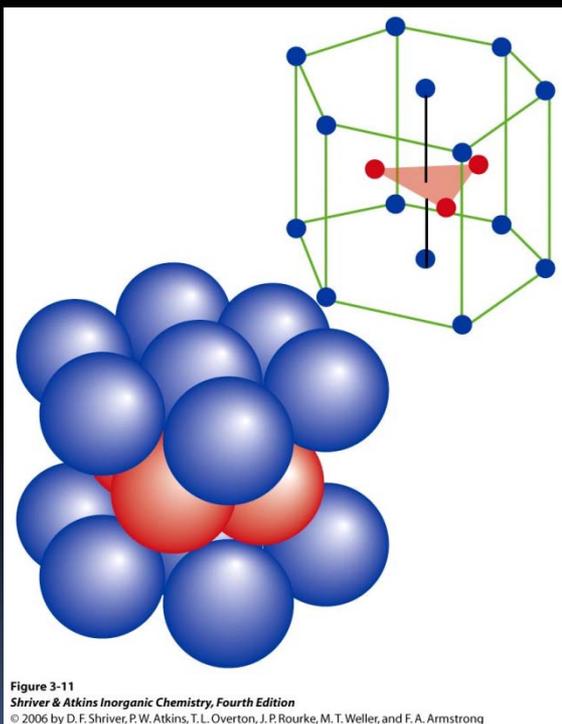
(c)



(d)

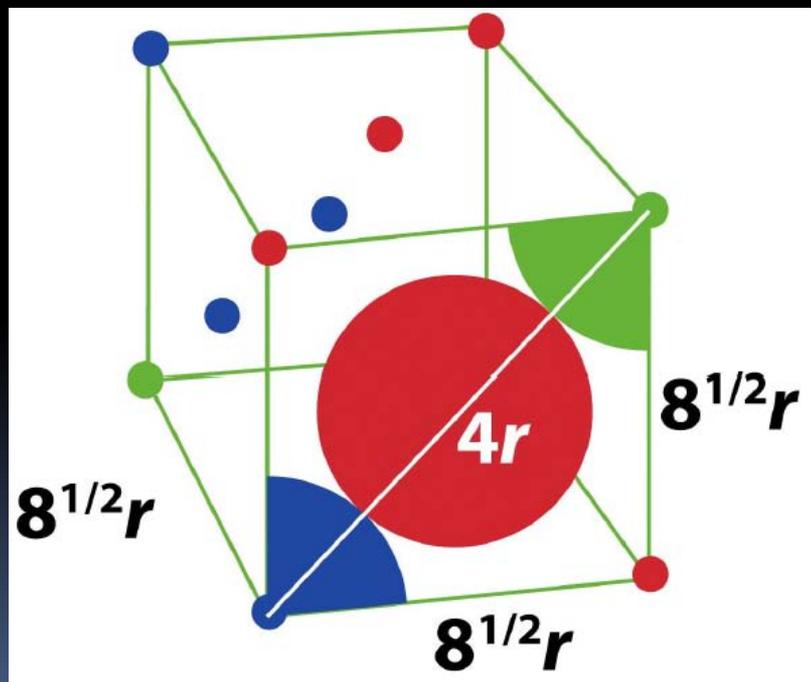
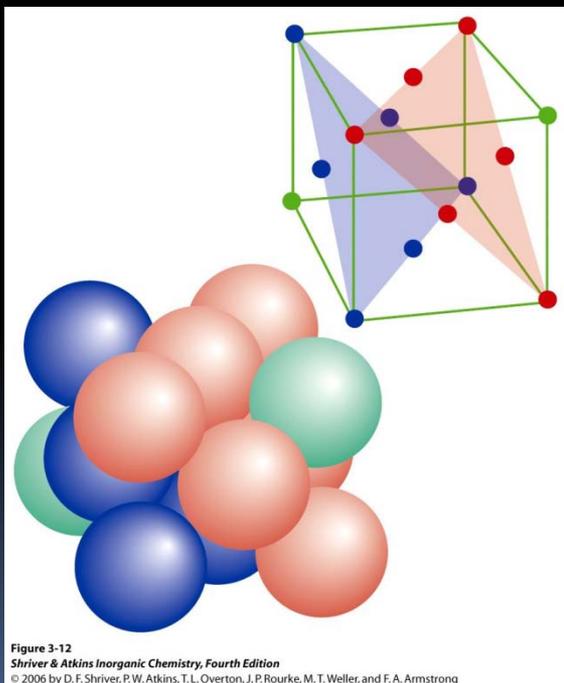
# Hexagonal Close Packing (hcp)

