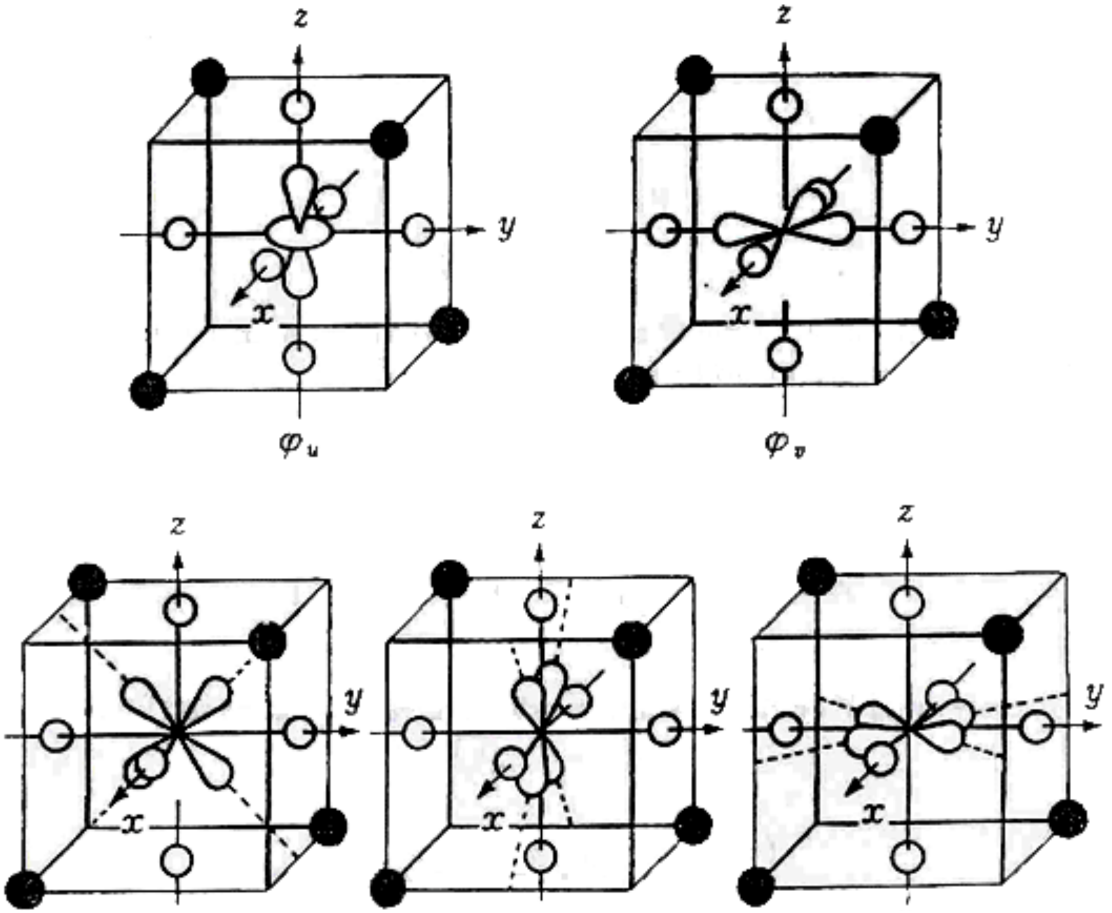
D ORBITAL SPLITTING IN NON-OCTAHEDRAL GEOMETRIES

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:

