MODULE 1 : QUANTUM CHEMISTRY

Q1. What is the role of doping on the band structures of solids?

Answer Role of doping on the band structures of solids is to enhance the conductivity of Semiconductors.

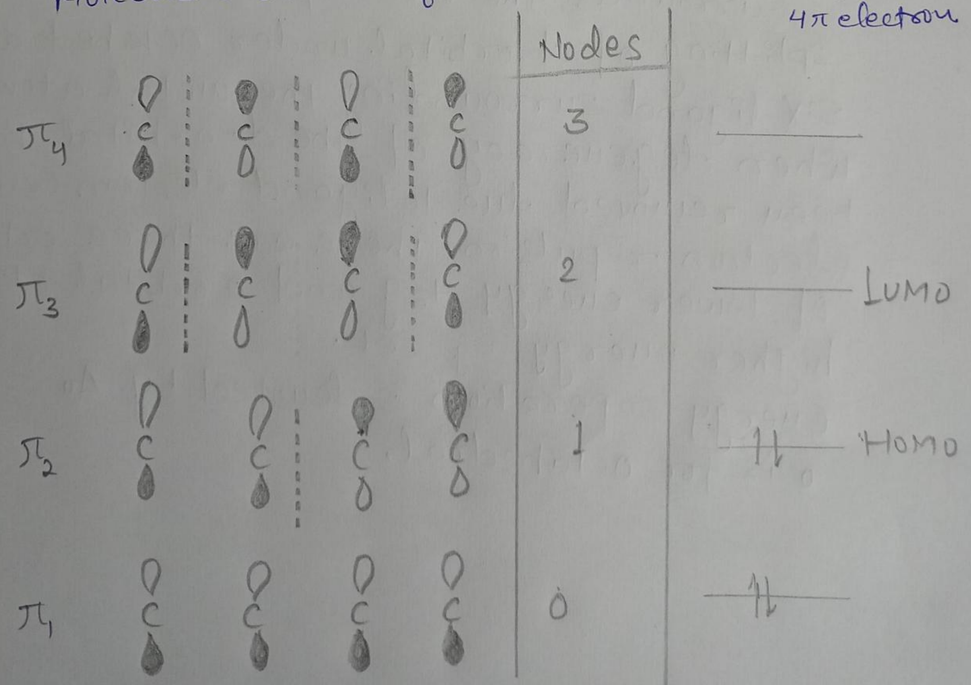
Q2. Give the schrodinger wave equation for a particle in 1-D box.

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

- V → potential energy
- E → Energy
- h → plank's constant
- ψ → schrodinger wave function.

Q3. Draw the Pi-molecular orbitals for butadiene.

Answer Molecular orbital for Butadiene



Q4. Give three main postulates of CFT. Explain the splitting of d orbitals under octahedral, tetrahedral and square planar ligand field.

Answer Three main postulates of crystal field theory are as follows:

(i) The attraction between the central metal and the ligand in a complex is purly electrostatic.

(ii) Ligands are treated as point charges in case of anions or point dipoles in case of neutral molecules.

(iii) The five d orbitals in an isolated gaseous metal have same energy and their degeneracy is maintained if a spherically symmetrical field of negative charges surrounds the metal ion.

Splitting of d-orbital under octahedral.

Six ligand surrounding the metal atom and when degeneracy of the d-orbital has been removed due to ligand electron-metal electron repulsion. There are three orbital of lower energy t_{2g} and 2 orbital of higher energy e_g set.

Energy seperation is denoted by Δ_o

o is for octahedral.

(ii) Splitting of d orbital under tetrahedral

Four ligand are surrounding the metal atom. When degeneracy of the d-orbitals has been removed due to ligand electron - metal electron repulsion. There are three orbital higher energy which is t_2 and two orbital of lower energy, e ($d_{x^2-y^2}$, d_{z^2}). $t_2 \rightarrow d_{xy}, d_{yz}, d_{xz}$

Here, 'g' subscript is not used because tetrahedral complexes lack symmetry.

