1 Exercise: Relaxation Theory

We will try to investigate the behavior of spin relaxation as a function of various parameters for a simple system that we can analyze using numerical simulations in MATLAB (or any other matrix-calculation package). We assume an isolated heteronuclear ^{15}N-^{1}H two-spin system attached to a rigid molecule that undergoes isotropic rotational tumbling with a correlation time τ_c. The spectral-density function for isotropic rotational tumbling is given by

$$J(\omega) = \frac{2}{5}\frac{\tau_c}{1 + (\omega\tau_c)^2} \; . \qquad\qquad [1.1]$$

We will look at the relaxation properties of the nitrogen atom due to dipolar coupling to the directly bound proton as well as the axially symmetric CSA tensor of the ^{15}N nucleus. The anisotropy of the dipolar coupling is defined by

$$\delta^{(IS)} = -2\frac{\mu_0 \gamma_I \gamma_S \hbar}{4\pi r_{IS}^3} \qquad\qquad [1.2]$$

and the magnitude of the axially symmetric chemical-shielding tensor is characterized by $\omega_0^{(S)}\sigma_{zz}^{(S)}$. The constants are given by:

$$
\begin{aligned}
\mu_0 &= 4\pi \cdot 10^{-7} \text{ N A}^{-2} \\
\hbar &= 1.05457 \cdot 10^{-34} \text{ J s} \\
\gamma_H &= 2.675 \cdot 10^{8} \text{ (T s)}^{-1} \\
\gamma_N &= -2.716 \cdot 10^{7} \text{ (T s)}^{-1}
\end{aligned}
\qquad . \qquad [1.3]
$$

We will use this simple spin system to look at different relaxation-rate constants. If not specified differently, we assume a static magnetic field of 14.1 T and a distance of 1.1 Å.

1.1 T_1 Dependence on Magnetic Field and Correlation Time

The longitudinal one-spin auto-relaxation time of the S spin (^{15}N) is given by

$$\frac{1}{T_{1S}} = \Gamma_{S_z, S_z} = \left(\frac{\delta^{(IS)}}{4}\right)^2 [J(\omega_I - \omega_S) + 3J(\omega_S) + 6J(\omega_I + \omega_S)] + \frac{3}{4}(\omega_0^{(S)}\sigma_{zz}^{(S)})^2 J(\omega_S). \quad [1.4]$$

- Calculate T_{1S} as a function of the correlation time τ_c assuming that the chemical-shielding tensor is $\sigma_{zz}^{(S)} = 0$ ppm. A reasonable range for τ_c is from 10^{-12} to 10^{-5} s. Generate a double-logarithmic plot of T_{1S} vs. $\omega_0^{(S)}\tau_c$. Where do you observe a minimum of the T_{1S} time? Rationalize the position of the minimum by discussing the form of the spectral-density function.

- Calculate and plot T_{1S} for chemical-shielding tensor values of $\sigma_{zz}^{(S)} = 50$ ppm and 150 ppm. What do you observe?

- Calculate T_{1S} as a function of the static magnetic field B_0 between 1 and 30 T for correlation times τ_c of 10^{-12}, 10^{-10}, and 10^{-8} s. We assume that the chemical-shielding tensor is $\sigma_{zz}^{(S)} = 0$ ppm.

1.2 T_2 Dependence on Magnetic Field and Correlation Time

The transverse one-spin auto-relaxation time of the S spin (^{15}N) is given by

$$\frac{1}{T_{2S}} = \Gamma_{S^+, S^+} = \frac{(\delta^{(IS)})^2}{32}[4J(0) + J(\omega_I - \omega_S) + 3J(\omega_S) + 6J(\omega_I) + 6J(\omega_I + \omega_S)] \\ + \frac{1}{2}(\omega_0^{(S)}\sigma_{zz}^{(S)})^2 J(0) + \frac{3}{8}(\omega_0^{(S)}\sigma_{zz}^{(S)})^2 J(\omega_S) \quad [1.5]$$

- Calculate T_{2S} as a function of the correlation time τ_c assuming that the chemical-shielding tensor is $\sigma_{zz}^{(S)} = 0$ ppm. Generate a double-logarithmic plot of T_{2S} vs. $\omega_0^{(S)}\tau_c$. Rationalize why the T_2 relaxation time shows no minimum but decreases continuously with increasing correlation time.

- Calculate and plot T_{2S} for chemical-shielding tensor values of $\sigma_{zz}^{(S)} = 50$ ppm and 150 ppm. What do you observe?

- Calculate T_{2S} as a function of the static magnetic field B_0 between 1 and 30 T for correlation times τ_c of 10^{-12}, 10^{-10}, and 10^{-8} s. We assume that the chemical-shielding tensor is $\sigma_{zz}^{(S)} = 0$ ppm.

