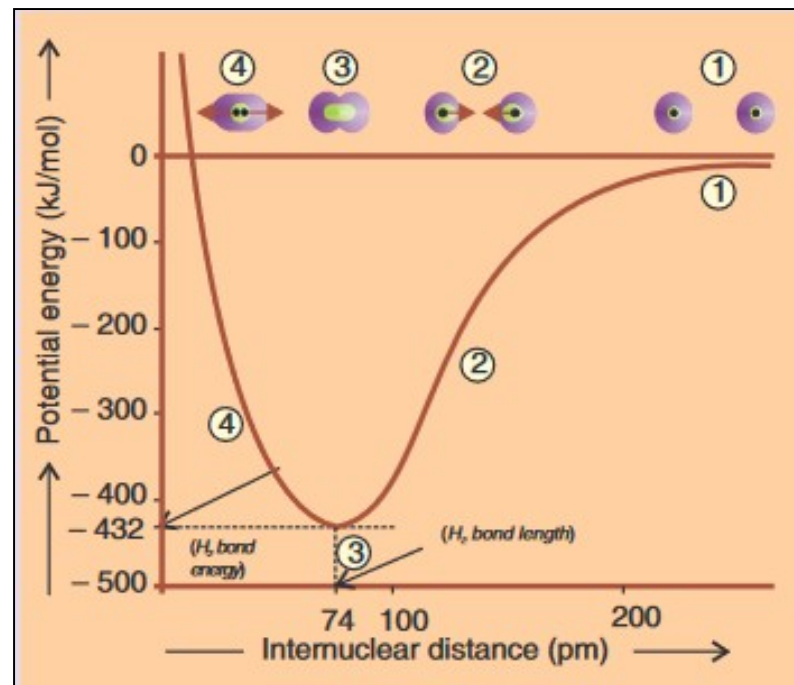
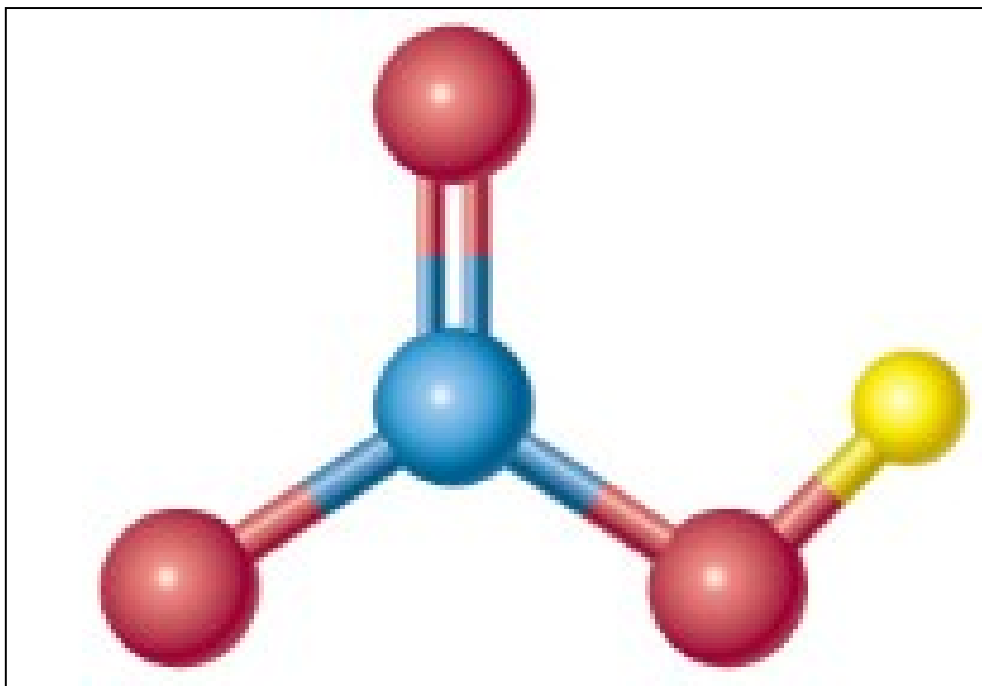


Wolaita Sodo University
Department of Chemistry
Course: Chemistry for
Remedial Program
Chapter-2: Chemical Bonding and Structure



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Inorganic Chemistry)**

Chapter 2

Chemical Bonding and Structure

2.1. Introduction

What is chemical bonding?

- **Chemical bond** is a strong force of binding between two or many atoms in compounds, molecules or ions.

Why do atoms combine?

- Everything wants to be more stable. It is easy to lie down than stand up; bonding is natural way of allowing the elements to lie down the energies of combining species.
- Atoms are bonded together to:
 - ✓ attain **noble gas** electronic configuration.
 - ✓ have **stability**.

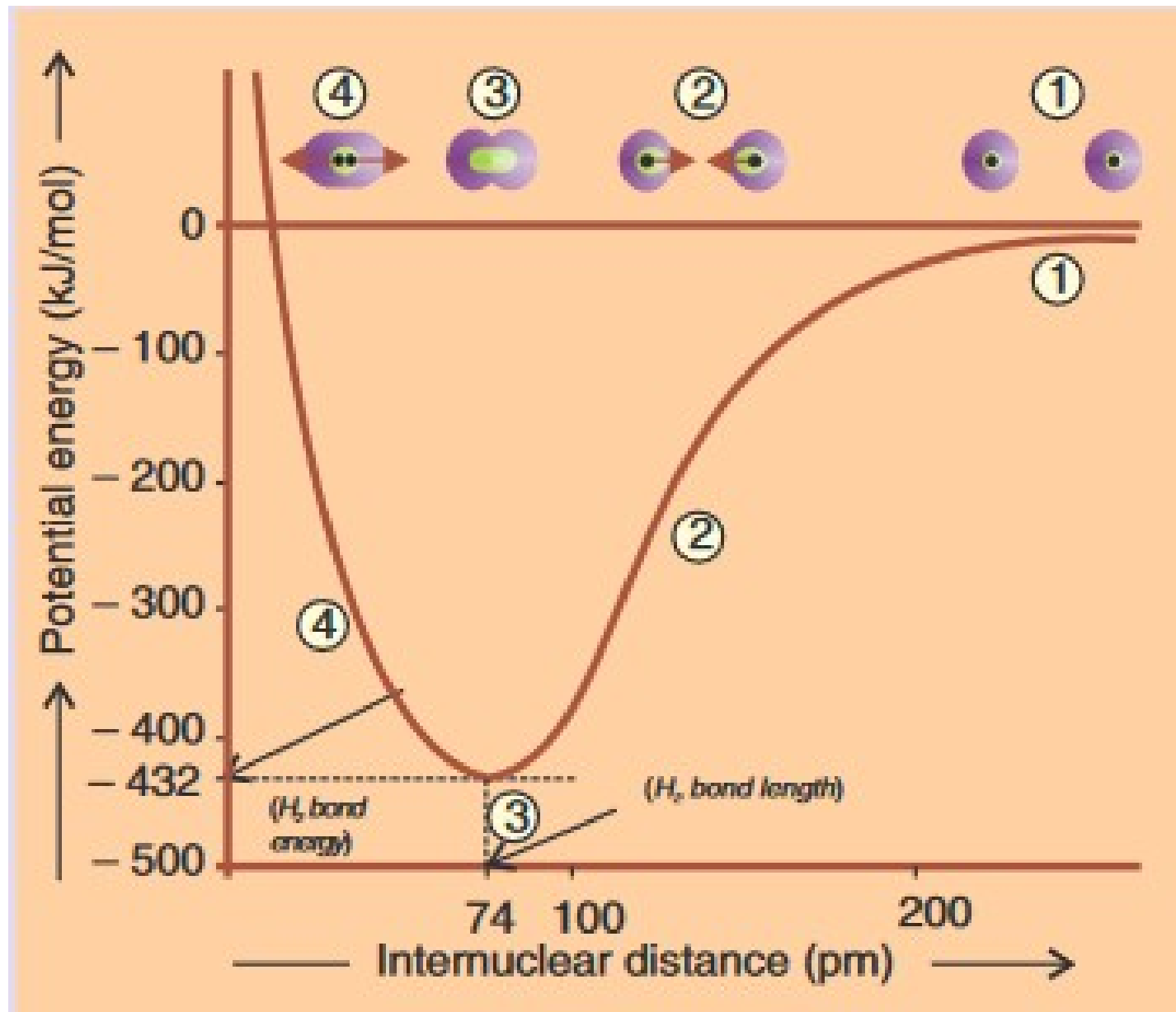


Figure: Potential-energy curve for H_2 : The stable molecule occurs at the bond distance corresponding to the minimum in the potential-energy curve

2.2. Types of Chemical Bonding

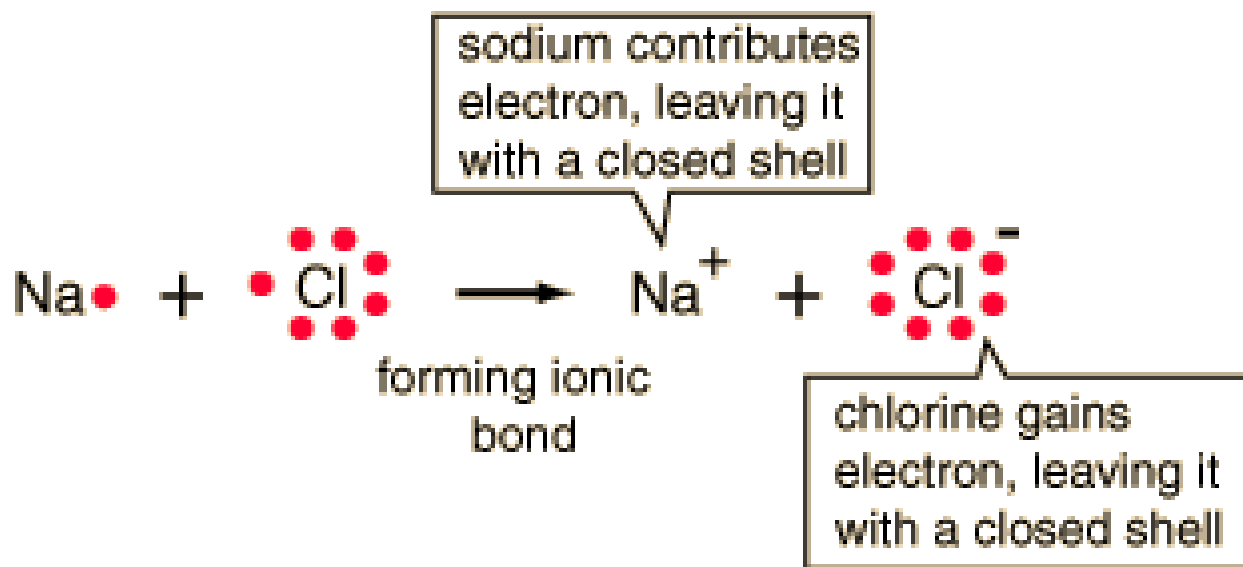
- Chemical bonds are basically classified into three types consisting of
 - (i) Ionic or electrovalent bond
 - (ii) Covalent bond and
 - (iii) Metallic bond.
- Mostly, **valence electrons** in the outer energy level of an atom take part in the chemical bonding.

2.2.1. THE IONIC BONDING

- Electrons are completely ***transferred*** from one atom to another. It is formed between electropositive species (***metals***) and electronegative species (***nonmetals***).
- In the process of either losing or gaining negatively charged electrons, the reacting atoms form **ions**.

Cont'd...

- The **electrostatic force** of attraction between oppositely charged ions results in the formation of **ionic bond or electrovalent** bond.
- **Example:** Consider the formation of some ionic bandings b/n Na^+ and Cl^- ions:



- *Examples* of ionic compounds include: NaCl , MgO , MgBr_2 , CaC_2 , HCl , Li_3N ...

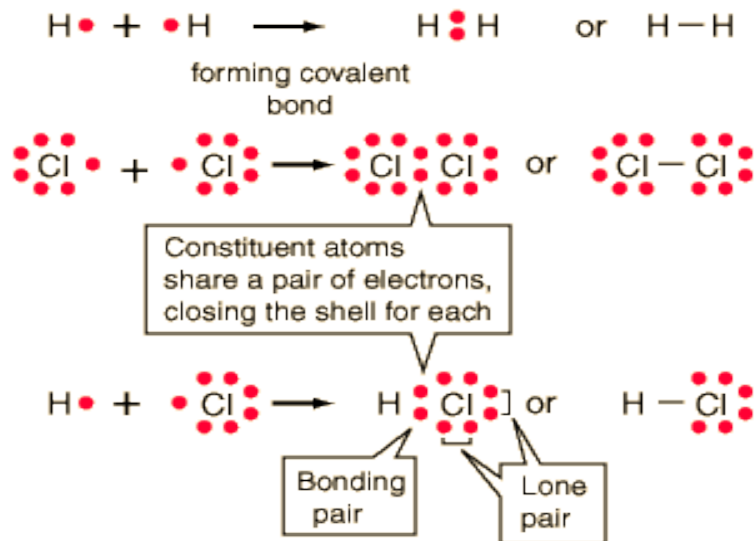
General Properties of Ionic Compounds

- Ionic compounds usually exist in the form of *crystalline solids*.
- Ionic compounds have **high melting point** and high **boiling point** due to strong attraction of force between ions.
- Ionic compounds are generally **soluble in water** and other **polar solvents** having high dielectric constants.
- Ionic compounds are good conductors of electricity in the solutions or in their molten states.
- In ionic - compounds, each ion is surrounded by oppositely charged ions **uniformly distributed** all around the ion. *i.e.*, Ionic bonding is ***non-directional***.

