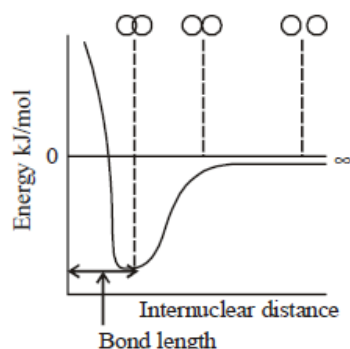


Chemical Bonding

The attractive force which holds various constituents (atoms, ions, etc.) together in different chemical species is called a chemical bond.

Cause of Bonding:

Energy Factor: When two atoms approach each other, the attractive and repulsive forces operate between them. The distance at which the attractive forces balance the repulsive forces is known as the bond distance, the potential energy of the system is minimum and the bond is said to be formed.



Stability Factor(Octet rule): Atoms enter into chemical bonding to acquire the stable inert gas electronic configuration(Octet). They can do so by losing, gaining or sharing of electrons.

Types of Chemical Bond:

Depending upon the mode of acquiring the stable electronic configuration, the chemical bonds may be

- Ionic or electrovalent bond
- Covalent bond
- Coordinate or dative bond
- Metallic bond
- Hydrogen bond
- Weak van der Waal's forces of attraction

Ionic Bond (By Kossel and Lewis):

Ionic bond is formed by the complete transference of one or more valence electrons of one atom to the valence shell of the other atom. Both atoms are converted into ions and have the electronic configuration of nearest noble gases. *The electrostatic attraction between oppositely charged ions, which always tends to decrease the potential energy of the system is known as the ionic bond.*

Factors affecting the formation of Ionic Bond:

(i) Ionisation energy : The lower the value of the ionization energy of an atom greater will be the ease of formation of cation from it.

(ii) Electron affinity (E) : The higher the electron affinity of an atom the greater will be the ease of formation of anion from it.

(iii) Lattice Energy : The amount of heat evolved when one mole of ionic compound is formed from positive and negative ions in the crystalline form is known as the **lattice energy**. The stability of ionic compounds increases as lattice energy increases.

Lattice Energy: Lattice energy is the energy change upon formation of one mole of a crystalline ionic compound from its constituent ions, which are assumed to initially be in the gaseous state.

It is a measure of the cohesive forces that bind ionic solids. The size of the lattice energy is connected to many other physical properties including solubility, hardness, and volatility. Since it generally cannot be measured directly, the lattice energy is usually deduced from experimental data via the Born–Haber cycle.

The lattice energy of an ionic compound depends strongly upon the charges of the ions that comprise the solid, which must attract or repel one another via Coulomb's Law. More subtly, the relative and absolute sizes of the ions influence lattice energy. London dispersion forces also exist between ions and contribute to the lattice energy via polarization effects. For ionic compounds made of molecular cations and/or anions, there may also be ion-dipole and dipole-dipole interactions if either molecule has a molecular dipole moment.

Born–Landé equation:

In 1918] Born and Landé proposed that the lattice energy could be derived from the electric potential of the ionic lattice and a repulsive potential energy term.

$$\Delta U_{\text{lattice}} = -\frac{N_A M z^+ z^- e^2}{4\pi\epsilon_0 r_0} \left(1 - \frac{1}{n}\right)$$

where

N_A is the Avogadro constant;

M is the Madelung constant, relating to the geometry of the crystal;

z^+ is the charge number of the cation;

z^- is the charge number of the anion;

e is the elementary charge, equal to 1.6022×10^{-19} C;

ϵ_0 is the permittivity of free space, equal to 8.854×10^{-12} C² J⁻¹ m⁻¹;

r_0 is the nearest-neighbor distance between ions; and

n is the Born exponent (a number between 5 and 12, determined experimentally by measuring the compressibility of the solid, or derived theoretically).

Calculating the average values of Born Exponent (n):

Electronic Structure of ion	n	Examples
He	5	Li ⁺ , Be ²⁺
Ne	7	Na ⁺ , Mg ²⁺ , F ⁻
Ar	9	K ⁺ , Ca ²⁺ , Cl ⁻
Kr	10	Rb ⁺ , Br ⁻
Xe	12	Cs ⁺ , I ⁻

e.g. n for Li⁺ =5, Cl⁻ =9, hence for LiCl $n=(5+9)/2=7$

The Born–Landé equation above shows that the lattice energy of a compound depends principally on two factors:

- As the charges on the ions increase, the lattice energy increases (becomes more negative),
- when ions are closer together the lattice energy increases (becomes more negative).

Barium oxide (BaO), for instance, which has the NaCl structure and therefore the same Madelung constant, has a bond radius of 275 picometers and a lattice energy of -3054 kJ/mol, while sodium chloride (NaCl) has a bond radius of 283 picometers and a lattice energy of -786 kJ/mol. The bond radii are similar but the charge numbers are not, with BaO having charge numbers of (+2, -2) and NaCl having (+1, -1); the Born–Landé equation predicts that the difference in charge numbers is the principal reason for the large difference in lattice energies.

Closely related to this widely used formula is the Kapustinskii equation, which can be used as a simpler way of estimating lattice energies where high precision is not required.

Kapustinskii equation:

$$U_L = K \cdot \frac{\nu \cdot |z^+| \cdot |z^-|}{r^+ + r^-} \cdot \left(1 - \frac{d}{r^+ + r^-} \right)$$

where $K = 1.20200 \times 10^{-4} \text{ J} \cdot \text{m} \cdot \text{mol}^{-1}$

$d = 3.45 \times 10^{-11} \text{ m}$

ν is the number of ions in the empirical formula,

z^+ and z^- are the numbers of elementary charge on the cation and anion, respectively, and

r^+ and r^- are the radii of the cation and anion, respectively, in meters.

Kapustinskii replaced r_0 , the measured distance between ions, with the sum of the corresponding ionic radii. In addition, the Born exponent, n , was assumed to have a mean value of 9. Finally, Kapustinskii noted that the Madelung constant, M , was approximately 0.88 times the number of ions in the empirical formula.

Born–Haber cycle:

The Born–Haber cycle is an approach to analyze reaction energies. The cycle is concerned with the formation of an ionic compound from the reaction of a metal (often a Group I or Group II element) with a halogen or other non-metallic element such as oxygen. Born–Haber cycles are used primarily as a means of calculating lattice energy (or more precisely enthalpy, which cannot otherwise be measured directly).

The Born–Haber cycle applies only to fully ionic solids such as certain alkali halides. Most compounds include covalent and ionic contributions to chemical bonding and to the lattice energy, which is represented by an extended Born–Haber thermodynamic cycle. The extended Born–Haber cycle can be used to estimate the polarity and the atomic charges of polar compounds.

Example: Formation of NaCl:

The heat of the formation of sodium chloride (ΔH_f°) from the sodium metal and chlorine gas can be experimentally measured.



The formation of ionic solid sodium chloride from solid sodium metal and gaseous chlorine is not a single-step process but goes through several processes. Heat changes of all the processes except the lattice energy can be experimentally measured.

The processes or steps in the formation of sodium chloride are as follows:

1. Solid sodium atom sublimates to gaseous atom by absorbing heat energy (ΔH_{sub}).



Sublimation energy $\Delta H_{\text{sub}} = +107 \text{ kJ/mol}$

2. Gaseous sodium atom absorbs the ionization energy to release one electron and forms a gaseous sodium ion.



Ionization energy $\Delta H_{\text{IE}} = +502 \text{ kJ/mol}$

3. Diatomic gaseous chlorine breaks into two individual atoms by absorbing bond energy, such that each chlorine atom absorbs half of the bond energy of the chlorine molecule.



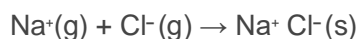
Bond dissociation energy of chlorine = $(1/2) \Delta H_{\text{diss}} = (1/2) 242 = +121 \text{ kJ/mol}$

4. Chlorine atom accepts an electron to form a chloride ion and releases energy equivalent to electron affinity.



Electron affinity = $\Delta H_{\text{EA}} = -355 \text{ kJ/mol}$

5. Gaseous sodium ion and gaseous chloride ion combine to form a solid sodium chloride molecule and releases energy equivalent to lattice energy.



Lattice energy = $\Delta H_{\text{LE}} = U = ?$

The summation of enthalpy of all the processes (from step 1 to step 5) give the net enthalpy of the formation of solid crystalline sodium chloride from sodium and chlorine in their standard conditions of solid and gas, respectively. This should be equal to the experimentally measured enthalpy of the formation of solid sodium chloride.

$$\text{So, } \Delta H_f^0 = \Delta H_{\text{sub}} + \Delta H_{\text{IE}} + (1/2) \Delta H_{\text{dis}} + \Delta H_{\text{EA}} + U$$

$$\text{or } \Delta H_f^0 - (\Delta H_{\text{sub}} + \Delta H_{\text{IE}} + (1/2) \Delta H_{\text{dis}} + \Delta H_{\text{EA}} + U) = 0$$

$$\text{or } 411 + 107 + 502 + 121 - 355 + U = 0$$

Here, except lattice energy, all other enthalpies can be experimentally measured.

$$\text{The lattice energy of the sodium chloride solid} = U = \Delta H_f^0 - (\Delta H_{\text{sub}} + \Delta H_{\text{IE}} + \frac{1}{2} \Delta H_{\text{dis}} + \Delta H_{\text{EA}}).$$

$$= -411 - 107 - 502 - 121 + 355$$

$$= -786 \text{ kJ/mol}.$$

Characteristics of Ionic Compounds:

- 1) Ionic compounds are usually solid. The ionic bonds hold the atoms strongly due to electrostatic attraction. The ionic compounds have high lattice energy, making them stable solids at room temperature.
- 2) Ionic compounds are soluble in polar solvents like water but are insoluble in non-polar solvent like benzene. The ionic compounds can break up due to ion-dipole interaction, where the polar solvent molecules can solvate the individual ions. The solvation energy must exceed the lattice energy.
- 3) The ionic compounds form a strong lattice due to strong electrostatic force operating over longer distances. Higher energy is required to disrupt their physical structure and as a result, ionic compounds usually have a very high melting point and boiling point.
- 4) The electrostatic attraction of the ionic bonds helps them in organising crystal structures. Crystal structures are arrangements of ions in repetitive units extended in three dimensions. This makes ionic solids highly dense.
- 5) Ionic crystals are however quite brittle. Applying pressure from outside, such as hammering, pushes the like charges too close to each other which results in strong repulsive force. This increases their brittleness.
- 6) Ionic forces are non-directional, i.e, the electrostatic forces act in all directions equally. That is why ionic compounds do not have any isomers .
- 7) Solid ionic compounds cannot conduct electricity, however, in molten state, they can conduct electricity owing to the dissociation of charges.

Variable Electrovalency: There are two main reasons for showing variable valency

- **Inert pair effect in p-block elements:** The elements of III A group show +3 oxidation state mainly. But as we go down the group the oxidation state +1 becomes more and more pronounced. Similarly the elements of IV A group show +4 oxidation state in general but as we go down the group the +2 state becomes more and more pronounced.

