Pulsed nuclear magnetic resonance

Aims and Objectives

- Understand the basic theory of nuclear magnetic resonance from a classical viewpoint.
- Understand the longitudinal and transverse relaxation times.
- Measure the resonant frequency and the two relaxation times in some samples.

Introduction

In nuclear magnetic resonance (NMR), the nuclei of atoms are exposed to a magnetic field. This causes the nuclei to precess around the field axis at a frequency which can be determined electronically. For a particular magnetic field, this frequency is specific to particular nuclei. The magnetic field seen by the nucleus is the sum of an 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 at radio frequencies (RF) by placing a sample inside a coil driven by a pulsed RF oscillator. The oscillating magnetic field tips the nuclear spins over so that they subsequently precess in the steady magnetic field. The resultant precessing magnetic moment induces a voltage in a pick-up coil that is amplified and rectified in order to display the NMR signal from the sample.

In this experiment, you will study the simplest nucleus, the hydrogen nucleus, to understand the basic features of NMR.

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

Nucleus	Spin J	Nuclear moment μ_N	$\gamma/2\pi$ (Larmor frequency at 1 T) MHz
^{1}H	1/2	2.79	42.6
D,^{2}H	1	0.86	6.5
^{4}He	0	0	-
^{12}C	0	0	-
^{13}C	1/2	0.70	10.7
^{19}F	1/2	2.63	40.1
^{127}I	5/2	2.79	8.5

Table 1: Properties of a selection of interesting nuclei.

associated magnetic moment μ. To this extent, the nucleus may be pictured as a small, spinning bar magnet. Classically, the nucleus could have any value of M_I or μ, but these values are constrained by quantum mechanics. The angular momentum, $M_I = \hbar I$, where I is the spin quantum number for the nucleus, has either integer or half-integer values. μ is also constrained, and is normally expressed in terms of the value for the proton (called the nuclear magneton), $\mu_N = \frac{e\hbar}{2m_n}$, where m_N is the proton mass. μ and M_I point in the same direction along the axis of spin. Both μ and I are specific to particular nucleus; example values are given in Table 1.

The nuclear gyroscope

The problem of a bar magnet precessing in a magnetic field is closely analogous to the theory of a classical gyroscope precessing in a gravitational field. Consider the nucleus as a small, classical, spinning sphere with angular momentum M_I and magnetic moment μ, pointing at an angle θ to the z direction (see Figure 1). Left alone, it will remain in that position.

A magnetic field produces a torque on the moment, which tries to align the moment with the magnetic field. Because the moment also has an associated angular momentum, the angle between the moment and the magnetic field must remain constant at θ, and so the moment will precess around the magnetic field at an angular frequency

Can you derive this?

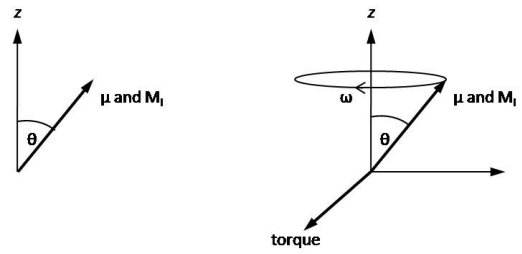


Figure 1: The magnetic moment in a steady field.

$$\omega_L = \frac{\mu}{M_I} B. \tag{1}$$

This is known as *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. The ratio

$$\gamma = \frac{\mu}{M_I} = \frac{\mu}{\hbar I} \tag{2}$$

is called the *gyromagnetic ratio* of the nucleus, such that $\omega_L = \gamma B$. Some values for γ are given in Table 1.

Addition of a alternating field

Figure 2 illustrates the basic principle of pulsed NMR. Initially, the magnetization M is parallel to the steady magnetic field B along the z-axis (Fig. 2a). A pulsed RF magnetic field B_{RF} is then applied along the x-axis, perpendicular to the steady field (Fig. 2b). If the frequency of the RF pulse is tuned to resonance (i.e. $\omega = \omega_L$), the spins precess around the RF field at angular frequency γB_{RF} during the pulse. A resonant pulse of duration Δt therefore tilts the spins through the angle $\Delta\theta = \gamma B_{RF} \Delta t$.

