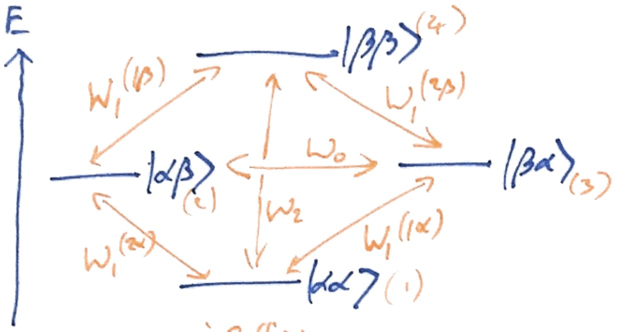
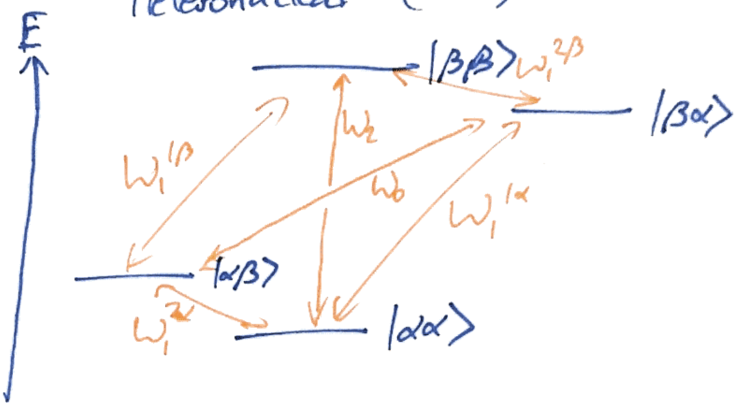
Longitudinal Relaxation + Cross-relaxation

Consider a 2-spin system and its energy levels:

Homonuclear (I_1, I_2):



Heteronuclear (IS):



$W_1^{2\alpha}$ — spin 1 in α state — spin 2 flips
W_1 — single quantum transition

As discussed last week, fluctuating local magnetic fields can induce transitions between states.

In general, transition rates depend on 3 factors:

$$W = aY^2 j(\omega)$$

a — constant from Hamiltonian
Y — strength of fluctuations in field
$j(\omega)$ — spectral density at transition frequency associated with W.

e.g. for dipolar interaction between 2 spins:

$$W_1^{1\alpha} = W_1^{1\beta} = \frac{3}{40} b^2 j(\omega_1) \qquad W_0 = \frac{1}{20} b^2 j(\omega_1 - \omega_2)$$

$$W_1^{2\alpha} = W_1^{2\beta} = \frac{3}{40} b^2 j(\omega_2) \qquad W_2 = \frac{3}{10} b^2 j(\omega_1 + \omega_2)$$

$$b = \frac{\mu_0 \gamma_1 \gamma_2 \hbar}{4\pi r^3}$$

Recall — semiclassical approximation in which $W_{\alpha\to\beta} = W_{\beta\to\alpha}$
— but instead of populations we analyse perturbations from equilibrium, $\Delta n = n - n_0$.

Consider rate of change in populations (actually Δn but for simplicity will write n only):

$$\frac{dn_1}{dt} = -\text{loss to other states} + \text{gains from other states}$$
$$= -\left(W_1^{2\alpha} + W_1^{1\alpha} + W_2\right) n_1 + W_1^{2\alpha} n_2 + W_1^{1\alpha} n_3 + W_2 n_4$$
$$\frac{dn_2}{dt} = -\left(W_1^{2\alpha} + W_0 + W_1^{1\beta}\right) n_2 + W_1^{2\alpha} n_1 + W_0 n_3 + W_1^{1\beta} n_4$$

etc.

