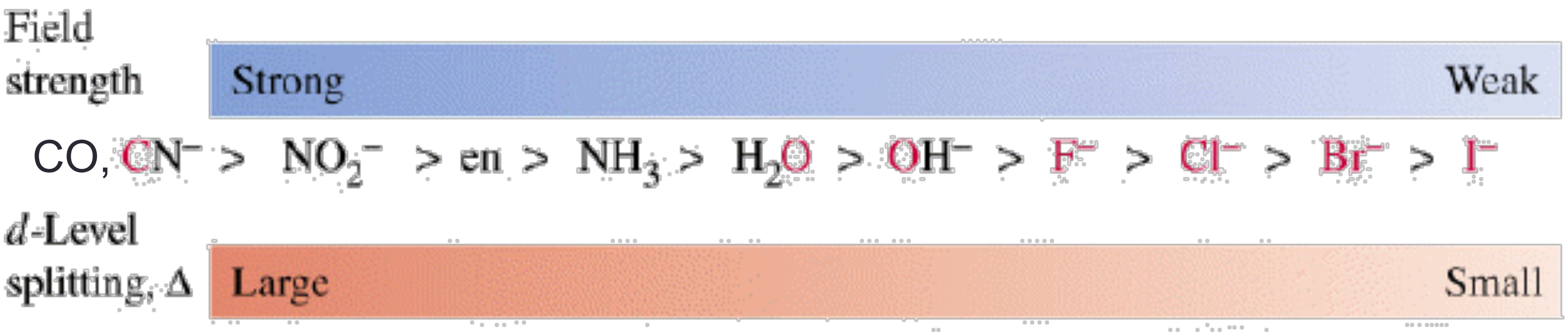
D-ORBITAL SPLITTING AND THE SPECTROCHEMICAL SERIES

MFT Ch 10

The spectrochemical series

Next week's lab will explore this!

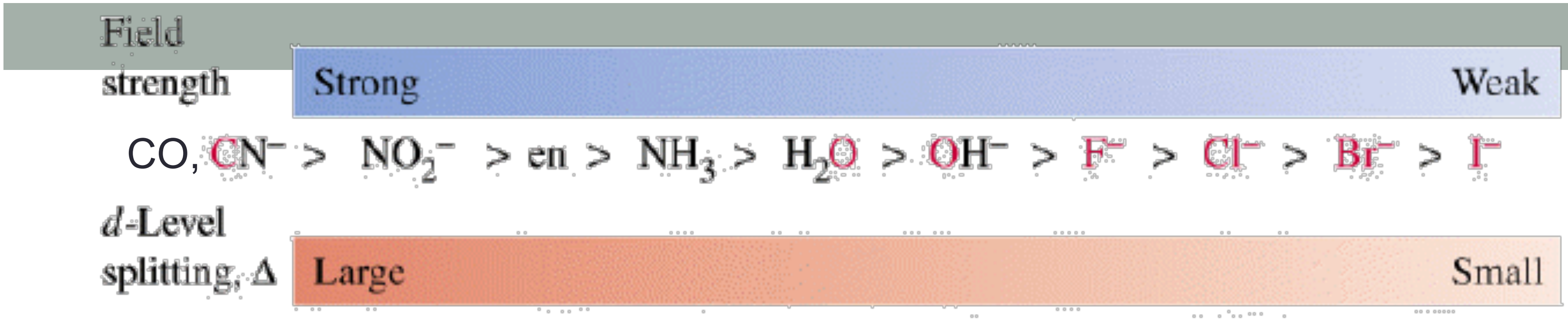
- The spectrochemical series ranks ligands in the order of their 'field strength'



CO, $CN^- > NO_2^- > en > NH_3 > H_2O > OH^- > F^- > Cl^- > Br^- > I^-$

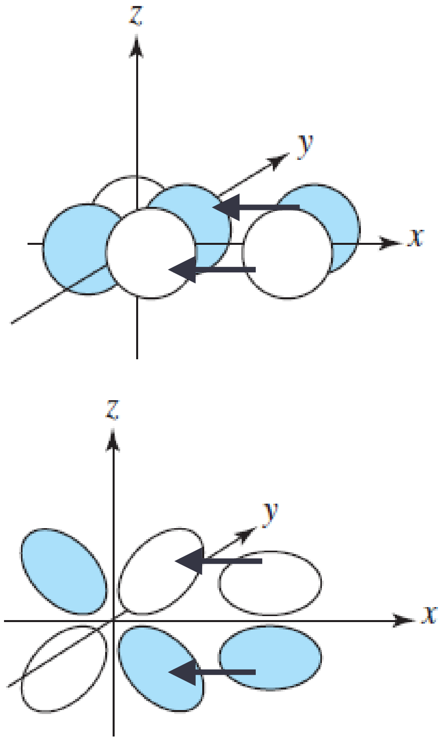
- Strong field ligands produce complexes with a large Δ_o
- Weak field ligands produce complexes with a small Δ_o

- Strong field ligands are pi acceptors, weak field ligands are pi donors



CO, $CN^- > NO_2^- > en > NH_3 > H_2O > OH^- > F^- > Cl^- > Br^- > I^-$

π donor ligands have interaction between filled p orbital on ligand and metal d orbital



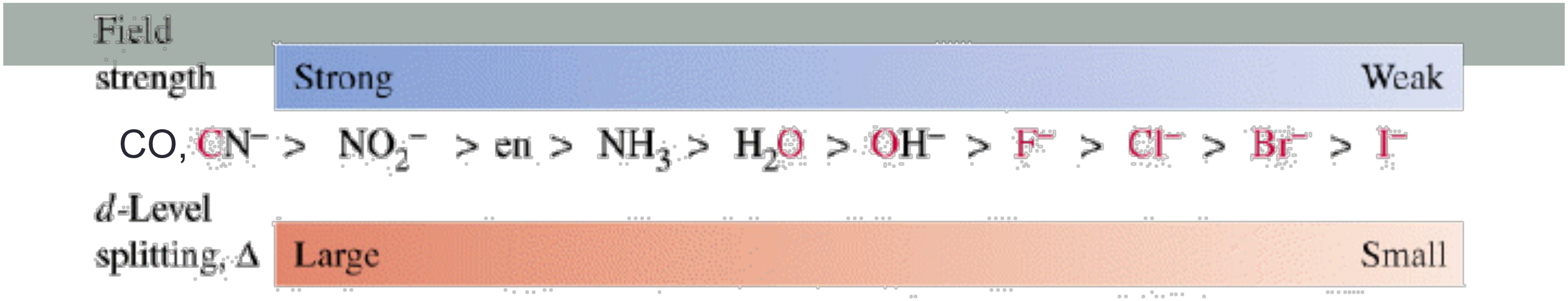
Metal d_{xz} orbital
Ligand p_z orbital

π donor ligands have multiple lone pairs on donor atom (one pair can be a σ donor, another a π donor). Halides are typical examples.

