

# **Engineering Chemistry UNIT-1-A-ii**

**INTRODUCTION TO ENGG. CHEMISTRY  
PART A: i) ATOMS TO MOLECULES TO MATERIALS  
FOR ENGINEERS-ii. Co-Ordination complexes**

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**To rationalize how the shapes of atomic orbitals are transformed into the orbitals occupied in covalently bonded species,**

**we need the help of two bonding theories:**

**Valence Bond (VB) Theory**

**Molecular Orbital (MO) Theory**

## **VALENCE BOND THEORY [text]**

**Developed in 1927 by HEITLER and LONDON**

**For maximum electron density and overlapping  
i.e. stable bond formation-**

- i) The electrons should have opposite spins and**
- ii) The greater overlapping of the electron clouds.**

## VALENCE BOND THEORY [text]

**Linus Pauling and J.C. Slater extended this theory:**

**a) Extent of overlapping of the electron wave functions determine the strength of a bond**

**[ maximum overlap=strongest bond]**

**b) Out of two orbitals of identical stability or energy the one with more directionally concentrated would form a stronger bond.**

**Linus Pauling and J.C. Slater extended this theory:**

**a) Extent of overlapping of the electron wave functions determine the strength of a bond**

**[ maximum overlap=strongest bond]**

**b) Out of two orbitals of identical stability or energy the one with more directionally concentrated would form a stronger bond.**

**c) s-spherically symmetrical**

**d) The direction of bond forming orbitals will decide the direction. e.g.  $P_x - P_x$  overlap will be in x direction.**

**e) When a bond is formed along x-direction,  $P_y, P_z$  orbitals will remain as it is.**

- In order for a covalent bond to form between two atoms, **overlap** must occur between the orbitals containing the valence electrons.
- The **best overlap** occurs when two orbitals are allowed to meet “**head on**” in a straight line.
- When this occurs, the atomic orbitals merge to form a single bonding orbital and a
- “**single bond**” is formed, called a **sigma ( $\sigma$ ) bond**.

