PULSED NUCLEAR MAGNETIC RESONANCE

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INTRODUCTION

Basic scientific research has contributed significantly to the development of various fields and industries. In fact, certain techniques developed in the laboratory have proven so powerful that they are simultaneously utilized by several different fields. One such technique is pulsed nuclear magnetic resonance (NMR). For example, NMR is used by chemists to study the static structure of molecules and by physicians to image any of a number of body parts, an NMR technique that is known as magnetic resonance imaging (MRI) in the medical field. In order to fully understand the principles of this powerful tool, we must look toward quantum mechanical theory.

BASIC PRINCIPLES

Basic quantum mechanics states that an elementary system such as the nucleus has an intrinsic angular momentum. In the case of the nucleus, spin angular momentum is given by the equation

$$S = \hbar\sqrt{I(I+1)}, \qquad (1)$$

where I is a spin quantum number. According to the indeterminacy that is an inherent part of quantum theory, the value of S can only be known in one direction; thus if we restrict the orientation of the spin angular momentum of a nucleus by specifying the spin angular momentum in that direction, let this be the z-direction, then

$$S_z = m\hbar, \qquad (2)$$

where m is an integer or half-odd integer ranging from -I to I.

The fact that an intrinsic magnetic moment μ is associated with the nucleus can easily be understood if we think of spin angular momentum in the classical sense and take into consideration that the nucleus carries a charge. (See Figure 1.) The magnetic moment is given by

$$\mu = \gamma\hbar I \qquad (3)$$

where γ is the gyromagnetic ratio of a specific nucleus; for a hydrogen nucleus, this value is $2.68 \times 10^8\, rad/s\cdot T$.

If we place a sample, such as water, with hydrogen molecules that possess intrinsic magnetic moments in a static magnetic field H_0, the interaction energy between one of the magnetic moments μ and the magnetic field is given by

$$E = -\bar{\mu}\cdot\overline{H_o}. \qquad (4)$$

If we identify the static field with the z-direction, then

$$E_m = -\gamma S_z H_o = -\gamma m\hbar H_o. \qquad (5)$$

For spin one-half particles, to which our discussion will be limited, m can have a value of $\pm 1/2$. This demonstrates that there is a splitting of energy levels, called Zeeman splitting, due to the interaction of a magnetic moment (spin) with a static magnetic field. (See Figure 2.) This splitting of energy levels corresponds to the two possible alignments of a spin with the static field -- parallel or anti parallel to the field, the former being the lower of the two energy levels.

The energy difference between the two Zeeman states is given by the equation

$$\Delta E = \gamma\hbar H_o. \qquad (6)$$

Thus if we irradiate the system with a time-varying electromagnetic field of angular frequency ω where

$$\hbar\omega = E = \gamma\hbar H_o, \qquad (7)$$

transitions will be induced between the two energy levels. If we place a sample of water in a fixed static field H_0 the frequency of the electromagnetic radiation is restricted by the condition

$$\omega = \gamma_p H_o. \qquad (8)$$

Spins in the lower energy state will be excited to the higher energy state by the energy of the electromagnetic radiation and vice-versa. When the electromagnetic radiation is turned off, we observe the relaxation of the system, as the spins return to their equilibrium distribution and give up energy to the lattice in the process. However, there is more to this simple description as we will discuss using thermodynamics and the phenomenon of the precession of a magnetic moment in a magnetic field.

Consider a sample of water that is placed in a static magnetic field H_0. The energy level of N magnetic moments will split into the Zeeman states, with N_- spins in the higher energy level and N_+ spins in the lower energy level. If the lattice that these spins are in is assumed to be characterized by a single constant temperature T and to have a heat capacity that is large compared with the interaction energy between the spins and H_0, an assumption that is valid for room temperature, then the ratio of N_+ to N_- at thermal equilibrium is given by the Boltzmann factor

$$\frac{N_+}{N_-} = e^{\Delta E/kt} = e^{\gamma\hbar H_o/kT}. \qquad (9)$$

In the presence of a magnetic field $H_o = 2500G$ at room temperature $T = 295K$, the ratio indicates that more spins will be in the lower energy level than in the higher energy level

$$\frac{N_+}{N_-} = 1.00000173. \qquad (10)$$

Therefore, a net movement of spins from the lower energy level to the higher energy level occurs when we irradiate the system by electromagnetic radiation.