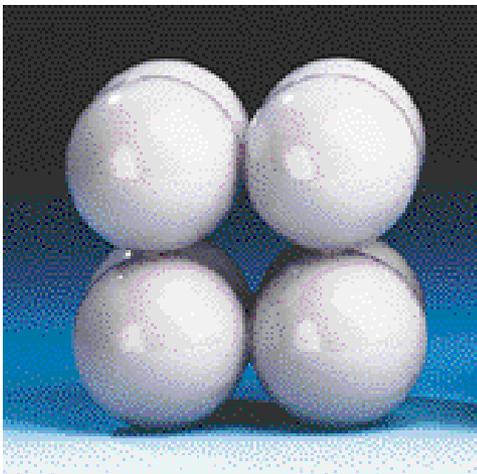
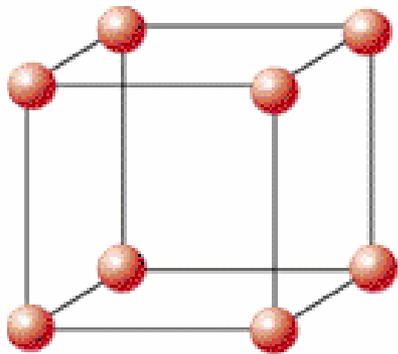
- Pattern: ABABAB...
- Number of balls in a unit cell = ?



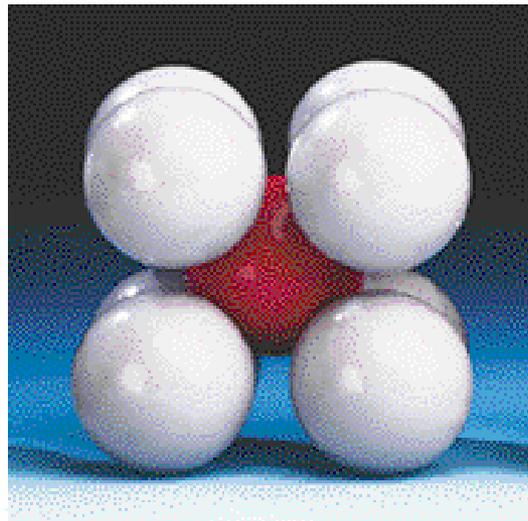
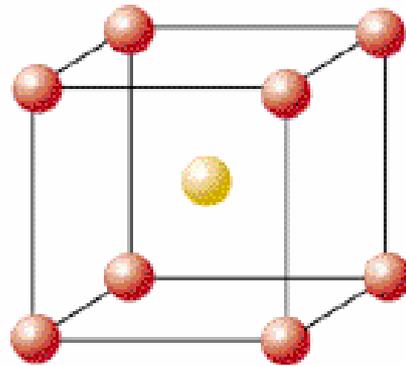
# Cubic Close Packing (ccp)

- Also called **face centered close packing (fcc)**
- Pattern: ABCABCABC...
- Number of balls in a unit cell = ?

