

Crystal Field Theory

Spectroelectrochemical Series

$I^- < Br^- < S^{2-} < SCN^- < Cl^- < NO_2^- < N^{3-} < F^- < OH^- < C_2O_4^{2-} < O^{2-} < H_2O < NCS^- < CH_3C\equiv N < py < NH_3 < en < bpy < phen < NO_2^- < PPh_3 < CN^- < CO$

$Mn^{2+} < Ni^{2+} < Co^{2+} < Fe^{2+} < V^{2+} < Fe^{3+} < Co^{3+} < Mo^{3+} < Rh^{3+} < Ru^{3+} < Pd^{4+} < Ir^{3+} < Pt^{4+}$

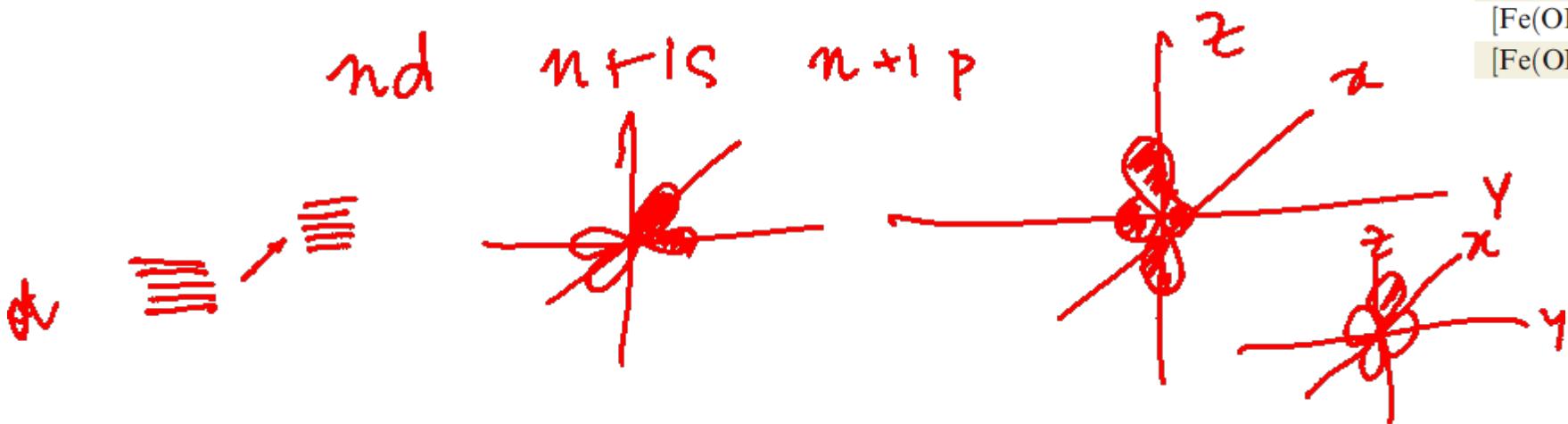
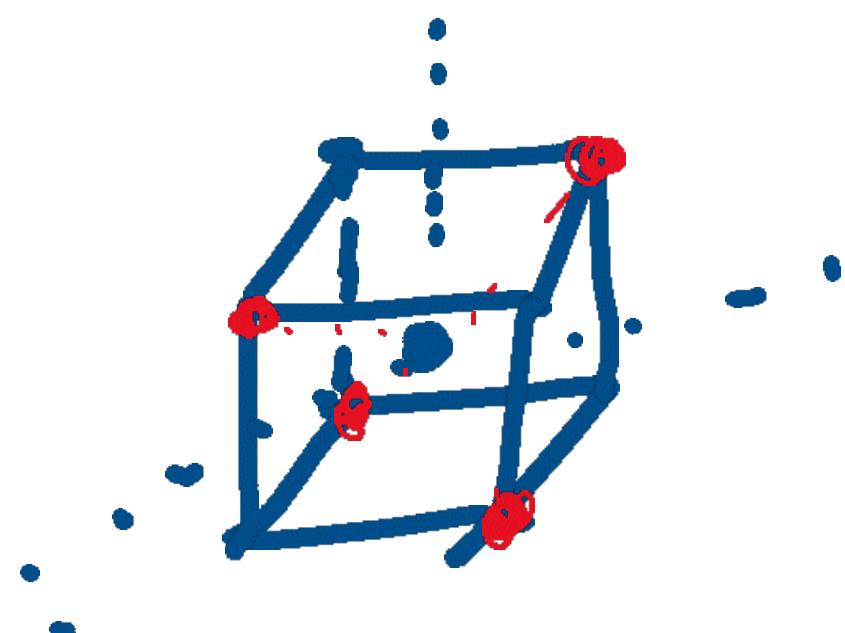


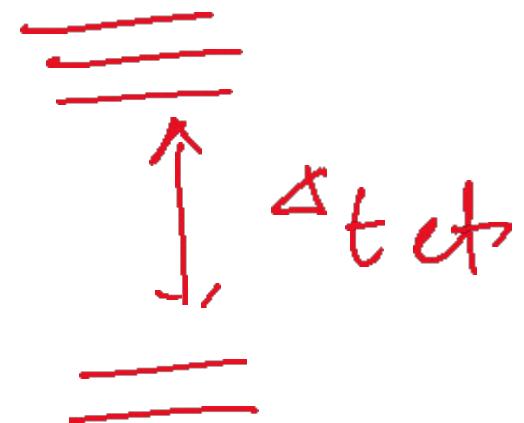
Table 20.2 Values of Δ_{oct} for some *d*-block metal complexes.

