Mark and Olson, Experiments in Modern Physics.

Chapter 9

NUCLEAR MAGNETIC RESONANCE

9.1 INTRODUCTION

One of the very important postwar achievements in physics is the study of nuclear magnetism. This work grew out of the intensive development of radar during the war. The first actual nuclear magnetic resonance experiments were performed during 1946–1948 by Felix Bloch[1] of Stanford University and E. M. Purcell[2] of Harvard Uni-

versity. Both experimenters observed transitions between different orientation states of protons in an external magnetic field. Rapid strides in technique were made shortly after the first experiments were performed, and within a few years a large number of nuclear magnetic moments had been measured by many different workers. In addition to the measurements of nuclear magnetic moments, nuclear magnetic resonance experiments also contributed to the understanding of internal magnetic fields in crystals, and many important experiments have been performed in solid-state and molecular physics.

9.2 LARMOR PRECESSION

Nuclear magnetic resonance is closely related to the Zeeman effect in atomic spectroscopy. Both are caused by the precession in an external magnetic field of magnetic moments modified by quantum mechanical rules which define the behavior of atomic and nuclear systems. The quantum description of precessing magnetic moments was first derived for atoms and was then extended to nuclei when it was discovered that nuclei also possess magnetic moments. This same sequence will be followed here.

An electron moving in an orbit around a nucleus has an angular momentum and, also, a magnetic moment associated with the current produced by the charge moving in the orbit. The magnetic and mechanical moment vectors point in opposite directions because of the negative sign of the electronic charge. If the orbit is circular and has a radius r, the mechanical moment is

$$p = m_e v r = m_e r^2 \omega \tag{9.1}$$

and the magnetic moment is

$$\mu = -iA = -i\pi r^2 \tag{9.2}$$

where ω is the angular velocity of the charge, i is the current due to the electron moving in the orbit. The electron current is determined by the following expression:

$$i = e\nu = \frac{e\omega}{2\pi} \tag{9.3}$$

Assume the atom is now placed in an external magnetic field as shown in Fig. 9.1. The magnetic field H exerts a torque on the magnetic moment which tries to line up the moment with the field. The torque, which is the vector product of the magnetic field H and the magnetic moment $\boldsymbol{\mu}$, is given by

$$\mathbf{T} = \boldsymbol{\mu} \times \mu_0 \mathbf{H} \qquad \text{or} \qquad T = \mu\mu_0 H \sin\theta \tag{9.4}$$

The quantity μ_0 is the permeability of free space and equals $4\pi \times 10^{-7} \simeq 12.57 \times 10^{-7}$ webers/amp-m.) This torque, which points out of the plane of the paper, is equal to the time rate of change of angular momentum. Thus

$$\frac{d\mathbf{p}}{dt} = \mathbf{T} \qquad \text{or} \qquad \frac{dp}{dt} = \mu\mu_0 H \sin\theta \tag{9.5}$$

The rate of change of angular momentum is perpendicular to the angular momentum vector **p**, so that the vector precesses around the

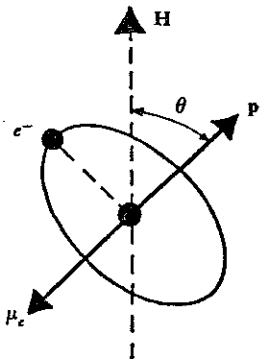

FIGURE 9.1

Orientation (relative to an external magnetic field) of the orbital angular momentum and resulting magnetic moment vectors of orbiting electron.

direction of the field. The frequency of precession can be computed with the help of Fig. 9.2. The change in the angular momentum in terms of the angle $d\alpha$ is

$$dp = p \sin\theta \, d\alpha \tag{9.6}$$

Substituting Eq. (9.6) into Eq. (9.5) gives

$$\mu\mu_0 H \sin\theta = p \sin\theta \frac{d\alpha}{dt} \tag{9.7}$$

The frequency of precession ν is equal to $(1/2\pi)(d\alpha/dt)$, so that

$$2\pi\nu = \frac{\mu}{p} \mu_0 H \tag{9.8}$$

Using Eqs. (9.1), (9.2), and (9.3) for the mechanical moment, the

magnetic moment, and the current, respectively, gives

$$\nu_L = \frac{\mu_0}{2\pi}\frac{eH}{2m_e} \tag{9.9}$$

The frequency given in Eq. (9.9) is called the Larmor frequency. Note that the Larmor frequency is independent of the angle between the mechanical moment and the magnetic field. The Larmor frequency is the characteristic precessional frequency of an atomic orbital electron in an external magnetic field.

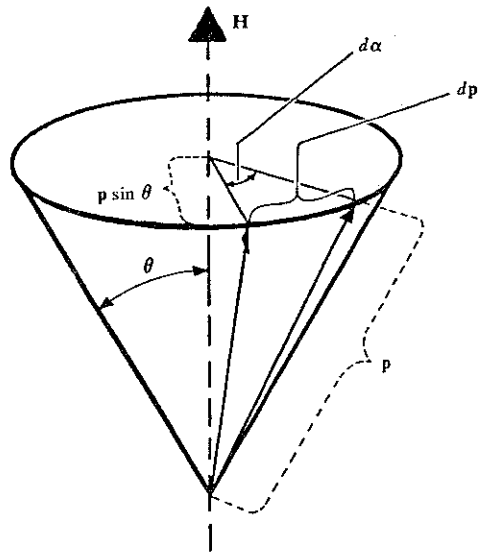

FIGURE 9.2

Angular momentum vector displacement caused by interaction force between the magnetic moment and the external field.

The magnetic field in Fig. 9.2 does not change the orientation of the magnetic moment with respect to the field direction, that is, the angle θ is a constant. It can easily be seen that a magnetic field component perpendicular to H is necessary to cause θ to change. Furthermore, this perpendicular component cannot be simply a static field, since this would only add vectorially to H and thus change the axis around which the moment precesses. The perpendicular component should rotate with the same angular frequency as the angular momentum vector p. Such a rotating field can be applied, but in practice it is generally easier to use a linearly oscillating field which is perpendicular to H. A sinusoidally oscillating field can always be split into two circularly

polarized components. In this case one of the two rotating field vectors precesses around the fixed field at the same rate as the magnetic moment. The other circularly polarized component rotates in the opposite direction with an apparent frequency (with respect to the precessing moment) equal to twice the Larmor frequency.

