(34) **Today**

Section 10.1 Experimental Data Used in when Describing Bonding in Coordination Compound

Section 10.2 Crystal Field Theory

Next Class (35)

Section 10.2 Crystal Field Theory

Section 10.3 Ligand Field Theory

The Final is Scheduled for Wednesday, December 20 from 10:10 to 12:10

Hand in reworked test 3 at the final.

Crystal Field Theory

Electrostatic approach where d orbital splitting is explained using an ionic model

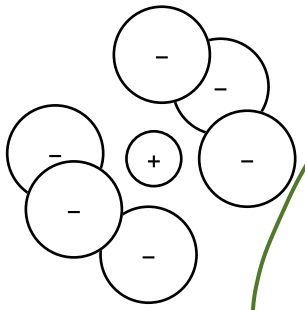
e^- ligands are attracted like ions to the ⊕ metal

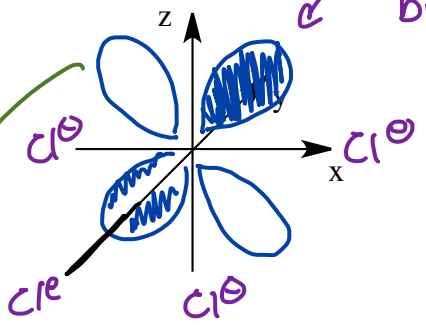
the e^-'s on the ligands repel the e^-'s in the metal d orbitals

$e^- - e^-$ repulsion changes the energy of the e^-'s in the metal d orbitals

Ligand Field Theory

MO approach that describes bonding in terms of ligand HOMO/LUMO interactions with metal orbitals

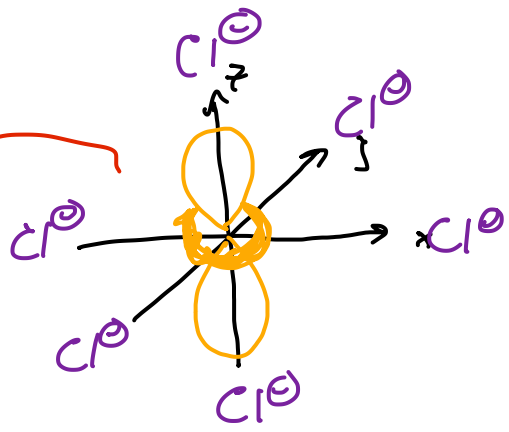




T_{2g} d_{xz}

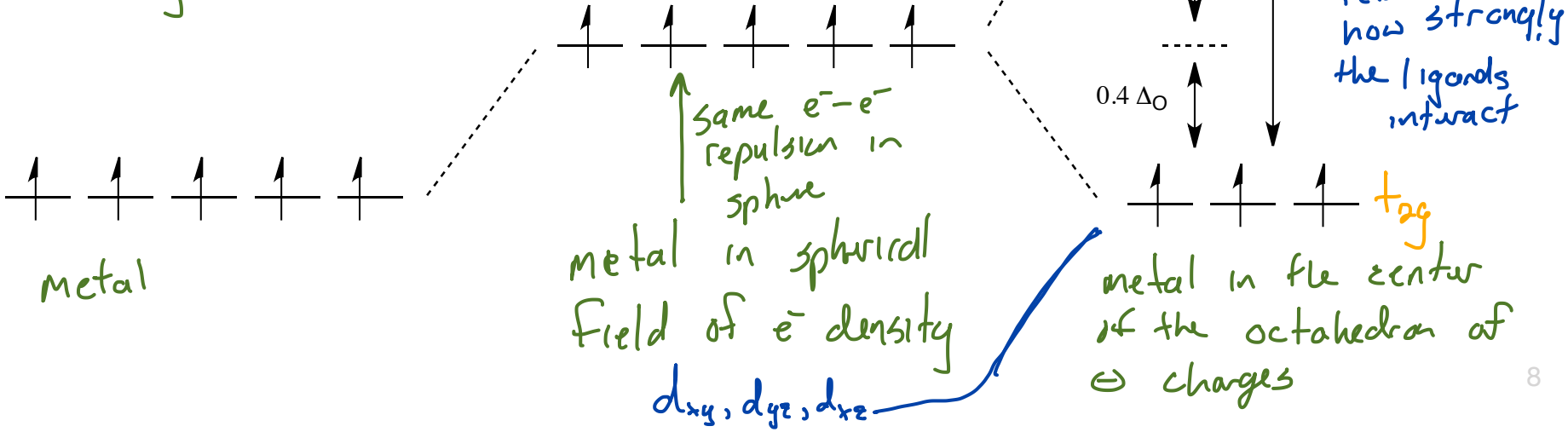
Cl⊖ hidden behind orbital

e⁻'s in the d_{xz} orbital experience no (or less) e⁻ – e⁻ repulsion with the Cl⊖ e⁻'s because they are farther away