Complex	Δ / cm^{-1}	Complex	Δ / cm^{-1}
$[TiF_6]^{3-}$	17 000	$[Fe(\text{ox})_3]^{3-}$	14 100
$[Ti(OH_2)_6]^{3+}$	20 300	$[Fe(\text{CN})_6]^{3-}$	35 000
$[V(OH_2)_6]^{3+}$	17 850	$[Fe(\text{CN})_6]^{4-}$	33 800
$[V(OH_2)_6]^{2+}$	12 400	$[CoF_6]^{3-}$	13 100
$[CrF_6]^{3-}$	15 000	$[Co(\text{NH}_3)_6]^{3+}$	22 900
$[Cr(OH_2)_6]^{3+}$	17 400	$[Co(\text{NH}_3)_6]^{2+}$	10 200
$[Cr(OH_2)_6]^{2+}$	14 100	$[Co(\text{en})_3]^{3+}$	24 000
$[Cr(\text{NH}_3)_6]^{3+}$	21 600	$[Co(\text{OH}_2)_6]^{3+}$	18 200
$[Cr(\text{CN})_6]^{3-}$	26 600	$[Co(\text{OH}_2)_6]^{2+}$	9 300
$[MnF_6]^{2-}$	21 800	$[Ni(\text{OH}_2)_6]^{2+}$	8 500
$[Fe(OH_2)_6]^{3+}$	13 700	$[Ni(\text{NH}_3)_6]^{2+}$	10 800
$[Fe(OH_2)_6]^{2+}$	9 400	$[Ni(\text{en})_3]^{2+}$	11 500

Octahedral



4 coordinated



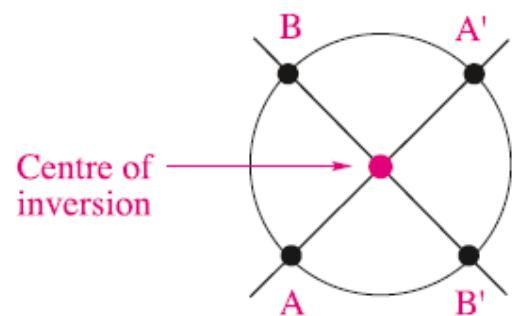
$$\Delta_O = \frac{4}{9} \Delta_{tet}$$

Simple symmetry concept

The two sets of d orbitals in an octahedral field are labelled e_g and t_{2g} (Fig. 20.3). In a tetrahedral field (Fig. 20.8), the labels become e and t_2 . The symbols t and e refer to the degeneracy of the level:

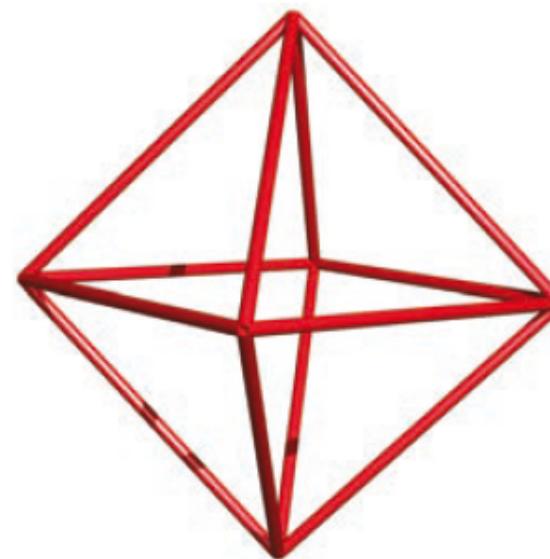
- a triply degenerate level is labelled t ;
- a doubly degenerate level is labelled e .

The subscript g means *gerade* and the subscript u means *ungerade*. *Gerade* and *ungerade* designate the behaviour of the wavefunction under the operation of *inversion*, and denote the *parity* (even or odd) of an orbital.

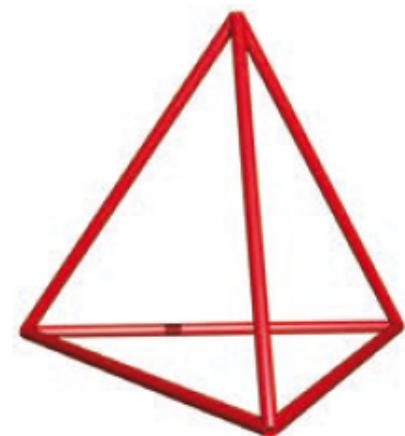


Point A is related to A' by passing through the centre of inversion. Similarly, B is related to B'.

The u and g labels are applicable *only* if the system possesses a centre of symmetry (centre of inversion) and thus are used for the octahedral field, but not for the tetrahedral one:

