

Metal pi-Complexes

Dr Bina Rani
Univ. Prof. of Chemistry
Magadh Mahila College (P.U.)
Patna

M.Sc. 2nd Semester, CC6 Course
Inorganic Chemistry

①

Bonding and structure in metal Carbonyl

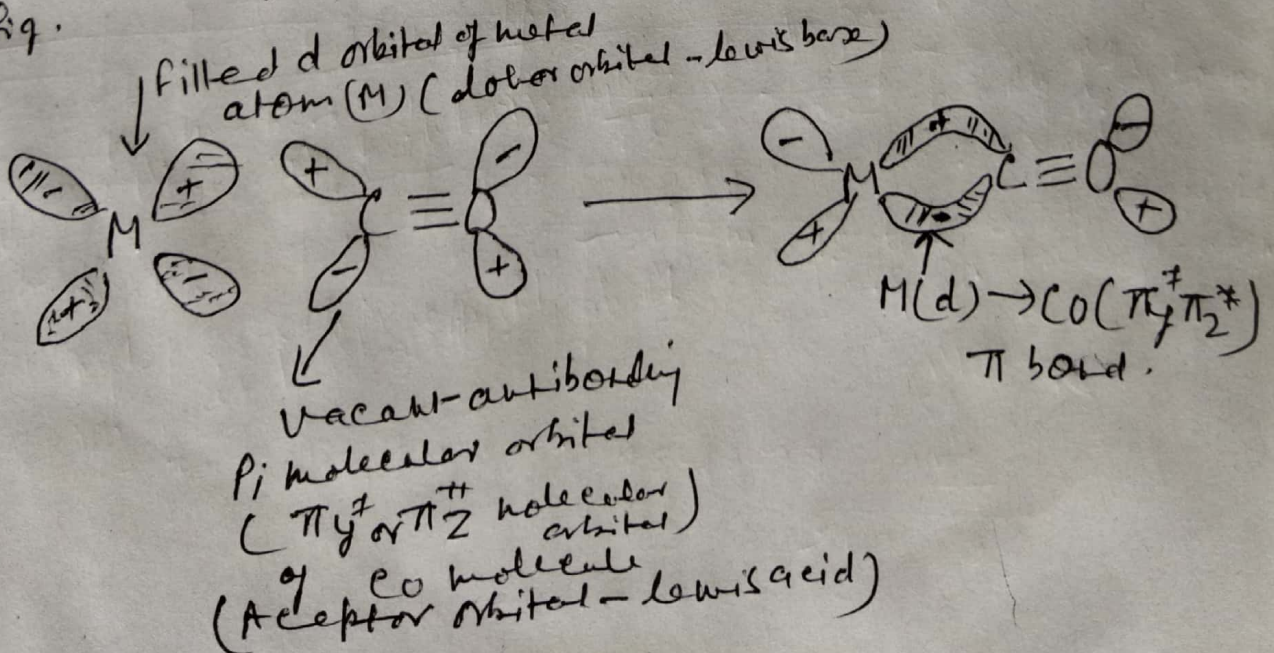
Different types of bonds found in metallic Carbonyls

1. $:O \equiv C \rightarrow M$ coordinate σ bond.

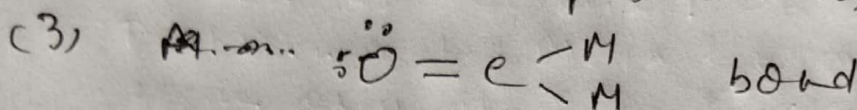
Formation of $:O \equiv C \rightarrow M$ coordinate σ bond on the basis of valence bond theory, the structure of CO molecule is $:O \equiv C:$. When CO molecule gets linked as a terminal carbonyl group with a transition metal (M) in low oxidation state (0, -1, +1). Here only the lone pair of electrons on C-atom (and not on oxygen atom) is donated to the vacant hybrid orbital of the metallic atom. This is because of the fact that C is less electronegative than O-atom.

2. Formation of $M \rightarrow CO$ π bond.

$M \rightarrow CO$ π -bond is formed by the donation of a pair of electrons from the filled d-orbital of the metal atom into the vacant antibonding π molecular orbital (ie, π_y^* or π_z^* molecular orbital) of CO molecule. in fig.