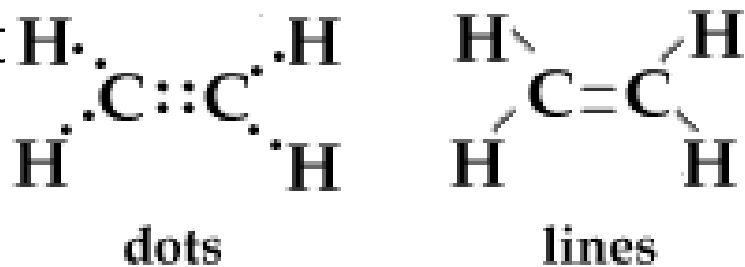
2.2.2. THE COVALENT BONDS

- *Covalent bonds* involve **sharing of a pair of valence electrons** by two atoms
- When two atoms have a small difference in their tendencies to lose or gain electrons, we observe electron sharing and covalent bonding.
- This type of bonding most commonly occurs between nonmetal atoms (although a pair of metal atoms can sometimes form a covalent bond).

Example:



- **Multiple covalent bonds** are common for certain atoms depending upon their valence configuration.
- For example, in ethylene (C_2H_4), a **double** covalent bond results from the sharing of two sets of valence elect



- Ator $:\text{N}:::\text{N}: \quad \quad \quad :\text{N} \equiv \text{N}: \quad \text{sample of a triple covalent bond.}$
- The **polarity** of a covalent bond is defined by any difference in electro-negativity between the two atoms participating in the covalent bond formation.
- Bond polarity describes the **distribution of electron density** around two bonded atoms.

- For two bonded atoms with similar electronegativities, the electron density of the bond is **equally distributed** (shared) between the two atom, this is a **non-polar covalent bond**.

- The electron density of a covalent bond is *shifted* **towards the atom with the largest electro-negativity.**



Polar covalent bond

Non- polar

Coordinate Covalent Bond

- A **coordinate covalent bond** (also called a **dative bond**) is formed when one atom donates (contribute) **both of the electrons** to form a single covalent bond.

Example: $\text{BF}_3 + \text{:NH}_3$



- As boron does not have a full outer shell, it is able to accept an electron pair from

Properties of covalent compounds

- The covalent compounds **do not exist as ions** but they **exist as molecules**.
- The **m.pt.** and **b.pt.** of covalent compounds are generally **low**.
- Covalent compounds are generally insoluble or **less soluble in water and other polar solvents**. However, these are soluble in non-polar solvents.
- They are poor conductors of electricity in the fused or dissolved state.
- Molecular reactions are quite **slow** because *energy is required to break covalent bonds*.
- Since the covalent bond is **localized** in between the nuclei of atoms, it is **directional** in nature.

The Octet Rule

- States that an atom tends to gain, lose or share electrons until there are **eight** electrons in its valence shell (the nearest noble gas configuration at its row).
- The octet rule guides us in allotting electrons to the atoms in a Lewis structure; in a few cases, however, we set the rule aside.

Example: $\text{Na}^+ = 1s^2 2s^2 2p^6 = 2:8 \Rightarrow$ Configuration of Ne.

$\text{Cl}^- = 1s^2 2s^2 2p^6 3s^2 3p^6 = 2:8:8 \Rightarrow$ Configuration of Ar.

Note: - Hydrogen follows a special configuration called **Duet rule** (2 electrons in its outer most shell).

1) Electron deficient molecules

- Cpds containing either Be or B are often electron deficient, *i.e.*, they have fewer than 8 electrons around Be or B atom.

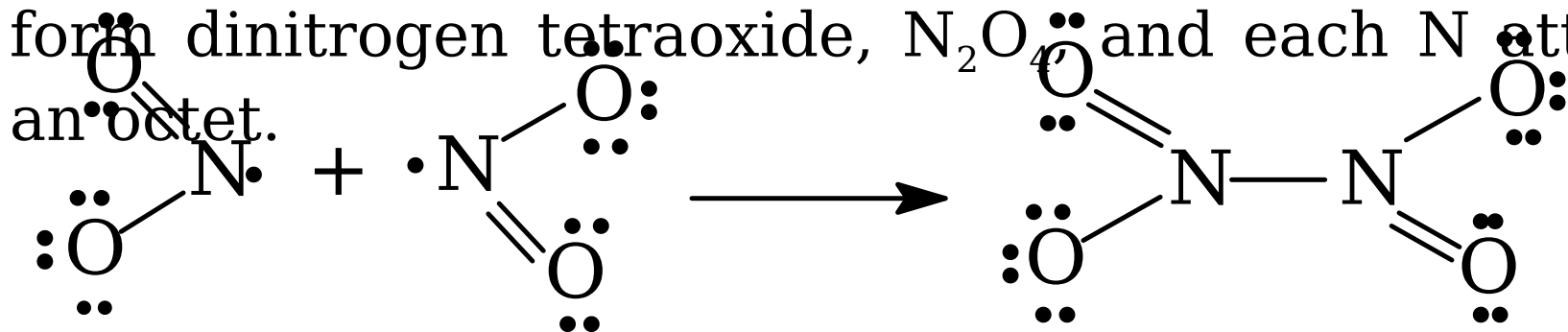
Example: BH_3 , BeCl_2 , BF_3 , etc.

2) Odd electron molecules

- A few molecules contain an odd number of valence electrons, so they cannot possibly have all their electrons in pairs.
- Such species, called *free radicals*, contain a lone (unpaired) electron, which makes them paramagnetic and extremely reactive.
- Free radicals can react with each other to pair up their lone electrons.

Example: NO, NO₂, etc.

- When two NO₂ molecules collide, for example they form dinitrogen tetroxide, N₂O₄, and each N attains an octet.



3) Expanded valence shells (more than octet electron)

- Many molecules or ions have more than eight valence electrons around the central atom from period 3 or higher, those in which d-orbitals are available.

Example: PCl_5 , SF_6 , I_3^- , etc.

Theories of Bonding

1) Lewis Theory of Covalent Bonding

- ***The Lewis structure (or Lewis formula)***- is two-dimensional structural formula consists of electron-dot symbols that depict each atom and its neighbors.
- The bonding pairs that hold them together, and the lone pairs that fill each atom's outer level (valence shell) - **octet rule**.

Steps to assign Lewi's dot formula

1. Write the electron configuration of the combining atoms and determine the valence shell electrons of each atom.
2. Add the valence shell electrons of all combining atoms (charge on the molecule:
 - (i) if the molecule is positively charged, subtract the number of charges from the total valence electrons;
 - (ii) if the molecule is negatively charged add the number of charge to the total valence shell electrons.
3. Decide the central atom:
 - (iii) The atom with fewer numbers is taken as central atom.
 - (iv) Large sized and relatively electropositive atoms are always selected as central atom.

4. Share a pair of electron between central atom and surrounding atom (form a **temporary single bond**).
5. Complete the octet starting from the **surrounding atom**.
6. Put any remaining as after the surrounding atoms complete their octet is put as ***lone pair*** on the central atom.
7. If the central atom has less than an octet, you must form multiple bonds so that each atom has an octet

Solution

1) We count the valence electrons

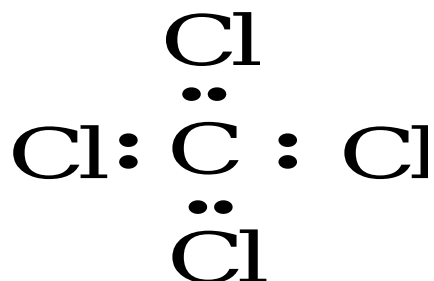
Carbon is group IVA contributes $4e^-$,

Chlorine Group VIIA contributes $7e^-$ each

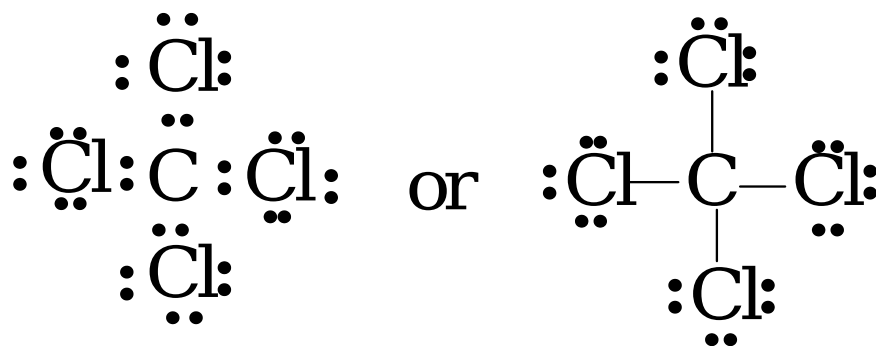
$28e^-$

Cont'd...

2) Distributing electrons by placing pairs in each bond gives



3) This has used $8e^-$ so there are $32 - 8 = 24e^-$ left.
Complete the valence shells of Cl atoms.



4) This has used $24e^-$, none are left. Each atom has an octet & therefore, this is the Lewis structure for CCl_4 .

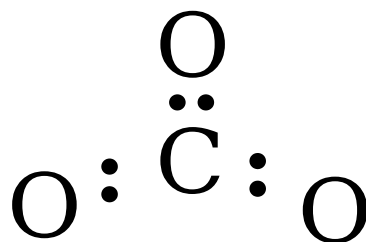
Problem 2: What is the Lewis structure for the carbonate ion, CO_3^{2-} ?

Solution:

1) This time we have an ion whose formula suggests the atom arrangement



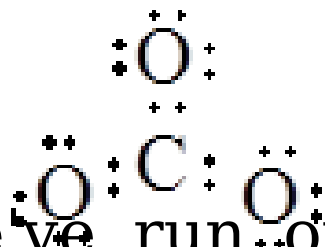
2) Counting valence electrons; carbon supplies $4e^-$, each oxygen supplies $6e^-$, & the negative charge adds $2e^-$, the total is $4 + 18 + 2 = 24e^-$. Placing a pair in each bond gives.



⇒ This has used $6e^-$, leaving $18e^-$.

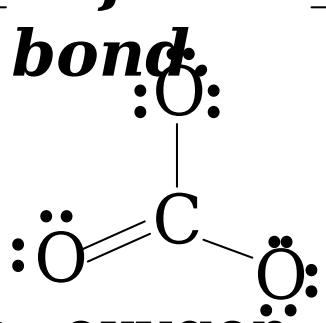
3) The 18 electrons are used to complete the octet around oxygen.

Cont'd...



➡ This time we've run out of electrons, but C doesn't have an octet.

4) Now, ***move one of the unshared pairs on oxygen into one of the bonds.***

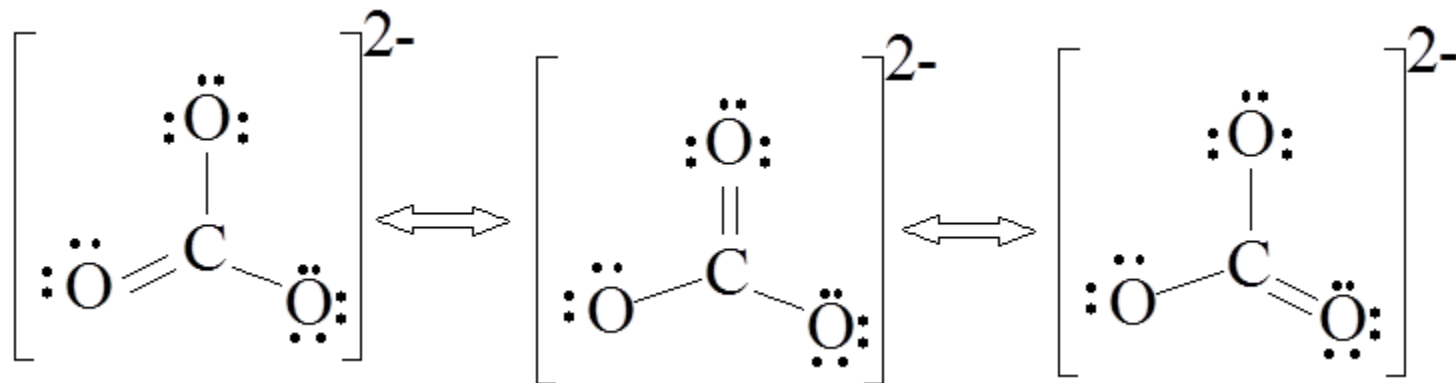


➡ Notice that the oxygen hasn't lost the pair, but carbon completes its octet by sharing it.

5) Finally we should be sure to indicate the charge on the ion by enclosing the Lewis structure in brackets with the charge outside.

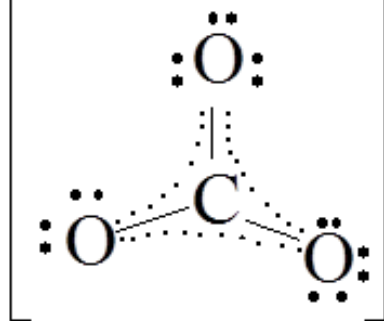
RESONANCE STRUCTURES

- ❖ Some molecules have structures that are not expressed correctly by single Lewis structure.
- ❖ For example consider the carbonate ion (CO_3^{2-}), whose Lewis structure was indicated in example 2,
- ❖ The three Lewis structures shown in figure below differ only in the position of the double bond.



- Such Lewis structures are said to be **resonance structures**.

- Each of these structures is known as **Resonance contributor**.
- The most stable Lewis structures is assumed to be a **hybrid of all resonance contributors**
- Thus, the resonance hybrid structure of carbonate ion is a $\left[\text{O}=\text{C}(\text{O})\text{O} \right]^{2-}$ as follows.



Activity

Write all resonance contributors and the most probable (resonance hybrid) structures of each of the following structures:



II) Sidwick-powell theory (Valence Shell Electron Pair Repulsion (VSEPR) Theory)

- This theory was proposed for the first time by Sidwick and Powell in 1940 and developed by Gillespie and Nyholm in 1957.
- This theory is very useful in predicting the ***geometry*** or ***shape*** of polyatomic molecules or ions of non-transition elements.
- According to this theory, ***“the shape of a given species (molecule or ion) depends on the number and nature of electron pairs surrounding the central atom of the species.”***
- **Molecular Geometry** is the general shape of a molecule as determined by the relative position of atomic nuclei.

