

Unit I: Atomic Structure and Bonding Theories

Quantum-mechanical model of atom, Schrodinger wave equation, significance of Ψ and Ψ^2 , applications to particle in a box and hydrogen atom; Molecular orbital theory – bonding in homo and hetero nuclear diatomic molecules – energy level diagrams of N₂, O₂, NO and CO; π -molecular orbitals of butadiene and benzene; VSEPR theory and molecular shapes.

Maharshi Kanada – [600 BCE] originated the idea that Anu (atom) was an indestructible particle of matter, and hence eternal. He believed atoms to be minute objects invisible to the naked eye which come into being and vanish in an instant. Kanada also put forward the idea that atoms could be combined in various ways to produce chemical changes in presence of other factors such as heat.

Atoms consist of three tiny kinds of particles called subatomic particles: protons, electrons, and neutrons. The protons (+ve) and the neutrons (neutral) present at the centre of the atom called the nucleus and the electrons (-ve) fly around above the nucleus in a small cloud. Atom is electrically neutral.

The word atom is from Greek means indivisible and the idea that all matter ultimately consists of small particles, called atoms was conceived by John Dalton in 1808.

Quantum-mechanical model of atom:

Classical mechanics (based on Newton's laws of motion) explains the motion of all macroscopic particles and fail to explain the motion of tiny particles like electrons. Max Planck proposed quantum theory at the beginning of 20th century. Based on the ideas of quantum theory, a new mechanics called quantum mechanics was developed in the mid-1920s. Then Erwin Shrodinger developed quantum mechanics or wave mechanics on the bases of de Broglie's principle and Heisenberg's principle.

Louis de Broglie explains the dual nature of the electron. All particles behave with wave and particle properties at the same time.

$$\lambda = \frac{h}{mv}$$

The momentum of a particle in motion is inversely proportional to the wavelength of the waves associated with it. But it is insignificant for heavy particles because de Broglie's wavelength is too small to measure.

Werner Heisenberg: proposed Heisenberg's Uncertainty Principle. It is impossible to know both the position and momentum of an electron simultaneously with perfect accuracy. This quantum mechanical model of the atom treats an electron like a wave. Mathematically,

$$(\text{error in position}) \times (\text{error in momentum}) \geq \frac{h}{4\pi}$$

$$\Delta x \cdot \Delta p \geq \frac{h}{4\pi}$$

$$\Delta x \cdot m \Delta v \geq \frac{h}{4\pi}$$

When position and momentum of an electron not known accurately at a particular time, then the concept of Bohr's model is meaning less to think of orbits. However, it is possible only to predict or state the probability of locating an electron of a particular energy in a given region of space at a given time.

Erwin Shrödinger: The Shrödinger's quantum mechanical model explains the behaviour of an electron in an atom by an equation developed by him.

Since the electron shows wave like nature, the classical wave equation describes the wave motion of a particle along the x-axis by the equation

$$\psi = A \sin \frac{2\pi x}{\lambda} \quad \text{--- (eq 1)}$$

ψ = wave function

A = Constant

X = displacement of wave in the given direction x

λ = wave length

On differentiating the equation -1 twice w. r. t. 'x'

$$\frac{\partial \psi}{\partial x} = A \left(\frac{2\pi}{\lambda} \right) \cos \frac{2\pi x}{\lambda}$$

$$\frac{\partial \psi}{\partial x} = \frac{2\pi A}{\lambda} \cos \frac{2\pi x}{\lambda} \quad \text{--- (eq 2)}$$

$$\frac{\partial^2 \psi}{\partial x^2} = \frac{2\pi A}{\lambda} \left(-\sin \frac{2\pi x}{\lambda} \right) \frac{2\pi}{\lambda}$$

$$= -\frac{4\pi^2 A}{\lambda^2} \sin \frac{2\pi x}{\lambda} \quad \text{--- (eq 3)}$$

With respect to equation 1, equation 3 can be written as

$$\frac{\partial^2 \psi}{\partial x^2} = -\frac{4\pi^2}{\lambda^2} \psi$$

$$\frac{\partial^2 \psi}{\partial x^2} + \frac{4\pi^2}{\lambda^2} \psi = 0 \quad \text{--- (eq 4)}$$

According to Bohr's theory the total energy (E) of electron is

$$E = KE + PE$$

$$E = \frac{1}{2} mv^2 + V \quad \text{----- (eq 5)}$$

(m = mass & v is velocity of moving electron)

From de Broglie's explains

$$\lambda = \frac{h}{mv}$$

$$mv = \frac{h}{\lambda}$$

$$m^2v^2 = \frac{h^2}{\lambda^2}$$

$$\begin{aligned} KE &= \frac{1}{2}mv^2 \\ &= \frac{1}{2} \frac{m}{m} mv^2 \\ &= \frac{1}{2} \frac{m^2v^2}{m} \\ &= \frac{m^2v^2}{2m} \end{aligned}$$

Dividing with '2m' on both sides

$$\frac{m^2v^2}{2m} = \frac{h^2}{2\lambda^2m} \quad \text{--- (eq 6)}$$

On substituting the KE value from equation- 6 in to equation- 5

$$E = \frac{h^2}{2\lambda^2m} + V$$

$$\frac{1}{\lambda^2} = (E - V) \frac{2m}{h^2} \quad \text{--- (eq 7)}$$

On substituting the $\frac{1}{\lambda^2}$ value in equation- 4

$$\frac{\partial^2 \psi}{\partial x^2} + \frac{4\pi^2 2m}{h^2} \psi (E - V) = 0$$

$$\frac{\partial^2 \psi}{\partial x^2} + \frac{8\pi^2 m}{h^2} (E - V) \psi = 0$$

This is the Shrödinger wave equation for a particle in one direction. Then for an electron with the wave motion in the three dimensional phase (i.e. along x, y, z axis) is

$$\frac{\partial^2 \psi}{\partial x^2} + \frac{\partial^2 \psi}{\partial y^2} + \frac{\partial^2 \psi}{\partial z^2} + \frac{8\pi^2 m}{h^2} (E - V) \psi = 0 \quad \text{--- (eq 8)}$$

Where x, y, z are space coordinates;

m = mass of electron;

\hbar = Plank's constant;

E = Total energy of electron;

V = potential energy of electron

ψ = amplitude of the wave called as wave function

$\frac{\partial^2 \psi}{\partial x^2}$ = represents the second derivative of ψ w.r.t. to 'x' and so on

On simplification Shrödinger wave equation - 8

$$\frac{\partial^2 \psi}{\partial x^2} + \frac{\partial^2 \psi}{\partial y^2} + \frac{\partial^2 \psi}{\partial z^2} + \frac{2m}{\hbar^2} (E - V) \psi = 0 \quad \text{--- (9)}$$

$$\hbar = \frac{h}{2\pi}$$

Since $\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} = \nabla^2$ is the *Laplacian operator*, then the equation -9 can be written as

$$\nabla^2 \psi + \frac{2m}{\hbar^2} (E - V) \psi = 0 \dots \dots \dots (10)$$

This Shrödinger wave equation treated an electron like a wave and predicted the probable location of an electron around the nucleus called the atomic orbital.

When the proper value of E are substituted in Shrödinger's equation, the solution of this equation give wave function (ψ) or Eigen-function. These values of ψ corresponds to certain definite (discrete) energy values are called Eigen-values corresponds to Bohr's orbitals.

Significance of ψ and ψ^2 : The wave function ψ by itself has no physical Significance. It represents the amplitude of electron wave

According to the Theory of propagation of light and sound waves, the *square of the amplitude* of the wave proportional to the *intensity* of the light or sound. Similarly the ψ^2 (square of ψ) at a point is proportional to the probability of finding an electron with definite energy within a certain region around the nucleus or proportional to the density of electrons.

Case-1: If ψ^2 is zero, then the probability of finding an electron at that point is negligible.

Case-2: If the wave function is imaginary, this quantity represents the probability of ψ^2 , as a function of x, y, and z co-ordinates of the system and it varies form one space region to another.

- For a one-dimensional problem, this region is a space between x and $x + d_x$
- for a two-dimensional problem, this region is an electron of area
- for a three-dimensional problem, this region is an element of volume

Thus the probability of finding the electrons in different regions is different. This shows the agreement with uncertainty principle. Evidently, ψ^2 can be interpreted as probability density. If ∂v is a finite volume ($\partial v = \partial x \cdot \partial y \cdot \partial z$), then $\psi^2 \partial v$ gives the probability of finding the electron in the region having a volume ∂v .

The main significance of Shrödinger's equation is

- This Quantum-mechanical model of atom is updates to Bohr Model. Electrons are not in circular orbits around nucleus and electrons are in a 3-D region around the nucleus
- Solution to this equation is a wave that describes the quantum aspects of a system. This quantum mechanical model describes the probable location of electrons in atoms by describing principal energy level, energy sublevel, orbital (in each sublevel) and spin.

Particle in a box

(Or) Particle in a one dimensional potential box (Or) Particle in potential well (Or) Show that the energies of a particle in a potential box are quantized
 (Or) Derive the equation for Eigen energies and Eigen function of a particle, also known as the infinite potential well or the infinite square well

In quantum mechanics, the particle in a box model describes a particle free to move in a small space surrounded by impenetrable barriers. Let us consider box of width 'L', infinite depth and having infinitely hard walls. Let 'm' be the mass of particle moving with velocity 'v' along x-direction between two rigid walls A & B. The particle will not lose any energy in collision with walls, hence its total energy remains constant 'E'. When the particle is in motion, the potential energy is minimum (inside V=0) and outside the box is V=∞.

$$\text{Schrödinger wave equation in one dimension} \quad \frac{\partial^2 \psi}{\partial x^2} + \frac{2m(E - V)}{\hbar^2} \psi = 0$$

$$\frac{\partial^2 \psi}{\partial x^2} + \frac{2mE}{\hbar^2} \psi = 0 \quad (\text{here } V = 0) \quad \dots \dots \quad (1)$$

$$\frac{\partial^2 \psi}{\partial x^2} + k^2 \psi = 0 \quad \text{where } k^2 = \frac{2mE}{\hbar^2}$$

Eq-1 is the wave equation for a particle inside a potential well in x direction.

