# Chemical Bonding and Molecular Structure

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## Chemical Bonding

A chemical bond is an attractive force which holds various constituents (such as atoms, ions) together in different chemical species.

## Kossel-Lewis Approach to Chemical Bonding

- Lewis postulated that atoms attain the stable octet when they are chemically bonded.
- **Lewis symbols**
- Notations to represent valence electrons in an atom
- Example:

- Significance of Lewis symbols – The number of dots represents the number of valence electrons.
- Octet rule- Atoms tend to gain, lose or share electrons so as to have eight electrons in their valence shells.
- **Lewis dot structure**

Representation of molecules and ions in terms of the shared pairs of electrons and the octet rule

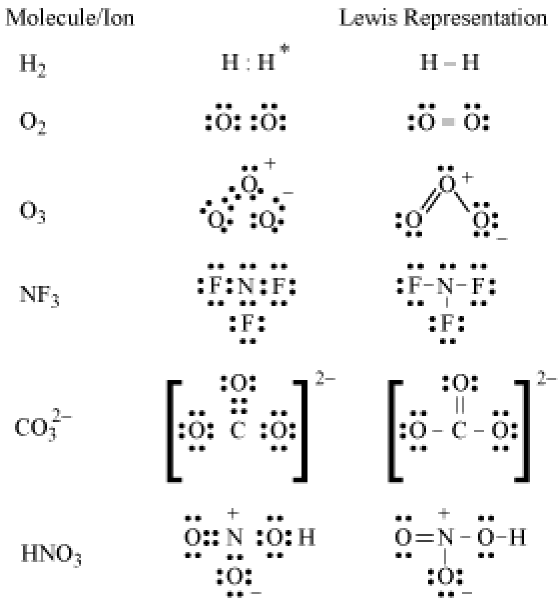
Steps to writing Lewis dot structure:

- Add the valence electrons of the combining atoms. This will give the total number of electrons required to write the structure.
- One negative charge means the addition of an electron. Similarly, one positive charge implies the removal of an electron from the total number of electrons.
- The chemical symbol of the atoms and the skeletal structure of the compound should be known. Then, distribute the total number of electrons as bonding shared pairs between the atoms in proportion to the total bonds.

- The least electronegative atom occupies the central position of the molecule/ion. For example in $NF_3$, nitrogen occupies the central position whereas the three fluorine atoms occupy the terminal positions.

- When the shared pairs of electrons have been accounted for single bonds, utilise the remaining electron pairs for either multiple bonding or count them as lone pairs. Here, the basic requirement is that each bonded atom gets an octet of electrons.

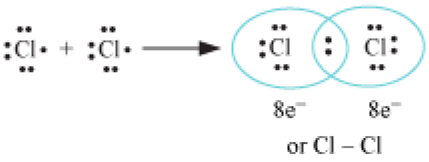
- Lewis representation of some molecules



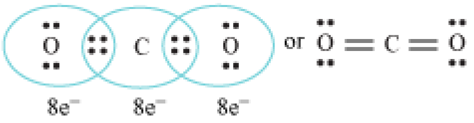
(*- Each hydrogen atom attains the electronic configuration of helium i.e. a duplet of electrons)

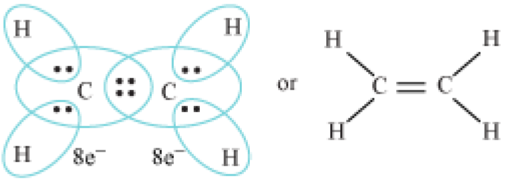
- **Covalent bond**

- Single covalent bond – Sharing of one electron pair

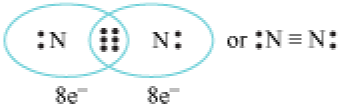


- Double bond – Sharing of two electron pairs





- Triple bond – Sharing of three electron pairs



$N_2$ molecule

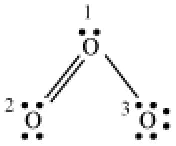
$C_2H_2$ molecule

- **Formal Charge**

$$\left[\begin{array}{l}\text{Formal charge (F.C)}\\ \text{on an atom in a}\\ \text{Lewis structure}\end{array}\right] = \left[\begin{array}{l}\text{Total number of}\\ \text{valence electrons}\\ \text{in the free atom}\end{array}\right] - \left[\begin{array}{l}\text{Total number of}\\ \text{nonbonding (lone}\\ \text{pair electrons)}\end{array}\right] - \frac{1}{2}\left[\begin{array}{l}\text{Total number of}\\ \text{bonding (shared}\\ \text{electrons)}\end{array}\right]$$

- Example:

  Lewis structure of $O_3$ is



F.C. on the O-1 atom $= 6 - 2 - \frac{1}{2}(6) = +1$

F.C. on the O-2 atom $= 6 - 4 - \frac{1}{2}(4) = 0$

F.C. on the O-3 atom $= 6 - 6 - \frac{1}{2}(2) = -1$

- Smaller the formal charge on the atoms, lower is the energy of the structure.
- The concept of formal charge is based on covalent bonding in which electron pairs are equally shared by neighbouring atoms.

- Limitations of the octet rule:

- Incomplete octet of the central atom

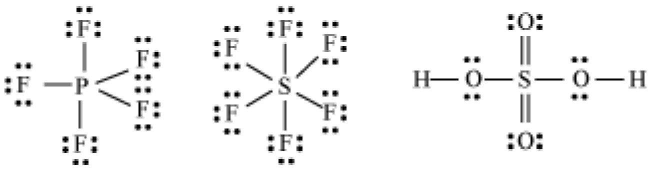
  Examples: LiCl, $BeH_2$, $BCl_3$

- Odd electron molecules

  Examples: NO, $NO_2$

- Expanded octet

  Examples: $PF_5$, $SF_6$, $H_2SO_4$



$PF_5$ 10 electrons around the P atom

$SF_6$ 12 electrons around the S atom

$H_2SO_4$ 12 electrons around the S atom

Some other drawbacks of octet rule:

- It is based upon chemical inertness of noble gases. However, some noble gases can combine to form compounds such as $XeF_2$, $KrF_2$, $XeOF_2$, etc.

- It does not account for shape of molecules

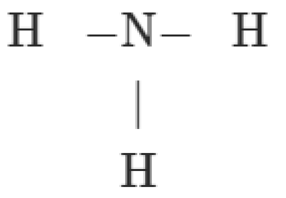
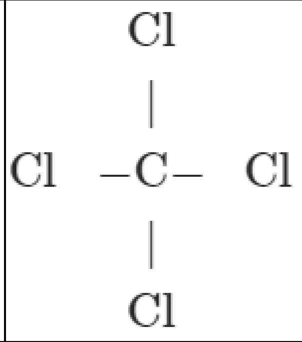
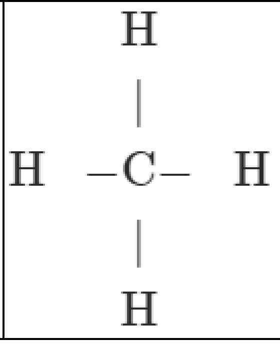
- It does not explain the relative stability of molecules

**Conditions for Formation of Covalent Bond**

- Presence of four or more electrons in the outermost shell of an atom (exception H, Be, B and Al)

- High electronegativity of both the atoms
- High electron affinity for both the atoms
- High ionisation energy of both the atoms
- Electronegativity difference between combining atoms should be zero or very low

### Formation of Some Covalently Bonded Molecules

| Compound | Molecule | Type and Number of Covalent Bonds |
|---|---|---|
| Hydrogen ($H_2$) | H−H | One single bond |
| Chlorine ($Cl_2$) | Cl−Cl | One single bond |
| Nitrogen ($N_2$) | N≡N | One triple bond |
| Water ($H_2O$) | H−O−H | Two single bonds between O and H |
| Ammonia ($NH_3$) |  $\begin{array}{ccc} \mathrm{H} & -\mathrm{N}- & \mathrm{H} \\ & \vert & \\ & \mathrm{H} & \end{array}$ | Three single bonds between N and H |
| Carbon tetrachloride ($CCl_4$) |  $\begin{array}{ccc} & \mathrm{Cl} & \\ & \vert & \\ \mathrm{Cl} & -\mathrm{C}- & \mathrm{Cl} \\ & \vert & \\ & \mathrm{Cl} & \end{array}$ | Four single bonds between C and Cl |
| Methane ($CH_4$) |  $\begin{array}{ccc} & \mathrm{H} & \\ & \vert & \\ \mathrm{H} & -\mathrm{C}- & \mathrm{H} \\ & \vert & \\ & \mathrm{H} & \end{array}$ | Four single bonds between C and H |

