Pulsed nuclear magnetic resonance Set 3 - with temperature control

Aims and Objectives

- Understand the basic theory of nuclear magnetic resonance from a classical viewpoint.
- Understand the longitudinal and transverse relaxation times.
- Use NMR in a systematic study involving changing samples or conditions.

Introduction

In nuclear magnetic resonance (NMR), the nuclei of atoms are exposed to a steady magnetic field. Nuclei having a magnetic moment precess around the field axis at a frequency which is determined by the nucleus and the total field it is exposed to. The magnetic field seen by the nucleus is the sum of the applied field and local fields produced by neighbouring atoms. The exact precessional frequency and the relaxation modes of the precession are therefore affected by the local environment of the nuclei. A measurement of these parameters is a powerful tool for investigating the local environment of chosen nuclei and has important applications in studies ranging from fundamental physics and chemistry, through forensic science to whole body magnetic resonance imaging.

NMR can be observed by placing a sample within a coil of wire and using sensitive electronics to detect the EMF induced in the coil by the motion of the magnetic nuclei. Moreover, the same coil can be driven by a pulse of current at the correct frequency, which can reorient the nuclei so that they subsequently precess in the ambient field.

Background

To understand NMR it is necessary to recall some basic properties of a nucleus. In addition to mass and charge, many nuclei have a net angular momentum M_I, and an associated magnetic moment μ, which results from the rotational motion of the charge.

Nucleus	Spin I	Magnetic moment μ	(Gyromagnetic ratio γ) / 2π (MHz/T)
^{1}H	1/2	2.79	42.6
D, ^{2}H	1	0.86	6.5
^{12}C	0	0	-
^{16}O	0	0	-
^{19}F	1/2	2.63	40.1

Table 1 – Properties of a few nuclei. μ is given in units of $\mu_N = e\hbar/2m_p$

The ratio μ/M_I is known as the gyromagnetic ratio γ, and varies between nuclei because of their varying internal structure and spin. Example values are given in Table 1.

In the following description, we will mostly ignore the quantum nature of nuclear spin, and treat the aggregate of all the nuclei in the sample classically. Also we pass lightly over the fact that the thermal energy around room temperature ($\approx 25 \times 10^{-3}$ eV) is much larger than the energy difference between a nucleus being aligned or anti-aligned with a typical field ($\approx 10^{-7}$ eV), so that the nuclear spins are *almost* completely randomised. The magnetisation we are discussing is the small magnetically-driven imbalance.

The nuclear gyroscope

A constant magnetic field B applies a torque τ to any magnetic moment μ that is not aligned with the field: $\tau = \mu \times B$. In a static system, the torque tends to align the moment with the field, but when the moment is associated with an angular momentum M_I, the torque causes the moment to precess around the field direction at an angular frequency

$$\omega_L = \frac{\mu}{M_I} B,$$

see Figure 1.

This gyroscopic effect is called *Larmor precession*, and ω_L is the Larmor frequency. It is independent of the angle θ, and is characteristic of a particular nucleus for a given field.

Addition of a alternating field

Figure 2 illustrates the basic principle of NMR. Initially, the magnetization M is parallel to a steady magnetic field B along the z-axis (Fig. 2a). A second, alternating,

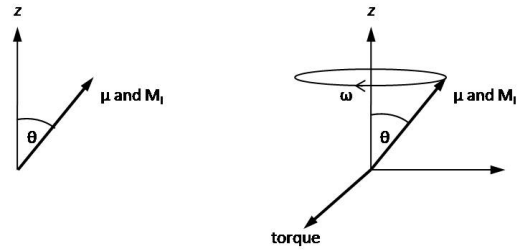

Figure 1 – The magnetic moment in a steady field along z. The torque is out of the page, and the change in angular momentum must be in the direction of the torque. Hence the tip of μ starts to describe a circle as shown.

magnetic field B_{RF} is then applied along the x-axis, perpendicular to B. Its frequency ω is adjusted so that $\omega = \omega_L$, and the nuclear moments are driven at their resonant frequency. The frequency is typically several megahertz, in the radio frequency range, so the alternating field is called the RF field. It is applied using a coil of wire driven by a transmitter.

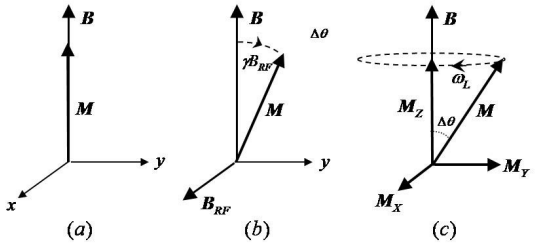

Figure 2 – Magnetization M (a) before, (b) during, and (c) after an RF pulse with frequency ω_L.