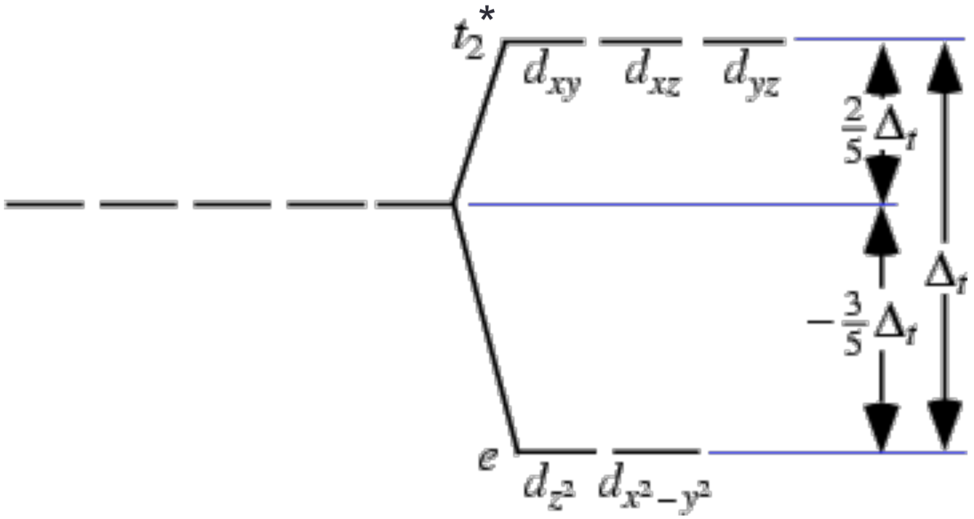


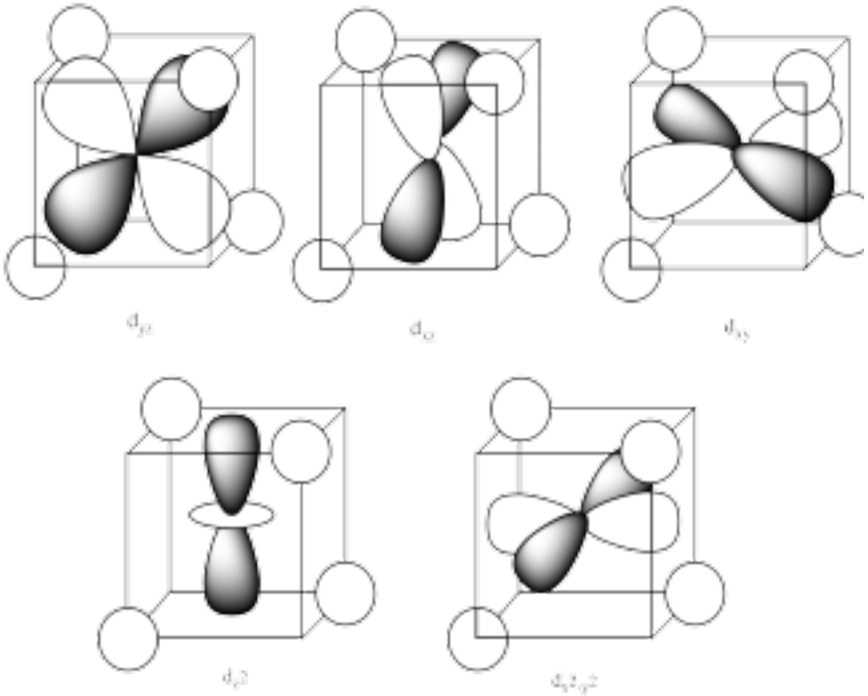
d orbitals inscribed into a cube with octahedral ligand set (white circles) and tetrahedral ligand set (black circles). Octahedral ligands are on the face of the cubes whereas tetrahedral ligands are on the corners. Their interactions with the orbitals are thus opposite from each other.

Note: d orbitals not shaded properly in this image

d orbital splitting in Tetrahedral geometry

opposite of octahedral splitting!

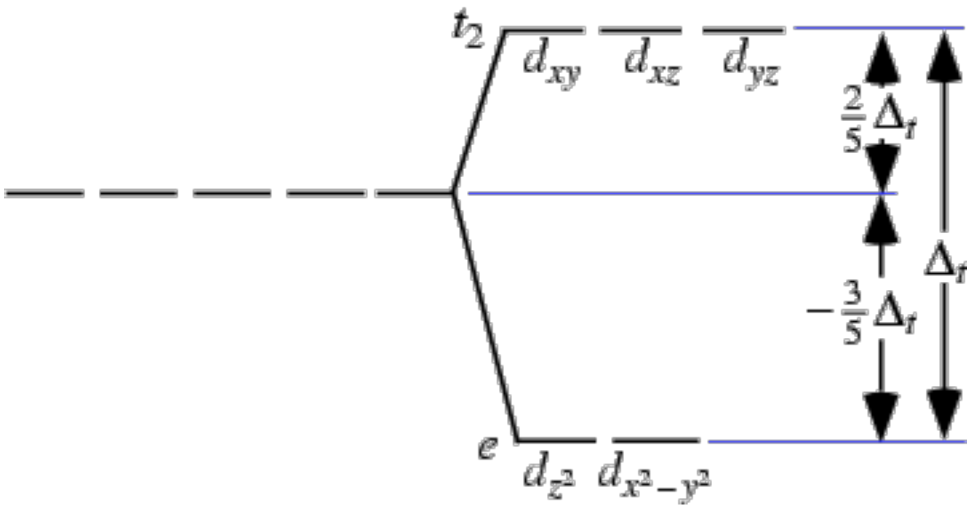




Note that SALC treatment for σ ligands gives you $\Gamma_\sigma = A_1 + T_2$. These correspond to s orbital (A_1) and dxy, dxz, and dyz orbitals (T_2) (see MFT 10.3.5). Thus t_2 orbitals here are antibonding (t_2^*), e are nonbonding.