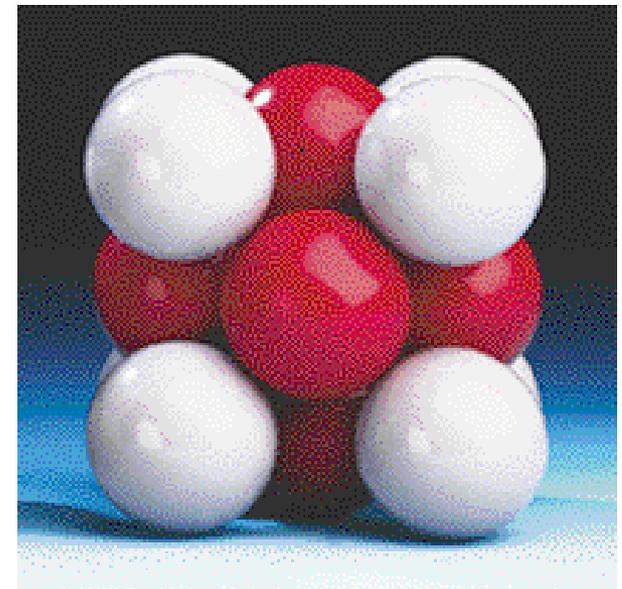
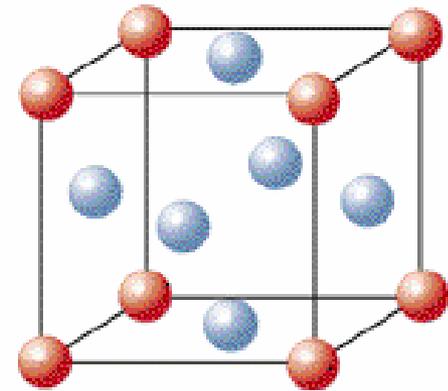




