Today

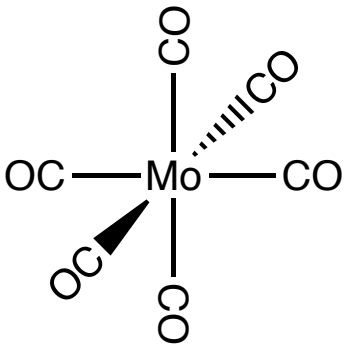
Ligand Field Theory Section 10.3

Next Class

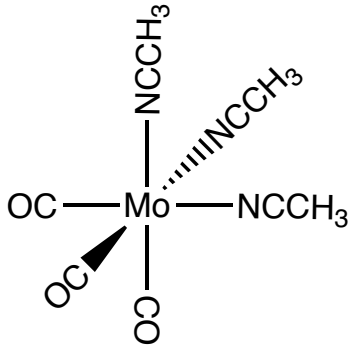
Ligand Field Theory Section 10.3

Rework Test 3 and hand in on Wednesday, December 15

Rework Project 2 by 12/21



$:NH_3$



$:C\equiv O:$ $:N\equiv C-CH_3$

$[:C\equiv N:]^-$

Isoelectronic

Isolobal "same" MO's at the N end of the molecule

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		

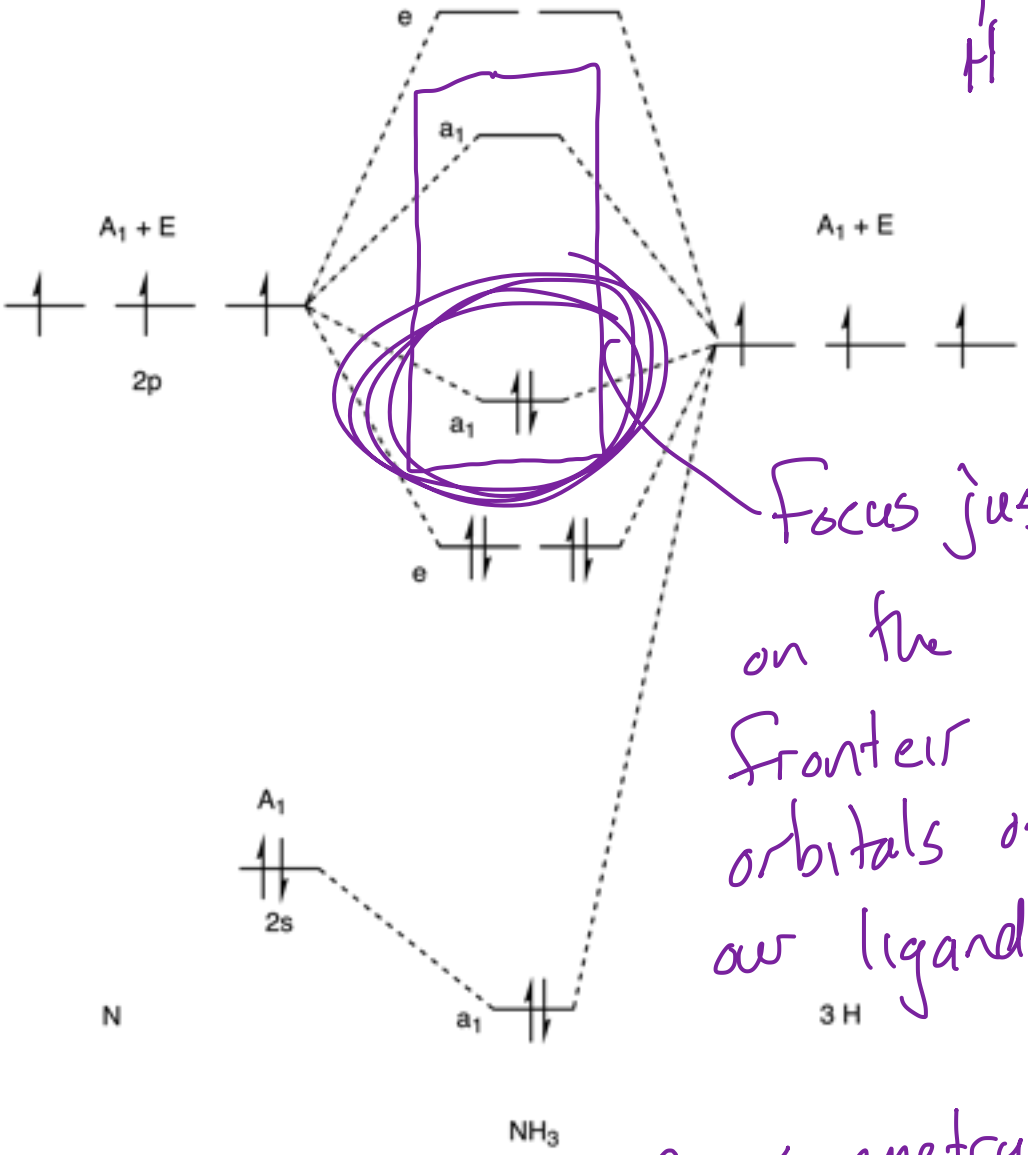