The two s electrons (ns^2) in the valence shell tend to remain inert and do not participate in formation of bonds. This is called inert pair effect. Thus the inert pair effect is the main cause of variable valency in p block elements.

- **Small energy difference between ns and (n-1)d sub shells:** in transition elements and ns and (n-2) sub shells in inner transition elements. In transition elements the variation in oxidation state is due to involvement of incomplete d-orbitals in addition to electrons of ns orbital. So the electrons from both the energy levels can be used for bonding, e.g. Iron, mercury, and copper show variable valency.

Similarly, inner transition elements show variable valency due to incomplete filling of f-orbitals. So in addition to ns electrons, the electrons from f-orbitals may be used for chemical bond formation.

Covalent Bond (By Lewis and Langmuir):

According to G. N. Lewis atoms may also combine by sharing of electrons present in their outermost shells and attain noble gas electronic configuration. One shared pair of electrons constitute a single bond, two electron pairs constitute a double bond and so on. The bonds thus formed are known as covalent bonds.

VALENCE BOND THEORY : A covalent bond is formed by the overlapping between two half filled atomic orbitals having electrons with opposite spin.

Types of Covalent Bonds:

1. **σ bond:** It is formed by head-on overlap of orbitals. In s bond, the electron density is concentrated in between two atoms, and along the line joining the two atoms.



Figure 3.20 Different types of overlaps in σ bond: (a) $s-s$ overlap; (b) $s-p$ overlap; and (c) $p-p$ overlap

Keeping the internuclear distance same, the relative strength of bond resulting from three kinds of overlap is: $s-s < s-p < p-p$.

The order of bond strength can be explained on the basis of the fact that more the area of overlap, higher will be the strength. Since the p orbital has directional property, $p-p$ overlap provides more area for overlap for the same internuclear distance.

2. **π bond:** It is formed by sideways overlap of orbitals and it merely shortens the bond length.

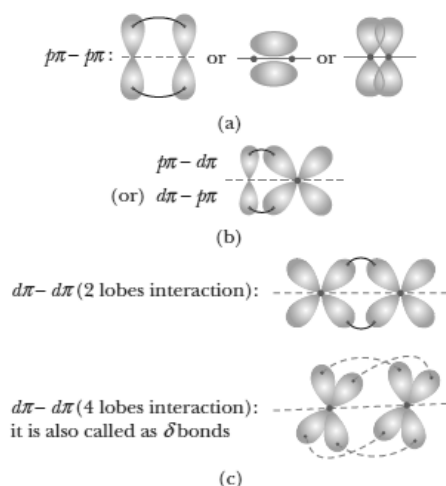


Figure 3.22 Different types of overlaps in π bond: (a) $p\pi-p\pi$ overlap; (b) $p\pi-d\pi$ or $d\pi-p\pi$ overlap; (c) $d\pi-d\pi$ overlap.

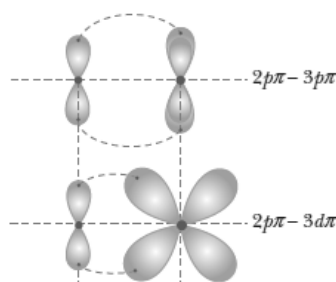


Figure 3.23 Nature of overlap between p and d orbitals in π bond formation.

The relative strength of the π bonds increases when the intermolecular distance decreases and the order is:

$$2p\pi - 2p\pi > 2p\pi - 3d\pi > 2p\pi - 3p\pi > 3p\pi - 3p\pi$$

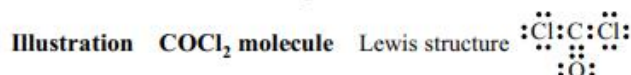
Due to the inclined nature of the d orbital, it is more close in case of $2p\pi - 3d\pi$ overlap and strength of bond is more as compared to $2p\pi - 3p\pi$.

The shape of the molecule is determined by the σ bonds (and lone pairs) but not by the π bonds.

Formal Charge and Lewis Structure : The formal charge on an atom is the difference between the valence electrons in an isolated atom and the number of electrons assigned to that atom in a Lewis structure. The equation for computing formal charge is

$$\text{Formal charge} = \text{Valence electrons on free atom} - \text{Number of (Nonbonding} + \frac{1}{2} \text{ bonding) electrons in a Lewis structure}$$

The sum of the formal charges of atoms in a Lewis structure is equal to the charge on the molecular species.



Atom	Valence electrons in a free atom	Electrons in Lewis structure		Formal Charge
		Nonbonding	bonding	
Cl	7	6	2	$7 - (6 + \frac{1}{2} \times 2) = 0$
O	6	4	4	$6 - (4 + \frac{1}{2} \times 4) = 0$
C	4	0	8	$4 - (0 + \frac{1}{2} \times 8) = 0$

Utility of Formal Charge : Computing formal charge of atoms in a molecule or ion helps deciding a plausible Lewis structure of the species. The guiding principles are as follows.

- Amongst the several Lewis structures, the species having the lowest magnitude of formal charge is the preferred structure.
- Amongst Lewis structures having similar distribution of formal charges, the one having negative formal charges on the more electronegative atoms is the preferred structure.

Covalent character of an ionic bond : Fajan Rules:

An ionic compound has partial covalent character and vice versa. The partial covalency in an ionic compound may be explained qualitatively with the help of Fajan rules described in the following.

- **High Charge and Small Size of the Cation**: cationic electronic charge to penetrate partially into the anionic electronic cloud resulting into the partial covalent bond character to the ionic bond. e.g. $\text{BeCl}_2 > \text{MgCl}_2 > \text{CaCl}_2 > \text{SrCl}_2 > \text{BaCl}_2$
- **High Charge and Large Size of the Anion** : The electronic cloud of such an anion is most easily polarized by the cation. $\text{NaI} > \text{NaBr} > \text{NaCl} > \text{NaF}$
- **Electronic configuration of cation**: It has been observed that a cation having 18 ($s^2p^6d^{10}$) electrons in outermost shell (pseudo noble gas configuration) can polarize the anion more than cation having 8 (s^2p^6) noble gas electronic configuration. Hence CuCl is more covalent than NaCl . Similarly AgCl is more covalent than KCl .







Exceptions to the octet rule:

The octet rule is broken in a significant number of cases:

1. For example, for atoms such as Be and B which have less than four outer electrons. Even if all the outer electrons are used to form bonds an octet cannot be attained. For example, in BeCl_2 and BCl_3 , total number of electrons on the central atom are 4 and 6 respectively.
2. The octet rule is also broken where atoms have an extra energy level which is close in energy to the p level, and may accept electrons and be used for bonding. PF_3 obeys the octet rule, but PF_5 does not. PF_5 has ten outer electrons, and uses one 3s, three 3p and one 3d orbitals. Any compound with more than four covalent bonds must break the octet rule, and these violations become increasingly common in elements after the first two periods of eight elements in the periodic table.
3. The octet rule does not work in molecules which have an odd number of electrons, such as NO and ClO_2 , nor does it explain why O_2 is paramagnetic and has two unpaired electrons.

Sidgwick–Powell theory: They suggested that for molecules and ions that contain only single bonds, the approximate shape can be predicted from the number of electron pairs in the outer or valence shell of the central atom. Bond pairs and lone pairs were taken as equivalent, since all electron pairs take up some space, and they repel each other. Repulsion is minimized if the electron pairs are orientated in space as far apart as possible. Based on this theory, the following molecular shapes were suggested depending on number of electron/lone pairs in the valence shell.

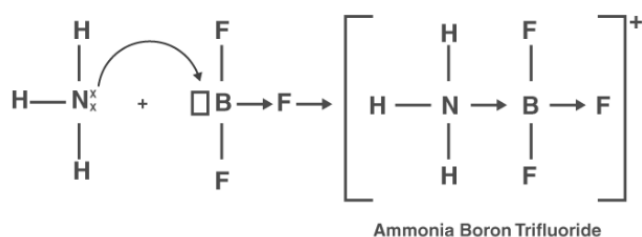
Molecular shapes predicted by Sidgwick–Powell theory:

Number of electron pairs in outer shell	Shape of molecule		Bond angles
2	linear		180°
3	plane triangle		120°
4	tetrahedron		109°28′
5	trigonal bipyramid		120° and 90°
6	octahedron		90°
7	pentagonal bipyramid		72° and 90°

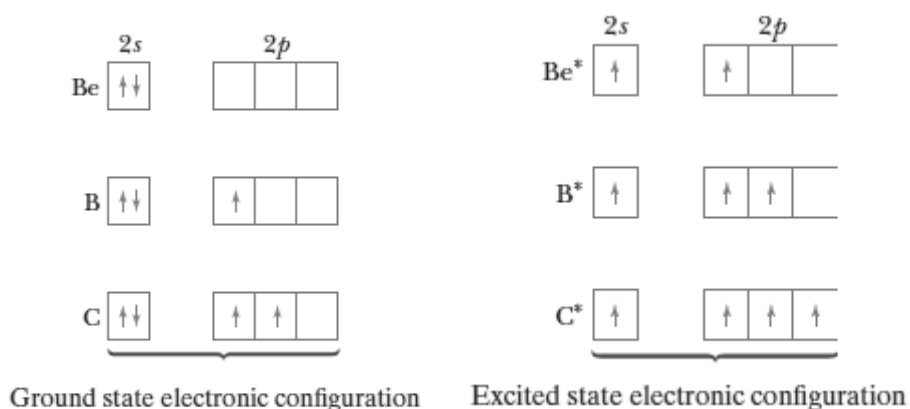
Coordinate Bond:

A coordinate bond is a special type of covalent bond in which the electron pair is shared from one atom only. In other words, both the electrons that form the shared pair are from the same atom. The coordinate bonds can also be alternatively referred to as Dative bonds or dipolar bonds. The bonding of metal ions to ligands involves this kind of interaction. This type of interaction is central to Lewis acid–base theory.

Example: Formation of Ammonia Boron Trifluoride.



Hybridization: Initially it was considered that unpaired electrons in the valence shell of an atom and only the pure atomic orbitals are involved in the bond formation, except when coordinate covalent bonds are formed. This can explain the formation of molecules like H_2 , HX (where $X = F, Cl, Br, I$), X_2 , H_2O , NH_3 , etc. However, the formation of BeH_2 , BH_3 and CH_4 (like compounds) cannot be explained, since Be has no unpaired electron in its ground state, and B and C also have 1 and 2 unpaired electrons respectively. The valence bond theory was modified to explain the formation of such compounds. It was suggested that in all such cases, a pair of electrons gets unpaired and one of the electrons is excited to the next available vacant orbital of slightly higher energy. The driving force for this process is the energy released in the bond formation by unpaired electrons. Accordingly, the number of unpaired electrons in Be, B, and C is **2, 3, and 4 respectively**.



