NUCLEAR MAGNETIC RESONANCE

The phenomenon of nuclear magnetic resonance will be used to study magnetic moments of nuclei.

Theory:

In addition to its well-known properties of mass, charge, and intrinsic angular momentum (spin), the atomic nucleus possesses in general a magnetic moment. The classical analogy explaining the existence of a nuclear magnetic moment is that of a spinning, charged sphere.

The classical magnetic moment of a spinning sphere with charge $q$ and mass $M$ uniformly distributed throughout its volume is:

$$\vec{\mu} = \frac{q}{2M} \vec{L}$$

where $\vec{\mu}$ is the magnetic moment and $\vec{L}$ is the angular momentum.

If this charged, spinning sphere (a magnetic dipole with magnetic moment $\vec{\mu}$) is placed in a uniform magnetic field $\vec{B}$, the (classical) energy is

$$E = -\vec{\mu} \cdot \vec{B}$$

To obtain the correct (quantum mechanical) expression for the energy due to the nucleus being placed in a magnetic field, the correct relation between $\vec{\mu}$ and $\vec{L}$ must be used, and the quantization of angular momentum must be considered. The correct relation between $\vec{\mu}$ and $\vec{L}$ is

$$\vec{\mu} = g \frac{e}{2M} \vec{L} = \gamma \vec{L}$$

where $g$ (the Lande splitting factor) and $\gamma$ (the gyromagnetic ratio) are numbers characteristic of a particular nuclear isotope in a particular nuclear energy state. The symbol $M$ denotes the proton mass and $e$ the proton charge. It is usual to express the angular momentum in terms of $\vec{I}$, the nuclear spin vector, using the relation $\vec{I} = \vec{L} / h$ where $h = h/2\pi$ and $h = $ Planck’s constant. Thus:

$$\vec{\mu} = \gamma \frac{h}{2\pi} \vec{I}$$

The largest observable value of $\vec{I}$ in a given direction, denoted $I$, and called the spin (or spin quantum number), is integral or half-integral. That is, it can only have values such as 0, $\frac{1}{2}$, 1, $\frac{3}{2}$ ... Each nuclear ground state is characterized by just one value of $I$. Substituting into the energy expression,

$$E = -\vec{\mu} \cdot \vec{B} = -\gamma h \vec{I} \cdot \vec{B} = -\gamma h \frac{h}{2\pi} \vec{I} \cdot \vec{B}$$

(5)
where \( \hat{B} \) is a unit vector in the direction of \( \vec{B} \). However, the quantization of spin (angular momentum) leads to discrete energy levels rather than a continuous range of energies. The expression \( \vec{I} \cdot \hat{B} \) can be interpreted as ‘the component of \( \vec{I} \) in the direction of \( \vec{B} \)’. According to quantum mechanics, the only permitted values of \( \vec{I} \cdot \hat{B} \) are \(-I, -I + 1, \ldots, I - 1, I\). The expression \( \vec{I} \cdot \hat{B} \) (i.e. the component of \( \vec{I} \) in a preferred direction) is given the symbol \( m \) and called the spin magnetic quantum number. Thus, substituting into the energy equation,

\[
E = -\gamma \hbar m B \quad m = -I, -I + 1, \ldots, I - 1, I
\]

Consider a sample of protons (hydrogen nuclei) placed in a magnetic field. Since the spin of the proton is \( \frac{1}{2} \), there are two energy states, corresponding to \( m = \pm \frac{1}{2} \), which are occupied when protons are placed in a magnetic field. The energy difference between these two states is

\[
\Delta E = -\gamma \hbar B\left(-\frac{1}{2}\right) - (-\gamma \hbar B\left(-\frac{1}{2}\right)) = \gamma \hbar B
\]

\[
\Delta E = (2.6752 \times 10^8 \text{ s}^{-1}\text{T}^{-1})(1.0546 \times 10^{-34} \text{ J} \cdot \text{s}) \cdot B
\]

\[
\Delta E = (2.821 \times 10^{-26} \text{ J/T}) \cdot B
\]

If radiation of the frequency \( \Delta E/\hbar \) \( (= \nu_o) \) is supplied to the protons in the magnetic field \( B \), transitions between the two possible energy states will occur. This ‘resonance’ condition can be written as

\[
\nu_o = \left(\frac{2.821 \times 10^{-26} \text{ J/T}}{\hbar}\right) \cdot B
\]

\[
\nu_o = (4.2576 \times 10^7 \text{ s}^{-1}\text{T}^{-1}) \cdot B
\]

\[
\nu_o = (42.576 \text{ MHz/T}) \cdot B
\]

From a quantum mechanical calculation, it is found that for protons in a magnetic field, being supplied with electromagnetic energy of the resonance frequency, the probability of a transition from the lower energy state to the higher (absorption) is exactly equal to the probability of a transition from the higher energy state to the lower (stimulated or induced emission). If the number of nuclei (protons) in each state is the same, then no net absorption of power will occur and no resonance can be observed. However, if the protons are in equilibrium with their surroundings, then each energy state will be populated according to the Boltzmann distribution. Thus there will be a (small) excess of protons in the lower energy state. It is this excess that allows observation of resonance.

