Pulsed NMR

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Abstract

Two unknown samples were probed via pulsed nuclear magnetic resonance (NMR), where parameters such as time between pulses, pulse width, and the pulse frequency were all tuned. The resulting radio-frequency magnetic feedback was measured, and the spin-lattice relaxation time (T_1) and spin-spin relation time (T_2) was measured for each sample. T_1 was found to be 62.41 ± 43.02 and 35.28 ± 0.05 ms, for sample 1 and 2, respectively, while T_2 was found to be 0.0201 ± 0.0004 and 0.0155 ± 0.003 ms for sample 1 and sample 2, respectively.

1 Introduction

Pulsed nuclear magnetic resonance (NMR) is a technique used by physicists and chemists alike to investigate the identity and properties of materials through the resonance of the nucleus with an external magnetic field. It is also the basis of magnetic resonance imaging (MRI) machines used for medical diagnoses. Its appeal lies in its ease of use, its non-destructive probing, and its ability to probe a variety of materials, as long as they have spin 1/2 nuclei. Hydrogen (^1H) is a spin 1/2 nuclei, and present in all organic materials, and is the nucleus that is investigated here.

Magnetic resonance is possible because the nuclei have properties of both charge and an intrinsic angular momentum (spin), and in this sense a nuclei can be thought as tiny spinning bar magnet. This means the nuclei can either be aligned or anti-aligned with a static magnetic field (defined to be in the $+\hat{z}$ direction), with the balance of nuclei in each state being dependant on temperature. However, the transition to thermal equilibrium magnetization of the nuclei does not happen instantaneously: it reaches its equilibrium of states following exponentially saturating behavior. If M_0 is thermal equilibrium magnetization per unit volume, then the total magnetization per unit volume of the sample is:

$$M_z(t) = M_0(1 - 2e^{-t/T_1})$$

Where T_1 is called the spin-lattice relaxation time, unique to each material being probed. The lattice refers to the surroundings of the nuclei, as energy must flow to and momentum must be transferred from the nuclei to the surroundings as the nuclei align to the magnetic field and flip their spin.

There is, of course, an accompanying precessional motion in the xy plane. For hydrogen nuclei, they precess with the given frequency:

$$f_0 = (4.258\text{MHz/kilogauss})B_z$$

This frequency does depend on environmental factors such as temperature, and deviates slightly for each proton in the sample due to inhomogeneous static magnetic fields or interactions with a neighbor's magnetic field.

This precessional motion of each nuclei is randomly distributed in the xy plane, so there is only net magnetization along the z-axis. If a rotating magnetic field is applied in the xy plane through an alternating-current applied to Helmholtz coils with frequency equal to f_0, the net magnetization changes. Looking in the frame of the rotating magnetic field, the net magnetization rotates around this applied magnetic field. By pulsing this magnetization, the transient orientation of the magnetization can be controlled. A pulse of the right length can be applied so there is net magnetization in the xy plane, dubbed a 90^o pulse. After the pulse is applied, the nuclei will then relax into magnetization equal to that of thermal equilibrium. Not all protons have the same precession frequency, and so after the pulse they will fall out of phase to return to their previously magnetized state. This will be an exponential decay, with a time constant of T_2, called the spin-spin relaxation time. The corresponding decay plot of magnetization in the x or z axis over time is the free-induction decay (FID).

FID cannot be easily directly measured due to non-uniformities in the magnet. So instead, spin-echo decay can be used. A 90^o pulse can be applied to put the magnetization of all nuclei in the xy plane, some time passes (τ) as the magnetic moments of the nuclei can go out of phase from one another due to their differing precession frequencies, and then a 180^o pulse is applied. This

causes the magnetization of the nuclei to flip, decay back into phase (at time 2τ, and then continue to precess out of phase once again. This creates a measurable echo signal. Some loss of $M_{x,y}$ magnetization occurs compared to the FID due to fluctuation in local magnetic fields. The height of the echos can be expressed as:

$$M_{x,y} = M_0 e^{-2\tau/T_2} \tag{1}$$

So, by measuring the echo height at multiple τ, the resulting exponential can be fit to find T_2.

Rough pulse widths (t_w) can be determined by measuring the magnetic field:

$$t_w = \frac{\theta}{\gamma B_1} \tag{2}$$

Where θ is the desired angle,γ is the known gyromagnetic ratio of a proton, and B_1 is the strength of the oscillatory magnetic field. This must be adjusted to account for local environmental conditions such as temperature.