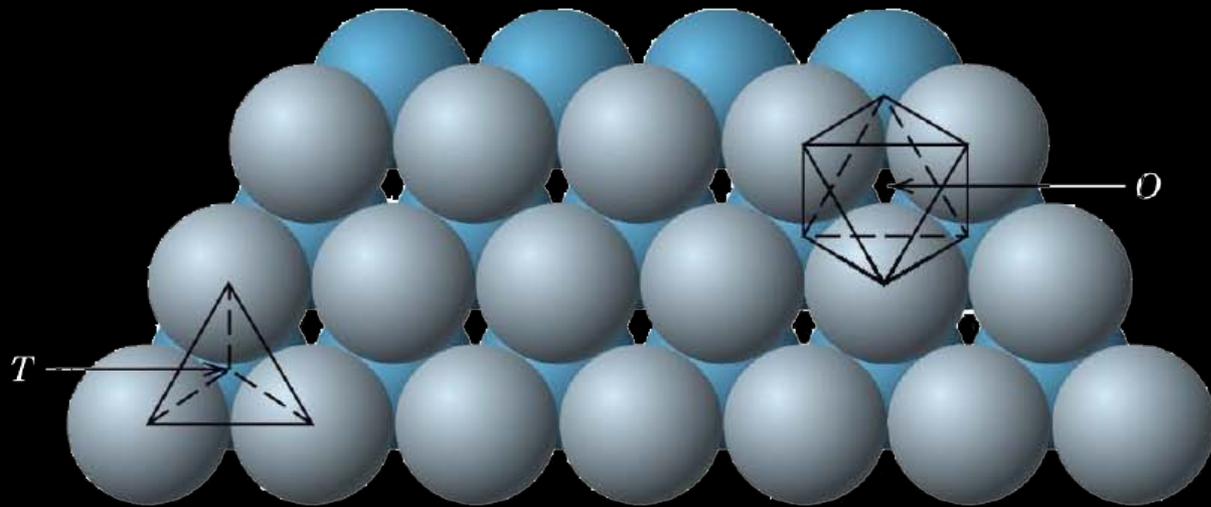
simple cubic



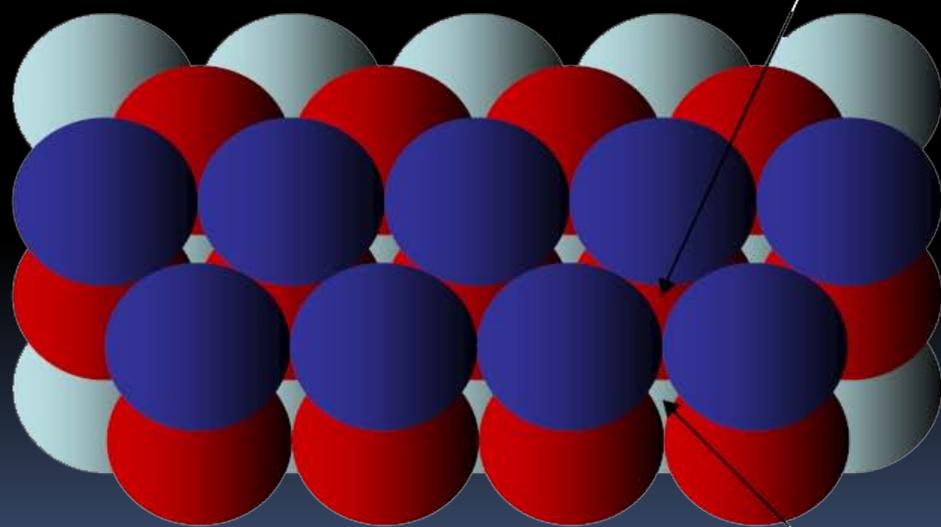
body-centered cubic



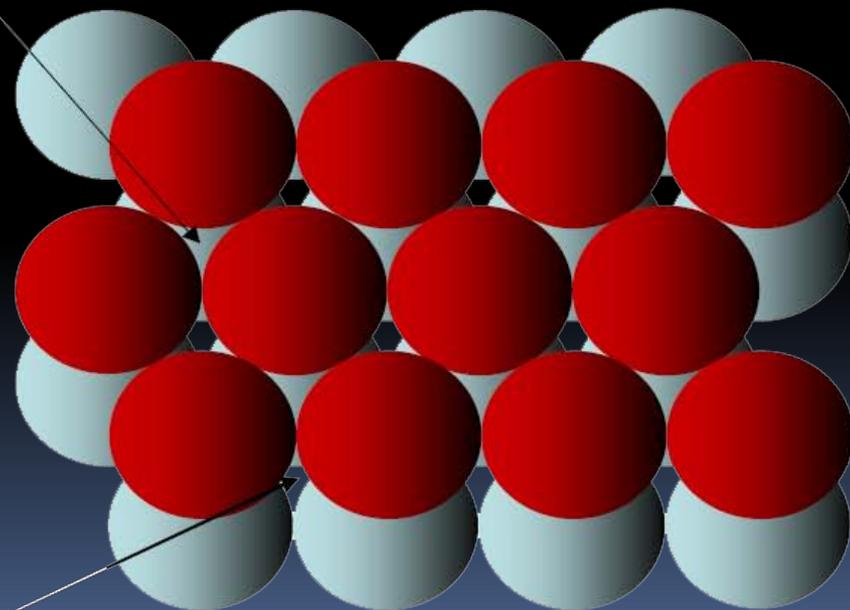
face-centered cubic



Tetrahedral site



