Typical Ox. States for 1st Row TM
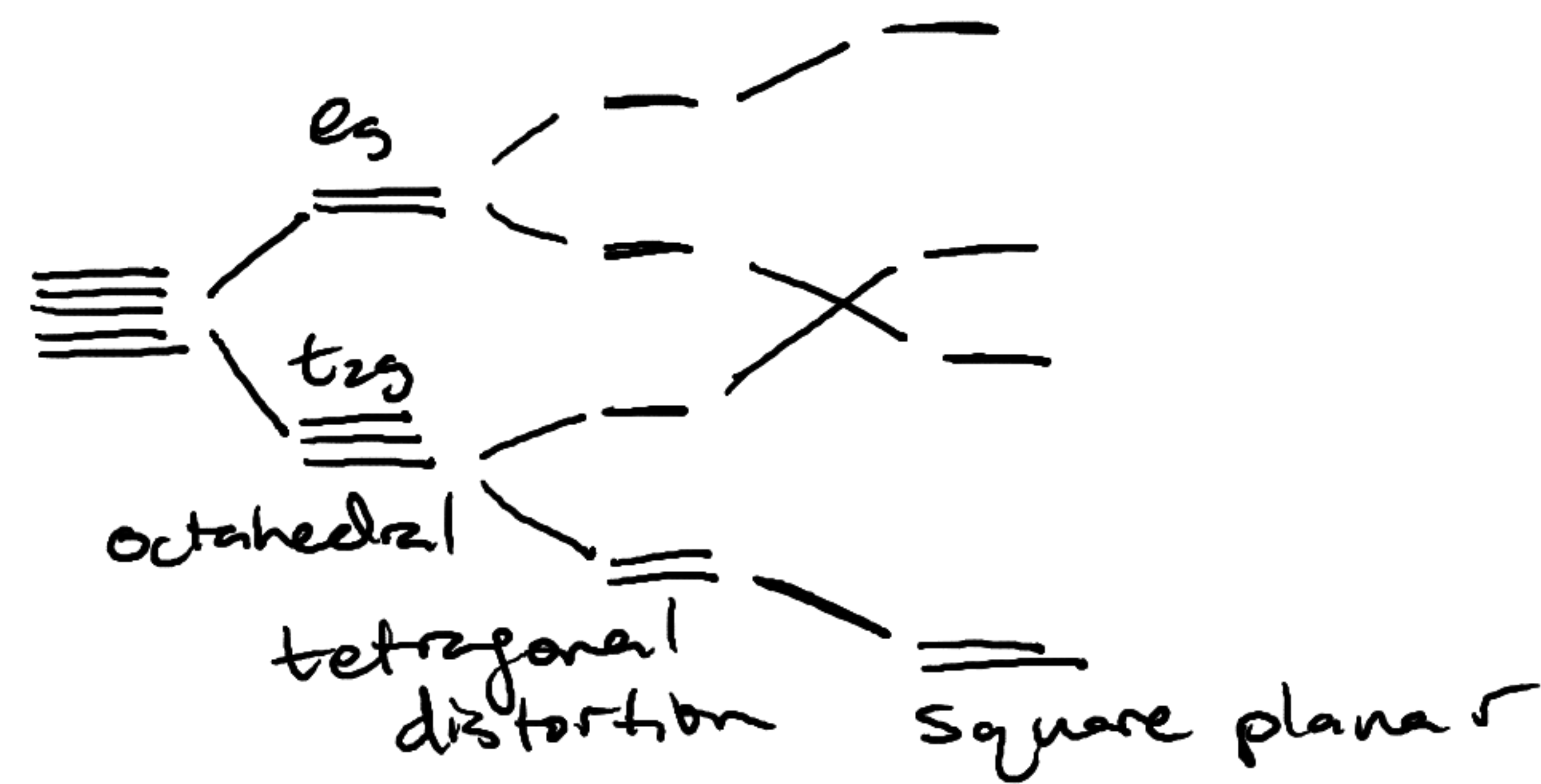
Sc(III) Ti(IV) V(III) Cr(II) Mn(II)
         (IV)   (IV)   (III)   high spin
                 (V)

Fe(II) Co(II) Ni(II) Cu(I) Zn(II)
(III)   (III)

