NMR summer school, Windischleuba, 2023: Workshop set 3

The aim of this exercise is to work out the behaviour of thermal equilibrium magnetisation under the repetition of many spin-echo elements.

The setup is as follows:

- Our sample consists of an ensemble of molecules containing an isolated spin-1/2. For example acetone-2-^{13}C. For simplicity we ignore the proton spins of the methyl groups.
- We know from experimental observations that the carbon spin will experience spin relaxation once its been perturbed from its thermal equilibrium.
- We assume that relaxation is caused by dipolar couplings to our solvent molecules.
- We further assume that these effects induce an external random magnetic field (erf), in example: $H_{\mathrm{erf}}(t) = -\gamma \vec{I} \cdot \vec{B}_{\mathrm{rand}}(t) = -\gamma(B_x^{\mathrm{erf}}(t) I_x + B_y^{\mathrm{erf}}(t) I_y + B_z^{\mathrm{erf}}(t) I_z)$.

We now want to construct a relaxation superoperator $\hat{\Gamma}_{\mathrm{erf}}$ which captures the relaxation effects due to $H_{\mathrm{erf}}(t)$. Remember that when using spherical tensor operators the expression for the relaxation superoperator is given by:

$$\hat{\Gamma}_{\mathrm{erf}} = -\frac{1}{2} \sum_{m=-1}^{+1} J_{\mathrm{erf}}(m\omega_0) \hat{T}_{1m}^{\dagger} \hat{T}_{1m}, \tag{1}$$

where $J_{\mathrm{erf}}(\omega)$ is the spectral density describing the external random field flucutations.

In a second step we then have to thermalise the relaxation superoperator. To this end we construct the thermalisation superoperator $\hat{\Theta}$

$$\hat{\Theta} = \hat{\mathbb{1}} - |\rho_{\mathrm{eq}})(\mathbb{1}|. \tag{2}$$

The thermalised superoperator is then given by

$$\hat{\Gamma}_{\mathrm{erf}}^{\theta} = \hat{\Gamma}_{\mathrm{erf}} \hat{\Theta}. \tag{3}$$

Q1. The external random field Hamiltonian is given in terms of Cartesian operators. How does the same Hamiltonian look in terms of spherical tensor operators?

Q2. The external random field are assumed to be isotropic. This means:

- $\overline{B_x^{\mathrm{erf}}(0) B_x^{\mathrm{erf}}(\tau)} = B_{\mathrm{rms}}^2 e^{-|\tau|/\tau_c}$, $\overline{B_y^{\mathrm{erf}}(0) B_y^{\mathrm{erf}}(\tau)} = B_{\mathrm{rms}}^2 e^{-|\tau|/\tau_c}$, $\overline{B_z^{\mathrm{erf}}(0) B_z^{\mathrm{erf}}(\tau)} = B_{\mathrm{rms}}^2 e^{-|\tau|/\tau_c}$
- $\overline{B_x^{\mathrm{erf}}(0) B_y^{\mathrm{erf}}(\tau)} = 0$, $\overline{B_x^{\mathrm{erf}}(0) B_z^{\mathrm{erf}}(\tau)} = 0$, $\overline{B_y^{\mathrm{erf}}(0) B_z^{\mathrm{erf}}(\tau)} = 0$

What does the spectral density $J_{\mathrm{erf}}(\omega)$ look like?

Q3. From now on we assume the so-called "fast-motiton-limit". This means the correlation time is very short and the spectral density for all values of ω is given by $J(\omega) = J(0)$. What does the spectral density in the fast-motion-limit look like?

Q4. What does $\hat{\Gamma}_{\mathrm{erf}}$ (in the fast-motion-limit) look like when you put all of this together? In example insert the correct spectral density and spherical tensor operators into equation (1).

Q5. Consider now the Liouville space basis given by the operators $\mathcal{B}_{\mathcal{L}} = \{\frac{1}{\sqrt{2}}\mathbb{1}, \sqrt{2}I_z, I^-, I^+\}$. Calculate the superoperator matrix representation $[\hat{\Gamma}_{\text{erf}}]_{\mathcal{B}_{\mathcal{L}}}$. **Hint**: $[I_z, I^{\pm}] = \pm I^{\pm}$ and $[I^+, I^-] = 2I_z$

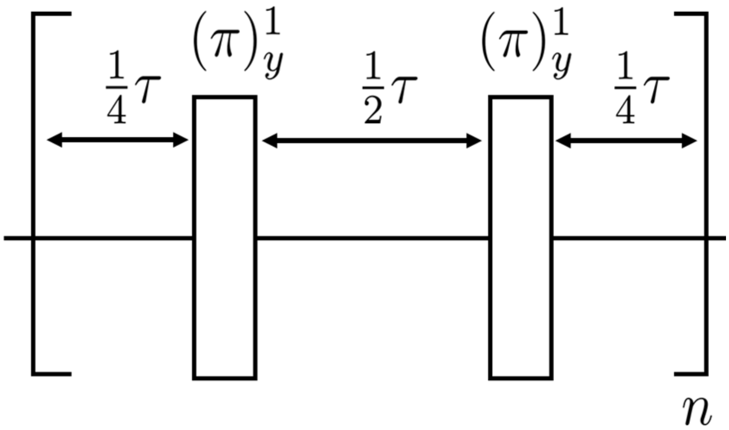
Q6. Following equation (2) we will need the thermal equilibrium density operator ρ_{eq} to thermalise the relaxation superoperator. What is $|\rho_{\text{eq}})$ in the high-temperature limit for $H_0 = \omega_0 I_z$? **Tip:** It might be useful to abbreviate $\beta = \hbar/(k_B T)$ to simplify the notation.

Q7. What is the superoperator matrix representation $[\hat{\Theta}]_{\mathcal{B}_{\mathcal{L}}}$ with respect to $\mathcal{B}_{\mathcal{L}} = \{\frac{1}{\sqrt{2}}\mathbb{1}, \sqrt{2}I_z, I^-, I^+\}$?

Q8. Calculate the superoperator matrix representation for $\hat{\Gamma}^{\theta}_{\text{erf}}$ with respect to $\mathcal{B}_{\mathcal{L}}$, in example $[\hat{\Gamma}_{\text{erf}}]_{\mathcal{B}_{\mathcal{L}}} \cdot [\hat{\Theta}]_{\mathcal{B}_{\mathcal{L}}}$.

Consider now the application of the following pulse sequence:

Figure 1: Repeated spin-echo application



Q9. What is the effect of a $(\pi)_y$ rotation onto each of the basis elements $\mathcal{B}_{\mathcal{L}} = \{\frac{1}{\sqrt{2}}\mathbb{1}, \sqrt{2}I_z, I^-, I^+\}$? From this knowledge derive the superoperator matrix representation $[(\pi)_y]_{\mathcal{B}_{\mathcal{L}}}$

Q10. Consider now the "average" relaxation superoperator: $\frac{1}{2}\{\hat{\Gamma}^{\theta}_{\text{erf}} + (\hat{\pi}_y)\hat{\Gamma}^{\theta}_{\text{erf}}(\hat{\pi}_y)\}$. Calculate the superoperator matrix representation $[(\pi)_y]_{\mathcal{B}_{\mathcal{L}}} \cdot [\hat{\Gamma}^{\theta}_{\text{erf}}]_{\mathcal{B}_{\mathcal{L}}} \cdot [(\pi)_y]_{\mathcal{B}_{\mathcal{L}}}$. Combine this with the result of Q7 to derive the average relaxation superoperator.

Q11. What does this matrix physically mean? Which NMR experiment did we just derive?