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Research in nuclear magnetism

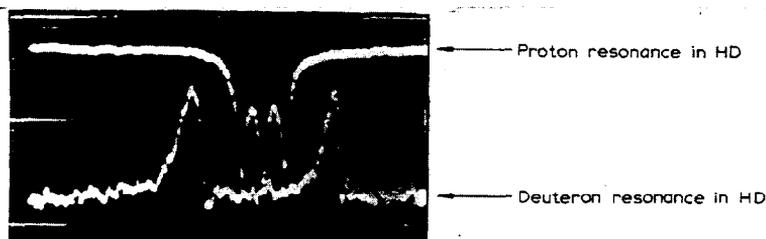
Nobel Lecture, December 11, 1952

Professor Bloch has told you how one can detect the precession of the magnetic nuclei in a drop of water. Commonplace as such experiments have become in our laboratories, I have not yet lost a feeling of wonder, and of delight, that this delicate motion should reside in all the ordinary things around us, revealing itself only to him who looks for it. I remember, in the winter of our first experiments, just seven years ago, looking on snow with new eyes. There the snow lay around my doorstep - great heaps of protons quietly precessing in the earth's magnetic field. To see the world for a moment as something rich and strange is the private reward of many a discovery. But I am afraid it has little bearing on the sober question we must, as physicists, ask ourselves: What can we learn from all this about the structure of matter? It is my privilege to tell you now of some of the things that can be learned.

Let us begin with the most direct application of nuclear induction methods, the measurement of nuclear magnetic moments. The basis for this is the resonance condition

$$f = \frac{\mu H_0}{Ih}$$

in which f is the frequency of precession of the axis of nuclear spin in a magnetic field of strength H_0 , and μ is the magnetic moment of the nucleus. The number I is the nuclear spin quantum number, an integer or half-integer, and h is Planck's constant. Now H_0 , except for a certain slight correction, is simply the field of the magnet in which the substance has been put, and it can be measured. The frequency of precession, once it is detected, is easily measured with high accuracy, and thus one can determine the quantity μ/Ih . However, for practical reasons, it is hard to measure the strength of a magnetic field very precisely. This difficulty is avoided if one is content to measure the *ratio* of the magnetic moments for two different nuclear species. We could, for example, compare the precession frequencies f_H and f_D for protons and deuterons exposed to the *same* magnetic field H_0 . A mixture of light



$$\frac{\mu(^2\text{H})}{\mu(^1\text{H})} = 0.307012189 \pm 30$$

Fig. 1. Simultaneous display of deuteron and proton resonances in HD. The proton trace is inverted. (T. F. Wimett, *Massachusetts Institute of Technology.*)

and heavy water, H_2O and D_2O , might serve as our sample. Then $f_{\text{D}}/f_{\text{H}}$ is the ratio of the magnetic moment of the deuteron to that of the proton, apart from the simple factor $I_{\text{D}}/I_{\text{H}}$, which is the ratio of the spins, in this case 2. In this way the magnetic moments of many different nuclei have been measured, relative to the moment of the proton, with great precision.

To show what accuracy can be achieved, let me describe one example, a very recent experiment by T. F. Wimett in the laboratory of Professor Bitter of the Massachusetts Institute of Technology. The ratio of the deuteron moment to the proton moment had been carefully determined before by Anderson and Smaller at Chicago, and by K. Siegbahn and Lindström here at the Nobel Institute. Wimett has now refined this measurement still further using as his sample the gas HD. This substance has a certain advantage: the two different nuclei are not only in the same vessel, but in the same molecule, so there is no doubt that the magnetic field at each is the same. Fig. 1 shows simultaneous traces of the proton resonance and the deuteron resonance in a field of about 15,000 gauss. You will notice at once that the resonances are not simple. The proton resonance is a triplet line, almost fully resolved, while the deuteron resonance is a cleanly resolved doublet. This has an interesting explanation, to which I shall return near the end of my lecture, but it has no direct bearing on this experiment except to emphasize the extraordinary resolution. The separation of the deuteron doublet is only 0.07 gauss, 1 part in 200,000 of the applied field. By carefully lining up the central proton peak with each deuteron peak, in turn, a measurement reliable to about 1 part in 10 million can be made. The determination of the exact frequency ratio is accomplished by an elaborate scheme of harmonic mul-

tiplication. Wimett's result, which he kindly gave to me just a few days before I left Cambridge, is

$$\frac{\mu(\text{D})}{\mu(\text{H})} = 0.307012189 \pm 0.000000030$$

Table 1. Magnetic moments of the neutron (n), deuteron (^2H), triton (^3H), and ^3He , relative to the moment of the proton (^1H).