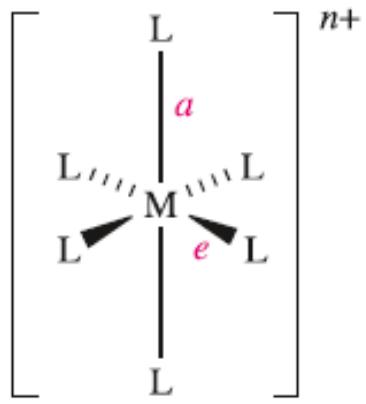


Octahedron has a centre of symmetry

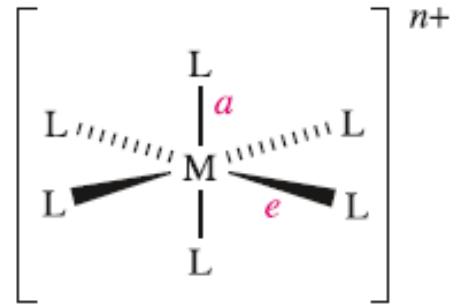


Tetrahedron has no centre of symmetry

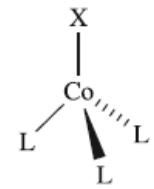
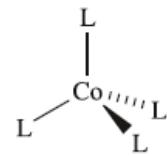
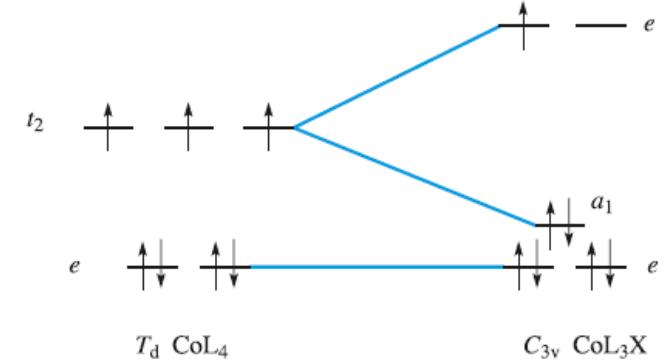
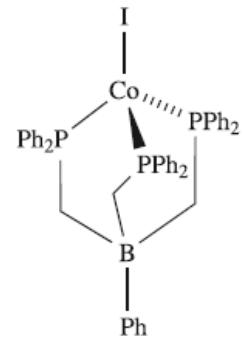
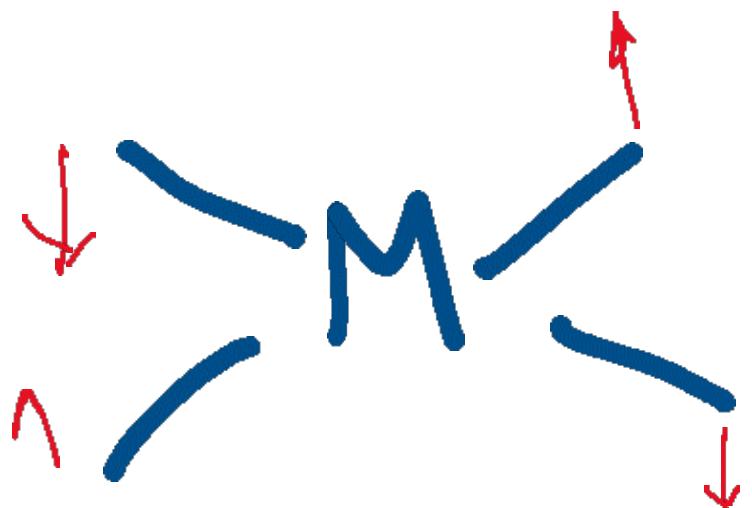
For more on the origins of symmetry labels: see Chapter 5.

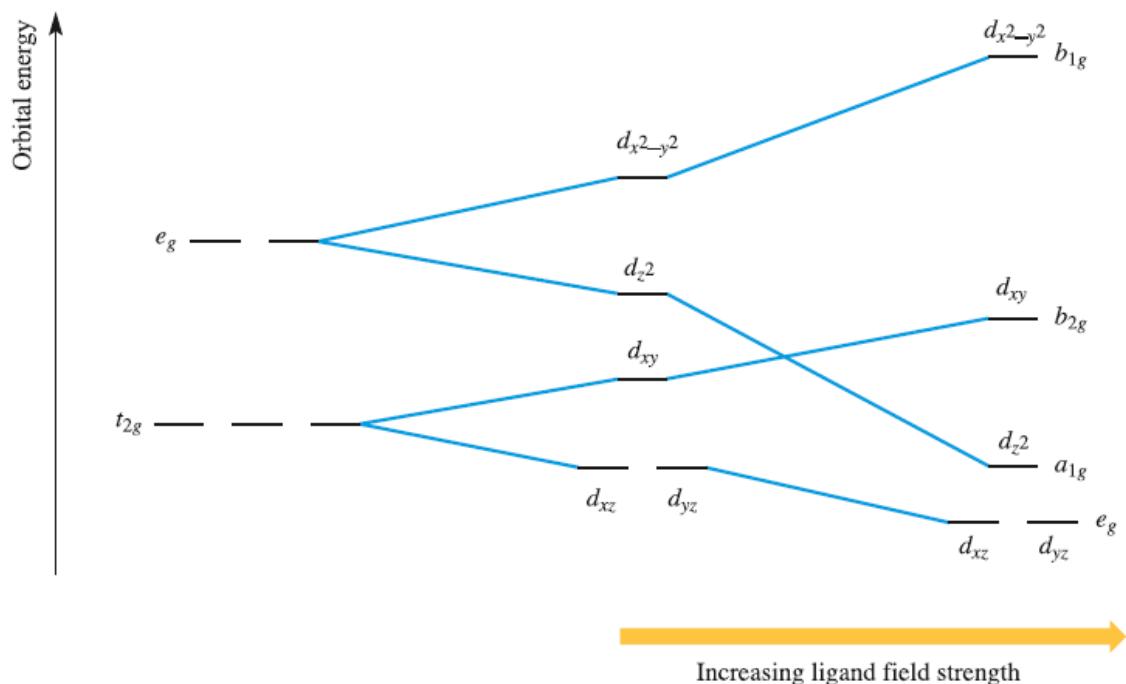
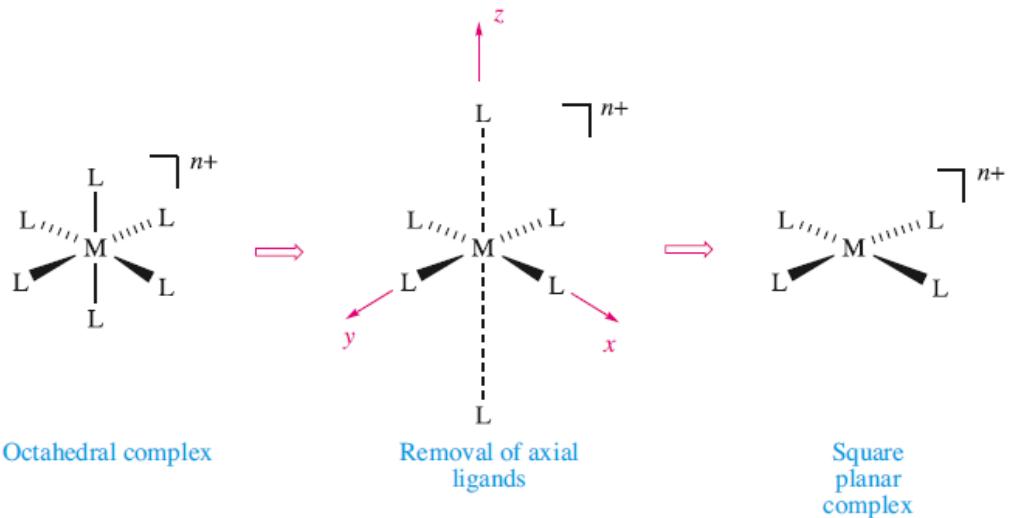


