Fundamentals of Nuclear Magnetic Resonance Absorption. I

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Fundamentals of Nuclear Magnetic Resonance Absorption. I*†

G. E. Pake
Washington University, Saint Louis, Missouri

CONTENTS OF PART I*

A. Introduction

THE magnetic properties of the nucleus have interested the physicist ever since they were first postulated to explain the hyperfine structure of spectral lines. It was supposed that the nucleus is, in general, a small magnet whose interaction with the atomic electrons splits the energy levels between which the electrons make the transitions responsible for atomic line spectra. With the development of spectroscopic equipment of high resolving power, it ultimately became possible to determine certain nuclear spins and to measure a number of nuclear magnetic moments to about two significant figures.[1]

Considerably more accurate measurements were obtained in molecular beam experiments,[2,3] which were pioneered under O. Stern and which later flourished under Rabi at Columbia University. An outstanding addition to beam technique was the magnetic resonance method[2,3] which the Rabi group applied to these experiments. The most recent developments in the study of nuclear magnetic moments have applied the magnetic resonance principle to solids, liquids, and gases in their normal physical states, and the compilation of data concerning nuclear magnetism has become even more rapid.

The new resonance techniques, devised simultaneously and independently by the Purcell and Pound group[4,5] at Harvard and the Bloch and Hansen group[6,7] at Stanford, require relatively simpler equipment than do the beam experiments. (Indeed, a bridge-type apparatus similar to that of Bloembergen, Purcell, and Pound is part of an outstanding undergraduate program in physics directed by Professor Frank Verbrugge at Carleton College.) Further, the new methods seldom require the alteration of the physical or chemical form of the sample containing the nucleus whose magnetic properties are to be studied.

In addition to the extremely important advances in measurement of nuclear magnetic properties which the new methods provide, they also afford means for investigating establishment of the thermal equilibrium essential to magnetic methods for attaining very low temperatures. And the width and shape of the resonance has yielded information concerning crystal structure,[8,9] phase transitions in solids,[10] and hindered internal motions in solids.[11] An excellent intro-

* The concluding portion of this article will appear in a later issue of this Journal.

† Assisted by the joint program of the ONR and AEC.

[1] H. Kopfermann, *Kernmomente* (Edwards Brothers, Inc., Ann Arbor, 1945), Chapter II.

[2] D. R. Hamilton, *Am. J. Physics* **9**, 319 (1941).

[3] J. B. M. Kellogg and S. Millman, *Rev. Mod. Physics* **18**, 323 (1946).

[4] Purcell, Torrey, and Pound, *Physical Rev.* **69**, 37 (1946).

[5] Bloembergen, Purcell, and Pound, *Physical Rev.* **73**, 679 (1948), referred to as BPP throughout the following pages.

[6] Bloch, Hansen, and Packard, *Physical Rev.* **69**, 127 (1946).

[7] F. Bloch, *Physical Rev.* **70**, 460 (1946); Bloch, Hansen, and Packard, *Physical Rev.* **70**, 474 (1946).

[8] G. E. Pake, *J. Chem. Physics* **16**, 327 (1948).

[9] Gutowsky, Kistiakowsky, Pake, and Purcell, *J. Chem. Physics* **17**, 972 (1949).

[10] N. L. Alpert, *Physical Rev.* **75**, 398 (1949).

[11] H. Gutowsky and G. E. Pake, *J. Chem. Physics* **18**, 162 (1950).

ductory paper by Purcell,[12] titled "Nuclear magnetism in relation to problems of the liquid and solid states," skillfully presents certain potentialities of nuclear magnetism in structural studies to the reader who is without previous background in the subject.

One should not infer from the foregoing that molecular beams are in any sense outmoded. The very effects which reflect the structure of the sample tend, for many substances, to render the new techniques less effective in measuring the asymmetry of the nuclear charge distribution (the electric quadrupole moment). Nor have the Purcell and Bloch experiments offered competition to their contemporary cousin, microwave spectroscopy,[13] or to molecular beams in the determination of nuclear spins. Instead of seeking to eliminate one another, these three experimental approaches—molecular beams, microwave spectroscopy, and nuclear resonance absorption (Purcell) or nuclear resonance induction (Bloch)—supplement each other to provide versatile means for probing phenomena involving the magnetic and electric moments of nuclei.

The present article attempts to discuss one of these new methods, the nuclear resonance absorption technique of Purcell and Pound, in such a way as to be of value to the first-year graduate student of physics, and the material is substantially that used in introducing nuclear magnetism to graduate students at Washington University, where research begins with the inception of graduate study. A knowledge of the Bohr frequency condition is assumed, but no familiarity with quantum mechanics is required. A few results are taken bodily from quantum mechanics and are accompanied by remarks which, it is hoped, will put the student on the alert in his future studies for transition probabilities, the uncertainty principle, and other paraphernalia of quantum mechanics.

The closely allied nuclear induction experiment is not treated here, inasmuch as the pioneering articles on this subject by Bloch and his collaborators[7] provide in one place a lucid and sufficiently comprehensive treatment. These papers are quite as valuable to the beginning graduate student as to the front line researcher, for Bloch takes full advantage of the validity of the classical equations of motion in determining the nuclear magnetization. Lack of familiarity with quantum mechanics is thus much less of a stumbling block for the student when he reads these papers than when he turns to existent literature on nuclear absorption.

For the expert physicist who has specialized in other branches of his subject and wishes to become acquainted with the short history of this new nuclear technique, it is hoped that the present article can at least serve as a partially complete guide to the literature.

B. Magnetic and Angular Momentum Properties of the Nucleus

1. The Nuclear Magnet and its Vector Model

In addition to its well-known properties of mass, charge, and intrinsic angular momentum (spin), the atomic nucleus possesses in general a magnetic moment, that is, it behaves much as if it were a bar magnet. Although elementary textbooks often define the magnetic moment of a magnet as the product of its magnetic pole strength and the distance between its two poles, physicists believe that free magnetic poles do not exist and that a more accurate picture involves circulating electric currents or "current whirls." The magnetism of a bar of iron is attributed to "current whirls" of a kind within the iron atoms, and similarly the magnetism of the nucleus may be considered as originating with circulating currents in the nucleus. Since the existence of an intrinsic angular momentum of the nucleus implies a circulation of mass within it, it should not be surprising that the magnetic moment and angular momentum are related to each other. Indeed, classical models of the nucleus predict that these two vectors should be collinear and that their lengths should always be in the same ratio. For example, if one computes the magnetic moment of a spinning spherical shell with charge q and mass M uniformly distributed over its surface, he obtains a magnetic moment

$$\boldsymbol{\mu} = \frac{q}{2Mc}\mathbf{p}, \tag{1.01}$$

[12] E. M. Purcell, *Science* **107**, 433 (1948).
[13] See the review article by W. Gordy, *Rev. Mod. Physics* **20**, 668 (1948).

TABLE I. Nuclear spins, nuclear magnetic moments in units of the nuclear magneton, and the nuclear resonant frequency for $H_0=10{,}000$ gauss. The third column is taken from Taub and Kusch, *Physical Rev.* **75**, 1481 (1949); for the limits of error of these numbers, see this reference. The last column does not utilize all the significant figures of the fifth column, but instead indicates to one decimal place the magnitude of the resonant frequency in megacycles sec^{-1}. Nuclear magnetic moments obtained from hyperfine structure are generally known to about two significant figures, and are not included in this table. In addition, no exception has yet been found to the empirical rule that nuclei with even A and Z have zero spin and zero magnetic moment.

