I. INTRODUCTION

A. OVERVIEW OF THE INSTRUMENT

Congratulations, you have acquired for your students the most versatile, sensitive, rugged and reliable nuclear magnetic resonance spectrometer designed specifically for instruction. The specifications of this unit rival any research grade unit in this frequency range in terms of sensitivity, stability, capabilities and state-of-the-art electronics. And yet, the unit was designed from the outset for student instruction. By that we mean that students, and not a computer, set all of the experimental parameters. Students can make many mistakes including miswiring the spectrometer and incorrectly setting any and all of the parameters without damaging the unit. For the one case where incorrect wiring might do some damage, the unit has special connectors which make those connections impossible with the cables provided.

All of the data is presented in analog form for examination on a digital storage oscilloscope or a computer. Students (and faculty) can then choose how they wish to perform data reduction or analysis. No proprietary software programs are needed to operate the unit, so no software updates are needed. TeachSpin is convinced that the “volt” will never go out of style, and that the mode of data storage and analysis is a choice best left to the individual user. Although data storage and analysis hardware and software is changing so rapidly that what is “hot” today may be obsolete tomorrow, your TeachSpin spectrometer, with its analog output signals, will be capable of taking research grade data long into the future.

Our first NMR instrument PS1-A,B is no longer available because some of its essential electronics components are no longer being manufactured. (It continues, however, to teach students pulsed NMR spectroscopy of protons at more than 170 institutions all over the world.) PS2-A is a completely redesigned spectrometer. The many differences and innovations are presented in the following list.

1. Students can study NMR signals from two types of nuclei, protons (hydrogen nuclei) and fluorine. Since the field of the permanent magnet is constant, this is accomplished by changing the spectrometer frequency.
2. PS2-A is both a pulsed and a continuous wave (CW) spectrometer.
3. The unit has both amplitude (envelope) and phase sensitive detection built into its receiver.
4. The RF probe head has a single coil and a 50 Ω input impedance; a matched unit.
5. The field and frequency have increased to 21 MHz proton for resonance.
6. The magnetic field is stabilized to 1 part in $2 \times 10^6$ over a 20 minute interval.
7. Adjustable electric shim coils that can be used to increase the magnetic field homogeneity are part of the RF sample probe system. They can also be used to create known gradients for measuring diffusion as well as for one-dimensional imaging.
8. The homogeneous high magnetic field allows direct detection of inequivalent fluorine and protons nuclei (chemical shifts) in the free induction decay signal.
9. A Lock-In detection module can detect CW signals from solids with wide lines.

10. Both magnetic field and RF frequency sweeps are built in for studying CW resonance.

11. Digital clock stability in both the RF frequency and the pulse width synthesis are integral to the design.

12. The receiver recovery time (after pulse) has been improved by a factor of five to approximately 15 µs, making signals from “soft” solids available for study.

The electronics system was designed by Dr. Norman Jarosik of the Princeton University Physics Department. Norman is a staff scientist in the “gravity Group” and the chief engineer of WMAP, the satellite that has been sensing and mapping the anisotropies in the microwave radiation left over from the Big Bang of the early universe. He also designed the PS-1 A and B whose well deserved reputation for reliability, as well as sensitivity, is known world-wide. Norman has been involved with TeachSpin from its 1992 inception.

Nuclear magnetic resonance is a large and mature field of physics. There certainly is a lot to learn and a real potential for a student to explore his or her own ideas in this area, perhaps even to find a real research project. We cannot think of a better instrument for students to pursue their own open-ended sets of experiments. But a new student should not be intimidated by the prospect of learning this vast subject. TeachSpin has outlined a manageable way to begin the study of NMR. Students can begin with straight-forward experiments that will develop their confidence and understanding and then branch out to more advanced measurements. This instrument is accessible, after all, it was designed from the moment of inception for the student. Enjoy!