## Valence Bond Theory:

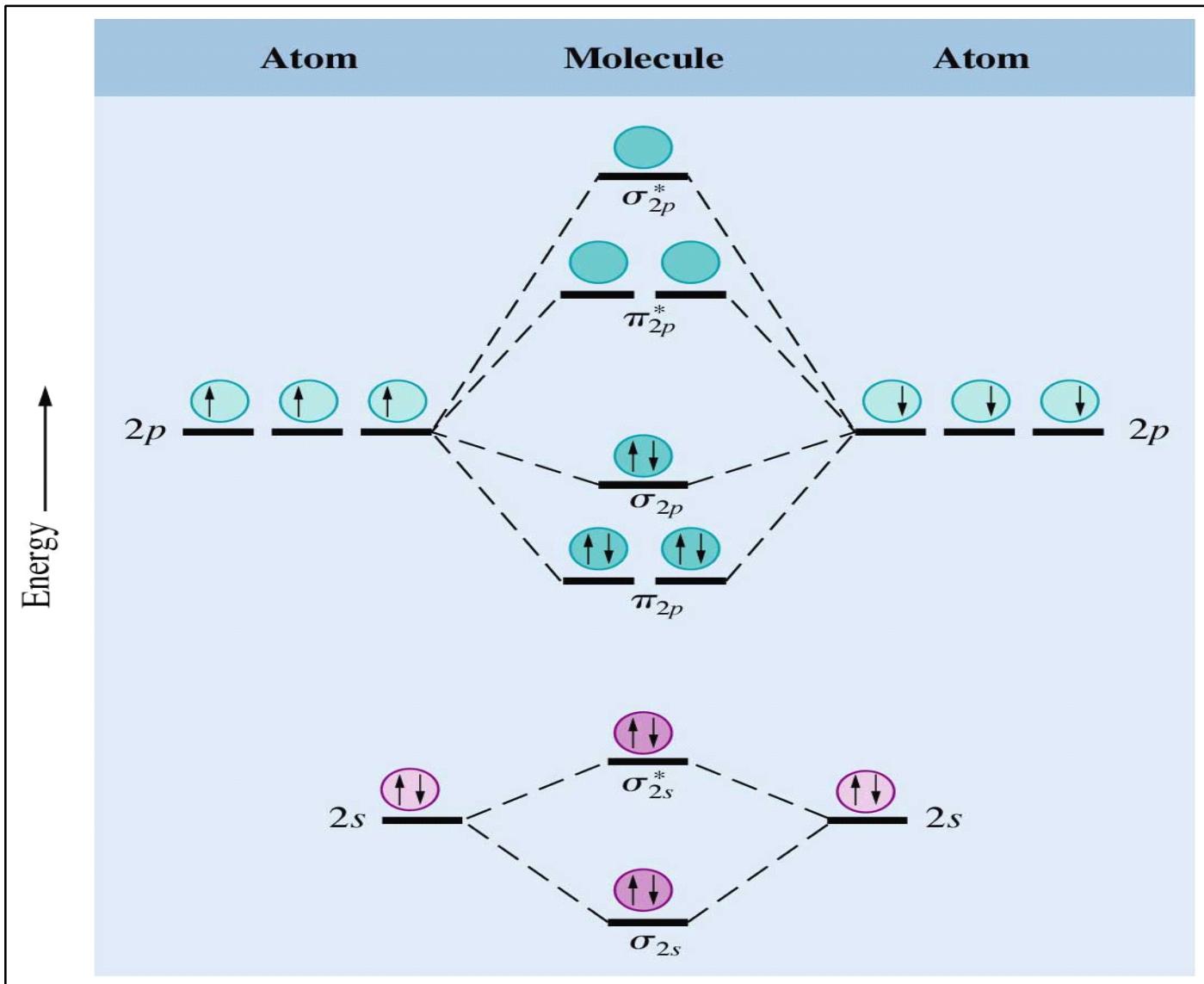
- $\text{H}_2$  forms due to overlap of two 1s orbitals.
- $\text{F}_2$  : Electron densities from p-subshell electrons overlap to produce a bond in  $\text{F}_2$ .
- $\text{CH}_4$ : The 1s orbital of hydrogen must overlap with the 2s and 2p orbitals of carbon.

## LIMITATIONS of VALENCE BOND THEORY [text]

**VBT doesn't explain :**

- a] the formation of coordinate bond**
- b] The formation of odd electron molecules**  
**e.g.  $\text{H}_2^+$  ,  $\text{NO}$ ,  $\text{O}_3$  etc. where no electron pairing takes place.**
- c] the paramagnetic nature of Oxygen.**
- d] structure of molecules involving resonance and hybridization.**

# **MOLECULAR ORBITAL THEORY**

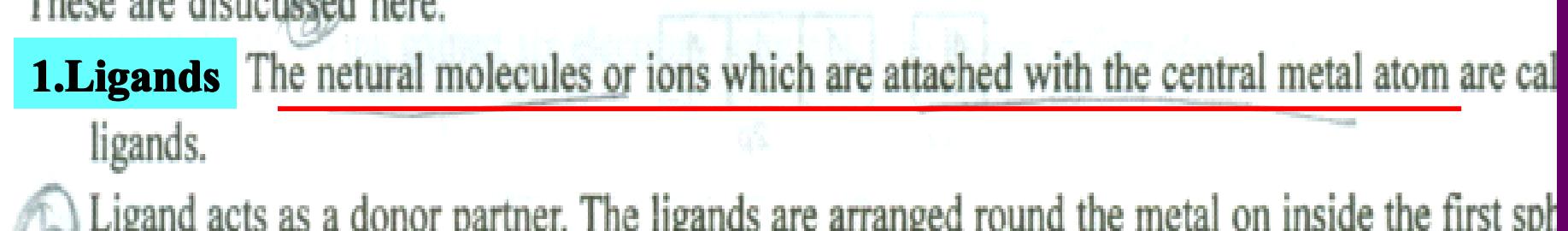


**Fig. 10.34 MO Diagram of  $\text{N}_2$**

## Valence Bond Theory for Complex ion or Coordination Compounds.

It is necessary to understand the some important terms used in the study of inorganic compounds. These are discussed here.

