PHYSICAL REVIEW VOLUME 81, NUMBER 5 MARCH 1, 1951

The Time Average Magnetic Field at the Nucleus in Nuclear Magnetic Resonance Experiments*†

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(Received September 13, 1950)

For the high precision measurement of a nuclear gyromagnetic ratio by the Purcell or Bloch resonance methods, accurate knowledge of the time average magnetic field H_{Av} at the positions of the nuclei is necessary. The various component fields contributing to H_{Av} are listed. An experimental study is made of two of these fields: the magnetic shielding field in molecules and the magnetization field of paramagnetic ions added to a sample. In an earlier paper accurate computed values were given of the magnetic shielding field for free atoms and monatomic ions. The effect of these fields on the attainable precision in the measurement of nuclear moments is discussed.

I. INTRODUCTION

In a nuclear magnetic resonance experiment, using the Purcell technique of resonance absorption[1,2] or the Bloch technique of nuclear induction,[3–5] the nuclei are not isolated but are contained in atoms, ions, or molecules. These in turn contribute to the composition of a macroscopic sample of matter which is used in the experiment. It should be expected, therefore, that the effective (i.e., time average), magnetic field to which the resonating nuclei are exposed will not be exactly the same as the externally applied field, since the latter field will induce certain small internal fields in the sample. The purpose of the present paper is to investigate the magnitude and characteristics of these internal fields under various experimental conditions.

For nuclei with gyromagnetic ratio $\gamma=\mu/I\hbar$, the resonance condition may be written

$$\omega_{\text{res}}=\gamma H_{Av}, \tag{1}$$

where H_{Av} is the time average value of the magnetic field at the position of one of the nuclei, the average to be taken over a long time interval,[6] and ω_{res} is the corresponding angular Larmor frequency and hence the radiofrequency which must be applied to induce the maximum resonance absorption in the sample. Since magnetic fields are difficult to measure with high precision, it is customary to measure the ratio of two nuclear magnetic moments (we assume the spins are known), by comparison of their Larmor frequencies in the "same" magnetic field. If this condition could actually be satisfied, we would have, for two nuclear species A and B,

$$\mu_A/\mu_B=(I_A/I_B)(\omega_{\text{res}A}/\omega_{\text{res}B}). \tag{2}$$

It is, presently, possible to measure a frequency ratio in the radiofrequency region with a precision of 1 part in 10^6 or better, and resonance line widths in liquids have been reported as small as 1 part in 10^5 of the applied magnetic field. Estimating conservatively that the center of a resonance line can be determined to within 10 percent of the line width, we see that the present attainable precision inherent in the measurement of a nuclear moment ratio by the Purcell or Bloch techniques is of the order of 1 part in 10^6. However, evidence is presented in this paper to show that even though both nuclear species are exposed to the same external field H_0, the field H_{Av} at the two may be significantly different. Hence, to utilize this high precision, accurate knowledge of the internal fields contributing to H_{Av} is of prime necessity.

It will be assumed that the electronic state of the atom, ion, or molecule which contains the resonating nucleus is characterized by zero permanent magnetic moment. If this were not the case, the field acting at the nucleus due to such a moment would generally be considerably stronger than the applied field, so that the above nuclear resonance phenomenon would be obliterated completely. Also, we will not be concerned with fluctuating fields at the nucleus having a time average, of zero, since such fields do not affect the resonance condition, Eq. (1). For example, there is the so-called local field H_{loc} defined by Bloembergen, Purcell, and Pound[2] (hereafter referred to as BPP), as being the instantaneous sum of the dipole fields at one nucleus due to all its neighbors. Although the local field can have a magnitude of several gauss, it generally fluctuates in a random manner with almost zero average, since nuclear magnetization is small. It is further found

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* From a thesis submitted in partial fulfillment of the requirements for the degree of Ph.D. in Physics at the Massachusetts Institute of Technology. A preliminary report of these findings was presented at the meeting of the American Physical Society, New York, February 2, 1950; [Phys. Rev. 78, 339 (1950)].

† This work has been supported in part by the Signal Corps, Air Materiel Command, and ONR.

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[1] Purcell, Torrey, and Pound, Phys. Rev. 69, 37 (1946).

[2] Bloembergen, Purcell, and Pound, Phys. Rev. 73, 679 (1948). This reference is referred to in the text as BPP.

[3] Bloch, Hansen, and Packard, Phys. Rev. 69, 127 (1946).

[4] F. Bloch, Phys. Rev. 70, 460 (1946).

[5] Bloch, Hansen, and Packard, Phys. Rev. 70, 474 (1946).

[6] By a long time interval is meant a time longer than molecular configuration times in the sample. The definition of H_{Av} as the time average field at one nucleus is valid only if the applied magnetic field is perfectly homogeneous over the sample volume and all nuclei experience the same structural surroundings. If either of these conditions is not met, H_{Av} would be defined as the weighted mean of the time average fields for all the nuclei.

that in most liquids it fluctuates at a rate much higher than the nuclear Larmor frequency. It is for this reason that the natural line width of a resonance in a liquid is so extremely small, the observed width being usually determined solely by the inhomogeneity of the applied magnetic field over the sample volume.[7] On the other hand, in the case of solid substances where the structures are rigid in the sense that molecular configuration times are considerably longer than the nuclear precession time, the local field will result in a broadening of the resonance line by, perhaps, several orders of magnitude. Indeed, in some cases a statistical analysis shows that the local field may give rise to a fine structure in the broad resonance line. Such a fine structure has been observed in certain single crystals and crystalline powders[8, 9] and, surprisingly, it has recently been observed in a liquid.[10] It should be stressed, however, that the center of symmetry of a resonance line possessing this type of fine structure will be at the same position at which a single resonance line would occur for the same nucleus.[11] The analysis indicates that there is a higher statistical weighting around certain values of H_{loc}; the average of H_{loc} over all the nuclei in the sample is zero.

II. THE FIELDS CONTRIBUTING TO H_{Av}

For a liquid, the time average field at the nucleus may be divided into three significant components

$$H_{\text{Av}}=H_0+H'+H''. \tag{3}$$

(1). H_0 is the external or magnet field and is, of course, the chief component of the field H_{Av}. In the majority of past nuclear moment ratio measurements, separate samples have been used, placed side by side in the magnet field. Often elaborate precautions have been taken to insure that the field H_0 is the same at both samples, but, in any event, this method is undesirable in that an additional source of error is introduced. To insure that both nuclear species see the same space average field H_0, it is desirable to use a single sample containing both types of nuclei. Also, in this way, any asymmetry in resonance line shape due to nonuniformity in H_0 over the sample volume will be duplicated; hence, in determining line centers no error is introduced by this factor. Descriptions of the single-sample technique as applied to the Bloch and Purcell type of experiments have been given in the literature.[12, 13]

(2). H' is the magnetic shielding field at the nucleus due to the induced motions of the electrons of the atom or molecule containing the nucleus.

For an atom or monatomic ion, in which case Larmor's theorem is valid, this field is given by[14]

$$H'=\frac{eH_0}{3mc^2}\int_0^\infty\frac{\rho(r)dr}{r}=\frac{eH_0}{3mc^2}v(0), \tag{4}$$

where $\rho(r)$ is the radial charge density of the electrons at a distance r from the nucleus, and $v(0)$ is the electrostatic potential produced at the nucleus by the atomic electrons. In a previous paper[15] the author has given computed values of $v(0)$ for all atoms and singly-charged ions which have been treated by the Hartree or Hartree-Fock self-consistent field method. By interpolation and the use of Eq. (4), H'/H_0 values for all neutral atoms are given. It is estimated from experimental evidence as to the accuracy of the self-consistent field method that these values can be trusted to within 5 percent except for the heaviest atoms, where the relativity effect becomes important.

In diatomic and polyatomic molecules and ions there is an additional component of the magnetic shielding field which is attributed to a second-order paramagnetism. The existence of this component was only recently reported by various observers,[16–18] although some months before the experimental discovery it was suggested to the author by Professor F. Bitter that a second-order paramagnetic field should exist at the nucleus of normally diamagnetic atoms and molecules owing to a Paschen-Back type of uncoupling of the paired electron spins characteristic of diamagnetism. That, for atoms, the energy required for uncoupling is great is seen by the fact that the Paschen-Back effect becomes important only for magnetic fields of the order of 10^5 gauss or greater. Bitter pointed out, however, that for molecules, where the excited states are closer together, the uncoupling would be expected to begin at much lower field strengths and, hence, might be observed experimentally.

It is well known from the theory of molecular diamagnetism[19] that the molar susceptibility of $^1\Sigma$ molecules consists of two terms, *viz.*,

$$\chi_{\text{mol}}=-\frac{Ne^2}{6mc^2}\sum\langle r^2\rangle_{\text{Av}}+\frac{2}{3}N\sum_{n\neq0}\frac{|(0|m^0|n)|^2}{E_n-E_0}, \tag{5}$$

where N is here the Avogadro number. The first term is the ordinary Pauli expression for the diamagnetism of atoms (the summation now to be extended over all the electrons in the molecule), while the second gives

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[7] If the nuclei possess an electric quadrupole moment, the resonance line may be considerably broadened because of the interaction of the quadrupole moment with the fluctuating inhomogeneous electric fields in a liquid.

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

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

[10] W. G. Proctor and F. C. Yu, Phys. Rev. **78**, 471 (1950).

[11] Another source of resonance fine structure is the nuclear electric quadrupole interaction in crystalline substances having lower than cubic symmetry. R. V. Pound, Phys. Rev. **79**, 685 (1950).

[12] Bloch, Levinthal, and Packard, Phys. Rev. **72**, 1125 (1947).

[13] W. C. Dickinson and T. F. Wimett, Phys. Rev. **75**, 1769 (1949). The technique described in this paper was introduced by F. Bitter.

[14] W. E. Lamb, Jr., Phys. Rev. **60**, 817 (1941).

[15] W. C. Dickinson, Phys. Rev. **80**, 563 (1950).

[16] W. D. Knight, Phys. Rev. **76**, 1259 (1949).

[17] W. C. Dickinson, Phys. Rev. **77**, 736 (1950).

[18] W. G. Proctor and F. C. Yu, Phys. Rev. **77**, 717 (1950).

