Determination of Nuclear Gyromagnetic Ratios I

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Nuclear magnetic resonance absorption peaks have been observed for seventeen nuclear species. The technique used in observing the resonances involves the use of super-regenerative oscillators and is different in many respects from the bridge method of Purcell and the nuclear induction method of Bloch. Resonance absorption has been observed for the following nuclei: H^1, H^2, Li^7, Be^9, B^{11}, F^{19}, Na^{23}, Al^{27}, P^{31}, Cu^{63}, Cu^{65}, Br^{79}, Br^{81}, Rb^{85}, Rb^{87}, I^{127}, and Cs^{133}. By comparison of various resonance peaks with the proton resonance peak observed simultaneously in the same magnetic field, values for nuclear gyromagnetic ratios and nuclear magnetic moments can be determined in terms of the gyromagnetic ratio and the magnetic moment of the proton. The following frequency ratios have been obtained:

Nucleus	Ratio of resonance frequency to proton frequency in same magnetic field
H^2	0.15355 ±0.03%
Li^7	0.38862 ±0.02
B^{11}	0.32076 ±0.03
F^{19}	0.94086 ±0.02
Na^{23}	0.26454 ±0.03
Al^{27}	0.26062 ±0.04
Cu^{63}	0.26515 ±0.02
Cu^{65}	0.28404 ±0.03
Br^{79}	0.25059 ±0.02
Br^{81}	0.27014 ±0.02
Rb^{87}	0.32718 ±0.05
I^{127}	0.20003 ±0.04

I. INTRODUCTION

SINCE the pioneer work of Purcell and his collaborators[1] on nuclear magnetic resonances in solids and liquids, several different methods have been developed for observing these resonances. Purcell employed a radiofrequency bridge, one arm of which included a coil containing a sample mounted in a strong magnetic field H, which could be modulated at a low audiofrequency. When the Larmor condition

$$h\nu = \mu H_R/I = gH_R \qquad (1)$$

was realized by variation of H, radiation of radiofrequency ν was absorbed by the sample and the bridge was unbalanced. By proper adjustment of the bridge, either absorption or dispersion effects could be observed.[2] In the contemporaneous work of Bloch and his colleagues[3–5] an entirely different approach to the problem was employed. Whereas in Purcell's method, it was necessary to work at extremely low radiofrequency power levels in order to avoid "saturation effects," which appear as a result of the de-population of the lower energy levels, Bloch's method involved the use of high radiofrequency power and involved adiabatic processes. In Bloch's experiment the sample was placed in a coil mounted with its axis perpendicular to a strong magnetic field; this coil formed a part of a radiofrequency oscillator. Resonances were observed by noting voltages induced at resonance in a second coil mounted with its axis perpendicular to the axis of the first coil and to the direction of the strong magnetic field; this is the so-called "nuclear induction" experiment. The ultimate sensitivities of the two methods are apparently the same.

Since the original work of Purcell[1] and Bloch,[3] other methods of detecting nuclear magnetic resonances have been developed by Roberts,[6] Pound,[7] and more recently by Torrey.[8]

In the work of Roberts, resonances were observed by noting the variation occurring in the output of a super-regenerative oscillator when condition (1) was realized; Roberts also reported experiments with an auto-dyne oscillator, which he found to be less sensitive than the super-regenerative oscillator. Pound has developed an ingenious method of detection which embodies principles similar to those involved in Roberts' work with the auto-dyne oscillator; Pound's system is arranged to permit an automatically controlled slow variation of frequency in a constant magnetic field and has been particularly effective in searching for magnetic resonances. An amplifier with an extremely narrow pass band can be used. Torrey has recently reported the development of a method using pulses of radiofrequency radiation; this method seems particularly well suited for studies of spin-lattice relaxation times.

Our own experiments[9–11] have been done with super-regenerative oscillator circuits operated under conditions apparently different from those used in Roberts' experiment. A super-regenerative oscillator consists of a vacuum-tube circuit which would execute normal oscillations at a radiofrequency were it not for an audiofrequency "quench voltage" which is applied to one of the tube elements in such a manner as to prevent the radiofrequency oscillations from attaining their normal amplitude; this type of oscillator can also be considered an amplitude-modulated radiofrequency oscillator with the amplitude-modulation occurring at the quench-

* Charles E. Coffin Fellow.
[1] E. M. Purcell, H. C. Torrey, and R. V. Pound, Phys. Rev. **69**, 37 (1946).
[2] Bloembergen, Purcell, and Pound, Phys. Rev. **73**, 679 (1948).
[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] A. Roberts, Rev. Sci. Inst. **18**, 845 (1947).
[7] R. V. Pound, Phys. Rev. **72**, 527 (1947).
[8] H. C. Torrey, Phys. Rev. **75**, 1326 (1949).
[9] J. R. Zimmerman and D. Williams, Phys. Rev. **73**, 94 (1948).
[10] J. R. Zimmerman and D. Williams, Phys. Rev. **74**, 1885 (1948).
[11] J. R. Zimmerman and D. Williams, Phys. Rev. **75**, 198 (1949).

voltage frequency. The spectrum of a super-regenerative oscillator consists of a central frequency ν_0 plus a large group of "side-bands" of frequency $\nu_0 \pm n\nu_q$, where n is an integer and ν_q is the quench frequency. In our work, ν_0 was of the order of 7 mc/sec. and the quench frequency was of the order of 10 kc/sec.; thus, the spectrum of our oscillator consisted of a central frequency of approximately 7 mc/sec. plus a large number of side-bands spaced at 10-kc/sec. intervals. The relative intensities of the various spectral components depend upon the conditions at which the oscillator is operated; for example, the relative intensities are functions of the bias voltages of the various electrodes in the tube, the quench voltage, the quench frequency, etc.