Z	Nucleus	A	Spin	$\mu=gI$	$\nu_0=g\mu_0\hbar^{-1}H_0$ for $H_0=10^4$ gauss (megacycles/sec)
0	n	1	1/2	−1.9135	29.1
1	H	1	1/2	2.7935	42.6
1	H	2	1	0.8576	6.5
1	H	3	1/2	2.9797	45.4
2	He	3	1/2	2.13	32.5
3	Li	6	1	0.8223	6.3
3	Li	7	3/2	3.2571	16.5
4	Be	9	3/2	−1.177	6.0
5	B	10	3	1.8012	4.6
5	B	11	3/2	2.6893	13.7
6	C	13	1/2	0.7025	10.7
7	N	14	1	0.404	3.1
7	N	15	1/2	±0.280	4.3
9	F	19	1/2	2.6291	40.1
11	Na	22	3	1.7464	4.4
11	Na	23	3/2	2.2178	11.3
13	Al	27	5/2	3.6419	11.1
15	P	31	1/2	1.1318	17.3
17	Cl	35	3/2	0.8222	4.2
17	Cl	37	3/2	0.683	3.5
19	K	39	3/2	0.391	2.0
19	K	40	4	−1.291	2.4
19	K	41	3/2	0.215	1.1
29	Cu	63	3/2	2.2266	11.3
29	Cu	65	3/2	2.3850	12.1
31	Ga	69	3/2	2.0145	10.3
31	Ga	71	3/2	2.559	13.0
38	Br	79	3/2	2.1061	10.7
38	Br	81	3/2	2.2700	11.5
37	Rb	85	5/2	1.3534	4.1
37	Rb	87	3/2	2.7510	14.0
49	In	113	9/2	5.489	9.3
49	In	115	9/2	5.502	9.3
53	I	127	5/2	2.8105	8.6
55	Cs	133	9/2	3.316	5.5
56	Ba	135	3/2	0.8364	4.3
56	Ba	137	3/2	0.9354	4.8
81	Tl	203	1/2	1.6121	24.6
81	Tl	205	1/2	1.6280	24.8

where $\mathbf{p}$ is the angular momentum of the spinning shell and c is a constant numerically equal to the velocity of light in free space.

We shall see that the nucleus does not conform accurately to this model nor to any other proposed simple model (nor even, thus far, to any complex one!), and that the resonance absorption phenomenon to be discussed here provides one of the experimental methods for learning the relation between the nuclear magnetic moment and the vector $\mathbf{p}$. However, nuclear magnets differ only in magnitude and/or sign from the prediction of Eq. (1.01), and it is customary to write

$$\boldsymbol{\mu}=g\frac{e}{2Mc}\mathbf{p}, \tag{1.02}$$

where g, called the *gyromagnetic ratio*, is a number characteristic of a given nuclear species in a given nuclear energy state. The symbol M denotes the proton mass and e the proton charge.

Since the nuclear moment is proportional to the intrinsic angular momentum or *spin* of the nucleus, it is worth while to review the special properties of this vector according to modern physics. The angular momentum of any particle or system of particles is found to be easily expressible in terms of a fundamental unit $\hbar$, which is Planck's constant divided by 2π. The quantity usually denoted "the spin" is defined as $1/\hbar$ times the largest observable value of the time average of a component of $\mathbf{p}$ in a given direction. We shall usually be concerned with magnetic fields and we select the direction of an applied magnetic field $\mathbf{H}$ as the direction of interest to us:

$$\text{"the spin"}=(1/\hbar)(p_H)_{\max}=I. \tag{1.03}$$

It is found experimentally and theoretically that the nuclear spin I can have integral or half-integral values. Each nuclear ground state is characterized by just one value of I, which is tabulated under the column marked "Spin" in Table I.

A general expression for all the permitted values of p_H is

$$p_H=m\hbar, \tag{1.04}$$

where $m=I, I-1, I-2, \cdots, -I+1, -I$. Since quantum-mechanical arguments show that the value of $\mathbf{p}\cdot\mathbf{p}$ is $I(I+1)\hbar^2$, the length of the angular momentum vector is

$$|\mathbf{p}|=[I(I+1)]^{\frac{1}{2}}\hbar. \tag{1.05}$$

One can apply these relations to find the length of the component at right angles to the $\mathbf{H}$-direction. Consider the proton, which has been found experimentally to have $I=\frac{1}{2}$. When $p_H=m\hbar$, with $m=+\frac{1}{2}$, the length of the vector is $|\mathbf{p}|=(\sqrt{3}/2)\hbar$ and the perpendicular component

is

$$p_\perp = (\sqrt{2}/2)\hbar, \tag{1.06}$$

which is even greater than $(p_H)_{\max}$. As I increases, $(p_H)_{\max}$ and $|\mathbf{p}|$ become more nearly equal. For an object which is massive (compared to a nucleus), such as a spinning baseball, $(p_H)_{\max}$ and $|\mathbf{p}|$ are to all intents and purposes equal for measurable values of $\mathbf{p}$.

2. *The Larmor Precession; Energy in the Magnetic Field*

If a magnet of dipole moment $\boldsymbol{\mu}$ is placed in a magnetic field $\mathbf{H}$, a torque is exerted on the magnetic dipole,

$$\mathbf{L} = \boldsymbol{\mu} \times \mathbf{H}. \tag{2.01}$$

Newton's law for rotational motion states that the rate of change of angular momentum of a system is equal to the torque applied to it, or

$$d\mathbf{p}/dt = \mathbf{L}. \tag{2.02}$$

Since the torque on a nucleus with magnetic moment $\boldsymbol{\mu}$ is given by Eq. (2.01), it follows that

$$d\mathbf{p}/dt = \boldsymbol{\mu} \times \mathbf{H}. \tag{2.03}$$

But since $\boldsymbol{\mu} = g(e/2Mc)\mathbf{p}$, we have

$$d\mathbf{p}/dt = -g(e/2Mc)\mathbf{H} \times \mathbf{p}, \tag{2.04}$$

which is the equation of motion for a vector $\mathbf{p}$ of constant magnitude precessing with angular velocity

$$\boldsymbol{\omega}_0 = -g(e/2Mc)\mathbf{H}. \tag{2.05}$$

To see this, note that (Fig. 1)

$$d\mathbf{p} = \boldsymbol{\omega}_0 \times \mathbf{p}\, dt \tag{2.06}$$

gives the proper direction to $d\mathbf{p}$, as well as the proper magnitude.

We therefore conclude that if a nucleus of magnetic moment $\boldsymbol{\mu} = g(e/2Mc)\mathbf{p}$ is placed in a magnetic field, the magnetic moment vector (or the angular momentum vector) precesses with the angular frequency [Eq. (2.06)] regardless of the angle between $\boldsymbol{\mu}$ and $\mathbf{H}$. This is called the *Larmor precession frequency.*

Recalling the arguments of Sec. 1, we see that the vector model of the nucleus is easily described in terms of the magnetic moment as follows. The nuclear magnetic moment of a nucleus with spin I is a vector of length

$$|\boldsymbol{\mu}| = g(e/2Mc)[I(I+1)]^{\frac{1}{2}}\hbar; \tag{2.07}$$

it has a component

$$\mu_H = g(e\hbar/2Mc)m \quad [m = I, I-1, \cdots, -I] \tag{2.08}$$

along the direction of an externally applied magnetic field $\mathbf{H}$, and a component of length

$$\mu_\perp = g(e\hbar/2Mc)[I(I+1) - m^2]^{\frac{1}{2}} \tag{2.09}$$

which is perpendicular to the external field and precesses with an angular frequency of magnitude

$$\omega_0 = g(e/2Mc)H. \tag{2.10}$$

Since, as may be derived from Eq. (2.01), the potential energy U of a magnetic moment $\boldsymbol{\mu}$ in a magnetic field $\mathbf{H}$ is, apart from an additive constant,

$$U = -\boldsymbol{\mu} \cdot \mathbf{H} = -\mu_H H, \tag{2.11}$$

the energy of our nuclear dipole in a state characterized by m is

$$U(m) = -g(e\hbar/2Mc)mH, \tag{2.12}$$

and a nucleus of spin I has, in general, $2I+1$ energy levels (one for each value of m) accessible to it in consequence of its interaction with a magnetic field $\mathbf{H}$. These are called the Zeeman levels, inasmuch as they are similar to those responsible for the Zeeman splittings in atomic

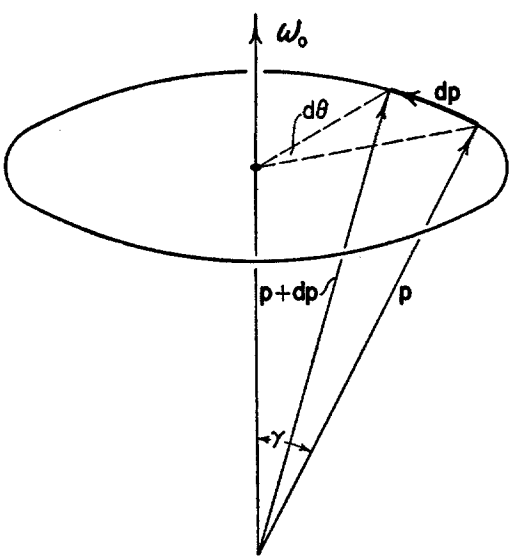

FIG. 1. Vector diagram used to illustrate the differential equation obeyed by a precessing angular momentum vector of constant magnitude.

spectra. It should be noted explicitly that the foregoing equations are valid whether g is negative or positive.