$\frac{\mu(\text{n})}{\mu(^1\text{H})} = -0.685001 \pm 3$	$\frac{\mu(^2\text{H})}{\mu(^1\text{H})} = 0.30701225 \pm 10$
$\frac{\mu(^3\text{H})}{\mu(^1\text{H})} = 1.066636 \pm 10$	$\frac{\mu(^3\text{He})}{\mu(^1\text{H})} = -0.7618150 \pm 12$

The results of four earlier experiments of this sort are listed in Table 1. Of course the neutron experiment is a very special one, and Professor Bloch has already described his elegant method for detecting the neutron precession frequency. The other values were obtained by various investigators¹ in the way I have just indicated. These numbers provide a very stringent test of any theory of nuclear structure. A wholly satisfactory theory ought to be able to predict them. As you know, we are very far from having such a theory now. But even so, the high accuracy is not all wasted. The moment of the deuteron is not *quite* equal to the sum of the moments of its separate parts, the neutron and proton. Thanks to the extreme precision of the experimental values, this small but significant discrepancy is itself fixed quite accurately.

As we leave the simplest nuclei and proceed through the Periodic Table, the situation changes a little. The experimental precision is just as high, but one must apply to the measured frequency ratios a small correction to take account of the magnetic shielding effect of the atomic electrons. This correction increases rapidly with atomic number. Until better atomic wave functions are available, it cannot be calculated reliably enough to support the six figure accuracy of the resonance measurement. There is one important exception. For two isotopes of the same element, the correction cancels out. Accurate moment ratios for isotopic pairs are of considerable interest, especially if the hyperfine structure interval for the two isotopes can be determined. A. Bohr and Weisskopf² have shown that such a comparison can reveal something about the internal structure of the nucleus.

Perhaps the greatest present need, through most of the Periodic Table, is for spin values and only moderately precise moment values, to help test the promising shell theories of nuclear structure. Nuclear induction methods will surely continue to contribute to this task. Spin determinations in particular, which depend on careful intensity measurements, are likely to receive more attention.

The experimental physicist often needs to measure the intensity of a magnetic field. Until recently a precise magnetic field measurement has been a formidable undertaking, but it is such no longer. At the National Bureau of Standards in Washington, Hipple and his collaborators³ have measured the proton precession frequency and, at the same time, have measured in absolute units the intensity of their magnetic field. All the resources of the Bureau were brought to bear on the latter measurement, and an accuracy of 1 part in 40,000 was achieved. Knowing their result, an experimenter anywhere in the world can determine absolute magnetic intensities to the same precision, using equipment no more elaborate than an ordinary radio receiver. He need only determine the proton precession frequency in the field in question. Few physical quantities are as easy to measure accurately as a radio frequency, thanks to modern electronic techniques and the availability, in most countries, of standard-frequency broadcasts.

Already a number of experiments have been performed in which the nuclear resonance has served as a standard of reference. Certain ones are of special interest because they have improved our knowledge of the fundamental atomic constants. In each of these experiments two *different* magnetic resonance phenomena have been observed at the same time in the same magnet. The phenomena involved are indicated in Fig. 2. The precession of the proton moment (Fig. 2 a) we have already described; it is detected and measured in a nuclear induction experiment. The electron has an intrinsic spin and magnetic moment and also precesses in a magnetic field (Fig. 2 b). For the same field strength, the electron's spin-precession frequency is about 700 times greater than the proton precession frequency. A bare proton, moving in a magnetic field, revolves in a circular orbit with a certain frequency (Fig. 2 c). This is the familiar principle of the cyclotron and we might name the associated frequency the « proton cyclotron frequency ». A free electron in a magnetic field likewise revolves in a circular orbit, with a frequency that we may call the « electron cyclotron frequency ». These « cyclotron frequencies » are governed simply by the particle's charge-to-mass ratio. If any pair of these resonance phenomena are compared, in the same magnetic field,

