ation, which could easily cause falsification of the relative intensities.

We wish to acknowledge helpful discussions with Professor L. Nordheim and the assistance of Mr. R. L. Carter in obtaining the photographs.

Note added in proof: Through a private communication, Dr. J. M. Jauch has informed us of an error in his intensity formulae (reference 5). The errors involve the values of $Q(J)$, $A_{J-1,J}$ and $A_{J,J+1}$, which should be

$$Q(J)=\frac{(2J-1)(J-1)(J+1)^3+(2J+3)(J+2)J^3}{2J+1}+[J(J+1)-1]^2$$

$$A_{J-1,J}=K^2(2J-1)/3J^3(J+1)$$

$$A_{J,J+1}=K^2(2J+3)/3J(J+1)^3$$

rather than the expressions given in the original paper. The corrected forms give values in agreement with the results of the present paper.

PHYSICAL REVIEW VOLUME 73, NUMBER 7 APRIL 1, 1948

The Hyperfine Structure of Hydrogen and Deuterium*

JOHN E. NAFE AND EDWARD B. NELSON
Columbia University, New York, New York

(Received December 17, 1947)

The atomic-beam magnetic resonance method has been applied to measure the h.f.s. separation of the ground state of H and D by observing frequencies of the r-f field required to induce transitions among certain of the magnetic levels of the h.f.s. multiplets in magnetic fields of the order of 1 gauss. The resonance minima were of the theoretical width for transitions which are field independent in the first order. For deuterium we find $\nu_D = 327.384 \pm 0.003$ Mc which agrees with our previously reported value within the precision claimed for that quantity. For hydrogen we find $\nu_H = 1420.410 \pm 0.006$ Mc which is less than the value previously reported by 0.06 percent. The ratio of the measured h.f.s. separations, ν_H/ν_D, is 4.33867 ± 0.00004.

The h.f.s. separations, ν_H and ν_D, may be calculated from known values of the magnetic moment of the proton, μ_p, and the magnetic moment of the deuteron, μ_d. The measured ν_H and ν_D are larger than the calculated values by 0.24 percent and 0.26 percent, respectively. The ratio ν_H/ν_D may be calculated from the known ratio μ_p/μ_d using the ordinary reduced mass correction (discussed in the section entitled "Discussion of Results" of this paper). This ratio is independent of α^2 and R_∞. The calculated ratio is found to be higher than our value by 0.017 percent. This discrepancy is 18 times the probable error in our measurements.

1. INTRODUCTION

THIS paper describes a precision measurement of the hyperfine structure separation of the ground state for the atoms H and D. The experiment depends on the application of the atomic-beam magnetic resonance method previously applied in investigations of the radio-frequency spectra of atoms.[1-3] The h.f.s. separation, ν_H, for hydrogen and the corresponding quantity, ν_D, for deuterium are obtained directly in terms of a fundamental time standard, and depend neither on a knowledge of the gyromagnetic ratio of the nuclear or atomic systems nor on a measurement of magnetic field intensity. None of the experimentally determined constants of physics enter into the measurement.

The h.f.s. splitting of a $^2S_{\frac{1}{2}}$ state in consequence of the perturbing field at the position of the electron produced by the magnetic moment of the nucleus has been calculated by Fermi.[4] The separation, ν, of the h.f.s. doublet terms expressed in absolute frequency units was found to be

$$\nu=(8\pi/3h)(2I+1/I)\mu_0\mu_N\psi^2(0), \qquad (1)$$

where I is the nuclear spin in units of $\hbar$, μ_0 is the Bohr magneton, μ_N is the nuclear magnetic moment in absolute units, and $\psi(0)$ is the

* Publication assisted by the Ernest Kempton Adams Fund for Physical Research of Columbia University.

[1] P. Kusch, S. Millman, and I. I. Rabi, Phys. Rev. **57**, 765 (1940).

[2] S. Millman and P. Kusch, Phys. Rev. **58**, 538 (1940).

[3] J. R. Zacharias, Phys. Rev. **61**, 270 (1942).

[4] E. Fermi, Zeits. f. Physik **60**, 320 (1930).

Schroedinger wave function evaluated at $r=0$. The earliest experiments[5,6] performed in this laboratory for the measurement of the nuclear magnetic moment of the proton, μ_p, and of the deuteron, μ_d, made use of Eq. (1) to compute the values of the moments from indirectly measured values of ν_H and ν_D. More recently, μ_p and μ_d have been obtained from the very accurate measurement by Millman and Kusch.[7] Since these latest values of the moments do not depend on the theory of the h.f.s. splitting they may be used in Eq. (1) to compute values of ν_H and ν_D for comparison with the experimental values reported in this paper.

Preliminary results of these experiments were reported in a letter to the editor of this journal.[8] Further study has revealed that the precision claimed in this letter for the value of ν_H was considerably overestimated. A revised method has been adopted in the case of hydrogen in which the resonance frequency of principal importance for the determination of ν_H is quite insensitive to drift of the magnetic field intensity. The method previously employed in the case of deuterium has not been changed. An improvement in the technique used in the measurement of frequency has resulted in a substantial improvement in the precision of the values of ν_H and ν_D over those previously reported.