Called ‘weak field’!

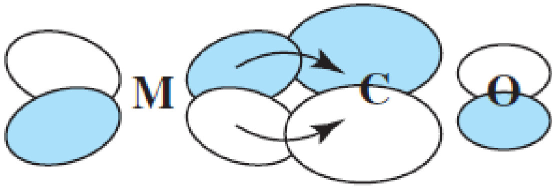
Exception: O-based ligands are not good π donors , O is too electronegative. H_2O is considered σ only, HO^- is a very slightly better π donor (three lone pairs!), so is ‘weaker’ field that H_2O

Note: NH_3, with only one lone pair, is only a σ donor, is stronger field than H_2O

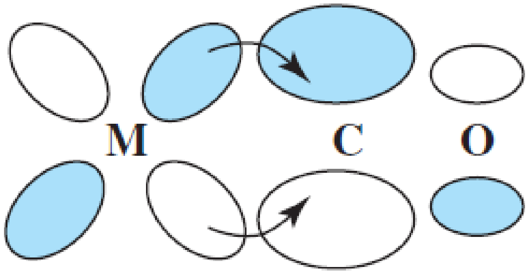


CO, $CN^- > NO_2^- > en > NH_3 > H_2O > OH^- > F^- > Cl^- > Br^- > I^-$

π acceptor ligands have interaction between empty π* orbital on ligand and metal d orbital



π Acceptance



π Acceptance

π acceptor ligands are multiply bonded species that have empty π* orbitals to accept electron density from the metal center

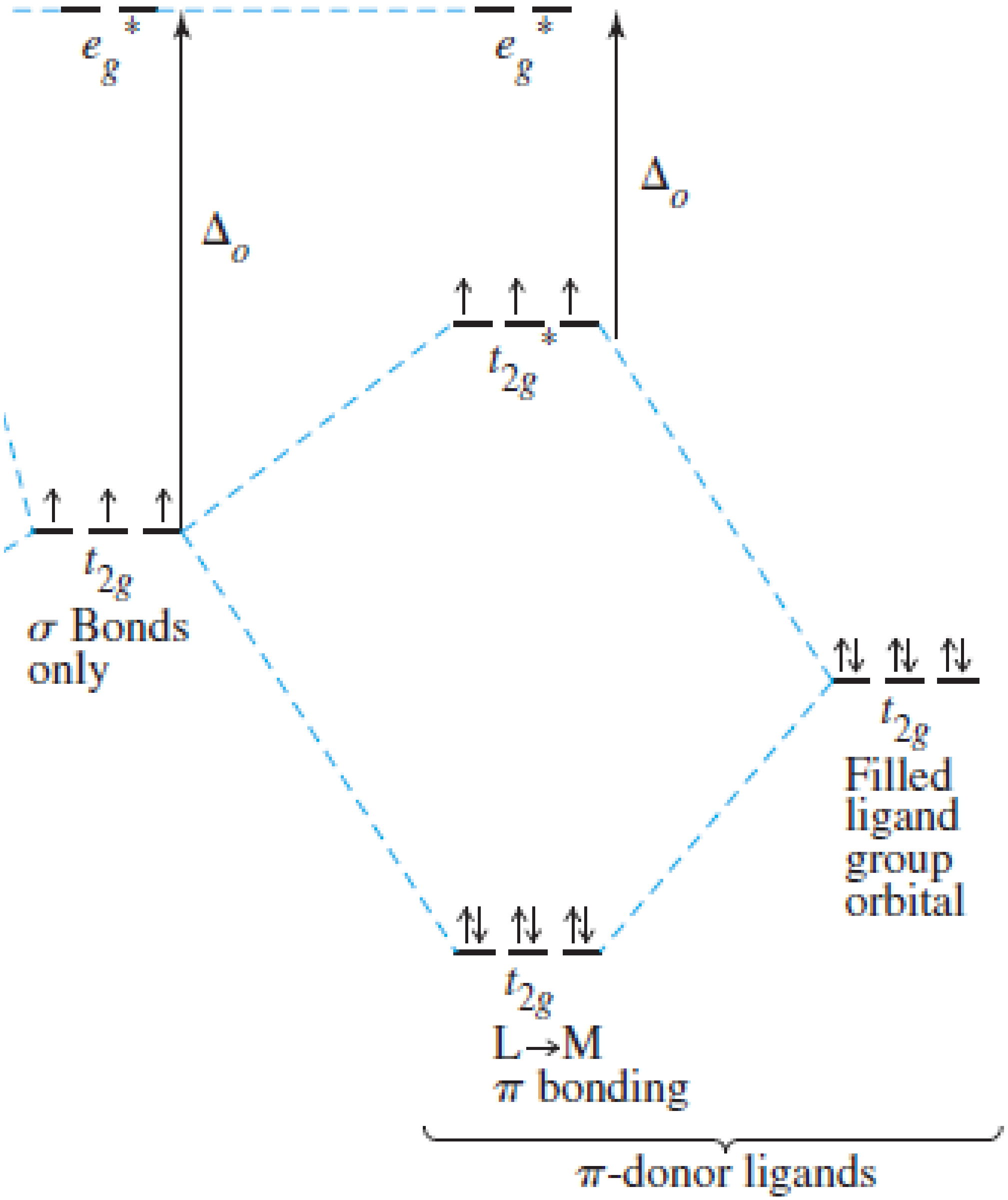
Called ‘strong field’!

Affect of π interactions on d orbital splitting

- Both π donor and acceptor ligands have the right symmetry to interact with the t_{2g} orbitals on the metal, so π interactions will change this from a nonbonding orbital set to an orbital set with more bonding or antibonding character π donor ligands interact with t_{2g} non bonding orbitals.

