XMCD Sum Rules

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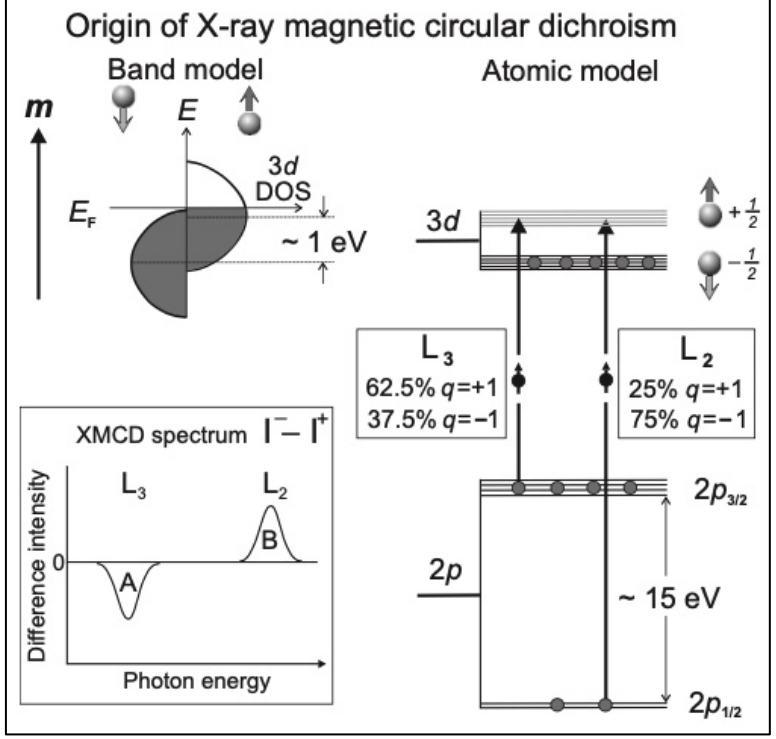
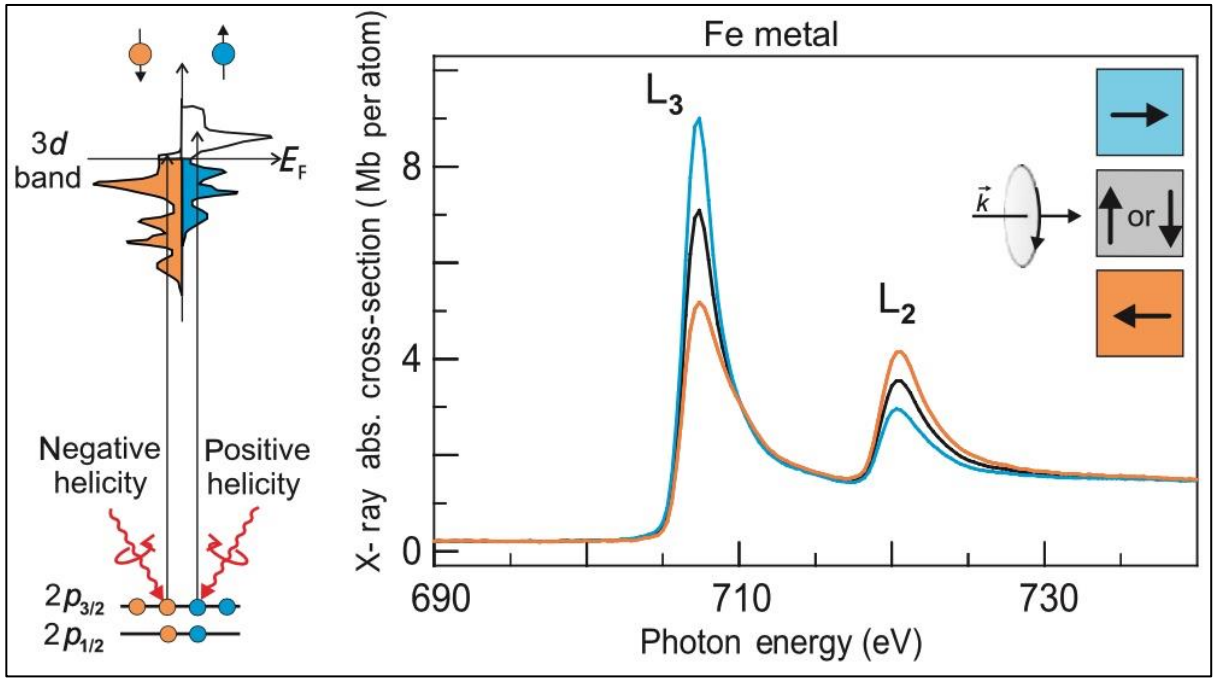
Xu Group Meeting