Resonance can be observed by measuring the absorption of the supplied electromagnetic energy as a function of its frequency. At the resonance frequency, this absorption should abruptly increase.
As power is supplied to the system at the resonance frequency, the excess number of protons in the lower energy state will decrease and soon no more absorption will be observed. This is called saturation. However, the spin-lattice interaction between the protons and their surroundings, causing an energy transfer from the spin system to the surroundings due to Brownian motion and lattice vibration, tends to restore the Boltzmann distribution, and allow further power absorption. The spin-lattice interaction (also called relaxation) is characterized by a time constant $T_1$. The shorter $T_1$, the more power can be supplied without reaching saturation, and hence the stronger the resonance signal.

There is also an interaction between neighbouring nuclear spins (spin-spin interaction) which causes a slight shift in the energy states for each proton in the applied magnetic field. This causes a broadening of the resonance signal, since there is no longer a well-defined frequency at which power absorption will occur. In order to facilitate observation of the resonance signal, paramagnetic ions may be added to the sample to broaden the resonance signal. Signal broadening also results from inhomogeneity of the external magnetic field.

Careful study of the signal obtained in a nuclear magnetic resonance experiment leads to information concerning crystal structure and chemical binding in the sample. The technique of observation of nuclear magnetic resonance is also used to study magnetic moments of various substances. Finally, a more practical application of NMR is the accurate measurement of magnetic fields. An accuracy of 1 part in $10^5$ can be obtained for magnetic fields from $10^2$ to $10^5$ gauss (0.01 to 10 T).

A relatively recent application of NMR is in diagnostic medical imaging (MRI – magnetic resonance imaging).

MRI is based on two principles:
1. the magnetic resonance frequency depends on the value of the magnetic field;
2. the relaxation time depends on the nature of the surroundings of the resonating nuclei.

In MRI the hydrogen nuclei (proton) concentration is measured. By providing a magnetic field that varies uniformly across the subject, protons at different positions will have different resonance frequencies. Measurement of the relaxation times of these hydrogen nuclei gives an indication of the types of tissues surrounding the hydrogen nuclei.

Thus by applying the appropriate magnetic field gradients and detecting the proton resonant signal in sufficient detail, MRI provides a ‘picture’ of a two-dimensional ‘slice’ through the subject at any desired location.

Advantages of MRI over x-ray imaging are its more-detailed images of soft tissues and its non-ionizing nature.

**Apparatus:**

The sample probe consists of a 7 mm glass tube filled with glycerine (a good source of hydrogen nuclei (protons)). The tube is surrounded by a coil to provide the high frequency electromagnetic energy.
To observe the resonance signal, the external magnetic field is modulated. A pair of Helmholtz coils powered at ac line frequency is used for this, one coil placed on either side of the sample. The entire arrangement is placed between the polefaces of an electromagnet (see Figure 1).

![Diagram of NMR apparatus](image)

**Figure 1**

A marginal oscillator (Alpha Scientific Laboratories, Inc. Model AL 675 NMR-EPR) is used to produce the radio frequency (rf) electromagnetic power and to detect resonance. If the marginal oscillator is approximated as a constant current source, then at resonance the power loss increases suddenly due to absorption in the sample. This is detected as a voltage drop which is amplified and detected on an oscilloscope. The advantages of the marginal oscillator are compactness and simplicity but it cannot be used to study the resonance signal in detail.

To better understand how the apparatus is used, refer to Figure 2, a plot of energy vs. time.
Since the Helmholtz coils are connected to a power unit (A.C. Sweep AL 679) oscillating at 60 Hz, the net magnetic field experienced by the sample (the sum of the Helmholtz field and the electromagnet field) is

\[ B_{\text{net}} = B + B' \sin[(377 \text{ rad/s}) \cdot t] \]

Thus the energy difference between spin states of the sample, \( \Delta E \), also oscillates sinusoidally, between the values

\[ \gamma \hbar (B + B') \text{ and } \gamma \hbar (B - B') \]

The magnitude of \( B' \) with respect to \( B \) is greatly exaggerated in Figure 2.