### Difference between Properties of Ionic and Covalent Compounds

| Ionic Compounds | Covalent Compounds |
|---|---|

| | |
|---|---|
| The constituent particles are ions. | The constituent particles are molecules. |
| They exist as hard solids. | They exist as gases, liquids or soft solids. |
| They have high melting and boiling points | They have low melting and boiling points. |
| They are good conductors of electricity in the aqueous or molten state. | They do not conduct electricity. |
| They ionise in solution and behave as electrolytes. | Only polar compounds form ions in aqueous solutions. |
| They undergo dissociation. | They do not undergo dissociation. |
| They are soluble in water. | They are soluble only in organic solvents. |
| They undergo fast chemical reactions. | They undergo slow chemical reactions. |

## Ionic or Electrovalent Bond & Bond Parameters

- Formation of ionic compound depends upon

- ease of formation of positive and negative ions
- arrangement of positive and negative ions

## Ionisation Enthalpy ($\Delta_i H$)

- Enthalpy change when a gas phase atom in its ground state loses an electron

$M_{(g)} \rightarrow M^+_{(g)} + e^-$

- Always positive

- Lower the ionisation enthalpy, more easily is the positive ion formed.

## Electron Gain Enthalpy

- Enthalpy change when a gas phase atom in its ground state gains an electron

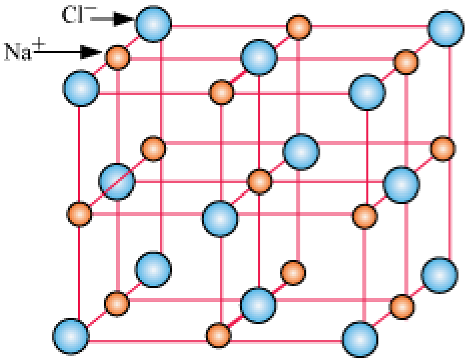
$X_{(g)} + e^- \rightarrow X^-_{(g)}$

- May be positive or negative

- Higher the negative value of electron gain enthalpy, more easily is the negative ion formed.

- Ionic bond is formed more easily between an element with low ionization enthalpy and element with high negative value of electron gain enthalpy

### Crystal Structure of NaCl (rock salt)



Rock salt structure

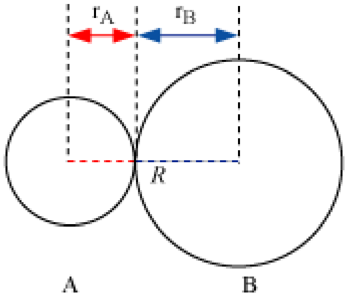
### Lattice Enthalpy

- Energy required to separate completely one mole of a solid ionic compound into gaseous constituent ions
- Higher the lattice enthalpy, more stable is the ionic compound.

### Bond Parameters

### Bond Length

- Equilibrium distance between the nuclei of two bonded atoms in a molecule



Bond length (R) = $r_A + r_B$

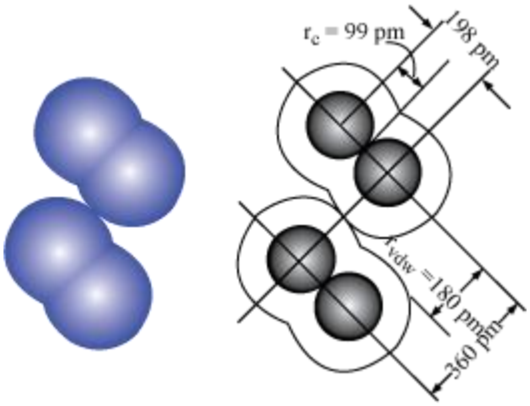
- **Covalent radius:**

  Radius of an atom's core which is in contact with the core of an adjacent atom in a bonded situation

- Van der Waals’ radius:

  Overall size of the atom which includes its valence shell in a non-bonded situation

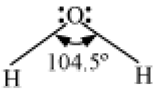
- Covalent and van der Waals’ radii in a chlorine molecule:



Here, inner circles correspond to the size of the chlorine atom.

### Bond Angle

- Angle between orbitals containing bonding electron pairs around the central atom in a molecule/complex ion



### Bond Enthalpy ($\Delta_a H$)

- Energy required to break one mole of a particular type of bond between two atoms in gaseous state
- Example:

  $O_2 (O{=}O)_{(g)} \rightarrow O_{(g)} + O_{(g)}$ ; $\Delta_a H^\theta = 498$ kJ mol$^{-1}$

- Larger the bond enthalpy, stronger is the bond.
- Mean or Average Bond Enthalpy

$$= \frac{\text{Total bond dissociation enthalpy}}{\text{Number of bonds}}$$

**Bond Order**

- Represents the number of bonds between two atoms in a molecule

- Examples:

| Molecule | Bond Order |
|---|---|
| $H_2$ | 1 |
| $O_2$ | 2 |
| $N_2$ | 3 |
| CO | 3 |

- Isoelectronic species have identical bond order.

- Examples:

| Isoelectronic species | Bond order |
|---|---|
| $F_2$ and $O_2^{2-}$ | 1 |
| $N_2$, CO, and $NO^+$ | 3 |

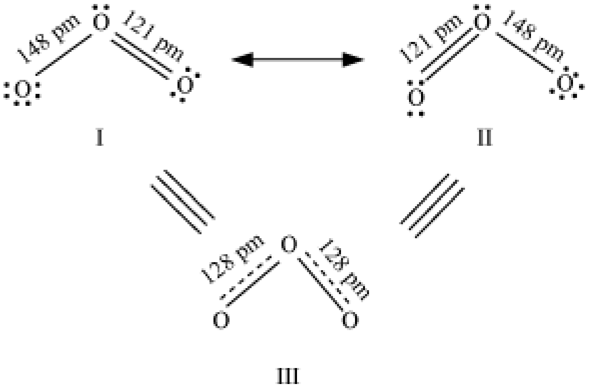
- With the increase in bond order:
- bond enthalpy increases
- bond length decreases

**Resonance Structures**

- Equivalent Lewis Structures
- Also known as canonical structures

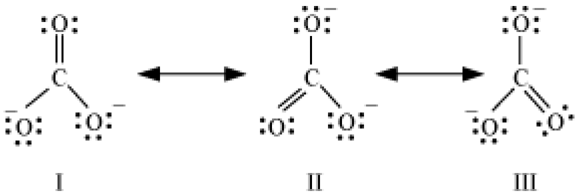
- Example:

- Resonance structures of ozone ($O_3$)



Here, I and II are resonance structures. III is the resonance hybrid.

- Resonance structures of carbonate ion $\left(CO_3^{2-}\right)$:



Here, I, II, and III are resonance structures.

- Resonance stabilises a molecule.
- Energy of resonance hybrid is less than that of any one of the resonance structures.
- Resonance averages the bond characteristics as a whole.

**Important**

Canonical structure does not have real existence.

Molecule does not exist in one canonical form for a certain fraction of time and in another for other fractions of time.

There is no equilibrium between canonical forms.

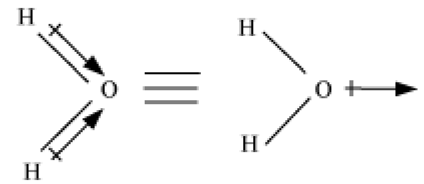
A molecule has only a single structure which is the resonance hybrid.