Recall : XAS of d-orbitals in Ni, Co

- Partially filled d-orbitals; look for $L_{2,3}$ transitions
  - $2p_{1/2} \Rightarrow 3d : L_2$
  - $2p_{3/2} \Rightarrow 3d : L_3$
- Band model: net moment due to difference between majority/minority electrons
- Energy difference due to spin-orbit splitting in p-orbitals
  - "Orbital quenching" in d-orbitals suppresses orbital moment





Recall : QM Description of Absorption

- Polarized photon (linear, RCP, LCP) sets interaction Hamiltonian between initial, final states
- Determination of non-zero matrix elements sets spin, radian, angular selection rules for absorption
  - Most complex part is angular component

The polarization dependent *X-ray absorption resonance intensity* in the *dipole approximation* is given by

$$I_{\text{res}} = \mathcal{A}\,|\langle b|\,\boldsymbol{\epsilon}\cdot\boldsymbol{r}|a\rangle|^2\,. \tag{9.60}$$

The proportionality factor, given by

$$\mathcal{A} = 4\pi^2\frac{e^2}{4\pi\epsilon_0\hbar c}\,\hbar\omega \tag{9.61}$$

contains the dimensionless *fine structure constant* α_{f}

$$\alpha_{\text{f}} = \frac{e^2}{4\pi\epsilon_0\hbar c} = \frac{1}{137.04}. \tag{9.62}$$

The intensity I_{res} has the dimension [length$^2\times$ energy] and is usually expressed in units of [Mb eV], where $1\,\text{Mb} = 10^{-22}\,\text{m}^2$.

$$P_z^0 = r\,C_0^{(1)} = r\,\cos\theta = z, \tag{9.71}$$

$$P_z^{\pm} = r\,C_{\pm1}^{(1)} = \mp r\frac{1}{\sqrt{2}}\,\sin\theta\,\text{e}^{\pm\text{i}\phi} = \mp\frac{1}{\sqrt{2}}\,(x \pm \text{i}y). \tag{9.72}$$

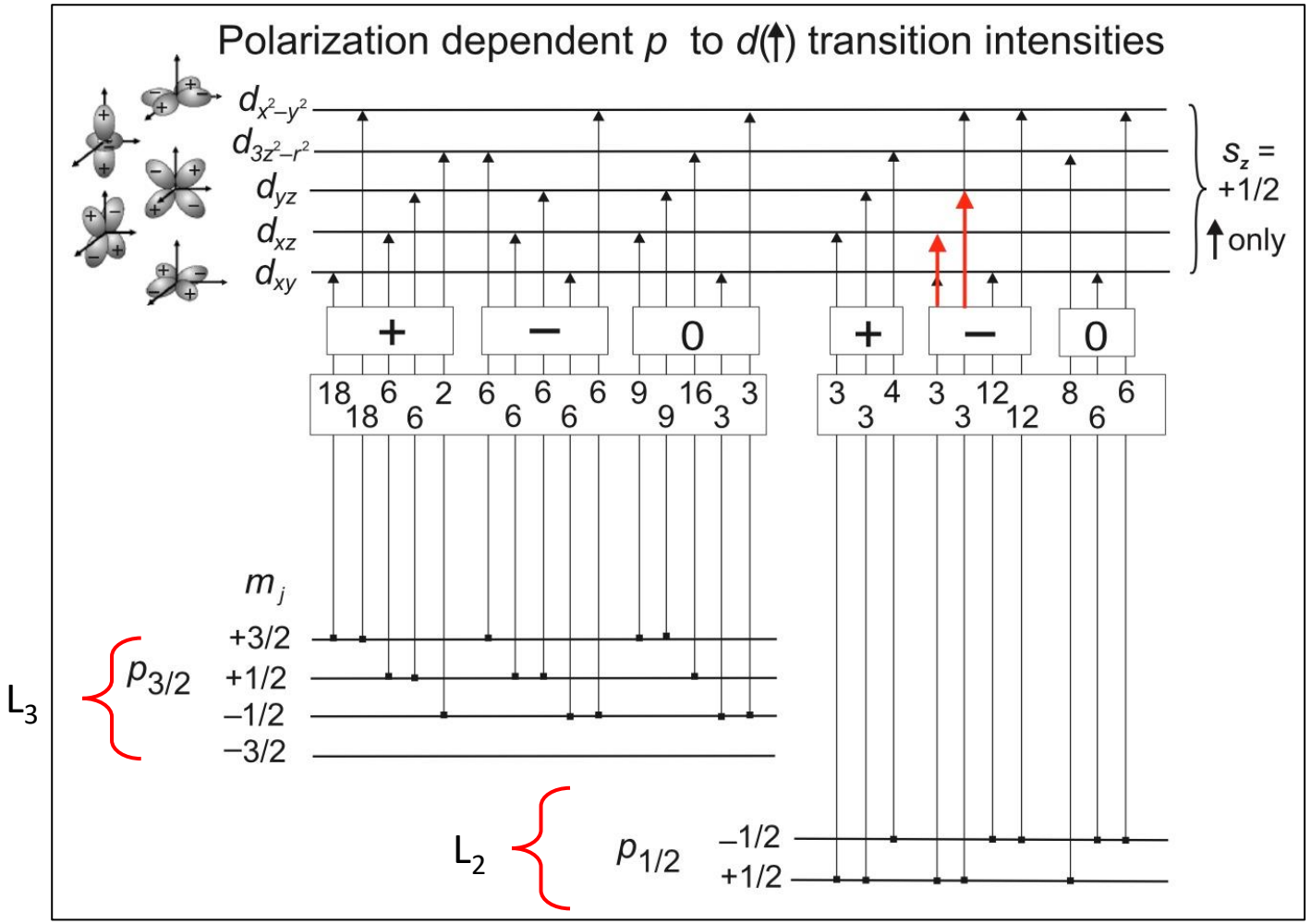
$$\langle b|\,P_\alpha^q\,|a\rangle = \underbrace{\delta(m_s', m_s)}_{\text{spin}}\;\underbrace{\langle R_{n',l}(r)|r|R_{n,c}(r)\rangle}_{\text{radial}}\;\underbrace{\sum_{m_c,m_l,p} e_{\alpha,p}^q\,\langle l, m_l|\,C_p^{(1)}\,|c, m_c\rangle}_{\text{angular}}, \tag{9.80}$$