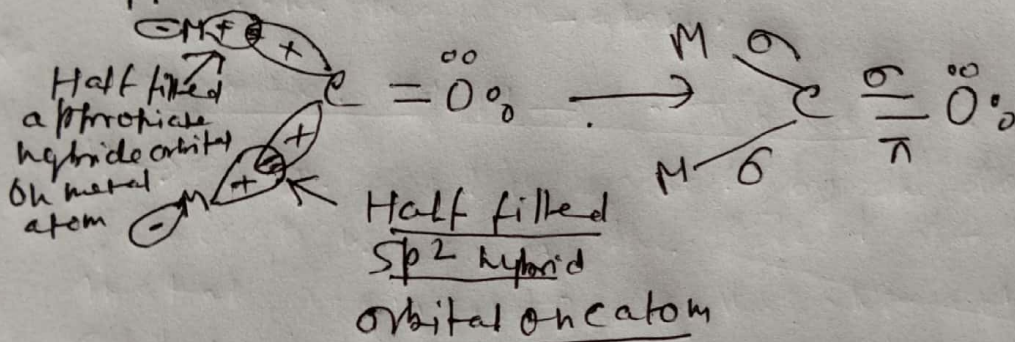


Formation of $OC \rightarrow M, \sigma$ and $M \rightarrow CO, \pi$ -bonds in metallic carbonyls shows that for the formation of $OC \rightarrow M$ σ -bond, CO molecule should have filled sp hybrid orbital and the metallic atom should have suitable vacant hybrid orbital. On the other hand for the formation of $M \rightarrow CO$ π bond, the metal atom should have filled d -orbital and CO molecule should have vacant antibonding π molecular orbital, i.e. metallic carbonyl have double bonding which can be represented as $OC \xrightarrow[\pi]{\sigma} M$.



This bond is found in bridged polynuclear carbonyls & formation of different bonds in

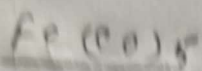
$M \begin{matrix} \nearrow \\ \searrow \end{matrix} \overset{\cdot\cdot}{C} = \overset{\cdot\cdot}{O}$ system has been depicted in fig.



formation of two $(M-C)$ σ bonds in $M \begin{matrix} \nearrow \\ \searrow \end{matrix} \overset{\cdot\cdot}{C} = \overset{\cdot\cdot}{O}$ by the overlap of two singly-filled sp^2 hybrid orbitals on C -atom and two appropriate singly-filled hybrid orbitals on two M -atoms.

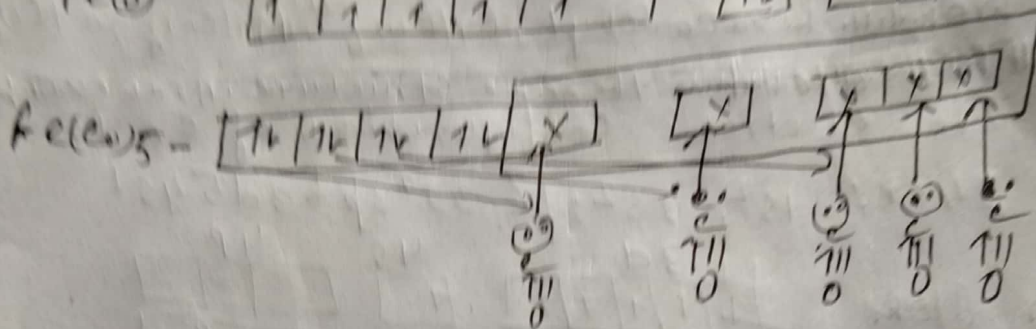
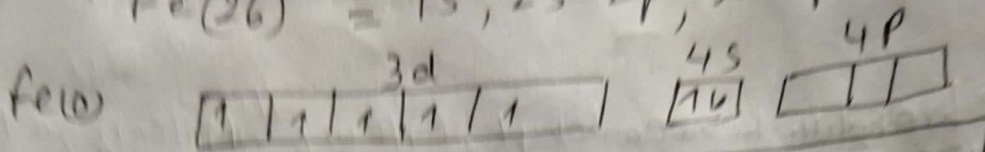
(4) $M \cdots M$ bond :- These are many carbonyls which contain one or more $M \cdots M$ bonds. Examples of carbonyls containing $M \cdots M$ bonds are $M_2(CO)_8$, $M_2(CO)_{10}$, and $M_3(CO)_{12}$ etc.