B. OUTLINE OF THE PHYSICS

B.1 Brief History

In 1946, nuclear magnetic resonance (NMR) in condensed matter was discovered simultaneously by Edward Purcell at Harvard and Felix Bloch at Stanford using different instrumentation and techniques. Both groups, however, placed a sample containing magnetic nuclei in a uniform magnetic field and observed the response of those nuclei to a continuous (CW) radio frequency magnetic field as the field was tuned through resonance. This discovery opened up a new type of spectroscopy which has become one of the most important tools available to physicists, chemists, geologists, and biologists.

In 1950, Erwin Hahn, a postdoctoral fellow at the University of Illinois, again placing his sample of condensed matter in a uniform magnetic field, explored the response of the magnetic nuclei to pulse bursts of these same radio frequency (RF) magnetic fields. Hahn was interested in observing transient effects on the magnetic nuclei after the RF bursts. During these experiments, he observed a “spin echo” signal; that is, a signal from the magnetic nuclei that occurred after a two pulse sequence, at a time equal to the delay time between the two pulses. This discovery, and his brilliant analysis of the experiments, gave birth to a new technique for studying magnetic resonance. This pulse method originally had only a few practitioners, but now it is the method of choice for most laboratories. For the first twenty years after its discovery, continuous wave (CW) magnetic
resonance apparatus was used in almost every research chemistry laboratory, and no commercial pulsed NMR instruments were available. However, since 1966 when Ernst and Anderson showed that high resolution NMR spectroscopy can be achieved using Fourier transforms of the transient response, and cheap fast computers made this calculation practical, pulsed NMR has become the dominant commercial instrumentation for most research applications.

Widely used in physics and chemistry to characterize materials, NMR is a microscopic method in the sense that it probes the nuclei and their immediate surroundings. Within a certain solid, for instance, there may be a variety of local magnetic fields. A magnetic measurement by a magnetometer measures an average field. NMR, on the other hand, is capable of measuring the local field at atomic nuclei. Another example would be a molecule containing a several atoms of the same element, for instance carbon, in various different configurations. The NMR signal will be different for each one of these configurations. The microscopic nature of the NMR measurement makes it extremely useful, and often unique. Of course, in order to have a signal of detectable magnitude, we need many molecules of the same configuration to occur within the sample. The nuclei investigated in this set of experiments, hydrogen (proton) and fluorine, are very abundant and give particularly strong signals.

This technology has also found its way into medicine. MRI (magnetic resonance imaging; the word “nuclear” being removed to relieve the fears of the scientifically illiterate public) scans are revolutionizing radiology. This imaging technique seems to be completely noninvasive, produces remarkable three dimensional images, and has the potential to give physicians detailed information about the inner working of living systems. For example, preliminary work has already shown that blood flow patterns in both the brain and the heart can be studied without dangerous catheterization or the injection of radioactive isotopes. Someday, MRI scans may be able to pinpoint malignant tissue without biopsies. MRI is only in its adolescence, and we will see many more applications of this diagnostic tool in the coming years.

You have purchased a pulsed and CW NMR spectrometer designed specifically for teaching. The PS2-A is a complete spectrometer, including the magnet, magnet temperature controller, pulse generator, oscillator, pulse amplifier, sensitive receiver, linear amplitude and phase-sensitive detector, sample probe, gradient coils with dedicated current regulated supply and a CW lock-in detector. You need only supply the oscilloscope and the substances you wish to study. Now you are ready to learn the fundamentals of both CW and pulsed nuclear magnetic resonance spectroscopy.

