THE CONSTRUCTION AND OPERATION OF A NUCLEAR MAGNETIC RESONANCE PROBE

by

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INTRODUCTION

Nuclear magnetic resonance is a branch of spectroscopy which is concerned with the energy levels of atomic nuclei in magnetic fields and the transitions induced between them through absorption or emission of electromagnetic radiation. The nuclear magnetic resonance experiment is basically a particular measurement of the behavior of a nucleus placed in a magnetic field. Thus we are actually using nuclei to probe the magnetic field and investigating the effect of the field on the probe.

Some atomic nuclei possess magnetic moments in addition to acting as point electrostatic charges. In some ways, certain nuclei behave as though they are nonspinning spherical bodies with nuclear charge distributed evenly over their surfaces. A nucleus of this type does not have a magnetic moment because there is no circulation of the nuclear charge. The nuclear quadrupole moment for such a nucleus is zero, and when a unit electric probe charge approaches such a nucleus it experiences an electrostatic field whose magnitude is independent of the direction of approach. These nuclei are said to have their nuclear spin value equal to zero and have no nuclear magnetic moment.

Many atomic nuclei in their ground state have a nonzero spin angular momentum $I\hbar$ so that the spinning nucleus has circulating charge which generates a magnetic field resulting in a dipole moment, $\mu = \gamma \hbar I$, collinear with the angular momentum.

Nuclei with spin 1/2 have a spherical charge distribution which means that a probing charge approaching the nuclei

experiences the same electrostatic field regardless of the direction of approach, and therefore, as with the spherical nonspinning nuclei, the electric quadrupole is zero. For nuclei with spin greater than 1/2, the electric quadrupole moment is not zero and gives a measure of the asymmetry of the nuclear charge distribution.

An important property of spinning nuclei is that the projection of their magnetic moment vectors appear to have only preferred values in any given direction, such as along the axis of an externally applied magnetic field. The permitted values of the component of the vector moment along the direction of interest can be described by a set of magnetic quantum numbers m, which are derivable from the nuclear spin I and the relation

$$m = I, I - 1, I - 2, \ldots, -I$$

For an isolated nucleus in a steady magnetic field H_0, the length of the nuclear angular momentum vector is

$$\left[I(I + 1)\right]^{\frac{1}{2}} \hbar$$

but the only measurable components of this vector are given by $m\hbar$, where m may take on any of the (2 I + 1) values in the series

$$I, I - 1, \ldots, -(I - 1), -I$$

If I is 1/2, the possible magnetic quantum numbers are +1/2 and -1/2.

In the absence of a magnetic field there is no preference for one or the other of the two possible magnetic quantum numbers for a nucleus with I equal to 1/2. If there is a large assemblage of such nuclei, then there would be as many nuclei with m equal +1/2 as there would be with m equal -1/2. In a magnetic field,

the nuclei will tend to assume the magnetic quantum number +1/2 which represents alignment with the field. Thus in the presence of a magnetic field, m = +1/2 represents a lower energy state than m = -1/2, provided the gyromagnetic ratio γ is positive. However, the tendency of the nuclei to assume the magnetic quantum number +1/2 is opposed by thermal agitation. The nuclear moment, field strength, and temperature can be used to calculate the equilibrium numbers of the nuclei in each quantum state by the Boltzmann distribution law. At room temperature in a magnetic field of 1000 gauss, thermal agitation is so important relative to the energy gained by alignment of the nuclei that only a very slight excess of the nuclei go into the more favorable quantum state, as shown by

$$\frac{N(+1/2)}{N(-1/2)} = \exp\left(\frac{\gamma \hbar H}{kT}\right) = 1.00000066$$

Nuclear magnetic resonance is primarily concerned with transitions of the nuclei in a magnetic field between energy levels which are expressed by the different magnetic quantum numbers. There is no direct magnetic interaction between the nuclei and the electrons which surround them. Thus a problem is posed with regard to the transfer of the energy of the nuclei to and from their surroundings. The energy-transfer problem may be restated in the following way. Consider an assemblage of nuclei in the absence of a magnetic field. As stated before, there will be exactly equal numbers of nuclei with the magnetic quantum numbers +1/2 and -1/2. In the presence of a magnetic field, this distribution corresponds to an infinitely high temperature because the

state with the magnetic quantum number -1/2 is now energetically less favorable than the +1/2 state and only an infinitely high temperature could produce sufficient thermal agitation to keep the nuclear magnets from having some net alignment in the field direction. In order to achieve the equilibrium distribution of nuclei between the two possible spin states at a lower temperature, it is necessary that energy be lost to the surroundings by nuclear "relaxation". One would not expect the relaxation to be a simple process, since the nuclei are not able to collide with one another of the surrounding electrons and convert their energy due to an external magnetic field into molecular vibration, rotational, or translational energy. Transfer of energy back and forth among nuclei in various magnetic quantum states and their surroundings can be achieved with the aid of another property which may be ascribed to magnetic nuclei, called nuclear precession.

When a nucleus with a magnetic moment and angular momentum is placed in a magnetic field, it precesses around the axis of the field with an angular velocity ω, which is directly proportional to the magnetic field H_0. The proportionality constant γ between the angular velocity of precession and the magnetic field H_0 is called the gyromagnetic ratio. All nuclei of the same charge and mass number in the same nuclear state have the same gyromagnetic ratio. Thus all protons precess at the same angular velocity when the magnetic field strength at the nucleus is the same. In general, γ is either positive or negative but for the proton γ is positive.

