Spherical polar coordinates

Δ OPA

$\cos\theta = \dfrac{OA}{OP}$

$OA = z$

$OB = x$

$OC = y$

$\Rightarrow \cos\theta = \dfrac{z}{r}$

$\Rightarrow \boxed{z = r\cos\theta}$

ΔOPg

$\sin\theta = \dfrac{OB}{OP} \Rightarrow OB = (OP)\sin\theta = r\sin\theta$

$\cos\phi = \dfrac{OB}{Og} \Rightarrow OB = (Og)\cos\phi \Rightarrow \boxed{x = (r\sin\theta)\cos\phi}$

$\sin\phi = \dfrac{Bg}{Og} \Rightarrow Bg = (Og)\sin\phi = r\sin\theta\sin\phi$

$\boxed{y = Bg = OC = r\sin\theta\sin\phi}$

$$\boxed{\begin{array}{l} x = r\sin\theta\cos\phi \\ y = r\sin\theta\sin\phi \\ z = r\cos\theta \end{array}}$$

The spherical symmetry of an atom, the wave functions are satisfactorily expressed in terms of spherical polar co-ordinates system with nucleus at the origin, changing from the cartesian co-ordinates to polar co-ordinates, the schrodinger wave equation assumes the following form from standard schrodinger equation

$$\dfrac{d^2\psi}{dx^2} + \dfrac{d^2\psi}{dy^2} + \dfrac{d^2\psi}{dz^2} + \dfrac{8\pi^2 m}{h^2}(E-V)\psi = 0$$

$$\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial\psi}{\partial r}\right) + \frac{1}{r^2\sin^2\theta}\frac{\partial^2\psi}{\partial\varphi^2} + \frac{1}{r^2\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial\psi}{\partial\theta}\right)$$
$$+ 8\pi^2\mu(E-V) = 0$$

μ = reduced mass.

Where r, θ, φ are the polar co-ordinates of the electron with respect to the nucleus (N) as origin (fig. ① & ②)
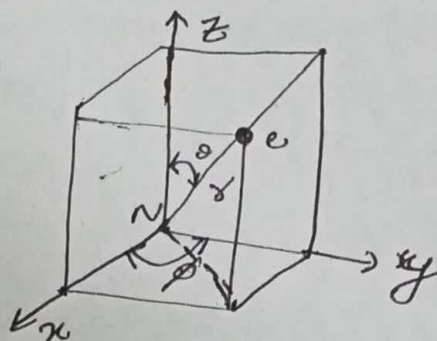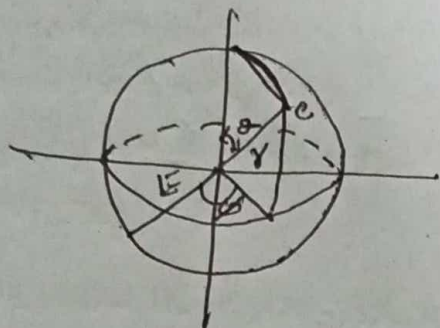
Mathematically, wavefunction $\psi(r,\theta,\varphi)$ can be expressed as

$$\psi(r,\theta,\varphi) = R_{(r)} \cdot \Theta_{(\theta)} \cdot \phi_{(\varphi)}$$

where $R_{(r)}$ is a function that depends on the distance from nucleus

* depends on the quantum numbers n, l (principal and azimuthal quantum numbers, respectively).

⊖ $\Theta_{(\theta)}$ = function of θ depends on l & m_l (magnetic quantum number)

$\phi_{(\varphi)}$ = function of ϕ depends on m_l.

* The total wave function $\psi(r,\theta,\varphi)$ gives the total probability of finding an electron is called atomic orbital.

* The wavefunction $\psi(r,\theta,\varphi)$ = product of two function

(i) radial & (ii) angular wave function.

probability distribution & shapes of orbitals

s-orbital An s-electron has no preferred direction in space; there is equal chance of finding it in any direction around the nucleus. Graphically shown below fig
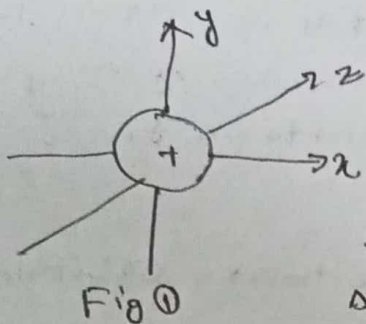
In this diagram, the nucleus of the atom is at the origin and the surface of the sphere represents the probability of finding the s-electron which is therefore same in all directions.

Fig ①

P-orbital

A P-level has an accomodation for six electrons distributed over three p-orbitals, to each value of the principal quantum number (n).