**Polarity of Bonds**

- Dipole moment (μ) = Charge (Q) × Distance of separation (*r*)
- Unit = Debye (D)

  1 D = $3.33564 \times 10^{-30}$ C m

- Example: Dipole moment of $H_2O$

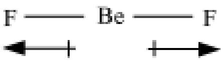


Bond dipole

Resultant dipole moment

Net Dipole moment, μ = 1.85 D

- Example: Dipole moment of $BeF_2$

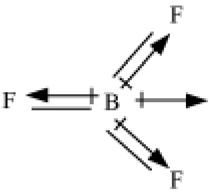


Bond diploes in $BeF_2$

Total Bond moment in $BeF_2$

Net Dipole moment, μ = 0

- Example: Dipole moment of $BF_3$

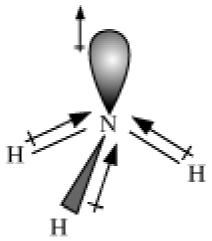


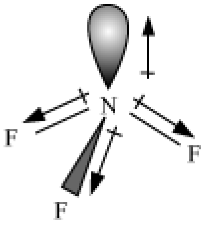
Bond dipoles

Total dipole moment

Net Dipole moment, μ = 0

- Comparison between the dipole moments of $NH_3$ and $NF_3$





Resultant dipole moment in $NH_3$ = $4.90 \times 10^{-30}$ C m

Resultant dipole moment in $NF_3$ = $0.80 \times 10^{-30}$ C m

- Covalent character of ionic bond in terms of Fajan's rule:

- Smaller the size of the cation and larger the size of the anion, greater is the covalent character of ionic bond.

- Greater the charge on the cation, greater is the covalent character of the ionic bond.

- Cations with outer electronic configuration of the type $ns^2np^6nd^{10}$ (typical of transition metal cations) have greater polarising power than the ones with a noble gas configuration, $ns^2np^6$ (typical of alkali and alkaline earth metal cations).

**Valence Shell Electron Pair Repulsion (VSEPR) Theory**

- Shapes of covalent molecules can be predicted with the help of this theory.

- Postulates:

- The shape of a molecule depends upon the number of valence shell electron pairs (bonded or non-bonded) around the central atom.
- Pairs of electrons in the valence shell tend to repel each other as their electron clouds are negatively charged.
- The electron pairs tend to occupy those positions in space, which minimize repulsions and thus maximize distance from one another.
- The valence shell is taken as a sphere with the electron pairs localizing on the spherical surface at maximum distance from one another.
- A multiple bond is treated as a single electron pair and the two or three electron pairs of a multiple bond are treated as a single super pair.
- The VSEPR model is applicable to any such structure where two or more resonance structures can represent a molecule.

- Decreasing order of repulsive interaction of electron pairs:

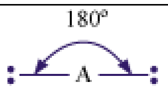
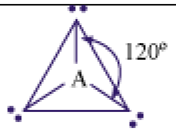
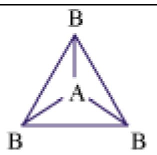
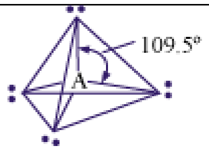
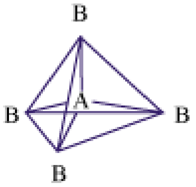
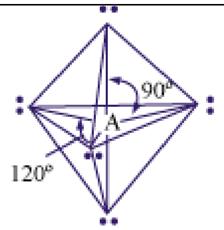
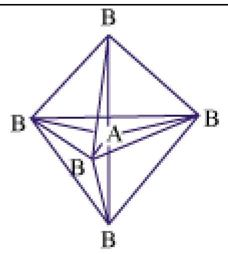
Lone pair (lp) – Lone pair (lp) > Lone pair (lp) – Bond pair (bp) > Bond pair (bp) – Bond pair (bp)

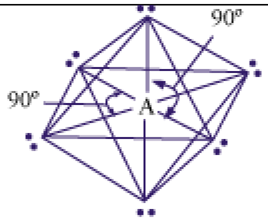
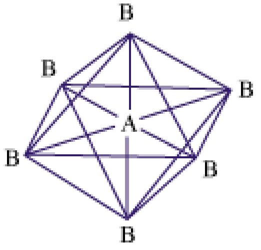
- Reason for greater repulsion between lp – lp: The lone pairs occupy larger space than the bond pairs.

- Molecules are classified into the following two categories to predict the geometrical shapes of molecules using VSEPR theory.

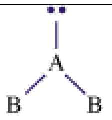
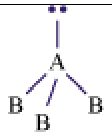
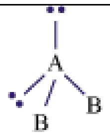
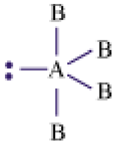
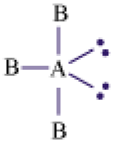
- Molecules in which the central atom has no lone pair
- Molecules in which the central atom has one or more lone pairs

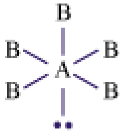
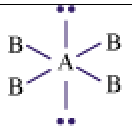
**Geometry of molecules in which the central atom has no lone pair of electrons:**

| Number of electron pairs | Arrangement of electron pairs | Molecular geometry | Examples |
|---|---|---|---|
| 2 |  <br>Linear |  <br>Linear | $BeCl_2$,<br>$HgCl_2$ |
| 3 |  <br>Trigonal planar |  <br>Trigonal planar | $BF_3$ |
| 4 |  <br>Tetrahedral |  <br>Tetrahedral | $CH_4$, $NH_4^+$ |
| 5 |  <br>Trigonal bipyramidal |  <br>Trigonal bipyramidal | $PCl_5$ |

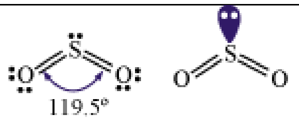
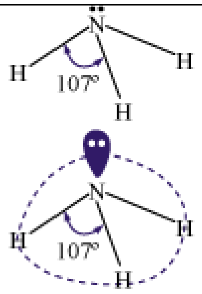
| | | | |
|---|---|---|---|
| 6 |  <br>Octahedral |  <br>Octahedral | $SF_6$ |

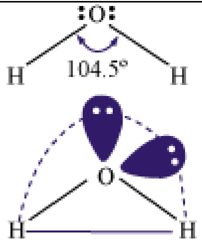
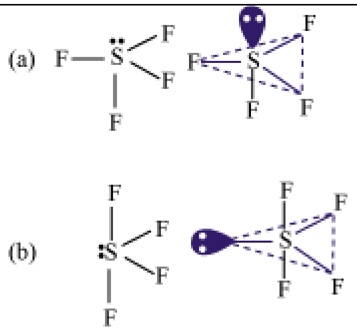
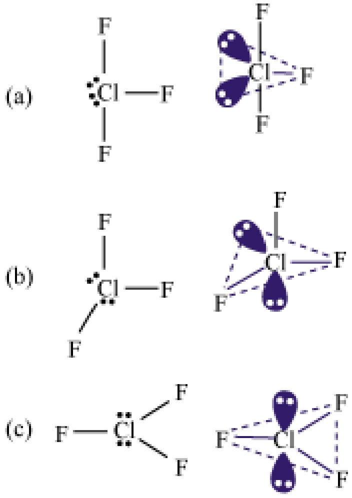
### Shape (geometry) of some simple molecules/ions with central ions having one or more lone pairs of electrons (E):

| Molecule type | No. of bonding pairs | No. of lone pairs | Arrangement of electron pairs | Shape | Examples |
|---|---|---|---|---|---|
| $AB_2E$ | 2 | 1 |  <br>Trigonal planar | Bent | $SO_2$, $O_3$ |
| $AB_3E$ | 3 | 1 |  <br>Tetrahedral | Trigonal pyramidal | $NH_3$ |
| $AB_2E_2$ | 2 | 2 |  <br>Tetrahedral | Bent | $H_2O$ |
| $AB_4E$ | 4 | 1 |  <br>Trigonal bi-pyramidal | See saw | $SF_4$ |
| $AB_3E_2$ | 3 | 2 |  <br>Trigonal bi-pyramidal | T-shape | $ClF_3$ |

| | | | | | |
|---|---|---|---|---|---|
| $AB_5E$ | 5 | 1 |  <br>Octahedral | Square pyramid | $BrF_5$ |
| $AB_4E_2$ | 4 | 2 |  <br>Octahedral | Square planar | $XeF_4$ |