d_{z^2}

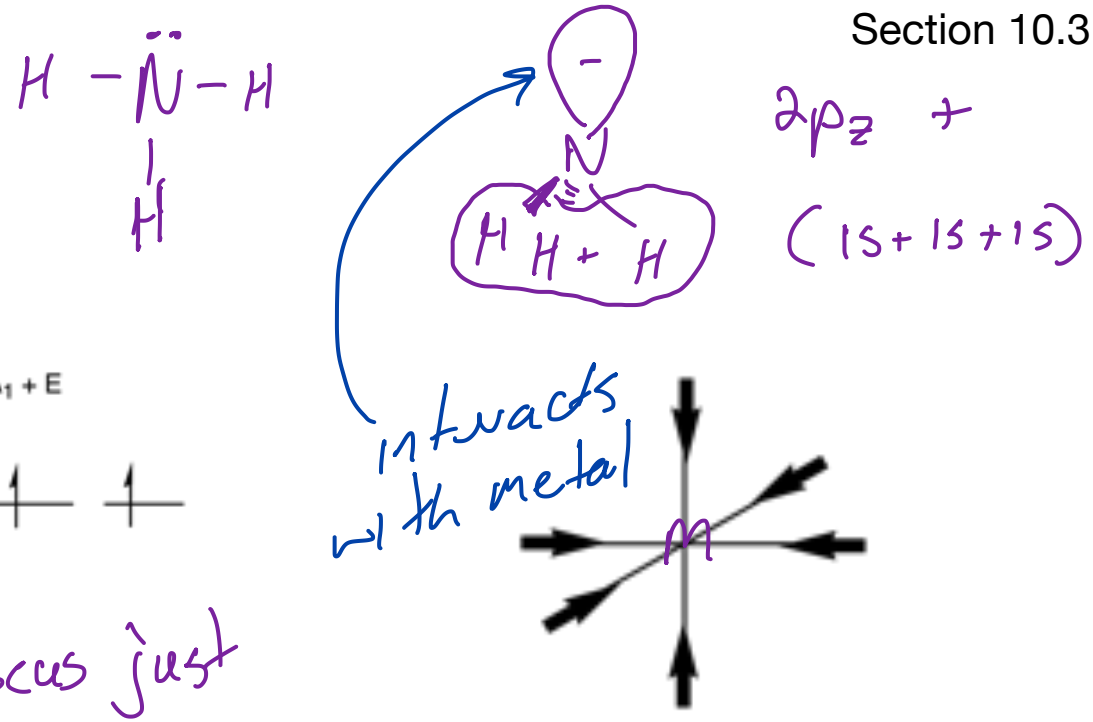
2 d orbitals are oriented along the x, y, z axes E_g

3 d orbitals are oriented between the axes T_{2g}

Ligand Field Theory: σ Donors

MO Diagram for NH_3





Focus just on the frontier orbitals of our ligands

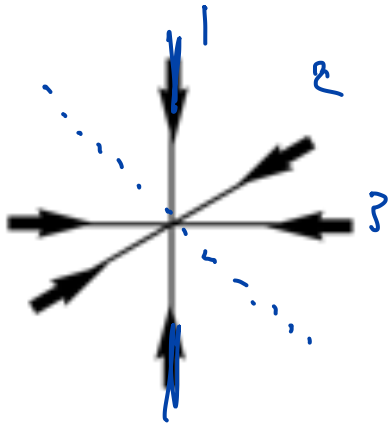
σ donors have lp e⁻'s that they can point directly at a metal

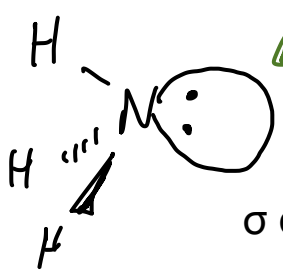
a_1 symmetry is what we would call σ in a linear molecule

