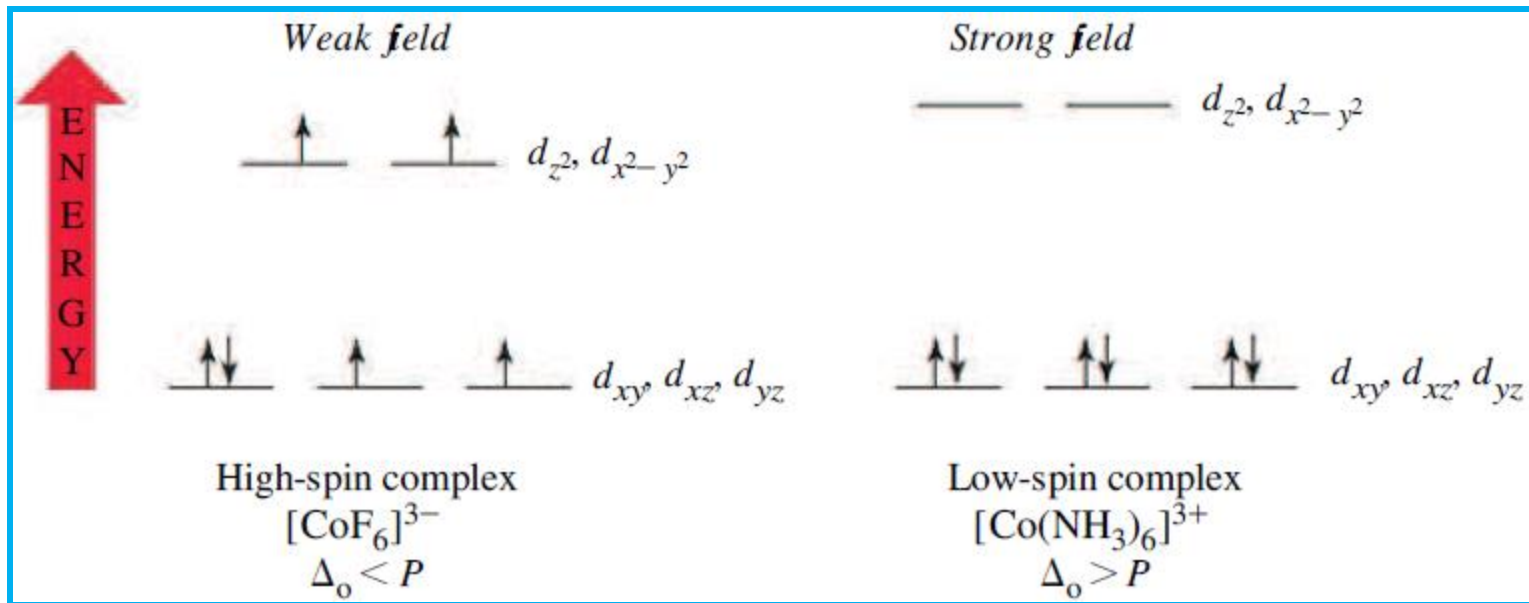


Crystal Field Stabilization Energy: High & Low Spin Octahedral Complexes

- CFSE for d^4 weak field case = $[3 \times 0.4 \Delta_o - 1 \times 0.6 \Delta_o] = 0.6 \Delta_o$
- CFSE for d^4 strong field case = $4 \times 0.4 \Delta_o = 1.6 \Delta_o$
- The different electron configurations are referred to as **high spin** (for the weak field case) and **low spin** (for the strong field case).
- The possibility of high and low spin complexes exists for configurations d^5 - d^7 as well.