The property of magnetic nuclei which corresponds to precession provides a means whereby energy may be transferred back and forth between the nuclei and their surroundings. Consider a magnetic field vector arranged so as to rotate perpendicularly to a magnetic field at an angular velocity other than the angular velocity of the precessing nuclei, the rotating field vector and the precessing nuclear magnetic vectors cannot remain in phase and there will be no effective interaction between them. On the other hand, if the rotating field vector has the same angular velocity as the precessing nuclear vectors, it will remain in phase with them and can exert a magnetic torque tending to flip over the nuclei, and hence change their magnetic quantum numbers. If the nuclear magnetic quantum numbers change, energy is transferred to or from the agency producing the rotating field vector. Thus can an assemblage of nuclear magnets immersed in a magnetic field come to thermal equilibrium with its surroundings.

An important mechanism for relaxation of a group of nuclei at a nonequilibrium spin temperature utilizes atomic and molecular thermal motion as follows. Suppose a magnetic nucleus is surrounded by others of its type contained in atoms undergoing violent thermal motions. The thermal motions of the nuclei produce random oscillatory magnetic fields which can have frequency components with frequencies equal to the precession frequencies of the relaxing nuclei and can act as a rotating magnetic field vector so as to permit the magnetic orientation energy to be converted to thermal energy. The rate of relaxation by this mechanism depends on the temperature, the concentration of magnetic

nuclei, and the viscosity of the medium. The process can be expressed in terms of a relaxation time, which is the mean lifetime of the excess of nuclei in the excited state.

As might be expected, thermal motions of substances with unpaired electrons are particularly effective in inducing thermal relaxation. Thus transitions between states with various magnetic quantum numbers which have different energies because of an applied magnetic field may be induced by thermal motions of magnetic nuclei or paramagnetic substances or else by an external rotating magnetic field which has a frequency equal or very nearly equal to the precession frequency of the nuclei.

The phenomena of nuclear magnetic resonance is the measurement, under appropriate conditions, of the absorption of energy by the dipole moments from an external rotating magnetic field which has a frequency equal to the frequency of precession of the nuclei.

If a magnetic dipole is in an inhomogeneous field it will have an unbalanced force acting upon it. Stern and Gerlach (2) utilized this fact and passed a beam of atoms which possessed a magnetic moment through an inhomogeneous field and from the magnitude of the deflection calculated the atomic magnetic moments. They found that the measurable values of the component of an atomic moment do not form a continuous range, but instead form a discrete set corresponding to the space quantization of the atom in the magnetic field.

Rabi (3) introduced the resonance method to greatly improve the beam method, but it was Purcell, Torrey, and Pound (4), and

Block, Hansen, and Packard (5, 6) who carried out the first successful nuclear magnetic resonance experiments in bulk matter.

A nuclear magnetic resonance spectrometer consists basically of a magnet, radio-frequency (rf) transmitter or oscillator, and a suitable rf detector. When a sample of a material comprised of atoms having nuclei with magnetic moments is placed in the magnetic pole gap and subjected to the rf field of the oscillator, absorption of rf energy occurs when the equation $\omega = \gamma H$ is satisfied. Upon absorption of the rf energy, a voltage is induced in a coil wound around the sample and then this voltage is amplified and displayed on an oscilloscope.

Purcell and Block employed different methods to search for nuclear magnetic resonance. In Purcell's apparatus the sample of matter was placed between the two pole faces of a magnet and surrounded with a coil which produced the second rotating field. When the frequency was just right, energy was absorbed by the sample from the rotating field and this absorption was recorded by a sudden dip in the strength of the signal reaching a radio receiver.

Block's group, on the other hand, devised an instrument which recorded the event by an induction of a voltage. As the protons in the sample absorbed energy from the field and flipped over, the motion of their magnetic fields induced a voltage in a second coil and this signal was registered on an oscilloscope.

Purcell and Block used such samples as paraffin and water, and thus observed proton resonance.

THEORY

The approach followed by Block (3) will be used to derive the theory for nuclear magnetic resonance.

First consider a nucleus with magnetic moment $\underline{\mu}$ in a magnetic field $\underline{H}_0$. The magnetic field $\underline{H}_0$ exerts a torque $\underline{T} = \underline{\mu} \times \underline{H}_0$ on the magnetic moment which is equal to the time rate of change of the angular momentum $\underline{a}$.

$$\underline{\mu} \times \underline{H}_0 = \underline{T} = \frac{d\underline{a}}{dt} = \frac{1}{\gamma} \frac{d\underline{\mu}}{dt} \qquad (1)$$

Now consider a unit volume of nuclei where the vector sum of the magnetic moments is equal to the magnetization $\underline{M}$. Since $\underline{\mu} = \gamma \underline{a}$, where $\underline{a}$ is the angular momentum for each nucleus, then the magnetic moment is parallel to the angular momentum for each nucleus and upon summing over a unit volume we obtain

$$\underline{M} = \gamma \underline{A}$$

where $\underline{A}$ is the total angular momentum for all the nuclei in the unit volume, and

$$\frac{d\underline{M}}{dt} = \frac{d\underline{A}}{dt} = \underline{M} \times \underline{H} \qquad (2)$$

Now consider the behavior of these nuclei when the sample is subjected to two external fields. Let the first field be a constant magnetic field in the z direction and the second a comparatively weak oscillating field in the x direction. For the present all other fields shall be neglected.

