

(33) Today

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

Section 10.2 Crystal Field Theory

(35) Second Class from Today

Section 10.3 Ligand Field Theory

Section 10.5 The Jan-Teller Effect

Section 10.6 Four and Six-Coordinate Preferences

Next Class (34)

Section 10.2 Crystal Field Theory

Section 10.3 Ligand Field Theory

Magnetic Susceptibility is related to magnetic moment

magnetic moment
 $\mu = 2.828 (\chi T)^{1/2}$

spin quantum #
 $\mu_{S+L} = g[S(S + 1) + [1/4 L(L + 1)]]^{1/2}$

magnetic susceptibility

or with some approximating.... $\mu_S = (n(n + 2))^{1/2}$ (n is the number of unpaired electrons)

For metals in the 4th period the spins of the e⁻'s dominate
 and magnetic moment is related to the total spin magnetic moment (the spin quantum number S)

S = sum of the unpaired spins for all e⁻'s on the metal

↑↓ paired spins cancel out $S = +\frac{1}{2} + -\frac{1}{2} = 0$

and the orbital angular momentum (L) is the maximum possible sum of the m_l values for an electron configuration

L is determined by adding up all the m_l values

2p	↑↑	$m_l = 0$
2s	↑↓	$m_l = 0$
1s	↑↓	$m_l = 0$

$m_l = 1, 0, -1$

↑ pair e⁻'s here first

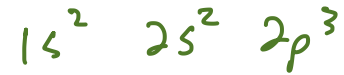
S and L | write e⁻ config

for N



$$S = 0 + 0 + \frac{1}{2} + \frac{1}{2} + \frac{1}{2} = \frac{3}{2}$$

$\uparrow \quad \uparrow$
 $+\frac{1}{2} + -\frac{1}{2} \quad m_l \quad 1 \quad 0 \quad -1$

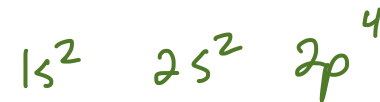


$$L = 0 + 0 + 0 + 0 + 1 + 0 + -1 = 0$$

for O

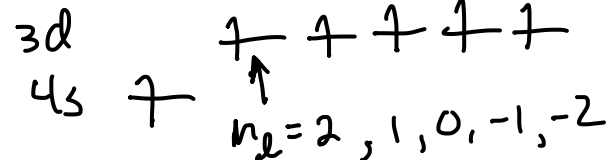


$$S = 0 + 0 + 0 + \frac{1}{2} + \frac{1}{2} = 1$$

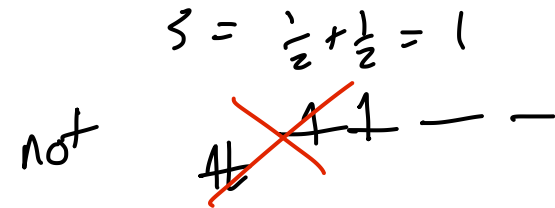
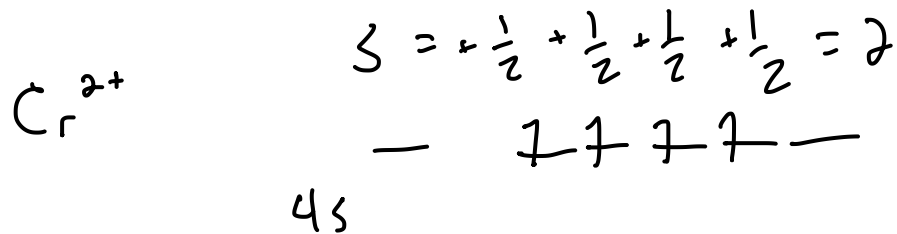
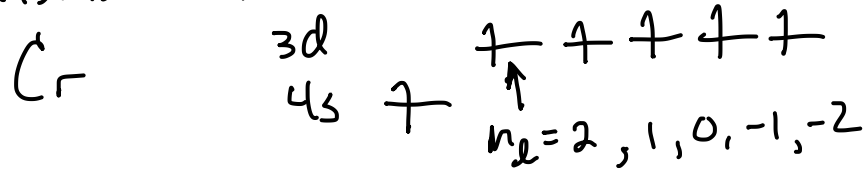


