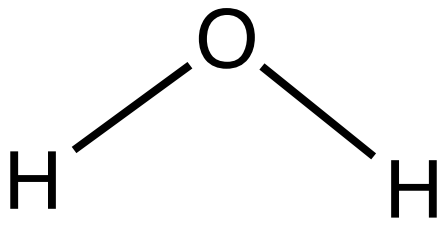
- The following slides are composed of a selection of slides from Lecture 10 through Lecture 17.

VIBRATIONAL MODES

Application 2: Molecular Vibrations and Vibrational Spectroscopy



- A molecule with N atoms has 3N degrees of freedom
  - Translational modes: T_x, T_y, and T_z (movement of the whole body)
  - Rotational modes: R_x, R_y, and R_z (rotations of the whole body)
  - Vibrational modes: displacement of atoms from their mean positions

- H_2O, N = 3 has 3 x 3 = 9 degrees of freedom

Normal modes/fundamental vibrations

- A vibrational mode is a molecular vibration where some or all atoms vibrate together with the same frequency in a defined manner (and some can be detected by IR, Raman)

- **Non-linear molecules** have 3N – 6 vibrational modes
  - 3N – (T_x, T_y, T_z) – (R_x, R_y, R_z)
- **Linear molecules** have 3N – 5 vibrational modes
  - 3N – (T_x, T_y, T_z) – (R_x, R_y)

  (rotation around z-axis does not change molecule, so doesn't count)

- H_2O: 3 x 3 -6 = 3 vibrational modes

Finding vibrational modes

1) **Find Γ_{3N}** The first step in this process is making a ***reducible representation*** of all possible molecular motions Γ_{3N} (aka Γ_{total})

2) **Use the reduction formula** *to determine irreducible representations that make up reducible representation* Γ_{3N}

3) **Determine which representations represent translational and rotational movements, the remaining are vibrations**

4) **Determine if any of the vibrations are IR or Raman active**

This procedure takes into account ALL of the atoms in a molecule!

Simplified procedure for looking only at selected vibrational modes

This procedure is much simpler, looks only at specific bonds in a molecule:

1) Determine $\Gamma_{A\text{-}B}$ (how many A-B bonds are unmoved?)
   In the case of CO bonds, we call this Γ_{CO}
2) Use reduction formula to find irreducible representations.
3) Determine how many IR and Raman active stretches there are based off the irreducible representations

Character table for D_{4h} point group

	E	$2C_4$ (z)	C_2	$2C'_2$	$2C''_2$	i	$2S_4$	σ_h	$2\sigma_v$	$2\sigma_d$	linears, rotations	quadratic
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	R_z	
B_{1g}	1	-1	1	1	-1	1	-1	1	1	-1		x^2-y^2
B_{2g}	1	-1	1	-1	1	1	-1	1	-1	1		xy
E_g	2	0	-2	0	0	2	0	-2	0	0	(R_x, R_y)	(xz, yz)
A_{1u}	1	1	1	1	1	-1	-1	-1	-1	-1		
A_{2u}	1	1	1	-1	-1	-1	-1	-1	1	1	z	
B_{1u}	1	-1	1	1	-1	-1	1	-1	-1	1		
B_{2u}	1	-1	1	-1	1	-1	1	-1	1	-1		
E_u	2	0	-2	0	0	-2	0	2	0	0	(x, y)	

Character table for C_{2v} point group

	E	C_2 (z)	σ_v(xz)	σ_v(yz)	linear, rotations	quadratic
A_1	1	1	1	1	z	x^2, y^2, z^2
A_2	1	1	-1	-1	R_z	xy
B_1	1	-1	1	-1	x, R_y	xz
B_2	1	-1	-1	1	y, R_x	yz

Steps for determining SALCs/group orbitals

1) **Determine the point group of your molecule.** If the molecule is $D_{\infty h}$, use the D_{2h} character table. $C_{\infty v}$, use C_{2v}.

