Magnetic Resonance

PART I—NUCLEAR MAGNETIC RESONANCE

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Magnetic resonance is the name of a phenomenon discovered less than sixteen years ago, which from the start has had a high theoretical importance and is now attaining a notable practical value. Nuclear magnetic resonance occurs when a substance containing magnetic nuclei is exposed to crossed magnetic fields, one being steady and the other oscillating, and the strength of the former field and the frequency of the latter are matched in a particular way. When these are properly matched, the nuclei are turned over in the steady field, and energy is absorbed from the oscillating field. Another way of describing the effect is to say that resonance occurs when the applied frequency is equal to the frequency of precession of the nuclei in the steady field. This phenomenon illustrates very clearly some of the fundamental laws of Nature. For the purposes of nuclear physics it is used to determine the magnetic moments of nuclei and their relaxation-times in the substance that contains them. It is also used for chemical analysis, for measurement of magnetic fields, for analysis of crystal structure and for locating changes of phase of the substance containing the nuclei. Magnetic resonance of electrons is similar, but for a fundamental reason is confined almost exclusively to free atoms of certain kinds, to ferromagnetic substances and to certain strongly paramagnetic salts. For these last it serves to throw light on the fields prevailing within the crystals.

"Magnetic" is an ancient word in physics and so is "resonance," but "magnetic resonance" is something new. It is the name of a phenomenon which is sharp and clearcut and easy to evoke, which springs directly from the ultimate magnetic particles of matter, which illustrates the fundamental laws of these, and which has found and still is finding uses of importance. There are two types of it, the nuclear and the electronic. Nuclear magnetic resonance is the theme of the first part of this article: it will recur from time to time in the second part (to appear in a later issue of this JOURNAL) but the main topic of that second part will be electronic resonance. It is fitting that they should be treated in this order, for the nuclear type of resonance is less distorted by complexities than is the other. Perhaps it is not premature to say that while nuclear magnetic resonance always goes by that name, the electronic type is usually called "paramagnetic resonance" or "ferromagnetic resonance."

Nuclear magnetic resonance was realized in 1937, in molecular-beam experiments. The war distracted physicists, and the next great step was not made until after — but very soon after — the armistices. In the winter months of 1945–46 the phenomenon was produced in liquids and in solids. The news burst upon the world from the pages of *The Physical Review* in the early weeks of 1946, causing among physicists an immediate and an immense sensation. Of some discoveries one wonders how they came to be made at all, of others one wonders afterward why they were not made earlier. Nuclear magnetic resonance is of the latter class. But this is a discovery that could not have been made *much* sooner than it was, for it required the apparatus and techniques of short-wave radio and microwaves, and these are recent.

The work of 1945 was done by two independent groups three thousand miles apart, using somewhat different experimental methods and expounding the theory in somewhat different ways. The differences are really superficial, and in the course of time will probably be minimized; but the two streams of later work that rose from those two sources are still distinguishable. The methods are called the nuclear resonance absorption method and the nuclear induction method: I treat them in this order. A sketchy account of the molecular-beam method will follow upon these, and then several of the applications — which of these are major and which are minor must be left for history to decide.

On the first few pages, and on many thereafter, the talk will be of protons. Protons are the commonest material particles in Nature, electrons excepted (neutrons are also an exception but not an important one here, as they are seldom found free). Protons also have the happy attribute called "spin ½" soon to be explained, which simplifies the exposition greatly. This is one of the rare fields of physics in which the simplest case, the commonest case, and the most useful case, are all three of them one and the same.

PROTON RESONANCE ABSORPTION

To begin with, there must be a sample containing hydrogen, protons being the nuclei of ordinary (as distinguished from heavy) hydrogen atoms. It may be pure hydrogen in gaseous, liquid or solid form, or any one of countless compounds of hydrogen. I first take water for the sample, and enumerate the other particles in water. There are the nuclei of the common isotope of oxygen, oxygen 16: they are non-magnetic and produce no resonance. There are the nuclei of rarer isotopes of oxygen and hydrogen: they will be mentioned later. There are the electrons: they are reserved for Part II of this article. We are now left with the protons.

The sample is placed between the poles of a magnet, Fig. 1, so that it is in a magnetic field which should be homogeneous and is usually strong. The strength of the field is denoted by H, and its direction is always that of the z-axis (and usually vertical). I should like to call it "the steady field," but usually it is modulated during the experiments, so I shall call it "the big field". Actually it can be very small, but nearly always it is between 8,000 and 15,000 gauss, and 10,000 gauss is a good figure to keep in mind.

The big field must not be the sole magnetic field applied to the sample. There must also be an alternating or oscillating field — stationary electromagnetic waves, formed in a solenoid (or sometimes in a resonant cavity). Such waves comprise, as Maxwell taught us long ago, an alternating electric field and an alternating magnetic field. In most of the uses of electromagnetic waves it is the electric field that counts, and the magnetic field is remembered only as something demanded by Maxwell's equations to keep the electric field going. In this application the electric field takes a back seat, and it is the magnetic field that counts. This oscillating magnetic field must be at right angles to the big field; we lay the x-direction along it. Its amplitude, to be denoted

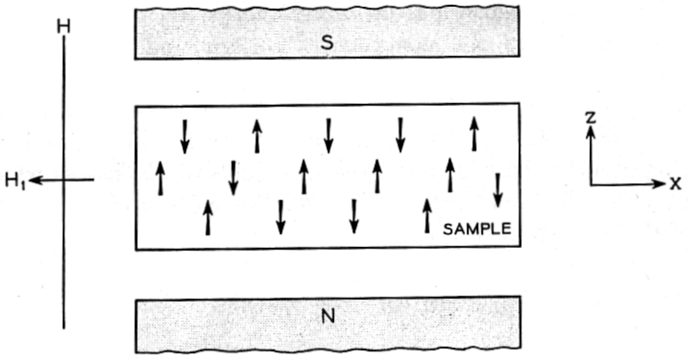

Fig. 1 — Scheme of the apparatus for observing nuclear magnetic resonance. The detecting circuits are omitted. The nuclei indicated by the arrows are of "spin ½," protons for example.

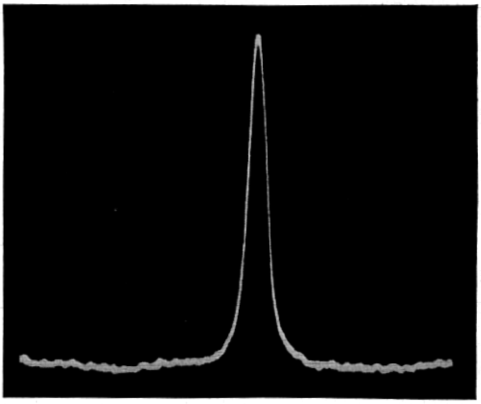

Fig. 2 — Peak of nuclear resonance absorption. This is the first peak to be published other than those obtained with molecular beams. It pertains to protons in water. (Courtesy of E. M. Purcell).

by H_1, is of the order of a small fraction of one gauss up to several gauss. Its frequency must be of the order of tens of megacycles. To be more specific, the effect that is sought with protons is located at 42.6 mc when H is 10,000 gauss.