The *X-ray absorption resonance intensity* for different X-ray propagation directions α and polarization states q can be written as

$$I_{\text{res}} = \mathcal{A}\,|\langle b|\,P_\alpha^q|a\rangle|^2, \tag{9.75}$$

where $\mathcal{A}$ is given by (9.61) and the polarization dependent dipole operators P_α^q with $\alpha = x, y,$ or z and $q = +1, 0,$ or -1 are listed in Table A.4.

Goal : Calculate all transition elements for *p* ⇨ d orbitals



Orbital quenched d-states

Matrix element under polarity ±,0 x-ray

Initial SOC p-states

Example of Calculation

$$|d_n, \uparrow\downarrow\rangle = |d_n\rangle \otimes |\uparrow\downarrow\rangle, \alpha = |\uparrow\rangle, \beta = |\downarrow\rangle$$

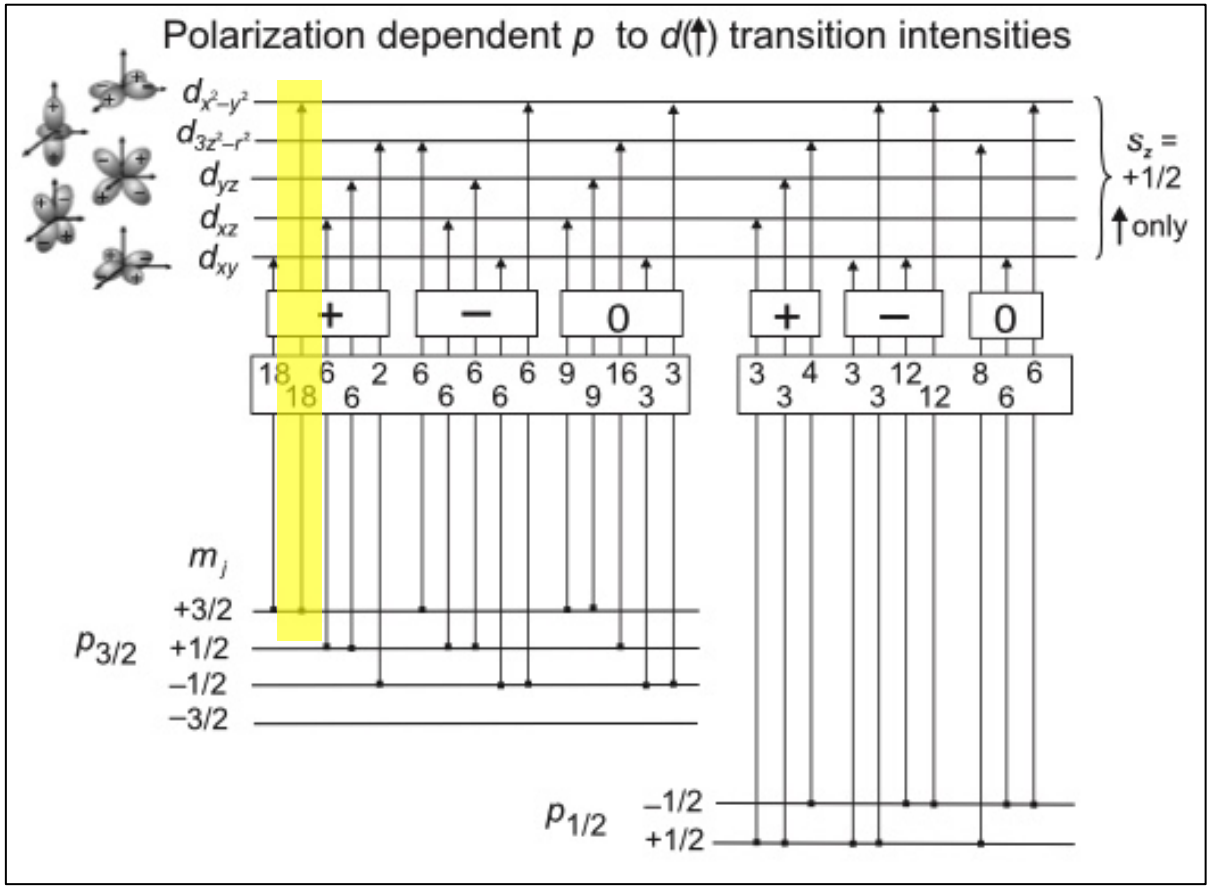
$$|d_{x^2-y^2}, \uparrow\rangle = \frac{1}{\sqrt{2}}\left(Y_{2,-2}\alpha + Y_{2,2}\alpha\right)$$