[19] J. H. Van Vleck, *Electric and Magnetic Susceptibilities* (Oxford University Press, London, 1932), Chapter X.

the contribution of the high frequency matrix elements of the orbital paramagnetic moment of the molecule, the summation to be extended over all the *n*-excited states of the molecule. According to Van Vleck,[19] the existence of this second term is based physically on the fact that the nuclei in a diatomic or polyatomic molecule act at different attracting centers and so exert a torque on the electrons. This torque causes a continual transfer of angular momentum back and forth between the electrons and nuclei of the molecule, with the result that although the mean orbital angular momentum of a $^1\Sigma$ molecule is zero, the mean square value is not zero. It is found experimentally that the large majority of molecular compounds are diamagnetic, showing that the first term in Eq. (5) is usually larger than the second. There are a few instances where the second term predominates, with the substance showing a feeble, temperature-independent paramagnetism.

From the two terms of Eq. (5) can in principle be found the net additional fields at the nuclei of a molecule due respectively to the diamagnetism and second-order paramagnetism of all the other molecules in the sample. As will be shown below, the field due to the diamagnetic term almost always can be neglected, hence, also the field due to the second term. It cannot be concluded from this, however, that the *internal* diamagnetic and second-order paramagnetic fields (i.e., the fields at the nuclei of a molecule due to the extra-nuclear electrons of the molecule itself) are negligible. Indeed, since the internal diamagnetic shielding field H' for atoms constitutes an important correction in nuclear resonance experiments, the existence in some cases of a significant internal second-order paramagnetic component in molecules might well be expected.

In a theoretical treatment of the problem, Ramsey[20] obtains an expression for the total molecular shielding field consisting of a diamagnetic and a second-order paramagnetic term. Owing to the choice of the coordinate origin at the nucleus at which the field is desired, his expression for the diamagnetic term becomes identical with Eq. (4) except that the integration is extended over all the electrons in the molecule rather than only the one atom containing the resonating nucleus. Because of the $1/r$ dependence of $v(0)$, perturbations of the valence electrons of an atom by molecular binding have little effect on the atomic value of $v(0)$.[15] Also, except possibly for the lightest atoms, contributions to $v(0)$ from electrons belonging to other atoms of a molecule would be relatively small. (Examples: for an F_2 molecule the contribution of the electrons of one F atom to the value of $v(0)$ at the nucleus of the other atom would be about 7 percent of the $v(0)$ value for a free F atom. For a $GaCl_3$ molecule the contribution of the electrons of the three chlorine atoms to the value of $v(0)$ at the nucleus of the Ga atom would be only about 3 percent of the $v(0)$ value for a free Ga atom.) Hence, to a first approximation, except for the lightest atoms, values of the internal diamagnetic correction H'/H_0 for free atoms can also be used for the diamagnetic term in Ramsey's expression.

The second term of Ramsey's expression for the molecular shielding H'/H_0 is of the same general form as the second term in Eq. (5), although more complicated. Unfortunately, the numerical evaluation of this term would be difficult for most molecules, since knowledge of wave functions of the excited states of the molecule would be needed. However, for the important case of molecular hydrogen, Ramsey[20] has been able to calculate the second-order paramagnetic term utilizing the experimentally measured value of the spin-rotational interaction constant for the H_2 molecule.[21] The diamagnetic term Eq. (4) for molecular hydrogen has been calculated by Anderson[22] using Nordsieck's wave functions. Thus, the total shielding field is found to be[23]

$$H'/H_0=(-3.24+0.56)\times 10^{-5}=-2.68\times 10^{-5}.$$

Although for H_2 the second-order paramagnetic term is only about 17 percent of the diamagnetic term, no similar prediction can be made concerning more complex molecules. Van Vleck[19] points out that for molecules in which the nuclear field is less nearly centro-symmetric than is the case for H_2 the second term in the expression for the molecular susceptibility Eq. (5) would be expected to become more important. He also points out that this term would be expected to be particularly large for molecules formed out of atoms whose ground states were not ^1S. Similar predictions can, hence, be made about the importance of the internal second-order paramagnetism. It is, indeed, conceivable that in some cases the second-order paramagnetic term could be larger than the diamagnetic term in Ramsey's expression so that the shielding field H'/H_0 would have a positive value.

(3). H'' is the magnetization field due to any paramagnetic ions that might be added to the sample for the purpose of shortening the spin-lattice relaxation time T_1 of the nuclear spin system. The inverse time T_1^{-1} is a measure of the rate at which energy absorbed by the nuclear spin system can be transferred to the atomic lattice. If T_1 is excessively long, the population of the $2I+1$ nuclear energy levels, originally governed by the Boltzmann factor $\exp(\mu H_0 m/IkT)$, becomes equalized as resonance is approached with a resulting decrease in the rate of absorption. This "heating up" of the nuclear spins is referred to as saturation and causes distortion of the resonance line shape as well as decrease of the signal-to-noise ratio. The large fluctuating magnetic fields associated with paramagnetic ions create better

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[20] N. F. Ramsey, Phys. Rev. **78**, 699 (1950).

[21] Kellogg, Rabi, Ramsey, and Zacharias, Phys. Rev. **57**, 677 (1940).

[22] H. L. Anderson, Phys. Rev. **76**, 1460 (1949).

[23] E. Hylleraas and S. Skavlem, Phys. Rev. **79**, 117 (1950), obtain by an essentially different method a value for this shielding constant between 2.66×10^{-5} and 2.95×10^{-5}.

TABLE I. Bulk diamagnetic susceptibility χ_{vol} for some common liquids.

Liquid		$-\chi_{vol}\times 10^6$
HNO_3		0.700
H_2O		0.721
$(C_2H_5)_2O$	Ethyl ether	0.546
$C_2H_4O_2$	Acetic acid	0.552
C_6H_6	Benzene	0.636
C_2H_6O	Ethyl alcohol	0.587
CCl_4	Carbon tetrachloride	0.685
Cl_2	(Liquid)	0.887

spin-lattice coupling,[24] thus shortening T_1. The line broadening associated with a shortening of T_1 will not be observed for small enough ionic concentrations, since, as previously mentioned, the natural line width in liquids is usually much less than the observed line width which is due to inhomogeneities in H_0. Since any observable line broadening lowers precision, there is usually an optimum ionic concentration in any particular case.

In past nuclear moment ratio measurements, where paramagnetic ions have been used, one of the following three assumptions has generally been made as to the effect of the magnetization field (our H''), on the precision of the experiment:

(a) On adding paramagnetic ions to one of two samples used in a moment comparison, the concentration is small enough so that any field shift would be negligible.

(b) On adding the same concentration of paramagnetic ions to both samples, both nuclear species would experience the same magnetization field. This assumption also is made when paramagnetic ions are added to a single sample containing both nuclear species.

(c) When only one nuclear resonance is needed in an experiment (e.g., comparison of proton and neutron moments), by using a spherically shaped sample, the field H'' would be exactly zero.

The validity of these assumptions may be tested by means of experimental data presented in Sec. V.

In addition to the three significant field components in liquids discussed above, the following fields should be listed as also contributing to H_{Av}:

(4). The bulk diamagnetic field. From random values of χ_{vol} for liquids given in Table I it is seen that diamagnetic volume susceptibilities are quite small and do not vary considerably from liquid to liquid. Referring to Table I, we might expect the maximum difference in χ_{vol} for liquids to be about 5×10^{-7}. The corresponding fractional field difference $\Delta H/H_0$ would vary from zero for spherical samples to about 1 part in 10^6 for transverse cylindrical samples. (Sec. V.) In the experiments reported below the smallest fractional field difference that could be detected between two samples was about 5 parts in 10^6 so that differences in bulk diamagnetic field could be neglected. Of course, when both nuclear species are contained in a single sample, they both will experience the same diminution of field strength due to bulk diamagnetism.

In the case of solids, χ_{vol} may be somewhat larger than for liquids, but due to the broad resonance lines characteristic of solids, the bulk diamagnetic field can always be neglected.

(5). The static nuclear paramagnetic field. The volume susceptibility of a sample due to nuclear dipole alignment is given by the Curie law, *viz.*,

$$\chi_0=[(I+1)/I](N\mu^2/3kT), \tag{6}$$

where N is the number of nuclei per cc with moment μ and spin I, and T is the absolute temperature. As an example of the magnitude of χ_0, we might take water with its high density of protons. Thus,

$$(\chi_0)_{H_2O}\approx 3.2\times 10^{-10}. \tag{7}$$

Since the contribution to H_{Av} would be of the order of $\chi_0 H_0$, it is seen that nuclear dipole orientation is a perfectly negligible factor. The contribution to H_{Av} of the field due to orientation of molecular rotation moments will likewise be negligible, since these moments are known to be of the same order as nuclear moments.

(6). It is shown by Bloch and Siegert[25] for the special case of nuclei with spin $\frac{1}{2}$ that the use of a linear oscillating rather than a rotating r-f field necessitates replacing the resonance field value H_0 by an effective value $H_0{}^*=H_0(1-H_1{}^2/16H_0{}^2)$, where H_1 is the amplitude of the r-f field.[26] In resonance absorption experiments and modern nuclear induction experiments $H_1/H_0\approx 10^{-4}$ to 10^{-6}. Hence, not only would this result in a negligible shift in the resonance curve, but in a moment ratio measurement the resonances from both nuclear species would be shifted in the same direction and by about the same amount.

(7). The field due to electronic paramagnetism in metals.[27] Knight[16] found that the nuclear resonance frequency for an atom in the metallic state is usually appreciably greater than the resonance frequency when the atom is in a nonmetallic compound. These frequency shifts are of the order of a few tenths of one percent and have been attributed[28] to the large probability density near the nuclei of the conduction electrons in a metal, resulting in an enormous concentration of the local magnetic susceptibility in the vicinity of the nuclei. The obvious precaution is to use only nonmetallic compounds in a moment comparison.

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[24] The reader is referred to BPP for a detailed theoretical treatment of the effect of paramagnetic ions on spin-lattice relaxation.

[25] F. Bloch and A. Siegert, Phys. Rev. **57**, 522 (1940).

[26] Professor Ramsey has pointed out to the author that this same result can be derived classically, independent of the nuclear spin value, by using a simple rotating coordinate system method.

[27] Powdered metallic samples can be used in resonance experiments provided the metal particles are sufficiently insulated from one another so that the sample is a nonconductor. In some cases (e.g., Al, Cu) F. Bitter has found that a pure metal powder can be used; the surface oxidation of the metal particles provides adequate insulation.

[28] Townes, Herring, and Knight, Phys. Rev. **77**, 852 (1950).