Finally there must be circuits and detectors for measuring the absorption of the electromagnetic wave-energy in the sample. These are well known to those proficient in the art: we pass them over.

Now of the two quantities H and ν either is to be varied while the other is to be kept constant, and the absorption is to be measured. Usually H is varied while ν is kept constant, and the data consist of a plot of absorption against H for a set value of ν.

When such a curve is plotted it proves to be, in the main, a smoothly-sloping curve, of no interest in the present connection. What *is* of interest is that it is interrupted by a magnificent peak of extraordinary sharpness, deserving to be called a needle. Probably there is nothing that can please an experimenter more than a curve with a fine sharp peak: here he has it. Fig. 2 exhibits the first such peak on record. But neither Fig. 2 nor any other picture can convey an adequate idea of the sharpness of the peak, for the distance from this imposing feature to the axis of the ordinates at field-strength zero may be, and often is, tens of thousands of times as great as the breadth of the peak. (With the induction-method, peaks have been distinguished from each other that are separate by only a millionth of the value of H at which they are found). This needle has the narrowness that is characteristic of fine lines in optical spectra; and this is as it should be, for a spectrum-line is just what it is, even though it lies in the radiofrequency range and for technical reasons appears on a scope instead of on a photographic film.

The peak is the phenomenon of magnetic resonance. We shall now interpret it in terms of theory somewhat oversimplified, for it is not the office of these opening paragraphs to introduce all of the complexities of quantum mechanics.

In Fig. 1, inside the rectangle which represents the sample, appear a number of arrows. These are symbols of the protons. In other circumstances we might imagine the protons as solid balls, in still others we might imagine them as centres of force; but for the present purpose we are regarding them as tiny bar-magnets, and the arrows symbolize the directions in which they are pointing. It is necessary to label these directions with perfect clearness. The figure has been drawn with the south pole-piece of the big magnet (the one responsible for the big field H) above. The point of each arrow represents the *north* pole of the protonic magnet.

Thus the arrows pointing upward represent protons in the orientation into which the big field would like to turn the protonic magnets, and would indeed succeed in turning them if they were literal compass-needles in literal compasses. The arrows pointing downward represent protons in the opposite orientation. I will call these, for shortness, the "up" orientation and the "down" orientation. Evidently if the physicist could reach into the sample with fingers or with forceps and turn a proton from the up orientation into the down one, he would be doing work upon the proton at the expense of energy from his muscles. Well, he cannot reach into the sample with fingers or with forceps and grasp and turn a proton. But he can reach into the sample with the oscillating field and turn the protons, and this is the experiment we are considering. Magnetic resonance is the turning of protons from the up orientation into the down one, from the orientation or "level" of lesser energy into the orientation or level of greater energy.

But why does the effect occur at one frequency only? And what determines that frequency? To cope with this problem we shall have to introduce symbols, equations, and quantitative reasoning.

The first step is to evaluate the work required to turn the proton, or, in other words, the energy-difference between the two orientations or levels. It shall be denoted by W, and the magnetic moment of the proton by μ_p. We proceed by strictly classical reasoning. The torque exerted on the proton by the magnetic field H is $-\mu_p H \sin \theta$. Here θ stands for the angle between the direction of the steady field and the direction in which the magnetic moment of the proton is pointing. We have admitted the existence of only two values of θ, viz. the values 0° and 180°; more will be said about this later; but for the duration of this particular argument we shall have to admit all values of θ from 0° to 180°. The value of W which we are seeking is the integral of $\mu_p H \sin \theta$ from 0° to 180°, from the up orientation to the down one. It is easily obtained:

$$W = -\int_{0^\circ}^{180^\circ} \mu_p H \sin \theta d\theta = 2\mu_p H \tag{1}$$

Having arrived at equation (1) by strictly classical reasoning, we must now approach equation (2) by a starkly quantal argument. Immense amounts of evidence have shown that when energy is absorbed from electromagnetic waves of frequencies ν in the optical range of the spectrum and in the X-ray range, not to speak of other ranges, it is invariably absorbed in parcels or quanta equal to $h\nu$, h standing as always for Planck's constant. If this doctrine is sometimes difficult to assimilate when applied to the optical spectrum, how much more difficult it is to accept when applied to waves of radio frequencies! Yet here also it is to be accepted, so we put:

$$W = h\nu \tag{2}$$

Now we transfer the value of W from equation (1) to equation (2), and arrive at the destination:

$$H = \tfrac{1}{2}h\nu/\mu_p \tag{3}$$

In this equation h is known with very great accuracy, and μ_p had also been measured when the first experiments upon magnetic resonance were made, though not with nearly the accuracy that physicists now claim for it. It remains only for the experimenter to insert for ν the value of the frequency in his experiment and for H the value of the fieldstrength at which the peak appears. The test is whether the two sides of the equation agree. Needless to say, the test has been brilliantly passed.

Quantum-theory has entered into this argument in more ways than the one which led to equation (2). I return now to the fact that we have arrived at equation (3) by postulating two, and only two, "permitted" orientations of the protonic magnets in the steady field. This is illustrated by the presence, in Fig. 1, of arrows pointing up and arrows pointing down but no arrows pointing slantwise. We might have assumed that there are protons, and therefore arrows, pointing in every direction. We might have assumed that there is a proton pointing, say, at angle

76°13′ to the vertical, and that it can absorb a quantum $h\nu$ of just the right energy to turn it to the angle 118°36′. This would have led to the inference that instead of absorption confined to the fieldstrength $h\nu/2\mu_p$ corresponding to the actual peak, there would be absorption at every fieldstrength from $h\nu/2\mu_p$ on upwards toward infinity. The experiment frustrates this inference, and so declares for the two and the only two permitted orientations. One did not have to wait for this experiment to learn this fact: it has been known for thirty years, both as a consequence of quantum mechanics and as a fact of experience. However this is a very pretty proof of it.

We now must generalize equation (3) so as to make it take care of all nuclei and not the proton only; and in the course of this process we shall meet the actor behind the scenes who determines the permitted orientations. His names are *spin* and *angular momentum.*

THE GENERAL EQUATION FOR NUCLEAR MAGNETIC RESONANCE

We are now en route to the general equation of which (3) is the special case appropriate to the proton. Our first step takes us to the deuteron or nucleus of heavy hydrogen. Its magnetic moment differs from that of the proton, so we must write μ_d instead of μ_p. More significant is the fact that the deuteron has three permitted orientations in the big field instead of two. The orientations of proton and deuteron are shown in the first and third columns of Fig. 3; beside them are horizontal lines depicting their energy-values, energy being measured vertically upward from an arbitrary zero.