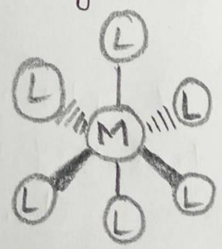
Splitting of d orbital under tetrahedral

(iii) square planar ligand field.

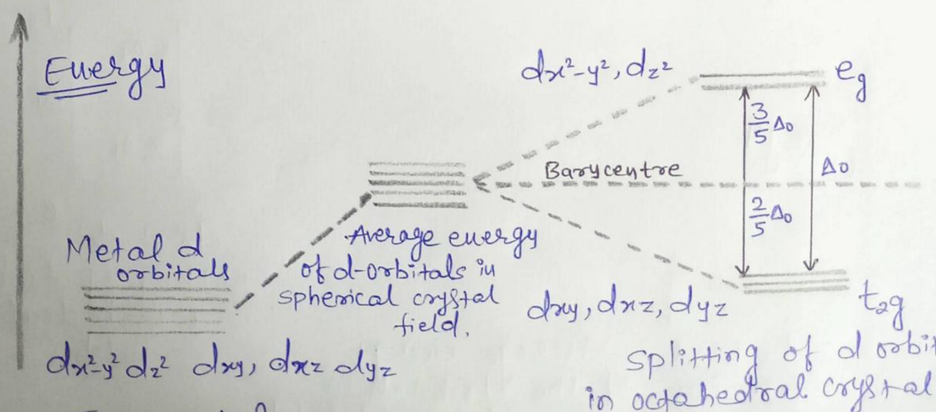
Four ligand are surrounding the metal and when degeneracy of the d-orbital has been removed. Then, there are 3 orbitals of lower energy t_{2g} and two for higher e_g establish.

5. Explain crystal field splitting in octahedral complexes.

Answer



L – Ligand
M – Metal



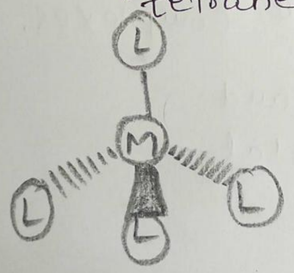
Splitting of d orbitals in octahedral crystal field.

6. Define and explain CFT.

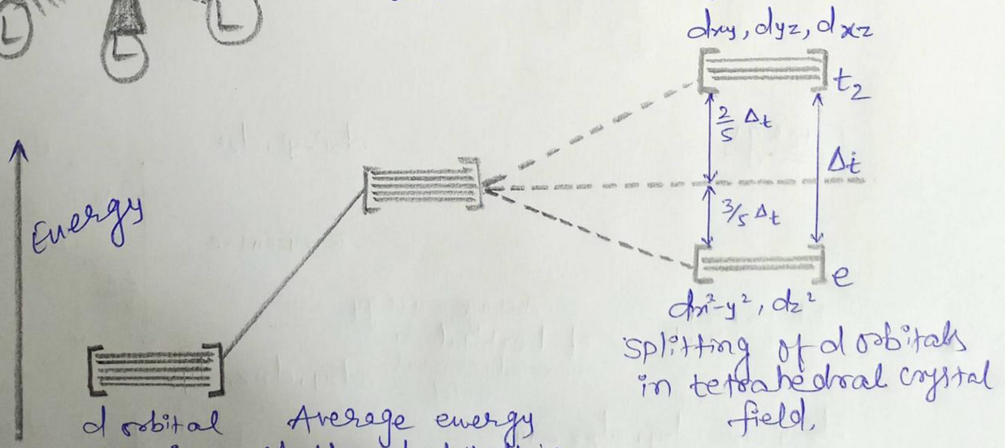
Answer The crystal field theory (CFT) is an electrostatic model which considers the metal-ligand bond to be ionic arising purely from electrostatic interaction between the metal ion and ligand.
Here, ligand are treated as point charge and point dipole in case of anions and neutral molecules respectively.
Five d-orbitals in an isolated gaseous metal are degenerated. When degeneracy of the d orbitals is lifted. It results in splitting of the d orbitals. The pattern of splitting depends upon the nature of the crystal field.