Structure of some Carbonyls



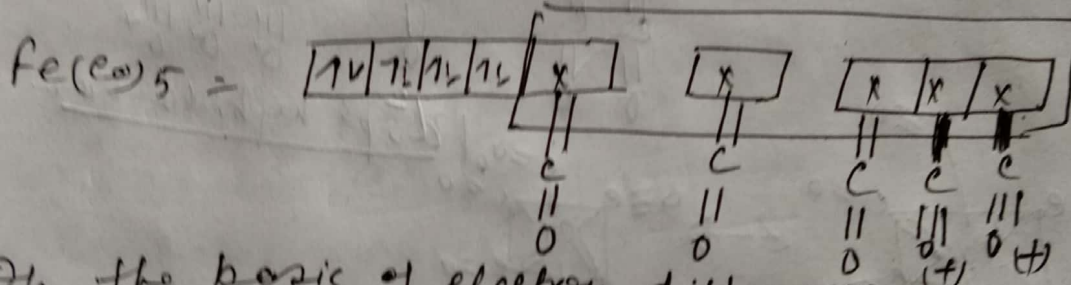
The electronic configuration of iron atom is

$Fe(26) = 1s^2, 2s^2 2p^6, 3s^2 3p^6, 3d^6 4s^2$

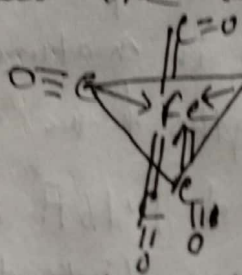


dsp^3 hybridisation.

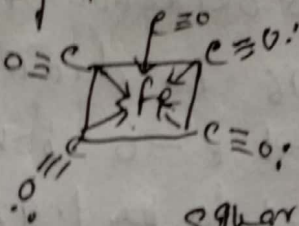
Five lone pairs of electron of five CO molecules are donated to these five dsp^3 hybrid orbitals and form five σ bonds. Thus $Fe(CO)_5$ molecule becomes diamagnetic. In principle, $Fe(CO)_5$ molecule can have any of the two geometry, trigonal bipyramidal and square pyramidal.



On the basis of electron diffraction and X-ray studies the $Fe-C_{axial}$ and $Fe-C_{basal}$ bond lengths are equal to 1.797 and 1.842 Å respectively, X-ray study has shown that these bonds are almost of the same length.