$$|p_{3/2}, +\tfrac{3}{2}\rangle = Y_{1,1}\alpha$$

$$\left\langle d_{x^2-y^2}\middle|C^{(1)}_{+1}\middle|p_{3/2}, +\tfrac{3}{2}\right\rangle$$

$$= \frac{1}{\sqrt{2}}\left\{\langle 2,-2|C^{(1)}_{+1}|1,1\rangle + \langle 2,2|C^{(1)}_{+1}|1,1\rangle\right\}$$

$$= \frac{1}{\sqrt{2}}\sqrt{\frac{4\cdot 3}{2\cdot 3\cdot 5}} = \frac{1}{\sqrt{5}}$$



Squares of matrix element, multiplied by 90

Example of Calculation

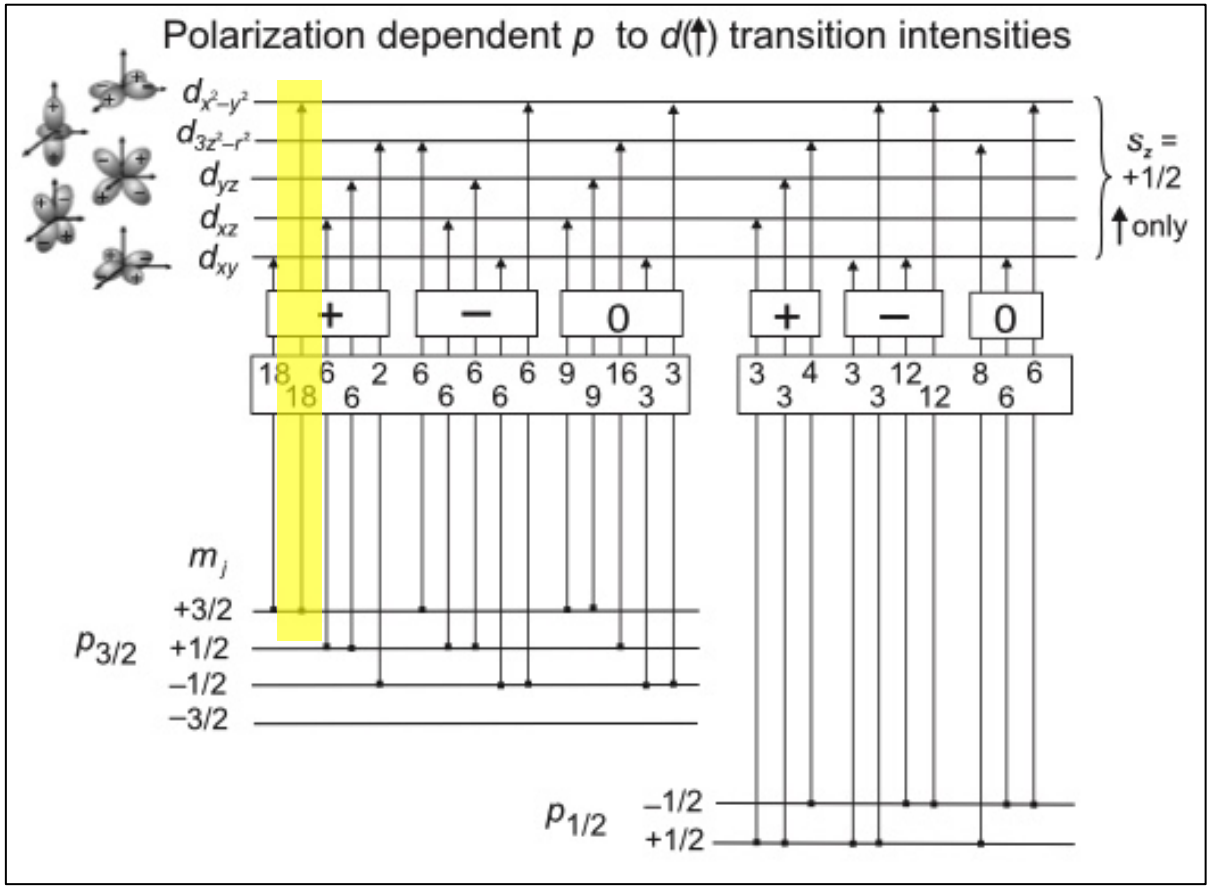
$$|d_{x^2-y^2},\downarrow\rangle = \frac{1}{\sqrt{2}}\left(Y_{2,-2}\beta + Y_{2,2}\beta\right)$$