1. Electron pairs will arrange themselves to be as far apart as possible so that the repulsion between them is at minimum.

2. Lone pair of electrons takes more room on the surface of atom than that of bonding pairs. According to the VSEPR theory, the repulsion of electron pair is in the following order:

Lone pair-Lone Pair > Lone Pair- Bond Pair > Bond Pair- Bond Pair

3. The repulsive force decreases sharply with increasing bond angle

4. The geometries that minimize the repulsion between groups of electrons have been mathematically established.

Table 2.1: The basic sets of five geometries, general formula of molecules, bond angles and examples.

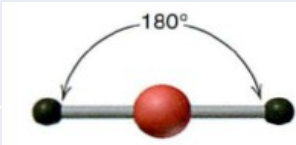
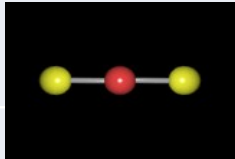
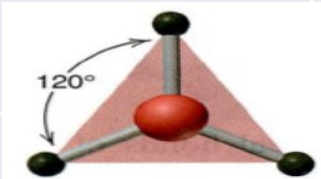
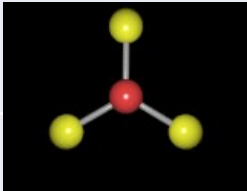
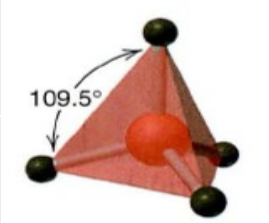
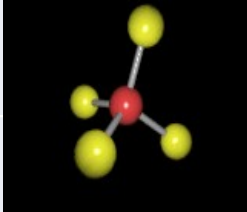
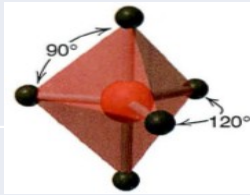
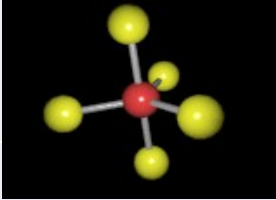
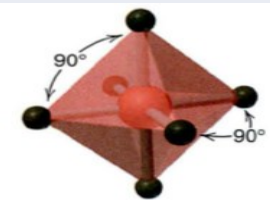
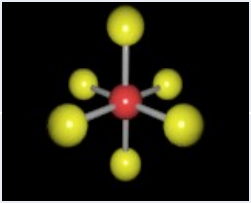
Geometry General description	General formula	Angles	Examples	3-D view of geometry	2-D view
Linear	AX_2	180°	$BeCl_2$, CO_2 , CS_2		
Trigonal-planar	AX_3	120°	BCl_3 , CO_3^{2-} , SO_3		
Tetrahedron	AX_4	109.5°	CH_4 , CCl_4 , NH_4^+ , SiF_4 , BF_4^- , ClO_4 , PO_4^{3-}		
Trigonal bipyramid	AX_5	$90^\circ, 120^\circ$	PF_5 , PCl_5 , AsF_5		
Octahedron	AX_6	90°	SF_6 , SeF_6 , PF_6^- , SiF_6^{2-}		

Table 2.2: Summary of the electron pair geometry and molecular geometry.

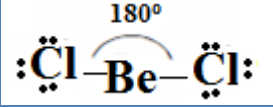
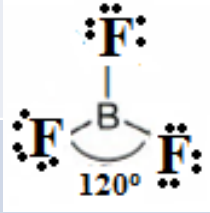
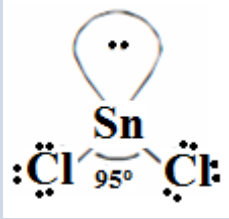
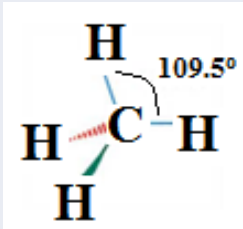
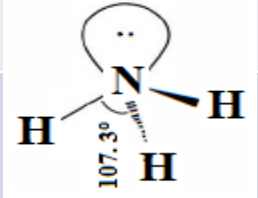
Electro pairs			Electro pair geometry	Molecular Geometry	Example	Other Examples
Total	Bonding pair	Lone pair				
2	2	0	Linear	Linear		
3	3	0	Trigonal planar	Trigonal planar		BeF ₂ , HCN, CS ₂ , CO ₂
3						SO ₃ , NO ₃ ⁻ , CO ₃ ²⁻
	2	1	Trigonal planar	Bent(V-shape)		SO ₂ , PbCl ₂ , SnBr ₂ , O ₃ , SnCl ₂
4	4	0	Tetrahedral	Tetrahedral		SiCl ₄ , SO ₄ ²⁻ , ClO ₄ ⁻

Table 2.2 (Cont'd...)

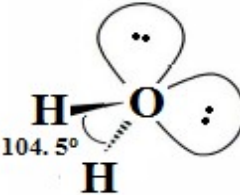
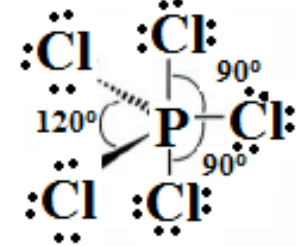
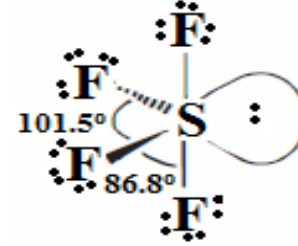
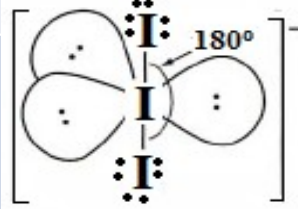
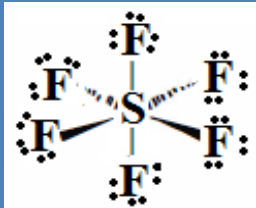
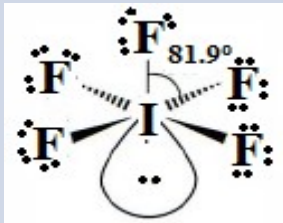
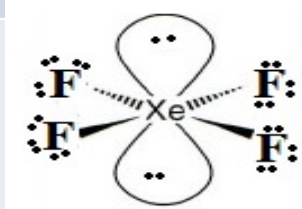
4	2	2	Tetrahedral	Bent (angular)		OF ₂ , SCl ₂
5	5	0	Trigonal bipyramidal	Trigonal bipyramidal		PF ₅ , AsF ₅ , SOF ₄
	4	1	Trigonal bipyramidal	Distorted tetrahedral (See Saw)		SF ₄ , IF ₄ ⁺ , XeO ₂ F ₂ , IO ₂ F ₂ ⁻
	3	2	Trigonal bipyramidal	T-shape		ClF ₃ , BrCl ₃

Table 2.2 (Cont'd...)

6	6	0	Octahedral	Octahedral		IOF ₅ , SCl ₆
	5	1	Octahedral	Square pyramidal		TeF ₅ ⁻ , BeF ₅ , XeF ₅ ⁺
	4	2	Octahedral	Square planar		ICl ₄ ⁻

- Generally the **electron pair geometry** depends on the **number of electron pairs** around central atom.
- Where as, the **Molecular geometry** depends on both the number of electron pairs and the nature (**bonding** and **lone pair**) of **electron pairs** around central atom.

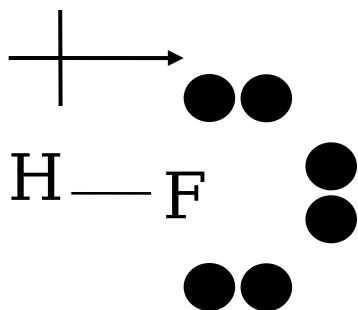
Merits of Knowing Shape of Covalent Compounds

- Knowing the shape (geometry) of covalent molecules is a key to understand its physical and chemical behavior.
- One of the most important and far-reaching effects of molecular shape is molecular **polarity**, which can influence melting and boiling points, solubility, chemical reactivity, and even biological function.

Bond Polarity

In general, a covalent bond is:

- **Dipole Moments**
 - polar if it occurs between two different atoms.
 - nonpolar if it occurs between two identical atoms.
 - It is a measure of the polarity of a bond.
 - Is often represented by a special arrow.



Arrow points toward more EN atom.

Polarity of Diatomic Molecules

- **Diatomic Molecules** - molecules made of only two atoms.
 - If atoms are the same, molecule is nonpolar.
 - If atoms are diff., molecule is polar.

NOTE: *Polar does not mean charged.*

- Is Cl_2 polar or nonpolar?
- Is CO polar or nonpolar?

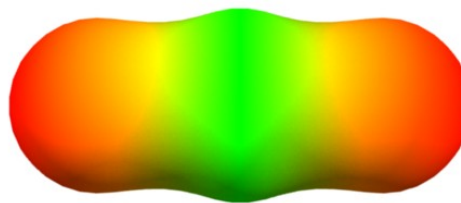
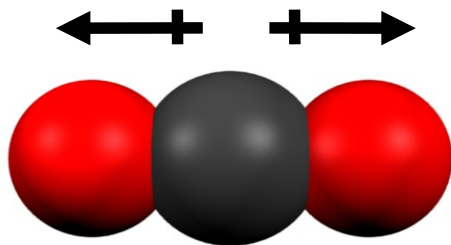
Molecules With 3 or More Atoms

- A molecule with 3 or more atoms is:
 - Polar if its central atom has lone pairs OR
 - If the outer atoms are not all the same.
 - Nonpolar if its central atom has no lone pairs AND
 - All the outer atoms are identical.

Example: CO₂ vs. H₂O

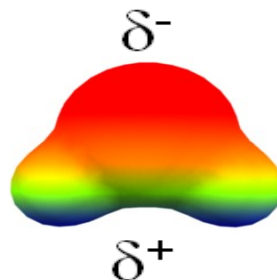
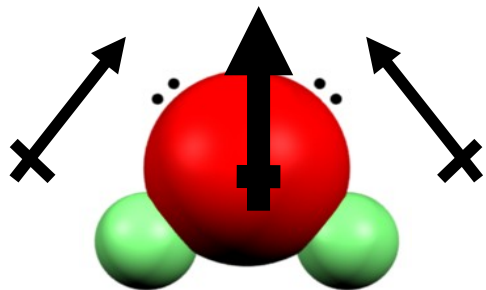
i) Consider the Lewis structure $\ddot{\text{O}}=\text{C}=\ddot{\text{O}}$

⇒ This molecule is nonpolar.



ii) Consider the Lewis structure $\text{H}-\ddot{\text{O}}-\text{H}$

⇒ This molecule is polar.

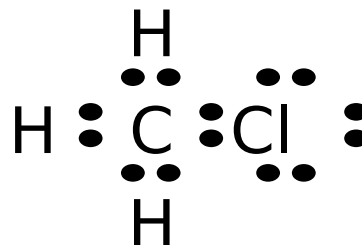
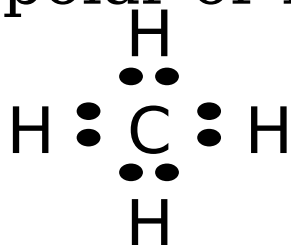


Exercise: CH_4 vs. CH_3Cl

- Neither CH_4 nor CH_3Cl has any lone pairs on the central carbon atom.

⇒ Is CH_4 polar or nonpolar?

⇒ Is CH_3Cl polar or nonpolar?



Properties of Polar Molecules

- Polar molecules tend to align when placed in an electric field with the positive end of the molecule oriented toward the negative plate and the negative end toward the positive plate.
- We can use an electrically charged object to attract polar molecules, but nonpolar molecules are not attracted.
- Polar solvents are better at dissolving polar substances, and nonpolar solvents are better at dissolving nonpolar substances.
- Molecules are always randomly distributed in the liquid state in the absence of an electric field. When an electric field is applied, polar molecules like HF will align to the dipoles with the field direction.

III)The Valence Bond Theory (VBT)

- The **VBT** was proposed by Heitler and London to explain the formation of covalent bond quantitatively using quantum mechanics.
- Later on, Linus Pauling improved this theory by introducing the concept of **hybridization**.
- The main postulates of this theory are as follows:
 - i)A covalent bond is formed by the ***overlapping of two half filled valence atomic orbitals*** of two different atoms.
 - ii)The electrons in the overlapping orbitals get paired and confined between the nuclei of two atoms.
 - iii)The electron density between two bonded atoms increases due to overlapping. This confers

VBT...

- As the two atoms are brought more closely together, however, the **repulsion of the atomic nuclei becomes more important than the electron-nucleus attraction** and the bond become unstable.
- For each bond, then, there is a condition of **optimal orbital overlap** that leads to a **maximum bond strength** (bond energy) at a particular internuclear distance (**bond**

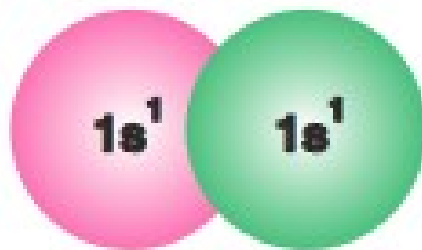


Figure: Atomic orbital overlap and bonding in H₂

VBT...

- The **s orbital** is **spherical**, but **p** and **d** orbitals have particular orientations.
- Thus, in p & d orbitals, more electron density is in one direction than in another.
- The bond involving p or d orbitals will tend to be oriented in the **direction that maximizes overlap**.