ROTATING FRAME OF REFERENCE

Before proceeding with the discussion of the rotating frame of reference, we must calculate the net magnetic moment of a sample of water in a magnetic field H_0. As the thermodynamics portrait illustrated, there are more spins parallel to H_0 than anti parallel. This means that the net magnetization will point along the direction of H_0. (See Figure 3.) Since our discussion pertains to hydrogen nuclei, it is important to remember that there are two hydrogen nuclei per molecule of water. Magnetization M is related to the net spin per unit volume of the sample, a quantity that is related to H_0 by the constant χ

$$\overline{M} = \chi \overline{H_O} \text{ where} \qquad (11)$$

$$\chi = \frac{N\gamma^2\hbar^2 I(I+1)}{[3kT]}. \text{ [Ref. }^1\text{]} \qquad (12)$$

In essence, χ is the ratio of the concentration of spins parallel to H_0 and anti parallel to H_0. For a fixed volume of water and a fixed value of H_0, we can calculate the net magnetization using the above information.

We must also note a magnetic moment placed in a magnetic field aligns itself with the field only if it can give up or gain some energy. If the energy of the magnetic moment remains constant, then the magnetic moment precesses about the magnetic field with a fixed frequency ω. We will not treat the specifics of the derivation of this frequency; it is sufficient to say that the precessional frequency, known as the Larmor frequency, is given by Equation 8.

In order to induce transitions between Zeeman states, the water sample is irradiated by an electromagnetic field H_1. Let H_1 be a field oscillating in the plane perpendicular to H_0. An oscillating field can be vectorally represented by two vectors rotating in opposite senses in the x-y plane. If H_1 satisfies the resonance condition

$$\omega_L = \gamma_p H_1, \qquad (13)$$

then H_1 can be depicted as rotating about H_0 at the Larmor frequency. As soon as H_1 is introduced, the net magnetization M will begin to tip towards the x-y plane and to process about both H_o and H_1; we can simplify this complex scenario if we study it from a rotating frame of reference. (See Figure 4.) If we choose a rotating frame of reference that rotates at the Larmor frequency, then M will appear to be stationary and so will H_1. M will then begin to precess about H_1 at the Larmor frequency -- which is equivalent to the tipping of M towards the x-y plane. The duration and intensity of H_1 can be controlled in order to tip M exactly into the x-y plane; such a pulse of H_1 is called a $\pi/2$ pulse. When the net magnetization is in the x-y plane, it has no component in the z-direction. This corresponds to an equal population of spins in each of the Zeeman states. Thus the first step of NMR has been completed. This process as seen from the more complex laboratory frame of reference is depicted in Figure 5.

T_1, T_2, and T_2* RELAXATION TIMES

We will discuss these relaxation times using the portrait of the net magnetization previously developed. The spin-lattice relaxation time T_1 is the time that it takes for the net magnetization M to return to thermal equilibrium once the H_1 pulse has been turned off. This relaxation time characterizes the method by which spins in the water sample give up the energy that they had absorbed to the lattice. But this is not the only relaxation time that characterizes a water sample. An individual spin in a water sample is not just subject to the static and oscillating magnetic fields described above. Instead, the spin will also perceive a magnetic field as a result of the precession of spins and as a result of magnetic impurities around it. Magnet inhomogeneity will also cause spins in different areas of the sample to perceive different magnetic fields. The result is that spins will precess at slightly different frequencies, and the net magnetization can no longer be portrayed by one vector. Instead, net magnetization must be portrayed by several different vectors precessing at slightly different frequencies which eventually leads to total dephasing of the magnetization and a decay of the measured signal. (See Figure 6.) The dephasing of M due to spin-spin interactions is characterized by the relaxation time T_2, while T_2* is a measurement of the dephasing of M due to magnet inhomogeneity. In most cases, dephasing of M due to magnet inhomogeneity dominates the signal decay.