2. GENERAL DISCUSSION

The normal, $^2S_{\frac{1}{2}}$, state of H and D is split in the absence of an external magnetic field into an h.f.s. doublet of which one component is specified by a value of the total angular momentum $F=I+\frac{1}{2}$ and the other by $F=I-\frac{1}{2}$, where I is the nuclear spin. Each component of the h.f.s. doublet is split further in the presence of an external magnetic field into $2F+1$ magnetic levels. These are usually designated by the quantum numbers F and m_F appropriate for the region of very weak field ($\mu_0 H \ll \Delta W$). The quantum number m_F, the projection of F along the direction of the magnetic field, may take on any of the values $F, F-1, \cdots, -F$. At higher magnetic field intensities the quantum numbers F, m_F are no longer appropriate because of the partial decoupling between I and J. The projection, m, of the total angular momentum remains quantized, however, and the m associated with a given level is numerically the same as the m_F value specifying the level is very weak field. The energies of the magnetic levels are given, in any magnetic field, by the Breit-Rabi[9] formulae,

$$W_{I\pm\frac{1}{2}} = -\frac{\Delta W}{2(2I+1)} + g_I \mu_0 H m \pm \frac{\Delta W}{2}\left(1+\frac{4mx}{(2I+1)}+x^2\right)^{\frac{1}{2}}, \quad (2)$$

where ΔW is the h.f.s. separation in energy units, g_I is the nuclear gyromagnetic ratio, μ_0 is the Bohr magneton, and H is the magnetic field intensity. The quantity x appearing in this equation is proportional to the magnetic field intensity

TABLE I. The transitions between magnetic levels arising from the h.f.s. doublet of H and D which are observable with the atomic beam apparatus used in these experiments, and the expressions for the transition frequencies.

	Transition $(F, m \leftrightarrow F', m')$	Line designation	Frequency
H	$(1, 1 \leftrightarrow 0, 0)$	π_1	$\nu_H\{\frac{1}{2}(1+x)+\frac{1}{2}(1+x^2)^{\frac{1}{2}}+g_I(\mu_0 H/\Delta W)\}$
	$(1, 0 \leftrightarrow 0, 0)$	σ_1	$\nu_H(1+x^2)^{\frac{1}{2}}$
	$(1, -1 \leftrightarrow 1, 0)$	π_2	$\nu_H\{-\frac{1}{2}(1-x)+\frac{1}{2}(1+x^2)^{\frac{1}{2}}+g_I(\mu_0 H/\Delta W)\}$
D	$(\frac{3}{2}, \frac{3}{2} \leftrightarrow \frac{1}{2}, \frac{1}{2})$	π_1'	$\nu_D\{\frac{1}{2}(1+x)+\frac{1}{2}(1+\frac{2}{3}x+x^2)^{\frac{1}{2}}+g_I(\mu_0 H/\Delta W)\}$
	$(\frac{3}{2}, \frac{1}{2} \leftrightarrow \frac{1}{2}, \frac{1}{2})$	σ_1'	$\nu_D(1+\frac{2}{3}x+x^2)^{\frac{1}{2}}$
	$(\frac{3}{2}, \frac{1}{2} \leftrightarrow \frac{1}{2}, -\frac{1}{2})$ *	π_2'	$\nu_D\{\frac{1}{2}(1+\frac{2}{3}x+x^2)^{\frac{1}{2}}+\frac{1}{2}(1-\frac{2}{3}x+x^2)^{\frac{1}{2}}+g_I(\mu_0 H/\Delta W)\}$
	$(\frac{3}{2}, -\frac{1}{2} \leftrightarrow \frac{1}{2}, \frac{1}{2})$ *		$\nu_D\{\frac{1}{2}(1+\frac{2}{3}x+x^2)^{\frac{1}{2}}+\frac{1}{2}(1-\frac{2}{3}x+x^2)^{\frac{1}{2}}-g_I(\mu_0 H/\Delta W)\}$
	$(\frac{3}{2}, -\frac{1}{2} \leftrightarrow \frac{1}{2}, -\frac{1}{2})$	σ_2'	$\nu_D(1-\frac{2}{3}x+x^2)^{\frac{1}{2}}$
	$(\frac{3}{2}, -\frac{1}{2} \leftrightarrow \frac{3}{2}, -\frac{3}{2})$	π_3'	$\nu_D\{-\frac{1}{2}(1-x)+\frac{1}{2}(1-\frac{2}{3}x+x^2)^{\frac{1}{2}}+g_I(\mu_0 H/\Delta W)\}$

* Unresolved doublet.

[5] I. I. Rabi, J. M. B. Kellogg, and J. R. Zacharias, Phys. Rev. **46**, 157, 163 (1934).
[6] J. M. B. Kellogg, I. I. Rabi, and J. R. Zacharias, Phys. Rev. **50**, 472 (1936).
[7] S. Millman and P. Kusch, Phys. Rev. **60**, 91 (1941).
[8] J. E. Nafe, E. B. Nelson, and I. I. Rabi, Phys. Rev. **71**, 914 (1947).
[9] G. Breit and I. I. Rabi, Phys. Rev. **38**, 2082 (1931).

and is given by

$$x=\frac{(g_J-g_I)\mu_0 H}{\Delta W}, \tag{3}$$

where g_J is the electronic g factor.

