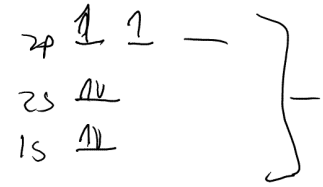
^2p Electrone Configuration $\Rightarrow$ Free ion terms ^3P, ^1D, ^1S

① Hunds Rule $\Rightarrow$ Maximal multiplicity $\Rightarrow$ lowest energies



— lowest energy config for p^2 $\therefore$ ^3P is lowest energy term since it has highest multiplicity.

② If 2 or more term symbols share the maximal multiplicity, the lower energy term will have a larger value of L

^4F is lower in energy than ^4P

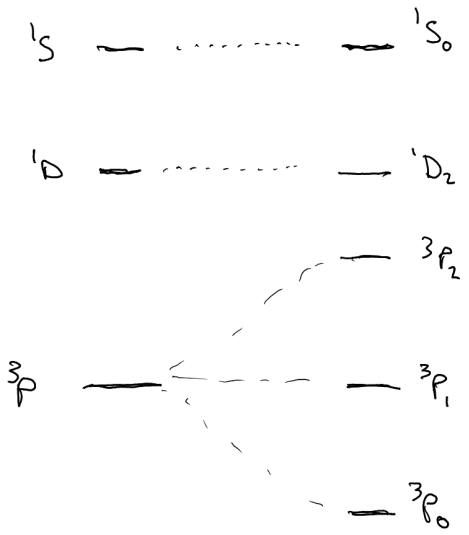
$L=3$ $L=1$

Multielectron systems Spin + Angular orbital momenta can interact...

↳ Spin-Orbit Coupling ($L \times S$ interacts to give a new QN $\Rightarrow$ J)

$^{(2S+1)}L_J$ $\quad J = L+S,\ L+(S-1),\ L+(S-2) \ldots L-S$

p^2



^1S $L=0$; $S=0$ $\therefore J=0$

^1D $L=2$; $S=0$ $\therefore J=2$

^3P $L=1$; $S=1$ $\therefore J=2,1,0$

When Valence set is less than half filled, the low J will be lowest in Energy

" " " is half or greater filled, the low J would be highest " "