★ These three orbitals are at right angles to each other & the three angular probability distributions are dumbbells shaped along the three coordinate and are named as p_x, p_y, p_z orbitals. The different shapes are shown in Fig. ②


P_x P_y P_z
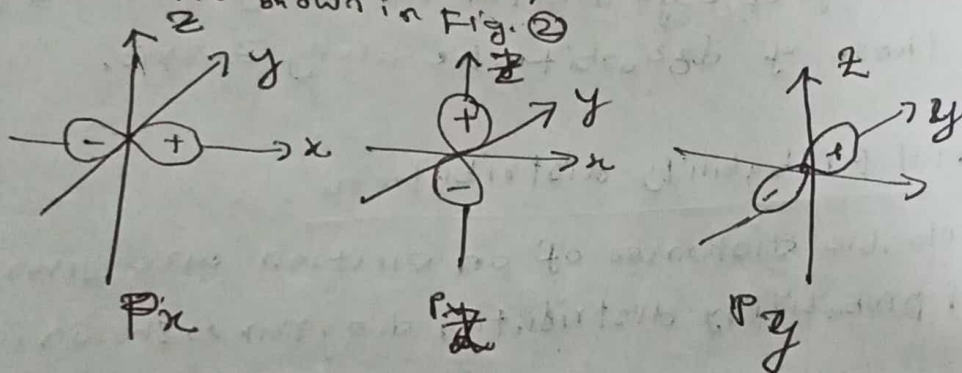
★ P_x orbital = the electron will be found in the direction of x-axis.

P_y orbital = the electron will be found in the direction of y-axis.

P_z orbital = the electron will be found in the direction of z-axis.

d-orbital

The angular probability distribution of five d-orbitals can accomodate ten electron. These five orbitals are d_{xy}, d_{yz}, d_{zx}, $d_{x^2-y^2}$, d_{z^2}. The shapes are shown in Fig ③

d_{xy} d_{xz} d_{yz} $d_{x^2-y^2}$

d_{z^2}
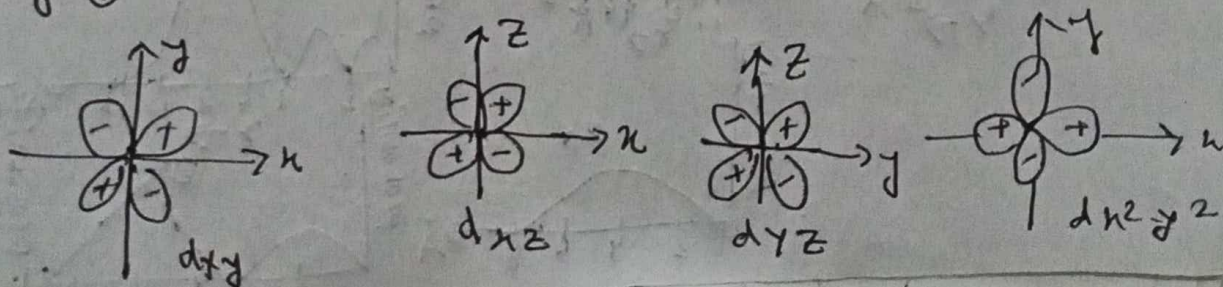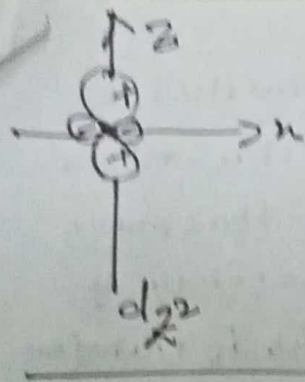
* All the d-orbitals are equivalent in energy in the absence of magnetic field and are said to be five fold degenerate.

* The sets of the three orbitals namely d_{xy}, d_{yz}, d_{zx} have their lobes lying symmetrically in between the co-ordinated axes indicated by the subscripts to d, e.g the lobes of d_{xy} orbital are pointing or lying in between the x & y axes. This set is referred to as t_{2g} set.

* The set of two orbitals i.e, $d_{x^2-y^2}$ & d_{z^2} orbitals form e_g set having their lobes along the axes.
The lobes of $d_{x^2-y^2}$ orbital lie along the x & y axes while those of d_{z^2} orbital lie along z-axis.

Radial probability distribution

* The probable distances of an electron are given by radial probability distribution diagram as shown in Fig. ⊕

* In these diagrams, the probability of finding an electron at a distance 'r' from the nucleus is plotted against 'r' (distance from the nucleus) to get 1s, 2s, 2p, 3s, 3p & 3d orbitals.

* The probability of finding an electron at nucleus is zero.

* The distributions vary according to the principal quantum number (n). The larger the value of the principal quantum number the farther is the electron from the nucleus.
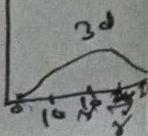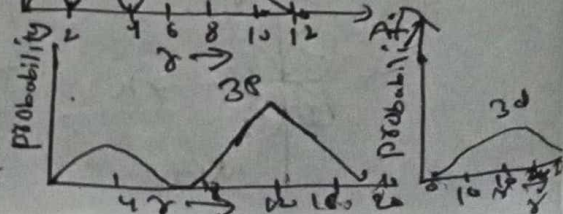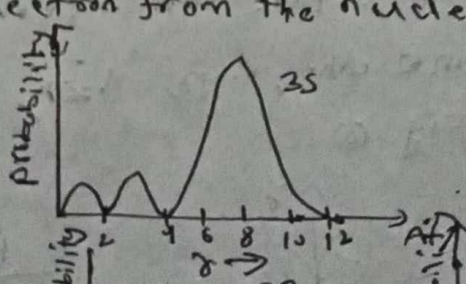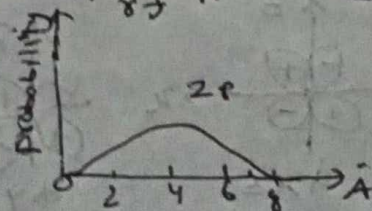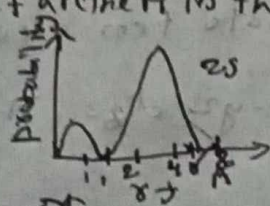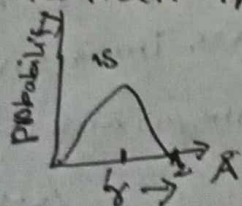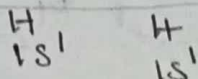
Molecular orbital theory

