University of Tasmania

Third year laboratory work

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Nuclear magnetic resonance

April 28, 2022

Safety

This experiment involves the use of a strong static magnetic field. A serious hazard is posed to anyone with ferrous surgical implants and/or bioelectronic devices. Magnetically susceptible jewelry should be removed and particular care should be taken with any form of magnetic storage media and analogue watches, as exposure to the field may result in permanent damage.

Nuclear magnetic resonance

Summary

In this experiment, we study the fundamental principles of nuclear magnetic resonance.

Objectives and learning outcomes

- Investigate the fundamental principles of nuclear magnetic resonance
- Measure the values of the spin-lattice and spin-spin times ($T1$ and $T2$) for mineral oil
- Investigate the use of magnetic gradients in NMR and their application to MRI

Introduction

Nuclear magnetic resonance (NMR), and notably the related technique of Magnetic Resonance Imaging (MRI) has become ubiquitous in modern healthcare, in addition to being an invaluable tool in myriad other fields. At its core, NMR is a quantum mechanical phenomenon arising from the interaction between an atom and an external radiation field.

In conventional NMR, one normally considers the nucleus of the hydrogen atom (a proton) in a strong external magnetic field. The nuclear spin $I = 1/2$ and therefore will have quantised projections on the external field of $m_I = \pm 1/2$, corresponding to the spin being either aligned or anti-aligned with the field. The energy difference between the aligned (ground) state and anti-aligned (excited) state has an energy difference determined by the external field strength as dictated by the Zeeman shift. Nuclear magnetic resonance occurs when radiation is applied to the proton and the energy of the applied radiation is equal to that of the energy spacing between the different spin alignments, and thus transitions between spin states can occur. Whilst this principle is relatively simple, it has been exploited with great success, from the generation of extremely sensitive chemical probes to magnetic sensors with unparalleled sensitivity, and of course to non-invasive imaging techniques. Here we shall study the basic principles of NMR and see how they apply to MRI.

It should be noted that NMR is notoriously conceptually challenging to understand, the notes here are designed as a rough guide to the content but you are expected to do detailed research on the theoretical underpinnings of NMR prior to attempting any of the experiments, especially those involving MRI.

Nuclear magnetic resonance

A single spin

Consider a single particle of spin$-1/2$ in a magnetic field $\mathbf{B}$. The interaction Hamiltonian of the system is given by

$$\hat{H}' = -\hat{\boldsymbol{\mu}} \cdot \mathbf{B} \tag{1}$$

where $\hat{\boldsymbol{\mu}}$ is the magnetic dipole moment of the spin. By convention, we define the magnetic field along z such that the spin interaction $-\hat{\boldsymbol{\mu}} \cdot \mathbf{B} = -\mu_z B_0$, where B_0 is the strength of the field along z. Under these conditions, the energy separation between the two spin states is given by

$$\Delta E = -\gamma \hbar B_0 \tag{2}$$

where γ is the gyromagnetic ratio. If we then resonantly couple radiation of frequency ω into the system, the energy of the photon must match that of the energy splitting, namely

$$\hbar\omega = \gamma\hbar B_0. \tag{3}$$

When the above equation is satisfied, the frequency ω is denoted ω_L and is known as the Lamor frequency. The Lamor frequency is an important quantity as not only does it define the energy difference between the aligned and anti-aligned spin states, but it is also the frequency at which precession of the spin vector around the magnetic field vector occurs.

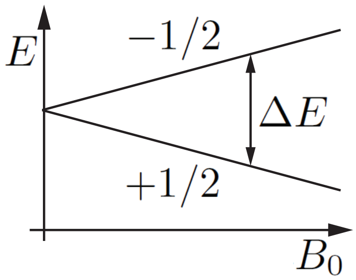

Figure 1: The energy level structure of a spin−1/2 system in an external magnetic field

Exercise 1

Verify equation 2 given that $\hat{\boldsymbol{\mu}} = \gamma\hat{\mathbf{S}}$, where $\hat{\mathbf{S}}$ is the usual spin operator.