π donor orbitals are lower in energy than d orbitals (remember, these are nonbonding p orbitals on the ligand)

This causes t_{2g} orbitals that we associate with Δ_o to become antibonding in nature, raising their energy, and making Δ_o smaller in magnitude



π acceptor ligands interact with t_{2g} non bonding orbitals.

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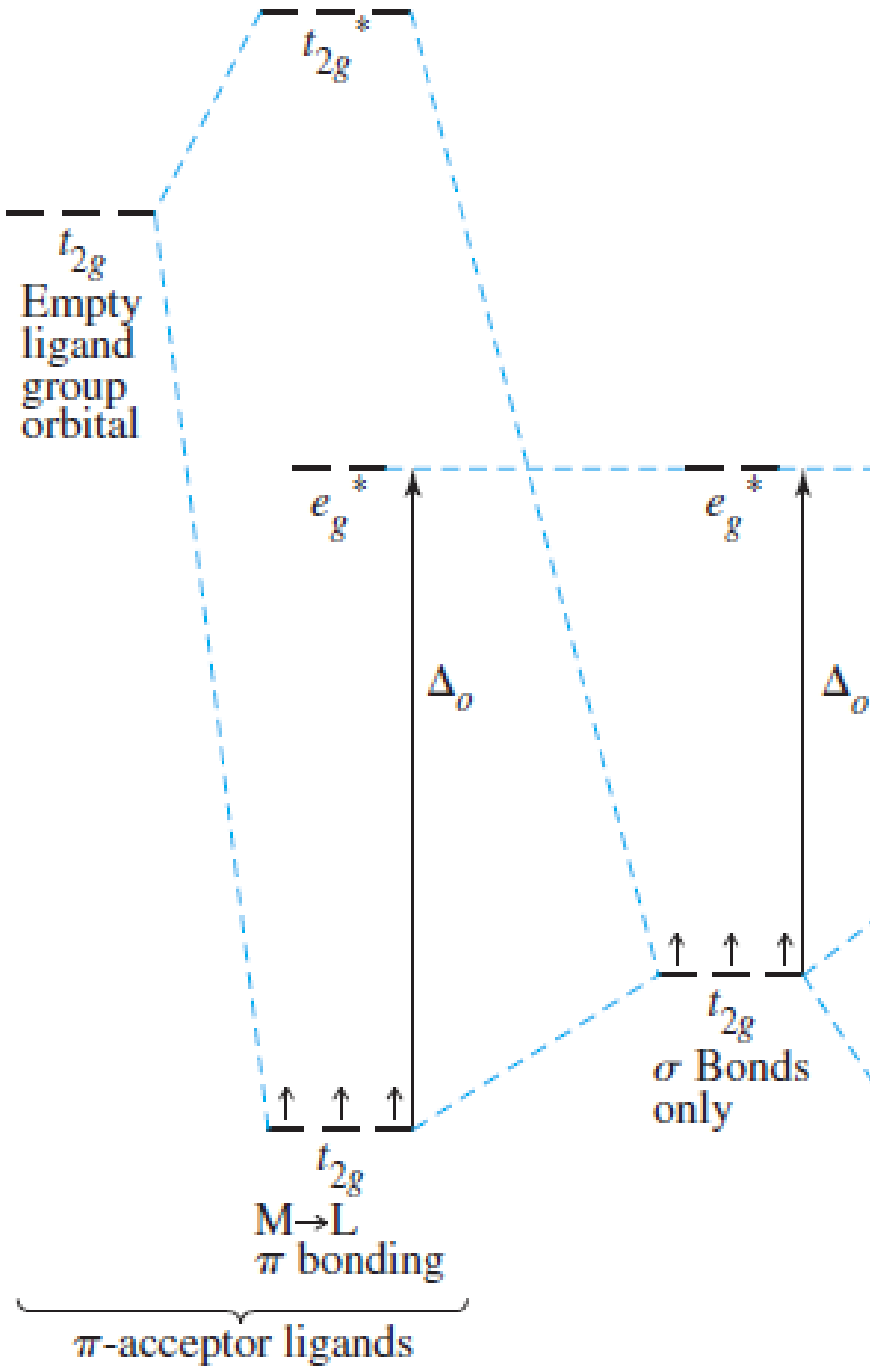
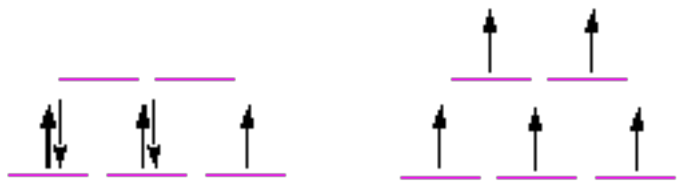


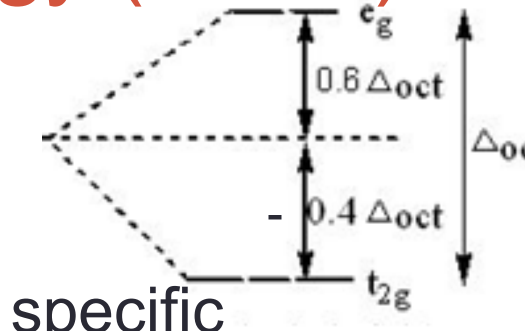
Ligand Field Stabilization Energy (LFSE)