Linear combination of atomic orbitals, LCAO

Homonuclear diatomic molecule

H_2 molecule   H   H $1s^1$ $1s^1$

Let, two H-atoms designated by H_A and H_B containing two 1s-atomic orbitals (A.O) overlap to form molecular orbitals. The expression for Molecular orbital (MO) will be one bonding (ϕ_B) and the other antibonding (ϕ_A).

$$\left. \begin{array}{l} \phi_B = \psi_A(1s) + \psi_B(1s) \\ \phi_A = \psi_A(1s) - \psi_B(1s) \end{array} \right\} \quad\quad (1)$$

The two conditions can be represented pictorially as shown below
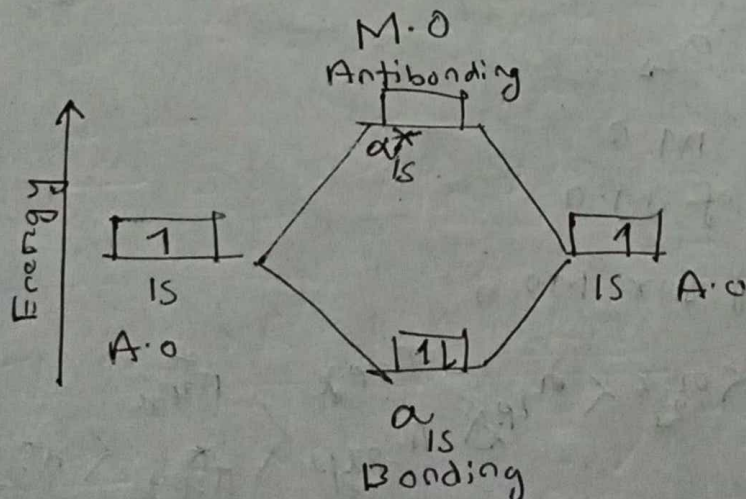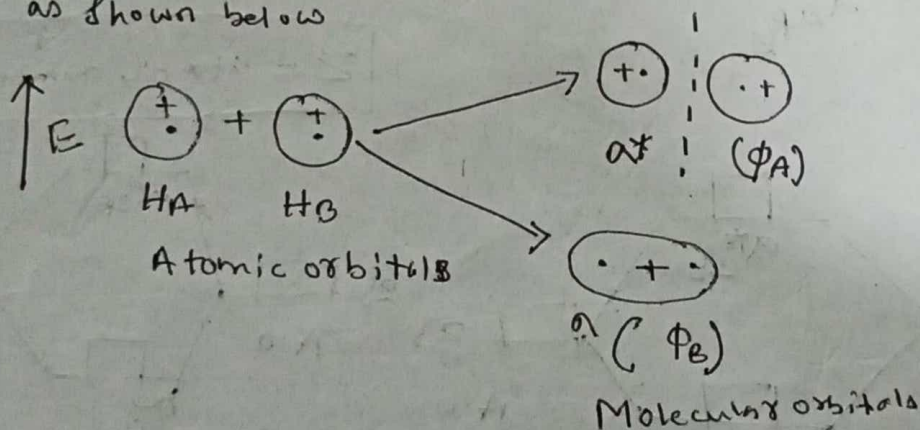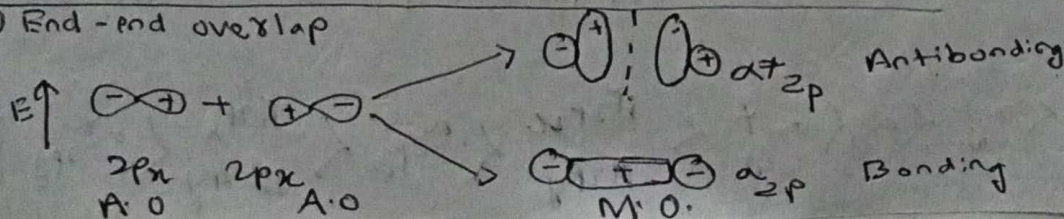

