Inorganic

Orbitals interactions in metals: LFSE

Last Time

- Ligand Field Theory

- Dative interactions between transition metals and π-donating ligands

- Dative interactions between transition metals and π-accepting ligands (metal $d\pi$-backbonding)

- Ligand Field Stabilization Energies (LFSE)

- Demystifying the spectrochemical series

Lecture Topics

- Crystal field splitting for other geometries

- Tetrahedral crystal field stabilization energies

- Periodic trends in the stabilities of transition metal compounds

- The Irving Williams Series

The Spectrochemical Series - Ligands

Δ_{oct} increases along spectrochemical series:

$I^- <$ Br$^- <$ [NC**S**]$^- <$ Cl$^- <$ F$^- <$ [OH]$^- <$ [ox]$^{2-} \approx$ H$_2$O $<$ [**N**CS]$^- <$ NH$_3 <$ en $<$ bpy $<$ phen $<$ [CN]$^- \approx$ CO

Weak Field Ligands
(Smaller Δ_{oct})

Strong Field Ligands
(Larger Δ_{oct})

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

The spectrochemical series is an empirical generalization that can also be applied to metal ions.

Tetrahedral Geometry (T_d)

In tetrahedral molecular geometries, none of the atomic orbitals for the metal ion point directly at the ligands.