Low spin

d^5



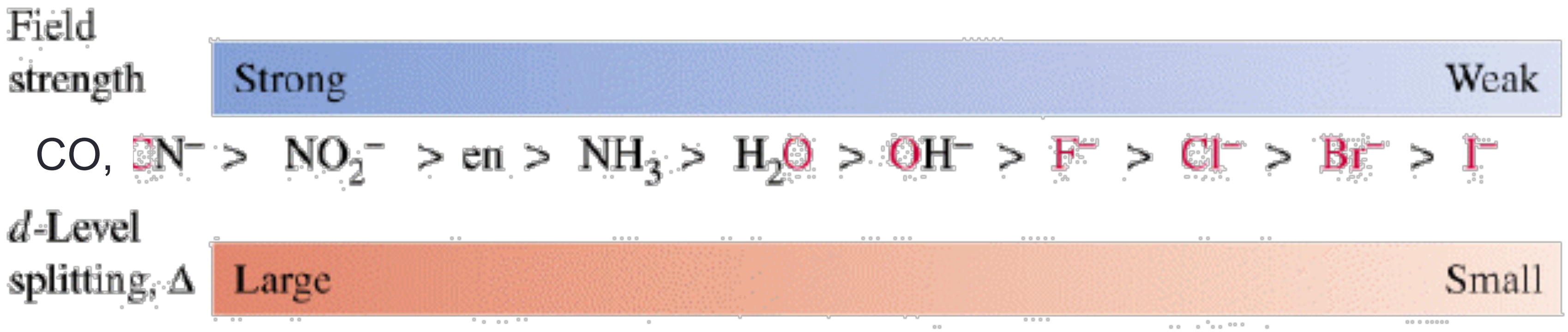
High spin



- LFSE: stabilization energy associated with a specific electronic configuration

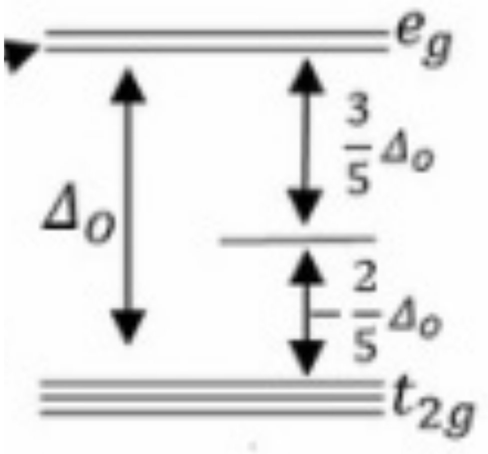
This is for octahedral geometry! Other geometries will have similar types of calculations but numbers are different

- LFSE = $(-2/5\Delta_o)$ x (# of t_2g electrons) + $(3/5\Delta_o)$ x (# of e_g electrons)
- LFSE for low spin d^5: $(-2/5\Delta_o)*5 = -2\Delta_o$
- LFSE for high spin d^5: $(-2/5\Delta_o)*3 + (3/5\Delta_o)*2 = 0$
- More negative values are more stable, (however if Δ_o is small, so is the LFSE, so h.s. complexes are observed!)

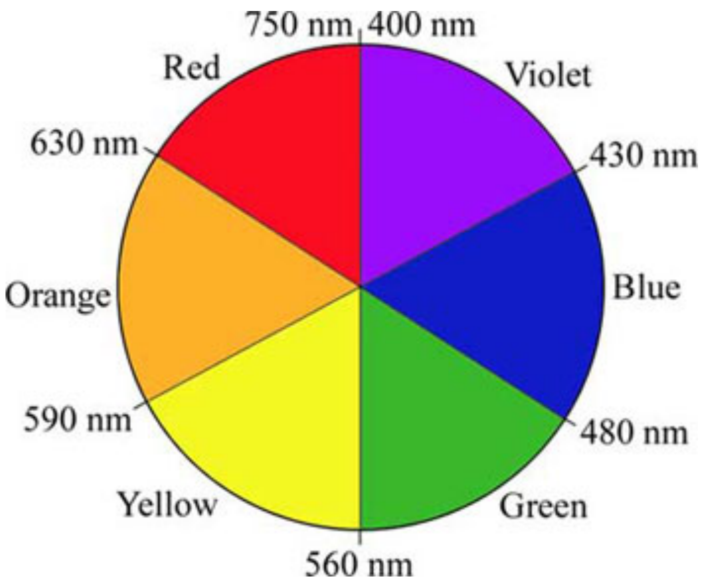


CO, $CN^- > NO_2^- > en > NH_3 > H_2O > OH^- > F^- > Cl^- > Br^- > I^-$

LFSE = $(-2/5\Delta_o)$ x (# of t_2g electrons) + $(3/5\Delta_o)$ x (# of e_g electrons)



$\mu_S = g\sqrt{[S(S+1)]}$



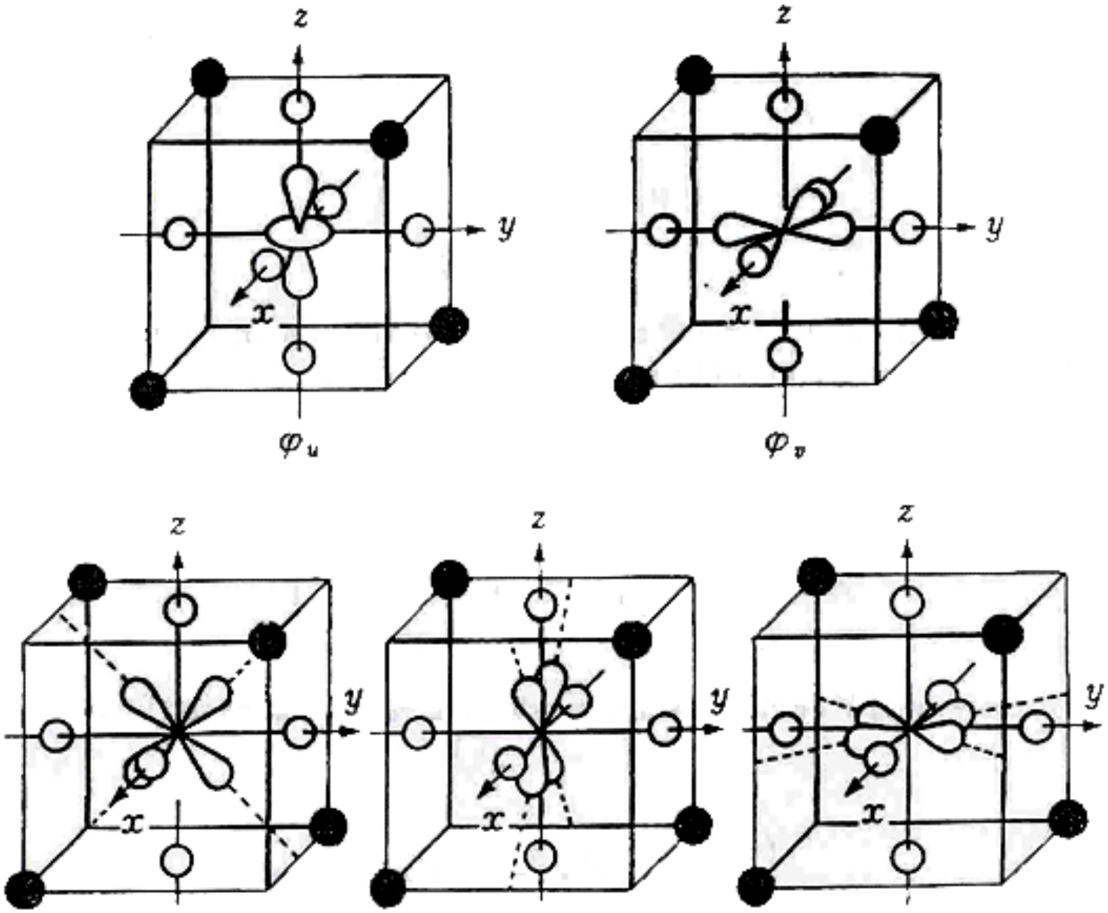
- Δ_o increases with increasing charge on metal
- Δ_o increases going down a group, 4d, 5d metals typically have only low spin configurations because of their large Δ_o