Let the general solution of above equation is $\psi(x) = A \sin kx + B \cos kx$ $\dots \dots \quad (2)$

Where A and B are constants

For calculation of A, B; let us apply the boundary condition-1 $\psi(x) = 0$ at $x = 0$ $\dots \dots \quad (3)$

boundary condition-2 $\psi(x) = 0$ at $x = L$ $\dots \dots \quad (4)$

Applying 1st boundary condition, [on substituting Eq.-3 in Eq-2] $0 = A \sin 0 + B \cos 0$

$$B = 0 \quad \dots \dots \quad (5)$$

Applying 2nd boundary condition, [on substituting Eq.-4 & 5 in Eq-2]

Then Eq.2 can be written as

$$0 = A \sin kL + 0 \cos kL$$

$$A \sin kL = 0$$

It means $A = 0$ (or) $\sin kL = 0$

but A,B cannot be zero at the same time; so $A \neq 0$

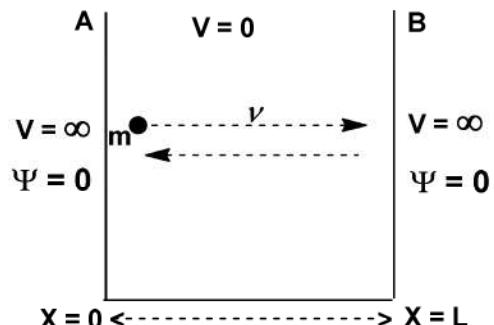
$$\therefore \sin kL = 0 \rightarrow kL = n\pi \quad (\text{where } n = 1, 2, 3, \dots)$$

$$k = \frac{n\pi}{L} \quad \dots \dots \quad (6)$$

On square the equation 6 on both sides

$$k^2 = \frac{n^2\pi^2}{L^2} \quad \dots \dots \quad (7)$$

On comparing Eq.(1) & (7) $k^2 = \frac{2mE}{\hbar^2} = \frac{n^2\pi^2}{L^2}$ (Where $n = 1, 2, 3, \dots$)



$$\boxed{E = \frac{n^2 \pi^2 \hbar^2}{2mL^2}} \quad \text{or} \quad \boxed{E = \frac{n^2 \hbar^2}{8mL^2}} \quad \dots \dots \dots \quad (8)$$

From above Eq. it is clear that energy is inversely proportional to mass and square of length. But energy is quantized, hence it cannot vary continuously. E_1 is called zero point energy system.

The lowest energy level of the particle is obtained when $n=1$.

$$\text{When } n = 1 \text{ then } E_1 = \frac{\pi^2 \hbar^2}{2mL^2}$$

$$\text{When } n = 2 \text{ then } E_2 = \frac{4\pi^2 \hbar^2}{2mL^2} = 4E_1$$

$$\text{When } n = 3 \text{ then } E_3 = \frac{9\pi^2 \hbar^2}{2mL^2} = 9E_1$$

$$\therefore \text{In general the energy level is } E_n = n^2 E_1 \quad \dots \dots \dots \quad (9)$$

From the above equations it is clear that particles in the box are having discrete energy values, these energy values are called Eigen values of energy [E_1, E_2, E_3, \dots]. If $E = 0$ then Ψ inside the box become Zero, which is wrong. So $E \neq 0$.

The permitted energy levels for the motion of the particle in three dimension in the box is given by

$$E = \frac{n_x^2 \hbar^2}{8mL^2} + \frac{n_y^2 \hbar^2}{8mL^2} + \frac{n_z^2 \hbar^2}{8mL^2}$$

$$E_{nx, ny, nz} = (n_x^2 + n_y^2 + n_z^2) \frac{\hbar^2}{8mL^2}$$

$$\text{For cubic box } L_x = L_y = L_z = L$$

$$n_x = n_y = n_z = 1$$

$$\text{Then } E = (1^2 + 1^2 + 1^2) \frac{\hbar^2}{8mL^2}$$

$$\therefore E = \frac{3\hbar^2}{8mL^2}$$

Now for a cubical box of all sides the energy level corresponding to three different states with quantum numbers (2,1,1) (1,2,1) and (1,1,2)

$$E = \frac{6\hbar^2}{8mL^2}$$

Scientific processes that atoms can have up to seven principle energy levels of electrons around the nucleus.

Wave function inside the box:

Normally, ψ_n may be +ve or -ve but $|\psi|^2$ is always +ve, So $|\psi|^2$ gives the probability of finding the particle at a given point. This value varies for different quantum number (n). For example $|\psi_1|^2$ has its maximum value in the middle of the box, while $|\psi_2|^2$ is equal to zero there.

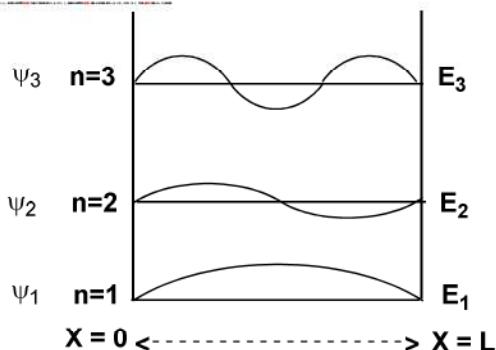


Fig-a: Elecetron wave function

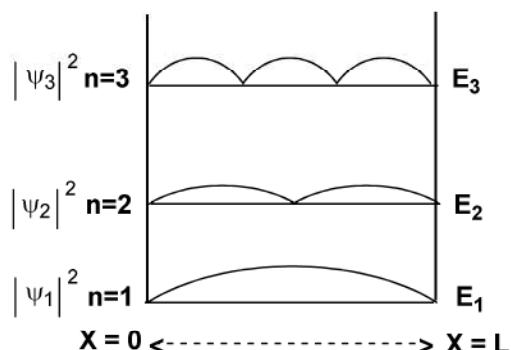


Fig-b: corresponding probability density

Fig. (a) & (b): Ground state, first, second excited states of an electron in potential well

Substitute Eq. 5 and Eq.6 in Eq.2.....Then Eq.2 can be written as

$$\psi(x) = A \sin \frac{n\pi}{L} x \quad \dots\dots\dots (10)$$

For calculation of 'A' in Eq (10), let us impose normalization conditions. i,e, equalizing the probability density to unity. $|\psi|^2 = 1$.

$$\text{Net density is } \int_0^L |\psi|^2 dx = 1$$

$$\int_0^L A^2 \sin^2 \left(\frac{n\pi x}{L} \right) dx = 1$$

$$A^2 \int_0^L \frac{1}{2} \left(1 - \cos \frac{2n\pi x}{L} \right) dx = 1$$

$$\frac{A^2}{2} \left[x - \left(\frac{L}{2n\pi} \right) \sin \frac{2n\pi x}{L} \right]_0^L = 1$$

$$\frac{A^2 L}{2} - 0 = 1 \quad \rightarrow \quad \frac{A^2 L}{2} = 1$$

$$A = \sqrt{\frac{2}{L}}$$

∴ Normalized wave function (Eq.10) is

$$\psi(x) = \sqrt{\frac{2}{L}} \sin \frac{n\pi}{L} x$$

Wave-Mechanical Model of hydrogen atom:

Apply the Schrödinger wave equation to the electron present in a hydrogen atom by assume its proton (nucleus) to be stationary.

$$\frac{\partial^2 \psi}{\partial x^2} + \frac{\partial^2 \psi}{\partial y^2} + \frac{\partial^2 \psi}{\partial z^2} + \frac{8\pi^2 m}{h^2} (E - V) \psi = 0 \quad \dots \dots \dots 1$$

The electrostatic potential energy (V) of an electron at a distance 'r' from the nucleus is given by

$$V = \frac{-e^2}{(4\pi \epsilon_0)r} \quad \dots \dots \dots 2$$

Substitute eq-2 in eq.- 1

$$\frac{\partial^2 \psi}{\partial x^2} + \frac{\partial^2 \psi}{\partial y^2} + \frac{\partial^2 \psi}{\partial z^2} + \frac{8\pi^2 m}{h^2} \left(E + \frac{e^2}{(4\pi \epsilon_0)r} \right) \psi = 0 \quad \dots \dots \dots 3$$

Spherical form Schrödinger wave equation is obtained on transferring the Cartesian coordinates of the Eq-3 into spherical coordinates (r, θ, ϕ). The r, θ, ϕ which are defined in Figure.

Finally, the solution of Schrödinger wave equation in spherical form is

$$\psi(r, \theta, \phi) = R(r) \Theta(\theta) \Phi(\phi) \quad \dots \dots \dots 4$$

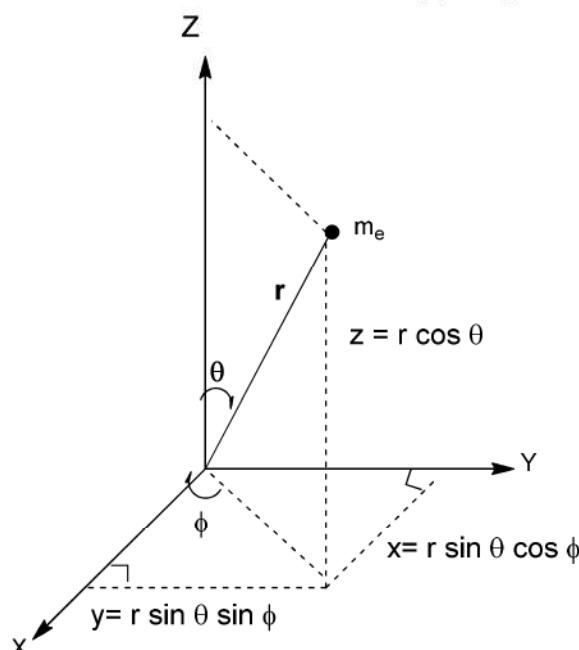


Fig: Spherical coordinates

Where $\psi(r, \theta, \phi)$, is known as total wave function, $R(r)$ is the radial wave function and other two are angular wave functions. The radial part explains the energy and angular part explains the shape of the orbitals

$$\psi(r, \theta, \phi) = R(r) Y(\theta, \phi) \longrightarrow 5$$

- i. The radial wave function $R(r)$ describes variations of wave function ψ of the electron along a radius vector from the nucleolus keeping θ and ϕ constant. Therefore, $R(r)$ deals with the distribution of the electron charge density as a function of distance (r) from the nucleus.
- ii. The angular function $Y(\theta)$ describes variations of ψ with ' θ ' keeping r and ϕ constant.
- iii. Another angular function $Y(\phi)$ describes variations of ψ with ' ϕ ' keeping r and θ constant

$R(r)$ depends on two quantum numbers n and ℓ can be denoted as $R_{n,\ell}(r)$ or simply $R_{n,\ell}$. The angular wave functions depend on the quantum numbers ℓ and m

$$\Psi_{n,\ell,m}(r, \theta, \phi) = R_{n,\ell}(r) Y_{\ell,m}(\theta, \phi) \longrightarrow 6$$

This equation shows that the total wave function besides depending on r, θ, ϕ , also depends on the quantum numbers n, ℓ and m . Each permitted combination of n, ℓ and m gives a distinct wave function and hence a distinct orbital.