Product operators (density matrices) of interest are related to differences between energy levels:

$$I_{1z} = \left(|\alpha\rangle - |\beta\rangle\right) \otimes E_2$$
$$= (n_1 - n_3) + (n_2 - n_4)$$
$$I_{2z} = (n_1 - n_2) + (n_3 - n_4)$$
$$2I_{1z}I_{2z} = (n_1 - n_3) - (n_2 - n_4) = (n_1 - n_2) - (n_3 - n_4)$$

Putting this all together:

cross-relaxation

cross-correlated relaxation

self-relaxation of spin 1

$$\frac{dI_{1z}}{dt} = -R_1^{(1)} I_{1z} - \sigma I_{2z} - \Delta^{(1)} 2I_{1z}I_{2z}$$

Restoring populations at equilibrium:

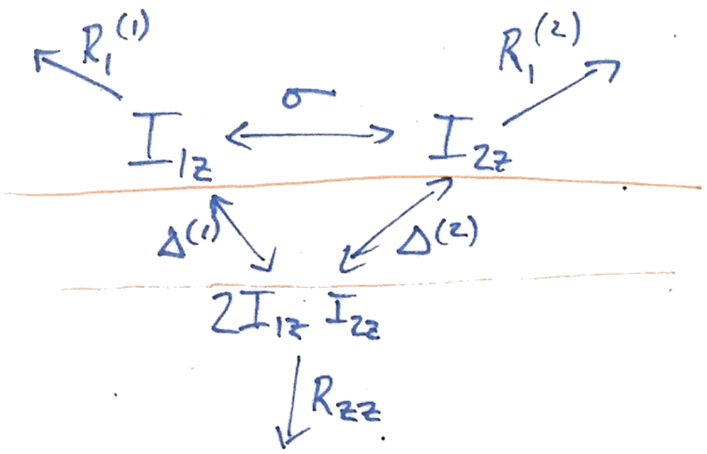
$$\frac{dI_{1z}}{dt} = \frac{d\left(I_{1z} - I_{1z}^{(0)}\right)}{dt} = -R_1^{(1)}\left(I_{1z} - I_{1z}^{(0)}\right) - \sigma\left(I_{2z} - I_{2z}^{(0)}\right) - \Delta^{(1)} 2I_{1z}I_{2z}$$

zero at equilibrium

$$\frac{dI_{2z}}{dt} = -R_1^{(2)}\left(I_{2z} - I_{2z}^{(0)}\right) - \sigma\left(I_{1z} - I_{1z}^{(0)}\right) - \Delta^{(2)} 2I_{1z}I_{2z}$$

$$\frac{d\, 2I_{1z}I_{2z}}{dt} = -\Delta^{(1)}\left(I_{1z} - I_{1z}^{(0)}\right) - \Delta^{(2)}\left(I_{2z} - I_{2z}^{(0)}\right) - R_{zz} \cdot 2I_{1z}I_{2z}$$

More graphically:



$$R_1^{(1)} = W_1^{1\alpha} + W_1^{1\beta} + W_0 + W_2$$
$$R_1^{(2)} = W_1^{2\alpha} + W_1^{2\beta} + W_0 + W_2$$
$$\sigma = W_2 - W_0$$
$$\Delta^{(1)} = W_1^{1\alpha} - W_1^{1\beta}$$
$$\Delta^{(2)} = W_1^{2\alpha} - W_1^{2\beta}$$
$$R_1^{zz} = W_1^{1\alpha} + W_1^{1\beta} + W_1^{2\alpha} + W_1^{2\beta}$$

$\Delta^{(1)} = \Delta^{(2)} = 0$ for pure dipolar relaxation
– but not for CSA

NOE:

Transient: $I_{1z}(0) = I_{1z}^{\circ}$ $\quad I_{2z}(0) = -I_{2z}^{\circ}$

$$\Longrightarrow \frac{dI_{1z}}{dt} = 2\sigma_{12} I_{2z}^{\circ}$$

Steady state: $I_{2z} = 0$ $\quad \dfrac{dI_{1z}}{dt} = 0$

$$\Rightarrow I_{1z} \text{ at SS} = I_{1z}^{\circ} + \frac{\sigma_{12}}{R_1^{(1)}} I_{2z}^{\circ}$$