Application of 18-electron rule

(i) To explain the stability of transition metal organometallic complexes:

$V(CO)_6$ vs $[V(CO)_6]^-$

DIY

(ii) Prediction of the number of metal metal bonds in polynuclear complexes:

| Sl. No.	Molecule	Total valence electron(s) (TVE) [A]	$(18 \times n) - A$ [B] [n=no. of the metals in the complex]	Total M–M bonds $(\frac{B}{2})$	Bonds per metal
[i]	$Fe_2(CO)_9$	34	36−34=2	$\frac{2}{2}=1$	$\frac{34}{2}=17; 1$
[ii]	$Fe_3(CO)_{12}$	48	54−48=6	$\frac{6}{2}=3$	$\frac{48}{3}=16; 2$
[iii]	$Co_4(CO)_{12}$	60	72−60=12	$\frac{12}{2}=6$	$\frac{60}{4}=15; 3$
[iv]	$Ir_4(CO)_{12}$	60	72−60=12	$\frac{12}{2}=6$	$\frac{60}{4}=15; 3$
[v]	$(\eta^4-C_4H_4)_2Fe_2(CO)_3$	30	36−30=6	$\frac{6}{2}=3$	$\frac{30}{2}=15; 3$

(iii) Possibility of dimerization or polymerization:

$Mn(CO)_5$ bearing 17 electron complexes, undergo dimerization to form $Mn_2(CO)_{10}$ to maintain 18 electron rule.

(iv) Extensive study of different reaction of organometallic compounds viz. oxidative addition, reductive elimination, insertion etc. are well understood from the concept of 18-electron rule.

Limitations of 18-e rule:

(i) 18-electron rule works well for the low-valent metals with strong π-acceptor ligands. Therefore this rule is not applicable to organometallic compounds of main group metals as well as those of lanthanide and actinide metals. Moreover this rule often breaks down for early and late d-block metals.

(ii) 18 electron rule fails to explain the binding mode of coordinated ligands (example, coordinated CO ligand). According to 18 electron rule $Mn_2(CO)_{10}$ has two possible structures:
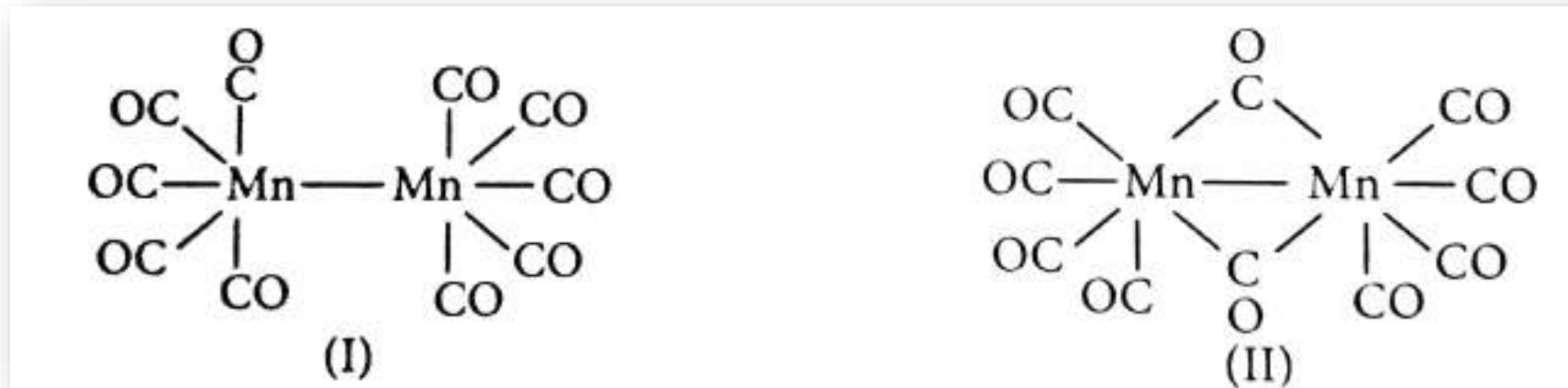

In the above example, both structure satisfy the 18 electron rule, but final structure can be drawn from the stretching frequency data of the coordinated CO. From stretching frequency data of coordinated CO Structure I is the final structure of $Mn_2(CO)_{10}$

(iii) The 18 electron rule fails when bonding of organometallic clusters of moderate to big sizes (six metal atoms and more) are considered. The bonding of clusters and their stabilities are therefore considered under other electron counting methods.