$$|p_{3/2},+\tfrac{3}{2}\rangle = Y_{1,1}\alpha$$

$$\left\langle d_{x^2-y^2},\downarrow \left| C^{(1)}_{+1} \right| p_{3/2},+\tfrac{3}{2} \right\rangle$$

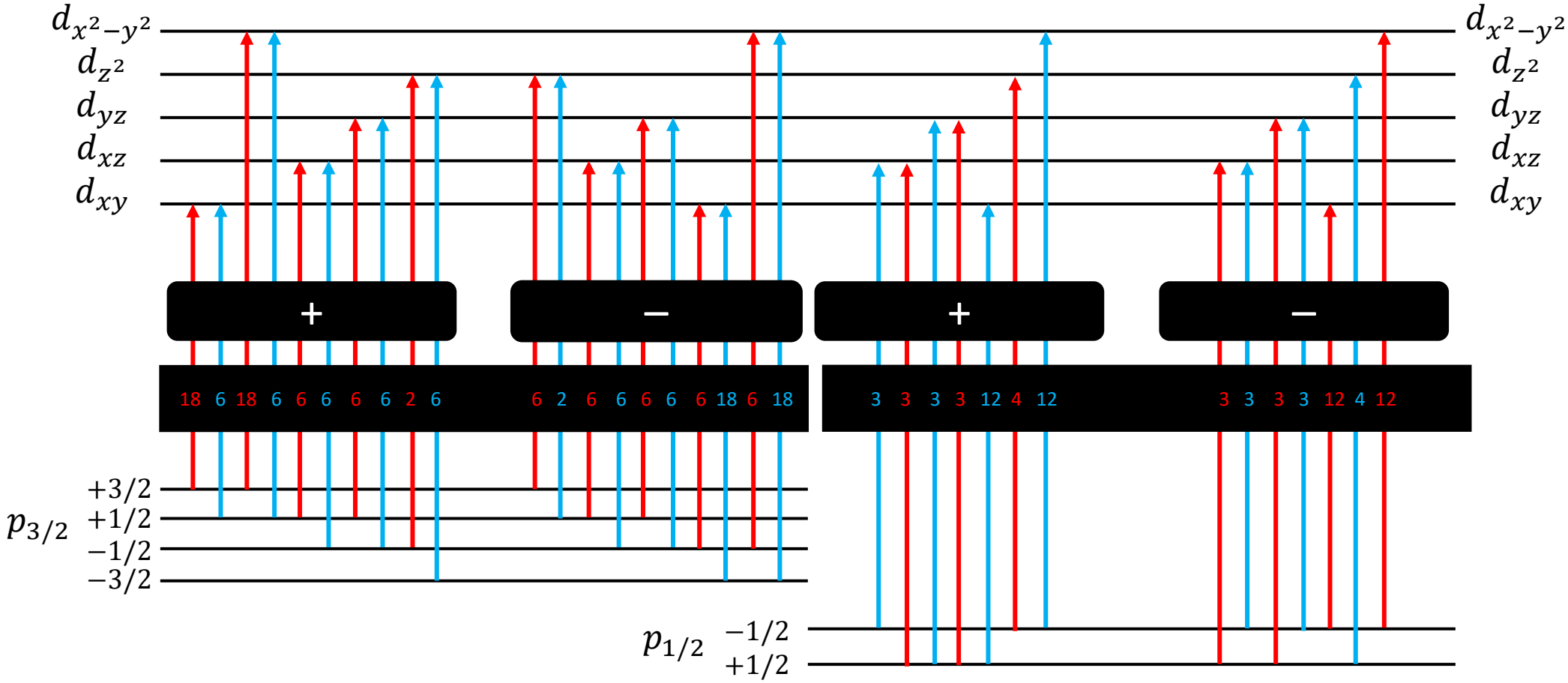
$$= 0$$