Trigonal bipyramidal structure $Fe(CO)_5$

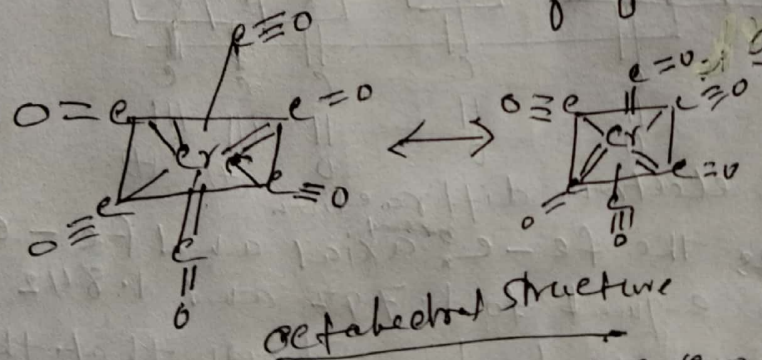
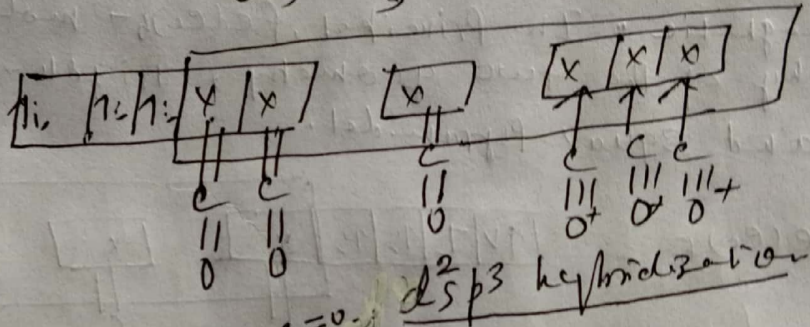
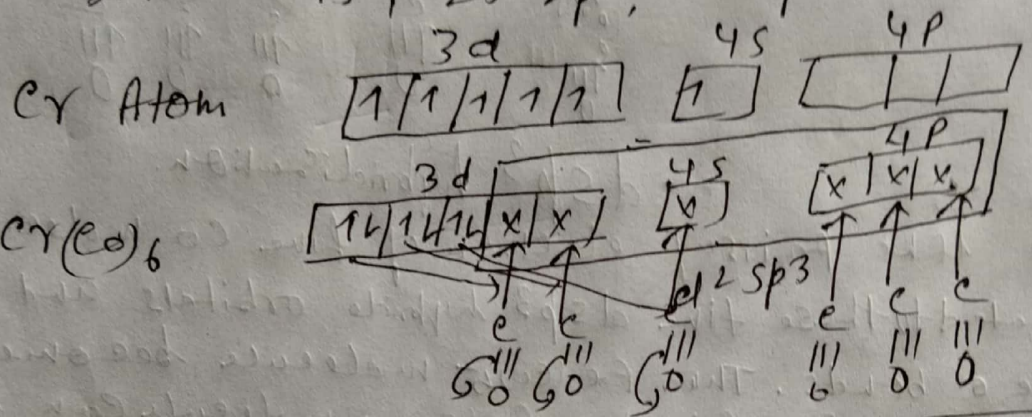


Square pyramidal structure $Fe(CO)_5$

dsp^3 hybridization of Fe-atom. Trigonal bipyramidal shape of $Fe(CO)_5$ molecule suggests that Fe-atom which is in zero oxidation state is dsp^3 hybridised.

chromium hexacarbonyl, $Cr(CO)_6$, $Mo(CO)_6$, $W(CO)_6$
 All atoms have the same structure. As an example - Cr.
 The electronic configuration of Cr is

24 Cr: $1s^2, 2s^2 2p^6, 3s^2 3p^6 3d^5 4s^1$

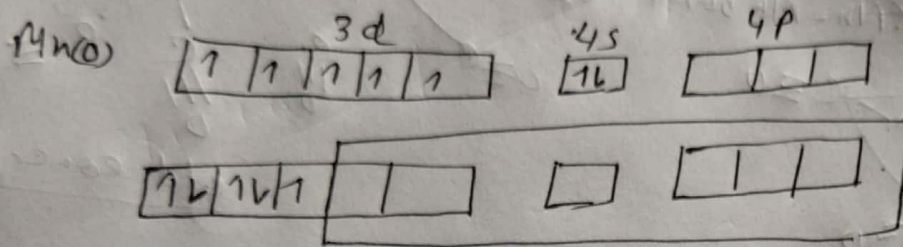
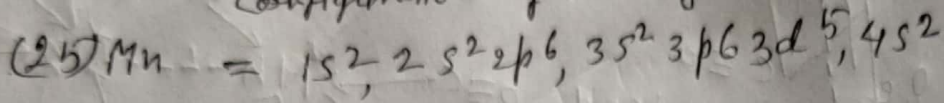


Octahedral geometry of $Cr(CO)_6$ suggested that Cr-atom which is zero oxidation state is d^2sp^3 hybridized.