III. EXPERIMENTAL TECHNIQUE FOR MEASUREMENT OF RESONANCE LINE SHIFTS

The theoretical and physical principles of nuclear magnetic resonance absorption have been given in detail by BPP. The radiofrequency bridge technique and modulation method described there is, in all essentials, that used for the work reported in this paper. Figure 1 is a block diagram of the circuit and equipment employed. The magnet is an iron-core, water-cooled electromagnet designed by F. Bitter. The gap width is $2\frac{1}{2}$ in. and the pole faces are 8 in. in diameter with rims adjustable for maximum field homogeneity. The current is supplied by a bank of submarine batteries. For a field of 7000 gauss, with the magnet windings connected in series, 50 volts and about 45 amp are required; this current can be maintained for 8 hours or more with no observable steady drift due to the batteries. The current is monitored by a galvanometer and a Rubicon potentiometer which measure the voltage drop across a low resistance shunt placed in series with the magnet circuit. The exact resistance of the shunt is unimportant, since it is never necessary to measure the absolute value of the current. For the slow variation of the magnet field through resonance, a motor-driven rheostat is used. Small fluctuations in battery current limit the slowness with which the field may be varied. For the work reported here, a sweep rate of approximately 1 gauss/min was used although a considerably slower rate can be attained easily.

The experimental problem is the detection and measurement of shifts in resonance position which are usually small compared with the resonance line width. By a shift in resonance position is meant that on varying some parameter in the sample (e.g., the concentration of paramagnetic ions), the nuclear resonance under investigation occurs at a slightly different value of applied field H_0, holding the radiofrequency at a constant value. Such a shift is interpreted as arising from a small change in the time average field H_{Av} experienced by the nuclei, necessitating an equal and opposite change in the applied field H_0 in order that the resonance condition Eq. (1) be satisfied.

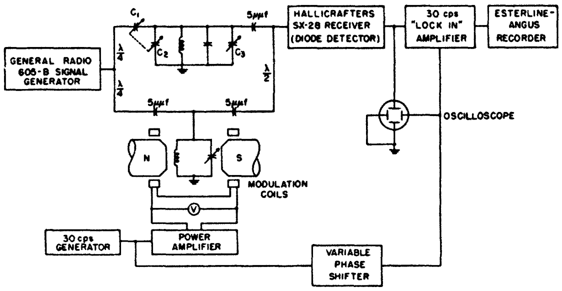

FIG. 1. Block diagram of nuclear resonance absorption bridge circuit. Two such r-f bridges, both fed by a single frequency generator, were used for the experiments.

The method developed for the measurement of these small shifts consisted in the use of two identical r-f bridge circuits, each with separate receiver, 30-cps narrow-band, lock-in amplifier, and recording milliammeter, but both coupled to the same G. R. 605-B signal generator. A nuclear species in the "standard" sample of the one bridge gives a resonance at a constant field position with which to compare the resonance position of the same nuclear species in the "variable" sample of the other bridge. Any frequency drift of the generator will shift both resonances the same fractional amount and, hence, will have no effect on the measurement of a shift. The sample coils for the two bridges consisted of No. 30 copper wire wound on 10-mm o.d. cylindrical glass sample holders placed side by side in a single brass box. The liquid sample materials were contained in either 8-mm o.d. spherical bulbs blown at the end of 3-mm glass tubing or in 8-mm o.d. long cylindrical test tubes; in either case a snug fit was made with the inside of the sample holders. Since both the sample coils were driven at the same frequency, they had to be well shielded from each other to prevent any coupling between the two bridges. Although it is desirable that the samples be placed very close together so that they will experience as small a magnetic field gradient as possible, a limit is set by the lowering of the Q of the coils when they are placed too close to the brass shield between them. It was found that the coil Q's were only slightly lowered for the center-to-center distance between sample holders of 16.5 mm.

In order that the nuclear resonances from identical samples in the two bridges will occur simultaneously as the magnet field is varied slowly through resonance, the sample box must be so adjusted in the magnet that the position of zero-field gradient (maximum field), is just halfway between the two sample coils. A rough adjustment is made easily by means of oscilloscope observation of the proton resonance, using only one bridge. Then, with identical samples in both sample holders and using both bridges, final adjustment is made, by means of a positioning mechanism on the magnet, until the resonance curves from the two samples occur simultaneously on the respective Esterline-Angus recorder tapes. After adjustment of the sample box in this manner, the proton derivative of absorption curve[29] (qualitatively similar to a dispersion curve), had a peak-to-peak width of about 0.3 gauss in a field of 7000 gauss. This can be compared with a peak-to-peak width of about 0.1 gauss, when the sample is in the position of zero field gradient. The width between the two small minima for a derivative of dispersion curve was found, in general, to be closely twice the peak-to-peak width for a derivative of absorption curve.

A resonance shift is measured as follows. Identical samples are placed in the two sample holders. The two resonances are traversed, first, with the magnet

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[29] With the modulation method used in these experiments the output of the lock-in amplifier reproduces the derivative of the original absorption or dispersion resonance curves (see reference 2 for details).

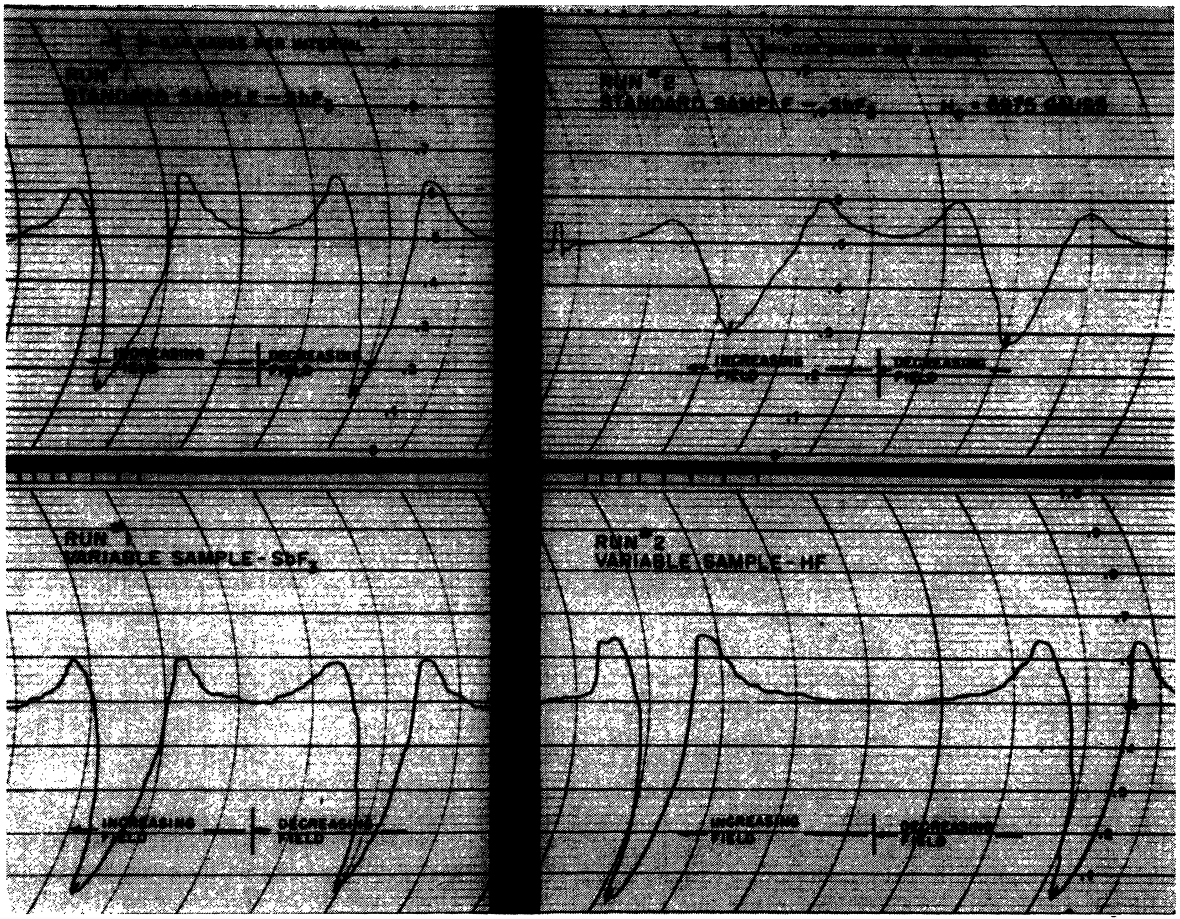

FIG. 2. Record of two runs. In Run No. 1 the F^{19} resonance in SbF_3 was simultaneously observed in both bridges. In Run No. 2 the variable sample was changed to HF, the standard sample remaining SbF_3. Note the large resonance shift. The SbF_3 resonance curves are wider in Run No. 2 than in Run No. 1 due to the nonlinearity in sweep rate of the motor-driven rheostat. In Run No. 2, due to the wider separation of the two HF resonances, a larger section of the rheostat had to be traversed. The SbF_3 resonances were traversed at the end of the rheostat where the rate was slowest, hence, the broadness.

current increasing, then with the magnet current decreasing, and, then, once more with the magnet current increasing. We will call such a series of three resonance pairs a run. On traversing the second pair of resonances in a run the recorder tapes are simultaneously marked by means of a relay switch for equal intervals of current as read from the galvanometer scale. A second run is now made, the outer pairs of resonances being for decreasing rather than increasing magnet current as for the first run. This procedure eliminates error due to the effect of hysteresis, to be mentioned below. The variable sample is now removed and, for example, a definite concentration of paramagnetic ions added. Replacing the sample, two more runs are made in the same manner. It was usual practice after a series of runs were made, changing the variable sample several times, to end the experiment by once more making the variable sample identical to the standard sample. Thus, if the sample box had been moved accidentally or if the relative field at the two samples had changed for any other reason, this would have been detected.

An illustration of two runs (F^{19} resonances), is given in Fig. 2. For lack of space only two of the three pairs of resonances are shown in each run. The sections of tape in the upper and lower left hand corner constitute the first run in which the two samples were identical—both containing an aqueous solution of SbF_3. It is seen that the resonances occur practically simultaneously. The sections of tape in the upper and lower right-hand corner constitute the second run in which the variable sample is now HF. The standard sample, of course, is left unchanged. The current calibration is seen in the upper left-hand corner of each section of tape. The large shift observed here is attributed to a difference in the molecular shielding field between SbF_3 and HF. It is a much larger shift than is usually observed on addition of paramagnetic ions.