$$L = 0 + 0 + 0 + 0 + 1 + 1 + 0 - 1 = 1$$

transition metals

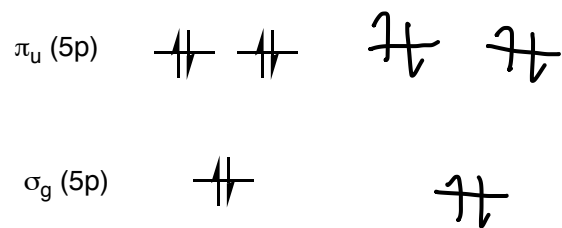
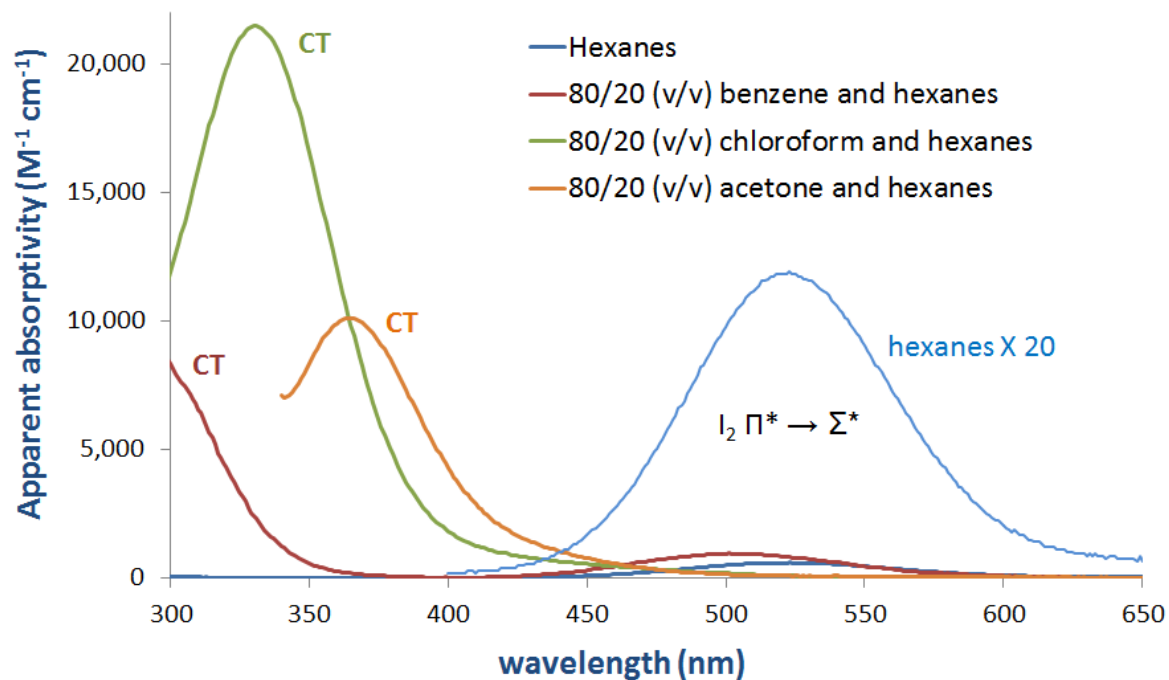
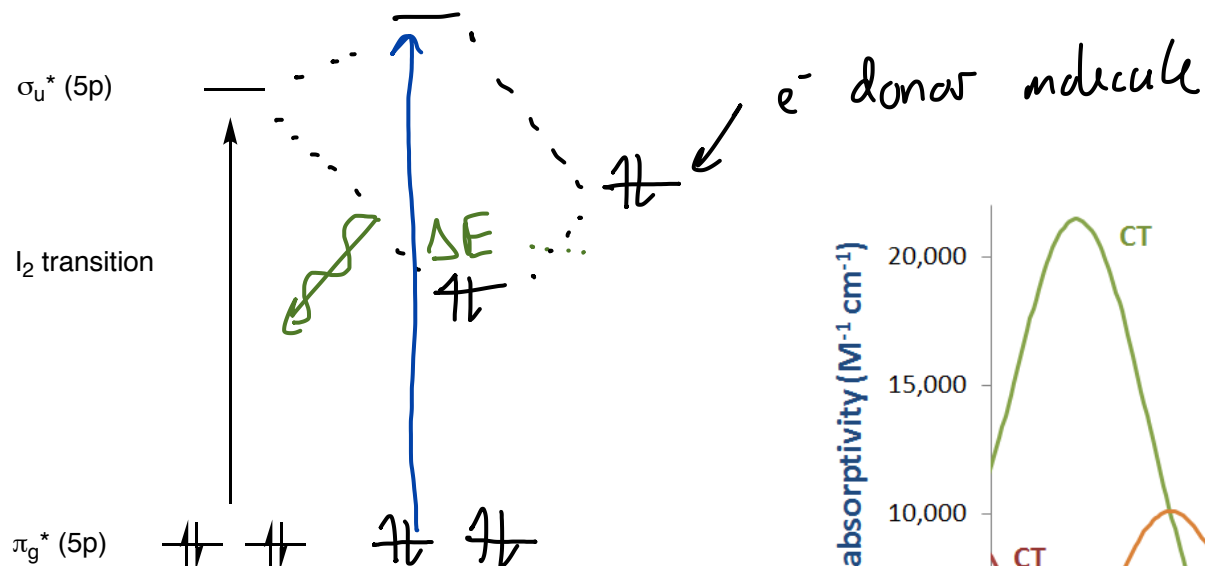