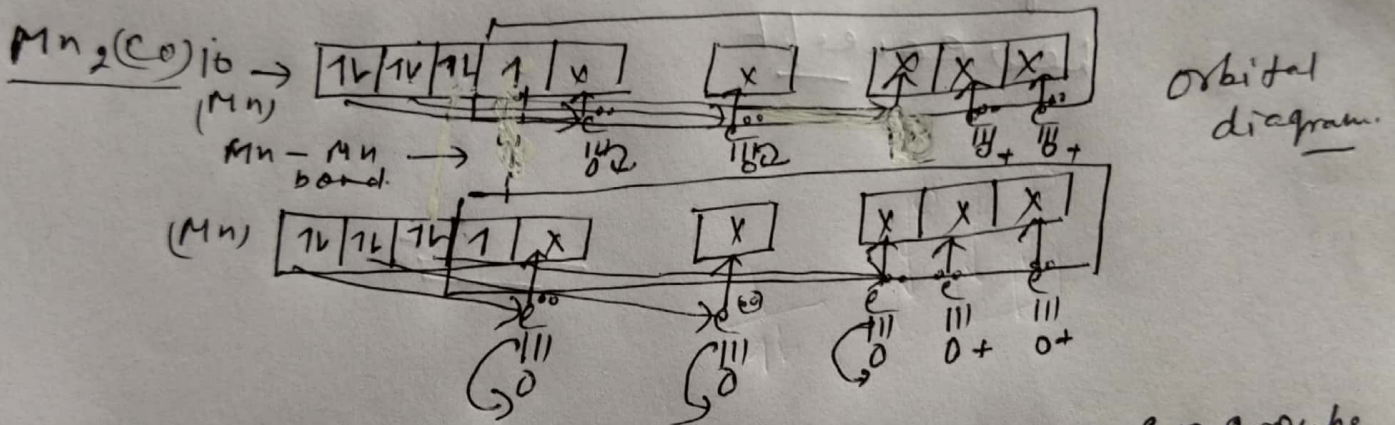
Since $Cr(CO)_6$ is diamagnetic in nature, Cr-e and e-o bond lengths have been found to be equal to 1.92 \AA and 1.16 \AA respectively. Each of the six CO groups are linked to the metal atom by a σ bond, out of six CO groups three are also linked by π bonds to the metal atom.

Structure of $Mn_2(CO)_{10}$, $Tc_2(CO)_{10}$ and $Re_2(CO)_{10}$ molecules

All these molecules have the same structure. As an example let us consider the structure of $Mn_2(CO)_{10}$.
 electronic configuration of manganese is



d^2sp^3 hybridisation

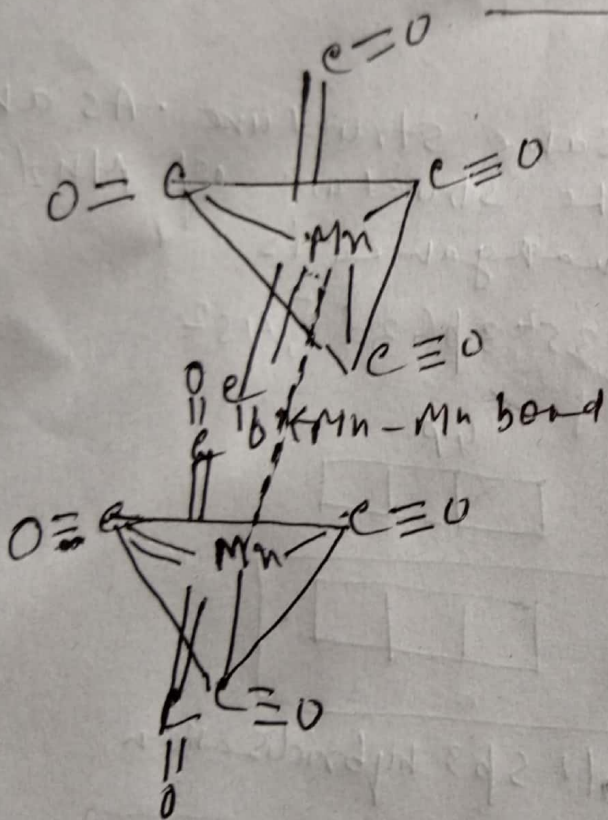


This diagram clearly shows that three CO groups form $Mn-\pi C \equiv O$ and two CO groups form $Mn-C \equiv O$ type of bonding. One electron of each d^2sp^3 -hybrid orbital overlaps to form metal-metal bond.