**FCC**

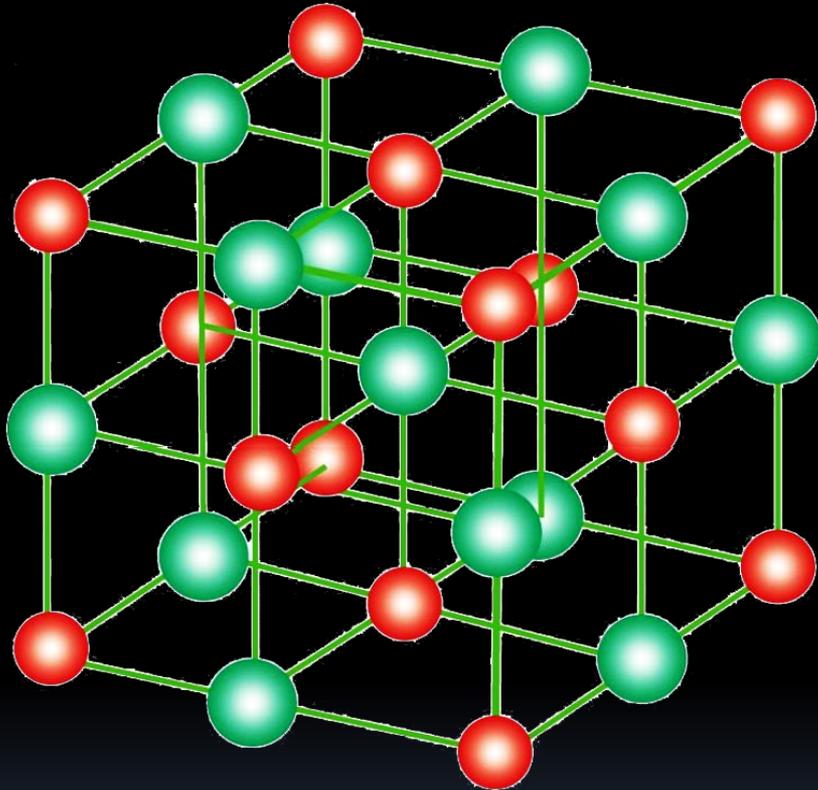


**HCP**

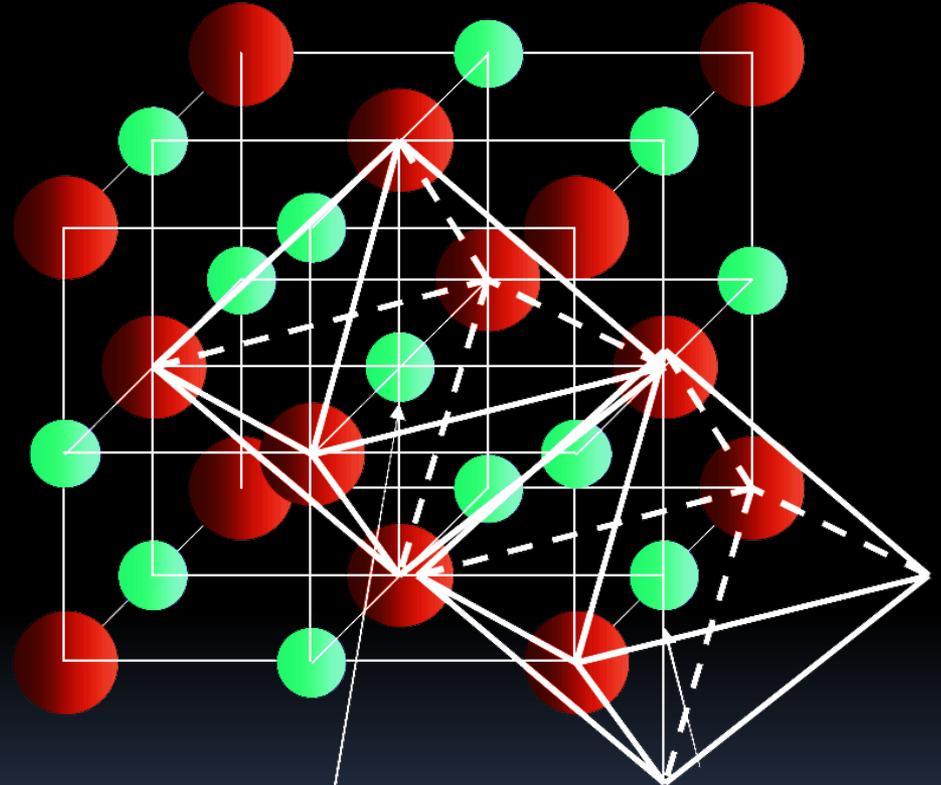
Octahedral site

# NaCl (MX) structure

Octahedral ( $O_h$ ) sites