The effect of applying the oscillating field ($H_0 \sin 2\pi\nu_L t$) can be readily understood if the precessing vectors are viewed from a coordinate system which rotates around the fixed field with an angular velocity $2\pi\nu_L$. The magnetic moment and one of the rotating components will be in phase with each other and will thus appear as "constant" vectors in the new coordinate system. The magnetic moment vector will precess around the in-phase component, thus changing the angle θ. Since the fixed field H is very much larger than the maximum value of the oscillating field, the angle θ changes only slightly during each cycle of the Larmor precession. The oscillating magnetic field is thus usually regarded as a small perturbation on the strong constant field. The out-of-phase component of the oscillating field will not change θ. It can be shown that it causes the magnetic moment vector to perform small oscillations around some equilibrium value of θ, but no net change in θ occurs. If the oscillating field is applied with any frequency other than the Larmor frequency, neither of the rotating field components will be in phase with the moment and thus will cause no net change in θ.

9.3 ENERGY LEVELS AND TRANSITIONS

The potential energy of a magnetic moment vector $\boldsymbol{\mu}$ in a magnetic field H is a function of the angle between the vectors. The torque defined in Eq. (9.4) tries to line up the vectors $\boldsymbol{\mu}$ and H so that they are parallel. This state of the system has the lowest potential energy, whereas the state in which $\boldsymbol{\mu}$ and H point in opposite directions has the highest potential energy. The work done to rotate the magnetic moment from the lowest energy position ($\theta = 0$) to a position where the angle θ has a finite value is

$$E = \int_0^\theta T \, d\theta' = \mu\mu_0 H \int_0^\theta \sin\theta' \, d\theta' = \mu\mu_0 H(1 - \cos\theta) \quad (9.10)$$

To change the orientation of the magnetic moment, energy must either be emitted or absorbed. It has already been shown that this energy can be supplied by an oscillating magnetic field applied to the sample at the proper "resonant" (Larmor) frequency, hence the name magnetic resonance.

To understand how energy is transferred to the system in a real

situation, some elementary knowledge of quantum mechanics is necessary. An angular momentum vector p has only a certain number of discrete orientations with respect to an external axis. This result is based on the well-known Stern-Gerlach experiment[3] in which the various discrete components of a magnetic-mechanical moment system are separated using a nonhomogeneous magnetic field. It was shown

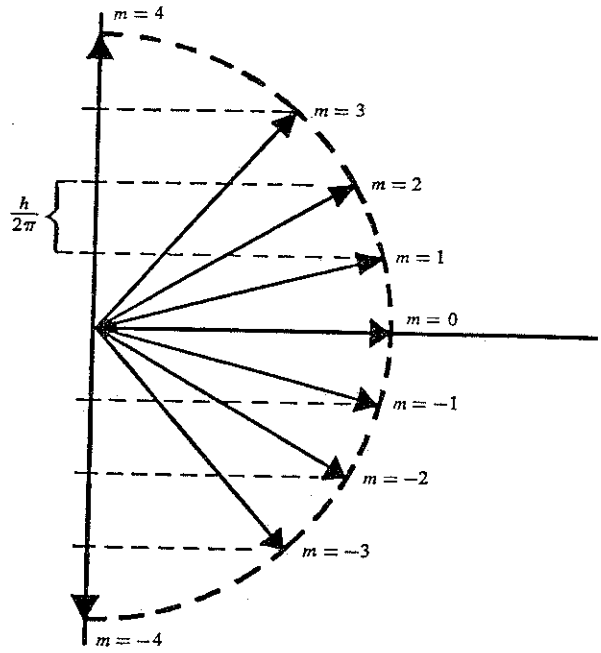

FIGURE 9.3

Possible orientations relative to an external field direction of an angular momentum vector of quantum number $l = 4$.

that the component of the angular momentum with respect to the field axis z is

$$p_z = \frac{mh}{2\pi} \tag{9.11}$$

where m is an integer and h is Planck's constant. The values of m range between $-l$ and $+l$, where l is the orbital angular momentum quantum number. The situation is illustrated in Fig. 9.3 for the case when the maximum component of the angular momentum along the magnetic field is 4. The change in energy between successive orientations of the

moment system can be calculated using Eq. (9.10). The energy change is

$$\Delta E = \mu\mu_0 H \sin\theta\,\Delta\theta = \Delta(\mu\mu_0 H\cos\theta) \tag{9.12}$$

This expression can be rewritten in terms of the Larmor frequency, using Eq. (9.8),

$$\Delta E = \Delta(p\cos\theta)\,2\pi\nu_L \tag{9.13}$$

The quantity in parenthesis in Eq. (9.13) is the z component of the angular momentum vector **p**. From Eq. (9.11) it is obvious that any change in this component must be equal to at least $h/2\pi$. Thus

$$\Delta E = h\nu_L \tag{9.14}$$

which is the spacing between the energy levels of a magnetic-mechanical moment system in a magnetic field. It is interesting to note that Eq. (9.14) is also the statement governing the emission and absorption of radiant energy derived in Appendix II. The major problem in magnetic resonance experiments is to detect the energy associated with the transitions corresponding to the different orientations of the magnetic moments in the external field.

The introduction of quantized angular momenta in Eq. (9.11) leads to the more usual manner in which the relationships between transition energies and magnetic moments are written. Starting again with Eq. (9.8), the quantized mechanical moment is given by

$$p = \frac{h}{2\pi} I \tag{9.15}$$

where I may be of either integer or, as will be seen later, half-integer value. Substituting (9.15) into (9.8) gives

$$\nu_L = \frac{\mu}{hI}\,\mu_0 H \tag{9.16}$$

and since $\Delta E = h\nu_L$

$$\Delta E = \frac{\mu}{I}\,\mu_0 H \tag{9.17}$$

It is customary to write Eq. (9.14) in terms of a quantity called the "Bohr magneton," μ_B, which is defined as

$$\mu_B = \frac{e\hbar}{2m_e} \tag{9.18}$$

so that in the case of quantized angular momenta, Eq. (9.17) can be rewritten as

$$\Delta E = (\mu/\mu_B I)\mu_B\mu_0 H \tag{9.19}$$

by multiplying the numerator and denominator by μ_B. The factor $(\mu/\mu_B I)$ is called the Lande g factor so that