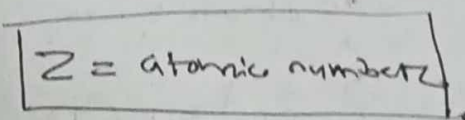Atomic orbitals → Molecular orbitals

Fig :- Molecular orbital diagram of H_2
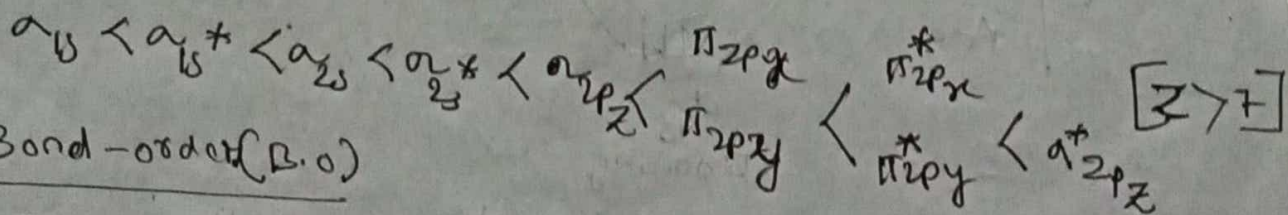
Molecular orbitals from p-atomic orbitals.

① End-end overlap

⑥ side-by-side overlap

$2P_z$ $2P_z$
A.O A.O

$\pi^* 2P_z$

M.O

Energy ↑

$\sigma^* 2P_z$

$\pi^* 2P_x$ $\pi^* 2P_y$

2p [x y z]   2p [x y z]
A.O   A.O

$\pi 2P_x$ $\pi 2P_y$

$\sigma 2P_z$

σ^*_{2s}

2s [ ]   2s [ ]
A.O   A.O

σ_{2s}

M.O

σ^*_{2p} Z<7

$\pi^* 2P_x$ $\pi^* 2P_y$

2p [n y z] $\sigma 2p_z$ 2p [n y z p]
A.O   A.O

$\pi 2P_x$ $\pi 2P_y$

Z>7

Z = atomic number

σ^*_{2s}

2s [ ]   2s [ ]
A.O   A.O

σ_{2s}

Fig: Order of energy of M.O.

The order of energy for MO is

$\sigma_{1s} < \sigma_{1s}^* < \sigma_{2s} < \sigma_{2s}^* < \sigma 2p_z < \dfrac{\pi 2p_x}{\pi 2p_y} < \dfrac{\pi^* 2p_x}{\pi^* 2p_y} < \sigma^* 2p_z$ [Z>7]

Bond - order (B.O)

$B.O = \dfrac{N.B. - N.A.}{2}$

N.B. = no. of electrons in bonding M.O
N.A. = no. of electrons in antibonding M.O

$\sigma_{1s} < \sigma_{1s}^* < \sigma_{2s} < \sigma_{2s}^* < \dfrac{\pi 2p_x}{\pi 2p_y} < \sigma 2p_z < \dfrac{\pi^* 2p_x}{\pi^* 2p_y} < \sigma^* 2p_z$ [Z<7]

· $\underline{Be_2 \text{ molecule}}$ $Be_4 = 1s^2 2s^2$

$Be_4 = 1s^2 2s^2$
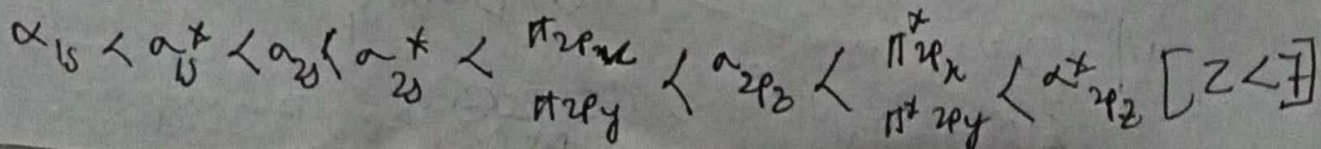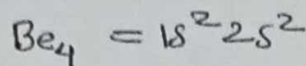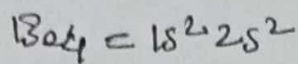
Electronic configuration of Be_2 molecule
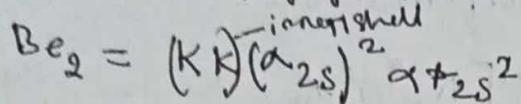
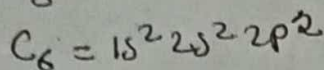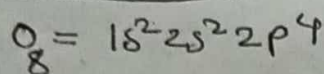$$Be_2 = (KK)\overbrace{(\sigma_{2s})^2}^{\text{inner shell}} \sigma^*_{2s}{}^2 \qquad B.o = \frac{2-2}{2} = \frac{0}{2} = 0/\!/.$$
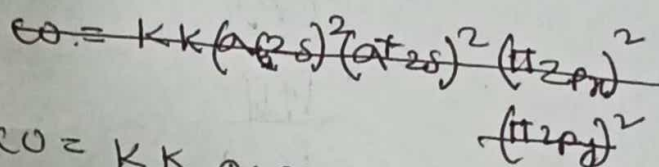
∴ Be_2 molecule is not stable to form.

Molecular orbital energy level diagram of heteronuclear diatomic molecules.