↳ Spin-wavefunctions not compatible under transition rules



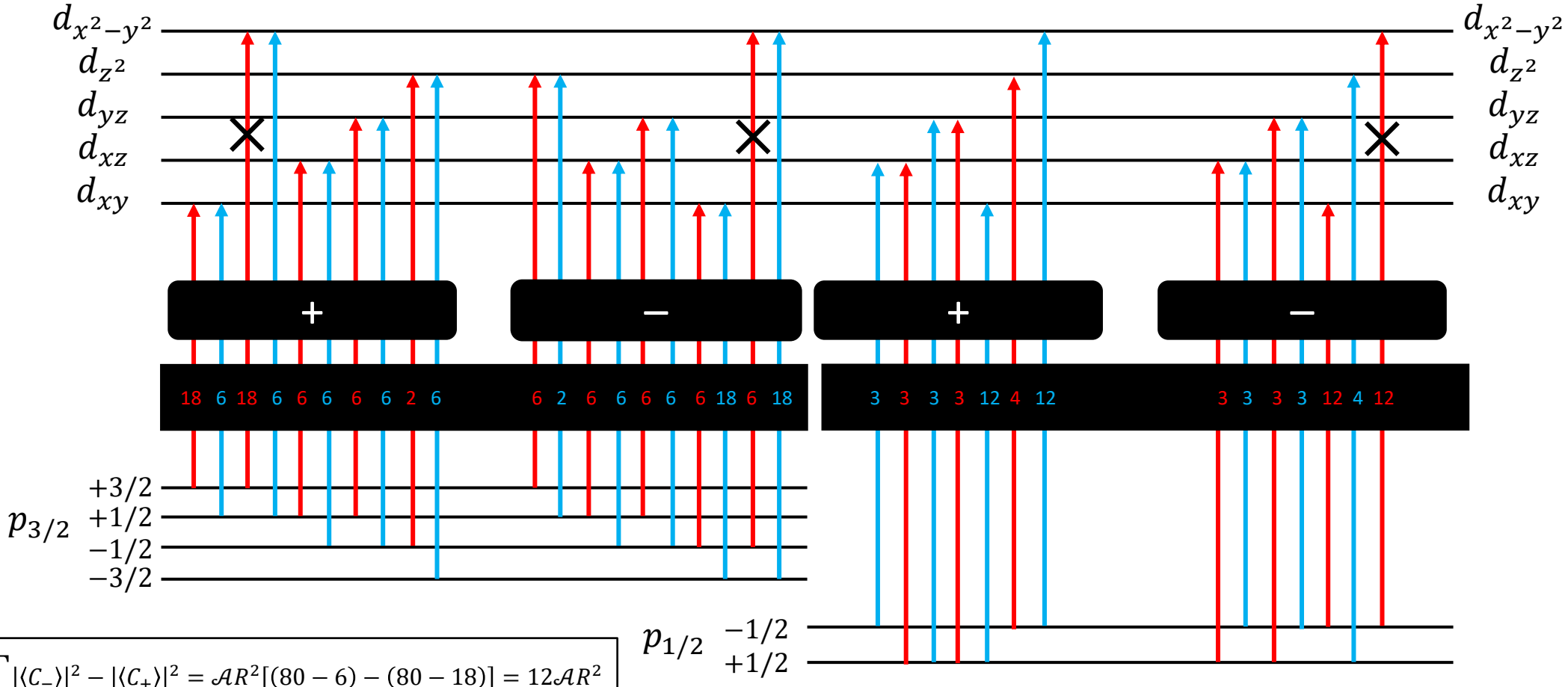
Squares of matrix element, multiplied by 90

Full $L_{2,3}$ Transition Intensities



If Some *d*-Orbitals Occupied

(↑ in d_{xx-yy})