Hence Be, B, C can show covalency of 2, 3 and 4 respectively. Apart from this, the existence of PF_5 , SF_6 , IF_7 , XeF_2 , XeF_4 , XeF_6 can also be well explained by this theory.

If purely atomic orbitals were involved in bonding, then in the formation of methane molecule the three C–H bonds will be formed by the p–s overlap and the fourth C–H bond will be formed by the s–s overlap. Since the s–s overlap may take place from any direction, there is no certainty of the location of the fourth H atom. But in reality, this is not observed, instead we observe that

1. All $\widehat{\text{HCH}}$ bond angles are identical with a value of $109^\circ 28'$.

2. All C–H bond lengths and strengths are identical.

So to explain the above observations, the theory of hybridization was introduced.

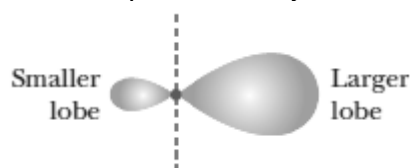
Hybridization can be defined as the mixing of pure atomic orbitals of comparable energy.

Features of hybrid orbitals:

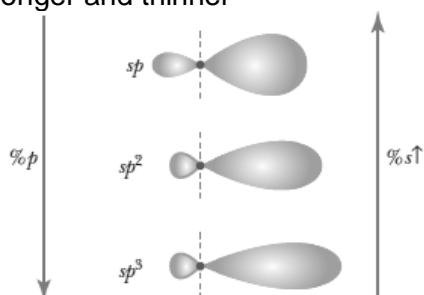
1. The number of hybrid orbitals of equal energy formed is same as the number of atomic orbitals that are mixed. All the hybrid orbitals formed have identical characteristics. For example, one s orbital and three p orbitals are mixed to form four sp^3 hybrid orbitals, which are of equal energy; and each sp^3 hybrid orbital has 25% s character and 75% p character.

Hybridization type	% s	% p	% d
sp	50	50	–
sp^2	33.33	66.67	–
sp^3	25	75	–
sp^3d	20	60	20
sp^3d^2	~ 16.5	50	~ 33
sp^3d^3	~ 14	~ 43	~ 43

2. The shape of each hybrid orbital is such that one lobe is small and the other lobe is large



3. As the % s character increases in a hybrid orbital, the hybrid orbital becomes bulkier and shorter. On the other hand as the % p or % d character increases, the orbital becomes longer and thinner



3. As the % s character increases in a hybrid orbital, the hybrid orbital becomes bulkier and shorter. On the other hand as the % p or % d character increases, the orbital becomes longer and thinner.

steric number(S.N.): It is the number of atoms bonded to the central atom of a molecule plus the number of lone pairs on the central atom.

S.N. $= (Q + \frac{R}{2})$, where Q = number of s bond pairs, R = number of unshared electrons on the central atom. Hence, $\frac{R}{2}$ = number of lone pairs of electrons on the central atom.

Relation between steric number, hybridization and geometry of molecules

Steric number	Hybridization	Orientation of the hybrid orbital in space or electronic geometry around the central atom	Angles between hybrid orbitals
2	sp	Linear 	180°
3	sp^2	Trigonal planar 	120°
4	sp^3	Tetrahedral (Td) 	$109^\circ 28'$
5	sp^3d	Trigonal bipyramidal (TBP) 	Axial (a) and equatorial (e) : 90° e and e : 120° a and a : 180°
6	sp^3d^2	Octahedral (Oh) 	Between two adjacent orbitals : 90° Between two opposite orbitals : 180°
7	sp^3d^3	Pentagonal bipyramidal (PBP) 	a and a : 180° a and e : 90° e and e : 72°

VALENCE SHELL ELECTRON PAIR REPULSION (VSEPR) THEORY:

This theory may be summarized in the following points:

1. Electron pairs tend to minimize repulsions and these are in the order:
lone pair–lone pair > lone pair–bond pair > bond pair–bond pair. (Here bond pair refers to a single bond.) Shapes of the molecules depend upon repulsions between bond pair and lone pair electrons.
2. The double bond is in need of more space as compared to the single bond. The repulsion order in relation to the bonds is as follows:
double bond – double bond > double bond – single bond > single bond – single bond.
3. Keeping the central atom (having lone pair) same, if the electronegativity of the surrounding atom increases, the bond angle will decrease provided no other factors like size and back bonding play any role.
4. Keeping the surrounding atoms same, if the electronegativity of the central atom (having the lone pair) increases, the bond angle increases.
5. Sometimes the lone pair may be transferred from filled shell of an atom to unfilled shell of the adjacent bonded atom. This phenomenon of transferring electron is known as 'back bonding'.

Effect of lone pair: If the lone pair(s) is (are) present, the bond angles get distorted and the shape of the molecule can be visualized from the three-dimensional figure obtained after placing the bond pairs and lone pair(s) in a manner such that the repulsion between them is minimised. (The location of the lone pair will not be considered in the shape determination because electrons are not visible).

Shapes of the species undergoing different hybridizations:

1. For sp hybridization

The steric number is 2.

The possible values of $(Q + \frac{R}{2})$ are

$2 + 0 \Rightarrow$ Linear geometry, e.g. BeH_2 , BeCl_2 , BH_2^+ , NO_2^+

or $1 + 1 \Rightarrow$ Linear geometry, e.g. CO .

2. For sp^2 hybridization

The steric number is 3.

The possible values of $(Q + \frac{R}{2})$ are

$3 + 0 \Rightarrow$ Trigonal planar geometry, e.g. BX_3 , AlCl_3 , AlBr_3 , CH_3^+ , CO_3^{2-} , NO_3^- etc.

or $2 + 1 \Rightarrow$ Bent / V-shaped / Angular geometry, e.g. NO_2^- , SnCl_2 , SO_2 etc.

3. For sp^3 hybridization

The steric number is 4.

The possible values of $(Q + \frac{R}{2})$ are

$4 + 0 \Rightarrow$ Tetrahedral geometry, e.g. BH_4^- , NF_4^+ , NH_4^+ , SiF_4 , PH_4^+ etc.

or $3 + 1 \Rightarrow$ Pyramidal geometry, e.g. NH_3 , SnCl_3^- , SO_3^{2-} , SeO_3^{2-} etc.

or $3 + 1 \Rightarrow$ Angular / V-shaped / Bent geometry, e.g. H_2O , Cl_2O , NH_2^- etc.

4. For sp^3d hybridization

The steric number is 5.

The possible values of $(Q + \frac{R}{2})$ are

$5 + 0 \Rightarrow$ TBP geometry, e.g. PCl_5 , PF_5 , SbF_5 , PCl_2F_3 , PCl_3F_2 , XeO_3F_2 , etc.

or $4 + 1 \Rightarrow$ See-saw geometry, e.g. SF_4 , SF_2Cl_2 , XeO_2F_2 .

or $3 + 2 \Rightarrow$ T-shaped geometry, e.g. ClF_3 , XeF_3^+ , BrF_3 , XeOF_2 , etc.

or $2 + 3 \Rightarrow$ Linear geometry, e.g. XeF_2 , ICl_2^- , $[\text{I}(\text{CN})_2]^-$ etc.

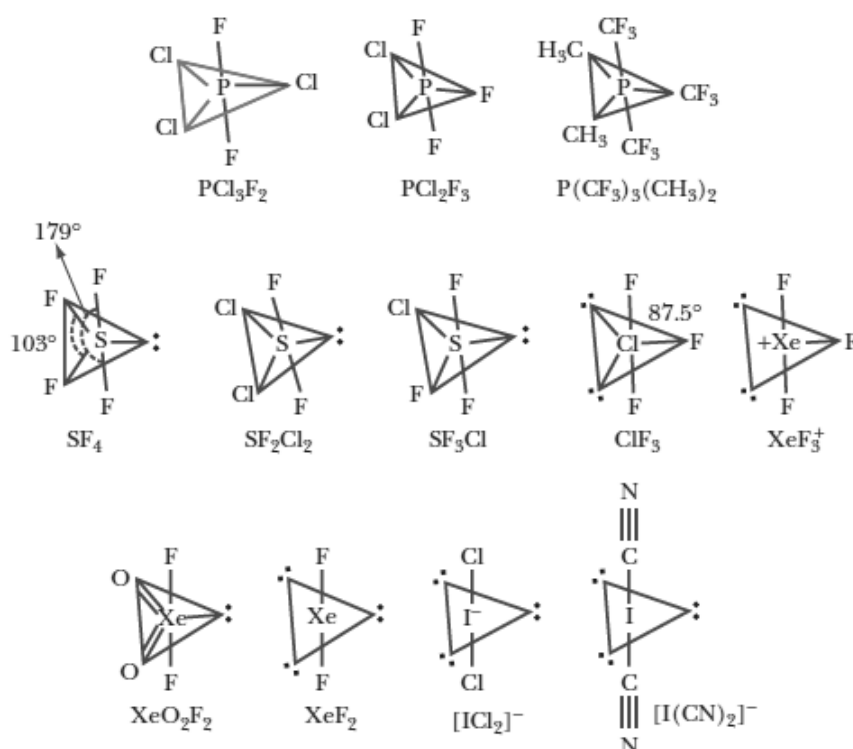
The relative location of the bond pair and the lone pair is decided by **Bent's rule**, which states that the more electronegative atom prefers to stay in the orbital having less s character, while the lone pair prefers to stay in the orbital having more s character. Alternatively, it may be stated as follows. For TBP geometry, the more electronegative atom prefers to stay in the axial position, while the lone pair

Prefers to stay in the equatorial position. The above statement is explained through the following concepts:

It is suggested that $sp^3d = sp^2 + pd$, i.e. all five hybrid orbitals in sp^3d hybridization are not equal, and the concept of unequal hybridization (kind of failure of hybridization theory) starts here. So the equatorial set of orbitals is made of sp^2 hybrid orbitals, while the axial set is made of pd hybrid orbitals. It is also supported by the fact that in PCl_5 , $d_{P-Cl}(a)$ is greater than $d_{P-Cl}(e)$.

The order of energy required to remove an electron from a particular orbital having the same principal quantum number is $s > p > d > f$. This follows the order of proximity of orbitals to the nucleus. We know that the more electronegative atom attracts the bond pair towards itself, and this kind of withdrawing of electrons will be easiest when the attached orbital of it from the central atom consists of minimum or nil s character. Hence, the more electronegative atom prefers the orbitals having less s character or axial position in the TBP geometry.