C_4 2×

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 0 2 2 0 0 0 4 2

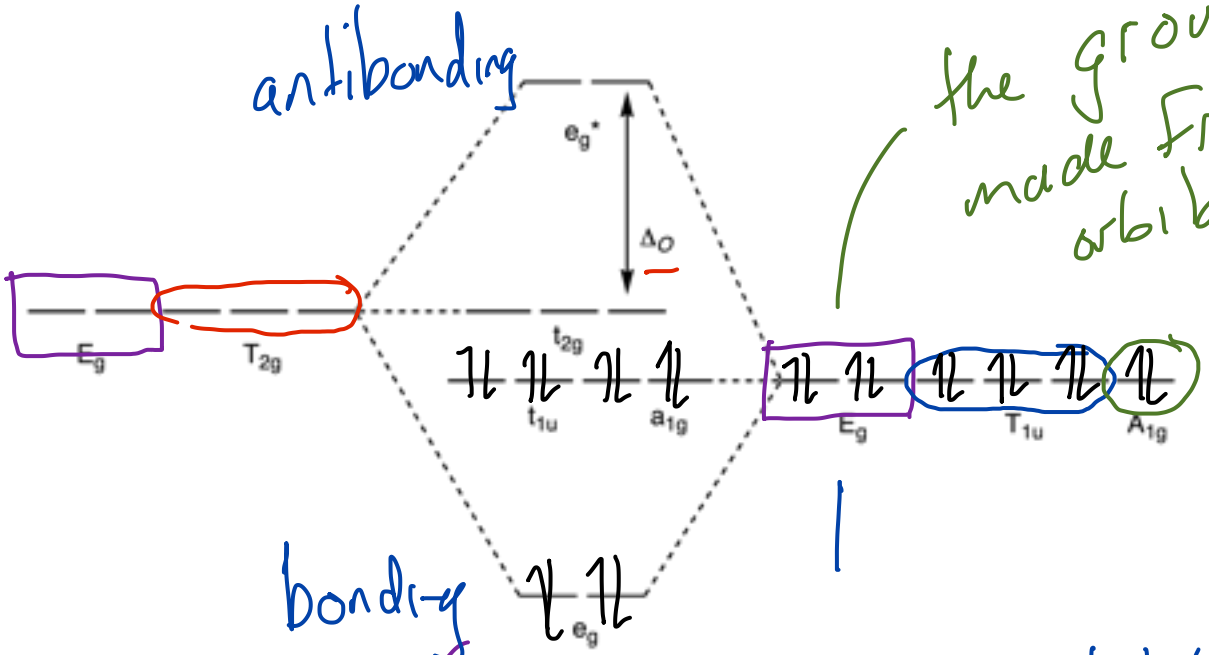




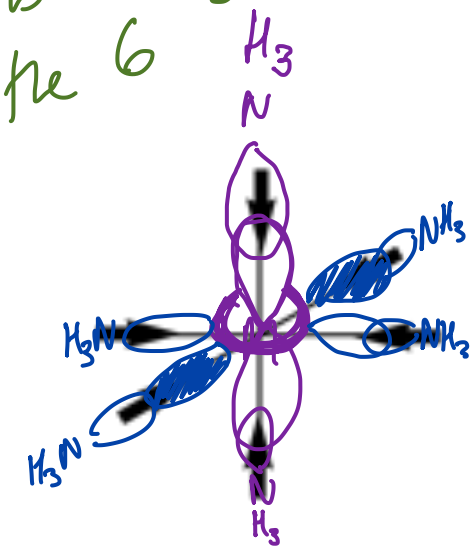
eg' identically symmetrical

metal