An ensemble of spins

Whilst it is possible to isolate single spins, it is very difficult. Normally we are considering macroscopic samples and thus were are considering of order 10^{23} spins. We need therefore consider the statistical qualities of the system, not just the single-particle nature of the system. In the case of a single spin, the direction of the magnetisation vector $\mathbf{M}$ is exactly that of the spin vector $\mathbf{S}$; however, in the statistical mixture the magnetisation vector is the vector addition of all spin vectors in the sample.

Exercise 2

What fraction of spins would you expect to find in the excited state at room temperature? What can you say about the magnetisation vector under these conditions? For reference, typical values of ω_L are of the order 10s of megahertz.

In order to understand the transient effects in the spin system, it is important to visualise what is occurring on a microscopic level. Namely, that there are a large number of spins undergoing precession around the magnetic field vector, either aligned or anti-aligned. Let's consider the ground state, where spins are aligned to the field: the precession of an individual spin results in the precession of the local magnetisation vector, but the magnetisation vector of neighbouring spin, which is also undergoing precession, will in all likelihood be pointing in a different direction. Certainly, the projection of the spin onto the magnetic field will be the same, but the components perpendicular to the field will likely be different. Put another way, the precession of one spin is *out of phase* with the other spin, which means when we take an ensemble average means there will be no component of the magnetisation vector perpendicular to the magnetic field (see figure 2). For spins in the ground state, the magnetisation vector will be parallel to the applied field and for spins in the excited state, the magnetisation vector will be antiparallel to the applied field.

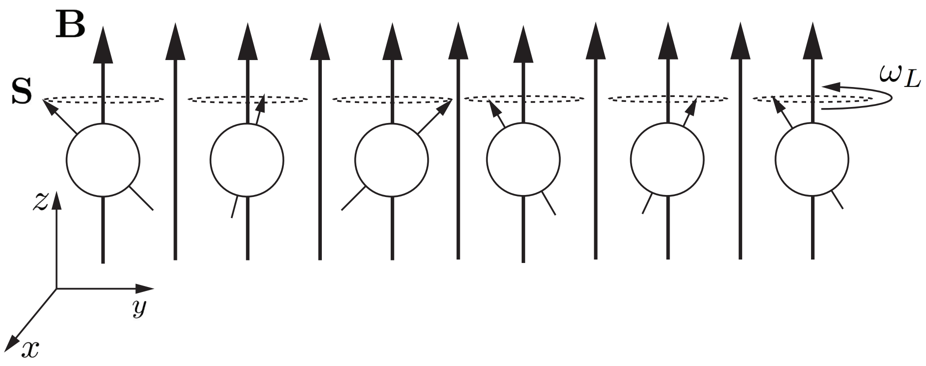

Figure 2: An ensemble of ground state spins undergoing precession out of phase

Transverse magnetisation: the classical interpretation

Suppose we introduce a radiation field with frequency ω_L directed such that there is a rotating magnetic field $\mathbf{B}'$ which oscillates perpendicular to the static field B_0. In the frame of a spin undergoing precession around the $z-$axis, there is now an orthogonal static magnetic field around which the spin will also undergo precession. There is thereby a deflection of the magnetisation vector away from being purely along z and into the $x - y$ plane.

Transverse magnetisation: the quantum interpretation

If we apply a coupling radiation field resonant with the energy-level splitting due to the external magnetic field, we can induce transitions between the spin states and therefore that we can induce a change in the magnetisation of the ensemble. In a two-level system with a coupling field and all spins initially in the ground state, the transient excited state population ρ_e for resonant coupling can be calculated from the optical Bloch equations with the result

$$\rho_e(t) = \sin^2\left(\frac{\Omega t}{2}\right) \tag{4}$$

where Ω is the Rabi frequency, which is determined by the strength of the coupling between the radiation field and the spin system.