Nuclear magnetic resonance is a vast subject. Tens of thousands of research papers and hundreds of books have been published on NMR. We will not attempt to explain or even to summarize this literature. Some of you may wish to do only a few simple experiments with the apparatus and achieve a basic conceptual understanding, while others may aim to understand the details of the density matrix formulation of relaxation processes and do some original research. The likelihood is that the majority of students will work somewhere in between these two extremes. In this section we will provide a brief theoretical introduction to many important ideas of PNMR. This will help you get started and can be referred to later. These remarks will be brief, not completely worked out from first principles, and not intended as a substitute for a careful study of the literature and published texts. An extensive annotated bibliography of important papers and books on the subject is provided at the end of this section.
B.2 Theory

Magnetic resonance is observed in systems where the magnetic constituents have both a magnetic moment and an angular momentum. Many, but not all, of the stable nuclei of ordinary matter have this property. In “classical physics” terms, magnetic nuclei act like a small spinning bar magnet. For this instrument, we will be concerned with only two nuclei, the nucleus of hydrogen, which is a single proton, and the nucleus of fluorine which contains both protons and neutrons. Both nuclei can be thought of as small spinning bar magnets with a magnetic moment $\mu$ and an angular momentum $J$, which are related by the vector equation:

$$\mu = \gamma J$$

(1.1)

The proportionality factor $\gamma$ is called the “gyromagnetic ratio” and its values are unique to each kind of nucleus in the experiment.

The nuclear angular momentum is quantized in units of $\hbar$ as:

$$J = \hbar I$$

(1.2)

where $I$ is the “spin” of the nucleus.

The magnetic energy $U$ of the nucleus in an external magnetic field is:

$$U = -\mu \cdot B$$

(1.3)

If the magnetic field is in the $z$-direction, then the magnetic energy is:

$$U = -\mu_z B_0 = -\gamma \hbar I_z B_0$$

(1.4)

Quantum mechanics requires that the allowed values $I_z$, $m_1$, be quantized as

$$m_1 = I, I - 1, I - 2, I - 3 \ldots -I.$$  

(1.5)

Both of the nuclei we are investigating, the proton (hydrogen nucleus) and the fluorine nucleus have spin one half ($I = 1/2$). Therefore, the allowed values of $I_z$ are simply

$$m_1 = \pm 1/2$$

(1.6)

This means that there are only two magnetic energy states for these nuclei when residing in a constant magnetic field $B_0$. These states are described in Figure 1.1.

The energy separation between the two states, $\Delta U$, can be written in terms of an angular frequency or as

$$\Delta U = \hbar \omega_0 = \gamma \hbar B_0$$

or

$$\omega_0 = \gamma B_0$$

(1.7)

Figure 1.1 Energy State Separation in a Magnetic Field
Equation 1.7, $\omega_0 = \gamma B_0$ describes the fundamental resonance condition.

For the proton:

$$\gamma_{\text{proton}} = 2.675 \times 10^8 \text{ rad/sec-tesla}$$  \hfill (1.8)

For Fluorine:

$$\gamma_{\text{fluorine}} = 2.517 \times 10^8 \text{ rad/sec-tesla}$$

For the proton, the numerical relationship between the resonant frequency and the constant magnetic field is worth remembering:

$$f_{\text{proton}} \text{ (MHz)} = 42.58 B_0 \text{ tesla}$$  \hfill (1.9)

If a one milliliter (ml) sample of water (containing about $7 \times 10^{19}$ protons) is placed in a magnetic field in the z-direction, a nuclear magnetization in the z-direction eventually becomes established. This nuclear magnetization occurs because of unequal population of the two possible quantum states. If $N_1$ and $N_2$ are the number of spins per unit volume in the respective states, then the population ratio ($N_2 / N_1$), in thermal equilibrium, is given by the Boltzmann factor as:

$$\frac{N_2}{N_1} = e^{\frac{\Delta U}{kT}} = e^{\frac{\hbar \omega_0}{kT}}$$  \hfill (1.10)

and the magnetization is

$$M_z = (N_1 - N_2) \mu$$  \hfill (1.11)

The thermal equilibrium magnetization per unit volume for $N$ magnetic moments is

$$M_0 = N \mu \tanh\left(\frac{\mu B}{kT}\right) \approx N \mu^2 \frac{B}{kT}$$  \hfill (1.12)

where $N = N_1 + N_2$

This magnetization does not appear instantaneously when the sample is placed in the magnetic field. It takes a finite time for the magnetization to build up to its equilibrium value along the direction of the magnetic field (which we define as the z-axis). For most systems, the z-component of the magnetization is observed to grow exponentially as depicted in Figure 1.2. The differential equation that describes such a process assumes that the rate of approach to equilibrium is proportional to the difference between the equilibrium value $M_0$ and the instantaneous value $M_z(t)$:

$$\frac{dM_z(t)}{dt} = \frac{M_0 - M_z}{T_1}$$  \hfill (1.13)

where $T_1$ is called the spin-lattice relaxation time.