The RF field B_{RF} is normally applied as a pulse of duration Δt. During this time, the nuclear moments precess slowly around the RF field at angular frequency γB_{RF}, while they also precesss around B. A resonant pulse of duration Δt therefore tilts the spins through the angle $\Delta\theta = \gamma B_{RF}\Delta t$, see Fig. 2b. They are then left precessing about the steady field B at the new tilt angle, Fig. 2c.

The angle of tilt $\Delta\theta$ is controlled by adjusting the RF pulse length Δt. Two important cases are a 90° pulse, where M is rotated through 90° into the xy plane, and a 180° pulse where M is completely reversed.

After the RF pulse, the spins precess around the steady field B at the Larmor frequency ω_L. The magnetization M in Fig. 2c therefore also precesses, and the x and y components oscillate as

$$M_x = M\sin\Delta\theta\sin\omega_L t \quad \text{and} \quad M_y = M\sin\Delta\theta\cos\omega_L t. \tag{1}$$

Show that the signal is maximal for a 90° pulse.

The oscillating component M_x induces a voltage at the Larmor frequency in the same coil that was used to apply the pulse. A sensitive radio receiver is used to measure this voltage, and hence the component of the nuclear magnetisation in the x direction. This signal provides the basis for the pulsed NMR technique used here and in MRI.

Relaxation times

The energy of a magnetic moment μ in a magnetic field B is given by $U = -\mu \cdot B$, and so this is a *minimum* when the moment μ points along the field direction, i.e. the $+z$ direction, and a maximum when the moment points exactly opposite to the field direction.

For isolated nuclei in a magnetic field, the energy must stay constant and so nuclei turned at an angle θ to the z-axis will continue to precess forever at the same angle. In any real system, however, there are energy losses and the nuclei relax exponentially towards their minimum energy state (i.e. aligned parallel to the field) with a time constant T_1. This is known as the *longitudinal relaxation time*. Depending on the sample, T_1 can range from a fraction of a second to hours.

There is additional effects which can cause very rapid decay of the detected signal, faster than T_1. The receiving coil responds to the x-component of the total magnetic moment of all the precessing nuclei within it. So long as the nuclei remain aligned with each other, this remains constant. But if the precessing nuclei get out of phase with each other, the net moment can fall to zero, even though they are still precessing. These effects are observed as a *transverse relaxation time* T_2. Since the total moment decays with time constant T_1, the observed $T_2 \leq T_1$.

Try sketching this.

This dephasing can occur if there are small local variations in the field. A nucleus in a field $B + \delta B$ precesses at a frequency $\omega = \omega_L + \delta\omega$, so nuclei experiencing different δB get out of step. This can be caused by:

(i) Static variations in the local magnetic field caused by various nearby ions. This makes NMR sensitive to the local environment of the nuclei, which is very useful. It can be described by a decay time T_2.

(ii) Inhomogeneities in the field of the magnet. Unfortunately, no magnet is perfect, and its field inhomogeneity is reponsible for a dephasing time constant T_{2i}.

The finally observed transverse relaxation time T_2^* is a combination of these effects:

Why add reciprocals?

$$\frac{1}{T_2^*} = \frac{1}{T_2} + \frac{1}{T_{2i}}$$

Fortunately, the techniques described below can remove the effect of T_{2i}.

Liquids vs. solids

The longitudinal relaxation T_1 is an inelastic process - the spins relax back to the $+z$ axis as they lose energy. T_1 is long in a solid because it relies on the presence of small fluctuating magnetic fields, which in a quantum mechanical picture, couple the states pointing in the $+z$ and $-z$ directions. In a solid, these fluctuations are very small and relaxation is largely due to coupling of the nuclear spins to the lattice via paramagnetic impurities.

In a liquid, the molecules move rapidly past each other in a continual state of thermal motion, causing rapid fluctuations in the local field seen by each nucleus. This has very different effects on the longitudinal and transverse relaxation times:

- for the *longitudinal* relaxation, it enhances the coupling between the spin-up and spin-down states, providing a mechanism for relaxing the moments back along the $+z$ direction and hence dramatically reducing T_1.
- it has the opposite effect on the transverse relaxation, because the atoms move past each other on a timescale which is short compared with the dephasing time in the $x-y$ plane. It actually averages out the variations in the local field which cause transverse relaxation, and results in a substantial increase in T_2.