On solving these equations it is found the wave function (ψ) exists only if electrons total energy has the value given by

$$E_n = \frac{me^4}{8n^2 h^2 \epsilon_0^2} \longrightarrow 7$$

Then for Hydrogen atom

$$E_n = -\frac{13.6}{n^2} \text{ eV} \longrightarrow 8$$

Where $n=1, 2, 3, \dots$ these values are same as calculated by Bohr's known as principle quantum numbers. The ' n ' value determines not only the energy of orbit but also the probable location of the atom's electrons in element at various distances from the nucleus and also the atomic radius.

' ℓ ' is Azimuthal quantum number, it can have any integral value ranging from 0 to $(n-1)$.

' m ' is magnetic quantum number, it can have values range from $-\ell$ to $+\ell$ including zero.

The shape of an atomic orbital is mainly determined by ℓ and m and is independent of n . By substituting these n, ℓ and m values in Schrödinger wave Eq-6 gives the orbitals representation.

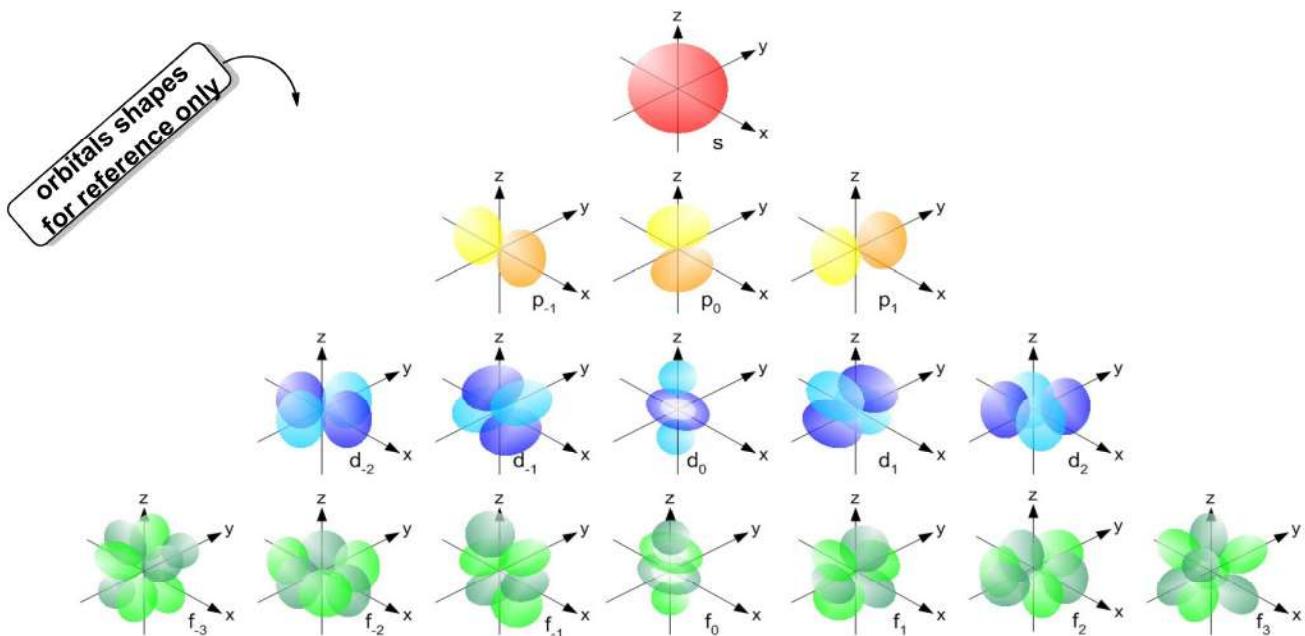
's' orbital – spherical 'p' orbital – Dumbbell 'd' orbital – double dumbbell shape

'f' orbital – have very diffused shape. This indicates it has no definite shape.

Significance of quantum numbers:

Principle (n) Main energy Level (Symbol)	Azimuthal (ℓ)		Magnetic (m)	
	values 0 to (n-1)	sub energy	values $-\ell \text{ to } +\ell$	sub-sub energy*
1 (K)	0	1s	0	S
2 (L)	0	2s	0	S
	1	2p	-1, 0 +1	2P _x , 2P _z , 2P _y
3 (M)	0	3s	0	S
	1	3p	-1, 0 +1	3P _x , 3P _z , 3P _y
	2	3d	-2 -1 0 +1 +2	d _{xy} , d _{yz} , d _z ² , d _{zx} d _x ² -y ²
4 (N)	0	4s	0	S
	1	4p	-1 0 +1	P _x , P _z , P _y
	2	4d	-2 -1 0 +1 +2	d _{xy} , d _{yz} , d _z ² , d _{zx} d _x ² -y ²
	3	4f	-3 -2 -1 0 +1 +2 +3	f _{xz} ² , f _{yz} ² , f _{xyz} , f _z ³ , f _{z(x} ² -y ² _{), f_{x(x}²-3y²_{, f_{y(3x}²-y²}}

*Note: the p-orbital with m=0 has zero component of angular momentum about z-axis and is called P_z orbital.
 $m = \pm 1$ refers px or py orbitals. In the same way 3d orbitals have different orientations of the angular momentum with z axis.



Molecular orbital theory – bonding in homo and hetero nuclear diatomic molecules

Milliken developed this theory to explain the formation of i) chemical bond ii) relative bond strengths, iii) magnetic behaviour iv) shape of molecules.

Postulates of MO theory:

1. The atomic orbitals overlap to form a new orbital known as molecular orbital. As a result, the atomic orbitals lose their individual identity.

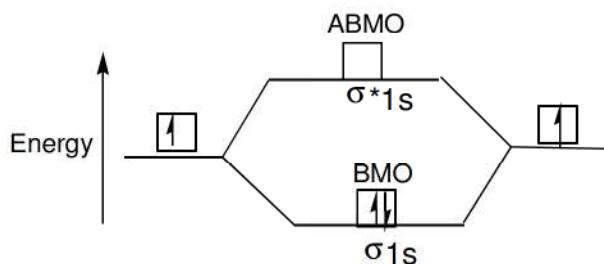
- The number of MOs formed is equal to the number of AOs combined
 - Only those AOs are combined to form MOs which have comparable energy, and orientations. **For ex:** 1s can combine with 1s and not with 2s as they have energy gap. Further, If 'x' is the molecular axis, i.e. p_x oriented in line of s-orbitals but p_y , p_z are perpendicular then the possible combination may takes place between s – p_x , but not between s – p_y , s – p_z atomic orbitals.
 - These MOs are two types. They are bonding molecular orbital (BMO) and anti-bonding molecular orbital (ABMO).
 - According to MOT the formation of bonding and anti-bonding molecular orbitals can be explain based on **Linear combination of atomic orbitals (LCAO) method:** _____

According to LCAO method the molecular orbital wave function is a linear combination (addition or subtraction) of the wave function of the individual atomic orbitals ψ_A and ψ_B .

This shows that BMO obtained by addition of overlap of two atomic orbitals (ψ_b^2) has lower energy than either of two atomic orbitals ψ_A and ψ_B . This leads to formation of a stable chemical bond and is termed as bonding molecular orbital.

$\therefore \Psi_a^2 < (\Psi_A^2 + \Psi_B^2)$ by an amount equal to $2\Psi_A.\Psi_B$

This indicates that ABMO obtained by subtraction of overlap of two atomic orbitals (ψ_a^2) has higher energy than either of two atomic orbitals ψ_A and ψ_B . Evidently such orbitals cannot lead to the formation of a chemical bond and is termed as anti-bonding molecular orbital.



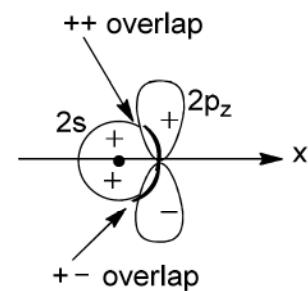
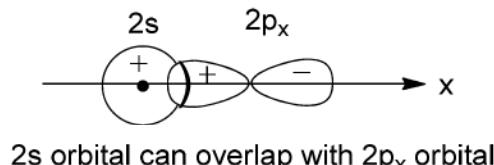
6. BMO has lower energy than the corresponding AOs and ABMO has higher energy than the corresponding AOs.
7. Axial overlap of orbitals yields σ bond formation and side-by-side overlap of yields π bond formation.
8. The BMOs are represented by σ , π , δ , Ψ etc. while ABMOs are represented by σ^* , π^* , δ^* , Ψ^* etc.
9. It is important to note that the energies of MOs is less than the sum of energies of two atomic orbitals consequently the resulting molecule is more stable.
10. The shapes of molecular orbitals depend upon the type of combining atomic orbitals.
11. The molecular orbitals (MOs) are the energy states of a molecule, in which the electrons of the molecule are filled just like in case of atomic orbitals (AOs)
12. The filling of electrons in MOs takes place by same rule as for atomic orbitals, like they follow, Aufbau, Pauli exclusion, and Hund's rule
13. The maximum capacity of a MO is two electrons with opposite spins
14. MOs gives electron probability distribution (Ψ^2) around a group of nuclei
15. If a molecule contains one or more unpaired electrons in its MOs it is paramagnetic in nature and if all electrons are paired then it exhibits diamagnetic behavior. Greater the number of unpaired electrons in the MOs higher is the paramagnetic character.

16. Bond order = $\frac{\text{number of electrons in BMO} - \text{number of electrons in ABMO}}{2}$

When no. of electrons in BMO is equal to no. of electrons in ABMO, then no bond will be formed between the atoms and molecule does not exist (having 0 or -ve values).
Greater the value of bond order (+ve), greater the stability of the molecule. .