One guesses from the aspect of Fig. 3 that the deuteron will show three peaks of magnetic resonance; for it seems possible for the deuteron to be turned from orientation *a* to orientation *b*, from *b* to *z* and from *a* all the way to *z*. But of these three conceivable "transitions" the third

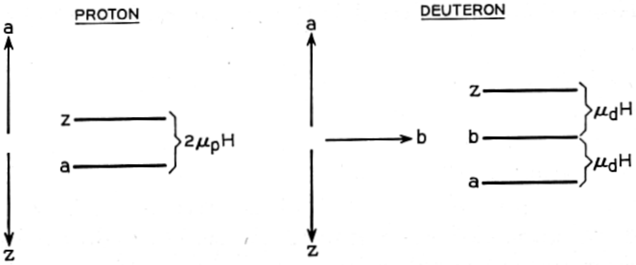

Fig. 3 — Orientations and energy-levels of protons and deuterons in a magnetic field, according to the "old" quantum-theory.

does not occur at all: the theorists know the reason why, and call it a "forbidden" transition. As for the other two, the mere symmetry of the picture shows that they involve equal absorptions of energy and therefore contribute coincident peaks. There is therefore only one distinguishable peak, and we have to find the value of H at which it appears. This is easily done. Going back to equation (1), we integrate the integrand which there appears from 0° to 90° (or from 90° to 180°); and so we come to the analogue of equation (3) which applies to the deuteron:

$$H = h\nu/\mu_d \tag{4}$$

In the course of this argument we have met with an example of two general rules: *no matter how many permitted orientations there are, transitions occur only between consecutive ones, and these permitted transitions always agree in energy-absorption, so that there is never more than one peak.* Yet equation (4) differs from equation (3), because in the right-hand member $h\nu/\mu$ — and now I am using μ as the general symbol for magnetic moment — is multiplied by ½ for the proton and by one for the deuteron. Now, ½ is the value of the spin of the proton and one is the value of the spin of the deuteron. We generalize from these two instances: we use I as the general symbol for the spin; and we arrive at the following:

$$H = (I/\mu)h\nu \tag{5}$$

The generalization is sound; and *equation (5) is the fundamental equation of nuclear magnetic resonance.*

I now have to interpret the word "spin." Spin is a particular measure of the angular momentum of the nucleus. That a magnetic nucleus has angular momentum is surely not surprising. We are trained to ascribe magnetism to the motion of charged bodies: an electric current flowing in a loop has the same magnetic field as a bar-magnet. When a nucleus is observed to have a magnetic moment and an angular momentum, it is natural to correlate one property with the other: one does not quite know how far the analogy may safely be pressed, but at least it is helpful.

But what sort of a measure of the nuclear angular momentum is the quantity I? The answer to this question is confused by the fact that in our times there have been two forms of quantum theory: the "new" quantum mechanics which is undoubtedly more competent in general, and the "old" quantum theory of the nineteen-twenties which is certainly more simple in the present case. Desire to be clear has led me to employ the older theory up to now, but conscience obliges me to introduce the new one.

In the old theory, I is the nuclear angular momentum in terms of the unit $h/2\pi$. Two of the permitted orientations, which I will call the "extreme" ones, are straight along and straight against the field-direction. For these, the projections of the angular momentum upon the field-direction are $+Ih/2\pi$ and $-Ih/2\pi$. For the proton $I = \frac{1}{2}$, and the two extreme orientations are the only ones.

In the new theory, the nuclear angular momentum in terms of the unit $h/2\pi$ is $\sqrt{I(I + 1)}$. For the two extreme orientations, the projections of the angular momentum on the field-direction are $+Ih/2\pi$ and $-Ih/2\pi$, just as they were in the old theory. But now these orientations are no longer straight along and straight against the field-direction. They must be inclined, one to the up direction and the other to the down direction, at the angle of which the cosine is $I/\sqrt{I/(I + 1)}$.

Thus I has partly changed its meaning: it is still the maximum permissible projection, upon the field-direction, of the nuclear angular momentum in terms of the unit $h/2\pi$, and this is what it was before; but it is no longer the magnitude of the nuclear angular momentum. So also has μ changed a part of its meaning. It is the maximum permissible projection, upon the field-direction, of the magnetic moment of the nucleus, and this it was before; but it is not the magnitude of the nuclear magnetic moment. The language of this subject has not been well adjusted to this change. Fortunately I is called the "spin," which does not necessarily convey the impression that it is quite the same thing as angular momentum; but μ is still called the "magnetic moment," and in the new quantum mechanics this is a mistake.

Fig. 4 is Fig. 3 redrawn in the spirit of quantum mechanics. The arrows now represent angular momentum and magnetic moment jointly,

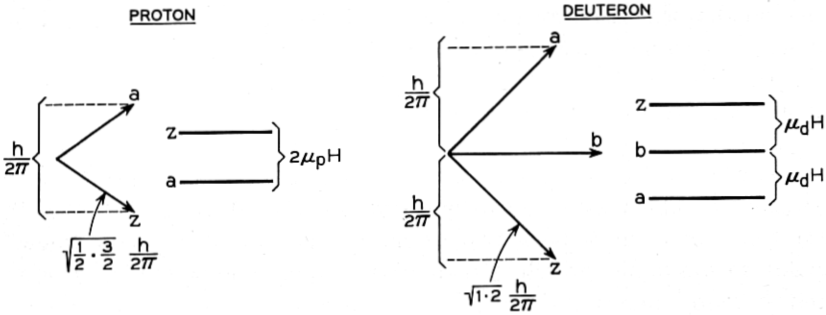

Fig. 4 — Orientations and energy-levels of protons and deuterons in a magnetic field, according to quantum mechanics.

but the numbers affixed to them are the values of angular momentum. The energy-levels in the second and fourth columns are often known as "Zeeman levels." I take this occasion to complete the statement about the allowed orientations, which in recent paragraphs has been made for the extreme orientations only. The projections of the nuclear angular momentum upon the field-direction are

$$+Ih/2\pi,\ +(I-1)h/2\pi,\ \cdots,\ -(I-1)h/2\pi,\ -Ih/2\pi.$$

From this principle combined with the fact that transitions occur only between consecutive levels, follows rigorously equation (5), which I derived in a looser way.

Spins are ascertained in various ways, usually from their influence on the electrons surrounding the nuclei, which manifests itself in details of optical spectra and in cleverly-designed molecular-beam experiments. They are always integer multiples of ½. Important instances of nuclei of spin ½ are the proton and the nucleus F^{19}. The neutron and the electron also belong in this category, as we shall see later on. The deuteron has already provided us with an important instance of a nucleus of spin one. Spins as high as $9/2$ are certainly known, and this is probably not the limit. Nuclei of spin zero are common: I have already mentioned one of them, oxygen 16. Such nuclei do not produce magnetic resonance; we shall have nothing to do with them.