① $\underline{Co \text{ molecule}}$

$O_8 = 1s^2 2s^2 2p^4$ The electronic configuration

$C_6 = 1s^2 2s^2 2p^2$

$CO = KK (\sigma_{2s})^2 (\sigma^*_{2s})^2 (\pi_{2p\pi})^2$
$(\pi_{2p\gamma})^2$

$CO = KK\ \sigma_{2s}{}^2\ \sigma^*_{2s}{}^2\ \pi_{2p\pi}{}^2$
$\pi_{2p\gamma}{}^2\ \sigma_{2p_z}{}^2$

$B.o = \frac{8-2}{2} = 3.$
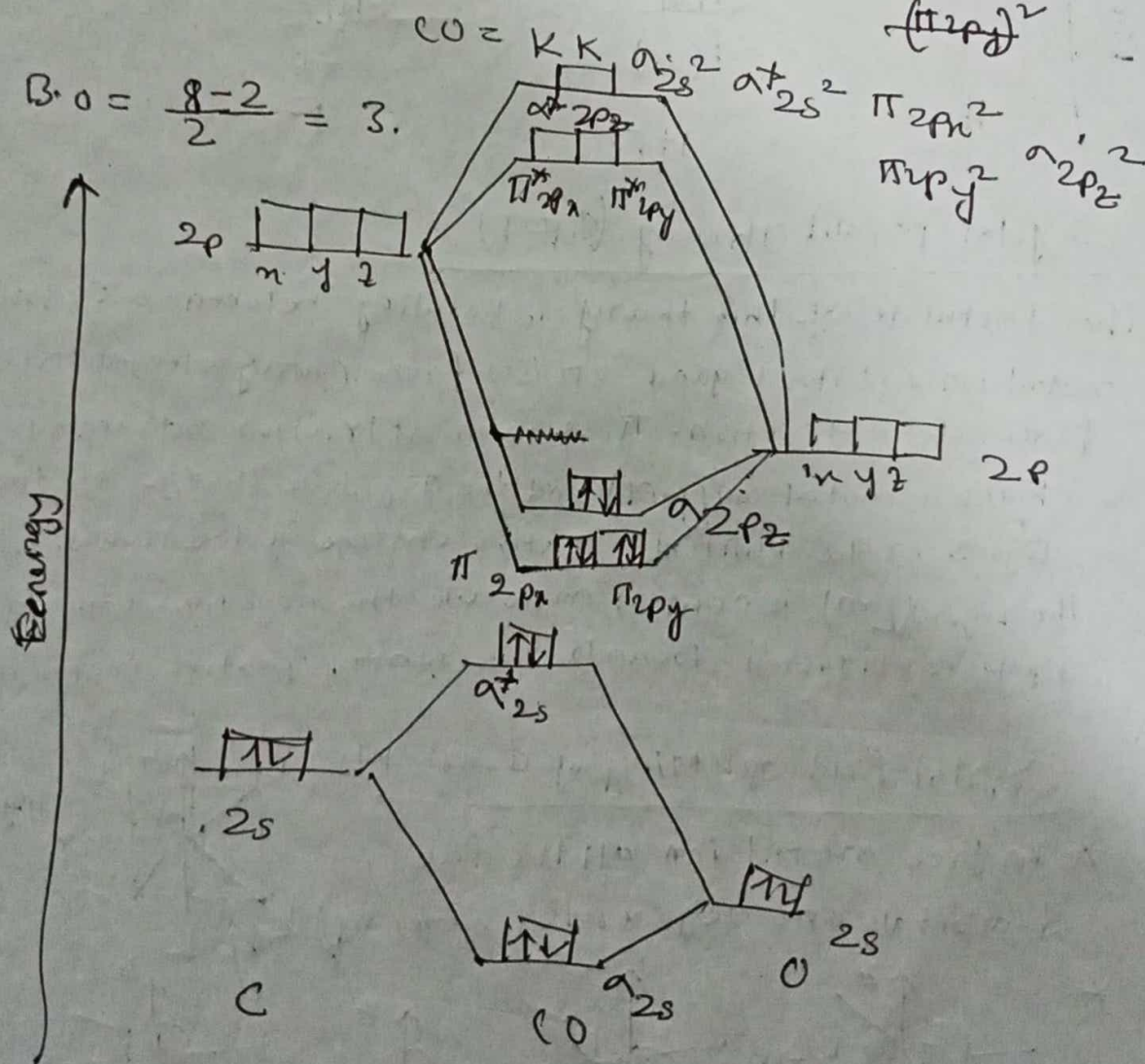
MO energy level diagram for CO.

HF molecule

$H_1 = 1s^1$, $F_9 = 1s^2 2s^2 2p^5$
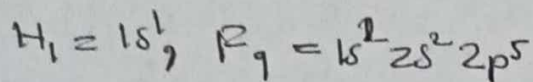
Electronic configuration of HF molecule is