σ donors



the group orbitals σ donor made from the 6 orbital

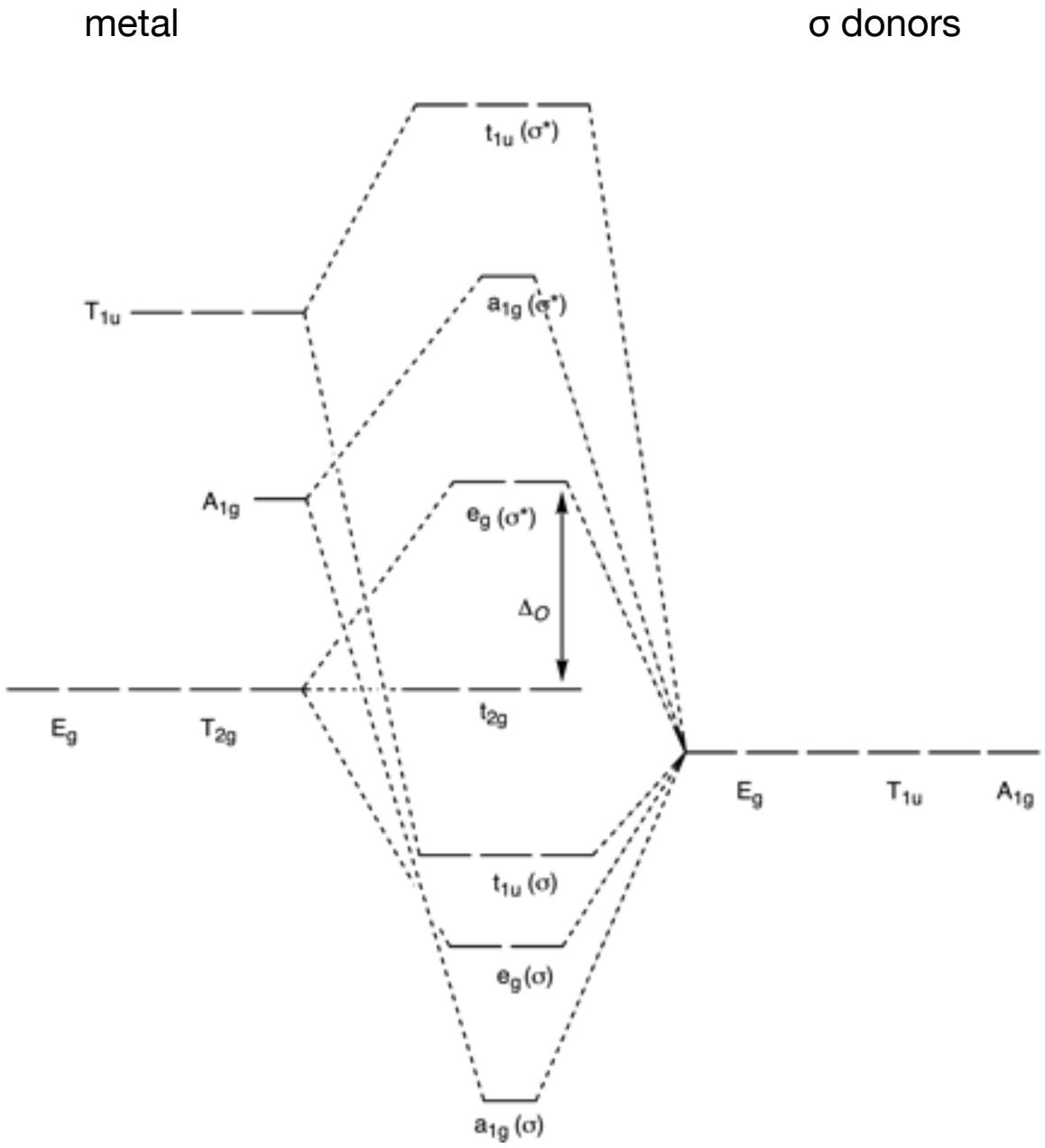


set of orbitals for the SALC's from NH_3

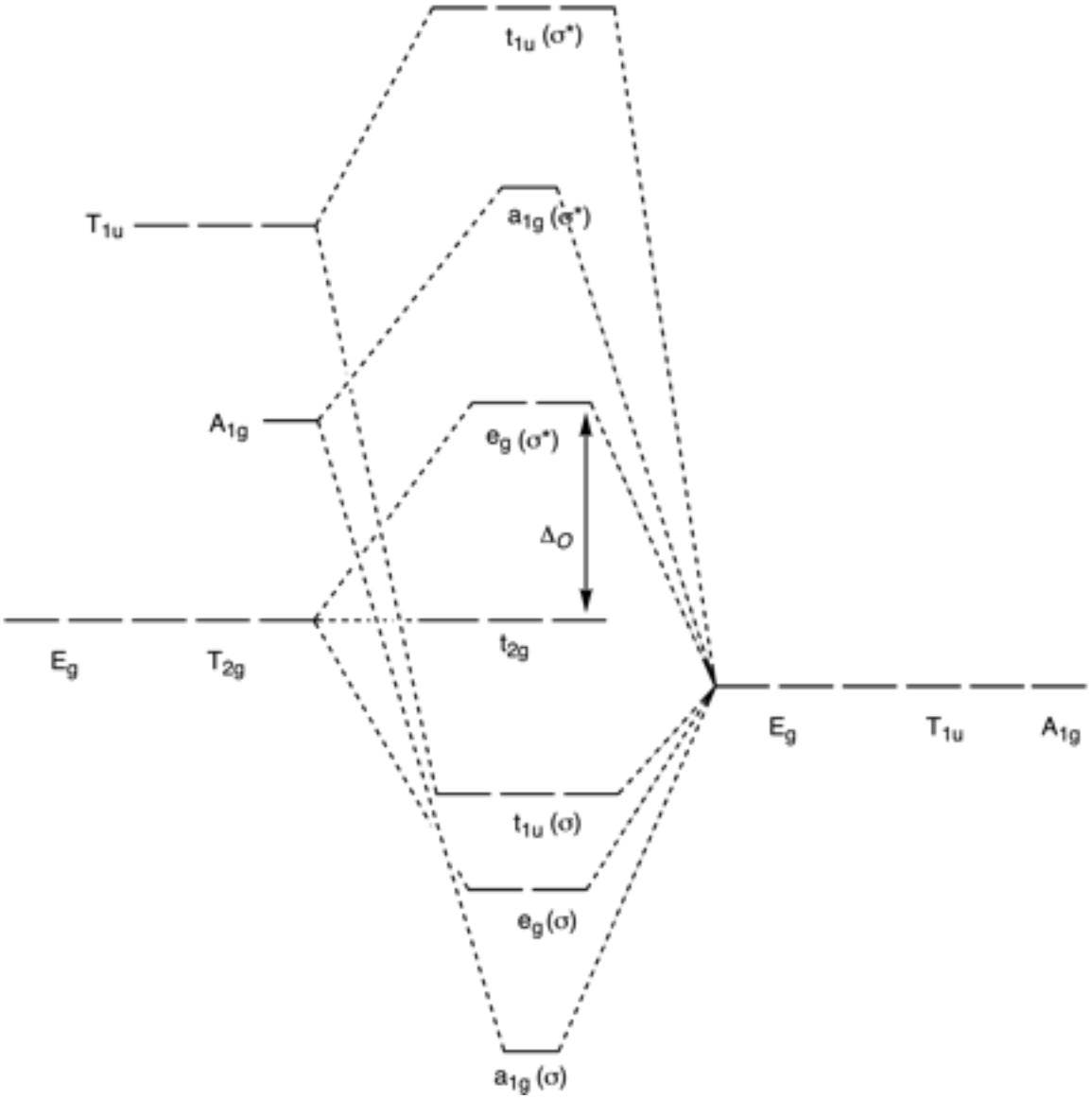
t_{2g} are the d_{xy}, d_{xz}, d_{yz}