A brief table shall conclude this section. To what has already been stated it adds the number of permitted orientations corresponding to each value of spin.

Spin	½	1	$3/2$	I
Number of orientations	2	3	4	$2I+1$
H for peak	$(1/2)h\nu/\mu$	$h\nu/\mu$	$(3/2)h\nu/\mu$	$(I/\mu)h\nu$

THE LARMOR PRECESSION AND NUCLEAR INDUCTION

Now we go back to first principles, make a fresh start, and arrive by a different route at the equation for magnetic resonance. On this route we meet with a vivid justification of the use of the name "resonance."

Resonance implies a tuning or a matching between an applied frequency and a frequency either actually or potentially present in the substance in question. A piano-wire, a membrane, the air in an organ-pipe, an electrical circuit comprising capacity and inductance, all resonate to the frequency which is that of their own natural vibrations. No mention has yet been made of a frequency peculiar to the nucleus which is matched by the applied frequency when magnetic resonance occurs. There is indeed such a natural frequency, not however a frequency of vibration; it is a frequency of *precession*. Precession is a concept well known to astronomers and to such physicists as have to do with gyroscopes, perhaps not so well known as it should be to others.

In Fig. 5, the vertical is again the direction of the big magnetic field. The arrow represents the angular momentum of the nucleus, which I now denote by p. The magnetic field H exerts a torque on the nucleus. I have already given an expression for this torque, but I gave it in the language of the "old" quantum-theory. To employ this expression with as little apparent change as possible, I introduce the symbol μ_0 for the magnetic moment of the nucleus, and reserve μ for the maximum permissible projection of μ_0 on the field-direction. The torque now appears on the right-hand side of the following, purely classical, equation:

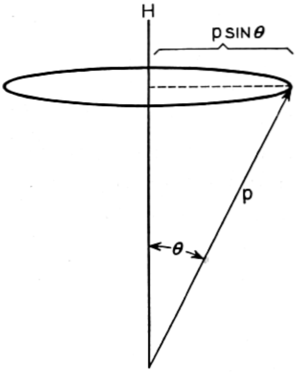

Fig. 5 — Illustrating the Larmor precession.

$$dp/dt = \mu_0 H \sin \theta \qquad (6)$$

This is a vectorial equation, but I will endeavor to express its vectorial content by words instead of symbols. Fix the attention on the tip of the arrow. The torque makes it describe a circle of radius $p \sin \theta$ in the horizontal plane, with a frequency which I denote by ν. Its peripheral speed in this circle is ν multiplied by the circumference of the circle, therefore $\nu \cdot 2\pi p \sin \theta$. This speed is dp/dt. Putting its value into (6), we observe with pleasure that θ vanishes from the scene: the result is going to be the same for all orientations of the magnet: this is it:

$$H = 2\pi p\nu/\mu_0 \qquad (7)$$

Making the substitutions that have already been describe, we get:

$$H = (I/\mu)h\nu \tag{8}$$

and this is none other than formula (5), the fundamental equation of magnetic resonance. The precession-frequency is the resonance-frequency.

This precession is often called the "Larmor precession," and the frequency given by (5) or (8) is called the "Larmor frequency." The name is a posthumous honor; Larmor died before magnetic resonance was discovered; his theory was applied to the Zeeman effect, the effect of magnetic fields upon optical spectra.

It is not hard to believe that when the applied frequency coincides with the Larmor frequency, something drastic must happen to the precession. The theory has been worked out on a classical basis. I will not pursue it into its details; but at least the first step should be taken.

I have said that the alternating field is perpendicular to the big field. We take the x-direction as its direction. The magnetic field, or magnetic vector as I will henceforth call it, has then $H_1 \cos 2\pi\omega t$ for its x-component (I use ω for the frequency so as to distinguish it from the Larmor frequency) and zero for its y-component. Now imagine a vector, of constant magnitude $(\frac{1}{2})H_1$, lying in the xy-plane, pointing away from the z-axis and revolving around this axis *clockwise* with frequency ω. Its x-component will be $(\frac{1}{2})H_1 \cos 2\pi\omega t$, its y-component will be $-(\frac{1}{2})H_1 \sin 2\pi\omega t$. Imagine another such vector revolving *counterclockwise*. Its x-component will be $(\frac{1}{2})H_1 \cos 2\pi\omega t$, its y-component will be $(\frac{1}{2})H_1 \sin 2\pi\omega t$. (It is evident that we have chosen their phases so as to bring about this result). The sum of these two vectors has $H_1 \cos 2\pi\omega t$ for its x-component and zero for its y-component. But this is the vector that we started out with. In the language of optics, we have resolved a plane-polarized wave into two circularly-polarized ones.

The foregoing is pure mathematics. Now comes the physics. Of these two revolving vectors, one is whirling in exact unison with the precessing magnet when ω is exactly equal to the Larmor frequency, the other is rushing round and round in the opposite direction. Our intuition tells us that the former may be expected to produce a great effect on the precession, the latter a small one. The latter is not always negligible, but may be neglected here. Thus in this artful way we have substituted a circularly-polarized field for the actual plane-polarized one.

The theory further leads to the prediction that when resonance exists, the precession will be exaggerated in such a way as to produce an alternating magnetic flux across the xz plane. Now I describe an actual experiment, the first of its type.

The sample is water (or something else) in a spherical container. Around the container are wrapped two coils at right angles to one another. The coil of which the axis is parallel to the x-axis produces the alternating field. The coil of which the axis is parallel to the y-axis is connected with a rectifier and a detector. At resonance there is an alternating magnetic flux through the latter coil, and by the operation of the rectifier this is converted into a signal on the scope. The signal locates the resonance-frequency as accurately as does the peak in the absorption-method. This is the phenomenon called "nuclear induction."

I terminate this section by mentioning a paradox resulting from precession. Everyone has seen a compass-needle turning to point to the north: it is natural to infer that when a magnetic field is applied to a piece of matter, the elementary magnetic particles of which the nuclei (and also the electrons) are examples will automatically turn to point along the field. Yet the analogy fails and the inference is false: the nuclei do not turn to point along the field, but each of them maintains a constant angle with the field while it precesses. It seems to follow that matter cannot be magnetized by a magnetic field, but again the inference is false. Animistically speaking, the field makes the nuclei want to turn into its direction, but they cannot fulfill their desire without assistance from something other than the field. This something-other is not absent, and in the section on "relaxation" we shall meet with it.

THE MOLECULAR-BEAM EXPERIMENT

There are three methods for detecting and locating nuclear magnetic resonance, and we have now considered two of them. In one of these, the resonating nucleus makes itself manifest by absorbing energy; in the other, that of nuclear induction, by radiating energy; in the one which is to come, by simply failing to turn up at the scene of the measurement. This singular attribute is that of the molecular-beam experiment, which (I repeat) was done before the others and so receives the credit of revealing nuclear magnetic resonance. Molecular-beam experiments are so remarkable that it is hard to speak of them without yielding to temptation to say more than is essential to the purpose, but here the temptation must be withstood.

