Pulsed nuclear magnetic resonance Set 2 - Deluxe model

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 steady 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 by placing a sample in a steady magnetic field, and additionally applying to the sample an RF field produced by a coil driven by an 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 the RF coil that is amplified and processed 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?

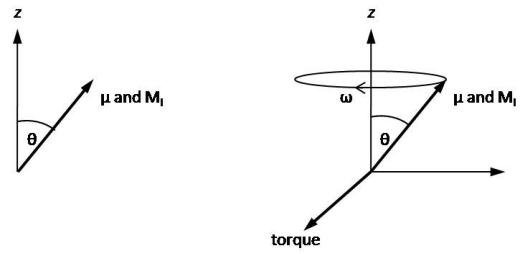


Figure 1: The magnetic moment in a steady field.

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

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

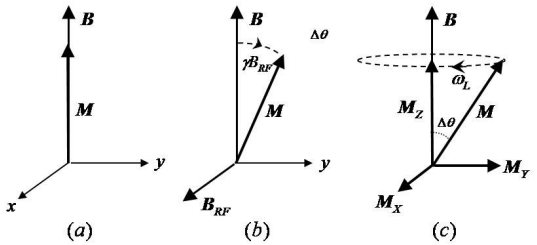


Figure 2: Magnetization M (a) before, (b) during, and (c) after an RF pulse with frequency ω_L.

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_x induces a voltage at the Larmor frequency in the RF coil. 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?*

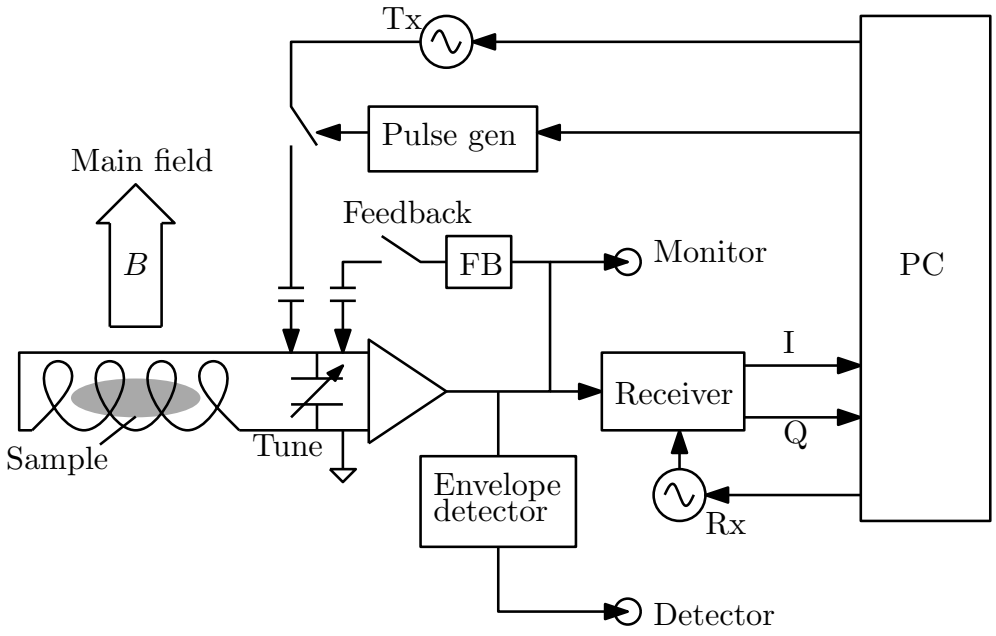


Figure 3: Block diagram of the NMR electronics unit. In CW (continuous wave) mode, the feedback circuit is completed, causing it to oscillate at a frequency determined by the sample coil and the tuning capacitor. The magnetic response of the sample perturbs the amplitude of this oscillation, which is read out using the envelope detector. Alternatively, in pulsed mode, 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.

Resonant absorbtion

In continuous wave mode, a small oscillating field is applied to the sample by means of a small coil that is just outside the sample tube. The oscillating field is perpendicular to the direction of the field from the main magnet, and its frequency is adjusted using the manual tuning knob. When the frequency of the oscillating field is equal to the Larmor frequency, power is absorbed by the sample, as those nuclei that are anti-aligned with the main field are rotated to align with it. The oscillator is designed so that its amplitude depends on this power loss, so the Larmor resonance can be seen

as a peak in the loss, as the field of the main magnet is swept through that satisfying Eq. 1.