APPARATUS

Before we can explore relaxation time measurements, the apparatus that we used in this particular NMR experiment merits discussion. (See Figure 7.) There are essentially two main stages to a pulsed NMR experiment -- when the pulse is on and the water sample is being irradiated by electromagnetic radiation and when the pulse is off and relaxation processes are being measured. A pulse is generated by using a stable frequency synthesizer, a radio frequency (RF) synthesizer in this case, that is eventually connected to a coil that lies in the plane perpendicular to H_o, the x-y plane. The RF synthesizer produces a continuous oscillating voltage that induces an oscillating electromagnetic field in the coil. This signal must be amplified and turned into a pulse whose width can be controlled. The RF power amplifier can be gated by a direct current pulse. This means that the RF signal will be transmitted to the power amplifier only when the direct current pulse is on, and thus the width of the dc pulse controls the width of the RF pulse. The RF amplifier, however, has a 50Ω input and output impedance. In order to have maximum power transfer, all circuit elements following the RF amplifier must have 50Ω input impedances. The circuit element that follows the RF amplifier is the sample coil; the coil is mainly inductive and partially resistive at the operating frequency of 10 MHz. Therefore, a tank circuit of two variable capacitors needs to be connected to the sample coil for impedance matching. It is essential to be able to control the capacitance of the capacitors because the impedance of the sample coil changes when different samples are placed in the coil, since they are dielectric materials. For a specific sample, we tune the tank circuit to give an impedance of 50 Ω in series with the coil.

When the pulse is turned off, the magnetic moments in the sample precess at various frequencies, given by $\omega = \gamma (H + \Delta H)$. Processing magnetic moments will cause a changing net magnetization in the x-y plane that will also induce an electromagnetic field in the sample coil, which we measure as a voltage signal. Therefore, the sample coil serves both as a transmitter of the RF pulse to the sample and as a detector of the relaxation processes. However, the voltage signal is in the micro volt range and so it must be amplified by a series of low-noise RF amplifiers. These amplifiers are quite sensitive and cannot survive a voltage input much larger than 1 V. Since the amplified pulse leaving the amplifier is usually tens of volts, it would destroy the amplifiers if it were allowed to reach them. A series of crossed diode pairs and a quarter-wavelength ($\lambda/4$) cable are used to solve this problem.

Diodes operate to let current flow in one direction if the voltage difference across them is larger than a turn-on voltage, 0.6 V for the diodes we used in this experiment. Otherwise, current cannot flow in either direction and they behave as open elements in the circuit. When the pulse is on, the voltage across the crossed diode pairs is much larger than 0.6 V so they are shorted; they allow the signal to pass through them unhindered. Here is where the role of the $\lambda/4$ cable comes in. At a frequency of 10 MHz, the wavelength of the RF pulse in a coaxial cable is about 20 meters. A $\lambda/4$ cable is therefore 4 m in length and has the following property. At 10 MHz, it has a high impedance when connected to crossed diode pairs to ground. The pulse will thus travel to the 50 Ω impedance tank circuit instead of the large impedance $\lambda/4$ cable. After the pulse is turned off, the micro volt signal voltage from the sample cannot short the diodes that follow the RF amplifier. The signal will travel through the $\lambda/4$ cable to the RF amplifiers, where it will be amplified and then multiplied with the continuously oscillating RF signal by the mixer. If two signals of about the same frequency (f) are multiplied together, the result is a superposition of two signals, one signal of about a frequency of 2f and the other with a frequency corresponding to the small frequency difference between the two signals. A 100 kHz low-pass filter is the final circuit element that the signal encounters before being displayed on the oscilloscope. This low-pass filter cuts out the 2f signal and noise at frequencies larger than 100 kHz. The signal displayed on the oscilloscope is a beat pattern between the RF input frequency and the Larmor frequency, so it becomes relatively easy to see when the system is at resonance, in other words when the condition of Equation (8) is satisfied.