**1. Ligands** The natural molecules or ions which are attached with the central metal atom are called ligands.

A hand-drawn diagram showing a central metal atom represented by a circle with a cross inside. Four lines extend from this central circle to four surrounding circles, each representing a ligand molecule or ion.

Ligand acts as a donor partner. The ligands are arranged round the metal on inside the first sphere of attraction in perfect geometry.

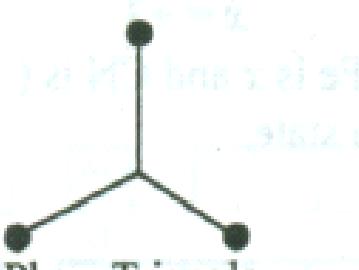
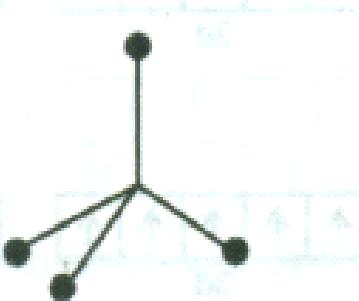
**2. Coordination number** It is the total number of atoms of the ligands, that can coordinate to central metal ion.

**3. Coordination sphere** The central metal ion and the ligands that are directly attached to it enclosed in a square bracket are called coordination sphere.

## Valence Bond theory (V.B.T)

1. The central metal atom or ion in the complex makes available an adequate number of empty orbitals for the formation coordination compound with suitable ligands. The number of empty orbitals made available for the purpose is equal to the coordination number of the central atom or ion.
2. Hybrid orbital: The atomic orbitals (*s*, *p* and *d*) of the metal hybridise to give an equal number of new orbitals of equivalent energy called hybrid orbitals.
3. The *d* orbitals involved in the hybridisation may be inner (*n*-1) or the outer (*n*) orbitals.
4. Each ligand has at least one orbital containing a lone pair of electrons.
5. The empty hybrid orbitals of metal ion overlap with the orbitals of ligands to form metal ligand bond ( $M \leftarrow L$ ).

**Table. 1.2: Hybridisation and shapes of complex ions or molecules.**

S.No.	Hybridised orbital	Bondangle	Molecular Geometry	Example
1.	sp	180°	 <b>Linear</b>	$[\text{Ag}(\text{NH}_3)_2]^+$ , $[\text{Ag}(\text{CN})_2]^-$
2.	sp <sup>2</sup>	120°	 <b>Plane Triangle</b>	$[\text{HgI}_3]^-$
3.	sp <sup>3</sup>	109° 28'	 <b>Tetrahedral</b>	$[\text{Ni}(\text{CO})_4]$ , $[\text{Zn}(\text{NH}_3)_4]^{+2}$

**Table. 1.2: Hybridisation and shapes of complex ions or molecules.**

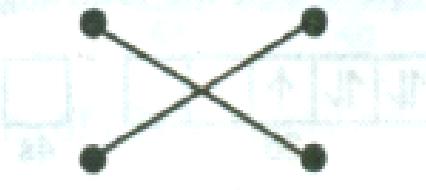
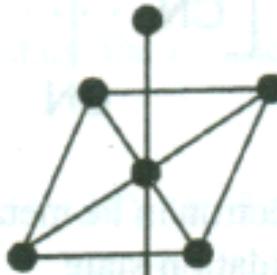
S.No.	Hybridised orbital	Bondangle	Molecular Geometry	Example
4.	$dsp^2$	$90^\circ$	 <b>Square Planar</b>	$[\text{Ni}(\text{CN})_4]^{2-}$ , $[\text{Cu}(\text{NH}_3)_4]^{2+}$
5.	$dsp^3$	$120^\circ$ and $90^\circ$	 <b>Trigonalbipyramidal</b>	$[\text{Fe}(\text{CO})_5]$ , $[\text{Cu}(\text{Cl})_5]^{3-}$

Table. 1.2: Hybridisation and shapes of complex ions or molecules.