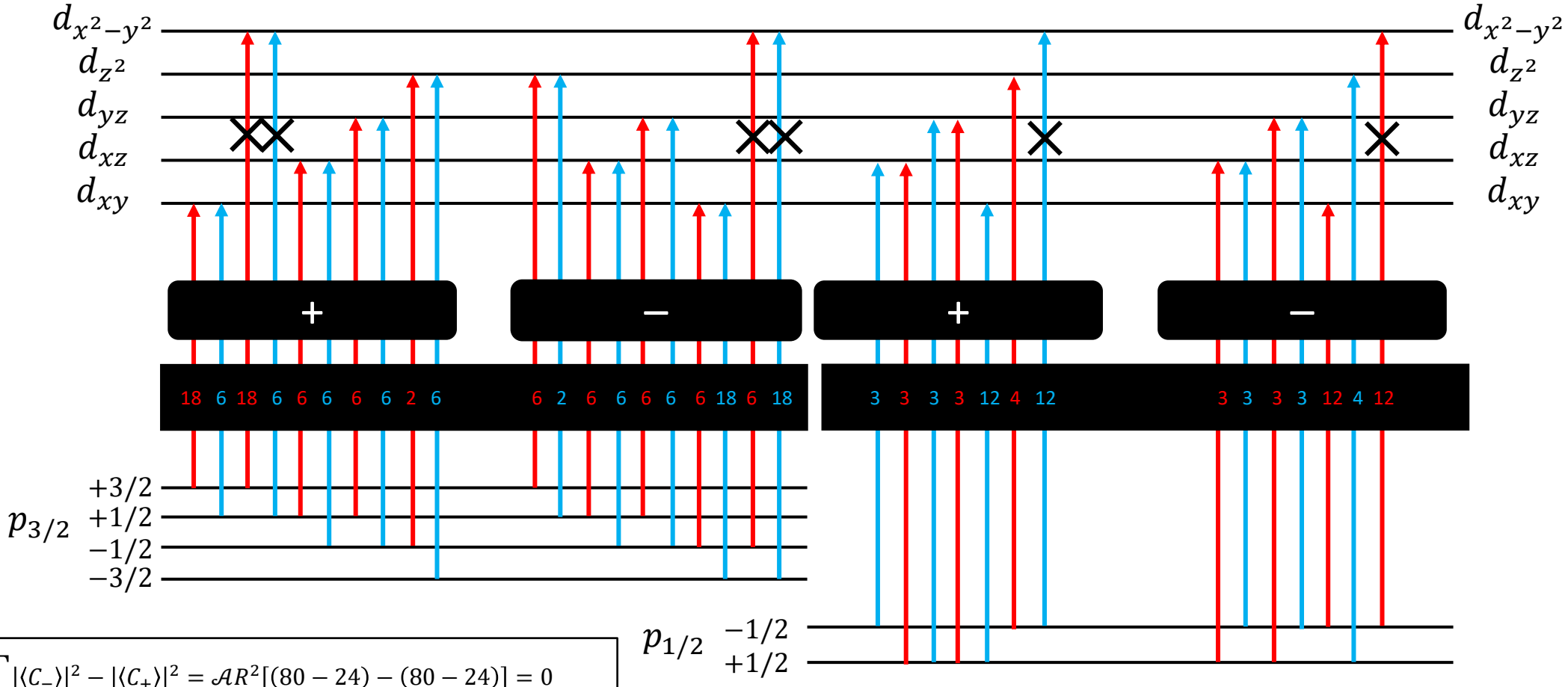


$$\Delta I_{L_3} = \mathcal{A}R^2 \sum |\langle C_- \rangle|^2 - |\langle C_+ \rangle|^2 = \mathcal{A}R^2[(80-6)-(80-18)] = 12\mathcal{A}R^2$$

$$\Delta I_{L_2} = \mathcal{A}R^2[(40-12)-(40-0)] = -12\mathcal{A}R^2$$

If Some *d*-Orbitals Occupied

(↑ & ↓ in $d_{xx\text{-}yy}$)