Conditions for the formation of molecular orbital:

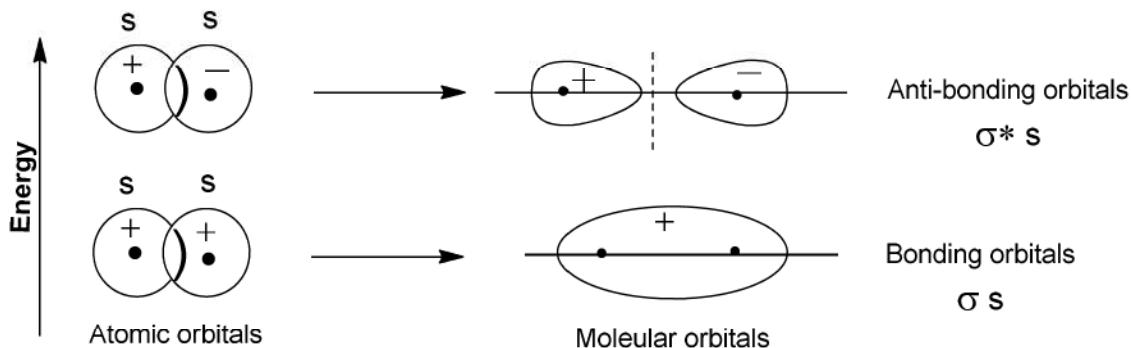
- i) The energy of combining atomic orbital should be of similar magnitude
1s can combine with 1s and not with 2s as they have energy gap
- ii) The overlapping atomic orbitals should possess same symmetry about the molecular axis.



iii) Combination of atomic orbitals takes place only, if overlapping takes place to a considerable extent

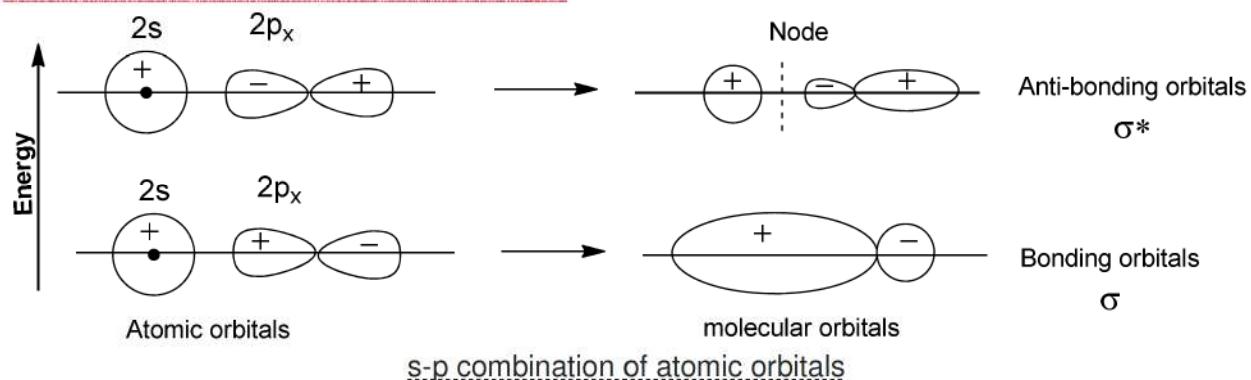
The pictorial representation of the formation of BMOs and ABMOs from AOs is shown below:

Combination of 's' orbitals: The combination of two similar s-orbitals gives only σ and σ^* MOs.



σ and σ^* molecular orbitals are formed by the combination of two 's' atomic orbitals

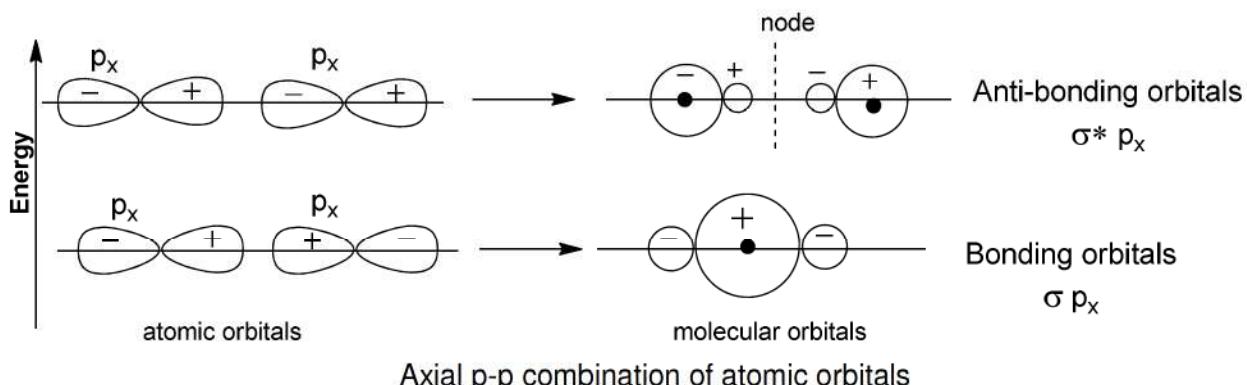
Combination of 'p-s' orbitals: This combination also gives only σ and σ^* M.O.s. This is possible only along molecular axis i.e. if x is the molecular axis, then only p_x -orbital overlap with 's' orbitals along molecular axis, . . .



Combination of 'p' orbitals: In this case two types of molecular interaction can be studied depending on the way in which they overlap with each other.

i) Axial p-p interactions: (combination of two p_x orbitals)

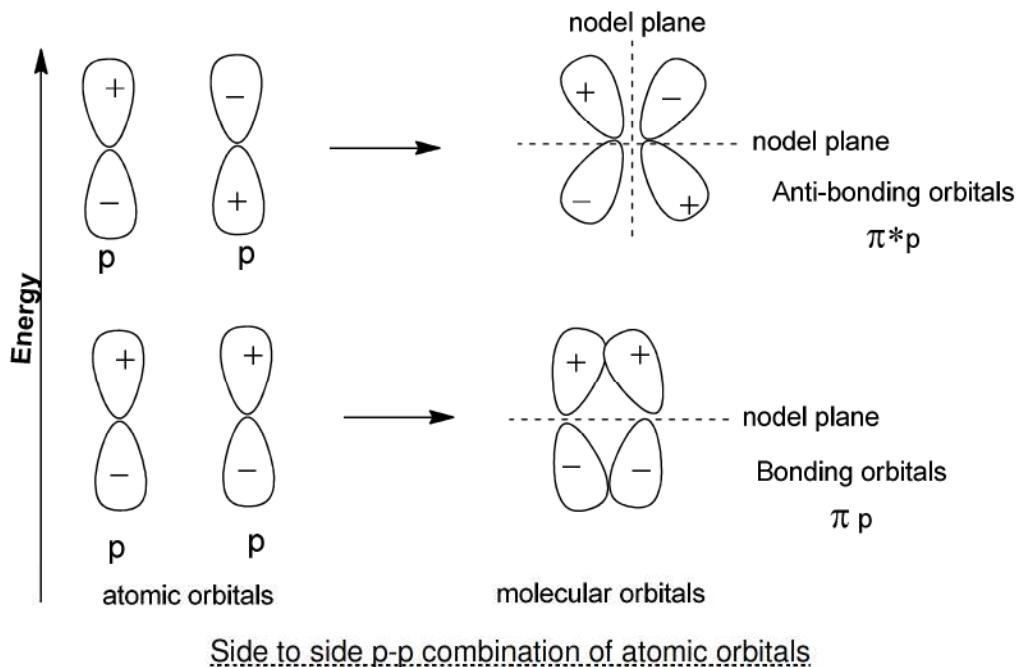
When two p_x orbitals overlap end to end, they create $\sigma 2p_x$ and $\sigma^* 2p_x$ orbitals.



Axial p-p combination of atomic orbitals

ii) Side to side p-p interactions: (combination of two p_y or two p_z orbitals)

The side-by-side overlap of two p orbitals gives rise to a π p bonding molecular orbital and a π^* p anti-bonding molecular orbital.



With this it is clear, the interaction of AOs to form the MOs is possible only if the symmetry considerations are taken care.

- If s- p_x combination is allowed then s- p_y and s- p_z combination is disallowed because p_x lies along the molecular axis.
- Similarly, If x- axis is the molecular axis only p_x-p_x , p_y-p_y and p_z-p_z combinations are allowed, whereas p_x-p_y , p_x-p_z and p_y-p_z , combinations are disallowed. p_y-p_y and p_z-p_z combination will produce π M.Os and π^* M.Os. These πp_y and πp_z as well as $\pi^* p_y$ and $\pi^* p_z$ MOs have the same energy, i.e. these are degenerate orbitals.

Order of MOs energy levels: The order of energy levels of the MOs can be determined experimentally from spectroscopic studies.

The energy levels of O₂ through Ne₂ MOs are in the following order.

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

This sequence has been found to hold for O₂, F₂ etc.

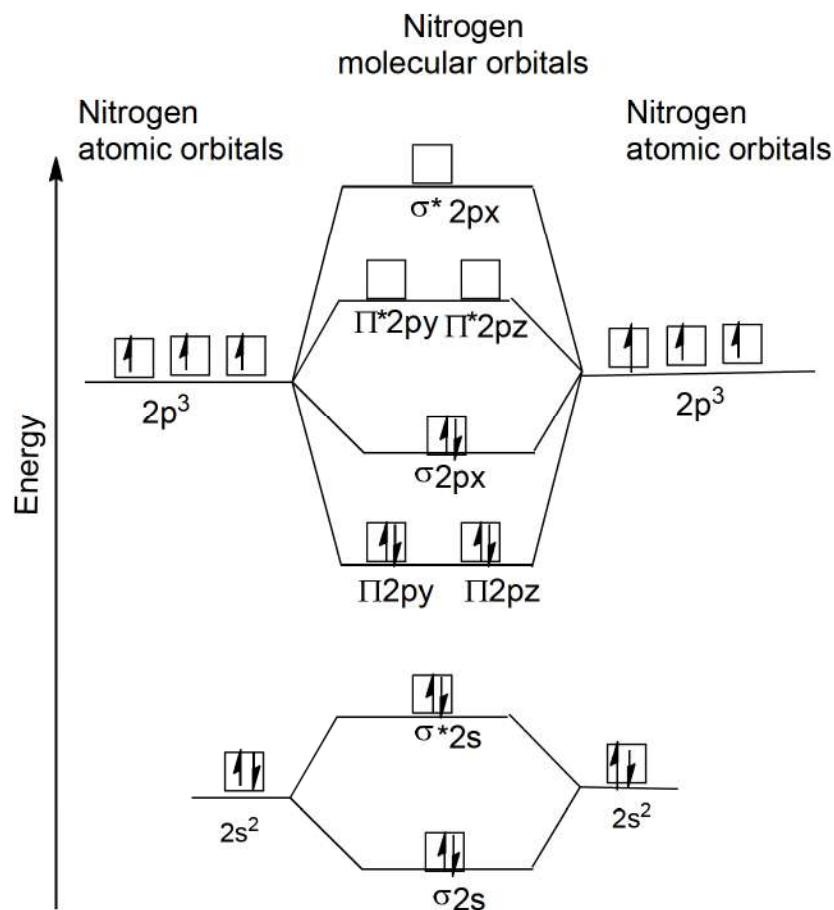
But for Li₂ through N₂ molecules $\sigma 2p_x$ is of slightly higher energy than $\pi 2p_y$, $\pi 2p_z$ MOs due to certain well established reasons and hence the sequence becomes.