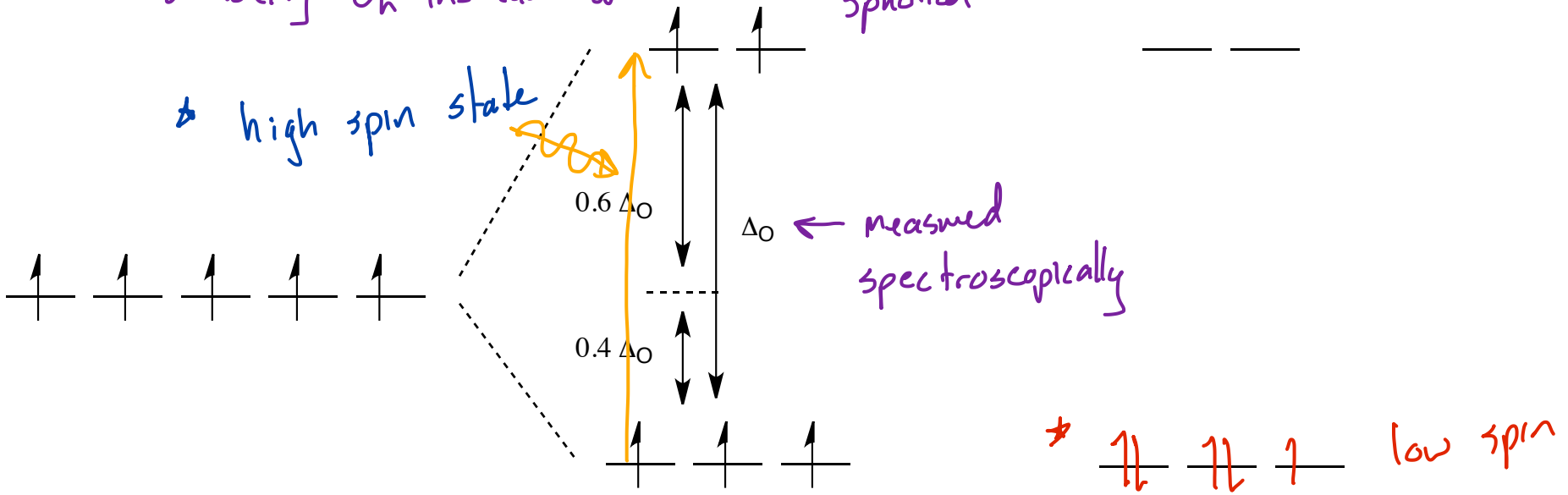
E_g d_{z^2}

e⁻'s in the d_{z^2} orbital would experience greater e⁻–e⁻ repulsion



Crystal Field Stabilization Energy compares the energy of the electrons in a spherical field to the energy of the electrons in an octahedral field

How much stabilization do we get due to the field being O_h instead of spherical



CFSE = $E_{Octahedral}$ - $E_{spherical}$

$E_{spherical}$ = 0 + pairing energy

$E_{octahedral}$ = (# e^- x -0.4Δ_O) + (# e^- x 0.6Δ_O)

$-1.2\Delta_O$ + $1.2 \cdot \Delta_O$

$3 \times -0.4\,\Delta_O$ $2 \times 0.6\Delta_O$

The energy of the photon needed to excite an e^- from the low to high E d orbitals gives us Δ_O.

* The ligand interaction was weak so the metal is in a high spin state
* The ligand interaction is strong enough that pairing e's becomes favorable as compared to occupying the higher E e_g orbitals

Compares the energy of the metal ion in a spherical field of electron density to the energy of the metal ion in an octahedral field (or the appropriate field for the geometry of the complex)

Δ_O can be determined using spectroscopic techniques

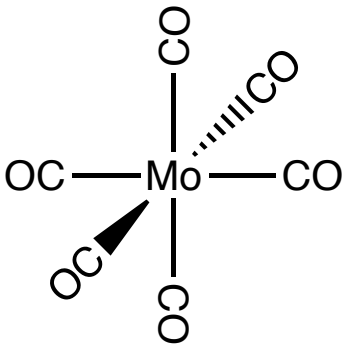
Number of unpaired spins can be determined by using magnetic spectrometry

Finding the Δ_o and electronic structure of the metal allows us to compare the relative effect that ligands have on a metal