The field dependence of the magnetic levels arising from the h.f.s. doublet is shown for $H(I=\frac{1}{2})$ in Fig. 1a and for $D(I=1)$ in Fig. 1b. In the presence of an oscillating magnetic field of appropriate strength, frequency, and polarization with respect to the fixed magnetic field, the atom may undergo a transition from one to another of the magnetic levels consistent with the selection rules, $\Delta F=\pm 1$ or 0, $\Delta m=\pm 1$ or 0. Transitions in which m is unchanged (σ transitions) can be induced if the r-f field has a component parallel to the direction of the steady field. Transitions in which m changes by ± 1 (π-transitions) can be induced if the r-f field has a component perpendicular to the direction of the steady field.

The transitions among the magnetic levels of H and D which have been observed in this experiment, together with the equations for the frequencies of these lines, are listed in Table I. The states involved in a given transition are indicated with the notation $(F, m\leftrightarrow F', m')$ where F, m and F', m' are the quantum numbers which describe the weak field levels from which the levels in question may be derived by an adiabatic transformation. The frequencies of these transitions are designated by the letters π or σ, to indicate the polarization, with numerical subscripts attached in order of decreasing frequency of the lines. These frequencies plotted against x are shown for H in Fig. 2a and for D in Fig. 2b. The magnetic field intensity corresponding to $x=1$ is about 507 gauss for H and about 117 gauss for D.

The lines shown in Fig. 2 which approach ν_H or ν_D in frequency as the magnetic field approaches zero become, in very weak field, the Zeeman components of the multiplet $F\leftrightarrow F-1$. The Zeeman components $(1, -1\leftrightarrow 0, 0)$ for H and $(\frac{3}{2}, -\frac{3}{2}\leftrightarrow\frac{1}{2}, -\frac{1}{2})$ for D cannot be observed with the present apparatus. These components are omitted from Fig. 2. The lines $(1, 0\leftrightarrow 0, 0)$ for H and $(\frac{3}{2}, \frac{1}{2}\leftrightarrow\frac{1}{2}, -\frac{1}{2})$, $(\frac{3}{2}, -\frac{1}{2}\leftrightarrow\frac{1}{2}, \frac{1}{2})$ for D each become independent of the magnetic field near zero field. These are the central components of the two Zeeman patterns. Because these lines are field independent in the first-order, observations of the frequencies of these lines are particularly useful for the precise determination of ν_H and ν_D.

3. METHOD

The value of ν_H has been computed from the results obtained by two different experimental

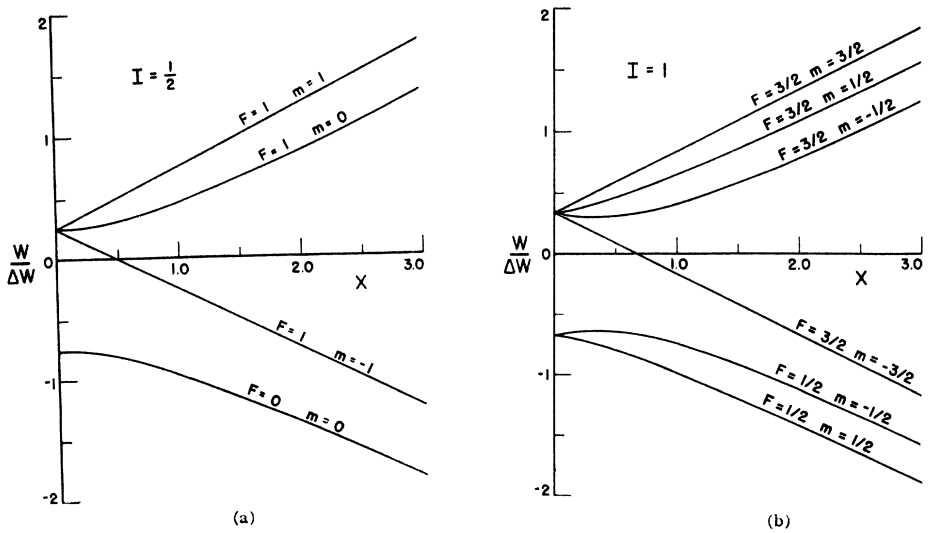

FIG. 1. The magnetic field dependence of the magnetic levels arising from the components of an h.f.s. doublet (a) for the case in which $J=\frac{1}{2}$, $I=\frac{1}{2}$ (hydrogen) and (b) for the case in which $J=\frac{1}{2}$, $I=1$ (deuterium). Each level is labeled by the quantum numbers F and m appropriate in the region of very weak magnetic field.

procedures. The first method utilized the fact that the difference in frequency of the lines $(1, 1\leftrightarrow 0, 0)$ and $(1, 0\leftrightarrow 1, -1)$, at the same value of the magnetic field, gives ν_H directly. This method has the disadvantage that both transition frequencies depend nearly linearly on the magnetic field intensity. The observed lines are broadened because of inhomogeneities in the field. Careful monitoring of the current in the magnet which produces the uniform field is necessary so that the drift of the field intensity may be minimized.