Conceive a narrow stream of hydrogen-containing molecules coming along the (horizontal) axis of y, and cutting across a big magnetic field parallel to the (vertical) axis of z. This big field differs from that of

Fig. 1 in one important way: it is *non-uniform*, increasing in strength from (say) the bottom to the top. In one respect the protons behave just as they do in a sample in a uniform field: roughly half of them are pointing up and the other half pointing down. But in the non-uniform field the "up" protons experience a net force pushing them upward and the "down" protons a net force pushing them down. (Visualizing each of the protons as a tiny bar-magnet, one sees that the fieldstrength is bigger where the upper pole of the magnet is than where the lower pole is). The beam is parted into two diverging pencils, the one containing the "up" protons only and the other the "down" protons only; I call the first the "up" pencil and disregard the second.

The "up" pencil now passes through a region just like that implied in Fig. 1: a magnetic field which is big and vertical and *uniform*—H will stand for its strength—and an oscillating field with the magnetic vector parallel to the x-direction. If in this second region some of the protons are turned by the oscillating field into the "down" orientations, that will make no difference to their course across the remainder of the second region where H is uniform. But beyond the second region lies a third where again there is a big field that is non-uniform. In this third region the "up" protons go one way and the "down" protons go another. The detector lies athwart the first way; the "down" protons will miss it.

The detector-reading is plotted against H for a set value of ν. One might think that two curves would be plotted, one with the alternating field off and the other with it on, and that the latter would be systematically lower than the former. But the latter will be lower than the

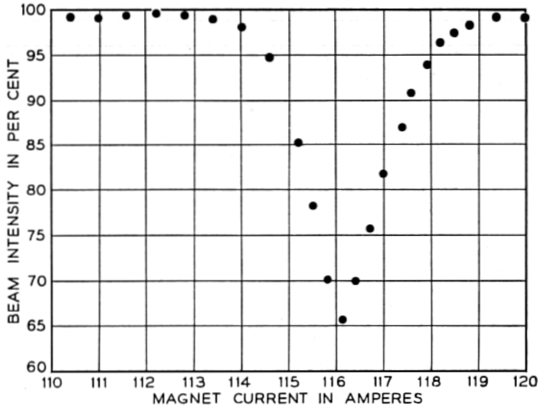

Fig. 6 — Negative peak or valley of nuclear resonance absorption obtained by the molecular-beam method. It pertains to lithium nuclei in lithium chloride molecules. This was the first experimental evidence of nuclear magnetic resonance. (I. I. Rabi, J. R. Zacharias, S. Millman and P. Kusch).

former only in the immediate vicinity of the value of H which conforms to equation (3); for the protons are turned over only when the Larmor frequency agrees very nearly with the applied frequency. Accordingly one keeps the alternating field on all the time and plots a single curve; and this is marked by a fine sharp peak, but this time a peak that points *downward*, Fig. 6, for it testifies to the absence of the overturned protons that have missed the detector.

The first experiment of this kind was done on molecules of lithium chloride. The reader may have been puzzled that I spoke of a beam of *molecules* and then of the deflection of *protons:* the protons, or whatever other magnetic nuclei are being studied, carry the molecules with them. In the experiments on LiCl, the peaks of lithium and of chlorine were found in different parts of the curve. Later the proton-resonance was discovered by using molecules of KOH and NaOH, and confirmed with molecules of H_2 and HD (the latter being a hydrogen molecule of which one nucleus is a proton and the other a deuteron). It is from this molecule of HD that the proton-resonance, and for that matter the deuteron-resonance also, stand out most clearly and sharply. In H_2 and in D_2 the resonances are perturbed and multiplied, but for reasons which are well understood so that the theory is strengthened instead of being weakened; but to describe these pretty things would be confusing unless they were explained, and to explain them would take us far afield.

SOME APPLICATIONS OF NUCLEAR MAGNETIC RESONANCE

The first of the uses of nuclear magnetic resonance is of interest mainly to the nuclear theorist. He wants to know (I/μ) for as many nuclei as possible; and this knowledge may be found by locating the resonance-peaks, and applying to their values of H and ν the equation (3) or (5) which I repeat:

$$H = (I/\mu)h\nu \tag{9}$$

Anyone who is going to burrow into the literature of this subject must be apprised beforehand, or else find out the hard way, that this simple statement is variously expressed. Here is a sad case of the ruination of a beautiful terminology by carelessness. The terms which have been ruined are "gyromagnetic ratio" and "magneto-mechanical ratio." The former ought to mean, as originally it did mean, the ratio of angular momentum to magnetic moment. The latter ought to mean the ratio of magnetic moment to angular momentum. Both have by now been used in both these senses, and there are variants within each sense, depending on the unit that is preferred by the user. The appearance of either "gyromagnetic ratio" or "magneto-mechanical ratio" in a paper is a red light warning the reader to make sure just what the author means by it. In this paper both of these terms are discarded with regret.

An experimenter may give his value of (μ/I) directly, or may give his value of g, which is (μ/I) expressed in terms of a peculiar unit. The peculiar unit is $eh/4\pi m_p c$, in which m_p stands for the rest-mass of the proton and the other symbols have their normal meanings. This unit got into the picture because there was a doctrine that (μ/I) for the proton ought to be just two of it. This was based on an analogy with the electron which, to the consternation of theorists and the complication of Nature, proved to be fallacious. Reported values of g range from nearly 6 to 0.143; the proton has one of the two highest values, the triton or nucleus of hydrogen 3 has the other. Since all these values may be described without much extravagance as being "of the order of 2," the use of g remains convenient.*

Many people say that they have measured μ. Formally this is all wrong, but practically it is usually all right, for in most if not all cases I is known from experiments of other kinds. Most of these people give the value of μ in "nuclear magnetons." This means that they are giving the value of gI, as is seen from the following equation which resumes in notation what I just said in words, and provides the definition of g:

$$\mu = gI(eh/4\pi m_p c) \tag{10}$$

The quantity in brackets is called "nuclear magneton."

Now that this tiresome but necessary passage is behind us, we can review the results.

Values of gI — or of some other of the quantities catalogued above — have been published for about forty nuclei. The values of gI available toward the end of 1950 were gathered together and published in an article to which I give the reference in a footnote.† The largest is about twenty-five times the smallest: this is a wide range of variation, yet not so wide as that of the nuclear charges or the nuclear masses. Isotopes of one another may have values nearly the same or considerably different; the same is true of isobars. Most of the values are positive: this

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* It is perhaps not premature to mention that in optical spectroscopy and in electronic magnetic resonance, the symbol g is used with a similar but not an identical meaning.