7. Briefly discuss crystal field splitting in tetrahedral complexes.

Answer



— d orbital spliting in tetrahedral crystal.



splitting of d orbitals in tetrahedral crystal field.

Q8. What is the significance of ψ and ψ^2.

Answer ψ - A wave function and refers to the amplitude of electron wave. i.e., probability amplitude. It can be positive, negative and Imaginary.

ψ^2 - It is known as probability density and determines the probability of finding an electron at a point within the atom.

Q9. Derive the expression for E and ψ for a particle in 1-Dimensional box.

Answers let ψ be the function that describes all the states of the particles in a one-D box. As we know, the wave function as well as the energy both are the obtained as this 2nd order differential equation is solved.

$\therefore \hat{H}\psi = E\psi$ ------- (i)

↳ Hamiltonian operator.

After putting the value of one-Dimensional Hamiltonian in equation (i), we get

$$\Rightarrow \left[\frac{-h^2\partial^2}{8\pi^2 m \partial x^2} + V\right]\psi = E\psi \quad -(ii)$$

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

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

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

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

Equation (vi) is the schrodinger wave equation for a particle moving along one dimension only. After putting the value of potential inside the box in eq^n (vi) i.e., $V=0$ we get.

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

Now Consider

$$k^2 = \frac{8\pi m E}{h^2} \quad ---(\text{vii b.})$$

$$\frac{\partial^2\psi}{\partial x^2} + k^2\psi = 0 \quad --(\text{viii})$$

The general solution of eq (viii) is:

$$\boxed{\psi = A\sin kx + B\cos kx} \quad --(\text{viii b})$$

Here, eq (viii) cannot be used to find different physical properties of corresponding quantum mechanical states because of some unknown parameter like A, B and k.

(i) The first boundary condition : ψ must vanish when $x=0$ i.e.,

$$\therefore 0 = A\sin k(0) + B\cos k(0)$$
$$\Rightarrow 0 = 0 + B\cos k(0)$$
$$\Rightarrow B = 0$$

Putting it on eq (viii b), we get

$$\psi = A\sin kx + 0\cos kx$$

$$\boxed{\psi = A\sin kx} \quad --(\text{ix})$$

· (ii) The second boundary Condition:

ψ must vanish when $x = a$ i.e.,

$$0 = A \sin ka$$

$$\sin ka = 0 \quad --(x)$$

$$\sin n\pi = 0 \quad ---(xi)$$

where,

$n = 0, 1, 2, 3, 4, \ldots \infty.$

Comparing eq (x) and (xi), we conclude that

$$\sin ka = \sin n\pi = 0$$

$$ka = n\pi$$

$$k = \frac{n\pi}{a} \quad --(xii)$$

After putting the value of k in eq (ix)

$$\psi = A \sin \frac{n\pi x}{a} \quad ---(xiii)$$

The only parameter that is still unknown is A, which can be also obtained by the condition of normalization i.e., the function must define the state completely.

$$\therefore \int_0^a \psi^2 = A^2 \int_0^a \sin^2\left(\frac{n\pi x}{a}\right) = 1$$

$$\Rightarrow \quad A^2 \cdot \frac{a}{2} = 1$$

$$\Rightarrow \quad A^2 = \frac{2}{a} \Rightarrow A = \sqrt{\frac{2}{a}} \quad ---(xiv)$$

After putting the value of A in eq (xiii), we get

$$\psi = \sqrt{\frac{2}{a}} \sin \frac{n\pi x}{a} \quad ---(xv)$$

Since the function ψ also depends upon the discrete variable n,

$$\psi_n = \sqrt{\frac{2}{a}} \sin \frac{n\pi x}{a} \quad ---(xvi)$$

For first quantum mechanical state i.e. $n=1$

$$\psi_n = \sqrt{\frac{2}{a}} \sin \frac{\pi x}{a}$$

Similarly, we can write expression for $\psi_2, \psi_3, \psi_4, \psi_5$ and so on. The $u=0$ is permitted by the boundary condition.

we still didn't use it in eq^n (xvi), because it makes the whole function to collapse to zero.