The central frequency may be easily identified by the method mentioned by Roberts;[6] small changes in quench frequency produce changes in side-band frequency but do not produce appreciable changes in the central frequency ν_0. In normal operation of our equipment, the central-frequency component was more intense than any of the side bands. Any of the frequencies

$$\nu = \nu_0 \pm n\nu_q \quad (n=0, 1, 2, 3\cdots) \tag{2}$$

is capable of producing a resonance absorption provided condition (1) is fulfilled. This fact can be used to advantage in *search* for resonances: for example, if the power level of the central frequency is so high as to produce saturation, one or more of the side-bands can be used for observing the absorption. Furthermore, as the search process involves changing the magnetic field H slowly while watching an oscilloscope display, it is usually easier to recognize a *series* of absorption peaks corresponding to the frequencies in (2) than to recognize a single peak which might be lost in the random noise signals.

Variations in the output of the super-regenerative oscillator when resonance occurs may be produced by absorption processes involved in transitions between energy levels or by the effects of nuclear-induction signals on the oscillator itself. Both effects are probably present; Roberts[6] reports that in his apparatus the latter effect was dominant. The relative magnitude of the circuit responses to the two effects depends upon conditions of operation. In our work, the radiofrequency power level was kept low, and the effects of resonance upon the circuit was analogous to the introduction of a resistive element in the tank circuit; the principal effect was a large variation of power level which could readily be observed by means of an a-m receiver. The chief effect observed was therefore more closely related to the Purcell experiment than to the Bloch experiment.

A small change in oscillation frequency could also be observed at resonance by means of an f-m receiver. The observed variation in frequency was small compared to the observed variation in amplitude. That the amplitude variation was dominant was further verified by comparison of the proton signal observed by means of an a-m receiver with the proton signal observed by means of an audio amplifier circuit which was insensitive to variations in radiofrequency. Although the a-m receiver proved more sensitive, the shapes of the proton signals obtained by the two methods showed marked similarity.

In initial search for nuclear magnetic resonances only one oscillator coil was placed in the strong magnetic field. In quantitative measurements two mutually perpendicular coils were mounted in the magnetic field; a proton sample was placed in one coil and a sample containing another nucleus was placed in the other coil. By simultaneous observation of resonances for the proton and for the other nucleus, the gyromagnetic ratio of the second nucleus could be determined in terms of the gyromagnetic ratio of the proton. Experimental details are given in the following section.

II. EXPERIMENTAL METHODS

The sample, S_x, to be investigated was placed within a small coil, L, in the homogeneous field of an electromagnet, M. This coil was the tank coil of a simple LC oscillator, the oscillations being interrupted by an external 10–15-kc quench voltage from an audio oscillator. When the condition of resonance, $h\nu = gH_R$, was realized by varying H, the energy absorbed from the tank circuit of the oscillator caused a marked change in the output of the oscillator. This change in output can be detected by several methods, two of which will be described briefly. A more detailed description of the apparatus will be given elsewhere in the near future.

(A) Direct Audio Detection

A block diagram of the experimental arrangement used in this method is shown in Fig. 1a. An audio bandpass amplifier, designed to suppress both 60-c and 10-kc frequencies, was used to detect any variation of the audio components in the plate current of the oscillator. By subjecting H_0 to a small 60-c modulation, amplitude variations occurring at resonance could be observed as amplitude signals on an oscilloscope as

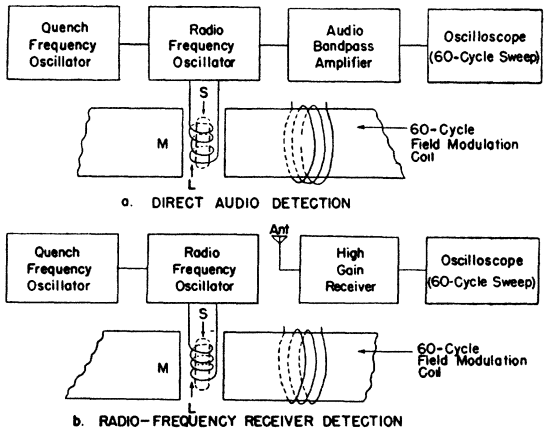


FIG. 1. Block diagram of apparatus used in search for nuclear magnetic resonances.

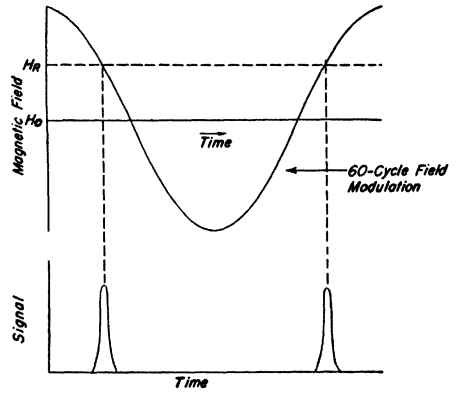


FIG. 2. Magnetic field applied to sample. H_0 is the large field (6000–7000 gauss) applied to sample. A small 60-cycle modulation (10–30 gauss) is superposed. Resonance absorption occurs at field H_R. On the oscilloscope employed trace length intervals $|\Delta l|$ are proportional to magnetic field variations $|\Delta H|$ when H_0 is adjusted so that $H_0=H_R$.

shown schematically in Fig. 2, where for a given frequency of the LC oscillator, H_R corresponds to the resonance condition $h\nu=gH_R$. These two oscilloscope "pips" coalesce into a single one if H_0 is increased to the value where H_R becomes tangent to the field modulation curve. Since no r-f tuning was required by this method, search for nuclear resonances could be carried out by varying the frequency of the r-f oscillator and holding H_0 constant.