$$\Delta E = g\mu_B\mu_0 H \tag{9.20}$$

and

$$g = (\mu/\mu_B I) \tag{9.21}$$

For the case of an electron moving in a circular orbit, it can be shown that $g = 1$ so that substituting Eq. (9.18) into (9.20) and using (9.14) leads to the correct expression for the Larmor frequency (9.9). It can be shown that $g = 1$ for all classically rotating objects having uniform charge-to-mass ratios throughout their volumes. The same is not true, however, in the case of the intrinsic angular momentum, or spin, of the electron. It is known that the value of the electron spin is $I = \frac{1}{2}$, while the magnetic moment associated with this spin is equal to one Bohr magneton, μ_B. Therefore, the g factor defined in Eq. (9.21) is equal to 2 for the electron spin. This result is a consequence of the complete relativistic theory of the electron. In general, a group of magnetic and mechanical moments may be coupled together in such a way that g can take on noninteger values.

9.4 NUCLEAR MAGNETISM

Nuclei also possess magnetic moments. These were first discovered when atomic spectra, particularly for hydrogen and deuterium, were investigated with spectrographs having ultrahigh resolution. It was found that many spectral lines were split into multiplets with very small separations. This phenomenon is called hyperfine structure and was explained by W. Pauli[4] as being caused by the interaction between the atomic and nuclear magnetic moments. The unit used to express nuclear magnetic moments is the "nuclear magneton," μ_N, which is identical to the "Bohr magneton" defined in Eq. (9.18) except that electron mass, m_e, is replaced by proton mass, m_p. Nuclear moments are thus about 1830 times smaller than atomic magnetic moments.

The magnetic moment of the proton has been measured by determining the Larmor frequency of protons in a magnetic field, H. The associated energy splitting was found to be

$$\Delta E = 2.8\mu_N\mu_0 H \tag{9.22}$$

Thus, it can be said that the proton possesses a magnetic moment of 2.8 nuclear magnetons. The value of the g factor of the proton is 5.56, which can be obtained by substituting μ_N for μ_B in Eq. (9.21) and remembering that the intrinsic spin of the proton is $I = \frac{1}{2}$. The reason

for the large g factor of the proton is not understood, and all attempts at making an accurate quantitative prediction of the proton magnetic moment have failed.

The frequencies necessary to observe transitions between various nuclear orientation states can be easily estimated. For protons, the g factor is 5.56, so that

$$\nu_L = 5.56 \frac{\mu_0}{2\pi} \frac{eH}{2m_p} \tag{9.23}$$

To evaluate this expression, a word about the units used to measure magnetic fields is in order. The magnetic field H is measured in units of ampere-turns/meter, and H is determined by the configuration of the field coils and the magnitude of the current in them. The magnetic induction B resulting from the field H is defined as $B = \mu_0 H$ in free space and is measured in units of webers/square meter. The magnetic induction is determined by the properties of a material, and for the same field H, different values of B occur in different materials. In this case $B = \mu H$, and μ is the permeability of the material.

In practice, the important quantity is B, for it defines the field strength the nuclear magnetic moment resides in. It will be assumed for the remainder of the chapter that the materials investigated have a permeability equal to that of free space (i.e., $\mu = \mu_0$ and so the symbol μ will be reserved to stand only for magnetic moments). Thus, for an assumed induction of one-tenth of a weber/square meter, the proton Larmor frequency is

$$\nu_L = \frac{5.56}{2\pi} \frac{eB}{2m_p} \simeq 4 \times 10^6 \text{ cycles/sec} \tag{9.24}$$

(To relate this quantity of B to the corresponding units in the Gaussian system, it is convenient to remember that 1 weber/m^2 = 10^4 gauss.) This frequency corresponds to short-wave radio frequencies used in communications. Power must be supplied to the sample with a radio-frequency oscillator operating at this frequency. The energy of the nuclear reorientation transitions considered here is

$$\begin{aligned} E &= h\nu_L = 6 \times 10^{-27} \times 10^6 = 6 \times 10^{-21} \text{ ergs} \\ &= 4 \times 10^{-9} \text{ ev} \end{aligned} \tag{9.25}$$

This energy is very small indeed. It serves to define the energy scale of the phenomena investigated in nuclear magnetic resonance experiments. A typical sample in a proton resonance experiment might consist of a tenth of a cubic centimeter volume of water or roughly 10^{22} protons. If the spin orientations of all the protons in the sample are flipped

simultaneously, the total energy involved is roughly

$$E_T = 4 \times 10^{-9} \times 10^{22} \approx 4 \times 10^{13} \text{ ev}$$
$$\approx 20 \text{ ergs} \tag{9.26}$$

This energy is also very small, corresponding to a few microwatts if it were delivered continuously at the rate of 20 ergs/sec. Actually, not all the protons in a given sample are flipped when radio-frequency power of the correct frequency is applied. The actual power which can be absorbed by the sample under a given set of conditions is determined by the temperature, the applied magnetic field, and the interaction between the nuclear spins and the lattice. It can be calculated quite easily from certain simple assumptions.

When a magnetic field is applied to a sample containing an assembly of protons, there exists a difference in the number of protons with their spins parallel ($m = \frac{1}{2}$) and those with their spins antiparallel ($m = -\frac{1}{2}$) to the field. This difference is determined by the Boltzmann factors. If there are N_0 protons in the sample, the number of protons having $m = \frac{1}{2}$ is given by the relation

$$N_{\frac{1}{2}} = \frac{N_0}{2} e^{\mu B/kT} \tag{9.27}$$

and for $m = -\frac{1}{2}$ it is

$$N_{-\frac{1}{2}} = \frac{N_0}{2} e^{-\mu B/kT} \tag{9.28}$$

In practice μB is always much smaller than kT, so that the exponentials can be expanded. Thus the difference between the two populations is

$$\Delta N = N_{\frac{1}{2}} - N_{-\frac{1}{2}} = \frac{N_0}{2}\left(1 + \frac{\mu B}{kT}\right) - \frac{N_0}{2}\left(1 - \frac{\mu B}{kT}\right)$$
$$= N_0 \frac{\mu B}{kT} \tag{9.29}$$

At room temperature, and for a magnetic induction of one-tenth of a weber per square meter, the quantity $\mu B/kT$ of Eq. (9.24) is approximately 10^{-7}. Thus, in a sample of 10^{22} protons, the excess population in the lower energy state is only 10^{15} protons.