(iv) d^8-transition metal has a tendency to form square planar 16-electron complexes. It is well known that square planar 16 electron complexes of d metals result in completely filled orbitals, except the high energy $d_{x^2-y^2}$ orbital. This can happen for the d metals of groups 8-11. Group 8 metals shows the least and group 11 the highest tendency to become 16e. When these metal are 16e, they normally becomes square planar complexes viz. $[PtCl_4]^{2-}$, $[AuMe_4]^-$, $RhClL_3$ (L=PR_3)

Late transition metals with d^8 electronic configuration eg. Rh(I), Ir(I), Pd(II), Pt (II) have a tendency to form square plannar 16VSE (Valance Shell Electron) complexes. Similarly, d^{10} complexes tend to form trigonal 16 VSE complexes. As the atomic number increases, the d-shell is stabilized (Lowers in energy). The occupied d_z^2 orbital (perpendicular to the plane) is no longer involved in ligand bonding. (Electronic effect)
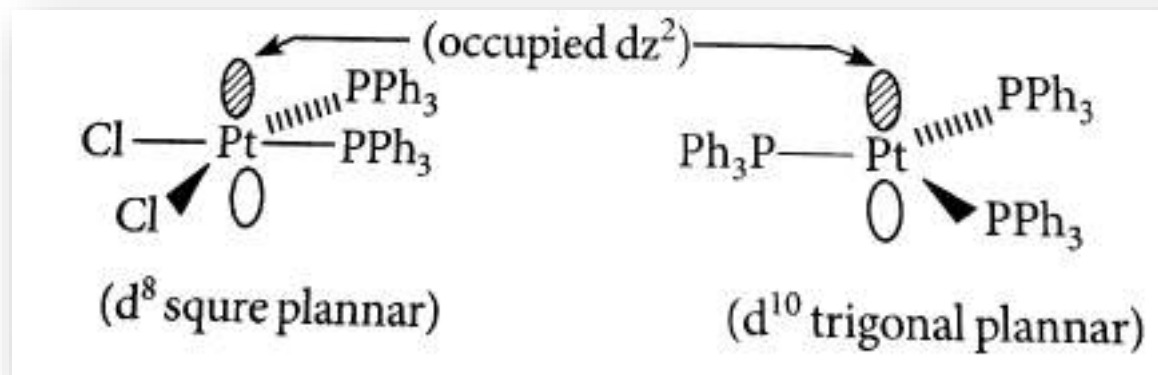
$(d^8$ squre plannar) $(d^{10}$ trigonal plannar)

Transition metal organometallic compounds mainly belong to any of the three categories.
Class I : Complexes for which the number of valence electrons do not obey the 18 VSE (valence shell electron) rule.
Class II : Complexes for which the number of valence electrons do not exceed 18
Class III: Complexes for which the valence electrons exactly obey the 18 VE rule.