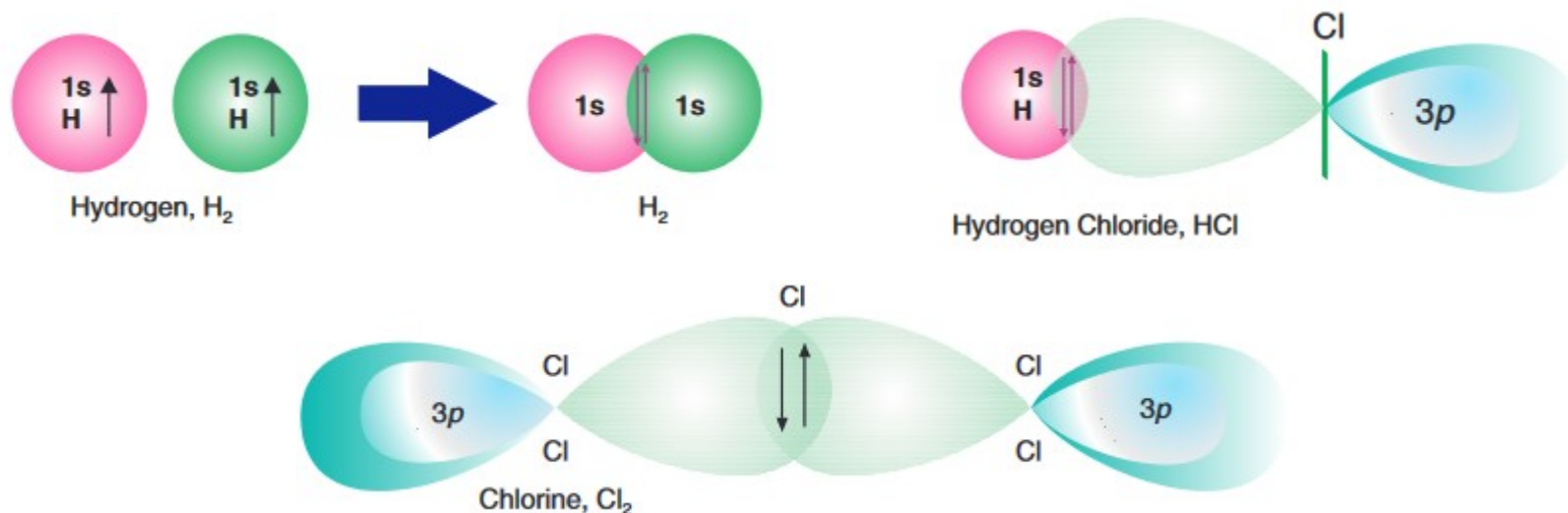


Figure: s-s, s-p and p-p orbital overlapping and spin pairing in 3-D molecules

Sigma(σ -) and Pi (π -) Bonds

- Based on the pattern of overlapping, covalent bonds are classified as sigma- and pi- bonds.

i) σ -bond

- The covalent bond formed due to overlapping of atomic orbital along the **inter-nucleus axis** (***head on overlapping***) is called **σ -bond (sigma bond)**
- It is a stronger bond and **cylindrically** symmetrical.
- The σ -bond (overlapping) is further classified as σ_{s-s} overlapping, σ_{s-p} overlapping and σ_{p-p} overlapping (See the following figure).

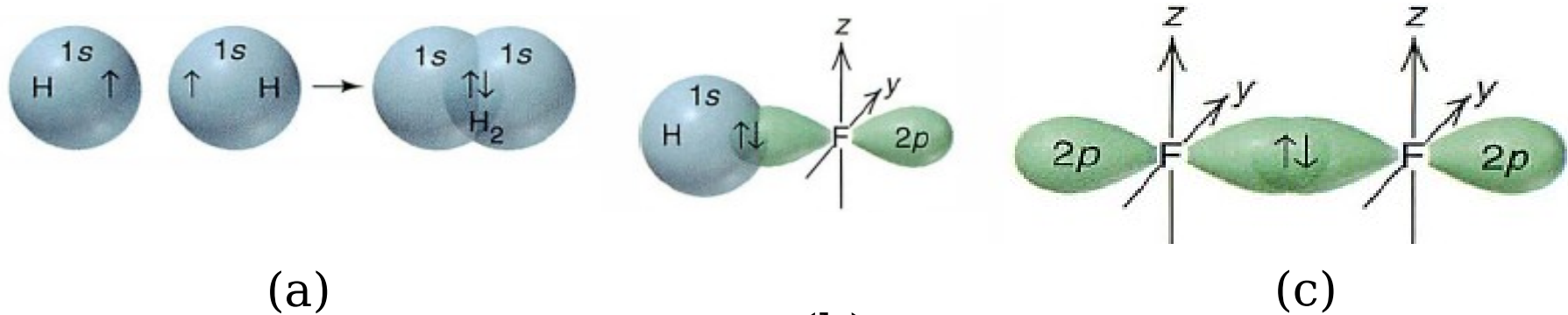


Figure: (a) σ_{s-s} , σ_{s-p} and σ_{p-p} overlapping in various molecules

ii) π -bond

- The covalent bond formed by **sidewise overlapping** of atomic orbitals is called **π -bond**.
- In **π -bond**, the electron density is present **above and below** the **inter-nuclear axis**.
- It is relatively not strong π bond since the electrons are bonding atoms.

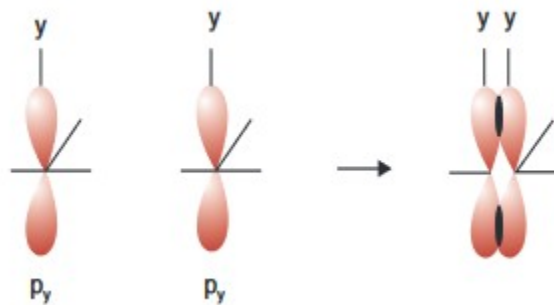


Figure: p-p sideways overlap

Orbital Hybridization

- The old version of valence bond theory is limited to diatomic molecules only.
- For example, the covalent bond in H_2 , O_2 , Cl_2 , N_2 , HCl , etc. molecule can be explained by the orbital overlapping of the two atoms.
- However, it could not explain the structures and bond angles of molecules with more than three atoms.
***E.g.** It could not explain the structures and bond angles of H_2O , NH_3 etc.*
- In order to explain the structures and bond angles of molecules, Linus Pauling modified the valence bond theory using **hybridization concept**.
- **Definition:** ***Orbital hybridization** is the intermixing of two or more atomic orbitals of similar energy to give identical and degenerate new type of orbitals.*

Orbital hybridization...

- Only atomic orbitals of same atom with almost same energy can participate in the hybridization.
- The completely-filled or half-filled or even empty orbitals can undergo hybridization.
- The combination of orbitals belonging to different atoms is called **bonding**.
- The new orbitals that are formed due to hybridization are known as **hybrid orbitals**, which have mixed characteristics of atomic orbitals.
- The shapes of hybrid orbitals are identical. Usually they have one big lobe associated with a small lobe on the other side.
- The hybrid orbitals are **degenerate** i.e., they have similar energy.

Orbital hybridization...

Example: If three atomic orbitals hybridize, the number of hybrid orbitals formed will be equal to 3.

- The hybrid orbitals are filled with those electrons which were present in the parent atomic orbitals.
- The filling up of electrons in them follows **Pauli's exclusion** principle and **Hund's rule**.
- ➡ The hybrid orbitals participate in the **σ bond** formation with other atoms.
- The hybrid orbitals are oriented in space so as to minimize repulsions between them. *This explains why the atomic orbitals undergo hybridization before bond formation.*
- The bond angles in the molecule are equal to or almost equal to the angles between the hybrid orbitals forming the σ bonds.
- The shape of the molecule is determined by the *type*

Types of Hybrid Orbitals

i) *sp* hybridization

- When two electron groups surround the central atom, we observe a linear shape, which means that the bonding must have a linear orientation.
- VB theory explains this by proposing that mixing two nonequivalent *sp* hybrid orbitals that lie **180° apart**.
- Characterized by the central atom of **linear molecules**.

Example: CO₂, BeCl₂, etc.

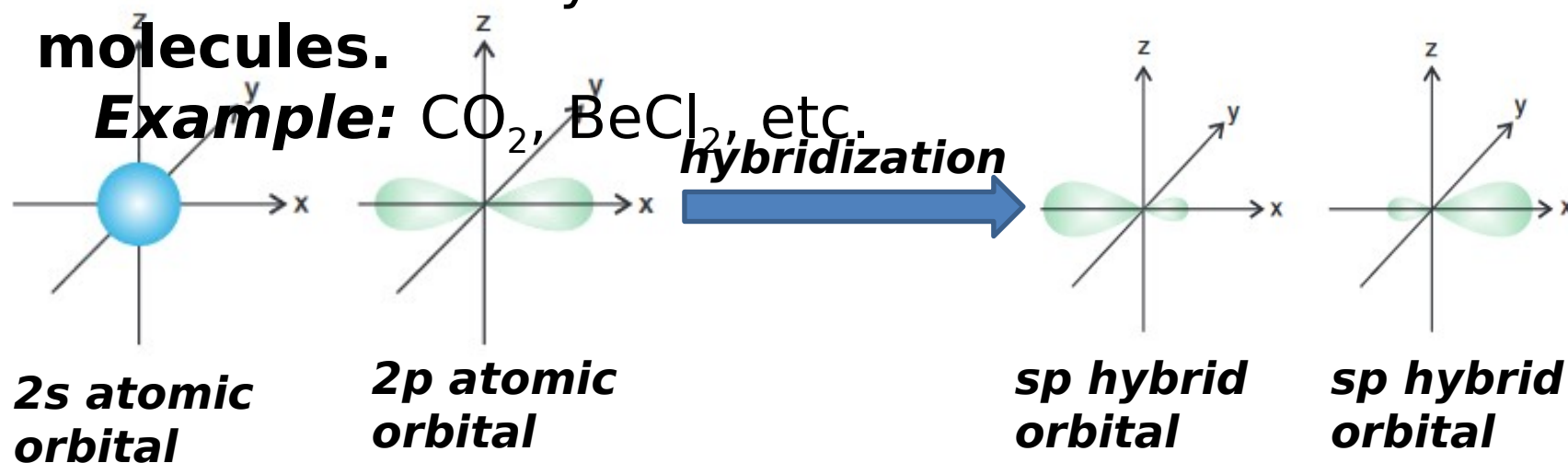
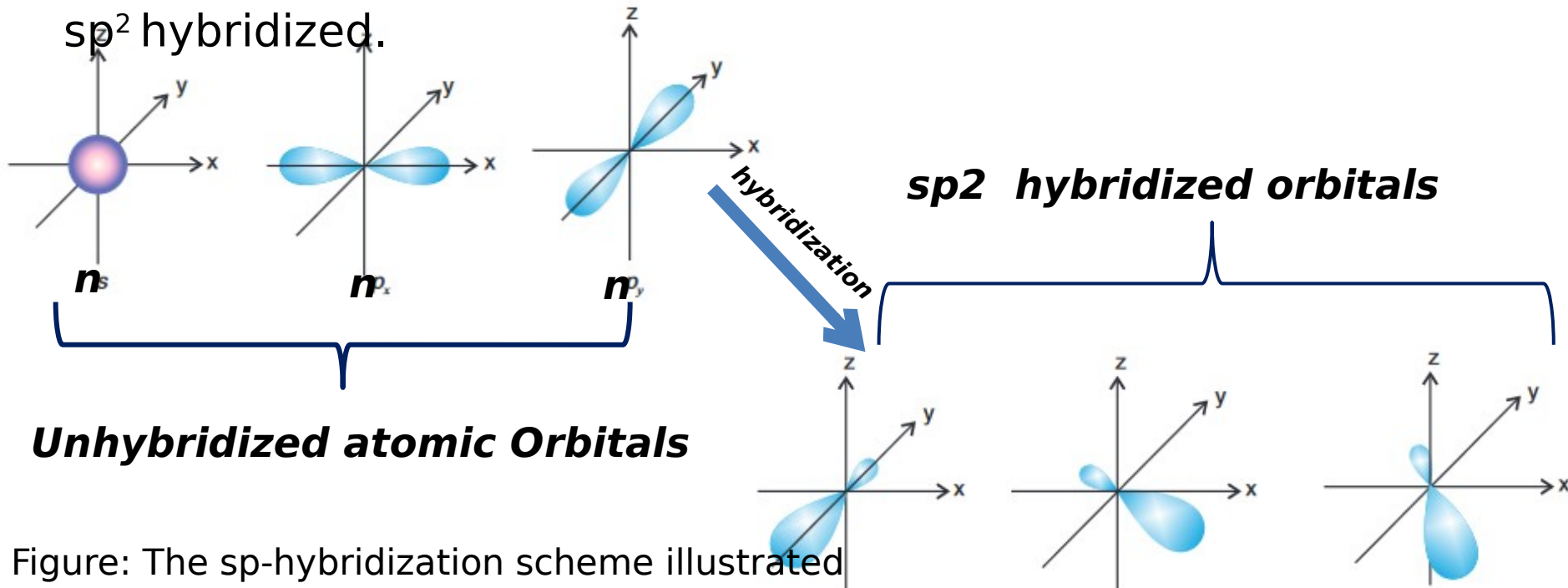


Figure: The *sp*-hybridization scheme illustrated⁴⁰

ii) sp^2 Hybridization

- In order to rationalize the **trigonal planar** electron group arrangement and the shapes of molecules based on it.
- The mixing of **one s** and **two p orbitals** of the central atom to give three hybrid orbitals that point toward the vertices of equilateral triangle.
- Each of **sp^2 hybrid** orbitals are **120°** apart.
- VB theory proposes that the central B atom in the **BF_3** molecule is sp^2 hybridized.