2) **Take stock of the valence orbitals** of both the central and non-central atoms in the molecule

3) **Find $\Gamma_{orbital}$** for all the valence orbitals of the non-central atoms. If they are H's, you only determine **Γ_{1s}**. If it is a 2nd row p-block element, you calculate **Γ_{2s}, Γ_{2pz}, Γ_{2px}, Γ_{2py}**

4) **Use the reduction formula** to determine the irreducible representations that make up the $\Gamma_{orbital}$'s

5) **Determine the orbitals on the central atom that match the irreducible representations from 3.** These are the orbitals that can interact with the outer atoms

6) **Determine what the group orbitals look like by matching them with the central atom orbitals determined in 4.**

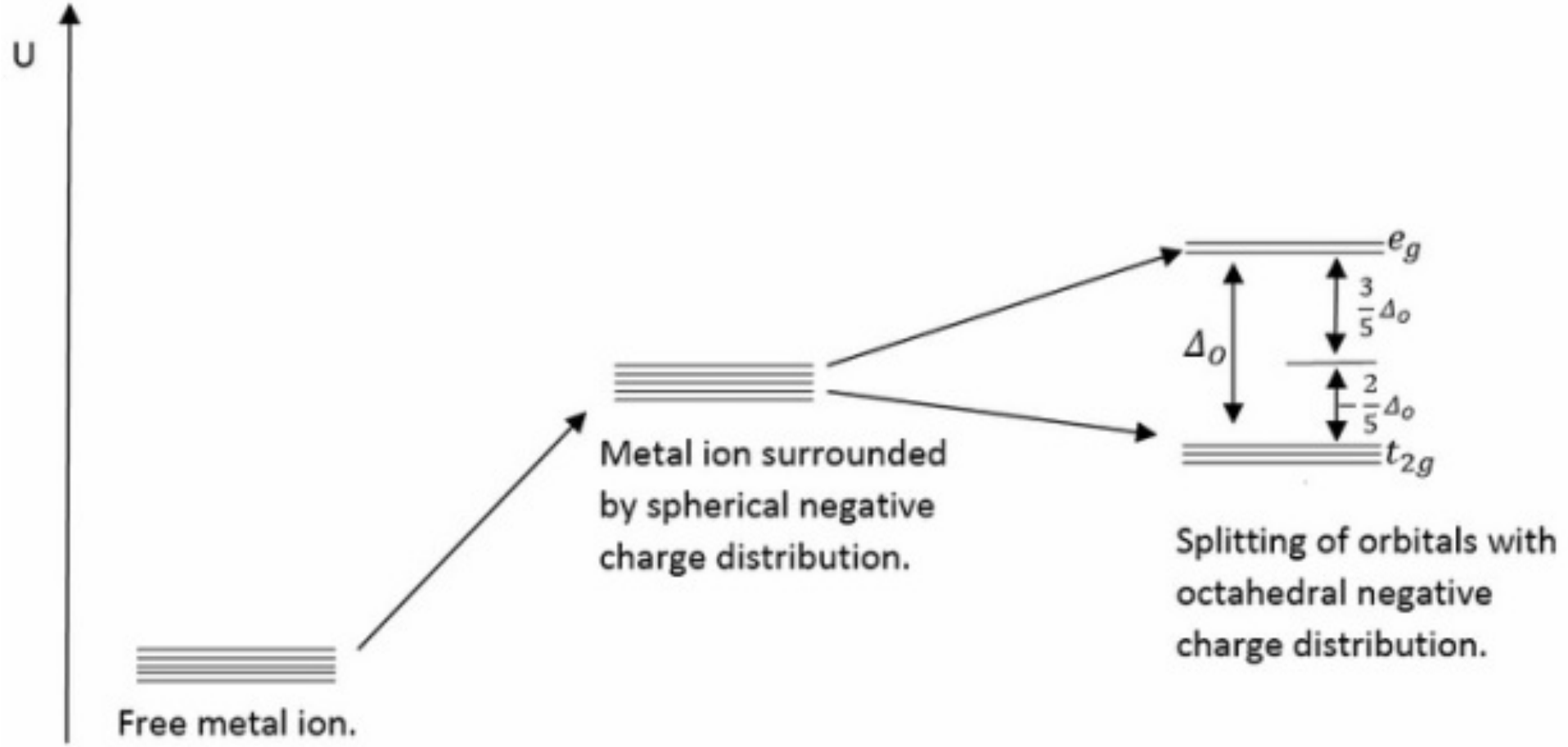
D_{3h}	E	$2C_3$	$3C_2$	σ_h	$2S_3$	$3\sigma_v$		
A_1'	1	1	1	1	1	1		$x^2 + y^2, z^2$
A_2'	1	1	−1	1	1	−1	R_z	
E'	2	−1	0	2	−1	0	(x, y)	$(x^2 - y^2, xy)$
A_1''	1	1	1	−1	−1	−1		
A_2''	1	1	−1	−1	−1	1	z	
E''	2	−1	0	−2	1	0	(R_x, R_y)	(xz, yz)