The current calibration is changed to a magnetic field calibration as follows. The magnet field is centered

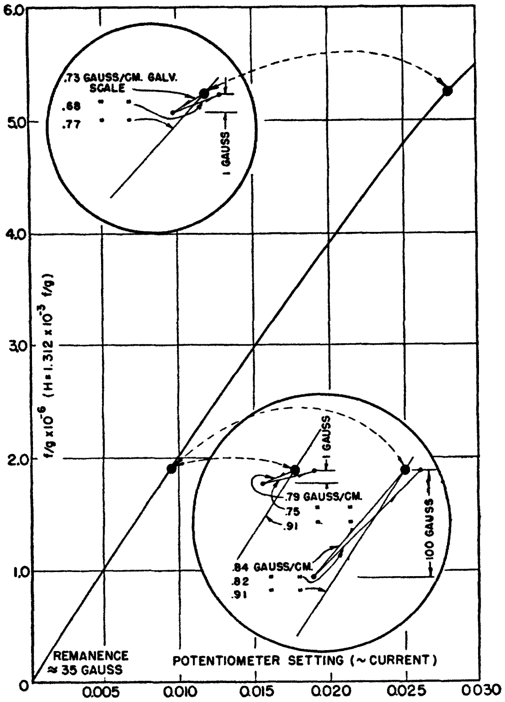

FIG. 3. Effect of hysteresis in magnetic field calibration.

on a resonance and the radiofrequency measured with a Zenith BC-221-T frequency meter. Then, the signal generator is slightly changed in frequency and the magnet current changed until the resonance is once more centered. The corresponding galvanometer deflection is read; and from the relation $dH = d\omega/\gamma$, the galvanometer scale is calibrated in gauss/cm. It is important to warn that even when there is no saturation of the magnet field, it is incorrect to write $di/i = dH/H$ and, hence, determine dH with the potentiometer alone. This ignores the phenomenon of reversible magnetization, which means only that at any point on the i *vs* H curve for an iron-core electromagnet a small hysteresis curve is traced out. For this reason, as seen in Fig. 3, the field calibration is slightly dependent on whether the magnet current is increasing or decreasing. By making the calibration several times in each direction, an average calibration is obtained which can be trusted to 10 percent in accuracy. Also, as seen in Fig. 3, the calibration depends on the magnitude of the field change dH. Care was taken to calibrate the field over about the same field increment as was actually traversed for the resonances.

The determination of a resonance shift from a run consists in the measurement and comparison of distances *between* the three resonance centers on each tape. This eliminates any systematic errors which might arise from time lags in the apparatus. The importance of estimating accurately the centers of the resonance lines is obvious, particularly in the case of shifts much smaller than the line width. It was rarely possible experimentally to traverse in succession the three pairs of resonance curves in a run without one or both bridges drifting slightly from the desired balance. This causes a slight dissymmetry in the resulting resonance curves due to a mixing of dispersion and absorption. In order to be able to determine the true line center when such dissymmetries occur, an analysis was made of "mixed" resonance line shapes[30] using Gaussian shape functions given by Pake and Purcell.[31] (According to the criteria given by these authors the gaussian derivative curves fit our experimental curves much better than the corresponding Lorentz curves.) On the basis of this analysis, Fig. 4 illustrates an "impure" derivative of dispersion-type curve, where the difference between the true and observed line center is 5 percent of the line width, measured between the two minima. In some cases the actual resonance field shift which is to be measured is not much larger than this.

It was found over a large range of experiments that the smallest resonance shift of the variable sample with respect to the standard sample that could be detected was about 0.03 gauss in a field of 7000 gauss. This corresponds to a shift equal to about 1/20th of the line width of a derivative of dispersion-type curve; or stated differently, to a shift of 4 to 5 parts in 10^6 with respect to the applied field. The accuracy to which this shift could be measured was also found to be about 5 parts in 10^6 of the applied field. Hence, a shift of 0.03 gauss could only be measured to an accuracy of the order of the shift itself, while a shift of 0.3 gauss could be measured to an accuracy of about 10 percent. Because of the uncertainty attached to the magnetic field calibration, it is felt that an accuracy of 10 percent is the best that can be quoted—even for shifts larger than 0.3 gauss.

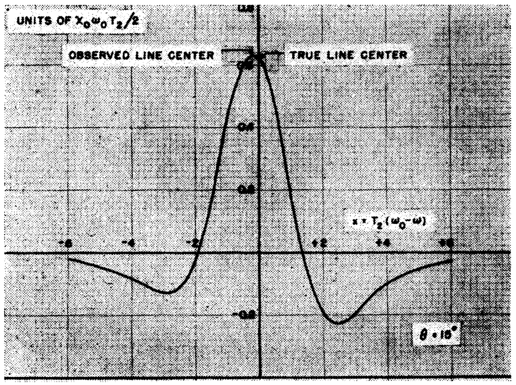

FIG. 4. Line shape (gaussian), of an "impure" nuclear magnetic resonance. If $d\chi''/dx$ represents the derivative of an absorption curve and $d\chi'/dx$ the derivative of a dispersion curve, the equation of the above curve is $(d\chi'/dx)\cos\theta + d\chi''/dx \sin\theta$, where θ is the circuit "balance factor." Any experimental curve more distorted than the one shown above was rejected.

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[30] On request, the author will gladly furnish the results of this analysis to other workers in this field.

[31] G. E. Pake and E. M. Purcell, Phys. Rev. 74, 1184 (1948).

IV. THE MAGNETIC SHIELDING FIELD FOR MOLECULES

Knight[16] was the first to observe a dependence of nuclear resonance position on chemical compound. In a letter reporting shifts of the nuclear resonance in several metals, he briefly mentioned observing shifts of the P^{31} resonance of about 0.01 percent among some phosphorous compounds. Independently, the author[17] reported a dependence of the F^{19} resonance on the chemical compound, and Proctor and Yu[18] reported an even more pronounced effect for the N^{14} resonance. With this indication that such a dependence was not uncommon, a survey was made of the nuclear resonance positions in different chemical compounds of several light elements. In the data given below for each element, the shielding field in different molecules is compared with the shielding field in the molecule for which the nuclear resonance is found to come at the ***highest*** value of applied magnetic field (i.e., zero or lowest non-zero contribution of second-order paramagnetism, assuming that the diamagnetic contribution is closely the same in all cases). This is rather an arbitrary procedure, since there may be other molecular compounds, not observed here, in which the resonance comes at a still higher applied field. Thus, it is impossible to determine the absolute value of the second-order paramagnetic field for any molecule, unless for the standard compound it is known that the resonating nucleus is contained in a simple diamagnetic ion or atom rather than a molecule. The second-order paramagnetism would be zero in this case, and a comparison with other molecular compounds would determine the absolute value of the second-order paramagnetic contribution for those molecules.

(A) Hydrogen

Proton resonances were compared with each other in acetone, mineral oil (Nujol), distilled water, glacial acetic acid, ethyl alcohol, glycerin, benzene, and anhydrous ether. No shifts could be detected within the accuracy of the experiment of about 5 parts in 10^6 with respect to the applied field. It would, no doubt, be expected that any shifts occurring in the proton resonance position would be quite small, since the single covalent bond which the hydrogen atom forms would be about the same from one compound to another.[32] Since the total shielding correction H'/H_0 for molecular hydrogen is only 2.7×10^{-5}, it is seen that a difference in shielding of less than about 20 percent between the above molecules would not have been detected. An important experiment will be a comparison of the proton resonance in water and in mineral oil with the proton resonance in gaseous or liquid hydrogen, preferably to an accuracy of 1 part in 10^6. It is only for H_2 that the total magnetic shielding has been computed, while in most high precision measurements the proton resonance from mineral oil or H_2O is used as a standard.

(B) Lithium

The series of Li^7 compounds listed in Fig. 5 were compared in a field $H_0=6950$ gauss. No shifts were observed within the experimental accuracy. This is, no doubt, because the Li atoms in solution are entirely ionized—losing their loosely bound valence electron and becoming positive ions. Hence, there would be no second-order paramagnetism.

(C) Boron

The data obtained for the different B^{11} compounds compared in a field $H_0=7100$ gauss is given in Table II. The resonances in BCl_3 and BBr_3 come at nearly the same position, but there is a noticeable shift between the resonances in these compounds and the resonance in $BF_3{:}O(C_2H_5)_2$. This is not surprising, since the BF_3 forms a bond with the ether molecule. Also, Pauling[33] points out that BF_3 differs from BCl_3 and BBr_3 in that the B−F bond has a greater ionic character (63 percent for B−F; 22 percent for B−Cl).

(D) Fluorine

The data for the different F^{19} compounds compared in a field $H_0=6975$ gauss are given in Table III. It would be expected that NaF and KF in aqueous solution would be entirely ionized. Therefore, it is surprising to find that the resonances in BeF_2, BF_3, and HF occur at a higher applied field than those in NaF and KF. Since the second-order paramagnetic field must always be an aiding field, resonances in compounds that are not totally ionized would be expected to occur at a lower applied field than those in NaF and KF. The only plausible explanation for this is that the diamagnetic contribution may be slightly greater for BeF_2, BF_3, and HF than for the F^- ions in the NaF and KF solutions. Indeed, when the observed resonance shifts in a light element such as fluorine are much smaller than the magnitude of the internal diamagnetic field for the atom ($H'=3.2$ gauss for F^{19} at $H_0=7000$ gauss), this might well be the case.

According to the analysis made by Ramsey,[20] the molecular shielding field should be linearly proportional to the applied field. Thus, the difference of this field between different molecules also should be proportional to the applied field. This was checked experimentally by also observing the F^{19} shifts at a field $H_0=2500$ gauss. From Table IV it is seen that the average ratio

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[32] G. Lindstrom, Phys. Rev. **78**, 817 (1950), finds that the deuteron-proton moment ratio differs by 4(±3) parts in 10^6 depending on whether the proton sample was paraffin oil or H_2O. Such a small difference might well be due to a difference in the bulk diamagnetic field between the two substances. Also H. S. Gutowsky and C. J. Hoffman, Phys. Rev. **80**, 110 (1950), report that the magnetic shielding in mineral oil is (3±1.5) parts in 10^6 to (8±1.5) parts in 10^6 higher than in benzene, CF_3CO_2H, HBF_4, $CHCl_3$, concentrated HCl, and HNO_3.

[33] L. Pauling, *The Nature of the Chemical Bond* (Cornell University Press, 1940), Chapter VII.