(B) Radio Frequency Receiver Detection

A block diagram of the apparatus used in this method of detection is shown in Fig. 1b. When nuclear absorption occurs, there is a decrease in the radiated r-f power. This change in output of the oscillator was observed by means of a high gain receiver. The quench frequency modulation appearing in the output of the receiver was filtered out by the I.F. crystal band selector unit of the receiver. In searching for nuclear resonances, high sensitivity was obtained by using a crystal I.F. band width of about 300 cycles. Once resonances were found, the sensitivity of the oscillator was adjusted by variation of quench frequency and voltage so that the I.F. band width in the receiver could be broadened to 1000 cycles. This width was large enough to give a good representation of the true resonance absorption curves. As in the previous method, H_0 was subjected to a small 60-c modulation. The audio output of the receiver was then displayed on the oscilloscope. The sweep of the oscilloscope was synchronized with the magnetic field modulation, and the 60-c sweep was of such a wave form as to give a horizontal beam displacement approximately linear in time; departures from linearity were such that length intervals Δl on the horizontal trace were proportional to magnetic field variations ΔH in the immediate vicinity of the "pips" when $H_R=H_0$ in Fig. 2.

(C) Search Techniques

In initial search for nuclear resonances, the receiver detection method was employed because of its greater sensitivity as compared with that of the audio detection method. In Fig. 3 are shown typical absorption peaks observed with the "search" oscillator. A narrow crystal I.F. band width of 300 cycles/sec was used to increase the sensitivity of the apparatus. No attempt was made to obtain a true representation of the actual shape of the resonance curves for these pictures. In making frequency measurements, to be explained later, a broad I.F. band width was necessary to give an accurate reproduction of the absorption peaks. Some of the curves in Fig. 3 have two peaks and others appear to have only one. This can be explained by the fact that, for the narrow crystal I.F. setting, the amplitude of one peak can be enhanced and the other one suppressed by slightly detuning the receiver. The transient effect known as the "wiggles" can also be seen in several of the photographs in Fig. 3. These "wiggles" always occur *after* the magnetic field has passed through resonance; comprehensive discussions of this phenomenon have been given elsewhere.[2,12]

(D) Frequency Measurements

Making use of both the audio and receiver detection methods as shown in Fig. 4, one can measure the gyromagnetic ratio of an unknown nucleus in terms of the proton gyromagnetic ratio. Suppose that a sample, S_x, of an unknown nucleus is placed in the coil of oscillator B and a sample, S_p, of the proton is placed in the coil of oscillator A. With oscillator B remaining at a fixed frequency, the magnetic field, H_0, is then varied until a nuclear resonance indication appears on the oscilloscope trace. Then the frequency of oscillator A is varied until the proton resonance occurs at the same magnetic field H_R. These two resonances are observed simultaneously on an oscilloscope by use of an electronic switch. A typical double trace of F^{19} and H^1 is shown in Fig. 5. The resonance "pips" of the lower trace (H^1) are brought into coincidence with those of the upper trace by varying the frequency of oscillator A, the coil of which contains the proton sample.

It can be seen from Fig. 5 that two smaller proton resonances occur in addition to the two main resonances. These are merely side-band absorptions characteristic of super-regenerative oscillators described earlier in this paper. The side-bands serve several useful purposes. If the magnetic field H_0 is varied over a small range, the distance between one of the main resonances and its accompanying sideband will remain constant provided a portion of the oscilloscope sweep is linear with respect to magnetic field variations. Provided a portion of the sweep is found to be linear in gauss, the total sweep in gauss can be estimated, since the sweep is also linear in

[12] B. A. Jacobsohn and R. K. Wangsness, Phys. Rev. **73**, 940 (1948).

frequency and the distance between the main resonance and its sideband is merely the frequency of the audio quench voltage.

In Fig. 5a, the total sweep, i.e., twice the amplitude of the 60-c modulation, is 25 gauss; the distance between the main proton resonance "pips" and the corresponding sidebands is about 4 gauss or 15 kc.; the half-power widths of the F^{19} and H^1 resonances are approximately 1 gauss and 0.5 gauss, respectively. Figure 5b shows an expanded trace of the coincident F^{19} and H^1 amplitude "pips." This expansion gives an indication of what might be termed the resolving power of the instrument. As indicated in the discussion of frequency measurements and field inhomogeneities given below, the half-power resonance widths of the unknown samples apparently are not at present the limiting factors in the accuracy of the experiment. The proton resonance half-width is less than that of any of the nuclei to be measured.

Using the comparison method, one can write $h\nu = gH$ and $h\nu^1 = g^1H$ where ν is the frequency of oscillator B, and ν^1 is the frequency of oscillator A, g is the gyromagnetic ratio of nuclei in S_x, and g^1 is the gyromagnetic ratio of the proton. If the field H_0 is homogeneous throughout the region of S_p and S_x, then $g = (\nu/\nu^1)g^1$. When an oscilloscope double trace as in Fig. 5 is obtained, frequency measurements of oscillator A and oscillator B are obtained by tuning the frequencies of these oscillators, ν^1 and ν, in on the frequency calibration receiver of Fig. 4, and then zero beating these frequencies with a calibrated GR 805C signal generator. The coincident matching shown in Fig. 5 is displayed while frequency measurements are being made and serves to monitor the oscillator frequencies. Any drift in frequency of either oscillator A or B would be easily observed if such drift were to occur. This method of comparison, of course, is independent of magnetic field