When the oscillating magnetic field is applied, it can induce transitions in both directions. That is, the protons may gain energy from the radio-frequency field or they may give energy to the radio-frequency field. (For a complete discussion of absorption and stimulated emission of electromagnetic energy, see Chapter 11.) The rate at which energy is absorbed from the oscillating field by a group of protons is very close to the rate at which the protons give energy to the radio-frequency field. This is because the spontaneous emission term in this case is

negligible (i.e., for $n_r + 1$, the $n_r \gg 1$). Therefore any net energy absorbed by the sample from the radio-frequency field depends only on the population difference between the two orientation states. If the states are equally populated, no net energy is absorbed or emitted.

In the case of the proton sample considered, the excess population in the lower energy state ($m = \frac{1}{2}$) is 10^{15} protons. When the applied radio-frequency field has changed half of these protons (5×10^{14}) to the higher energy state, equilibrium is reached, and no further change in population occurs. At this point the sample is said to be saturated. This situation exists only if there is no other mechanism for reorienting the protons. In all practical cases, the interaction between the proton magnetic moment and the fields of other magnetic moments (usually large atomic moments) in the sample material provides a means by which the proton spins can be reoriented independent of the radio-frequency field. Thus, if a sample is saturated by the radio-frequency field (i.e., the populations are made equal) and the radio-frequency field is then turned off, the proton moments will return to the thermal equilibrium of Eqs. (9.27) and (9.28). The characteristic decay time for reaching equilibrium is called the "relaxation time."

From the arguments outlined in the foregoing paragraphs it is obvious that the radio-frequency power absorbed by the sample will depend on a competition between the tendencies of the applied radio-frequency field to saturate the sample and the relaxation mechanism to return the spin distribution to thermal equilibrium. To observe resonance absorption, a significant fraction of the population difference must be available so that transitions can occur. It is clear that the energy absorbed will generally be very much smaller than the amount calculated in Eq. (9.26).

To observe resonance signals from protons, a small glass tube filled with water is used as a sample. Since the relaxation time of pure water is quite long ($\sim$3.6 sec), it is necessary to add some paramagnetic ions to obtain easily observable proton resonance signals. These ions have large permanent magnetic moments, and they help to randomize the proton spins more rapidly, thus reducing the relaxation times to values smaller than 10^{-3} sec. Therefore a large excess proton population is always available in the lower energy level to absorb radio-frequency energy when the magnetic field and resonance frequency are properly adjusted.

9.5 EXPERIMENTAL METHODS

Nuclear resonance experiments are usually conducted using an apparatus of the kind shown in Fig. 9.4. The permanent magnet or electro-

magnet supplies the constant magnetic field in which the nuclei precess. The modulating field is provided by the two coils shown. The function of the modulating coil is to vary the value of the magnetic field while the frequency of the radio-frequency field is held constant, so that, at least for some values of the magnetic field, H, the condition of Eq. (9.23) is satisfied. This is easier than holding the magnetic field constant and varying the oscillator frequency to sweep through the resonant condition of Eq. (9.23). The oscillating radio-frequency magnetic field is

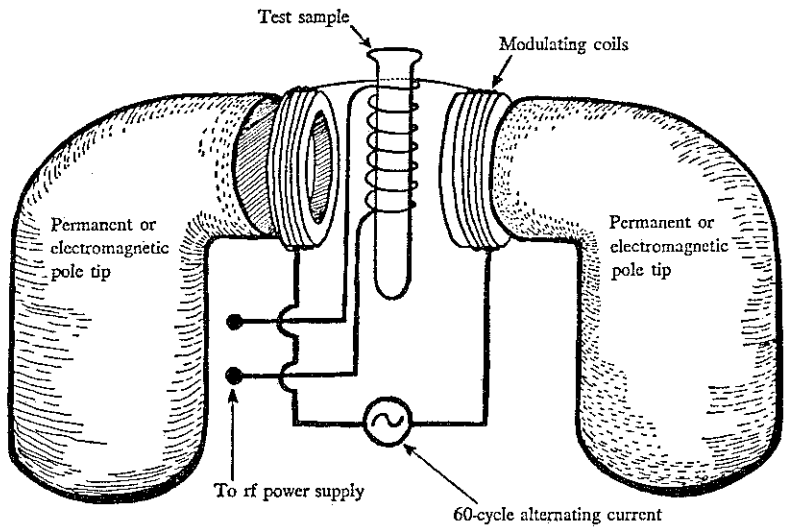

FIGURE 9.4

Experimental configuration showing magnet poles, modulating coils, and the resonance sample, using the marginal oscillator or bridge methods of resonance detection.

perpendicular to the external field. The modulated field is shown in Fig. 9.5. The magnetic induction B_0 has a value of approximately 0.10 weber/m^2 in most cases, so that the appropriate Larmor frequencies for nuclear systems are of the order of a few megacycles. The modulating field usually has a peak value of the order of 2.5×10^{-4} webers/m^2 gauss, so that the external field is given by an expression of the form

$$B(t) = B_0 + B_1 \sin \omega t \tag{9.30}$$

where typically $B_0 = 0.10$ weber/m^2

$B_1 = 2.5 \times 10^{-4}$ webers/m^2

The resonance condition can be observed in a number of different ways. One common method is to observe a change in the power emitted by the oscillator which supplies the radio-frequency perturbing field. The coil in which the sample resides is part of the LC-tuned circuit in the oscillator. When the resonance condition [Eq. (9.23)] is fulfilled, the impedance of L changes, since a small amount of energy is absorbed by the sample. This change can be detected as a change in the bias voltage on the collector of a transistor. The oscillator is usually adjusted in such a way that the feedback signal from the LC circuit to the oscillator