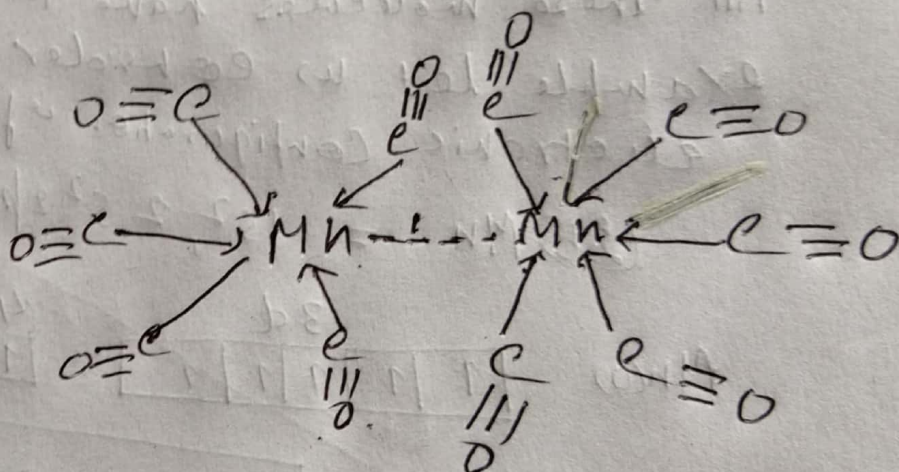
$Tc_2(CO)_{10}$ and $Re_2(CO)_{10}$ also have the $Mn_2(CO)_{10}$ structure. The metal-metal bond length in Mn, Re and Tc are - 2.92 \AA , 3.02 \AA and 3.04 \AA respectively.

Mn-atoms get paired and hence $Mn_2(CO)_{10}$ shows diamagnetic character. Infrared spectra shows that there is no absorption frequency in the neighbourhood of 1800 cm^{-1} indicating the absence of bridging CO group in the molecule. X-ray diffraction analysis shows that there is direct M-M-bonding in the molecule.

Orbital diagram of $Mn_2(CO)_{10}$



new concept



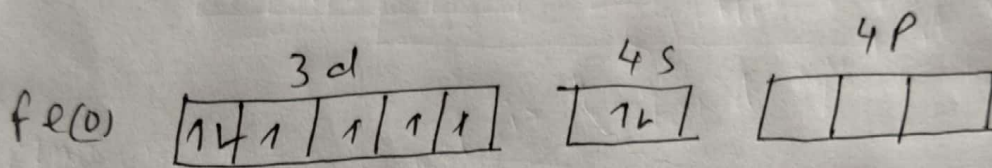
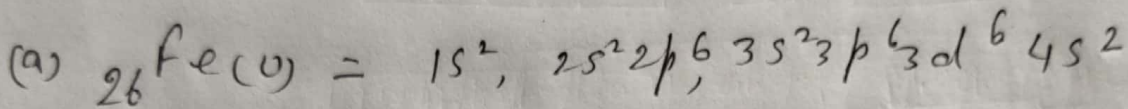
old concept

Structure of $Fe_2(CO)_9$ molecule

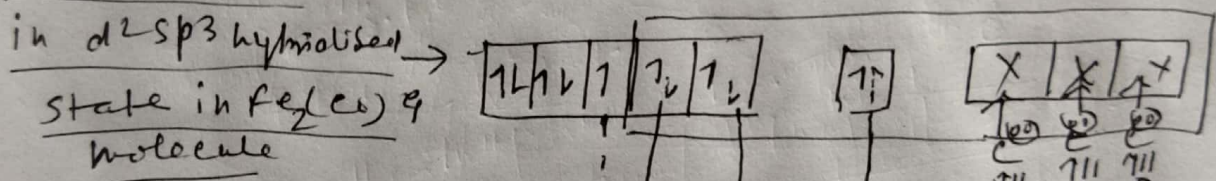
On the basis of IR and X-ray studies, it is revealed that $Fe_2(CO)_9$ molecule consists Fe-Fe δ -bond and there are two types of CO molecules e.g.