At first glance such a result may not appear anything special, but is it saying the probability of a spin being found in the excited state oscillates between 0 and 1 at a rate determined by Ω. Indeed there are many implications from the above result, but the observation that if a pulse of radiation is present for time τ such that $\Omega\tau = \pi$ means that a spin in the ground state will be transferred into the excited state. Such a pulse is known as a π pulse and can be used to flip the magnetisation of a sample. Less intuitively, a $\pi/2$ pulse (which satisfies $\Omega\tau = \pi/2$) means that the excited-state probability evaluates to $\rho_e(t) = 1/2$. By definition, this also means that the ground-state probability is then $\rho_g = 1 - \rho_e = 1/2$. Indeed, the state is described by a superposition of the ground and excited states with equal weighting. In contrast to the classical system which consists of two discrete states either aligned or anti-aligned to the external field, quantum mechanics allows for the superposition of these states and thus states which cannot be expressed classically. An important implication of these superposition states is that the spin vector $\mathbf{S}$ will have a non-zero component perpendicular to the magnetic field.

Exercise 3

What is the Bloch sphere? How does it aid in the visualisation of NMR?

Free-induction decay

By now we should have an understanding of a spin ensemble system in an external magnetic field: by coupling radiation of the correct frequency, we can induce a change in the magnetisation of the sample. By placing pickup coils orthogonal the magnetic-field axis, any transverse magnetisation will result in an induced current which we can amplify and detect. Importantly, the magnetisation vector will *always* rotate at the Lamor frequency, meaning that we can mix the detected signal with our emission frequency in a process known as demodulation. This should allow us to detect the free-induction decay from our sample.

Exercise 4

Remembering that the detected signal is demodulated, how will we know when the radiation source frequency matches the Lamor frequency?

The final point that must be discussed before we can look for a signal is *what does a signal look like?* To answer this, we must look at the experimental setup, a schematic of which is shown in figure 3. Here, a sample of mineral oil (the source of protons) is placed in a strong magnetic field and radiation is applied to the sample through a radio-frequency (RF) coil; the same coil can be used as an antenna for spins undergoing precession in the $x - y$ plane. Consider what signal we would expect if we put in a perfect $\pi/2$ pulse: the magnetisation vector will rotate into the $x - y$ plane, but will it remain indefinitely? The answer is unsurprisingly no; there are two primary decay mechanisms, one characterising the loss of longitudinal magnetisation and another characterising the loss of transverse magnetisation. These decay mechanisms are characterised by decay times $T1$ and $T2$ respectively, the so called spin-lattice and spin-spin relaxation times.

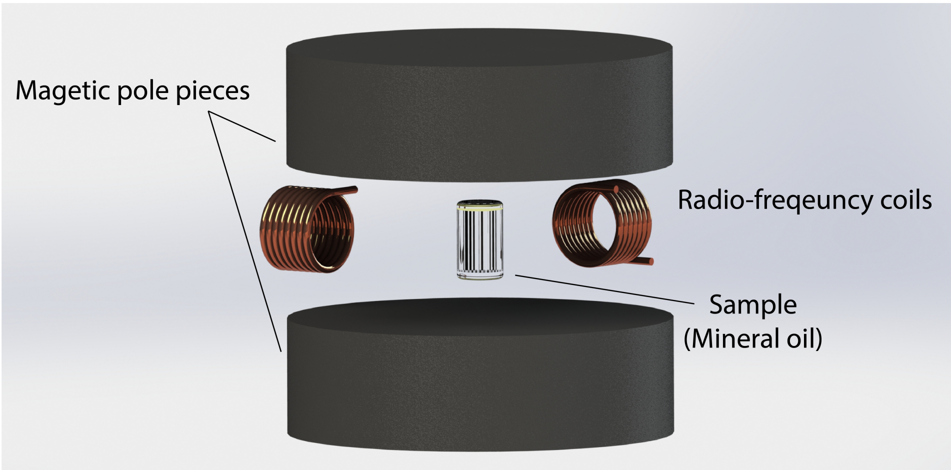

Figure 3: A schematic of the experimental setup . A sample of mineral oil is placed in a magnetic field and radio-frequency coils allow from the transmission and reception of RF signals.