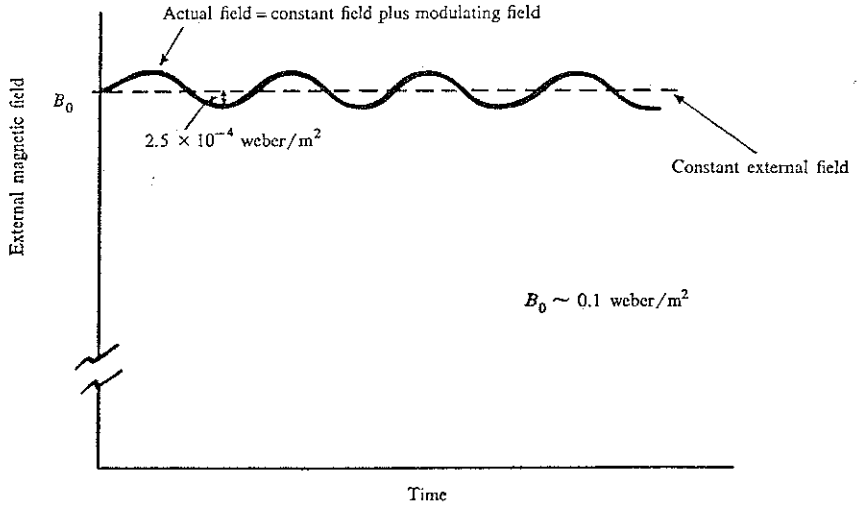

FIGURE 9.5

External field resulting from the superposition of the constant and oscillating fields.

transistor is just barely positive, that is, the oscillations are just sustained. In this condition even a small change in the load may stop the oscillator completely, thus causing a large, observable effect. A schematic diagram of the system used to observe the nuclear resonance signal is shown in Fig. 9.6 and the oscillator circuit[5] is shown in Fig. 9.7. The horizontal sweep of the oscilloscope is driven by the 60-cycle modulating coil signal. The vertical sweep is connected to the output of the oscillator. If the oscillator frequency is not correct [i.e., does not fulfill the resonance condition of Eq. (9.23)], then the oscilloscope pattern observed is that shown in the left panel of Fig. 9.8; if the resonance condition is properly satisfied, the pattern shown in the right-hand panel is observed.

The radio-frequency coil of the oscillator circuit in Fig. 9.7 should consist of 10 to 20 turns (depending on the frequency range desired) wound on a $\frac{1}{4}$-in. diameter core. The wire used should be about No. 20 lacquered copper wire. The radio-frequency coil and the modulating coils can be combined into an integral head for convenient use. A piece of brass ($1\frac{1}{2}$ in. OD $\times$ 1 in. high) can be used as a form on which the

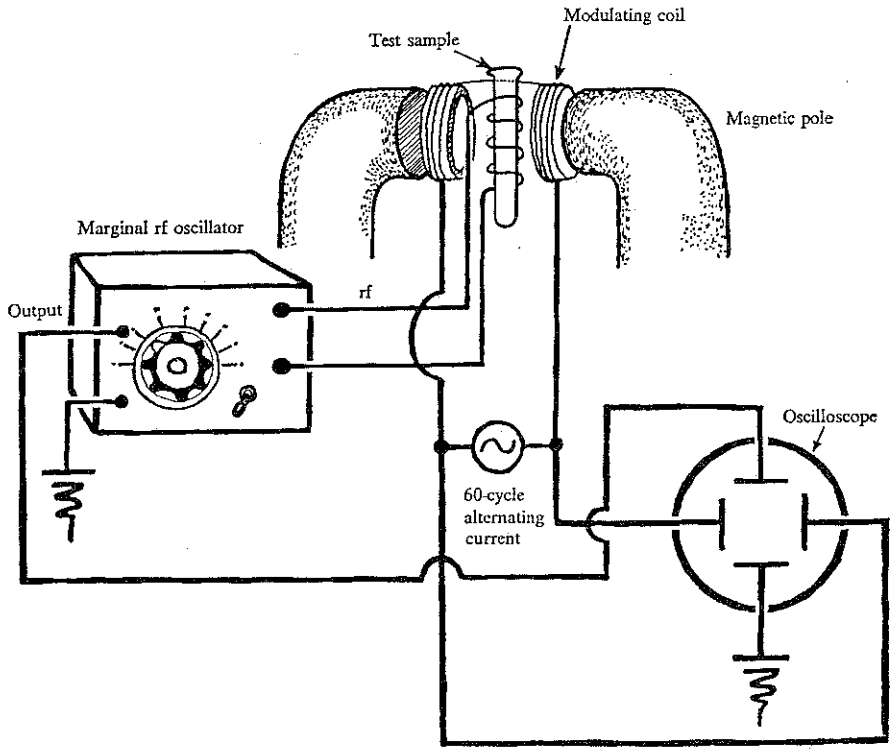

FIGURE 9.6

Experimental configuration for using the marginal oscillator for nuclear magnetic resonance measurements.

modulating coils are wound. The radio-frequency coil is wound on the inside with a hole cut in the brass form to facilitate inserting various samples. The radio-frequency power can be fed down an extra brass tube which acts as a coaxial lead and thus shields the radio-frequency circuit. This head is shown in Fig. 9.9.

Another method commonly used to observe the resonance signal is to pick up directly the radio-frequency energy emitted when the nuclei