Does not account for stabilization due to bonding

organometallic complex

covalent bond between C + Mo



O_h

$:C\equiv O:$

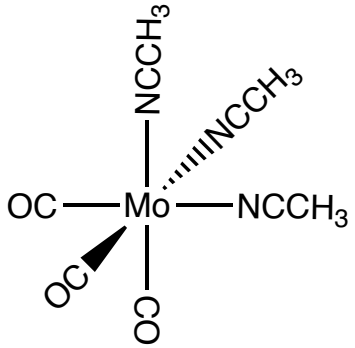
↑ ↑ and π bonds

lone-pair e⁻'s

$:NH_3$

↑

lone-pair e⁻'s



pseudo-O_h

$:N\equiv C-CH_3$

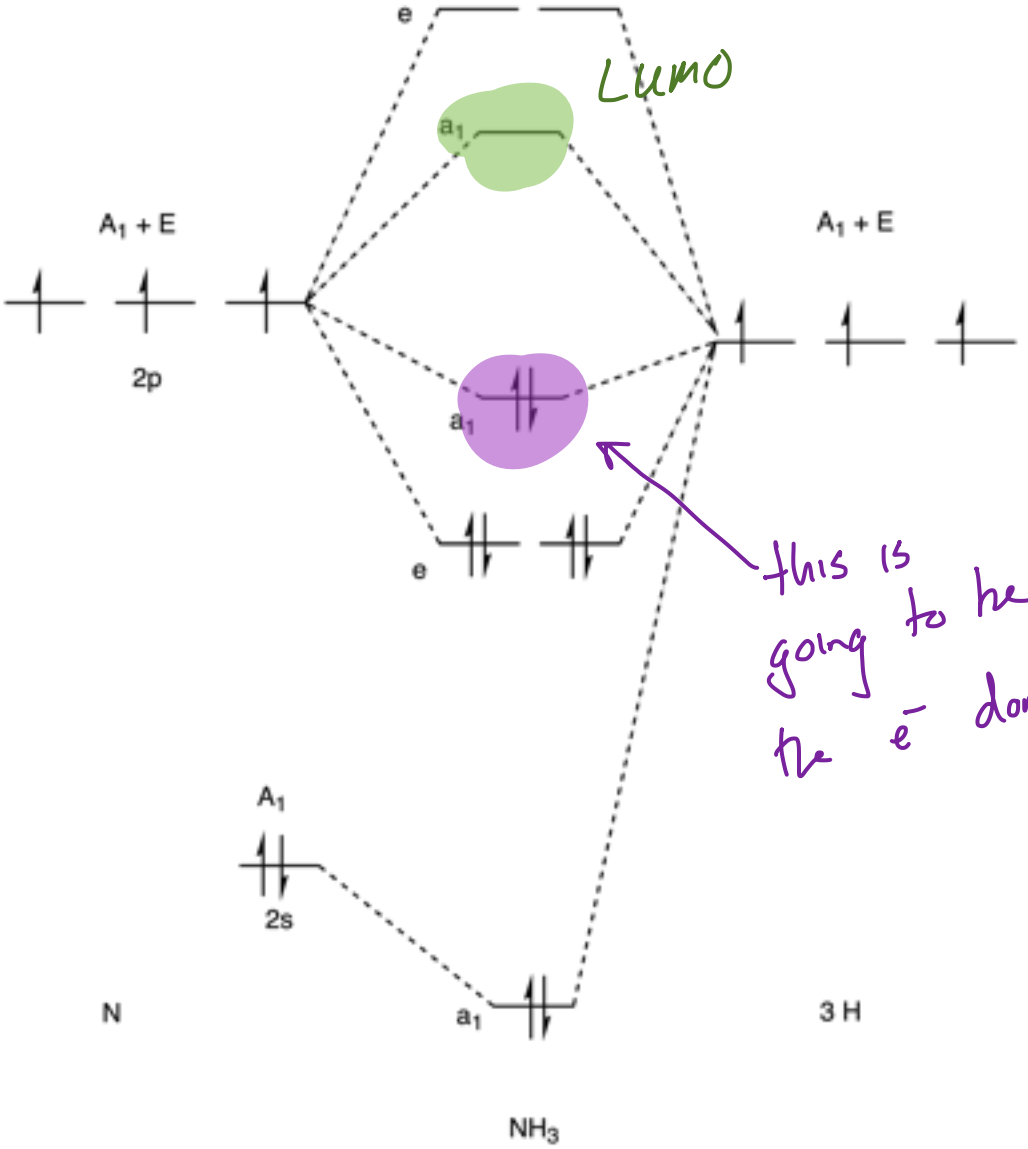
↑ ↑ and π bonds

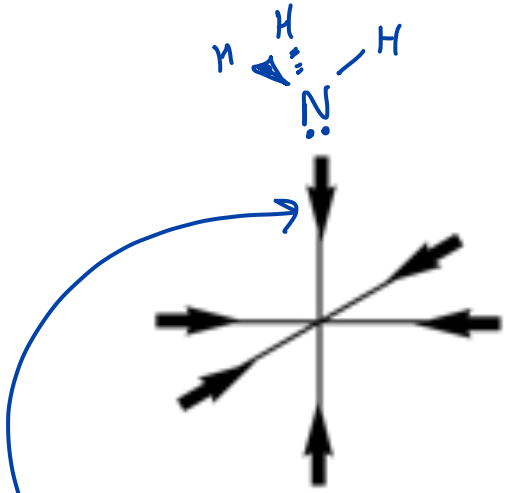
metal d orbitals have E_g + T_{2g} symmetry

O_h	E	8 C_3	6 C_2	6 C_4	3 C_2*	i	6 S_4	8 S_6	3 σ_h	6 σ_d	* (C_4^2)	
A_{1g}	1	1	1	1	1	1	1	1	1	1		$x^2 + y^2 + z^2$
A_{2g}	1	1	-1	-1	1	1	-1	1	1	-1		
E_g	2	-1	0	0	2	2	0	-1	2	0		($2z^2 - x^2 - y^2$, $x^2 - y^2$)
T_{1g}	3	0	-1	1	-1	3	1	0	-1	-1	(R_x, R_y, R_z)	
T_{2g}	3	0	1	-1	-1	3	-1	0	-1	1		(xy, yz, xz)
A_{1u}	1	1	1	1	1	-1	-1	-1	-1	-1		
A_{2u}	1	1	-1	-1	1	-1	1	-1	-1	1		
E_u	2	-1	0	0	2	-2	0	1	-2	0		
T_{1u}	3	0	-1	1	-1	-3	-1	0	1	1	(x, y, x)	
T_{2u}	3	0	1	-1	-1	-3	1	0	1	-1		

d_{z^2}

MO Diagram for NH_3





this bond has σ symmetry ... so

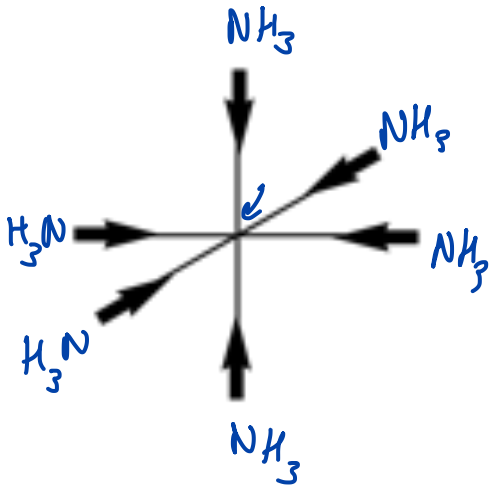
NH_3 is a σ e^- donor

To describe bonding the symmetry of the 6 SALC must be determined

metal d orbitals

no symmetry match with the metal d orbitals and these ligand SALCs

O_h	E	8 C_3	6 C_2	6 C_4	3 C_2*	i	6 S_4	8 S_6	3 σ_h	6 σ_d
A_{1g}	1	1	1	1	1	1	1	1	1	1
A_{2g}	1	1	-1	-1	1	1	-1	1	1	-1
E_g	2	-1	0	0	2	2	0	-1	2	0
T_{1g}	3	0	-1	1	-1	3	1	0	-1	-1
T_{2g}	3	0	1	-1	-1	3	-1	0	-1	1
A_{1u}	1	1	1	1	1	-1	-1	-1	-1	-1
A_{2u}	1	1	-1	-1	1	-1	1	-1	-1	1
E_u	2	-1	0	0	2	-2	0	1	-2	0
T_{1u}	3	0	-1	1	-1	-3	-1	0	1	1
T_{2u}	3	0	1	-1	-1	-3	1	0	1	-1