The effect of the lone pair on bond angles makes them bent, see-saw and T-shaped as shown below:

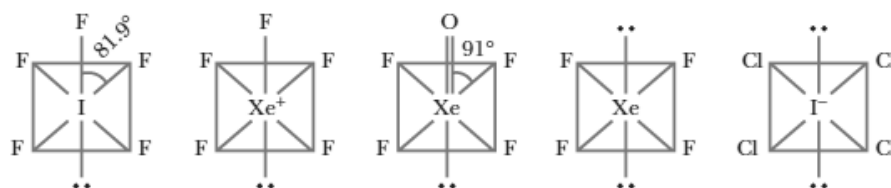


5. For sp^3d^2 hybridization: The steric number is 6.

The possible values of $(Q + \frac{R}{2})$ are

- $6 + 0 \Rightarrow$ Octahedral geometry, e.g. SF_6 , $TeCl_6$, XeO_6^{4-} , XeO_2F_4 , etc.
- or $5 + 1 \Rightarrow$ Square pyramidal geometry, e.g. IF_5 , XeF_5^+ , $XeOF_4$, etc.
- or $4 + 2 \Rightarrow$ Square planar geometry, e.g. XeF_4 , $[ICl_4]^-$, etc.

Structures of some molecules with sp^3d^2 hybridization are shown below:



In case of IF_5 and $[XeF_5]^+$, distortion is observed in the shape because the lone pair–bond pair repulsion is

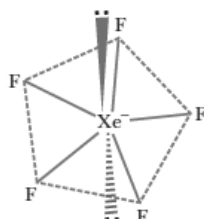
greater than the bond pair–bond pair repulsion. But in case of XeOF_4 , the lone pair–bond pair repulsion is almost equal to the double bond–single bond pair repulsion. Hence, the distortion is very less and the double bond repels slightly more here as compared to the lone pair, and the $\widehat{\text{OXeF}}$ angle is 91° .

6. For sp^3d^3 hybridization:

The steric number is 7.

The possible values of $(Q + \frac{R}{2})$ are

- a. $7 + 0 \Rightarrow$ PBP geometry, e.g. IF_7 .
- b. $6 + 1 \Rightarrow$ This can have the following geometries
 - (i) Distorted octahedral geometry, e.g. XeF_6 , IF_6^- , etc., when the lone pair is present in stereochemically active s orbital.
 - (ii) Perfect octahedral geometry, e.g. $[\text{ICl}_6]^-$, $[\text{TeCl}_6]^{2-}$, $[\text{SbCl}_6]^{3-}$, etc., where the lone pair is present in stereochemically inactive s orbital.
- c. $5 + 2 \Rightarrow$ Pentagonal planar geometry, e.g. $[\text{XeF}_5]^-$.



Pentagonal planar structure of $[\text{XeF}_5]^-$

The structure of $[\text{XeF}_5]^-$ is shown above. It appears contradictory that the two lone pairs are at the axial position in $[\text{XeF}_5]^-$, while in case of ClF_3 two lone pairs are at the equatorial position. It can be understood by an alternative statement of **Bent's rule**, i.e. **"the orbital occupying more space around the central atom will have more s character"**. For TBP geometry, one axial orbital is having three neighbouring orbitals which are all at 90° , while one equatorial orbital is having four neighbouring orbitals, out of which two are at 90° and the other two are at 120° . Hence, the equatorial orbital occupies more space as compared to the axial orbital and will have more s character.

However, this generalization does not hold true when the atoms surrounding the central atom are different. For example, the bond lengths observed in PCl_3F_2 and PCl_2F_3 are as follows:

PCl_3F_2 : $d_{\text{P-F}}$ (a) = 159.6 pm; $d_{\text{P-Cl}}$ (e) = 200.5 pm

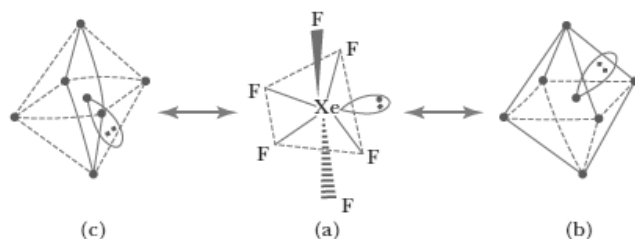
PCl_2F_3 : $d_{\text{P-F}}$ (a) = 159.1 pm; $d_{\text{P-F}}$ (e) = 153.8 pm; $d_{\text{P-Cl}}$ (e) = 200.2 pm

It can be concluded that in such cases the orbital length (axial) is always greater than orbital length (equatorial) but not the bond length.

Similarly for PBP geometry, one axial orbital is having five neighbouring orbitals and all are at 90° , while one equatorial orbital is having four neighbouring orbitals, out of which two are at 90° and other two are at 72° . Hence the axial orbital occupies more space as compared to the equatorial orbital and the axial orbital has more s character. Thus the two lone pairs in PBP geometry occupy the axial position and this clearly explains the structure of $[\text{XeF}_5]^-$.

Again according to this theory, the position of the lone pair in XeF_6 molecule should be in axial position and the shape should be pentagonal pyramidal. But this is not observed and the actual shape of molecule is octahedral. This implies that the lone pair is placed at the equatorial position, and this explains the structure of XeF_6 shown in the following figures:

According to Figure, μ_{expected} for XeF_6 is not equal to zero. But $\mu_{\text{real}}(\text{XeF}_6) \sim \text{zero}$. To explain the above facts, it is considered that the actual molecule is in dynamic equilibrium of all the three structures shown in Figure. Here it is considered that the lone pair is present in the **stereochemically active s orbital** and similar structure is observed in IF_6^- . But anions like $[\text{SbX}_6]^{3-}$, $[\text{TeX}_6]^{2-}$ ($\text{X} = \text{Cl}$,

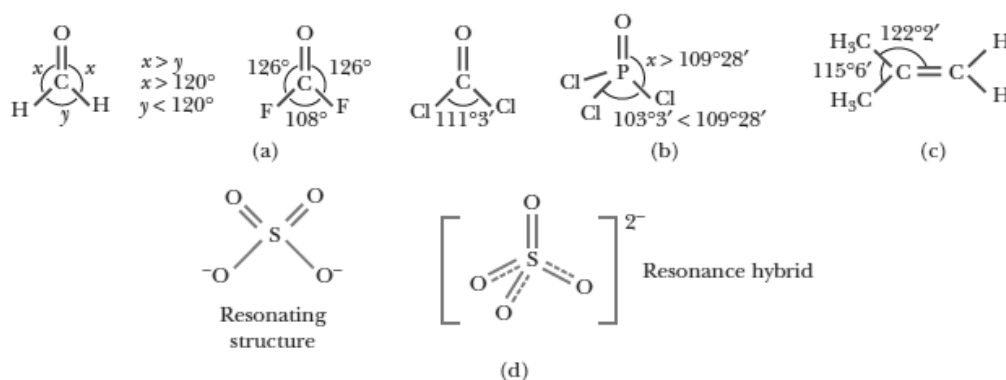


Br, I), $[\text{BrF}_6]^-$, $[\text{ICl}_6]^-$ have been assigned perfectly octahedral structure on the basis of X-ray crystallography and the lone pair is present in **stereochemically inactive s orbital**.

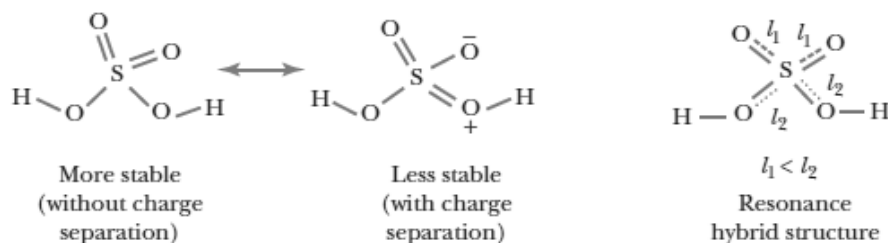
Effect of double bond:

The effect of double bond is illustrated below for trigonal geometry and tetrahedral geometry

It shows that in SO_4^{2-} , all OSO bond angles are identical ($109^\circ 28'$) due to presence of resonating structures.



However, in case of H_2SO_4 , all OSO angles are not identical because resonating structures are not identical as in SO_4^{2-} , and their contribution is also not identical. This is shown below:



The double bond – double bond repulsion is more as compared to double bond – single bond and single bond – single bond repulsion. Hence OSO angles are not identical, also there are two kinds of S–O bond lengths.

Note: Similar explanation is also applicable for HCO_2^- and HCO_2H , NO_3^- and HNO_3 , NO_2^- and HNO_2 , PO_4^{3-} and H_3PO_4 , etc.

Effect of electronegativity:

1. When the central atom having lone pair is the same with different surrounding atoms: As the surrounding atoms become more and more electronegative they pull the bonding electrons further away from the central atom. This causes the reduction of repulsion between bond pairs and hence bond angle, e.g.

NH_3 and NF_3	H_2O and F_2O
107° and 102°	104.5° and 103.1°

In absence of lone pair, the effect of electronegativity is not observed.

CH_4 and CF_4
$109^\circ 28'$ and $109^\circ 28'$

Bent's rule is also consistent with Gillespie's VSEPR model, and may provide alternative rationalization for effect of electronegativity. So it is restated as: '*more electronegative atom not only prefers to stay in the orbital*

having more *p* character but also can increase the *p* character in its attached orbital from the central atom depending on the circumstance'. e.g.

$d_{\text{C-Cl}}$ in CH_3Cl (1.78\AA) $>$ $d_{\text{C-Cl}}$ in CF_3Cl (1.75\AA)

2. When the surrounding atom is the same with different central atom having lone pair: Opposite effect of case-1 is observed.

NH_3	PH_3	AsH_3	SbH_3
107°	93.8°	91.8°	91.3°
H_2O	H_2S	H_2Se	H_2Te
104.5°	92°	91°	89.5°

The effect of electronegativity as postulated in VSEPR theory explains the order of the angle for the above molecules but cannot rationalize very small angles ($\sim 90^\circ$) in PH_3 , AsH_3 ..., H_2S , H_2Se ... etc. with respect to NH_3 and H_2O respectively.

To explain this, **Drago** suggested an empirical rule which is compatible with the energetics of hybridization. It states that if the central atom is in the third row or below in the periodic table, the lone pair will occupy a stereochemically inactive *s* orbital, and the bonding will be through *p* orbitals, and bond angles will be nearly 90° if the electronegativity of the surrounding atom is ≤ 2.5 .

The above rule is based upon the relation between hybridization and bond angle for two or more equivalent *s-p* hybrid orbitals, where the fraction of *s* character (*S*) or fraction of *p* character (*P*) is given by the relationship:

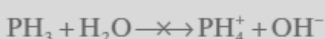
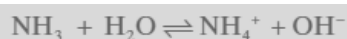
$$\cos \theta = \frac{S}{S-1} = \frac{P-1}{P} \quad (\text{for } 90^\circ < \theta < 180^\circ)$$

For example, for AsH_3 , $\widehat{\text{HAsH}}$ angle is 91.8° , and from calculation it can be shown that each As-H bond consists of almost 97% *p* character and 3% *s* character. Hence, it can be concluded that there is no hybridization or the extent of hybridization is very less for PH_3 , AsH_3 , SbH_3 , H_2S , H_2Se and H_2Te molecules.