The d_{xy}, d_{yz}, and d_{xz} orbitals do not point directly at the ligands, but they are closer to the ligands than the d_{z^2} and $d_{x^2-y^2}$ atomic orbitals.
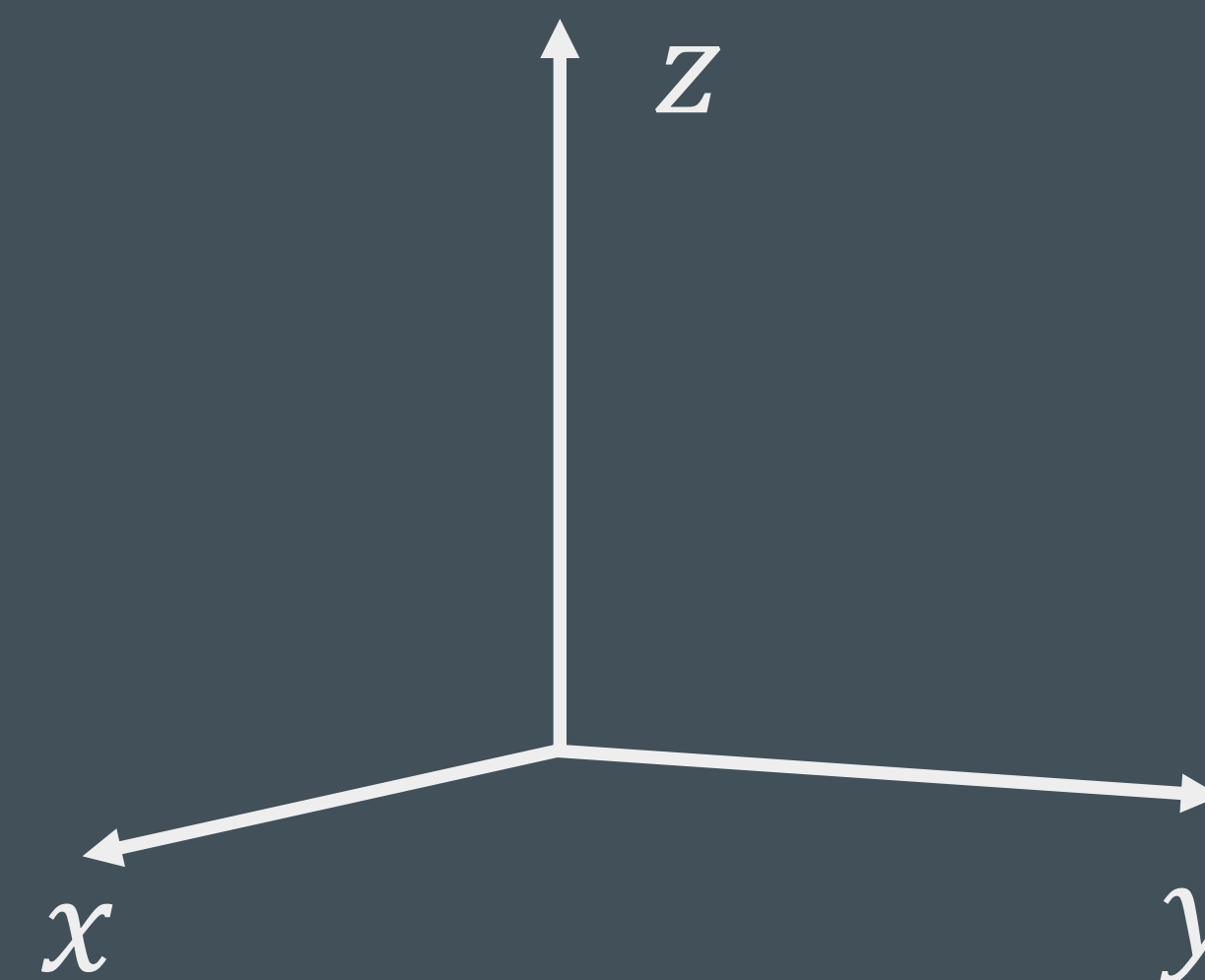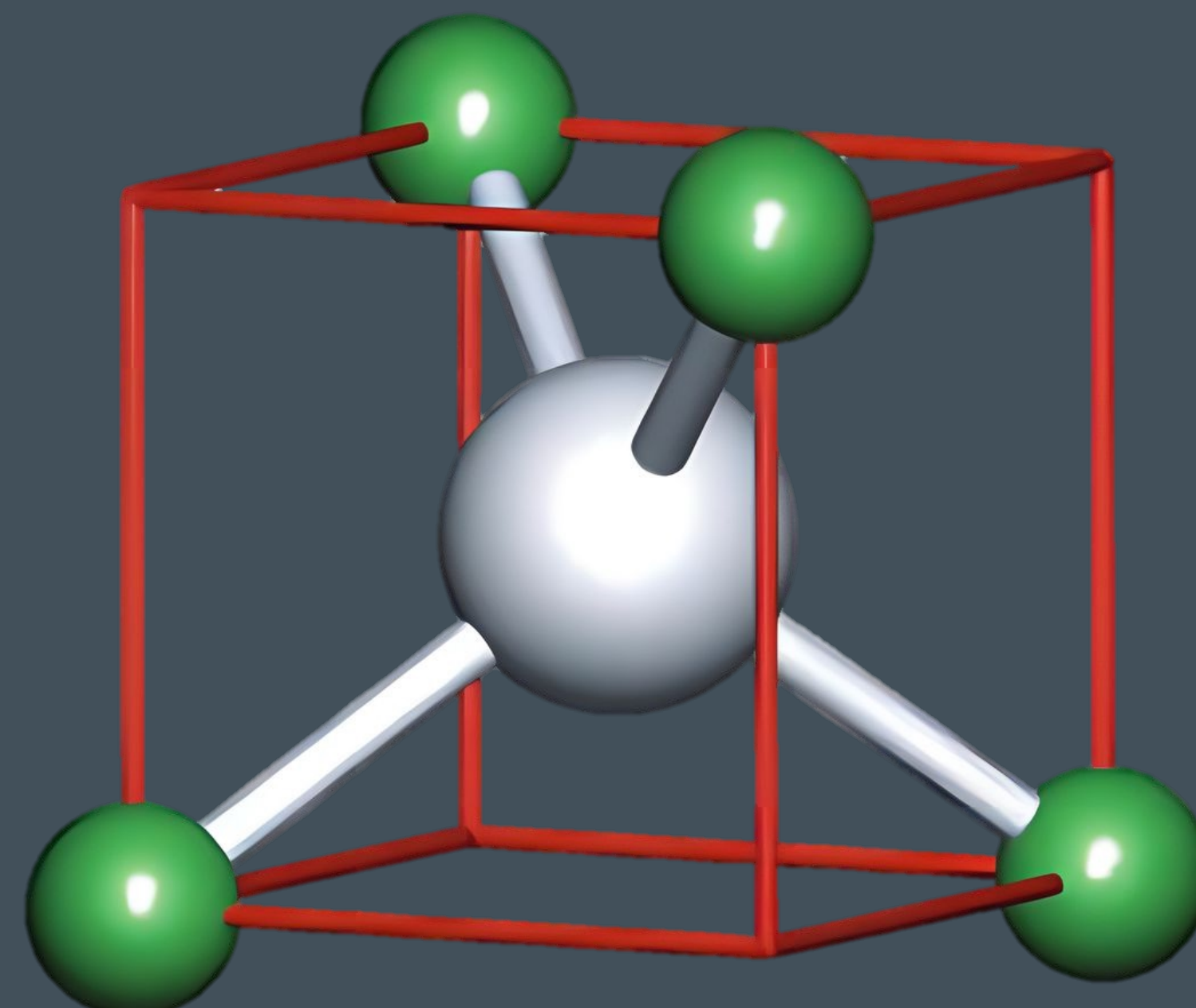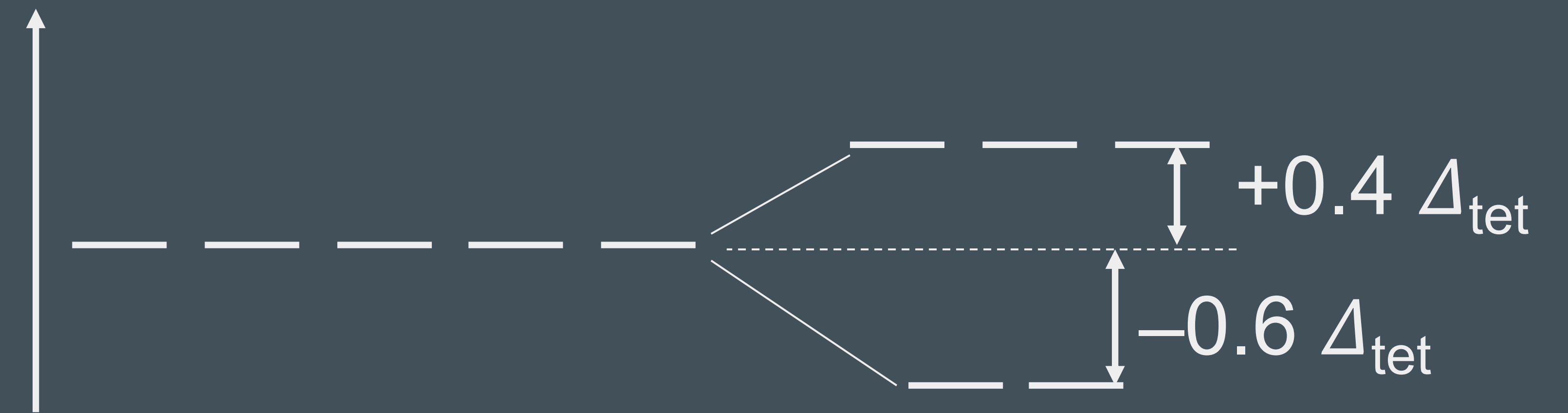
Tetrahedral Geometry (T$_d$)