If the longitudinal and the transverse relaxation time have been measured, one can determine the correlation time of the molecule as

$$\tau_c = \frac{1}{2}\sqrt{\frac{1}{\omega_S^2}\left(6\frac{T_1}{T_2}-7\right)} \, . \tag{1.6}$$

- Back calculate the correlation time from the T_1 and T_2 values calculated for the chemical-shielding tensor of $\sigma_{zz}^{(S)} = 0$ ppm. Plot the back calculated values against the input correlation times. In which range of correlation times is Equation [1.6] valid? Derive Equation [1.6] from the analytical Equations [1.4] and [1.5] for T_1 and T_2.

1.3   Coupled Relaxation Modes

If we look at longitudinal relaxation in a heteronuclear two-spin system, we find that all three relaxation modes are coupled and can be described by a system of coupled differential equations.

$$\frac{d}{dt}\begin{bmatrix} \langle I_z\rangle(t) \\ \langle S_z\rangle(t) \\ \langle 2I_zS_z\rangle(t) \end{bmatrix} = -\begin{bmatrix} \Gamma_{I_z,I_z} & \Gamma_{S_z,I_z} & \Gamma_{2I_zS_z,I_z} \\ \Gamma_{S_z,I_z} & \Gamma_{S_z,S_z} & \Gamma_{2I_zS_z,S_z} \\ \Gamma_{2I_zS_z,I_z} & \Gamma_{2I_zS_z,S_z} & \Gamma_{2I_zS_z,2I_zS_z} \end{bmatrix}\begin{bmatrix} \langle I_z\rangle(t) - \langle I_z\rangle_{eq} \\ \langle S_z\rangle(t) - \langle S_z\rangle_{eq} \\ \langle 2I_zS_z\rangle(t) - \langle 2I_zS_z\rangle_{eq} \end{bmatrix} \tag{1.7}$$

If we neglect cross-correlated cross relaxation, the system simplifies into two sub blocks.

$$\frac{d}{dt}\begin{bmatrix} \langle I_z\rangle(t) \\ \langle S_z\rangle(t) \\ \langle 2I_zS_z\rangle(t) \end{bmatrix} = -\begin{bmatrix} \Gamma_{I_z,I_z} & \Gamma_{S_z,I_z} & 0 \\ \Gamma_{S_z,I_z} & \Gamma_{S_z,S_z} & 0 \\ 0 & 0 & \Gamma_{2I_zS_z,2I_zS_z} \end{bmatrix}\begin{bmatrix} \langle I_z\rangle(t) - \langle I_z\rangle_{eq} \\ \langle S_z\rangle(t) - \langle S_z\rangle_{eq} \\ \langle 2I_zS_z\rangle(t) - \langle 2I_zS_z\rangle_{eq} \end{bmatrix} \tag{1.8}$$

The four relevant relaxation-rate constants are given by

$$\Gamma_{I_z, I_z} = \left(\frac{\delta^{(IS)}}{4}\right)^2 [J(\omega_I - \omega_S) + 3J(\omega_I) + 6J(\omega_I + \omega_S)] + \frac{3}{4}(\omega_0^{(I)}\sigma_{zz}^{(I)})^2 J(\omega_I)$$

$$\Gamma_{S_z, S_z} = \left(\frac{\delta^{(IS)}}{4}\right)^2 [J(\omega_I - \omega_S) + 3J(\omega_S) + 6J(\omega_I + \omega_S)] + \frac{3}{4}(\omega_0^{(S)}\sigma_{zz}^{(S)})^2 J(\omega_S)$$

$$\Gamma_{2I_z S_z, 2I_z S_z} = \left(\frac{\delta^{(IS)}}{4}\right)^2 [3J(\omega_I) + 3J(\omega_S)] + \frac{3}{4}(\omega_0^{(I)}\sigma_{zz})^2 J(\omega_I) + \frac{3}{4}(\omega_0^{(S)}\sigma_{zz}^{(S)})^2 J(\omega_S)$$

$$\Gamma_{S_z, I_z} = \left(\frac{\delta^{(IS)}}{4}\right)^2 [-J(\omega_I - \omega_S) + 6J(\omega_I + \omega_S)]$$

$$. \quad [1.9]$$

- Calculate the time evolution of the S_z magnetization after a 180° inversion pulse, i.e., for an initial condition $\sigma_0 = -S_z$ by solving the differential equation [1.8] assuming isotropic rotational tumbling at correlation times of $\tau_c = 10^{-8}$ and 10^{-10} s assuming that the chemical-shielding tensor is $\sigma_{zz}^{(S)} = 0$ ppm. Compare the curve with a mono-exponential buildup towards thermal equilibrium with a time constant of T_{1S}. Discuss the results.

- If we saturate the protons by applying on-resonance cw irradiation on the I spin during the relaxation delay, the system of differential equations is modified. We can assume that $\langle I_z \rangle(t) = 0$. Calculate the time evolution of the S_z magnetization after a 180° inversion pulse under these conditions analytically. What is now the rate constant with which the system relaxes towards the steady-state equilibrium value.

