2.4.1.4. Nuclear Magnetic and Quadrupole Resonance. 2.4.1.4.1.* †

Principles of the Method. 2.4.1.4.1. Introduction. Since their introduction by Purcell, et al.,¹ and by Bloch et al.,² the techniques of nuclear magnetic resonance and nuclear induction have been successfully used in the precision determination of the magnetic moments of over 100 nuclei and the spins of about 25. The subsequent observation of nuclear quadrupole resonance absorption in solids by Dehmelt³ and by Pound⁴ has resulted in the measurement of nuclear electric quadrupole moments for some 20 nuclei. These experiments are all so closely interrelated that they will be collectively treated. The method is a modified extension of Rabi's principle of magnetic resonance (see Section 2.4.1.2) to nuclei contained in matter of normal density; here the resonance condition is observed by a macroscopic electromagnetic absorption or dispersion in contrast to the deflection and subsequent detection of free atoms. It should also be noted that the method is the nuclear analog of microwave paramagnetic resonance absorption (see Section 2.4.1.3).

Consider a nucleus characterized by its angular momentum \( I \hbar \) and total magnetic moment \( \mu = \gamma I \hbar \). Here \( \mu \) represents the component along \( I \) of the resultant magnetic moment of the individual nucleons, which are so tightly coupled by nuclear forces in comparison to the energies involved in magnetic resonance that the assumed proportionality between \( \mu \) and \( I \) is completely justified. The maximum possible components of \( I \) and \( \mu \) in any given direction are called the spin \( I \) and the magnetic moment \( \mu \).⁵ The proportionality factor \( \gamma = \mu/I\hbar \) is here called the gyromagnetic ratio; for protons, \( \gamma \cong 2.67 \times 10^4 \text{ sec}^{-1} \text{ oersted}^{-1} \). The interaction of the nucleus with an applied dc magnetic field \( H \) will be given by the usual magnetic dipole term \( \mathcal{K}_M = -\mu \cdot H = -\gamma I \cdot H \). The \( 2I + 1 \) equally spaced energy levels (see Fig. 1) are given by \( E_m = -\gamma \hbar H_0 m \) where \( I \geq m \geq -I \), if we assume \( H \) is directed along

† See also Vol. 2, Chapter 9.7; Vol. 3, Chapter 4.1; Vol. 4, A, Chapter 4.4.
³ H. G. Dehmelt, Am. J. Phys. 22, 110 (1954), which see for earlier references.
⁵ \( \mu \) is in Gaussian units, which are used throughout this section; the unit of magnetic field \( H \) is the oersted. Sometimes nuclear magnetic moments are given in units of the nuclear magneton \( \mu_0 = e\hbar/2mc = 5.05 \times 10^{-24} \text{ erg/oersted} \). Usually experiments are performed in magnet air gaps in which \( H \) (oersteds) = \( B \) (gauss) to high precision; for this reason, the literature of magnetic resonance often specifies the magnetic field in units of the gauss.

*Sections 2.4.1.4.1 through 2.4.1.4.7.2 are by C. D. Jeffries. Section 2.4.1.4.7.3 is by G. Feher.
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the z axis with magnitude $H_0$. Consider now a large number of such nuclei which are immersed in a lattice, i.e., a reservoir of thermal energy, such as the protons in a sample of water or a crystal of ice. Because of thermal agitation, there will be relaxation processes which tend to bring the system of proton spins into thermal equilibrium with the lattice.

We can describe the system by assigning Boltzmann population factors to the energy levels. Between an adjacent pair of levels there will exist the population ratio:

$$\frac{N(m)}{N(m+1)} = \exp\left[-\frac{E_m}{kT} + \frac{E_{m+1}}{kT}\right]$$

(typical value at room temperature). Now if electromagnetic radiation at the Larmor frequency $\omega_0 = \left[E_m - E_{m+1}\right]/\hbar = \gamma H_0$ radians/sec is applied to the system, stimulated magnetic dipole transitions may occur according to the selection rule $\Delta m = \pm 1$. However, there will be more stimulated absorption ($\Delta m = -1$) than stimulated emission ($\Delta m = +1$) because of the slight excess population in the lower state of any pair of levels. Thus there will be a net resonant absorption of electromagnetic energy by the system, resulting in a slight heating of the lattice. For $H_o$ fields of a few thousand oersteds, $\nu_0 = \omega_0/2\pi$ is of the order of 10 Mc/sec, and the resonance absorption can be detected by straightforward radio frequency techniques, e.g., by wrapping a coil around the sample and observing by means of a bridge the loss factor of the coil for frequencies in the neighborhood of $\nu_0$. As in related phenomena, the absorption is accompanied by a dispersion which can be observed by adjusting the

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Fig. 1. (a) Energy levels of a magnetic dipole with spin $I = \frac{3}{2}$ in a magnetic field. (b) Additional splitting due to nuclear electrical quadrupole interaction with electric field gradient in a crystal.

---

bridge to detect the change in reactance of the coil. Thus by observing
the resonance frequency \( v_0 \) in a known magnetic field, one obtains in a
relatively simple experimental arrangement the nuclear gyromagnetic
ratio \( \mu/I\hbar \), from which the magnetic moment \( \mu \) may be determined if the
spin \( I \) is known. Furthermore, as shown later, the spin may be determined
from the amplitude of the resonance absorption.

If \( I \geq 1 \), the nucleus may be further characterized by an electric
quadrupole moment and there may be in addition to \( 3c_I \) an interaction
of the form \( \mathcal{K}_Q = Q \cdot \Delta E \), which represents the dyadic product of the
nuclear quadrupole moment operator \( Q \) with the electric field gradient
tensor \( \Delta E \) at the nuclear site. The nuclear electric quadrupole moment,
declared explicitly in reference 44, is a measure of the deviation from
spherical symmetry of the nuclear charge distribution. Although the
quadrupole interaction may be averaged to zero in the rapid tumbling of
liquids, we find in single crystals that the magnetic energy levels are
shifted unequally (see Fig. 1) by this additional term, so that resonance
absorption between pairs of levels may be observed at several different
frequencies. In the case of zero applied magnetic field, resonance absorp-
tion between pure quadrupole levels may be observed. The measurement
of the resonance frequencies determines the product \( QQ \) of a principal
value \( q \) of the electric field gradient tensor with the scalar quadrupole
moment \( Q \). Calculated values of \( q \) must be used to obtain \( Q \) from the
data; consequently the precision in the determination of \( Q \), in this or
any other method, is about two or more orders of magnitudes lower than
for \( \mu \). However the precise ratio of the quadrupole moments for two
isotopes can be easily measured. Furthermore the spin \( I \) is explicitly
given by the number of resonance lines.