To observe the resonance, ensure the PC-controlled pulse generator is not running, and switch on both the Feedback and LF boost switches on the control box. The function generator should be connected to the coils wound on the main magnet, monitored using one channel of the oscilloscope, and set to provide a 15 Hz ramp of 10 V p-p amplitude. Connect the Detector output of the control box to the other oscilloscope channel. Glycerine is a good sample to start with; you should have a test tube containing 2-3 cm of glycerine, with a rubber O-ring at the top to protect the fixed glass sample holder. Lower the test tube into the fixed glass sample holder with care – a contaminated or broken sample holder will bring the experiment to a halt.

Adjust the Tune control to centre the NMR resonance on the field sweep.

Measuring the gyromagnetic ratio γ for the proton

The Monitor output of the control box allows a frequency counter to display the frequency of the oscillating field. By inserting a Hall probe in place of the sample, you can measure the magnetic field B. From these measurements, you should be able to obtain a value for γ. Ideally, you should do this with the smallest possible sweep of the main field, so decrease this, while adjusting the tuning to keep the resonance centred.

You will notice that the resonance is not a simple peak. Can you explain why there are additional wiggles after the resonance (think about the relaxation times)? It can be revealing to look at the wiggles when sweeping slower or faster than 15 Hz.

Pulsed NMR

Pulsed mode operation is controlled by the NMR application on the PC. The frequency of the applied RF pulses is controlled by the Tx ("transmit") frequency setting. 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 between zero and seven B pulses. The whole cycle is repeated at a rate set by the repetition 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 close to 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.

Investigation of pulsed NMR signal

A good sample to start with for pulsed mesurements is mineral oil (any kind). The CW detector used previously will also display the reponse to pulses, but in order to acquire data with the computer, you must turn the Feedback switch off, as the RF receiver is otherwise overwhelmed by the small oscillations used by the CW circuit. The PC always takes 50,000 readings for each pulse sequence; you can control the sample rate (given in kilosamples per second) and hence the time scale of the display. Since 50,000 readings is likely to be more than you need in a data file, the "Save Every" setting reduces the density of samples in any data file you save.

Turn off the ramp generator and Feedback switch, and start the pulsed NMR application. Set the Tx and Rx frequencies to the Larmor frequency you measured in CW mode. Start with a single A pulse, about 10 μs wide. Adjust the scales, pulse width, and Tune knob on the control box, to optimise The NMR pulse response. You can discriminate between the real NMR signal and the direct effect of the Tx pulse on the receiver by briefly removing the sample. Now investigate the effect of B pulses and the various controls. Sketch some representative examples.

The response to a single pulse is shown schematically in Figure 4.

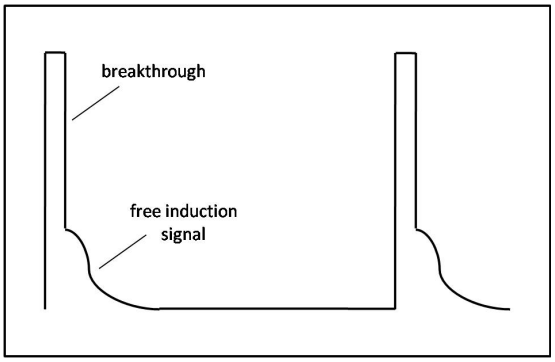


Figure 4: Schematic single pulse response

The tall spike is partly the pulse itself, but mainly the receiver amplifier recovering from the huge overload that the pulse constitutes. It can be ignored except as a way of seeing where the pulse occurred. The decaying part is the NMR signal. It is called the *free induction signal* to distinguish it from the CW signal obtained if the RF field is left on continuously. Optimise the size of the signal. Try the effect on its amplitude

of altering the first pulse width, the tuning, and also changing the repetition 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.

A better value for the gyromagnetic ratio γ of the proton

Previously, we found the Larmor frequency by adjusting the RF frequency to find the absorbtion peak, and hoping we could locate its centre. Now that we can see the free decay signal, we can just measure its frequency. The in-phase (or quadrature) receive channel oscillates at a frequency that is the difference between the incoming signal and the Rx local oscillator.