transition metals



Cr²⁺ is a d⁴ metal... e⁻'s are lost from the s orbitals first.

Electronic Spectra



the photon that is absorbed gives information about the difference in energy between two orbitals in a complex

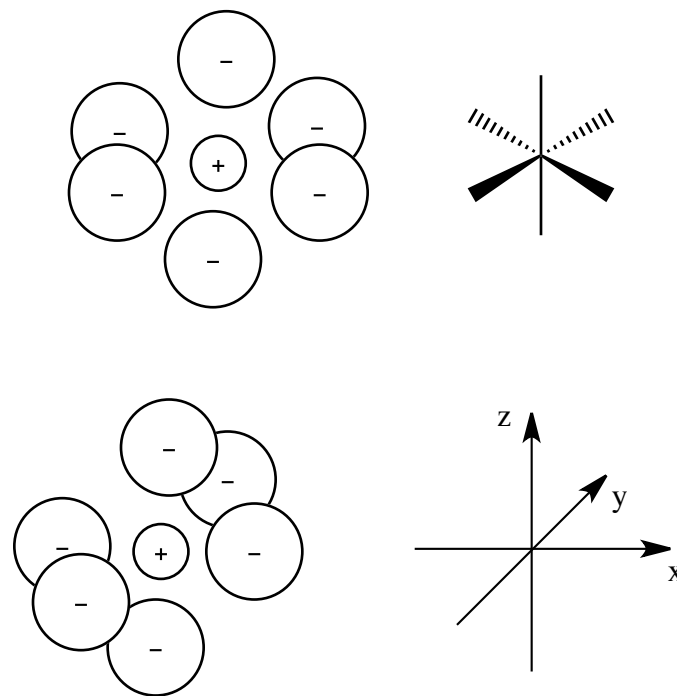
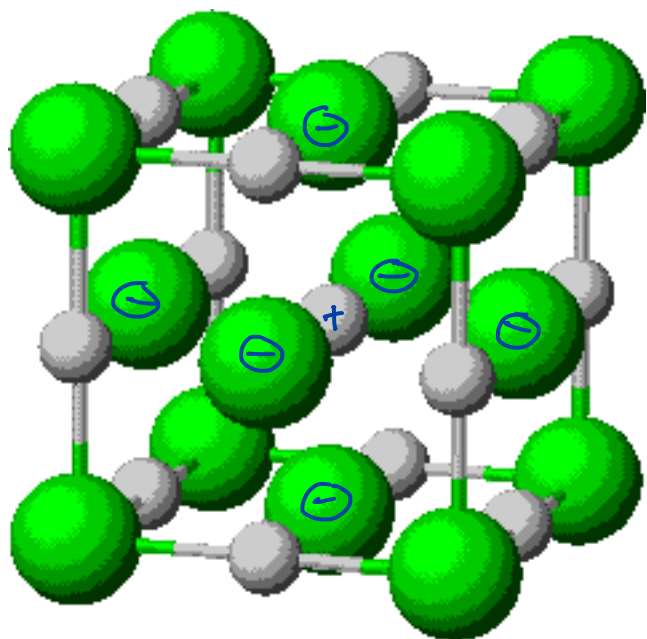
Crystal Field Theory

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

(all of the d orbitals will not have the same E... why?