Figure 1.2 Magnetization vs. time for a sample placed in a magnetic field
If the unmagnetized sample is placed in a magnetic field, so that at $t = 0$, $M_z = 0$, then direct integration of equation 1.13, with these initial conditions, gives:

$$M_z(t) = M_0(1 - e^{\frac{-t}{T_1}})$$  \hspace{1cm} (1.14)$$

The rate at which the magnetization approaches its thermal equilibrium value is characteristic of the particular sample. Typical values range from microseconds to seconds. What makes one material take 10 microseconds to reach equilibrium while another material (also with protons as the nuclear magnets) takes 3 seconds? Obviously, some processes in the material make the protons “relax” towards equilibrium at different rates. The study of these processes is one of the major topics in magnetic resonance.

Although we will not attempt to discuss these processes in detail, a few ideas are worth noting. In thermal equilibrium, more protons are in the lower energy state than the upper. When the unmagnetized sample was first put in the magnet, the protons occupied the two states equally that is ($N_1 = N_2$). During the magnetization process energy must flow from the nuclei to the surroundings, since the magnetic energy from the spins is reduced. The surroundings which absorb this energy are referred to as “the lattice”, even for liquids or gases. Thus, the name “spin-lattice” relaxation time for the characteristic time of this energy flow.

However, there is more than energy flow that occurs in this process of magnetization. Each proton has angular momentum (as well as a magnetic moment) and the angular momentum must also be transferred from the spins to the surroundings during magnetization. In quantum mechanical terms, the “lattice” must have angular momentum states available when a spin goes from $m_1 = -1/2$ to $m_1 = +1/2$. In classical physics terms, the spins must experience a torque capable of changing their angular momentum. The existence of such states is usually the critical determining factor in explaining the enormous differences in $T_1$ for various materials. Pulsed NMR is ideally suited for making precise measurements of this important relaxation time. The pulse technique gives a direct and unambiguous measurement, where as CW spectrometers require a difficult, indirect, and imprecise technique to measure the same quantity.

What about magnetization in the x-y plane? In thermal equilibrium the only net magnetization of the sample is $M_z$, the magnetization along the external constant magnetic field. This can be understood from a simple classical model of the system. Think of placing a collection of tiny current loops in a magnetic field. The torque $\tau$ on the loop is $\mu \times B$ and that torque causes the angular momentum of the loop to change, as given by:

$$\tau = \frac{d\mathbf{J}}{dt} \hspace{1cm} \text{or} \hspace{1cm} \mathbf{\mu} \times \mathbf{B} = \frac{d\mathbf{J}}{dt}$$  \hspace{1cm} (1.15)$$
For our nuclei, equation 1.15 becomes:

$$\mathbf{\mu} \times \mathbf{B} = \frac{1}{\gamma} \frac{d\mathbf{\mu}}{dt} \quad (1.16)$$

Equation 1.16 is the classical equation describing the time variation of the magnetic moment of the proton in a magnetic field. It can be shown from equation 1.16 that the magnetic moment will execute precessional motion, depicted in 1.3. The precessional frequency $\omega_0 = \gamma B_0$, is just the resonant frequency in equation 1.7.

If we add up all the magnetization for the $10^{20}$ nuclei in our sample in thermal equilibrium, the $\mu_z$ components sum to $M_z$, but the $x$ and $y$ components of the individual magnetic moments add to zero.