The total external field has the components

$$H_z = H_0 \quad H_y = 0 \quad H_x = 2 H_1 \cos \omega t \qquad (3)$$

The linear oscillating field H_x of amplitude $2H_1$ may be regarded as the superposition of two rotating fields both of amplitude H_1, but rotating in opposite directions. Only the field rotating with its angular velocity in the same direction as the magnetization vector can exert an effective torque on the magnetization vector since it only can maintain a constant phase relationship to the magnetization vector. Thus we now have

$$H_z = H_0 \quad H_y = \mp H_1 \sin \omega t \quad H_x = H_1 \cos \omega t \tag{4}$$

If we let θ denote the angle between H_0 and the magnetization vector, we can write

$$\begin{aligned} M_x &= M \sin \theta \cos \omega t \\ M_y &= \mp M \sin \theta \sin \omega t \\ M_z &= M \cos \theta \end{aligned} \tag{5}$$

Equation (2) is satisfied if θ is constant and chosen such that

$$\tan \theta = \frac{\gamma H_1}{\gamma H_0 \mp \omega} \tag{6}$$

where the minus and plus sign before ω depend upon whether γ is positive or negative. If we denote the resonant value of the magnetic field by H^* and let

$$H^* = \frac{\omega}{|\gamma|} \tag{7}$$

then (6) becomes

$$\tan \theta = \frac{H_1}{H_0 - H^*} \tag{8}$$

If we let

$$\delta = \frac{H_0 - H^*}{H_1} = \cot \theta \tag{9}$$

then equations (5) become

$$M_x = \frac{M \cos \omega t}{\sqrt{1+\delta^2}}$$

$$M_y = \frac{M \sin \omega t}{\sqrt{1+\delta^2}} \qquad (10)$$

$$M_z = \frac{M}{\sqrt{1+\delta^2}}$$

As the magnetic field H_0 approaches its resonance value H*, then δ goes to zero and θ approaches $\pi/2$.

Although these equations have been derived on the basis of constant ω and H_0, they are equally valid provided these quantities vary slowly enough that

$$\left| \frac{d\delta}{dt} \right| \ll \left| \delta H_1 \right| \qquad (11)$$

If the amplitude of H_1 is constant, then there are two means by which δ and thus the components of equation (10) can vary. Either the field H_0 can be held constant and the frequency of the oscillating field H_1 be varied, thus varying the value of the resonance field H* which satisfies $\omega = \gamma H$, or else the frequency ω, and therefore H*, can be held constant and H_0 be varied slowly. It will be assumed from here on that ω is held constant and H_0 is varied such as to satisfy equation (11). Another way of expressing the condition (11) is by stating that the magnetic field H_0 must pass through an interval $\Delta\delta$ during a time Δt which is long comparable to

$$t_1 = \frac{1}{|\gamma H_1|} \qquad (12)$$

The above considerations can now be used to describe an experimental arrangement whereby an induced voltage signal can be detected.

If we have a coil wound around the sample with its axis in the y direction, we can find an expression for the voltage induced in this coil at resonance. An expression for My is given by equation (10) and the corresponding induction is given by

$$B_y = 4\pi M_y \tag{13}$$

If there are N turns in the receiver coil and the cross-sectional area of the sample is a, then we have for the effective flux through the coil

$$\Phi = 4\pi N a M_y$$

$$= \mp 4\pi N a M \frac{\sin \omega t}{\sqrt{1+\delta^2}} \tag{14}$$

Faraday's law gives us

$$= \pm \frac{4\pi}{c} N a M \omega \frac{\cos \omega t}{\sqrt{1+\delta^2}} \tag{15}$$

where have assumed that the time variation of δ is slow enough that we may neglect it compared to the time derivative of cos ωt. This signal voltage is a maximum at resonance.

$$H_0 = \frac{\omega}{|\gamma|} = H^*$$

Substituting $M = \chi H$, we obtain

$$V = \pm \frac{4\pi}{c} N a \chi H_0 \omega \frac{\cos \omega t}{\sqrt{1+\delta^2}} \tag{16}$$

Equation (16) gives for the amplitude of the induced voltage

$$\nu_r = \frac{4\pi}{c} N a \gamma H_0 \omega \qquad (17)$$

The preceding considerations are qualitative since they only take into consideration those nuclear reorientations which are due to external fields. Effects due to atomic electrons and neighboring nuclei have been neglected. The importance of the atomic moments depends upon the substance under consideration. There are many substances, water for example, where the electron spins are paired off and thus their effect can be justifiably neglected. Many substances have permanent atomic moments and in such cases these moments cannot be neglected; however, we shall not consider substances with permanent atomic moments.

In order to better understand the effects of neighboring nuclei, we must further consider nuclear relaxation. There are actually two varieties of relaxation. The first, discussed in the introduction, has to do with the establishment of thermal equilibrium between an assemblage of nuclear moments with different quantum numbers. This is "longitudinal" relaxation, since it results in establishment of an equilibrium value of the nuclear magnetization along the axis of the magnetic field H_0. When the assemblage is placed in a magnetic field and relaxation takes place, there is an increase in the sample magnetization along the field axis as more of the nuclei drop into the lower state with magnetic quantum number +1/2. The characteristic longitudinal relaxation time is designated as T_1.

The other variety of relaxation may be illustrated as follows. Consider a group of nuclei which are precessing in phase

about the axis of a common magnetic field. If the nuclei were all centered on the same point, their magnetic moment vectors would be precessing together like a bundle of sticks tied together. If we take the magnetic field axis to be the z axis, the nuclei precessing in phase produce a resultant rotating magnetic vector which has a component in the xy plane. If by any process the nuclei tend to lose their phase coherence, their resultant will move toward the z axis and the macroscopic component of magnetization in the xy plane will go to zero. This type of relaxation is commonly referred to as "transverse" relaxation, and its rate is expressed in terms of the characteristic time T_2.