**Shapes of molecules containing bond pair and lone pair:**

| **Molecule type** | **No. of bonding pairs** | **No. of lone pairs** | **Arrangement of electron pairs** | **Shape** | **Examples** |
|---|---|---|---|---|---|
| $AB_2E$ | 2 | 1 |  | Bent | Theoretically, the shape should have been triangular planar. However, in actuality, it is bent or v-shaped. The reason for this is that the lone pair−bond pair repulsion is greater than the bond pair−bond pair repulsion. Therefore, the angle is reduced to 119.5° from 120°. |
| $AB_3E$ | 3 | 1 |  | Trigonal Pyramidal | If there had been a bp in place of a lp, the shape would have been tetrahedral. However, one lone pair is present, and the repulsion between lp and bp (greater than the bp−bp repulsion) causes the angle between the bond pairs to reduce to 107° from 109.5°. |

| | | | | | |
|---|---|---|---|---|---|
| $AB_2E_2$ | 2 | 2 |  | Bent | The shape would have been tetrahedral had there been only bp. However, two lps are present, so the shape is distorted tetrahedral or angular. The reason for this is that the lp−lp repulsion is greater than the lp−bp repulsion, which in turn is greater than the bp−bp repulsion. Thus, the angle reduces to 104.5° from 109.5°. |
| $AB_4E$ | 4 | 1 |  | See-saw | The lp is present at the axial position in (a). So, there are three lp−bp repulsions at 90°.<br>The lp is at the equatorial position in (b), and there are two lp−bp repulsions. Therefore, the arrangement shown in (b) is more stable. This shape is described as a distorted tetrahedron, a folded square or a see-saw. |
| $AB_3E_2$ | 3 | 2 |  | T-shaped | The lp is at the equatorial position in (a). As a result, there are lesser lp−bp repulsions as compared to the others where the lone pairs are at the axial position. Therefore, the shape in (a) is the most stable (T-shaped). |

## Valance Bond Theory and the Concept of Hybridisation

### Limitations of Lewis approach

It failed to explain:

- the formation of a chemical bond
- the shapes of polyatomic molecules
- difference between bond dissociation energies and bond lengths of various molecules containing same kind of bonds. For example, both $H_2$ and $F_2$ contain a single covalent bond, but have different values of the same quantities.

**Limitations of VSEPR theory**

- Although it gave the geometry of simple molecules, it could not explain them.
- It was not useful in predicting shapes of many compounds, like transition metal complexes. Thus, it had limited applications.

To overcome these limitations, two new theories were given. These were-

- Valence bond theory
- Molecular orbital theory

**Valence Bond Theory**

Introduced by Heitler and London (1927); developed further by Pauling and others

**Theory:**

- Consider two hydrogen atoms A and B approaching each other to form a covalent bond. $N_A$, $N_B$, $e_A$, and $e_B$ represent the nucleus and electrons of atoms A and B respectively.
- When the atoms are at large distance from each other, there is no force of attraction between them.
- As the distance reduces, the following forces start developing in them:

Attractive forces –

1. Between the nucleus and the electron of the same atom ($N_A$- $e_A$, $N_B$ - $e_B$)

2. Between the nucleus and the electron of different atoms ($N_A$- $e_B$, $N_B$ - $e_A$)

Repulsive forces –

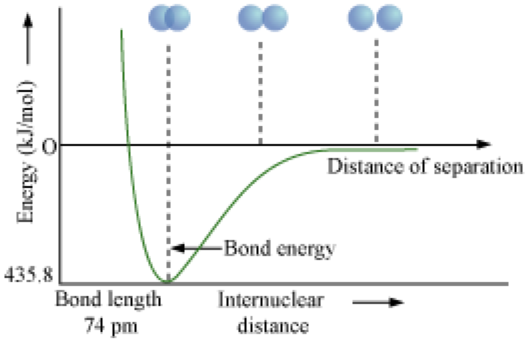
1. Between the electrons of the two atoms ($e_A$ - $e_B$)

2. Between the nuclei of the two atoms ($N_A$ - $N_B$)

- Experimentally, the attractive forces are found to be stronger than the repulsive ones. Therefore, the two atoms approach each other, and the potential energy also drops during the process.

- When the two forces balance each other, a state of minimum energy is attained. At this point, the two atoms are said to be bonded. The distance between them is called the bond length (in case of H-atoms, the bond length is equal to 74 pm).

- Also, during bond formation, energy is released. This released energy is called bond enthalpy. The minimum of the given curve represents bond energy, which is 435.8 kJ for hydrogen.



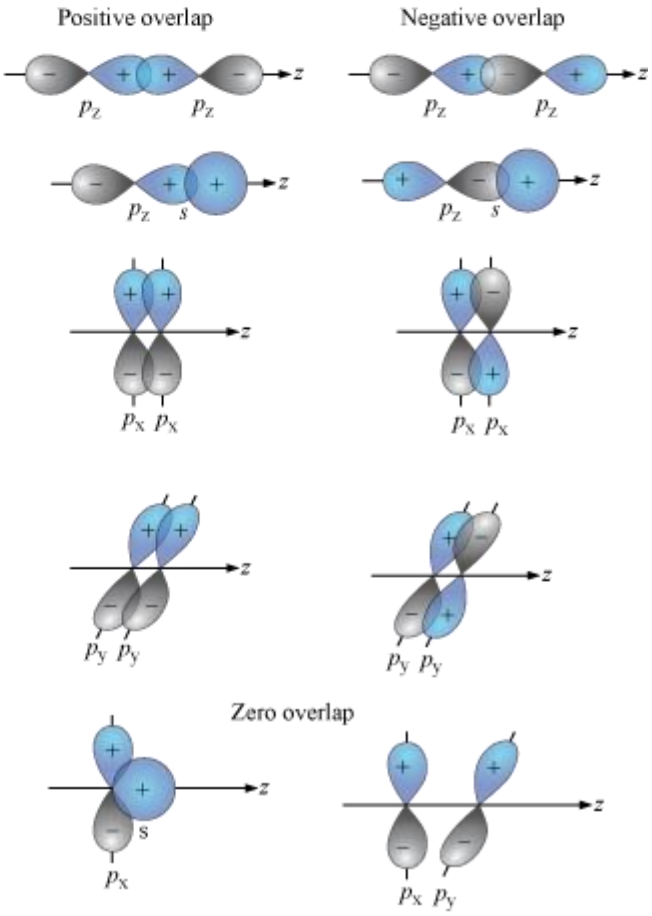
The potential energy curve for the formation of $H_2$ molecule as a function of internuclear distance of the H atoms

- It can be observed in the above figure that when the two H-atoms form a bond, they overlap each other slightly. This represents overlapping of atomic orbitals. (Hence, this theory introduces the concept of atomic orbitals, stating that covalent bonds are formed by the overlapping of singly filled atomic orbitals containing electrons having opposite spins.)

- More the extent of the overlapping, stronger will be the bond.

**Overlapping of Atomic Orbitals**

- The overlap between various atomic orbitals can be positive, negative or zero. The given figure shows the various possible overlappings for *s* and *p* orbitals.



- Two types of covalent bonds can be formed based on the type of overlapping:
- Sigma bond (head-on or axial overlap) – bond formed by head-to-head overlap along the inter-nuclear axis. This type of overlapping results in the formation of sigma bonds. It is of the following types

  (i) *s-s*

  (ii) *s-p*

  (iii) *p-p*

-
- Pi ($\pi$) bond (sideways overlap) – lateral overlapping takes place as the axes of the orbitals remain parallel to each other, and perpendicular to the inter-nuclear axis
- As the extent of overlapping in the case of a sigma bond is more than it is in the case of a pi bond, the sigma bond is stronger.

Now, we know that

- *s* orbital is spherical in nature and can overlap from any direction.
- *p* orbitals are arranged in *x*, *y* and *z* directions, and have an angle of 90° among themselves.

In the case of methane ($CH_4$), 1*s* orbitals of 4 H atoms overlap with 2*s*, $2p_x$, $2p_y$ and $2p_z$ orbitals of C. Thus, three bonds (formed by the overlapping of 1*s* and 2*p* orbitals) should be at an angle of 90° with each other, and the position of the fourth bond (formed by the overlapping of 1s and 2*s* orbitals) cannot be known. However, we know that the geometry of $CH_4$ is tetrahedral, and all the bond angles are equal (109.5°).