Figure 1.3

For the $x$-components of every nucleus to add up to some $M_x$, there must be a definite phase relationship among all the precessing spins. For example, we might start the precessional motion with the $x$-component of the spins lined up along the $x$-axis. But that is not the case for a sample simply placed in a magnet. In thermal equilibrium, the spin components in the $x$-$y$ plane are oriented randomly. Thus, in thermal equilibrium there is no transverse ($x$ or $y$) component of the net magnetization of the sample. As we shall soon see, however, there is a way to create such a transverse magnetization using radio frequency pulsed magnetic fields. The idea is to quickly rotate the thermal equilibrium magnetization $M_z$ into the $x$-$y$ plane and thus create a temporary $M_x$ and $M_y$. Let’s see how this is done.

Equation 1.16 can be generalized to describe the classical motion of the net magnetization of the entire sample. It then becomes

$$\frac{d\mathbf{M}}{dt} = \gamma \mathbf{M} \times \mathbf{B} \quad (1.17)$$

where $\mathbf{B}$ is any magnetic field, including time dependent rotating fields.

Suppose we apply not only a constant magnetic field $B_0 \hat{k}$, but a rotating (circularly polarized) magnetic field of angular frequency $\omega$ the $x$-$y$ plane so the total field is written as

$$\mathbf{B}(t) = B_1 \cos \omega t \hat{i} + B_1 \sin \omega t \hat{j} + B_0 \hat{k} \quad (1.18)$$
The analysis of the magnetization in this complicated time dependent magnetic field can best be carried out in a non-inertial rotating coordinate system. The coordinate system of choice is rotating at the same angular frequency as the rotating magnetic field with its axis in the direction of the static magnetic field. In this rotating coordinate system, the rotating magnetic field appears to be stationary and aligned along the \( x^* \) axis (Figure 1.4). However, from the point of view of the rotating coordinate system, \( B_0 \) and \( B_1 \) are not the only magnetic fields. An effective field along the \( z^* \) direction, of \(-\frac{\alpha}{\gamma} \hat{k}^*\) must also be included.

Let’s justify this new effective magnetic field with the following physical argument.

Equations 1.16 and 1.17 predict the precessional motion of a magnetization in a constant magnetic field \( B_0 \hat{k} \). Suppose one observes this precessional motion from a rotating coordinate system which rotates at the precessional frequency. In this frame of reference the magnetization appears stationary, in some fixed position. The only way a magnetization can remain fixed in space is if there is no torque on it. If the magnetic field is zero in the reference frame, then the torque on \( M \) is always zero no matter what direction \( M \) is oriented. The magnetic field is zero (in the rotating frame) if we add the effective field \(-\frac{\alpha}{\gamma} \hat{k}^*\) which is equal to \( B_0 \hat{k}^* \)

Transforming the magnetic field expression in equation (1.18) into such a rotating coordinate system, the total magnet field in the rotating frame \( B^* \) is

\[
B^*_{eff} = B_1 \hat{i}^* + (B_0 - \frac{\alpha}{\gamma} \hat{k})
\]

(1.19)

Figure 1.4 is a representation of Equation 1.19. The classical equation of motion of the magnetization as observed in the rotating frame is then

\[
\frac{dM}{dt} \bigg|_{rot} = \gamma M \times B^*_{eff}
\]

(1.20)

which shows that \( M \) will precess about \( B^*_{eff} \) in the rotating frame.

\[†\]What is actually applied is an oscillating field \( 2B_1 \cos \omega t \hat{i} \). But that can be decomposed into two counter rotating fields \( B_1 (\cos \omega t + \sin \omega t) + B_1 (\cos \omega t - \sin \omega t) \). One of the counter rotating fields can be shown to have no practical affects on the spin system and can be ignored in this analysis.
Suppose now, we create a rotating magnetic field at a frequency \( \omega_0 \) as such that

\[
\frac{\omega}{\gamma} = B_0 \quad \text{or} \quad \omega = \gamma B_0 = \omega_0
\]  

(1.21)