S.No.	Hybridised orbital	Bondangle	Molecular Geometry	Example
6.	$sp^3d$	$90^\circ$	 <p>Square Pyramidal</p>	$[SbF_5]^{2-}$ , $[IF_5]$
7.	$d^2sp^3$ , $sp^3d^2$	$90^\circ$	 <p>Octahedral</p>	$[Fe(CN)_6]^{3-}$ , $[Fe(F)_6]^{3-}$

## Applications of V.B.T

1.  $[\text{K}_4\text{Fe}(\text{CN})_6]$  or  $[\text{Fe}(\text{CN}_6)]^{3-}$



$$\text{Fe} = 26$$

The atomic number of Fe = 26

Atomic configuration of Fe  $1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 4s^2, 3d^6$

Oxidation state of Fe in  $[\text{Fe}(\text{CN})_6]^{3-}$  is

$$x + 6(-1) = -3$$

$$x = +3$$

[Here oxidation number of Fe is x and CN is (-1)]

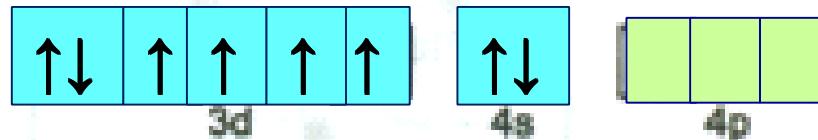
Now Fe is in **(+3)** oxidation state.

[Here oxidation number of Fe is  $x$  and CN is  $(-1)$ ]

Now Fe is in (+3) oxidation state.

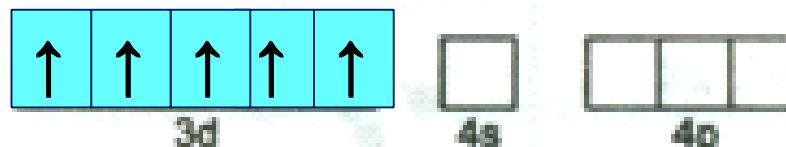
Fe is in GS

**Fe = 26**

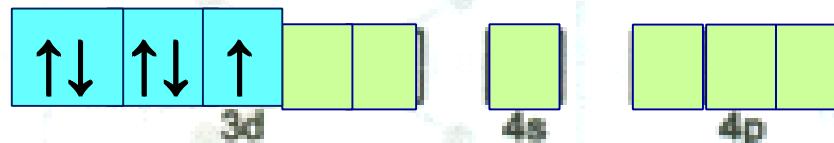


Fe is in (+3)O.s

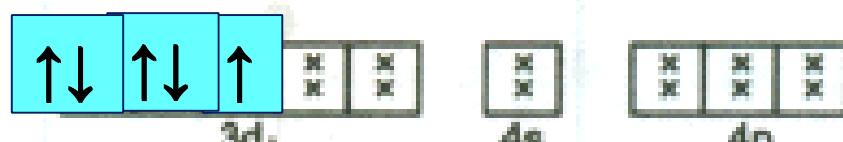
**(+3)**



Due to influence of strong ligand CN, the rearrangement of Fe electrons takes place.



After hybridisation on filling the electrons of CN in empty orbitals of Fe metal.



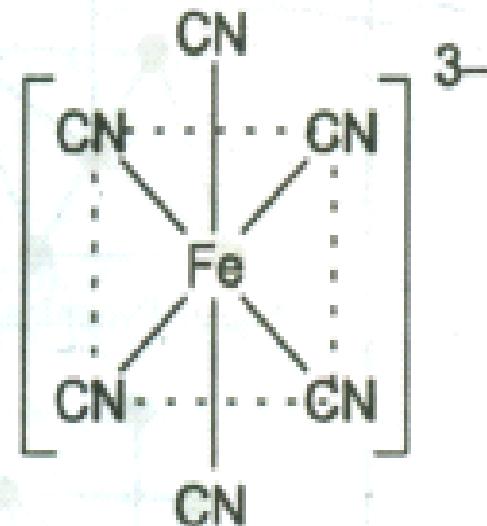
**$d^2s\ p^3$**

**paramagnetic**

Two  $d$ , one  $s$  and three  $p$  orbital hybridised with each other to form  $[\text{Fe}(\text{CN})_6]^{3-}$ , therefore hybridisation is  $d^2sp^3$  and the shape of the molecule is octahedral.