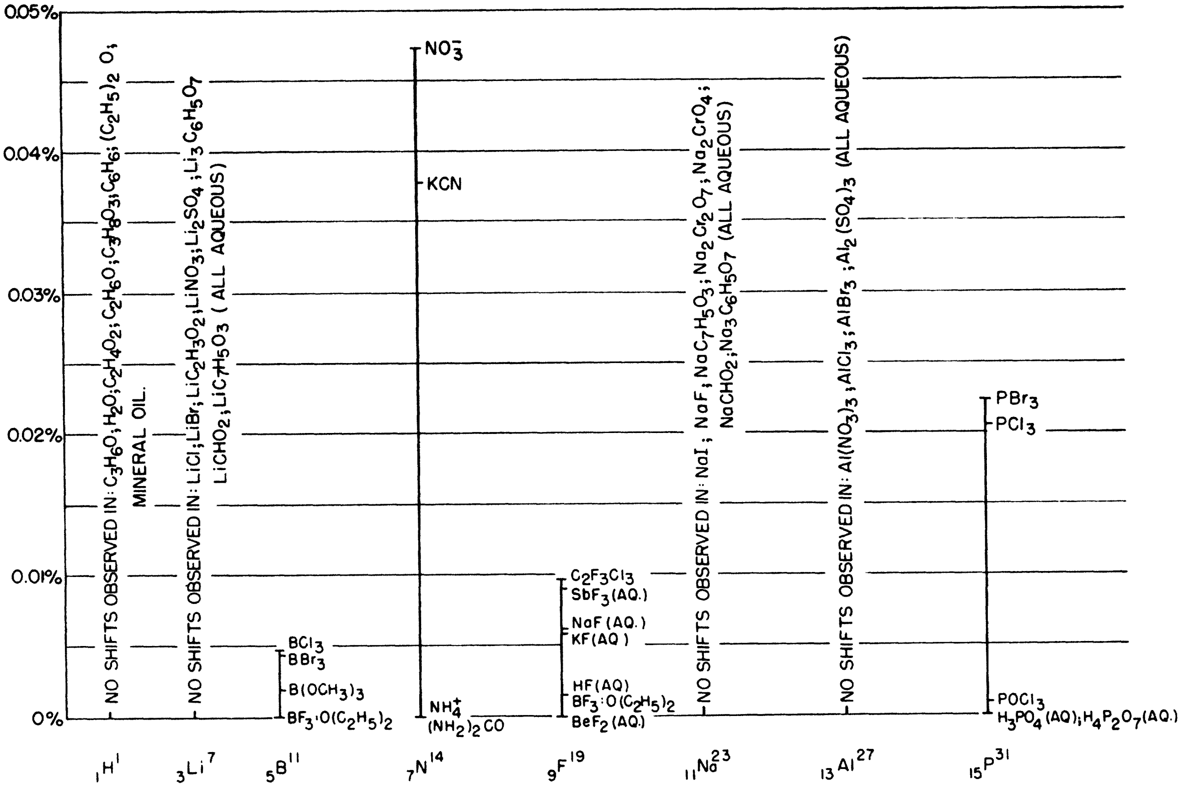

FIG. 5. Percentage differences in the magnetic shielding H'/H_0 for molecules of several light elements.

of the shifts at the two field strengths is 2.5. Since the ratio of the applied fields is 2.8, it can be stated that within the experimental error the molecular shielding field is, indeed, linearly proportional to H_0. In the work of Proctor and Yu[18] on shifts in N^{14}, linearity in the field dependence was also observed.

(E) Sodium

The series of Na^{23} compounds listed in Fig. 5 were compared in a field $H_0=6950$ gauss. As for Li^7, the observance of no shifts can be attributed to the ionic form of the Na compounds in aqueous solution. It would be interesting to obtain some metal-organic compounds containing Li and Na to compare with the aqueous solutions of the salts. A shift should be observed due to the bonding of the Li and Na atoms into the organic molecule.

TABLE II. Differences in the magnetic shielding field for some B^{11} compounds. $H_0=7100$ gauss. The resonance in $BF_3:O(C_2H_5)_2$ was observed at the highest value of applied magnetic field.

Compound	$\Delta H'$ (gauss)	$\Delta H'/H_0$ (%)
$BF_3:O(C_2H_5)_2$	0.00	0.00
$B(OCH_3)_3$	0.13	0.0018
BBr_3	0.31	0.0044
BCl_3	0.33	0.0046

(F) Aluminum

In the series of Al compounds listed in Fig. 5 no shifts were observed within the experimental error. Again, this can be attributed to complete ionization in the aqueous solution, since it would be extremely unlikely that the second-order paramagnetism would be exactly the same for all the molecules compared.

(G) Phosphorus

A comparison of several P^{31} compounds was made at a field $H_0=5800$ gauss. The results are given in Table V. It is seen that a large shift occurs between those compounds where the phosphorous exhibits a valency of 3

TABLE III. Differences in the magnetic shielding field for some F^{19} compounds. $H_0=6975$ gauss. The resonance in BeF_2 (aq) was observed at the highest value of applied magnetic field.[a]

Compound	$\Delta H'$ (gauss)	$\Delta H'/H_0$ (%)
BeF_2 (aq)	0.00	0.00
HF (aq) and $BF_3:O(C_2H_5)_2$	0.10	0.0014
KF (aq)	0.40	0.0057
NaF (aq)	0.42	0.0060
SbF_3 (aq)	0.63	0.0090
$C_2F_3Cl_3$	0.67	0.0096

[a] These values are 36 percent smaller than those previously listed by the author (reference 17), owing to an unfortunate error in magnetic field calibration. H. S. Gutowsky and C. J. Hoffman, Phys. Rev. **80**, 110 (1950), have checked the F^{19} shifts reported here and their values are in essential agreement with those given above. They also give the magnetic shielding for several other F^{19} compounds.

TABLE IV. Resonance field separations for F^{19} compounds at two different values of applied field strength.

Compounds compared	Separation at 6975 gauss	Separation at 2500 gauss	Ratio
SbF_3 and BeF_2	0.63 gauss	0.23 gauss	2.8
SbF_3 and HF	0.53	0.22	2.4
$C_2F_3Cl_3$ and HF	0.57	0.26	2.2

and those in which a valency of 5 is exhibited. In the former compounds, such as PCl_3 and PBr_3, only the three $3p$ orbitals of the phosphorous are used in bond formation. When a valency of five is exhibited, however, as in $POCl_3$ and H_3PO_4, not only the three $3p$ orbitals are used but also the $3s$ orbital and one $3d$ orbital. Hence, a very different electronic structure would be expected and a resulting large difference in the second-order paramagnetism. It is noted from Table V that the P^{31} resonances in P_2O_5 (aq) and $H_4P_2O_7$ (aq) come at exactly the same position as in H_3PO_4. This is confirmation of the fact that these compounds do not retain their molecular form in aqueous solution but decompose to H_3PO_4.

V. THE MAGNETIZATION FIELD OF PARAMAGNETIC IONS

To obtain an expression for H'', the component of H_{Av} due to a given concentration of paramagnetic ions added to the sample, we follow the method introduced by Debye[34] for electric dipoles. It is assumed that the applied field H_0 is homogeneous over the sample volume and that the sample container is in the shape of an ellipsoid so that the magnetization[35] $M=\chi H_0$, created by the paramagnetic ions, will be homogeneous. The field H'' may be thought of as consisting of three components

$$H''=H_1+H_2+H_3. \qquad (8)$$

The field H_1 (not to be confused with the r-f field H_1), is ascribed to the induced magnetic poles on the surface of a small hypothetical sphere[36] with its center at the nucleus. This is the so-called Lorentz or cavity field and has the value $(4\pi/3)M$. The field H_2 is the familiar demagnetizing field, defined by $H_2=-\alpha M$, where α is the demagnetizing factor.[37] It might be expected that the remaining field H_3 due to those paramagnetic ions inside the hypothetical sphere would be exactly zero, since the interaction energy $\boldsymbol{\mu}\cdot\mathbf{H}_3$ of the nuclear magnetic moment μ with this field involves an isotropic averaging of $(-1+3\cos^2\theta)$ over the volume of the sphere. However, it is found experimentally that H_3 may differ significantly from zero; anticipating this, we define an "interaction factor" $q=H_3/M$. The full expression for H'' hence becomes

$$H''=[(4\pi/3)-\alpha]M+qM. \qquad (9)$$

TABLE V. Differences in the magnetic shielding field for some P^{31} compounds. $H_0=5800$ gauss. The resonance in H_3PO_4 (aq) was observed at the highest value of applied magnetic field.

Compound	$\Delta H'$ (gauss)	$\Delta H'/H_0$ (%)
H_3PO_4 (aq); $H_4P_2O_7$ (aq); and P_2O_5 (aq)	0.00	0.00
$POCl_3$	0.05	0.0009
PCl_3	1.18	0.020
PBr_3	1.30	0.022

Two sample shapes were used experimentally: a spherical sample for which $\alpha=4\pi/3$ and an "infinite" transverse cylindrical sample for which $\alpha=2\pi$. This was done mainly as a check on the validity of Eq. (9), since, if a significantly different value of q is found for the two sample shapes, all other conditions being the same, the reasoning leading to Eq. (9) would have to be re-examined.

TABLE VI. Experimental values of μ_{eff} for paramagnetic ions used in experiments.

Paramagnetic ion	Experimental μ_{eff} (solutions) M.I.T.	Van Vleck
Ni^{++}	3.26	3.23
Co^{++}	5.00	4.6–5.0
Cu^{++}	1.82	1.8–2.0
Fe^{++}	5.45	5.33
Mn^{++}		5.2–5.96
Cr^{+++}		3.68–3.86
Er^{+++}		9.4–9.6

The first column of Table VI lists those paramagnetic ions used in the experiments. The second column lists $\mu_{\text{eff}}=(3\chi kT/N\beta^2)^{\frac{1}{2}}$ (T is the absolute temperature, N the number of paramagnetic ions per cc, and β the Bohr magneton), calculated from susceptibilities measured at M.I.T. for several of the saturated paramagnetic solutions used.[38] In the third column are listed experimental values of μ_{eff} as given by Van Vleck.[39] The agreement between the M.I.T. values and those given by Van Vleck is so satisfactory that confidence was felt in using the average values of Van Vleck for the remaining solutions in Table VI where the susceptibility was not measured at M.I.T. From μ_{eff} the magnetization M required in Eq. (9) is obtained. It should be mentioned that the field H'' differs from the experi-

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[34] P. Debye, Physik. Z. **13**, 97 (1912).

[35] The rigorous definition of M is $M=\chi H_i$, where H_i is the field inside the sample. However, the difference between H_i and H_0 is negligible, since paramagnetic permeabilities are so nearly unity.

[36] The radius of this sphere should be small on a macroscopic scale but large enough so that the nucleus at its center will experience negligible fluctuations in field owing to thermal movement of the ions outside of the sphere.

[37] Actually, the magnetization is not quite homogeneous, since the sample to which paramagnetic ions were added was necessarily in a position where a gradient of the magnet field existed. Thus, there would be a "magnetization charge" per unit volume as well as the magnetic poles on the surface which we have considered. It was determined experimentally, however, that this effect was negligible, the resonance shifts being the same whether the sample was in its normal position or shifted to a position of zero-field gradient.

