Freie Universität Berlin

Advanced Laboratory Course

Pulsed Nuclear Magnetic Resonance (NMR)

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Abstract

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1 Introduction

1.1 What is NMR?

NMR = Nuclear Magnetic Resonance is phenomenon in which atomic nuclei interact with electromagnetic radiation due to their magnetic dipole. It has applications in material measurement, especially in medecine (MRI machines).

1.2 Why nuclei have spin? Which samples will you measure and what exactly will give you the signal in the experiment?

From quantum mechanical theory, recall that protons and neutrons have a property called "spin", which behaves like angular momentum. So also the nuclei have spin, namely a spin system composed of protons and neutrons, and the interaction strength of the EM radiation depends on spin (i.e. quantum state) and type of nucleus (element). As a consequence, nuclei with L = 0 (where L is the angular momentum quantum number of the nucleus) do not interact, and are thus "invisible", e.g. ^{12}C, ^{16}O.

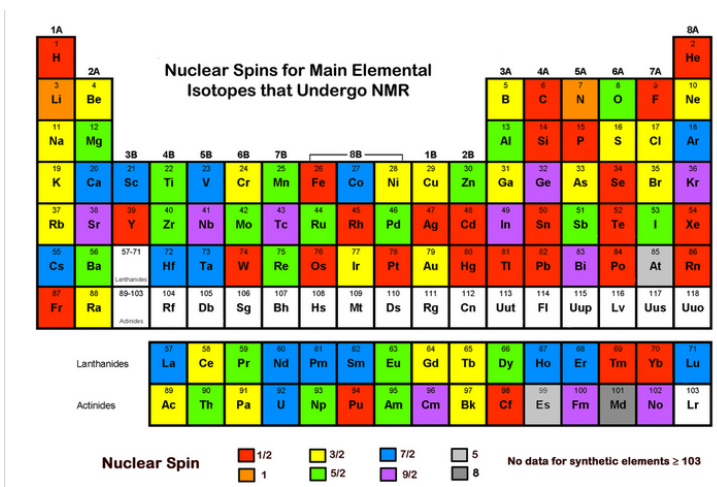

Figure 1: Table illustrating nuclear spins for different elements [**mri_questions_nuclear_spin**]

1.3 How do you understand "spin"? What is the gyromagnetic ratio of a proton?

The gyromagnetic ratio (γ) is defined as the ratio of the magnetic moment to the angular momentum.

$$\gamma = \frac{\mu}{L}$$

More intuitively, this can be thought of as "how strongly a given configuration interacts with a B-field", or "how much magnetic moment you get per angular momentum". The gyromagnetic ratio of a proton $\gamma_{proton} \approx 2.68 s^{-1} T^{-1}$ (there is some theory around why this is the value but it is not relevant right now). Recall as well that the energy of a magnetic moment μ in a magnetic field B is $-\mu B$

1.4 What happens to a nuclear spin in a magnetic field (Zeeman splitting, Larmor precession, Larmor frequency)

A magnetic field will cause the particles to align their magnetic dipoles with the field. They can align with the field, in what is called the α state, or antiparellel to it, in what we call the β state. The difference between these two energy states will be

$$\Delta E = \frac{\gamma \hbar B_0}{2\pi}$$

Note that this split is proportional to the applied magnetic field. When we consider that spin quantum number $m_I \in -I, ..., I$, we get

$$E = E_0 - \frac{\hbar \gamma B_0 m_I}{2\pi}$$

Larmor procession is procession that will occur by the magnetic moments around the applied B-field. This behaves as expected with a classical gyroscope, we call its frequency the **Larmor frequency** and it is

$$\omega_L = \gamma B_0$$

(do we need to show the derivation?)

1.5 Ensemble of spins. Populations of the spin levels. Macroscopic magnetization vector. Dynamics of the magnetization vector in the external magnetic field.

Without an external magnetic field, the sum of all magnetic moments cancels, and thus no population difference between two spin states can exist (equal distribution of spin up-spin down particles). However, when we introduce an external magnetic field, a difference in the population of two spin states occurs, which results in a net magnetization parallel to the applied field.