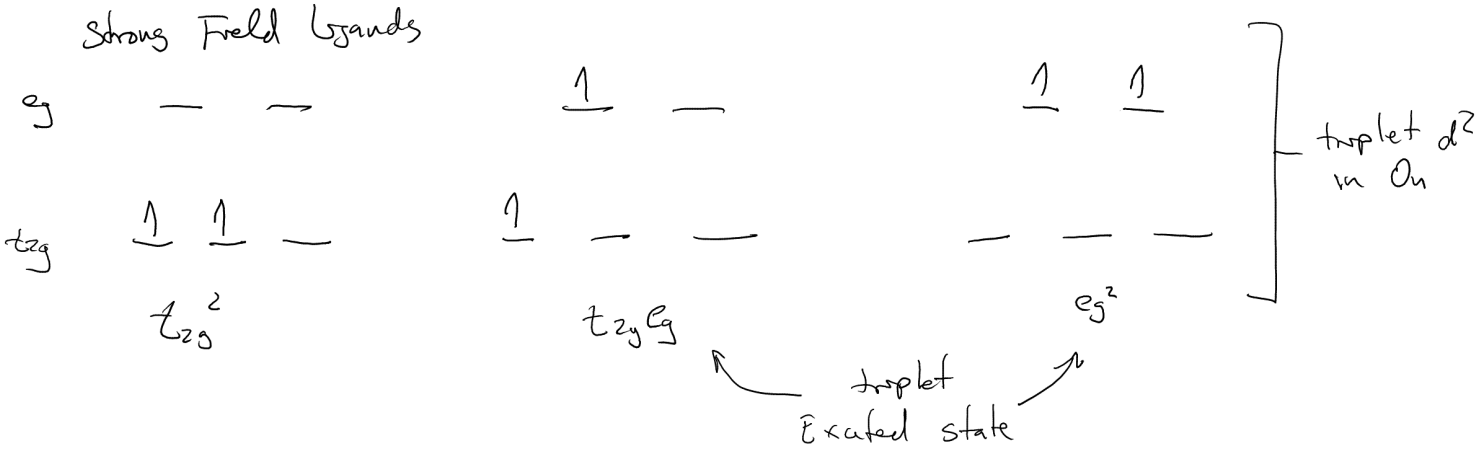
3P is Free ion term

$V^{3+} \Rightarrow d^2 \Rightarrow {}^3F, {}^3P, {}^1G, {}^1D, {}^1S$

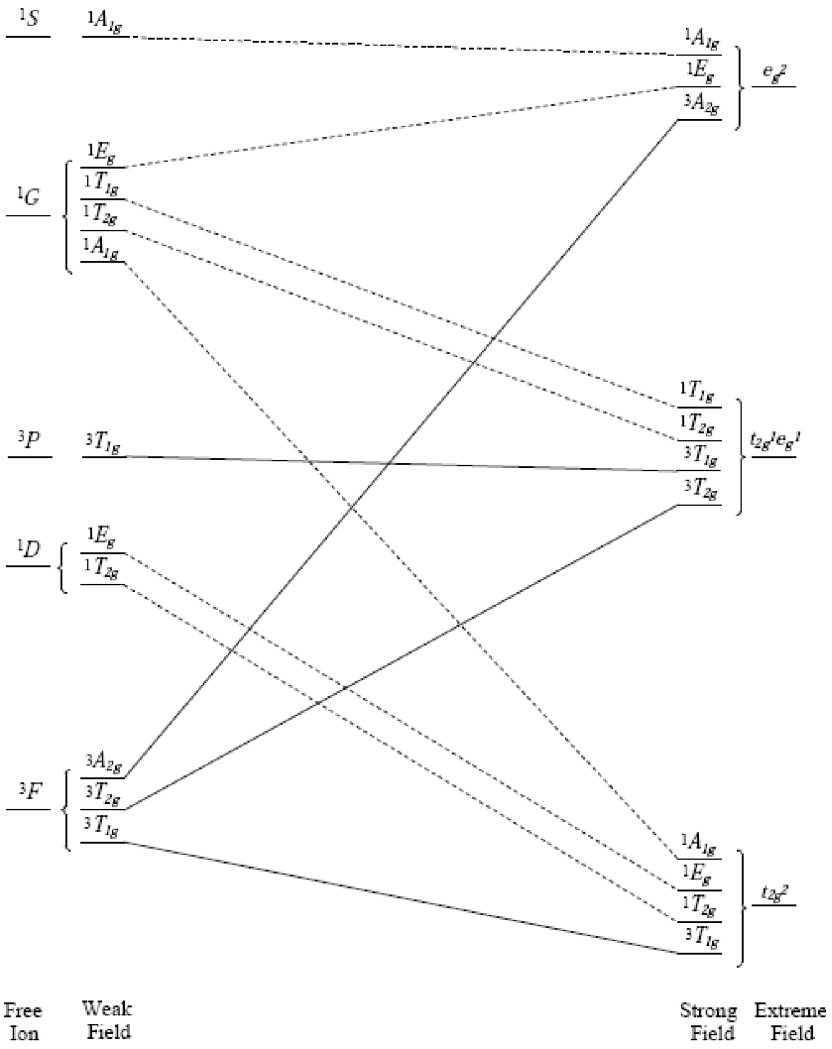
Free Ion Config ↗ (No ligand Field)

↑ ↑ _ _ _ 5 degenerate d-orbitals.

Strong Field Ligands



d^2 Correlation Diagram



Selection Rules

① Laporte Selection Rule.

transitions between states of the same parity are forbidden

(g) ⇸ (g) is not allowed...