PULSE SEQUENCES

As previously mentioned, the pickup coil lies in the x-y plane, so it detects changes in the net magnetization in that plane. A $\pi/2$ pulse tips the net magnetization into the x-y plane, but M begins to dephase because different spins in different parts of the sample are in different static magnetic fields due to spin-spin interactions and field inhomogeneity. The dephasing of M causes the signal that is detected right after the $\pi/2$ pulse to decay; this signal, seen on the oscilloscope screen is called a free-induction decay (FID) and is depicted in Figure 8[2]. The decay signal contains information about both the relaxation times of T_2 and T_2*. There is a clever pulse sequence, however, that can in essence reverse the dephasing of spins due to inhomogeneity of the magnet, and allows us to take T_2 and T_2* data separately.

The pulse sequence is a $\pi/2$ pulse followed by a π pulse a time τ afterwards. M is in the x-y plane following the $\pi/2$ pulse; dephasing due to random spin-spin interactions and magnet inhomogeneity causes certain spins to process at faster frequencies than other spins. A time τ later, spins have dephased by a certain amount. If the π pulse is applied at this time, the magnetization will be tipped towards the -z direction and back through to the x-y plane. The spins that were precessing at a faster frequency are now behind those that are precessing at a slower frequency, but the precessional frequencies are the same. Therefore at a time τ later, the spins are back in phase again. The signal that appears on the oscilloscope will be two FID's back-to-back with the maximum amplitude occurring at a time 2τ after the $\pi/2$ pulse; this signal is known as a spin-echo. However, the amplitude of the spin-echo has decayed since the $\pi/2$ pulse. (See Figure 9.) This decay in amplitude is due to the random spin-spin interactions and is thus a measurement of T_2, while the width of the spin-echo is a measurement of twice T_2*.

The pulse sequence to measure T_1 is a series of $\pi/2$ pulses spaced at regular intervals Δt apart. Each $\pi/2$ pulse will be followed by an FID signal whose amplitude will increase exponentially according to the value of the relaxation time T_1. (See Figure 10.)

EXPERIMENTAL DATA

Before data on relaxation times could be gathered, the current to field characteristics and the hysteresis of the electromagnet producing H_o had to be studied. Next we began collecting data to measure the relaxation times of a deionized water sample. We started out by measuring T_2 using the relationship between the exponential decay of the spin-echo signal and the time between the $\pi/2$ and π pulses. We measured a time T_2 that was shorter than we expected; we expect T_2 to be on the order of seconds for a pure water sample. Instead, we observed a rapid partially non-exponential decrease in the amplitude of the spin-echo. We found that this effect is documented in Farrar and Becker. (See Figure 11.)[3]

Incorrect measurements were made as a result of the diffusion of water molecules throughout the sample. If a water molecule, during the time of spin-echo amplitude measurement, diffuses to another part of the sample where it is subject to different magnetic fields, due to magnet inhomogeneity, then its spins will begin to precess at a different frequency. Data using the spin-echo will only be correct if spins continue to precess at the same frequency throughout the measurement process.

Since we could not correct magnet inhomogeneity, we began searching for samples where water molecules were localized such as in cell structures of celery or whose movement was restricted such as in a gelatin sample. We took T_2 measurements of these samples. Although the decay was less rapid, the T_2 measurements were not significantly increased.

There are various pulse sequences, documented in Farrar and Becker, to measure relaxation times without the interference of diffusion effects; these remain to be tried in future NMR experiments. Although results from the NMR experiment were inconclusive, the experiment proved to be a good introduction to the basic principles of NMR. Once relaxation time measurements are understood, then we can turn our attention to understanding the use of these relaxation time measurements in chemistry and medical imaging.

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[1] For a mathematical derivation, see Robert Schumacher. Introduction to Magnetic Resonance. W.A. Benjamin, Inc.: New York, 1970, pp. 28-30.

[2] Becker, Edwin D. and Thomas C. Farrar. Pulse and Fourier Transform NMR. Academic Press: New York, 1971, p. 20.

[3] Becker and Farrar, p. 45.