Based upon the above discussion, we can explain the following facts.

a. PH_3 has much lower solubility in water as compared to that of NH_3 .

b. The formation of PH_4^+ is difficult as compared to that of NH_4^+



c. The complexing ability of NH_3 is much higher as compared to that of PH_3 .

These three observations can be explained on the basis that the lone pair donating ability for P in case of PH_3 is much less because the lone pair resides at almost pure *s* orbital. In case of NH_3 , the lone pair is present in one sp^3 hybrid orbital and can be donated easily.

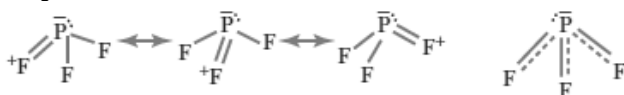
Back bonding:

The phenomenon of back bonding involves transfer of lone pair from filled shell of an atom to the unfilled shell of the adjacent bonded atom.

It is a kind of coordinate *p* bonding which may be partial or full, depending on the relative donating and accepting ability of the donor and acceptor atoms. In general, the donor atoms are the second period elements carrying lone pairs, such as F, O, N, C; sometimes Cl, Br, I, P, S can also act as donor atoms depending on circumstance.

1. Back bonding with F as donor atom

a. Considering the electronegativity of the surrounding atoms, the expected bond angle order for PH_3 and PF_3 is $\text{PH}_3 > \text{PF}_3$. But in reality, it is $\text{PH}_3 < \text{PF}_3$. This is due to back bonding in PF_3 which is shown in Figure.

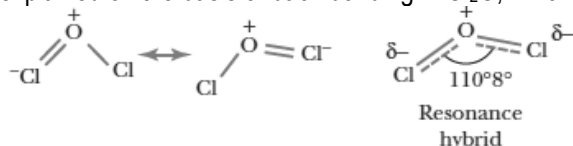


Due to back bonding the partial double bond character develops in a bond causing a decrease in the bond length.

d_{B-F} in BF_3 is less than that in BF_4^- because back bonding is not possible in BF_4^- due to the non-availability of vacant orbital in B atom under sp^3 hybridization.

2. Back bonding with O as donor atom:

a. The expected bond angle order for H_2O , Cl_2O and F_2O is $H_2O > Cl_2O > F_2O$ based on the electronegativities of the surrounding atoms. But in reality, the order is $Cl_2O (110^\circ 8') > H_2O (104^\circ 5') > F_2O (103^\circ 2')$. This is also explained on the basis of back bonding in Cl_2O , which is not possible in H_2O and F_2O .



b. $(CH_3)_2O$ forms a complex with BF_3 easily, while $(SiH_3)_2O$ cannot do so because the availability of the lone pair on O atom decreases due to back bonding from O atom to vacant $3d$ orbital of Si atom. C atom has no such vacant orbital for back bonding.

3. Back bonding with N as donor atom:

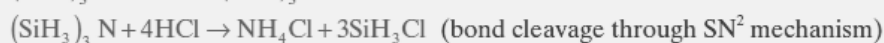
a. The bond angle order is:

$NCl_3 (107^\circ 45') > NH_3 (107^\circ) > NF_3 (102^\circ)$.

This is due to very slight back bonding in NCl_3 from $2p$ orbital of N to $3d$ orbital of Cl the extent of which is very less because only one lone pair is distributed over three chlorine atoms.

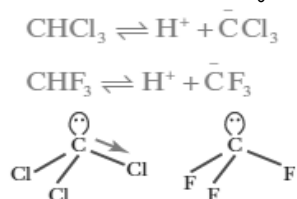
b. $(CH_3)_3N$ is pyramidal while $(H_3Si)_3N$ is planar. This can be explained on the basis of back bonding. In case of $(CH_3)_3N$, there is no back bonding, however $2p\pi - 3d\pi$ in $(SiH_3)_3N$ makes it planar and N atom is forced to adopt sp^2 hybridization.

It is also observed that $(CH_3)_3N$ is more basic as compared to $(SiH_3)_3N$ due to the same reason and they behave differently towards HCl .



4. Back bonding with C as donor atom:

$CHCl_3$ is more acidic than CHF_3 which is explained as follows:



The lone pair on C atom gets delocalized through $2p\pi - 3d\pi$ bonding in ClC_3^- , which is not possible in case of FC_3^- .

THE EXTENT OF d ORBITAL PARTICIPATION IN MOLECULAR BONDING:

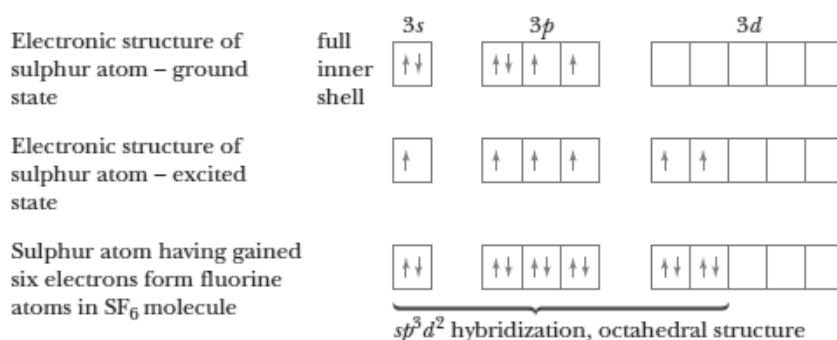
The bonding in PCl_5 may be described using hybrids of the $3s$, $3p$ and $3d$ atomic orbitals for P – see below. However, there are doubts as to whether d orbitals can take part and this has led to the decline of valence bond theory.

Electronic structure of phosphorus atom – ground state	full inner shell	$3s$ 	$3p$ 	$3d$
Phosphorus atom – excited state				
Phosphorus having gained five electrons from chlorine atoms in PCl_5 molecule				
		sp^3d hybridization, trigonal bipyramid		

However, *d* orbitals are in general too large and too high in energy to mix completely with *s* and *p* orbitals. The difference in size is illustrated by the mean values for the radial distance for different phosphorus orbitals: $3s = 0.47 \text{ \AA}$, $3p = 0.55 \text{ \AA}$ and $3d = 2.4 \text{ \AA}$. The energy of an orbital is proportional to its mean radial distance, and since the $3d$ orbital is much larger it is much higher in energy than the $3s$ and $3p$ orbitals. It would at first seem unlikely that hybridization involving *s*, *p* and *d* orbitals could possibly occur.

Several factors affect the size of orbitals. The most important is the charge on the atom. If the atom carries a formal positive charge then all the electrons will be pulled in towards the nucleus. The effect is greatest for the outer electrons. If the central P atom is bonded to a highly electronegative element such as F, O or Cl, then the electronegative element attracts more than its share of the bonding electrons and the F or Cl atom attains a δ^- charge. This leaves a δ^+ charge on P, which makes the orbitals contract. Since the $3d$ orbital contracts in size very much more than the $3s$ and $3p$ orbitals, the energies of the $3s$, $3p$ and $3d$ orbitals may become close enough to allow hybridization to occur in PCl_5 . Hydrogen does not cause this large contraction, so PH_5 does not exist.

In a similar way the structure of SF_6 can be described by mixing the $3s$, three $3p$ and two $3d$ orbitals, that is sp^3d^2 hybridization.



The presence of six highly electronegative F atoms causes a large contraction of the *d* orbitals, and lowers their energy, so mixing may be possible. A second factor affecting the size of *d* orbitals is the number of *d* orbitals occupied by electrons. If only one $3d$ orbital is occupied on an S atom, the average radial distance is 2.46 \AA , but when two $3d$ orbitals are occupied the distance drops to 1.60 \AA . A further small contraction of *d* orbitals may arise by coupling of the spins of electrons occupying different orbitals.

It seems probable that *d* orbitals do participate in bonding in cases where *d* orbital contraction occurs.

METALLIC BOND :

It has been found that metals have generally low ionization energies indicating that valence electrons are weakly bound to the atomic kernel (or core). Metals contain few valence electrons and valence orbitals which are empty. Thus valence electrons are completely delocalised and are frequently exchanged between atoms. The atoms thus acquire a positive charge and are arranged in a regular fashion (lattice structure). The valence electrons form an "electron gas" or "sea of electrons" (electron sea model). The attractive interaction between the mobile electrons and a number of $+ve$ ions constitutes a weak bond known as metallic bond.

CONSEQUENCES OF METALLIC BOND :

- 1. Electrical conductivity** - It is due to presence of mobile valence electrons.
- 2. Thermal conductivity** - On heating one part of metal, the K.E. of electrons is increased and they conduct heat to the other parts of the metal.
- 3. Metallic lustre** - The mobile electrons are promoted to excited states by absorption of light and on coming back from the excited state light of all wavelengths in the visible region is emitted. The surface, therefore emits metallic lustre.
- 4 Malleability** - Metals can be made thin sheets
- 5. Ductility** - Metals can be drawn into wires since metal kernels can easily be shifted.
- 6. Electrical conductivity decreases with temperature** - It is due to random motion of mobile electrons which increases with increase of temperature.

Polar Covalent Bond: Each atom in a molecule has its own ability to attract the bonded pair of electrons. This ability is known as electronegativity. (such as H_2 , O_2 , F_2 , Cl_2 , etc.) is shared equally by both atoms.

However, for heteroatomic molecules like HCl, HI etc. the bond pair of electrons is closer to the atom having larger electronegativity. Consequently, this atom acquires a partial negative charge while the other atom acquires equal partial positive charge. Because of the charge separation, the covalent bond between these two atoms is said to be a polar covalent bond.

Dipole Moment : The polarization of bonded pair of electrons between two atoms is expressed in terms of physical quantity known as dipole moment. It is defined as : $\mu = (\delta q) \times r$.

where δq is the partial charge separation between two atoms and r is the distance between the two atoms.

Representation of Dipole Moment: Dipole moment is a vector quantity, i.e. it has magnitude as well as direction. In chemistry, dipole moment is indicated by the crossed arrow as shown in the following.

positive end \rightarrow negative end

that is, it is directed from positive end to the negative end.

Unit of Dipole Moment In SI system, unit of dipole moment = (unit of δq) (unit of r) = C m

In CGS system, unit of dipole moment = (esu) (cm)

Most molecules have dipole moment of the order of 10^{-18} esu cm. This value of dipole moment is known as 1 debye (written as 1 D).

$$1 \text{ D} = 10^{-18} \text{ esu cm} = (10^{-18}) \left\{ (1 \text{ esu}) \left(\frac{1.6 \times 10^{-19} \text{ C}}{4.8 \times 10^{-10} \text{ esu}} \right) \right\} (10^{-2} \text{ m}) = 3.33 \times 10^{-30} \text{ C m}$$

Dipole Moment of a Polyatomic Molecule: Each bond in a molecule has a dipole moment, known as bond moment. The dipole moment of a molecule is obtained by the vector addition of these bond moments.