From the broad field of nuclear magnetic and quadrupole resonance
absorption, we discuss here only those aspects of direct interest to nuclear
physics. For details we refer to more general and extensive treat-ments.7–11

2.4.1.4.1.2. The Bloch Phenomenological Theory. The simple optical
model of magnetic resonance absorption given above does not take into
consideration the interactions of the spin system with itself or with the
lattice. Detailed treatments of these relaxation processes have been

11 T. P. Das and E. L. Hahn, Nuclear quadrupole resonance spectroscopy. Solid
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given,\textsuperscript{1,12–14} but from the viewpoint of nuclear physics it is sufficient
to consider the original phenomenological treatment of Bloch in which
these effects are represented by two empirical relaxation times.\textsuperscript{2} Con-
sider $n$ identical nuclei per unit volume of spin $I$ and magnetic mo-
ment $\mu$ under the influence of an applied field $H$ with the components:
$H_x = 2H_1 \cos \omega t$, $H_y = 0$, $H_z = H$; here $H$ is a large and uniform field;
$H_1$ is a small oscillating field applied by means of a coil around the sample
to induce magnetic dipole transitions. Following Ehrenfest's theorem one
assumes that $M$, the resultant magnetization per unit volume of all the
nuclei, obeys the classical equation of motion $dM/dt = \dot{M} = \gamma M \times H$
in the absence of relaxation effects. These are next taken into account
as follows: owing to thermal processes in which the spin system exchanges
energy with the lattice, it is assumed that the longitudinal component
of the magnetization $M_z$ approaches its thermal equilibrium value $M_0$
in a characteristic thermal relaxation time $T_1$ according to the relation:
$\dot{M}_z = -(M_z - M_0)/T_1$. Here $M_0$ is given by the familiar Curie formula
$M_0 = \frac{I + 1}{I} \frac{n\mu^2}{3kT} \frac{H_o}{1 + 1} \frac{n\gamma\hbar^2}{3kT} \omega_0$ \hfill (2.4.1.4.1)

where $T$ is the absolute temperature of the sample and $k$ is Boltzmann's
constant. It is also assumed that the transverse components $M_x$, $M_y$
will vanish exponentially in a characteristic time $T_2$ according to the relations
$\dot{M}_x = -M_x/T_2$; $\dot{M}_y = -M_y/T_2$. The time $T_2 \leq T_1$ and is called the
transverse or total relaxation time, and is essentially the characteristic
time for incoherence of $M_x$, $M_y$ due to processes in which, the total energy
of the spin system does not change; more specifically, there may be
mutual spin flips, or variations of the locally effective value of $H$
throughout the sample due to the dipole fields of neighboring nuclei. By the
Fourier theorem the resonance linewidth $\Delta \omega \approx 1/T_2$, unless there is
appreciable inhomogeneous broadening\textsuperscript{14a} due, e.g., to magnetic field
nonuniformities. In the following we assume that there is no appreciable
inhomogeneous broadening, as is often the case for liquids but not for
solids.

The total effect of both applied fields and internal interactions is then
approximately given by the phenomenological equations:

$\dot{M}_x = -M_x/T_2 - \gamma M_y H$

$\dot{M}_y = -M_y/T_2 + \gamma (M_z 2H_1 \cos \omega t - M_y H)$ \hfill (2.4.1.4.2)

$\dot{M}_z = -(M_z - M_0)/T_1 - \gamma M_z 2H_1 \cos \omega t.$


\textsuperscript{14} A. G. Redfield, \textit{IBM J. Research Develop.} 1, 1 (1957).

In the Purcell technique\(^1\) the experimentally observed quantity is essentially a bridge unbalance voltage \(V_p\) proportional to \(M_z\). In the Bloch technique\(^2\) of nuclear induction, an additional coil is wound around the sample along the \(y\) axis (see Fig. 3), and one observes the induced voltage \(V_y \propto M_y\). In either technique, resonance is usually observed by noting the periodic change in \(V_p\) or \(V_y\) as the applied field \(H\) is periodically swept through the resonance value \(H_0 = \omega_0 / \gamma\) by superposing on the dc field a small modulation field \(H_m \cos \Omega t\). From the nature of Eqs. (2.4.1.4.2), it is seen that the exact shape of the resonance curves \(V_p(H)\) and \(V_y(H)\) will depend upon the rate at which the resonance is swept through, i.e., upon whether or not the passage through the resonance line in a time \(\tau\) is adiabatic in the Ehrenfest sense \((\tau \gg 1/\gamma H_1)\), and also upon the ratios \(\tau / T_1\) and \(\tau / T_2\). Perhaps the simplest and most common case is that of adiabatic slow passage: resonance is swept through so slowly that \(M_z\) continuously reaches its steady-state value under the influence of \(H_1\) and the relaxation processes. This requires \(\tau >> T_1, T_2, 1/\gamma H_1\). Another interesting case is that of adiabatic fast passage in which \(\tau >> 1/\gamma H_1, \tau << T_1, T_2\); this has the property of reversing the algebraic sign of \(M_z\), i.e., turning over the magnetization during the passage. Still another case of experimental interest is that of nonadiabatic passage (very small \(H_1\)) with \(\tau \lesssim T_2\), which gives rise to transient oscillation or "wiggles."\(^1,15\) These and other modulation effects have been treated,\(^16-20\) but here we will be chiefly concerned with the adiabatic slow passage case for which Eqs. (2.4.1.4.2) yield these solutions, if \(H\) is considered to be the variable and \(\Delta H = (H_0 - H)\) is the deviation from the resonance value:

\[
\begin{align*}
M_z &= u \cos \omega t - v \sin \omega t \\
M_y &= - (u \sin \omega t + v \cos \omega t) \\
M_x &= \frac{1 + (T_2 \gamma \Delta H)^2}{1 + (T_2 \gamma \Delta H)^2 + (\gamma H_1)^2 T_1 T_2} M_0 \\
u(H) &= \frac{|\gamma|^2 H_1 T_2 \Delta H}{1 + (T_2 \gamma \Delta H)^2 + (\gamma H_1)^2 T_1 T_2} M_0 \quad \text{(dispersion mode)} \\
v(H) &= - \frac{|\gamma|^2 H_1 T_2}{1 + (T_2 \gamma \Delta H)^2 + (\gamma H_1)^2 T_1 T_2} M_0 \quad \text{(absorption mode)}
\end{align*}
\]