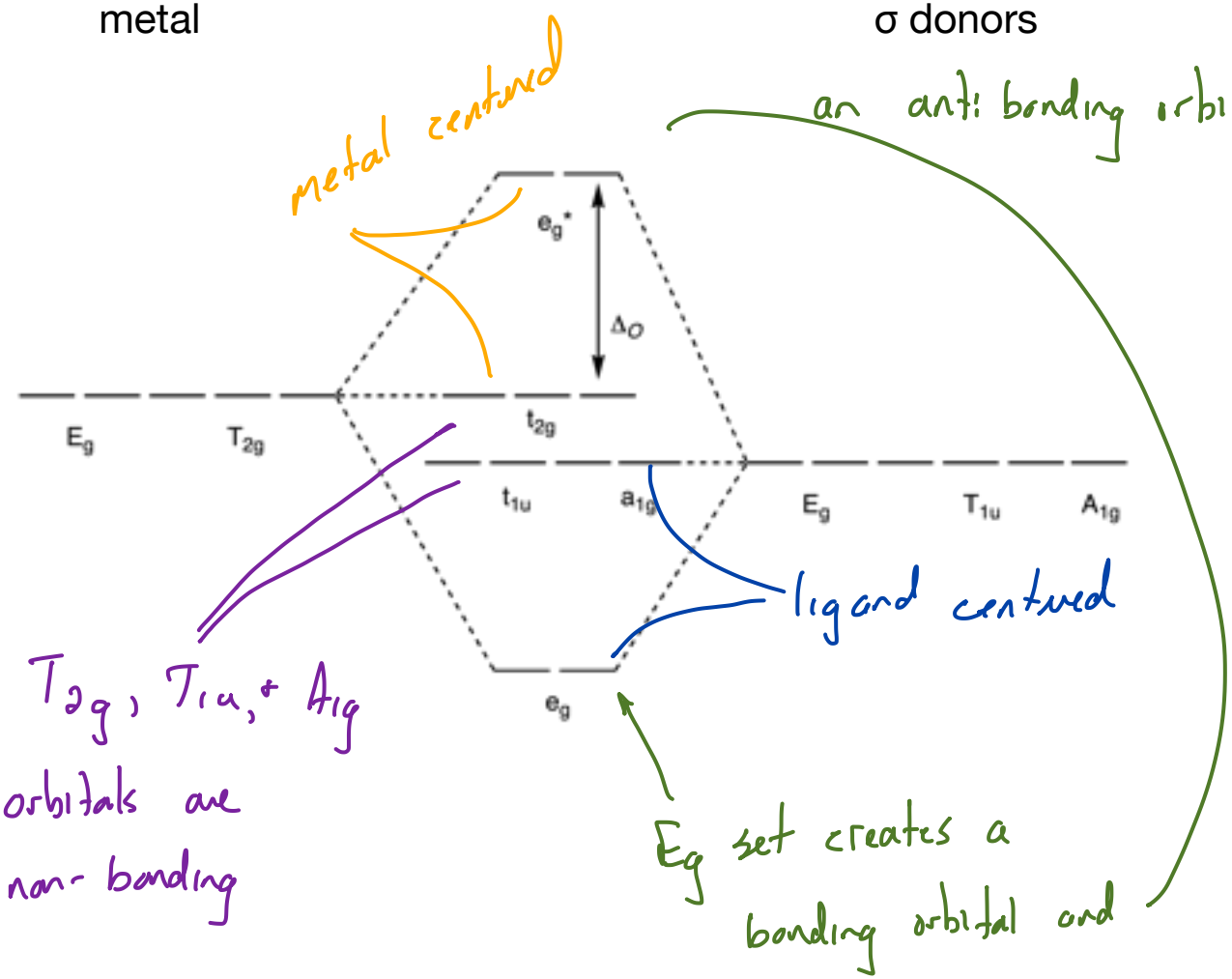
Γ 6 0 . . . . . .

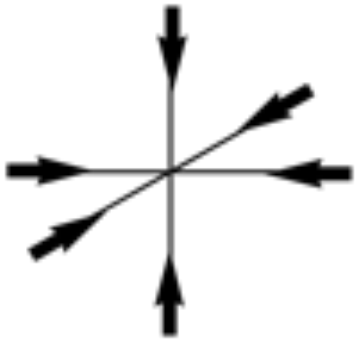
linear algebra to determine symmetry of the σ donor SALC's on the N