Now,

From eq (xii) and (viib)

$$k^2 = \frac{8\pi^2 m E}{h^2} = \frac{n^2\pi^2}{a^2}$$

$$\boxed{E_u = \frac{u^2 h^2}{8ma^2}} \quad ---(xvii)$$

The energy of different quantum mechanical states can be obtained by putting $n=1,2,3,..\infty$ in equation.

Hence, we have obtained the expression for E and ψ for a particle in one-dimensional box

Q10. Draw and explain molecular orbital diagram of O_2 and compare its bond order and magnetic properties with O_2^+, O_2^-, O_2^{2-}.

	Bond order	Magnetic property
O_2	$\frac{1}{2}$[Bonding - Anti-bond] $\frac{1}{2}[10-6] = 2$	paramagnetic
O_2^+	$\frac{1}{2}[10-5] = 2.5$	paramagnetic
O_2^-	$\frac{1}{2}[10-7] = 1.5$	Paramagnetic
O_2^{2-}	$\frac{1}{2}[10-8] = 1$	diamagnetic.

Higher is the bond order, stronger is the bond, and higher is the stability.
The decreasing order of the stability is
$O_2^+ > O_2 > O_2^- > O_2^{2-}$.

Q11. What are intrinsic and extrinsic semiconductor?

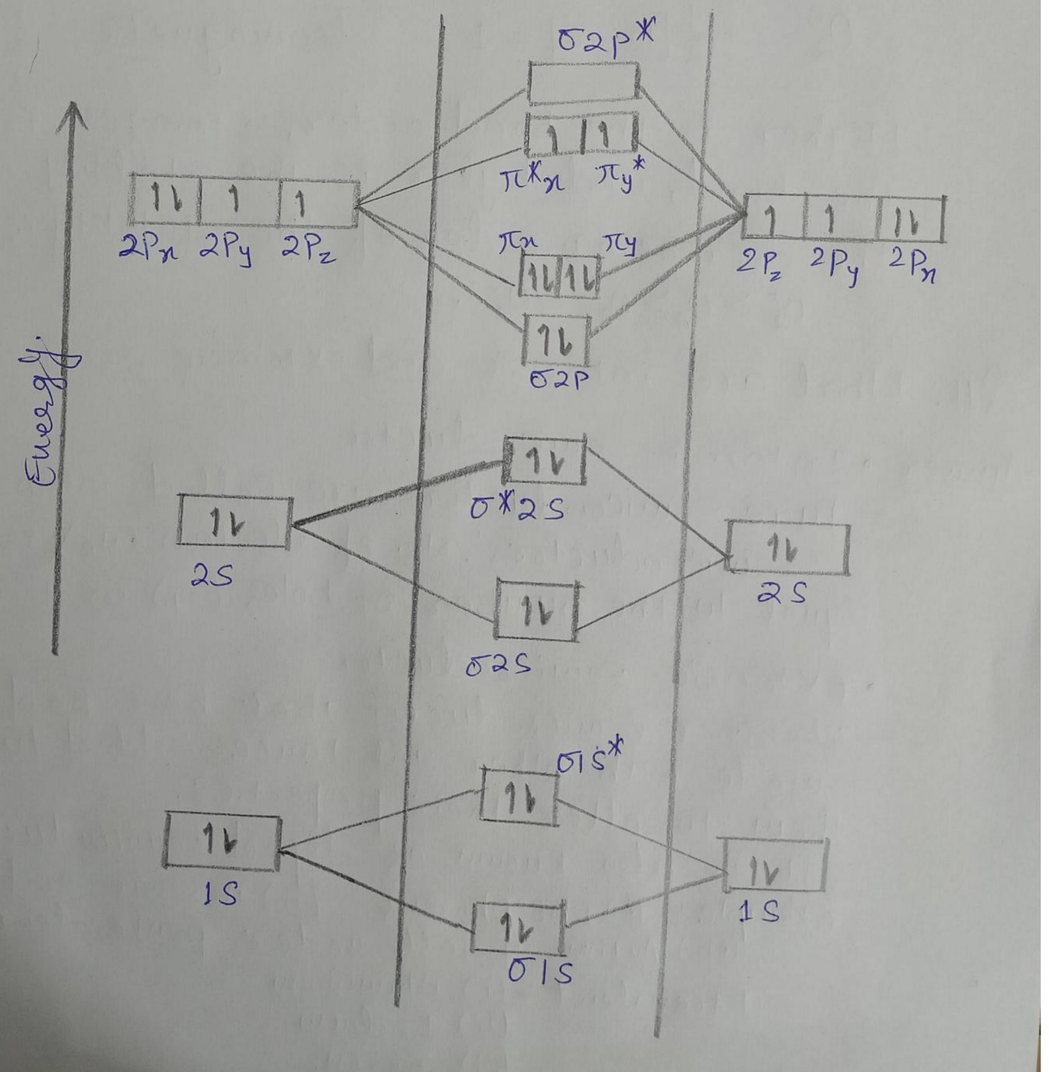
Answer • Intrinsic Semiconductor
– Pure Semiconductors are called 'intrinsic semiconductors'. No. of electron (n_e) is equal to the number of holes (n_h) in this.
• Extrinsic Semiconductor
– Intrinsic semiconductor that have had made with other substances added to them to alter their properties.
It is also known as doped semiconductor.
Example: (i) phosphorous (ii) Arsenic and (iii) Antimony falls under pentavalent
Tetravalent – (i) Aluminium
(ii) Indium
(iii) Boron.