In Eq. (2.4.1.4.3b) the \((-)\) sign is to be taken for positive \(\gamma\), the \((+\) sign

for negative $\gamma$. In the nuclear induction technique, e.g., there will be induced into the receiver coil along the $y$ axis a voltage

$$V_y \propto M_y = \mp (u \omega \cos \omega t - v \omega \sin \omega t).$$

Because of incomplete decoupling with the transmitter coil along the $x$ axis, there will also be induced into the receiver coil a leakage voltage $V_e = A \sin \omega t + B \cos \omega t$, which may generally be considerably larger than $V_y$. By adjusting the phase of this leakage voltage by means of flux steering paddles and/or phase shifting networks, one can make either $A/B \ll 1$ or $A/B \gg 1$. Thus the total receiver coil voltage $V_y + V_e$ can be made essentially proportional to either $v$ or $u$; i.e., one may observe either the absorption or the dispersion (or any combination). Similar considerations hold for the Purcell single coil technique: by adjusting the balance of an rf bridge containing the coil as an element, one can make the total bridge unbalance voltage $V_p + V_e$ at nuclear resonance proportional to either the imaginary or the real part of the complex nuclear susceptibility corresponding to the absorption $v$ or the dispersion $u$, respectively. Note that whereas the algebraic sign of the nuclear induction signals are dependent upon the sign of the gyromagnetic ratio $\gamma$, those of the single coil signals are not. This is due to the circumstance that two (crossed) coils are needed to establish the sense of a rotating field.

The shape of experimentally observed homogeneously broadened resonance curves for protons in $\text{H}_2\text{O}$ under adiabatic slow passage conditions are shown in Figs. 2a and 2b. They follow closely the form expected from Eqs. (2.4.1.4.3): the absorption $v$ has a maximum at resonance ($\Delta H = 0$) and a half-width at half-maximum $H_{1/2} = 1/\gamma T_2$, provided the rf field $H_1$ is small enough so that $(\gamma H_1)^2 T_1 T_2 \ll 1$. As $(\gamma H_1)^2 T_1 T_2$ is increased, $v$ increases to a maximum value at

$$(\gamma H_1)^2 T_1 T_2 = 1$$

after which it decreases while the line width increases. This behavior is called saturation: the transition probability between two levels due to a sufficiently large $H_1$ can considerably exceed the transition probability due to thermal relaxation processes, resulting in a population difference, and hence a signal, considerably less than that at thermal equilibrium. The dispersion $u$, on the other hand, does not display this saturation effect. Both $u$ and $v$ have the same maximum value: $(M_0/2) \cdot (T_2/T_1)^{1/2}$. The magnitude of the received signal $V_z$, which is proportional to $\omega u$ or $\omega v$, will thus have the optimum value:

$$(V_z)_{opt} \propto \mu^3 \frac{I + 1}{I^2} \frac{nH_0^2}{3kT} \sqrt{T_2 \over T_1} \propto \mu(I + 1) \frac{n\omega_0^2}{3kT} \sqrt{T_2 \over T_1} \quad (2.4.1.4.4)$$
Equation (2.4.1.4.4) shows clearly that to make the signals as large as possible the highest available static magnetic field (and hence frequency) should be used. It is possible in the case of liquids to shorten $T_1$ by the addition of paramagnetic ions until $T_1 \approx T_2$. This gives optimum signal heights which, for equal numbers of nuclei, are proportional to $\mu(I + 1)$.

Fig. 2. Oscilloscope traces of signals for protons in 1 cc of H$_2$O as observed at $H_0 \approx 3300$ oersteds with apparatus of Fig. 3. A 40-cps modulation field is used, sweeping through resonance twice in each cycle, the phase being shifted to separate the two traces. In (a) and (b) are shown the adiabatic-slow-passage dispersion and absorption modes, respectively, observed in a 1.0 molar aqueous solution of Fe(NO$_3$)$_3$. In (c) and (d) are shown the nonadiabatic-passage dispersion and absorption modes, respectively, observed in a 0.01 M aqueous solution of FeCl$_3$; note the characteristic "wiggles."

at constant frequency and to $\mu^2(I + 1)/I^2$ at constant field. Tables are available giving these relative sensitivity figures for all nuclei for which $\mu$ and $I$ are known.

Figures 2c and 2d show observed signals for protons in H$_2$O under nonadiabatic conditions. Such signals are frequently observed in prac-
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For the absorption mode, the resonance field $H_0$ lies on the line of symmetry of the figure.\textsuperscript{16}

The phenomenological theory given above yields the so-called Lorentx line shapes of Eq. (2.4.1.4.3); these are usually observed for liquids under slow passage conditions. However, in viscous fluids or solids the assumed model is not valid, and the observed line shapes are often nearly Gaussian; we refer to Pake and Purcell\textsuperscript{21} for a general discussion of line shapes.

2.4.1.4.2. EXPERIMENTAL APPARATUS. Since the early experiments, there have been many changes and improvements in the apparatus used to observe nuclear magnetic resonance resulting in greatly improved sensitivity and resolution. For example, with present-day techniques, the resonance of the deuterons in 1 cc of ordinary water may be observed several times above the noise background; relative line widths as small as $H_{1/2}/H_0 \approx 10^{-8}$ have been measured for protons. The details of various experimental apparatus have been given adequately in the literature to which we refer. The two coil nuclear induction arrangement of Bloch et al.\textsuperscript{2} has been modified for various applications by Proctor,\textsuperscript{22} Weaver,\textsuperscript{21} Redfield,\textsuperscript{24} Arnold,\textsuperscript{25} and others. The single-coil bridge method of Purcell et al.\textsuperscript{1} has been adapted to a more readily tunable twin-tee bridge by Torrey,\textsuperscript{26} Anderson,\textsuperscript{27} Collins,\textsuperscript{28} and others. Another notable single-coil method is the regenerative detector of Pound and Knight,\textsuperscript{29} Roberts,\textsuperscript{30} and others, in which the absorption is detected by its reaction on an oscillator. Other related techniques have also been described.\textsuperscript{31} In experiments in which the nuclear magnetic resonance is split by quadrupole interaction, any of the preceding methods may be used. In zero magnetic field experiments, where there is no preferred axis of orientation, only the single-coil methods will work. Circuits developed particularly for this case have been described by Dehmelt,\textsuperscript{32} Wang,\textsuperscript{33} Livingston,\textsuperscript{34} and others.