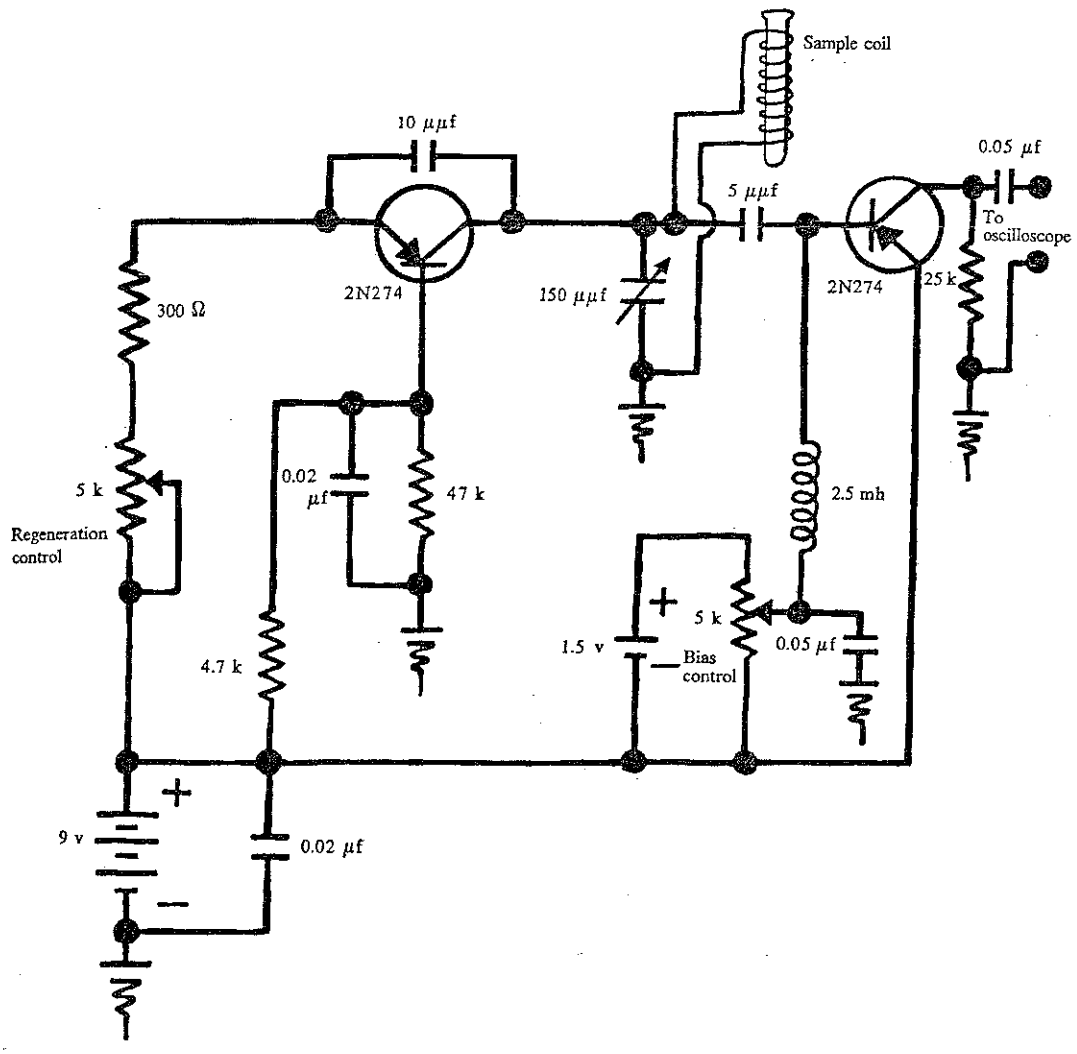

FIGURE 9.7

Schematic diagram of a transistorized marginal oscillator circuit.

in the sample change their orientations. The system is similar to the one shown in Fig. 9.4 except that another pickup coil must be used. This system is shown in Fig. 9.10. The pickup coils are located as shown, with their axis perpendicular to the radio-frequency exciting coil and also to the external field. The principal difficulty with this method is that it is hard to make certain that the pickup coils do not

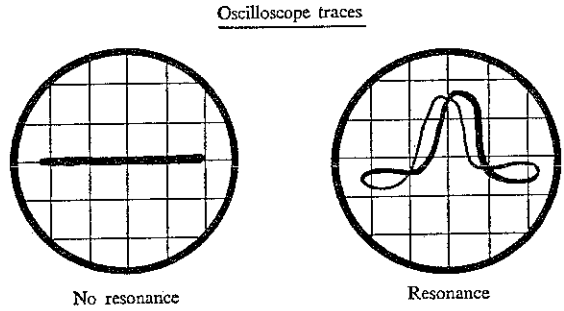

FIGURE 9.8

Oscilloscope traces of the marginal oscillator output for nonresonance and resonance cases.

see the signal from the excitation coil. The pickup coils can only detect an H field along their own axes; hence they should not see the radio-frequency energy radiated by the oscillator coil provided that they are carefully aligned. The radio-frequency signal from the reorienting magnetic moments within the sample has a component of an H vector parallel to the axis of the pickup coils. This component will be detected by the pickup coils. The output from the pickup coils is fed to a conventional radio-frequency receiver and the output signal from the receiver may be displayed in a manner similar to that used in the marginal oscillator method. The oscilloscope's horizontal sweep is con-

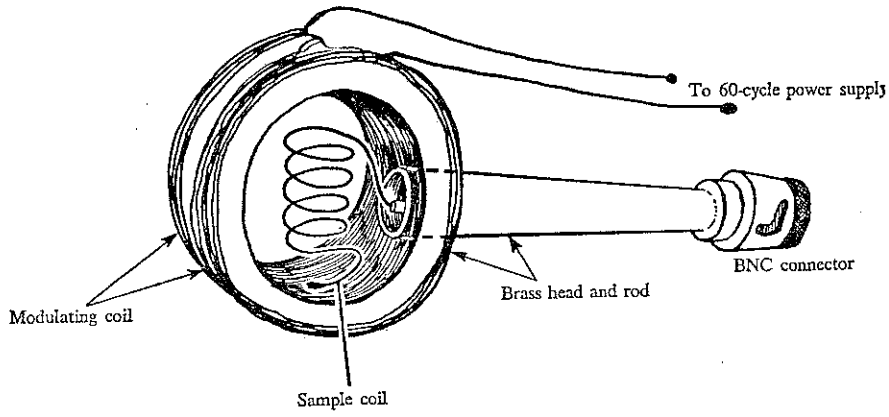

FIGURE 9.9

Marginal oscillator resonance head containing modulating and resonance coils with shielded radio frequency feed.

trolled by the modulator signal and the vertical sweep is actuated by the radio-frequency receiver output signal. The oscilloscope trace is similar to that shown in Fig. 9.8.