The splitting of the *d* orbitals is inverted compared with that for a regular octahedral structure and the energy difference (Δ_{tet}) is smaller.

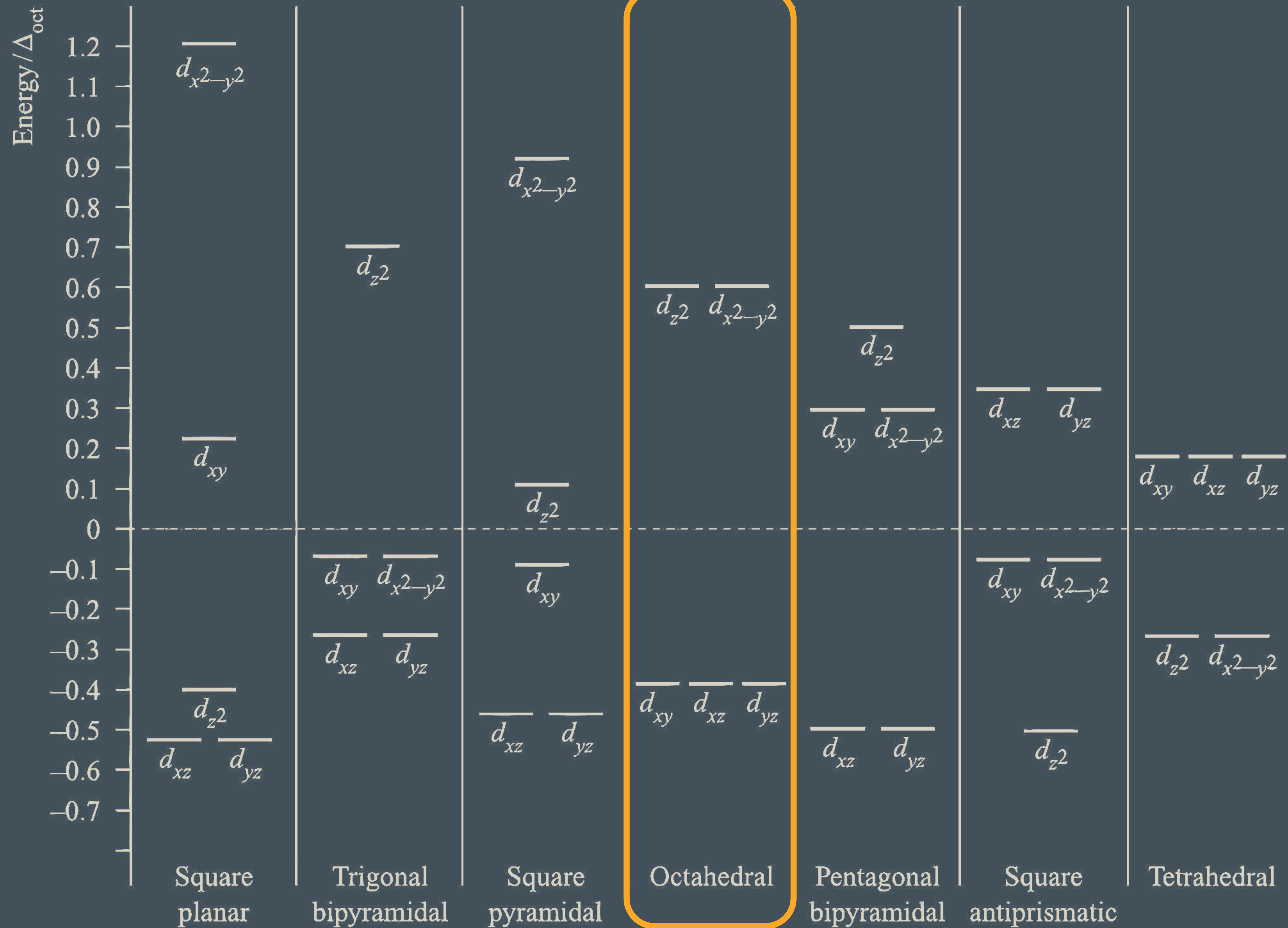$$\Delta_{tet} = \frac{4}{9}\Delta_{oct}$$

Tetrahedral Geometry (T_d)