[38] The author is greatly indebted to Mr. O. J. VanSant, Jr. for the measurement of these susceptibilities.

[39] J. H. Van Vleck, reference 19, pp. 243 and 285.

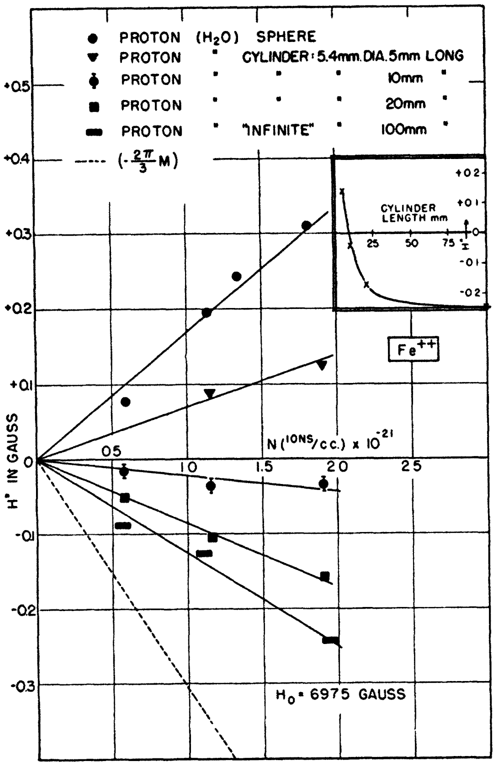

FIG. 6. Illustration of the dependence of H'' on sample shape. $FeCl_2$ added to H_2O. Proton resonance.

mentally measured resonance shift by the small amount which the external magnetization field from the paramagnetic ions in the variable sample contributes to the total field at the standard sample. Thus, for the dimensions used, it was calculated that there was an opposing field of $0.04M$ at the standard sample when the variable sample was spherical and $0.14M$ when the variable sample was cylindrical.

To determine the length of the transverse cylinder needed to approximate an infinite cylinder, H'' was measured *vs* concentration of Fe^{++} ions for a series of cylinders of increasing length. The results are shown in Fig. 6. From the insert which is a plot of H'' *vs* cylinder length for a concentration $N = 2\times10^{21}$ ions/cc, it is seen that the 100-mm cylinder closely approximates the infinite case. This length was, subsequently, used, care being taken that the cylinder was placed in the sample holder so that the r-f coil was at the center of the cylinder length. The dotted line in Fig. 6 (also in Figs. 7, 8, and 9), represents the field H'' for an infinite cylinder if the interaction factor q were zero. For a spherical sample H'' would be always zero if q were zero. Hence, it is seen that for Fe^{++} ions in H_2O the proton q value is positive—the measured q being $+1.1$ for both the spherical and "infinite" transverse cylindrical samples.

Figure 7 illustrates what was found in general; that for a given paramagnetic ion, the field H'' depends strongly on the resonating nucleus. Another finding illustrated in Fig. 7 is that H'' is the same, within the experimental error, for the proton and deuteron resonances in water. It would, of course, be expected that the magnetization field shift for two isotopes in the same chemical compound would be identical. The proton and deuteron isotopes furnish a good test of this in that the radiofrequencies for resonance in the same magnetic field H_0 are considerably different (29.5 and 4.5 Mc, respectively, in a field $H_0 = 6975$ gauss), so that if the magnetization field were in any way influenced by the r-f field, this should be observed.

Figure 8 illustrates two findings. First, as shown by the fluorine resonance shifts in HF and SbF_3, we see that H'' may depend not only on the resonating nucleus but also on the chemical compound containing the nucleus. (The shift shown in Fig. 8 for the fluorine resonance in HF on addition of Co^{++} ions was the largest of any observed.) Second, Fig. 8 confirms the fact that the field H'' is linearly proportional, within experimental error, to the applied field H_0 for a given concentration of paramagnetic ions. Thus, the ratio of the field strengths is 3.0, and the ratio of H'' at the two fields is 2.7.

Figure 9 shows one of the few cases in which a negative interaction factor was measured.

A complete summary of the experimental results is given in Table VII as a tabulation of interaction factors.

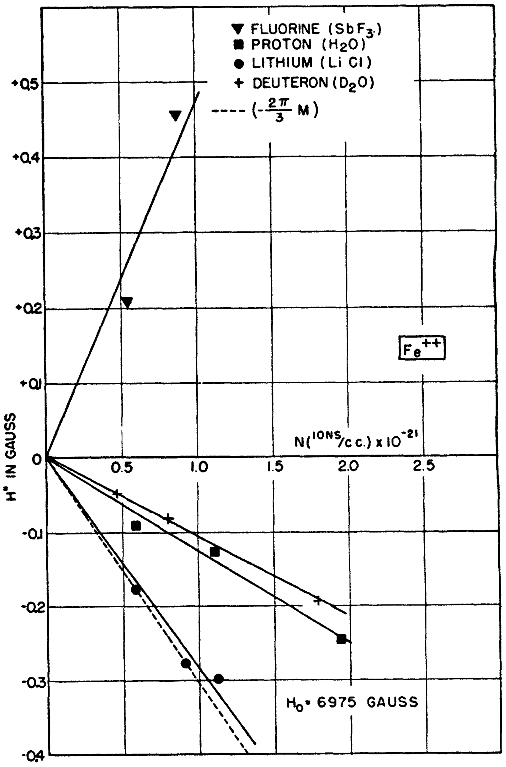

FIG. 7. Illustration of the dependence of H'' on resonating nucleus. $FeCl_2$. "Infinite" cylinder.

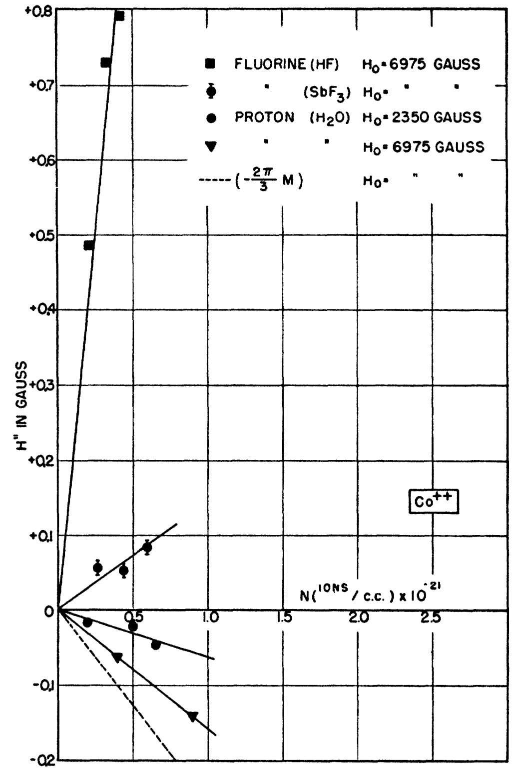

Fig. 8. Illustration of the dependence of H'' on chemical compound containing resonating nucleus and of the linear dependence of H'' on applied field H_0. $CoCl_2$. "Infinite" cylinder.

The general consistency of the experimental data is indicated by the agreement between the interaction factors for the corresponding cylindrical and spherical cases. The amount of disagreement can be attributed partly to general experimental error and partly to meniscus effect and lack of perfect sphericity for the spherical sample. For this reason, more confidence should be given the q values listed for the cylindrical case.

It was felt originally by the author that the deviations in the nuclear resonance shifts from those which would be predicted naively on the basis of the simple Debye theory (i.e., $q=0$), might be similar in origin to those in the electric case. When the concentration of molecules with electric dipole moments is sufficiently high, it is thought that several molecules combine to form a temporary unit very likely having a resultant electric dipole moment quite different from that of a single molecule. However, the magnetic analogy is not a very good one, since such association effects would constitute a sort of incipient ferromagnetism which, although not unknown for paramagnetic salts, particularly at extremely low temperatures, would not be expected to occur in solutions, due to the higher magnetic dilution.

It was suggested by Professor E. M. Purcell (private communication), that there might be a spin-dependent, electron exchange process occurring between the paramagnetic ions and the normally diamagnetic ions containing the resonating nuclei, whence the latter would for a small fraction of the time be in a paramagnetic state. This exchange process would have to take place at a much higher frequency than the nuclear Larmor frequency, otherwise abnormal resonance line broadening would be observed. This explanation gives a simple reason for the fact that interaction factors are large for a negative ion such as fluorine and small for a positive ion such as lithium. In the former case, the exchange process would be facilitated by electrostatic attraction between the positive paramagnetic ions and the negative fluorine ions, while, in the latter case, there would be a mutual repulsion of the positive ions. Although this exchange process might play an important part in some cases, it would not seem to allow for the exceptional cases where a negative value of q is measured.

The most plausible theory for explaining the type of shifts observed was suggested by Dr. N. Bloembergen. It is well known that the paramagnetic ions in crystals are often under the influence of strong and generally asymmetric electric fields due to neighboring atoms. Under the influence of these fields, the paramagnetic ions may exhibit a magnetic anisotropy; that is, the measured susceptibility will depend on the orientation of the crystal axis with respect to the applied magnetic field. Bloembergen suggested that there might be a

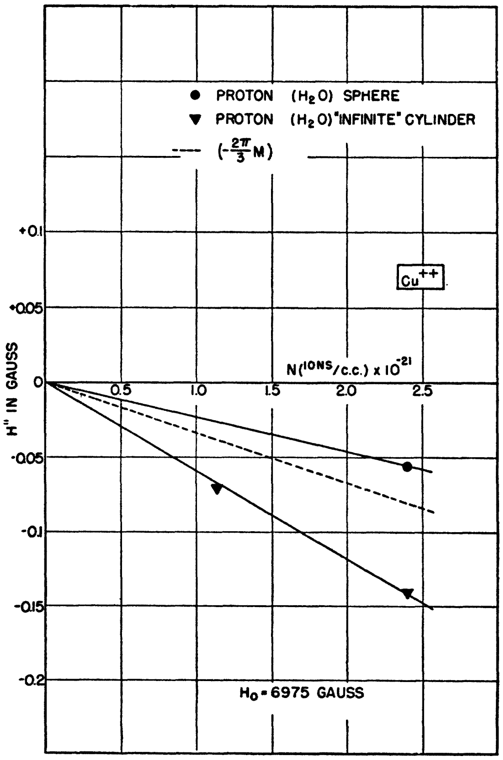

Fig. 9. Example of a negative interaction factor. $CuCl_2$ added to H_2O. Proton resonance.