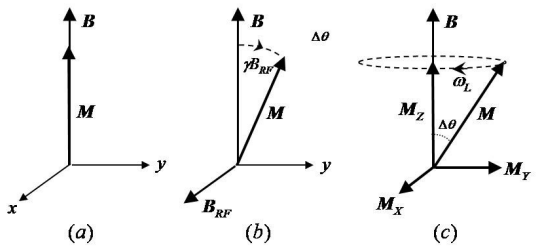


Figure 2: Magnetization M (a) before, (b) during, and (c) after an RF pulse with frequency ω_L.

Hence, 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°, 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

$$M_x = M \sin\Delta\theta \sin\omega_L t \quad \text{and} \quad M_y = M \sin\Delta\theta \cos\omega_L t. \tag{3}$$

The oscillating component M_y induces a voltage at the Larmor frequency in a pick-up coil oriented along the y-axis. This 'free induction' signal provides the basis for the pulsed NMR technique used here and in MRI.

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

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*. In a solid, T_1 can range from seconds to many hours.

There is an additional effect which can cause very rapid decay of the detected signal. Spin-spin interactions between adjacent nuclei expose each individual nucleus to a *net* magnetic field, which is typically slightly different to the applied field, and randomly fluctuates with time.

A nucleus in a field $B + \delta B$ precesses at a frequency $\omega = \omega_L + \delta\omega$. As the sign and amplitude of δB varies the nuclei rapidly become dephased in the $x-y$ plane, on a timescale typically much faster than T_1 (often less than 1 μs). The detected signal therefore decays exponentially in a dephasing time T_2, even though the nuclei are all still oriented approximately 90 ° to the z-axis. T_2 is called the *transverse relaxation time*.

Try sketching this.

T_2 is defined by the relaxation of the detected signal. For a solid, the dephasing effects take place on a timescale very short compared with T_1, and so the observed relaxation is determined by dephasing. If there were no dephasing effects, the *detected* signal

would still decay as the moments relaxed along the z-axis. T_1 therefore becomes the limiting value of T_2 as dephasing effects tend to zero.

Spin-spin interactions are not the only cause of dephasing. It may also occur due to variations in the static local magnetic fields caused by inhomogeneities in the magnet and *static* local fields caused by polarization by the applied field of the electron clouds around the various ions. This results in a transverse relaxation time with time T_2^*, which is clearly shorter than T_2.

Liquids vs. solids

The longitudinal relaxation T_1 is an inelastic process - the spins relax back to the $+z$ axis as they lose energy. Spin-spin relaxation, on the other hand, is an elastic process. 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 spin-spin 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 spin-spin relaxation and results in a substantial increase in the *transverse* relaxation time 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 Watson 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 $M = (N\mu^2 B)/k_B T$ and the corresponding angular momentum will be M/γ.

Can you show this?

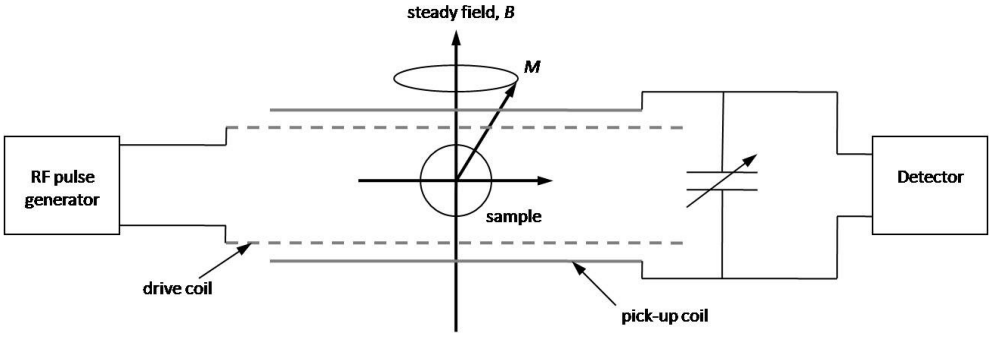


Figure 3: Schematic of the experimental setup in the Newport instrument.

A short pulse of RF current at the Larmor frequency is then applied through the drive coil, which in turn produces a short pulse of RF magnetic field at the sample. This tilts the magnetic moment of the sample at an angle to the steady B field (see above). The moment then precesses around the steady B field at the Larmor frequency. This precession can be observed by detecting the emf induced in the pick-up coil by the rotating moment.

The pick-up coil is rotated at an angle of 90° around the steady field axis relative to the drive coil in order to reduce direct pick-up from the drive pulse. The detector is a simple diode/smoothing circuit which turns the a.c. pick-up signal into a d.c. level of proportional amplitude which can then be fed into an oscilloscope.

What is the capacitor for?