\textsuperscript{34} R. Livingston, \textit{Ann. N. Y. Acad. Sci.} 55, 800 (1952).
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Well-engineered apparatus of both the single- and double-coil types are now commercially available.\textsuperscript{35,36}

All techniques essentially measure the same thing: the components of the nuclear magnetization given by $u$ and $v$ in Eq. (2.4.1.4.3). The exception is that in the regeneration detectors only the absorption mode may be detected; also the range of operation of the applied rf field $H_1$ is somewhat restricted so that optimum sensitivity may not be achieved for very short or very long relaxation times. On the other hand, the regeneration detector is basically the simplest, since it does not involve a separate transmitter and receiver and is easily tunable with a single variable condenser; no frequency-sensitive balance conditions are involved as in the single-coil bridge method and in nuclear induction. These latter methods have the advantage, however, that they operate over wide ranges of $H_1$ and may be preset to observe the dispersion under optimum signal conditions: $(\gamma H_1)^2T_1T_2 > 1$. This feature is particularly useful in searching for weak signals. Current practice in most nuclear induction arrangements is to gang and track the transmitter and receiver so that single knob frequency control is available. Independent in-phase and out-of-phase leakage controls facilitate a rapid adjustment of the desired mode of operation. The sign of nuclear magnetic moments can be determined only with the nuclear induction arrangement.

Permanent magnets may be used to provide a highly stable moderate field (~5 to 8 kilo-oersteds) with a minimum of upkeep. Greater flexibility is usually desired, however, and electronically regulated precision electromagnets of the Stanford type\textsuperscript{37} have been widely used. They provide a continuously variable field from 0 to 15 kilo-oersteds with a stability of 1 in $10^6$ or better. To prevent excessive broadening of the resonance lines by field nonuniformities within the sample, large diameter poles (~12 in.) and/or shimming by thin ferromagnetic materials or auxiliary coils is usually resorted to. For nuclear moment determinations, an inhomogeneity $\delta H \approx 1/\gamma T_2 \leq 0.1$ oersted over a typical sample volume of 1 cc is desirable. Otherwise it is difficult to shorten $T_1$ by the addition of paramagnetic ions to make $T_1 \approx T_2$.

An upper limit of the signal-to-noise ratio to be expected with a nuclear induction apparatus, for example, can be calculated approximately as follows: the voltage induced at resonance into a cylindrical receiver coil of $N$ turns and diameter $d$ by a sample completely filling the coil will be $V = N\pi d^2 M_y \times 10^{-8}$ volt. If the sample does not com-

\textsuperscript{35} Varian Associates, Palo Alto, California.
\textsuperscript{36} Perkin-Elmer Corporation, Norwalk, Connecticut.
\textsuperscript{37} Available from Varian Associates (reference 35); Pacific Electric Motors, Oakland, California; Harvey-Wells Corp., Framingham, Massachusetts.
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completely fill the coil, the voltage will be correspondingly less because of incomplete flux linkage. For slow passage homogeneously broadened lines, the maximum value of $M_y = (M_0 \omega / 2) \sqrt{T_2 / T_1}$. If the coil is resonated with a capacitor in a parallel resonant circuit of quality factor $Q$, the available rms signal voltage across this resonant circuit then will be

$$V_s = QV_y = \left[ n_\pi^2 N d^2 Q H_0^2 \gamma^6 (I + 1) I h^2 / 6 \sqrt{2} kT \right] \sqrt{T_2 / T_1} \times 10^{-8} \text{ volt.}$$  \hspace{0.5cm} (2.4.1.4.5)

Taking the typical values $d = 1 \text{ cm}; N = 10 \text{ turns}; Q = 100; H_0 = 10,000 \text{ oersteds}; \gamma \approx 4 \times 10^3 \text{ rad/oersted for deuterons}; I = 1; n = 6.6 \times 10^{22} / \text{cc for } D_2 O; T = 300^\circ K; T_1 \approx T_2$, one finds $V_s \approx 2 \times 10^{-4} \text{ volt}$. The rms Johnson noise voltage across the same circuit will be $V_n = \sqrt{4 k T R \Delta \nu}$ volts, where $\Delta \nu$ is the bandwidth of the receiver in cps, and $R = Q \omega L$ is the shunt resistance of the resonant circuit. For cylindrical coils of length $\approx$ diameter $d$, $L \approx 0.7 N^2 d \times 10^{-8} \text{ henry}$. The signal-to-noise ratio then becomes

$$\frac{V_s}{V_n} \approx \frac{n(I + 1) I}{f} \sqrt{\frac{Q H_0^2 \gamma^6}{T_1 \Delta \nu}} \times 2 \times 10^{-55} \hspace{0.5cm} (2.4.1.4.6)$$

where the factor $f \geq 1$ takes into account all additional noise, e.g., in the amplifier, and is here called the noise figure of the apparatus. It is possible to achieve $f \approx 2$ in practice. From Eq. (2.4.1.4.6) one finds that an over-all working rule for the actual observable signal-to-noise ratio in a typical apparatus at room temperature under optimum conditions [$T_1 \approx T_2; (\gamma H_1)^2 T_1 T_2 \approx 1$] is:

$$\frac{V_s}{V_n} \approx n(\Delta \nu)^{1/2} \frac{I + 1}{I^{5/2}} \left( \frac{\mu_I}{\mu_0} \right)^{5/2} H_0^{5/2} \times 2 \times 10^{-25} \hspace{0.5cm} (2.4.1.4.7)$$

where $\mu / \mu_0$ is the nuclear magnetic moment in units of the nuclear magneton, $H_0$ is the field in oersteds, $n =$ number of nuclei/cc in sample, $\Delta \nu =$ apparatus bandwidth in cps. Similar considerations for the single coil method have been given by Pound.\textsuperscript{1} The general conclusion is that for all the methods, about $10^{20}$ nuclei are required to give a visible signal for the typical values $I \sim 1, \mu \sim \mu_0, H \sim 10^4 \text{ oersteds}.$

A block diagram for a nuclear induction spectrometer is shown in Fig. 3. Strong signals are simply displayed on an oscilloscope by using a modulation field $H_m$ several times the linewidth, requiring a bandwidth $\Delta \nu \sim 10^3$ cps. For weak signals, a modulation field approximately $\frac{1}{10}$ the linewidth is often used in conjunction with a narrow band ($\Delta \nu \approx 0.1$ cps) lock-in amplifier to record the derivative of the absorption, as shown.
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Fig. 3. Block diagram of nuclear induction spectrometer.