the E_g set of SALCs from NH_3 interact

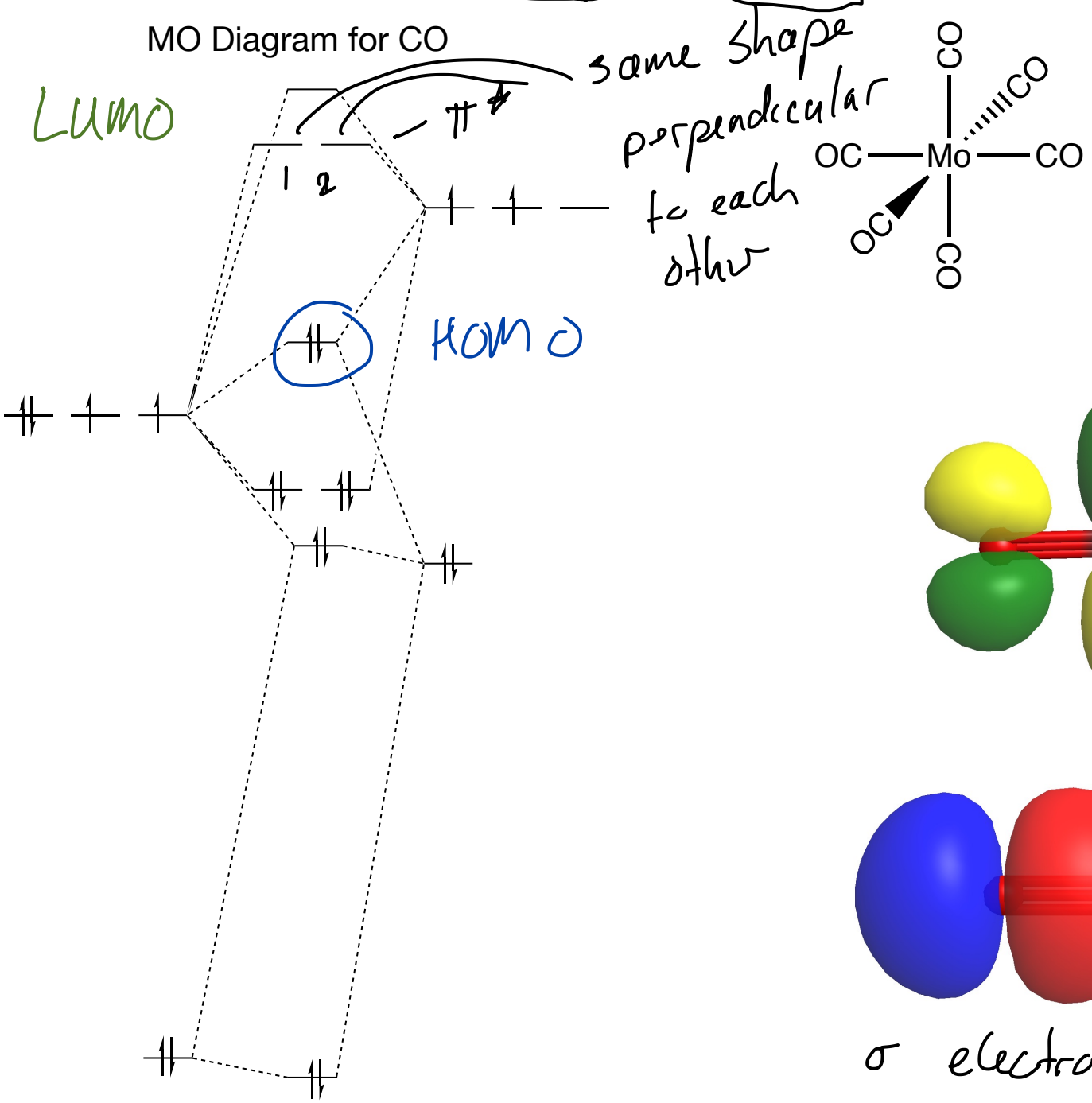
the d_{z^2} + $d_{x^2-y^2}$ after all, the σ donating orbitals on the NH_3 are aligned on the x, y, z axes