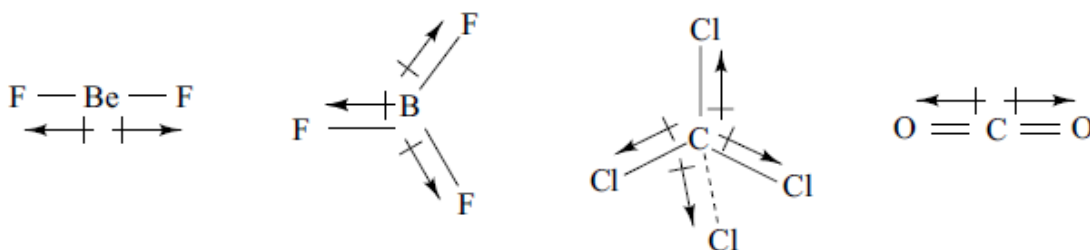
Illustration: The bond moment of O-H bond is 1.52 D. The bond angle of H_2O is 105° .

Therefore, the resultant dipole moment is:

$$\mu_{\text{H}_2\text{O}} = 2\mu_{\text{OH}} \cos(105^\circ/2) = 2 (1.52 \text{ D}) (0.609) = 1.85 \text{ D}$$

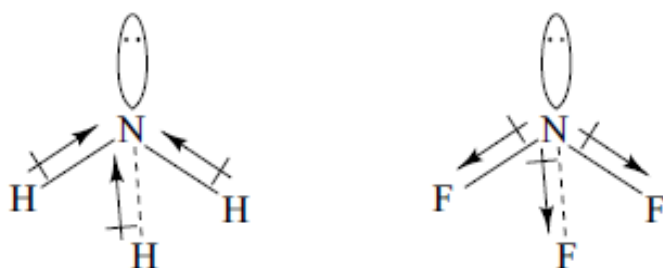
Nonpolar Polyatomic Molecule

The dipole moment of a nonpolar polyatomic molecule is zero inspite of the fact that the bond moments of the molecule is not zero. This is due to the fact that the individual bond moments in the molecule is symmetrically placed so that their vector additions is zero, e.g.



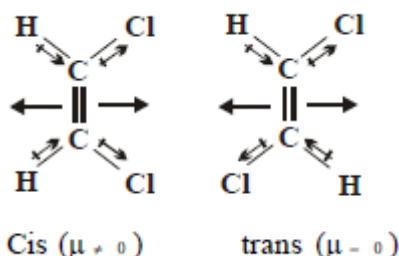
- **Comparison of Dipole Moments of NH_3 and NF_3 :**

Both NH_3 and NF_3 have pyramidal shapes with lone pair of electrons on nitrogen atom.

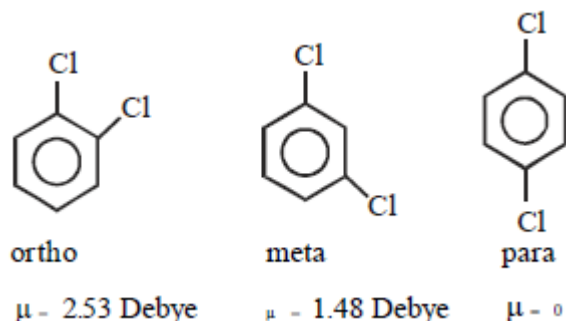


In NH_3 , orbital dipole acts in the same direction as the sum of bond vectors of the three N-H bond bonds. In NF_3 , orbital dipole acts in the opposite direction to the sum of bond vectors of the three N-F bond bonds. These facts make the dipole moment of NH_3 ($\mu = 1.57 \text{ D}$) larger than that of NF_3 ($\mu = 0.24 \text{ D}$).

- Cis and trans isomers can be distinguished by dipole moments, usually cis isomers have higher dipole moment and hence higher polarity e.g.



- Among disubstituted benzene, dipole moment is greatest for ortho isomer, zero for para isomer and less than that of ortho for meta isomer. $o > m > p$. e.g.



- Per Cent Ionic Character of a Polar Bond:** The per cent ionic character of a polar bond is defined as:

$$\text{Per cent ionic character} = \frac{\mu_{AB}}{\mu_{\text{ionic}}} \times 100$$

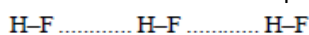
where $\mu_{\text{ionic}} = (e r_{AB})$ corresponds to 100% ionic character of the bond.

Illustration The bond moment of O — H bond is 1.52 D. If bond length O — H is 95 pm, its per cent ionic character will be

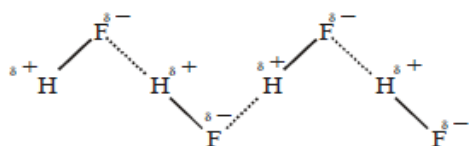
$$\text{Per cent ionic character} = \frac{\mu_{\text{OH}}}{e r_{\text{OH}}} \times 100 = \frac{(1.52 \text{ D})(3.33 \times 10^{-30} \text{ C m / 1 D})}{(1.6 \times 10^{-19} \text{ C})(95 \times 10^{-12} \text{ m})} \times 100 = 33.3 \%$$

HYDROGEN BOND :

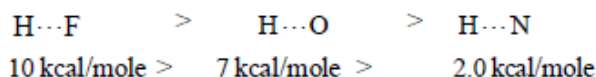
It may be defined as the force of attraction existing between hydrogen atom covalently bonded to highly electronegative atom (N, O or F) and the electronegative atom belonging to another molecule of the same or different substance. It is represented by dotted lines, e.g.



The chains possess a **Zig-Zag** structure



Hydrogen bond is purely electrostatic in nature. It is a weak bond, the strength of the strongest being about 5 - 10 kcal per mole. The more the electronegativity of atom involved in H - bonding, the more is the bond strength eg.



Types of hydrogen bonds - Hydrogen bond is of two types

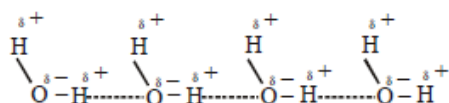
- (i) **Intermolecular** H-bonding (Association). H-bonding involving two or more molecules.
- (ii) **Intramolecular** H-bonding (chelation). H-bonding taking place within single molecule.

(I) Applications of intermolecular H-bonding.

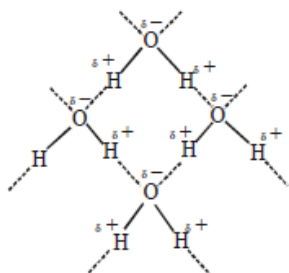
(a) Water - Water has the lowest molecular weight among the hydrides of group 16 elements yet it has the highest melting and boiling points.

	H ₂ O	H ₂ S	H ₂ Se	H ₂ Te
Melting point	0°C	-85.5°C	-66°C	-51.2°C
Boiling point	100°C	-60.4°C	-41.5°C	+2°C

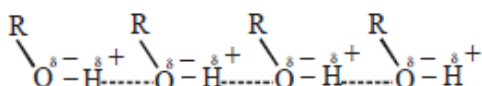
It is due to intermolecular H - bonding through which water molecules associate.



(b) Ice has less density than water - In crystal structure of ice every water molecule is associated with four other water molecules by H-bonding in a tetrahedral fashion. It gives rise to cage like tetrahedral structure of ice with large empty spaces. On melting the ice H-bonds are broken and space between water molecules decreases and density of water increases upto 4°C. Above 4°C more H - bonds are broken, the water molecules move apart from each other and the density again decreases. Thus water has maximum density at 4°C.

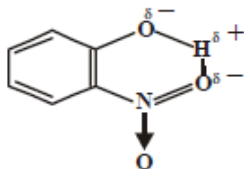


(c) Alcohols & Ethers- The marked difference between the melting and boiling points of alcohols and corresponding ethers is also due to association in alcohol molecules, which is absent for ether molecules.



(II) Applications of Intramolecular H - bonding.

Volatile character of nitrophenols - o-nitrophenol is more volatile (b.pt 214°C) as compared to meta (b.pt 290°C) and para (b.pt 279°C). It is due to chelation.

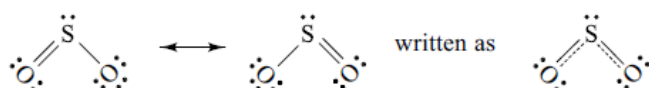


In meta and para isomer chelation is not possible due to the formation of desired size of ring. They therefore associate to some extent and have higher B.P.

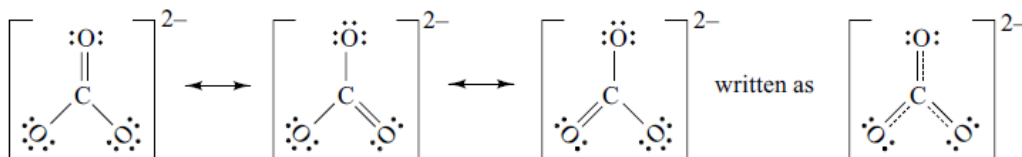
Concept of Resonance:

distribution of electrons over a given skeleton of atoms in a molecule. None of the individual structures adequately explains the characteristics of the molecule. However, these can be explained if the actual structure of the molecule is considered as the superposition of individual structures. This phenomenon is known as resonance and the individual structures are known as resonating structures.

Illustrations



The resonance hybrid of the two Lewis structures makes both the S — O bond lengths equal in size.



Molecular Orbital Theory:

Molecular orbital theory provides the explanation for the formation of bond in a molecule on the lines very similar to those of atomic orbitals. In the molecular orbital theory, the valency electrons are considered to be associated with all the nuclei in the molecule. Thus the atomic orbitals *from different atoms* must be combined to produce molecular orbitals. Electrons may be considered either as particles or waves. An electron in an atom may therefore be described as occupying an

atomic orbital, or by a wave function ψ , which is a solution to the Schrodinger wave equation. Electrons in a molecule are said to occupy molecular orbitals. The wave function describing a molecular orbital may be obtained by one of two procedures:

1. Linear combination of atomic orbitals (LCAO).
2. United atom method.

LCAO Method:

Consider two atoms A and B which have atomic orbitals described by the wave functions $\psi(A)$ and $\psi(B)$. If the electron clouds of these two atoms overlap when the atoms approach, then the wave function for the molecule (molecular orbital $\psi(AB)$) can be obtained by a linear combination of the atomic orbitals $\psi(A)$ and $\psi(B)$:

$$\psi(AB) = N(c_1\psi(A) + c_2\psi(B))$$

Where N is a normalizing constant chosen to ensure that the probability of finding an electron in the whole of the space is unity, and c_1 and c_2 are constants chosen to give a minimum energy for $\psi(AB)$. If atoms A and B are similar, then c_1 and c_2 will have similar values. If atoms A and B are the same, then c_1 and c_2 are equal.