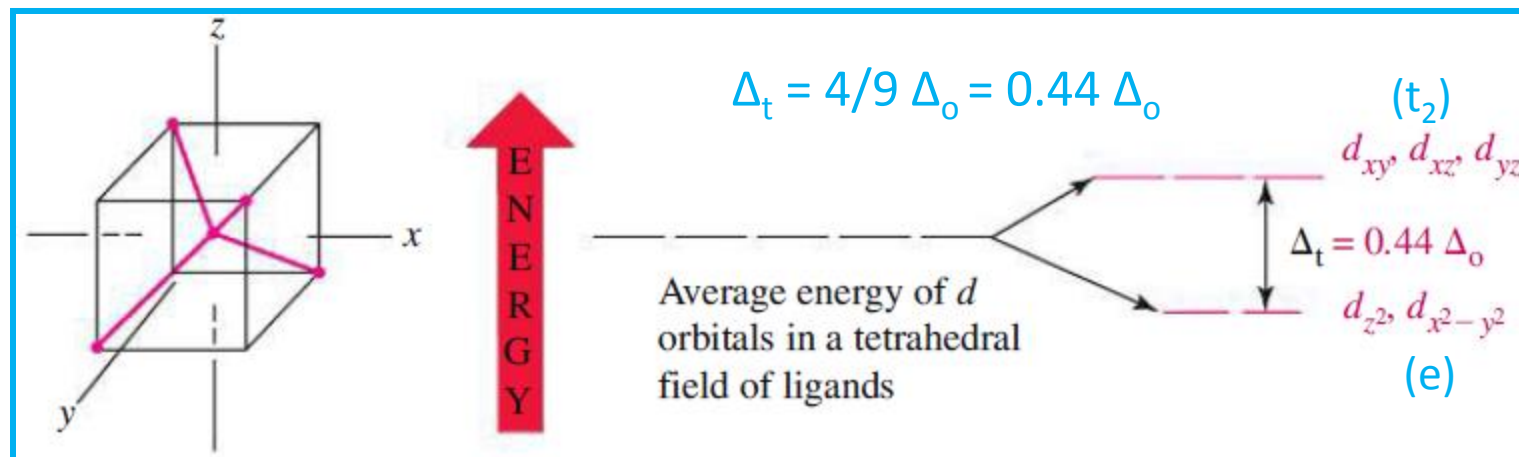
Crystal Field Stabilization Energy: High & Low Spin Octahedral Complexes

- **Electron-pairing energy (P):** Energy required to change two electrons with parallel spin in different degenerate orbitals into spin-paired electrons in the same orbital.
- **Two terms** contribute to pairing energy:
 - a) **loss in the exchange energy** which occurs upon pairing the electrons.
 - b) **Coulombic repulsion** between the spin-paired electrons.
- **CFSE for $(t_{2g})^x(e_g)^y$ configuration** = $(0.4x - 0.6y)\Delta_o - pP$ (considering pairing energy)

p = total number of electron pairs compared to corresponding high-spin configuration; P = mean pairing energy

Free Ion	CFSE	
	High Spin	Low Spin
d^4	$0.6\Delta_o$	$1.6\Delta_o - P$
d^5	$0\Delta_o$	$2.0\Delta_o - 2P$
d^6	$0.4\Delta_o$	$2.4\Delta_o - 2P$
d^7	$0.8\Delta_o$	$1.8\Delta_o - P$

Crystal Field Theory: Tetrahedral Complexes



- Imagine a tetrahedral molecule inside a cube with metal ions in the center of the cube. The ligands occupy the four alternate corners of the cube leaving the rest four corners empty.
- The two 'e' ($d_{x^2-y^2}$ and d_{z^2}) orbitals point to the center of the face of the cube while the three 't₂' (d_{xy} , d_{yz} and d_{zx}) orbitals point to the center of the edges of the cube.
- Thus, the t₂ orbitals are nearer to the direction of approach of the ligands than the e orbitals. (The ligands do not directly approach any of the metal d orbitals)

Crystal Field Theory: Tetrahedral Complexes

▪ Why almost all tetrahedral complexes are high spin?

- There are only 4 ligands in the tetrahedral complex and hence the ligand field is roughly $2/3$ of the octahedral field.
- The direction of ligand approach in tetrahedral complex does not coincide with the d-orbitals. This reduces the field by a factor of $2/3$. Therefore Δ_t is roughly $2/3 \times 2/3 = 4/9$ of Δ_o .
- As a result, all tetrahedral complexes are **high-spin** since the Δ_t is normally smaller than the pairing energy. Hence, low spin configurations are rarely observed. Usually, if a very strong field ligand is present, **square planar** geometry will be favored.

▪ When do we expect tetrahedral geometry?

- Small metal ions and large ligands (Cl^- , Br^- and I^-) because then ligand-ligand repulsions cancel the energy advantage of forming more metal-ligand bonds.
- Metal ions with zero CFSE (d^0 , d^5 , d^{10}) or small CFSE (d^2 and d^7).
- **Examples:** MnO_4^- (d^0), FeCl_4^- (d^5 , h.s.), CoCl_4^{2-} (d^7 , h.s.), ZnCl_4^{2-} (d^{10})