The energy difference of states leads to a difference in population

$$\frac{N_{upper}}{N_{lower}} = exp(\frac{-\Delta E}{kT}) = exp(\frac{-h\nu}{kT}) = exp(\frac{\gamma h B_0}{2\pi kT})$$

The strength of the signal observed will be

$$S(t) = N_{tot} P sin(\theta) \gamma B cos(\omega t)$$

Where P, the polarization is defined as

$$P = \frac{N_\uparrow - N_\downarrow}{N_\uparrow + N_\downarrow} = \frac{\gamma \hbar B_0}{2kT}$$

Is it necessary to show the derivation here?
At $T = 300K$ and $B_0 = 1T$ for protons we have $P = .0000034$ [**pirl_youtube_mri**]

More generally a sample in thermal equilibrium will have

$$S = \frac{N_{tot} \gamma^3 \hbar^2 B_0^2}{4kT}$$

We define the Boltzmann Magnetization M_0 as

$$M_0 = \sum \vec{\mu} \cdot density \cdot P = \frac{N \gamma^2 \hbar^2 B_0}{4kT} =_0 B_0$$

1.6 Magnetic resonance: What is resonating?

If we apply a B field to a nuclear with magnetic moment that is not already aligned with the field, it will experience Larmor precession. This precession will emit a specific frequency depending on the gyromagnetic ratio and

magnitude of the applied B-field, that we can measure. If we apply this perpendicular B-field at the Larmor frequency, we can induce resonance. Thus the spinning nuclei will precess with a frequency proportional to the applied magnetic field, i.e.:

$$\nu_L = \frac{\gamma B_0}{2\pi}$$

1.7 Rotating frame vs. laboratory frame. Dynamics of the magnetization vector: Blochs equations of motion.

After the nuclei have been pulsed, their magnetic moments proceed in a corkscrew pattern as they process and reconverge around the baseline magnetic field B_0. This is easier to describe mathematically in a rotating reference frame centered on a nucleus with rotation rate equal to the Larmor frequency. Here we can just look at the behavior of the components of the nucleus magnetic moment in the $B0$ and B_1 directions, as one decays and the other approaches μ

1.8 /2 pulse. FID (free induction decay) with no relaxation processes. How do we detect an FID from an ensemble of magnetic nuclei? Sketch a setup.

FID can be observed from the procession of the ensemble of magnetic moments around the applied constant magnetic field B_0 when an orthogonal pulse is applied close to the Larmor frequency.

1.9 Relaxation times. T1 vs. T2 vs. T2*. You should know the differences between them.

Since we need to observe many nuclei in aggregate to have a measurable effect, the nuclei need to all be precessing in phase. They will randomly become out of phase over time after the aligning pulse has been applied due to each other's magnetic fields, and other non-uniform magnetic fields. This leads to the overall signal strength decaying according to the Free Induction Decay (FID).

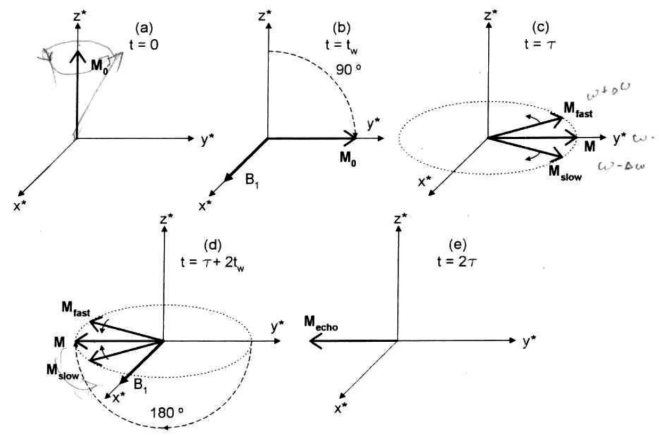

Figure 2: Schematic illustrating each stage of FID [**pulsed_spectrometer_manual**]

$$S(t) = Acos(\omega t)e^{-t/T_2}$$

The nuclei will also converge over time back to being in line with the base magnetic field, by the following magnitization

$$M(t) = M_0(1 - e^{-t/T_1})$$

Where T_1 represents the rate at which the nuclei return to allignment with the base magnetid field.

1.10 Bloch equations

The Bloch equations refer to the following electrostatic relations. Definitionally, the torque is the cross product of the magnetic moment with the applied B-field.

$$\vec{T} = \vec{M} \times \vec{B}$$

We also can describe the torque as

$$\vec{T} = \frac{\partial \vec{J}}{\partial \vec{t}}$$

And writing the magnetic moment as the sum of parts, and substituting the gyromagnetic ratio

$$\vec{M} = \sum_i \mu_i = \sum_i \gamma \vec{J}_i$$

$$\frac{\partial \vec{M}}{\partial t} = \gamma \frac{\partial}{\partial t} \vec{J} = \gamma \vec{T} = \gamma (\vec{M} \times \vec{B})$$

