

# Nuclear Magnetic Resonance

Ksenija Kovalenka

10485506

*School of Physics and Astronomy*

*The University of Manchester*

(Dated: November 5, 2021)

Nuclear magnetic resonance technique was used to determine the gyromagnetic ratios of proton and fluorine, later to high precision. They were obtained to be  $\gamma_p = (2.66 \pm 0.04) \times 10^8 \text{ s}^{-1}T^{-1}$  and  $\gamma_f = (2.5182 \pm 0.0008) \times 10^8 \text{ s}^{-1}T^{-1}$ , respectively. Spin-lattice relaxation times were investigated in aqueous glycerol and ferric nitrate solutions. For pure water, the value of relaxation time was obtained to be  $T_1 = (1600 \pm 200) \text{ ms}$  and for glycerol it was  $T_1 = (54 \pm 5) \text{ ms}$ .

## I. INTRODUCTION

Nuclear Magnetic Resonance (NMR) phenomenon refers to the absorption of the radio waves by nuclei in the magnetic field. Resonance was first successfully observed by Gorter in 1936 in lithium fluoride and potassium crystals [1]. Later, the main use of NMR for probing chemical structures was developed. Nowadays, NMR techniques allow to determine the composition and molecular structure of the unknown compounds, and test the purity of the known ones. It also underlays magnetic resonance imaging, widely used in diagnostics [2]. In this report, the important properties related to the NMR are discussed for a number of sample substances.

## II. THEORY

### A. The Gyromagnetic Ratio

In classical picture, nuclear spin in the magnetic field is described similarly to a gyroscope in the gravitational field, precessing about the direction of the field with some specific frequency. It can then absorb electromagnetic radiation, when the frequency of radiation reaches the precession frequency, called Larmor frequency.[3]

In quantum mechanics, such absorption is described by fine splitting of energy levels of an atom due to nuclear spin interaction with the external field. Photons are absorbed by nuclei when they transition in between levels, which only happens at the specific frequency corresponding to the energy gap.

Each nucleus has a total angular momentum  $\mathbf{J}$  and magnetic moment  $\boldsymbol{\mu}$ , which are parallel. Thus, the following proportionality relation can be written:

$$\boldsymbol{\mu} = \gamma \mathbf{J}, \quad (1)$$

where  $\gamma$  is the gyromagnetic ratio, unique for each nucleus. For a spin  $\frac{1}{2}$  particle, possible quantum numbers of  $\mathbf{J}$  are  $j = \pm \frac{1}{2}\hbar$ . Magnetic energy of a nucleus in the magnetic field  $\mathbf{B}$  is given by the Hamiltonian

$$H = -\boldsymbol{\mu} \cdot \mathbf{B} = \mp \frac{1}{2} \gamma \hbar B_z, \quad (2)$$

where  $B_z$  is the component of magnetic field in the z direction. The z-axis is arbitrary, so  $B_z$  becomes the magnitude of the field  $B$ . This gives an energy gap  $\Delta E$  of

$$\Delta E = \gamma \hbar B_z. \quad (3)$$

Equating it to the energy of the photon, produces the key relation for determining the gyromagnetic ratio of chosen nucleus as follows

$$\gamma \hbar B = \hbar \omega \quad (4)$$

$$\omega = \gamma B, \quad (5)$$

where  $\omega$  is the angular velocity of the radiation [4].

### B. Spin-Lattice Relaxation Time

A sample exposed to the static magnetic field becomes magnetised. It does so by transitioning nuclear spins to be aligned with the external field to minimise energy of the system, transferring the excess energy to the surroundings. Such process will continue to be observed until it reaches the limit of the surroundings to receive energy, corresponding to the Boltzmann distribution of the population

$$\frac{N_-^0}{N_+^0} = e^{-\Delta E/kT} = e^{-\gamma \hbar B/kT}, \quad (6)$$

where  $T$  is the temperature of the surroundings,  $k$  is the Boltzmann constant,  $N_+^0$  and  $N_-^0$  are the equilibrium populations of spins  $+\frac{1}{2}$  and  $-\frac{1}{2}$ , respectively.

The differential equation for the difference in spin populations  $n = N_- - N_+$  can be formed and solved, if the probabilities of up and down energy transitions  $W \uparrow$  and  $W \downarrow$  are introduced. It follows that

$$\frac{dN_+}{dt} = N_- W \downarrow - N_+ W \uparrow \quad (7)$$

$$\frac{dn}{dt} = N(W \downarrow - W \uparrow) - n(W \downarrow + W \uparrow) = \frac{n_0 - n}{T_1}, \quad (8)$$

where  $N$  is the combined population number.  $n_0$  and  $T_1$  are constants derived from the probabilities and population numbers for simplicity. The solution is

$$n = n_0 + Ae^{-t/T_1}, \quad (9)$$

which defines  $T_1$  as the characteristic relaxation time for a magnetised sample to return to the thermal equilibrium spin population due to interactions with surroundings and  $n_0$  as the population difference it is approaching.  $A$  is the initial population difference at time zero. It can be shown that absorption power is directly proportional to the spin population difference. Therefore, if the sample becomes magnetised, its ability of absorbing radiation reduces exponentially with the characteristic time  $T_1$  [5].