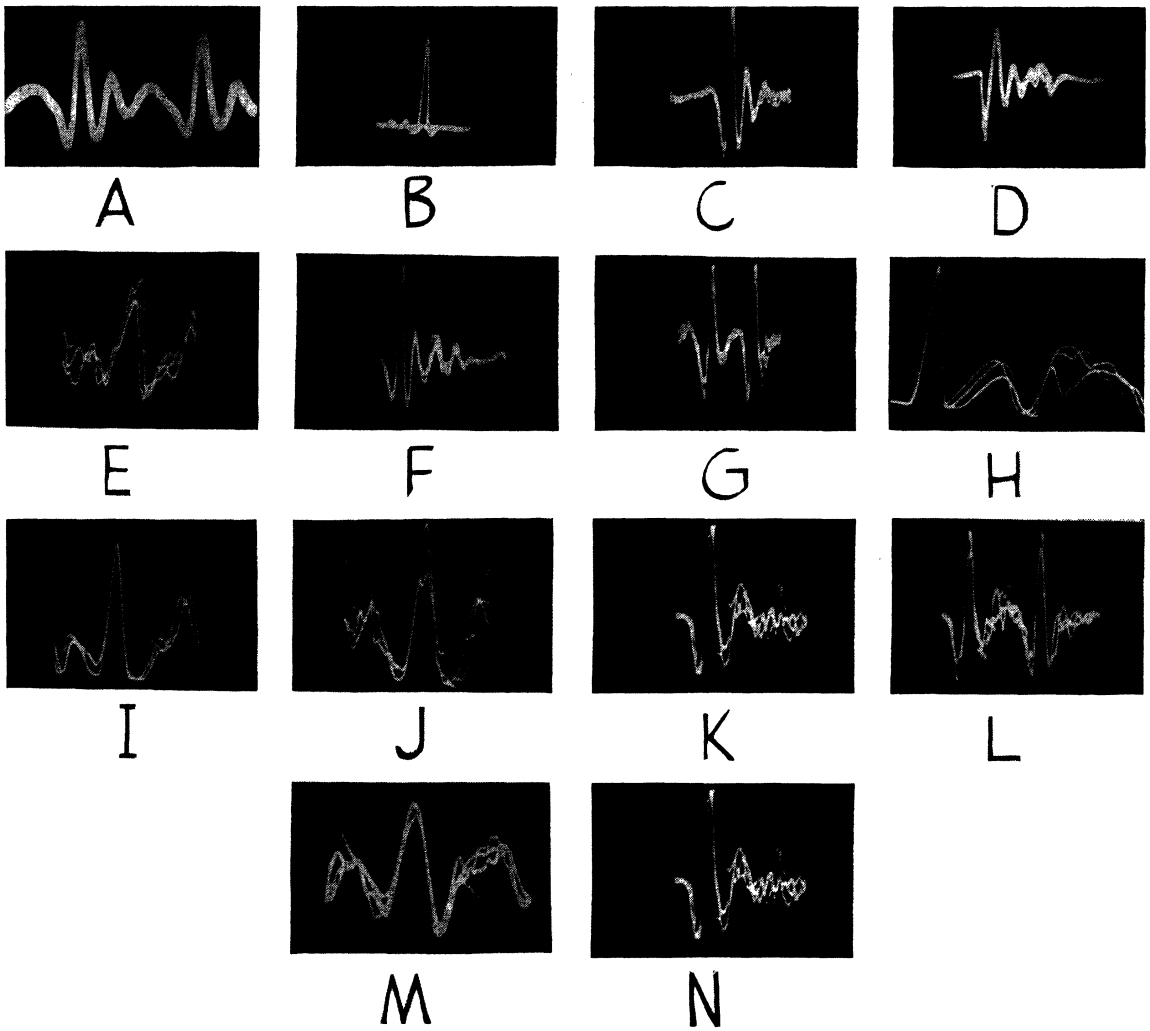


FIG. 3. Oscilloscope displays observed in search for resonances: (A) proton, (B) proton (audio detection), (C) deuteron, (D) lithium, (E) boron,[11] (F) fluorine,[19] (G) sodium,[23] (H) aluminum,[27] (I) copper,[63] (J) copper,[65] (K) bromine,[79] (L) bromine,[81] (M) rubidium,[87] and (N) iodine.[127] (Note: the oscilloscope sweep in (B) is different from that described.)

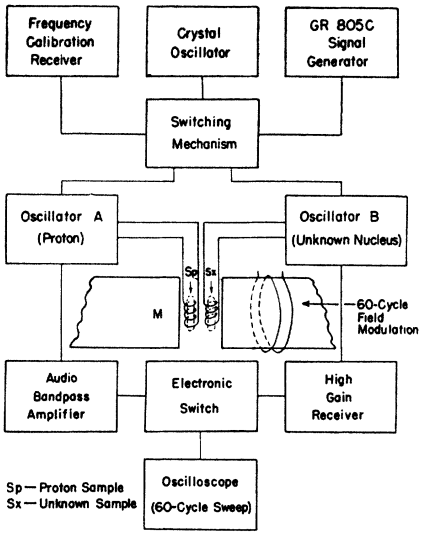


FIG. 4. Block diagram of apparatus used in determining frequency ratios. The coils containing samples S_p and S_x are actually placed with their axes perpendicular to each other and to the applied field.

fluctuations once the resonance "pips" have been matched.

For calibrating the signal generator, a 100-kc crystal oscillator is used as a secondary standard, the one-hundredth harmonic being tuned to WWV at 10 mc. Then, in terms of the harmonics of the crystal oscillator, the signal generator is calibrated at intervals of 0.1 mc over the expected frequency ranges of the oscillators A and B. By means of a vernier attachment, dial readings can be made to 0.001 percent of the operating frequency. Allowing a three-hour warm-up period, frequency measurements can be repeated with an accuracy of 0.01 percent.

(E) Field Inhomogeneities

The maximum inhomogeneity of the magnetic field over the region occupied by *one* of the samples can be estimated by observing directly the half-power resonance width of the protons in the given sample. Since even for the relatively large samples used, half-widths of proton signals are less than 0.5 gauss in a magnetic field of 6500 gauss for both S_p and S_x in Fig. 4, uncertainties due to this effect are small in comparison with other effects which limit the accuracy of the experiment.