When we only have the B_0 field applied along the z-axis, we get the following set of coupled differential equations

$$\frac{\partial}{\partial t} M_x(t) = \gamma M_y B_0 - M_x/T_2$$
$$\frac{\partial}{\partial t} M_y(t) = -\gamma M_x B_0 - M_y/T_2$$
$$\frac{\partial}{\partial t} M_z(t) = -(M_z - M_0)/T_1$$

Which have solutions

$$M_x(t) = [M_x(0) cos(\omega t) - M_y(0) sin(\omega t)] e^{-t/T_2}$$
$$M_y(t) = [M_x(0) sin(\omega t) - M_y(0) cos(\omega t)] e^{-t/T_2}$$
$$M_z(t) = M_{eq} + [M_z(0) - M_{eq}] e^{-t/T_1}$$

1.11 Spin echo. Pulse sequences.

Suppose we give a pulse B_1. Subsequently we apply another pulse with the same magnitude and opposite direction of B_1 at time τ after the first pulse. All the magnetic moments became out of phase due to inhomogeneities in the constant magnetic field. Assuming these inhomogeneities are constant, this second pulse will reverse the trajectory of all these moments, and will reconverge at their initial configuration from the first pulse after another interval of τ.

1.12 T2 and T2* measurements

T2* is the decay rate of the signal when we take into account imperfections in the applied fields. A proton has $\gamma = 42.6MHz/T$, so if we change $B = 1T$ to $B = 1.000001T$ (an error of order 10^{-6}), this can produce a change of

$$\Delta\omega = \gamma\Delta B = 267.5rad/s$$

Assuming our decay is still perfectly exponential with the inhomogeneity, and the effect of the inhomogeneity can be represented as a single exponential term, we have

$$S(t) = S_0 e^{-t/T_2^*} = S_0 e^{-t/T_2} e^{-\gamma\Delta Bt}$$

$$\frac{1}{T_2^*} = \frac{1}{T_2} + \gamma\Delta B$$

(do we need to talk about wy this assumption is valid? The Lorenztian distribution?)

Any magnetic field will have some inhomogeneity, which will put a lower bound on our error no matter how high we raise T_2

1.13 T1 (spin-lattice relaxation time) measurement.

Spin lattice relaxation time is our T1 relaxation time, spin-spin is our T2 relaxation time.

The Carr-Purcell method involves applying a 90° pulse, following by a series of 180° pulses separated by some time τ, which is short compared to either of the relaxation times. This causes the moments to become coherent again after the diffuse following the first pulse. Repeating this process allows us to see this process multiple times. The Meiboom-Gill enhancement applies a 90° shift at each successive pulse, which eliminates some of the error accumulation from the Carr-Pucell method

2 Experimental Setup

We will use a light mineral oil and several concentrations of $CuSO_4$ samples and observe it with a TeachSpin PS2-A pulse spectrometer. The sample is positioned in a coil, which is inside the B_0 field. This coil firstly acts as an

transmitter, i.e. it supplies a RF wave that changes the net magnetization of the sample. Then, after the signal has been applied, the same coil acts as a "receiver" (pickup coil), and records the precession of the B field in the x-y plane.

The PS2-A Synthesizer module is used to produce the oscillating RF signal that "tips" the spins, altering the net magnetization of the sample. Then the Pulse Programmer module is used to determine the duration and number of the RF pulses. Finally, the Receiver takes care of the amplification of the RF signal going into the coil, and directs the incoming RF resulting from the sample to the oscilloscope.

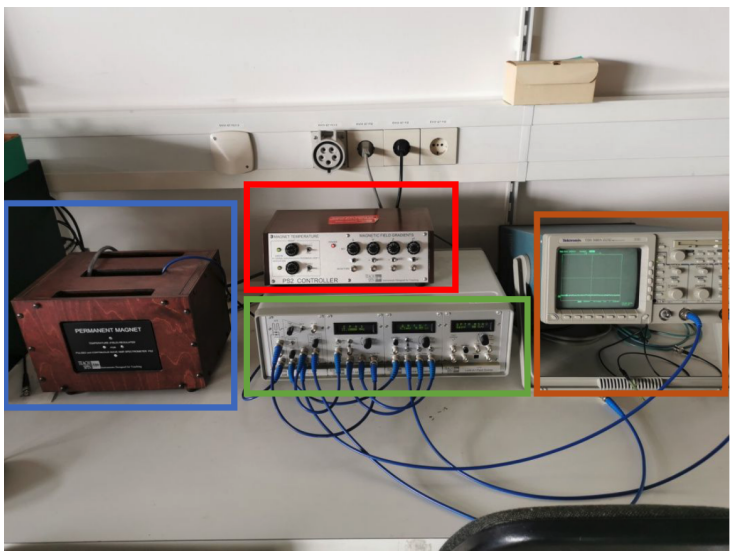

Figure 3: blue box - permanent magnet
red box - magnetic field gradients
green box spectrometer console including rf synthesizer, pulse programmer and receiver unit
brown box oscilloscope.[**experimental_setup_manual**]