Answer Electronic Configuration for an atom of O in the ground state is $1s^2 2s^2 2p^4$.

Then, O_2 molecule have 16 electrons

For the molecular orbital diagram, the electronic Configuration of oxygen molecule

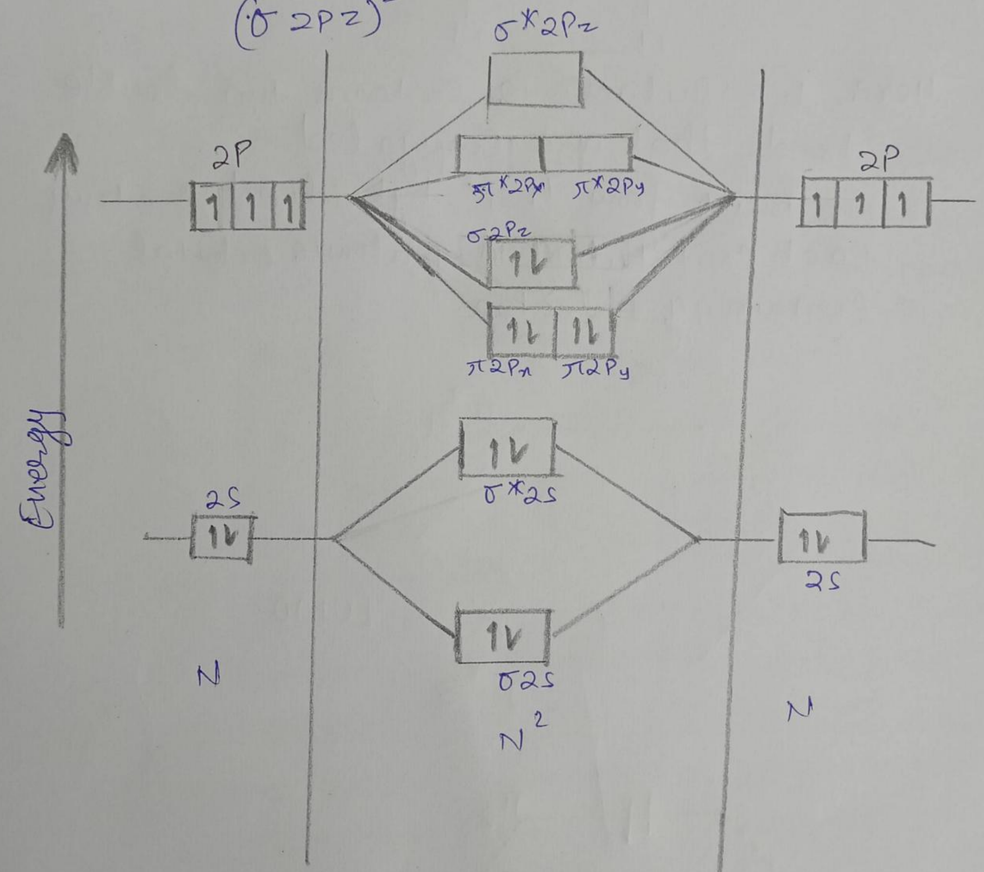
$O_2 :- \sigma 1s^2 \sigma^* 1s^2 \sigma 2s^2 \sigma^* 2s^2 \sigma 2p^2 \pi 2p_x^2 \pi 2p_y^2 \pi^* 2p_x^1 \pi^* 2p_y^1$.