The mean value of the magnetic field in the region occupied by S_p as compared with that in the region occupied by S_x is, however, of considerable significance in evaluating the gyromagnetic ratios. Suppose that S_p and S_x are both aqueous solutions of some compound containing unknown nuclei X. Then, first by comparing the H^1 resonance in oscillator A with the X resonance in B, and second by reversing this comparison procedure, the "inhomogeneity" between the two regions can be readily determined.

Let the superscript r denote the first comparison procedure, the superscript s denote the second comparison procedure, g^1 be the gyromagnetic ratio of H^1, g be the gyromagnetic ratio of X, H_A be the magnetic field in the region of S_p in Fig. 4, H_B be the magnetic field in the region of S_x in Fig. 4.

Then, for procedure r,

$$\begin{aligned} h\nu_B{}^r &= gH_B{}^r, \\ h\nu_A{}^r &= g^1H_A{}^r, \end{aligned} \tag{3}$$

and for procedure s,

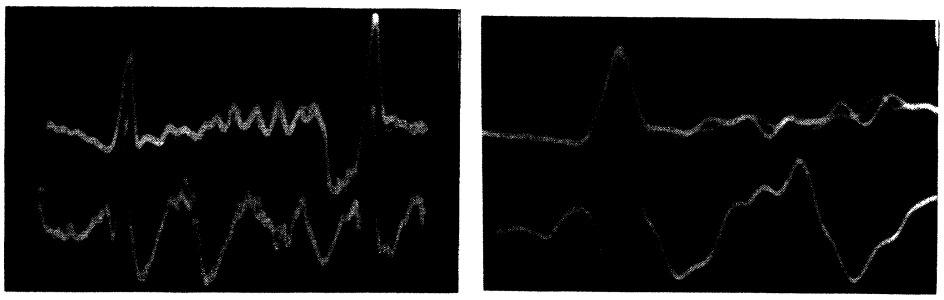
$$\begin{aligned} h\nu_B{}^s &= g^1H_B{}^s, \\ h\nu_A{}^s &= gH_A{}^s. \end{aligned} \tag{4}$$

The magnetic field was in the range 6000–7000 gauss for all resonance measurements of unknown nuclei reported here, and the magnetization curve of the magnet material over this field range is essentially linear. To a good approximation over this range of magnetic field values, the ratio H_A/H_B is constant and the relationship between H_A and H_B may be represented by

$$\begin{aligned} H_A{}^r &= (k+1)H_B{}^r, \\ H_A{}^s &= (k+1)H_B{}^s, \end{aligned} \tag{5}$$

where k is the constant of inhomogeneity. A solution of Eqs. (3)–(5) yields two useful expressions,

$$\begin{aligned} k+1 &= (\nu_A{}^r\nu_A{}^s/\nu_B{}^r\nu_B{}^s), \\ g &= (\nu_B{}^r/\nu_A{}^r)(k+1)g^1. \end{aligned} \tag{6}$$



A B

FIG. 5. Oscilloscope displays used comparing resonance frequencies of fluorine^{19} and the proton. In each photograph the upper trace shows the resonance for fluorine and the lower shows the proton resonance. The half-width of the proton peak is approximately 0.5 gauss.

In the determination of $(k+1)$, ten resonance frequency measurements using procedure r and ten comparisons using procedure s were obtained, the frequencies used in s corresponding to those used in r. The average value of $(k+1)$ obtained was

$$(k+1)\ (\text{average}) = 1.0011 \pm 0.0001.$$

Since both S_x and S_p cover the same regions of the magnetic field for all measurements, this factor of inhomogeneity was assumed to be the same for all gyromagnetic ratio measurements.

III. EXPERIMENTAL RESULTS

(A) Accuracy of Frequency Measurements

The experimental results for H^2, Li^7, B^{11}, F^{19}, Na^{23}, Al^{27}, Cu^{63}, Cu^{65}, Br^{79}, Br^{81}, Rb^{87}, I^{127} are summarized in Table II. Magnetic resonances for the nuclei Be^9, P^{31}, Rb^{85}, and Cs^{133} have also been observed by the receiver detection method of Fig. 1b. The resonance frequencies of these latter nuclei are being measured and will be reported later.

Each value listed in Table II represents the average of ten careful frequency-ratio determinations. Each of these determinations was made at a different value of the magnetic field H_0. A sample set of data for F^{19} is shown in Table I. The average deviation of the frequency ratio with sign disregarded was 0.02 percent.

In general, the average deviations for the individual measurements of a given unknown nucleus are about 0.03 percent. Since the error in estimating the inhomogeneity of the magnetic field might be as much as 0.01 percent, and since the frequency calibration of the GR 805C signal generator is allowed a variation of 0.01 percent of the measured frequency, it is easily seen that for any accuracy beyond that of the present average deviation, further refinement in frequency measurements and in the measurement of field inhomogeneities must be made. These factors, frequency measurements and determinations of field inhomogeneity, are the limitations of the accuracy in the present experiments.

(B) Summary of Results Obtained on Various Samples

A discussion of the results obtained on various samples containing the nuclei under investigation is desirable, since the intensity of the resonance peaks is strongly dependent upon the material used as a sample.

The basic datum obtained for any given nucleus in the present experiment is the ratio of its resonance frequency to the resonance frequency of the proton in the same *applied* magnetic field. In comparing our results with those of others, we have chosen to reduce their published results to a similar frequency ratio. Some of the earlier results have been stated in terms of the proton magnetic moment as determined by Millman and Kusch,[13] and others have been stated in terms of this value after application of the Schwinger[14] correction. Some of the values given in published summaries[15,16] include a correction for diamagnetism of the electrons,[17] which should be applied in calculation of a nuclear magnetic moment in view of the fact that the magnetic field at the nucleus is slightly different from the applied field. In view of the recent determination of the absolute value of the proton moment,[18] it seems desirable at present to use the measured frequency ratio as a basis of comparison. Actual values of the nuclear moments can be obtained in terms of the new value for the proton by using measured values of the spin and applying a suitable diamagnetism correction.