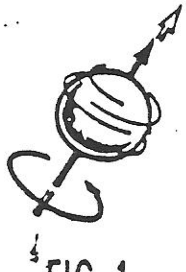

FIG 1

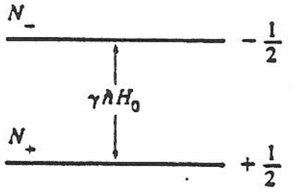

FIG 2

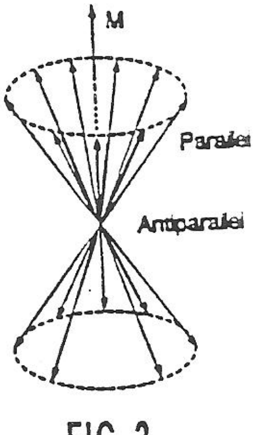

FIG 3

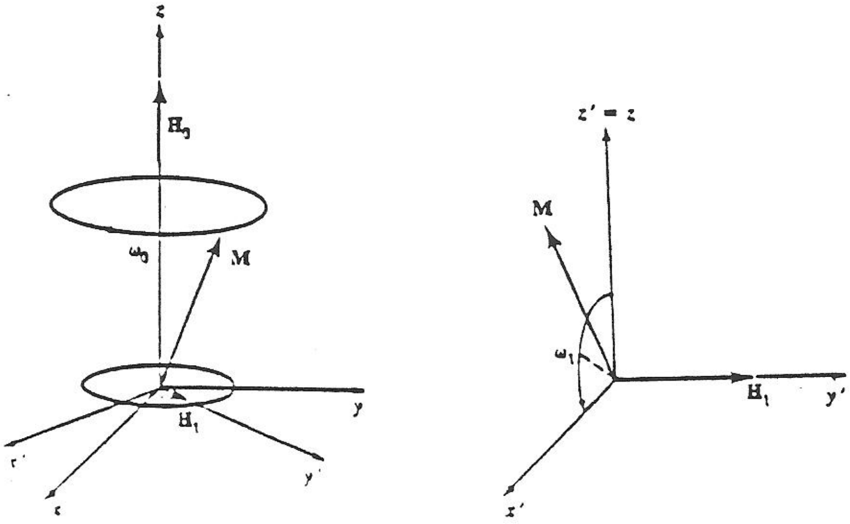

FIG 4

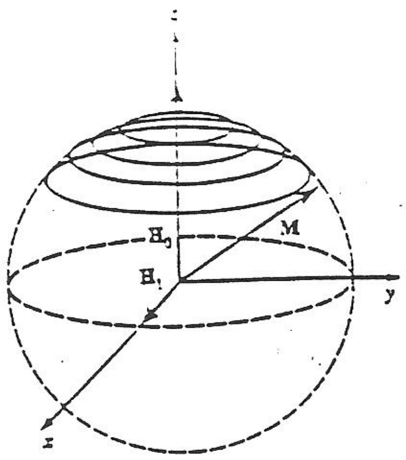

FIG 5

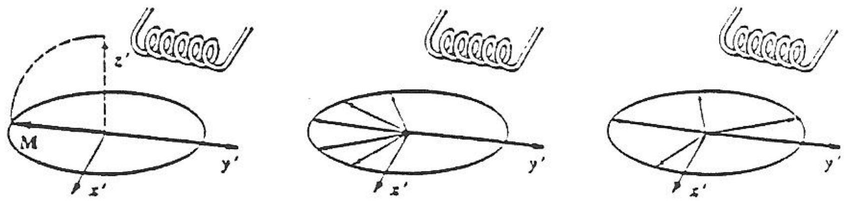