There are several factors which can contribute to transverse relaxation, and these may be classified as intrinsic in the nature of the sample or arising from the equipment used. The homogeneity of the applied magnetic field will be extremely important as an external factor. If the assemblage of nuclei under consideration is in a nonhomogeneous field, the nuclei will not have identical precession frequencies, and if they start off in phase they will soon get out of phase because of their different precession rates. In many cases the inhomogeneity of the applied magnetic field will be the most important factor determining T_2. Also the nucleus of one atom may have one type of molecule as a neighbor while another nucleus may have a quite different molecule as a neighbor. Such nuclei will be subjected in general to different magnetic fields and have different precession frequencies, thus permitting them to lose phase coherence. This effect will be most important in viscous media (5) where the molecules

move slowly with respect to one another. If the viscosity is low and the molecules tumble rapidly relative to the relaxation time of their nuclei, the fluctuations in the local magnetic fields are effectively averaged to zero and T_2 is therefore increased. Both T_1 and T_2 are important in determining the character of nuclear magnetic resonance signals.

In the first part of the development of the theory we considered only the external means by which the magnetization vector can be reorientated. Now we must also introduce those changes in the magnetization which are due to internal effects. A rigid quantum mechanical treatment shall not be attempted, but instead a semi-macroscopic description shall be given.

In order to obtain this description of the total change of the nuclear magnetization $\underline{M}$, terms will be introduced which contain the essential features of the longitudinal and transverse relaxation times. It will be assumed that the changes in the transverse components of the magnetization $\underline{M}$ due to internal effects are governed by the equations

$$M_x = -\frac{M_x}{T_2} \qquad (18)$$

$$M_y = -\frac{M_y}{T_2}$$

and the change in the longitudinal component M_z is given by

$$M_z = -\frac{(M_z - M_0)}{T_1} \qquad (19)$$

Adding these internal changes to the changes caused externally $\gamma\, M \times H$, we have Bloch's equations

$$\dot{M}_x - \gamma(M_y H_z - M_z H_y) + \frac{M_x}{T_2} = 0$$

$$\dot{M}_y - \gamma(M_z H_x - M_x H_z) + \frac{M_y}{T_2} = 0 \qquad (20)$$

$$\dot{M}_z - \gamma(M_x H_y - M_y H_x) + \frac{M_z}{T_1} = \frac{M_0}{T_1}$$

where M_0 is the equilibrium value of M_z. Consider the projection of $\underline{M}$ (6) on the XY plane Mxy. Movement of Mxy so as to produce a change in My will cause a current to be induced in the receiver coil around the sample with its axis along y. It is useful to consider Mxy to be made up of two magnetic components u and v which are in phase with the rf field H_1 and 90 degrees out of phase with H_1, respectively, so that Mxy = u + iv.

$$M_x = u \cos \omega t - v \sin \omega t$$
$$M_y = -u \sin \omega t - v \cos \omega t \qquad (21)$$

or in reverse

$$u = M_x \cos \omega t - M_y \sin \omega t$$
$$v = -M_x \sin \omega t - M_y \cos \omega t \qquad (22)$$

Substituting the equations (21) into (20) and using $\gamma H = \omega_0$, it follows that

$$\frac{du}{dt} = -(\omega_0 - \omega) - \frac{u}{T_2}$$

$$\frac{dv}{dt} = (\omega_0 - \omega)u - \frac{v}{T_2} - \gamma H_1 M_z \qquad (23)$$

$$\frac{dM_z}{dt} = \frac{M_0 - M_z}{T_1} + \gamma H_1 v$$

Since the receiver responds to My which is made up of both

u and v, we want to show how one can obtain a measure of one independent of the other.

H_0 is modulated but we shall consider the case where H_0 is practically constant and a steady signal is picked up in the receiver as if the magnetic field sweep were stopped on the side of peak of a resonance signal. Under these circumstances, Mxy has a constant length and rotates around the z axis at the frequency ω. The steady-state condition requires that

$$\frac{du}{dt} = \frac{dv}{dt} = \frac{dM_z}{dt} = 0 \tag{24}$$

Using these conditions with equations (23), we obtain

$$\begin{aligned} u &= -T_2\,(\omega_0 - \omega)v \\ v &= -\frac{\gamma T_2 H_1 M_z}{1 + T_2^2(\omega_0 - \omega)^2} \\ M_z &= M_0\,\frac{1 + T_2^2(\omega_0 - \omega)^2}{1 + T_2^2(\omega_0 - \omega)^2 + \gamma^2 H_1^2 T_1 T_2} \end{aligned} \tag{25}$$

Substituting the equation for Mz into that for v, gives

$$v = -\frac{\gamma H_1 M_0 T_2}{1 + T_2^2(\omega_0 - \omega)^2 + \gamma^2 H_1^2 T_1 T_2} \tag{26}$$

and

$$u = \frac{\gamma H_1 (\omega_0 - \omega) T_2^2\, M_0}{1 + T_2^2(\omega_0 - \omega)^2 + \gamma^2 H_1^2 T_1 T_2} \tag{27}$$

Assuming steady values for u, v, and Mz for some set values of H_0, H_1, M_0, T_1, and T_2, we can take a closer look at My which determines the signal. For the case where $\omega = \omega_0$, u = 0 and Mxy = iv. Thus from the definition of v, the vector Mxy must be 90 degrees out of phase with the rf field H_1 so that the field

along the Y axis due to My will have its maximum value when Hx is at its maximum value.