Ligand Field Theory

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



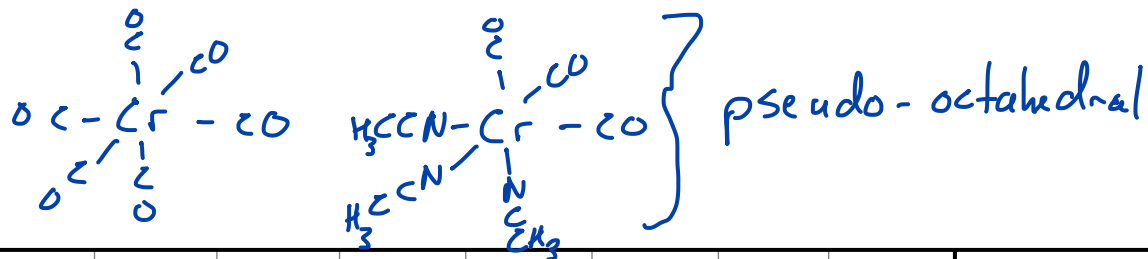
This Na^+ is in the middle of an O_h (octahedral) field of e^- density... the Cl^- are creating that field.

not so interesting for Na... no d e^- 's

Transition metals with d e^- 's... those e^- 's will experience repulsion to the e^- density supplied by the 6 Cl^- 's.

The amt. of repulsion depends on the symmetry of the orbitals.