It has been observed that 18-electron rule is not strictly obeyed. There are so many complexes with more than and fewer than 18 outer shell electrons are fairly common. We can explain stability of organometallic compounds from the concept of the **molecular orbital description** of bonding in complexes for **octahedral stereochemistry**. In an octahedral complex, all of the bonding orbitals (a_{1g}, t_{1u}, e_g and t_{2g}) are fully occupied and all of the antibonding orbitals are empty. Since there are nine bonding molecular orbitals, this will require 18 electrons, as predicted by the 18-electron rule.
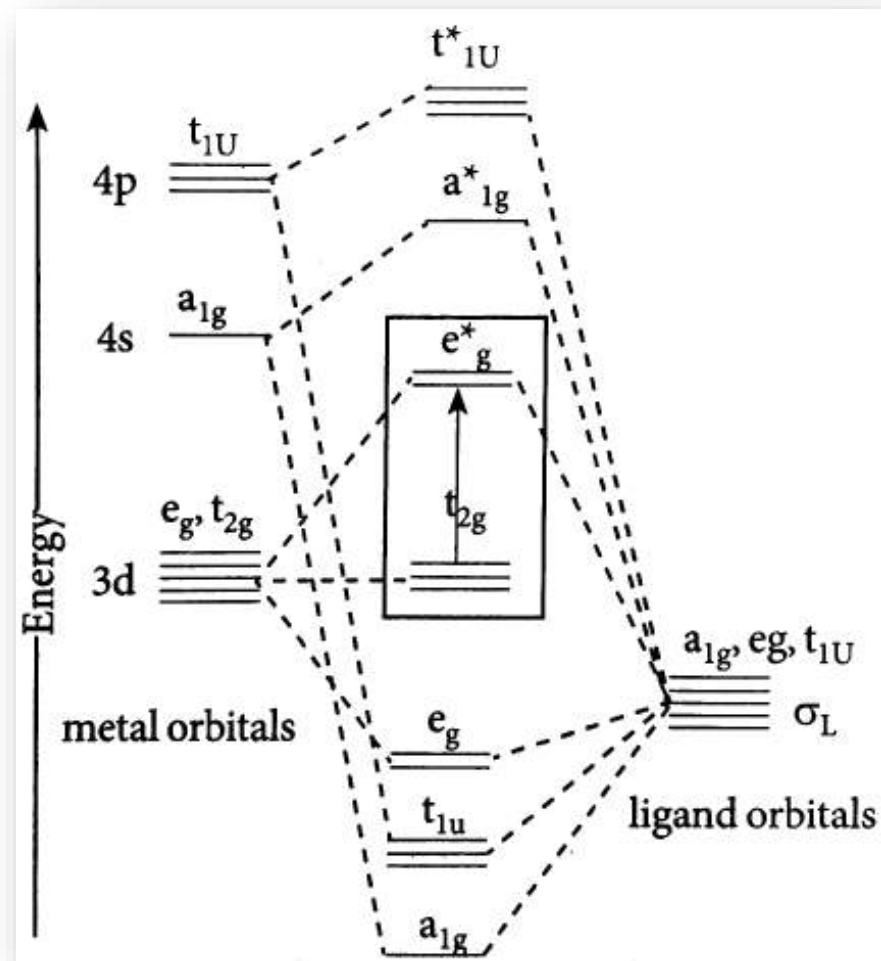
Class I: Δ_0 small; VSE > or < 18, M = First row transition metal.

In **class I complexes**, the Δ_0, is small and often applies to 3d metals and σ ligands at lower end of the spectrochemical series (weak field ligand).