Therefore, it is not possible to explain the geometry of various molecules (like $H_2O$, $CH_4$, and $NH_3$) only on the basis of overlapping.

To overcome this problem Pauling introduced the concept of **hybridisation**.

### Hybridisation

It states that atomic orbitals of slightly different energies combine to form a new set of equivalent orbitals (having the same energy and shape) known as hybrid orbitals.

These hybrid orbitals are more stable than atomic orbitals, and participate in bond formation.

**Salient features:**

1. Number of hybrid orbitals obtained = Number of atomic orbitals undergoing hybridisation

2. Hybrid orbitals are always identical in all respects.

3. To minimise electronic repulsion, they orient themselves in a preferred manner. Thus, the type of hybridisation indicates the geometry of a molecule.

**Conditions required for hybridisation:**

1. Orbitals in the valence shell should be hybridised.

2. Orbitals undergoing hybridisation should have almost equal energy.

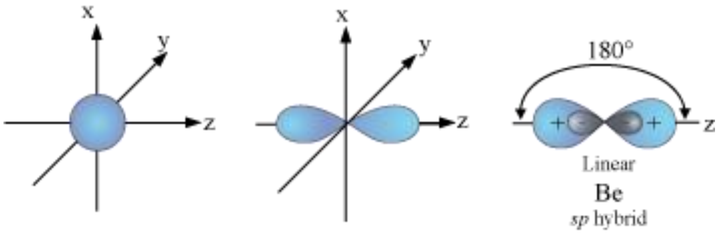
3. Promotion of electrons is not essential prior to hybridisation.

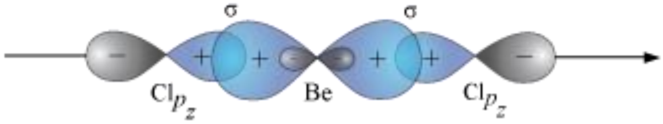
4. Half as well as fully filled orbitals of the valence shell can take part in hybridisation.

## Types of hybridisation:

- ***sp***

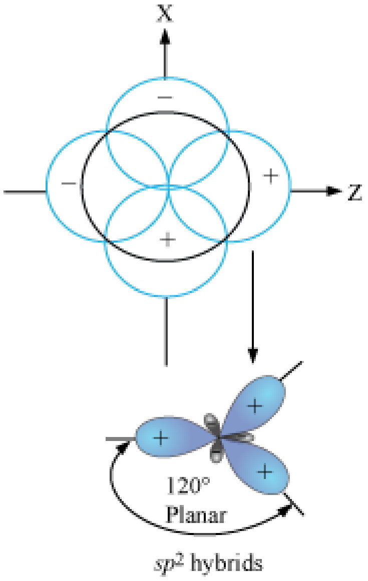
- Involves mixing of one *s* and one *p* orbital to give two *sp* orbitals
- Hybrid orbitals have 50% *s* and 50% *p* character.
- Also known as diagonal hybridisation. The molecules with sp hybridisation possess linear geometry.
- Example: $BeCl_2$ possesses *sp* hybridisation.

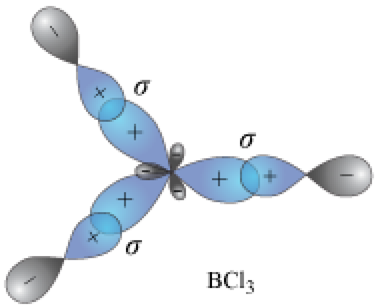




- ***sp***$^2$

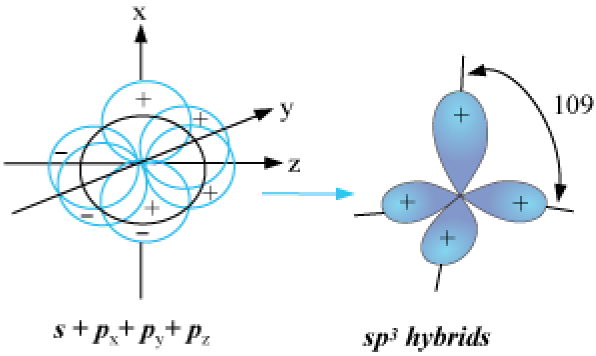
- Involves mixing of one *s* orbital and two *p* orbitals to give three *sp*$^2$ orbitals
- Hybrid orbitals have about 33% *s* and 67% *p* character.
- Three hybrid orbitals orient themselves in a trigonal planar fashion at an angle of 120°.
- Example: B in $BCl_3$ undergoes *sp*$^2$ hybridisation.

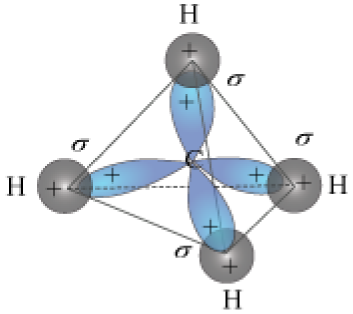




- ***sp*$^3$**

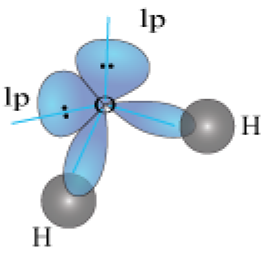
- Involves mixing of one *s* orbital and three *p* orbitals to give four *sp*$^3$ orbitals
- Hybrid orbitals have 25% *s* and 75% *p* character.
- Four hybrid orbitals orient themselves in such a manner that each orbital is directed toward the four corners of a tetrahedron.
- Example: C in $CH_4$ undergoes *sp*$^3$ hybridisation.



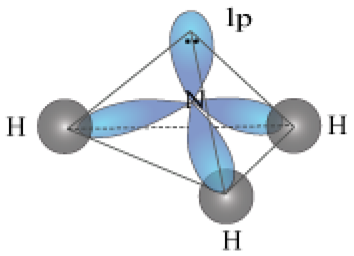


$CH_4$

The geometry of $H_2O$ and $NH_3$ can also be explained using *sp*$^3$ hybridisation. In a water molecule, the oxygen atom undergoes *sp*$^3$ hybridisation. Among the four hybrid orbitals, two contain the two lone pairs present on the O-atom, and the remaining two are involved in bonding. Similarly, in the case of $NH_3$, one *sp*$^3$ hybrid orbital contains a lone pair, and the remaining three are involved in bonding.



$H_2O$

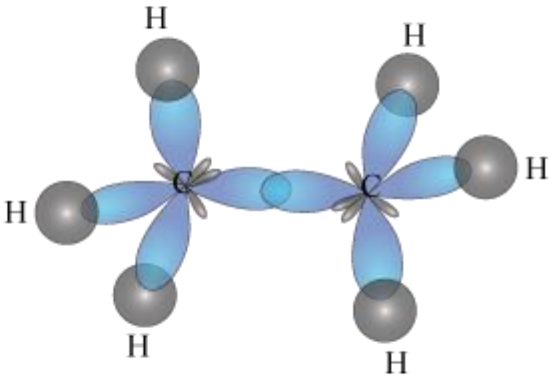


$NH_3$

**Some Other Examples of *sp*$^3$, *sp*$^2$ and *sp* hybridisation**

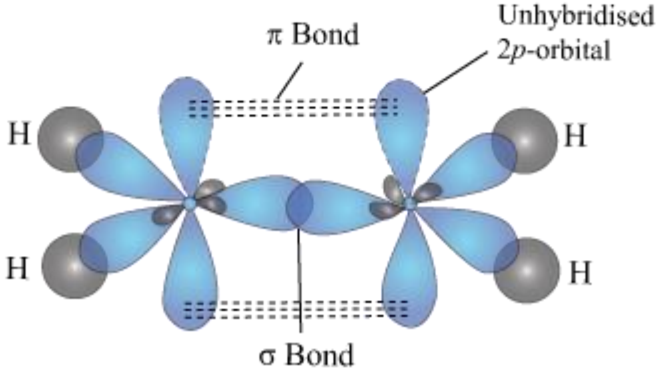
- **Hybridisation in $C_2H_6$**

- In $C_2H_6$, both the carbon atoms are *sp*$^3$ hybridised.
- One hybrid orbital from each C-atom is involved in C−C sigma bond.
- Remaining six hybrid orbitals form sigma bonds with six H-atoms.



