Transition Metal Complexes
Bonding

Bonding Theory

- Crystal Field Theory

  Coulomb Interactions

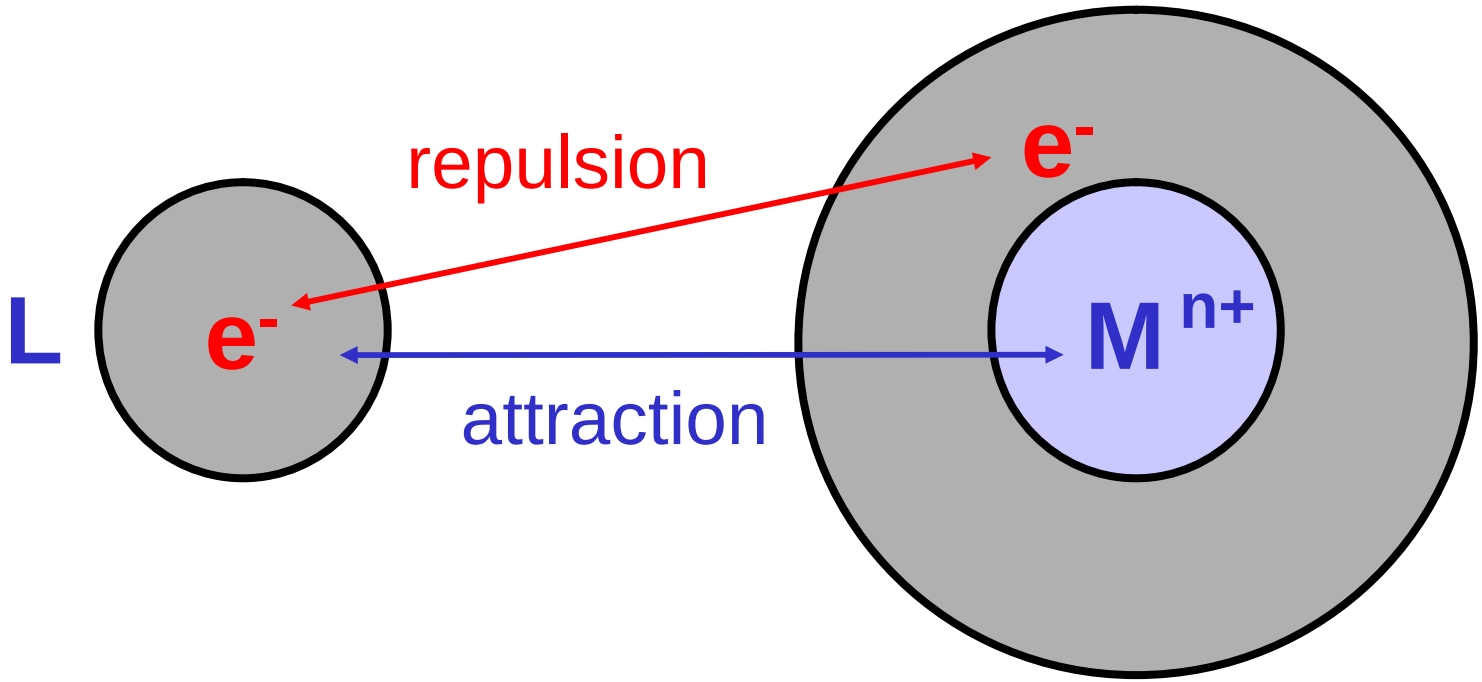
  – attraction between metal ion and ligand electrons

  – repulsion between metal electrons and ligand electrons
- Ligand Field Theory

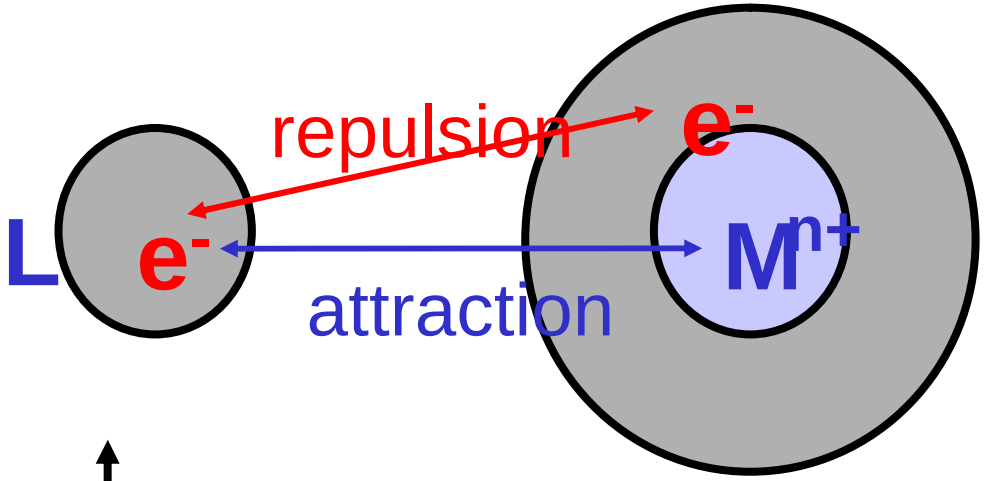
  MO Theory

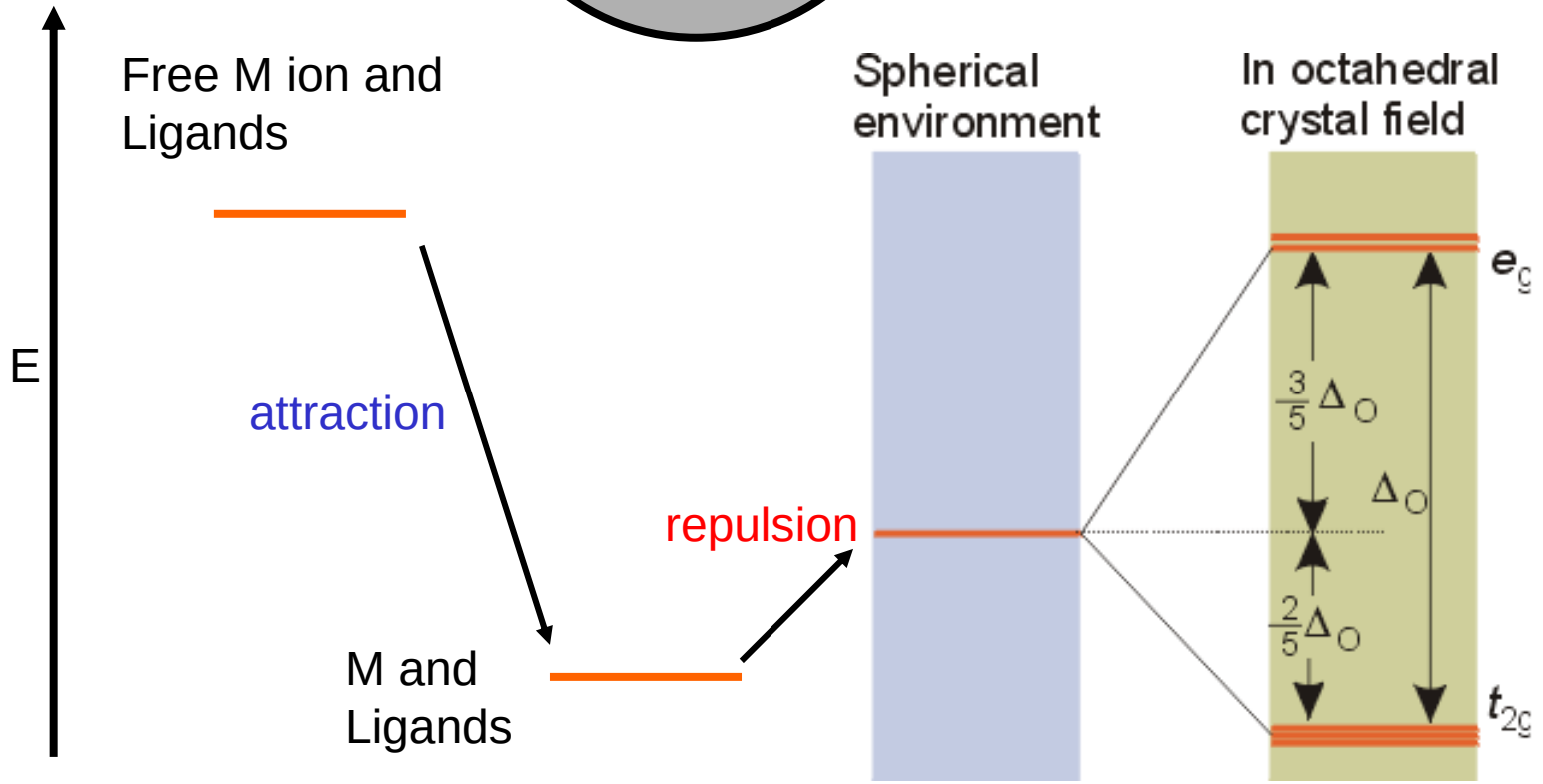
  Overlap of orbitals between ligands and metal