Alternatively, ν_H may be obtained from the measurement in very weak field of the frequencies of the lines $(1, 0\leftrightarrow 0, 0)$ and $(1, 1\leftrightarrow 0, 0)$. The first of these lines is the center component of the Zeeman pattern. Because the frequency of this line depends on field only in the second order, the line may be expected to be broadened very little by field inhomogeneities. The observed frequency should be quite insensitive to drift of the field. This is an important consideration in our experiments where the time required to map the lines may be several hours. The h.f.s. separation may be computed by direct use of the formulae of Table I. It is convenient, however, to use the approximation formula

$$\nu_H = \sigma_1 - \frac{2(\pi_1 - \sigma_1)^2}{\sigma_1}, \tag{4}$$

where π_1 and σ_1 are the observed transition frequencies defined in Table I. At $x=0.01$ for H, for example, π_1 and σ_1 differ by about 7 Mc out of 1420. The term to be subtracted from σ_1 to obtain ν_H, according to Eq. (4), is about 0.070 Mc and the first neglected term about 0.001 Mc.

In the case of D the frequencies of the line $(\frac{3}{2}, \frac{3}{2}\leftrightarrow\frac{1}{2}, \frac{1}{2})$ and of the unresolved doublet line $(\frac{3}{2}, \frac{1}{2}\leftrightarrow\frac{1}{2}, -\frac{1}{2})$; $(\frac{3}{2}, -\frac{1}{2}\leftrightarrow\frac{1}{2}, \frac{1}{2})$ may be combined to find ν_D in substantially the same way that the components of the Zeeman pattern may be used to compute ν_H. The doublet, or central component of the Zeeman pattern, is nearly field independent near zero field. Provided x is sufficiently small

$$\nu_D = \pi_2' - \frac{(\pi_1' - \pi_2')^2}{\pi_2'}, \tag{5}$$

where π_1' and π_2' refer to the frequencies of transitions listed in Table I.

The atomic-beam magnetic resonance method[1] was used to detect the occurrence of the transi-

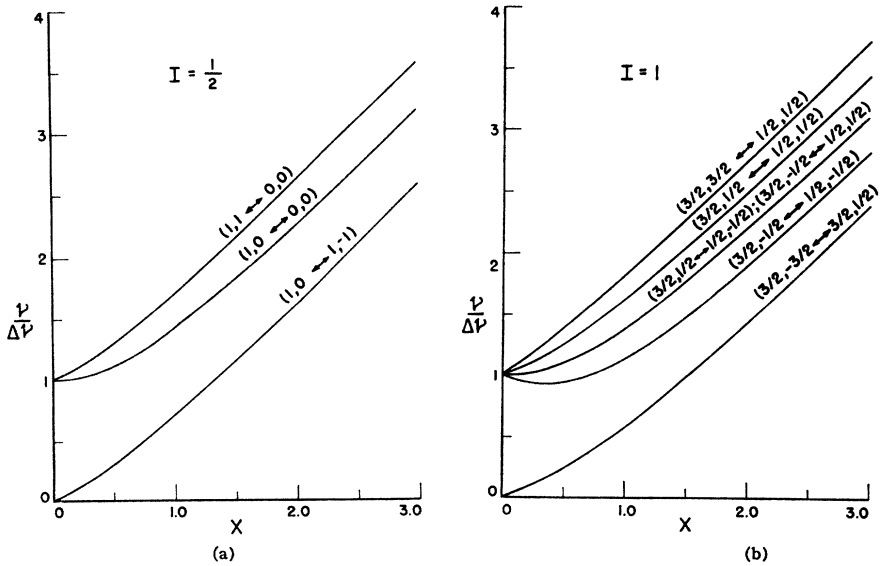

FIG. 2. The magnetic field dependence of the frequencies of transitions between magnetic levels arising from the components of the h.f.s. doublet for (a) hydrogen and (b) deuterium. The frequencies of transitions between levels which in high field have the same value of m_J have been omitted since these transitions are not observable with the apparatus used in these experiments.

tions described above. In this method a collimated beam of atoms in transit from the source to the detector traverses three magnetic fields. The fields of the first, or A magnet, and the last, or B magnet, are inhomogeneous. The directions of these fields are parallel but their gradients are oppositely directed. An atom with a given magnetic moment is acted upon by forces which are oppositely directed in the A and B fields. These fields may be so adjusted that there exist trajectories, leading from the source to the detector, for atoms of all speeds and in all magnetic levels. For focusing to be possible, an atom must remain in the same magnetic level while traversing the magnetic fields. Between the A and B magnets the beam traverses the gap of the third, or C magnet, in which the magnetic field is uniform and parallel to the A and B fields. An oscillating magnetic field is superimposed on the uniform field. At resonance, absorption or stimulated emission occurs for some of the atoms. Having undergone a transition between magnetic levels, the effective magnetic moment of these atoms in the B field is different from that required for focusing. If the change in the moment is sufficiently large (of the order of one Bohr magneton), those atoms which have undergone a transition are defocused and the intensity of the beam at the detector is reduced.