3. *The Nuclear Magneton and "The Magnetic Moment"*

The constant

$$\mu_0 = e\hbar/2Mc \tag{3.01}$$

is called the nuclear magneton, and nuclear magnetic moments are often measured in terms of it. The *Bohr magneton*, which is the unit of measure for electronic magnetic moments, may be found from Eq. (3.01) by substituting the electron mass for the proton mass. Note that electronic magnetic moments are of the order of 1000 times larger than nuclear moments. The values of the two magnetons are as follows:

$$\mu_0 = 5.049\times10^{-24} \text{ erg/gauss}$$
$$\mu_\beta = 0.9273\times10^{-20} \text{ erg/gauss.}$$

It is customary to let the vector $\mathbf{I}$ stand for the nuclear spin in units of $\hbar$. Then

$$\mathbf{I}\cdot\mathbf{I} = I(I+1)$$
$$I_H = m.$$

We can combine these definitions to express most conveniently the nuclear magnetic moment vector as

$$\boldsymbol{\mu} = g\mu_0\mathbf{I}. \tag{3.02}$$

The quantity colloquially referred to as "the magnetic moment" is

$$(\mu_H)_{\max} = gI\mu_0. \tag{3.03}$$

The dimensionless number gI is the "magnetic moment" measured in units of the nuclear magneton; it is the number tabulated in the fifth column of Table I.

4. *Thermal Agitation: The Curie Susceptibility*

We introduce the effects of thermal agitation on an assembly of magnets by carrying out a simple derivation of the so-called static Curie susceptibility.

The magnetic induction, or magnetic flux density, within a sample of matter may be written as

$$\mathbf{B} = \mathbf{H} + 4\pi\mathbf{M}, \tag{4.01}$$

where $\mathbf{H}$ is the magnetic field and $\mathbf{M}$ is the volume density of magnetic dipole moments or the magnetic moment per unit volume of the sample. In simple substances which are isotropic, the vector $\mathbf{M}$ is proportional to the applied magnetic field, as we shall find in our ensuing computation, and the proportionality factor χ is defined as the magnetic susceptibility:

$$\mathbf{M} = \chi\mathbf{H}. \tag{4.02}$$

Consider now a substance containing N nuclei per unit volume, and assume for simplicity that their nuclear magnets are all alike. Then we can compute the magnetic moment per unit volume, $\mathbf{M}$, if we know the number of nuclei in each energy state, since we already know from Eq. (3.08) the value of the static magnetic moment component along the field direction for each state m. The natural tendency is for a magnet to align itself parallel to an external field, for, as shown by Eq. (2.12), the potential energy is then a minimum. However, the energy possessed by each degree of freedom of the nucleus by virtue of its temperature is $\frac{1}{2}kT$, and a simple calculation shows that, even for the largest nuclear magnet in Table I, this thermal energy far exceeds the difference in energy between the parallel and antiparallel positions of the nuclear magnet in the field $\mathbf{H}$.

We therefore expect the collisions due to thermal agitation in the sample to play such havoc among the ranks of the nuclear magnets, which the external magnetic field $\mathbf{H}$ seeks to align, that there will be but a very small excess of nuclei in the lowest energy state. To illustrate this effect quantitatively, we compute from the Boltzmann factor the excess number of protons ($2I+1=2$) in the lower state at room temperature in a field of 20,000 gauss (usually the upper limit on fields obtainable in the laboratory).

Let the number of nuclei per unit volume with energy $U(m)$ be $N(m)$. Then the ratio of the population of the two proton states $m=\frac{1}{2}$ and $m=-\frac{1}{2}$ is, according to Boltzmann,

$$\frac{N(+\frac{1}{2})}{N(-\frac{1}{2})} = \frac{\exp[-U(\frac{1}{2})/kT]}{\exp[-U(-\frac{1}{2})/kT]} \cong 1 + g\mu_0\frac{H}{kT}, \tag{4.03}$$

since, at room temperature, $U(m)\ll kT$. Putting the numbers $H=20{,}000$ gauss, $kT=4\times10^{-14}$ erg, and $g=5.58$ for protons, one finds

$$N(+\tfrac{1}{2})/N(-\tfrac{1}{2}) = 1+14.1\times10^{-6}.$$

Thus, for every million nuclei in the upper energy state, there are one million and fourteen nuclei in the lower energy state. Clearly it is these fourteen protons in each two million which are responsible for the net nuclear magnetization of the sample.

To compute the Curie susceptibility for any nucleus characterized by $\alpha = g\mu_0 H/kT$, we require the sum

$$M_H = \sum_{m=-I}^{I} N(m)\mu_H(m) = K \sum_{m=-I}^{I} \exp[m\alpha] g\mu_0 m. \quad (4.04)$$

Since $\alpha \ll 1$, the constant K is easily evaluated from

$$N = \sum_{-I}^{I} N(m) = \sum_{-I}^{I} K \exp[m\alpha]$$

as $N/(2I+1)$. Thus Eq. (4.04) becomes

$$M_H = \frac{N}{2I+1} \sum_{-I}^{I} (1+\alpha m)\alpha \frac{kT}{H} m$$

$$M_H = \frac{N}{2I+1} \alpha^2 \frac{kT}{H} \sum_{-I}^{I} m^2. \quad (4.05)$$

Whether I is integral or half-integral, it may be shown that

$$\sum_{-I}^{I} m^2 = \tfrac{1}{3} I(I+1)(2I+1),$$

and the final result is

$$M_H = (N/3kT) g^2 \mu_0^2 I(I+1) H. \quad (4.06)$$

Comparison with Eq. (4.02) identifies the Curie susceptibility, which we denote by χ_0:

$$\chi_0 = (N/3kT) g^2 \mu_0^2 I(I+1). \quad (4.07)$$

Returning to our example, the proton, we see that Eq. (4.07) simply gives the magnetic moment per unit volume arising from the fourteen excess protons aligned parallel to **H** out of every two million protons in the sample. With reduced temperatures, the excess population in the lower energy state increases. Indeed, at very low temperatures the nuclear effect becomes so pronounced as to be experimentally measurable; the static Curie susceptibility of solid hydrogen has been measured directly by Lasarew and Schubnikow.[14]

C. Magnetic Resonance

5. Absorption and the Bohr Frequency Condition

On the basis of the Bohr frequency condition, one can use the results of Part B to conclude that nuclear resonance absorption may occur. Bohr's explanation of the hydrogen spectrum involved the postulate that a system characterized by two discrete energy states separated by energy ΔU may make a transition from one state to the other accompanied by either emission or absorption of a quantum of electromagnetic radiation of energy

$$\hbar\omega = \Delta U. \quad (5.01)$$

Whether the quantum is emitted or absorbed is determined by energy conservation for the transition in question.

In Part B a nucleus in a magnetic field was found to have $2I+1$ energy levels accessible to it, and if $I \neq 0$, transitions are possible. The energy difference between any two such levels in a constant external magnetic field $\mathbf{H}_0$ is

$$U(m'') - U(m') = g\mu_0 H_0 (m' - m''). \quad (5.02)$$

Only transitions in which m changes by $+1$ or -1 are permitted by a so-called *selection rule* and therefore transitions are permitted between adjacent states of an energy level scheme such as that of Fig. 2, which applies to a nucleus with $I = 5/2$. The selection rule applied to Eqs. (5.01) and (5.02) determines the frequency of the radiation emitted or absorbed by the nuclear magnetic dipole:

$$\hbar\omega_0 = g\mu_0 H_0, \quad (5.03)$$

which is precisely the Larmor frequency of Eq. (2.10). Protons in a field of 10,000 gauss precess at a frequency $\omega_0/2\pi = 42.6 \times 10^6$ sec^{-1}, which is in the radiofrequency range.

To summarize, if one subjects a sample containing nuclear magnets to radiation at the Larmor frequency, which is the order of megacycles in ordinary laboratory magnetic fields, a nucleus in a lower Zeeman energy state may ab-

[14] B. Lasarew and L. Schubnikow, *Physik. Zeits. Sowjetunion* 11, 445 (1937). If this reference is not available, see reference 1, pp. 224–225.