Note that, as defined, T_2 can never be greater than T_1, so that in a liquid, T_1 and T_2 will become comparable.

Experimental Method

Equipment

A schematic of the equipment is shown in Figure 3. The sample is placed in a nearly uniform steady magnetic field B produced by a permanent magnet. At T = 0 K, all N moments in the sample will point along the field direction. At temperature T the moment along the z axis will be $M = (N\mu^2 B)/k_B T$.

Can you show this?

Pulsed NMR

Pulsed mode operation is controlled by the NMR-lt application on the PC. The frequency of the applied RF pulses is controlled by the Tx ("transmit") frequency setting.

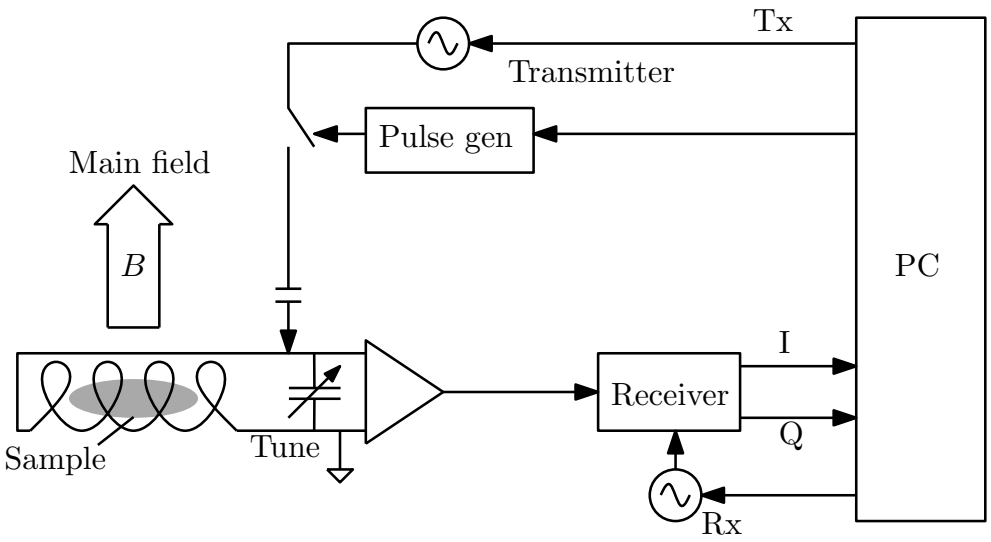

Figure 3 – Block diagram of the NMR-lt electronics unit. The PC applies one or more pulses of a field oscillating at the transmit (Tx) frequency, while reading back the response of the sample using a receiver tuned to the receive (Rx) frequency. The receiver provides the PC with the sample response both in phase with (I) and in quadrature with (Q) the Rx frequency, from which the PC can calculate the amplitude.

Their number and duration are controlled by the A and B width and timing controls. The only distinction between A pulses and B pulses is that A is the initial pulse, which is followed by zero or more B pulses. The whole cycle is repeated at a rate set by the repeat time.

Each pulse will tilt the magnetic moment of the sample as shown in Figure 2. The moment then precesses around the steady B field at the Larmor frequency. This precession is observed by means of the EMF induced in the RF coil by the rotating moment. The EMF is amplified and passed to a radio receiver whose tuning is controlled by the Rx ("receive") frequency setting, which is normally set the same as the Tx frequency. Both the in-phase and quadrature components (with respect to the Rx oscillator) of the received signal are passed to the computer, which is normally set to compute the magnitude of the received signal from them. See the NMR-lt software guide for details of the user interface.

Investigation of pulsed NMR signal

You should certainly begin with the tuning and spin echo investigations below. But the remainder of the techniques described are alternatives that you might apply to your sample of interest. See what works for you, and proceed with that.