In that case, \( B_{\text{eff}}^* = B_1 \), a constant magnetic field in the x* direction (Figure 1.5). Then, the magnetization \( M_z \) begins to precess about this magnetic field at a rate \( \Omega = \gamma B_1 \), (in the rotating frame). If we turn off the B₁ field at the instant the magnetization reaches the x-y plane, we will have created a transient (non-thermal equilibrium) situation where there is a net magnetization in the x-y plane. If this rotating field is applied for twice the time the transient magnetization will be - \( M_z \) and if it is left on four times as long the magnetization will be back where it started, with \( M_z \) along the z* axis. These are called:

- 90° or \( \pi/2 \) pulse \( \rightarrow M_z \rightarrow M_y 
- 180° or \( \pi \) pulse \( \rightarrow M_z \rightarrow -M_z 
- 360° or 2\pi pulse \( \rightarrow M_z \rightarrow M_z

Figure 1.5

In the laboratory (or rest) frame, where the experiment is actually carried out, the magnetization not only precesses about \( B_1 \), but rotates about \( \hat{k} \) during the pulse. **It is not possible, however, to observe the magnetization during the pulse.** Pulsed NMR signals are observed AFTER the transmitter pulse is over? But, what is there to observe AFTER the transmitter pulse is over? The spectrometer detects the net magnetization precessing about the constant magnetic field \( B_0 \hat{k} \) in the x-y plane. Nothing Else!

Suppose a 90° (\( \pi/2 \)) pulse is imposed on a sample in thermal equilibrium. The net equilibrium magnetization will be rotated into the x-y plane where, after the pulse, it will precess about \( B_0 \hat{k} \). But the x-y magnetization will not last forever. For most systems, this magnetization decays exponentially as shown in Figure 1.6. The differential equations which describe the decay in the rotating coordinate system are:

\[
\frac{dM_{x^*}}{dt} = -\frac{M_{x^*}}{T_2} \quad \text{and} \quad \frac{dM_{y^*}}{dt} = -\frac{M_{y^*}}{T_2}
\]

(1.22)

whose solutions are:

\[
M_{x^*} = M_0 e^{-\frac{t}{T_2}} \quad \text{and} \quad M_{y^*} = M_0 e^{-\frac{t}{T_2}}
\]

(1.23)

where the characteristic decay time \( T_2 \) is called the **Spin-Spin Relaxation Time.**
One simple way to understand this relaxation process, from the classical perspective, is to recall that each nucleus is itself a magnet and produces a magnetic field at its neighbors. Therefore, for a given distribution of nuclei, there must also be a distribution of local fields at the various nucleus sites. Thus, the nuclei precess about $B_0\hat{k}$ with a distribution of frequencies, not a single frequency $\omega_0$.

**Figure 1.6**

Even if all the nuclei begin in phase (after the 90° pulse), they will soon get out of phase and the net x-y magnetization will eventually go to zero. A measurement of $T_2$, the decay constant of the x-y magnetization, gives information about the distribution of local fields at the nuclear sites.

From this analysis, it would appear that the spin-spin relaxation time $T_2$ can be determined by simply plotting the decay of $M_x$ (or $M_y$) after a 90° pulse. This signal is called the free precession or free induction decay (FID). If the field of the magnet were perfectly uniform over the entire sample volume, then the time constant associated with the free induction decay would, in fact, be $T_2$. But, in most cases, it is the nonuniformity of the magnet’s field over the sample that is responsible for the observed decay constant of the FID. At its center, the PS2-A’s magnet has sufficient uniformity to produce at least a .3 millisecond decay time. Using the electric shim coils (See Section II.F), students can improve the homogeneity so that decay time due to the magnet (called $T_2^*$ in the jargon) is as long as 5 milliseconds, and, possibly, longer. Thus, for a sample whose $T_2 < 5$ ms, the free induction decay constant is also the $T_2$ of the sample. But what if $T_2$ is actually 5 msec or longer? The observed decay will still be about 5 ms. Here is where the genius of Erwin Hahn’s discovery of the spin echo plays its crucial role.