Crystal Field Theory



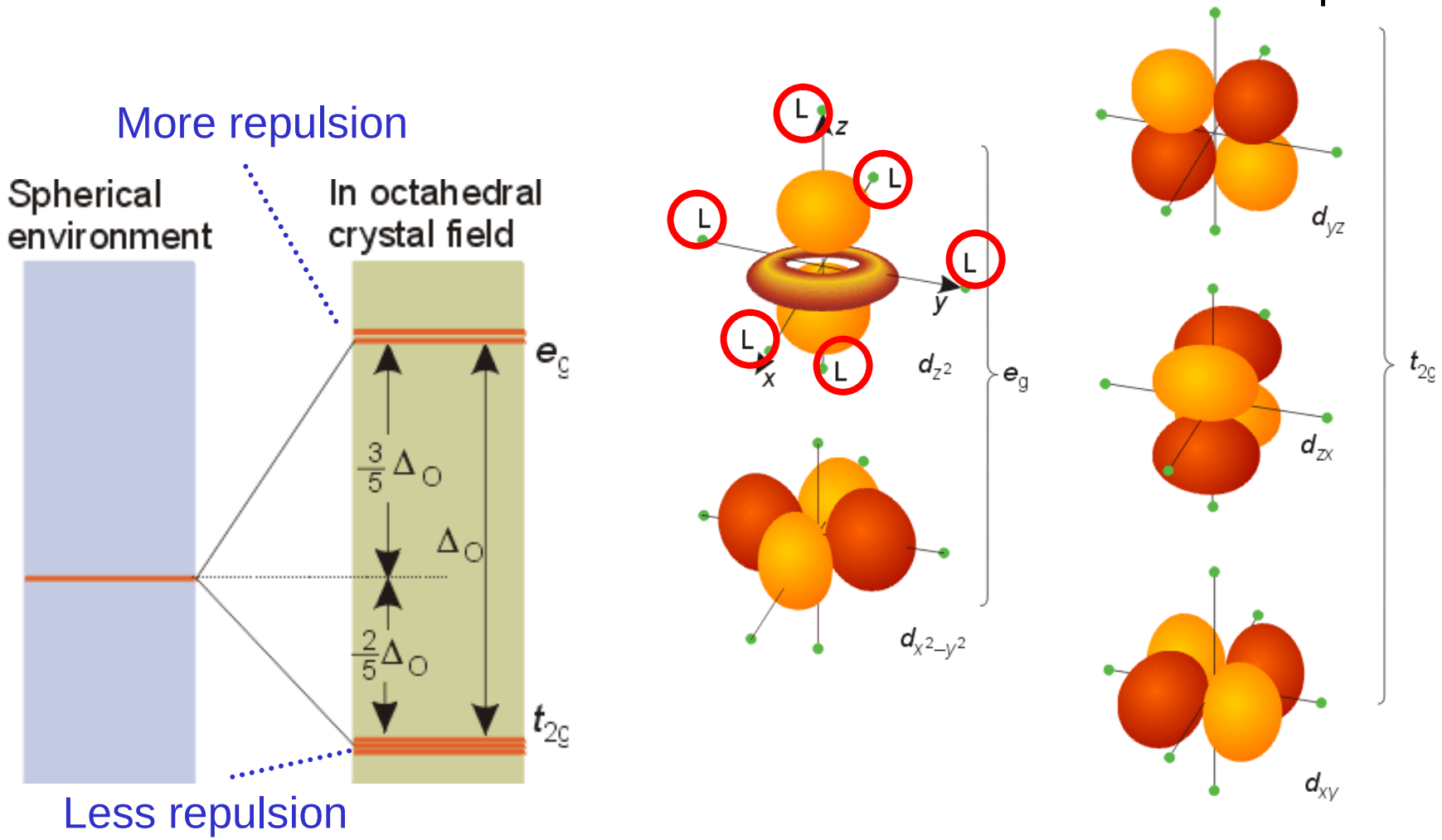
Crystal Field Theory





Splitting of d Orbitals in O_h Field

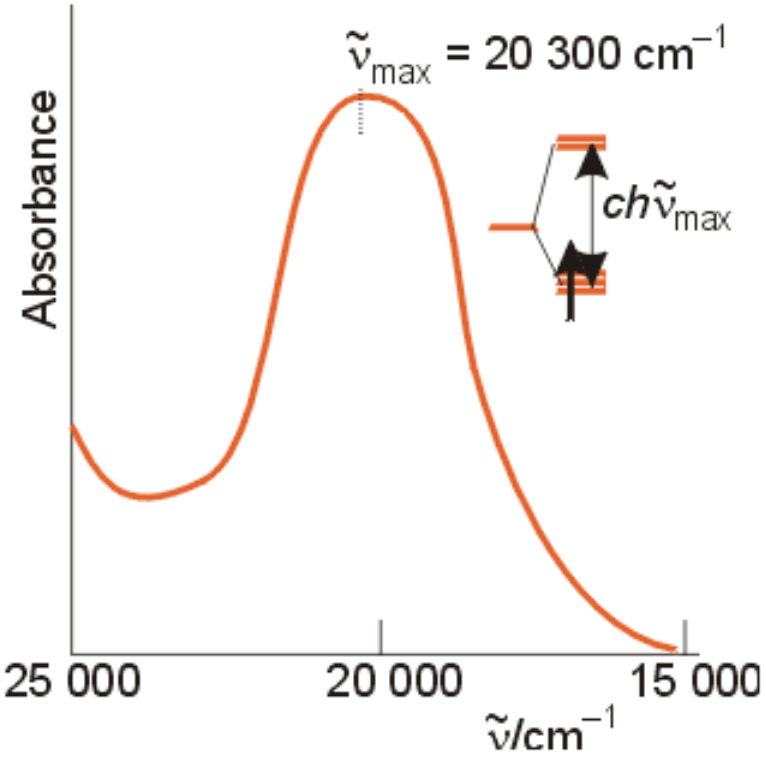
Δ_o: Ligand Field Splitting Parameter (10 D_q)



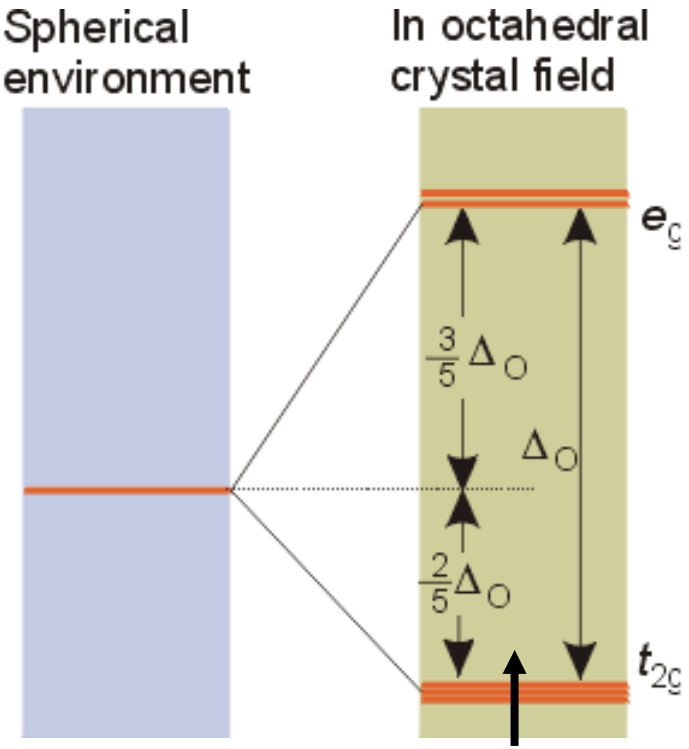
Factors Affecting the Magnitude Crystal Field Splitting

- Identity of the ligand
- Charge on the metal
- Position in a group
- Geometry and coordination number

Absorption Spectrum of $[Ti(OH_2)_6]^{3+}$



$e_g \longleftarrow t_{2g}$



Variation of Δ_o in Octahedral Ti(III) Complexes

- Ti(III) is a d^1 complex and exhibits one absorption in its electronic spectrum due to transition of the electron from the t_{2g} orbitals to the e_g orbitals. The energy of the absorption corresponds to Δ_o.