† Pake, G. E., American Journal of Physics, **18**, pp. 438–52, pp. 473–86, 1950. The table is on p. 440 of the October issue.

means that the angular momentum and the magnetic moment are parallel. A few are negative: for these (one of which is the neutron) the angular momentum and the magnetic moment are anti-parallel.

These values of μ (for, I repeat, gI is μ expressed in terms of a particular unit) are useful as challenges and as aids to the nuclear theorists. They are challenges, because the μ-value of a given nucleus is something to be explained; they may be aids, because a theory may be fortified by giving the right value of μ or confuted by leading to a wrong one. Now, nuclear theory is difficult, and by and large it is not so far advanced that it can demand experimental values accurate to let us say, the legendary "sixth place of decimals." This is a piece of temporary good fortune, for two reasons.

First, the strength of the big field H may not be known with adequate accuracy at the place where the nuclei are. It can however be ignored if one is concerned only to measure the ratio of the (μ/I) values of two nuclei. The experimenter has then to put into his apparatus successively samples containing the two kinds of nuclei, or a single sample containing them both: the ratio of the frequencies at which the resonance-peaks appear is the ratio of the (μ/I) values, and H vanishes in the division. Often the comparison-nucleus is the proton, so that many published values of gI come ultimately from ratios in which gI for the proton stands in the denominator. Such ratios are frequently adequate for the testing of theories, and their accuracies may be very good indeed, even attaining the sixth significant figure. (The basic determination of μ for the proton itself will be mentioned in Part II.)

Second, the true field which the nuclei experience may be slightly different from the big field H, because of local fields within the substance. This is of course an admission that our fundamental equation, (5) or (9) in this article, can be wrong. So it can be, and this is a development that may be thought distressing. But such developments are almost the rule in physics, whenever the art of measurement is bettered; and in the present case the errors in equation (9) must be regarded as felicitous, for they lead to some of the most fascinating applications of nuclear resonance.

Thus when ammonium nitrate, NH_4NO_3, is put into the apparatus, there are two peaks of nitrogen instead of one. They are not far apart — if for the frequency in use one is at $H = 10{,}000$ gauss the other is at 9,997. The formula NH_4NO_3 suggests, and the diagram of the molecule would confirm if we had it here, that the two nitrogen nuclei are differently placed in the molecule: one may say that they have different atomic surroundings. Thus the position of either of the peaks is distinctive not of nitrogen alone, but of nitrogen in its particular surroundings. These same surroundings might recur in several different types of molecule, or might be confined to one. The formula of ethyl alcohol may be written as $CH_3 \cdot CH_2 \cdot OH$. This compound presents three proton-peaks, Fig. 7, separated by a few per cent of one gauss when the big field is of the order of 10,000: they have been ascribed to protons in the three "groups" CH_3 and CH_2 and OH. To identify a group is to perform a process of chemical analysis, and this is a nascent application of nuclear magnetic resonance.

This is a good place to speak of the efficacy of nuclear resonance in revealing the presence of chemical elements or of individual isotopes. The proton is one of the easiest nuclei to discern in this way, largely owing to its relatively high magnetic moment. It has been calculated that $2 \cdot 10^{16}$ protons suffice to give a detectable "signal" by the induc-

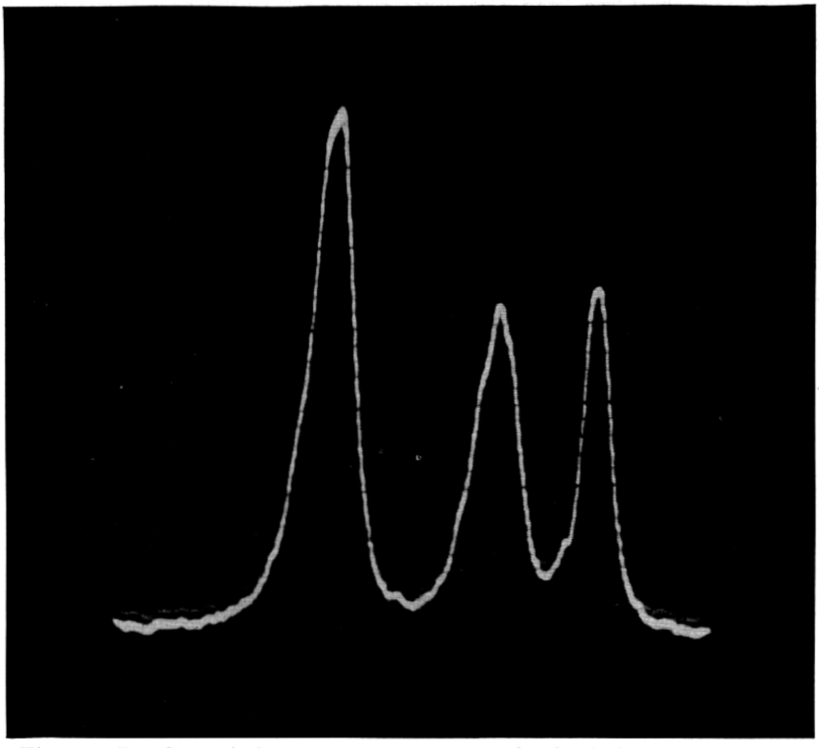

Fig. 7 — Breakup of the proton resonance peak of ethyl alcohol into three peaks, each believed to arise from protons in distinctive 'groups" within the molecule. (Courtesy of M. E. Packard).

tion-method; a small capsule of gaseous hydrogen at a pressure of only one atmosphere will show the resonance of protons. The second isotope of hydrogen is normally present in that substance in an abundance of only 1.5 parts in ten thousand, the second isotope of oxygen exists only in an abundance of four parts in ten thousand; neither was discovered for more than a decade after the search for isotopes was well under way; but both of them have been detected by nuclear resonance.

Another application is to crystallography. In the crystal called gypsum, each proton is exposed to a magnetic field of the order of ten gauss from its neighboring protons. The resonance-peak is split into two or three or even four, depending on the inclination of the big field to the crystal axes. It would take many pages to describe this effect in detail, but it is so intelligible that one may deduce from it the positions of the protons in the crystal lattice. Nuclear resonance in fact seemed called to play a great role in crystallography, since the principal tool of the crystallographer has been the diffraction of X-rays, and this will not disclose the presence nor *a fortiori* the locations of protons in a crystal lattice. However this promising child of resonance has apparently been throttled in its cradle, for the still newer art of neutron-diffraction has proved itself adequate for finding the protons in a lattice.

Another application is to the measurement of magnetic field strengths. One sees that if proton-resonance is produced at a measured frequency in a steady field of which the magnitude H is unknown, H may be determined by equation (3) with an accuracy contingent on the accuracy with which μ_p is known, and this is pretty high. This has become a common method of measuring magnetic field strengths.