A primary consideration in the design of this apparatus has been the production of an atomic beam of high intensity at the detector. This requires that the source-detector distance be small and that a high beam be used. (The length of the path of the beam in this experiment is unusually short, 33 cm). Both of these requirements lead to a reduction in the deflection of the beam for this is proportional to the gradient of the magnetic field and roughly proportional to the square of the length of the magnets. Certain components of the Zeeman pattern of the multiplet ($F \leftrightarrow F-1$) in both H and D could not be observed because the change in the effective atomic moment of the atom (of the order of a nuclear magneton) was insufficient to cause a measurable defocusing of the beam.

4. APPARATUS

The apparatus used in this experiment is similar to that described by Kusch, Millman, and Rabi[1] for the measurement of the h.f.s. of the alkali atoms, but modified in the manner described by Kellogg, Rabi, Ramsey, and Zacharias[10] to permit the study of gas beams. The vacuum envelope of the apparatus is an 8-inch brass tube which is divided into three sections, each section being pumped separately, so that the magnet chamber is isolated from the higher pressure source chamber. A schematic drawing of the apparatus is given in Fig. 3. When hydrogen was admitted to the system through the source slit at a rate equivalent to 1.8 cc at

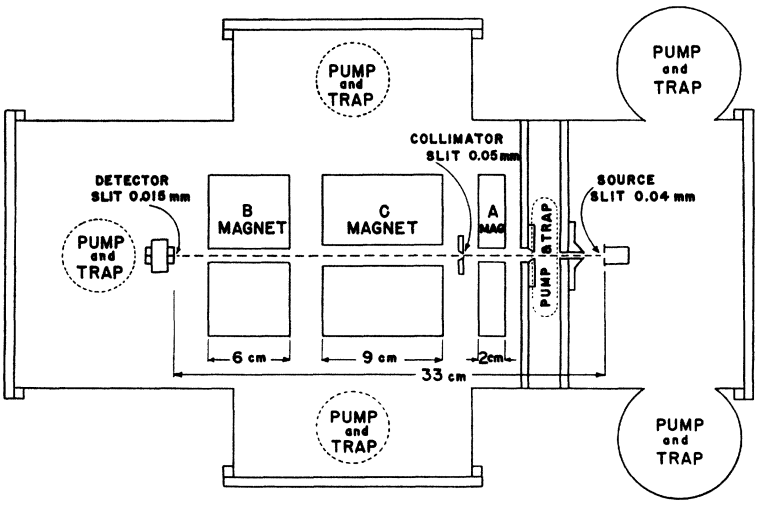

FIG. 3. Schematic diagram of the atomic beam apparatus. Longitudinal dimensions from source to detector are drawn to scale.

[10] J. M. B. Kellogg, I. I. Rabi, N. F. Ramsey, Jr., and J. R. Zacharias, Phys. Rev. 58, 728 (1939).

N.T.P. per minute, the pressures in mm of Hg in the source, intermediate, and magnet chambers were about 2×10^{-4}, 2×10^{-5}, and 1×10^{-6}, respectively. The diffusion pumps were equipped with dry-ice cooled traps; liquid-nitrogen cooled traps were not used.

The vertical clearance in the deflecting magnets is 1.0 cm; the gap width is 2.3 mm. A beam height of 6 mm was used. The ratio of gradient to field, averaged over the height of the beam, was about unity. A current of 35 amperes through the 11 turn, water-cooled magnet winding deflects the reoriented atoms sufficiently to completely defocus the beam. The magnet which produces the homogeneous field has faces at the air gap which are 9.0 cm long and 4.3 cm high. These faces were surface ground and lapped as was the 0.25-inch spacer. The intensity of the homogeneous field was determined in each experiment from the frequency separation of the Zeeman components.

Atomic hydrogen (or deuterium) was produced in a 5-meter Wood's discharge tube. Moist hydrogen (or deuterium) was admitted through capillaries at the rate of about 1.8 cc at N.T.P./min to the ends of the discharge tube from a manifold in which the pressure of the gas was approximately atmospheric. The pressure in the discharge tube was about $\frac{1}{4}$ mm of Hg. Measured values of beam intensity were corrected for the drift caused by the slow decrease in time of the manifold pressure. The discharge was excited by a 13,000 volt, 60 cycle transformer, using a resistive load in the primary to stabilize the discharge. The source is similar to that described by K.-R.-Z.[6] The source slit is 0.04 mm wide and 6 mm high and is formed by microscope cover glasses, waxed over the opening through the water jacket into the discharge tube. The atomic portion of the beam caused about 75 percent of the observed deflection of the galvanometer. This was demonstrated by increasing the current in one of the deflecting magnets until no further reduction in beam intensity was observed.