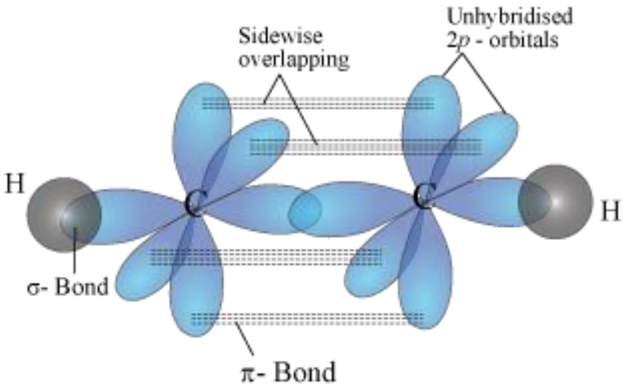
- **Hybridisation in $C_2H_4$**

- In $C_2H_4$, both the carbon atoms are $sp^2$ hybridised.
- One hybrid orbital from each C-atom is involved in C−C sigma bond.
- The *p*-orbital that has not participated in hybridisation, participates in C−C pi bonding. Thus, $C_2H_4$ contains a C−C double bond.
- Remaining four hybrid orbitals form sigma bonds with four H-atoms.



- **Hybridisation in $C_2H_2$**

- In $C_2H_2$, both the carbon atoms are *sp* hybridised.
- One hybrid orbital from each C-atom is involved in C−C sigma bond.
- The two *p*-orbitals that have not participated in hybridisation, participate in two C−C pi bonds. Thus, $C_2H_2$ contains a C−C triple bond.
- Remaining two hybrid orbitals form sigma bonds with two H-atoms.

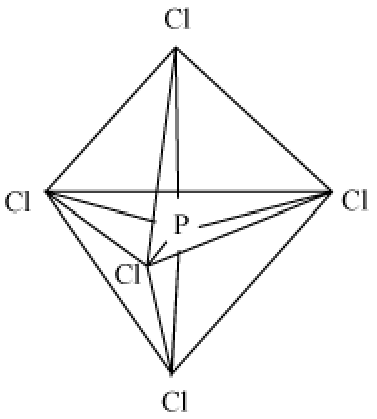


### Hybridisation involving *d*-orbitals

- Elements present in the third group contain the *d*-orbital in addition to the *s* and *p* orbitals. Also, the energy of 3*d* orbitals is comparable to 3*s* and 3*p* as well as 4*s* and 4*p* orbitals. Thus, the orbitals that can participate in hybridisation are
- 3*s*, 3*p*, and 3*d*
- 3*d*, 4*s* and 4*p*
- However, the energy gap between 3p and 4*s* orbitals is large enough to prevent them from mixing.
- Important hybridisation involving *d*-orbitals are:

| **Shapes of molecules / ions** | **Hybridisation** | **Example** |
|---|---|---|
| Square planar | $dsp^2$ | $[Ni(CN)_4]^{2-}$ |
| Trigonal bipyramidal | $sp^3d$ | $PCl_5$ |
| Square pyramidal | $sp^3d^2$ | $BrF_5$ |
| Octahedral | $sp^3d^2/d^2sp^3$ | $SF_6/[Co(NH_3)_6]^{3+}$ |

### Formation of $PCl_5$

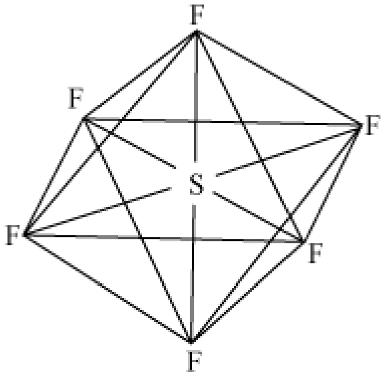


- The five $sp^3d$ hybrid orbitals orient themselves in a trigonal bipyramidal manner, which is the geometry of $PCl_5$.

- Notice that all the P−Cl bonds in the molecule are not equivalent. Three bonds that are present in one plane are called equatorial bonds and have an angle of 120° between them.

- The other two bonds are called axial bonds and are at 90° with the equatorial plane.

**Formation of $SF_6$**



- The six $sp^3d^2$ hybrid orbitals orient themselves in an octahedral manner, which is the geometry of $SF_6$.

### Molecular Orbital Theory

### Salient Features of Molecular Orbital (MO) Theory

- The electrons in a molecule are present in various molecular orbitals as the electrons of atoms are present in various atomic orbitals.

- Molecular orbitals are formed by the combination of atomic orbitals of comparable energy and proper symmetry.

- An electron in an atomic orbital is under the influence of only one nucleus while in a molecular orbital, it is under the influence of two or more nuclei depending upon the number of atoms in the molecule. Thus, an atomic orbital is mono-centric while a molecular orbital is polycentric.

- The number of molecular orbitals formed is equal to the number of combining atomic orbitals. When two atomic orbitals combine, two molecular orbitals are formed. One is called bonding molecular orbital and the other is called antibonding molecular orbital.

- The bonding MO has greater stability than anti-bonding MO as bonding MO has lower energy than antibonding MO.

- A molecular orbital gives the electron probability distribution around a group of nuclei in a molecule such as an atomic orbital that gives the electron probability distribution around a nucleus in an atom.

- The molecular orbitals are filled in the same way as atomic orbitals are filled according to the Aufbau's principle obeying the Pauli's exclusion principle and the Hund's rule.

**Formation of Molecular orbitals: Linear Combination of Atomic Orbitals (LCAO)**

**Application of LCAO to Homonuclear Diatomic Hydrogen Molecule**

$\psi_{MO} = \psi_A \pm \psi_B$

Where, $\psi_{MO}$= Wave function representing molecular orbital of hydrogen molecule

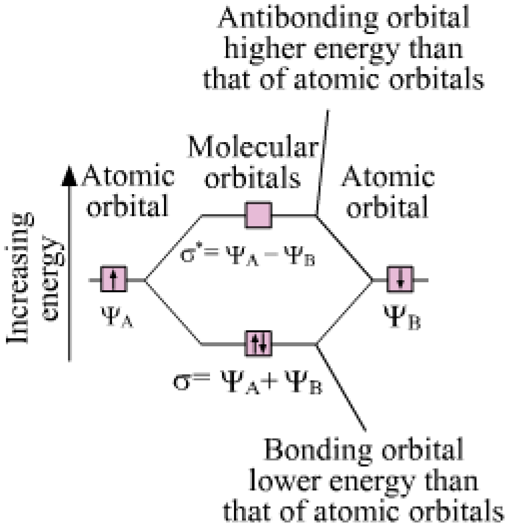
$\psi_A$, $\psi_B$= Wave functions representing atomic orbitals of hydrogen atoms A and B respectively

- Two molecular orbitals

  Bonding molecular orbital, $\sigma = \psi_A + \psi_B$

  Antibonding molecular orbital, $\sigma^* = \psi_A - \psi_B$

- Energy level diagram depicting formation of bonding and anti-bonding molecular orbitals of hydrogen molecule:



- The energy of a bonding MO is always lower than that of an antibonding M.O.

**Conditions for the Combination of Atomic Orbitals**

- The combining atomic orbitals must have the same or nearly the same energies.
- The combining atomic orbitals must have the same symmetry about the molecular axis.
- The extent of overlapping between the combining atomic orbitals must be maximum.