The experimental problem in determining nuclear magnetic resonance absorption is to measure the component of the field due to My, which is in phase with Hx, since this corresponds to v (absorption or v mode) without interference from the component of the field due to My which is out of phase with Hx and corresponds to u (dispersion or u mode). This is achieved by permitting some of the field Hx to "leak" into the receiver coil. Similarly, if we arrange to "leak" an Hy component we can look at the u mode without interference from the v mode.

The magnitude of the absorption mode signal S induced in the receiver coil under conditions of slow passage can be partially expressed by the following general equation in terms of some variables of practical interest.

$$S = \text{const } N \frac{I+1}{I} \frac{\mu^2 H_0^2}{3kT} \frac{\gamma^2 H_1 T_2}{1 + T_2^2(\omega_0-\omega)^2 + \gamma^2 H_1^2 T_1 T_2} \tag{28}$$

where N = number of nuclei in the volume of the receiver coil

I = nuclear spin number

μ = nuclear magnetic moment

k = Boltzmann's constant

T = absolute temperature

The signal strength decreases with temperature because thermal agitation opposes the lining up of the nuclei in the direction of the field H_0. It can be seen that for small values of the rf field H_1, such that

$$\gamma^2 H_1^2 T_1 T_2 << 1 \qquad (29)$$

the signal is proportional to $H_1 T_2$ at the peak of the absorption curve where $\omega = \omega_0$.

$$S = \text{const } H_1 T_2 \quad (\text{at } \omega = \omega_0) \qquad (30)$$

In these circumstances M_0 is approximately equal to Mz which means that the nuclear moments are practically at thermal equilibrium with their surroundings. If we define the resonance line width δv as the width of the absorption curve at half maximum amplitude $S_0/2$ on a plot of signal versus $\omega_0 - \omega$, then we can show that $\delta v = \frac{2}{T_2}$ as follows.

$$S = \text{const } \frac{T_2}{1 + (\omega_0 - \omega)^2 T_2^2}$$

$$= \text{const } T_2 \text{ when } \omega = \omega_0$$

$$\frac{S_0}{2} = \text{const } \frac{T_2}{2} = \text{const } \frac{T_2}{1 + (\delta v/2)^2 T_2^2}$$

$$T_2 = 2/\delta v \qquad (31)$$

T_2 is largely determined by magnetic field inhomogeneities for relatively nonviscous liquids. We can qualitatively describe the inhomogeneities by an effective irregulation of the z field of order H' where

$$T_2 = \frac{1}{|\gamma| H'} \qquad (32)$$

The magnitude of T_2 can be roughfully estimated (3) if H' is due to the neighboring nuclei whose motion can be neglected. We would expect that

$$H' \cong \frac{\mu}{r^3} \tag{33}$$

where μ is the magnetic moment of a neighboring nucleus and r is the distance of the nucleus from the point in question. Choosing $\mu = 10^{-23}$ erg/cm and $r = 2 \times 10^{-8}$ cm, this gives

$$H' = 1.0 \text{ gauss}$$

and with $\gamma = 10^4$ (cgs) we obtain

$$T_2 = 10^{-4} \text{ sec}$$

The above estimation for T_2 is only an illustration that T_2 can be much smaller than T_1. For example, T_1 for pure water is approximately 3 seconds (10).

When H_1 is large, the term $\gamma^2 H_1^2 T_1 T_2$ may well dominate the denominator of equation (28), resulting in

$$S = \text{const}' \frac{1}{H_1 T_1} \tag{34}$$

The nuclei are then said to be "saturated", and the rf power input is limited by the ability of longitudinal relaxation to transfer energy from nuclei to their surroundings. Resonance signals (7) may often be increased at large H_1 values by reducing T_1 with the aid of added paramagnetic ions such as Mn^{++}.

In a nuclear magnetic induction experiment, we may change the precession frequency of the nuclei by varying the applied magnetic field and keeping the oscillator frequency constant. At some value of the field ($H = \frac{\omega_0}{\gamma}$), the nuclear precession frequency becomes equal to the frequency of the rotating rf field produced by the oscillator, and energy may then be transferred from the rf field to the nuclei, causing some of them to go to

the higher energy state with m = -1/2. When the sample absorbs energy from the rf field, the rf field tends to tip the magnetic moments of the individual nuclei away from the magnetic field H_0. This causes the resultant of the magnetic moments to precess around the magnetic field H_0 at the precession frequency. This has the result that the macroscopic resultant is moved away from the field axis and produces a rotating component of magnetization in the x and y directions which precesses around the H field axis with the same angular velocity as the individual nuclei. This alternating field in the y direction induces a current in the receiver coil and thus generates a nuclear magnetic induction signal.

As the magnetic field H_0 is increased by the modulation of H_0, the nuclei increase their precessional frequencies and drop out of phase with the rotating rf field. At this point, transverse and longitudinal relaxation processes return the nuclear magnetization of the nuclei in the x, y, and z directions to the equilibrium values. As the oscillating y magnetization component decreases by transverse relaxation, the signal dies away in the receiver coil.