Bond length $a > e$

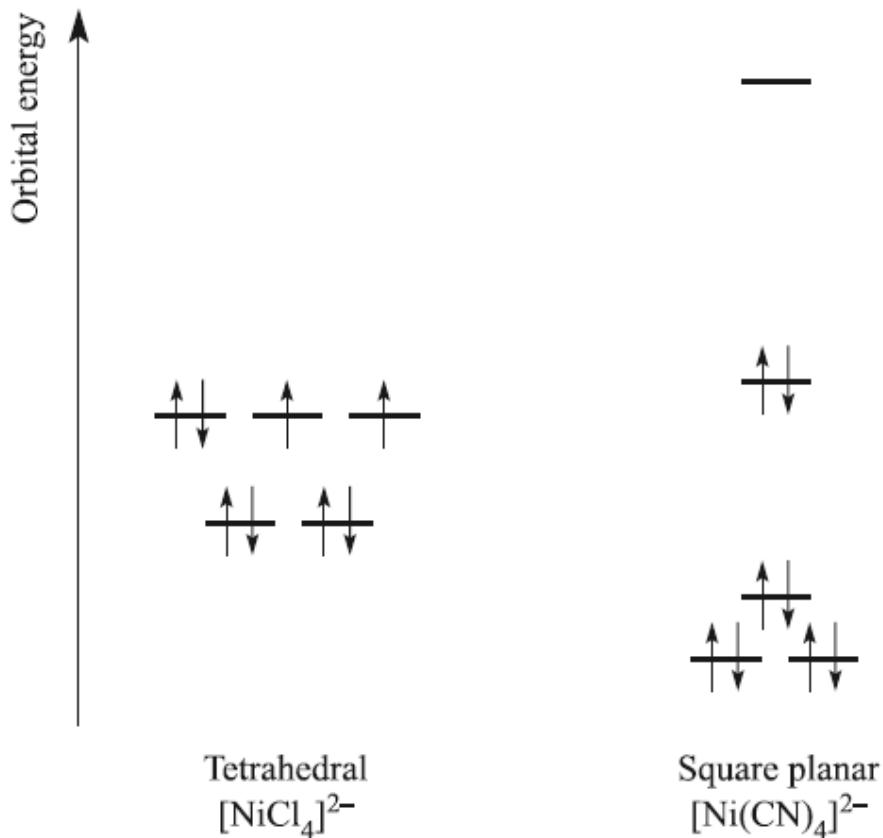


Bond length $a < e$

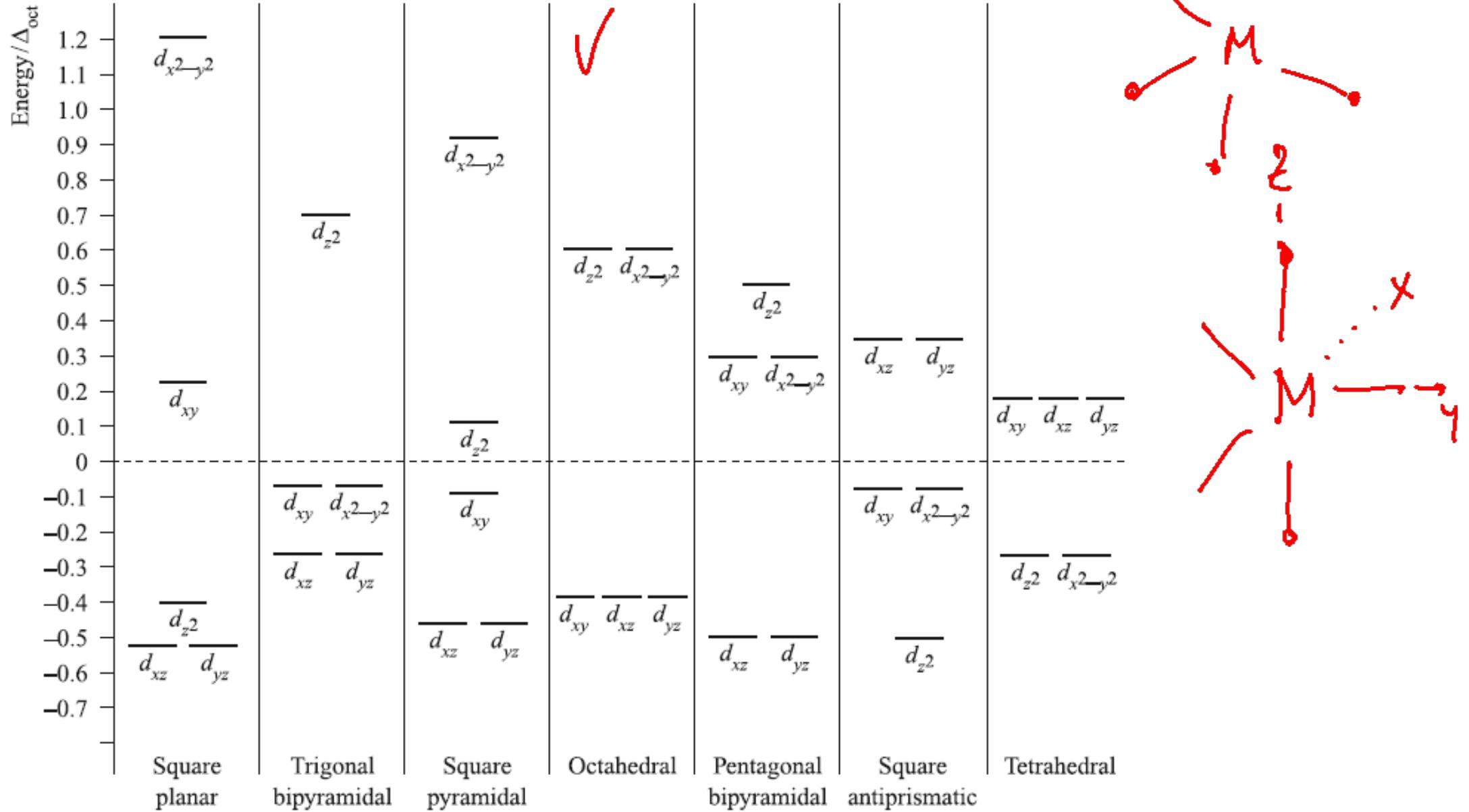




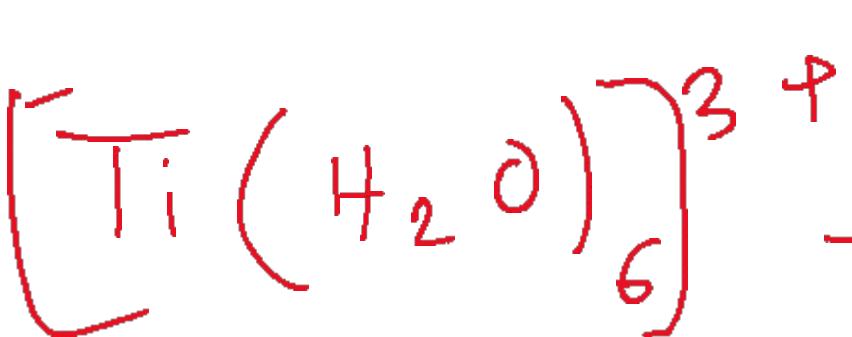
Consider the splitting diagrams shown in Fig. 20.11. For $[\text{Ni}(\text{CN})_4]^{2-}$ and $[\text{NiCl}_4]^{2-}$, the eight electrons occupy the d orbitals as follows:



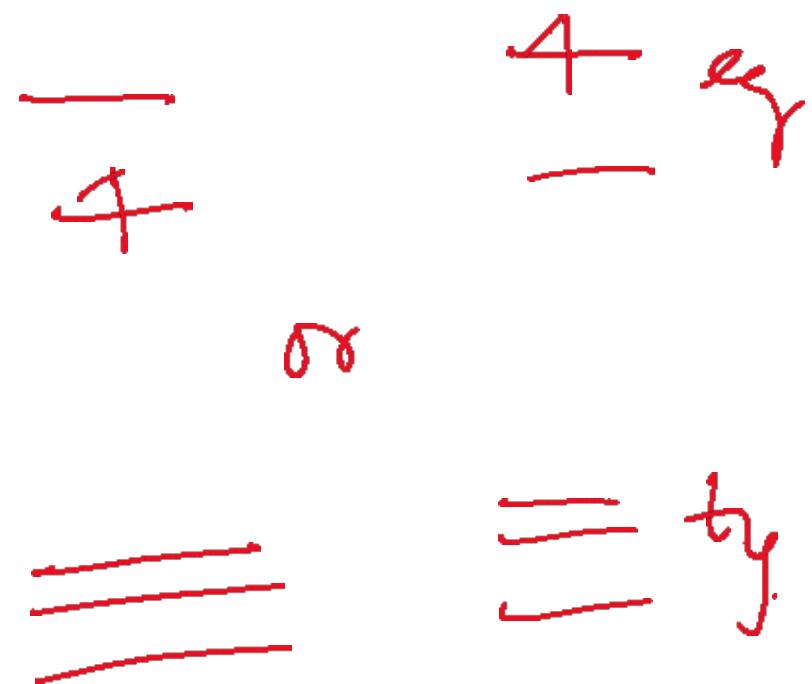
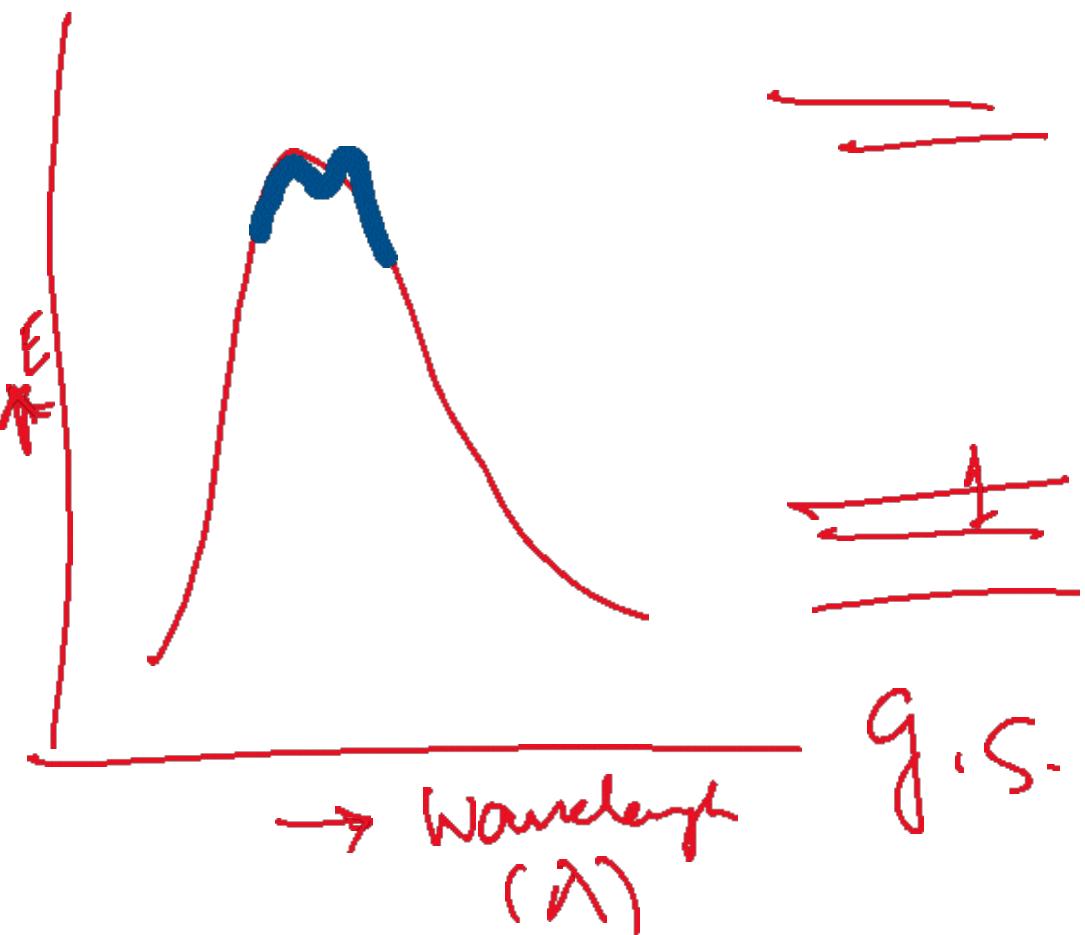
Thus, $[\text{NiCl}_4]^{2-}$ is paramagnetic while $[\text{Ni}(\text{CN})_4]^{2-}$ is diamagnetic.