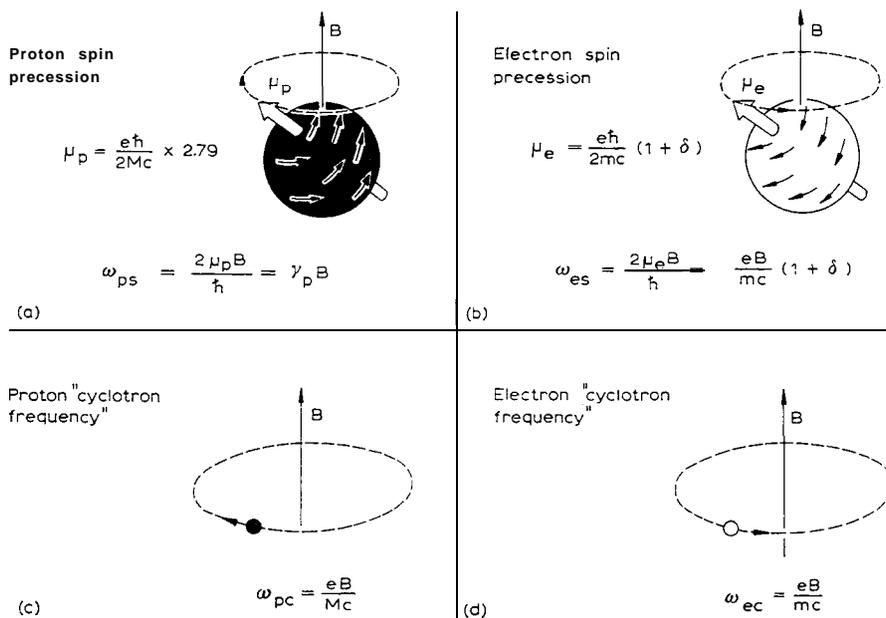


Fig. 2. Four elementary magnetic resonance phenomena.

the field strength cancels out and we are left with a relation between certain atomic constants. The experiment is thus reduced to the measurement of a frequency *ratio*.

The ratio of the proton spin-precession frequency to the proton cyclotron frequency has been determined by Hipple⁴, and by Bloch⁵, in ways very different but equally ingenious. (The direct result of this measurement is the value of the proton moment in nuclear magnetons.) In my laboratory we have measured the ratio of the proton precession frequency to the cyclotron frequency of free electrons⁶. The precession of the spin of a truly free electron has not been observed, but Kusch and his collaborators at Columbia, by combining the techniques of atomic beams and nuclear induction, have determined very precisely the ratio of the proton's precession frequency to that of the spinning electron in the hydrogen atom⁷. The results of these experiments have in one way or another improved the accuracy of the following constants of atomic physics: the Faraday, F ; the specific charge of the electron, e/mc ; the ratio of the mass of the proton to that of the electron, M/m ; the dimensionless *fine-structure constant*, $2\pi e^2/\hbar c$. They have also helped to test the new theoretical advances in quantum electrodynamics led by Schwinger.