RELAXATION

If anyone were asked to guess the most important use of nuclear magnetic resonance, he would have two good reasons for choosing the study of relaxation. More pages of the scientific journals have been devoted to it than to any other application. Moreover, the discoverers spoke of it almost as soon as they spoke of the discovery; one has the feeling that they were so confident of the discovery, that as soon as it was made they considered it much less important for its own sake than as a tool.

"Relaxation" is a word that entered long ago into physics. Its general meaning is the gradual self-adjustment of a system to a sudden change in conditions. In the immediate instance the system is our sample in the big magnetic field; the sudden change in conditions is the starting or the stopping of the oscillating field; and what gradually adjusts itself is the distribution of the protons between the up and the down orientations. Now I will describe an experiment such as has been performed on protons in water.

Let the sample be placed in the big field some time — several hours will always be ample — before the experiment is to begin. The experimenter should know in advance the frequency of the Larmor precession, so that he can apply the oscillating field of proper frequency as soon as he and the sample are ready. The sample then enters into what I will call "the state of resonance." The experimenter is to measure the height of the peak as soon as the oscillating field is switched on: I call this initial stature A_0. The big field and the alternating field are now *both* to be kept on. The height of the peak, A, is to be measured from time to time, say once every tenth of a second (this has been done with movie techniques). It is found that A is a declining function of time; the peak is shrinking.

After a while, let the alternating field be switched off while the big field continues to be on. The state of resonance is now suspended. Again the height of the peak is to be recorded every tenth of a second. Needless to say, the alternating field must be on while the record is being made, but it shall be off all of the rest of the time, which is most of the time. It will be found that the peak is growing again. It is, in fact, trending back to its initial stature A_0, and the law of its rise is the exponential law:

$$A = A_0 [1 - \exp(-t/T_1)]^* \tag{11}$$

The constant T_1, which this experiment determines, is called the "spin-lattice relaxation-time." "Lattice" will be recognized as a term appropriate to crystals: in the literature of this subject it is however applied to all solids and liquids. Its meaning in this field may be put as follows: the "lattice" is all of the sample except the nuclear spins.

The actual experiment is not usually done quite as I just described it. The alternating field does not have to be switched on or off, because if its frequency is far from the Larmor frequency it is practically ineffectual. If the observer wants to end the state of resonance, he displaces H or ν away from the resonance-value; if he wants to restore it he brings H or ν back to the resonance-value. By modulating the big field with say a 60-cycle frequency, he may pass the system briefly

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[*] This formula implies that $A = 0$ when $t = 0$; the reader can recast it to cover the general case in which $0 < A < A_0$ at $t = 0$.

through the state of resonance 60 times in a second; and it is possible to record and measure A on every such passage.

The fall and the rise of A are due to a cause so obvious that the reader has probably guessed it already. The peak, we recall, is a peak of absorption due to the turning of "up" protons into the "down" direction. When an up proton is turned into the down direction it goes out of business as an absorber, and continues out of business so long as it remains in the down direction. Since there is a fall and since there is a rise, the sojourn in the down direction must be neither zero nor infinite. If it were zero there would be no fall, and if it were infinite there would be no rise. The shrinkage of the peak in the presence of magnetic resonance, and the growth of the peak after resonance is discontinued, are signs that the sojourn of a proton in the down direction is finite but not zero. We divine already that T_1 is a measure of the average of this sojourn.

The foregoing may seem to imply that the height A of the peak is proportional to the number of up protons in the sample; but this is not so, and A is proportional to something else which I call the "margin." To present it I use N_u for the number of upward-pointing protons, N_d for the number of downward-pointing protons, N_0 for their constant sum, μ in the sense defined before, k for Boltzmann's constant; and I write down the fundamental theorem of Boltzmann:

$$N_u/N_d = \exp(2\mu H/kT) \tag{12}$$

The "margin" is $(N_u - N_d)$. We find:

$$\begin{aligned} N_u - N_d &= N_d\,[\exp(2\mu H/kT) - 1] \\ &= N_0\,(\mu H/kT) \text{ approximately} \end{aligned} \tag{13}$$

We have approximated by supposing μH to be very small compared with kT, which it is indeed; and by supposing N_u and N_d each to be nearly half of N_0—this second approximation is retroactively verified, for on substituting (for instance) 20,000 oersteds for H and room-temperature for T, one finds that out of two million protons selected at random a million plus seven are pointed up and a million minus seven are pointed down. The margin is thus 14 in two millions; but it may also be regarded as seven in two millions, since if seven protons out of two million should be turned down the margin would vanish and the peak would vanish with it.

Why is the stature of the peak proportional to the margin and not to N_u? The point is, that in addition to turning protons from the up direction to the down direction, the alternating field also helps protons to turn from the down to the up direction. Processes of the first kind involve absorption, as we already know; processes of the second kind involve release of energy. What the detector receives, and what the peak makes manifest, is the net of the absorptions over the releases. (This effect of the alternating field in helping protons from the down to the up direction is called "stimulated emission").

Now we must scrutinize equation (13) more closely. It is evident that T stands for an absolute temperature: the question is, what is it the temperature of?

One supposes perhaps that T is the temperature of the sample — that is to say, the temperature which would be shown by a thermometer stuck into the sample or possibly into a surrounding bath. And this is indeed what is supposed when the peak has the stature A_0, signifying that the sample has stood long enough in the big field undisturbed by resonance or anything else. When A is A_0 and T is the temperature of the sample, (13) is right. But when A is less than A_0 because the peak is falling, has fallen or is rising, we must choose between saying that (13) is not right, and saying that (13) defines a temperature which is to be called the temperature of the spinning nuclei, or the "spin temperature" for short.

The second choice is made; and this is the most vivid language in which to describe the situation. In this language we say that the resonance elevates the spin-temperature, or heats up the spins; and that after resonance ceases, the spins cool down to the temperature of the lattice. Thus the study of relaxation becomes the study of the heating and the cooling of the spins with respect to the lattice — "lattice" being defined, I recall, as everything in the sample except the spins.

Recorded values of T_1 range from times of the order of hours down to times of the order of ten-thousandths of a second. The highest are exhibited by protons in ice at extremely low temperatures; protons in water have $T_1 = 2.33$ seconds; the lowest values are found in the presence of "magnetic impurities." The typical dependence of T_1 on temperature is represented by a curve with a single minimum.

The importance of "magnetic impurities" derives from the agent of relaxation. Relaxation is operated normally by the varying magnetic fields whereby the nuclei act on one another; these vary, as I shall presently say more fully, because the nuclei are wiggling in thermal agitation. But the magnetic fields of nuclei are comparatively small, and therefore normal relaxation is comparatively slow. Much bigger is the magnetic field of an electron, for the magnetic moment of an electron is 660 times as great as that of a proton. Now, it is indeed true that all atoms and molecules contain electrons; and one may properly wonder why they do not always dominate the relaxation. The reason is that in most atoms and most molecules the electrons are paired "anti-parallel" so that their magnetic moments neutralize each other. (We are to see in Part II that this confines the electronic type of resonance to certain very specialized types of substances). One can however introduce into a substance, water for example, atoms or ions for which the neutralization is incomplete. These have much bigger magnetic moments and magnetic fields than any nucleus, and they speed up the spin-lattice relaxation. There is one special case which I treat in more detail, because of its relevance in this connection and its importance in solid-state physics.