Due to the difference in energy levels, tetrahedral complexes are almost **always** high spin.
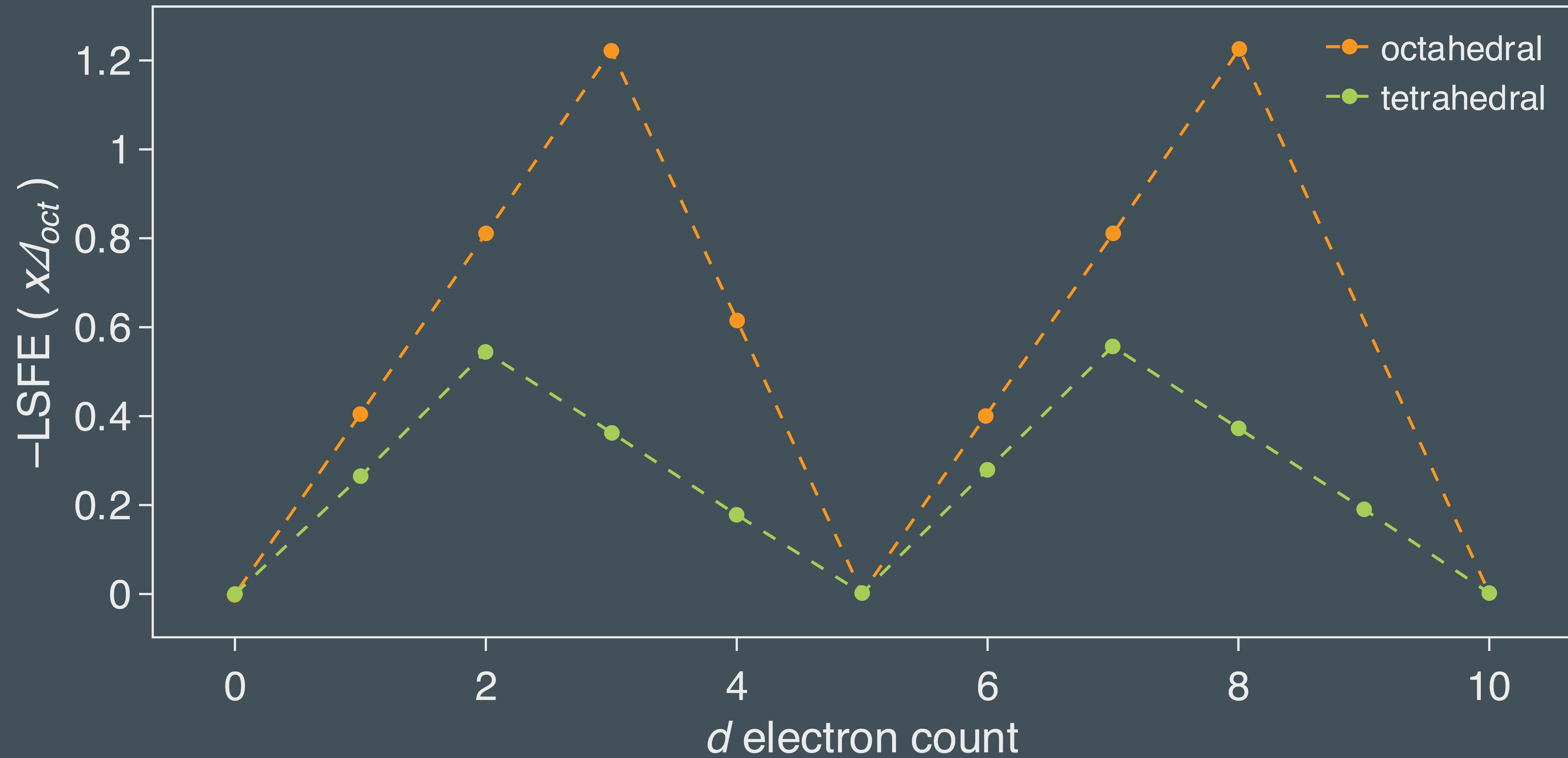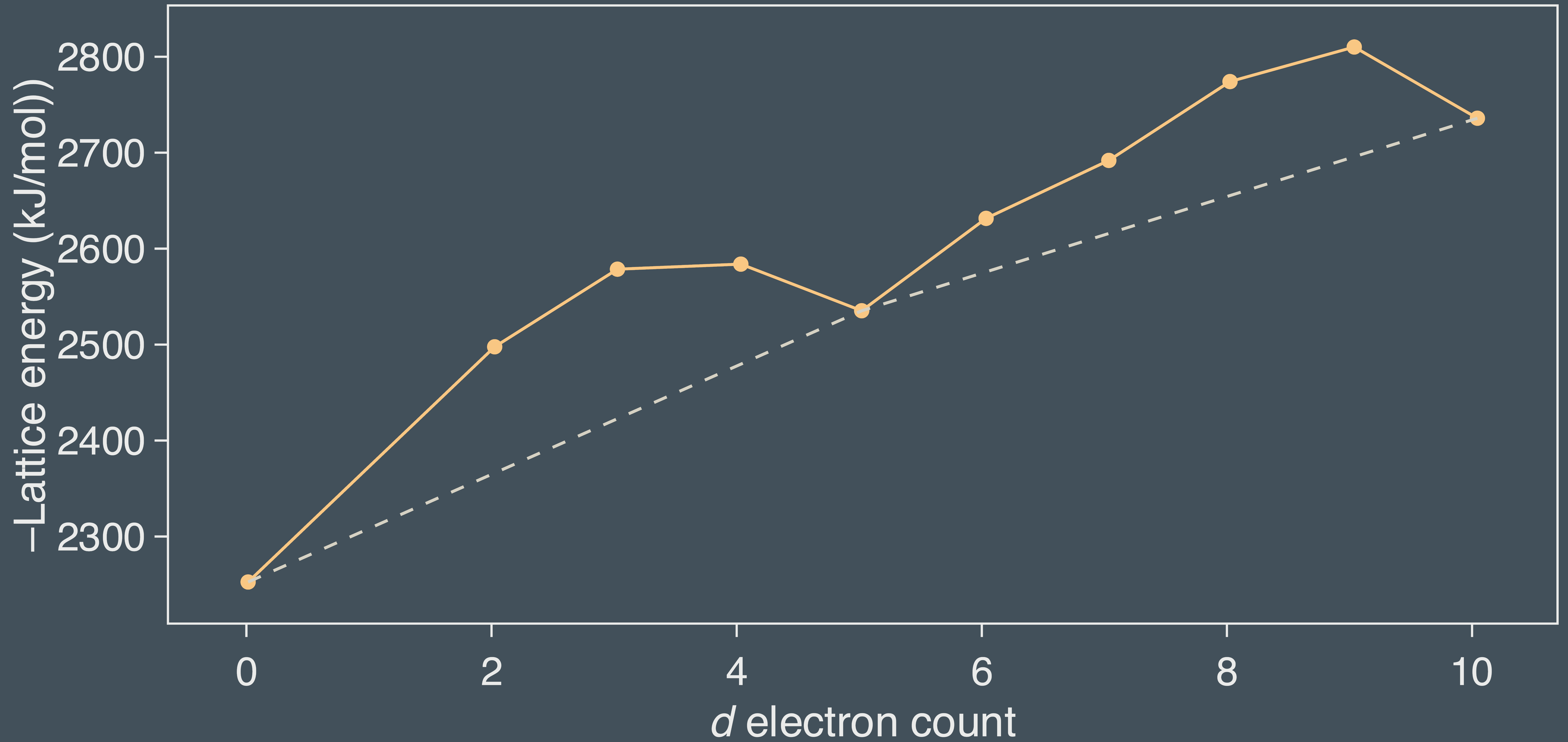
$$\Delta_{tet} = \frac{4}{9}\Delta_{oct}$$