FIG 6

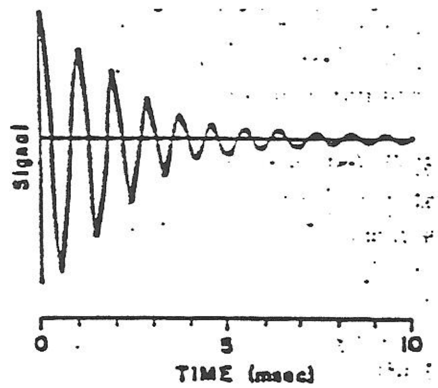

FIG 8

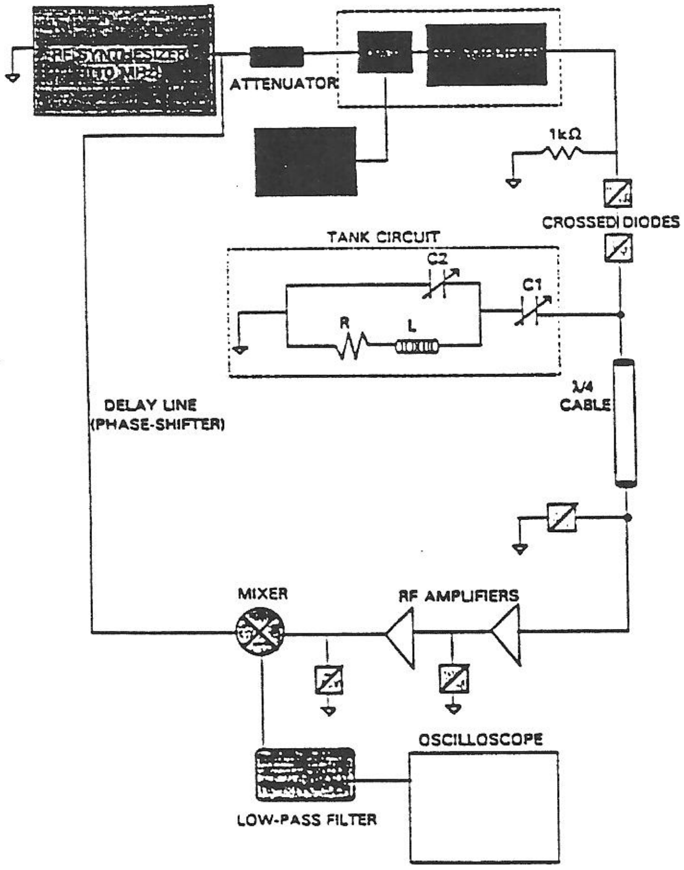

FIG 7

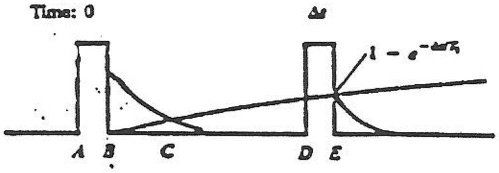

FIG 10

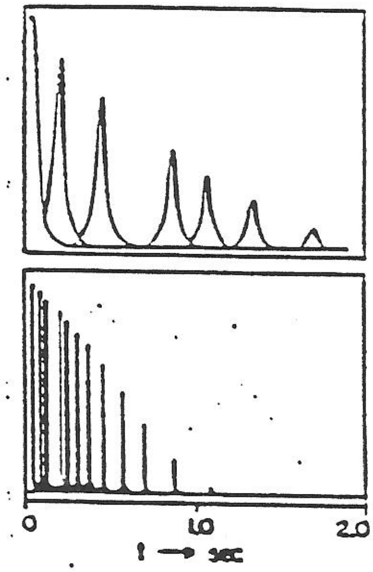

FIG 11

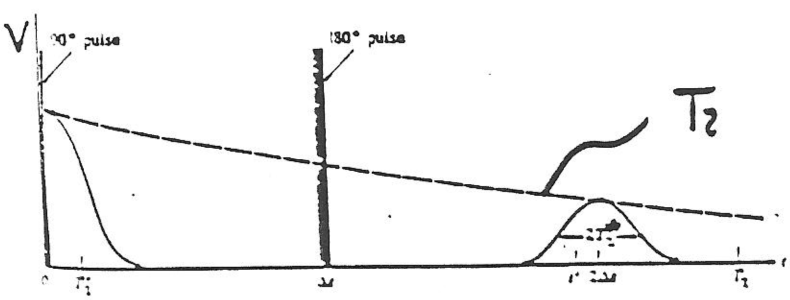

FIG 9