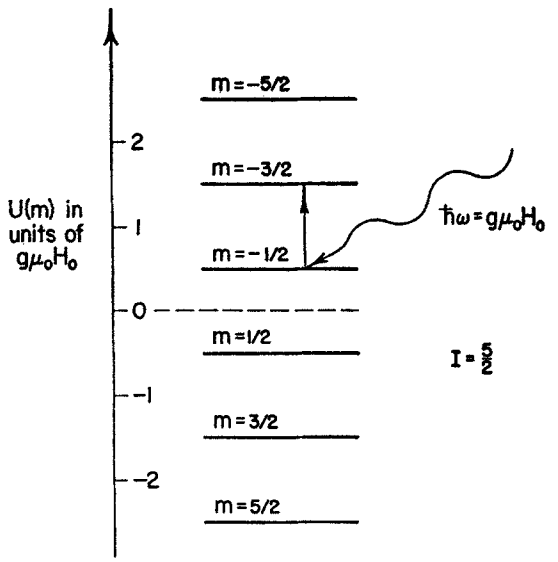

FIG. 2. Energy level diagram for a nuclear moment of spin 5/2, showing schematically the absorption of a quantum of radiation which induces a transition between a pair of adjacent Zeeman levels.

sorb a quantum of energy from the radiation field and make a transition to the next higher energy state. If the frequency of the radiation is not near the Larmor frequency, we expect little or no absorption, and hence the absorption is what physicists call a *resonance phenomenon.*

This cursory argument ignores entirely a number of important details. For example, are there sufficient excesses of nuclei in the lower energy states for a measurable net absorption to occur? If so, what means exist to maintain this distribution during the absorption process? And, are there any details about the radiation, such as its polarization, which are important? All of these questions will be dealt with in later sections.

6. *The Flopping Torque of a Precessing Magnetic Field*

Suppose that a small magnetic field $\mathbf{H}_1$ rotating with angular frequency ω is in some way placed at right angles to the constant magnetic field $\mathbf{H}_0$, where $H_1 \ll H_0$. The additional field $\mathbf{H}_1$ will produce a new torque $\mathbf{L}_{\text{flop}}$ which tends to tip the vector $\boldsymbol{\mu}$. Note, however, that if $\mathbf{H}_1$ rotates at a frequency appreciably different from the Larmor precession frequency of $\boldsymbol{\mu}$ in the large magnetic field, $\mathbf{L}_{\text{flop}}$ will change sense periodically with a frequency which is the difference between ω and ω_0. This is seen from Fig. 3 by noting that when $\mathbf{H}_1$ has the position OA with respect to $\boldsymbol{\mu}$, $\mathbf{L}_{\text{flop}}$ tends to tip $\boldsymbol{\mu}$ downward, but when $\mathbf{H}_1$ has position OB, its torque ($\mathbf{L}'_{\text{flop}}$) tends to tip $\boldsymbol{\mu}$ upward. This periodic change in sense of $\mathbf{L}_{\text{flop}}$ when ω and ω_0 differ appreciably leads to a zero time average for the flopping torque.

But when $\omega=\omega_0$, $\mathbf{L}_{\text{flop}}$ tends always to tip $\boldsymbol{\mu}$ in the same sense. If the vector $\boldsymbol{\mu}$ does tip and thus change its angle with respect to $\mathbf{H}_0$, energy must either be absorbed or emitted; again we are led to the resonance condition, this time by purely classical considerations.

The magnetic field $\mathbf{H}_1$ must *rotate* with angular frequency ω_0, whereas it seems natural to think of the electromagnetic radiation mentioned in Sec. 5 as possessing an *oscillatory* magnetic component. Indeed, the two points of view are reconcilable if one notes that an oscillatory field consists of two superimposed fields which rotate in opposite directions. Consider the field

$$\left.\begin{aligned} H_x &= 2H_1\cos\omega t \\ H_y &= 0 \\ H_z &= 0 \end{aligned}\right\}. \tag{6.01}$$

This is evidently expressible as the sum of the two fields,

$$\left\{\begin{aligned} H_x^{\text{right}} &= H_1\cos\omega t \\ H_y^{\text{right}} &= H_1\sin\omega t \\ H_z^{\text{right}} &= 0 \end{aligned}\right\}\left\{\begin{aligned} H_x^{\text{left}} &= H_1\cos\omega t \\ H_y^{\text{left}} &= -H_1\sin\omega t \\ H_z^{\text{left}} &= 0 \end{aligned}\right\}, \tag{6.02}$$

which rotate about the z axis with frequency ω, but in opposite directions. If the oscillating field Eq. (6.01) has $\omega=\omega_0$, one of its rotating components will follow the precessing vector $\boldsymbol{\mu}$ and produce transitions as discussed in this section. The oppositely rotating component is far off resonance, and its effect is negligible.

These considerations lead us to expect that the radiation which is to induce the transitions of Sec. 5 should be polarized with its magnetic vector at right angles to the large field $\mathbf{H}_0$.

7. *The Quantum-Mechanical Transition Probability*

The simple arguments of Secs. 5 and 6 attempt to make the absorption plausible, but a quantum-mechanical treatment is required to establish firmly the properties of the absorption by an

assembly of nuclear magnets. Quantum mechanics does not give us complete information as to the energy, angular momentum, and position of each nucleus at any time, but it does provide us with all that we need to know, namely, the *probability* that a nuclear magnetic moment initially in a state m will at some later time t be found in a state m'. This probability, expressed *per unit time*, will be denoted $P(m\rightarrow m')$.

If a nucleus in one of its Zeeman energy states is immersed in a radiation bath with energy in the frequency range $d\nu$ near ν given by $\rho(\nu)d\nu$, one expects the probability of a transition to be proportional to the number of quanta present with frequency near the Larmor frequency, that is, proportional to $\rho(\nu_0)$. In fact the quantum-mechanical result obtained by perturbation theory is

$$P(m\rightarrow m')=(2\pi/3\hbar^2)g^2\mu_0^2|\mathbf{I}_{mm'}|^2\rho(\nu_0). \quad (7.01)$$

The quantity $|\mathbf{I}_{mm'}|$, which is the so-called *matrix element* of the nuclear spin, is usually of order of magnitude unity; when $|m'-m|>1$ it vanishes, giving rise to the selection rule mentioned in Sec. 5.

For an isolated magnetic moment with $I=\frac{1}{2}$ in a constant magnetic field $\mathbf{H}_0$ perpendicular to which is a precessing smaller field $\mathbf{H}_1$, Rabi[15] computes the transition probability directly from the Schrödinger equation containing the time, without resorting to perturbation theory. He finds that the chance $C(\frac{1}{2}\rightarrow-\frac{1}{2})$ for a nucleus initially in state $m=\frac{1}{2}$ to be at a later time t in state $m=-\frac{1}{2}$ is

$$C(\tfrac{1}{2}\rightarrow-\tfrac{1}{2})=\frac{\sin^2\theta}{1+(\omega_0/\omega)^2-2(\omega_0/\omega)\cos\theta}\times\sin^2\left\{\frac{\omega t}{2}\left[1+\left(\frac{\omega_0}{\omega}\right)^2-2\frac{\omega_0}{\omega}\cos\theta\right]^{\frac{1}{2}}\right\}, \quad (7.02)$$

where $\tan\theta=H_1/H_0$; note that C is *not* a probability per unit time, but is rather the total probability at any time t. The ratio ω_0/ω is to be counted negative if the rotation of $\mathbf{H}_1$ is not in the same sense as the nuclear precession. In most experiments, $H_1\ll H_0$ and Eq. (7.02) becomes

$$C(\tfrac{1}{2}\rightarrow-\tfrac{1}{2})=\frac{\theta^2}{[1-(\omega_0/\omega)]^2+(\omega_0/\omega)\theta^2}\times\sin^2\left\{\frac{\omega t}{2}\left[\left(1-\frac{\omega_0}{\omega}\right)^2+\frac{\omega_0}{\omega}\theta^2\right]^{\frac{1}{2}}\right\}. \quad (7.03)$$

When resonance is obtained, that is, when $\omega=\omega_0$, a value of t can be found for which $C(\frac{1}{2}\rightarrow-\frac{1}{2})$ is as close to unity as one pleases. Moreover, when $\omega=-\omega_0$, $C(\frac{1}{2}\rightarrow-\frac{1}{2})$ becomes extremely small, confirming the conclusion of Sec. 7 that the wrong-rotating half of the oscillating field has negligible effect.

For higher values of the spin I, Majorana[16] has obtained the general formula for $C(m\rightarrow m')$.