It should be emphasized that relaxation begins as soon as the nuclei absorb energy from the rf field. If T_1 and T_2 are both extremely short, the signal strength at a given field value will be very small because both longitudinal and transverse relaxation destroy the components of magnetization in the x and y directions. On the other hand, if T_1 is very long, a "saturation" effect may be noted with respect to the signal strength because the energy absorbed by the nuclei from the rf field is not

readily dissipated to the surroundings. In this situation, the nuclei reach an equilibrium distribution between their magnetic quantum numbers which is determined by the relaxation time T_1. When T_1 is short, the nuclei remain more or less at thermal equilibrium with their surroundings and the absorption of energy then depends primarily on T_2.

DESIGN OF EQUIPMENT

We have seen in the introduction and theory that a sample which possesses a magnetic moment will, when placed in a suitable magnetic field H_0, absorb energy from an rf field at resonance and induce a voltage in a receiver coil wound around the sample. Equipment was designed to provide the rf field and detect the induced signal. The complete experimental arrangement is best understood in terms of the block diagram shown in Fig. 1, Plate I.

The steady magnetic field H_0 was provided by a Variflux variable permanent magnet made by Laboratory for Science. A plot of field strength versus gap width is given in Fig. 2, Plate I, for the 10-cm pole faces which were used. The pole faces could be made parallel by mechanical adjustments and the pole faces were shimmed. The field was adjusted by means of a Perkin-Elmer precision gauss meter so that it was homogeneous to one part in 10^4 over a three-cm circle which is larger than the sample cross-sectional area. It is this nonhomogeneity which is important in determining the transverse relaxation time T_2. Since the induced signal is proportional to H^2, it is desirable to have the field

EXPLANATION OF PLATE I

Fig. 1. Block diagram of the double-coil nuclear induction experiment. M = magnet, S = sweep coils, T = transmitter coil, R = receiver coils, A = oscilloscope.

Fig. 2. Plot of field strength H_0 (gauss) versus gap (cm) for the 10-cm pole faces for the Variflux magnet.

PLATE I

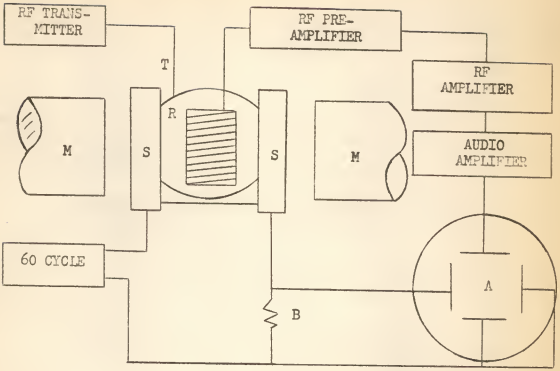


Figure 1

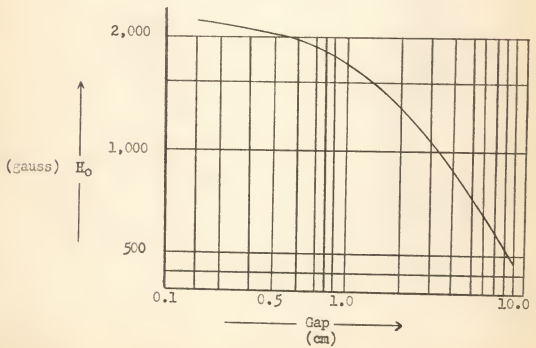


Figure 2

H_0 as large as possible. With a 5-megacycle rf oscillator the value of H_0 was restricted to 1180 gauss.

The nuclear induction "head" or probe used was a modification of the one used by Weaver (8). A sectional view is shown in Fig. 1, Plate II. The body of the probe was constructed of brass. The main body was machined from a 4-inch by 4-inch by 5/8-inch piece of brass. A 3½-inch by 3½-inch x 5/8-inch section was milled out of this and a 4-inch by 4-inch by 1/16-inch plate was soldered to one side. The other side was covered by a similar, but removable, plate which was held on by eight brass screws.

The transmitting coil was wound on blocks of lucite. Half of the coil was on a rigidly fixed piece of lucite while the other half was wound on a piece of lucite which was movable relative to a fixed block of lucite. The two were very accurately machined so as to allow relative motion in only one direction. The movable block was positioned by a screw and spring under compression. Hydrochloric acid was used to clean up the brass so as to remove any ferromagnetic material that might have been left while machine work was being done on the probe.

The receiving coil consisted of two layers of No. 24 copper wire of 10 turns each. The coil was one inch long and had an outside diameter of 39/64 inch and an inside diameter of 23/64 inch. The diameter of the sample, which was in a tube of outside diameter of 23/64 inch, was 17/64 inch, giving an effective sample volume of 0.9 cm^3.

Moving one half of the transmitting coil "tilts" the axis of

EXPLANATION OF PLATE II

Fig. 1. Schematic diagram of the nuclear induction probe with top plate removed. A = shield, F = fixed lucite blocks, M = sliding lucite block, S = screw and compressed spring, R = receiver coil, T = transmitter coil, G = ground connection for transmitter coil, V = v-mode control, and U = u-mode control, O = to input of receiver.

Fig. 2. Schematic diagram of u-mode control. R = resistance. (x, y, and z directions are consistent with the choice of coordinates used in the theory section.)

