

Experiment 355: Nuclear Magnetic Resonance

Aims

The primary aim of this experiment is to introduce the phenomenon of nuclear magnetic resonance (NMR). As with the Zeeman and Mossbauer effects, NMR provides a means of demonstrating the quantum mechanical nature of atomic systems. A second aim is to familiarise students with some simple applications of NMR, in particular, to the accurate measurement of magnetic field strengths (better than 1 part in 10^4) and to the study of certain properties of solids and liquids.

Introduction

The determination of magnetic field strengths using NMR is a standard technique. Such apparatus is in use in the AURA2 laboratory. The many more extensive and intriguing uses of NMR now current are discussed in texts in the library. In particular, NMR techniques now provide by far the best method of medical imaging.

An introduction to NMR theory is provided with the bench copy of this pamphlet. The introduction is an abstract from a book on NMR by E.D. Becker. This book can be found in the science library (538.3 B39). Both simpler and more extensive treatments can be found in other books on NMR and on solid state theory (references are given in the theory folder). You should read the theory in the folder or elsewhere and be sure that you follow the relevant sections as you proceed with the experiment.

Consult your demonstrator if you have any difficulties.

Apparatus

The NMR apparatus consists of an electromagnet with pole faces designed to produce a very homogeneous field \mathbf{B} in the centre of the gap. The electromagnet is driven by a variable but very stable direct current. A small coil, situated in the centre of the gap and with its axis perpendicular to \mathbf{B} , surrounds a sample tube and is used both to generate an oscillating magnetic field of frequency

$$\nu = \frac{\omega}{2\pi}$$

and to detect the magnetic resonance of nuclei in the sample material. The sample can be periodically swept through the resonant condition, $\omega = \omega_o$, either by frequency modulation of the radio-frequency driver or by modulating the field of the electromagnet with alternating current in the “Helmholtz” coils that embrace the pole gap.

In this apparatus the radio frequency is set to a suitable constant value by means of the tuning dial and it can be measured with a frequency meter. The magnitude of the radio-frequency field applied to the sample can be varied and calibrated with respect to the reading of the “RF level” voltmeter.

The “sweeping” or modulation field current is supplied at mains frequency and is also variable. (Note that the frequency of the field modulation is enormously less than the magnetic resonance frequency.) Varying the amplitude of the field modulation varies the rate at which the sample is swept through the resonance.

The oscilloscope time-base is driven in synchronism with the sweep field, and either a sinusoidal or linear time-base may be used. The “phase” control is provided to adjust the relative positions of the NMR signals.

Detecting the NMR signal

Very briefly, the method used to detect the NMR signal is as follows:

The sample is enclosed in a small coil of inductance L and resistance r tuned by capacitance C . The current

$$i = i_o \cos \omega t$$

is maintained in the coil at the resonant frequency

$$\nu = \frac{\omega}{2\pi} = \frac{1}{2\pi\sqrt{LC}}$$

by means of a feed-back circuit designed to hold i_o at constant amplitude. The feed-back power required to do this depends on the Q , defined by

$$Q = \frac{\text{mean energy stored in circuit}}{\text{energy dissipated per unit angular frequency}} = \frac{\frac{1}{2}Li_o^2}{\frac{1}{2}ri_o^2/\omega} = \frac{\omega L}{r}$$

For $Q \gg 1$ the series r is equivalent to a shunt $R = \omega LQ$, which gives an equivalent circuit (Fig. 1) more convenient for analysis. R is the shunt impedance (resistive) at resonance. A change in Q due to NMR absorption in the sample results in a change in R given by

$$\Delta R = \omega L \Delta Q$$

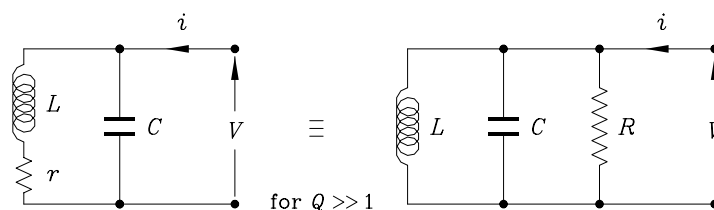


Figure 1: Equivalent series and parallel loss resistances

Since the resonant circuit is excited from a constant current source, the change in *rms* voltage across at the resonant frequency will be

$$\Delta V = \omega L \Delta Q i_o$$

and this signal, together with the inevitable “noise” fluctuations, is amplified and displayed on the oscilloscope. For more information see Rushworth and Turnstall, N.M.R. section 3.2.2, p. 58 and their Reference 97.