D ORBITAL SPLITTING IN NON-OCTAHEDRAL GEOMETRIES

In lieu of deriving full MOs for other geometries, we can derive d orbital splitting patterns for different geometries based on what we know about octahedral.

d orbital splitting in Tetrahedral geometry

Shortcut: Compare localization of ligands in octahedral vs tetrahedral geometry by inscribing both into a cube:

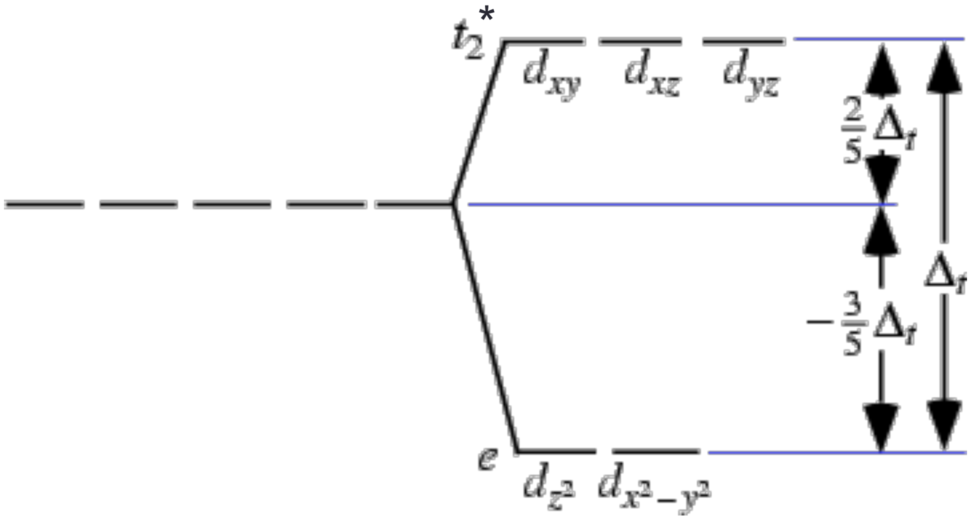


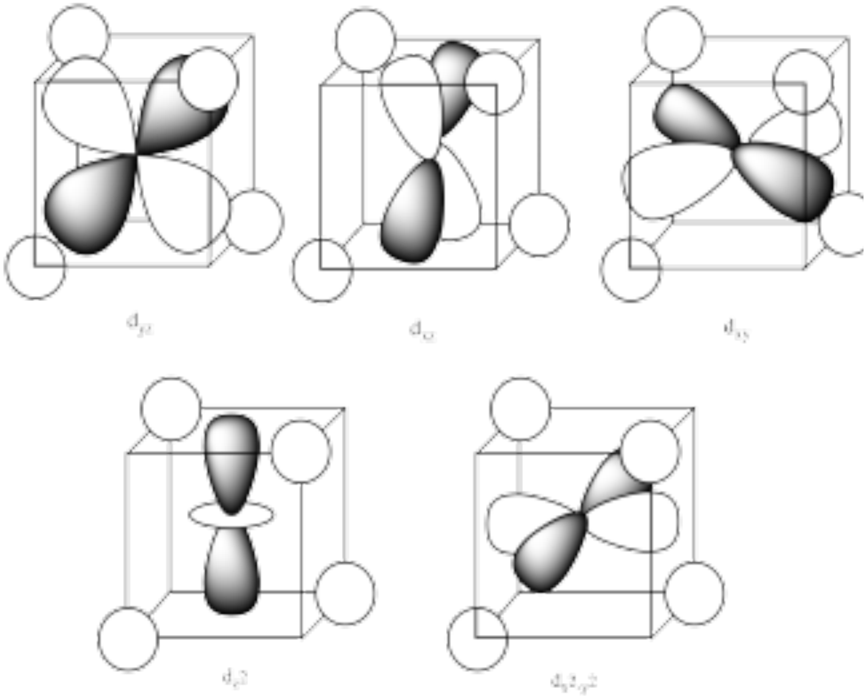
d orbitals inscribed into a cube with octahedral ligand set (white circles) and tetrahedral ligand set (black circles). Octahedral ligands are on the face of the cubes whereas tetrahedral ligands are on the corners. Their interactions with the orbitals are thus opposite from each other.

Note: d orbitals not shaded properly in this image

d orbital splitting in Tetrahedral geometry

opposite of octahedral splitting!