PLATE II

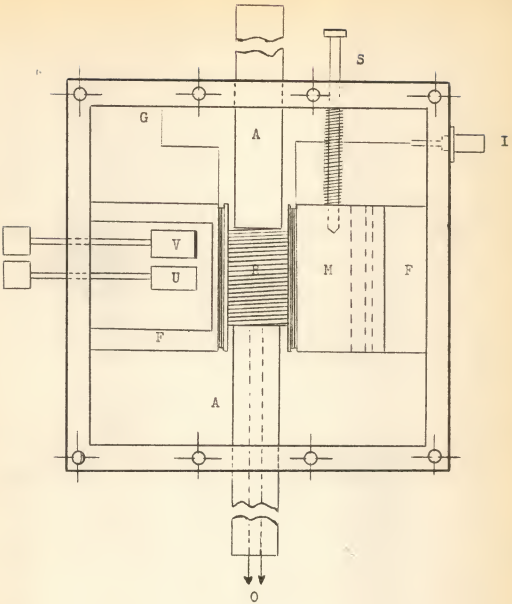


Figure 1

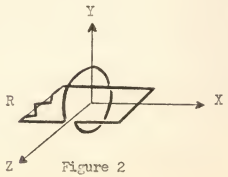


Figure 2

the rf field relative to the axis of the receiver coil, and thus varies the flux linkage between these two coils. The transmitting coil is made up of 20 turns of No. 30 copper wire on each block of lucite. The output from a James Knight model JKTO-43 5-megacycle oscillator was amplified by a Signal Corps model RT-46/TRC-10 transmitter which was used to drive the rf transmitter coils in the probe. The power for the oscillator was provided by a Sorensen Nobatron model Q28-1 d-c power supply. Care was taken so as not to exceed 28 volts. The stability of the oscillator was five parts in 10^8 per day.

The induced signal in the receiving coil is composed of an in-phase voltage and a voltage 90 degrees out-of-phase with the rf field in the transmitter coil. The in-phase component is the u-mode, or dispersion mode, described previously in the theory. The quadrature component, 90 degrees out-of-phase with the transmitter, is the v-mode, or absorption mode.

The tilting of the rf field produces a course balancing of the quadrature component. A fine v-mode control was provided by an additional control consisting of a circular piece of copper 3/8 inch in diameter and two mils thick mounted on the end of a lucite rod. The u-mode control used was similar to that used by Weaver (8) and consisted of an inductance loop and a series resistance of such a value that the total impedance was predominantly resistive. A diagram of the u-mode control is shown in Fig. 2, Plate II. Since the main rf field is predominantly in the x direction, the current induced in the circular loop does not change upon rotation about the x axis except to increase

slightly as it is moved in closer to the transmitter coils. However, the coupling of the receiver coil with the rectangular loop does change upon rotation. The control is mounted in a piece of lucite rod which is threaded so as to fit the corresponding threaded hole in the main body of the probe tightly. The combined effect of the three controls adjusts the magnitude and phase of the signal input to the preamplifier. The mechanical stability of the parts composing the head is quite critical since once the leakage has been adjusted to the desired level it is essential that it remain at that level.

In order to further minimize unwanted coupling with the receiver coil, the leads to the receiver coil were carefully shielded by a brass tube which extended from the bottom of the coil to outside the main body of the probe. The input connections to the transmitter coil and the output connector from the receiver coil on the end of the brass tube shield were made by coaxial cable.

In order to know that the signal from the probe is caused by the nuclear moments and not by some unknown cause, it is essential that the signal due to the nuclear moments be modulated in some known and controlled manner. The steady field H_0 was modulated at 60 cps with an amplitude of a fraction of a gauss by means of helmholtz coils wound around the pole faces. The amplitude of the 60-cycle modulating field could be varied from a few tenths of a gauss to about five gauss. This makes it unnecessary to try for extreme reduction of the leakage of H_1 into the receiver coil, since once the leakage has been reduced to a point

where it is, say, 10^3 times the induced signal, it may serve as a carrier upon which the induced signal appears, modulated at 60 cps. When the mean value of the magnetic field H_0 is close to the resonance value, the field is swept through the resonance value twice each cycle. The voltage drop across the resistor R is used to trigger the scope.

The signal from the receiver coil was amplified by an amplifier designed by Weaver (8). The amplifier had a gain of 50 and a noise figure of 25 decibels. The output of the amplifier was detected by a 1N34 diode which passed only the 60-cycle modulated envelope of the signal. The 60-cycle modulation was further amplified by Bureau of Ships type CML-50171 audio amplifier and then displayed on a Tektronix 515A oscilloscope. The audio amplifier had a continuously variable gain between zero and 10^5 with a noice level of 20 decibels when the gain was adjusted to a maximum.

Equation (17) can be used to estimate the magnitude of the induced voltage which might be expected. Using H_0 = 1180 gauss, a = 0.38 cm^2, γ = 3.4 x 10^{-6}, $\omega = 2\pi \times 5 \times 10^6$, and N = 20, we obtain

$$V_r = \frac{4\pi}{c} N a \gamma H \omega$$

$$= 400 \times 10^{-6} \text{ stat volts}$$

$$= 1.33 \times 10^{-6} \text{ volts}$$

In order to reduce the relaxation time of the proton resonance, paramagnetic catalyst were added to the samples. Both Mn^{++} and Fe^{+++} ions were used in various concentrations. A hole

in the main body of the probe allowed the sample to be inserted into the receiver coil without mechanically disturbing the alignment of the equipment.

CONCLUSIONS

With 40 volts across the transmitting coils and a 60-cycle 0.14-gauss sweep of the steady magnetic field H_0, proton resonance was observed in 0.1 and 0.01 molar solutions of $Fe(NO_3)_3$ and $Mn\ SO_4$. Resonance was not observed in distilled water because without an impurity the relaxation time was too long. Upon addition of a paramagnetic impurity, the relaxation time T_1 was induced, and the resonance signal was increased in accord with equation (34). However, upon adding enough impurity to give a 1.0 molar solution of either $MnSO_4$ or $Fe(NO_3)_3$, the relaxation time was reduced too much and resonance was not observed.

