(29) **Today**

Section 10.2 Crystal Field Theory

Section 10.3 Ligand Field Theory

Next Class (30)

Section 10.3 Ligand Field Theory

(31) **Second Class from Today**

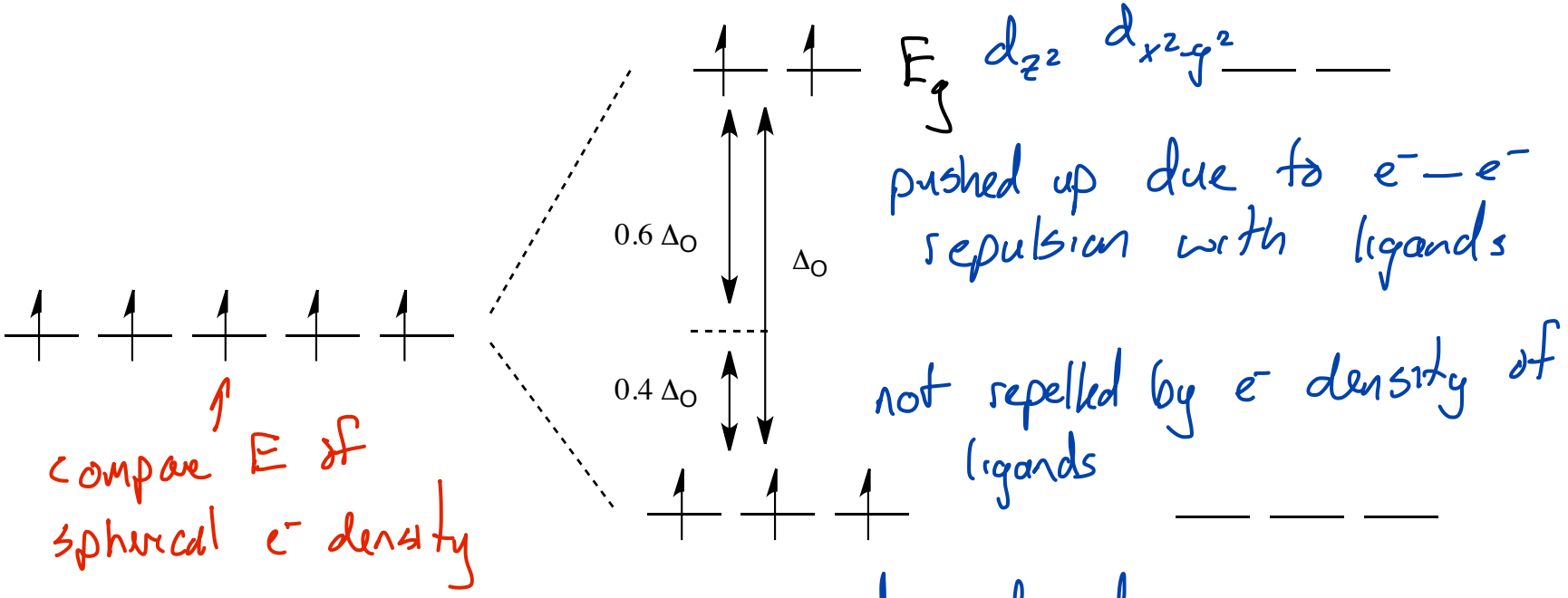
Section 10.5 The Jan-Teller Effect

Chap 12

Third Class from Today (32)

Chap 12

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



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

$E_{spherical} = 0 + \text{pairing energy}$

$E_{octahedral} = (\#\ e^- \times -0.4\Delta_O) + (\#\ e^- \times 0.6\Delta_O)$

Δ_o Gap determined spetrophotometrically

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)

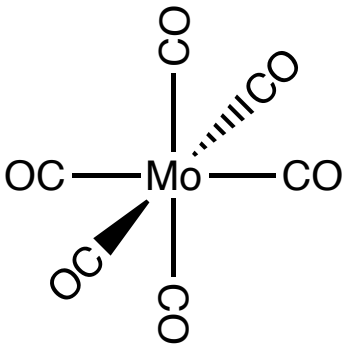
Δ_O can be determined using spectroscopic techniques