The probability of finding an electron in a volume of space dV is $\psi^2 dV$, so the probability density for the combination of two atoms as above is related to the wave function squared:

$$\psi_{(AB)}^2 = (c_1^2\psi_{(A)}^2 + 2c_1c_2\psi_{(A)}\psi_{(B)} + c_2^2\psi_{(B)}^2)$$

If we examine the three terms on the right of the equation, the first term $c_1^2\psi^2(A)$ is related to the probability of finding an electron on atom A if A is an isolated atom. The third term $c_2^2\psi^2(B)$ is related to the probability of finding an electron on atom B if B is an isolated atom. The middle term becomes increasingly important as the overlap between the two atomic orbitals increases, and this term is called the overlap integral. This term represents the main difference between the electron clouds in individual atoms and in the molecule. The larger this term the stronger the bond.

s-s combinations of orbitals:

Suppose the atoms A and B are hydrogen atoms; then the wave functions $\psi(A)$ and $\psi(B)$ describe the 1s atomic orbitals on the two atoms. Two combinations of the wave functions $\psi(A)$ and $\psi(B)$ are possible:

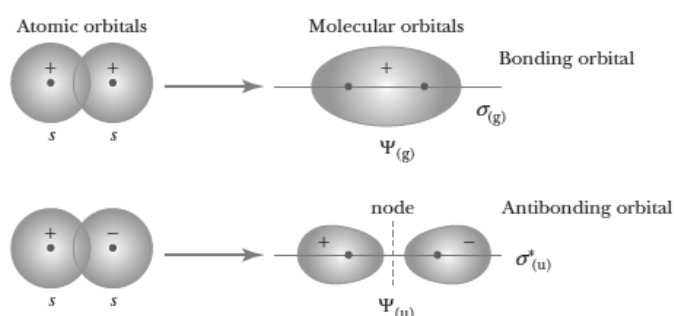
1. Where the signs of the two wave functions are the same.
2. Where the signs of the two wave functions are different.

Wave functions which have the same sign may be regarded as waves that are in phase, which when combined add up by constructive interference to give a larger resultant wave (**Bonding Molecular Orbital**). Similarly wave functions of different signs correspond to waves that are completely out of phase and which cancel each other by destructive interference (**Antibonding Molecular Orbital**). The signs + and - refer to signs of the wave functions, which determine their symmetry, and have nothing to do with electrical charges. The two combinations are:

$$\psi_{(g)} = N\{\psi_{(A)} + \psi_{(B)}\}$$

$$\psi_{(u)} = N\{\psi_{(A)} + [-\psi_{(B)}]\} \equiv N\{\psi_{(A)} - \psi_{(B)}\}$$

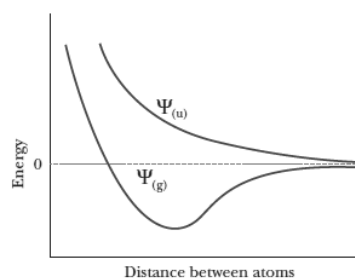
When a pair of atomic orbitals $\psi(A)$ and $\psi(B)$ combine, they give rise to a pair of molecular orbitals $\psi(g)$ and $\psi(u)$. The number of molecular orbitals produced must always be equal to the number of atomic orbitals involved. The function $\psi(g)$ leads to increased electron density in between the nuclei, and is therefore a **bonding**



molecular orbital. It is lower in energy than the original atomic orbitals. Conversely $\psi(u)$ results in two lobes of opposite sign cancelling and hence giving zero electron density in between the nuclei. This is an **antibonding molecular orbital** which is higher in energy.

The molecular orbital wave functions are designated $\psi(g)$ and $\psi(u)$; g stands for *gerade* (even) and u for *ungerade* (odd), **g** and **u** refer to the symmetry of the orbital about its centre. If the sign of the wave function is unchanged when the orbital is reflected about its centre (i.e. x, y and z are replaced by $-x$, $-y$ and $-z$) the orbital is **gerade**. An alternative method for determining the symmetry of the molecular orbital is to rotate the orbital about the line joining the two nuclei and then about a line perpendicular to this. If the sign of the lobes remains the same, the orbital is **gerade**, and if the sign changes, the orbital is **ungerade**.

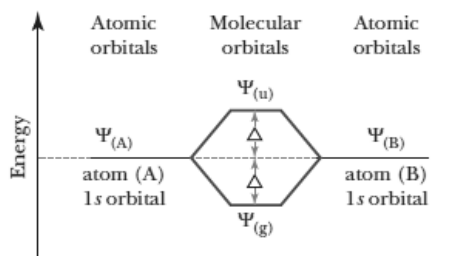
The energy of the bonding molecular orbital $\psi(g)$ passes through a minimum and the distance between the atoms at this point corresponds to the internuclear distance between the atoms when they form a bond. Consider the energy levels of the two 1s atomic orbitals, and of the bonding $\psi(g)$ and antibonding $\psi(u)$ orbitals.



The energy of the bonding molecular orbital is lower than that of the atomic orbital by an amount Δ . This is known as the stabilization energy.

Similarly the energy of the antibonding molecular orbital is increased by Δ . Atomic orbitals may hold up to two electrons (provided that they have opposite spins) and the same applies to molecular orbitals. In the case of two hydrogen atoms combining, there are two electrons to be considered: one from the 1s orbital of atom A and one from the 1s orbital of atom B. When combined, these two electrons both occupy the bonding molecular orbital $\psi(g)$. This results in a saving of energy of 2Δ , which corresponds to the **bond energy**. It is only because the system is stabilized in this way that a bond is formed.

Consider the hypothetical case of two He atoms combining. The 1s orbitals on each He contain two electrons, making a total of four electrons to put into molecular orbitals. Two of the electrons occupy the bonding MO, and two occupy the antibonding MO. The stabilization energy 2Δ derived from filling the bonding MO is offset by the 2Δ destabilization energy from using the antibonding MO. Since overall there is no saving of energy, He_2 does not exist, and this situation corresponds to non-bonding.

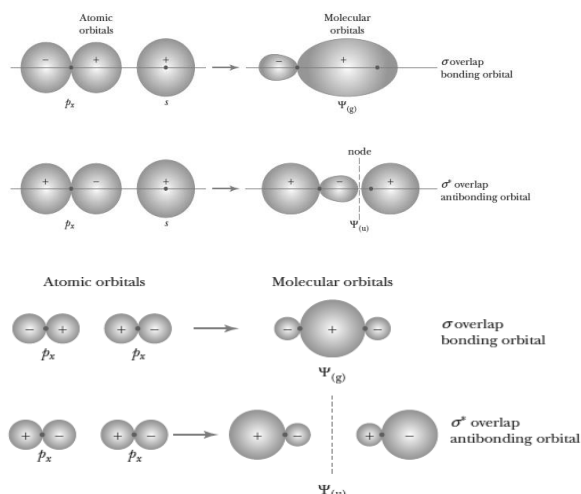


s-p combinations of orbitals:

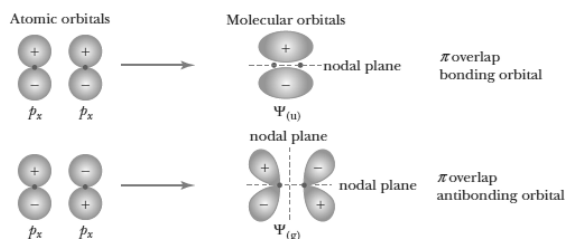
An s orbital may combine with a p orbital provided that the lobes of the p orbital are pointing along the axis joining the nuclei. When the lobes which overlap have the same sign this results in a bonding MO with an increased electron density between the nuclei. When the overlapping lobes have opposite signs this gives an antibonding MO with a reduced electron density in between the nuclei.

p-p combinations of orbitals:

Consider first the combination of two p orbitals which both have lobes pointing along the axis joining the nuclei. Both a bonding MO and an antibonding MO are produced.

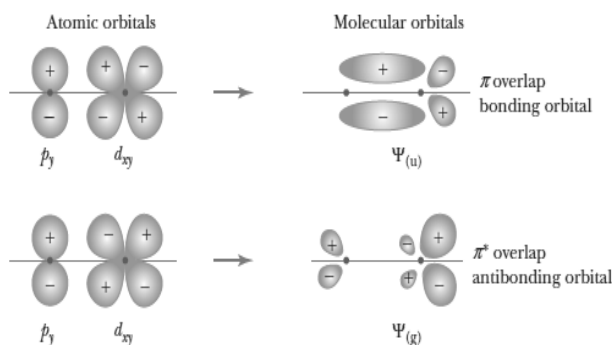


Next consider the combination of two p orbitals which both have lobes perpendicular to the axis joining the nuclei. Lateral overlap of orbitals will occur, resulting in π bonding and π^* antibonding MOs being produced



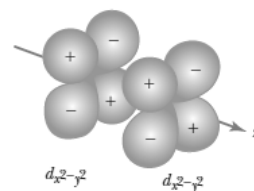
p-d combinations of orbitals:

A p orbital on one atom may overlap with a d orbital on another atom as shown, giving bonding and antibonding combinations. Since the orbitals do not point along the line joining the two nuclei, overlap must be of the π type. This type of bonding is responsible for the short bonds found in the oxides and oxoacids of phosphorus and sulphur. It also occurs in transition metal complexes such as the carbonyls and cyanides.



d-d combinations of orbitals:

It is possible to combine two d atomic orbitals, producing bonding and antibonding MOs which are called δ and δ^* respectively. On rotating these orbitals about the internuclear axis, the sign of the lobes changes four times compared with two changes with p overlap and no change for s overlap

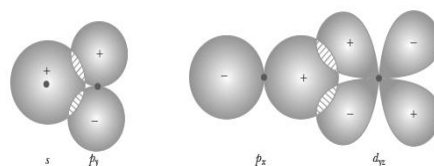


Non-bonding combinations of orbitals:

All the cases of overlap of atomic orbitals considered so far have resulted in a bonding MO of lower energy, and an antibonding MO of higher energy

To obtain a bonding MO with a concentration of electron density in between the nuclei, the signs (symmetry) of the lobes which overlap must be the same. Similarly for antibonding MOs the signs of the overlapping lobes must be different.

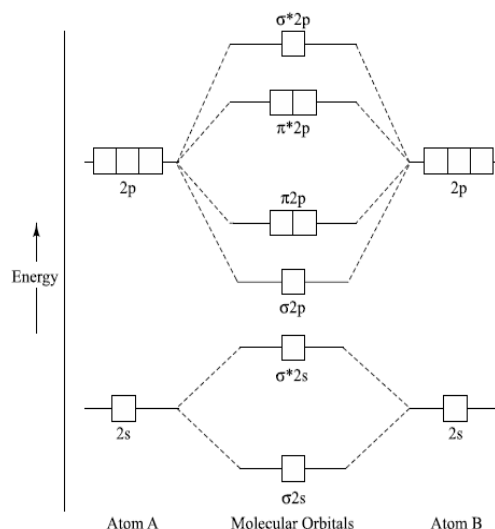
In the combinations as shown in Figure, any stabilization which occurs from overlapping + with + is destabilized by an equal amount of overlap of + with -. There is no overall change in energy, and this situation is termed non-bonding. It should be noted that in all of these non-bonding cases the symmetry of the two atomic orbitals is different, i.e. rotation about the axis changes the sign of one.