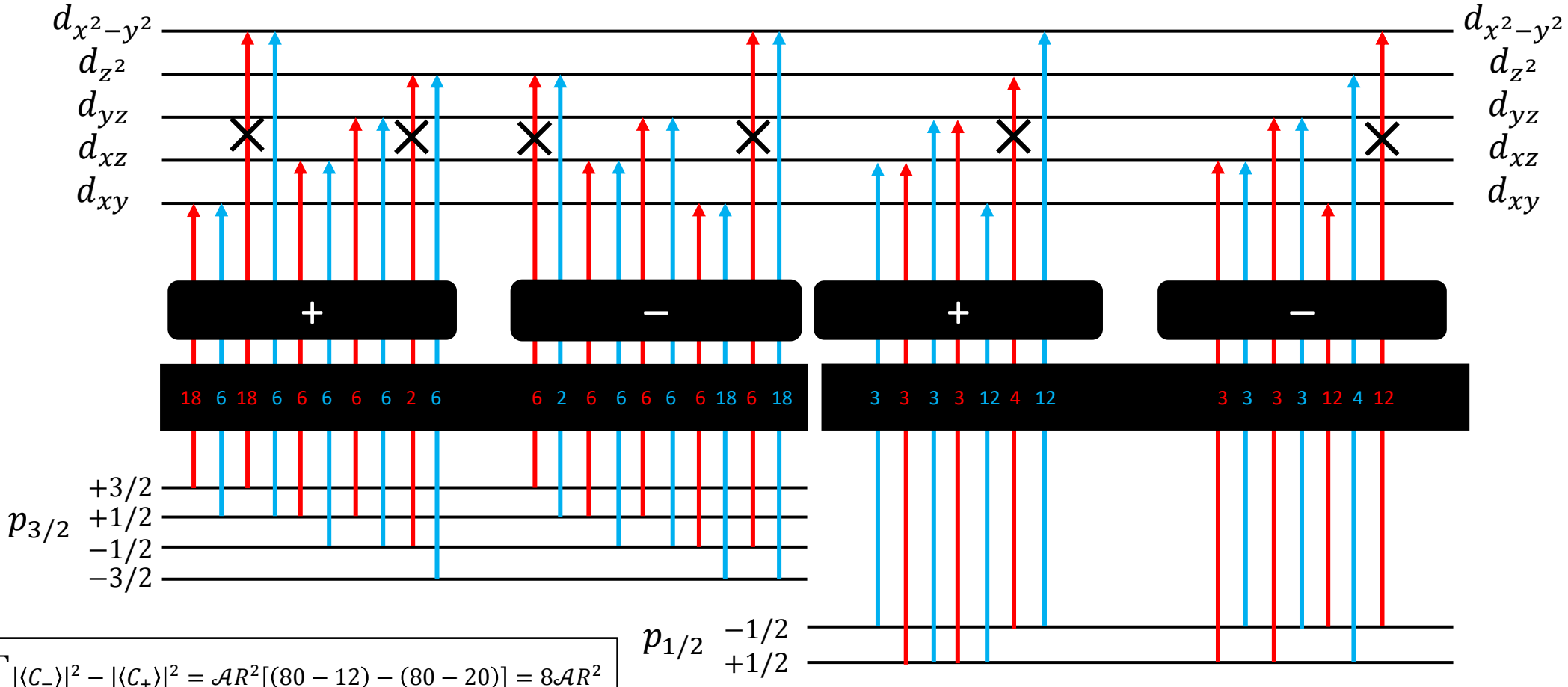


$$\Delta I_{L_3} = \mathcal{A}R^2 \sum |\langle C_- \rangle|^2 - |\langle C_+ \rangle|^2 = \mathcal{A}R^2[(80-24)-(80-24)] = 0$$

$$\Delta I_{L_2} = \mathcal{A}R^2[(40-12)-(40-12)] = 0$$

If Some *d*-Orbitals Occupied

(↑ in $d_{xx\text{-}yy}$ & ↑ in d_{zz})



$$\Delta I_{L_3} = \mathcal{A}R^2 \sum |\langle C_- \rangle|^2 - |\langle C_+ \rangle|^2 = \mathcal{A}R^2[(80-12)-(80-20)] = 8\mathcal{A}R^2$$

$$\Delta I_{L_2} = \mathcal{A}R^2[(40-12)-(40-4)] = -8\mathcal{A}R^2$$

Next : Orbital Rule

- Calculate $\langle I \rangle$ (which requires transitions of q=0 helicity light

$$\langle I \rangle = \frac{1}{3}\left(I_x^q + I_y^q + I_z^q\right) = \frac{1}{3}\left(I_\alpha^{-1} + I_\alpha^0 + I_\alpha^{+1}\right) \ . \qquad (9.87)$$

The *spin sum rule* links the angle averaged dichroism intensities with the size of the spin moment per atom according to

$$\langle -A + 2B \rangle = \frac{C}{\mu_B}\, m_s \ . \qquad (9.105)$$

where the constant C is the same as in the charge sum rule.

- Move from quenched *d*-orbitals to SOC d-orbitals
  - e.g. $\left|d_{3/2}, +3/2\right\rangle = \frac{1}{\sqrt{5}}\left(\sqrt{2}Y_{1,0}\alpha + Y_{1,+1}\beta\right)$

The *orbital moment sum rule* links the angle averaged dichroism intensities with the size of the average orbital moment per atom according to

$$-\langle A + B \rangle = \frac{3C}{2\mu_B}\, m_o \ . \qquad (9.106)$$

The constant C is the same as in the charge and spin sum rules.