If a 180^o pulse is then applied, then the magnetization in the z direction over time can be expressed as:

$$M_z = M_0(1 - 2e^{t/T_1}) \tag{3}$$

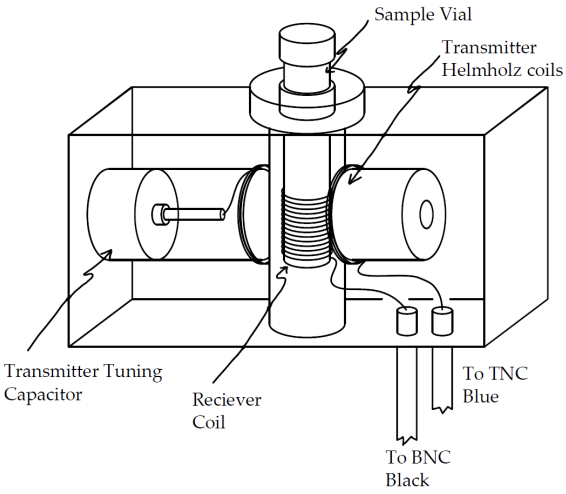

Figure 1: A diagram of the NMR, showing where the sample is placed, the transmitter Helmholtz coils where the oscillating magnetic field is applied, the receiver coils where the sample's signal is picked up, and the chamber where the sample is inserted [1]. In this diagram, the $+\hat{z}$ direction is coming out of the page.

2 Experimental Set-up

The NMR set-up is shown in 1, showing all the necessary components for pulsed NMR besides the permanent magnets. The permanent magnets would be drawn blocking the receiver coil as drawn and on the other side of the sample vial.

These signals are in the megahertz range, not easily processed by any oscilloscope. A mixer is used in order to view any signals in this range, both going in and coming from the NMR. Additionally, power amplification for the coils, signal amplification from the receiver, pulse generation, and a suitable oscillator are required electronic components. These components are provided in a all-in-one package via the TeachSpin apparatus. A block diagram of the components can be seen in figure 2.

For 180^o and 90^o pulses, equation 2 is a good starting point, but slight variations in the magnetic field over time or drifts in environmental conditions like temperature makes the calculated value only a good first guess. A 180^o pulse can be optimized by getting a material magnetized in the $\hat{z}$ direction with no external pulses, then making sure the signal is minimized after the pulse is applied, as the resulting magnetization should be entirely in the $-\hat{z}$ direction and give no measurable signal. Similarly, a 90^o pulse can be optimized through making sure that material

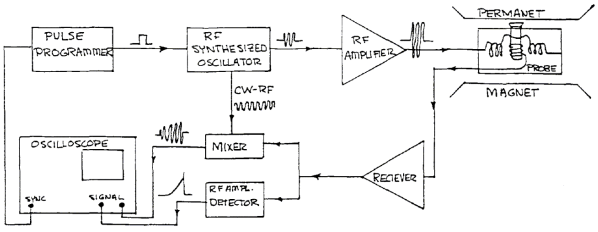

Figure 2: A block diagram of the provided TeachSpin apparatus [1].

with $+\hat{z}$ magnetization has a maximized signal after the pulse is applied, as all magnetization should then be in the xy plane.

The resonant frequency of the samples are unique to the samples due to their unique magnetic environments, and fluctuate with temperature and so must also be tuned. The module contains a mixer that allows the FID beat signal to be displayed as a signal the oscilloscope can read. The applied RF frequency is adjusted until the resulting beat frequency is zero, matching the applied frequency to the resonant frequency.

Once the setup is tuned, all signals received through the receiving coil are amplified and observed on the scope.

2.1 Measuring T_1

Because of the orientation of the transmitter coils, the experimental set-up can only measure magnetization in the xy plane, so equation 3 for magnetization in the $\hat{z}$ direction after a 180^o pulse seems useless. However, if a 90^o pulse is applied at some time τ all magnetization in the $\hat{z}$ direction gets pushed to the xy plane on its its echo signal, similar to what was discussed in measuring T_2. So, equation 3 describes the envelope of the resulting echos over varying τ. An example of one of these measurements can be seen in figure 3.

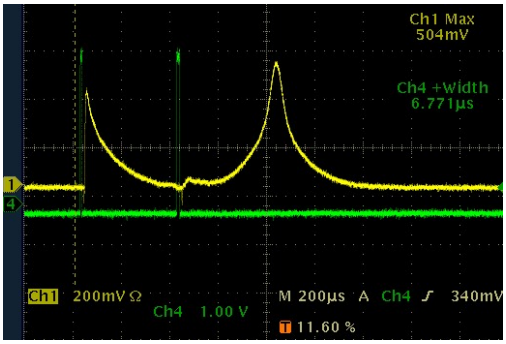

Figure 3: An oscilloscope screenshot showing both the applied pulses (green) and the resulting signal (yellow) in order to measure $T1$ for sample 2. The FID can be seen after the initial pulse, followed by the echo at a later time.