$H(1s^1) + F(1s^2 2s^2 2p^5) \rightarrow HF\left[K\,(2s)^2\,\sigma 2p_z^2\,2p_x^2\,2p_y^2\right]$
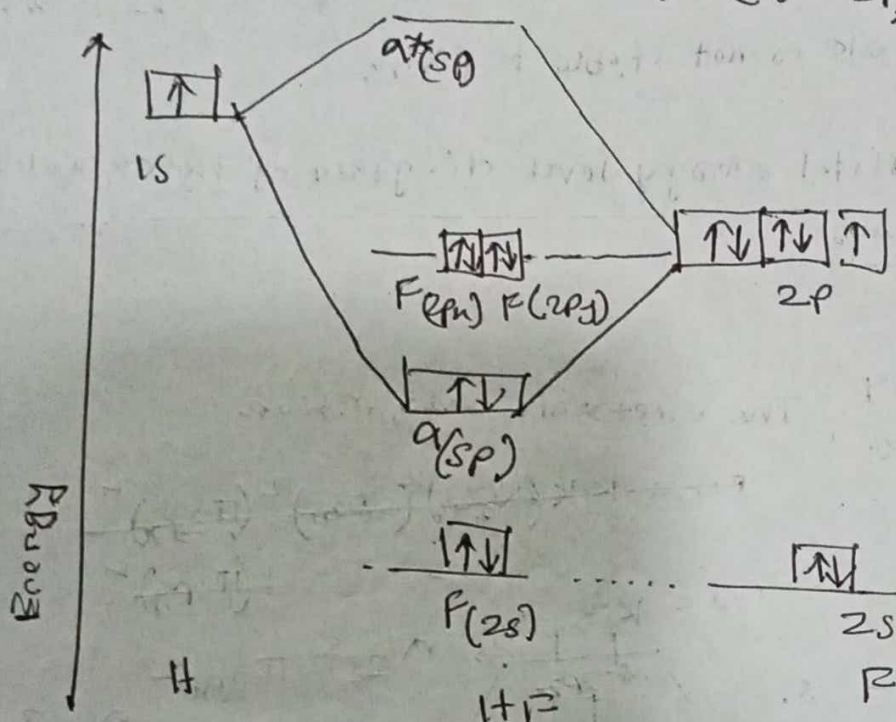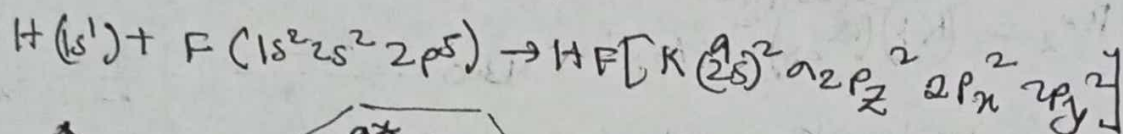
Crystal Field theory (CFT)

The postulate of this theory is: bonding between a central metal ion and its ligand arises from purely electrostatic force of attraction. That is an attraction between a positively charged metal ion (M^{n+}) and the negative charge o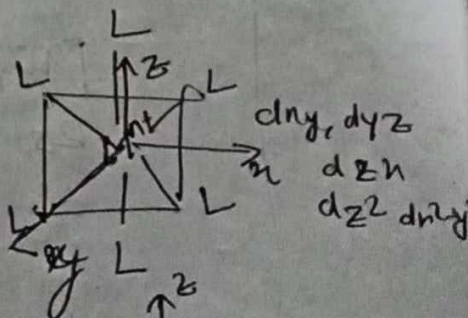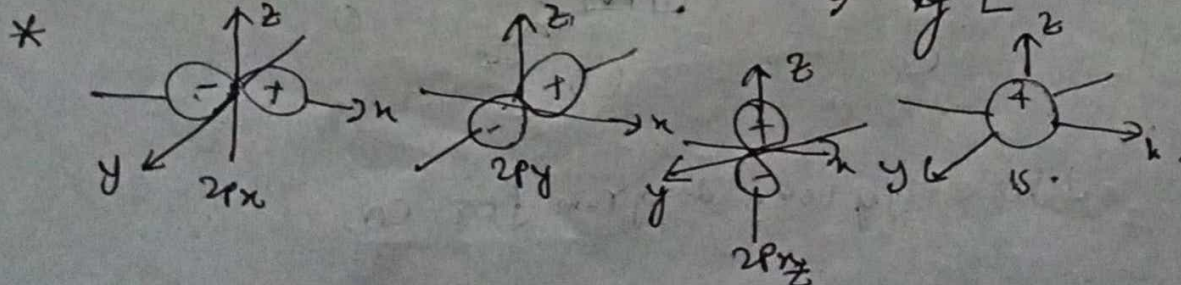f the ligand or the partial negative charge of the ligand. If the ligand (L^{-n}) is neutral molecule the negative end of the dipole is attracted towards the central positive metal ion.