3 Experiment Procedure

We will determine T_1 and T_2 for several concentrations of $CuSO_4$ and a light mineral oil by semi-logarithmic representation of the signal amplitudes over the time.

	light mineral oil	**.05 molar** $CuSO_4$	**.1 molar** $CuSO_4$	**.2 molar** $CuSO_4$
T_1				
T_2				

Table 1: Values we will find experimentally

4 Adjusting Parameters

We begin by looking at the FID after applying a 90° pulse, and do the following

- **Pulse Length Adjustment** We maximize the signal intensity by adjusting the length of the applied pulse
- **Frequency Adjustment** until we've further maximized the intensity, and there are no off-resonance induced oscillations
- Adjust the shimming coils to minimize inhomogeneities
- record T_2 after doing all the above
- Optimize the 180° pulse by varying tau and other parameters. Here we want to maximize the echo and reduce the second pulse's FID
- Perform Car-Purcell experiment and the Meiboom-Gibson improvement
- Measure T_1 values by building a $180^o - \tau - 90^o$ sequence, varying tau, plotting the FID max, inverting the FID until the zero crossing, and doing an exponential fit.

The resonant frequency for the mineral oil sample was determined to be 21.04581 MHz, and the length of the $\frac{\pi}{2}$ pulse was found to be $\tau_A = 2.8\mu$s and for the π pulse we had $\tau_B = 5\mu$s, which in consistent with the expectation that one should be double the other. However, there was a lot of margin of variation, meaning that the precise value of τ did not have large effects.

5 Determining the Free Induction Decay

In order to determine the Free Induction Decay time T_2^*, we are interested in the signal immediately after the $\frac{\pi}{2}$ pulse, which decays with an envelope of T_2^*. The data for this part was taken from the spin-echo measurements of the following section. Indeed, since multiple spectra for the measurements at different τs were recorded, an average of them was performed, such that it "killed" all the π signals, and only left the average of the $\frac{\pi}{2}$ signal (Figures 4 and 5), with enhanced precision.

This done, we are now interested in the envelope of this resulting decaying signal. It can be described as

$$S(t) = A \cdot e^{-\frac{t}{T_0}}$$

where A is the amplitude, and $T_0 \coloneqq T_2^*$. The fitted parameters were then obtained as ${T_2^*}_{0.1M} = 0.12$ms and ${T_2^*}_{0.2M} = 0.18$ms for the 0.1M and 0.2M concentrations respectively.

So we see a longer decaying time for the higher concentration sample. It was also noticed tat the amplitude of the 0.2M concentration was lower than the 0.1M concontration, which may be counterintuitive because with increasing concentration one would naively expect also an increased signal. More on this will be discussed later.

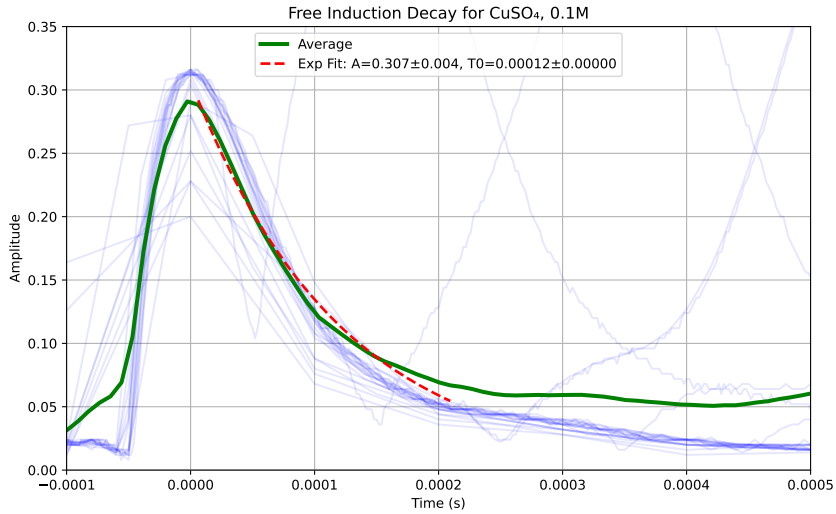

Figure 4: Free Induction Decay measurement for the 0.1M $CuSO_4$ sample. The data was taken from the spin-echo measurements of the following task, and was averaged so as to emphasize the $\frac{\pi}{2}$ pulse. The single measurements are plotted in light blue, and the average in green. A decaying exponential fit was then performed to read off T_2^*.