**$d^2s\ p^3$**

**$[\text{Fe}(\text{CN})_6]^{3-}$**



**paramagnetic**

There is presence of unpaired electron in Fe metal orbital, the magnetic behaviour is paramagnetic  
G.S  $\Rightarrow$  ground State, O.S  $\Rightarrow$  oxidation state



The atomic number of Fe = 26

Atomic configuration of Fe,  $1s^2, 2s^2, 2p^6, 3s^2, 2p^6, 4s^2, 3d^6$

Oxidation state of Fe in  $[Fe(CN)_6]^{4-}$  is

$$x + 6(-1) = -4, x = +2$$

(Here oxidation number of Fe is x and CN is (-1))

Now Fe is in **(+2)** oxidation state

Fe is in GS

1	1	1	1	1	1	4s	4p
3d							

Fe is in (+2)O.S

1	1	1	1	1	1	4s	4p
3d							

Due to influence of strong ligand CN, the rearrangement of Fe electrons takes place.

1	1	1	1	1	1	4s	4p
3d							

After hybridisation on filling the electrons of CN in empty orbitals of Fe metal.

1	1	1	x	x	x	4s	x	x	x
3d									

$d^6sp^2$

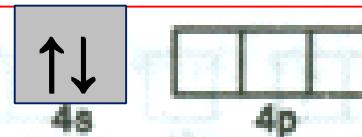
$K_4 [Fe(CN)_6]$

$[Fe(CN)_6]^{4-}$

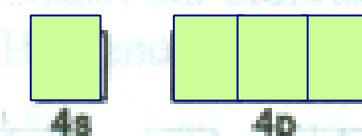
(Here oxidation number of Fe is  $x$  and CN is  $(-1)$ )

Now Fe is in **(+2)** oxidation state

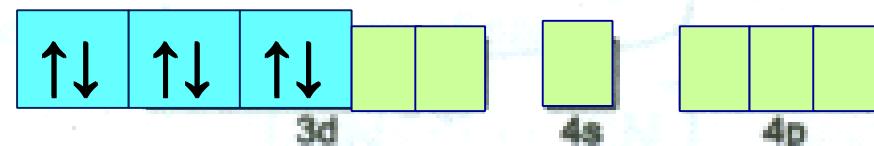
Fe is in G.S



Fe is in  $(+2)$ O.S



Due to influence of strong ligand CN, the rearrangement of Fe electrons takes place.



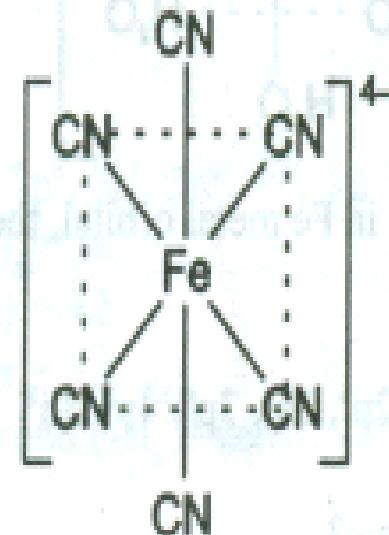
After hybridisation on filling the electrons of CN in empty orbitals of Fe metal.



**$d^2s^2p^3$**

**diamagnetic**

Two  $d$ , one  $s$  and three  $p$  orbitals hybridised with each other to form  $[\text{Fe}(\text{CN})_6]^{4-}$ , therefore hybridisation is  $\text{d}^2\text{sp}^3$  and the shape of the molecule ion is octahedral.



**diamagnetic**

There is no unpaired electron in Fe metal orbitals, the magnetic behaviour is diamagnetic.