d^1



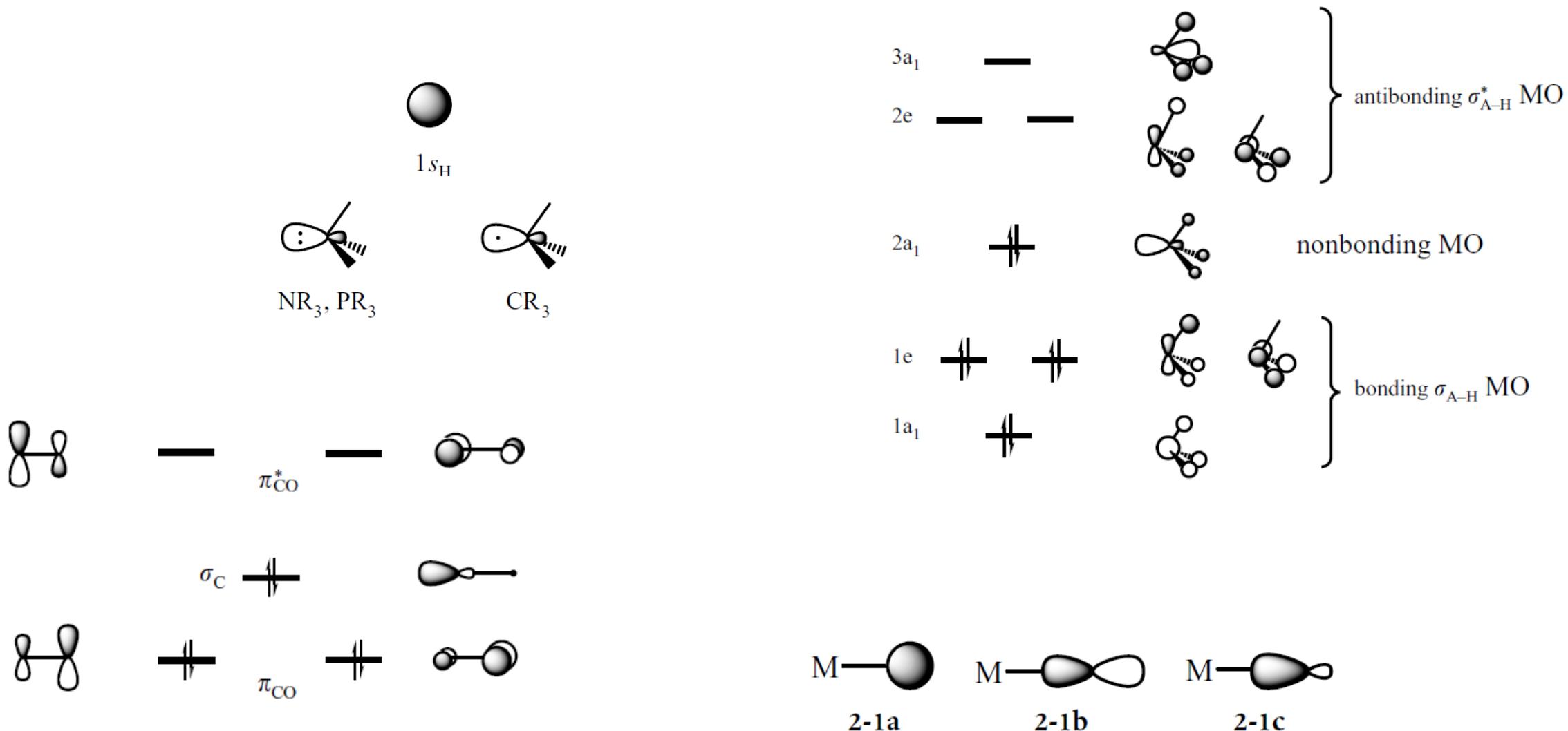
Electronic Spectra