- The same experiment, i.e., saturation of the I spin is the so-called steady-state NOE experiment. Calculate analytically the steady-state value of the NOE. What is the signal enhancement generated by the NOE? Calculate the signal enhancement numerically as a function of the correlation time assuming that the chemical-shielding tensor is $\sigma_{zz}^{(S)} = 0$ ppm.

2 Appendices

2.1 Matrix Properties

A real matrix A with elements A_{ij} is called *symmetric* if

$$A^T = A \qquad [2.1]$$

where A^T is the transpose of the matrix, i.e., for all elements the condition $A_{ij} = A_{ji}$ is fulfilled. The real matrix A is called *antisymmetric* if

$$A^T = -A \, , \qquad [2.2]$$

i.e., for all elements the condition $A_{ij} = A_{ji}$ is fulfilled. The real matrix A is called *orthogonal* if

$$A^T = A^{-1} \, . \qquad [2.3]$$

A complex matrix A with elements A_{ij} is called *hermitian* if

$$A^\dagger = A \qquad [2.4]$$

where $A^\dagger$ is the adjoint (transposed and complex conjugate) of the matrix, i.e., for all elements the condition $A_{ij} = A_{ji}*$ is fulfilled. The complex matrix A is called *unitary* if

$$A^\dagger = A^{-1} \, . \qquad [2.5]$$

The matrix representation of a Hamiltonian is always a Hermitian matrix. Form this it follows that the matrix representation of a propagator is always a unitary matrix and, therefore, the propagation of a density operator is always a unitary transformation.

2.2   Wigner Rotation Matrix Elements

2.2.1   Rank 0 Elements

Rank 0 tensors are quantities that transform like a scalar. They have only a single component, which is independent of the coordinate system. Therefore, the Wigner rotation matrix element is given by

$$\mathfrak{D}^0_{00} = d^0_{00}(\beta) = 1 .$$ [2.6]

2.2.2   Rank 1 Elements

Rank 1 tensor are vectors and their respective reduced Wigner rotation elements $d^1_{m', m}(\beta)$ are given by

Table 2.1: Reduced Wigner Rotation Matrix Elements of Rank 1

m'＼m	-1	0	+1
-1	$\cos^2\left(\dfrac{\beta}{2}\right)$	$\dfrac{\sin\beta}{\sqrt{2}}$	$\sin^2\left(\dfrac{\beta}{2}\right)$
0	$\dfrac{-\sin\beta}{\sqrt{2}}$	$\cos\beta$	$\dfrac{\sin\beta}{\sqrt{2}}$
+1	$\sin^2\left(\dfrac{\beta}{2}\right)$	$\dfrac{-\sin\beta}{\sqrt{2}}$	$\cos^2\left(\dfrac{\beta}{2}\right)$

2.2.3   Rank 2 Elements

Rank 2 tensors are second-rank tensors and the reduced Wigner rotation matrix elements are given by $d^2_{m',m}(\beta)$

Table 2.3: Reduced Wigner Rotation Matrix Elements of Rank 2

$m' \backslash m$	-2	-1	0	+1	+2
-2	$\left(\dfrac{1+\cos\beta}{2}\right)^2$	$\dfrac{1+\cos\beta}{2}\sin\beta$	$\sqrt{\dfrac{3}{8}}\sin^2\beta$	$\dfrac{1-\cos\beta}{2}\sin\beta$	$\left(\dfrac{1-\cos\beta}{2}\right)^2$
-1	$-\dfrac{1+\cos\beta}{2}\sin\beta$	$\cos^2\beta - \dfrac{1-\cos\beta}{2}$	$\sqrt{\dfrac{3}{8}}\sin(2\beta)$	$\dfrac{1+\cos\beta}{2} - \cos^2\beta$	$\dfrac{1-\cos\beta}{2}\sin\beta$
0	$\sqrt{\dfrac{3}{8}}\sin^2\beta$	$-\sqrt{\dfrac{3}{8}}\sin(2\beta)$	$\dfrac{3\cos^2\beta - 1}{2}$	$\sqrt{\dfrac{3}{8}}\sin(2\beta)$	$\sqrt{\dfrac{3}{8}}\sin^2\beta$
+1	$-\dfrac{1-\cos\beta}{2}\sin\beta$	$\dfrac{1+\cos\beta}{2} - \cos^2\beta$	$-\sqrt{\dfrac{3}{8}}\sin(2\beta)$	$\cos^2\beta - \dfrac{1-\cos\beta}{2}$	$\dfrac{1+\cos\beta}{2}\sin\beta$
+2	$\left(\dfrac{1-\cos\beta}{2}\right)^2$	$-\dfrac{1-\cos\beta}{2}\sin\beta$	$\sqrt{\dfrac{3}{8}}\sin^2\beta$	$-\dfrac{1+\cos\beta}{2}\sin\beta$	$\left(\dfrac{1+\cos\beta}{2}\right)^2$