Fig. 4. Recorded derivative of the dispersion signal of $\text{O}^{17}$ in 1 cc of natural $\text{H}_2\text{O}$; $H_0 \approx 10,000$ oersteds; $H_1 \approx 0.2$ oersted; $H_m \approx 0.3$ oersted; lock-in bandwidth $\Delta\nu \approx 0.1$ cps. [H. E. Weaver, *Phys. Rev.* 89, 923 (1953).]
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This narrow-banding technique usually reduces the noise by a factor of 100. The derivative signal from $^1\text{H}^1$ in natural $^2\text{H}_2\text{O}$ recorded under optimum conditions is shown in Fig. 4.

Figure 5 is a block diagram of an apparatus for observing pure quadrupole resonances.

![Block diagram of pure quadrupole resonance spectrometer.](image)

The resonance is modulated by applying periodically a magnetic field which causes Zeeman splitting.

2.4.1.4.3. Typical Procedures in Nuclear Magnetic Resonance.

The linewidth $H_{1/2} \approx 1/\gamma T_2$ is usually considerably narrower in non-viscous liquids than in solids because of the averaging out of the local dipole fields by the rapid tumbling motion in the former case. For this reason, and also because $T_1$ may be controlled by the addition of paramagnetic ions, liquid samples are usually used in the determination of nuclear moments by magnetic resonance. The nuclei in question are often contained in ions or complexes in aqueous solution. One usually chooses the most soluble compounds to maximize $n$. If the nuclei have an appreciable quadrupole moment, this will usually prove to be effective in providing sufficient thermal relaxation so that $T_1 \approx T_2$; in this case no paramagnetic ions need to be added. In fact, the quadrupole relaxation is sometimes so effective that the relaxation times are too short and the
line widths consequently too broad for the resonance to be seen. In these cases it is necessary to use a complex ion that is highly symmetrical so that the resultant electric field gradient is minimized. For example, the resonance of \( \text{As}^{75} \) can only be seen in the \( \text{AsO}_4^- \) or \( \text{AsS}_4^- \) complexes. Similarly, the resonance of \( \text{Zr}^{91} \) has been observed only in the compound \((\text{NH}_4)_2\text{ZrF}_6\). When it is desired to make \( T_1 \approx T_2 \) by the addition of paramagnetic ions (e.g., \( \text{Fe}^{++} \) or \( \text{Cu}^{++} \)), one may roughly assume that \( T_2 \) is determined by the known magnetic field inhomogeneity, and then use the approximate formula:

\[
\frac{1}{T_1} \approx \gamma^2 \mu_{\text{eff}} N_i (10\eta/kT) \text{sec}^{-1},
\]

where \( \gamma = \) gyromagnetic ratio of nucleus in rad/oersted; \( \mu_{\text{eff}} = \) magnetic moment in units of the Bohr magneton of the paramagnetic ion and has the typical values 2-6; \( N_i = \) number of paramagnetic ions per cc; \( \eta = \) viscosity of liquid; \( k = \) Boltzmann's constant; and \( T = \) absolute temperature.

The rare earth and transuranic elements are known to form only paramagnetic compounds and are not amenable to nuclear magnetic resonance studies in liquids because of the relatively huge (\(~10^6\) gauss) and randomly oriented magnetic field existing at the nuclear sites due to the hyperfine coupling with the unpaired electrons. Nuclear moments for these particular elements have been measured, e.g., by observing the hyperfine structure of the microwave paramagnetic resonance in single crystals (see Section 2.4.1.3). The other transition groups (3\textit{d}, 4\textit{d}, 5\textit{d}) can fortunately be made to form diamagnetic complexes and are amenable to both nuclear magnetic resonance and paramagnetic resonance studies. In some cases, one can also observe nuclear resonances in paramagnetic materials, as discussed in Section 2.4.1.4.7.2.

2.4.1.4.3.1. Magnetic Moment Measurements. The usual operation in a nuclear magnetic resonance experiment is to measure the ratio \( \gamma'/\gamma_p = \mu/2\mu_p I \), where \( \gamma = \mu/I\hbar \) is the unknown gyromagnetic ratio and \( \gamma_p = 2\mu_p/\hbar \) is the proton gyromagnetic ratio. It is sometimes more convenient to measure \( \gamma'/\gamma_d \), where \( \gamma_d \) is the deuteron gyromagnetic ratio, and then use the precisely known ratio \( \gamma_d/\gamma_p \). The unknown \( \mu \) in units of the nuclear magneton is then given by

\[
\mu/\mu_0 = 2I(\gamma/\gamma_p) \cdot (\mu_p/\mu_0).
\]  

The proton magnetic moment in units of the nuclear magneton, \( \mu_p/\mu_0 \), has been measured\(^{38\text{-}41} \) by comparing the magnetic resonance frequency to the cyclotron frequency of protons in the same magnetic field. The

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best value, as compiled by Cohen et al.,\textsuperscript{42} is $\mu_p/\mu_0 = 2.79275 \pm 0.00003$, including the diamagnetic correction.