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

Energy level diagrams for homo diatomic molecules (N_2 , O_2)

Energy level diagrams of N_2

The electronic configuration of each nitrogen atom is $1s^2 2s^2 2p^3$. $1s^2$ electrons of both N atoms belonging to KK MOs are non-bonding.



\therefore Electronic configuration of N_2 molecule is: (KK)⁴ ($\sigma 2s$)² < ($\sigma^* 2s$)² < ($\pi 2p_y = \pi 2p_z$)⁴ < ($\sigma 2p_x$)²

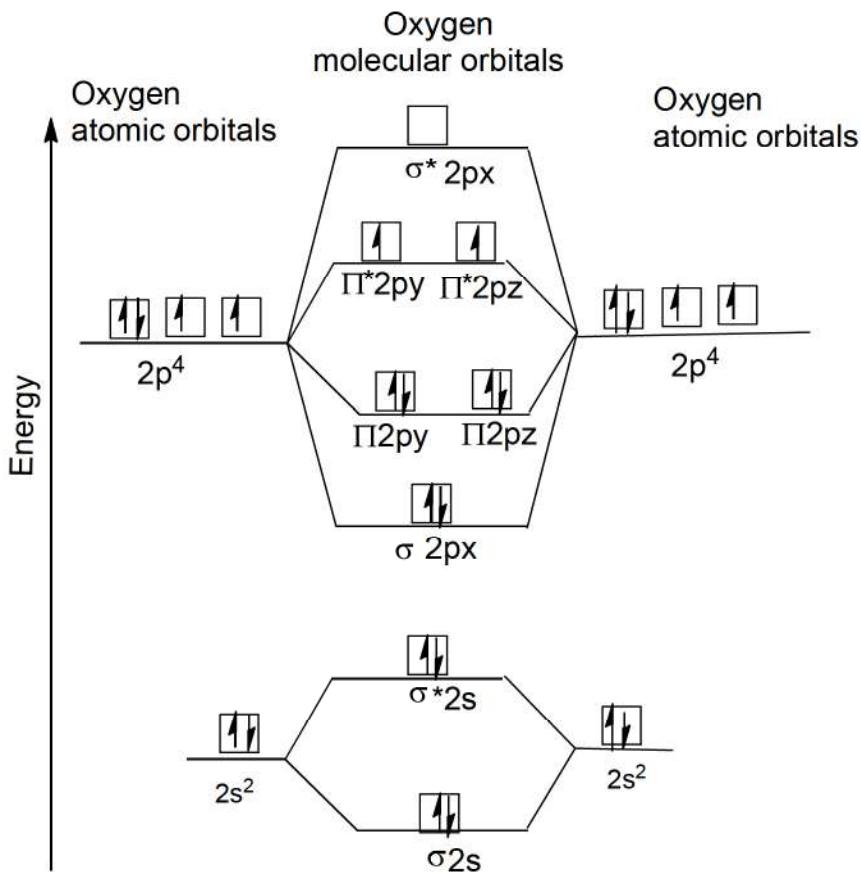
$$\text{Bond order} = \frac{\text{number of electrons in BMO} - \text{number of electrons in ABMO}}{2}$$

$$\text{Bond order} = \frac{8 - 2}{2} = 3$$

Bond order indicates nitrogen molecule contains a triple bond. Since all the electrons in bonding as well as anti-bonding molecular orbitals are paired it exhibits diamagnetic behaviour.

Energy level diagrams of O_2

The electronic configuration of each oxygen atom is $1s^2 2s^2 2p^4$. $1s^2$ electrons of both O atoms belonging to KK MOs are non-bonding.



\therefore Electronic configuration of O_2 molecule is:

$$(KK)^4 (\sigma 2s)^2 < (\sigma^* 2s)^2 < (\sigma 2p_x)^2 < (\pi 2p_y = \pi 2p_z)^4 < (\pi^* 2p_y)^1 = (\pi^* 2p_z)^1$$

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

$$\text{Bond order} = \frac{8 - 4}{2} = 2$$

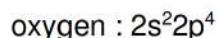
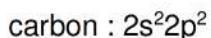
Bond order indicates oxygen molecule contains a double bond. The O_2 molecule exhibits paramagnetic behaviour, due the presence of two unpaired electrons in $\pi^* 2p_y$ and $\pi^* 2p_z$ molecular orbitals.

Energy level diagrams for hetero diatomic molecules (CO and NO)

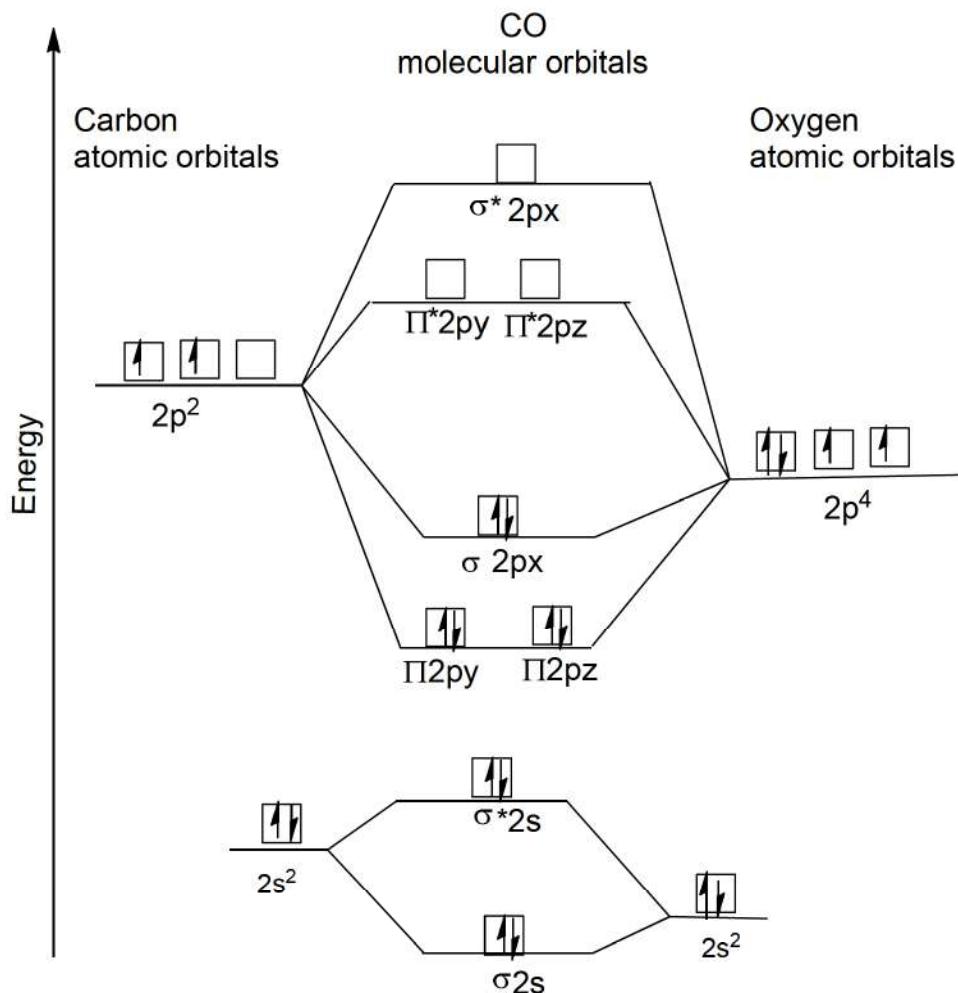
In hetero nuclear diatomic molecule the electron distribution between the two atoms is not symmetrical due to the difference in their energy levels. This leads to polar bonds, in which electron pairs is shared unequally by two atoms. During the formation of bonding molecular orbitals, the atomic orbital with lower energy makes the larger contribution and the anti-bonding molecular orbitals formed by atomic orbital with higher energy

Energy level diagrams of CO (Carbon monoxide)

This molecule is isoelectronic with N₂ molecule and has similar molecular electronic configuration and energy level diagram to that of N₂ molecule. There is only a minor difference in valence shell electron distribution in AOs of carbon and oxygen as follows.



The valence atomic orbitals of carbon and oxygen overlap with each other to form CO molecular orbitals.



∴ Electronic configuration of CO molecule is: (KK)⁴ (σ2s)² < (σ*2S)² < (Π2p_y = Π2p_z)⁴ < (σ2p_x)²

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

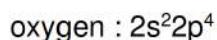
$$\text{Bond order} = \frac{8 - 2}{2} = 3$$

Bond order indicates the presence of a triple bond in the molecule. Further the molecular orbital configuration of CO is similar to the (isoelectronic) N₂.