Crystal field splitting of d-orbitals

* In free metal ion all the five d-orbitals are degenerate (same energy)

d_{xy}, d_{yz}
d_{zx}
$d_{z^2}, d_{x^2-y^2}$

3 dxy $3 d_{xz}$ $3 d_{yz}$ $3 d_{x^2-y^2}$

$3 d_{z^2}$: Boundary surface for the angular part of the wave function for $2s$, $2p$ & $3d$ orbitals.
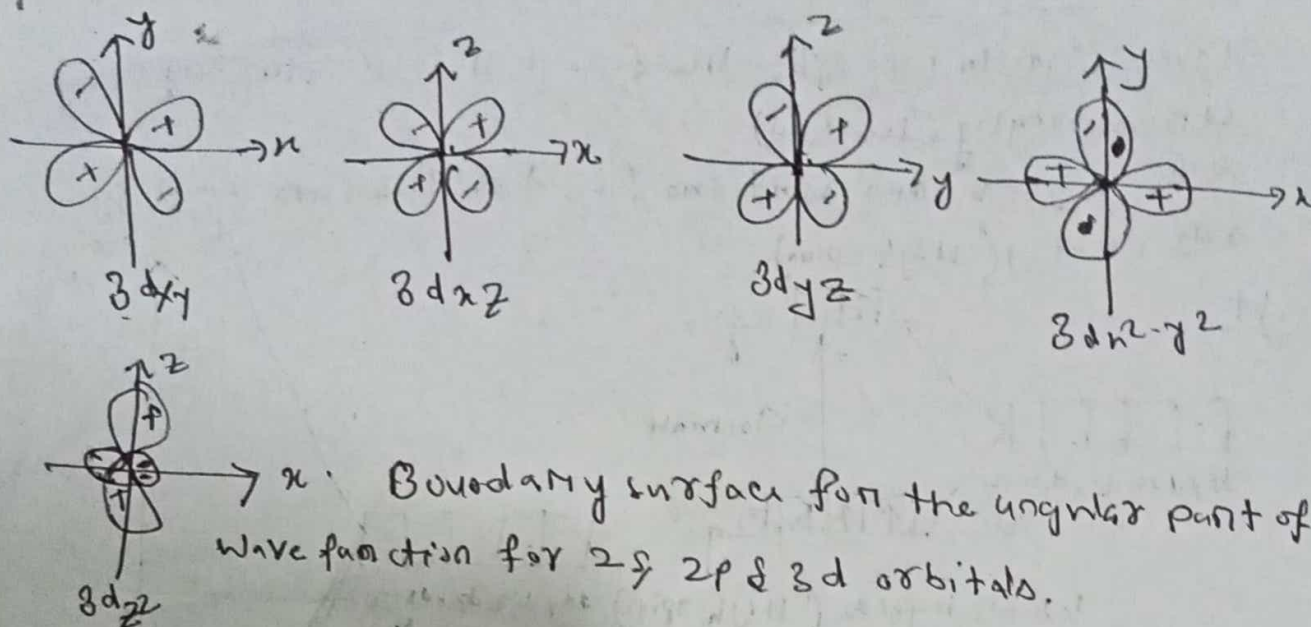
* When the six ligands approach the central metal atom along the
* axes they exert an electrostatic force of repulsion on the
d orbital electrons of the outermost shell i.e, the d electrons
are repelled by lone pair of electrons of the ligands. This
repulsion force raises the degenerate d orbitals of the metal
to a higher energy state. Since the lobes of d_{z^2} & $d_{x^2-y^2}$
orbitals (eg) sets of orbitals fall directly at the path of
of the approaching ligands, the electrons in these orbitals
experience a greater force of repulsion exerted by the
electrons of the ligands than that by the electrons of the
d_{xy}, d_{yz} & d_{zx} orbital (t_{2g}) set of orbitals which are directed
in space along x, y & z axes. Hence, eg have higher energy than
t_{2g}. The separation of five d-orbitals in the t_{2g} & eg sets
of different states is known as crystal field splitting.
* The energy difference between eg & t_{2g} sets of orbitals
is denoted by Δ_o or $10 D_q$ ($O = $ octahedral) $\Delta_o = $ crystal
field stabilisation energy (CFSE).