**Types of Molecular Orbitals**

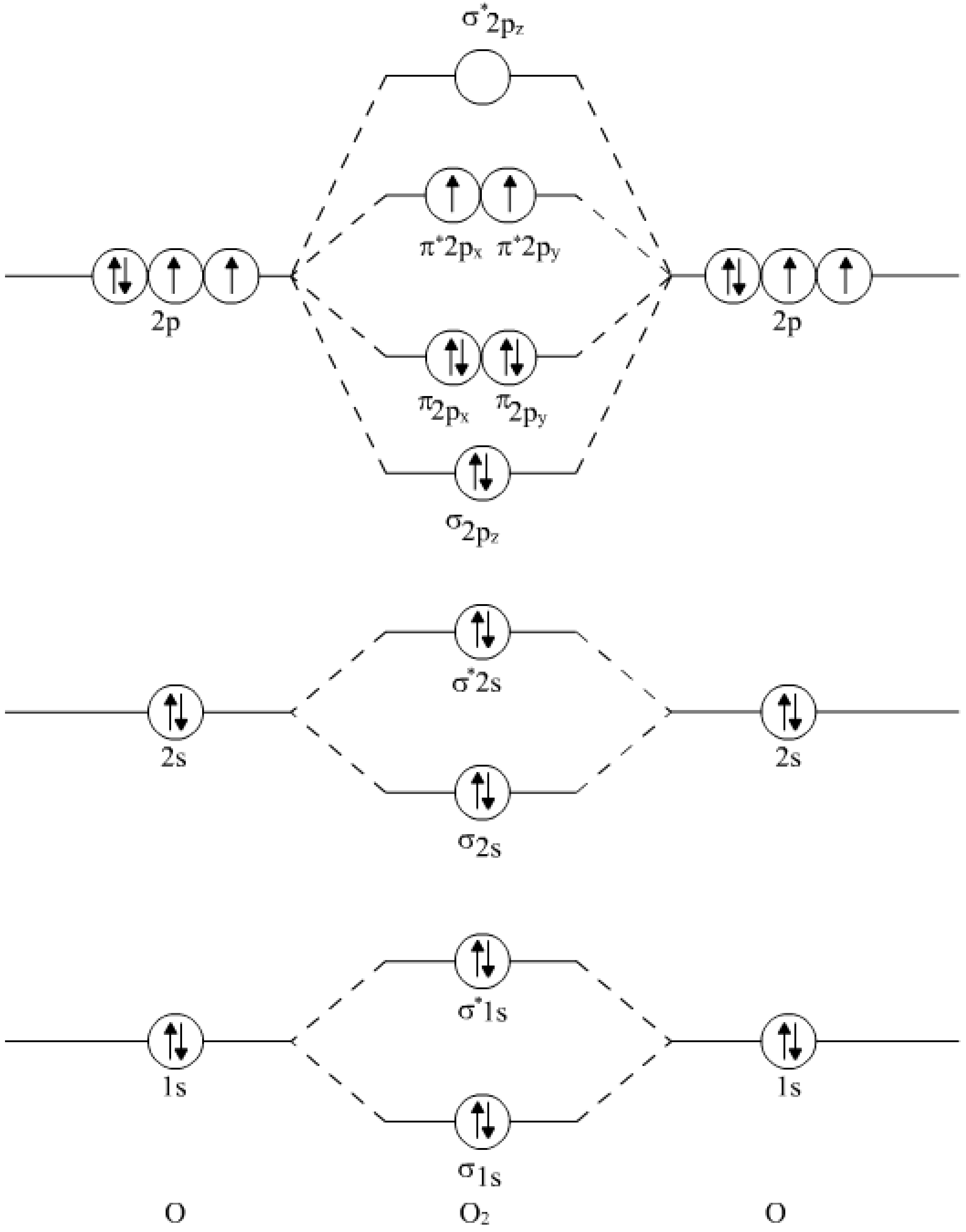
- σ (sigma), π (pi), δ (delta), etc.
- σ ––– symmetrical

  π ––– unsymmetrical

**Energy Level Diagram for Molecular Orbitals**

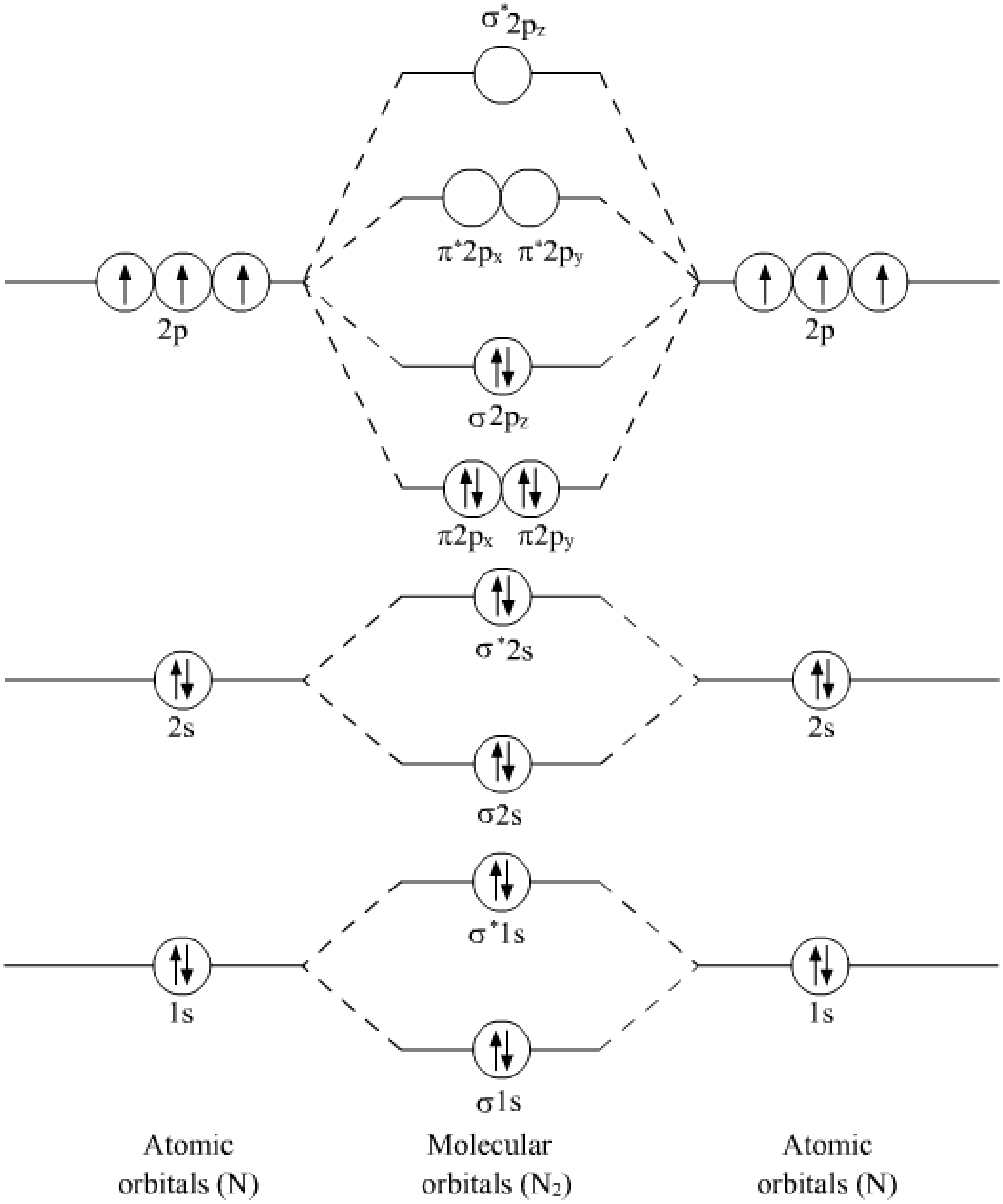
- Increasing order of energy for $O_2$ and $F_2$:

  $\sigma 1s < \sigma^*1s < \sigma 2s < \sigma^*2s < \sigma 2p_z < (\pi 2p_x = \pi 2p_y) < (\pi^*2p_x = \pi^*2p_y) < \sigma^*2p_z$



- Increasing order of energy for $Li_2$, $Be_2$, $B_2$, $C_2$, and $N_2$:

  $\sigma 1s < \sigma^*1s < \sigma 2s < \sigma^*2s < (\pi 2p_x = \pi 2p_y) < \sigma 2p_z < (\pi^*2p_x = \pi^*2p_y) < \sigma^*2p_z$



**Electronic Configuration and Molecular behaviour**

- Electronic configuration: Distribution of electrons among various molecular orbitals
- Information obtained from electronic configuration:
- Stability of molecules

If $N_b$= Number of electrons occupying bonding MO

$N_a$= Number of electrons occupying antibonding MO

Then,

(i) The molecule is stable if $N_b > N_a$

(ii) The molecule is unstable if $N_b \le N_a$

- Bond order:

  Bond order (b.o.) = $\frac{1}{2}(N_b - N_a)$

- Nature of bond:

  Single bond, if b.o. = 1

  Double bond, if b.o. = 2

  Triple bond, if b.o. = 3

- Bond length:

  Decreases with increase in b.o.