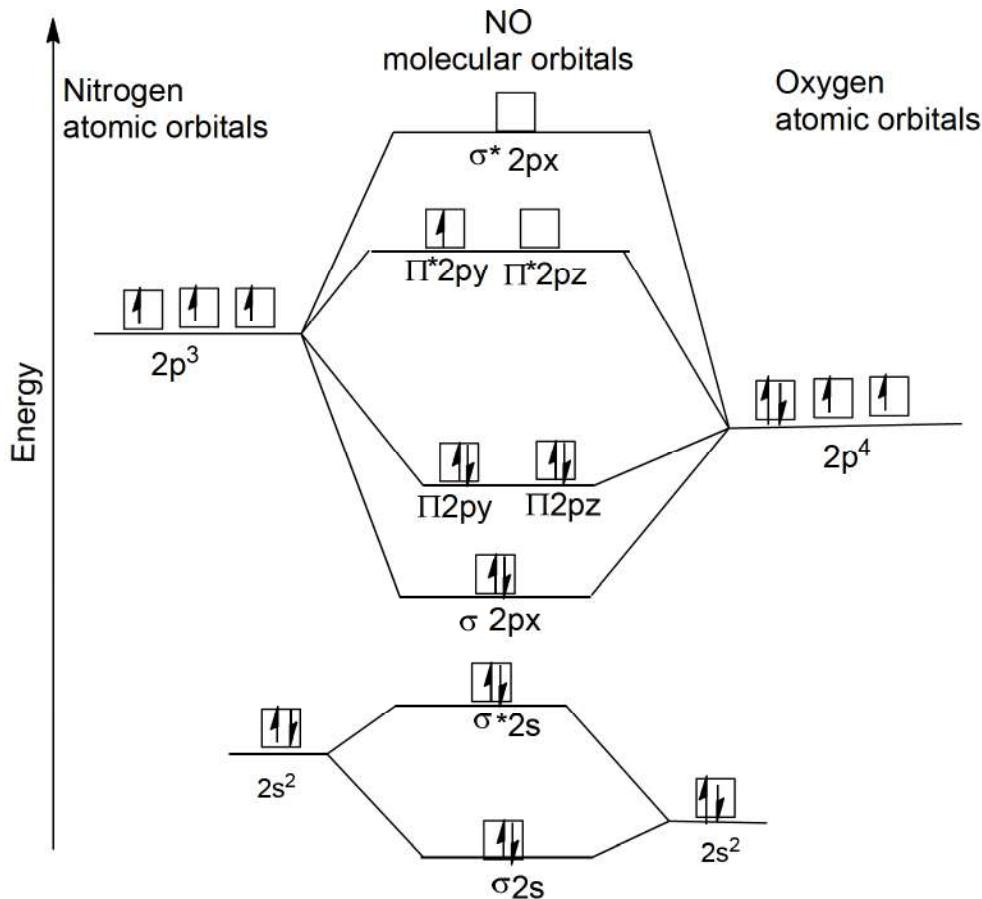
Since all the electrons in bonding as well as anti-bonding molecular orbitals are paired it exhibits diamagnetic behaviour

Energy level diagrams of NO (Nitric oxide)

The valence shell electron distribution in AOs of nitrogen and oxygen are as follows. The valence shell electronic configuration of carbon and Nitrogen are



The valence atomic orbitals of nitrogen and oxygen overlap with each other to form 'NO' molecular orbitals.



∴ Electronic configuration of NO molecule is:

$$(KK)^4 (\sigma 2s)^2 < (\sigma^* 2S)^2 < (\sigma 2p_x)^2 < (\pi 2p_y = \pi 2p_z)^4 < (\pi^* 2p_y)^1 = (\pi^* 2p_z)^0$$

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

$$\text{Bond order} = \frac{8 - 3}{2} = 2.5$$

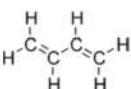
Since the bond order is +ve the NO molecule can exists. Further, there is significance energy difference between these atomic orbitals, their combination gives less effective molecular orbitals than N₂ or O₂, this results the bond between N and O is weaker than expected. However, The bond between N and O is 2.5 times as strong as a normal covalent bond.

Further this molecule exhibits paramagnetic behaviour, due the presence of two unpaired electrons in $\pi^* 2p_y$ and $\pi^* 2p_z$ molecular orbitals.

π -molecular orbitals:

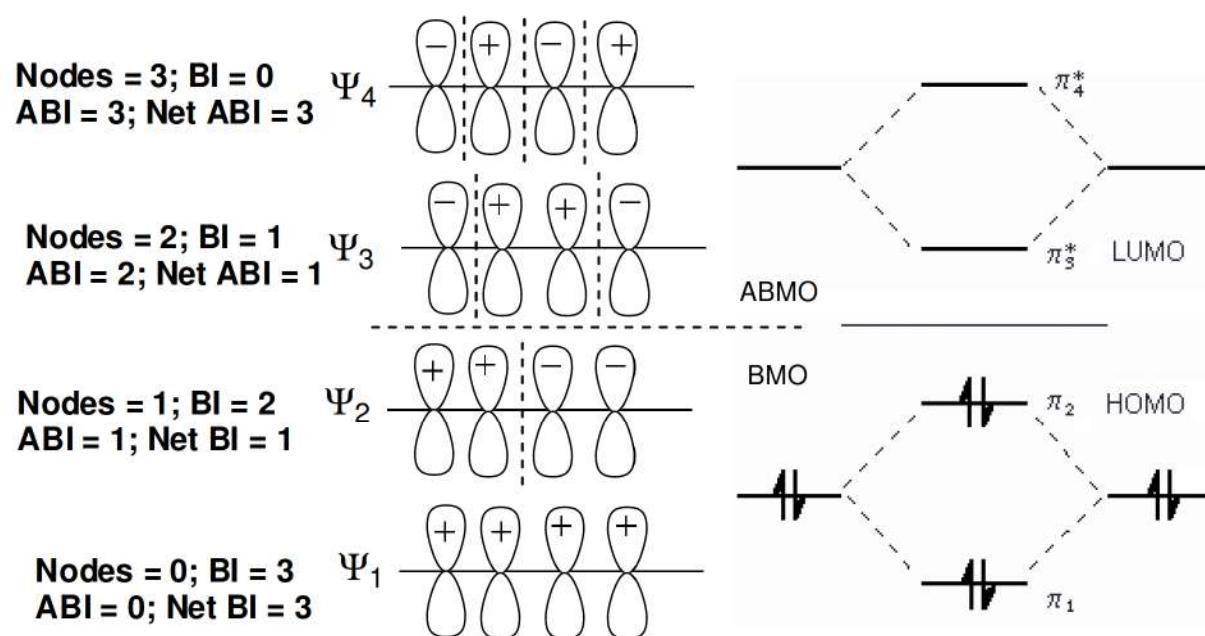
The number of molecular orbitals (n) for a π -system is equal to the number of contributing p orbitals.

π -molecular orbitals of butadiene:



The structure of 1,3-butadiene consists of two conjugated double bonds. The structure has four sp^2 hybridized carbon atoms. Each carbon atom contributes a 'p' atomic orbital which is not involved in hybridization consisting of one π electron, resulting in the arrangement of four π electrons from four p-orbitals which combine in four different ways and form four molecular orbitals designated by Ψ_1 , Ψ_2 , Ψ_3 , and Ψ_4 .

The bonding in π -molecular orbitals of butadiene is shown in the molecular orbital (MO) diagram.



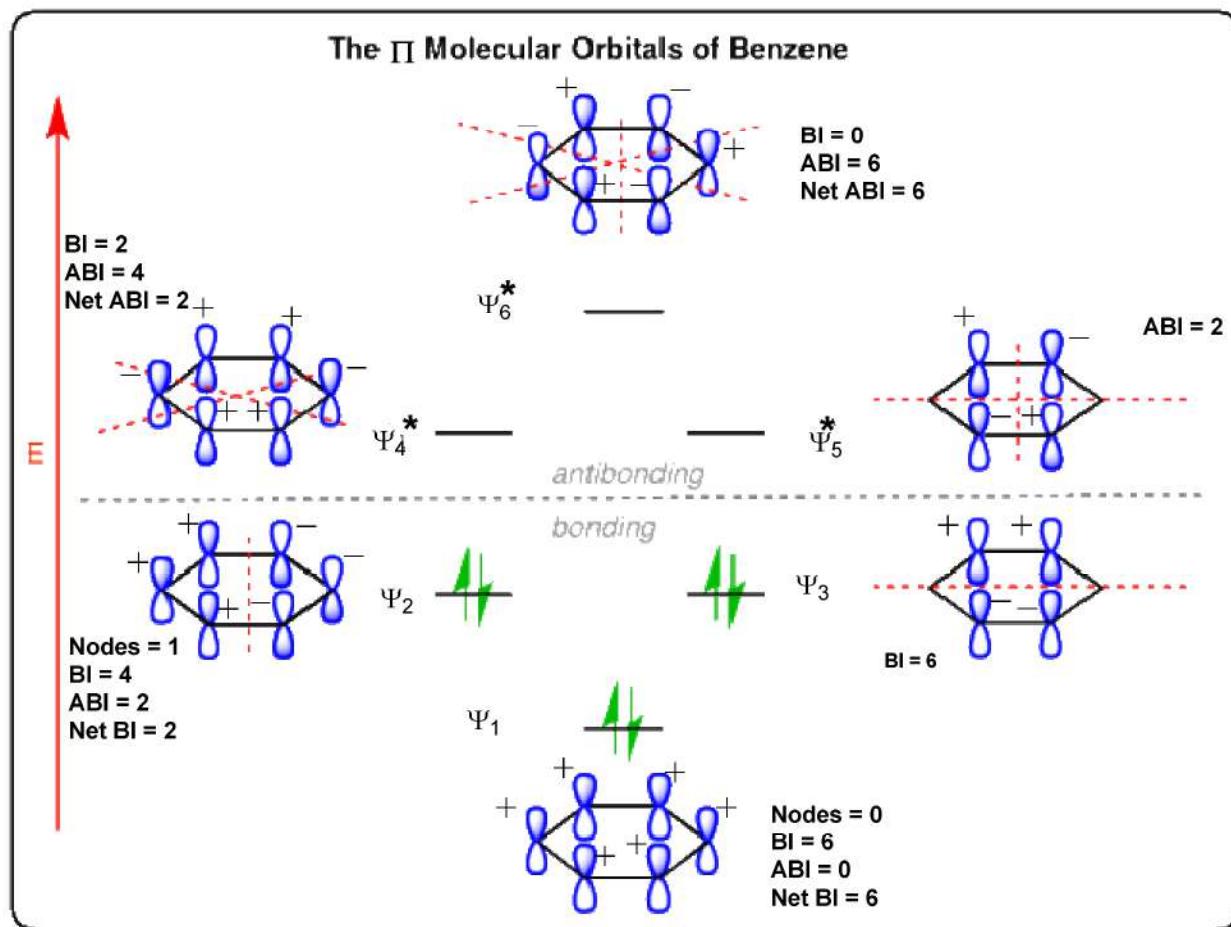
Molecular orbitals of 1,3-butadiene (Note: Ψ_n has $n-1$ nodes)

- Ψ_1 has bonding interactions in between C1-C2, C2-C3 and C3-C4. Therefore, there exists 3 bonding interactions (**BI**)
- Ψ_2 has bonding interactions between C1-C2 and C3-C4 and anti-bonding interactions (**ABI**) between C2-C3. Therefore, they have single anti-bonding interaction. It is the highest occupied molecular orbital (HOMO).
- Ψ_3 has bonding interactions between C2-C3 but anti-bonding interactions between C1-C2 and C3-C4. Therefore, they have single anti-bonding interaction. It is the lowest unoccupied molecular orbital (LUMO).
- Ψ_4 has anti-bonding interactions between C1-C2, C2-C3 and C3-C4. Therefore, they have 3 anti-bonding interactions.