similar directional effect on the g-factors of paramagnetic ions in liquids. A paramagnetic ion in a liquid is subjected to strong varying electric fields. These are responsible for the quenching of the orbital momentum, so that the effective magnetic moment of the ion is close to the "spin only" value. Although the average electric field in the liquid will have spherical symmetry, the field at any instant will deviate from the average. From an analysis made on this basis,[40] defining g as the value obtained from susceptibility measurements, i.e., $g=\mu_{\mathrm{eff}}/[S(S+1)]^{\frac{1}{2}}$, the following expression for q is obtained:

$$q=(16\pi b^3/45a^3)(g_{\parallel}^2-g_{\perp}^2)/g^2, \tag{10}$$

where $g_{\parallel}$ and $g_{\perp}$ are effective g values of the paramagnetic ion depending on whether the instantaneous angle between the axis of the internal electric field acting at the paramagnetic ion and the magnetic field H_0 is 0° or 90°, and b^3/a^3 is a rather crudely introduced geometrical factor, the magnitude of which depends on the closeness of approach between the ions of the liquid which contain the resonating nuclei and the added paramagnetic ions. Although Eq. (10) would clearly not offer any type of quantitative check of the experimental q values, it would seem that $g_{\parallel}^2-g_{\perp}^2$ for a liquid would have a value comparable to those observed in crystals. Also from Eq. (10), one would expect that the q value for a positive ion would be smaller than the value for a negative ion because of the difference in the average distance of approach in the two cases. Lastly, this theory would account for negative as well as positive q values, depending only on the relative magnitudes of $g_{\parallel}$ and $g_{\perp}$.

A confirmation of this theory is provided by the following experimental finding of Proctor and Yu.[18] For a solution of NH_4NO_3, without paramagnetic ions, the N^{14} resonance from the NH_4^+ complex was found to come at a higher magnetic field than the N^{14} resonance from the NO_3^- complex (for a fixed frequency). On addition of Mn^{++} ions the difference in field between the two resonances is found to increase. This is best explained by assuming that the q value for the NO_3^- complex is greater than that for the NH_4^+ complex as would be expected from the results given above.

VI. DISCUSSION: ATTAINABLE PRECISION IN NUCLEAR MOMENT MEASUREMENTS

Now that the various factors influencing the positions of nuclear resonances have been considered, an attempt will be made to analyze each factor as to its effect on the attainable precision in the measurement of nuclear moments by the resonance absorption and nuclear induction methods. Since the first successful application of these two methods in 1945, many nuclear moment ratio measurements have been published; the quoted precision ranges from about 1 part in 10^3 to 1 part in 10^6.

TABLE VII. Experimental values of the interaction factor q for "infinite" transverse cylindrical and spherical sample shapes.

Paramagnetic ion	Resonating nucleus	Chemical compound	q value cylinder	sphere
Ni^{++} (Cl_2)	H^1	H_2O	-1.0	-0.1
	F^{19}	SbF_3 (aq)	2.3	2.2
	Li^7	LiCl (aq)	0.9	
Ni^{++} (SO_4)	H^1	H_2O	0.0	0.0
	F^{19}	SbF_3 (aq)	3.5	2.5
	Li^7	LiCl (aq)	0.3	
Co^{++} (Cl_2)	H^1	H_2O	0.7	0.9
	F^{19}	SbF_3 (aq)	3.1	2.3
	F^{19}	HF (aq)	19.0	
Cu^{++} (Cl_2)	H^1	H_2O	-1.8	-1.5
Fe^{++} (Cl_2)	H^1	H_2O	1.1	1.1
	D^2	D_2O	1.2	
	F^{19}	SbF_3 (aq)	5.1	4.0
	Li^7	LiCl (aq)	0.0	
Mn^{++} (Cl_2)	Li^7	LiCl (aq)	0.5	
Cr^{+++} (Cl_3)	H^1	H_2O	-3.0	
	F^{19}	HF (aq)	6.0	
Er^{+++} (Cl_3)	H^1	H_2O	1.1	

Considering the evidence accumulated in the present paper, it would appear that the precision indices quoted in some of these measurements have been unjustifiably high. There is little doubt, however, that the resonance absorption and nuclear induction methods will replace all others for the high precision measurement of nuclear moments, and it is for this reason that the different factors which influence the precision of these measurements must be carefully noted and taken into account.

We first consider the effect of the atomic diamagnetic shielding correction on the precision to which the ratio of the nuclear moment μ_x to the proton moment μ_p can be measured. Setting $\mu_x/\mu_p=M$, $\omega_x/\omega_p=\Omega$, $H_x'/H_0=X$, and $H_p'/H_0=P$, we have

$$M=(I_x/I_p)\Omega_0=(I_x/I_p)\Omega_m(1-P)/(1-X), \tag{11}$$

where Ω_0 is the ratio of the Larmor precession frequencies in the same magnetic field H_0, and Ω_m is the measured ratio which will differ from the former because of the diamagnetic shielding. Differentiating Eq. (11), remembering that X and P are small compared with unity, gives closely

$$\Delta M/M=(\Delta\Omega_m/\Omega_m)+\Delta(X-P). \tag{12}$$

By employing a simple heterodyne technique in which a small beat frequency and one of the original frequencies are measured, rather than the two original frequencies, Ω_m can always be determined to a precision of 1 part in 10^5 or better. This assumes that the frequency-measuring meter is limited in precision to about 1 part in 10^4 as is usually the case. With more elaborate technique, it is possible to measure a frequency ratio to a precision of 1 part in 10^6 to 1 part in 10^7. Hence, we

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[40] N. Bloembergen and W. C. Dickinson, Phys. Rev. **79**, 179 (1950).

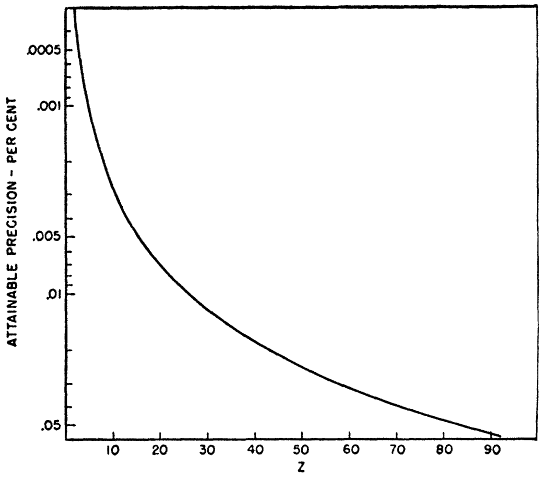

FIG. 10. Attainable precision in a nuclear moment ratio measurement as limited by the accuracy to which the atomic diamagnetic correction is known.

assume that the first term on the right side of Eq. (12) can always be neglected as compared with the second term. From an analysis of the accuracy of Hartree wave functions, it was estimated that values of H'/H_0 computed from these functions can be trusted to 5 percent.[15] Considering the agreement between the computation of Ramsey and that of Hylleraas and Skavlem for the shielding constant H_p'/H_0 of molecular hydrogen, it can also probably be given a maximum uncertainty of 5 percent.[41] Since $P \ll X$ for all but the lightest elements (e.g., $X/P = 11$ for ${}_5B$), Eq. (12) reduces to

$$\Delta(\mu_x/\mu_p)/(\mu_x/\mu_p) \cong 0.05 H_x'/H_0. \tag{13}$$

Figure 10 is a plot of Eq. (13) and gives the *limiting* precision attainable in a measurement of μ_x/μ_p considering the present accuracy to which the atomic diamagnetic correction can be quoted.[42]

An estimate will next be made of the largest concentration of paramagnetic ions that can be used in a ratio measurement if the resulting shift of resonances is to be neglected. For this purpose, we may assume conservatively that no resonance shifts will exceed the extraordinarily large shift found for the F^{19} resonance in HF on addition of Co^{++} ions (Fig. 8). This shift was 1 gauss in an applied field $H_0 = 7000$ gauss for a concentration $N(Co^{++}) = 0.5 \times 10^{21}$ ions/cc. Doubling this, to take into account the possibility that the shift occurring in the one nuclear species is of opposite sign to that in the other, gives a total shift of 0.028 percent for a 0.83-molar paramagnetic solution. Hence, for a measurement with precision 0.01 percent, a molarity of 0.3 would allow a shift equal to the precision limit. We might place as an upper limit a shift equal to $\frac{1}{3}$ the precision limit. Hence,

precision = 0.01 percent: maximum allowable
paramagnetic molarity of sample = 0.1 molar.

This allows a large safety factor, since most of the observed shifts were only of the order of $\frac{1}{10}$ to $\frac{1}{5}$ of the shift assumed in the above calculation.

Unfortunately, the effect of second-order paramagnetism on the precision of a nuclear moment measurement cannot be predicted in advance. It is necessary to compare the nuclear resonance position in several different molecular compounds containing the nucleus being measured. Even if no shifts are observed, it cannot be concluded with certainty that the second-order paramagnetism is zero for those compounds. However, it is improbable that this field would be the same in several different molecules—particularly if the atom containing the resonating nucleus did not exhibit the same valency in all the molecules examined. For atoms such as Li, Na, and Al, where no second-order paramagnetic shifts were observed for a series of compounds, it is safe to assume that the nuclei are contained in simple ions, so that the atomic diamagnetic correction may be directly applied. Of course, this is also the case when the resonating nucleus is contained in a free atom (e.g., He^3, $Xe^{129,131}$).

For current theoretical considerations regarding nuclear structure it is important that very precise values of the nuclear moment ratios of isotopic pairs be available. Fortunately, it is these ratios which can be measured most precisely by the resonance method. When both isotopes are contained in the same chemical compound, the magnetic shielding field will be the same for both nuclei.[43] It has been shown in the present paper that the shift of nuclear resonance due to added paramagnetic ions is closely the same for an isotopic pair (Fig. 7). Hence, it would seem that the nuclear moment ratio of an isotopic pair can be measured to a precision limited only by the resonance line widths and by the attainable precision in the measurement of the frequency ratio.[44]

An individual nuclear moment, of course, cannot be

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[41] If H_2O or mineral oil is used for the proton standard, we must assume that the comparison with the proton resonance in molecular hydrogen has been made.

[42] For the heavy elements ($Z \gtrsim 70$), the relativity effect makes it impossible to attach a 5 percent accuracy to the diamagnetic correction. The numerical coefficient in Eq. (13) would, hence, be slightly higher in this region. (See reference 15.)

[43] W. G. Proctor and F. C. Yu (private communication), have confirmed the validity of this statement for the isotopic pairs $N^{14,15}$ and $Cl^{35,37}$.