Ligand	Δ_o/cm^{-1}*
Br^-	11,400
Cl^-	13,000
$(H_2N)_2C=\underline{O}$	17,550
$\underline{N}CS^-$	18,400
F^-	18,900
H_2O	20,100
CN^-	22,300

*E = hν = hc/λ

Spectrochemical Series: Arrangement of ligands in order of increasing ligand field strength

Spectrochemical Series

- Order of ligand field strength with decreasing Δ_o:

  π acceptor > no π effect > weak π donor > π donor

  strong field ⟶ weak field

  CO > CN^- > PPh_3 > phen ~ NO_2^- > bipy > en > NH_3 ~ py > CH_3CN > $\underline{N}CS^-$ > H_2O > $C_2O_4^{2-}$ > OH^- > F^- > N_3^- > NO_3^- > Cl^- > $\underline{S}CN^-$ > S^{2-} > Br^- > I^-

- Order of metal with increasing Δ_o:

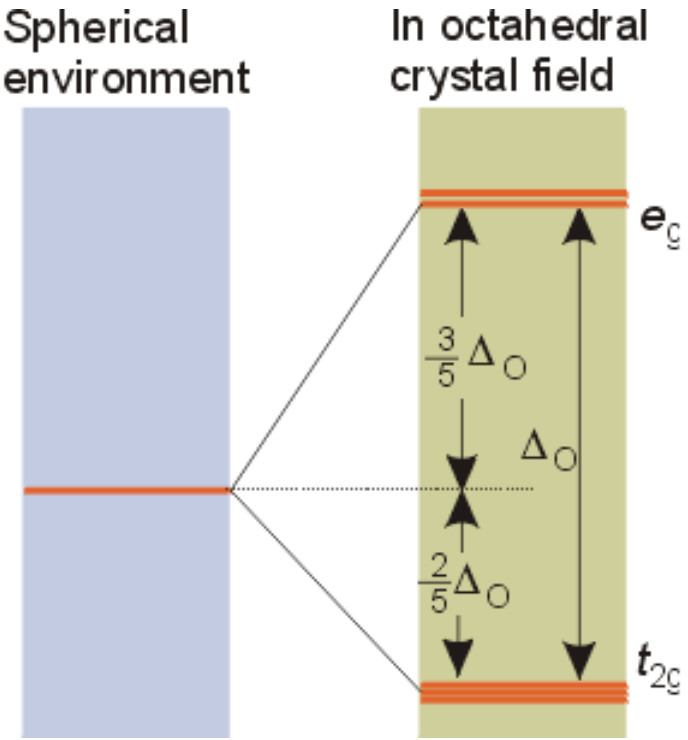
  Increases with increasing oxidation number

  Increases down a group

  Mn(II) < Ni(II) < Co(II) < Fe(II) < V(II) < Fe(III) < Co(III) < Mn(IV) < Mo(III) < Rh(III) < Ru(III) < Pd(IV) < Ir(III) < Pt(IV)

  weak field ⟶ strong field

Ligand Field Stabilization Energy (LFSE)

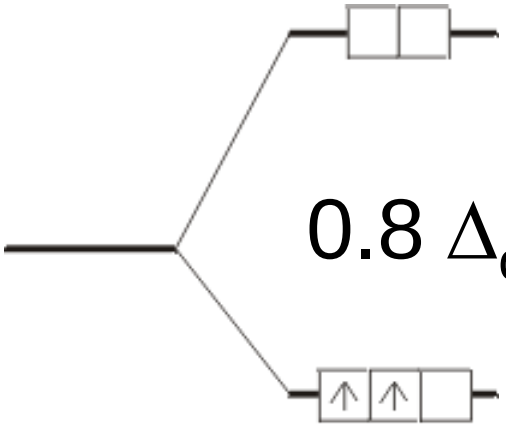


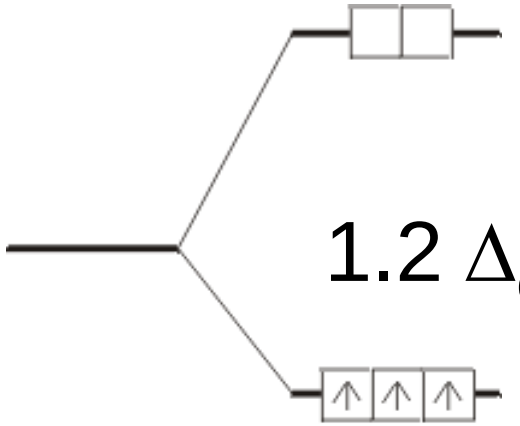
# of electrons

$$LFSE = (-0.4\,x + 0.6\,y)\,\Delta_o$$

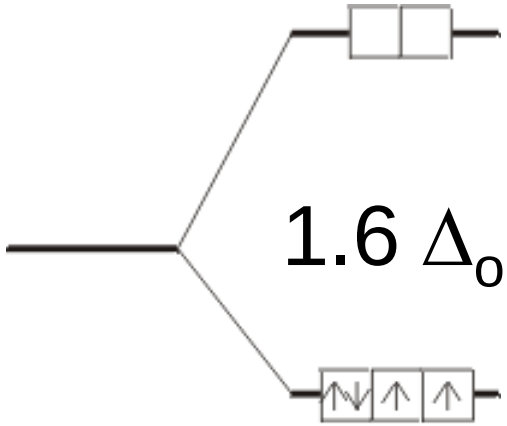
# of electrons

Strong Field and Weak Field

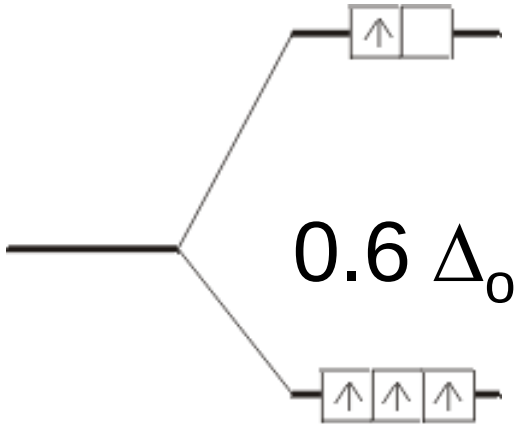




42 d^2



43 d^3



44 Strong-field d^4

45 Weak-field d^4

Pairing Energy

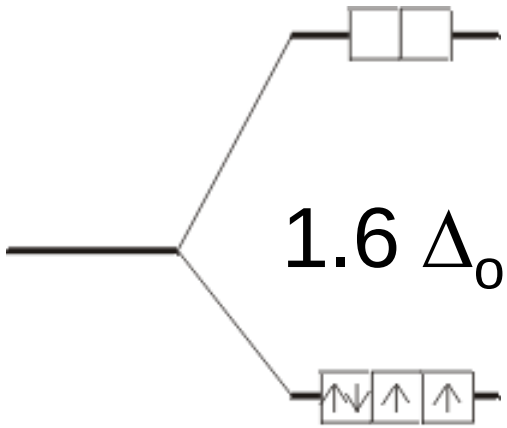
Pairing Energy:

Coulombic repulsion between electrons in the same orbital

1.6 Δ_o – P (pairing energy)	>	0.6 Δ_o	Strong Field
1.6 Δ_o – P (pairing energy)	<	0.6 Δ_o	Weak Field