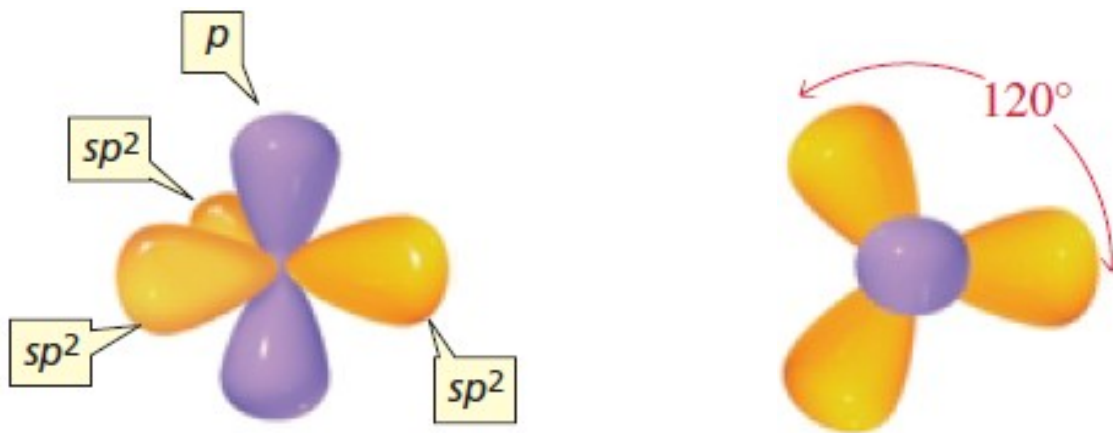


Figure: *The 3-D view of sp^2 hybrid orbitals*

- The figure above shows the three- sp^2 orbitals in the **trigonal plane**, with the third 2p orbital unhybridized and perpendicular to this plane.
- Each sp^2 orbital overlaps the 2p orbital of an F atom, and the six valence electrons- three from B and one from each of the three F atoms-form three bonding pairs.

iii) sp^3 Hybridization

- One s and all three p orbitals of the central atom mix and form four **sp^3 hybrid orbitals**, which point toward the ver

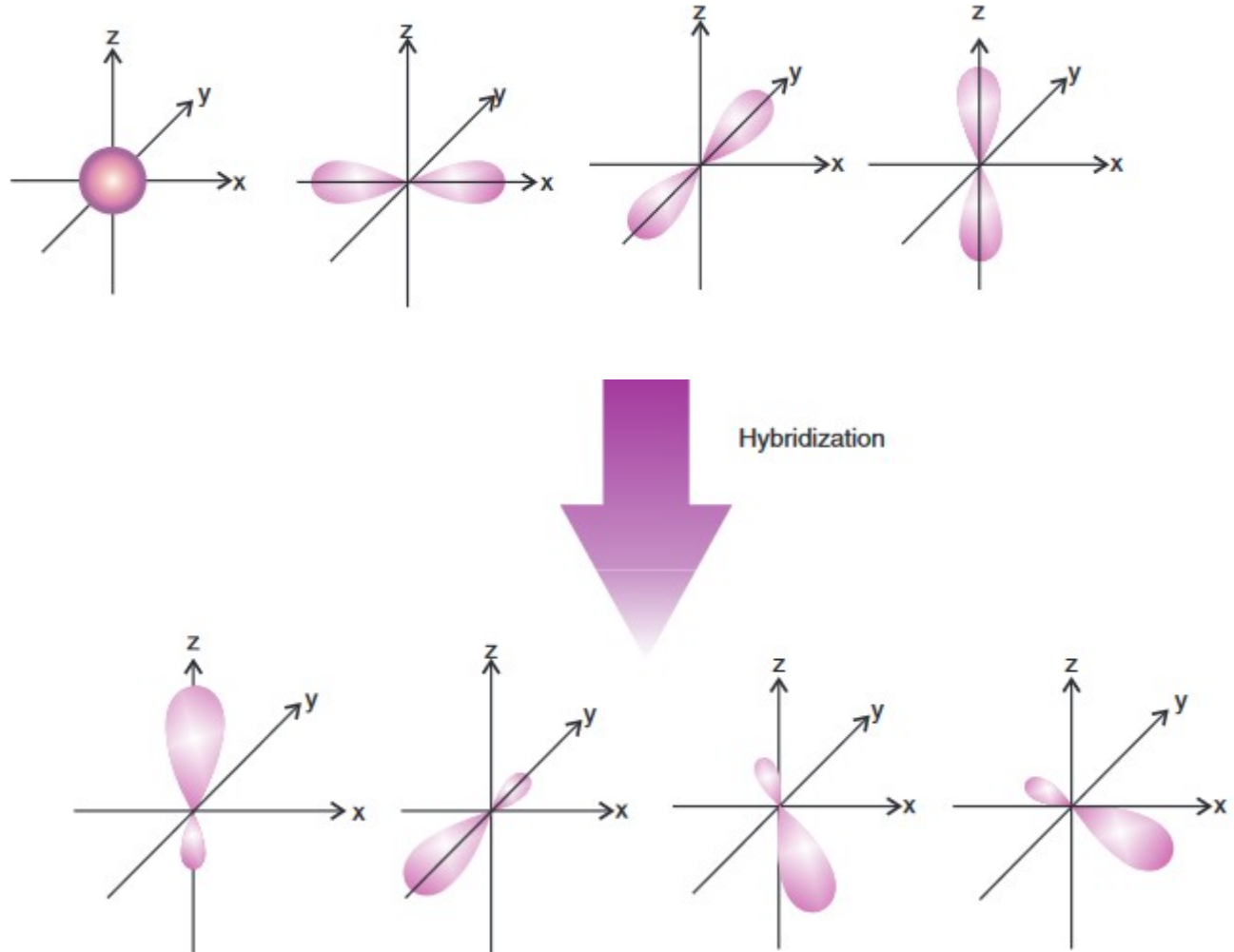
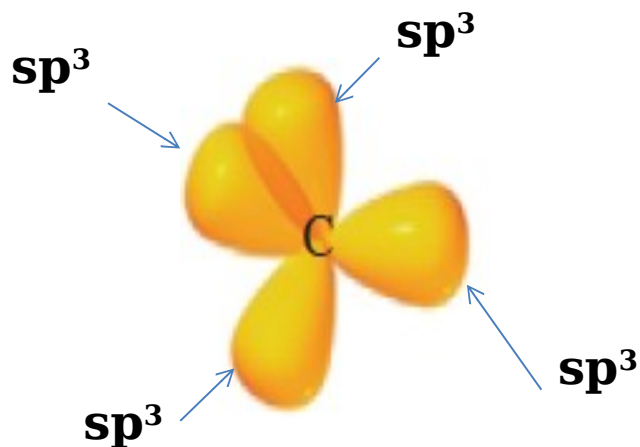


Figure: The sp^3 hybridization

- Its four valence electrons half fill the four sp^3 hybrids, which overlap the half-filled 1s orbitals of four H-atoms and form four C-H bonds.



The C atom in **methane** is sp^3 hybridized.

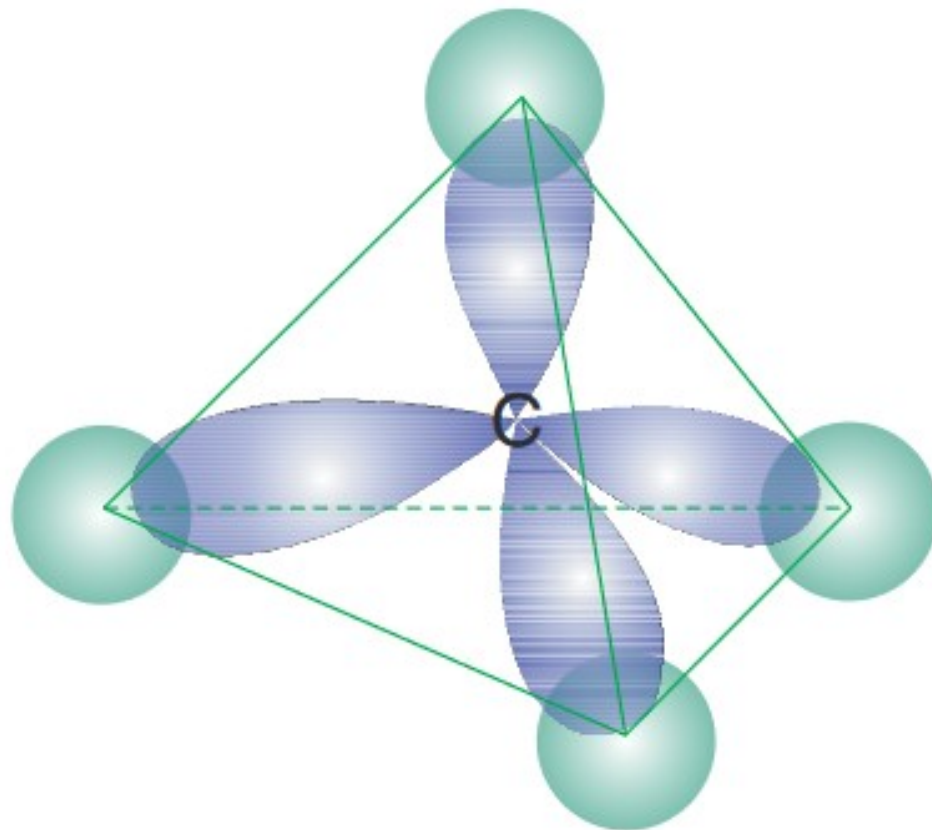


Figure: sp^3 Hybrid orbitals and bonding in methane scheme illustrated.

iv) sp^3d Hybridization

- One s, the three p, and one of the five d orbitals of the central atom mix and form five **sp^3d hybrid orbitals**.
- The central atom of **trigonal bipyramidal** shape of molecules such as **PCl_5** molecule are characterized by this type of hybrid

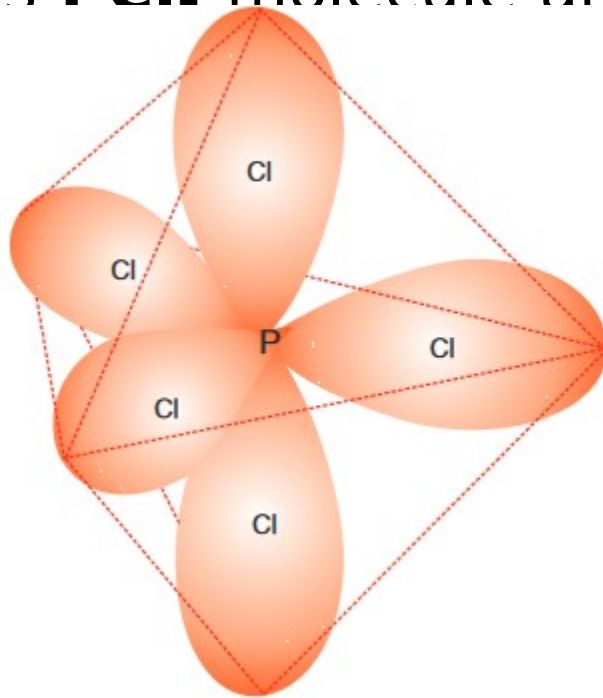


Figure: The sp^3d hybrid orbitals in the molecule of PCl_5

v) sp^3d^2 Hybridization

- The one s, the three p two of the five d orbitals of the central atom mix and form six **sp^3d^2 hybrid orbitals**, which point to the vertices of an **octahedron**.
- The central atom of **octahedral** shape of molecules such as **SF_6** is hybridized by this type of hybridization

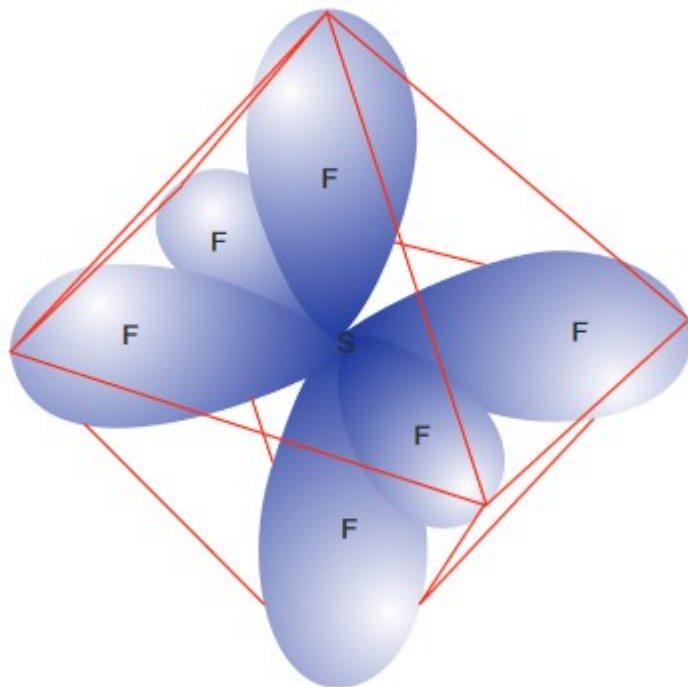


Figure: The sp^3d^2 hybridization in SF_6

iv) The Molecular Orbital Theory (MOT)

- Atomic orbitals are capable of combining or overlapping, to produce new electron distributions called molecular orbitals (MOs) – one MO for every AO.
- **Molecular orbital:** *is a region where electrons are most probably found around the nuclei of two or more atoms.*
- *Molecular orbitals are formed by the overlap of atomic orbitals.*

LCAO Methods

- In contrast to valence bond theory, in which one bonding orbital is formed because of the interaction of two atomic orbitals, in **MOT two molecular orbital results from the combination of two atomic orbitals.**

a) Bonding molecular orbital (BMO):

- Is the combination of atomic orbitals is additive, it results in forms bonding molecular orbitals

$$AO_A + AO_B = BMO_{AB}$$

where: AO is atomic Orbital and BMO is a **bonding molecular orbital**.