Experiment

1 Study of Proton NMR, and Measurement of Magnetic Fields

No trouble should be experienced in observing proton NMR signals so this is the first task to be attempted. As strong magnetic fields will be encountered it would be a good idea to

TAKE OFF YOUR WRISTWATCH

- (1) First check that the Teslameter is correctly calibrated. Use it to calibrate the magnetic field strength B versus current I for the uniform magnetic field of the large electromagnet.

Read the instructions on the magnet control panel. For some suitable field strength, e.g. 0.3 T (T=tesla = Wb/m² = 10⁴ gauss), calculate the NMR frequency for protons using the data in the Appendix.

- (2) Set the current (approximately) by using your magnetic calibration chart and select the appropriate oscillator coil. Handle coils by gripping the black base and line up the pins correctly before pressing into the female socket. Set the oscillator frequency using the coarse and fine frequency controls so that the frequency meter reads the calculated value.

Set R.F. level meter reading to about 10 on the $\times 10$ scale and insert either the tube packed with rubber bands or that containing paraffin oil.

- (3) Plug the field modulation coils into the “1A” socket (at the side of the control box), switch the oscilloscope to the “xy” mode and use the position controls to centre the spot on the screen. Set the CH1 gain at 1 V/div and CH2 at 20 mV/div. Turn on the 50 Hz sweep field.

“Tune in” the NMR signal with the fine frequency tuning knob.

Try the “phase” control on the field modulation, centre the NMR signals with the fine magnet-current control and work out the explanation of the effects each of these adjustments has on the display.

- (4) Record all relevant setting up details and observations. You may expect a slow drift in both magnetic field and oscillator frequency for about half an hour after switching on.
- (5) Measure the oscillator frequency with the frequency meter supplied and note that a change in the “R.F. level” setting requires returning the oscillator to the NMR frequency. Check, against the frequency meter, that this does not, however, shift the actual NMR frequency if the magnetic current remains unchanged.
- (6) Calculate the actual value of B from this frequency and compare with your calibration chart. Repeat this for a few B values and compare with your chart.
- (7) Spend a short time systematically manipulating the various controls in order to obtain a clear understanding of the variables governing the behaviour of the apparatus. Vary the oscillator tuning, fine and coarse magnet-current controls, the time-base phase and the modulation amplitude. (Note that the red lead to the field modulation coils must be plugged into the middle socket on the control box for the last operation.)
- (8) Switch on the linear time base by turning the time/div knob to about 2 ms, synchronise to a sub multiple of 50 Hz and examine the NMR signals on a linear time scale. Note that resonance occurs as the modulation field passes through zero when three or more signals are equally spaced on this time-base display. Indicate on a sketch of modulation-field against time where the NMR signals appear, with respect to the modulation cycle, when the NMR is not at a zero of the modulation field.
- (9) Devise a simple method for calibrating the modulation field amplitude ($\frac{1}{2}$ peak-to-peak excursion) in terms of the proton NMR frequency and hence in gauss. Consult a demonstrator if necessary.
- (10) Measure the sweep field amplitude with 1 ampere in the coils (socket marked “1 A”).
- (11) Estimate the width in gauss of the NMR signal at half maximum. Discuss the major contributions to this width. The true line width for protons in water is about 10^{-3} gauss. Does the width vary as the sample is moved away from the axis of the pole gap? If so, why?
- (12) From the above set of measurements estimate the accuracy with which the uniform field can be determined. This is best done using a low modulation field. Why?
- (13) Calculate the ratio of NMR frequencies for deuterons and protons using data from the Appendix. The deuteron signal is very weak. To find it, choose a value of B so that NMR frequencies for both protons and deuterons can be reached, find the proton signal and then shift to the deuteron frequency with a heavy water sample in the appropriate coil.

2 Detailed Study of NMR Signals

- (14) Observe and record in reasonable detail the following NMR signals for fixed frequency and modulation field settings. Note any changes in B -field fine-current settings required to locate the various NMR signals.

- (a) Signals for rubber, paraffin and lubricating oils.
- (b) The signal for deionized water as you quickly swing the fine current control onto the resonance value from below or above.
Wait a few seconds between repetitions of this.
- (c) Signals for the Fe^{+++} -doped water samples.