$$CFSE = [0.6 \times (eg) - 0.4 \times (t_{2g})] \Delta_o$$

d_{xy} d_{yz} d_{zx} $d_{x^2-y^2}$ d_{z^2}

d_{z^2} $d_{x^2-y^2}$ eg
$+0.6\Delta$
$-0.4\Delta_o$
Δ_o or $10 D_q$
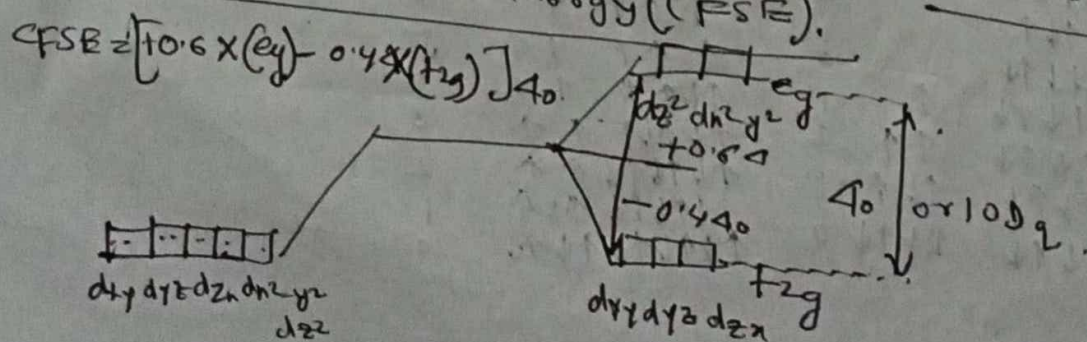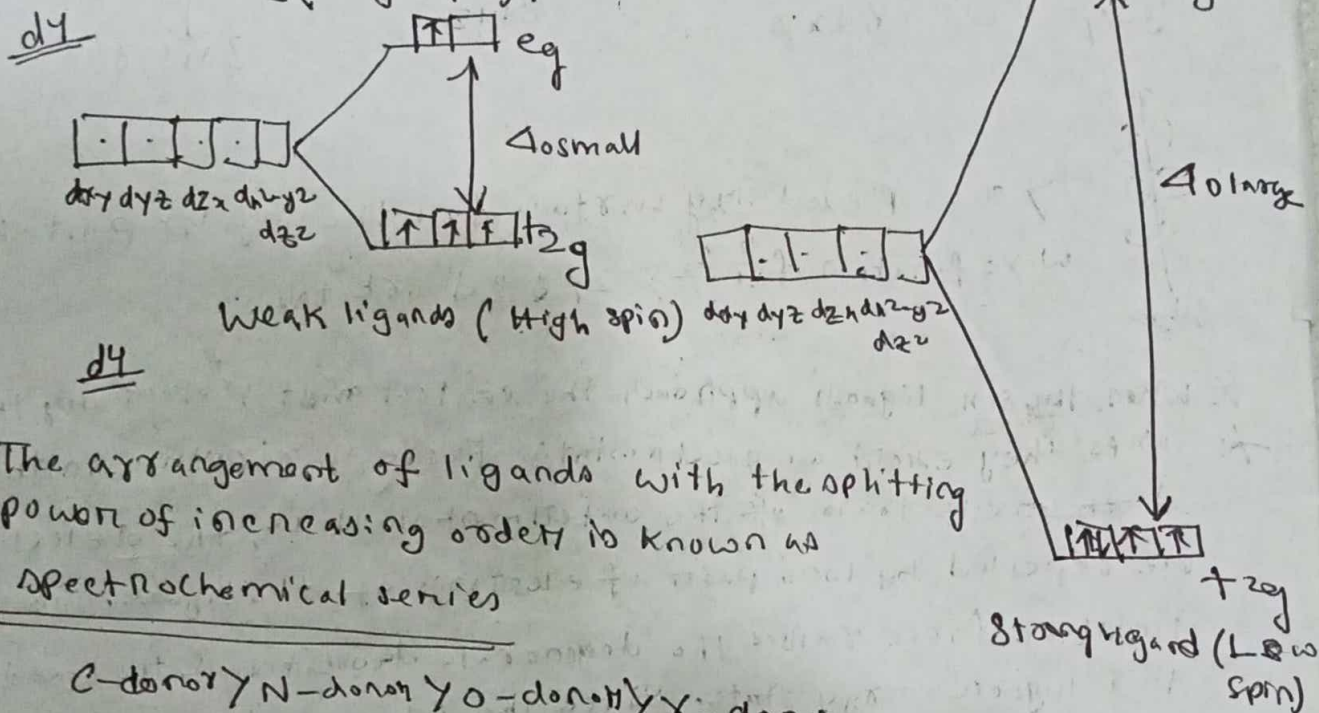d_{xy} d_{yz} d_{zx} t_{2g}

Fig:- crystal field splitting in an octahedral complex

Strong & weak Ligands

Strong ligands can split the five d-orbitals into t_{2g} & e_g sets strongly (low spin)

Weak ligands can split the five d-orbitals into t_{2g} & e_g sets weakly (High spin).

d4

Weak ligands (High spin)

Strong ligand (Low spin)

* The arrangement of ligands with the splitting power of increasing order is known as

Spectrochemical series

C-donor > N-donor > O-donor > X-donor

C-donor = CN^-, N-donor = NO_2^-, NH_3, O-donor = H_2O, OH^-

X-donor = $F^- > Cl^- > Br^- > I^-$

CFT & Magnetic properties of the complex

The magnetic moment μ is related to the unpaired electrons by the relation

$$\mu = \sqrt{n(n+2)} . B\mu \qquad n = no. \ of \ unpaired \ electron$$

	Strong Ligands		n	Weak ligands		n
	t_{2g}	e_g		t_{2g}	e_g	
d^1	↑		1	↑		1
d^2	↑ ↑		2	↑ ↑		2
d^3	↑ ↑ ↑		3	↑ ↑ ↑		3
d^4	↑↓ ↑ ↑		2	↑ ↑ ↑ ↑		4
d^5	↑↓ ↑↓ ↑		1	↑ ↑ ↑ ↑ ↑		5
d^6	↑↓ ↑↓ ↑↓		0	↑↓ ↑ ↑ ↑ ↑		4
d^7	↑↓ ↑↓ ↑↓	↑	1	↑↓ ↑↓ ↑ ↑ ↑		3
d^8	↑↓ ↑↓ ↑↓	↑ ↑	2	↑↓ ↑↓ ↑↓ ↑ ↑		2
d^9	↑↓ ↑↓ ↑↓	↑↓ ↑	1	↑↓ ↑↓ ↑↓ ↑↓ ↑		1
d^{10}	↑↓ ↑↓ ↑↓	↑↓ ↑↓	0	↑↓ ↑↓ ↑↓ ↑↓ ↑↓		0