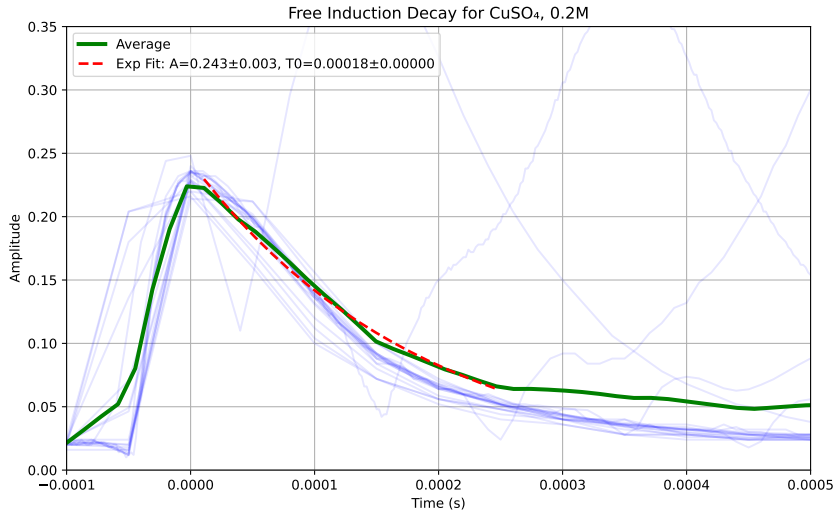

Figure 5: Free Induction Decay measurement for the 0.2M $CuSO_4$ sample. The data was taken from the spin-echo measurements of the following task, and was averaged so as to emphasize the $\frac{\pi}{2}$ pulse. The single measurements are plotted in light blue, and the average in green. A decaying exponential fit was then performed to read off T_2^*.

From the FID, we can then determine the magnetic field inhomegeneity, which, in the approximation $T_2^* \ll T_2$ is given by

$$\Delta B = \frac{\ln 2}{\gamma T_2^*}$$

. Plugging the numbers in (where $\gamma = 42.58 \frac{\mathrm{MHz}}{\mathrm{T}}$, we got for the 0.1M concentration

$$\Delta B \approx 135.6 \mu\mathrm{T}$$

and

$$\Delta B \approx 90.437 \mu\mathrm{T}$$

for the 0.2M concentration.

6 Determining T_2 using three different methods.

6.1 Spin echo method

In order to determine T_2 using the spin-echo method, we are interested in the amplitudes of the echo with respect to time. For this, we first optimized the π pulse by maximizing the echo and minimizing the FID of the second pulse. Then, we varied τ from around 0.0001s to 0.0130s, and plotted the resulting spectra in a single plot, which ensured proper alignment in time. Since different scales of the oscilloscope were used, alignment in time was crucial, and it was performed by manually shifting the $\frac{\pi}{2}$ pulse so that this peaked at time $t = 0$. Then, the peaks of the π pulse were detected for each of the t values (using the `peak_find` function in Python). The height of these peaks decreases exponentially and can then be fit into a decaying exponential function

$$S(t) = A \cdot e^{-\frac{t}{T_2}} + c$$

where A is again, the amplitude, T_2 is the spin-spin relaxation time and c is a shifting factor (irrelevant for our purposes here). The resulting fittings can be seen in Figures 6, 7 and 8, for the 0.05, 0.1 and 0.2M respectively. A trend that is noticeable can be seen by looking at the fitting parameters present in Table **??** - in particular, both T_2 and A decrease for increasing concentrations of the $CuSO_4$ sample.

Parameter	**0.05M**	**0.1M**	**0.2M**
A	0.5973 ± 0.0067	0.4984 ± 0.0034	0.3865 ± 0.0062
T_2 (s)	0.0199 ± 0.0005	0.0101 ± 0.0002	0.0045 ± 0.0002
c	-0.0532 ± 0.0073	0.0056 ± 0.0037	0.0243 ± 0.0068

Table 2: Fit Parameters for Spin-Echo Sequences of $CuSO_4$ at Different Concentrations (Hahn Echo Method)