At resonance, the expression (7.03) oscillates between 0 and 1 as time progresses. This hints at a result which is explicitly found by Rabi and also by the perturbation treatment, namely,

$$C(\tfrac{1}{2}\rightarrow-\tfrac{1}{2})=C(-\tfrac{1}{2}\rightarrow\tfrac{1}{2})$$
$$P(\tfrac{1}{2}\rightarrow-\tfrac{1}{2})=P(-\tfrac{1}{2}\rightarrow\tfrac{1}{2}). \quad (7.04)$$

The classical discussion made this seem likely, for there is nothing about the rotating field $\mathbf{H}_1$ which will turn off $\mathbf{L}_{\text{flop}}$ after the magnetic moment $\boldsymbol{\mu}$ has been tipped to a new position with respect to $\mathbf{H}_0$ (and, therefore, to a new energy).

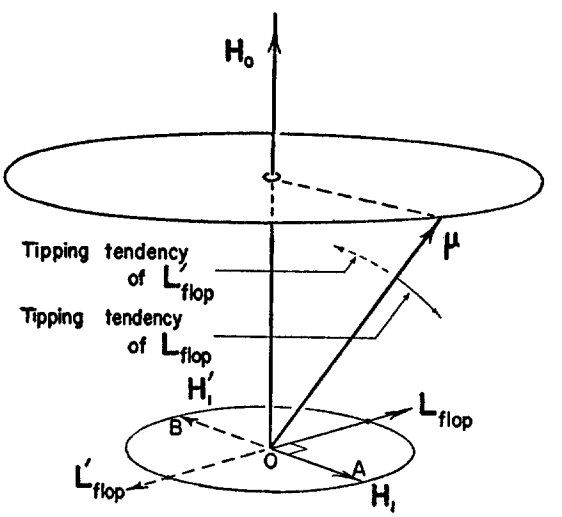

FIG. 3. Vector diagram illustrating the tendency of the small precessing magnetic field $\mathbf{H}_1$ to tip the magnetic moment vector as it precesses in a large constant field $\mathbf{H}_0$.

[15] I. I. Rabi, *Physical Rev.* 51, 652 (1937). See also J. Schwinger, *Physical Rev.* 51, 648 (1937).

[16] E. Majorana, *Nuovo Cimento* 9, 43 (1932). See also reference 3.

The reader is cautioned to use discretion in applying conclusions drawn from Eq. (7.03) to an assembly of *interacting* spins. First, as will be seen later, $C(\frac{1}{2}\rightarrow-\frac{1}{2})$ becomes quite small if ω_0/ω differs from unity by even a very small amount, and inhomogeneities in any laboratory magnetic field will make it impossible for a sizable fraction of the nuclei initially in state $m=\frac{1}{2}$ to have their C's near unity at any instant. Further, the nuclear magnets produce time varying local magnetic fields at their neighbors which, tend to spread ω_0 over an appreciable range only a small portion of which will be covered at any instant by a single monochromatic radiation source.

The equal probability found in Eq. (7.04) for transitions downward in energy (stimulated emission) and transitions upward in energy (absorption) emphasizes that, if a net absorption is to occur, there must at all times be the excess number of nuclear magnets which we found in Sec. 4 to exist in the lower energy states at thermal equilibrium. Otherwise, every absorptive transition will be balanced, on the average, by an emissive transition, and there will be no net energy exchange. We are thus brought to grips with the problem: how is thermal equilibrium among spin states established, and, once established, can it be maintained during a resonance experiment? The answer is found in the spin interactions to be discussed presently.

8. *The Spin-Lattice Relaxation Time, T_1*

Consider a sample containing nuclear magnetic moments which resides initially in a small magnetic field such as that of the earth. The Boltzmann factors for the various Zeeman energy states are almost exactly unity and the spins are essentially equally distributed among the $2I+1$ spin states. If this sample is thrust suddenly into the gap of an electromagnet which produces a field of 10,000 gauss, we ask how much time must elapse before the equilibrium excess numbers of nuclei will have found their way into the lower energy states. We are thus interested in the mechanism of the so-called *relaxation process* by which equilibrium is established. From a thermodynamic point of view, a relaxation process is thus any method of energy exchange between the system of nuclear spins and the lattice.

At the first instant after insertion into the magnetic field, and before equilibrium attains, the nuclear spins are still very nearly distributed in equal numbers among the $2I+1$ levels. A glance at Eq. (4.03) indicates that, since H_0, and therefore $U(m)$, is now large, the exponent can remain negligible only if the temperature T_S of the spin system is extremely high. In fact, for $I=\frac{1}{2}$, the excess number in the lower energy state defines at any time the spin temperature T_S. Our problem is that of describing the heat exchange between the lattice of vibrating atoms or molecules and the system of nuclear magnets, whose existence is usually well-sheltered by the enveloping electron closed-shells formed during the chemical combination which brought the lattice into being.

In order for the nuclear spins to "cool down," it is necessary that transitions from the upper spin states to the lower spin states occur more frequently than the reverse transitions. This seems at first thought to be incompatible with the result of Eq. (7.03) that the probabilities for transitions in both directions are equal. However, the present situation differs from that considered in Sec. 7 in that the entire system, consisting of lattice+radiation field+spins, is being left to itself to come to equilibrium at a definite temperature, whereas the monochromatic radiation field of Sec. 7 never comes to equilibrium with the nuclear spins at a common single temperature. Therefore the probabilities of Sec. 7 cannot be applied to the relaxation process without first taking into account certain properties and consequences of the equilibrium.

Let $N(p)$ and $N(q)$ be the equilibrium populations of two Zeeman levels p and q which differ in energy by U_p-U_q. Then a detailed balancing of the transitions between p and q will preserve equilibrium if

$$N(p)W(p\rightarrow q)=N(q)W(q\rightarrow p), \qquad (8.01)$$

where $W(p\rightarrow q)$ is the total probability per unit time of a single transition from p to q. But, at equilibrium, the Boltzmann factor governs $N(p)/N(q)$, and

$$\frac{W(p\rightarrow q)}{W(q\rightarrow p)}=\frac{N(q)}{N(p)}=\exp\left(\frac{U_p-U_q}{kT}\right). \qquad (8.02)$$

Now the probability of a single transition from

p to q cannot depend upon the population of q, and we must suppose that the total probabilities W are related to the quantum-mechanical probabilities P through the Boltzmann factor of the final state, even when equilibrium has not yet obtained:

$$W(p\rightarrow q)=P(p\rightarrow q)\exp(-U_q/kT). \quad (8.03)$$

We consider in detail the case $I=\frac{1}{2}$. Let the total number of spins be N, the population of the lower and upper energy states being respectively $N(+)$ and $N(-)$. Then, since $P(+\rightarrow-)=P(-\rightarrow+)=P$, we obtain

$$W(+\rightarrow-)=P\exp(-\tfrac{1}{2}g\mu_0H_0/kT)$$
$$W(-\rightarrow+)=P\exp(+\tfrac{1}{2}g\mu_0H_0/kT). \quad (8.04)$$

The excess number $n=N(+)-N(-)$ changes by 2 for each transition. This fact and the definition of the probabilities leads to the differential equation

$$dn/dt=2N(-)W(-\rightarrow+)-2N(+)W(+\rightarrow-). \quad (8.05)$$

Since $n\ll N$ for all cases of interest here, we substitute

$$W(+\rightarrow-)=P[1-\tfrac{1}{2}|g|\mu_0H_0/kT]$$
$$W(-\rightarrow+)=P[1+\tfrac{1}{2}|g|\mu_0H_0/kT], \quad (8.06)$$

obtained from Eq. (8.04), into Eq. (8.06) to find

$$dn/dt=2P(n_0-n), \quad (8.07)$$

where $n_0=N|g|\mu_0H_0/kT$ is the equilibrium value of n. Integration of Eq. (8.07) yields

$$n=n_0[1-\exp(-2Pt)]. \quad (8.08)$$

We note that the equilibrium excess number establishes in a fashion analogous to the charging of a capacitor of time constant $1/2P$. This characteristic time,

$$T_1=1/2P, \quad (8.09)$$

is called the *spin-lattice relaxation time* or the thermal relaxation time, and is the time required for all but $1/e$ of the equilibrium excess number to reach the lower energy state.

Theories of nuclear magnetic relaxation must compute P from Eq. (7.01). Waller[17] made one of the pioneering attempts in this direction. He examined the effect of the spectrum of vibrations and other lattice motions responsible for the specific heat of a solid. Such vibrations of the charged particles of the lattice lead to oscillatory currents and therefore to oscillatory local magnetic fields, the spectral intensity of which at the Larmor frequency should determine P according to Eq. (7.01). However, this mechanism leads to values of T_1 which are several orders of magnitude too large. Bloembergen, Purcell, and Pound[5] have studied relaxation in fluids and find that Brownian motions at the Larmor frequency provide the relaxation mechanism.