(g) → (u) is allowed

transitions between d-orbitals are technically forbidden
" " d + p-orbitals would be allowed

② Transition between states of different multiplicities are forbidden

$^4A_2 \longrightarrow {}^4T_1$ (allowed)

$^4A_2 \not\longrightarrow {}^2A_2$ (Forbidden)

Mechanisms for Relaxation of Selection Rules:

① Vibronic Coupling - Bond stretches + bends can eliminate an inversion center + allow for the electronic transition to take place

d-d transitions: $\varepsilon \sim 10 - 200\ cm^{-1}M^{-1}$

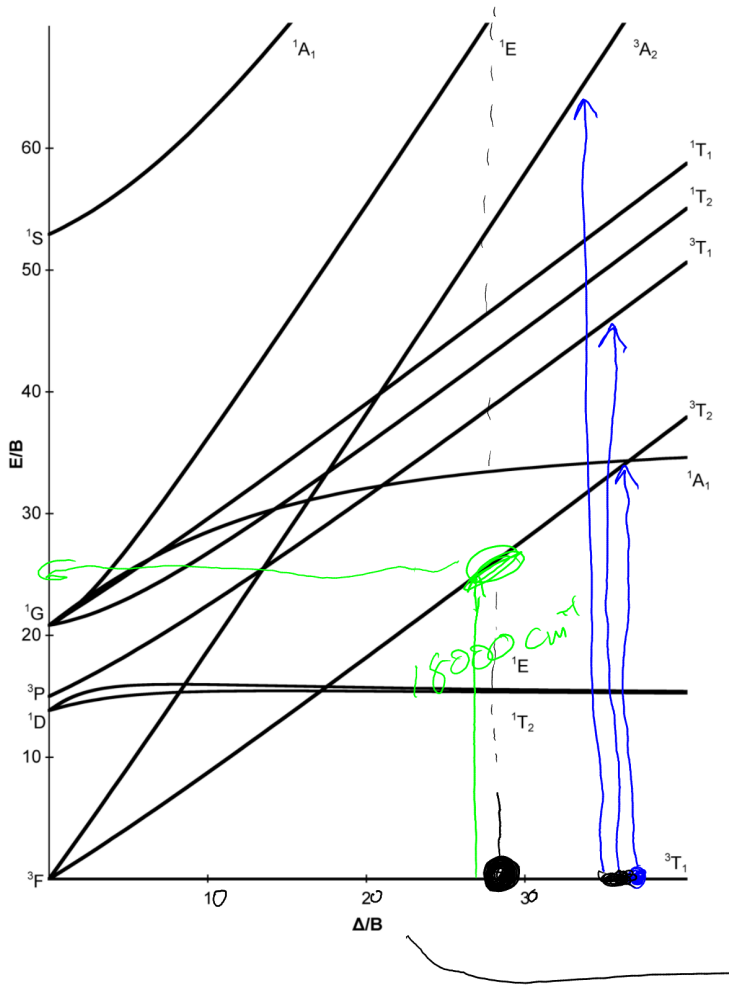
② Spin-Orbit Coupling - Mixing of L+S can relax the multiplicity constraint.

$Z \gtrsim 30$ (2nd + 3rd Row TM ions)

Tanabe-Sugano Diagrams - a special type of correlation diagram

Developed by Tanabe + Sugano in 1954 (J. Phys. Soc. Japan 1954, 9, 766)

TS-Diagram for d^2



$[V^{III}(OH_2)_6]^{3+}$

d^2

3 Spin allowed Transitions

ν_1 $^3T_{1g} \rightarrow {}^3T_{2g}$ ($17800\ cm^{-1}$)

ν_2 $^3T_{1g} \rightarrow {}^3T_{1g}$ ($25700\ cm^{-1}$)

ν_3 $^3T_{1g} \rightarrow {}^3A_{2g}$ ($38000\ cm^{-1}$)

Energy ↑

$\nu_1 = 17800 \rightarrow 1$

$\nu_2 = 25700 \rightarrow 1.44$

$\nu_3 = 38000 \rightarrow 2.13$

→ Strong Field

Δ/B

Weak Field

Δ = Field Strength

B = Racah Parameter

For $[V(OH_2)_6]^{3+}$ $\Delta/B = 30$ $B \approx 600\ cm^{-1}$

$\nu_1 = 18000\ cm^{-1} \Rightarrow \Delta/B$ of 30

ν_1

E

$18000/B = 30 \therefore B = 600\ cm^{-1}$