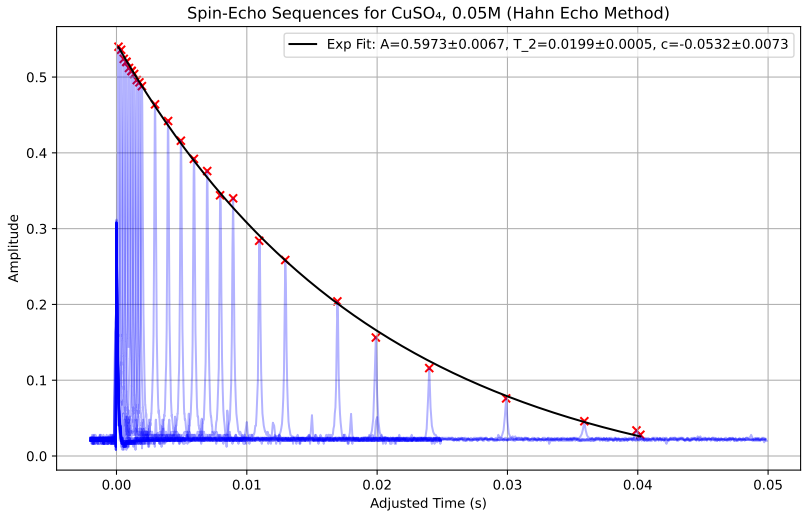

Figure 6: Spin-echo sequences for 0.05M $CuSO_4$ sample. Different values of τ are plotted in light blue, ranging from 0.0001s to around 0.013s.

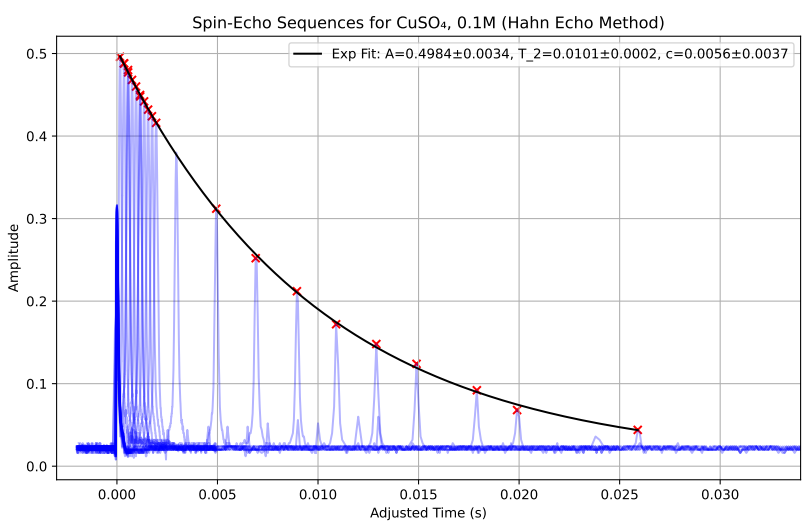

Figure 7: Spin-echo sequences for 0.1M $CuSO_4$ sample. Different values of τ are plotted in light blue, ranging from 0.0001s to around 0.013s.

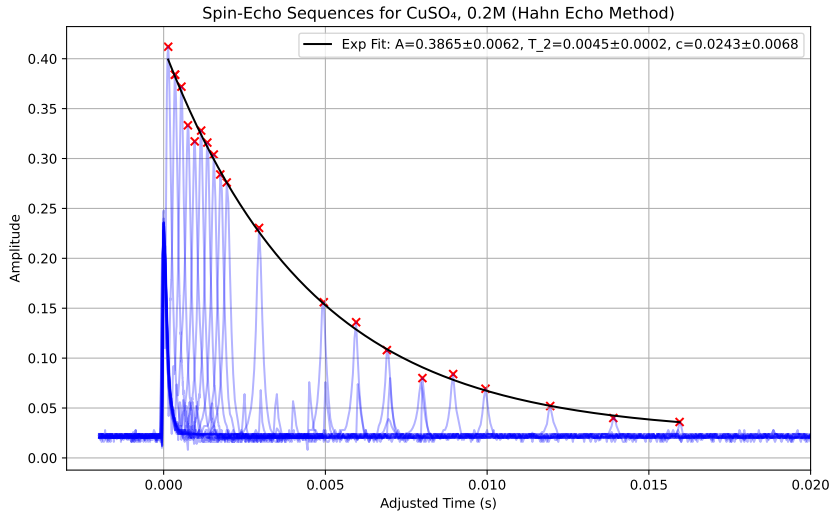

Figure 8: Spin-echo sequences for 0.2M $CuSO_4$ sample. Different values of τ are plotted in light blue, ranging from 0.0001s to around 0.013s.

6.2 Carr-Purcell Method

The principle of this method is the same as the previous one, with the difference that now we are automating the process of shifting τ by initiating a sequence of N spin-echo pulses. In our case, we chose N = 80 and $\tau = 0.0001s$.