The atomic number of Fe = 26

Atomic configuration of Fe,  $1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 4s^2, 3d^6$

Oxidation state of Fe in  $[\text{Fe}(\text{H}_2\text{O})_6]^{3+}$  is

$$x + 6(0) =$$

(+3)

$$x = +3$$

(Here oxidation number of Fe is  $x$  and  $\text{H}_2\text{O}$  is zero)

Now Fe is in (+3) O.S

Fe is in G.S.

1	1	1	1	1
3d				

1
4s

4p		

4d			

Fe is in (+3)O.S

1	1	1	1	1
3d				

4s

4p		

4d			

Since  $\text{H}_2\text{O}$  is weak ligand, therefore the rearrangement of Fe electrons does not take place.

After hybridisation on filling the electrons of  $\text{H}_2\text{O}$  in empty orbitals of Fe metal

1	1	1	1	1
3d				

X	
4s	

X	X	X
4p		

X	X	X	
4d			

paramagnetic

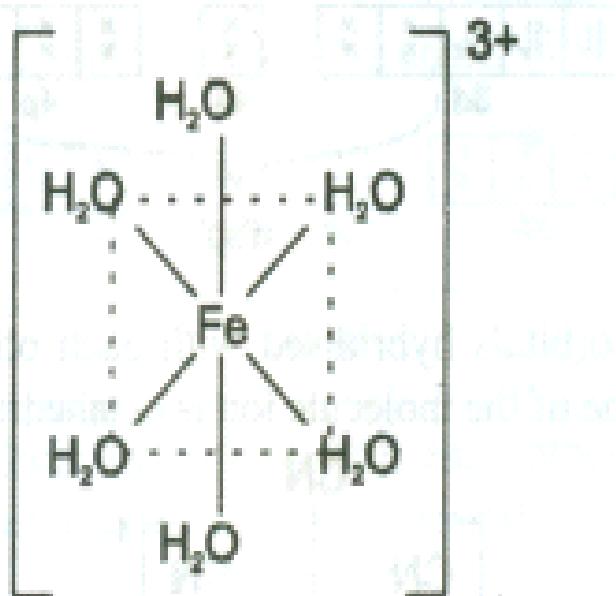
$\text{sp}^3\text{d}^2$



Fe = 26



Only *s*, three *p* and two *d* orbitals hybridised with each other to form  $[\text{Fe}(\text{H}_2\text{O})_6]^{3+}$ , therefore hybridisation is  $sp^3d^2$  and the shape of the molecule is octahedral.



**paramagnetic**

There is presence of unpaired electron in Fe metal orbital, the magnetic behaviour is paramagnetic.

4.  $[\text{Ni}(\text{CN})_4]^{2-}$

**Ni = 28**

The atomic number of Ni is 28

Atomic configuration of Ni,  $1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 4s^2, 3d^8$

Oxidation state of Ni in  $[\text{Ni}(\text{CN})_4]^{2-}$  is

$$x + 4(-1) = -2$$

$$x = +2$$

(Here oxidation number of Ni is  $x$  and (N is  $(-1)$ ))

Now Ni is in (+2) O.S

Ni is in GS.

1	1	1	1	1
3d				
4s				

1
4s
4p

Ni is in (+2)O.S

1	1	1	1	1
3d				
4s				

4s
4p

Due to influence of strong ligand CN, the rearrangement of Ni electrons take place.

1	1	1	1	1
3d				
4s				

4s
4p

After hybridisation on filling the electrons of CN in empty orbitals of Fe metal

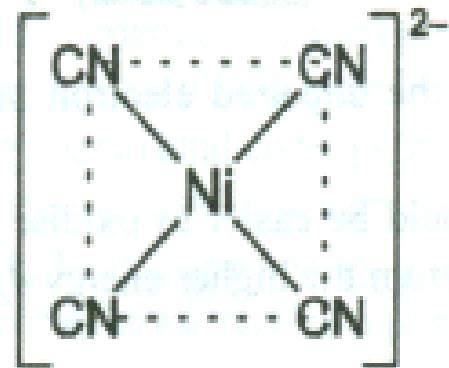
1	1	1	1	x
3d				
4s				

x	x	x
4s		
4p		

$d\text{s}^2$

**diamagnetic**

Only  $d$ , one  $s$  and two  $p$  orbitals hybridised each other to form  $[\text{Ni}(\text{CN})_4]^{2-}$ , therefore hybridisation is  $dsp^2$  and the shape of the complexion is square planar.