The Stern-Pirani detector used by us has been described by K.-R.-R.-Z.[10] The slits on the detector were formed by pressing the 4.5-mm jaws against 0.015-mm aluminum foil, forming a channel 0.015 mm wide, 3 mm high, and 4.5 mm long. The "fill-up" time of the detector is such that the galvanometer spot deflects to within 1/e of its final value in about 20 sec. A Leeds and Northrup Type H.S. galvanometer with a sensitivity of 0.05 microvolt/mm at 1 meter was used to detect the off-balance voltage of the Pirani gauge. The scale was placed 3 meters from the galvanometer. The heating current in the Pirani gauge was adjusted so that a typical deflection of the galvanometer caused by the beam was about 30 cm. A beam of hydrogen molecules with an intensity at the detector of about 3×10^{12} molecules/cm^2 sec. will produce a galvanometer deflection of about 1 cm. Readings were reproducible to within ±2 mm.

Radiofrequency magnetic fields were produced in the region of the homogeneous field by sending currents through two types of loops. The first one used produced an r-f field parallel to the beam (perpendicular to the homogeneous field) and induced π-transitions only. This loop was made of vertical sheets of copper, shorted below the line of the beam, and tapered from a coaxial line to a length of 6 cm at the line of the beam. In the second case, two rods, 3 cm long and lying parallel to the beam, were shorted at one end by a sheet of copper slotted to permit the passage of the beam. The plane of the rods was inclined at 45° to the direction of the homogeneous field. Radiofrequency current flowing in this loop produced a magnetic field having components parallel and perpendicular to the uniform field, thus both π- and σ-transitions could be induced. The transmission line from the oscillator was shorted by these loops. This line was not tuned. The current in the loop was varied either by changing the B supply voltage on the oscillator or by attenuating the output.

A coaxial line, tuned plate, tuned filament oscillator, driven by a 316-A tube was used for the frequency range 225–350 Mc. These frequencies were required in the measurements on deuterium and in the intermediate field measurements on hydrogen. Fine tuning was effected by changing the capacity across the end of the grid-plate line. Frequencies in the range 1400–1800 Mc, required in the experiments on hydrogen, were obtained from a grounded grid oscillator (APR-20) using a 2C40 tube and coaxial tuning elements. The stability of these oscillators is discussed in connection with the results.

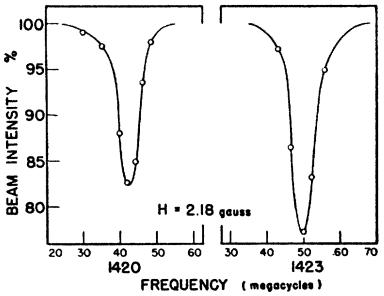

FIG. 4. The observed components of the multiplet $\Delta F=\pm 1$ in hydrogen. In order of increasing frequency these are the lines σ_1 and π_1 of Table I.

Frequencies were measured by heterodyning the output of the oscillator with harmonics of the output of a crystal-controlled, frequency multiplier. A 1N23 crystal was used as a simultaneous generator of harmonics of the standard frequency and mixer of these harmonics with the signal of unknown frequency. A General Radio frequency meter, Type 620-A, was used to measure the heterodyne frequency. These frequency meters are guaranteed to ± 0.01 percent. We have checked this meter against two other meters of the same type and found them to agree within the stated limit of accuracy. The frequency of the crystal, which furnishes calibration points for the heterodyne oscillator of the frequency meter, was checked against W.W.V. and found to deviate from its nominal value, 1 Mc, by only $+0.0012$ percent. Two crystal-controlled frequency multipliers were used. The first multiplied from 1 Mc to 100 Mc and the second from 1 Mc to 240 Mc. The final stage of the second multiplier is a push-pull tripler using an 832 tube to drive a parallel line. For each multiplier the frequency of the 5 Mc stage was compared frequently with that broadcast at 5 Mc by the Bureau of Standards, and the frequency of the 1-Mc oscillator adjusted so that the error in the 100-Mc or 240-Mc standard frequency was less than 1 part in 10^6.

Frequency measurements for the majority of the data on deuterium were made by comparing the frequency of the oscillator with the third harmonic (300 Mc) of the 100-Mc standard. The heterodyne frequencies were in the neighborhood of 30 Mc and could be measured to ± 0.002 Mc; thus, the frequency of the oscillator near 330 Mc could be measured to ± 0.002 Mc. With the 240-Mc frequency standard, frequencies could be measured to ± 0.0005 Mc, by heterodyning with the 4th harmonic (320 Mc) of the 80-Mc stage.

In the first measurements on hydrogen, the output of the 100-Mc frequency multiplier was too weak to permit the use of the higher harmonics necessary for measuring frequencies near 1420 Mc. A signal near 310 Mc from a Signal Corps test oscillator (TS-47/APR) was used to give strong harmonics in the range 1200–1800 Mc. The frequency of this oscillator was measured in the manner described above. A measurement of frequency near 1420 Mc consisted in a measurement of the frequency of the test oscillator, which was accurate to ± 0.001 Mc, and then the measurement of the frequency of the heterodyne signal between harmonics of the test oscillator frequency and the frequency in question. The drift in the frequency of the test oscillator was observed to be regular and less than 1 part in 10^5 for the time required to map an entire resonance curve and, therefore, caused no significant error in the final measurement of frequency. The accuracy of the final result was about ± 0.010 Mc.