- (i) Terminal M-C \equiv O groups (monomeric carbonyls)
- (ii) Ketonic bridge group $\begin{matrix} M \\ | \\ M-C=O \end{matrix}$

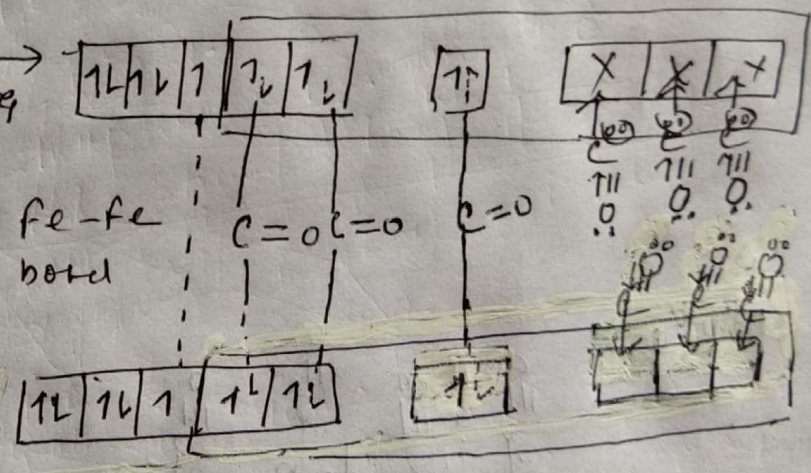
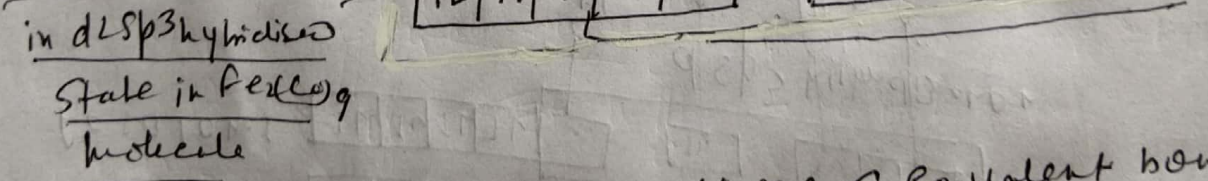
electronic configuration of Fe is:



(b) One Fe-atom



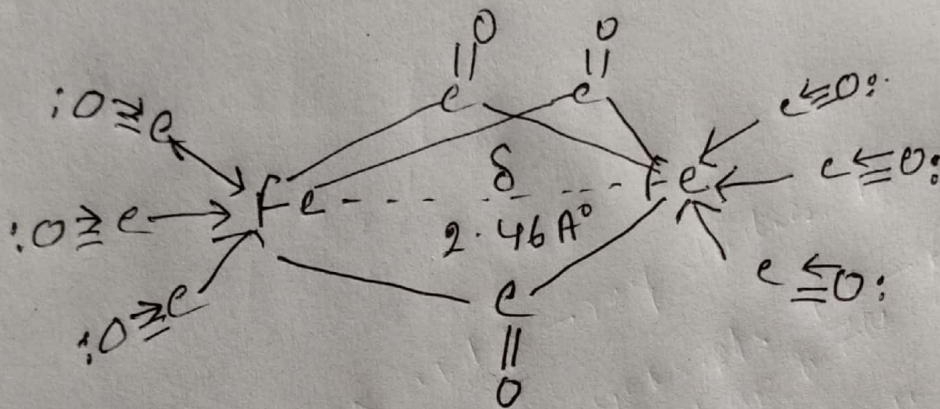
Other Fe-atom



Each iron atom forms three σ covalent bond and three bridging CO groups. In the molecule there is a Fe-Fe bond (molecule has no unpaired electron) Fe-Fe bond distance is quite short (2.64 \AA). One single bond between two Fe-atom. Since this bond is produced by the weak coupling of the unpaired electrons present in two 3d orbitals of two Fe atoms, it is called

Called fractional single bond and is represented as $Fe \cdots Fe$. This bond is a δ bond. The charge distribution ^{in this bond} is not symmetrical. This bond is longer in length than the normal single $Fe-Fe$ bond. $Fe_2(CO)_9$ is diamagnetic and obeys EAN or inert gas rule.

Structure of $Fe_2(CO)_9$ molecule



Bridging structure

Bond structure of $Fe_3(CO)_{12}$

$Fe_3(CO)_{12}$ molecule in solid state is formed by the replacement of one of the bridging CO group in $Fe_2(CO)_9$ by the unit $Fe(CO)_4$, the third Fe atom being equidistant from the other two.