**diamagnetic**

There is no of unpaired electron in Ni metal orbital, the magnetic behaviour is diamagnetic.

## Short Comings of Valence Bond Theory

### (i) Consider the complex



The atomic no of Cu is 29

Atomic configuration is  $1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 4s^2, 3d^{10}$

Oxidation state of Cu in  $[\text{Cu}(\text{NH}_3)_4]^{2+}$  is

$$x + 4(0) = +2$$

$$x = +2$$

(Here oxidation number of Cu is  $x$  and  $\text{NH}_3$  is zero)

Now Cu is in (+2) O.S

Cu is in G.S.

1	1	1	1	1	1	4s	4p

Cu is in (+2)O.S

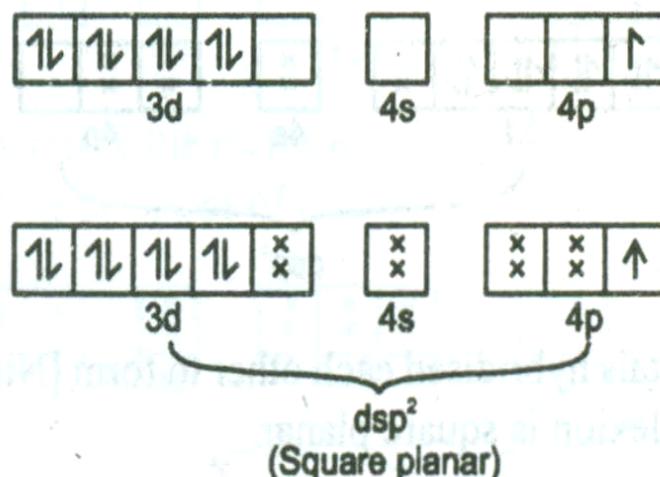
1	1	1	1	1	1	4s	4p

After hybridisation on filling the electrons of  $\text{NH}_3$  in empty orbitals of Cu metal.

1	1	1	1	1	1	4s	4p
x	x	x	x	x	x		

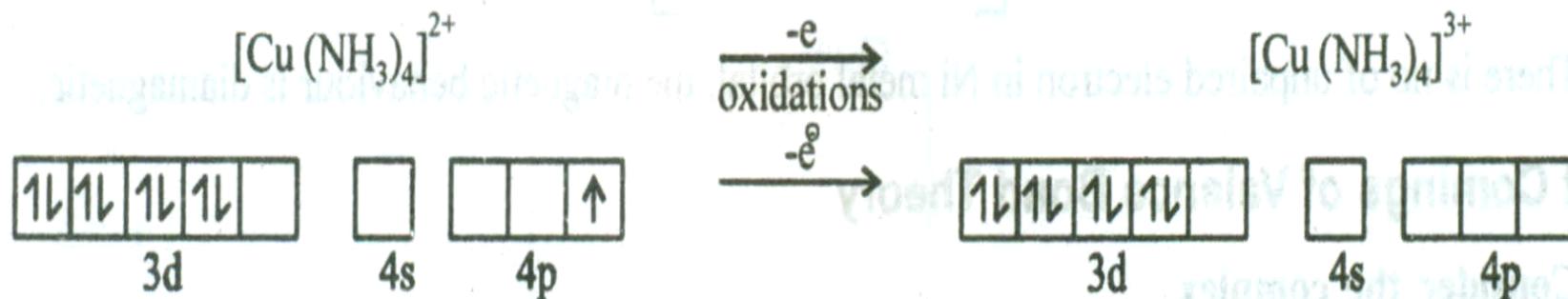
Only *s*, three *p* orbitals hybridised each other to form  $[\text{Cu}(\text{NH}_3)_4]^{2+}$ , therefore hybridisation is  $sp^3$  and the shape of the complex ion tetrahedral. But the compexion  $[\text{Cu}(\text{NH}_3)_4]^{2+}$  exists in square planer structure and therefore hybridisqt ion is  $dsp^2$ .