Crystal Field Theory

- Repulsive Forces
- 1) d orbitals “feel” a repulsive interaction from ligands that change the energy levels of the d orbitals
- 2) Extent of the repulsive interaction for each d orbital depends on where the ligands are in space (geometry!!!)

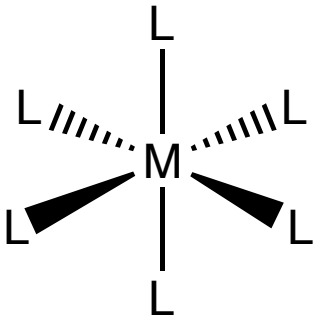
- The result is that depending on the geometry, different d orbitals will have different relative energies

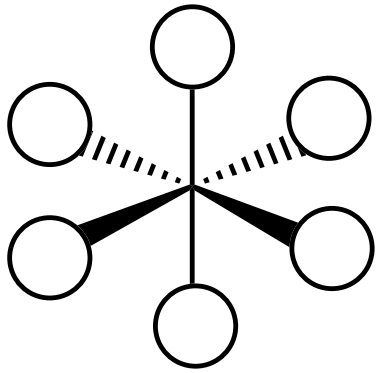
Octahedral crystal field splitting



LFT approach to octahedral metal complex bonding (MO approach)