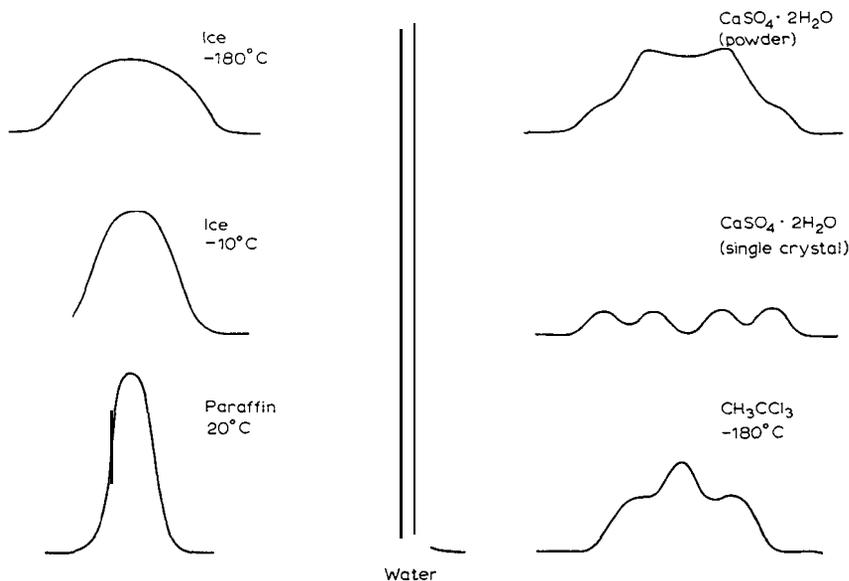


Fig. 3. Line shapes typical of the proton resonance in various substances. The line in water is not drawn to scale; it is actually much narrower and more intense than indicated.

We turn now to a very different subject, one whose rapid growth was surely not anticipated at the beginning of this work. That is the study of nuclear magnetism for the light it can throw on problems of molecular structure and molecular motion, problems rather close to physical chemistry. Indeed certain branches of this work are now being pursued in chemical laboratories. We are interested not in the mere occurrence of nuclear resonance at a particular frequency but in its finer details. The variety that we find is suggested by Fig. 3. Here are shown several line shapes typical of the proton magnetic resonance in a few simple substances. One way to record such a spectrum is to hold the applied magnetic field constant while slowly varying the frequency of observation. In every case the center of the resonance absorption occurs at very nearly the same frequency, in these substances. The line width, on the other hand, varies from some 50 kilocycles/second, in the case of ice at low temperature, to less than a few cycles/second, in the case of a liquid like water. (The true width of the resonance in water is too small to be shown properly in the diagram.)

The effects shown here can all be traced to the action of the nuclear magnets on one another. In ice, each hydrogen nucleus is subjected not only to the field of our magnet, which might be several thousand gauss, but to the

small magnetic field caused by each nearby proton in the crystal. Each nearest neighbor produces a field of a few gauss, more or less random in direction, with the result that the resonance absorption for the crystal as a whole is spread out over a corresponding interval in frequency. These « local magnetic fields » are present in water, too, but their effectiveness is destroyed by the rapid molecular diffusion characteristic of a liquid. Two adjoining molecules remain neighbors so short a time (about 10^{-10} seconds) that their mutual influence is very slight. Thus *molecular motion* is the key to the striking difference between crystals and fluids in respect to the width of the nuclear magnetic resonance.

In many crystals, atoms or molecules occasionally jump from one position to another. Although such events are rare by most standards, they may occur frequently enough to affect the width of the nuclear resonance line. In ice, for instance, the line is distinctly narrower at -10°C than at a much lower temperature. The narrowing indicates that each hydrogen atom undergoes a displacement within the crystal lattice several thousand times per second. The motion involved here is not the familiar thermal vibration of an atom in a perfectly elastic crystal, but an abrupt shift to a new site. Nuclear resonance studies have disclosed many unsuspected internal motions in crystals, and have helped to reveal the exact nature of motions already suggested by other physical or chemical evidence⁸.

If the magnetic nuclei in a crystal are clustered together in pairs, the action of the nuclear magnets on each other causes a doubling of the magnetic resonance line. Further distortion is caused by more remote neighbors, and the width of the pattern as a whole depends on the orientation of the nuclear pair with respect to the magnetic field. Rather complicated effects are possible, some of which are illustrated in Fig. 3. From a complicated effect that is also well understood, one can usually get a good deal of information. These magnetic interactions are now rather well understood. I shall mention only one recent application of the technique to a chemical problem.

Groups of three equidistant protons in randomly oriented crystals give, characteristically, a line with three humps. The methyl chloroform line, in Fig. 3, is an example. We have a complete quantitative theory of this line structure⁹. Last year Richards and Smith¹⁰ at Oxford, and quite independently Kakiuchi and others¹¹ in Tokyo, studied the proton resonance in perchloric acid monohydrate ($\text{HClO}_4 \cdot \text{H}_2\text{O}$) and certain related substances. This type of line was found. They were able to prove thereby that in those crystals the « hydronium » ion, OH^+ , exists, and to determine its dimensions.