d orbital splitting in Tetrahedral geometry

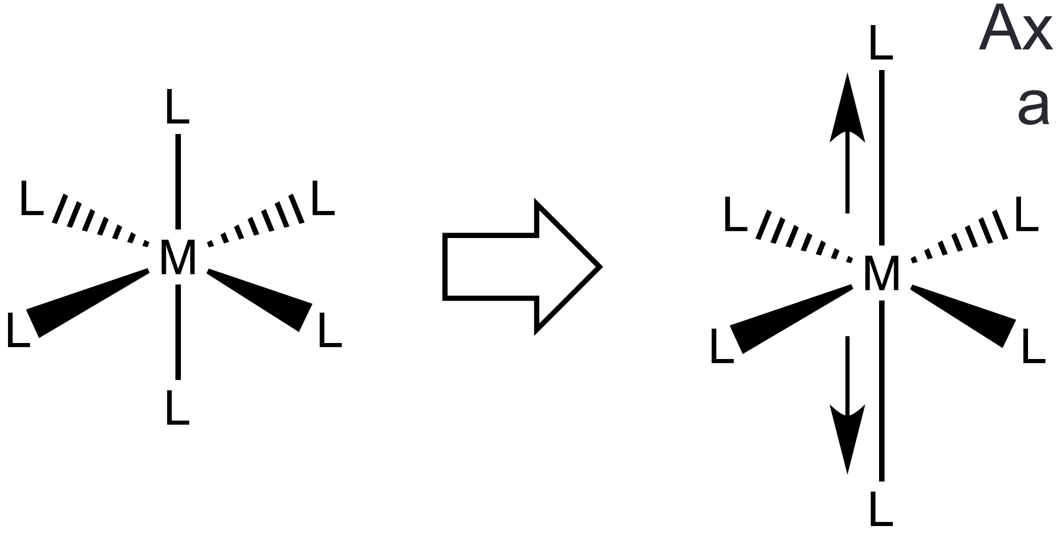
- Tetrahedral splitting, Δ_t, is not as large as Δ_o because only 4 ligands in tetrahedral vs. 6 ligands in octahedral
- $\Delta_t \approx 4/9\Delta_o$
- As a result of this smaller splitting, in practice tetrahedral complexes are high spin