The higher power, 240-Mc frequency standard was constructed to avoid the use of an intermediate frequency oscillator. As standard frequencies from this multiplier are obtained at 1440, 1680, $\cdots$ Mc, frequencies in the neighborhood of the h.f.s. of hydrogen, 1420.41 Mc, can be measured to 1 part in 10^6, an accuracy which exceeds the stability of the oscillator. It is to be noted that in our last and most reliable measurements on hydrogen the oscillator was stable to ± 0.003 Mc.

5. EXPERIMENTAL PROCEDURE

Transitions between the magnetic levels of the h.f.s. doublet in either H or D were located initially by fixing the frequency of the r-f field and then varying the C magnet current. In some cases it was necessary to reverse the current in the C magnet, relative to that in the A and B magnets, for their stray field in the vicinity of the r-f loop was about 5 gauss. After the transitions had been located, the magnet currents were held constant and the frequency varied to map the lines. As ν_H and ν_D were determined

mainly from the frequency of the field independent Zeeman components, a high degree of stability of the C magnet current was not required.

Drift of the galvanometer spot caused by thermal effects in the circuit, which amounted to about 1 cm/min., was averaged out by taking successive readings with the beam shutter open and closed. Readings were taken at intervals of 30 sec. The total time required to map a line was about 45 min. The field independent Zeeman component was mapped repeatedly in each run; the field dependent lines were mapped only often enough to determine the intensity of the magnetic field.

6. RESULTS

The h.f.s. separations, ν_H and ν_D, have been measured in magnetic fields of a few gauss and the measurements of ν_H have been repeated in fields of about 150 gauss. The low field measurements are the more reliable and the results are

$$\nu_H = 1420.410 \pm 0.006 \text{ Mc},$$
$$\nu_D = 327.384 \pm 0.003 \text{ Mc}.$$

The intermediate field measurements of ν_H agree with the low field results with a precision which exceeds the accuracy of the measurements. While the manuscript of this paper was in preparation results in good agreement with ours were reported by Nagle, Julian, and Zacharias.[11] A detailed discussion of results is given in this section.

Hydrogen

A weak field Zeeman pattern of the line $\Delta F = \pm 1$ in hydrogen, measured in a field of 2.18 gauss, is plotted in Fig. 4. The pattern is complete with the exception of the line $(1, -1 \leftrightarrow 0, 0)$ for which the change in the effective atomic moment is too small to cause a measurable defocusing of the beam. It is to be noted that the half-width of the σ-line $(1, 0 \leftrightarrow 0, 0)$ agrees with the value calculated from the uncertainty principle

$$\Delta\nu \Delta t \sim 1, \tag{6}$$

where $\Delta\nu$ is roughly the half-width of the line in frequency units and $\Delta t = l/v$ is the time required for the beam to traverse the r-f field of length l. We have assumed a temperature of 300°K for the source and have used the most probable velocity,[12] v, of the atom in the source. The inhomogeneity of the magnetic field, as estimated from the width of the π-line $(1, 1 \leftrightarrow 0, 0)$, would contribute only 6 kc to the width of the $(1, 0 \leftrightarrow 0, 0)$ line, even in the worst case. The frequency of the σ-line is almost exactly ν_H (Eq. (4)). The magnetic field is inhomogeneous to a degree indicated by the width of the π-line. The uncertainty of the correction applied to the

TABLE II. Results of weak and intermediate field measurements of the h.f.s. of hydrogen.

	$(1, 1 \leftrightarrow 0, 0)$ (Mc)	$(1, 0 \leftrightarrow 0, 0)$ (Mc)	$(1, 0 \leftrightarrow 1, -1)$ (Mc)	Field (gauss)	½-Width (Mc)	Stability of freq. (Mc)	ν_H (Mc)	Mean ν_H (Mc)
Section 1		1420.424		2.18	0.065	±0.003	1420.411	
Weak field	1423.48	1420.420		2.18	0.060	±0.003	1420.407	
		1420.425		2.18	0.065	±0.003	1420.412	
	1422.18	1420.417		1.26	0.110	±0.010	1420.413	
	1431.05	1420.566		7.59	0.080	±0.010	1420.409	
								1420.410±0.002
Section 2	1671.93			156.2	0.15	±0.005		
Intermediate field			251.41	156.2	0.19	±0.005	1420.45±0.07	
	1671.79			156.2	0.11	±0.005	1420.41±0.04	
			251.34	156.2	0.20	±0.005	1420.44±0.01	
	1671.77			156.2	0.16	±0.005		
	1661.12			149.5	0.16	±0.010		
			240.68	149.5	0.15	±0.010	1420.38±0.06	
	1661.00			149.5	0.14	±0.010	1420.40±0.08	
			240.52	149.5	0.19	±0.010		1420.42±0.03

[11] D. E. Nagle, R. S. Julian, and J. R. Zacharias, Phys. Rev. **72**, 971 (1947).
[12] H. C. Torrey, Phys. Rev. **59**, 293 (1941).

frequency of the σ-line to obtain ν_H on this account was less than 0.001 Mc.