It is well known that hydrogen atoms are very hard to locate by X-ray diffraction. Here is an opportunity for nuclear resonance studies to supplement, in special cases, the more general methods of structure analysis.

Many nuclei have, in addition to an intrinsic magnetic dipole moment, an *electric quadrupole moment*. This is a way of saying that the electric charge of the nucleus is not distributed evenly over a sphere. One may think of the nucleus as either an elongated or a flattened ellipsoid. If such a nucleus is put into a non-uniform electric field, it experiences a torque, and precesses. (You will recall that the slow precession of the earth's axis is a consequence of the ellipticity of the earth and the non-uniform gravitational fields of the moon and sun.) The nuclei in many crystals find themselves in non-uniform electric fields arising from their immediate atomic surroundings. A nuclear electric quadrupole moment then manifests itself in a splitting of the magnetic resonance line. To put it another way, the energy associated with each of the possible orientations of the nuclear spin in a magnetic field is somewhat altered by the electric effect. This is illustrated in Fig. 4. The trace in Fig. 4 is the nuclear resonance spectrum of ^{23}Na in a crystal of sodium nitrate. The line is widely split into a triplet by the quadrupole interaction. The number of components is always twice the nuclear spin I , so we have here a way of determining nuclear spins. This example is due to R. V. Pound who was the first to investigate these effects in crystals¹².

Another interesting and fruitful branch of nuclear magnetism is the study of nuclear relaxation, by which I shall mean here the attainment of thermal equilibrium between the nuclear spins and their environment. Professor Bloch has already referred to the crucial importance of relaxation in all these experiments. In the first experiment of Torrey, Pound, and myself this question gave us much concern. Our approach was somewhat different from Bloch's and was based on a theoretical paper of fundamental importance by Professor Waller¹³. Waller, in 1932, was dealing with relaxation in electronic paramagnetism, but Torrey was able to adapt his results to our case, with the conclusion that equilibrium should certainly be reached within several hours. We then designed the experiment so that, even if so long a time were required, the resonance could still be detected. As it turned out, the precaution was unnecessary, but that was our introduction to a fascinating problem that has occupied our attention ever since.

I believe we now have a good understanding of nuclear relaxation in many - though not all - physical systems. Experimentally, we find that the time to establish thermal equilibrium ranges widely from hours, in some substances,

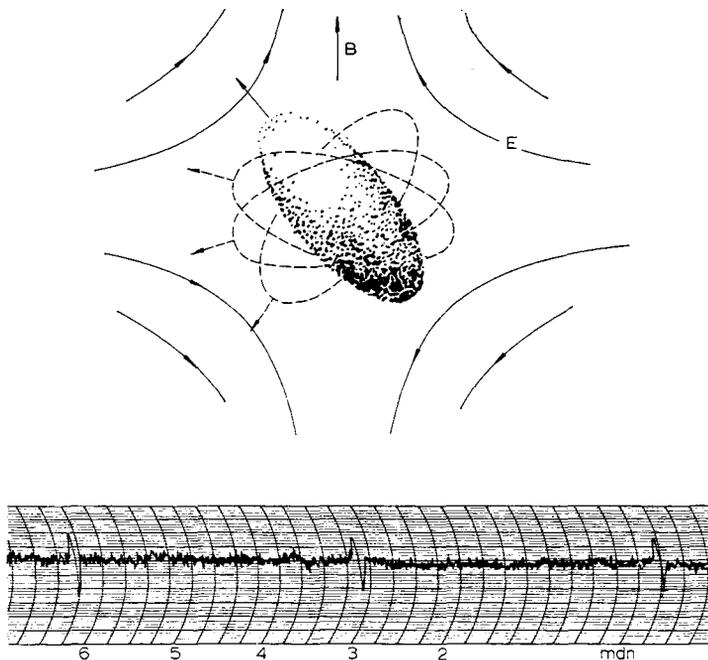


Fig. 4. A nucleus with an electric quadrupole moment in a uniform magnetic field (B) and a non-uniform electric field (E). Lower trace: ^{23}Na resonance in a single crystal of NaNO_3 , showing splitting of magnetic resonance line into a triplet.