- Magnetic nature:

  Diamagnetic, if all the MOs are doubly occupied; and paramagnetic, if one or more MOs are singly occupied

**Bonding in Some Homonuclear Diatomic Molecular**

**Bonding in some homonuclear diatomic molecules is as follows-**

**Hydrogen Molecule ($H_2$)**

- H−atom : $1s^1$
- $H_2$ : $(\sigma 1s)^2$
- Bond order $= \frac{N_b - N_a}{2} = \frac{2-0}{2} = 1$
- Bonded by single covalent bond

- Diamagnetic**:** as no unpaired electron

**Helium Molecule ($He_2$)**

- He-atom : $1s^2$
- $He_2$ : $(\sigma 1s)^2\ (\sigma^* 1s)^2$
- Bond order = $\frac{N_b - N_a}{2} = \frac{2-2}{2} = 0$
- Unstable and does not exist

**Lithium Molecule ($Li_2$)**

- Li-atom : $1s^2\ 2s^1$
- $Li_2$ : $(\sigma 1s)^2\ (\sigma^* 1s)^2\ (\sigma 2s)^2$

or, $KK(\sigma 2s)^2$, where KK = closed K shell structure $(\sigma 1s)^2\ (\sigma^* 1s)^2$

- Bond order = $\frac{N_b - N_a}{2} = \frac{4-2}{2} = 1$
- Diamagnetic
- Exists in vapour state

**Beryllium Molecule ($Be_2$)**

- Be−atom : $1s^2\ 2s^2$
- $Be_2$ : $(\sigma 1s)^2\ (\sigma^* 1s)^2\ (\sigma 2s)^2\ (\sigma^* 2s)^2$
- Bond order = $\frac{N_b - N_a}{2} = \frac{4-4}{2} = 0$
- Unstable and does not exist

**Carbon Molecule ($C_2$)**

- C-atom : $1s^2\ 2s^2\ 2p^2$

- $C_2$ : $(\sigma 1s)^2$ $(\sigma^* 1s)^2$ $(\sigma 2s)^2$ $(\sigma^* 2s)^2$ ($\pi 2p_x^2 = \pi 2p_y^2$)

  or, KK$(\sigma 2s)^2$ $(\sigma^* 2s)^2$ ($\pi 2p_x^2 = \pi 2p_y^2$)
- Bond order = $\frac{N_b - N_a}{2} = \frac{8-4}{2} = 2$
- Diamagnetic
- Both the bonds are pi bonds because four electrons are present in two pi molecular orbitals.

**Nitrogen Molecule ($N_2$)**

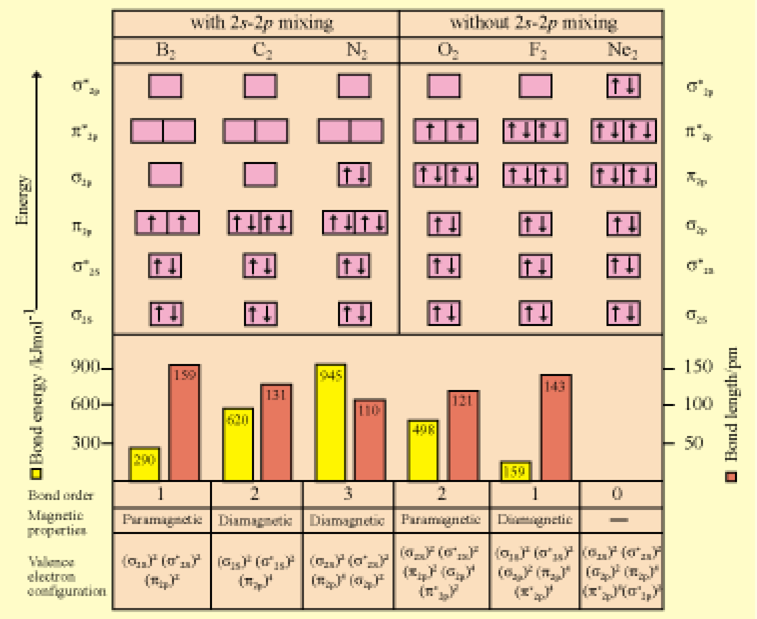
**Oxygen Molecule ($O_2$)**

- O-atom : $1s^2\ 2s^2\ 2p^4$
- $O_2$ : $(\sigma 1s)^2$ $(\sigma^* 1s)^2$ $(\sigma 2s)^2$ $(\sigma^* 2s)^2$ $(\sigma 2p_z)^2$ ($\pi 2p_x^2 = \pi 2p_y^2$) $(\pi^* 2p_x^1 = \pi 2p_y^1)$

  Or, KK $(\sigma 2s)^2$ $(\sigma^* 2s)^2$ $(\sigma 2p_z)^2$ ($\pi 2p_x^2 = \pi 2p_y^2$) $(\pi^* 2p_x^1 = \pi 2p_y^1)$
- Bond order $\frac{N_b - N_a}{2} = \frac{10-6}{2} = 2$
- Paramagnetic, because of two unpaired electrons

**Homonuclear Diatomic Molecules of the Second Row**

- Molecular orbital occupancy and molecular properties for $B_2$ through $Ne_2$



## Hydrogen Bonding

- Attractive force between hydrogen atom of one molecule and electronegative atom (F, O, or N) of another molecule
- Represented by dotted lines (------)

$$---\overset{\delta+}{H}-\underbrace{\overset{\delta-}{F}---\overset{\delta+}{H}}_{\text{Hydrogen bond}}-\overset{\delta-}{F}---$$

## Cause of Formation of Hydrogen Bonds

Hydrogen bond formation takes place when hydrogen is bonded to a strong electronegative atom. This formation is explained in the following flow chart:

| |
|---|
| Displacement of electron pair towards the electronegative atom |
| ↓ |
| Attainment of fractional positive charge by hydrogen atom and fractional negative charge by the electronegative atom |
| ↓ |
| Formation of a polar molecule having electrostatic force of attraction |
| ↓ |
| Formation of hydrogen bond |

## Dependence of H-bonding

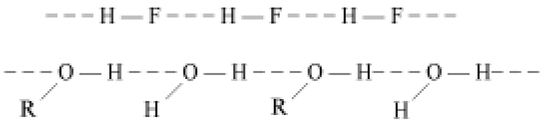
- The magnitude of H-bonding depends upon the physical state of the compound.
- $\xrightarrow[\text{Magnitude of H–bonding decreases}]{\text{Solid state > Liquid state > Gaseous state}}$

### Types of Hydrogen Bonds

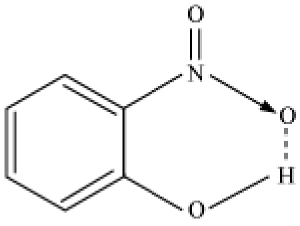
Two types: Intermolecular hydrogen bond

Intra-molecular hydrogen bond

- Intermolecular hydrogen bond:
- Formed between two different molecules of the same or different compounds
- Example:



- Intra-molecular hydrogen bond:
- Formed within the same molecule when hydrogen atom is present in between two highly electronegative atoms (F, O or N) within the same molecule
- Example:



*o* − Nitrophenol

### Importance of Hydrogen Bonding

- At normal temperature, water gets evaporated at a much less rate; this happens due to the formation of hydrogen bond. This helps in retaining a huge amount of water on the surface of earth.
- Water is stored in animal cell and plant cell due to the hydrogen bond.
- Hydrogen bond is formed between the components of the soil and the molecules of water.

- Clothes of artificial fibres, such as terrylene, etc. dry faster than clothes of cotton because of hydrogen bond.