Relative Energies of Molecular Orbitals-Correlation

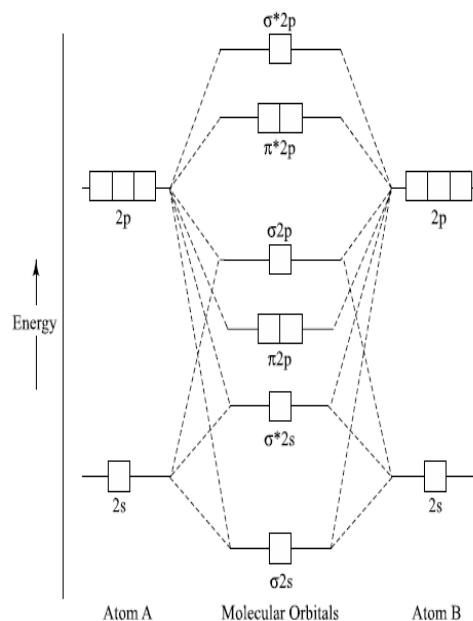
The adjacent diagram is expected for the orbitals of atoms of second period. In this diagram, $E(\sigma_{2p}) < E(\pi_{2p})$ since the end-to-end overlap of 2p orbitals is expected to be larger than side-ways overlap. found to be applicable only for O_2 and F_2 molecules. The relative energies of molecular orbitals is

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



For the molecules Li_2 to N_2 , the energy difference $2s(A)$ and $2p(A)$ is not large so that these two orbitals jointly combine with $2s(B)$ and $2p(B)$. This results in modification of relative energy of molecular orbitals which is shown below:

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



Bond order: It gives the number of bonds in a molecule. It is defined as

Bond Order = $\frac{(Nb - Na)}{2}$, where Nb and Na are total number of bonding and antibonding electrons respectively. The strength of a bond depends on the bond order of the molecule. The larger the bond order, the stronger the bond and larger the dissociation energy of the molecule.

Molecular Characteristics

Species	Valence electrons	Electronic Configuration	Bond Order [†]	Characteristics
H ₂	2	(σ1s) ²	$\frac{2-0}{2} = 1$	Diamagnetic as there is no unpaired electron
H ₂ ⁺	1	(σ1s) ¹	$\frac{1-0}{2} = \frac{1}{2}$	Relative to H ₂ , bond length increases, bond dissociation energy decreases Paramagnetic as there is one unpaired electron.
He ₂	4	(σ1s) ² (σ*1s) ²	$\frac{2-2}{2} = 0$	Does not exist as bond order is zero
He ₂ ⁺	3	(σ1s) ² (σ*1s) ¹	$\frac{2-1}{2} = \frac{1}{2}$	Expected to exist, paramagnetic
Li ₂	2	KK(σ2s) ²	$\frac{2-0}{2} = 1$	Diamagnetic
Be ₂	4	KK(σ2s) ² (σ*2s) ²	$\frac{2-2}{2} = 0$	Does not exist
B ₂	6	KK(σ2s) ² (σ*2s) ² (π2p _x) ¹ (π*2p _y) ¹	$\frac{4-2}{2} = 1$	Paramagnetic
C ₂	8	KK(σ2s) ² (σ*2s) ² (π2p _x) ² (π2p _y) ²	$\frac{6-2}{2} = 2$	Diamagnetic
N ₂	10	KK(σ2s) ² (σ*2s) ² (π2p _x) ² (π2p _y) ² (σ2p _z) ²	$\frac{8-2}{2} = 3$	Maximum number of bonds (1σ and 2π bonds) Maximum bond dissociation energy Minimum bond length, Diamagnetic
N ₂ ⁺	9	KK(σ2s) ² (σ*2s) ² (π2p _x) ² (π2p _y) ² (σ2p _z) ¹	$\frac{7-2}{2} = 2\frac{1}{2}$	Relative to N ₂ , bond dissociation energy decreases, bond length increases Paramagnetic
N ₂ ⁻	11	KK(σ2s) ² (σ*2s) ² (π2p _x) ² (π2p _y) ² (σ2p _z) ² (π*2p _x) ¹	$\frac{8-3}{2} = 2\frac{1}{2}$	— same —
O ₂	12	KK(σ2s) ² (σ*2s) ² (σ2p _z) ² (π2p _x) ² (π2p _y) ² (π*2p _x) ¹ (π*2p _y) ¹	$\frac{8-4}{2} = 2$	Paramagnetic as it contains two unpaired electrons
O ₂ ⁺	11	KK(σ2s) ² (σ*2s) ² (σ2p _z) ² (π2p _x) ² (π2p _y) ² (π*2p _x) ¹	$\frac{8-3}{2} = 2.5$	Relative to O ₂ , bond order is increased. Thus bond dissociation energy increases and bond length decreases Paramagnetic
Note: These effects are just opposite to those observed in going from N ₂ to N ₂ ⁺ .				
O ₂ ⁻	13	KK(σ2s) ² (σ*2s) ² (σ2p _z) ² (π2p _x) ² (π2p _y) ² (π*2p _x) ² (π*2p _y) ¹	$\frac{8-5}{2} = 1\frac{1}{2}$	Relative to O ₂ , bond order is decreased. Thus, bond dissociation energy decreases and bond length increases
Note: The species O ₂ ⁻ is expected to be less stable than O ₂ ⁺ due to larger electron-electron repulsion.				
F ₂	14	KK(σ2s) ² (σ*2s) ² (σ2p _z) ² (π2p _x) ² (π2p _y) ² (π*2p _x) ² (π*2p _y) ²	$\frac{8-6}{2} = 1$	Diamagnetic
Ne ₂	16	KK(σ2s) ² (σ*2s) ² (σ2p _z) ² (π2p _x) ² (π2p _y) ² (π*2p _x) ² (π*2p _y) ² (σ*2p _z) ²	$\frac{8-8}{2} = 0$	Does not exist

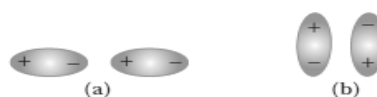
WEAK FORCES:

Attractive intermolecular forces

In the kinetic theory of gases, it is assumed that there are no forces of attraction between gas molecules. However, the fact that gases like O₂, H₂ etc. can be liquefied, implies that the molecules are aggregated together and are obviously held together by some forces of attraction. This kind of existence of intermolecular forces is also proved by other facts like non-ideal behaviour of real gases and Joule–Thomson effect, etc. There are three types of intermolecular attractive forces, which are described as follows and the sum of these three forces is called as van der Waals forces of attraction.

1. Dipole–dipole interaction (or Keesom forces):

These forces arise due to dipolar nature of a molecule. The opposite ends of two molecules are attracted Electrostatically in two ways, head–tail arrangement (fig-a) and anti-parallel arrangement



(fig-b). For fatty molecules, the head–tail arrangement is more stable. In other molecules, anti-parallel arrangement is more stable. Both the arrangements will have the same energy when the longer axis is 1.12 times as long as the shorter axis. Both the arrangements may exist together only when the molecule is having higher attractive forces than the thermal energy, and it is true for both solids and liquids. With increase in temperature, these orientations become more random. The hydrogen bonding is a special case of this type of interaction due to its high energy release.

2. Dipole–induced dipole interaction (or Debye forces):

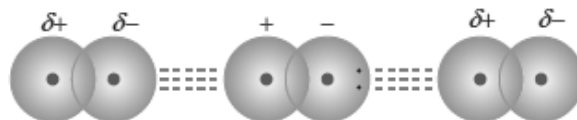
When the dipolar end of a polar molecule is introduced in the environment of a non-polar molecule, it can induce a dipole moment in the adjacent non-polar molecule. Then this induced dipole can interact electrostatically with the polarizing dipole.

This kind of interaction explains the solubility of noble gases in water, and formation of noble gas hydrates like $\text{Ar} \cdot 6\text{H}_2\text{O}$, $\text{Kr} \cdot 6\text{H}_2\text{O}$, and $\text{Xe} \cdot 6\text{H}_2\text{O}$. The solubility order for noble gases in water is: $\text{He} < \text{Ne} < \text{Ar} < \text{Kr} < \text{Xe}$. This is due to the increased polarizability of the larger inert gas molecules.



3. Instantaneous dipole–induced dipole interaction (London forces):

Molecules or atoms which have no permanent dipole are also attracted to each other and this is evident from the formation of liquid X_2 (where $\text{X} = \text{H}, \text{F}, \text{O}, \text{N}, \text{Cl}$, etc.) and liquid He . In such a molecule, at any point of time an instantaneous dipole is developed which induces dipole in the other nearby non-polar molecule, thereby producing dipole-induced dipole interactions. These interactions are known as London forces. On the time average these molecules are non-polar but at a particular moment, the molecule may become polar and the actual molecules may be a combination of all the three structure shown in the figure.



London forces work in polar and non-polar molecules and are dependent on the following factors and increases rapidly with increase in:

- (i) Number of polarizable electrons.
- (ii) Molecular weight.
- (iii) Molecular volume and surface area available for interaction.

Repulsive intermolecular forces

When the molecules come closer, the van der Waals forces increase gradually, but beyond a particular distance the electron–electron and nucleus–nucleus repulsions also increase, and finally the attractive and repulsive forces remain in equilibrium. The above repulsive energy is expressed by

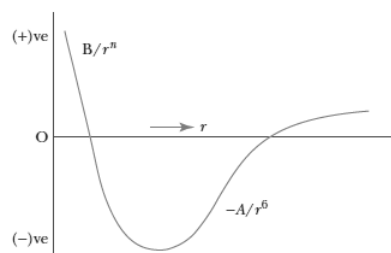
$$E_{\text{repulsive}} = \frac{B}{r^n} \quad \text{where } B \text{ is a constant, } n \text{ is of large value and depends upon the electronic configuration.}$$

Lennard–Jones potential

The net interaction energy (also called as Lennard–Jones potential) is expressed by E_T .

$$\begin{aligned} E_T &= E_{\text{attractive}} + E_{\text{repulsive}} \\ &= \frac{A}{r^6} + \frac{B}{r^n} \end{aligned}$$

The plot of E_T with r is shown in the Figure.



INTERACTIONS BETWEEN IONS AND COVALENT MOLECULES

1. Ion–dipole interactions: These interactions explain the solubilities of ionic compounds in polar solvents. When an ionic compound is dissolved in polar solvents, the positive end of the polar solvent gets oriented towards anion, while the negative end of the polar solvent gets oriented towards cation.

2. Ion–induced dipole interaction: The electrical field of an ion can polarize a non-polar molecule to induce a new dipole in the molecule. The electrostatic interaction between this ion and the induced dipole is called ion–induced dipole interaction. The formation of polyhalide ions like X_3^- ($X = \text{Cl}, \text{Br}, \text{I}$) and the solubility of ionic compounds in non-polar solvent can be explained on the basis of this interaction.