TABLE I. Typical data obtained in resonance frequency measurements (Fluorine[19]).

Fluorine frequency ν^{19}	Proton frequency ν^1	Observed ratio ν^{19}/ν^1	Corrected ratio $(\nu^{19}/\nu^1)(k+1)$
25.192	26.816	0.93944	0.94047
24.839	26.424	0.94002	0.94105
24.913	26.506	0.93990	0.94093
25.195	26.805	0.93994	0.94097
25.300	26.913	0.94007	0.94110
24.932	26.534	0.93962	0.94065
24.540	26.120	0.93951	0.94054
24.943	26.536	0.93997	0.94100
24.827	26.413	0.93995	0.94098
24.938	26.534	0.93985	0.94088
		Average	0.94086

Each unknown sample S_x had a volume of about 6 cc, corresponding to physical dimensions of 5 cm in length and of 1.25 cm in diameter. The proton sample, S_p, consisted of about 3 cc of water placed in a test tube 2.5 cm. in length and 1.25 cm in diameter. Both samples, S_x and S_p, always occupied the same regions of the magnetic field throughout the measurements of all nuclei reported here. A paramagnetic salt was sometimes used in S_x to reduce the relaxation time of the nuclei, thereby raising the upper limit of the power level of the oscillator beyond which saturation of the nuclear energy levels would occur. The frequency of oscillator B in Fig. 4 was set at values corresponding to resonance values of the magnetic field in the range 6000–7000 gauss.

Hydrogen[2]. The nuclear resonance of H^2 was observed in a 95 percent solution of deuterium oxide. Rabi's group[19,15] using the method of molecular beams was the first to measure accurately the gyromagnetic ratio of H^2. Their value for the frequency ratio is 0.1535 ± 0.001. Bloch[20] has recently announced a very precise measure-

[13] S. Millman and P. Kusch, Phys. Rev. **60**, 91 (1941).

[14] J. Schwinger, Phys. Rev. **73**, 416 (1948).

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

[16] J. Mattauch, *Nuclear Physics Tables* (Interscience Publishers, Inc., New York, 1946).

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

[18] Thomas, Driscoll, and Hipple, Phys. Rev. **75**, 902 (1949).

[19] Kellogg, Rabi, Ramsey, and Zacharias, Phys. Rev. **56**, 728 (1939).

[20] Bloch, Levinthal, and Packard, Phys. Rev. **72**, 1125 (1947), $(\mu'/\mu^2 = 3.257195 \pm 0.00002)$.

TABLE II. Summary of results.

Nucleus	Frequency ratios corrected $(\nu/\nu^1)(k+1)$
H^2	0.15355±0.00005
Li^7	0.38862±0.00002
B^{11}	0.32076±0.00009
F^{19}	0.94086±0.00017
Na^{23}	0.26454±0.00007
Al^{27}	0.26062±0.00011
Cu^{63}	0.26515±0.00005
Cu^{65}	0.28404±0.00009
Br^{79}	0.25059±0.00005
Br^{81}	0.27014±0.00005
Rb^{87}	0.32718±0.00016
I^{127}	0.20003±0.00007

ment which gives 0.1535063±0.00001 for the frequency ratio. Bitter,[21] using a bridge absorption method, reports a value of 0.153510±0.000003. Our corresponding value is 0.15355±0.00005.

Lithium^7. An aqueous solution of $Li(C_2H_3O_2)$ was used as the sample for observing nuclear resonance of Li^7. About 1 cc of the saturated solution of $CuCl_2$ was added to the lithium solution to act as a paramagnetic catalyst. With a radiofrequency level satisfactory for other materials, saturation of nuclear levels in the lithium sample occurred even in the presence of paramagnetic ions. However, this saturation does not occur for the side-band frequencies of the quenched r-f oscillator. Making use of the side-band characteristic of super-regenerative oscillators, one can vary the magnetic field H_0 to nuclear resonance corresponding to a side-band frequency instead of the center frequency of the r-f oscillator. The side-band frequency used in this case was 10.0 kc higher than the center frequency. A previous measurement[15] of the gyromagnetic ratio of Li^7 gives a value of 0.38873±0.00017 for the frequency ratio. The corresponding value found here is 0.38862±0.00002.

Boron^{11}. Strong resonances of both Na^{23} and B^{11} were observed in an aqueous solution of $Na_2B_2O_4$. However, only the measurements of B^{11} were obtained with this compound. There was no noticeable saturation of the nuclear levels at resonance. From molecular beam measurements[15] a value of 0.3081±0.0009 for the frequency ratio is obtained. In a recent private communication, F. Bitter reports a value of 0.32085±0.00006. These values are to be compared with the value 0.32076 ±0.00009 obtained in the present work.

Fluorine^{19}. Nuclear resonances were first observed in an organic liquid $CF_3-CCl=CCl-CF_3$. Much stronger resonances have since been observed in an aqueous solution of SbF_3. In the organic liquid saturation effects set in at a much lower power operating level of the r-f oscillator than does the aqueous solution of the antimony trifluoride. Previous measurements[15] gave a frequency ratio of 0.9410±0.0009 as compared with the value of 0.94086±0.00017 measured at this laboratory.

[21] Bitter, Alpert, Nable, and Poss, Phys. Rev. 72, 1271 (1947).