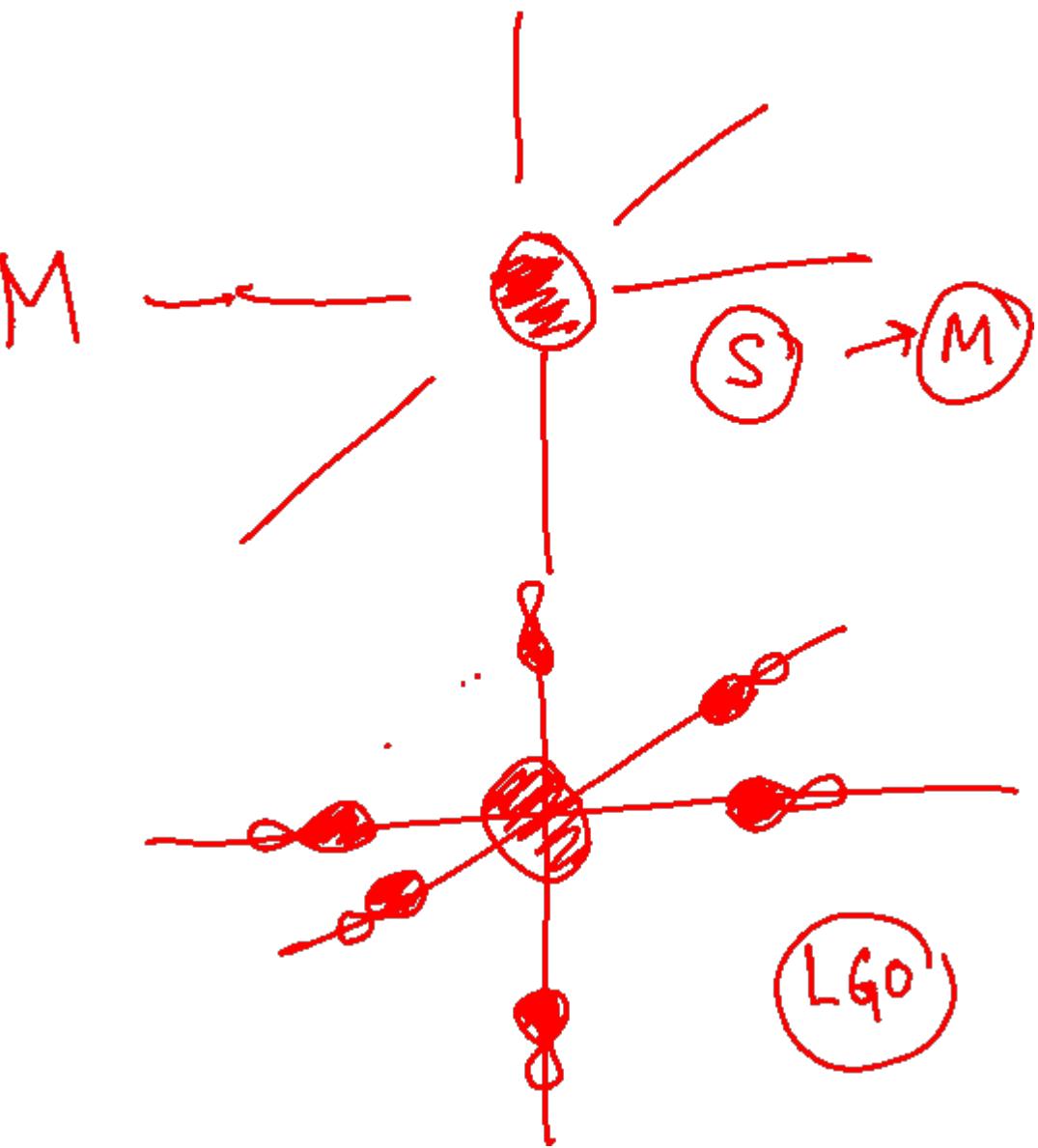
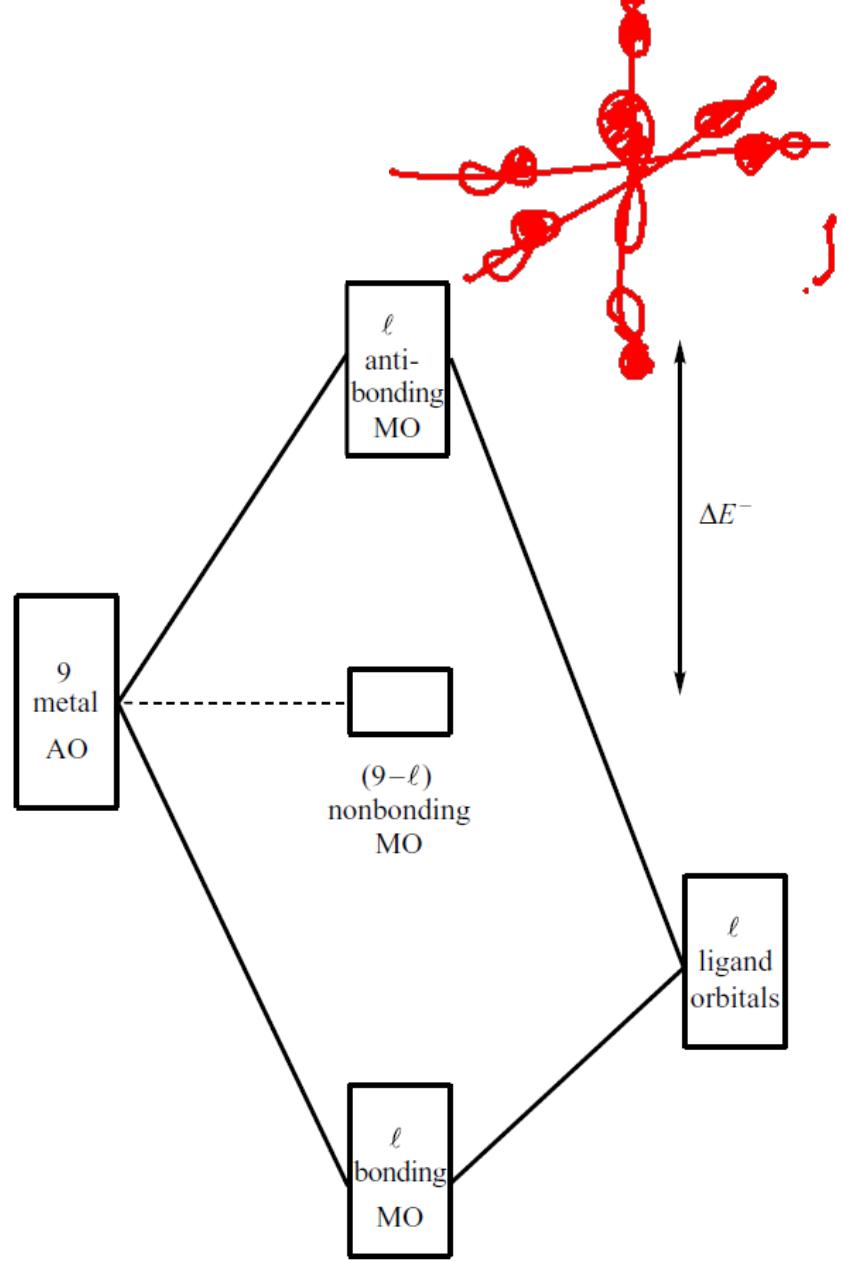