The ratio $\gamma/\gamma_p$ is usually measured as follows. A suitable sample is prepared containing both the unknown nuclei and the reference nuclei, H or D, as $H_2O$ or $D_2O$, for example. If the signals are large, they can be quickly found on the oscilloscope and, holding the dc magnetic field constant, the ratio of the resonance frequencies $\omega/\omega_p = \gamma/\gamma_p$ is measured by tuning the spectrometer to first one resonance and then the other, being careful in each case to adjust to a pure absorption mode so that the oscilloscope pattern is exactly symmetrical about its center point. A weak unknown signal is best found through searching at constant frequency with a narrow band recording spectrometer by slowly varying the field $H$ with a motor-driven current control. For optimum sensitivity, the dispersion mode is used under the following conditions: $T_1 \approx T_2$; $(\gamma H) T_1 T_2 \approx 2$; $H_m \approx H_{1/2}$. After the signal is located, the ratio $\omega/\omega_p = \gamma/\gamma_p$ may be measured in constant field by sweeping through the two resonances consecutively with a slow motor drive on the frequency control, and putting frequency markers on the recorder tapes. If the lines are reasonably sharp ($H_{1/2} \approx 0.1$ gauss) the ratio $\omega/\omega_p$ can be easily measured to 1 part in $10^5$ and with care to 1 in $10^6$. Such precision is not always warranted, because diamagnetic effects may cause the magnetic field at the unknown nucleus to differ slightly from that at the reference nucleus, thus violating slightly the assumed equality $\omega/\omega_p = \gamma/\gamma_p$. Necessary corrections are discussed in Section 2.4.1.4.5.2. The sign of $\mu$ is determined relative to $\mu_p$ by simply noting, with a nuclear induction spectrometer, whether the two signals have the same or opposite polarity when consecutively examined by varying the H field, leaving the spectrometer frequency and the leakage controls fixed.

2.4.1.4.3.2. Spin Measurements in Liquids. Under conditions of adiabatic slow passage and negligible saturation, we obtain from Eq. (2.4.1.4.3) for the signal voltage from the absorption mode at resonance $V_s \propto \gamma H_1 T_2 M_0 \omega \propto H_1 \omega^2 [T_2 \gamma^2 n(I + 1)I]$. Now $T_2 = 1/\gamma H_{1/2}$ and hence $[\gamma n(I + 1)I] \propto V_s H_{1/2}$, which, being the product of the signal height and the half-width is proportional to the area $A$ under the absorption curve if displayed as a function of the magnetic field. Thus, if we have two nuclei with identical resonance line shapes, and the two resonances are observed in turn by varying H while keeping $\omega$, $H_1$, and the apparatus sensitivity all constant, we can write;

$$\frac{A_1}{A_2} = \left(\frac{\gamma_1}{\gamma_2}\right) \left(\frac{n_1}{n_2}\right) \left(\frac{I_1 + 1}{I_1}\right) \left(\frac{I_2 + 1}{I_2}\right).$$

(2.4.1.4.9)

Thus we can determine the spin $I_1$ relative to $I_2$ by comparing the signal areas, knowing the gyromagnetic ratios and the relative nuclear concentrations in the sample. This signal area comparison can be made directly on the oscilloscope for strong signals, after making certain that both are observed under unsaturated adiabatic slow passage conditions.

Weak signals are usually examined by a narrow band differentiating type of apparatus which records the derivative of the resonance lines. To consider this case and to allow for other than Lorentzian line shapes, we rewrite the undifferentiated signal for unsaturated adiabatic slow passage conditions as

$V_s \propto n_2 \omega^2 \gamma |H_1(I + 1)I \cdot f(H)$,

where $f(H)$ is a resonance line shape function with a maximum value $f(H = H_0) = 1/H_{1/2}$ and so normalized that $\int_0^{\infty} f(H) \, dH = 1$. Now the differentiated signal recorded by the lock-in apparatus is proportional to

$G(H) = (\partial V_s/\partial H) \cdot H_m = \omega^2 H_1 H_m |\gamma| (I + 1)n f'(H)$.

The first moment $M_1$ of the differentiated signal will be

$M_1 \equiv \int_0^{\infty} G(H) \cdot (H - H_0) \, dH = \omega^2 H_1 H_m |\gamma| (I + 1)n$

as is seen from a partial integration and the normalization of $f(H)$. Thus for the differentiated signals of two nuclei observed in turn by varying $H$ while keeping $\omega$, $H_1$, and $H_m$ constant, we find

$M_1 = \frac{\gamma_1}{\gamma_2} \frac{n_2}{n_1} \frac{(I_1 + 1)I_1}{(I_2 + 1)I_2}$

(2.4.1.4.10)

The condition $(\gamma H_1)^3 T_1 T_2 \ll 1$, necessary for the validity of Eq. (2.4.1.4.10), must be experimentally checked by making for each resonance a saturation curve, i.e., a plot of $V_s$ versus $H_1$, from which an upper limit for a nonsaturating value of $H_1$ can be determined. Also the modulation field $H_m$ should be reasonably small, compared to $H_{1/2}$, to insure a true derivative in each case. In the event that the resonance curve is displayed as a function of frequency instead of field, then the area

$A' = \int_0^{\infty} V_s(v) \, dv$

so determined may be used in Eq. (2.4.1.4.9), if the right side is multiplied by $\gamma_1/\gamma_2$; similarly the first moment

$M_1' = \int_0^{\infty} G(v) \cdot (v - v_0) \, dv$

of the differentiated curve may be used in Eq. (2.4.1.4.10), if the right side is multiplied by $(\gamma_1/\gamma_2)^2$.

From Eq. (2.4.1.4.9), it is seen that the area ratio is proportional to

$I(I + 1) \propto 3, 15, 35, 63, 99, \ldots\ldots\ldots$, for odd nuclei, for example, so that increasingly greater accuracy of measurement is necessary to distinguish
between higher spin values. Particular care must then be taken to
ensure that there is no spurious signal height distortion by modulation
effects, etc.

It is evident that if \( J_1 \) and \( J_2 \) are both known for two isotopes, then
the first-moment ratio determines the relative isotopic abundance. This
is the basis of a simple nondestructive technique for measuring isotopic
abundance ratios to within a few per cent.\(^{43}\)

2.4.1.4.4. Quadrupole Resonances. 2.4.1.4.4.1. Quadrupole Splitting
of Magnetic Resonance. In crystalline samples one must consider the
total interaction \( \mathcal{H} = -\gamma H I \cdot H + Q \cdot \Delta E \). One of the simplest cases is
that in which the magnetic interaction term is much larger than the
quadrupole term. Using first-order perturbation theory; the energy levels
are found to be, for electric fields of axial symmetry,\(^4\)

\[
E_m(\theta) = -\gamma H m + \frac{e^2 q Q}{4I(2I-1)} \left[ 3m^2 - I(I + 1) \right] \left[ \frac{3}{2} \cos^2 \theta - \frac{1}{2} \right]
\]