John Teller Effect

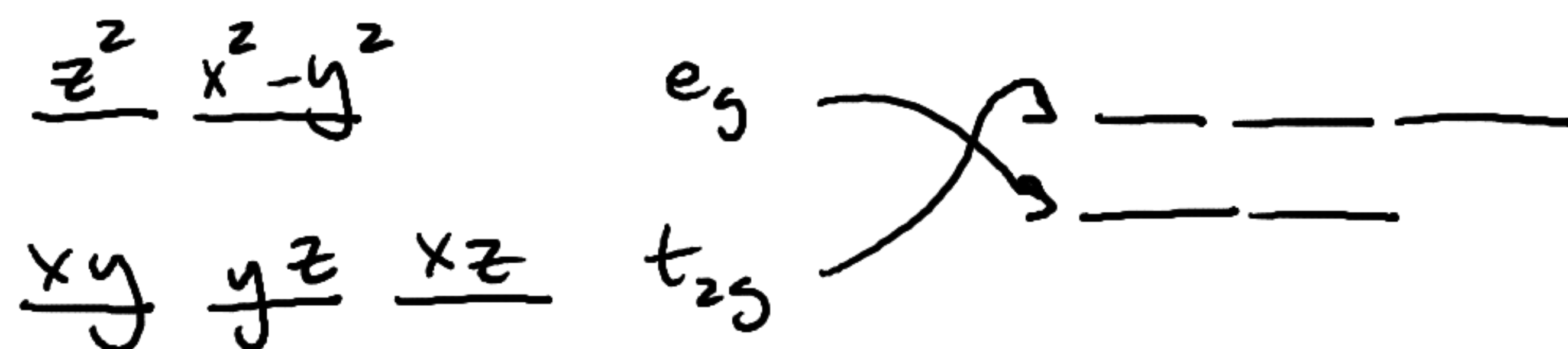If complex is degenerate $\Rightarrow$ It will charge config to obtain lower NRG

e_g

t_{2g}

octahedral

tetragonal distortion   square planar

High spin tetrahedral switches t_{2g} & e_g
   & changes splitting

$$\Delta_T = \frac{4}{9}\Delta_0$$

Common Splitting

Octahedral
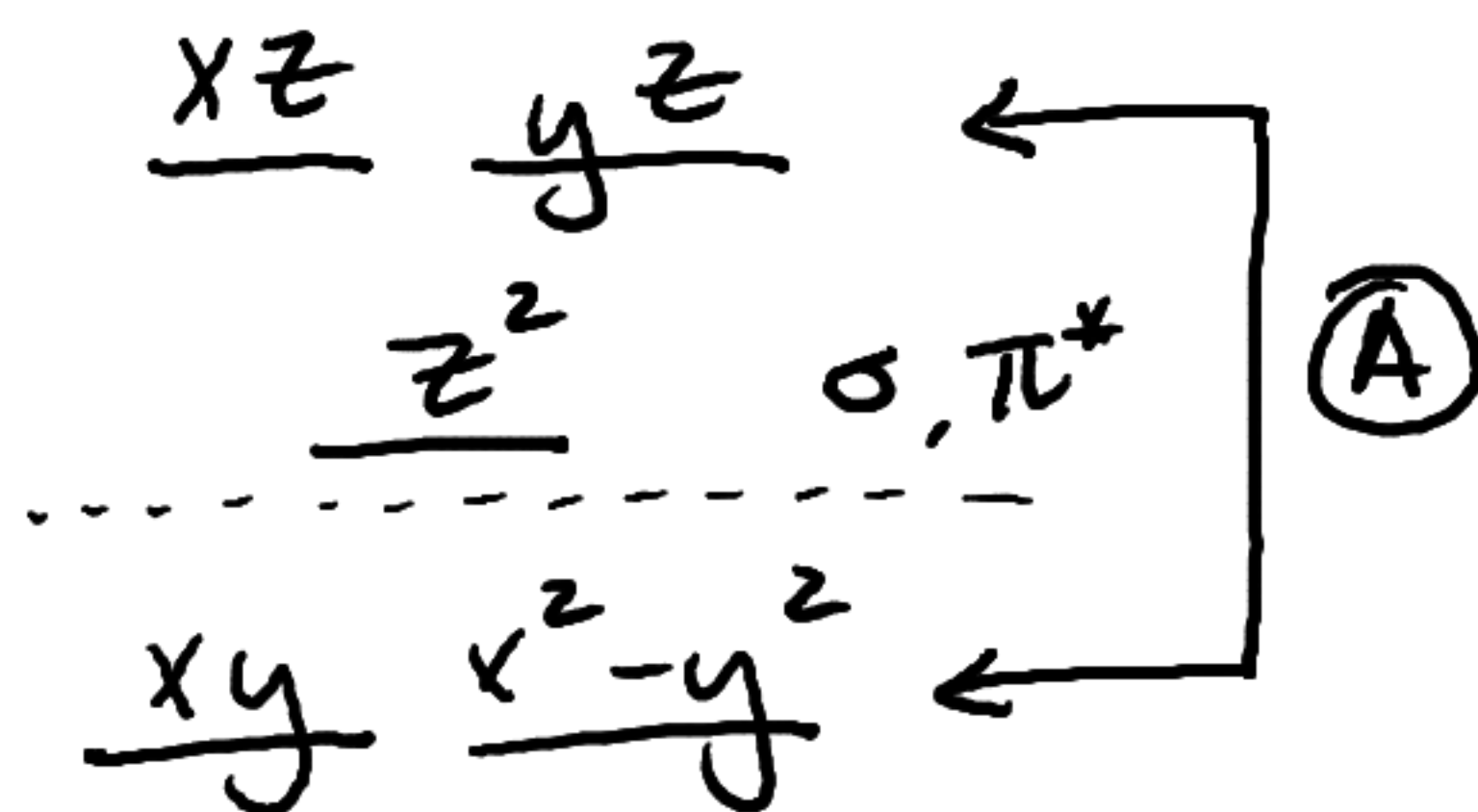
$\underline{z^2} \quad \underline{x^2-y^2}$ e_g