Initial tuning and measuring the gyromagnetic ratio of ^{1}H

Using a single (A) pulse around 10 μs long at the correct frequency for protons within the field of the magnet, try to find the free induction decay signal of the protons following a 90° pulse. The response to a single pulse is shown schematically in Figure 4. The big initial spike is just the transmitter pulse being picked up by the receiver. The

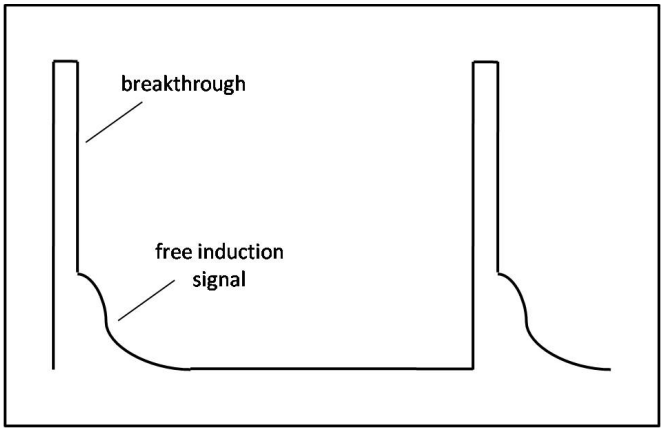

Figure 4 – Schematic single pulse response

decay that follows is the response of the hydrogen nuclei in a water- or oil- based sample. You can descriminate between this signal and other effects by briefly removing the sample tube.

Maximise the magnitude of the proton decay signal as follows:

- Make small adjustments of the Tx frequency
- Keep the Rx frequency equal to the Tx frequency
- Adjust the length of the pulse (aiming for 90°, which gives the biggest xy-plane moment)
- Keep the repetition rate slower than T_1, so every repetition starts from the same state
- Carefully move the magnet to find the most uniform field region (maximising T_2^*)

You may have to repeat the fine-tuning occasionally, because of small shifts in the sample position, or changes of the magnet temperature.

Once you see a signal, you can tune the frequency very precisely to the protons by switching to observe the in-phase component of the signal rather than the magnitude. This shows up as the beat frequency between the protons and Rx, so adjust Rx for

The receiver has a synchronous detector; essentially similar to a lock-in amplifier

the lowest possible beat frequency, then copy this to Tx and go back to displaying the magnitude.

From a measurement of the magnet's field and the proton frequency, you can calculate your own value for the gyromagnetic ratio of the hydrogen nucleus. Of course, γ is already known to standards-laboratory accuracy; this is, however, an excellent way to measure a magnetic field.

Measuring T_2^* and estimating T_1

The exponential decay time of the the free induction signal is T_2^*. You can fit and measure this. You may find that small movements of the sample and magnet can make it longer, which is a good thing.

Observe the effect of using too short a repetition time on the magnitude of the signal. This is related to T_1, and you should see big differences between pure water, oil and water slightly doped with $CuSO_4$.

The spin echo and measuring T_2

Using a second Tx pulse after the free induction signal has vanished, you can magically bring the signal back, see Figure 5. Using a single B pulse, nominally twice as long as

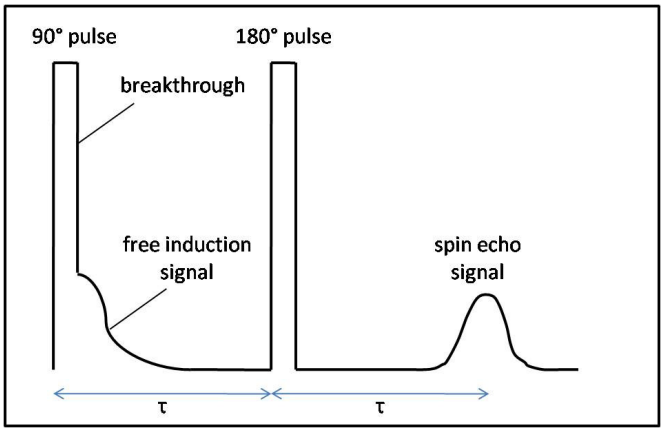

Figure 5 – Schematic 90° - 180° pulse sequence

the first pulse, so rotating the proton spins by 180°, the effects of field inomogeneity can be undone. By iterative adjustments of the pulse widths, maximise the size of the spin echo. Investigate how it changes as the delay time τ is varied.

Find out how this Hahn spin echo technique works. (Wikipedia has nice animation, see also Elster's web book[1]) It undoes only the dephasing associated with constant field variations of the magnet (T_{2i}); You can now see T_2 and T_1 effects more simply.

Pulse sequences

After a spin echo, the signal again decays. But you can coax the spins to stay in phase by repeating the B pulse as many times as you like, every 2τ. Best results are obtained by controlling the phases of the RF pulses, and pulse sequences are named after their inventors, see Carr [2], Meiboom [3], Gullion [4].

CPMG is a good sequence to try. See how long you can keep the spins coherent in a water sample.