O_h Point Group



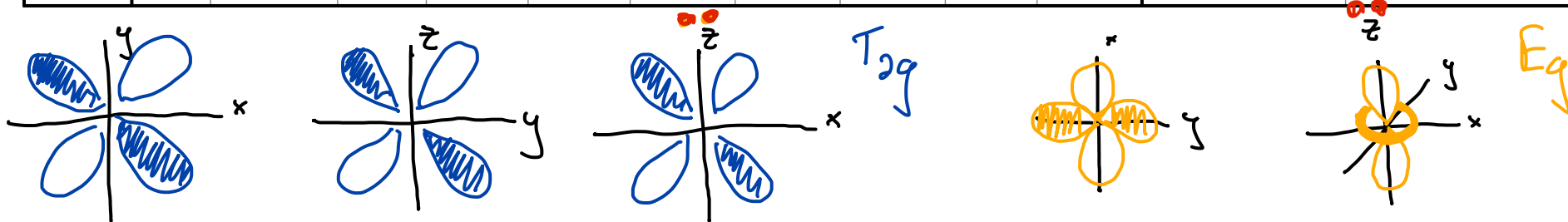
Review

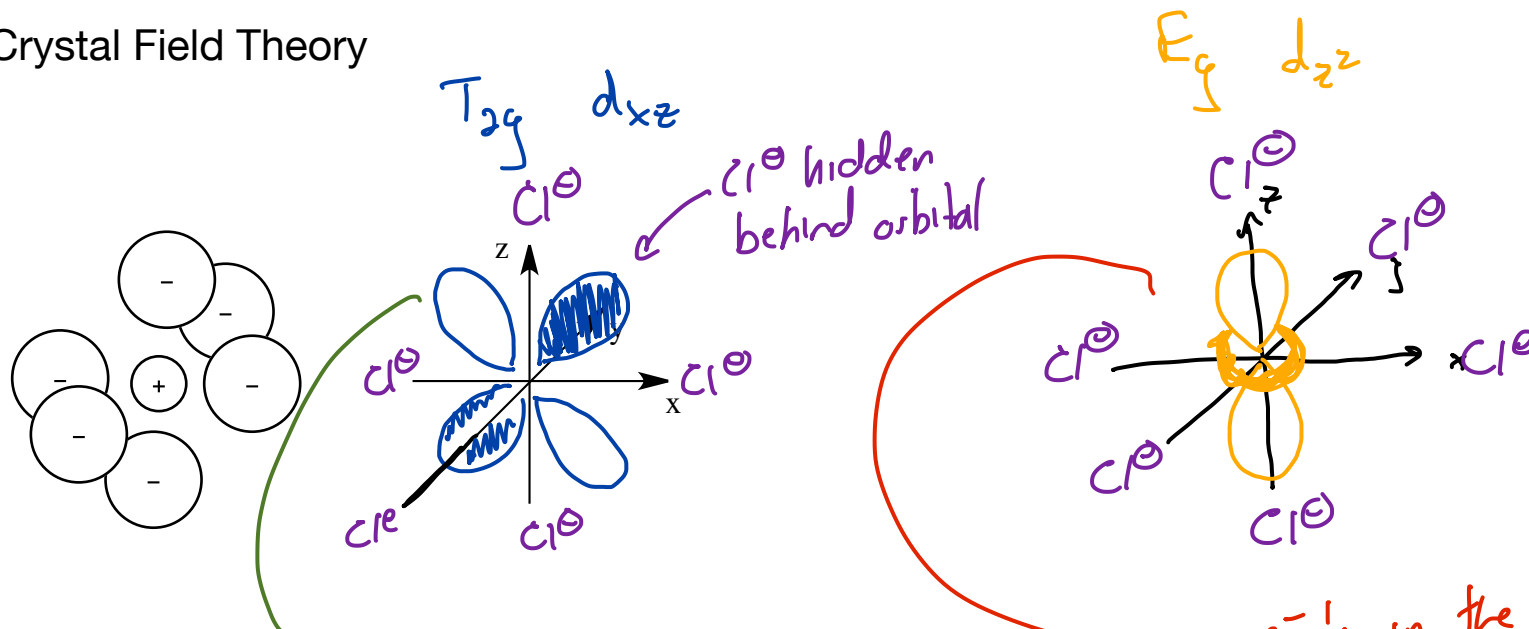
O _h	E	8 C ₃	6 C ₂	6 C ₄	3 C ₂ (C ₄ ²)	i	6 S ₄	8 S ₆	3 σ _h	6 σ _d		
A _{1g}	1	1	1	1	1	1	1	1	1	1		x ² + y ² + z ²
A _{2g}	1	1	-1	-1	1	1	-1	1	1	-1		
E _g	2	-1	0	0	2	2	0	-1	2	0		d _(2z² - x² - y²) , d _(x² - y²)
T _{1g}	3	0	-1	1	-1	3	1	0	-1	-1	(R _x , R _y , R _z)	
T _{2g}	3	0	1	-1	-1	3	-1	0	-1	1		d _(xy) , d _(yz) , d _(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		
T _{2u}	3	0	1	-1	-1	-3	1	0	1	-1		

orbitals aligned along z, and xy axes

orbitals aligned in between x + y + z axes

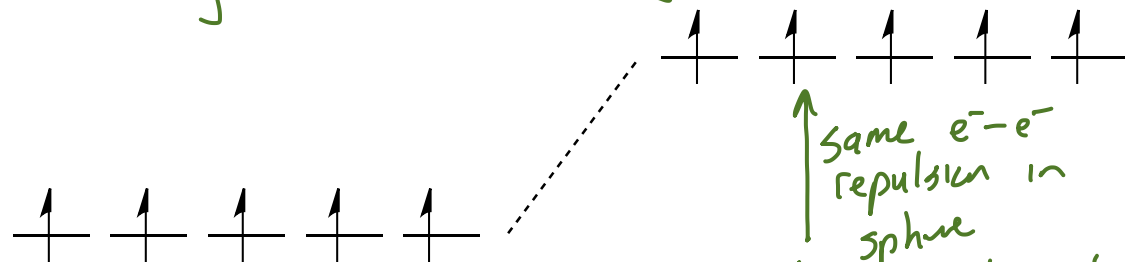
different symmetries means ligand e⁻'s interact differently with e⁻'s in metal d orbitals