down to fractions of a millisecond in others. I show only one example, and that mainly to clarify the meaning of the term relaxation. Fig. 5 is a plot of the gradual approach to equilibrium magnetization of an originally unmagnetized crystal of ammonium bromide. This can be called, quite properly, a *cooling curve*. The nuclear spins, in order to align themselves with the magnetic field, must give off energy to the crystal lattice. They are coupled so weakly to the lattice that the transfer of energy takes more than several minutes. Actually the approach to equilibrium is exponential, and the corresponding time constant, in this example 32 seconds, is what one calls the spin-lattice relaxation time.

It may seem astonishing, at first, that so long a time is associated with an atomic process. But in fact, if one looks at the problem more closely, it is hard to understand why the time is not much *longer*. Moreover this crystal, at a somewhat higher temperature, has a relaxation time of only 0.01 seconds! The explanation of this, and of similar behavior in a wide class of substances, lies in internal molecular motions other than mere vibration. It is

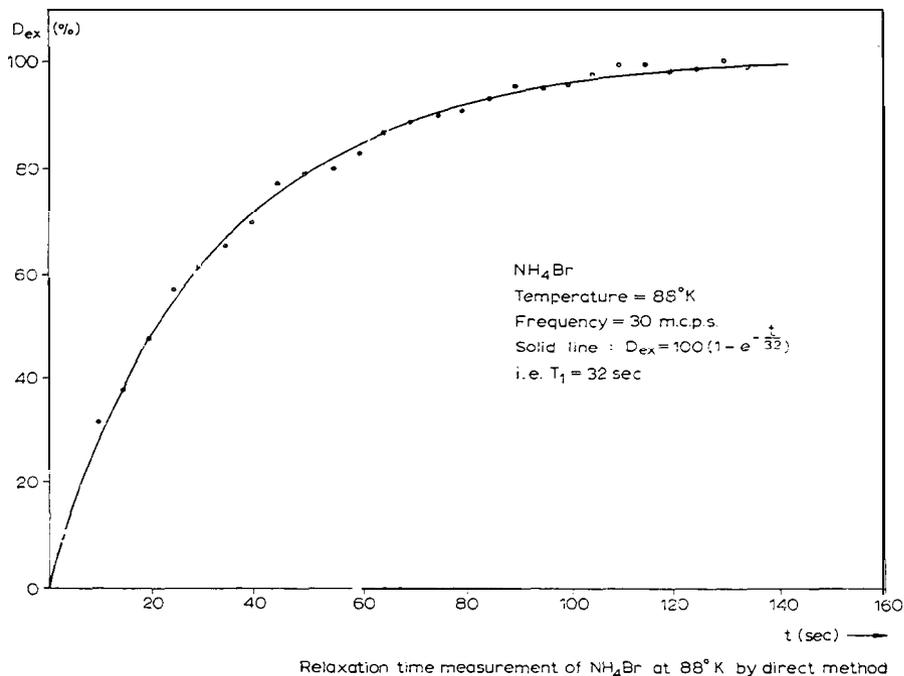


Fig. 5. The gradual approach to equilibrium magnetization. The ordinate is proportional to the intensity of nuclear polarization.

closely connected with the cause of line-narrowing, mentioned earlier. The particular motion occurring in the ammonium halides is a sudden rotation of the whole tetrahedral ammonium ion inside the cubic unit cell.

We have now a fairly general theory of nuclear relaxation¹⁴, a theory that has proved reliable enough to allow one to draw conclusions about the nature of the internal motion in a substance from the observed nuclear relaxation. My early collaborator, N. Bloembergen, has made essential contributions to this subject. Experimental work at Oxford and at Leiden has added much to our knowledge of other aspects of nuclear relaxation. In many respects this is only a new branch of a somewhat older subject, paramagnetic relaxation, in the study of which the Dutch laboratories, and especially Professor Gorter, have long led. The problem of nuclear relaxation has a special attraction for the low-temperature physicist, because, as Professor Simon pointed out many years ago, nuclear magnetization offers a way toward extremely low temperatures, providing the nuclear spins can exchange heat with something else.