Strong Field

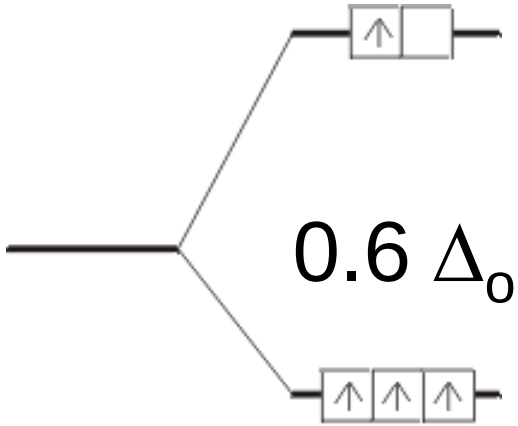
Low spin, 2 unpaired electrons



44 Strong-field d^4

Weak Field

High spin, 4 unpaired electrons



45 Weak-field d^4

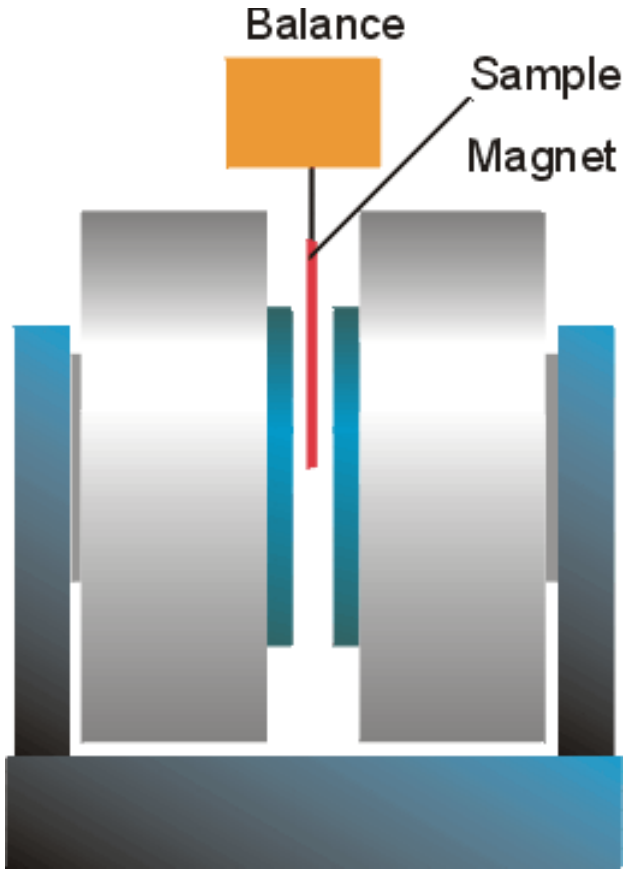
LFSE Δ_o and Δ_t

d^n	Example		Octahedral						Tetrahedral	
					N	LFSE			N	LFSE
0	Ca^{2+}	Sc^{3+}			0	0			0	0
1	Ti^{3+}				1	0.4			1	0.6
2	V^{3+}				2	0.8			2	1.2
3	Cr^{3+}	V^{2+}			3	1.2			3	0.8
			Strong Field				Weak Field			
4	Cr^{2+}	Mn^{3+}	2	1.6			4	0.6	4	0.4
5	Mn^{2+}	Fe^{3+}	1	2.0			5	0	5	0
6	Fe^{2+}	Co^{3+}	0	2.4			4	0.4	4	0.6
7	Co^{2+}		1	1.8			3	0.8	3	1.2
8	Ni^{2+}				2	1.2			2	0.8
9	Cu^{2+}				1	0.6			1	0.4
10	Cu^{+}	Zn^{2+}			0	0			0	0