Sodium^{23}. Na^{23} seems to give a strong resonance in most soluble sodium salts. Resonances were observed in aqueous solutions of NaI, NaBr, $NaAsO_2$, and $Na_2B_2O_4$. Although the concentration of Na^{23} nuclei in the $NaAsO_2$ solution was about the same as the concentration of Na^{23} nuclei in the other mentioned solutions, the nuclear resonance of Na^{23} in $NaAsO_2$ is much stronger than that which occurs in the others. Rabi[15] has reported a value corresponding to a frequency ratio of 0.26494 ±0.00028. In a private communication, F. Bitter reports a value of 0.26450±0.00003. Measurements made in the present study give the value 0.26454±0.00007.

Aluminum^{27}. Nuclear magnetic resonance absorption has been observed in aqueous solutions of both $AlCl_3$ and $Al_2(SO_4)_3$. Gyromagnetic ratio measurements were made with the $AlCl_3$ solution. Rabi[15] and his co-workers have reported a value giving a frequency ratio of 0.2603±0.0007. The average value determined here, 0.26062±0.00011, compares favorably with the above result.

Copper^{63} *and Copper*^{65}. The sample used was a mixture of Cu_2Cl_2 and a solution of $CuCl_2$. A considerable gain in nuclear absorption intensities of both Cu^{63} and Cu^{65} isotopes is obtained by the addition of the cupric ions. This increased intensity is, as earlier pointed out by R. V. Pound,[22] due to the cupric ion which decreases the relaxation time. Pound[23] has published the following frequency ratios for the isotopes of copper: $\nu(Cu^{63})/\nu(Na^{23})=1.0022$ and $\nu^{65}/\nu^{63}=1.0711$. Corresponding ratios computed from Table II are $\nu/(Cu^{63})/\nu(Na^{23})=1.0023$ and $\nu^{63}/\nu^{65}=1.0713$.

Bromine^{79} *and Bromine*^{81}. Nuclear resonances of both bromine isotopes were observed in NaBr and KBr aqueous solutions. Measurements were made with the NaBr solution. The only values published on the bromine isotopes are those reported by Pound.[23] He obtained $\nu^{81}/\nu^{79}=1.0778$ and $\nu^{81}/\nu(Na^{23})=1.0209$. Our corresponding values obtained from Table II are 1.0780 and 1.0212, respectively.

Rubidium^{87}. An aqueous solution of Rb_2CO_3 was employed for observing the nuclear resonance of Rb^{87}. It should be mentioned here that resonance absorption was also observed for Rb^{85} with the same sample; and, although Rb^{87} is only about one-third as abundant as Rb^{85}, the intensity of the Rb^{87} peak observed in the present experiment is considerably greater than that of Rb^{85}. Our value for the frequency ratio is 0.32718 ±0.00016 as compared with 0.3266±0.0010 by molecular beam methods.

Iodine^{127}. The absorption line resulting from I^{127} was first found by using an aqueous solution of NaI as a sample. A much stronger resonance was obtained from an aqueous solution of KI. Gyromagnetic measurements were made using the KI solution. Pound,[24] using his

[22] R. V. Pound, Phys. Rev. 73, 523 (1948).
[23] R. V. Pound, Phys. Rev. 72, 1273 (1947).
[24] R. V. Pound, Phys. Rev. 73, 1112 (1948).

recording radiofrequency spectrometer, found the ratio of the frequency of the I^{127} line to that of Na^{23} in a sample of NaI to be 0.75664. We have determined the same frequency ratio to be 0.75615.

IV. DISCUSSION OF RESULTS

From the results obtained thus far we are led to conclude that the sensitivity of the super-regenerative oscillator method of observing nuclear magnetic resonances is comparable with the sensitivities of the bridge and nuclear induction methods. The ultimate limitations of sensitivity have not yet been determined; these are of course determined by the effective noise factor associated with the oscillator and receiver or amplifier. The noise power can be decreased by decreasing the pass band of the receiver or amplifier. With 60-c modulation, the band width must of necessity be large, approximately 1000 cycles for a fair presentation of resonance line shapes; by decreasing the modulation frequency, one can decrease the band width. In observing a weak signal due to resonance absorption, there is an optimum radiofrequency power level which is probably determined by the spin-lattice relaxation time of the material used as a sample. The optimum power level had to be determined experimentally in the present work and there is at present no satisfactory method by which it can be calculated; it can be raised by adding magnetic catalysts. Further experimental work must be done before accurate estimates of ultimate sensitivity can be made.

An interesting check of some of the work done in the present study was made possible by the recent report of Bitter,[25] which appeared after the completion of our experimental work. Using two radiofrequency bridges, Bitter determined the ratio of resonance frequencies of several nuclei to the resonance frequency of the proton in the same magnetic field. In Table III is given a comparison of our results with those given by Bitter. In making the comparison, we have taken the ratio of our values for various nuclei to the corresponding values given by Bitter. It will be noted that in every case the results obtained by the two methods are in agreement within the limits stated. Except for B^{11} and Rb^{87} the frequency ratios obtained in the present work were slightly higher than the ones reported by Bitter. The average percentage difference between the values obtained by the two methods is 0.015 percent, which is extraordinarily good agreement in view of the fact that the details of the two experiments were quite different.

TABLE III. Comparison of present results with Bitter's results.

Nucleus	Present study / Bitter's results	Uncertainty: Present study	Uncertainty: Bitter
Li^{7}	1.0000	±0.0001	±0.0001
B^{11}	0.9997	3	2
Na^{23}	1.0002	3	1
Al^{27}	1.0002	4	1
Cu^{63}	1.0003	2	2
Cu^{65}	1.0004	2	2
Br^{81}	1.0004	2	3
Rb^{87}	1.0000	4	2

There is considerable room for improvement in our present methods of frequency measurements. If practical improvement in frequency measurements can be made, a more accurate determination of inhomogeneity factor k can also be made. It may then be advantageous to use smaller test samples in the hope of further reducing the widths of the observed resonance peaks. However, the agreement between our present results and those of Bitter indicates that fairly reliable results can be obtained with the super-regenerative oscillator even in its present form.