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

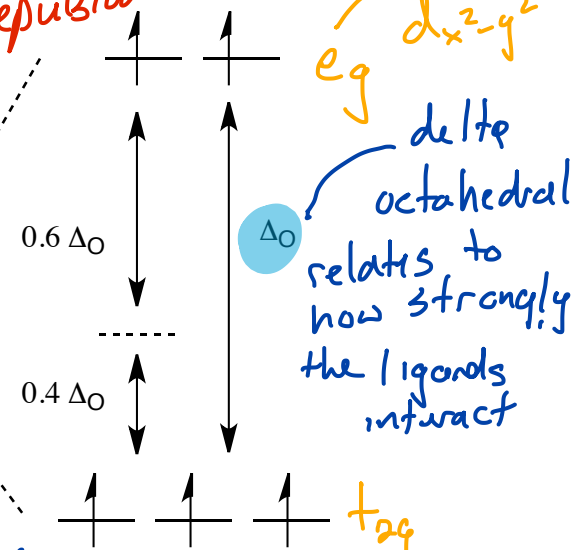
e^- 's in the d_{z^2} orbital would experience greater $e^- - e^-$ repulsion



metal

metal in spherical field of e^- density

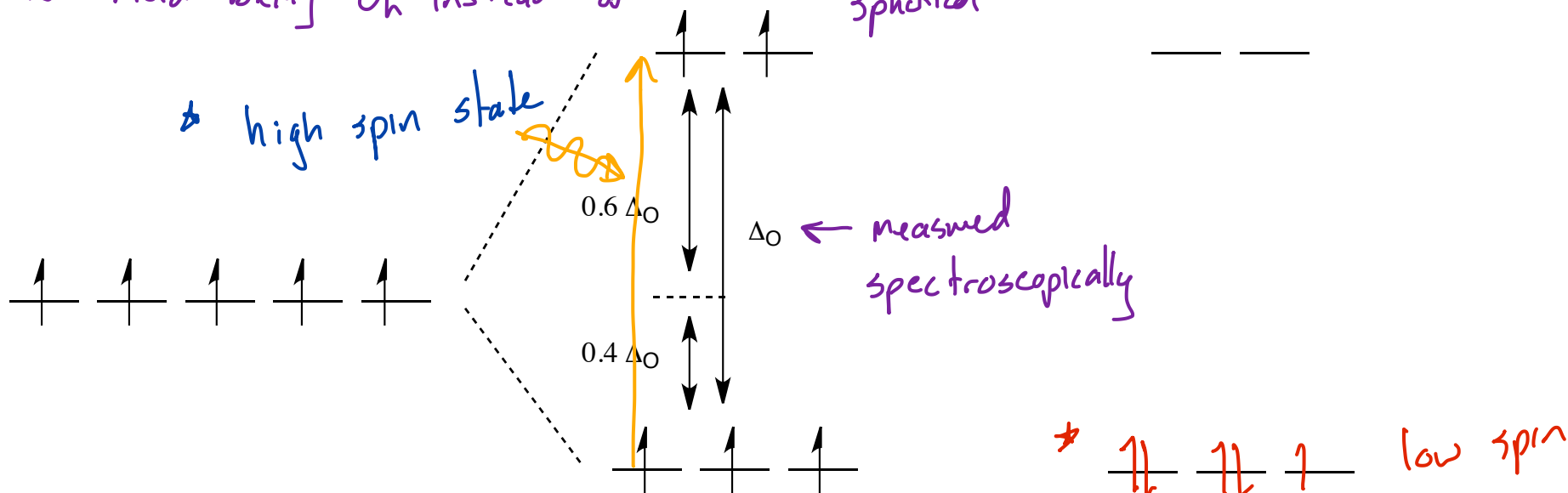
d_{xy}, d_{yz}, d_{xz}



metal in the center of the octahedron of Cl^- charges

Δ_o octahedral relates to how strongly the ligands interact

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 Oh instead of spherical



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

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

$E_{\text{Octahedral}} = (3 \text{ e}^- \times -0.4\Delta_o) + (2 \text{ e}^- \times 0.6\Delta_o)$

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 eg 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