+0.4 Δ_{tet}

–0.6 Δ_{tet}

Tetrahedral is always high spin
(always a weak field)

Ligand Field Stabilization Energies

Lattice Energies

LFSE and Equilibrium

We can also use LFSE to determine how easily we can replace ligands in solution (exchange).

We can do this because Δ_{oct} is ligand dependent.

The position of equilibrium will be related to the difference between two LFSEs.

Irving-Williams Series

The Irving-Williams series shows a "hump" that peaks at Cu^{2+} (d^9) and not at Ni^{2+} (d^8) as might be expected from a consideration of LFSEs.
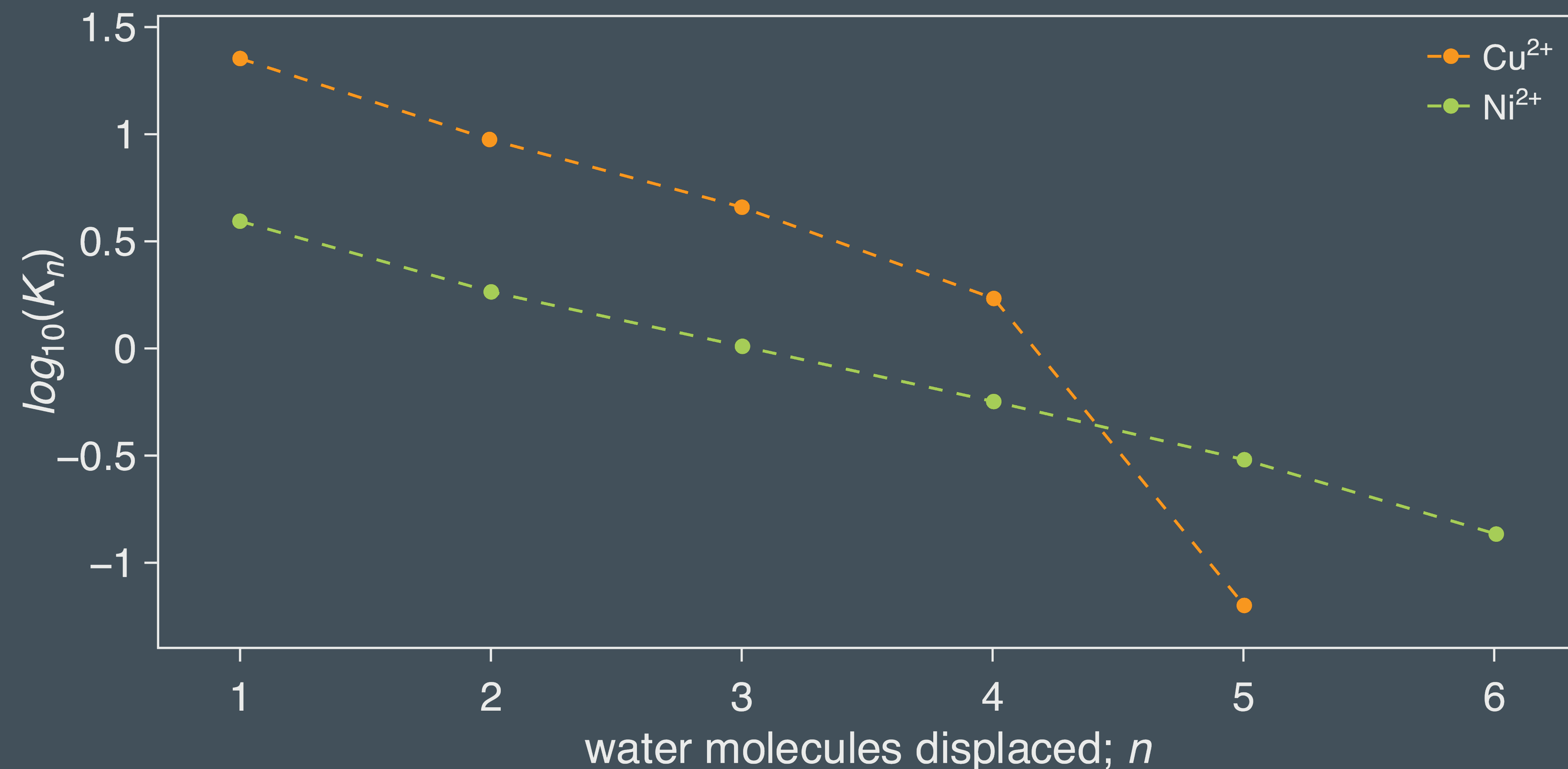
Overall stability constants for HS d-block metals

Metal ion	Mn^{2+}	Fe^{2+}	Co^{2+}	Ni^{2+}	Cu^{2+}	Zn^{2+}
$log\beta_3$ for $[M(en)_3]^{2+}$	5.7	9.5	13.8	18.6	18.7	12.1
$log\beta$ for $[M(EDTA)]^{2-}$	13.8	14.3	16.3	18.6	18.7	16.1

Irving-Williams Series

$Mn^{2+} < Fe^{2+} < Co^{2+} < Ni^{2+} < Cu^{2+} > Zn^{2+}$

Other considerations

So far we've assumed that all ligands are identical.

We have not yet explained *how* or *why* particular ligands are placed where they are in the spectrochemical series.

Next Time

- Pigments and the chemistry of color

- Electronic transitions in chemistry

- UV-vis absorption spectroscopy

- Molar Absorptivity

- Types of electronic transitions in metal complexes

- Selection Rules and Molar Absorptivity