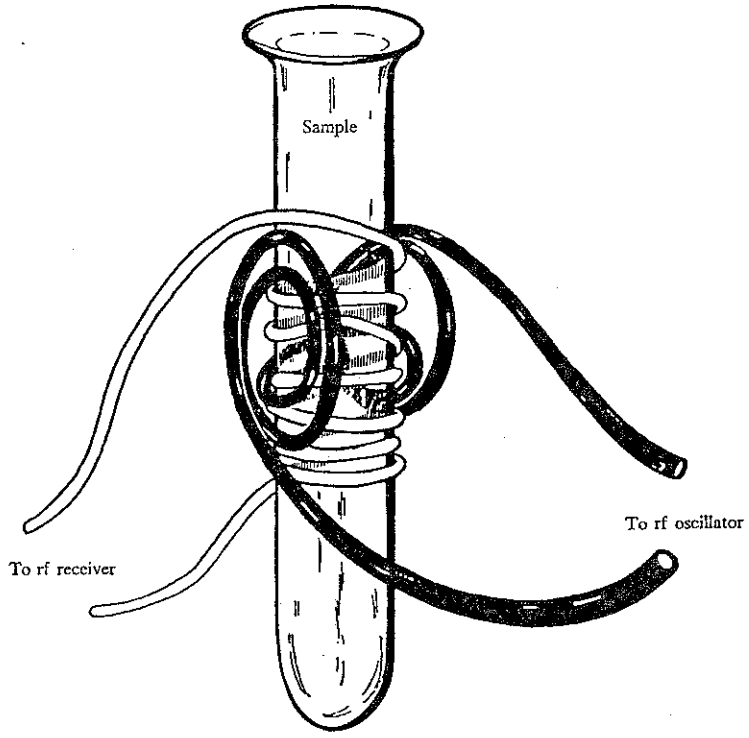

FIGURE 9.10

Crossed-coil arrangement for detecting energy radiated when magnetic moments flip under the resonance condition.

9.6 EXPERIMENTS

Measurement of the proton magnetic moment. A very precise measurement of the proton magnetic moment is possible by employing a technique where it is necessary only to determine frequencies. The Larmor frequency associated with the precession of the proton spins is

$$\nu_L = \frac{g}{2\pi}\frac{eB}{2m_p} \tag{9.31}$$

All the factors in Eq. (9.31) are known with great accuracy except B. One way to eliminate the measurement of B is to use the orbital motion of protons in the same magnetic field. In Chapter 11 the "omegatron"

has been described. The omegatron determines the cyclotron frequency of the orbital motion of protons in a magnetic field. The cyclotron frequency is given by

$$\nu_c = \frac{1}{2\pi}\frac{eB}{2m_p} \tag{9.32}$$

If the measurements of ν_L and ν_c are made in the same magnetic field, then the g factor is given by the ratio of the frequencies. From Eqs. (9.31) and (9.32),

$$\frac{\nu_L}{\nu_c} = g \tag{9.33}$$

Since frequencies can be measured with great accuracy, this method yields a very precise measurement of g for the proton. The proton magnetic moment can also be determined in terms of the Bohr magneton by using the electron rather than the proton cyclotron frequency.

Determination of nuclear magnetic moments. The magnetic moments of other nuclear species can be measured by using the equipment described in the previous sections. For example, if saturated aqueous solutions of either lithium or fluorine compounds are placed in the sample tube, the magnetic moments of Li^7 and F^{19} can be measured. Li^7 is the most abundant isotope of lithium (92.5 percent). It has a ground state spin of $\frac{3}{2}$ so that the nucleus has four possible orientations with respect to the external field instead of two, as was the case for the proton (see Fig. 9.11). However, spin values cannot be determined using nuclear magnetic resonance techniques because only the energy *change* for $\Delta m = \pm 1$ is measured by this method. This energy change is independent of the value of m and thus gives no information about the spin of the nucleus. Fluorine is monoisotopic (F^{19}) and has a ground state spin of $\frac{1}{2}$. Thus F^{19} behaves very much like the proton. The approximate g factors for Li^7 and F^{19} can be computed from the observed resonance frequencies and from certain simple assumptions about nuclear structure. The results are shown in Table 9.1.

With the equipment described in Sec. 9.5, the signal-to-noise ratio for the proton resonance signal shown in Fig. 9.8 is roughly 10 to 1. In order to observe resonance signals from various other species dissolved in the water, the concentration of ions must be of the order of 10 percent of the hydrogen (i.e., proton) concentration in the water. Compounds must therefore be found which are very soluble in water.

It is interesting to note that F^{19} has a magnetic moment quite close to that of the free proton, whereas the moment of Li^7 is somewhat larger. Nuclear magnetic moments are not yet well understood from a

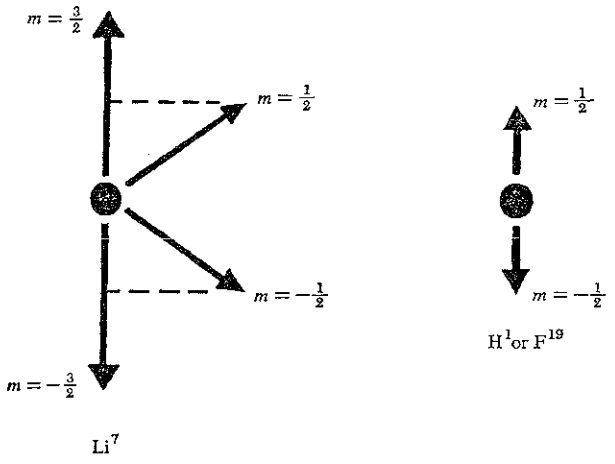

FIGURE 9.11

Possible spin states of Li^7 and F^{19}.

theoretical point of view. It is possible to make some general predictions about the expected trends, but no reliable quantitative statements can be made. Assume that F^{19} consists of a proton plus an O^{18} core (i.e., eight protons and ten neutrons) in which all the spins and moments cancel. If the proton is in a state having no orbital angular

TABLE 9.1

Magnetic moments and g factors for H^1, Li^7 and F^{19}

Isotope	*Spin*	*g*	*Magnetic moments in nuclear magnetons*
H^1	$\frac{1}{2}$	5.56	2.8
Li^7	$\frac{3}{2}$	2.16	3.2
F^{19}	$\frac{1}{2}$	5.24	2.7

momentum with respect to the core, the magnetic moment of F^{19} should be roughly equal to that of the free proton. This is what is observed, and it is therefore generally accepted that the structure of F^{19} is as assumed, that is, the proton is in an $S_{1/2}$ state with respect to the O^{18} core. In the case of Li^7 the situation is somewhat different. The magnetic moment (3.2 μ_N) is larger than the moment of the free proton. This means that the magnetic moment of Li^7 cannot be ascribed solely to the spin moment of the proton as was the case in F^{19}.

A possible explanation is that the Li^7 nucleus consists of a He^6 core with cancelled spins and moments and a proton moving around the core with an orbital angular momentum $l = 1$ (i.e., a P state). If the spin moment and the orbital moment are parallel, a magnetic moment larger than the one of the free proton would result. The proton is thus probably in a $P_{3/2}$ state (see Fig. 9.12).