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

Adjust the Rx frequency for a zero-frequency beat, and read off the frequency. Of course, γ is already known to standards-laboratory accuracy; this is, however, an excellent way to measure a magnetic field.

Measure T_2

Set the first (A) pulse to 90° and the repetition time to 200 ms or so. Set the number of secondary (B) pulses to 1, the A-B delay to 20 ms and the secondary pulse width to 180°. You should be able to obtain a trace like Figure 5.

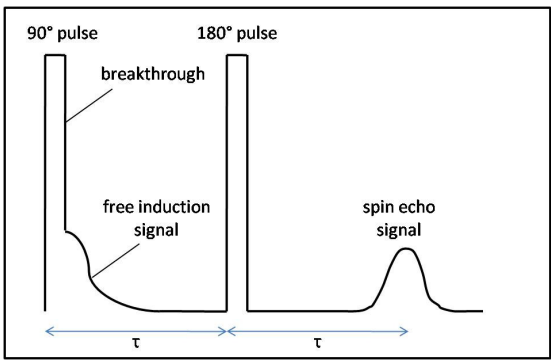


Figure 5: Schematic 90° - 180° pulse sequence

By iterative adjustment of the pulse width, Tx frequency, and the Tuning knob, 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 oil 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.

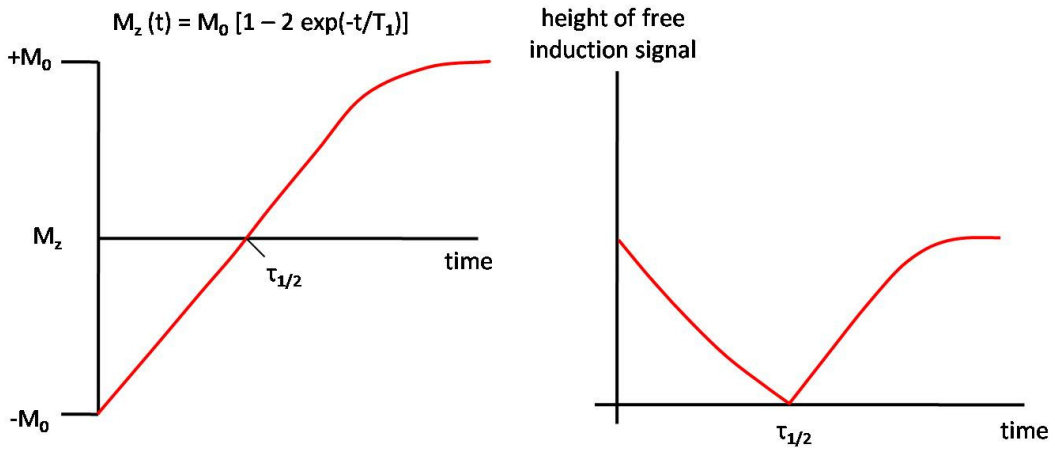
In practice, it is easier to set the spin-echo (i.e. 90°-180°) sequence first, making sure that the repeat time is sufficient to maximise the spin echo, and then reduce the duration

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.

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 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.

Further investigations

You should spend not more than two lab sessions studying the oil sample. You should spend at least two lab sessions on using NMR for a further investigation.

- 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 plain water and then very low concentrations. 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.
- Investigate a liquid - solid transition.
- Investigate the use of NMR for determining the moisture content of some systematically prepared samples.
- 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).
E. L. Hahn, *Nuclear induction due to free Larmor precession*, Physical Review **77**, 297 (1950).
E. L. Hahn, *Spin echoes*, Physical Review **80**, 580 (1950).
E. M. Purcell, H. C. Torrey and R. V. Pound, *Resonant absorption by nuclear magnetic moments in a solid*, Physical Review **69**, 37 (1946).

Textbooks

E. P. Andrew, *Nuclear Magnetic Resonance*, Cambridge University Press, Cambridge (1995).
C. P. Slichter, *Principles of Magnetic Resonance*, Harper and Row, New York (1963).
A. Abragam, *Principles of Nuclear Magnetism*, Clarendon Press, Oxford (1961).

Gyroscopes

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

EB 2009-08-20
MSC 2016-10-04