

Handed Out: Tuesday 2015/02/24

Due: Thursday 2015/03/05 (before class)

1. **Proton T_1 and T_2 versus correlation time.** Consider protons resonating at a Larmor frequency of $\omega_0 = 2\pi \times 400$ MHz. The protons are exposed to a random magnetic field with a root-mean-square amplitude of 0.2 mT and a correlation time of τ_c .

- On a Log-Log plot, graph T_1 and T_2 versus correlation time, with τ_c ranging from 1 ps to 1 μ s.
- Determine the minimum T_1 .
- Suppose that $T_1 = 100$ s at room temperature ($T = 298$ K) and that T_1 decreases upon heating. What is τ_c at room temperature?
- Is the spin-lattice relaxation in the extreme narrowing regime at room temperature?

2. **Linewidth of a Vibrational Resonance.** Consider the fragment of a protein sketched in Fig. 1. We wish to estimate the effect of the random motion of the oxygen atom on the linewidth of the N–H vibrational resonance.

Model the N–H bond as a one-dimensional quantum-mechanical harmonic oscillator of effective mass m and spring constant k_0 , and call the N–H vibrational coordinate x . The N–H bond is polar, and we will account for this by placing a partial charge of q_1 at the end of the harmonic oscillator spring. The oxygen we will model as a partial q_2 placed a distance r_0 away from the hydrogen along the direction of the N–H bond. The oxygen atom undergoes random excursions of size $\delta y(t)$ due to thermal motion. We may assume that

$$\sqrt{\delta y^2(t)} \ll r_0$$

The random motion of the oxygen will lead to two effects:

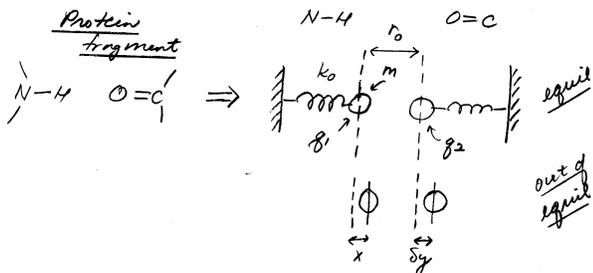


FIG. 1: Modeling the linewidth of the N–H vibrational resonance in a protein.

(a) A random electric field at the site of the hydrogen

$$\delta E_x(t) = \frac{1}{2} \frac{q_2}{\pi \epsilon_0} \frac{\delta y(t)}{r_0^3} \quad (1)$$

which will lead to a random force of $F(t) = q_1 \delta E_x(t)$ experienced by hydrogen.

(b) A random electric field gradient at the site of the hydrogen

$$\delta E'_x(t) = -\frac{3}{2} \frac{q_2}{\pi \epsilon_0} \frac{\delta y(t)}{r_0^4} \quad (2)$$

which will lead to a time-dependent shift in the N–H spring constant of approximately

$$\delta k(t) = q_1 \delta E'_x(t).$$

This random time-dependent shift in the spring constant will, in turn, cause a small random time-dependent shift in the resonance frequency of the N–H bond. In considering the effect of this shift below, you may assume that

$$\sqrt{\delta k^2(t)} \ll k_0.$$

Suppose the N–H bond is excited to some initial amplitude with an on-resonance laser. Use BPP theory to assess which of the two effects enumerated above will lead to the faster loss of initial amplitude. For the dominant relaxation mechanism, derive an expression predicting the decay time and suggest experiments to test your prediction.

3. **Spin lattice relaxation in the rotating frame.** Consider protons exposed to a rotating radiofrequency magnetic field in addition to a local random magnetic field and a static magnetic field. In the rotating frame, the Hamiltonian is

$$\mathcal{H}' = \omega_z(t) I_z + \omega_1 I_x + \frac{1}{2} I_+ \omega_-(t) e^{-i\omega_0 t} + \frac{1}{2} I_- \omega_+(t) e^{i\omega_0 t} \quad (3)$$

In class we showed how this Hamiltonian, minus the $\omega_1 I_x$ term, leads to both T_1 and T_2 relaxation. In this problem we want to explore how the new term, due to the irradiation, affects the relaxation.

(a) The natural approach to solving this problem is to transform it into a problem that we have already solved. This can be achieved by invoking a second interaction representation which removes the $\omega_1 I_x$ term from the rotating frame Hamiltonian \mathcal{H}' :

$$\sigma'' = U_2 \sigma' U_2^\dagger \quad (4a)$$

$$\mathcal{H}'' = U_2 \mathcal{H}' U_2^\dagger + i \dot{U}_2 U_2^\dagger \quad (4b)$$

What should U_2 be?

- (b) The next logical step is to use Bloembergen-Purcell-Pound theory to derive an equation governing the non-unitary evolution of σ'' :

$$\frac{d\sigma''}{dt} = -i[\mathcal{H}'', \sigma''] - \int_0^\infty [\mathcal{H}''(t), [\mathcal{H}''(t-\tau), \sigma'']] d\tau \quad (5)$$

The problem here is that we are interested in the rotating frame magnetization, which we calculate from the rotating frame density matrix σ' and not from the doubly-transformed σ'' . Substitute $\sigma'' = U_2 \sigma' U_2^\dagger$ and $\mathcal{H}'' = U_2 \mathcal{H}_f U_2^\dagger$ into the above equation and derive an equation for the evolution of σ' in terms of U_2 and \mathcal{H}_f .

- (c) Show that the rotating frame magnetization I_x evolves according to:

$$\frac{d}{dt} \langle I_x \rangle = - \int_0^\infty \langle [U_2^\dagger(\tau) \mathcal{H}_f(t-\tau) U_2(\tau), [\mathcal{H}_f(t), I_x]] \rangle d\tau \quad (6)$$

- (d) Use this result to show that, in the presence of phase $\phi = 0$ irradiation, I_x magnetization decays with a time constant T_x given by

$$\frac{1}{T_x} = \gamma^2 \langle B_z^2 \rangle J(\omega_1) + \frac{\gamma^2 \langle B_\perp^2 \rangle}{2} (J(\omega_0 + \omega_1) + J(\omega_0 - \omega_1)) \quad (7)$$

The time constant T_x is often called $T_{1\rho}$, shorthand for the "spin-lattice relaxation time in the rotating frame." This time constant gives us another window into the dynamics of random field fluctuations; T_x^{-1} is $\propto J(\omega_1)$ and $\omega_1 = -\gamma B_1 \sim 2\pi \times (1 \text{ to } 250 \text{ kHz})$ can be adjusted by tuning the strength of the transverse field.

Appendix A: Useful Information

BPP theory predicts that expectation value of an operator should evolve according to

$$\frac{d}{dt} \langle Q \rangle = - \int_0^\infty d\tau (\langle [\mathcal{H}(t+\tau), [\mathcal{H}(t), Q]] \rangle - \langle [\mathcal{H}(t+\tau), [\mathcal{H}(t), Q]] \rangle_{\text{eq}}) \quad (\text{A1})$$

For the quantum harmonic oscillator, we have $[a, a^\dagger] = 1$ and

$$X = \sqrt{\frac{\hbar}{2m\omega_0}} (a^\dagger + a), \quad (\text{A2a})$$

$$P = -i\sqrt{\frac{\hbar m\omega_0}{2}} (a^\dagger - a), \quad (\text{A2b})$$

$$\omega_0 = \sqrt{k/m}. \quad (\text{A2c})$$

A useful operator identity is

$$[A B, C] = A [B, C] + [A, C] B \quad (\text{A3})$$