$\underline{xy} \quad \underline{yz} \quad \underline{xz}$ t_{2g}

Tetrahedral

$\underline{\quad\quad} \quad \underline{\quad\quad}$

$\underline{\quad} \quad \underline{\quad} \quad \underline{\quad}$

Trigonal Planar (MX₃)

$\underline{xy} \quad \underline{x^2-y^2}$

$\underline{xz} \quad \underline{yz}$ $\underline{\quad\quad\quad}\uparrow$ rize due to L π interaction

$\underline{z^2}$ $\underline{\quad\quad\quad}\uparrow$ rise due to L direct interaction

Tetrahedral (MLX₃)

$\underline{xz} \quad \underline{yz}$

$\underline{z^2}$ σ, π^* Ⓐ

$\underline{xy} \quad \underline{x^2-y^2}$
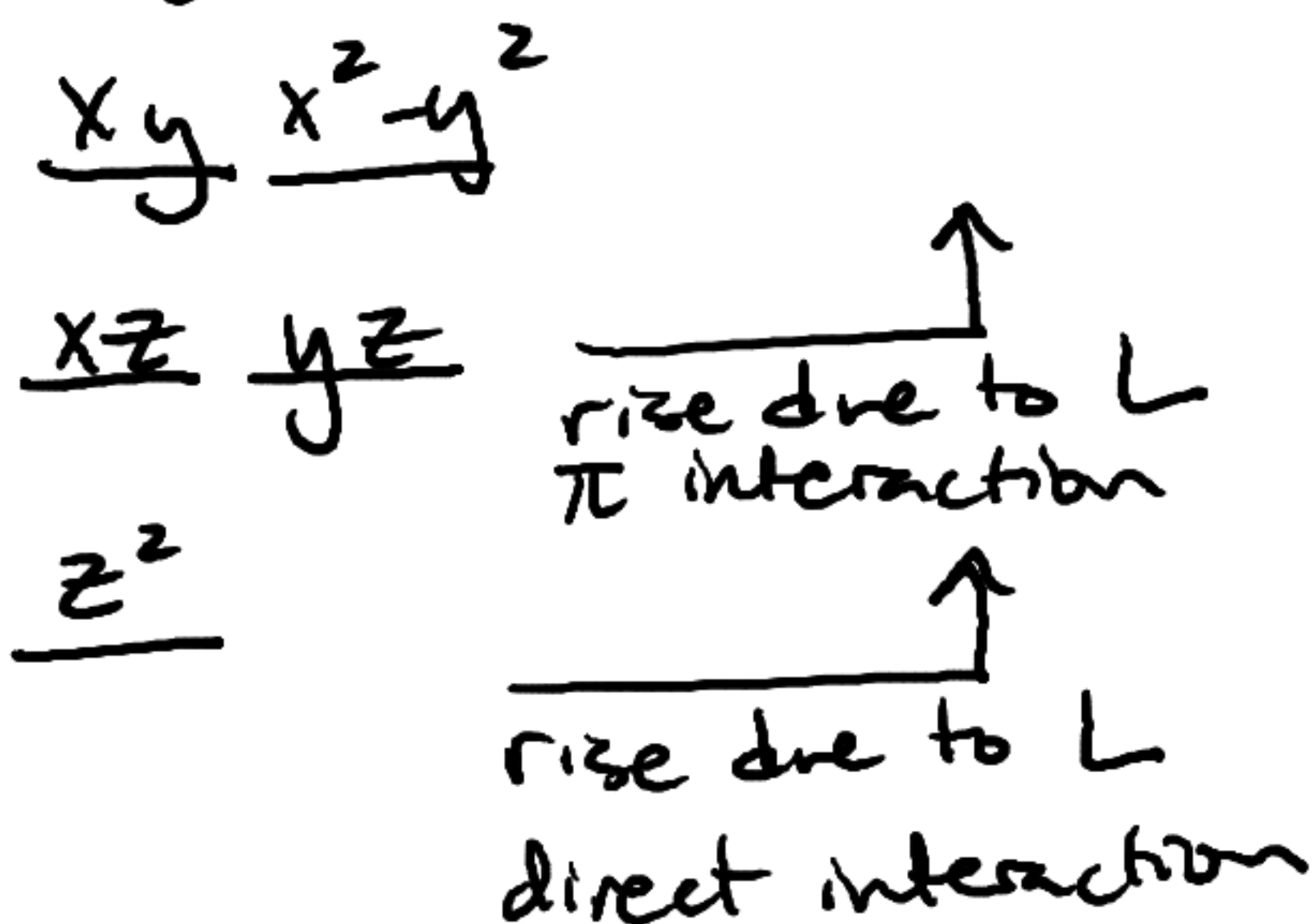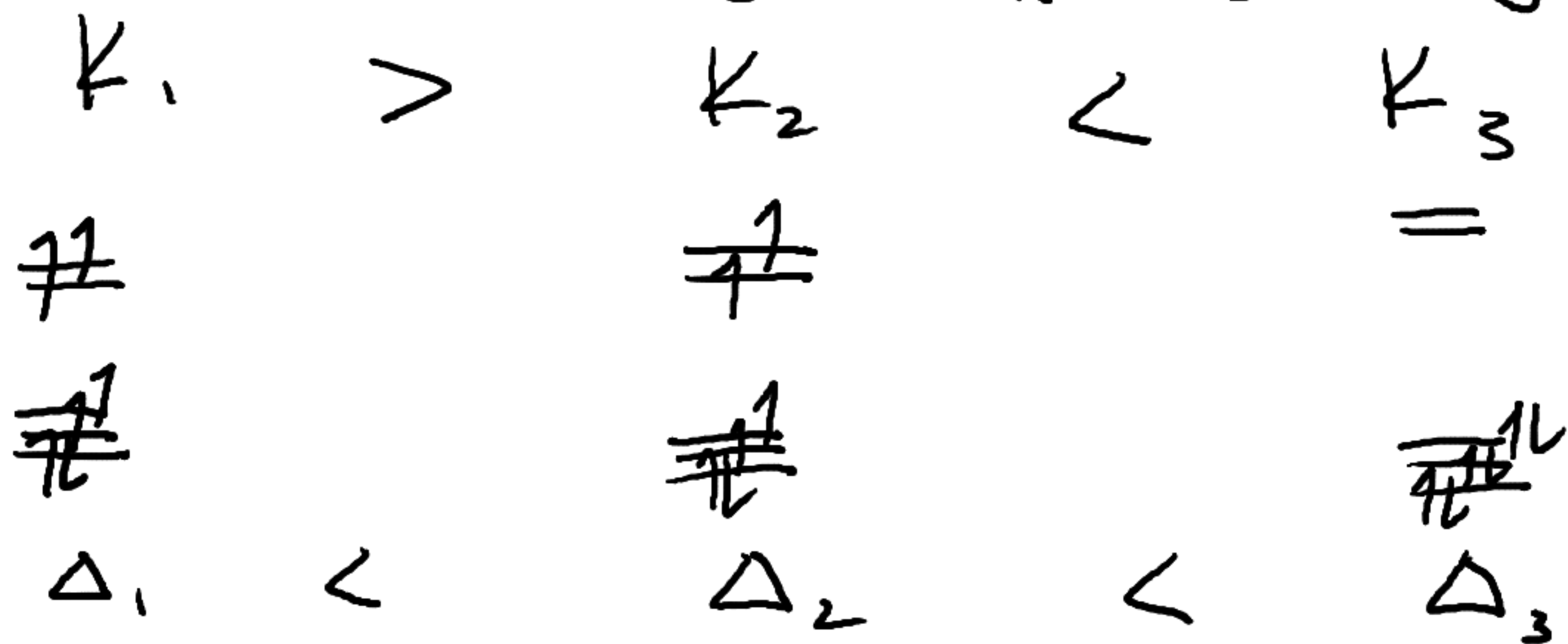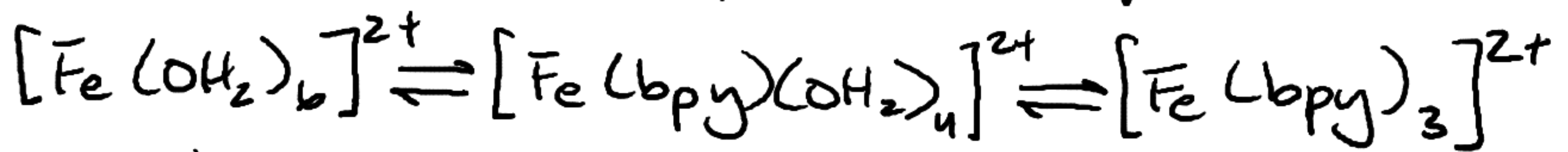
for L = π donor