Magnetic Measurements

- Paramagnetic:
  unpaired electrons

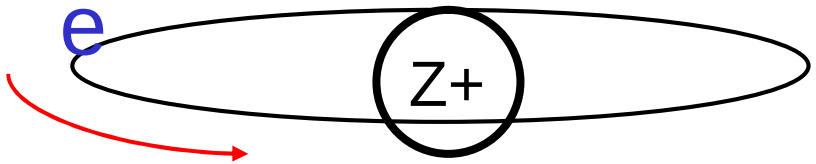
- Diamagnetic:
  all electrons paired



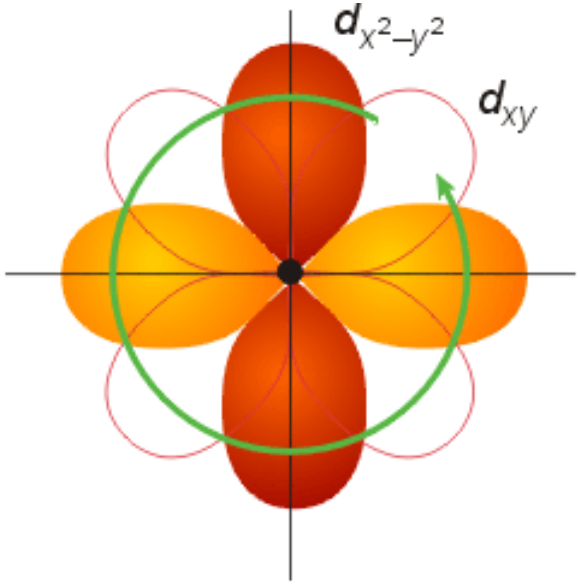
Origins of Magnetism

- Self spinning

- Spinning about nucleus



Origin of Orbital Angular Momentum



Spin-only Paramagnetism

- Magnetic Moment

$\mu = 2\{S(S+1)\}^{1/2}\ \mu_B$ $\qquad S = \Sigma s_i$

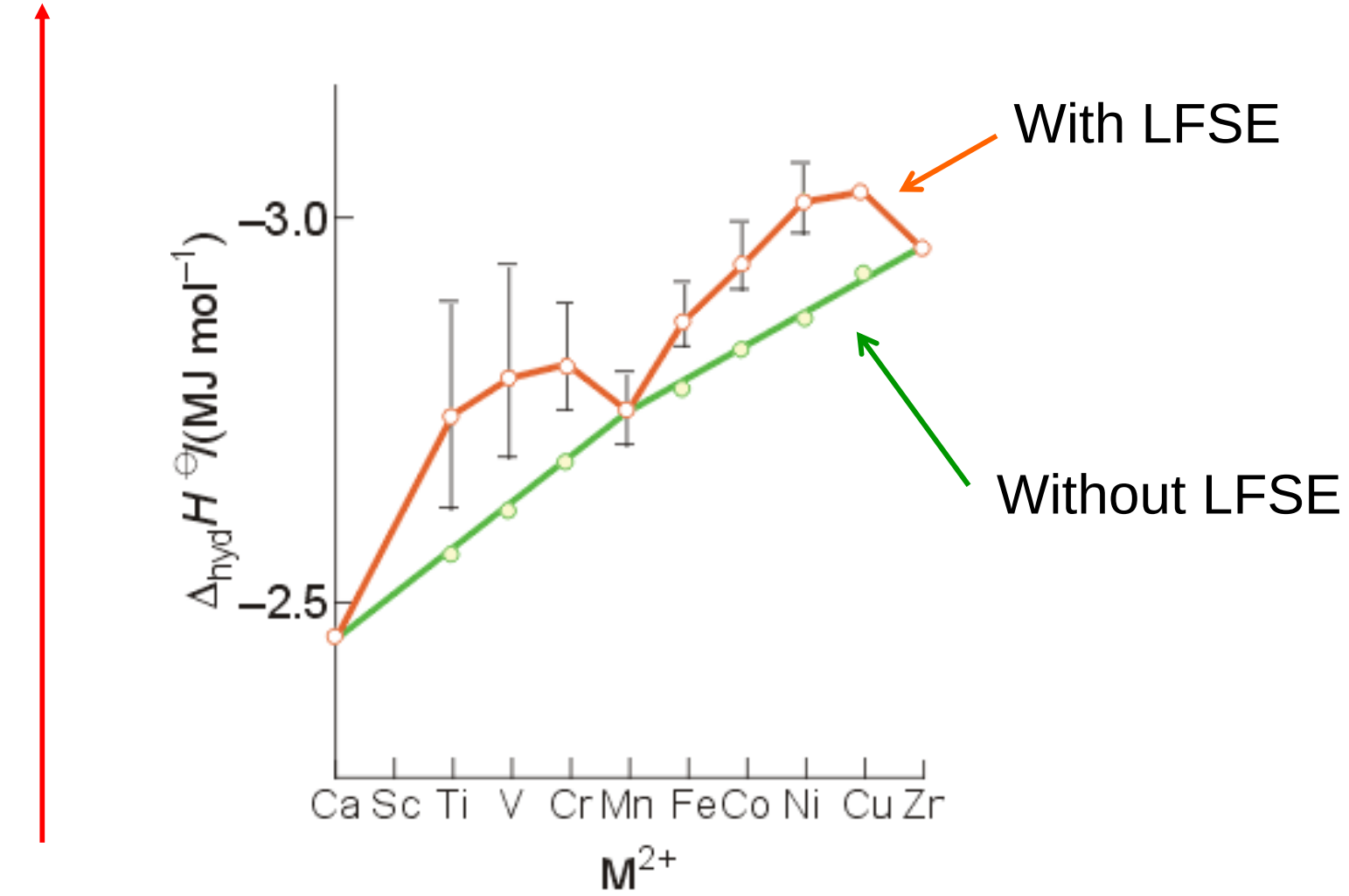
$= \{N(N+2)\}^{1/2}\ \mu_B$

μ_B : Bohr magneton, 9.274×10^{-24} J/T

Ion	*N*	*S*	μ / μ_B	
			Calc.	Exp.
Ti^{3+}	1	1/2	1.73	1.7 – 1.8
V^{3+}	2	1	2.83	2.7 – 2.9
Cr^{3+}	3	3/2	3.87	3.8
Mn^{3+}	4	2	4.90	4.8 – 4.9
Fe^{3+}	5	5/2	5.92	5.9