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

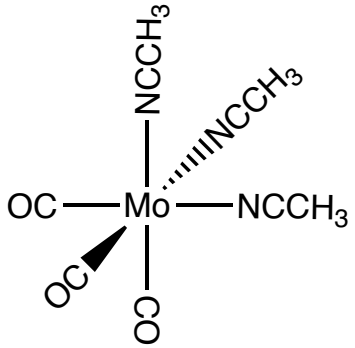
only talks about $e^- - e^-$ repulsion

Does not account for stabilization due to bonding



Octahedral geometry

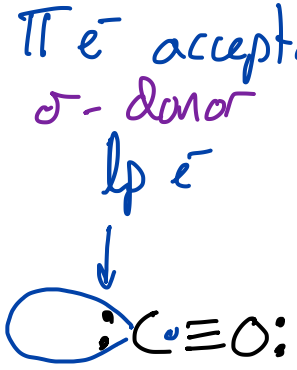
A member of the O_h pt. grp.

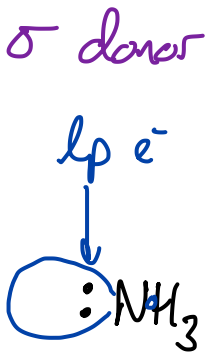


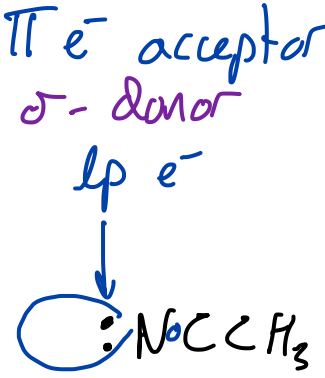
Octahedral geometry

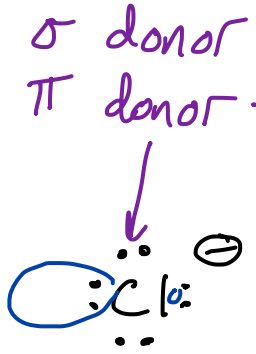
A member of the C_{3v} pt. grp

pseudo-O_h









can be used to make a σ bond σ donor ligands

Metal orbitals

metal s orbital

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		
A_{1g}	1	1	1	1	1	1	1	1	1	1	M 45	$x^2 + y^2 + z^2$
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		