After a coarse uncoupling of the rf field with the receiver coil was obtained by means of the screw adjustment, the remaining leakage was minimized by adjustment of the u-mode and v-mode paddles. If the out-of-phase component of the leakage was completely minimized by the u-mode paddle, and the in-phase component was incompletely minimized by the v-mode paddle, the absorption signal was obtained. On the other hand, if the in-phase component was completely minimized, and the out-of-phase component was incompletely minimized, the dispersion signal was obtained.

Figures 1(a) and 1(c), Plate III, show the oscilloscope display with no sample and thus indicate the noise level. Figure

EXPLANATION OF PLATE III

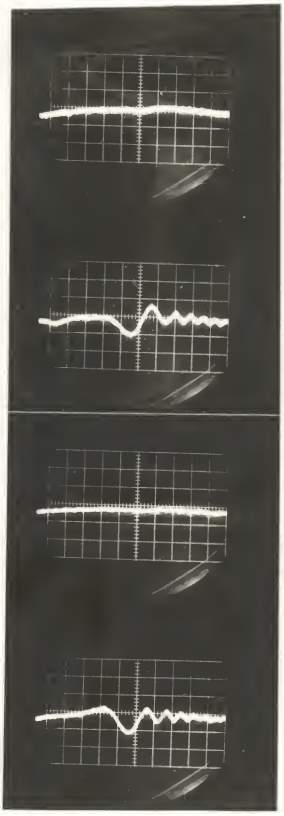
Fig. 1(a). Photograph of oscilloscope display with no sample in probe.

Fig. 1(b). Photograph of oscilloscope display with 0.01 molar solution of $Fe(NO_3)_3$ in probe with paddles adjusted to show dispersion mode.

Fig. 1(c). Photograph of oscilloscope display with no sample in probe.

Fig. 1(d). Photograph of oscilloscope display with 0.01 molar solution of $Fe(NO_3)_3$ in probe with paddles adjusted to show absorption mode.

PLATE III



(a)

(b)

(c)

(d)

Figure 1

1(d), Plate III, shows the absorption signal from a 0.01 molar solution of $Fe(NO_3)_3$ in water, and Fig. 1(b), Plate III, shows the dispersion signal for the same sample.

The resonance signal from the 0.01 molar solution of $Fe(NO_3)_3$ was one volt with an overall gain of 3.33×10^5 for the detection system. Thus the signal from the probe was three microvolts, which was larger than the 1.33 microvolts estimate from equation (17). The oscilloscope display of the signal could be increased above one volt by increasing the gain of the audio amplifier from 10^4 to 10^5 but only at the expense of a higher noise level.

The "wiggles" in the displayed signal occur after the magnetic field has passed through resonance. Nuclear spins which have been tipped over by the application of the rf field at their precessional frequency continue to precess in a coherent way after the magnetic field has changed to a nonresonant value. The changing nuclear precession rate comes alternately in and out of phase with the applied signal whose frequency remains constant. If the sweep rate were decreased so that the field went through resonance, say once every 30 minutes, then these "wiggles" should disappear.

Changes in the temperature of permanent magnet produced changes in the field H_0 which amounted to about 0.1 gauss per centigrade degree of room temperature with the field set at 1180 gauss. With the large heat capacity of the magnet, it responded very slowly to any changes in the room temperature. With a sweep rate of 60 cps this temperature-dependent drift of the magnet was not crucial. However, if the system were to be used at slow sweep

rates where the drift of the magnetic field became comparable to the sweep rate, then it would become critical.

The 0.1 molar solutions in both cases gave signals which were only one-fourth as large as the ones from the 0.01 molar solutions. The resonance signal from the 0.01 molar solution of $MnSO_4$ was only three-fourths of a volt compared to the one-volt signal from the $Fe(NO_3)_3$ 0.01 molar solution.

The line width of the resonance signal from all of the samples was 0.017 gauss and did not depend upon the sweep rate. This line width was determined mainly by the inhomogeneity in the H_0 field and agrees with gauss meter measurements of the field inhomogeneity.

The rf voltage across the transmitter coils was varied from 24 to 80 volts. The induced signal from the samples became larger as the rf field was increased but only at the expense of a higher noise level. Forty volts was chosen because it gave the maximum signal with a minimum of noise.

The sweep field was varied from 0.07 gauss up to 0.8 gauss. A 0.14-gauss sweep was chosen since decreasing it below 0.14 gauss did not increase the signal and increasing the sweep above 0.14 gauss decreased the signal strength.

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THE CONSTRUCTION AND OPERATION OF A NUCLEAR MAGNETIC RESONANCE PROBE

by

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If an external magnetic field is applied to a system of nuclei with magnetic moments and angular momentum, the nuclear magnetic moments will experience torques and will tend to be lined up parallel to the field. Although direct observation of such a lining up is difficult, it is possible, under appropriate conditions, for the moments to absorb energy from a magnetic field oscillating with a frequency in the radio-frequency region. Such absorption gives rise to what are called nuclear magnetic resonance spectra. It was the purpose of this research to build the equipment necessary for the observation of nuclear magnetic resonance spectra.

A 5-megacycle oscillator was used to provide the rf field and a variable permanent magnet was used to supply the external magnetic field. A nuclear induction "head" was built to house the rf coils and the receiver coil in which a voltage was induced by the precessing magnetic moments upon absorption of energy from the rf field. This voltage was amplified and displayed on an oscilloscope and photographed.