$\Gamma = E_g + T_{2u} + A_{1g}$

metal

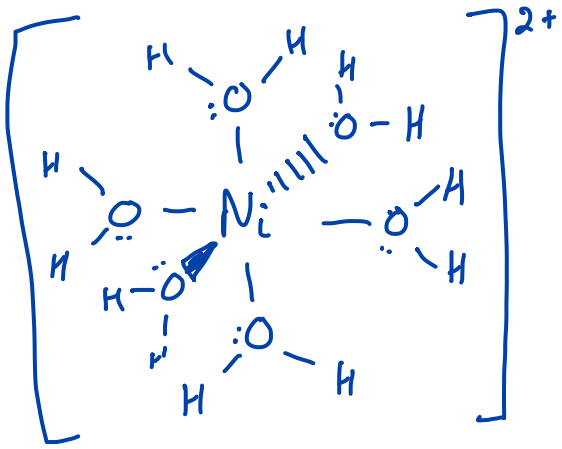
σ donors

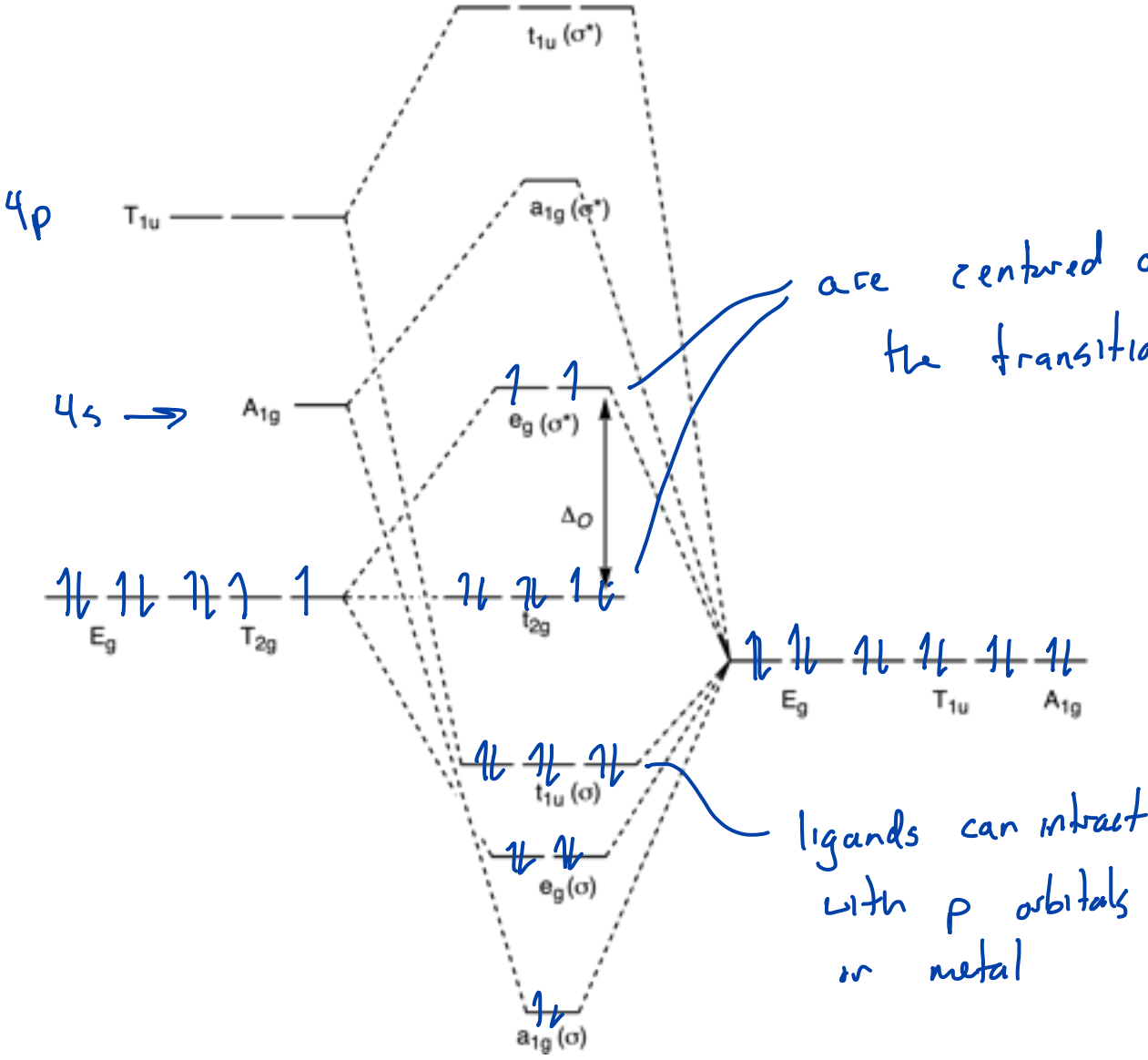




Ni^{2+} ← a d^8 metal

6 $H_2\ddot{O}:$



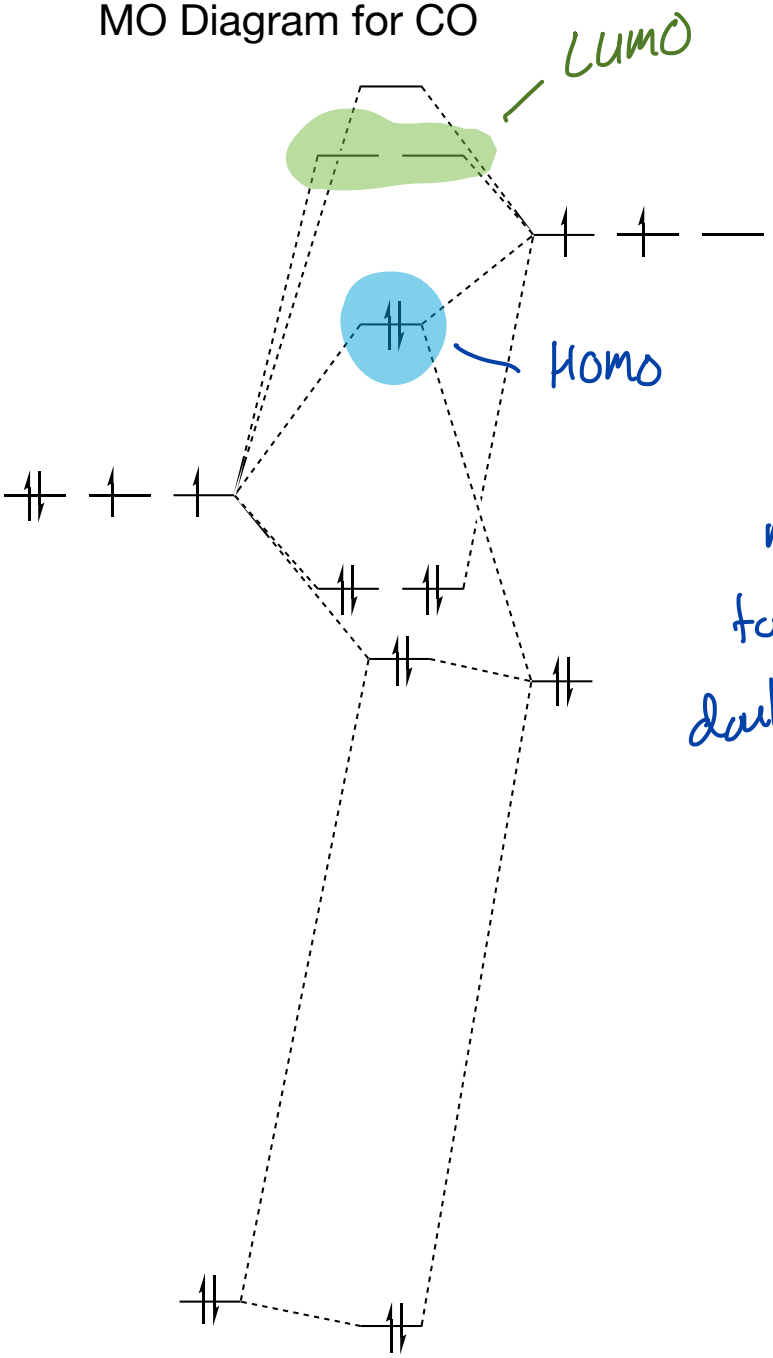


are centered on the transition metal

ligands can interact with p orbitals on metal

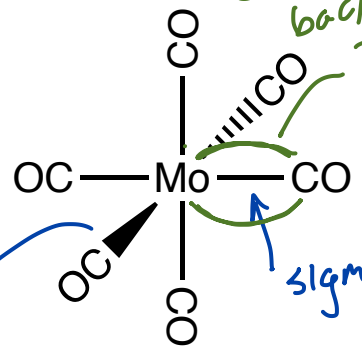
Ligand Field Theory π Interactions: π acceptor ligands