metal
σ donors
t_{1u} (σ*)
T_{1u}
a_{1g} (σ*)
A_{1g}
e_g (σ*)
Δ_O
t_{2g}
E_g
T_{2g}
E_g
T_{1u}
A_{1g}
t_{1u} (σ)
e_g(σ)
a_{1g} (σ)

Ni^{2+} 6 H_2O

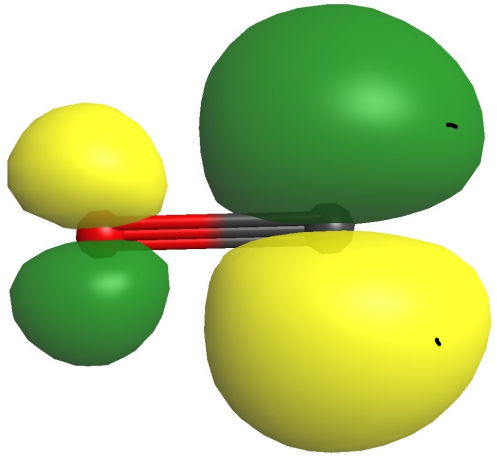


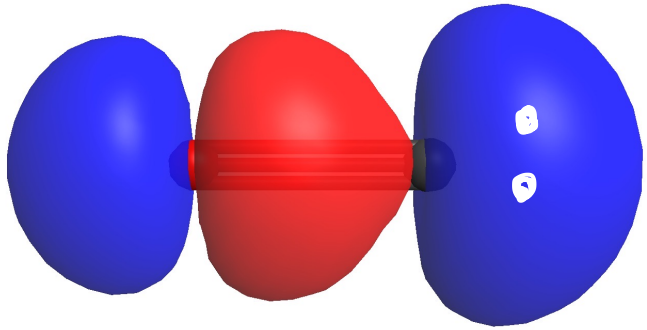
MO Diagram for CO



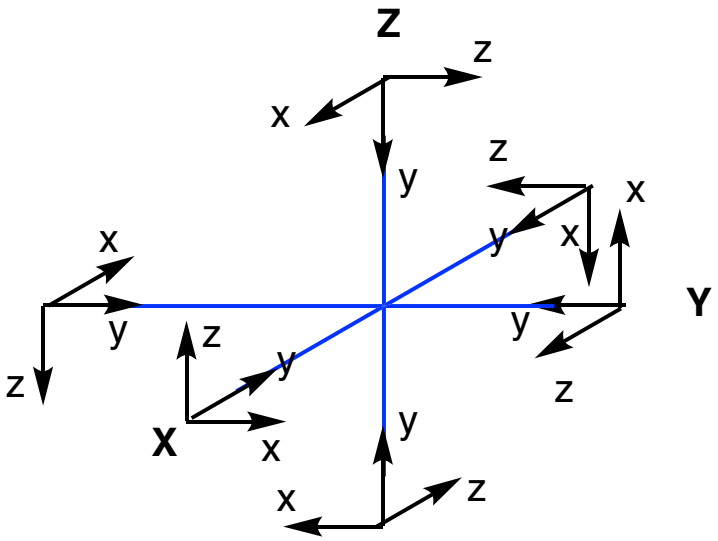