### III. EXPERIMENTAL APPROACH

#### A. Apparatus

The main setup used for performing NMR experiment is shown in Fig. 1.

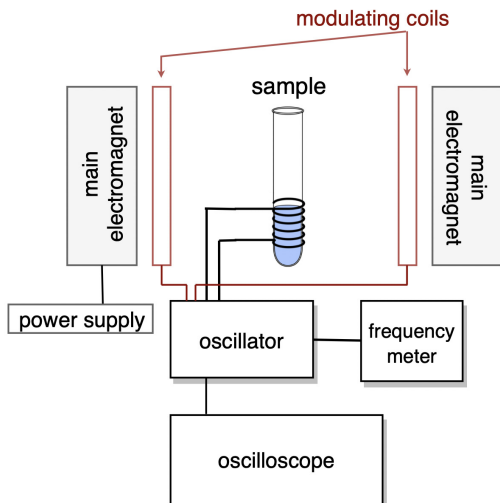


FIG. 1. Apparatus diagram, showing the setup of a sample, a magnet, modulating coils and analysing electronics. Radio frequency signal is transmitted via oscillator coil tightly wound around the sample.

It included a sample, a main electromagnet, providing uniform field and sweep coils, which modulate the main field, scanning through the resonance with mains frequency. Pure water, glycerol, ferric nitrate and a fluoro-carbon compound were used as samples. Electronics included an oscillator circuit, a frequency meter and an oscilloscope. Electromagnetic radiation with radio frequency was produced by the oscillator circuit in the cavity, where the sample was placed. Resonance was then tuning the Q factor of the oscillator circuit, allowing us to see the modulated amplitude of the radio waves on the

oscilloscope screen. Other output of the circuit was sent to frequency meter, allowing frequency measurements to high precision. Sinusoidal modulation was later replaced with two pulse waveform for measuring relaxation times.

Uniform magnetic field was measured using the hall effect probe, which had a dominant error compared to a frequency measurement of about 1 mT. Other required measurement such as peak height and difference between pulses for relaxation time part of the experiment were obtained using the cursor of the oscilloscope, with subsequent errors related to this procedure.

#### B. Analytical technique

For the first part of the experiment, two samples were used: glycerol and pure water. For a set constant frequency of radio waves, main magnetic field was gradually changed by varying current supply to the electromagnet until resonance peaks appeared on the oscilloscope screen. We have investigated the line width of the peaks at different horizontal and vertical positions of the sample to determine the position and size of the region of most uniform magnetic field. Then, fine tuning of the field was used to make peaks equally spaced, as it represents resonance occurring when the modulation field goes through zero. While doing so, the modulation amplitude was minimised, which allowed to find the required position more precisely. When peaks were equally spaced, modulation was switched off and the static field was recorded along with the frequency of radiation. Measurements were repeated at different frequencies and using Eq. (5) together with the linear fit,  $\gamma$  for proton resonance was determined.

As the dominant error was related to the magnetic field measurement (0.03% compared to 0.003% uncertainty in frequency measurement), the ratio of resonant frequencies was used to determine the gyromagnetic ratio of fluorine. Resonant frequencies for glycerol and fluoro-carbon compound were recorded for a fixed magnetic field values. A linear plot of two resonant frequencies and the literature value for proton  $\gamma_p$  [6] (known to high precision) was used to determine the  $\gamma_f$  for fluorine to high precision.

For finding spin-lattice relaxation time, two pulse waveform modulation was used instead of the sinusoidal scan. Each pulse scanned through the resonance once, time between pulses  $P_1$  and between pairs of pulses  $P_2$  was adjustable. As described in section II B, absorption power is reduced if the magnetised sample did not return to the equilibrium population so a reduction in the second peak height was observed. Measured peak difference is proportional to the population difference caused by relaxation of the spins, so using Eq. (9) allowed to determine  $T_1$  via a logarithmic plot against time between peaks  $P_1$ . Measurements and calculations for  $T_1$  were done for a range of aqueous glycerol and paramagnetic salt compounds to investigate the relaxation time dependence on

viscosity and paramagnetic ion concentration. Viscosity was calculated from glycerol concentration. Errors were estimated from the standard deviation of repeated measurements of the first peak.