(2.4.1.4.11)

where \( \theta \) is the angle between \( H \) and the axis \( x \) of field symmetry;
\( e = -2 \partial^2 V / \partial z^2 \), where \( V \) is the electrostatic potential at the nucleus
due to the surrounding electronic charges; \( Q = \) scalar nuclear electric
quadrupole moment.\(^44\) For crystalline fields of cubic symmetry, \( q \) van-
ishes; for fields of lower than axial symmetry, an additional parameter
\( \eta = (\partial^2 V / \partial x^2) - (\partial^2 V / \partial y^2) \) is introduced and Eq. (2.4.1.4.11) is modi-
fied.\(^11\) For a single crystal, the energy levels of Eq. (2.4.1.4.11) have the
discrete pattern as shown in Fig. 1 for a hypothetical spin \( I = \frac{3}{2} \). In
general, there are 21 possible transitions of the magnetic dipole type
(\( \Delta m = \pm 1 \)) between the levels. These can be induced by the applied
rf field \( H_1 \), and such resonances are readily observed by the magnetic
resonance techniques discussed above. In contrast to liquids, the nuclear
dipole-dipole interaction between neighboring nuclei is not averaged out,
with the result that usually \( T_2 \ll T_1 \) in diamagnetic crystals; for this
reason, the expected signal-to-noise ratio is less. A differentiating type
of spectrometer is usually used, and the lines are observed by varying
either the field or the frequency. A sample of \( \sim 1 \) gram is usually required.
The crystal is so mounted that \( \theta \) may be varied. At \( \theta = \arccos \left(1/\sqrt{3}\right) \),
the lines become nearly superposed, since by Eq. (2.4.1.4.11) the quad-

\(^{44}\) Q is defined [see, e.g., H. B. G. Casimir, Interaction between atomic nuclei and
electrons. *Teyler's Tweede Genootschap Haarlem* 11, 36 (1936)] as
\( Q = \int_0^1 \rho^2(3 \cos^2 \Theta - 1) \ d\rho \) integrated over the nuclear volume for the state \( m = I \), where \( \rho \) is the
nuclear charge density at a volume element \( d\rho \) at position \( r \) from the origin; \( \Theta \) is the
angle \( r \) makes with the nuclear spin axis.
rupole term vanishes to first order; higher order terms omitted from Eq. (2.4.1.4.11) may prevent an exact superposition.

For polycrystalline samples, one observes a much less discrete spectrum representing the spatially averaged values of $E_m(\theta)$.

In addition to those induced by the rf magnetic field $H_1$, transitions corresponding to $\Delta m = \pm 2, \pm 1$ could be induced by an applied rf electric field gradient. Sufficiently intense gradients cannot be produced electrically in the laboratory; they may be produced, however, by strong lattice vibrations induced by supersonic techniques.\footnote{M. Menes and D. I. Bolef, \textit{Phys. Rev.}, 109, 218 (1958).}

2.4.1.4.2. Pure Quadrupole Resonance. When single crystals are not available, and also when the quadrupole interaction is larger than the magnetic interaction, it is convenient to examine the so-called pure quadrupole spectrum. In zero magnetic field the energy becomes

$$E_m = \frac{e^2 q Q}{4 I (2I - 1)} [3m^2 - I(I + 1)] \quad (2.4.1.4.12)$$

for axially symmetric crystalline fields. Between these pure quadrupole levels an applied rf field $H_1$ may still induce magnetic dipole transitions ($\Delta m = \pm 1$) by acting on the nuclear magnetic moment. For half-integral spin there are $I - \frac{1}{2}$ such allowed transitions; for integral spin there are $I$ transitions. In a nonaxial field the levels are shifted but the $|m|$ degeneracy is not removed for half-integral spin; for integral spin, there is a splitting of the $\pm m$ levels, and additional lines are observed.

Since the energy, Eq. (2.4.1.4.12), is not orientation-dependent, powdered samples are usually used, and the resonances are observed with regenerative\footnote{W. G. Proctor and W. H. Tanttila, \textit{Phys. Rev.}, 101, 1757 (1956); W. Proctor and W. A. Robinson, \textit{Phys. Rev.}, 104, 1344 (1956).} or super-regenerative\footnote{W. G. Proctor and J. Tanttila, \textit{Phys. Rev.}, 101, 1757 (1956); W. Proctor and W. A. Robinson, \textit{Phys. Rev.}, 104, 1344 (1956).} detectors as the frequency is slowly varied. The signal is modulated by either Zeeman splitting, or by frequency-modulating the oscillator. Resonances over very wide ranges ($\sim 2$-700 Mc) have been observed.

2.4.1.4.3. Determinations of Nuclear Spin and Quadrupole Moments.

In both cases 2.4.1.4.4.1 and 2.4.1.4.4.2 above, by measuring the number of lines and the resonance frequency for each, one can obtain the spin $I$ and the coupling constant $e^2 q Q$ in single crystals or powdered samples. For two isotopes of the same element, $q$ will be the same, so the ratios of the nuclear quadrupole moments will be exactly equal to the ratio of the coupling constants. A number of such ratios have been measured.\footnote{W. G. Proctor and W. H. Tanttila, \textit{Phys. Rev.}, 101, 1757 (1956); W. Proctor and W. A. Robinson, \textit{Phys. Rev.}, 104, 1344 (1956).}

The sign of $Q$ cannot be determined by these methods. The general problem is to evaluate $q$ so that $Q$ can be determined from the measured
value of $e^2 q Q$. Moderately accurate values of $q$ have been estimated by the following procedures. The value of $q$ in the molecular solid is correlated with that for a free molecule; then, using the semiempirical considerations of Townes and Dailey, the $q$ for a free molecule is related to that for a free atom, which is then estimated by the established procedures of optical hyperfine structure, including the corrections of Sternheimer and Koster.

2.4.1.4.5. Corrections in Magnetic Resonance. The actual magnetic field at the nuclei may differ slightly from the applied magnetic field $H_0$ in which one observes magnetic resonance at frequency $\omega_0$. Several small corrections are necessary in calculating the gyromagnetic ratio $\gamma$ and one usually writes $\omega_0 / \gamma = H_0 + H_1 + H_1^1$. Here $H_1$ is the magnetic shielding field at the nuclei due to induced diamagnetic circulation of the electrons in the atom, ion, or molecule; and $H_1^1$ is the field at the nuclei due to the paramagnetism of the sample itself.