same shape perpendicular to each other

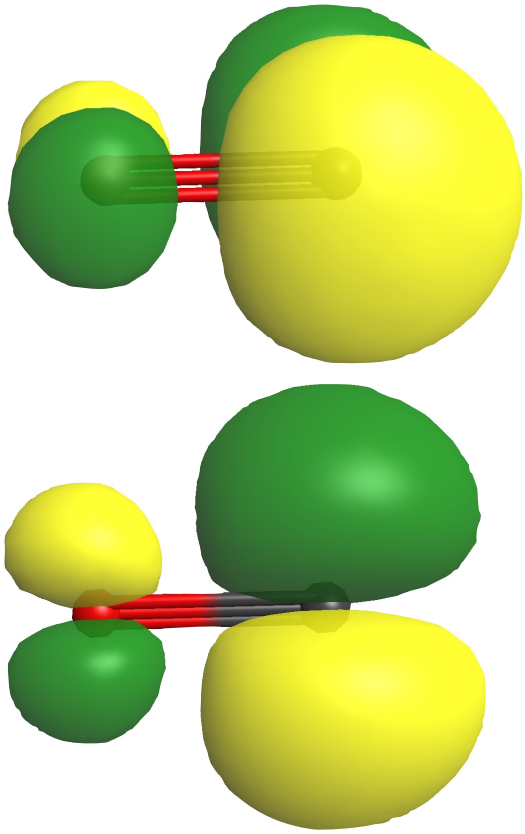
empty π orbital





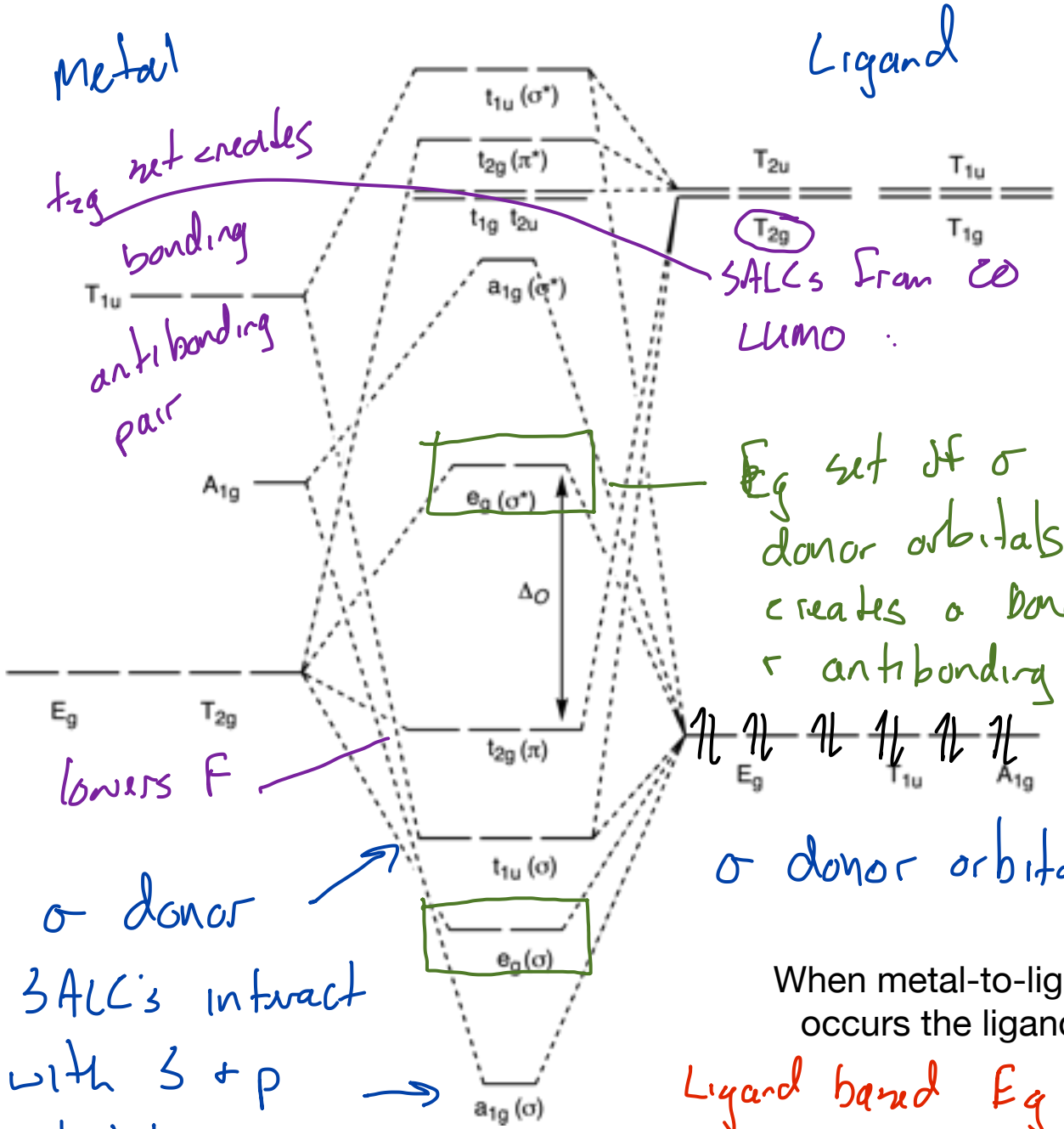
σ electron donor





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	$T_{1g} + T_{2g} + T_{1u} + T_{2u}$