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



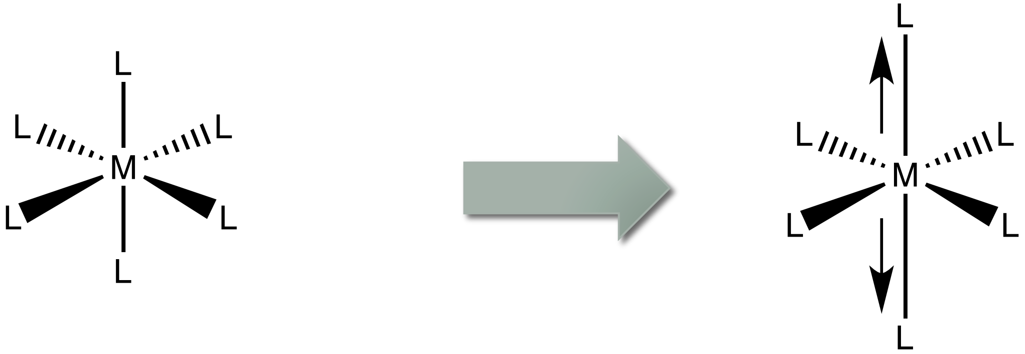
Axial distortion along z-axis

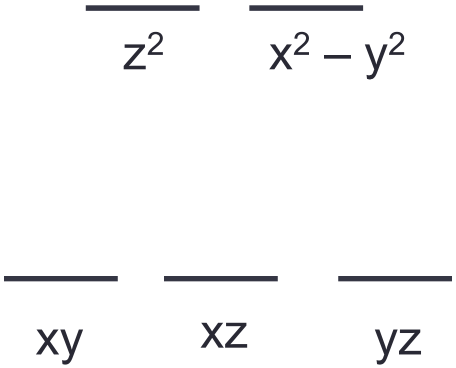
O_h symmetry

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



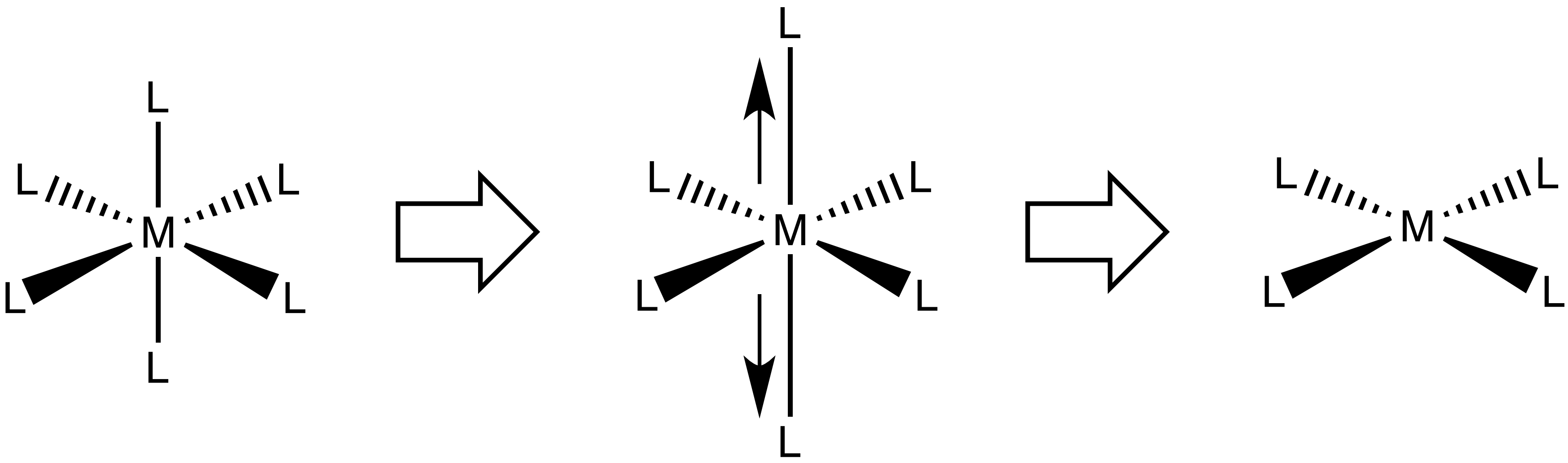


z^2 $x^2 - y^2$

xy xz yz

d orbital splitting in a square planar complex

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

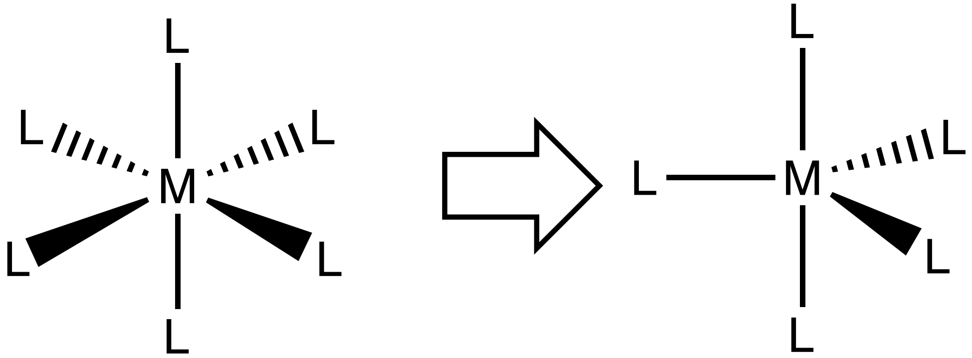


4-coordinate metal complexes: tetrahedral or square planar?