- The **energy of BMO is lower than** the energy of atomic orbital in an isolated atom.
- The electron density is concentrated b/n the two nuclei.
- Formation of BMO is **exothermic process** and **stabilizes** the molecule.

b) Anti Bonding molecular orbital (ABMO)

- Is formed by subtraction of atomic orbital that overlap.

$$AO_A - AO_B = (ABMO)^*_{AB}$$

- This combination forms an **antibonding MO**, which has a node between the nuclei, a region of zero electron density.

Types of Orbital Combination

i) s-s Combination

- When 1s- orbital from two different atoms A and B with the same size approach each other, they overlap to form sigma 1s- bonding molecular orbital ($\delta 1s_{AB}$).

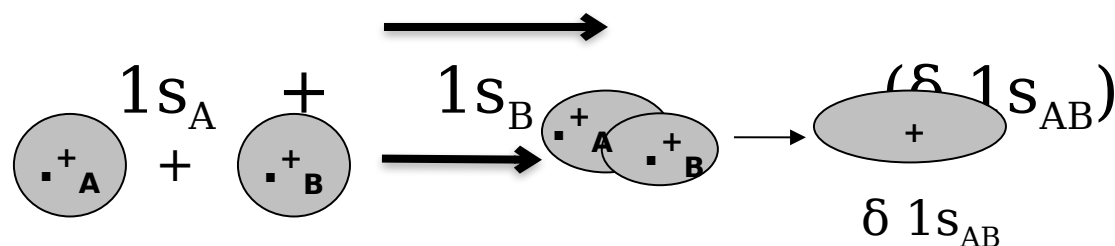


Figure: Formation of BMO from addition of two 1s atomic orbitals

- When 1s - orbital from two different atoms, A and B with opposite symmetry approach each other, they form sigma anti bonding 1s molecular orbital ($\delta^* 1s_{AB}$).

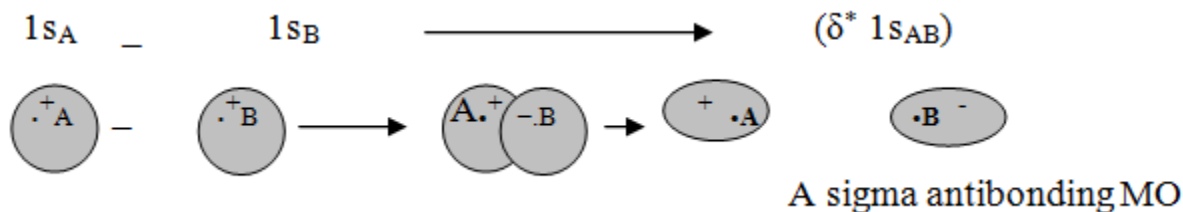


Figure: Formation of ABMO from subtraction of two 1s

p - p Combination

a) p-p combination of atomic orbitals along the internuclear axis (head on overlap)

- Two p_x atomic orbitals from two atoms lie along the internuclear axis of both atoms in symmetrical and anti-symmetrical approach.
- They overlap head on to form δ - bonding molecular orbital (δp_x) and δ^* -anti bonding molecular orbitals ($\delta^* p_x$).

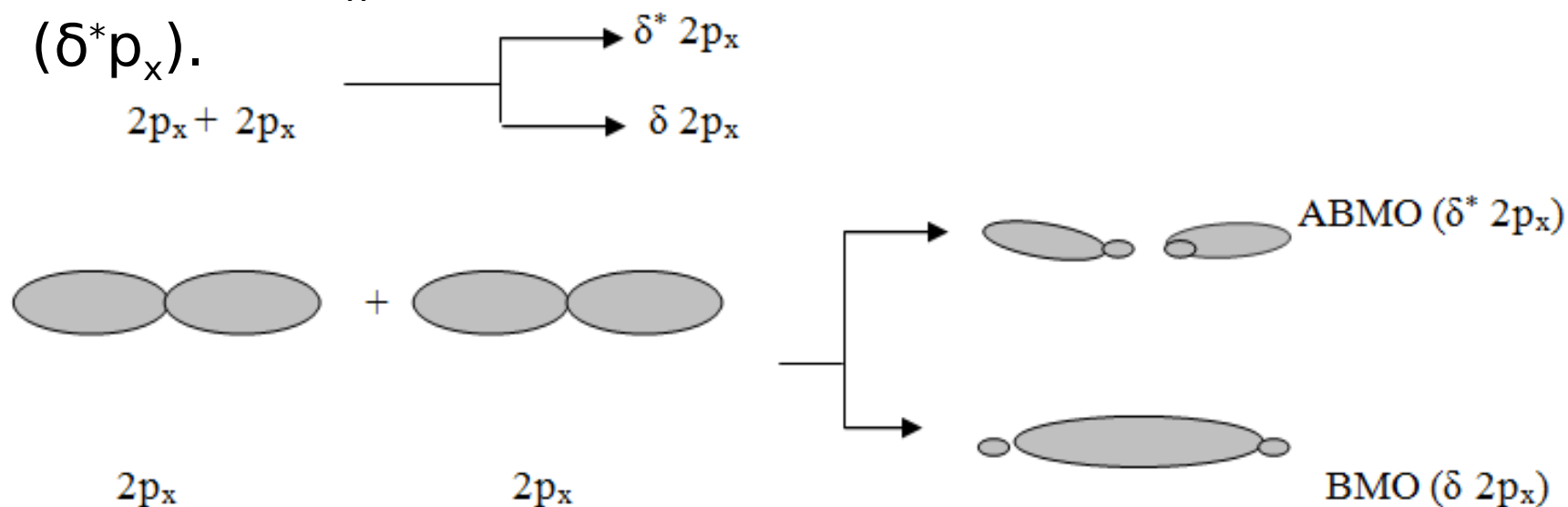


Figure: Head on combination of P- P atomic orbitals

b) Lateral (side way) overlap of p atomic orbitals

p_y and p_z atomic orbital from two atoms lie perpendicular to the internuclear axis and to each other.

- They overlap laterally (side to side) to form **π -bonding molecular orbital** ($\pi 2p_y$, $\pi 2p_z$) and **π -anti bonding**

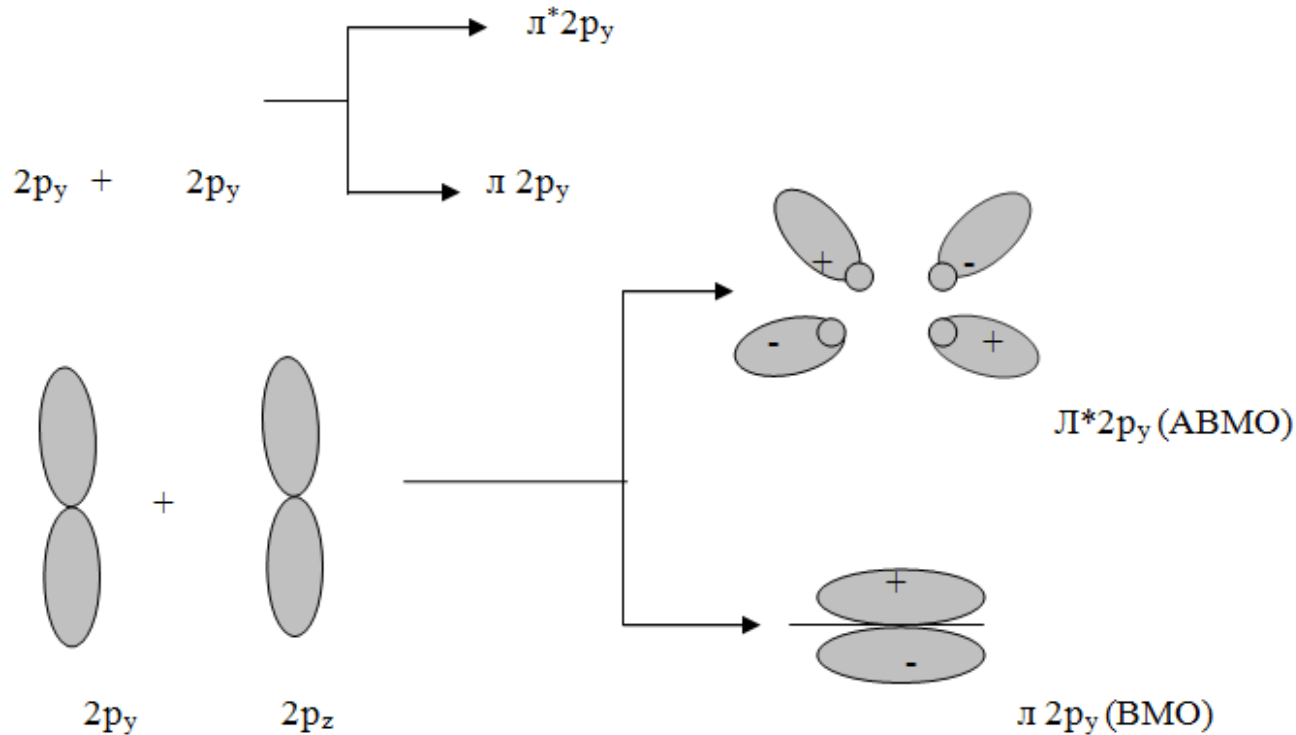


Figure: Sideway combination of P-P atomic

Electronic configuration in MOT

- The electronic configuration in MOT depends on:

- The Aufbau Principle:** fill electrons in to molecular orbital starting from lower energy molecular orbital.
- Pawel's Exclusion Principle:** each molecular orbital can contain a maximum of two electrons with opposite spin.
- Hund's rule:** if the molecular orbitals are degenerates (molecular orbitals with the same energy), electrons are filled in to **degenerate molecular** orbital singly with the same spin before pairing.

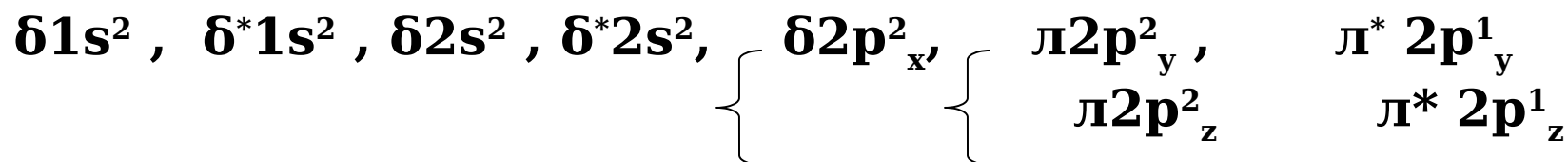
a) *Homonuclear diatomic molecules (Molecules made from atoms of atomic number 8-10) (for O_2 , F_2 , and Ne_2).*

-There is no interaction between 2s and 2p orbitals and the BMO resulted from head-on overlap of 2p atomic orbitals ($\delta 2p_x$) is lower in energy than that of p- Mos resulted from sidewise overlapping ($\pi 2p_y$ & $\pi 2p_z$). In this case, **δ - overlap is stronger than π - overlap.**

$\delta 1s$ $\delta^* 1s$ $\delta 2s$ $\delta^* 2s$ $\delta 2p_x$ $\pi 2p_y$ $\pi^* 2p_y$ $\delta^* 2p_x$ $\delta 3s$
 $\delta^* 3s$... $\pi 2p_z$ $\pi^* 2p_z$

Example: Write the molecular orbital electron configuration of O_2 molecule

O_2 involves 16 electrons



b) Homonuclear diatomic molecules (Molecules made from atoms of atomic number less than 8) (for N_2 , C_2 , and B_2).

- In these cases, interactions take place between the 2s and 2p atomic orbitals that are strong enough to swap the ordering of the σ_{2p} and π_{2p} molecular orbitals.



...

- The MO electron configuration becomes

Example: Write MO electron configuration of N_2^-

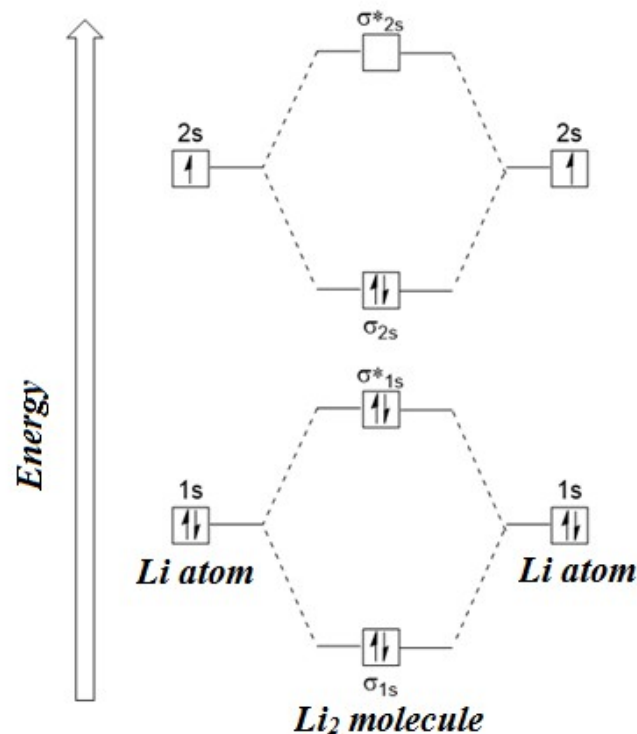
Solution: N_2^- involves 15 e^- $\delta 1s^2, \delta^* 1s^2, \delta 2s^2, \delta^* 2s^2, \left\{ \begin{array}{l} \pi 2p_y^2, \delta 2p_x^2, \pi^* 2p_y^1 \\ \pi 2p_z^2, \pi^* 2p_z^1 \end{array} \right.$

Molecular orbital Electron Configuration Energy Diagram

- The MO electron configurations can be indicated by the energy diagram.

Example 1: Draw the MO electron configuration Energy diagram for Li_2 molecule

Solution: The MO electron configuration of Li_2 molecule (having 6) is:
 $\delta 1s^2$, $\delta^* 1s^2$, $\delta 2s^2$.