MO Diagram for CO



metal d orbitals can donate e⁻ density back to CO

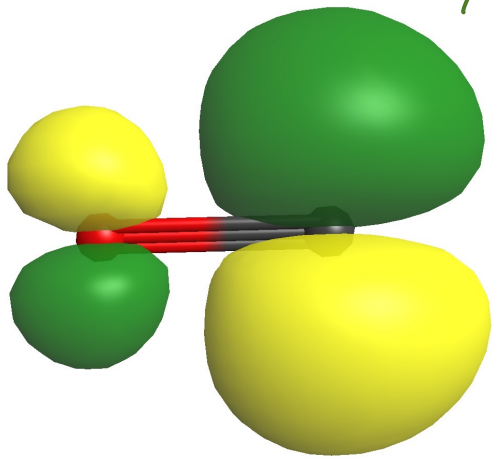
π e⁻ acceptor

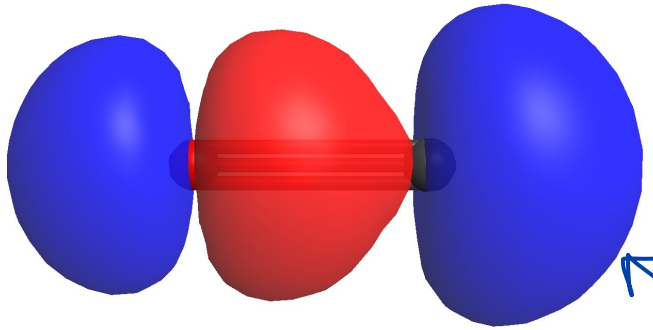


sigma donor

metal to C double bond

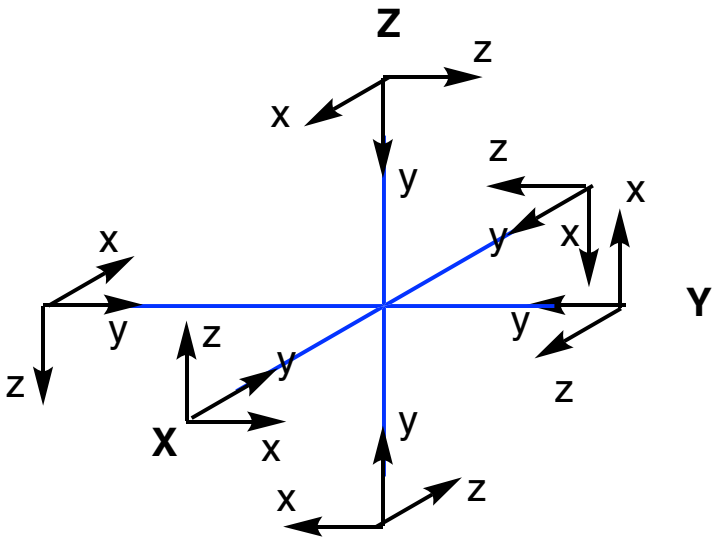
LUMO / π e⁻ acceptor

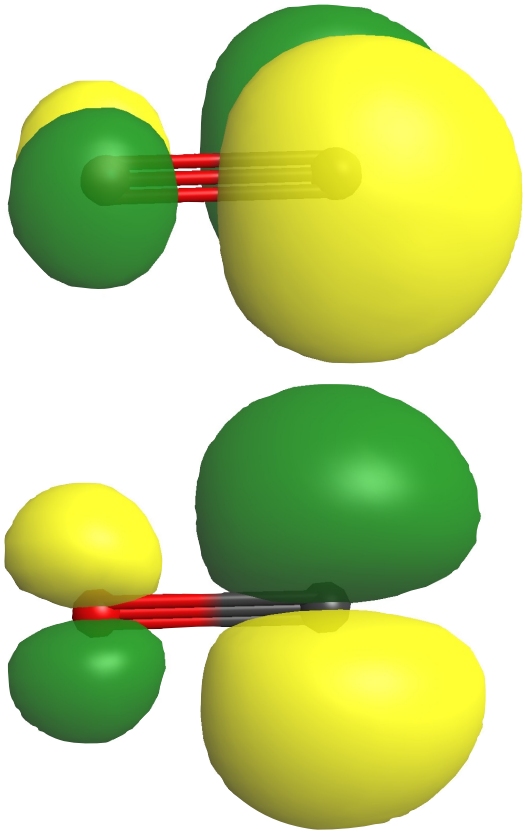




HOMO

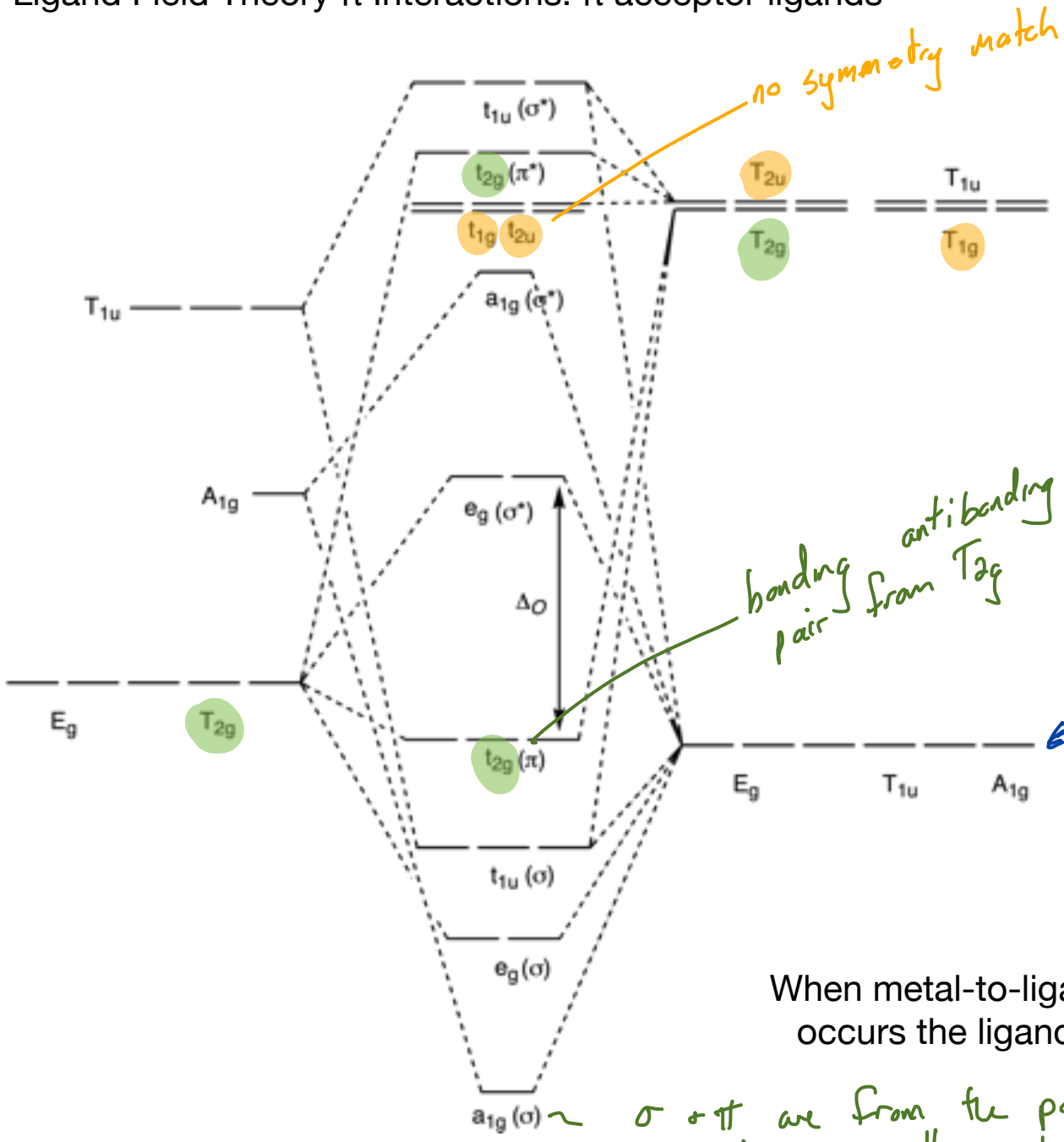
σ donor





O_h	E	8 C_3	6 C_2	6 C_4	3 C_2 (C_4^2)	i	6 S_4	8 S_6	3 σ_h	6 σ_d	
Γ_π	12	0	0	0	-4	0	0	0	0	0	$T_{1g} + T_{2g} + T_{1u} + T_{2u}$

SALCs for π acceptor orbitals on C≡O



π orbitals have the correct symmetry to interact with metal d orbitals in the T_{2g} set

σ orbitals have the correct symmetry to interact with metal d orbitals in the E_g set