Measure T_1 with the 90°-90° sequence

Immediately following a 90° pulse, the component of magnetization along the z-direction is reduced to zero. A second 90° pulse following shortly after the first one will produce a signal whose amplitude is proportional to and hence dependent on T_1 via

$$M_z(t) = M_0\Big[1 - \exp\Big(-\frac{t}{T_1}\Big)\Big] \qquad (2)$$

Where does this come from?

Sketch the results and determine T_1.

In practice, it is easier to set the spin-echo (i.e. 90°-180°) sequence first, making sure that the repeat time is sufficient to maximise the spin echo, and then reduce the duration of the secondary pulse to 90°. You should find that the first and secondary pulses have the same (maximum) amplitude. Now reduce the spacing between the first and secondary pulses, recording the amplitude of the free induction signal as you do so. Calculate T_1.

You should now be able to explain why using too short a recovery time for the first pulses reduces the amplitude of the free induction signal.

[1] https://mriquestions.com/spin-echo1.html
[2] HY Carr and EM Purcell, Phys Rev. 94 630 (1954) ("CP")
[3] S Meiboom and D Gill Rev. Sci. Inst. 29 688-691 (1958) ("CPMG")
[4] T Gullion, DB Baker and MS Conradi Journal of Magnetic resonance 89 479-484 (1990) ("XY"...)

Measure T_1 with the 180°-90° sequence

This is a quicker method for measuring T_1. The 180° pulse completely reverses the magnetization along the field direction. The vertical component of the magnetization will then recover its equilibrium value with a time constant T_1, passing through zero at time $\tau_{1/2}$ as shown in Figure 6.

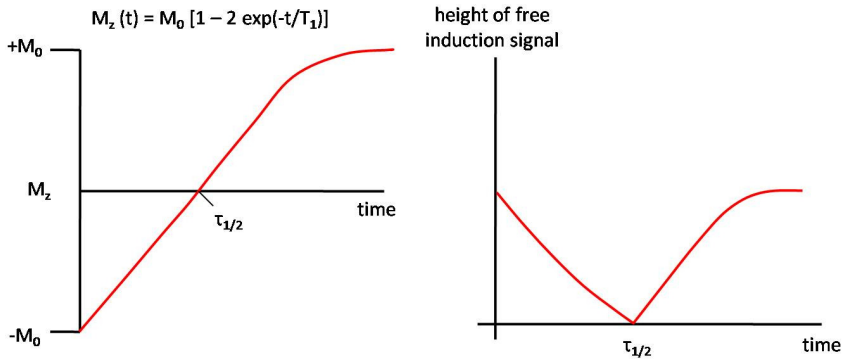

Figure 6 – 180 - 90 sequence

The amplitude of the free induction signal produced by the secondary 90° pulse is proportional to $M_z(t)$.

It is important to note that the magnitude signal does not contain sign information, and therefore does not change sign at $\tau_{1/2}$. What about I or Q?

Set up the 180°-90° sequence and vary the spacing of the secondary pulse in order to determine T_1. Again, you will find it easier to set up the spin echo (90°-180°) sequence first and maximise the spin echo signal, before readjusting the first and secondary pulse lengths.

Suggested further investigations

You should spend not more than two lab sessions on the initial investigations, above. Spend the rest of your time using NMR for a further investigation.

- This apparatus has a thermoelectric cooler stage that enables you to freeze a sample. You should be able to see changes in the decay times as the viscosity changes and a sample becomes solid. Ask a demonstrator to show you how the cooler and thermometry works.

- Water absorbed in porous rock behaves differently to pure water or pure rock. This is important to drilling and mining industries. Try some water in silica gel or molecular sieve as a porous material
- It is possible, if a little fiddly, to make up sample tubes containing variable concentrations of slightly magnetic ions, and see their effect on the relaxation times. Interpret your results and compare to the published literature.
- Compare the use of a Carr-Purcell sequence (many 180° pulses following the initial 90° pulse, to generate a sequence of echos) with the 90-180 method described above.

Recommended Reading

Research Papers

F. Bloch, *Nuclear induction*, Physical Review **70**, 460 (1946).
N. Bloembergen, E. M. Purcell and R. V. Pound, *Relaxation effects in nuclear magnetic resonance absorption*, Physical Review **73**, 679 (1948).
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A. Abragam, *Principles of Nuclear Magnetism*, Clarendon Press, Oxford (1961).

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D. Kleppner and R. J. Kolenkow, *An Introduction to Mechanics*, Ch. 7, McGraw-Hill (1973).

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