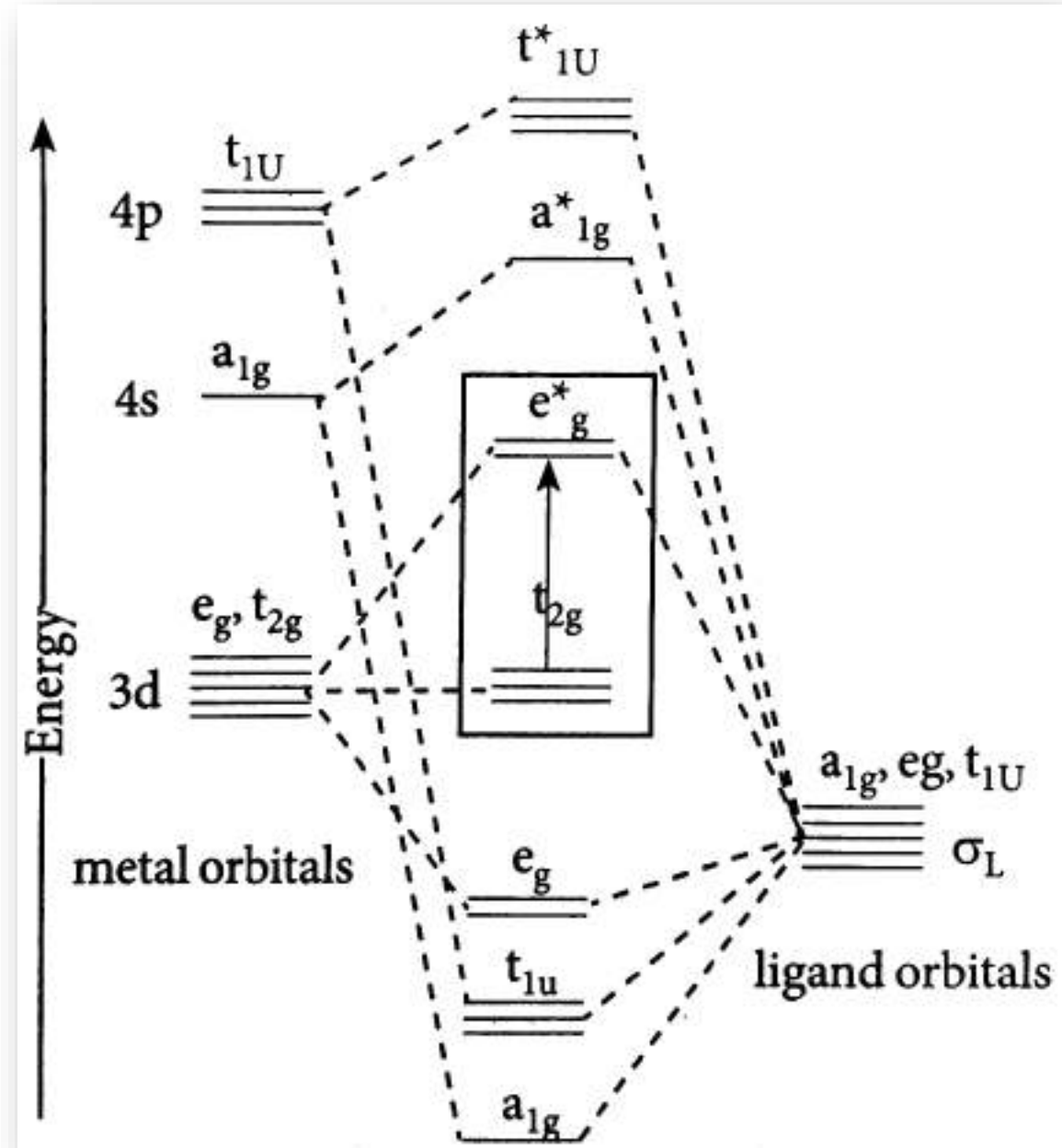In this case, t_{2g} orbital is non-bonding in nature and may be occupied by 0-6 electrons.

The e_g^* orbital is weakly antibonding and may be occupied by 0-4 electrons. As a result, 12-22 valence electron count may be obtained for this class of compounds.

Example-
$[Co(H_2O)_6]^{2+}$: 19 electrons,
$[Co(NH_3)_6]^{3+}$:18 electrons,
$[TiF_6]^{2-}$: 12 electrons.

Class II: VSE ≤ 18, M = 2nd/3rd row transition metal.