Thermal relaxation times thus far measured range from 10^{-4} sec or less in certain solutions containing paramagnetic ions to several hours for very pure ice crystals at liquid nitrogen temperatures. The value of T_1 for the protons in water at room temperature has been measured by Hahn[18] to be 2.33 ± 0.07 sec, in good agreement with the theory of BPP (see footnote 5). Relaxation for nuclear moments in solids, inadequately accounted for by Waller's theory, now appears to be explained by the presence of minute amounts of paramagnetic impurities, with their thousand-times larger magnetic moments.[19,20] These effects will be discussed in Part G.

9. *Spin-Spin Interactions*

The preceding section dealt with interactions between the system of nuclear spins and the lattice. In addition, each individual precessing nuclear moment interacts with neighboring spins through their magnetic fields. In fact, the total magnetic field at any single nucleus consists not only of the applied field H_0, but includes also the resultant of the local fields produced by the static components of neighboring magnetic dipoles. Depending upon the arrangement of its neighbors among the $2I+1$ values of μ_H, a given nucleus "sees" a slightly larger or slightly smaller field than that externally applied. One can estimate this effect by finding the magnitude of the local field which a nuclear magnetic dipole may be expected to produce at a distance of an angstrom unit or so,

$$H_{\text{loc}}\sim\mu_0r^{-3}\sim5 \text{ gauss}. \quad (9.01)$$

[17] I. Waller, *Zeits. f. Physik* **79**, 370 (1932).

[18] E. L. Hahn, *Physical Rev.* **76**, 145 (1949).

[19] J. F. Darby and B. V. Rollin, *Nature* **164**, 66 (1949).

[20] N. Bloembergen, *Physica* **15**, 386 (1949).

We can expect a dispersion or spread of values of the precession frequency because of the variation over these several gauss of the effective magnetic field at different nuclei throughout the sample. The magnitude of the precession frequency spread, $\delta\omega_0$, is then

$$\delta\omega_0 \sim g\mu_0\hbar^{-1}H_{\text{loc}} \sim 10^4 \text{ sec}^{-1}. \quad (9.02)$$

One can interpret this as meaning that, if two nuclei are known to be precessing in phase at time $t=0$, they may be expected to have lost their phase relationship within a time the order of $1/\delta\omega_0 \sim 10^{-4}$ sec.

A second process can occur to interrupt the phases of the precessing spins. If nuclei A and B are antiparallel to each other, the precessing component of A's magnetic moment produces at B a precessing magnetic field at nearly the proper frequency to produce a transition, and vice versa. It is, therefore, possible for A and B to flip each other over, leaving the net energy of the spin system unchanged. In effect, spins A and B have interchanged positions in the lattice, and this is often called a spin exchange or a spin-spin collision.

Though the spin-spin collision does not affect the total energy of the spin system, it does limit the lifetime of a spin state and leads, through the Heisenberg uncertainty relation, to an energy spread or dispersion. Since the relative phases of the two neighboring spins change appreciably during a time $1/\delta\omega_0$ (see the first part of this section), we can expect that nucleus A will require a time of that order of magnitude before its Larmor frequency becomes precisely equal to that of spin B, and the lifetime of a spin state should be limited by spin-spin collisions to times the order of $1/\delta\omega_0$. Then the energy levels are broadened by an amount δU given by

$$\delta U \cdot (1/\delta\omega_0) \sim \hbar \quad (9.03)$$

in accordance with the Heisenberg uncertainty principle. We again arrive at the conclusion that the relative phases of the precessing nuclear spins will be destroyed over times the order of $1/\delta\omega_0 \sim 10^{-4}$ sec, as a consequence of the interruption of a precessing state through spin-spin collisions.

The observable effect of these two phase-destroying processes arises through the spread in energy levels, that is, the dispersion of Larmor frequencies, which imparts to the absorption line a finite width. Later sections will be devoted to a detailed discussion of line width and its meaning in terms of the internal structure of the sample.

The quantum-mechanical calculation of line width verifies that both local field dispersion and spin exchange are real effects which broaden the line. The uniqueness of the two may be established by noting that unlike nuclear neighbors, by virtue of their appreciably different precession rates, should be unable to participate in spin-exchange processes, whereas their static components along $\mathbf{H}_0$ are still perfectly capable of dispersing the values of the total field at nuclei in the sample. Theory and experiment verify this fact.

D. The Bloch Formulation

10. Absorption and the Complex Susceptibility

Our point of view thus far has often been *microscopic*, that is, we have considered various phenomena in terms of the individual nucleus. In an actual experiment, of course, one deals with matter in bulk, and it is the *macroscopic* magnetic moment of the sample as a whole which he observes. The magnetic moment per unit volume of the sample $\mathbf{M}$ is related to the magnetic field $\mathbf{H}$ through the magnetic susceptibility χ, which is conveniently selected as the quantity to which the absorption will be related.

As in the familiar example of the magnetic absorption which leads to hysteresis losses in a transformer core, the energy absorbed by unit volume of the sample per second is

$$A = \frac{\omega}{2\pi}\int_{t=0}^{t=2\pi/\omega} \mathbf{H}\cdot d\mathbf{M}. \quad (10.01)$$

The integral itself represents the energy absorbed per cycle. It is convenient to represent the oscillatory magnetic field as the real part of a complex number

$$\mathcal{H} = 2H_1 \cdot \exp(i\omega t) \quad (10.02)$$

(script letters are used throughout to denote complex quantities). Then the physically observable magnetization is the real part of $\mathfrak{M}$ which is the product of the complex susceptibility

$\chi=\chi'-i\chi''$ and $\mathfrak{M}$:

$$M=\chi'(2H_1\cos\omega t)+\chi''(2H_1\sin\omega t). \quad (10.03)$$

Since $2H_1\cos\omega t$ is the applied field, the imaginary portion of the susceptibility is a measure of the out-of-phase component of magnetization.

If we take $\mathbf{M}$ and $d\mathbf{M}/dt$ to be collinear with $2\mathbf{H}_1$, the integral of Eq. (10.01) is quickly evaluated to yield

$$A=2H_1^2\omega\chi''. \quad (10.04)$$

The energy absorbed by the nuclear spin system is therefore proportional to χ'', the out-of-phase component of the nuclear magnetization. In the following section the resonance properties of χ'' will be demonstrated, thereby establishing *nuclear magnetic resonance absorption.*

11. The Bloch Equations

The equations of motion involving the nuclear magnetization $\mathbf{M}$ and the total magnetic field can be written from the discussions of earlier sections. These equations were first set up and solved by F. Bloch,[7] who sought a phenomenological description of the nuclear induction effect which is closely related to the absorption treated here.

Let the sample be placed in a large constant magnetic field $\mathbf{H}_0$ which lies along the z axis of a rectangular coordinate system, and suppose a small magnetic field to precess about the z axis. Then the magnetic field vector is taken to include $\mathbf{H}_0$ and the "left" rotating portion of Eq. (6.01):

$$\left.\begin{aligned} H_x&=H_1\cos\omega t\\ H_y&=-H_1\sin\omega t\\ H_z&=H_0 \end{aligned}\right\}. \quad (11.01)$$

The rotating field has its angular velocity vector along the direction of $-z$ because Eq. (2.05) indicates that a positive magnetic moment precesses in this sense. The equations which follow therefore treat absorption by an aggregate of nuclei with positive magnetic moments; the results will be equally valid for a negative moment if the $\mathbf{H}_1$ field precesses about $+z$, but no distinction will be necessary in the experimental situation which uses the oscillating field $H_x=2H_1\cos\omega t$, as both precessing components are present.

It is assumed for simplicity that the sample contains but one magnetic nuclear species, of which there are N per unit volume, and that this nucleus has spin I and magnetic moment gI nuclear magnetons. Although overlapping of two different nuclear resonances will seldom occur because the resonances are generally quite narrow, superposition will adapt the results which follow to any situation.