Suppose rf power of frequency \( v_1 \) is fed to the sample. Since, as shown in Figure 2, the rf energy (\( h v_1 \)) is always lower than the energy between states, no absorption can occur and no resonance signal is obtained. If the rf frequency is increased to \( v_2 \) then, as shown in Figure 2, absorption can occur and a resonance signal is produced, since the energy supplied (\( h v_2 \)) equals the energy between states twice for each cycle of the modulated magnetic field. By adjusting the frequency of the rf energy, the resonant frequency for the electromagnet field alone can be determined (i.e. \( h v_0 = \gamma \hbar B \)).
By measuring $v_0$ and $B$ at resonance the magnetic moment of the sample can be calculated. Alternatively, by measuring $v_0$ and knowing $\gamma$ a value for $B$ can be calculated.

Figure 3 is a block diagram of the electronics used in this experiment.
**Procedure and Experiment:**

1. Ensure that the dials on the Power Supply and Regulator are set to zero.

2. Turn on the water supply to cool the magnet windings.

3. Turn on the digital multimeter and set it to the 10 A DC scale.

4. Turn on the Power Supply and Regulator, and adjust the Regulator so that the pointer is within the black (controlled) region of the meter. The Regulator controls the current through the magnet, and the Power Supply is used to adjust the Regulator for proper regulation. Vary the current through the magnet using the controls of the two devices, always keeping the Regulator pointer within the black region, until you are familiar with the operation of the equipment.

5. Before continuing with the experiment, the magnet must be de-magnetized. This is done in a similar manner as was used for the β-ray Spectrometer magnet.

The current direction can be changed by placing the Regulator output cable in the other output socket (but only do this when the Power Supply is set to zero). Using the Power Supply dial alone (i.e. don’t worry about keeping the Regulator pointer in the regulation zone) increase the magnet current to 2.5 A, decrease to 0, change output cable connection, continue decreasing to –2.5 A, then increase to 0.

Repeat for current limits of 2.3 A and –2.3 A and proceed in 0.2 A steps until the cycle 0 → 0.1 A → 0 → –0.1 A → 0 has been completed. The magnet has now been de-magnetized.

*When demagnetizing, do not change the Regulator output cable connection until the Power Supply is set to 0.*

6. Turn on the oscilloscope. Set the scales at 0.1 V/cm (unless otherwise advised) and 2 ms/cm. Use ‘line’ or ‘ac’ triggering.

7. Turn on the Power Designs DC Supply and check that it is set for 9.20 V.

8. Turn on the AC Sweep unit and set the dial just slightly less than fully clockwise.

9. Turn on (plug in) the frequency counter.

10. Connect the 1.0-2.3 kG probe to the NMR-EPR marginal oscillator and the AC Sweep unit. Place the glycerine sample in the sample hole of the probe.

    Set the oscillator selector switch to ‘B’.

    Turn on the oscillator and adjust the oscillator current control until noise is observed on the oscilloscope trace.
Ensure that the probe (containing the glycerine sample) is placed in the centre of the polefaces of the electromagnet. Set the current in the magnet to 0.80 A and slowly adjust the oscillator frequency control until a resonance signal is obtained. (Resonance should occur at approximately 5.8 MHz.)

When the resonance signals are equally spaced on the oscilloscope trace, the oscillator frequency is equal to the resonance frequency \( v_0 \) corresponding to the magnetic field of the electromagnet. Why?

Record the resonance frequency.

Now remove the sample from the probe and measure the magnetic field by using the Hall probe.

*Ask your instructor to show you how to initialise and use the Hall probe.*

Repeat the measurements of resonance frequency and magnetic field for magnet currents of 0.95, 1.10, 1.25, and 1.40 A.

Set the current to 1.10 A, re-measure the resonant frequency and magnetic field for glycerine (protons) and then replace the glycerine sample with the Teflon rod (a source of fluorine nuclei) and measure the resonant frequency.

**Analysis:**

1. For the glycerine (proton) data, plot resonant frequency versus magnetic field. Compare the slope of the graph to the value predicted by equation (11). i.e. Determine the resonant frequency per magnetic field value for protons.

2. Calculate the resonant frequency per magnetic field value for fluorine.

**References:**

Fretter, *Introduction to Experimental Physics*, QC 41  
Halliday, *Introductory Nuclear Physics*, QC 173  
Melissinos, *Experiments in Modern Physics*, QC 33  