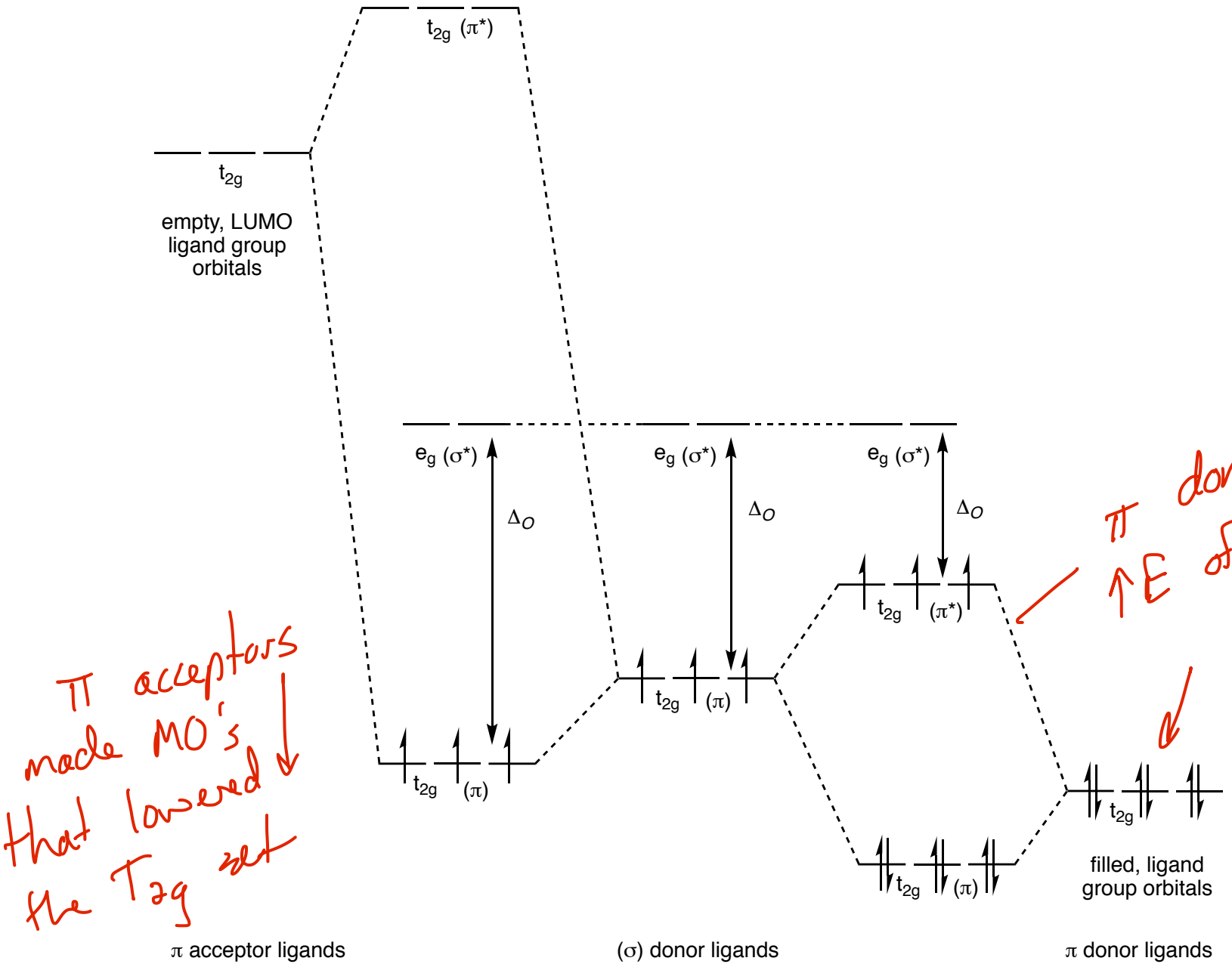
3 3 3 3



- 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
- π interactions increase Δ_O by lowering t_{2g} set
- σ interactions increase Δ_O by increasing e_g set

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

Ligand based Eg orbitals ↑ E of metal based Eg orbitals + ligand base T2g orbitals ↓ E of metal based T2g orbitals


t2g (π*)
t2g
empty, LUMO ligand group orbitals
eg (σ*)
Δo
t2g (π)
π acceptor ligands
eg (σ*)
Δo
t2g (π)
(σ) donor ligands
eg (σ*)
Δo
t2g (π*)
t2g (π)
filled, ligand group orbitals
π donor ligands
π acceptors made MO's that lowered the T2g set
π donor ligands ↑E of T2g set