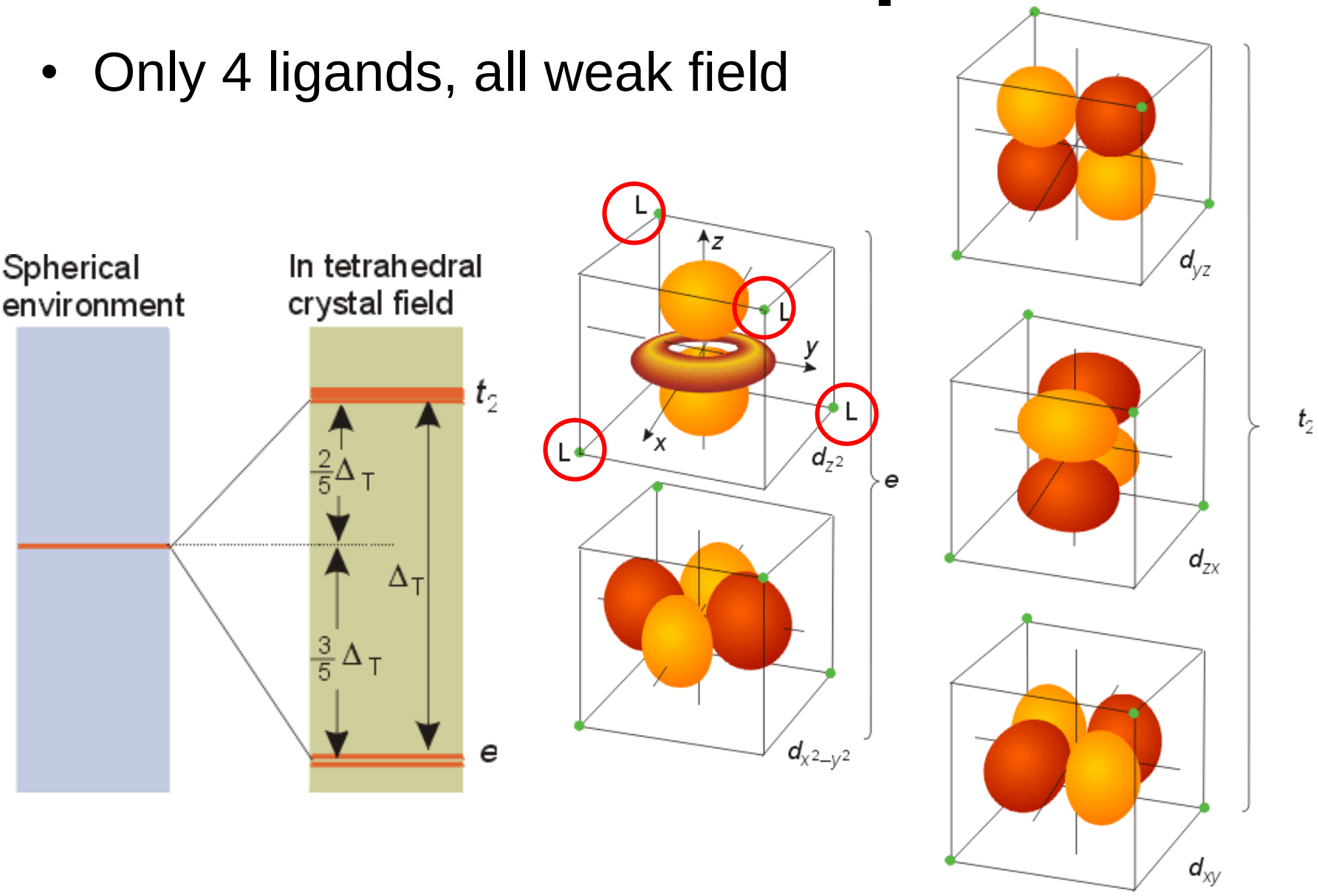
Thermochemical Correlations

More Stable



Tetrahedral Complexes

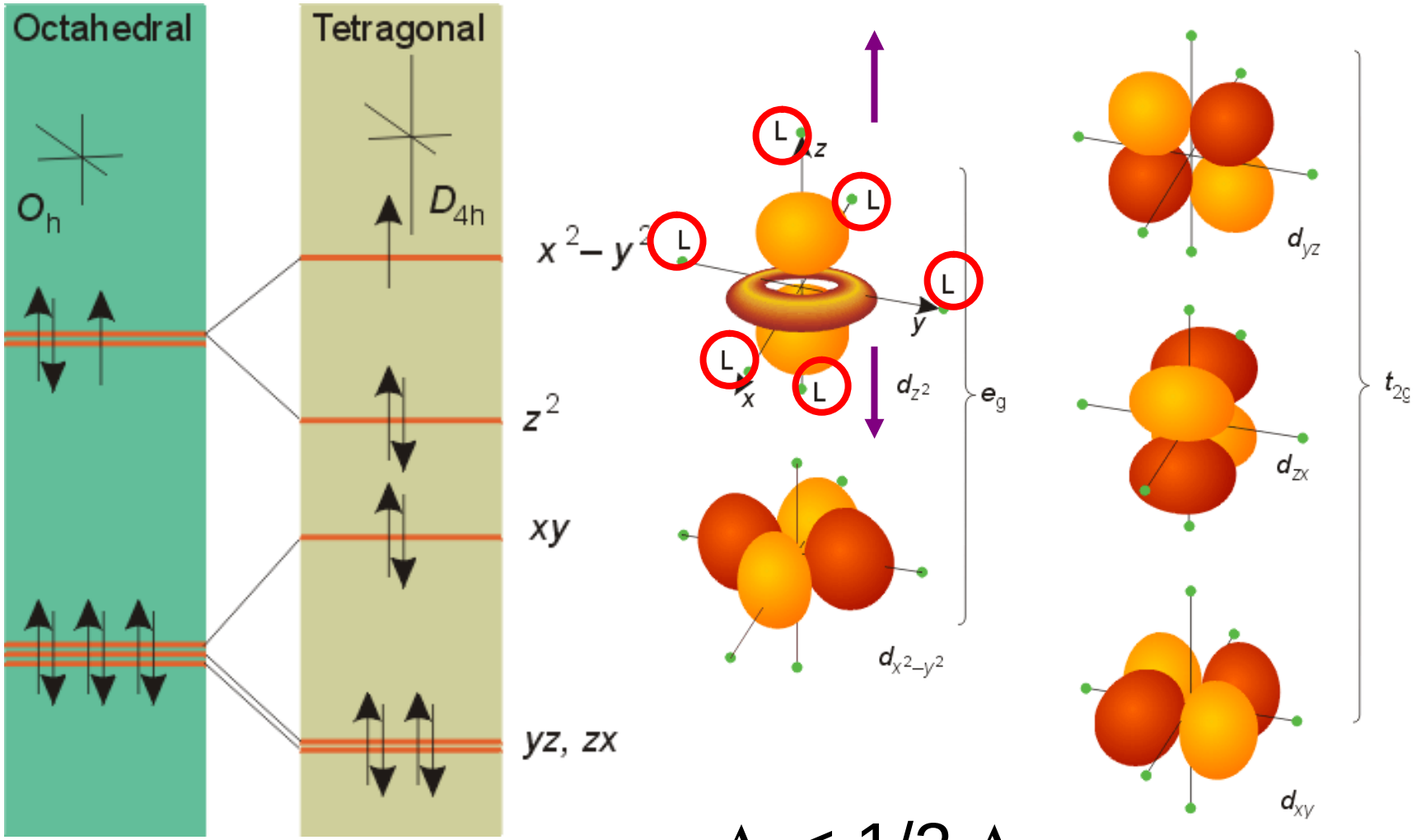
- Only 4 ligands, all weak field



LFSE Δ_o and Δ_t

d^n	Example		Octahedral						Tetrahedral	
					N	LFSE			N	LFSE
0	Ca^{2+}	Sc^{3+}			0	0			0	0
1	Ti^{3+}				1	0.4			1	0.6
2	V^{3+}				2	0.8			2	1.2
3	Cr^{3+}	V^{2+}			3	1.2			3	0.8
			Strong Field				Weak Field			
4	Cr^{2+}	Mn^{3+}	2	1.6			4	0.6	4	0.4
5	Mn^{2+}	Fe^{3+}	1	2.0			5	0	5	0
6	Fe^{2+}	Co^{3+}	0	2.4			4	0.4	4	0.6
7	Co^{2+}		1	1.8			3	0.8	3	1.2
8	Ni^{2+}				2	1.2			2	0.8
9	Cu^{2+}				1	0.6			1	0.4
10	Cu^{+}	Zn^{2+}			0	0			0	0