metal p orbitals

metal d orbitals

d_{xy} d_{xz} d_{yz}

metal d orbitals

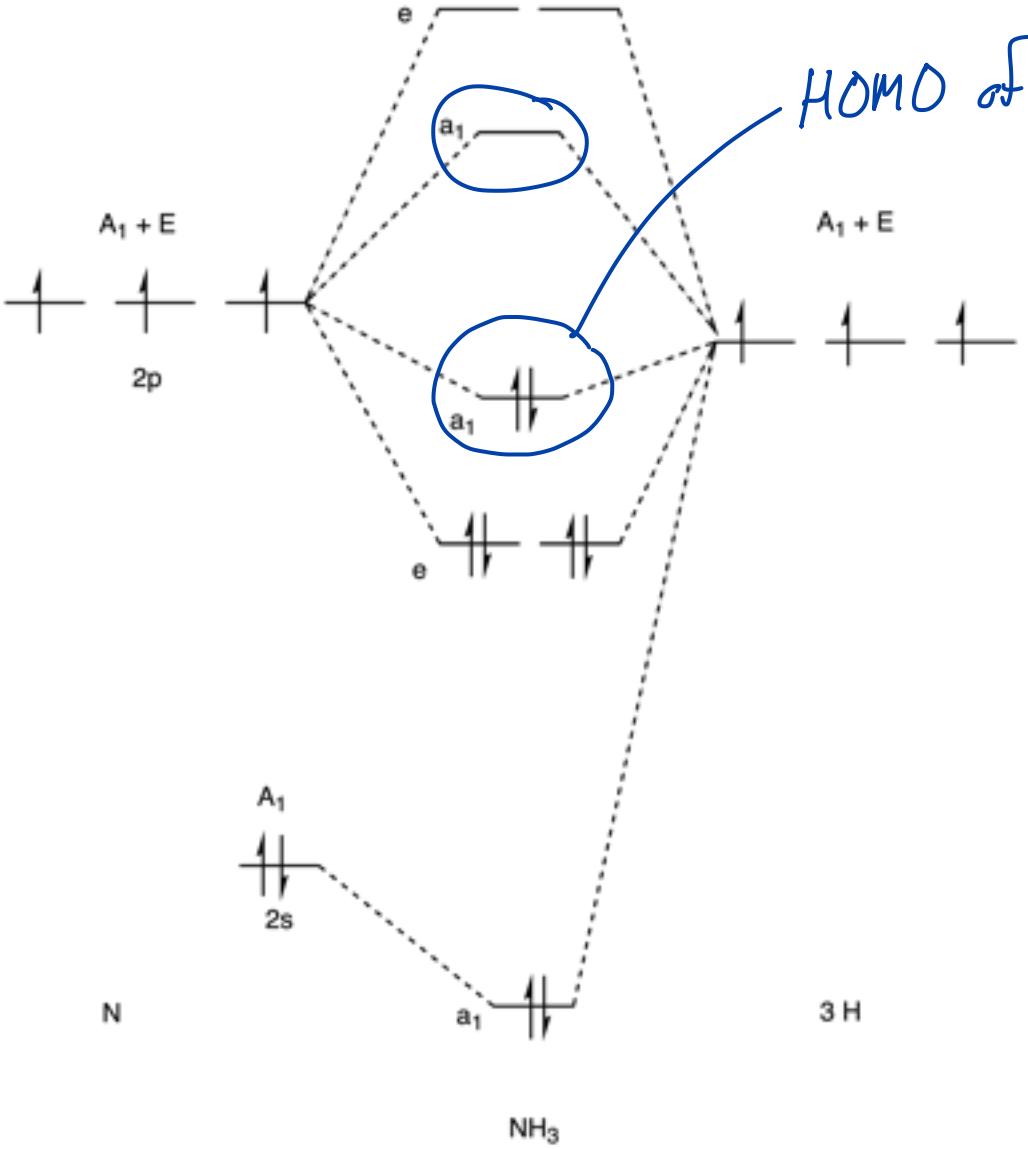
d_{z^2}, $d_{x^2-y^2}$

$x^2 + y^2 = z^2$

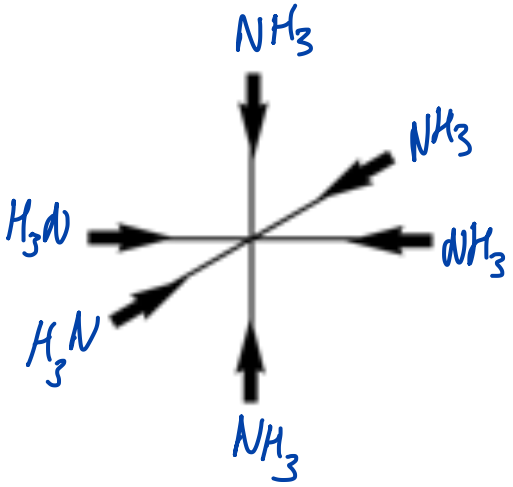
Ligand Field Theory: σ Donors

MO Diagram for NH_3

: NH_3 σ donor



HOMO of NH_3 is our σ-donor

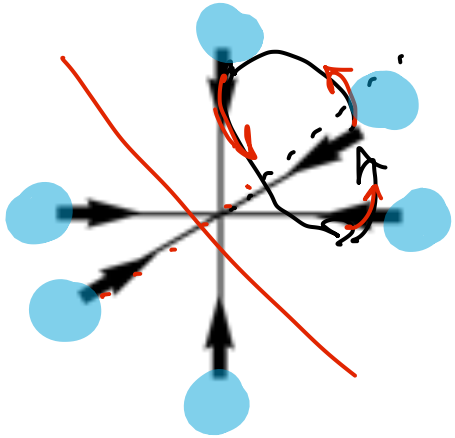


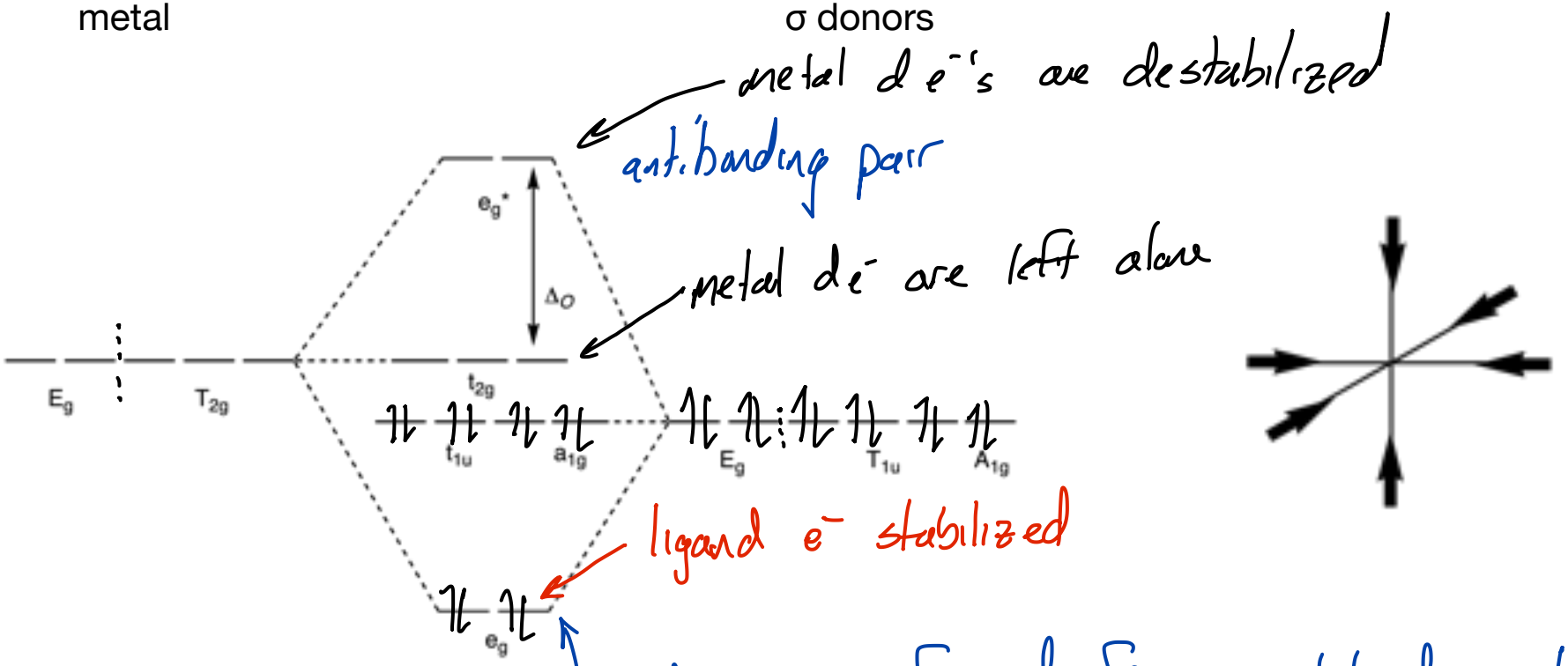