Arguments such as those made in the last paragraph illustrate one of the important ideas in modern nuclear physics, which is that the nucleus has a shell structure quite similar to that of an atom. In an odd A nucleus, A-1 nucleons pair off to form an even Z, even N core. The last nucleon then moves in a potential produced by this core, and

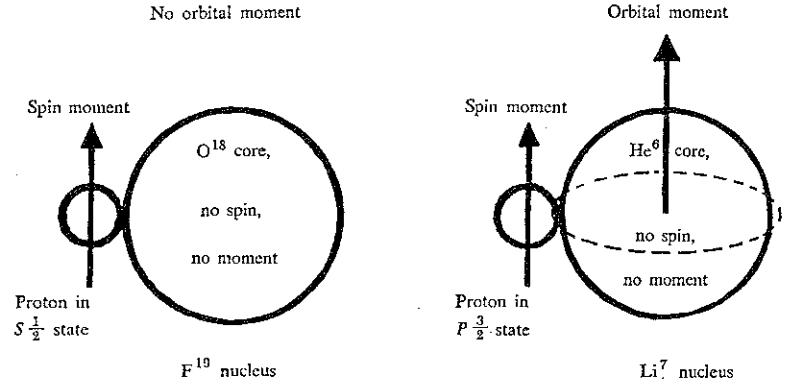

FIGURE 9.12

Possible models which would account for the observed magnetic moment of F^{19} and Li^7.

its motion is described by quantum numbers very similar to those used to describe the motion of an electron in an atom. This idea has been a very powerful aid in the description of several important nuclear phenomena.

Chemical shift. An important application of nuclear magnetic resonance is the study of the magnetic properties of materials. A proton in a material is always surrounded by atomic electrons. This electronic structure around each proton is always slightly diamagnetic, so that the precession of the electrons creates a new field H_D which opposes the externally applied field. The observed resonance frequency is therefore not quite the same as that observed if the protons were free but is that corresponding to free protons in a field $H_0 - H_D$. This effect is called the "chemical shift," for it is due to the electrons which determine the

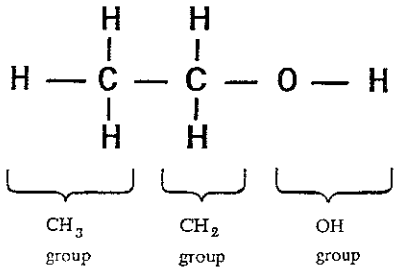

FIGURE 9.13

Molecular structure of ethyl alcohol.

chemical nature of the sample, and it shifts the resonance frequency from the value which would be observed for free protons.

An interesting example of the chemical shift is that of ethyl alcohol.[6] The chemical structure of ethyl alcohol is shown in Fig. 9.13. The protons in this material are distributed in such a way that they belong to three distinctly different chemical groupings, CH_3, CH_2, and OH. The electrons in each of these groupings have slightly different diamagnetic properties, so that the usual proton resonance signal is split into three different components as shown in Fig. 9.14. The intensity ratio of the three components is 1:2:3, which corresponds to the fact that the OH group has a single proton, the CH_2 group has two protons,

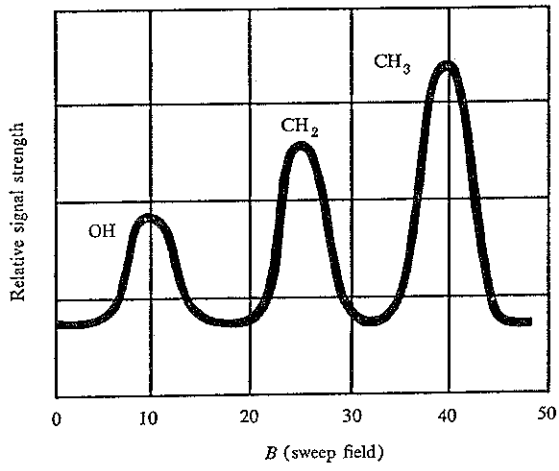

FIGURE 9.14

Proton resonance shifts for the three molecular groups of ethyl alcohol.

and the CH_3 group has three protons. The external field used in this experiment is roughly 0.9 weber/m^2. It is also interesting to note that the least affected frequency is that of the OH group and the one shifted most is the CH_3 group signal. This corresponds to the fact that the electrons in the OH structure are more tightly bound and hence less diamagnetic than those in the CH_2 and CH_3 structures. Also, it is important to notice that the chemical shift is quite small, about five parts per million. High-resolution instruments are therefore required to observe this effect.

It is obvious from the foregoing discussion that nuclear magnetic resonance is a powerful tool for determining the electronic environment of the nuclei which are being studied. Consequently, much can be learned about the detailed chemical structure of many complex molecules, particularly protein molecules encountered in biochemistry.

REFERENCES

1. Block, F., W. Hansen, and M. Packard: *Phys. Rev.*, **69**, 127, 946.
2. Purcell, E., H. Torrey, and R. Pound: *Phys. Rev.*, **69**, 37, 1946.
3. Stern, O.: *Z. Phys.*, **7**, 249, 1921; W. Gerlach and O. Stern, *Ann. Phys., Leipzig*, **74**, 673, 1924.
4. Pauli, W.: *Naturwissenschaften*, **12**, 741, 1924.
5. Singer, J. R., and S. D. Johnson: *Rev. Sci. Instr.*, **30**, 92, 1959.
6. Roberts, J. D.: "Nuclear Magnetic Resonance," McGraw-Hill Book Company, New York, 1959.

GENERAL BIBLIOGRAPHY

1. Andrew, E. R.: "Nuclear Magnetic Resonance," Cambridge University Press, London, 1955.
2. Ramsey, N. F.: Nuclear Moments and Statistics, Part III of "Experimental Nuclear Physics," edited by E. Segré, John Wiley and Sons, Inc., New York, 1953.
3. Slichter, C. P.: "Principles of Magnetic Resonance," Harper and Row, Publishers, Incorporated, New York, 1963.
4. Pople, J. A., W. G. Schneider, and H. J. Bernstein: "High-resolution Nuclear Magnetic Resonance," McGraw-Hill Book Company, New York, 1959.
5. NMR and EPR Spectroscopy, NMR-EPR Staff of Varian Associates, Pergamon Press, New York, 1960.