[44] Small discrepancies exist between some recent high precision measurements of the deuteron-proton moment ratio. Whether they have physical significance or are due to experimental causes has not yet been ascertained. A further investigation is now in process by T. Wimett at M.I.T.

quoted to a higher precision than that to which the standard moment used in the experiment is known. Recent measurements of the proton moment, involving different physical principles, give:

$$\mu_p = (1.4100 \pm 0.0002) \times 10^{-23}\ \text{ergs/gauss}^{45}$$
$$\mu_p = (15.2106 \pm 0.0007) \times 10^{-4} (e\hbar/2mc)^{46}$$
$$\mu_p = (15.2100 \pm 0.0002) \times 10^{-4} (e\hbar/2mc)^{47}$$
$$\mu_p = 2.79273 \pm 0.00006 (e\hbar/2M_p c).^{48}$$

All of these values include the diamagnetic correction for atomic hydrogen ($H'/H_0 = 1.8 \times 10^{-5}$), although the proton was contained in a molecule (H_2O, NaOH, mineral oil, and H_2O, respectively). This is probably of no importance considering the precision of the first value of μ_p, but the last three values will be improved when the actual molecular shielding correction is determined by a comparison with H_2. §

I wish to express my appreciation to Professor F. Bitter for the encouragement and guidance he has given during this investigation. Thanks are given to Professor N. F. Ramsey and Dr. J. Benedict for the privilege of several valuable discussions.

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[45] Thomas, Driscoll, and Hipple, Phys. Rev. **78**, 787 (1950).

[46] H. Taub and P. Kusch, Phys. Rev. **75**, 1481 (1949).

[47] J. H. Gardner and E. M. Purcell, Phys. Rev. **76**, 1262 (1949).

[48] Sommer, Thomas, and Hipple, Phys. Rev. **80**, 487 (1950).

§ *Note added in proof:* This comparison has been made recently by H. A. Thomas, Phys. Rev. **80**, 901 (1950). On the basis of Ramsey's calculated magnetic shielding value of 2.68×10^{-5} for H_2, he obtains 2.62×10^{-5} for H_2O and 2.84×10^{-5} for mineral oil (Petrolatum U.S.P.—Light). Also, H. S. Gutowsky and R. E. McClure, Phys. Rev. (to be published), have measured these shifts. Again based on Ramsey's value for H_2, they obtain 2.71×10^{-5} for H_2O and 3.05×10^{-5} for mineral oil (Nujol). The discrepancy between the H_2O values is not appreciably greater than the probable errors involved in the two measurements. However, Gutowsky (private communication) finds that the greater part of the difference between the mineral oil values is real and due to the different types of mineral oil used. Using an average value for the H_2O and mineral oil corrections the last two values of μ_p given above become, respectively, 15.2101×10^{-4} and 2.79275.

PHYSICAL REVIEW VOLUME 81, NUMBER 5 MARCH 1, 1951

An Increase of the Primary Cosmic-Ray Intensity Following a Solar Flare*

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(Received October 24, 1950)

An increase of 15.4±4.3 percent has been detected in the intensity of cosmic rays at altitudes between 95,000 and 100,000 feet, occurring approximately 19 hours after the commencement of the outstanding solar flare of May 10, 1949. The observations were conducted with a quadruple-coincidence counter train inclined at a zenith angle of 60°, and containing an interposed absorber of 1 cm of Pb. Complications introduced by atmospheric absorption, possible directional asymmetry, and multiplicative effects preclude a precise evaluation of the increase in terms of absolute primary particle intensity. The effect of the particles emitted by the sun during the chromospheric eruption does not manifest itself at altitudes below approximately 55,000 feet.

I. INTRODUCTION

SUDDEN increases in the cosmic ray intensity coincident with the occurrence of a solar flare have been registered on four occasions by instruments operating near sea level or at relatively low altitudes.[1–6] From the variation in the effect with altitude and latitude, as recorded by Compton-Bennett ionization chambers, which were completely shielded by 12 cm Pb, it was concluded[6] that the largest of these increases was attributable to the nucleonic component produced by relatively low energy charged primary particles accelerated by some solar mechanism.

It has been reported[7] recently that the rate of production in photographic emulsions of stars having 3 to 8 prongs exceeded the normal value at an altitude of 95,000 feet by 50±13 percent during the period 18:48–22:30 GMT on May 11, 1949, about 23 hours following the occurrence of the outstanding solar flare[8] of May 10, 1949. This bright chromospheric eruption, of importance 3+, the greatest possible on the scale of the International Astronomical Union, commenced at 20:00–20:03 GMT. Solar noise radiometer, ionospheric, and magnetic field measurements had all returned to normal before 22:20 GMT May 10, 1949, at which time the flare had subsided, but not disappeared, on

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

Extract from a dissertation submitted to the Graduate Council of Temple University in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

[1] S. E. Forbush, Phys. Rev. **70**, 771 (1946).

[2] A. Duperier, Proc. Phys. Soc. (London) **57**, 473 (1945).

[3] D. W. N. Dolbear and H. Elliott, Nature **159**, 58 (1947).

[4] H. V. Neher and W. C. Roesch, Revs. Modern Phys. **20**, 350 (1948).

[5] D. C. Rose, Phys. Rev. **78**, 181 (1950).

[6] Forbush, Stinchcomb and Schein, Phys. Rev. **79**, 501 (1950).

[7] Lord, Elston, and Schein, Phys. Rev. **79**, 540 (1950).

[8] A. H. Shapley and R. M. Davis, Science **110**, 159 (1949).

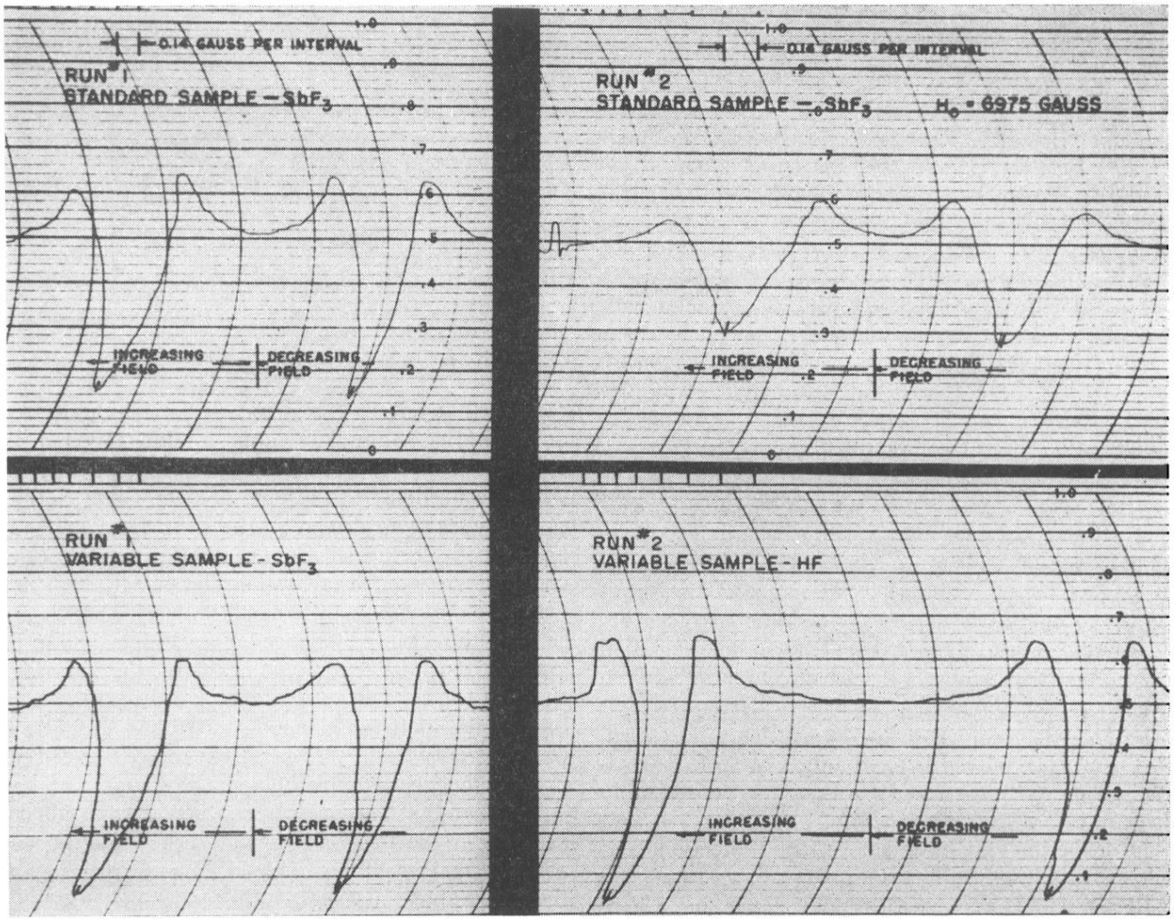

FIG. 2. Record of two runs. In Run No. 1 the F^{19} resonance in SbF_3 was simultaneously observed in both bridges. In Run No. 2 the variable sample was changed to HF, the standard sample remaining SbF_3. Note the large resonance shift. The SbF_3 resonance curves are wider in Run No. 2 than in Run No. 1 due to the nonlinearity in sweep rate of the motor-driven rheostat. In Run No. 2, due to the wider separation of the two HF resonances, a larger section of the rheostat had to be traversed. The SbF_3 resonances were traversed at the end of the rheostat where the rate was slowest, hence, the broadness.

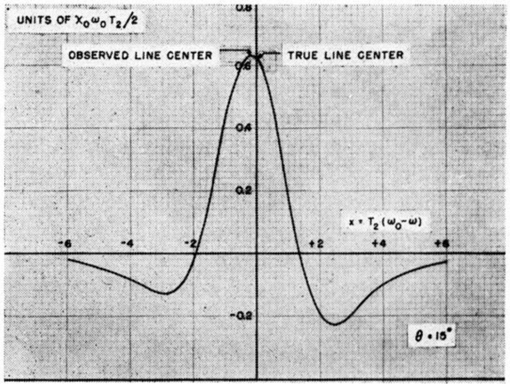

FIG. 4. Line shape (gaussian), of an "impure" nuclear magnetic resonance. If $d\chi''/dx$ represents the derivative of an absorption curve and $d\chi'/dx$ the derivative of a dispersion curve, the equation of the above curve is $(d\chi'/dx)\cos\theta + d\chi''/dx \sin\theta$, where θ is the circuit "balance factor." Any experimental curve more distorted than the one shown above was rejected.