The vector equation of motion for a single nuclear magnetic moment may be written from Eq. (2.03) as

$$d\boldsymbol{\mu}/dt=g(e/2Mc)\boldsymbol{\mu}\times\mathbf{H}. \quad (11.02)$$

Summing over all the nuclear moments in unit volume of the sample transforms Eq. (11.02) into

$$(d\mathbf{M}/dt)=\gamma\mathbf{M}\times\mathbf{H}, \quad (11.03)$$

where

$$\gamma=ge/2Mc=\omega_0/H_0. \quad (11.04)$$

The parentheses around $(d\mathbf{M}/dt)$ are intended to indicate that Eq. (11.03) represents but one of several contributions to $d\mathbf{M}/dt$, others arising from the processes discussed in Secs. 8 and 9. For example, the z-component of magnetization is proportional to the excess number in the lower energy states, and Eqs. (8.07) and (8.09) produce a spin-lattice contribution

$$(dM_z/dt)=(M_0-M_z)/T_1. \quad (11.05)$$

The final contribution arises through spin-spin processes, which were found in Sec. 9 to destroy phase relationships between the precessing ($x-$ and $y-$) components of the nuclear magnetic moments. This destruction of the $x-$ and $y-$ components may be expressed by the equations

$$\begin{aligned}(dM_x/dt)&=-M_x/T_2\\ (dM_y/dt)&=-M_y/T_2.\end{aligned} \quad (11.06)$$

Integration of each equation in (11.06) by itself quickly verifies that these components would die out to $1/e$ of their initial values after time T_2.

Upon evaluating the cross product in Eq. (11.02) and adding the contribution from Eqs. (11.05) and (11.06), one obtains the Bloch equations:

$$\begin{aligned} dM_x/dt&=\gamma[M_yH_0+M_zH_1\sin\omega t]-M_x/T_2\\ dM_y/dt&=\gamma[M_zH_1\cos\omega t-M_xH_0]-M_y/T_2\\ dM_z/dt&=\gamma[-M_xH_1\sin\omega t-M_yH_1\cos\omega t]\\ &\quad+(M_0-M_z)/T_1. \end{aligned} \quad (11.07)$$

The resonance absorption phenomenon we treat here is described largely by a particular solution of Eqs. (11.07) which is obtained in the Appendix. We shall be interested in M_x and M_z since the experimentally applied fields $2\mathbf{H}_1\cos\omega t$ and $\mathbf{H}_0$ are in these directions. We find

$$M_x=\tfrac{1}{2}\chi_0\omega_0T_2 \times\frac{(2H_1\cos\omega t)T_2(\omega_0-\omega)+2H_1\sin\omega t}{1+T_2^2(\omega_0-\omega)^2+\gamma^2H_1^2T_1T_2} \quad (11.08)$$

$$M_z=\chi_0H_0\frac{1+T_2^2(\omega_0-\omega)^2}{1+T_2^2(\omega_0-\omega)^2+\gamma^2H_1^2T_1T_2}, \quad (11.09)$$

where χ_0 is the Curie susceptibility in Eq. (4.07).

Comparison of Eq. (11.08) with Eq. (10.03) identifies the Bloch susceptibilities as

$$\chi'=\tfrac{1}{2}\chi_0\omega_0T_2\frac{T_2(\omega_0-\omega)}{1+T_2^2(\omega_0-\omega)^2+\gamma^2H_1^2T_1T_2}$$

$$\chi''=\tfrac{1}{2}\chi_0\omega_0T_2\frac{1}{1+T_2^2(\omega_0-\omega)^2+\gamma^2H_1^2T_1T_2}.$$

Finally, the absorption is obtained from Eq. (10.04) and the above value of χ''.

$$A=\omega H_1^2\chi_0\frac{\omega_0T_2}{1+T_2^2(\omega_0-\omega)^2+\gamma^2H_1^2T_1T_2}. \quad (11.10)$$

The key equation (11.02) into which Bloch introduced the interactions involving T_1 and T_2 is a classical one, and it may well be asked why we apply it with such confidence to the small nuclear domain under consideration. In the quantum-mechanical formalism, the magnetic moment $\boldsymbol{\mu}$ is replaced by an *operator*, and a procedure is developed for finding directly from the operator and the nuclear wave function the *expectation value* of the quantity the operator represents. It is a happy fact that the quantum-mechanical expression for the time derivative of the magnetic moment operator is identical in form to Eq. (11.02), $\boldsymbol{\mu}$ being replaced by the operator. Upon proceeding to take the expectation value of each member, one alters in no way the form of the equation, which is now satisfied by the expectation value of $\boldsymbol{\mu}$. This expectation value corresponds to the observable quantity in an experiment, and therefore Eq. (11.02) describes the system no matter how large or small its quantum numbers may be.

12. The Bloch Susceptibilities

a. No saturation effects.—Consider first the situation when

$$\gamma^2H_1^2T_1T_2\ll1. \quad (12.01)$$

For example, this condition, when applied to the proton resonance in water at 7000 gauss, requires that H_1 be about one milligauss or smaller. The susceptibilities of Eq. (11.09) then reduce to

$$\chi'=\tfrac{1}{2}\chi_0\omega_0T_2\frac{T_2(\omega_0-\omega)}{1+T_2^2(\omega_0-\omega)^2} \quad (12.02)$$

$$\chi''=\tfrac{1}{2}\chi_0\omega_0T_2\frac{1}{1+T_2^2(\omega_0-\omega)^2} \quad (12.03)$$

and the absorption is

$$A=2H_1^2\omega\chi''. \quad (12.04)$$

The factor ω in Eq. (12.04) may usually be replaced by ω_0 since the resonance is ordinarily quite narrow compared to the resonant frequency ω_0.

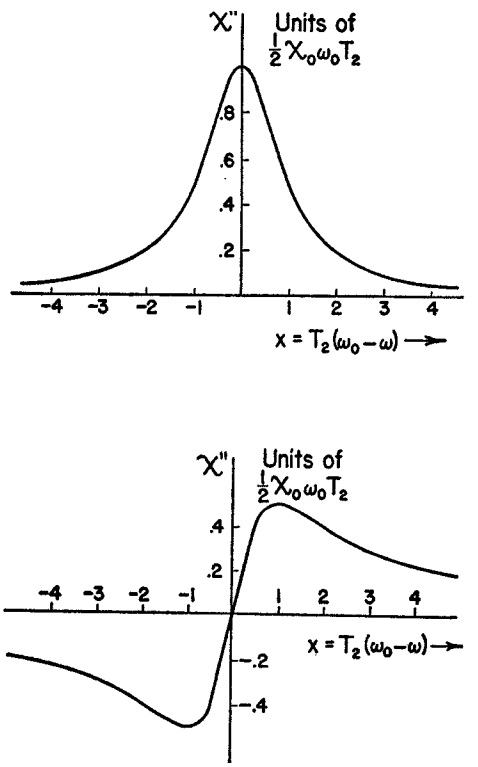

FIG. 4. The Bloch nuclear susceptibilities plotted against the dimensionless variable $x=T_2(\omega_0-\omega)$. These graphs apply to conditions of negligible saturation.

Equations (12.02) and (12.03) are plotted in Fig. 4 against an abscissa $x=T_2(\omega_0-\omega)$. The resonant character of the absorption is apparent, maximum absorption occurring at the Larmor frequency. Further, the half-width at half-maximum intensity occurs when

$$T_2|\omega_0-\omega|_{\frac{1}{2}}=1, \tag{12.05}$$

and thus $1/T_2$ is the half-width expressed as an angular frequency. The qualitative considerations of Sec. 9 are borne out: spin-spin processes fix the line width in a perfectly homogeneous external field.

The Bloch susceptibilities have the so-called Lorentz shape[21] which was first obtained in the simple classical analysis of radiation by a damped oscillator.[22]

b. Saturation effects.—We now remove the restriction Eq. (12.01) and increase H_1 until $\gamma^2H_1^2T_1T_2$ has a value of the order of unity. Under this condition, the nuclear spin system is said to be *saturated*, that is, it is soaking up radiofrequency energy to such an extent that the relaxation processes are unable to keep it at the lattice temperature. One can observe this directly from the expression (11.09) for M_z if χ_0 is replaced by its value in Eq. (4.07). The maximum value of M_z is then

$$M_z(\omega=\omega_0)=\frac{Ng^2\mu_0^2I(I+1)H_0}{3kT(1+\gamma^2H_1^2T_1T_2)}. \tag{12.06}$$

Equation (12.06) has a form that suggests the definition of an effective spin temperature,

$$T_S^{\text{eff}}=T(1+\gamma^2H_1^2T_1T_2), \tag{12.07}$$

since, if the constant field H_0 alone were applied at a real temperature equal to T_S^{eff}, Eq. (12.06) would give the equilibrium value of M_z which would arise. Thus the excess population in the lower energy states is reduced when $\gamma^2H_1^2T_1T_2$ is no longer negligible compared to unity.