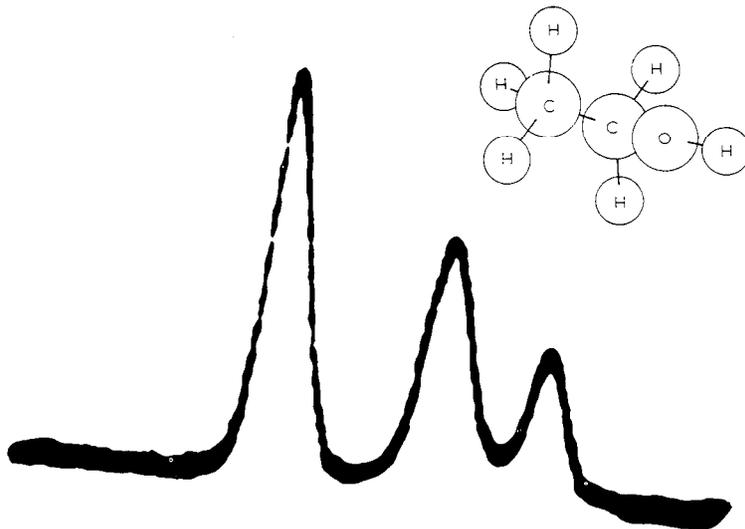


Fig. 6. The proton resonance in ethyl alcohol, observed with high resolution. The three lines arise from the CH₃ hydrogens, from the CH₂ hydrogens, and from the OH hydrogen, respectively.

There remain several puzzling aspects of nuclear relaxation. In trying to understand them we find ourselves still returning to some of the ideas advanced twenty years ago by Professor Waller. While I speak of theoretical contributions to nuclear magnetism, I must mention also Professor Van Vleck, who has put the theory of line-width on a rigorous basis, a notable advance.¹⁵

It is an old story in physics that higher resolving power leads to new effects. We remember that the magnetic moment of the nucleus was itself discovered through the hyperfine structure of lines in the visible spectrum. The nuclear resonance line in a liquid or gas can be remarkably narrow, as you have already seen. As soon as the reason for this was recognized, it became clear that the only practical limit on resolution was the inhomogeneity of the magnetic field applied to the specimen. Efforts were made in many laboratories to improve the magnets, and to use smaller specimens as well. With the improved resolution, it was found that identical nuclei, in the same applied field but in chemically different molecules, do not precess at exactly the same frequency. The explanation is simple: the magnetic field at an atomic nucleus differs slightly from the field externally applied because of the shielding effect of the electron cloud around the nucleus. In different molecules the atom's electron configuration will differ slightly, reflecting differences in

the chemical bond. The resulting resonance shifts have been called « chemical shifts ». They are only a nuisance to the experimenter interested in exact ratios of magnetic moments. But they are interesting to the physical chemist because they reveal something about the electrons that partake in the chemical bond.

Nolaboratory has more assiduously pursued high resolution than Professor Bloch's, where the striking example shown in Fig. 6 was discovered¹⁶. This is the proton resonance in ethyl alcohol, seen under very high resolution. Each lines comes from a chemically equivalent group of protons in the molecule, the intensity being proportional to the number of hydrogen atoms involved, 3 (methyl group), 2 (CH₂ group), and 1 (hydroxyl), respectively.

I can now return to the splitting observed in the proton and deuteron resonances in Fig. 1. This splitting does not arise from any effect on the applied field, but from an indirect coupling of the proton to the deuteron through the medium of the two electrons in the HD molecule. It is as much an intrinsic property of the HD molecule as is the optical spectrum of the molecule¹⁷. The splitting amounts to 43 cycles per second. I am sure we have only begun to explore the domain of very weak interactions - the « audio spectrum » of molecules, if I may call it that.

This has been a long story and a complicated one. We are dealing not merely with a new tool but with a new subject, a subject I have called simply nuclear magnetism. If you will think of the history of ordinary magnetism - the electronic kind - you will remember that it has been rich in difficult and provocative problems, and full of surprises. Nuclear magnetism, so far as we have gone, is like that too.

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