It should be noted that the absolute value of the envelope of the signals described in equation 3 is what is measured, as the circuitry in shown in figure 2 can only output positive voltages.

2.2 Measuring T_2

T_2 is more easily measured, with only one trial being necessary, with some slight additions to the theory. Multiple 180^o pulses can be applied after the initial 90^o pulse to record further decay rather than varying the width in between pulses. The applied pulses must be applied with alternating sign ($+180^o, -180^o$...). If this is not done, any small phase deviation in the pulse will quickly cumulative to produce large errors. The resulting signal from this train of pulses can be seen in figure 4.

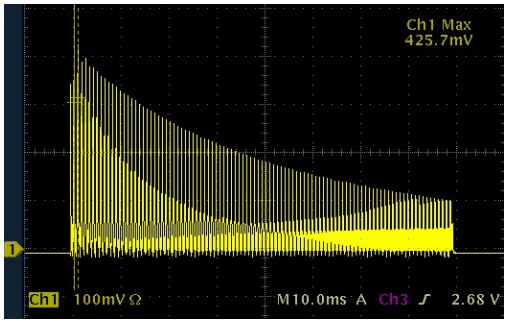

Figure 4: An oscilloscope screenshot showing the resulting signal (yellow) of a 90^o pulse followed by many 180^o pulses of alternating sign in order to measure $T2$. The behavior of a decaying exponential can clearly be seen.

3 Data Acquisition and Analysis

For T_1, data was collected by measuring the amplitude of the echo signal at varying τ, plotting the amplitude against τ, and fitting the resulting data to the absolute value of equation 3. Results can be seen below in figures 5 and 6.

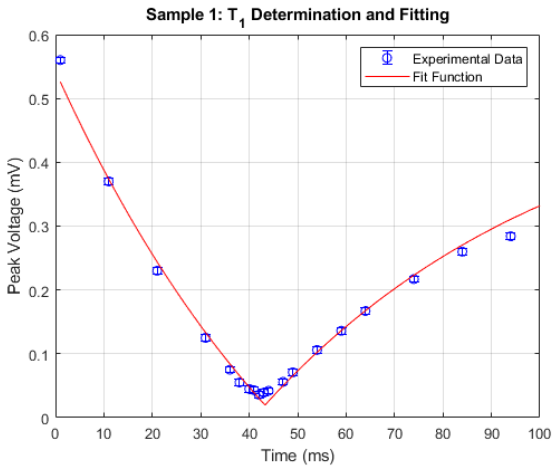

Figure 5: The data and fitting for T_1 of sample 1.

As show in in figure 4, many of the echos' amplitude and delay from the initial signal were recorded and fitted to equation 1. The results are shown below in figures 7 and 8.

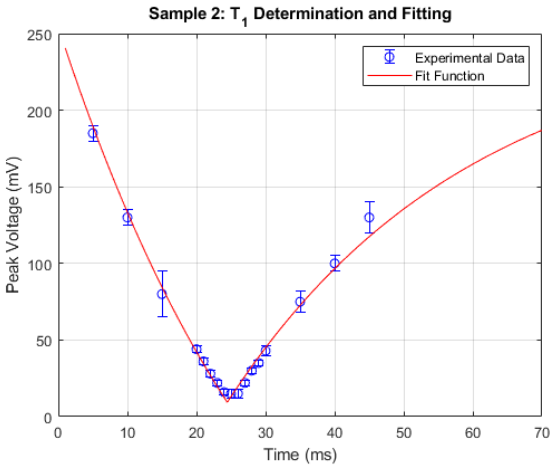

Figure 6: The data and fitting for T_1 of sample 2.

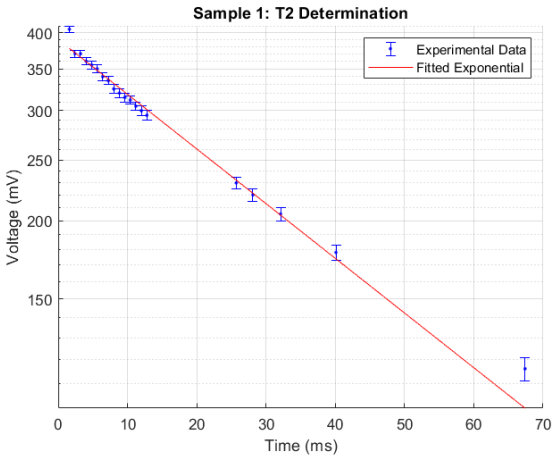

Figure 7: The data and fitting for T_2 of sample 1.