Q12. Write down the MOT electronic configuration and draw MOT orbital energy level diagram for N_2 molecule.

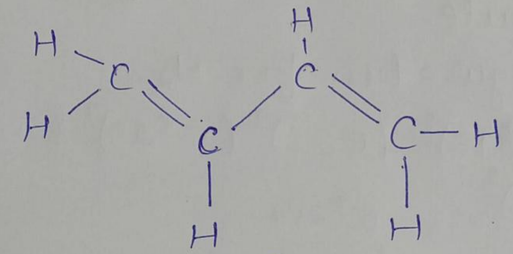
Answers MOT configuration for N_2.

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

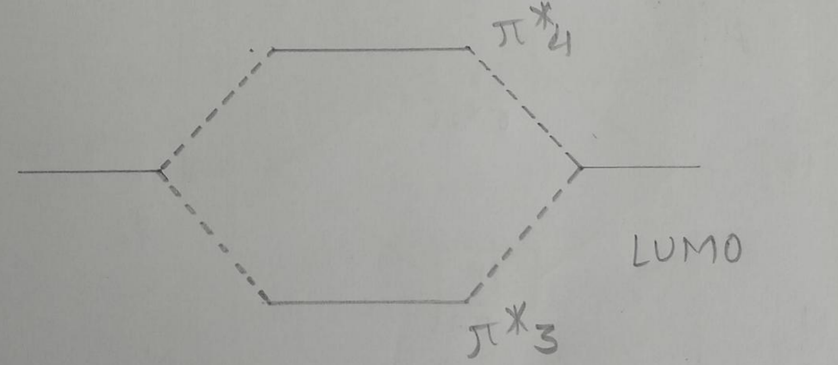


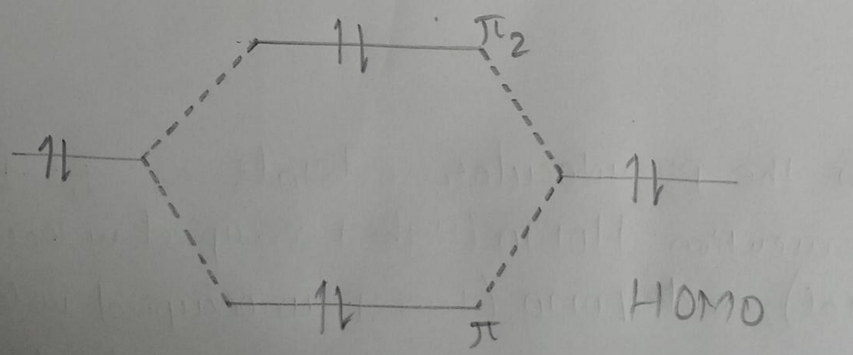
Q13. Draw the pi-molecular orbitals of 1,3-butadiene Also mention HOMO (Highest occupied molecular orbital) and LUMO (Lowest-unoccupied molecular orbital)