Tetragonal Complexes



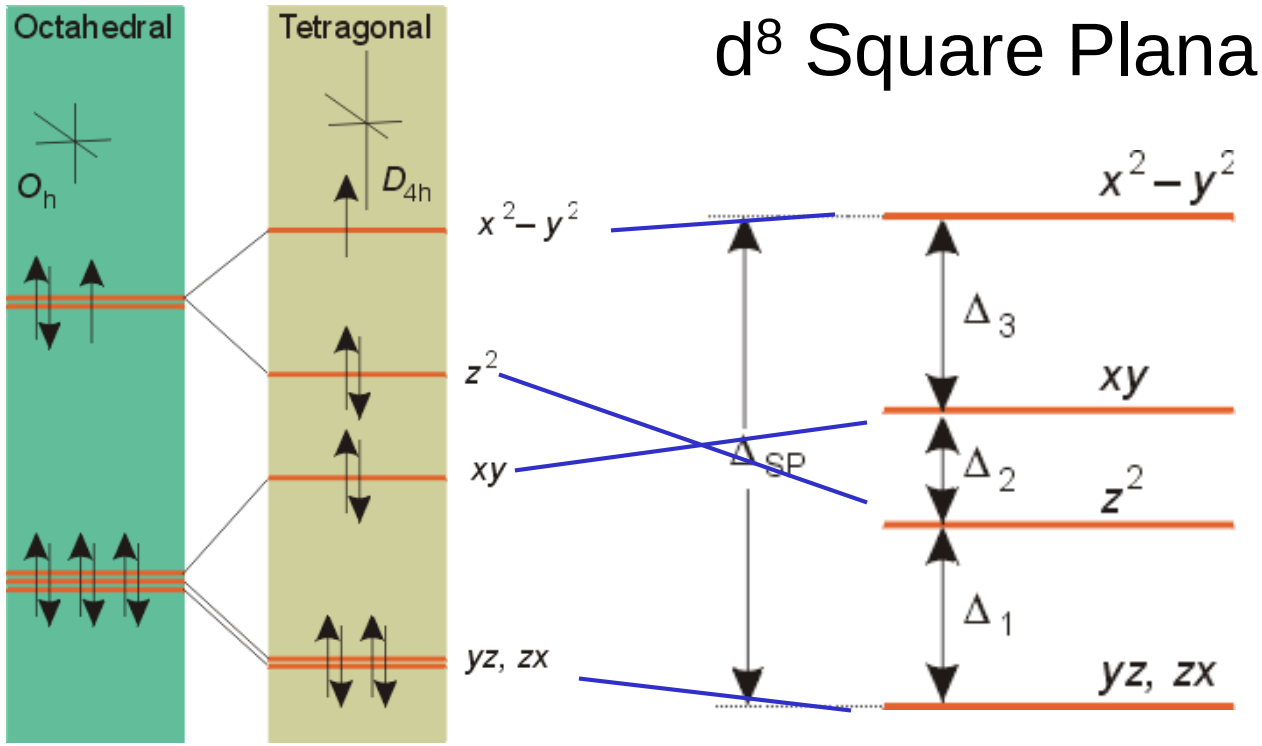
$\Delta_t < 1/2\ \Delta_o$

Square Planar Complexes

$\Delta_{sp} > \Delta_o$

$\Delta_{sp} \sim 1.3\ \Delta_o$

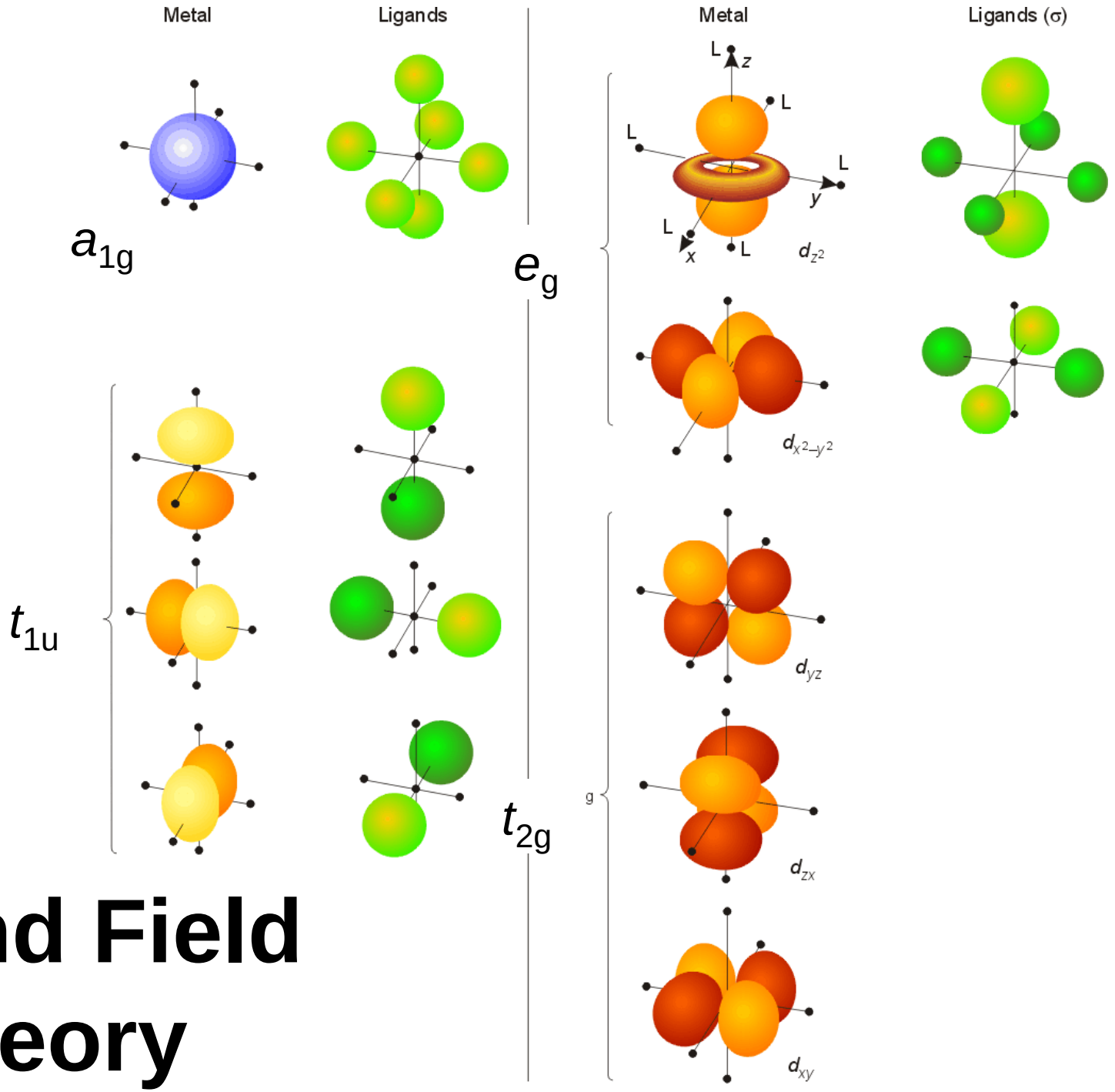
d^8 Square Planar stable



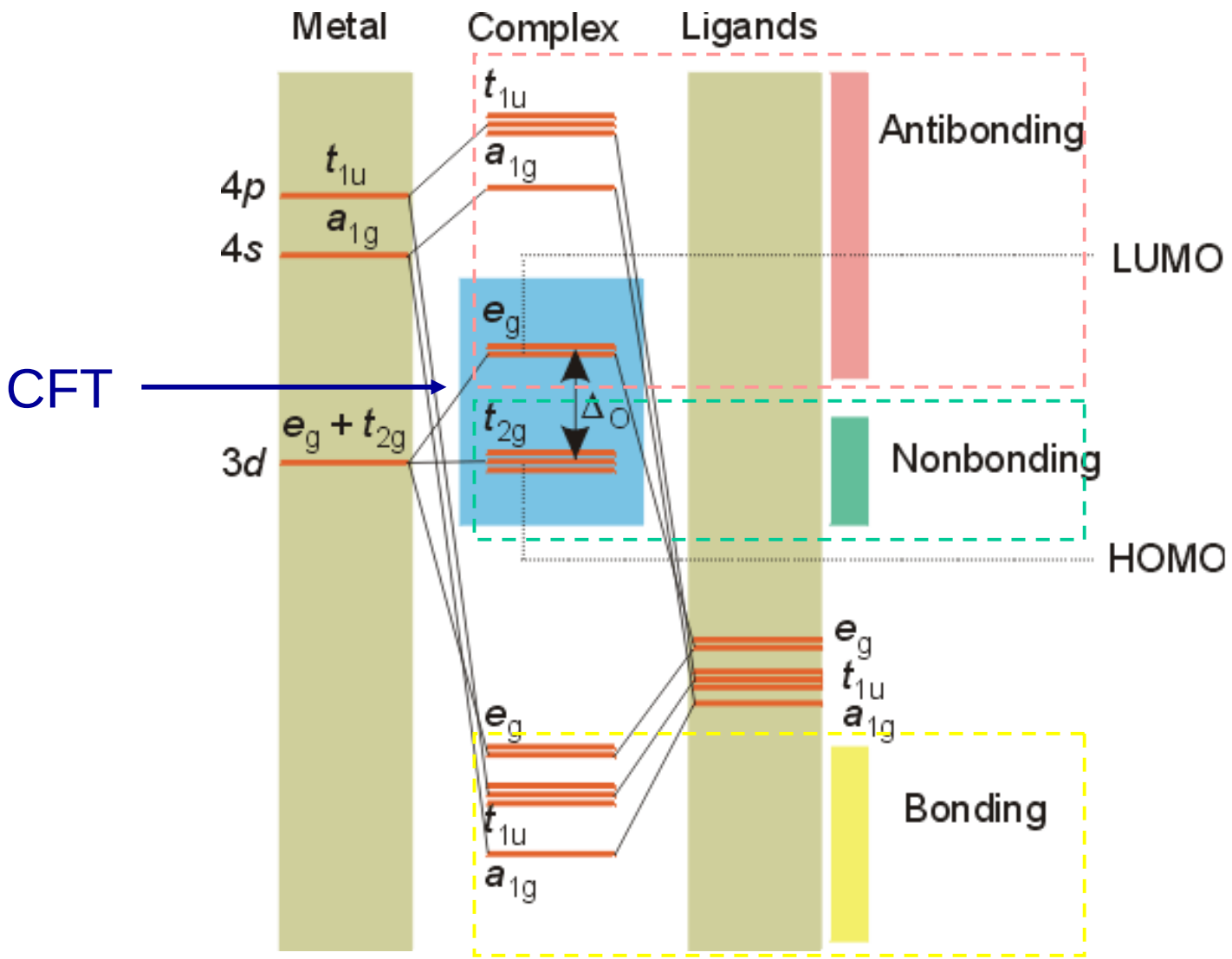
Jahn-Teller Effect

- If the ground electronic configuration of a linear complex is orbitally degenerate, the complex will distort so as to remove the degeneracy and achieve a lower energy.

Ligand Field Theory

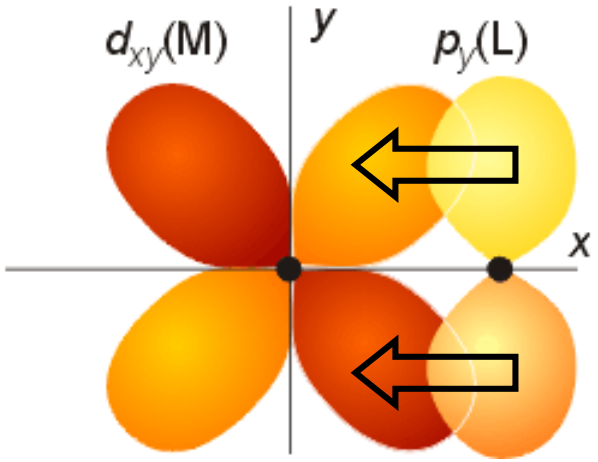


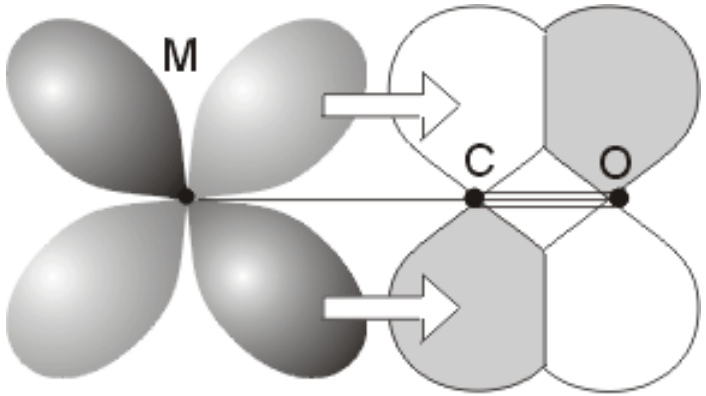
MO Energy Level Diagram



M-L π-Bonding

π-donor (π-base) and π-acceptor (π-acid)