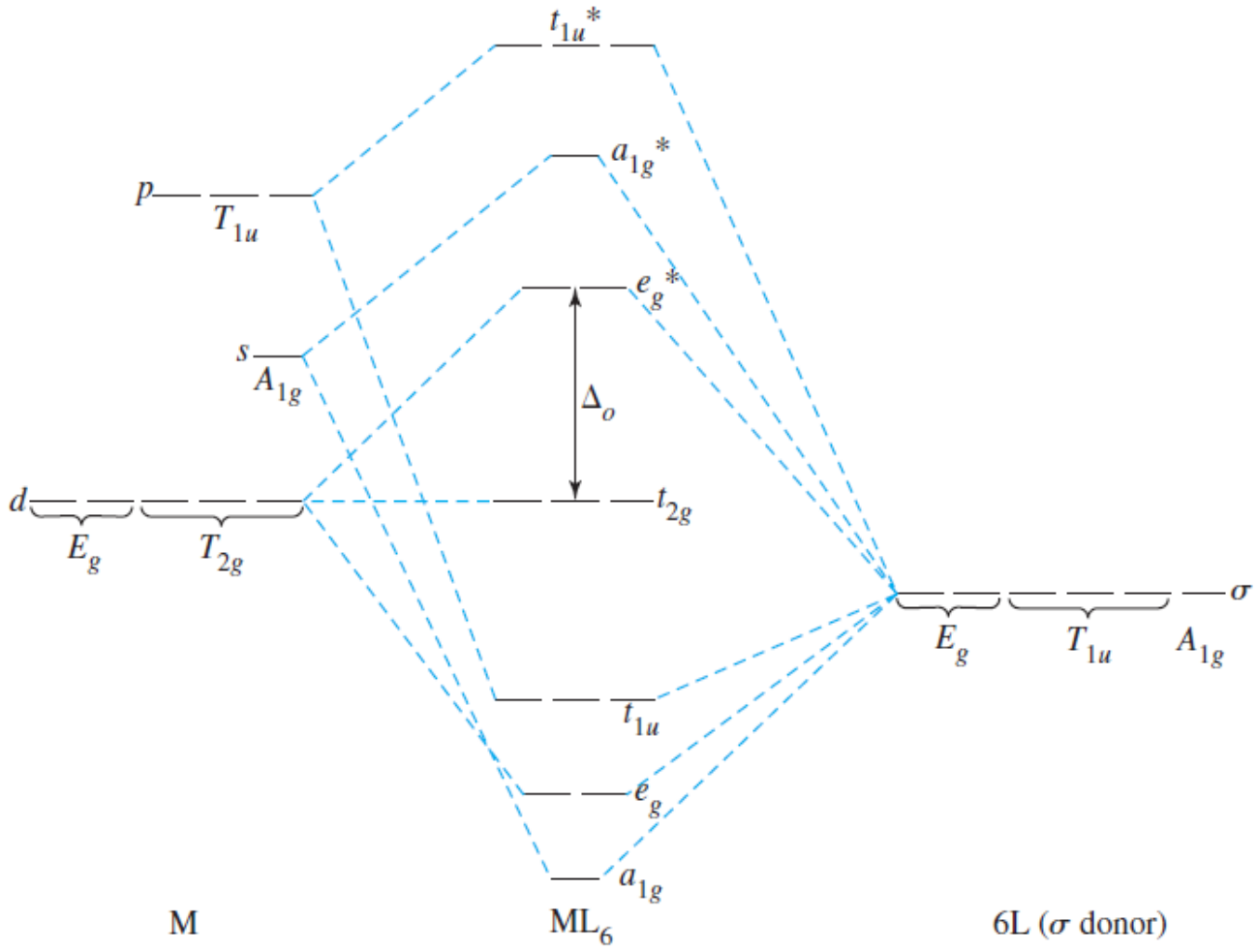
- Time to derive SALCs for an ML_6 complex!
- For now, we will just consider σ interactions between ligand and metal. You can derive SALCs by finding Γ_s
- The end result after using reduction formula?
- $\Gamma_s = A_{1g} + T_{1u} + E_g$





O_h	E	$8C_3$	$6C_2$	$6C_4$	$3C_2(=C_4^2)$	i	$6S_4$	$8S_6$	$3\sigma_h$	$6\sigma_d$		
A_{1g}	1	1	1	1	1	1	1	1	1	1		$x^2 + y^2 + z^2$
T_{1u}	3	0	−1	1	−1	−3	−1	0	1	1	(x, y, z)	
E_g	2	−1	0	0	2	2	0	−1	2	0		$(2z^2 - x^2 - y^2, x^2 - y^2)$