In class II complexes, Δ_0 spliting is large and it is applicable to 4d and 5d transition metals having high oxidation state and for σ bonding ligands in the intermediate and upper range of the spectrochemical series.
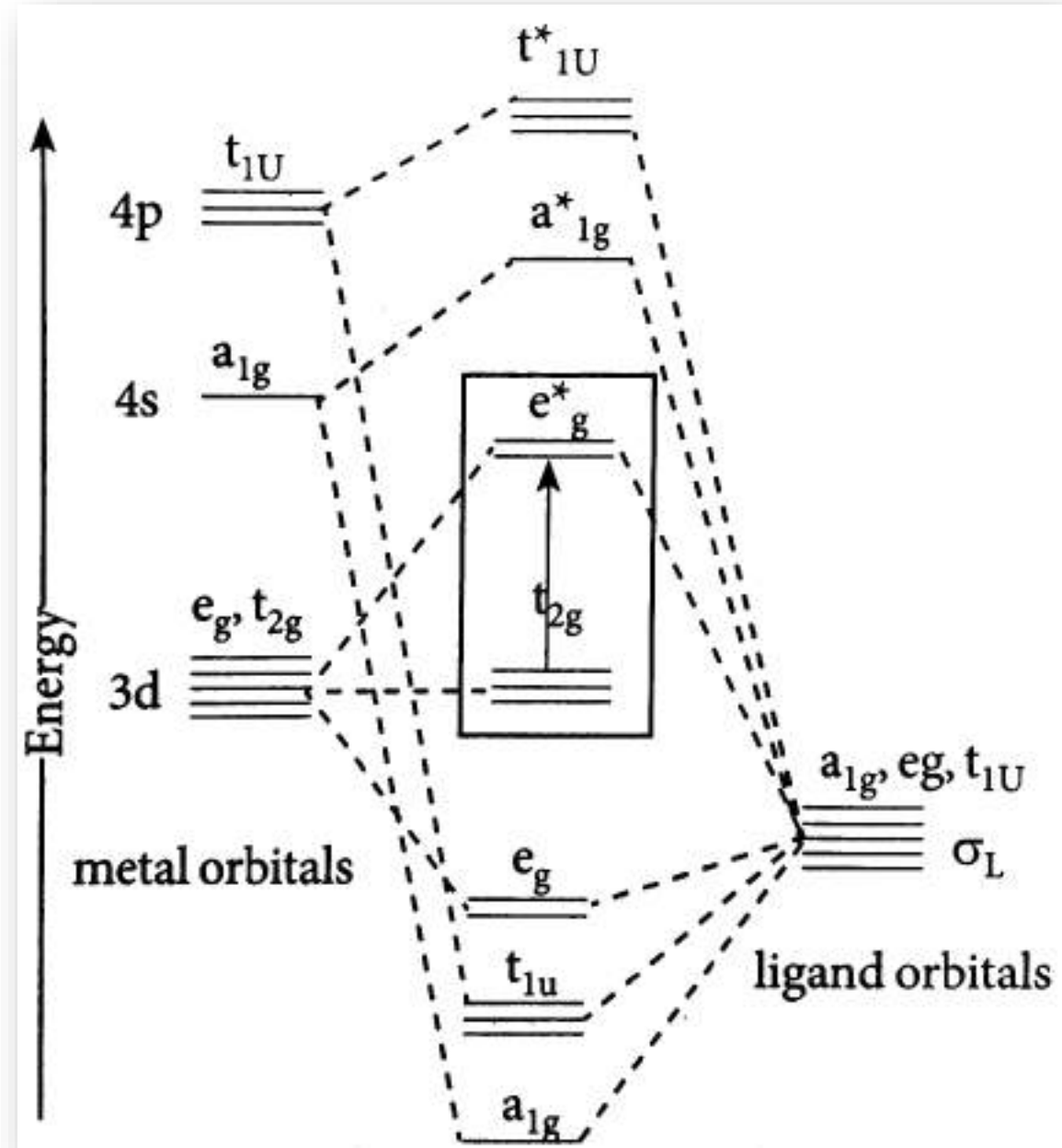
In this case, t_{2g}, orbital is essentially non-bonding in nature and can be filled by 0-6 electrons. The eg orbital is strongly antibonding and is not occupied at all.

Example:
WCl_6: 12 electrons,
$PtCl_4^{2-}$: 16 electron,
$[PtF_6]^{2-}$: 18 electrons.

Class III: VSE = 18 (organometallic complexes)

In this cases, Δ_0 splitting is the largest and is applicable to good σ-donor and π-acceptor ligands like CO, PF_3, alkenes or other ligands located at the upper end of the spectrochemical series.

The t_{2g} orbital becomes bonding owing to interactions with ligand orbitals and should be occupied by 6 electrons.

The e_g orbital is strongly antibonding and therefore remains unoccupied.

Examples:
$Fe(CO)_5$: 18 electrons
$\eta^5\text{-}CpCo(CO)_2$: 18 electrons

Note: Exceptions on steric ground: $(\eta^5\text{-}Cp)_2ZnCl_2$ (16 VSE), $V(CO)_6$: 17 VSE