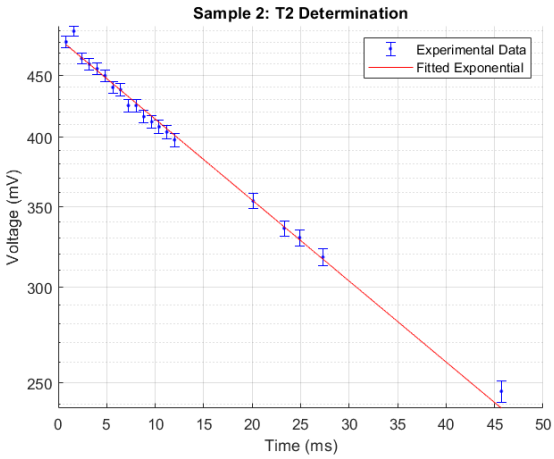

Figure 8: The data and fitting for T_1 of sample 2.

	T_1 *(ms)*	T_2 *(ms)*
Sample 1	62.41 ± 0.22	0.0201 ± 0.0004
Sample 2	35.28 ± 0.81	0.0155 ± 0.003

Table 1: The resulting T_1, T_2 times for both samples.

4 Conclusions

The results from fitting can be seen in table 1.

Sample 1's T_1 seems questionable due to a large uncertainty. This is likely explained by the pulses applied were not exactly of the intended phase, or the applied frequency not quite being the resonant frequeny, likely to to changes in temperature after tuning effecting these values. The resulting measured envelope deviated significantly from the absolute value of 3.

References

[1] HWS Physics. *Advanced Laboratory Manual*. Hobart and William Smith Colleges, 2019.

A Prelab Exercises I

1 Considering a collection of protons at T = 298.15K and in a magnetic field, B_o = 4kgauss. Fraction that are parallel to magnetic field:

$$\begin{aligned}\left[\frac{N_1}{N_2}\right] &= 1 - \exp\left[\frac{-\hbar\omega_o}{k_b T}\right] \\ &= 1 - \exp\left[\frac{-\hbar\gamma B_o}{k_b T}\right] \\ &= 2.741 * 10^{-10}\end{aligned}$$

where γ is the gyromagnetic ratio for a proton, N_1 is the aligned state, and N_2 is the anti-aligned state. For a population of 1 mL glucose, $\rho \approx 1 \frac{g}{mL}$, molecular formula $C_6H_{12}O_6$, through simple stoichiometry it can be found that leaves approximately $1.1 * 10^{13}$ more hydrogens that are aligned than anti aligned.

2 For the equations:

$$\begin{aligned}\dot{M}_x &= \gamma(\vec{M} \times \vec{B})_x \\ &= \gamma(M_y B_z - M_z B_y)\hat{x} \\ \dot{M}_y &= \gamma(\vec{M} \times \vec{B})_y \\ &= \gamma(M_z B_x - M_x B_z)\hat{y} \\ \dot{M}_z &= \gamma(\vec{M} \times \vec{B})_z + (M_0 - M_z)/T_1 \\ &= \gamma(M_x B_y - M_y B_x)\hat{z} + (M_0 - M_z)/T_1\end{aligned}$$

When $\vec{B} = B_o\hat{z}$:

$$\dot{M}_x = \gamma(M_y B_o)\hat{x}$$
$$\dot{M}_y = \gamma(-M_x B_o)\hat{y}$$
$$\dot{M}_z = \gamma(0)\hat{z} + (M_0 - M_z)/T_1$$

At t = 0, $M = -M_0\hat{z}$. So:

$$\ddot{M}_x = \gamma(-\gamma B_o M_x)$$
$$= \gamma\dot{M}_y B_o\hat{x}$$

which gives: $M_x = A\cos\gamma B_o t$. Similarly, $M_y = -A\sin\gamma B_o t$.