The absorption is also affected by saturation. Whereas the expression (12.04) for A increases directly with H_1^2, the general expression (11.10) approaches the constant value

$$A(\text{sat})=(\omega\omega_0\chi_0)/(\gamma^2T_1)$$

as H_1^2 is increased indefinitely.

[21] G. E. Pake and E. M. Purcell, *Physical Rev.* 74, 1184 (1948).

[22] See, for example, R. Becker, *Theorie der Electrizität* (Edwards Brothers, Inc., Ann Arbor, 1945), p. 139.

Appendix

To aid in obtaining the particular solution of the Bloch equations, define the complex numbers

$$\mathfrak{M}_+=M_x+iM_y$$
$$\mathfrak{M}_-=M_x-iM_y.$$

First add i times the second equation of (11.07) to the first, then subtract i times the second from the first, obtaining

$$d\mathfrak{M}_+/dt=\gamma[-iH_0\mathfrak{M}_+ +iH_1\mathfrak{M}_ze^{-i\omega t}]-\mathfrak{M}_+/T_2 \tag{1}$$

$$d\mathfrak{M}_-/dt=\gamma[iH_0\mathfrak{M}_- -iH_1\mathfrak{M}_ze^{i\omega t}]-\mathfrak{M}_-/T_2. \tag{2}$$

We remove the time dependence by letting

$$\left.\begin{aligned}\mathfrak{M}_+&=e^{-i\omega t}\mathfrak{N}_+\\ \mathfrak{M}_-&=e^{i\omega t}\mathfrak{N}_-\end{aligned}\right\}, \tag{3}$$

so that Eqs. (1) and (2) become, after substituting $\omega_0=\gamma H_0$,

$$\left.\begin{aligned}i\omega\mathfrak{N}_+&=i\omega_0\mathfrak{N}_+-i\omega_0(H_1/H_0)\mathfrak{M}_z+\mathfrak{N}_+/T_2\\ i\omega\mathfrak{N}_-&=i\omega_0\mathfrak{N}_--i\omega_0(H_1/H_0)\mathfrak{M}_z-\mathfrak{N}_-/T_2\end{aligned}\right\}. \tag{4}$$

Equations (4) yield $\mathfrak{N}_+$ and $\mathfrak{N}_-$:

$$\left.\begin{aligned}\mathfrak{N}_+&=\frac{\omega_0(H_1/H_0)\mathfrak{M}_z}{\omega_0-\omega-i/T_2}\\ \mathfrak{N}_-&=\frac{\omega_0(H_1/H_0)\mathfrak{M}_z}{\omega_0-\omega+i/T_2}\end{aligned}\right\}. \tag{5}$$

To evaluate $\mathfrak{M}_z$ we require the third equation of (11.07). We seek a solution characterized by a steady-state absorption, and it will be assumed that $\mathfrak{M}_z$ is time independent. This assumption is not so restrictive as to require that the spin and lattice temperatures be equal, but merely requires that the spin system reach equilibrium determined by the inflow of r-f energy, the relaxation times, and the lattice temperature; this equilibrium state may well correspond to a spin temperature appreciably higher than the lattice temperature.

The assumption $d\mathfrak{M}_z/dt=0$ combines with the identity

$$M_x\sin\omega t+M_y\cos\omega t=(1/2i)(\mathfrak{M}_+e^{i\omega t}-\mathfrak{M}_-e^{-i\omega t})$$

to yield from Eq. (12.07) that

$$\frac{\gamma H_1}{2i}[\mathfrak{M}_+ e^{i\omega t} - \mathfrak{M}_- e^{-i\omega t}] = \frac{\mathfrak{M}_z - M_0}{T_1}, \quad (6)$$

which on further rearranging becomes

$$\frac{M_0 - \mathfrak{M}_z}{T_1} = \omega_0 (H_1/H_0)\left(\frac{\mathfrak{M}_+ - \mathfrak{M}_-}{2i}\right). \quad (7)$$

The bracket of Eq. (7) is found directly from Eq. (5); it is real, allowing M_z to replace $\mathfrak{M}_z$ and, upon solving the resultant expression for M_z, one obtains

$$M_z = \chi_0 H_0 \frac{(\omega_0 - \omega)^2 + 1/T_2^2}{(\omega_0 - \omega)^2 + (1/T_2^2) + (\gamma^2 H_1^2 T_1/T_2)}. \quad (8)$$

The quantity M_x may be obtained from

$$M_x = \tfrac{1}{2}(\mathfrak{M}_+ + \mathfrak{M}_-) = \tfrac{1}{2}[\mathfrak{M}_+ e^{-i\omega t} + \mathfrak{M}_- e^{i\omega t}]$$

and Eqs. (5) as

$$M_x = \tfrac{1}{2}\omega_0 (H_1/H_0) M_z \left[\frac{e^{-i\omega t}}{\omega_0 - \omega - i/T_2} + \frac{e^{i\omega t}}{\omega_0 - \omega + i/T_2}\right]. \quad (9)$$

Since M_z is real and the terms in brackets are complex conjugates, the expression (9) is indeed real, and

$$M_x = \tfrac{1}{2}\omega_0 \chi_0 T_2 \times \left[\frac{(2H_1 \cos\omega t) T_2 (\omega_0 - \omega) + 2H_1 \sin\omega t}{1 + T_2^2(\omega_0 - \omega)^2 + \gamma^2 H_1^2 T_1 T_2}\right]. \quad (10)$$

List of Principal Symbols

$\boldsymbol{\mu}$ = magnetic moment vector
$\mathbf{p}$ = angular momentum vector
c = velocity of light in vacuum
M = mass of proton
e = charge on the proton
g = nuclear g-factor (dimensionless)
$\hbar = (2\pi)^{-1}$ times the Planck constant
$\mathbf{H}$ = magnetic field
$\mathbf{I}$ = nuclear spin vector (dimensionless)
m = magnetic quantum number (dimensionless)
I = nuclear spin (maximum value of m)
$\mathbf{L}$ = torque vector
ω_0 = angular frequency of Larmor precession
$U(m)$ = Zeeman energy of a magnetic moment in state m
$\mu_0 = e\hbar/(2Mc)$ = nuclear magneton
$\mu = gI$ = dimensionless number of nuclear magnetons: "the nuclear magnetic moment"
$\mathbf{B}$ = magnetic induction vector
$\mathbf{M}$ = volume density of magnetization
χ = magnetic susceptibility (dimensionless)
N = number of nuclear magnetic moments per unit volume
k = Boltzmann constant
T = absolute temperature, usually of the lattice
$N(m)$ = number of nuclei per unit volume in state m
χ_0 = nuclear Curie susceptibility
ω = angular frequency of incident radiation
$\mathbf{H}_1$ = rotating magnetic field
$\mathbf{H}_0$ = constant magnetic field vector
$P(m \to m')$ = transition probability per unit time
ν = frequency of radiation
$\rho(\nu)$ = energy density of radiation at frequency ν
$C(m \to m')$ = absolute transition probability
T_1 = spin-lattice relaxation time
T_S = temperature of the nuclear spin system
$W(p \to q)$ = total transition probability per unit time after detailed balancing
n = excess of nuclei per unit volume in lower Zeeman state (for $I = \frac{1}{2}$)
n_0 = equilibrium value of n for $T_S = T$
H_{loc} = magnetic field produced at a lattice point by neighboring nuclear moments
A = energy absorbed per second per unit volume
χ', χ'' = real and imaginary parts of $\chi = \chi' - i\chi''$
M_0 = equilibrium value of z-component of nuclear magnetization
T_2 = time for a freely precessing component of nuclear magnetization to fall to e^{-1} of its value; inverse measure of line width
$\gamma = ge/(2Mc)$ = ratio of angular Larmor frequency to magnetic field
$x = T_2(\omega_0 - \omega)$ = dimensionless variable
$\mathfrak{L}$ = complex inductance of coil containing nuclear sample
$\mathfrak{Y}$ = complex admittance
$\mathfrak{V}$ = complex potential difference
a = ratio of modulation amplitude (gauss) to line width (gauss)
G_r = gain of the receiver
D = deflection of "lock-in" meter
$s = \gamma^2 H_1^2 T_1 T_2$ = saturation factor
β = angular frequency of magnetic field modulation
ΔH = difference between H and its resonant value for applied radiofrequency ν
$p(\Delta H)$ = line shape for interacting pair
$f(\nu)$ = any normalized line shape on a frequency scale
$\langle(\Delta\nu)^2\rangle_{\text{Av}}$ = second moment of line shape
τ_c = correlation time
δH = separation (in gauss) between points of extreme slope of the absorption curve.