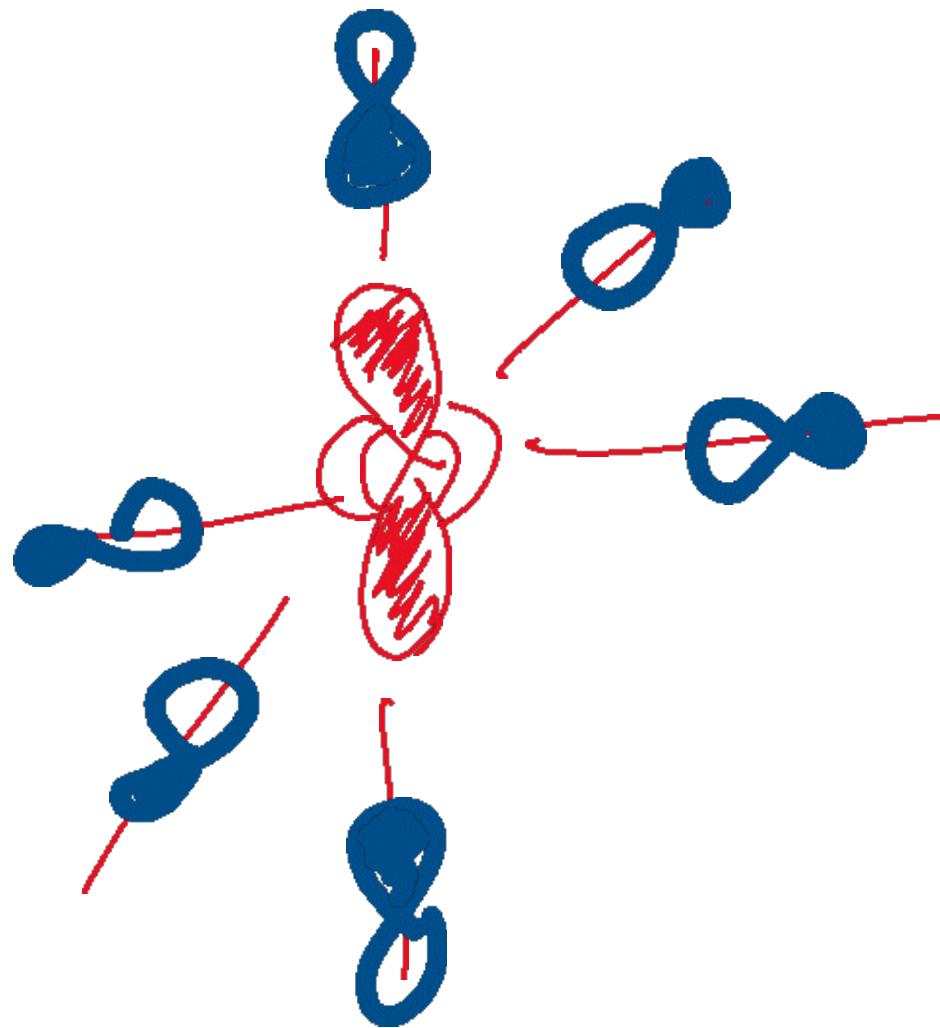
g.s.

Molecular orbital theory: octahedral complexes

Shape of Ligand Orbitals







Octahedral Complex

Tetrahedral Complex

Square-Planar Complex

Spectroelectrochemical series