The RF pulses are produced repetitively by gating a continuously running 2.7 MHz oscillator. There are two separately adjustable sorts of pule: *first* pulses and *secondary* pulses. The separation between successive first pulses is set by means of the knobs marked ‘repeat time‘. The duration of the each first pulse is set by a knob marked ‘first pulse width‘. You may also choose to follow each first pulse by a series of secondary pulses which may be a series of 0 (no secondary pulses), 1 or 8. The secondary pulse width and separation can be independently set by the four knobs in the section marked ‘secondary pulses’. The capacitor is adjusted by the knob marked ‘tuning’.

The box has three outputs:

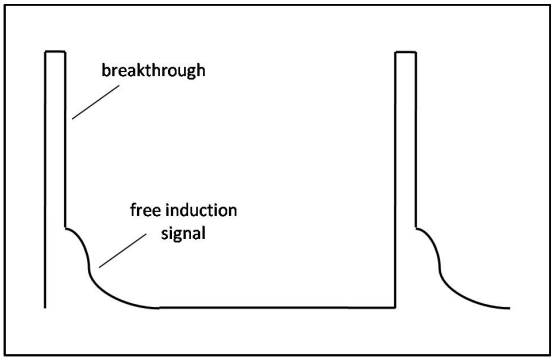
- *receiver* - detector output which should be connected to the oscilloscope.
- *sync* - this produces a short TTL pulse at the beginning of each initial pulse.
- *pulses* - this shows the gating pulses used to produce the RF pulses from the internal oscillator.

Investigation of outputs

Connect the 'receiver' and 'pulses' outputs to the two oscilloscope vertical inputs, and use the 'sync' pulses to trigger the 'scope. Set the number of secondary pulses to zero and investigate the effect of the first pulse width and recovery controls on what you see. The pulse you are observing on the detector output is a breakthrough signal, which should be ideally absent. Now investigate the effect of adjusting the various knobs in the secondary pulses section. Sketch some representative examples.

Observation of an NMR signal

Set the number of secondary pulses to zero and the recovery time to mid-range on x1. Set the oscilloscope so that you are observing the first two pulses. Put about 0.5 ml of liquid paraffin in a test tube to use as a sample. Lower the test tube into the coil set and observe the effect on the oscilloscope. By adjusting the first pulse width and the tuning knob, you should be able to get a signal like this:



The small decaying bit at the foot of the breakthrough signal is the NMR signal. It is called the *free induction signal* to distinguish it from the signal obtained if the RF field is left on continuously (not possible with this equipment). Maximise this signal on the 'scope. If you turn the gain too high, the oscilloscope's input amplifier will be saturated on the breakthrough pulse, and negative spikes will appear. Try the effect on the amplitude of the NMR signal of altering the first pulse width, the tuning, and also changing the recovery time. Estimate T_2^* from the free induction decay.

Two metal wires are available; lower them into the paraffin and explain the effects on the free induction signal.

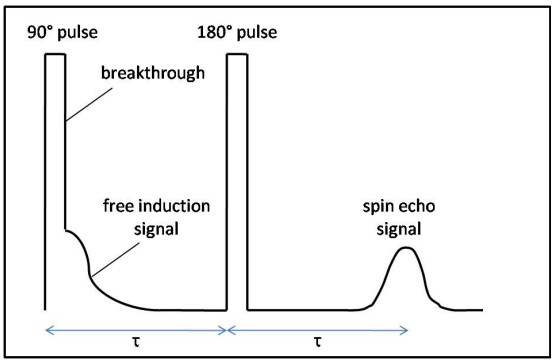
Measure the gyromagnetic ratio γ for the proton

To do this, you need a Hall probe to measure the magnetic field, and the 2-3 MHz RF generator. Turn off the NMR spectrometer in order to measure the permanent magnetic field associated with the Watson magnet. Turn it back on, and then wind a small coil of about ten turns of enamelled copper wire onto a former with a diameter of a few mm diameter and connect it in series with a 1 kΩ resistor to the output of the signal generator, before putting it into the field. By adjusting the amplitude and frequency of the signal generator you should be able to set up a beat pattern on the free induction signal from which you should be able to deduce the Larmor frequency and hence obtain a value for γ.

What does this do?

Measure T_2

Set the first pulse to 90° and the recovery time to 200 ms. Set the secondary pulse number to 1, the secondary pulse spacing to 20 ms and the secondary pulse width to 180°. You should be able to obtain a trace like this:



By iterative adjustment of the pulse width and tuning knobs, maximise the size of the spin echo.