With this information it is clear out of the four orbitals available, the molecular orbitals Ψ_1 and Ψ_2 are bonding molecular orbitals whereas the molecular orbitals Ψ_3 and Ψ_4 are anti-bonding molecular orbitals. The energy in molecular orbitals increases with the rise in the number of nodes.

π -molecular orbitals of Benzene

Each molecular orbital of benzene consist of a combination of the six p orbitals. Bonding interaction occurs when the orbitals to line up in a way that each lobe overlapping another p orbital has same signs.



Molecular orbitals of Benzene (Note: Ψ_n has $n-1$ nodes)

The order of energy levels: $\Psi_1 < \Psi_2 = \Psi_3 < \Psi_4 = \Psi_5 < \Psi_6$

The three π bonds of benzene are formed by the overlapping of six p orbitals on six adjacent carbon atoms. The six MOs are designated by Ψ_1 , Ψ_2 , Ψ_3 , Ψ_4 , Ψ_5 , Ψ_6 . Of these six MOs Ψ_1 , Ψ_2 , Ψ_3 are bonding molecular orbitals whereas Ψ_4 , Ψ_5 , Ψ_6 are antibonding orbitals. Each molecule orbital can accommodate two electrons having opposite spins. Therefore, addition of six electrons to the molecule orbitals beginning from the lowest energy molecule orbital results in the filling of all three bonding molecular orbital. The three higher energy antibonding orbitals

remain empty. Due to the presence of three filled bonding molecular orbitals in benzene, it possesses a closed bonding shell which makes Benzene stable.

VSEPR theory and molecular shapes:

Postulates of VSEPR Theory (Valence Shell Electron Pair Repulsion Theory)-

Sidgwick and Powell (1940) proposed VSEPR theory on the basis of repulsive interactions between valence electron pairs. Further this model was developed by Nyholm and Gillespie (1957).

- i) The geometry (shape) of a covalent molecule depends upon the number of valence shell electrons (bp and lp electrons) around the central atom.
- ii) The lps are localized on the central atom and bps are shared between two atoms. As a result, the lp electrons in molecule occupy more space as compared to bp electrons.
- iii) Electron pairs in valence shell tend to repel one another because their electron clouds are negatively charged. This repulsions brings deviations from original shapes and alterations in bond angles in the molecules.
- iv) The repulsive interaction between lone pair (lp) electrons and bonded pair (bp) electrons decreases as $lp - lp > lp - bp > bp - bp$
- v) The electron pairs orient themselves around the central atom in such a way that the repulsions between them are minimum. Therefore the molecule acquire low energy and maximum stability.
- vi) If all the hybrid orbitals of central atom contain only bond pair of electrons then the molecules will have regular geometry.
- vii) If hybrid orbitals of central atom contain lone pair and bond pair of electrons then the molecules will have irregular geometry. lp is also called as non-bonded electron pair.
 - a) The number of bps present on the central atom in a molecule = the number of bonded atoms attached to the central atom in a molecule.
 - b) The number of lps present on the central atom in a molecule =
$$\frac{\text{no. of valence electrons on the central atom} - \text{the no. of bonded atoms}}{2}$$

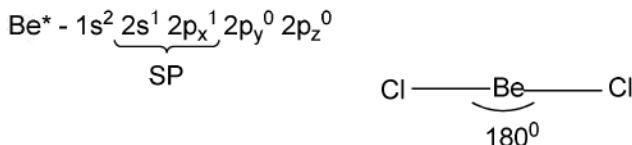
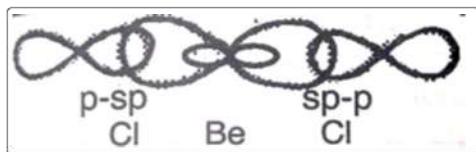
Based on these postulates, the following generalizations can be made, regarding the shapes of some simple molecules.

❖ Central atom surrounded by two valence-shell electron pairs:

Such a molecule always has linear arrangement of atoms with bond angle 180° , because such an arrangement keeps the two bp pairs of valence shell electrons as far apart as possible.

Ex: BeF_2 , BeCl_2

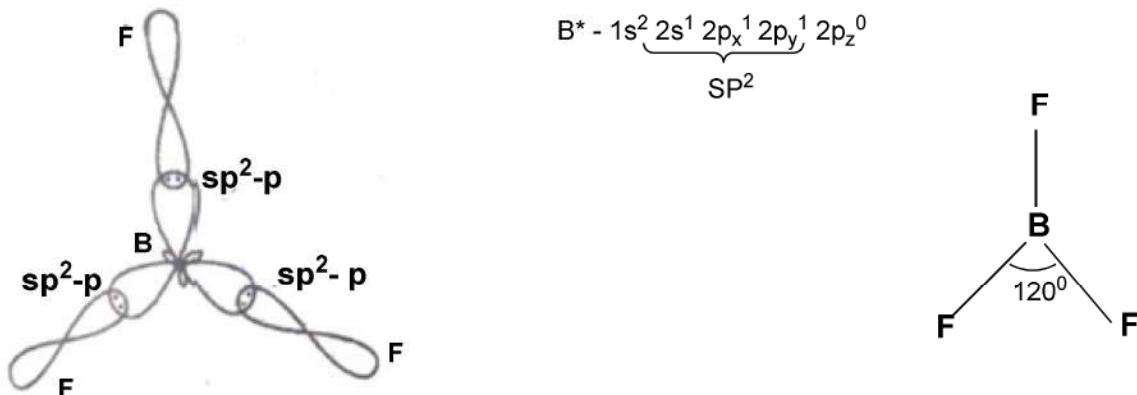
In BeCl_2 , the central atom is Be and its sp hybridized orbitals overlap with p_x orbitals of two chlorine atom to form two Be-Cl bonds (two σ sp-p bonds, linear shape, bond angle is 180°).



❖ Central atom surrounded by three valence-shell electron pairs:

Such a molecule always has triangular shape with a bond angle 120°. Ex: BF_3

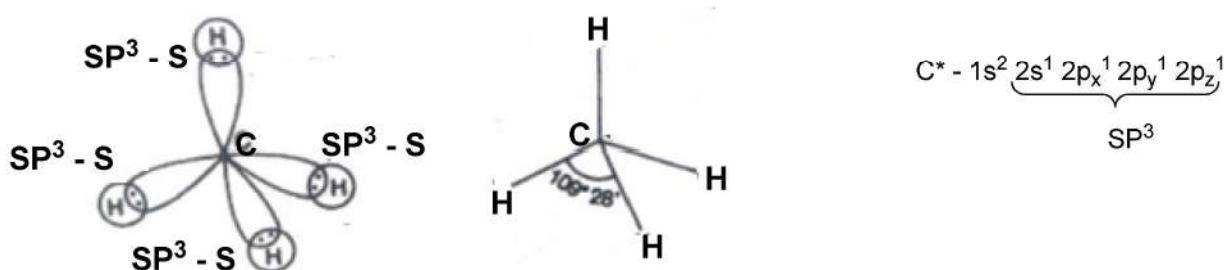
The central atom is B and its sp^2 hybridized orbitals overlap with p_x orbitals of three fluorine atom to form three B-F bonds (three σ sp^2 -p bonds, triangular shape, bond angle is 120°).



❖ Central atom surrounded by four valence-shell electron pairs:

Such a molecule always has tetrahedral shape with a bond angle 109°28'. This type of molecules may fall into three categories.

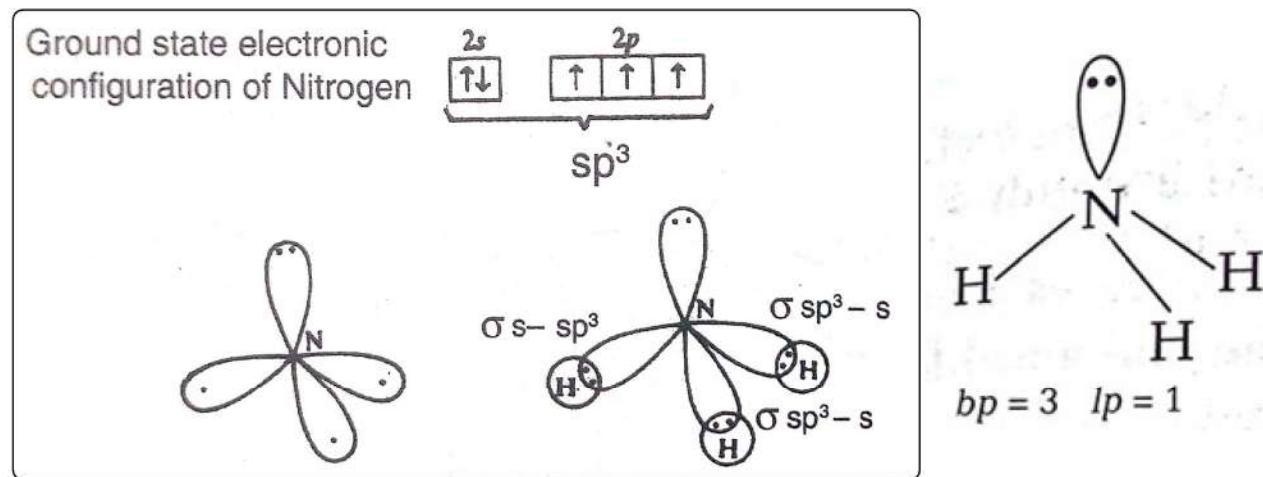
- i) Four bond pairs. Ex. CH_4
 - ii) Three bond pairs and one lone pairs. Ex. NH_3
 - iii) Two bond pairs and two lone pairs. Ex. H_2O
- i) Structure of methane (CH_4): In CH_4 the central atom is carbon. Each sp^3 hybrid orbital of carbon overlaps with s orbital of hydrogen to form 4 σ sp^3 – s bonds. (tetrahedral shape with a bond angle 109°28'). All the four electron pairs surrounding the central atom are bond pairs. i.e no lone pairs



Structure of ammonia (NH_3)

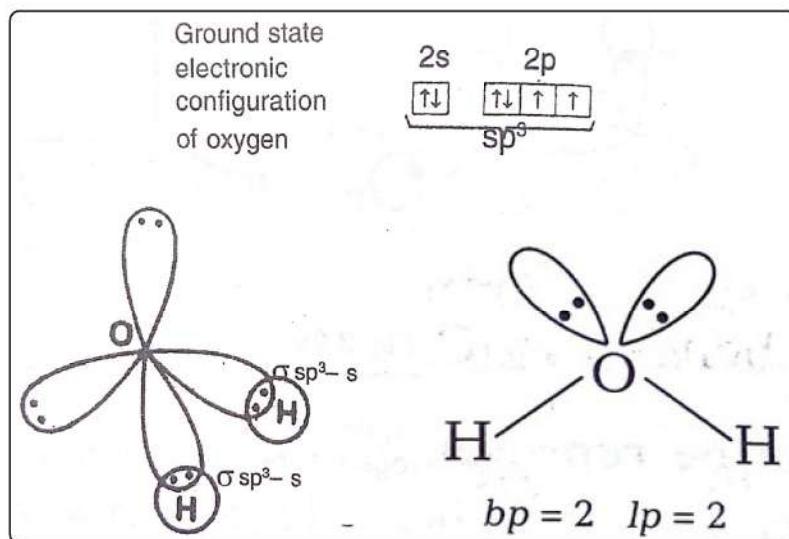
In NH_3 molecule the central atom is nitrogen. It has four electron pairs in its valence shell. Among these three are bond pairs and one is lone pair. Hence according to VSEPR theory to

minimise the repulsions between these 3-bps and 1-lp the structure of ammonia molecule changes from tetrahedral shape to pyramidal shape and the bond angle is 107° .