**4 atoms per unit cell**

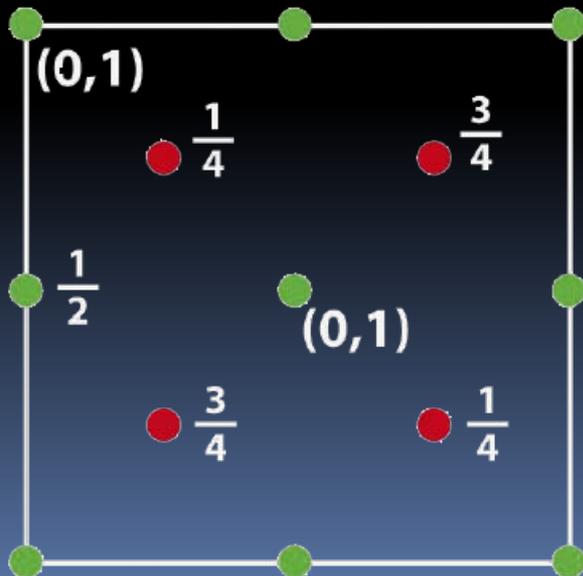
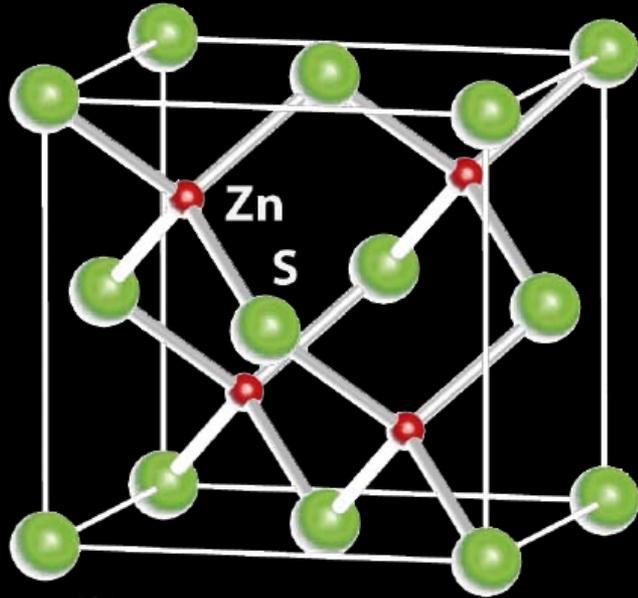


1 at the center

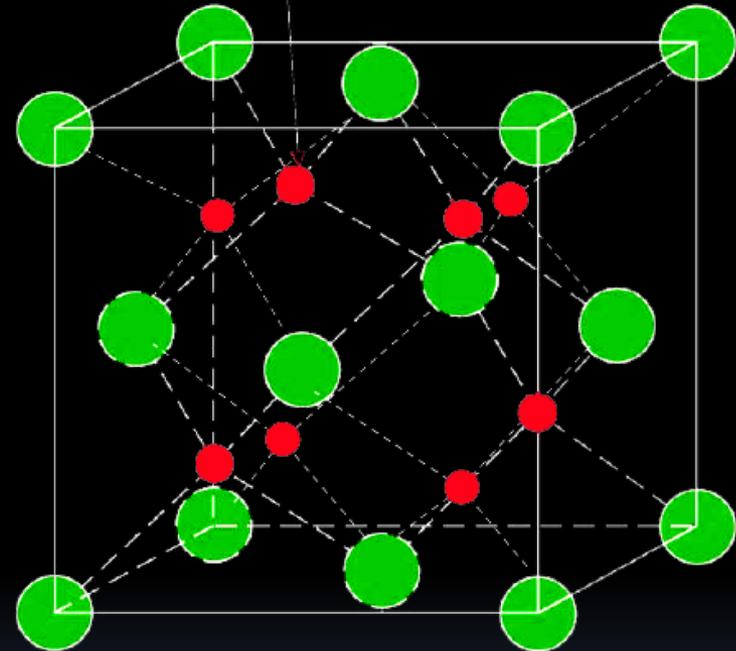
12 edge sites  
(each shared by 4 cells)