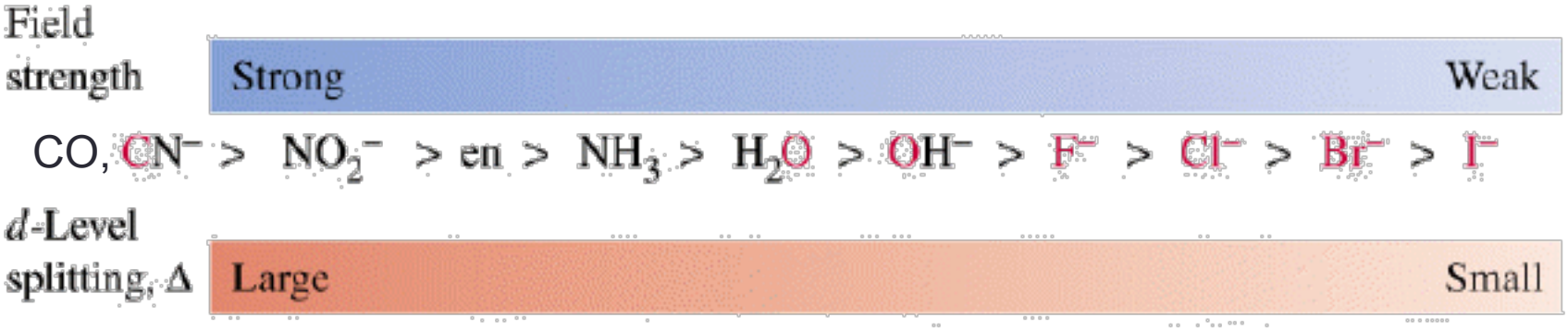
MO diagram of octahedral metal complex, sigma interactions only



The spectrochemical series

Next week's lab will explore this!

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



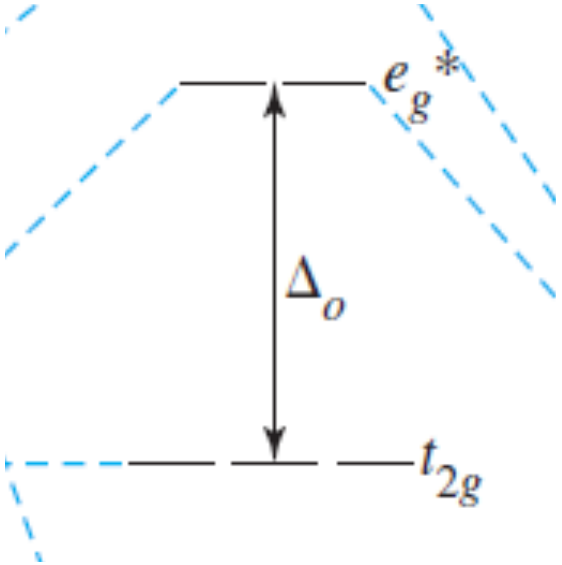
- Strong field ligands produce complexes with a large Δ_o
- Weak field ligands produce complexes with a small Δ_o

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

Δ_o contributes to many different properties of metal complexes

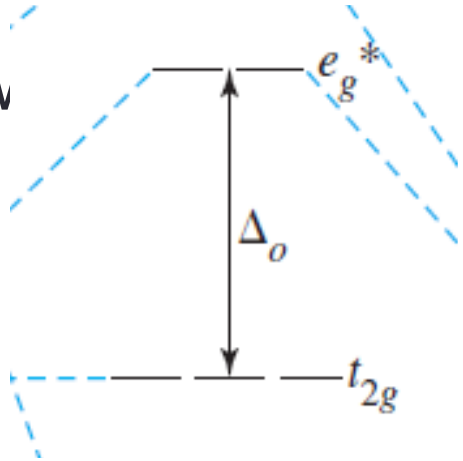
- The magnitude of Δ_o, in other words, the size of the energy gap between the t2g and eg* orbitals, can contribute to many different properties of metal complexes

- **Magnetic moment (high spin vs low spin)**
  - lab this week
- **Electronic spectra (UV-vis)**
  - lab next week
- **Kinetic stability (later lectures…)**