- Based on analysis of 13,000 **4-coordinate transition metal complexes**:

- d^0, d^1, d^2, d^5, and d^{10} prefer tetrahedral geometry
- d^8 shows strong preference for square planar geometry, especially for 4d and 5d metals. For 3d metals, weak field ligands typically favor tetrahedral structure, strong field square planar
- d^9 shows strong preference for square planar, though many structures are in between square planar and tetrahedral
- d^3, d^4, d^6, d^7 don’t show a preference for either tetrahedral or square planar

d orbital splitting in a trigonal bipyramidal complex

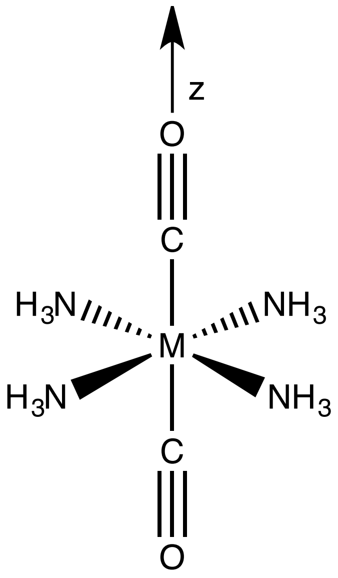


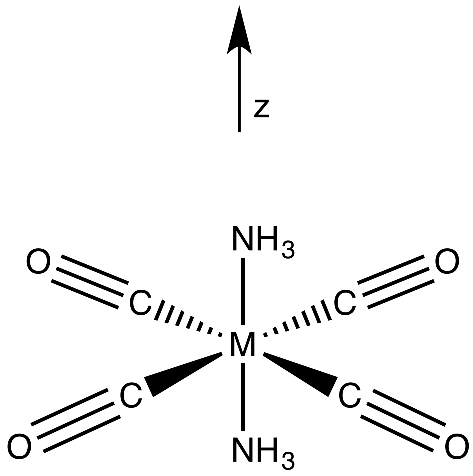
O_h symmetry

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

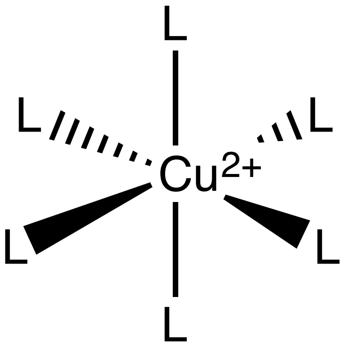
- Jahn-Teller Theorem: degenerate orbitals (same energy) cannot have different numbers of electrons

- 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)



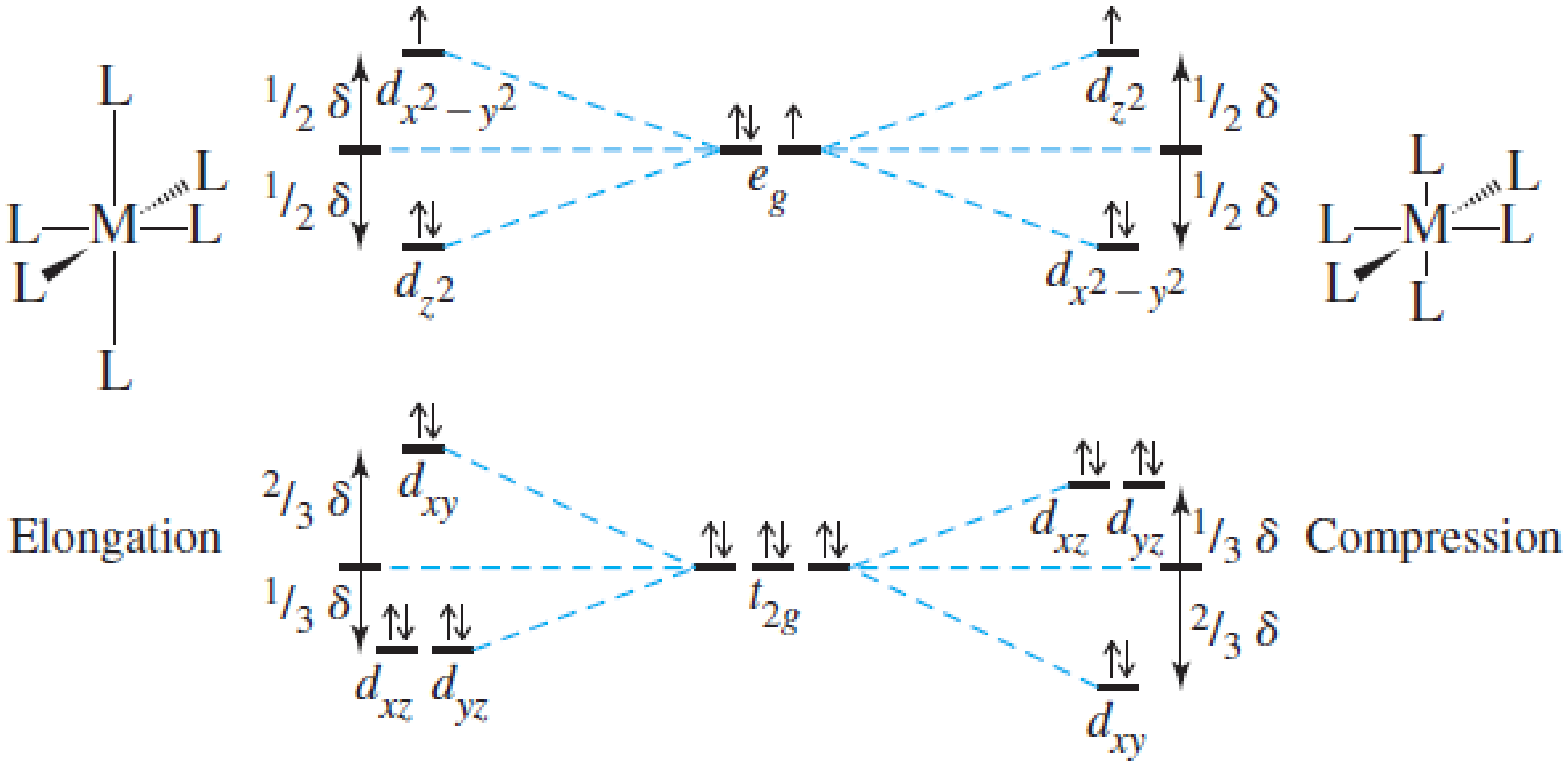
One e_g orbital has 2 electrons, one has 1 electron