There are crystals, of fluorite for instance, which occur colorless in Nature. These may be colored by exposing them to X-rays, or in other ways which we pass over here; and colored examples may also be found in Nature. Solid-state physicists have long been acquainted with these colorations, which they ascribe to what they call "F-centers." Various lines of reasoning have converged on the conclusion that an F-center is a cavity in the lattice (now I am using "lattice" in the normal sense, that of the crystallographers) in which a free electron is batting around like a wild animal in a cage. If this is so, then coloration of a colorless crystal by X-rays or otherwise should reduce its relaxation-time, and naturally-colored crystals should have lesser values of T_1 than those that are colorless. Experiment has ratified these inferences, and thus nuclear magnetic resonance has come to confirm the theory of the F-centres. So also has electronic resonance, since the F-centres display it with extreme clarity; but this is a topic for Part II.

The cause of relaxation has now been identified as the thermal agitation of the substance, working through the variation-in-time of the magnetic fields which act on every nucleus, weakly from its neighbor nuclei and strongly from any uncompensated electron that happens to be in the vicinity. In gases and liquids the nuclei cruise around, and so do the "magnetic impurities" if there are any; fieldstrengths change swiftly and relaxation tends to be rapid. In solids the atoms and their nuclei vibrate around fixed positions, and thermal agitation has come to be interpreted in the following way.

Nowadays one thinks of the solid sample as quivering with compressional waves, and perhaps torsional waves as well. These constitute the thermal agitation of the sample, and their various frequencies form its elastic spectrum. From this broad band of frequencies we isolate, in mind, the one which agrees with the frequency of the Larmor Precession. Think now of any two adjacent protons. The distance r between them will fluctuate in a complicated way as time goes on, but in this complicated motion we distinguish, again in mind, the component which has the frequency of the Larmor Precession. Well, according to earlier theory it is this component of the vibrations — be they interpreted as vibrations of the whole lattice or of two neighboring protons relative to each other — which helps the protons to turn from down to up, or for that matter from up to down. This is the channel by which energy passes to and fro between the lattice and the spins.

On submitting this idea to calculation it was found to give values of T_1 that are far too long. The next recourse was to take into account the "beat tones." Choose any frequency whatever in the elastic spectrum, and then another frequency differing from the first one by the frequency of the Larmor Precession. The sum of the two will present a beat frequency equal to that of the precession. This is a mathematical statement which seems as empty of physical meaning as — well, as seemed in its turn the assertion that the alternating magnetic vector H_1 directed along the x-axis is the sum of two circularly-polarized vectors. But the force between two neighboring protons is not linear (it is proportional to the inverse third-power of the distance r), and this gives physical meaning to the statement: the two frequencies conjointly act as if the beat-frequency were present. When these channels of communication between the spins and the lattice are added to the one first thought of, the calculated relaxation times come down into the order of magnitude of the real ones. More in the way of precise agreement can scarcely be hoped for, because of the effect of impurities on T_1.

Two other topics in the field of spin-lattice relaxation must at least be mentioned.

Some of the known values of T_1 are too low to be measured by observing the rise and fall of the resonance-peak. To indicate how these are measured, I recall that the energy of a wave-train is proportional to the square of its amplitude, H_1^2 in the present case. To speak of protons for simplicity: if T_1 were zero the number of protons in the "up" orientation would always be the same, and hence the height A of the peak would be proportional to H_1^2. But since T_1 is not zero the number of protons capable of absorbing goes down as H_1^2 goes up; and the curve of A against H_1^2 starts off tangent to the ideal straight line for $T_1 = 0$, but is concave-downward, drops away from the straight line and eventually will cease to rise.

We may pursue the argument one step farther. Here is the equation for the rate of change of N_u, the number of "up" protons:

$$dN_u/dt = (1/T_1)(N_{0u} - N_u) - bH_1^2N_u \tag{14}$$

Here N_{0u} stands for the number of "up" protons in the condition of equilibrium between the spin-temperature and the lattice-temperature. If we were dealing with the rise of the peak after the alternating field is shut off, the second term on the right would vanish, and we should be back at equation (11). We are however dealing here with the fall of the peak when the alternating field is on. One sees that eventually N_u will reach a constant value — it is said to "saturate" — and the peak a constant stature. If this saturation-value is measured and the value of b is known, T_1 can be computed. The saturation-value is measured, and b is determined from quantum mechanics.

Though I have tried to avoid giving the impression that the stature of the peak necessarily has its equilibrium-value A_0 before the oscillating field is first applied, I may not have quite succeeded. It would be a miracle if A were equal to A_0 at the moment when the sample is first put into the big field. Time must be allowed for the nuclei to adjust themselves or "relax" to the big field: it was because of this that I said at the beginning that the sample was to be placed in the big field several hours (a generous allowance of time, by the way) before the application of the alternating field. One would expect in general to find A much smaller than A_0, when the sample has just been exposed to the big field; on the other hand it could be greater than A_0 if the sample had previously been exposed to a field of greater strength than the field of the experiment.

Conceivably one might miss the peak altogether by looking for it too soon, if the relaxation-time were long; or by looking for it too late, after it had been reduced to its "saturation" stature. It may be that early attempts to find magnetic resonance were frustrated in these ways. Such dangers are now avoided by mixing the sample deliberately with magnetic impurities in order to diminish the value of T_1 : the peak of Figure 2 was obtained with water mixed with ferric nitrate. There is some reason also to conjecture that nuclear magnetic resonance might have been sought and found some years earlier than it was, but for an imperfect theory which indicated that the spin-lattice relaxation-time would be so long as to make it hopeless to look for the peak.

Students of the literature will find many allusions to another type of relaxation — the "spin-spin" relaxation, with a relaxation-time denoted by T_2. Except for the bare statement that the breadth of the peak varies inversely as the spin-spin relaxation-time, this topic must be left for some other occasion. It may be mentioned here, even though not explained, that the line-breadth diminishes suddenly when the substance melts, and may also decline at one or more temperatures where the substance is still a solid. Such temperatures are considered to be those at which some special type of molecular motion begins.

References and acknowledgements are to be appended to the second part of this article. Two names will however be mentioned in this place, those of Felix Bloch and Edward M. Purcell; for these are the names of the physicists to whom, on November 6, 1952, was awarded the Nobel Prize for the discovery of nuclear magnetic resonance by the techniques here respectively denoted as those of "nuclear induction" and "nuclear resonance absorption."