acceptor

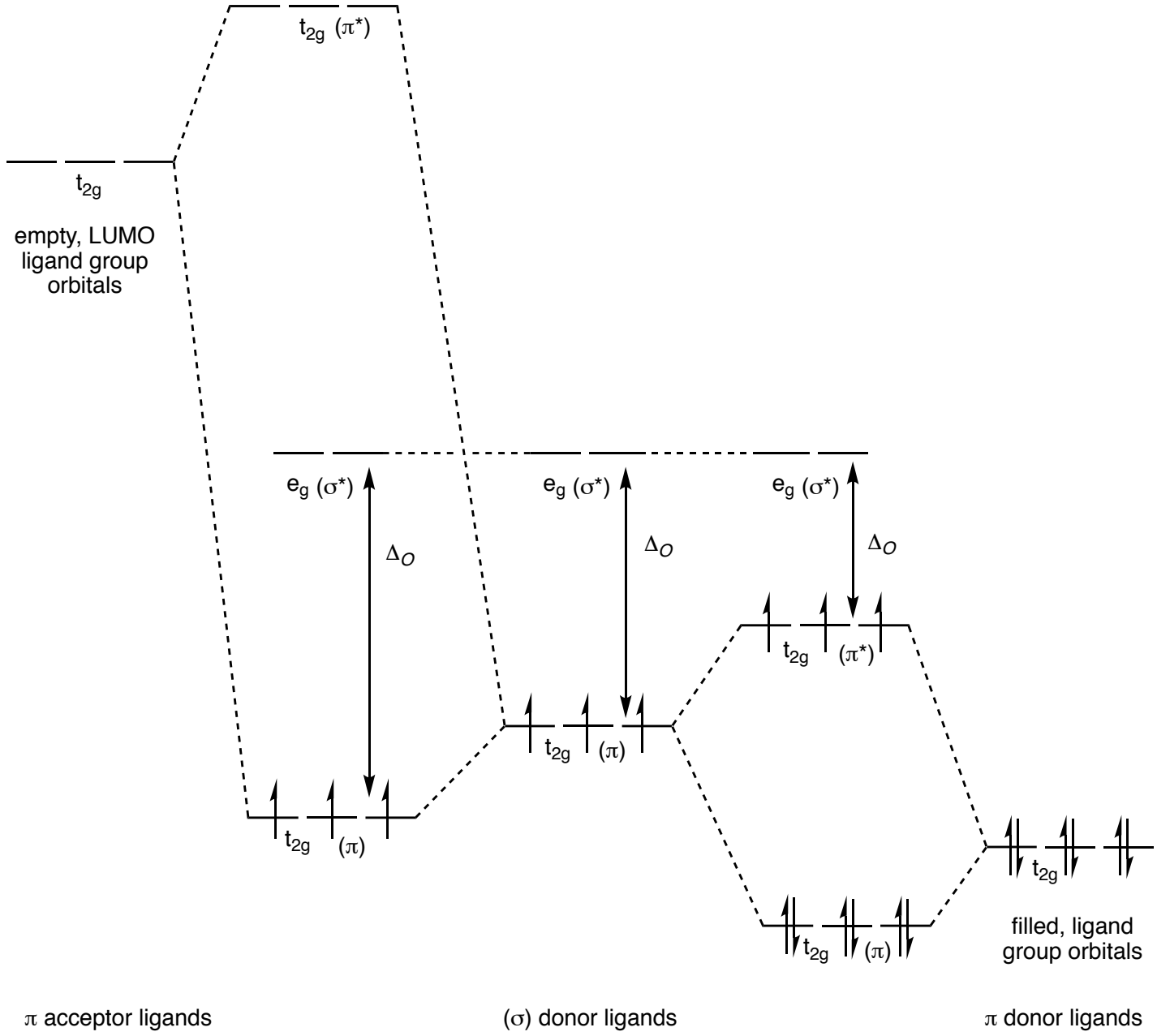
π interactions increase Δ_O by lowering t_{2g} set

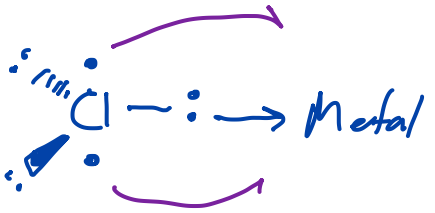
σ interactions increase Δ_O by increasing e_g set

C≡O is a σ donor... same SALCs as other σ donors

When metal-to-ligand bonding or π back-bonding occurs the ligand is a π acceptor

σ & π are from the point of view of 1 ligand to metal connection, not the overall symetry of the orbital

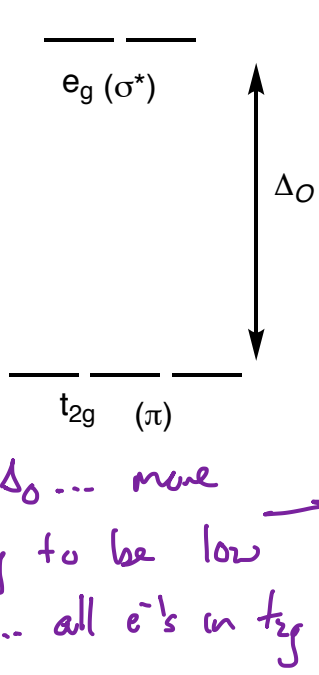

t2g (π*)
t2g
empty, LUMO ligand group orbitals
eg (σ*)
Δo
eg (σ*)
Δo
eg (σ*)
Δo
t2g (π*)
t2g (π)
t2g (π)
t2g
t2g (π)
filled, ligand group orbitals
π acceptor ligands
(σ) donor ligands
π donor ligands



σ donor
π donor

$Cl^{\ominus}$

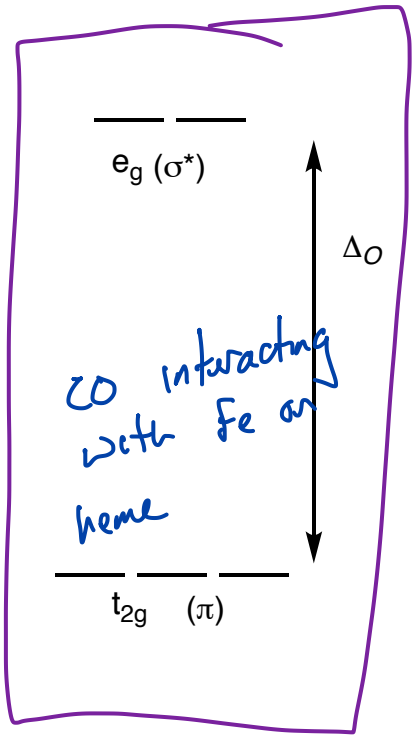
NH_3



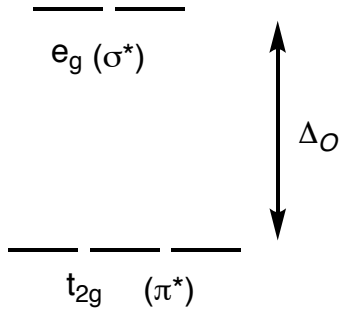
large Δ_o ... more likely to be low spin ... all e⁻'s in t_{2g}

σ donor ligands

$C\equiv O$



σ donor
π acceptor ligands



small Δ_o ... more likely to be high spin ... e⁻'s entering e_g set instead of pairing in t_{2g} set

σ donor ligands
π donor ligands

CO CN^- phen NO_2^- en NH_3 NCS^- H_2O F^- RCO_2^- OH^- Cl^- Br^- I^-

largest Δ_o

smallest Δ_o