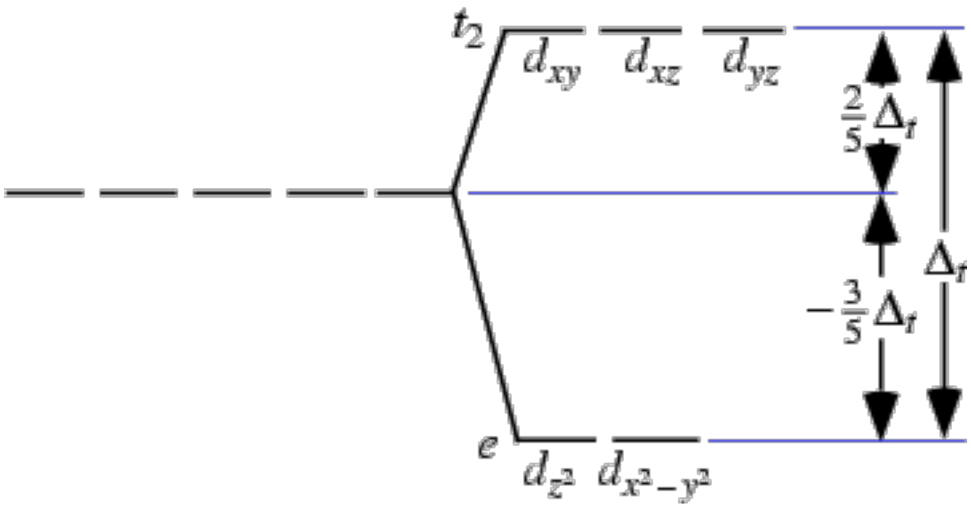




Note that SALC treatment for σ ligands gives you $\Gamma_\sigma = A_1 + T_2$. These correspond to s orbital (A_1) and dxy, dxz, and dyz orbitals (T_2) (see MFT 10.3.5). Thus t_2 orbitals here are antibonding (t_2^*), e are nonbonding.

d orbital splitting in Tetrahedral geometry

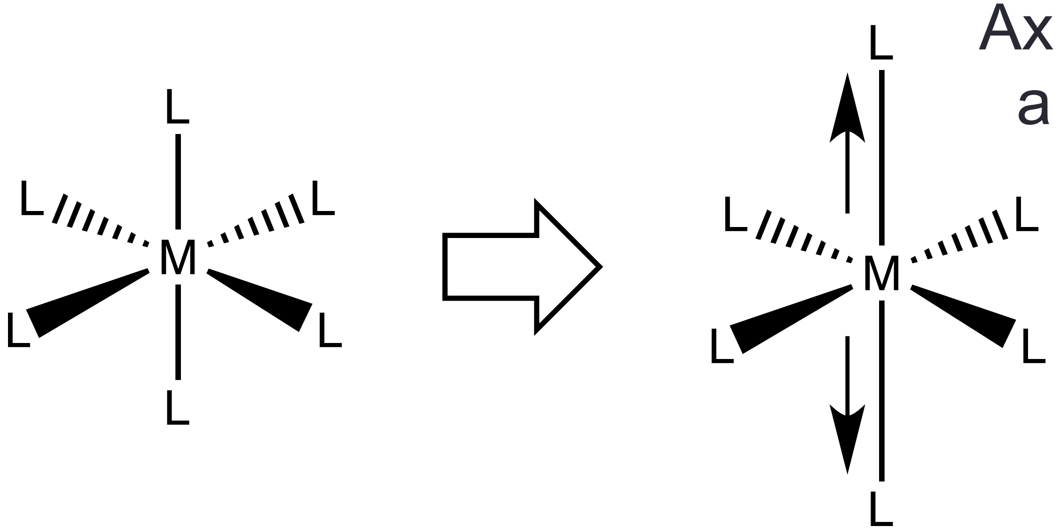
- Tetrahedral splitting, Δ_t, is not as large as Δ_o because only 4 ligands in tetrahedral vs. 6 ligands in octahedral
- $\Delta_t \approx 4/9\Delta_o$
- As a result of this smaller splitting, in practice tetrahedral complexes are high spin



LFSE can be calculated in tetrahedral just as in octahedral, except using the coefficients shown here

Note: coefficients used for LFSE calculations will give a LFSE = 0 d^{10} and high spin d^5 complexes

d orbital splitting in an axially-distorted octahedral complex



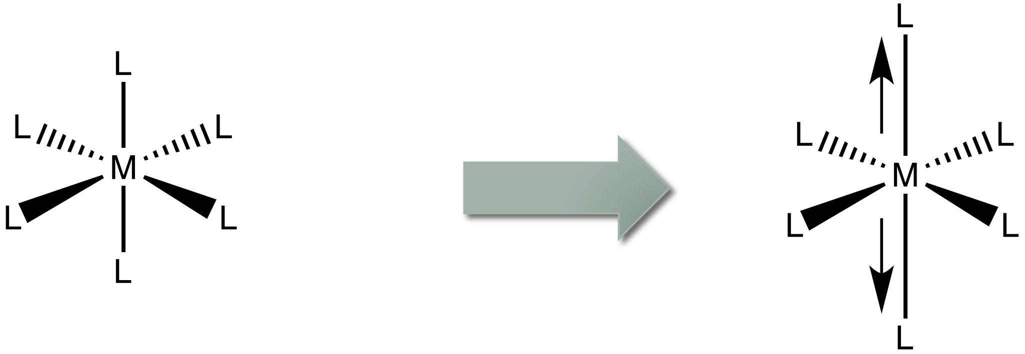
Axial distortion along z-axis

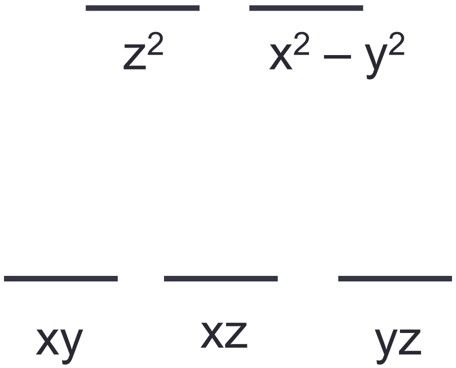
O_h symmetry

D_{4h} symmetry

Derivation: use octahedral d orbital splitting as a starting point, adjust orbital energy levels to take into account the distortion along the z axis