Before the invention of pulsed NMR, the only ways to measure the real $T_2$ were to improve the magnet’s homogeneity and to make the sample smaller. But, PNMR changed this.
Suppose we use a two pulse sequence, the first one $90^\circ$ and the second one, turned on a time $\tau$ later, a $180^\circ$ pulse. What happens? Figure 1.7 shows the pulse sequence and Figure 1.8 shows the progression of the magnetization in the rotating frame.

![Figure 1.7: A 90° - 180° Pulse Sequence](image1)

![Figure 1.8: Progression of the Magnetization in the Rotating Frame](image2)

- **a)** Thermal equilibrium magnetization $M_0$ along the z axis before the rf pulse.
- **b)** $M_0$ rotated to the y-axis after the $90^\circ$ pulse.
- **c)** The magnetization in the x-y plane is decreasing because some of the spins $\Delta m_{\text{fast}}$ are in a higher field, and other spins $\Delta m_{\text{slow}}$ are in a lower field static field.
- **d)** The spins are rotated $180^\circ$ (visualize flipping the entire x-y plane like a pancake on the griddle) by the pulsed if magnetic field.
- **e)** The rephasing the three magnetization “bundles” to form an *echo* at $t = 2\tau$. 
Study the diagrams in Figures 1.7 and 1.8 carefully. The 180° pulse allows the x-y magnetization to rephase to the value it would have had with a perfect magnet.

The echo process is analogous to an egalitarian and PC foot race for a kindergarten class, a race that makes all the children in the class winners, no matter how fast they can run. What if the race had the following rules? All the children are to line up at the starting line. At the first whistle, they are to run as fast as they can down the field. At the second whistle, they are to turn around and run back toward the starting line. First person back wins!! Of course, it is a tie, except for the ones who “interfere” with one another or fall down. As the children run away, the field spreads out with the fastest ones getting farther and farther ahead. At some point there is no semblance of order. On the trip back, as the faster ones overtake the slow pokes, who are now in the lead, the group comes together again “rephasing” as they pass the start line.

In Pulsed NMR, the 180° pulse is like that whistle. The spins in areas of larger field get out of phase by $+\Delta \theta$ in a time $\tau$. After the 180° pulse, they continue to precess faster than $M$ while the slower precessing spins do just the opposite. At $2\tau$ all the spins return to the in-phase condition and then again dephase.

Yet some loss of $M_{x,y}$ magnetization has occurred and the maximum height of the echo is not the same as the maximum height of the FID. This loss of transverse magnetization occurs because of stochastic fluctuation in the local fields at the nuclear sites which is not rephasable by the 180° pulse. These are the real $T_2$ processes that we are interested in measuring. To find the “real” $T_2$, we use a series of $90° > \tau > 180°$ pulse experiments, varying $\tau$, and then plotting the echo height as a function of time between the FID and the echo.

The transverse magnetization as measured by the maximum echo height is written as:

$$M_{xy}(2\tau) = M_0 e^{\frac{2\tau}{T_2}} \quad (1.24)$$

That’s enough theory for now. Let’s summarize:

1. Magnetic resonance is observed in systems whose constituent particles have both a magnetic moment and angular momentum.

2. The resonant frequency of the system depends on the applied magnetic field in accordance with the relationship $\omega_0 = \gamma B_0$ where

$$\gamma_{\text{proton}} = 2.675 \times 10^8 \text{ radian/sec-tesla}$$

or

$$f_{\text{proton}} = 42.58 \text{ MHz/tesla} \quad \text{(for protons)}$$

$$f_{\text{fluorine}} = 40.055 \text{ MHz/tesla} \quad \text{(for fluorine)}$$

3. The thermal equilibrium magnetization is parallel to the applied magnetic field, and approaches equilibrium following an exponential rise characterized by the constant $T_1$ the spin-lattice relaxation time.
4. Classically, the magnetization (which is the vector sum of the individual magnetic moments of the nuclei) obeys the differential equation

\[ \frac{dM}{dt} = \gamma (M \times B) \]

where \( B \) may be a time dependent field.