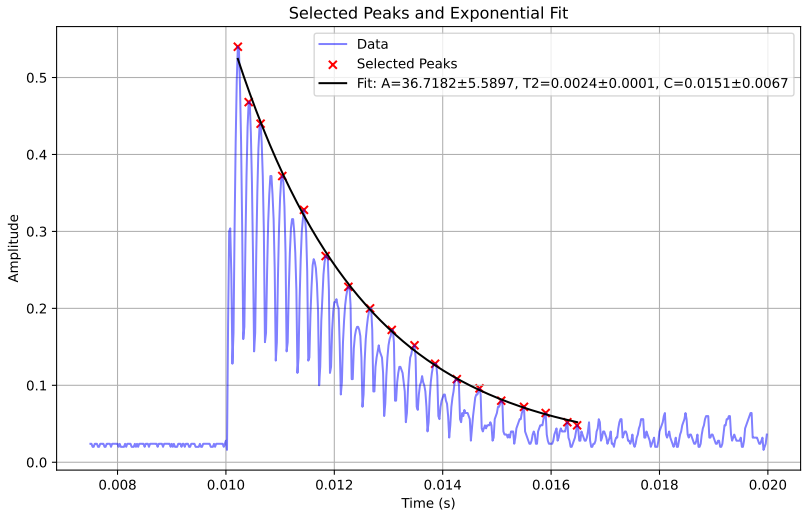

Figure 9: Carr-Purcell method for the 0.05M $CuSO_4$ sample.

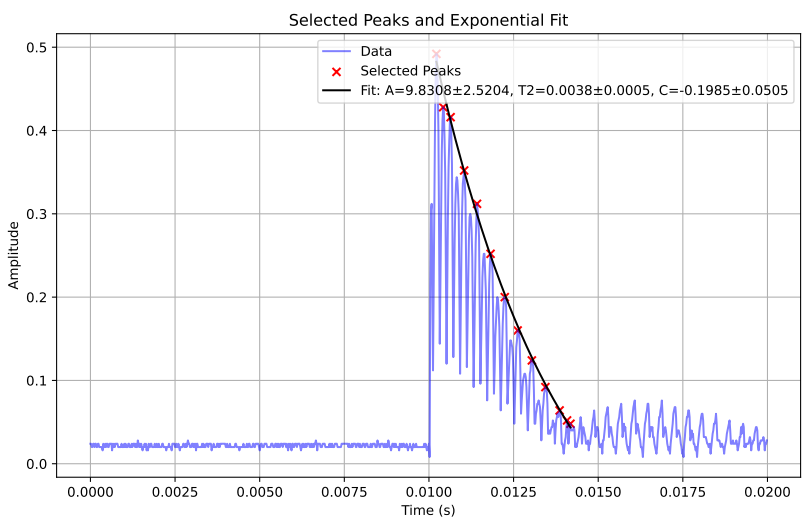

Figure 10: Carr-Purcell method for the 0.1M $CuSO_4$ sample.

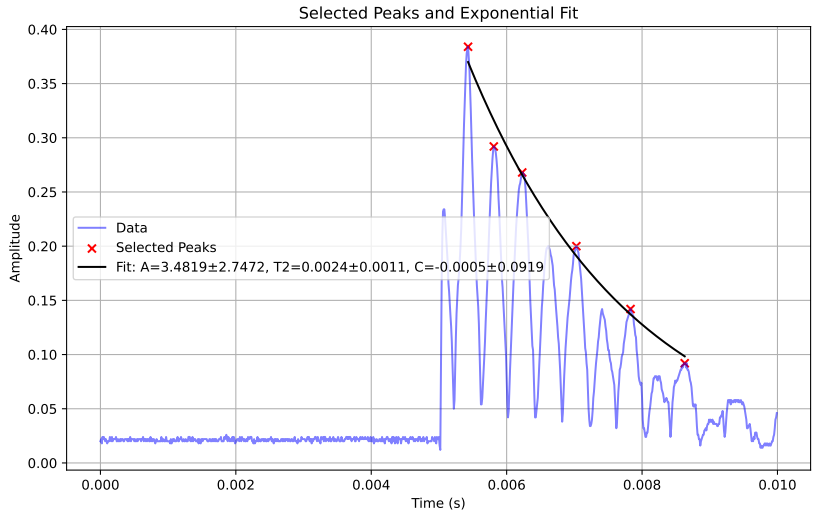

Figure 11: Carr-Purcell method for the 0.2M $CuSO_4$ sample.

6.3 Meiboom Gill Method

To perform the MG measurement, we turned on the MG switch of the setup, which takes care of applying the phase shift between the $\frac{\pi}{2}$ and π pulse, minimizing the flip angle error. Then, we used again N = 80 and $\tau = 0.0001$s to record the spectra for the different concentrations of our sample.