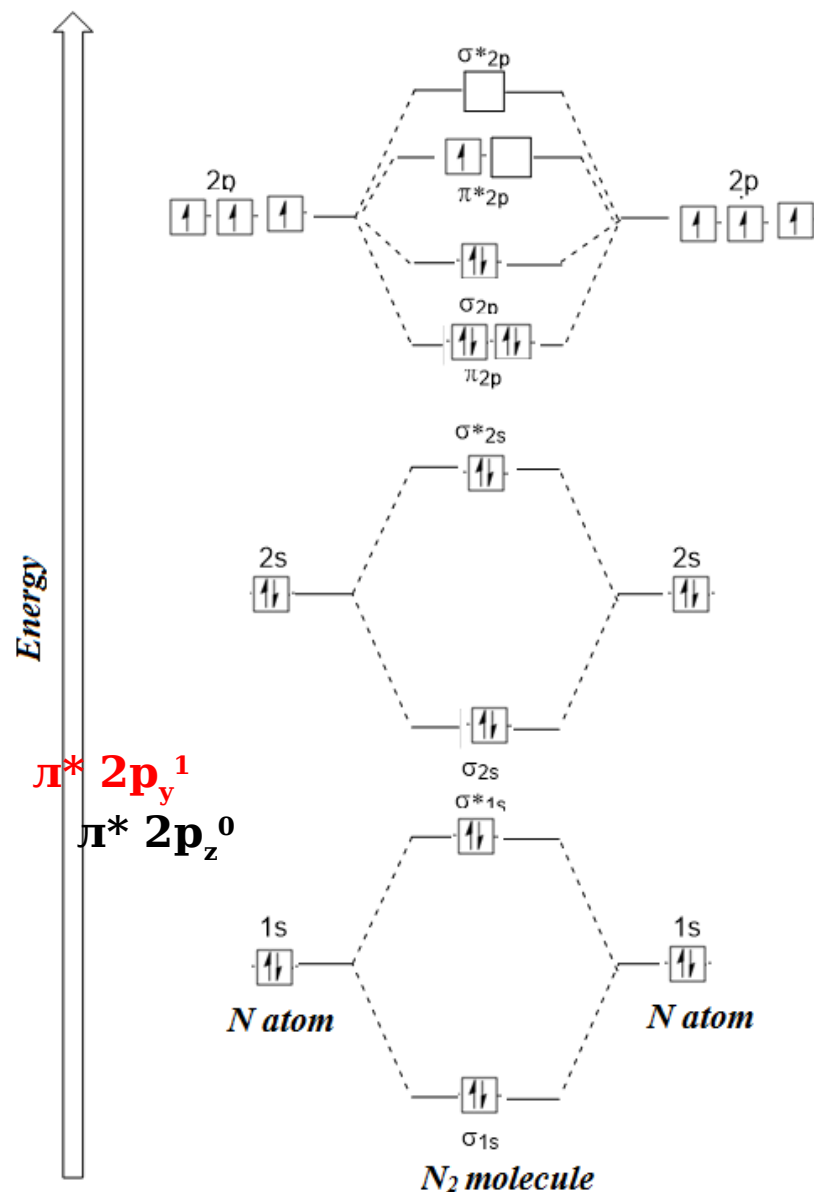


Example 2: Draw the MO electron configuration Energy diagram for **N₅⁻ molecule**

Solution:

▪ **Here, the** σ_{2p} MOs are at relatively higher energy state than π_{2p} because of interactions between the 2s and 2p atomic orbitals that are strong enough to swap the ordering of the σ_{2p} and π_{2p} molecular orbitals. Thus, the MO electron configuration of N_2 molecule, $\sigma_{1s}^2, \sigma_{1s}^{*2}, \sigma_{2s}^2, \sigma_{2s}^{*2}, \pi_{2p_y}^2, \pi_{2p_z}^2, \sigma_{2p_x}^2$, having 15 electrons is: $\pi_{2p_z}^2$

Exercise: Draw the MO electron configuration Energy diagram for O_2^- molecule



Bond Order of Molecules

Bond order (B.O.): is the number of bonding electron pairs between two atoms within a covalent molecule.

$$\text{Bond order} = \frac{\text{electrons in BMO} - \text{electrons in ABMO}}{2}$$

- Molecules with bond order $\frac{1}{2}$ or greater will be stable with respect to their atoms.
- Molecules with bond order zero will be unstable.
- The greater the bond order the more stable the molecule.

Example 1: Determine the bond order and stability of He_2

Solution : Total electron = $2+2=4$

Electronic configuration = $\sigma 1s^2, \sigma^* 1s^2$

$$\text{Bond order} = \frac{1}{2} (\# \text{ e- in BMO} - \# \text{ e- in ABMO})$$

$$= \frac{2 - 2}{2} = 0$$

Stability : Unstable. Because $B.O = 0$, Hence He_2 molecule does not exist.

Magnetic Property

- One of the advantages of molecular orbital theory over valence bond theory is its ability to explain the magnetic properties of covalent molecules.
- If the electronic configuration of a molecule contains **unpaired electron(s)**, the molecule is said to be **paramagnetic**.
- If the electronic configuration of a molecule contains all electrons paired, the molecule is said to be **diamagnetic**.

Example: Write the MO electron configuration of O_2^- molecule ion, calculate bond order, determine stability and its magnetic property.

Solution:

i) MO electron configuration, O_2^- has 17 electrons.

ii) Bond Order (BO)

$$\text{BO} = (\#e^- \text{ in BMO} - e^- \text{ in ABMO})$$

$$= (10 - 7)$$

$$= (3)$$

$$= 1.5$$

iii) Stability, $\square \text{O}_2^-$ molecule is **stable** because $\text{BO} \neq 0$.

iv) Magnetic Nature

$\square$ **Paramagnetic** because there is one unpaired electron in a MO.

2.2.3. Metallic bonding and bonding theories

Electron sea model and bonding in me

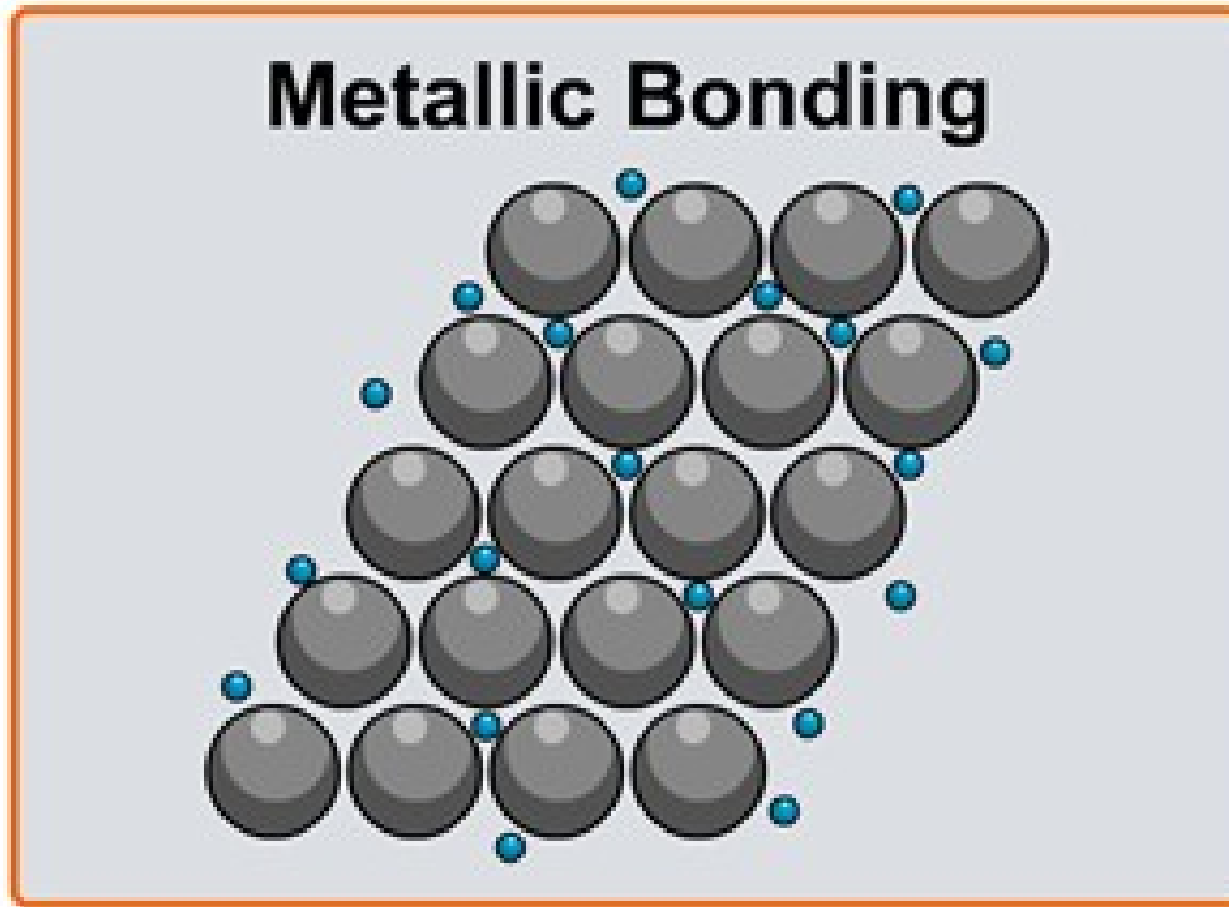


Figure: Electron sea model in metallic bond

Cont'd...

- The atoms in a pure metal are in tightly-packed layers, which form a regular **lattice** structure.
- Electrostatic forces of attraction between the positively charged nuclei and the negatively charged electrons hold the lattice together.
- A metal is therefore seen as a rigid framework of cations immersed in a '**sea**' of electrons that serve as the cement holding the three-dimensional cationic network together – **Metallic bonding**.

Cont'd...

- The outer electrons of the metal atoms separate from the atoms and create a '**sea of electrons**'.
- These electrons are **delocalized**, and so are free to move through the whole structure.
- The metal atoms become positively charged ions and are attracted to the sea of electrons. This attraction is called **metallic bonding**.

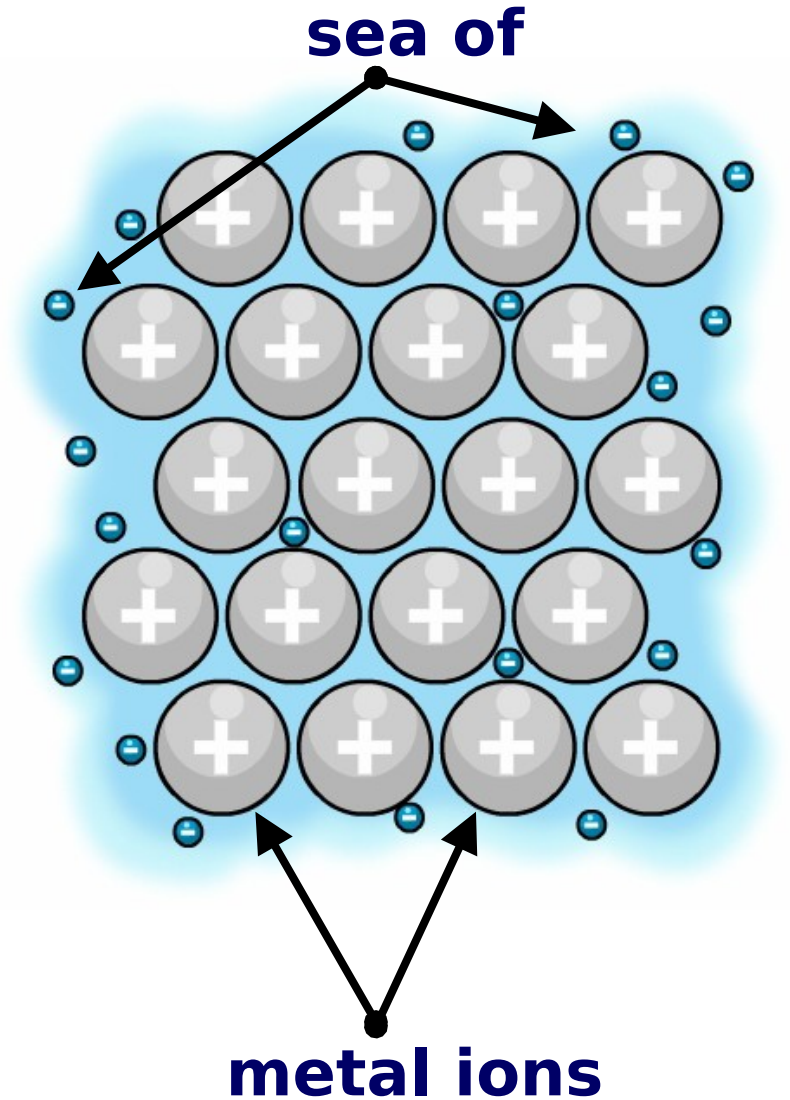


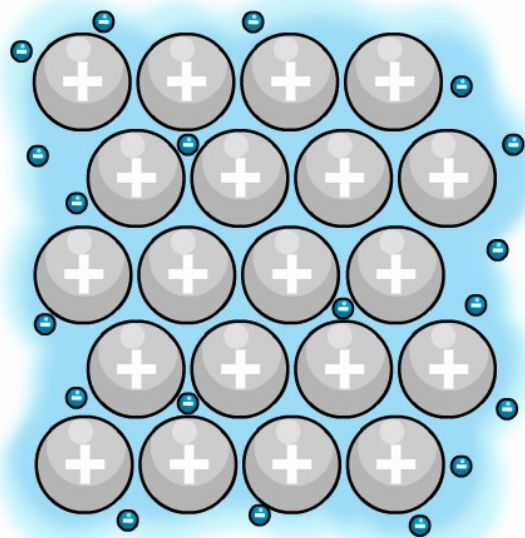
Figure: Illustration of delocalization of valance electrons in Electron-sea model

Properties of metals

- The properties of metals are related to their structure

i) Conduction of Heat and Electricity

- Delocalized electrons in metallic bonding allow metals to conduct heat and electricity.




heat

- For example, when a metal is heated, the delocalized electrons gain kinetic energy.
- These electrons then move faster, and so transfer the gained energy throughout the metal.
- This makes heat transfer in metals very efficient.
- ***Delocalized electrons also conduct electricity through metals in a similar way.***

Figure: Illustration of electronic structure of metal during thermal conduction

ii) High Melting Points of Metals

- Metals often have high melting points and boiling points. Gold, for example, has a melting point of 1064 °C and a boiling point of 2807 °C.
- This property is due to the strong attraction between the positively-charged metal ions and the sea of electrons.
- In metal extraction and other industrial processes, furnaces often run continuously to maintain the high temperatures needed to work with molten metals.
- The generally high melting points indicate that metallic bonding is quite strong.
- Melting points increase with an increase in the number of valence electrons to the sea, since there is a greater attractive force between the cations and the electrons.