d orbital splitting in an axially-distorted octahedral complex



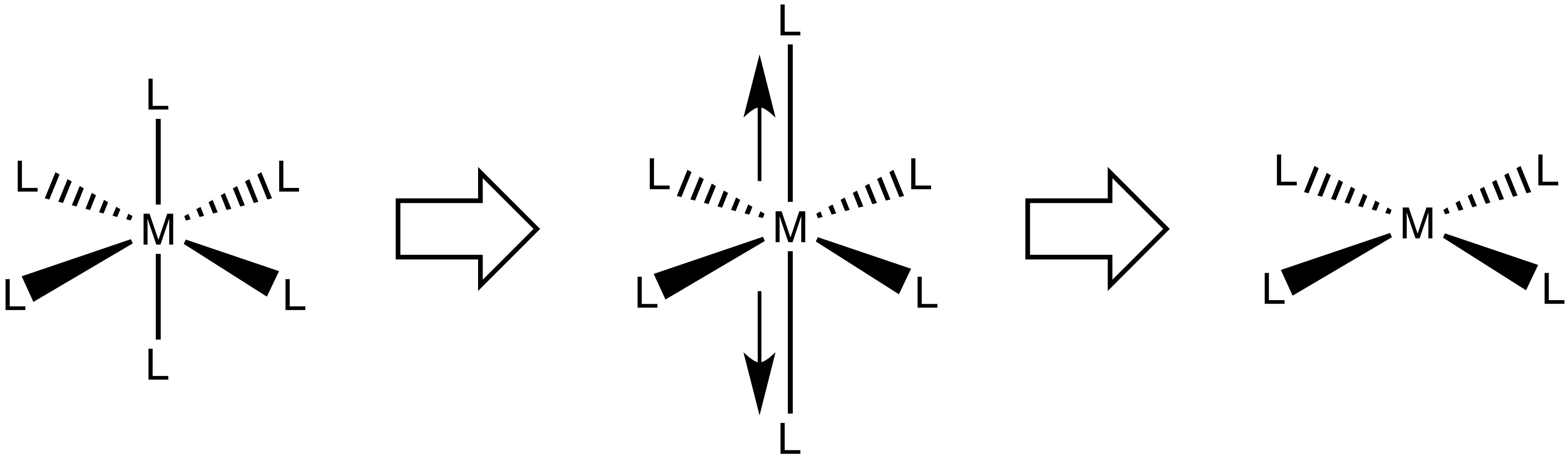


z^2 $x^2 - y^2$

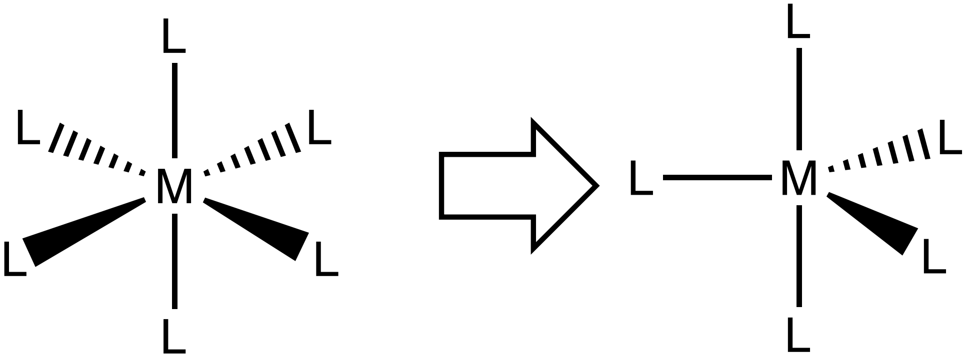
xy xz yz

d orbital splitting in a square planar complex

- Similar to axial distortion case, just ligands along z are no longer present



d orbital splitting in a trigonal bipyramidal complex

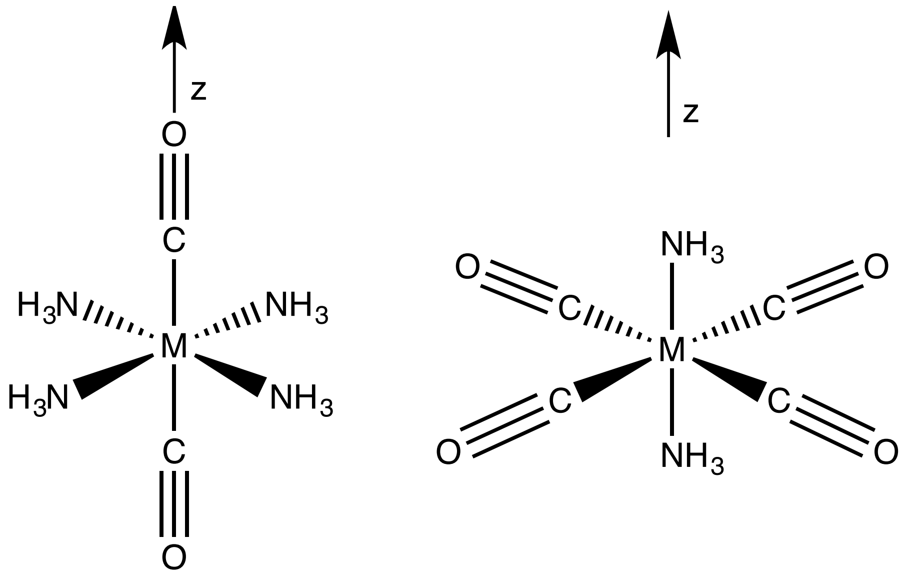


O_h symmetry

D_{3h} symmetry

Example d orbital splitting questions:

What would the d orbital splitting look like for these octahedral complexes compared to M(NH_3)$_6$? Take into account pi interactions from the CO ligands at either the axial or equatorial positions

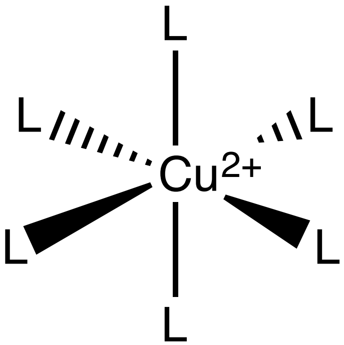


The Jahn-Teller Effect

- Jahn-Teller Theorem: degenerate orbitals (same energy) cannot have different numbers of electrons
- To account for this, molecules will distort so that orbitals are no longer degenerate
- Most commonly observed in octahedral complexes

The Jahn-Teller Effect

- Common J-T example: octahedral Cu^{2+} complexes (d^9)