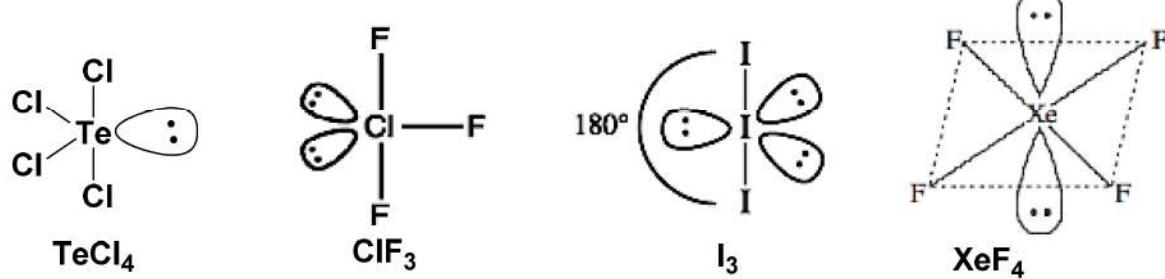


Structure of water (H_2O)

In H_2O molecule the central atom is oxygen. It has four electron pairs in its valence shell. Among these two are bond pairs and remaining two are lone pair. Hence according to VSEPR theory to minimise the repulsions between these 2-bps and 2-lps the structure of water molecule changes from tetrahedral shape to angular shape and the bond angle is $104^\circ 30'$.



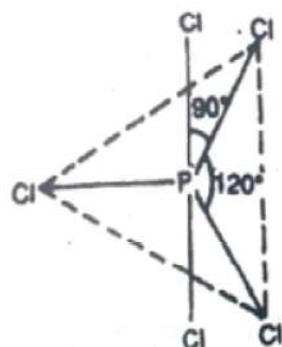
Shapes of few other molecules:



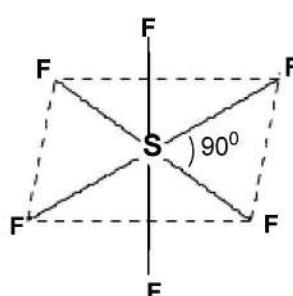
Shapes of some simple molecules in which the central atom has zero or more lone pairs of electrons:

Total number of electron pairs	Banded e ⁻ Pairs	Lone e ⁻ pairs	Shape	Example
2	2	0	Linear	BeCl ₂
3	3	0	Planar Triangular	BF ₃
	2	1	V-shaped	SnCl ₂
4	4	0	Tetrahedral	CH ₄
	3	1	Pyramid	NH ₃
	2	2	Angular	H ₂ O
5	5	0	Triangular bipyramidal	PCl ₅
	4	1	Irregular tetrahedral	TeCl ₄
	3	2	T-Shape	ClF ₃
	2	3	Linear	I ₃
6	6	0	Octahedral	SF ₆
	4	2	Square planar	XeF ₄
7	7	0	Pentagonal bipyramidal	IF ₇
	6	1	Distorted Octahedral	XeF ₆

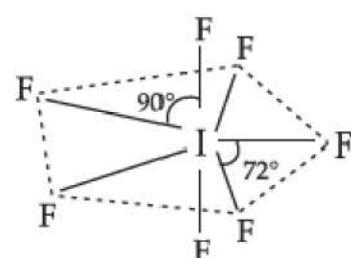
PCl₅



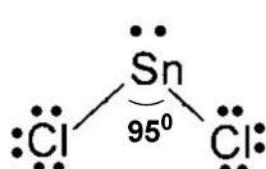
SF₆



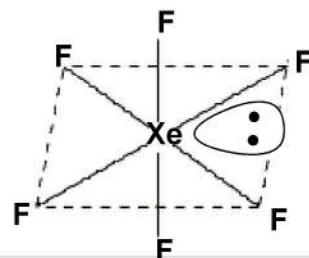
IF₇



SnCl₂



XeF₆



Solutions of the Schrödinger Wave Equation for a One-Electron Atom

n	ℓ	m_ℓ	Orbital	Solution
1	0	0	1s	$\psi_{1s} = \frac{1}{\sqrt{\pi}} \left(\frac{Z}{a_0}\right)^{3/2} e^{-\sigma}$
2	0	0	2s	$\psi_{2s} = \frac{1}{4\sqrt{2\pi}} \left(\frac{Z}{a_0}\right)^{3/2} (2 - \sigma) e^{-\sigma/2}$
2	1	0	2p _z	$\psi_{2p_z} = \frac{1}{4\sqrt{2\pi}} \left(\frac{Z}{a_0}\right)^{3/2} \sigma e^{-\sigma/2} \cos \theta$
2	1	± 1	2p _x	$\psi_{2p_x} = \frac{1}{4\sqrt{2\pi}} \left(\frac{Z}{a_0}\right)^{3/2} \sigma e^{-\sigma/2} \sin \theta \cos \phi$
			2p _y	$\psi_{2p_y} = \frac{1}{4\sqrt{2\pi}} \left(\frac{Z}{a_0}\right)^{3/2} \sigma e^{-\sigma/2} \sin \theta \sin \phi$
3	0	0	3s	$\psi_{3s} = \frac{1}{81\sqrt{3\pi}} \left(\frac{Z}{a_0}\right)^{3/2} (27 - 18\sigma + 2\sigma^2) e^{-\sigma/3}$
3	1	0	3p _z	$\psi_{3p_z} = \frac{\sqrt{2}}{81\sqrt{\pi}} \left(\frac{Z}{a_0}\right)^{3/2} (6\sigma - \sigma^2) e^{-\sigma/3} \cos \theta$
3	1	± 1	3p _x	$\psi_{3p_x} = \frac{\sqrt{2}}{81\sqrt{\pi}} \left(\frac{Z}{a_0}\right)^{3/2} (6\sigma - \sigma^2) e^{-\sigma/3} \sin \theta \cos \phi$
			3p _y	$\psi_{3p_y} = \frac{\sqrt{2}}{81\sqrt{\pi}} \left(\frac{Z}{a_0}\right)^{3/2} (6\sigma - \sigma^2) e^{-\sigma/3} \sin \theta \sin \phi$
3	2	0	3d _{z²}	$\psi_{3d_z^2} = \frac{1}{81\sqrt{6\pi}} \left(\frac{Z}{a_0}\right)^{3/2} \sigma^2 e^{-\sigma/3} (3 \cos^2 \theta - 1)$
3	2	± 1	3d _{xx}	$\psi_{3d_{xx}} = \frac{\sqrt{2}}{81\sqrt{\pi}} \left(\frac{Z}{a_0}\right)^{3/2} \sigma^2 e^{-\sigma/3} \sin \theta \cos \theta \cos \phi$
			3d _{yz}	$\psi_{3d_{yz}} = \frac{\sqrt{2}}{81\sqrt{\pi}} \left(\frac{Z}{a_0}\right)^{3/2} \sigma^2 e^{-\sigma/3} \sin \theta \cos \theta \sin \phi$
3	2	± 2	3d _{xy}	$\psi_{3d_{xy}} = \frac{1}{81\sqrt{2\pi}} \left(\frac{Z}{a_0}\right)^{3/2} \sigma^2 e^{-\sigma/3} \sin^2 \theta \sin 2\phi$
			3d _{x²-y²}	$\psi_{3d_{x^2-y^2}} = \frac{1}{81\sqrt{2\pi}} \left(\frac{Z}{a_0}\right)^{3/2} \sigma^2 e^{-\sigma/3} \sin^2 \theta \cos 2\phi$

Note: $\sigma = Zr/a_0$, where $Z = 1$ for hydrogen; $a_0 = \epsilon_0 b^2 / \pi m e^2 = 5.29 \times 10^{-11}$ m.

1 Mark Questions

1. Give the basic difference between AOs and MOs
The electrons in an atomic orbital is influenced by one nucleus and in molecular orbitals two or more nuclei depends on the number of atoms contained in a molecule.
2. Oxygen molecule is a paramagnetic –Justify
3. What is bond order? Mention its importance in molecular orbital theory
4. Why does He_2^+ exist while He_2 does not?
5. The bond order in O_2 is two while in N_2 it is three.
6. What are bonding and anti-bonding molecular orbitals?
7. Arrange the order of repulsions between bp and lp

Short and Long answer Questions

1. Draw the shapes of the two molecular orbitals derived from linear combination of atomic s-orbitals
2. What is LCAO approach? Explain
3. Elaborate the formation of σ and π molecular orbitals
4. Explain anti-bonding molecular orbitals has higher energy than bonding ones
5. Construct molecular energy level diagram for N_2 , NO molecules
6. Explain the paramagnetism in oxygen by molecular orbital theory. Sketch in energy diagram.
7. Discuss molecular orbital theory
8. Write the Schrödinger wave equation in Cartesian coordination and explain terms
9. What is Schrödinger wave equation? Explain the significance of ψ and ψ^2
10. Derive the Schrödinger wave equation for the wave mechanical model of an atom.
11. Derive Schrödinger wave equation particle in one dimension box.
12. Apply the Schrödinger wave equation to the electron present in a hydrogen
13. Derive the equation for Eigen energies and Eigen function of a particle
14. Mention the main postulates of VSEPR Theory. How this theory explain the shapes of the molecules?
15. Summarize your understanding of π -molecular orbitals of butadiene and benzene.

- ☞ This material consists of basic information
- ☞ Refer text book for more details

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