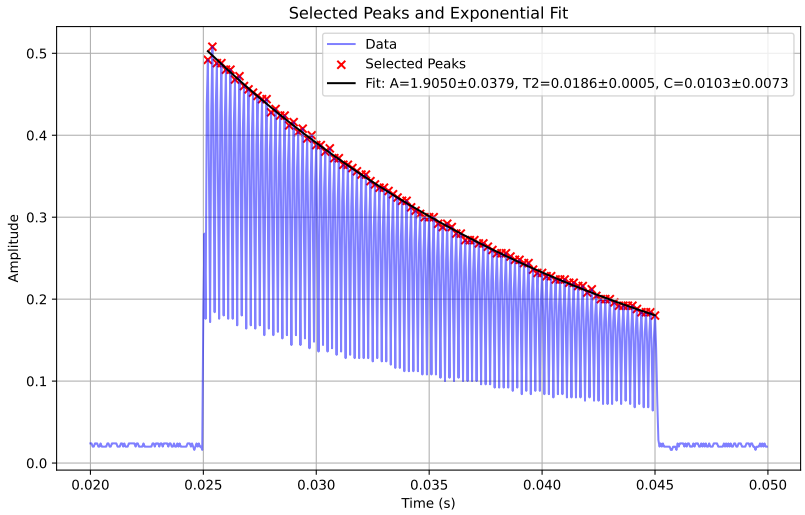

Figure 12: Meiboon-Gill method for the 0.05M $CuSO_4$ sample.

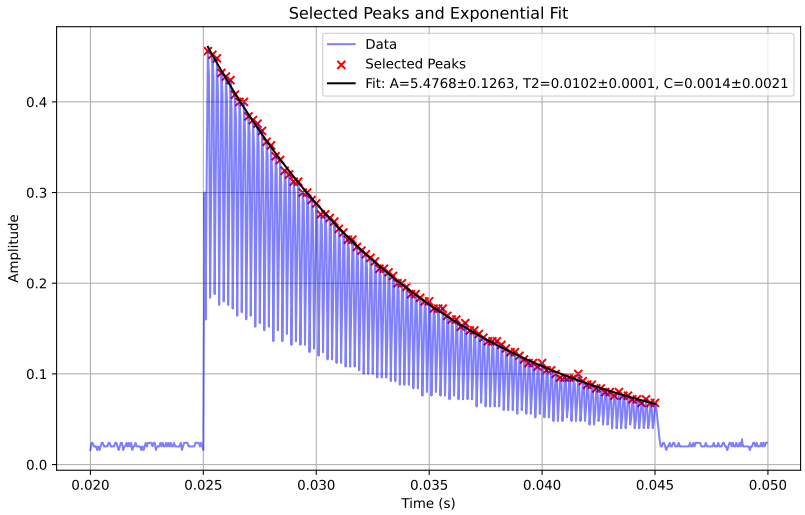

Figure 13: Meiboon-Gill method for the 0.1M $CuSO_4$ sample.

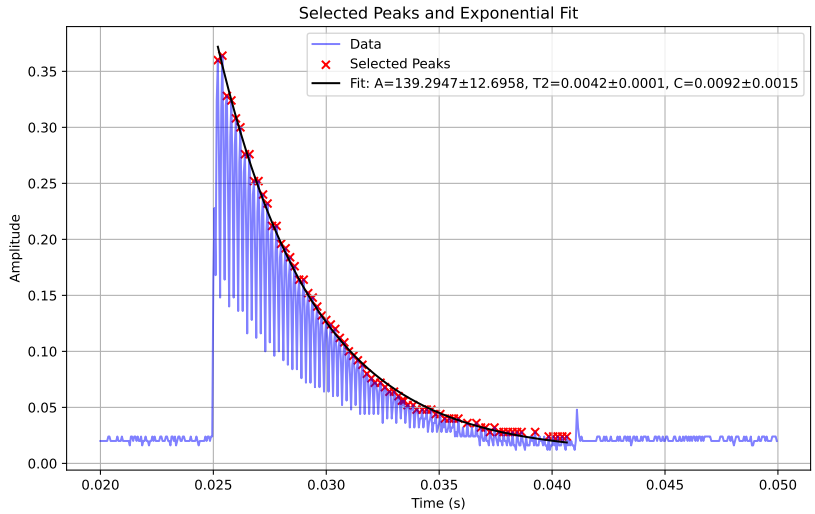

Figure 14: Meiboon-Gill method for the 0.2M $CuSO_4$ sample.

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