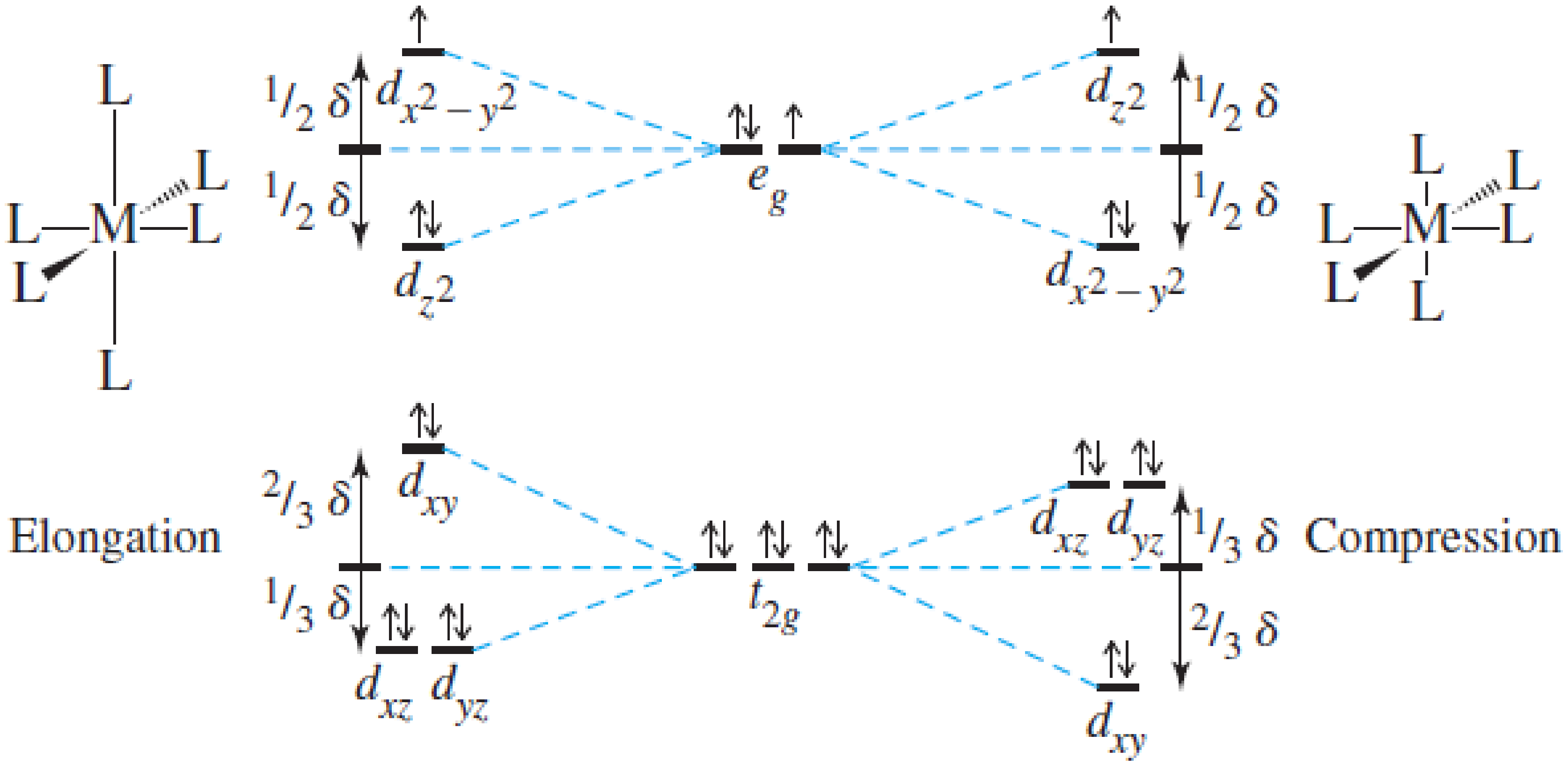
One e_g orbital has 2 electrons, one has 1 electron

→ Degenerate orbitals with unequal occupancy

→ Molecule will elongate or compress along an axis (convention if z axis) to relieve orbital degeneracy

The Jahn-Teller Effect

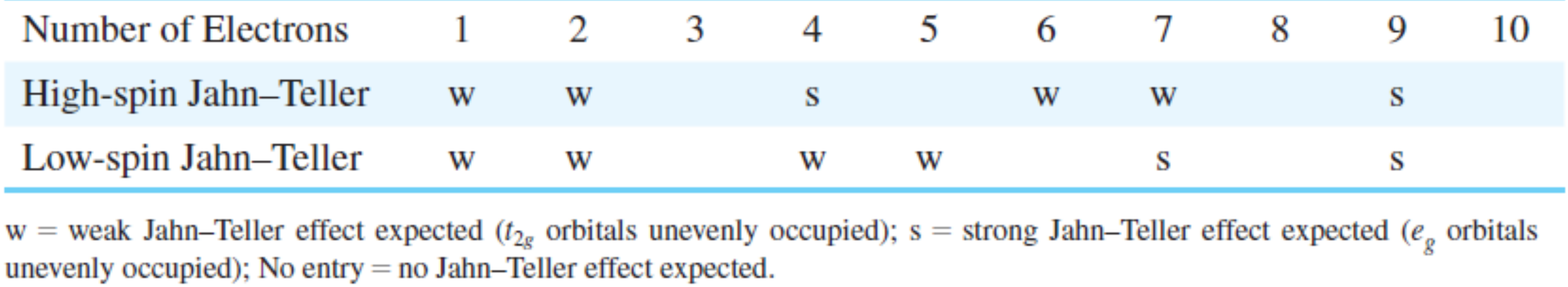
- Common J-T example: octahedral Cu^{2+} complexes (d^9)



The Jahn-Teller Effect

- Generally speaking, J-T effects are larger in complexes with unequal occupation in e_g orbitals compared to complexes with unequal occupation in t_{2g} orbitals

Table in section 10.5: expected J-T effects in octahedral transition metal complexes



Number of Electrons	1	2	3	4	5	6	7	8	9	10
High-spin Jahn–Teller	w	w		s		w	w		s	
Low-spin Jahn–Teller	w	w		w	w		s		s	

w = weak Jahn–Teller effect expected (t_{2g} orbitals unevenly occupied); s = strong Jahn–Teller effect expected (e_g orbitals unevenly occupied); No entry = no Jahn–Teller effect expected.