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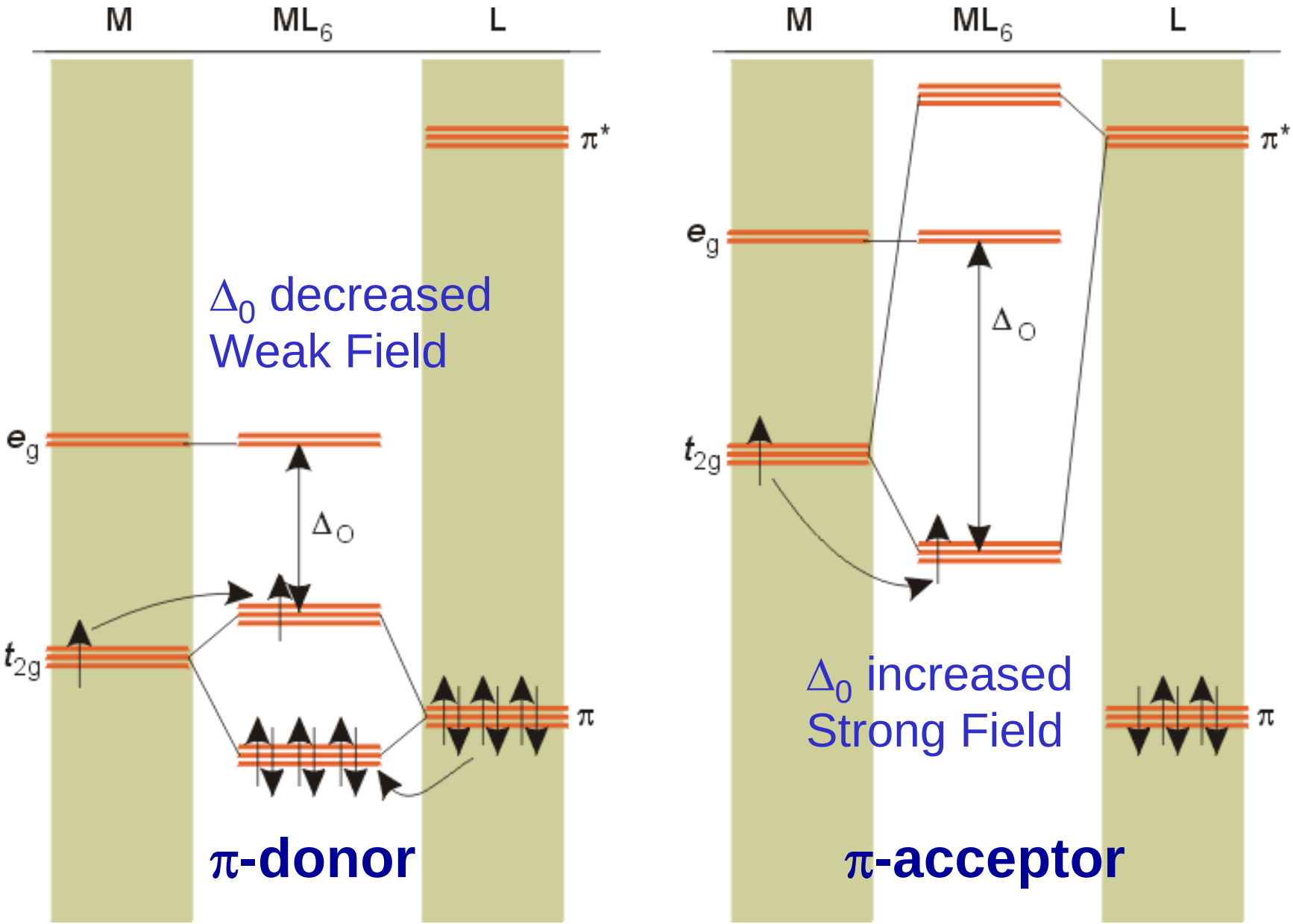
Effect of π-Interaction on Δ_o



M-L π-Bonding

- Order of ligand field strength with decreasing Δ_o:

  π acceptor > no π effect > weak π donor > π donor

  strong field ⟶ weak field

  $CO > CN^- > PPh_3 > phen \sim NO_2^- > bipy > en > NH_3 \sim py > CH_3CN > \underline{N}CS^- > H_2O > C_2O_4^{2-} > OH^- > F^- > N_3^- > NO_3^- > Cl^- > \underline{S}CN^- > S^{2-} > Br^- > I^-$

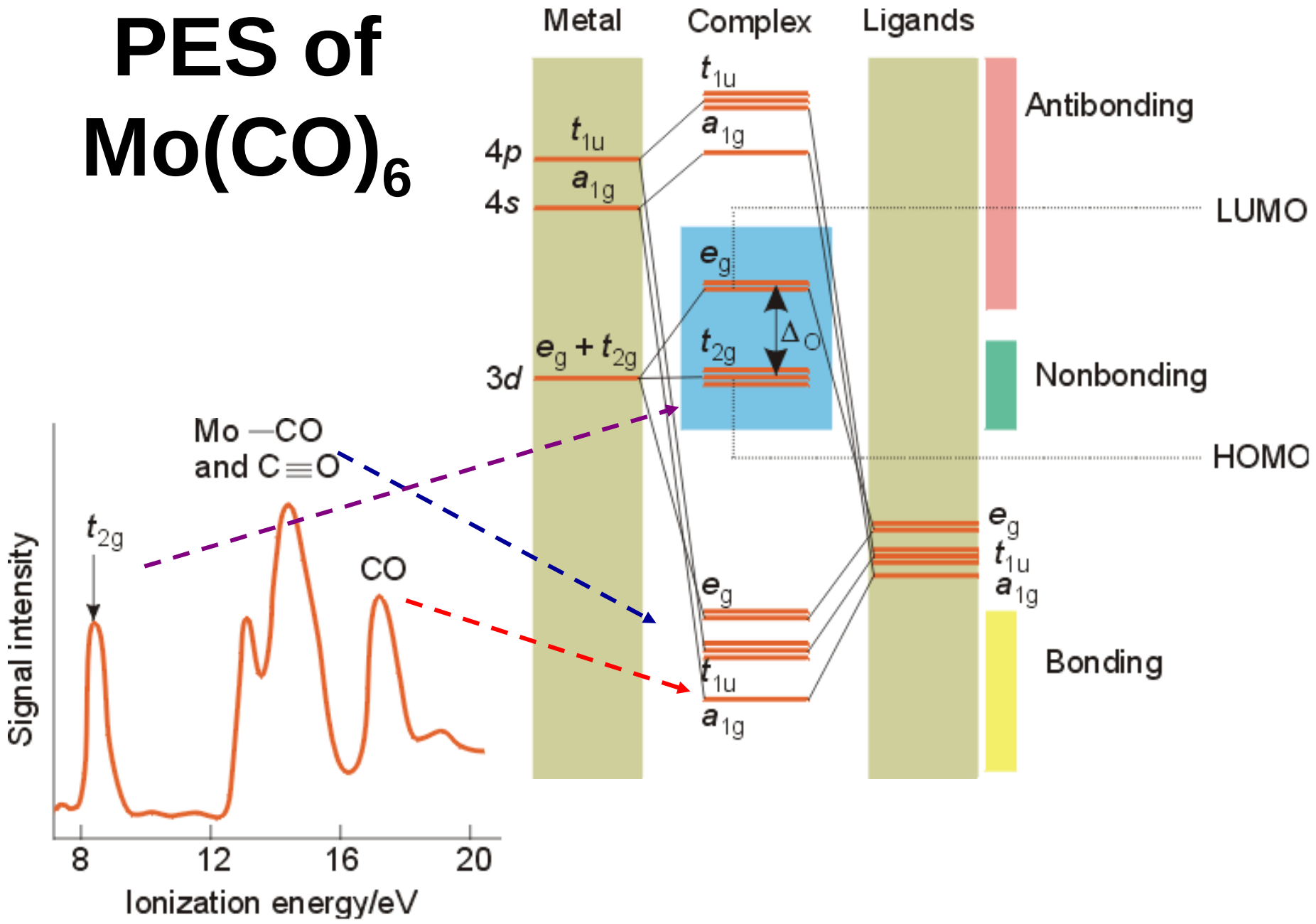
- Low Oxidation State Metal (electron rich)

  – π Acceptor Ligands

- High Oxidation State Metal (electron poor)

  – π Donor Ligands

PES of $Mo(CO)_6$


Metal
Complex
Ligands
Antibonding
Nonbonding
Bonding
LUMO
HOMO
4p
4s
3d
t_{1u}
a_{1g}
e_g
t_{2g}
$e_g + t_{2g}$
Δ_O
Mo —CO
and C≡O
CO
Signal intensity
Ionization energy/eV
8
12
16
20