#### IV. RESULTS

The gyromagnetic ratios for proton and fluorine were obtained as  $\gamma_p = (2.66 \pm 0.04) \times 10^8 \text{ s}^{-1}\text{T}^{-1}$  and  $\gamma_f = (2.5182 \pm 0.0008) \times 10^8 \text{ s}^{-1}\text{T}^{-1}$ , respectively. Both values agree with the accepted ones [6], although as expected from the procedure,  $\gamma$  for fluorine has much greater precision, with only 0.007% error.

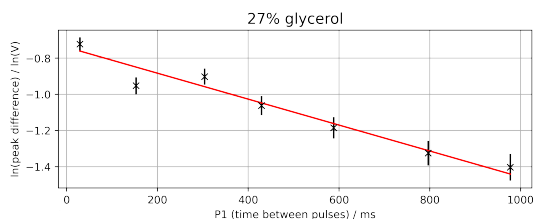


FIG. 2. Characteristic plot of logarithm of peak difference against time between peaks used for determining  $T_1$ .  $\chi_R^2 = 1.58$  for this plot.

The spin-lattice relaxation time dependence on viscosity and paramagnetic ion concentration are shown in Fig. 3. Characteristic plot for obtaining  $T_1$  for one of the solutions is shown in Fig. 2.  $T_1$  for pure water was obtained to be  $(1600 \pm 200) \text{ ms}$  and for glycerol  $(54 \pm 5) \text{ ms}$  [7] both values lie within the range suggested by previous finding.

Plots suggest a vague inverse proportionality trend in both cases, which was originally described by Bloembergen [8]. In general, the decrease of  $T_1$  with viscosity and number of paramagnetic ions in the compound can be expected from the increased coupling of the system with the surroundings allowing greater rate of energy transfer in both cases. However, the inverse proportionality re-

lation is heavily distorted by the chemical shift of each compound caused by the change in local environment of the resonating protons.

#### V. CONCLUSION

Main values, which this experiment aimed to obtain, were calculated consistently with the previously known results [6] [7]. Gyromagnetic ratios were obtained as  $\gamma_p = (2.66 \pm 0.04) \times 10^8 \text{ s}^{-1}\text{T}^{-1}$  and  $\gamma_f = (2.5182 \pm 0.0008) \times 10^8 \text{ s}^{-1}\text{T}^{-1}$  for proton and fluorine resonance, respectively. Plots are showing general trends justified physically, but a remain inconclusive in terms of specific model due to a number of various contributions to the system, which were not considered.

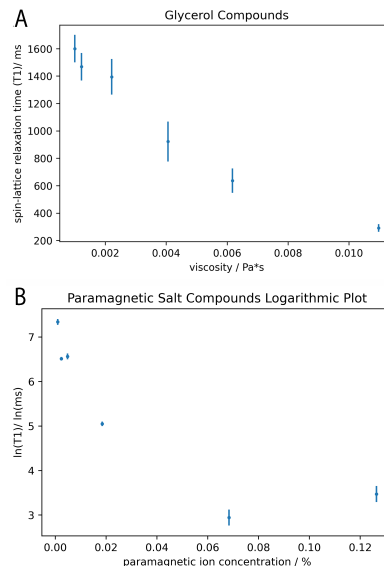


FIG. 3. Plots showing the spin-lattice relaxation time for different aqueous compounds. Plot A:  $T_1$  against the viscosity of the water-glycerol solutions. Plot B: natural logarithm of  $T_1$  against paramagnetic ion percentage concentration.

[1] E. Andrew and E. Szczesniak, A historical account of nmr in the solid state, *Progress in Nuclear Magnetic Resonance Spectroscopy* **28**, 11 (1995).  
[2] J. Branson, Nuclear magnetic resonance (nmr and mri), [https://quantummechanics.ucsd.edu/ph130a/130\\_notes/node271.html](https://quantummechanics.ucsd.edu/ph130a/130_notes/node271.html) (2013), accessed: 2021-10-02.  
[3] R. P. Feynman, *Lectures on physics*, Addison-Wesley **II** (1964).  
[4] E. R. Andrew, *Nuclear Magnetic Resonance* (Cambridge University Press, 1955).  
[5] C. Slichter, *Principles of Magnetic Resonance* (Harper and Row, 1963).

[6] A. U. Database, Nmr properties of commonly studied isotopes, <http://www.acadiau.ca/~bellis/resources/nmr/isotopes.tml>.  
[7] A. D. Wexler, J. Woissetschläger, U. Reiter, G. Reiter, M. Fuchsjäger, E. C. Fuchs, and L. Brecker, Nuclear magnetic relaxation mapping of spin relaxation in electrically stressed glycerol, *ACS Omega* **5**, 22057 (2020).  
[8] N. Bloembergen, E. M. Purcell, and R. V. Pound, Relaxation effects in nuclear magnetic resonance absorption, *Phys. Rev.* **73**, 679 (1948).