Exercise 5

What are the physical mechanisms that underpin the spin-lattice and the spin-spin relaxation times? Given these relaxation mechanisms, which signal would you expect to see following a perfect $\pi/2$ pulse?

Fundamentals of magnetic resonance

Remote operation of an experimental system requires particular attention to detail in order to ensure the system functions as you expect, but also to ensure that the system is not damaged.

Firstly, to control the apparatus, one must first take control of the machine used to interface with the apparatus.

To take control of this machine, establish a remote desktop connection to `SET-MAP-57450T2.utas.ad.internal` and log in using your university account. From here, open the `measure MRT` program. Provided the unit is connected you will now be able to run experiments.

Our first task it to observe a magnetic resonance signal and investigate the parameters which affect the quality of the signal. For all experiments, a sample of mineral oil will be placed in the static magnetic field as schematically shown in figure 3.

To begin, select the *MR-Frequency* experiment from the *Current lesson* window and click start. This will begin an simple experimental sequence where a burst of radiation at frequency ω will be emitted for a time defined in magnet settings (*Settings* $\rightarrow$ *Choose magnet*), set by default the be approximately a $\pi/2$ pulse (the exact duration is not currently important). You should now see a trace of the detected signal as a function of time; adjust the frequency until the optimum signal is found. Note that this setting a the frequency ω applies for all subsequent experiments. If you are having difficulty seeing a free-induction decay signal, the magnet is labelled with a resonant frequency for protons of 17.30 MHz at 22° C, which should provide a useful starting point.

Exercise 6

From your resonant frequency, calculate the strength of the magnetic field B_0 given the gyromagnetic ratio for the proton is $\gamma_H = 267.5 \times 10^6\,\mathrm{rad\ s^{-1}\ T^{-1}}$.

Now we have found the Lamor frequency for our system, we want to engineer the length of our pulses such that we can create $\pi/2$ and π pulses. Select the *MR-Excitationangle* experiment from the *Current lesson* window to have access to the pulse-length parameter τ; vary the parameter to study its effect, and find the values of τ for which $\pi/2$ and π pulses are created.

The quality of the observed signal is affected by a variety of parameters, but none more so than the magnetic field, after all, it is the value of the field that determines the precession frequency. Field inhomogeneity across the sample will act to reduce the signal amplitude and the value of $T2$, so by careful correction, both of these can be increased. Select the *B0inhomogenity* experiment from the *Current lesson* window to have access to the shim coils for the x, y and z directions, allowing for compensation of stray fields and field inhomogeneity. Adjust these values to obtain an optimum signal, noting that the Lamor frequency may need to be adjusted if the field is significantly altered.

Spin echo

Armed with an optimised magnetic field, and values for ω_L and τ, we are ready to perform our first non-trivial pulse sequence. Begin by selecting the *Spin Echo* experiment from the *Current lesson* window to start the spin-echo retrieval sequence. In this experiment, we are going to start with a $\pi/2$ pulse, wait for some time t and then apply a second pulse and observe what happens. The `Length 2 pulse` parameter controls the duration of the second pulse and the `Echotime` parameter controls the time delay between the pulses. Study the effect of the second pulse of the received signal and then adjust the pulse duration of the second pulse to make a π pulse.

Exercise 7

What is happening when the second pulse is a π pulse? What to you notice about the amplitude of the signal as you alter the echo time?

This concludes the introductory section into NMR; however, you will find that there are many other experiments in the *Current lesson* panel, which permit the study of other NMR phenomenon and importantly the quantitative assessment of various parameters. Below is a list of suggested tasks, for which it is suggested that you attempt in the order given, as knowledge acquired in a given task is required background for the subsequent task.

Tasks

1. Investigate the signal-to-noise limitations of NMR, with emphasis on the repetition time of the pulse sequence
2. Measure the values of $T1$ and $T2$ for mineral oil
3. Investigate the use of magnetic gradients in NMR and their application to MRI
4. Investigate 2-dimensional magnetic resonance imaging