Ⓐ occurs when L = π acceptor

Common Trends for Octahedral & Tetrahedral Geometry

- $M-L_6$ favored over L_4

- d^6 &/or low spin $\longrightarrow$ octahedral

- d^3 / d^8 $\longrightarrow$ octahedral

- high spin d^4 / d^9 prefer CN# = 6

$\longrightarrow$ tetragonal distortion

- d^2 / d^7 $\longrightarrow$ tetrahedral

- d^0 / d^{10} / high spin d^5 $\longrightarrow$ no preference

Coordination Equilibria

For octahedral complexes:
Reactant ligands & product ligands are in equilibrium

As reactant ligand becomes replaced, K decreases

Discrepancy occurs if e^- structure changes
(high spin to low spin)

$$[Fe(OH_2)_6]^{2+} \rightleftharpoons [Fe(bpy)(OH_2)_4]^{2+} \rightleftharpoons [Fe(bpy)_3]^{2+}$$

K_1 $>$ K_2 $<$ K_3

Δ_1 $<$ Δ_2 $<$ Δ_3

Chelate Effect

K of forming polydentate ligands
usually greater than corresponding monodentate
ligand
$\hookrightarrow$ greater increase in entropy

Irving Williams Series

for high spin M^{2+} of $\log(K)$

$Mn < Fe < Co < Ni < Cu > Zn$

$3\ e_g\ e^-$ due to
tetragonal distortion

The Trans- Effect

$$\mu = \left[\sqrt{n(n+2)} \right] \mu_\beta \qquad n = \text{\# of unpaired } e^-$$
$$S = \text{quantum \#}$$

$\uparrow CN \# = \uparrow$ bond length

e^- Counting

$$\text{Oxidation State} = \Sigma \left| \begin{array}{c} \text{anionic} \\ \text{ligand} \end{array} \text{charge} \right| + \text{overall charge}$$

d^n where $n = \overset{\text{column}}{\text{metal \#}} - \text{oxdn \#}$

$$\text{Valence } e^- = \overset{\text{column}}{\text{metal \#}} + \underset{\text{ligand}}{\Sigma \text{ anion}} e^-$$
$$+ \underset{\text{ligand}}{\Sigma \text{ neutral}} e^-$$
$$- \text{overall charge}$$

- Make sure to equally distribute e^- from bridging ligands between 2 metal centers

- In dimers, metals count like neutral ligand charge but valence count as 1 (due to equal sharing)

- coord. seems to favor interaction w/ 0