Now, considering: $\dot{M}_x = (M_o - M_z)/T_1$. Define:

$$U = M_z - M_0 \rightarrow \dot{U} = \dot{M}_z$$

So now:

$$\dot{U} = \frac{-U}{T_1}$$

Solving via separation of variables gives:

$$\frac{du}{dt} = \frac{-U}{T_1} \rightarrow \int\frac{du}{U} = \int\frac{dt}{T_1}$$

This gives: $U = B\exp\left(\frac{t}{T_1}\right)$. Subbing back for U:

$$M_z - M_0 = B\exp(t/T_1)$$

At t = 0: $M_z = -M_0$. So

$$-2M_0 = B \rightarrow M_z = M_0 - 2M_0\exp(t/T_1).$$

The magnetization is zero along the z-axis at:

$$0 = M_0 - 2M_0 exp(t_0/T_1)$$
$$\ln(M_0) = \ln(-2M_0)/T_1 t_0$$
$$t_0 = \frac{ln(M_0)}{\ln(2M_0)}T_1 = \ln(2)T_1$$

A sketch would be provided, but the equation for M_z over time is shown in figures 5 and 6 via the fit functions.

3 For a non-uniform magnetic field, each spin has a slightly different precession frequency. The net magnetization is the sum of the magnetic moments of each proton:

$$\vec{M} = \sum_{i=1}^{N}\mu_i$$

Where, in a reference frame rotating around the z-axis at the average frequency of the applied magnetic field (a star indicates the transformed axes:

$$\dot{\vec{\mu_i}} = \gamma\vec{\mu}\times\vec{b_i}\hat{z^*}$$
$$= -\gamma(\mu_{i,x}b_i)\hat{y^*} + \gamma(\mu_{i,y}b_i)\hat{x^*}$$

This set of differential equations gives:

$$\mu_y = A\cos(\gamma b_i t) \quad (1)$$
$$\mu_x = -A\sin(\gamma b_i t) \quad (2)$$

With $\mu_y(0) = \frac{e\hbar}{2mc}$, this gives: $A = \mu_y(0)$.

The angle deviation over time for the ith proton after an initial pulse can be expressed by looking at the deviation frequency:

$$\theta_i(t) = \gamma b_i t \quad (3)$$

Relating this to the expansion of the exponential:

$$e^{1/T_2 t} = 1 + (1/T_2)t + \frac{(1/T_2)^2}{2!}t^2 + \ldots \quad (4)$$

To show that de-phasing follows the exponential to first order, the time dependant terms of both equation 3 and 4 can be compared: $\gamma b_i t \sim (1/T_2)t$. This means $\gamma b_i = 1/T_2$.

On average: $1/T_2 = \gamma\sqrt{\langle b_i^2\rangle} = \sqrt{\langle\theta_i^2\rangle}$.

So, to first order, $\sqrt{\langle\theta_i^2\rangle}$ follows an exponential decay.

4 When a 90^o pulse is first applied to the sample, it causes the sample to have all of its net magnetization to be in one direction in the xy plane, and then it de-phases as previously discussed.

If μ_i, in the xy plane, is expressed as being a complex number with $\mu_{i,y}$ being projected onto the imaginary axis in the rotating frame and $\mu_{i,x}$ along the real axis in the rotating frame, then $\mu_i = e^{i(\gamma b_i t)}$.

During this de-phasing time, any given proton will have its magnetization drift according to its unique precession frequency, $w_i = \gamma * b_i$, meaning each of them will have some unique deviation from their initial magnetization in the xy plane. So, after time τ, the magnetization of any given proton can be expressed as:

$$\mu_i(\tau) = e^{i(w_i\tau)} \quad (5)$$

Meaning in the complex plane, the magnetization has deviated an angular distance of $w_i\tau$ over $\delta t = \tau$. If a 180^o pulse is then applied to the sample at time $t = \tau$, the magnetization of each proton flips about the x^* axis. This can be expressed as:

$$\mu_i(\tau^+) = e^{i(-w_i\tau)} \tag{6}$$

Where τ^+ indicates the time just after the pulse has been applied. This shows that now every proton has a angular deviation opposite of what they had before. Because of the flip, they will also be precessing according to the same equations, but just in the opposite direction in the complex plane. So, each proton is precessing from the angle $-w_i\tau$ back to their starting point. In order to travel an angular distance of $w_i\tau$ degrees, it previously took the proton τ seconds before the 180^o pulse. The precession frequency remains the same for individual protons barring any external environmental change, so it will once again take $\delta t = \tau$ seconds to travel$w_i\tau$ degrees. This means that after the 180^o pulse is applied at τ seconds, it takes and additional τ seconds for magnetization of all protons to be aligned once again, which is the spin echo. A total of 2τ seconds pass from the 90^o pulse to the time the spin echo occurs.

The protons (and their associated magnetization vectors) continue to follow the same equations of motion, just moving in the opposite direction, so all analysis from the pre-lab part 3 still holds to show that they de-phase in an exponential way, to first order.