Answer 1, 3-Butadiene



Here, 1,3-Butadiene contains two double bonds that are conjugated.
It built from 4 sp^2 hybridised C atoms each contributing a p atomic orbital containing 1 electron.





Q14. Explain the Complete LCAO Method.

Answers A linear Combination of atomic orbitals or LCAO is a quantum superposition of atomic orbitals and a technique for calculating molecular orbitals in quantum chemistry.

The condition that are required for a linear Combination of atomic orbitals are as follows:

(i) Same energy of combing orbital :
The Combining orbital must have same energy like 1s and 2P cannot be combine it will only Combine with 1s.

(ii) Same symmetry about the molecular axis.
If this factor will not be fullfilled then the electron density will be sparse.
e.g., the sub-orbitals of 2P have the same energy but still the $2P_z$ and $2P_x$ or $2P_y$ cannot Combine with as they have a different axis of symmetry.

(iii) Proper overlap between the atomic orbital.
Greater the extent of overlap of orbitals greater will be the nuclear density between the nuclei of the two atoms.

Q15. Calculate the Meffective (magnetic moment) of for Ni^{2+} and Co^{2+} metal ions.

Answer $Ni^{2+} \rightarrow [Ar]\ 4s^0\ 3d^8$ $\quad$ $Co^{2+} \rightarrow [Ar]\ 3d^7$

no. of unpaired $e^- = 2$ $\quad$ no. of unpaired $e^- = 3$

Magnetic moment $\rightarrow \sqrt{2(2+2)}$ $\quad$ $\rightarrow \sqrt{3(3+2)}$

$= \sqrt{8}$ $\quad$ $\rightarrow \sqrt{15}$

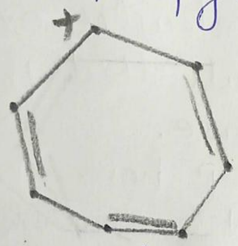
$= 2.83$ BM $\quad$ $= 3.87$ BM

Q16. Write the Huckel rule for Aromaticity of Compounds.

Answers (i) It should be in ring form and planar.
(ii) Every atom of the ring must be orthogonal to the plane of the ring.
(iii) There must be $4n+2\pi$ electrons present in a system of connected p orbitals
(iv) It must have a ring of p orbitals which doesn't have any sp^3 hybridized atoms.

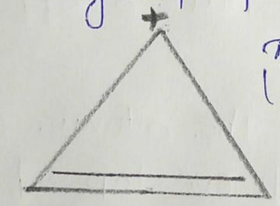
Q17. Predict the Tropylium cation, cyclopropenyl Cation, Cyclopentadiene are aromatic or not.

Answer — Tropylium cation. $[C_7H_7]^+$



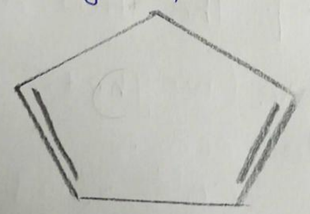
Aromatic
(i) because $6\pi^-$ electron which satisfied $(4n+2)$.

— cyclopropenyl cation. $[C_3H_3]^+$



Aromatic.
(i) because 2π electron.
Also, the Carbon atom are sp^2 hybridized.

— Cyclopentadiene $[C_5H_6]$



Not aromatic Compound because of the presence of a sp^3 hybridised ring.