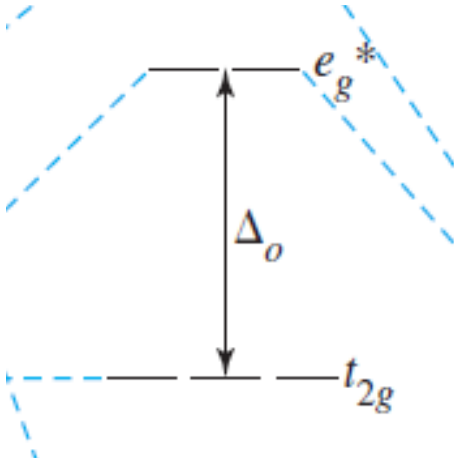
Octahedral d-d splitting

- For **M**:
  - Δ_o increases with increasing charge on metal (shorter, stronger bonds = more interaction = more splitting)
    - Δ_o (Fe^{2+}) < Δ_o (Fe^{3+})
  - Δ_o increases going down a group (larger d orbitals = more interaction with ligands = more splitting)
    - Δ_o (Fe^{2+}) < Δ_o (Ru^{2+})
    - Note: 4d, 5d metals typically have only low configurations because of their large Δ_o



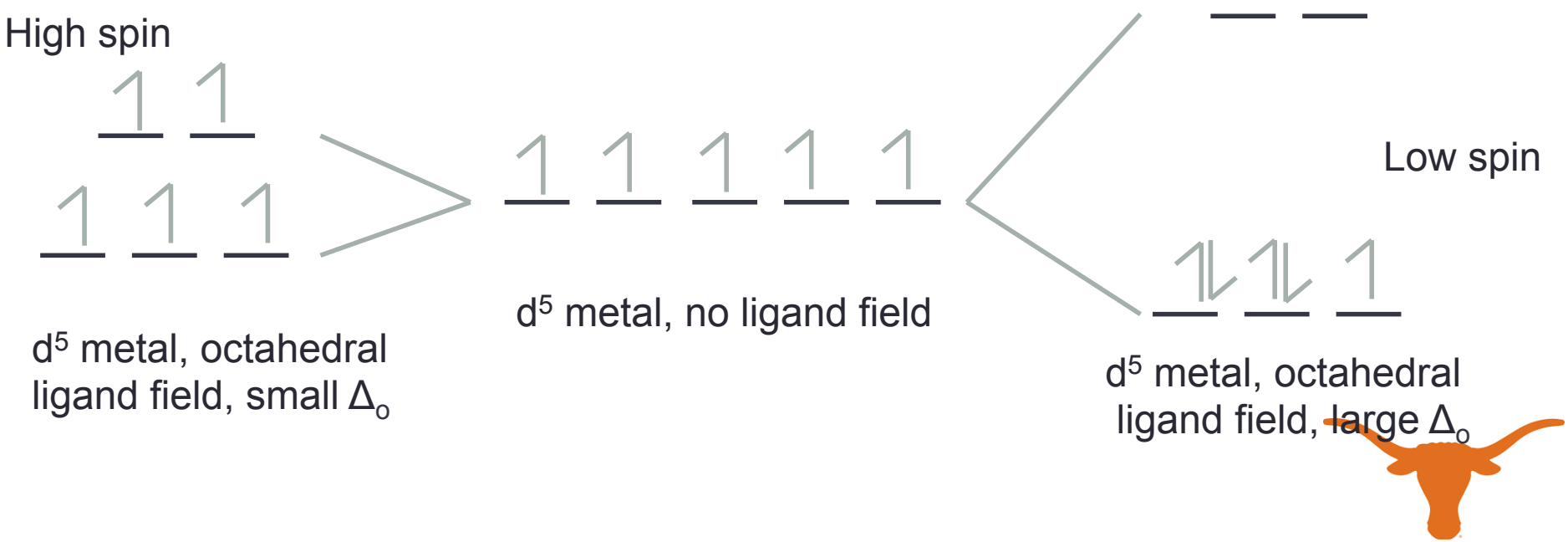
Octahedral d-d splitting

- For **L**:
  - Δ_o will depend on a number of characteristics of the ligand, most importantly, whether it can interact with the metal as a
    - sigma-only donor
    - sigma and pi donor
    - sigma donor and pi acceptor



Magnetic moment: High spin vs low spin complexes

- Low spin complexes: electrons fill lower energy d orbitals first (pairing energy < Δ_o)
- High spin complexes: electrons fill into lower and higher energy d orbitals before pairing (pairing energy > Δ_o)



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