The valence bond theory suggest that the transter of an unpaired 3d electron of Cu (II) to the higher energy  $4p_z$  orbital is essential to bring about  $dsp^2$  hybridisation.



However, the ESR spectra reveal that the unpaired electron in such complexes is not permanently located in the  $4p_z$  orbital of Cu(II).

Valence bond theory suggest that it would be easier to oxidise Cu(II) to Cu(III) in its square planar structure since the removal of electron from the higher energy  $4p_z$  orbital would be quite easy.



But it is contrary to facts for instance the oxidation of  $[\text{Cu}(\text{NH}_3)_4]^{2+}$  to  $[\text{Cu}(\text{NH}_3)_4]^{3+}$  does not occur at all.

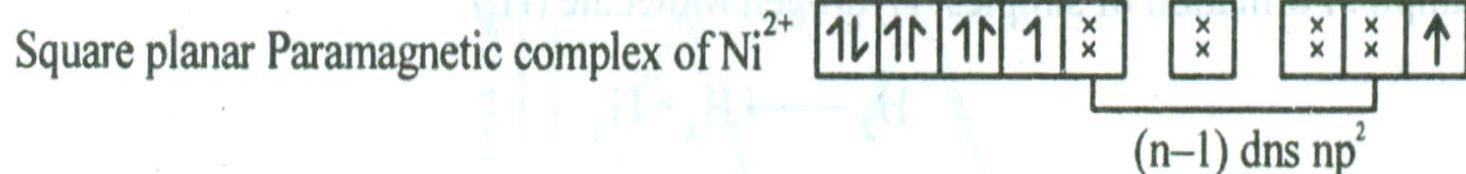
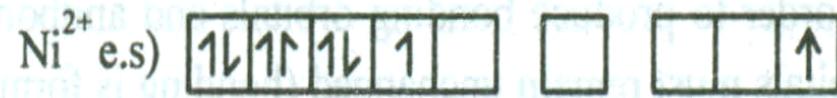
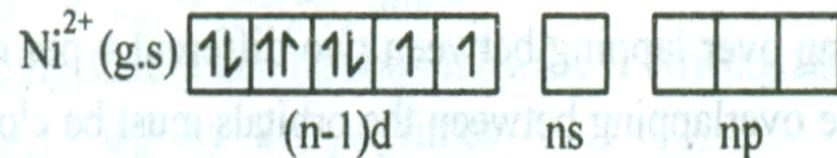
(ii) The valence bond does not satisfactorily explain why same complexes of a metal ion in a particular oxidation state are low spin (inner orbital), while some other are high spin (outer orbital) complex for eg.  $[\text{Cu}(\text{NH}_3)_6]^{3+}$  and  $[\text{CoF}_6]^{3-}$

(iii) The geometry of a complex and its magnetic behaviour is sometimes quite misleading square planar complex Ni (ii) should be diamagnetic as shown below.

$\text{Ni}^{2+}$  in G.S

$1\uparrow$	$1\uparrow$	$1\uparrow$	$\uparrow$	$\uparrow$			
					$1\uparrow$	$1\uparrow$	$1\uparrow$
						$1\uparrow$	$1\uparrow$
							$1\uparrow$

This may lead to the hybridisation  $(n-1)dsp^2$  Conclusion that all square planar complexes of Ni (ii) should be diamagnetic but actually it is not so. Some square planar complexes are paramagnetic.



Valence bond theory does make an attempt to explain this observation by postulating that in such complexes one of the unpaired  $(n-1)d$  electrons of  $\text{Ni}^{2+}$  gets transferred to the vacant  $4p_z$  orbital to vacate the  $(n-1)d$  orbital which is required for  $(n-1)d\ nsp^2$  hybridisation to form square planar complex. But it is difficult to explain why such excitation of electron of electrons occurs in one square planar complex but not in the other.