→ Degenerate orbitals with unequal occupancy

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

The Jahn-Teller Effect

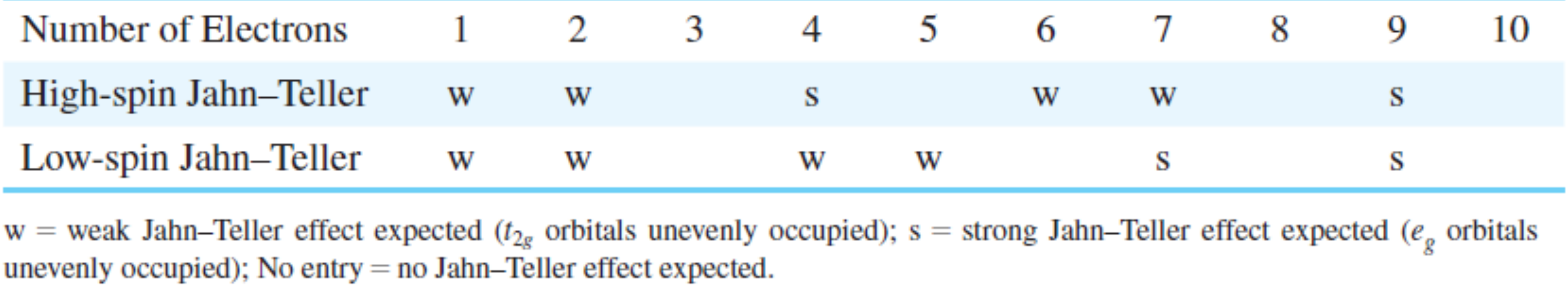
- Common J-T example: octahedral Cu^{2+} complexes (d^9)



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.

Example exam or quiz question

- Calculate the LFSE and μ_s for the following Fe^{2+} complexes:

  - $[Fe(CO)_6]^{2+}$
  - $[FeCl_6]^{4-}$
  - $[FeCl_4]^{2-}$

- Steps to solve this question:
  - 1) Determine the number of d electrons in the metal
  - 2) Determine the d orbital splitting pattern for the complex
  - 3) Determine if the complex will be high spin or low spin
  - 4) Calculate LFSE and μ_s

Example exam or quiz question

- Which of the following cobalt complexes is more likely to be high spin? Low spin? Why?
  - $[Co(OH_2)_6]^{2+}$
  - $[Co(OH_2)_6]^{3+}$

- What is the expected geometry for the following complexes?
  - $[Cu(NCCH_3)_4]^+$
  - $[Ni(CO)_4]^{2+}$
  - $[Ni(NH_3)_4]^{2+}$