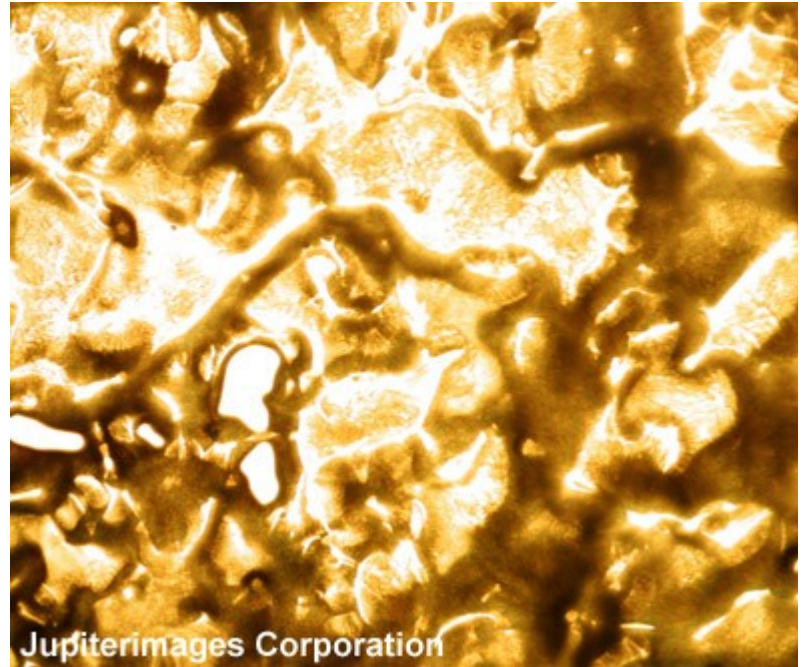


Figure: Molten gold

iii) Strength of Metals

- Metals are usually strong, not brittle. When a metal is hit, the layers of metal ions are able to slide over each other, and so the structure does not shatter.

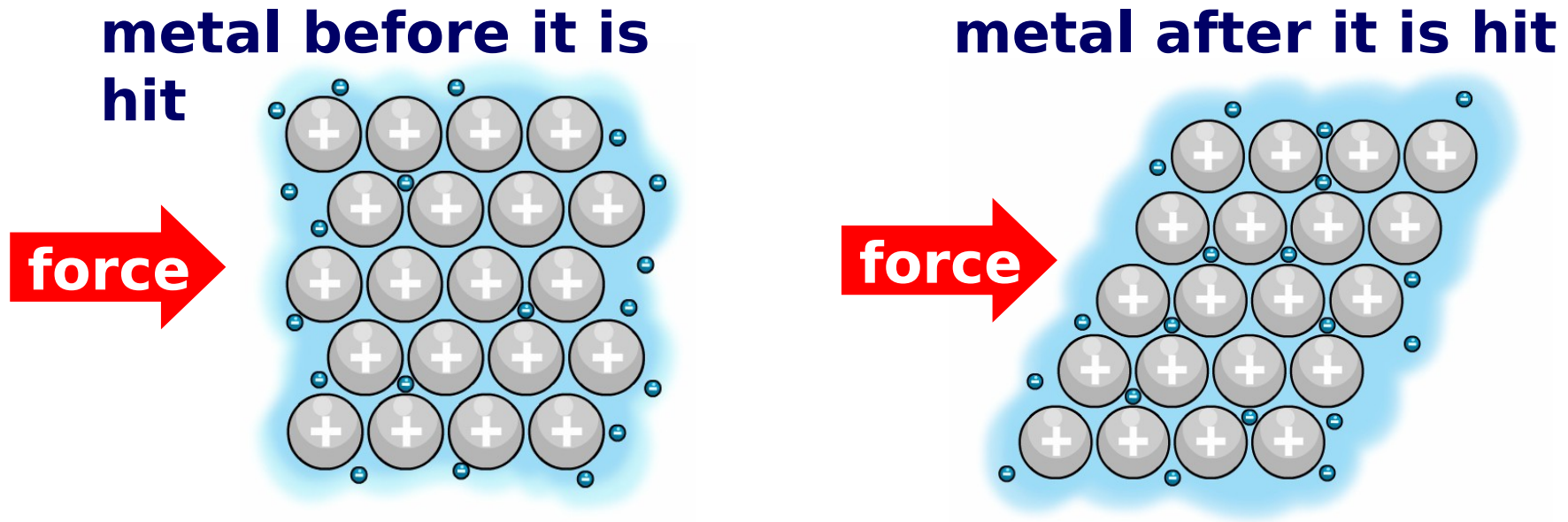


Figure: Sliding of metal atoms before and after being hammered

- The metallic bonds do not break because the delocalized electrons are free to move throughout the structure.
- This also explains why metals are malleable (easy to shape) and ductile (can be drawn into wires).

iv) Malleability and Ductility of Metals

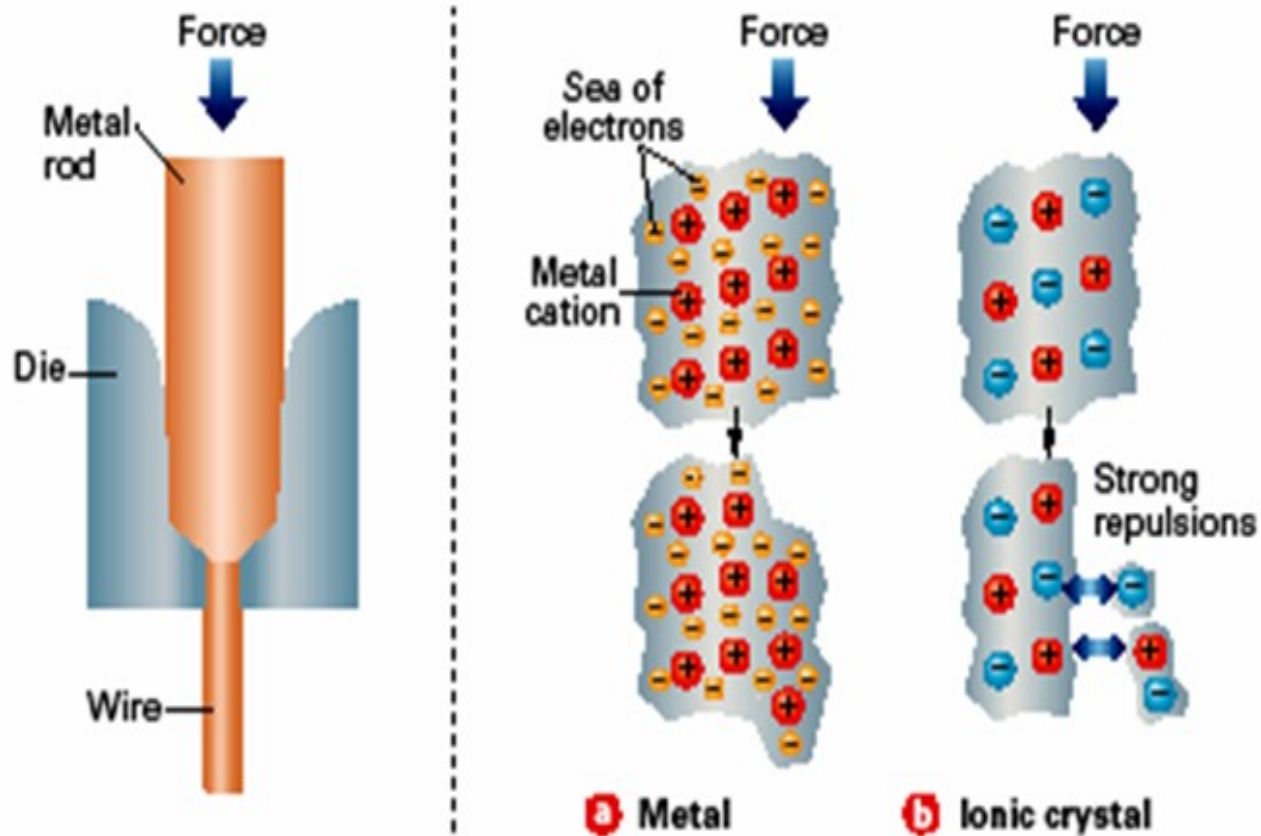
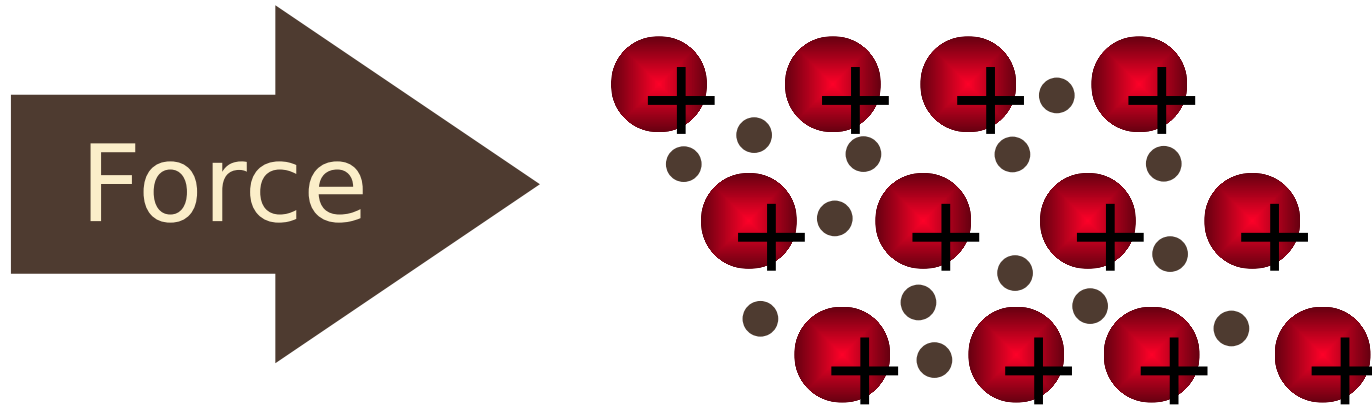


Figure: Comparison between metallic crystal and ionic crystal w.r.t malleability and ductility

Cont'd...

- Metals are malleable and ductile, rather than brittle, as a result of the **non-directional** nature of metallic bonds.
- The attractive forces exerted by the positive metal ions for the mobile electrons occur in all directions.
- This means that layers of atoms can move past one another without disrupting the force between the positive ions and the negative sea of electrons.

Malleability and Ductility (cont'd...)



- Mobile e-'s allow atoms to slide by
 - like ball bearings in oil.

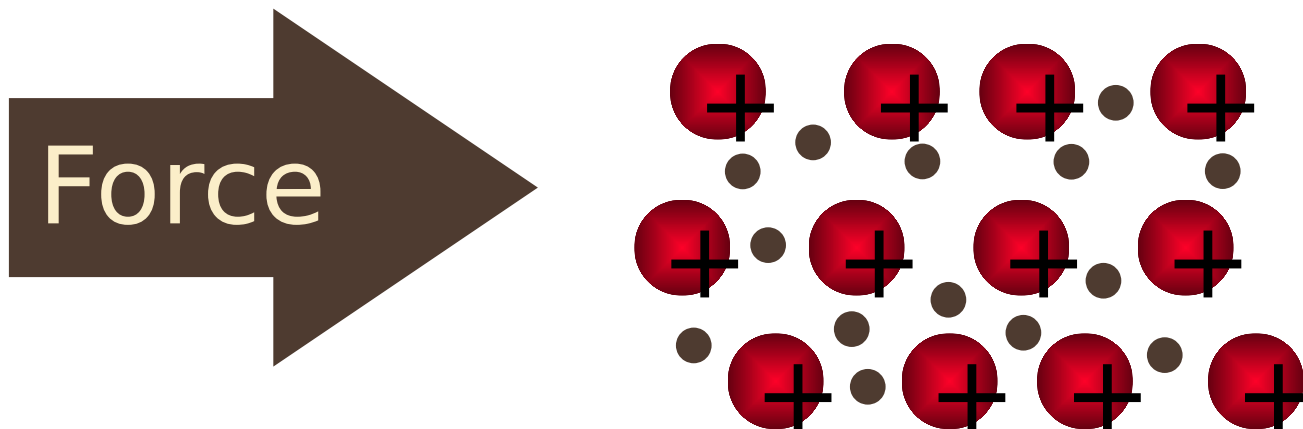


Figure: Malleability and Ductility illustrated

v) High Density

- Most metals have relatively high densities because metallic lattices are close-packed.

The End of Chapter 2

Thank
you

A fountain pen with a gold nib and a black barrel, positioned as if it has just finished writing the word 'you'. The pen is angled upwards and to the right, with its nib pointing towards the end of the word. The barrel has a textured, possibly rubberized, appearance.