Ligand Field Theory: σ Donors

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

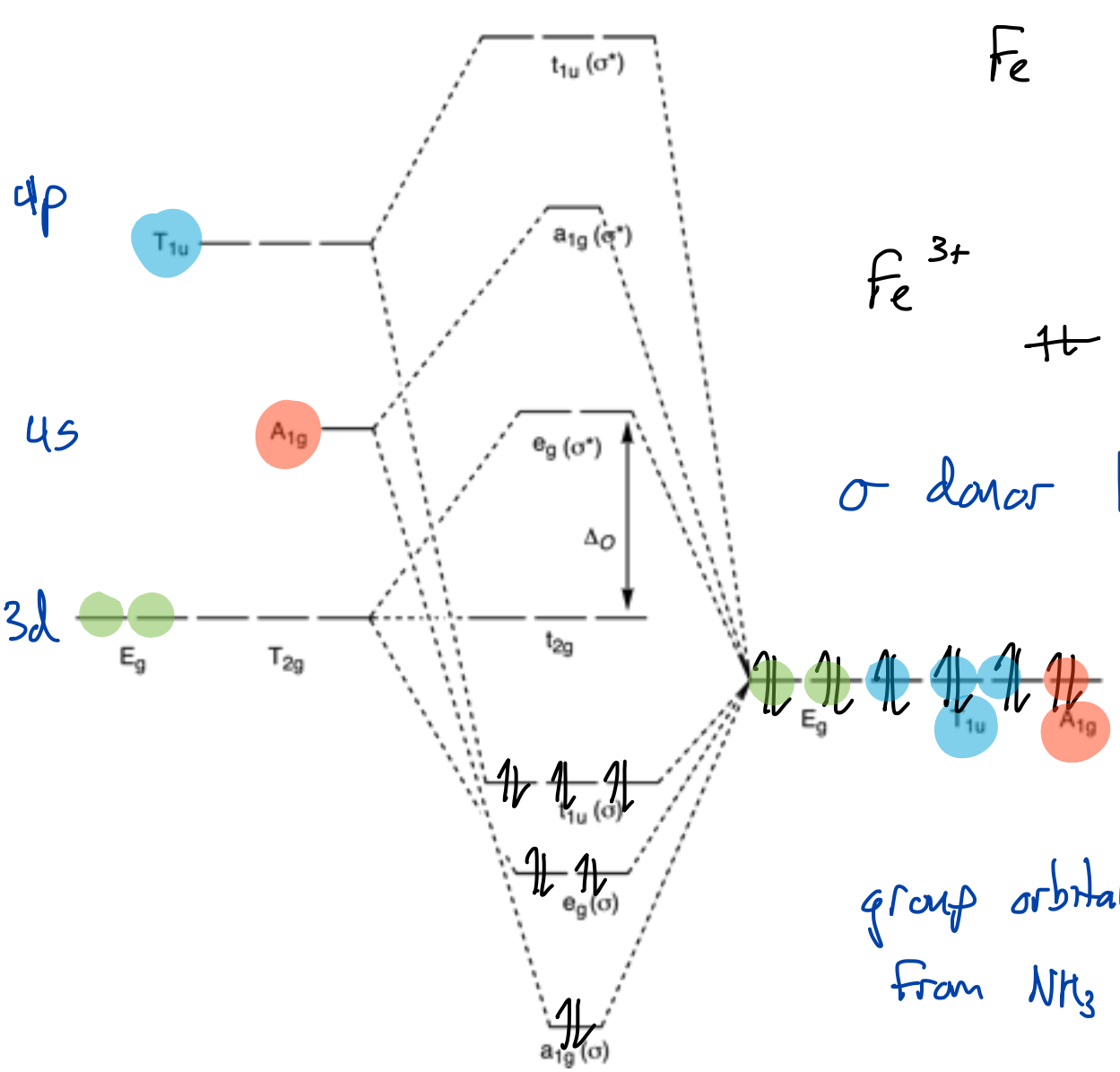
$\Gamma = 6 \quad 0 \quad 0 \quad 2 \quad 2 \quad 0 \quad 0 \quad 0 \quad 4 \quad 2$

$\Gamma = A_g + E_g + T_{1u}$

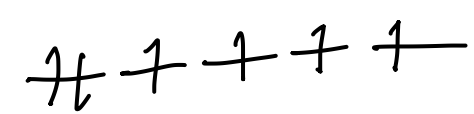



metal
σ donors
metal d e⁻'s are destabilized
anti.bonding pair
metal d e⁻ are left alone
e_g^*
Δ_O
E_g
T_{2g}
t_{2g}
t_{1u}
a_{1g}
E_g
T_{1u}
A_{1g}
ligand e⁻ stabilized
e_g
bonding pair formed from metal d + ligand Eg orbitals

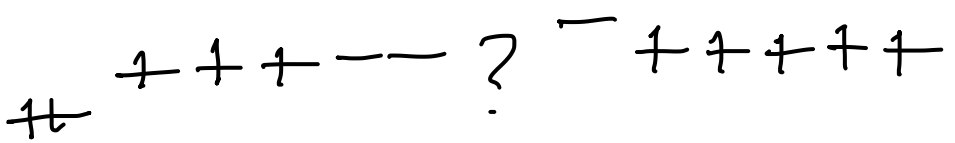
metal σ donors



Fe



Fe^{3+}



σ donor ligands ↑ the energy of the e_g set of d orbitals

group orbital from NH_3

σ donors increase E of e_g set of metal d orbitals