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[25] F. Bitter, Phys. Rev. **75**, 1326 (1949).

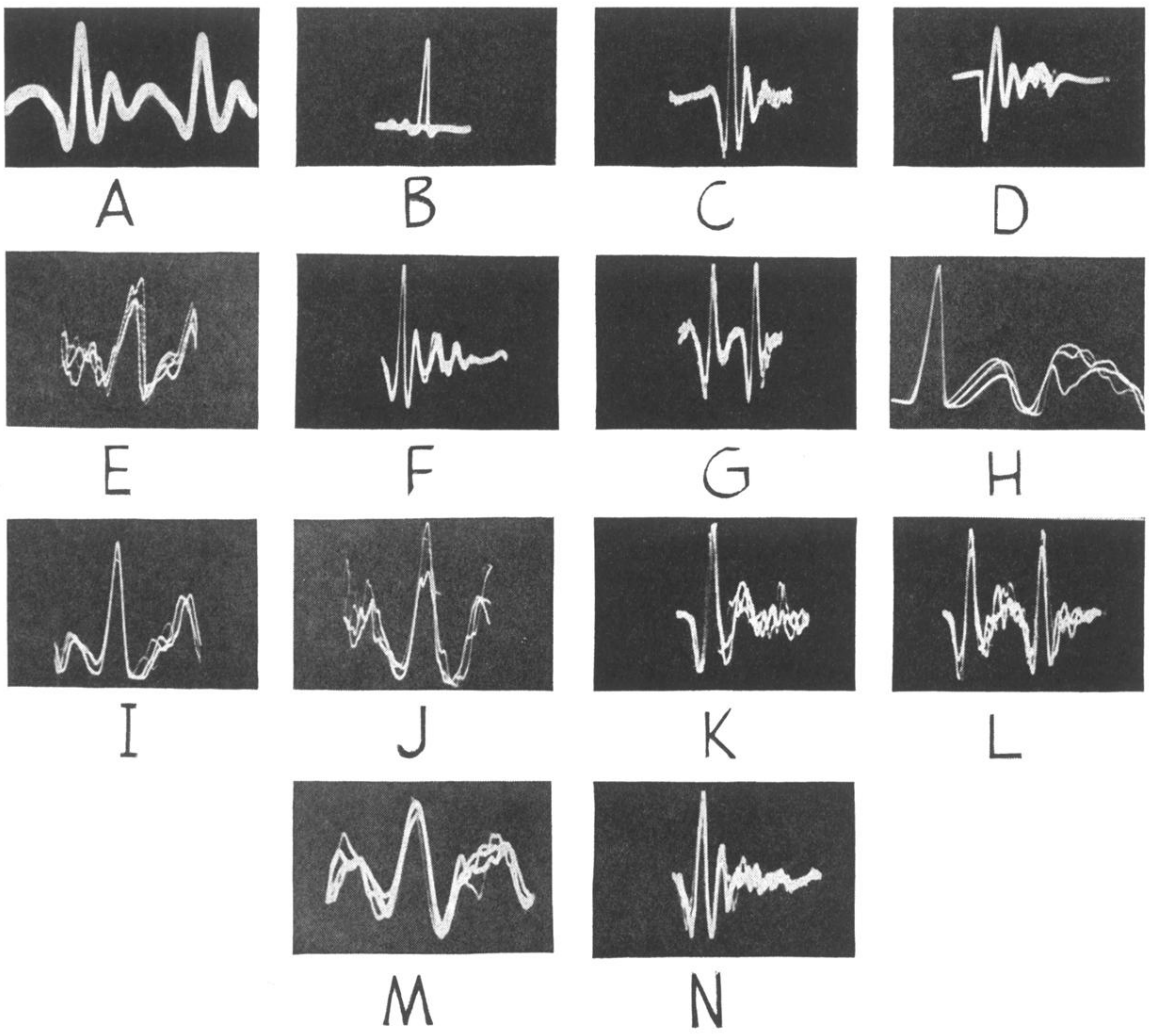
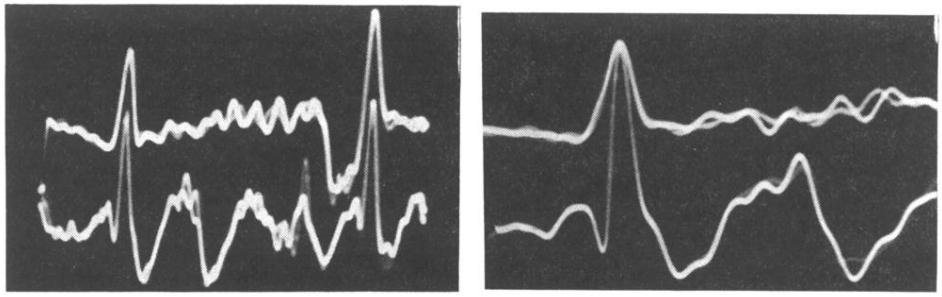


FIG. 3. Oscilloscope displays observed in search for resonances: (A) proton, (B) proton (audio detection), (C) deuteron, (D) lithium, (E) boron,[11] (F) fluorine,[19] (G) sodium,[23] (H) aluminum,[27] (I) copper,[63] (J) copper,[65] (K) bromine,[79] (L) bromine,[81] (M) rubidium,[87] and (N) iodine.[127] (Note: the oscilloscope sweep in (B) is different from that described.)



A B

FIG. 5. Oscilloscope displays used comparing resonance frequencies of fluorine[19] and the proton. In each photograph the upper trace shows the resonance for fluorine and the lower shows the proton resonance. The half-width of the proton peak is approximately 0.5 gauss.