Note that in very pure water relaxation effects are weak, and it takes several seconds for the proton spin states to return to thermal equilibrium when the equilibrium ratio is disturbed. The introduction of paramagnetic ions, e.g. Fe^{+++} , increases the relaxation rate.

- (15) Give a qualitative discussion of the details of and differences between these various signals in terms of relaxation effects and saturation. Discuss briefly the origin of the “wiggles” associated with a number of these signals.

Problems

- Assuming a magnetic field of 1 T (10^4 gauss) calculate the NMR frequencies for electrons, protons, deuterons, ^7Li and ^{19}F using constants listed in the Appendix.
- Show that a coil of n turns, cross-sectional area A m² and of high Q (≈ 100), tuned to resonance at f MHz and with a *rms* voltage V volts across it, generates an oscillating magnetic field at its centre of approximate amplitude

$$B_f = \frac{QV}{nAf\pi\sqrt{2}} \times 10^{-6} \text{ T}$$

Estimate the oscillating field amplitude (in gauss) in coil B (tuning range 4.7 to 14 MHz) for which

$$Q = 110, \quad n = 22 \text{ turns} \quad \text{and} \quad A = 1.2 \times 10^{-4} \text{ m}^2$$

when it is tuned to 10 MHz and the R.F. level meter indicates $10 \mu\text{A}$. (Note: there is a calibration graph of V rms vs I rms provided for the coil.)

- Show that if the polarizing magnetic field is

$$B(t) = B_o + B_m \sin \Omega t$$

the maximum rate of change of the field is

$$\left(\frac{dB}{dt} \right)_{\max} = \Omega B_m$$

Hence calculate the sweep rate (in gauss/s) in the magnet gap when the modulation coils are plugged into the 1A socket.

If the proton “line width” is of order 0.1 gauss and the NMR frequency is 10 MHz, estimate the number of complete precession periods made by a proton in the time required to sweep through the resonance.

List of Equipment

- Electromagnet and power Supply
- R.F. oscillator and power supply
- Decade scaler for R.F. oscillator output
- 3 R.F. coils (interchangeable)
- Sweep field control unit

6. Hitachi V202F oscilloscope
7. HP 5314A universal counter
8. Group 3 DTM-130 digital teslameter
9. 10-12 sample tubes (pyrex)
10. Samples rubber bands deionized water
 paraffin oil 10^{18} Fe⁺⁺⁺ ions/cm³ in water
 lubricating oil 10^{19} Fe⁺⁺⁺ ions/cm³ in water
 sodium arsenite 5×10^{20} Fe⁺⁺⁺ ions/cm³ in water
 heavy water
11. Calibration charts for: magnet field versus current
 R.F. oscillator frequency versus dial setting for each coil
 rms voltage across specimen versus R.F. level

R. Garrett

P. H. Barker

May, 2004.

Appendix

Physical Constants

electron mass	m_e	=	9.10831×10^{-31} kg
proton mass	m_p	=	1.67241×10^{-27} kg
electron charge	e	=	1.60206×10^{-19} C
electron charge/mass ratio	e/m_e	=	1.75890×10^{11} C kg ⁻¹
Planck constant	h	=	6.62517×10^{-34} J s = 4.1354×10^{-15} eV s
Planck constant/ (2π)	\hbar	=	1.05443×10^{-34} J s = 6.5817×10^{-16} eV s
Boltzmann constant	k	=	1.38044×10^{-23} J K ⁻¹
Avogadro constant	N	=	6.02486×10^{23} mol ⁻¹
nuclear magneton	μ_{nm}	=	$e\hbar/(2m_p) = 5.05038 \times 10^{-27}$ J T ⁻¹
proton magnetic moment	μ_p	=	$2.79275\mu_{nm} = 1.41044 \times 10^{-26}$ J / T
proton gyromagnetic ratio	γ_p	=	2.675×10^8 rad s ⁻¹ T ⁻¹

²H₁ : nuclear spin number $I = 1$ magnetic moment $\mu = 0.8574\mu_{nm}$

⁶Li₃ : nuclear spin number $I = 1$ magnetic moment $\mu = 0.8220\mu_{nm}$

⁷Li₃ : nuclear spin number $I = \frac{3}{2}$ magnetic moment $\mu = 3.2563\mu_{nm}$

¹⁹F₉ : nuclear spin number $I = \frac{1}{2}$ magnetic moment $\mu = 2.6275\mu_{nm}$