What is the origin of this spin echo signal?

Assume for the moment that the only cause of field inhomogeneity is that due to the Watson magnet. Let the average B field have a Larmor frequency and consider part of the sample at slightly higher field where the spins are precessing at angular frequency $\omega_L + \delta\omega$. Now move to a frame of reference rotating at ω_L.

The 90° pulse along the B_{RF} will tip this component into the $x-y$ plane, where it will initially be in phase with all of the other components in the sample, and so will contribute to the free induction signal. After a time τ it will have precessed through an angle $\Delta\omega\tau$ about the z-axis.

A 180° pulse applied at this moment will then rotate the magnetization through 180° around B_{RF}. The magnetization will then continue to precess in the same sense as before, and after a further time τ will be exactly 180° away from its position following the initial 90° pulse. *This will be true for all components of the magnetization from every part of the sample, irrespective of magnitude or the sense of* $\Delta\omega$. Therefore, all components of the magnetization will come back in phase a time τ after the 180° pulse. This produces the spin echo, and it removes effects due to inhomogeneities in the applied field due to the Watson magnet.

Hint: try sketching this.

If the relative precession of all of the spins could be reversed, the magnetization would *always* be restored to its full value and the amplitude of the spin echo would remain constant and equal to the amplitude of the initial free induction signal. The argument above only applies to inhomogeneities in the static magnetic field, cause by the magnet and fixed internal fields in the solids. It does not apply to the fluctuating internal fields responsible for the transverse relaxation time, which cause irreversible dephasing. The amplitude of the spin echo will then fall as $\exp(-\tau/T_2)$.

Measure this in the paraffin 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

$$M_z(t) = M_0\left[1 - \exp\left(-\frac{t}{T_1}\right)\right] \quad (4)$$

Where does this come from?

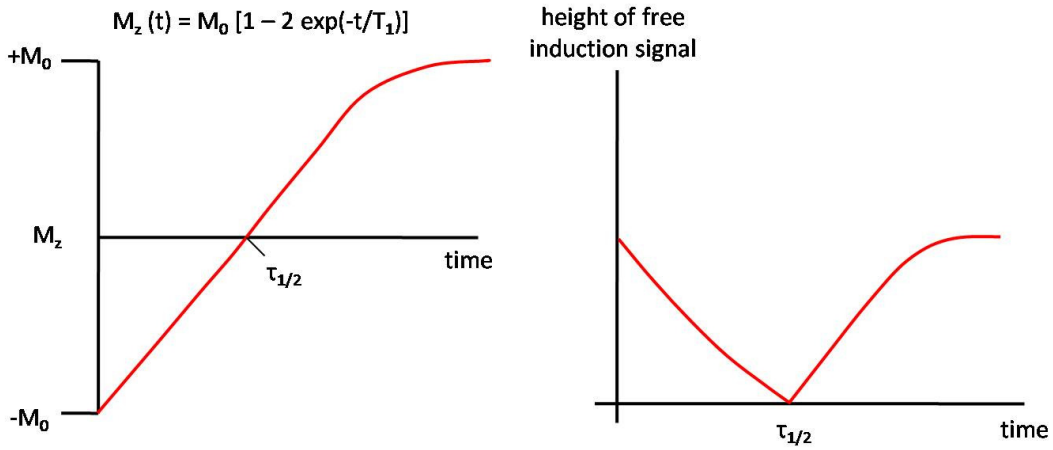
Sketch the results and determine T_1.

In practice, it is easier to set the spin-echo (i.e. 90°-180°) sequence first, making sure that the recovery 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.

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 below.



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 signal on the oscilloscope depends on the amplitude, but not the phase of the induced signal, and therefore does not change sign at $\tau_{1/2}$.

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.

Further investigations

You should spend not more than two lab sessions studying the paraffin. You should spend at least two lab sessions on the further investigations.

- Relaxation of protons in water by paramagnetic ions - make up solutions of known molar concentrations of copper sulphate in water and investigate how T_1 and T_2 vary with concentration. Start with a very low concentration. Copper sulphate solution contains Cu^{2+} ions, which carry an unpaired electron. They are therefore paramagnetic with a magnetic moment of $\sim 1\ \mu_B$. These ions produce a fluctuating magnetic field that acts upon the proton spins in the solution and reduces their relaxation times T_1 and T_2. Interpret your results and compare to the published literature.

Recommended Reading

Research Papers

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