**Net 4  $O_h$  sites/unit cell**

# ZnS structure

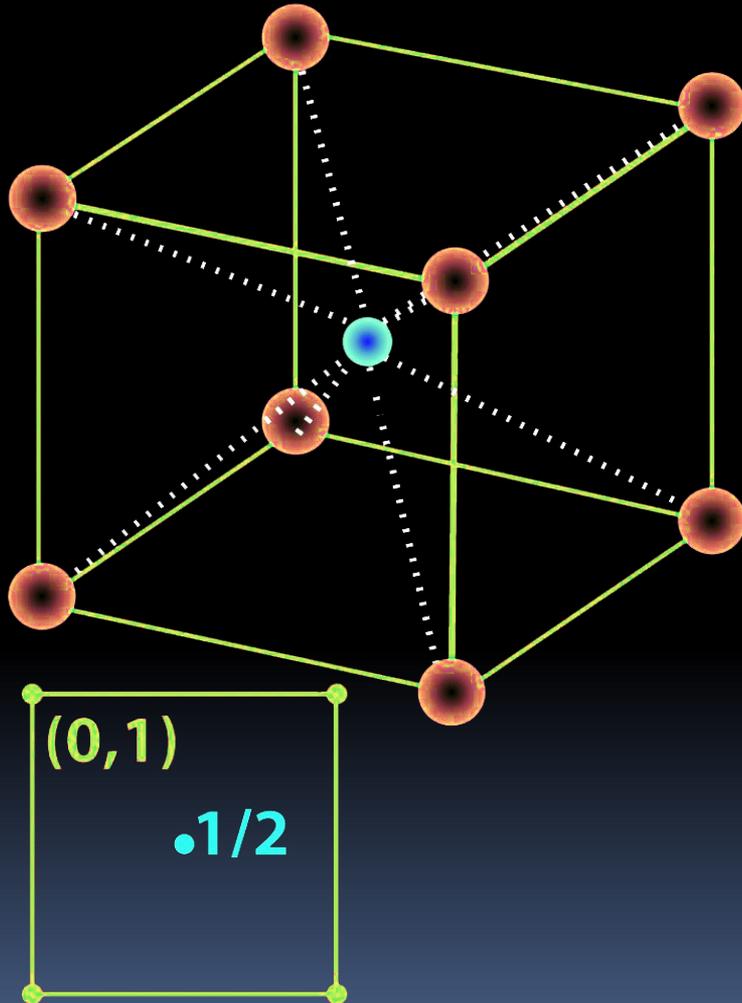


Tetrahedral ( $T_d$ ) sites

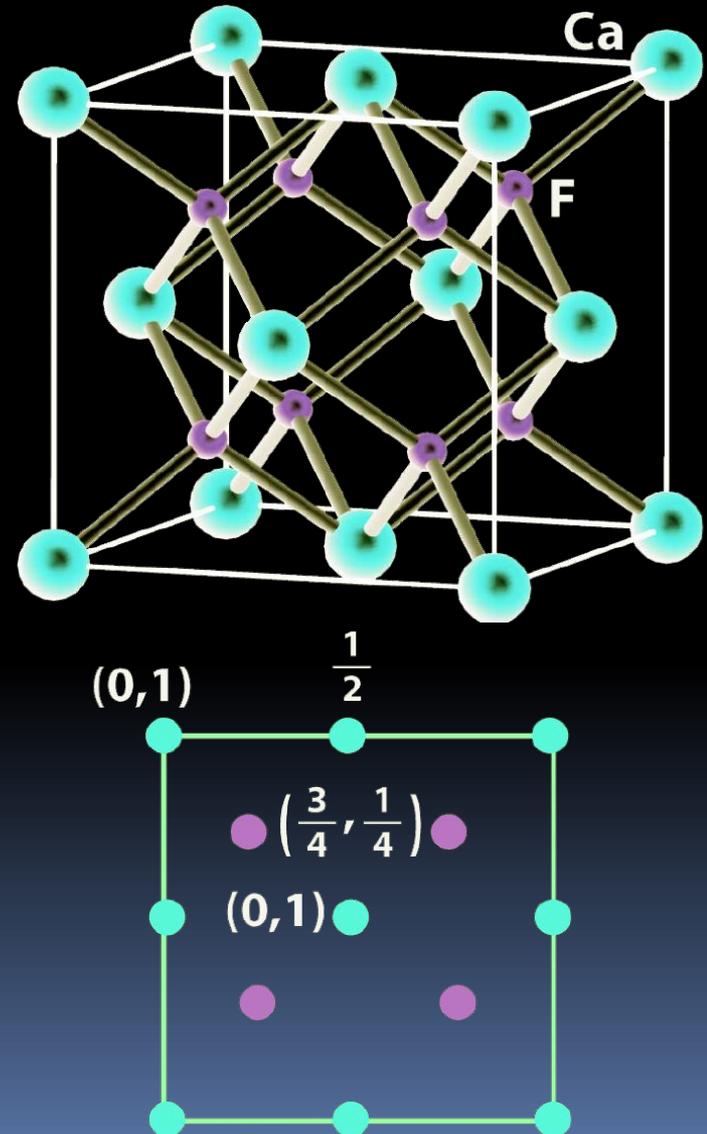


Net 8  $T_d$  sites/unit cell

# CsCl structure



# CaF<sub>2</sub> (MX<sub>2</sub>) structure



# Relationship between structures