5. Pulsed NMR employs a rotating radio frequency magnetic field described by

\[ B(t) = B_1 \cos \omega t \hat{i} + B_1 \sin \omega t \hat{j} + B_0 \hat{k} \]

6. The easiest way to analyze the motion of the magnetization during and after the rf pulsed magnetic field is to transform into a rotating coordinate system. If the system is rotating at an angular frequency \( \omega \) along the direction of the magnetic field, a fictitious magnetic field must be added to the real fields such that the total effective magnetic field in the rotating frame is:

\[ B_{\text{eff}}^* = B_1 \hat{i} + (B_0 - \frac{\omega}{k}) \hat{k} \]

7. On resonance \( \omega = \omega_0 = \gamma B_0 \) and \( B_{\text{eff}}^* = B_1 \hat{i} \). In the rotating frame, during the pulse, the spins precess around \( B_1^* \).

8. A 90° pulse is one where the pulse is left on just long enough (\( t_w \)) for the equilibrium magnetization \( M_0 \) to rotate to the x-y plane. That is;

\[ \omega_1 t_w = \pi/2 \text{ radians} \quad \text{or} \quad t_w = \frac{\pi}{2\omega_1} \]

But

\[ \omega_1 = \gamma B_1 \]  

(since, on resonance, \( B_1 \) is the only field in the rotating frame.)

So,

\[ t_w (90^\circ) = \frac{\pi}{2\gamma B_1} \text{ duration of the } 90^\circ \text{ pulse} \quad (1.25) \]

9. \( T_2 \) - the spin-spin relaxation time - is the characteristic decay time for the nuclear magnetization in the x-y (or transverse) plane.

10. The spin-echo experiments allow the measurement of \( T_2 \) in the presence of a nonuniform static magnetic field. For those cases where the free induction decay time constant, (sometimes written \( T_2^* \)) is shorter than the real \( T_2 \), the decay of the echo envelope’s maximum heights for various times \( \tau \), gives the real \( T_2 \).
C. REFERENCES

The following is a rather long list, and you certainly will not have the time all of them. In fact, you may only have time to read a rather small percentage of what is listed. But, you must take the time to read some of them so you have a basic understanding of magnetic resonance spectroscopy.

C.1 Books

A complete text with problems, clear explanations, appropriate for advanced undergraduate or graduate level students. Any serious student of magnetic resonance should own it. Everyone should read at least some of it. This reference contains a nearly complete bibliography of the important papers published in both NR and ESR spectroscopy. Consult this text for references to particular subjects.

A good introduction, with simplified mathematics, to the subject. Gives students a physical feel for the basic ideas of PNMR.

Don’t let the title ESR scare you away from using this excellent text. It has clear discussions of important ideas of magnetic resonance, such as the rotating coordinate systems etc.


This is Bloembergen’s Ph.D. thesis, reprinted, but it is like no other thesis you will ever read. Describes some of the classic ideas of magnetic resonance, still very worth reading, you will see why he is a Nobel Laureate.

This text is in a class by itself, but not easy for the beginner. Abragam has his own way of describing NMR. Important, but clearly for advanced students.

A good general discussion of theory, experimental methods, and applications of NMR.
C. Kittel “Introduction to Solid State Physics” 5th edition, Wiley, New York 1976 in Chapter 16. A reasonable place to begin the subject of magnetic resonance, very brief, not fully worked out, but a good first overview;


C.2 Papers


H. Y. Carr, E. M. Purcell: Effects of diffusion on free precession in nuclear magnetic resonance experiments. Phys Rev 94, 630-638 (1954) Anything Ed Purcell signs his name to is worth reading! This certainly is one such example. A must for PNMR.


K. Symon, “Mechanics” 3rd ed. Addison-Wesley, Reading, MA (1971) A good place to learn about rotating coordinate systems, if you don’t already understand them.