2.4.1.4.5.1. Diamagnetic Corrections. The field $H_1$ is proportional but opposite in sense to $H_0$ and is written as $H_1 = -\sigma H_0$, where $\sigma$ is the magnetic shielding factor. Lamb calculated theoretically $\sigma$ for free atoms, and values have been tabulated by Lamb and by Dickinson. They range from $\sigma \approx 2 \times 10^{-5}$ for hydrogen to $\sigma \approx 10^{-2}$ for uranium. Measured magnetic moments that have been multiplied by the correction factor $(1 + \sigma)$ are said to be diamagnetically corrected. If the resonances are observed in atoms or ions, the Lamb correction is probably adequate. However, many resonances are observed for nuclei contained in molecules, and Ramsey has calculated the additional corrections necessary. Unfortunately, they can be evaluated only for the protons in the H$_2$ molecule; the result, including the Lamb term, is $\sigma = 2.66 \times 10^{-5}$. By comparing the resonance frequency of protons in H$_2$ to those in the H$_2$O and in mineral oil, the shielding factors for the latter two are found experimentally to be $\sigma = 2.82 \times 10^{-5}$ and $\sigma = 2.60 \times 10^{-5}$, respectively. This shift in the resonance frequency for a given nucleus contained in different compounds is called the “chemical shift” and has been observed

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47 See, for example, T. P. Das and E. L. Hahn, Nuclear quadrupole resonance spectroscopy. Solid State Phys. Suppl. 1, Chapters 7-9 (1958).
51 R. M. Sternheimer, Phys. Rev. 84, 244 (1951); 86, 316 (1952); 96, 736 (1954).
for many nuclei. Although usually of the order of 0.01%, a few cases have been found where the shifts are as large as 1%. For this reason, it is important in measuring magnetic moments to observe the resonance in several different compounds, including free ions if possible; presumably the resonance which occurs at the lowest field (for fixed frequency) shows the least diamagnetic shielding. There are, of course, no diamagnetic corrections necessary in measuring the ratios of magnetic moments for two isotopes of the same element.

Special high-resolution techniques have been developed to study these chemical shifts from the viewpoint of structural chemistry.

2.4.1.4.5.2. Paramagnetic Corrections. The field $H^{11}$ due to the magnetization $M_p$ of added paramagnetic ions has been experimentally measured by Dickinson for different ions and geometries of the sample. For a spherical sample, the depolarization field $-\left(\frac{4\pi}{3}\right)M_p$ cancels the Lorentz field $\left(\frac{4\pi}{3}\right)M_p$ and one might expect the field $H^{11}$ to be zero; experimentally, this is not found to be so, probably because of spin-exchange interactions. Dickinson found that $H^{11}$ depends upon the sample geometry, the chemical compound containing the resonating nucleus, and the particular paramagnetic ion and its concentration. For example, a sample of $\text{H}_2\text{O}$ of roughly spherical proportions containing $\text{FeCl}_2$ has a measured value $H^{11} \approx 2cH_0 \times 10^{-8}$ oersted, when $c$ is the molarity (moles/liter) of $\text{FeCl}_2$. For long cylindrical shapes, $H^{11}$ may be negative. A general safety rule is, for $(H^{11}/H) < 10^{-4}$, it is necessary that $c < 0.3$ mole/liter.

In powdered metal samples, Knight has found that the paramagnetism of the conduction electrons contributes to $H^{11}$. This Knight shift in the resonance frequency may be as large as 1%; experimental and theoretical values have been tabulated for many metals.

2.4.1.4.6. Measurement of Magnetic Fields by Nuclear Magnetic Resonance. Driscoll and Bender have measured the proton gyromagnetic ratio, in absolute units by observing the resonance frequency $\omega_0$ in a magnetic induction field $B_0$, which was measured by a

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56 A summary of data is given by H. E. Walchli, in "A Table of Nuclear Moment Data," ORNL-1469 and supplements. Oak Ridge National Laboratory, Oak Ridge, Tennessee.


60 W. D. Knight, Phys. Rev. 76, 1259 (1949).


2.4. DETERMINATION OF SPIN, PARITY, AND NUCLEAR MOMENTS

They find \( \gamma_p = \omega_0 / B_0 = (2.67513 \pm 0.00002) \times 10^4 \text{ rad/sec/gauss} \), without diamagnetic correction. Correspondingly, this result can be used to measure a magnetic field in absolute units to high precision; one simply observes, in the field to be measured, the proton resonance frequency \( \nu_p \) of protons in liquid \( \text{H}_2\text{O} \) containing, say, 0.02 mole per liter of \( \text{FeCl}_2 \). The sample geometry may vary between a sphere and a long cylinder. The applied field is then given directly by the formula

\[
B \text{ (in gauss)} = 234.873 \times \nu_p \text{ (in Mc/sec)}.
\]

For high fields, it is sometimes more convenient to observe the deuteron resonance frequency \( \nu_d \) in \( \text{D}_2\text{O} \) (containing, say, 0.5 mole/liter of \( \text{FeCl}_2 \)), for which the following formula applies:

\[
B \text{ (in gauss)} = 1530.06 \times \nu_d \text{ (in Mc/sec)}
\]

For precision measurements of fields of a few gauss, the devices of Packard and Varian and Abragam et al. are particularly suitable.

2.4.1.4.7. SPECIAL METHODS. We discuss very briefly special methods, which, in addition to the usual steady-state methods described above, have some applications to nuclear physics.

2.4.1.4.7.1. Spin Echoes. By applying the rf field \( H_1 \) in the form of pulses instead of continuously, Hahn induced several transient responses of spin systems which he called spin echoes. This method is particularly useful for measurement of the relaxation times \( T_1 \) and \( T_2 \), and may be applied to spin systems either in magnetic interaction with a dc field, or in pure quadrupole interaction. In the latter case, unusually small quadrupole coupling constants have been measured by the use of transient double resonance techniques: signals from spin system \( A \) at a relatively high resonance frequency are observed as a function of a second relatively low frequency applied to a system \( B \), which is in weak interaction with system \( A \). At the resonance frequency of \( B \), the signal strength of \( A \) is observed to change. In effect, one has a high frequency, and hence high sensitivity, probe for weak interactions. This method would be particularly appropriate for measuring quadrupole coupling constants smaller than a few Mc/sec.

64 E. L. Hahn, Phys. Rev. 80, 580 (1950).