The results of three sets of measurements of ν_H are given in Section 1 of Table II. The frequencies of the π- and σ-transitions are given in columns 1 and 2, respectively, and the magnetic field in column 4. The observed half-width of the σ-line is in column 5. An estimate of the combined accuracy of the measurement of the frequency and the stability of the oscillator is given in column 6 and ν_H in column 7. The average of these results is $\nu_H = 1420.410 \pm 0.002$ Mc. The average deviation (0.002 Mc) of the 5 measurements from their mean is less than the average uncertainty in the frequency of any individual point, and is about 3 percent of the average half-width of the σ-lines. The accuracy of the determination of ν_H in any individual measurement is limited by the half-width of the line and not by the stability of the oscillator or the accuracy of the measurement of the frequency. As the reproducibility of the results may be fortuitous, we estimate the probable error to be 10 percent of the half-width of the σ-lines. The final result of the weak field measurements is

$$\nu_H = 1420.410 \pm 0.006 \text{ Mc.}$$

The results of the weak field measurements of ν_H have been confirmed by measurements in fields of intermediate strength (about 150 gauss). The results of two sets of measurements are given in Section 2 of Table II. The line $(1, 1 \leftrightarrow 0, 0)$ in column 1 and the line $(1, 0 \leftrightarrow 1, -1)$ in column 3 were mapped in succession in order that correction for the drift of the field might be made. The average of these results, $\nu_H = 1420.42 \pm 0.03$ Mc, agrees very well with the results obtained in weak fields. The average deviation (0.03 Mc) of these values from the mean is less than the maximum uncertainty in 4 of the 5 values. The lack of precision is caused by the excessive half-width of these field dependent lines and the drift of the magnetic field which shifted the lines by about 0.10 Mc. The agreement between ν_H obtained in weak and intermediate strength fields is 0.001 percent and exceeds the accuracy of the intermediate field measurements.

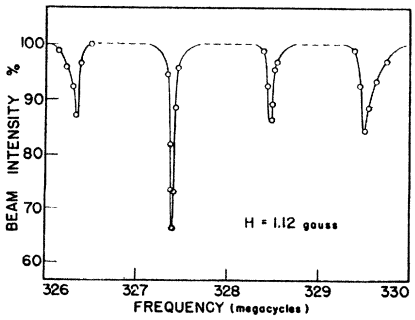

FIG. 5. The observed components of the multiplet $\Delta F = \pm 1$ in deuterium. In order of increasing frequency these are the lines σ_2', π_2', σ_1', and π_1' of Table I.

Deuterium

A weak field Zeeman pattern of the multiplet $\Delta F = \pm 1$ in deuterium, measured in a field of 1.12 gauss, is given in Fig. 5. The pattern is complete with the exception of the $(\frac{3}{2}, \frac{3}{2} \leftrightarrow \frac{1}{2}, \frac{1}{2})$ line for which the change in the effective atomic moment is too small to cause a measurable defocusing of the beam. The frequencies of the field independent unresolved doublet line, $(\frac{3}{2}, \frac{1}{2} \leftrightarrow \frac{1}{2}, -\frac{1}{2})$; $(\frac{3}{2}, -\frac{1}{2} \leftrightarrow \frac{1}{2}, \frac{1}{2})$, and the field dependent line, $(\frac{3}{2}, \frac{3}{2} \leftrightarrow \frac{1}{2}, \frac{1}{2})$, are used in Eq. (5) to obtain ν_D. The width of the unresolved doublet line agrees well with the calculated uncertainty width, particularly in the cases where the oscillator output was attenuated. The half-width of the $(\frac{3}{2}, \frac{3}{2} \leftrightarrow \frac{1}{2}, \frac{1}{2})$ line caused no significant error in the value of the second-order correction in Eq. (5).

Two series of measurements of ν_D have been made. The length of the r-f field and the method of measuring frequency were different in each case. The first series of measurements were made with the 6-cm r-f loop which induced π-transitions only. The expected minimum half-width of the lines is about 0.028 Mc. The frequency was measured by heterodyning the signal with harmonics of the 100-Mc crystal-controlled standard and could be measured to ± 0.002 Mc. Agreement within the stated accuracy was obtained when the frequency was checked against various harmonics of the 100-Mc standard. The results of these measurements are given in Section 1 of Table III. The frequencies of the field dependent π-line $(\frac{3}{2}, \frac{3}{2} \leftrightarrow \frac{1}{2}, \frac{1}{2})$ and the field independent doublet, $(\frac{3}{2}, \frac{1}{2} \leftrightarrow \frac{1}{2}, -\frac{1}{2})$; $(\frac{3}{2}, -\frac{1}{2} \leftrightarrow \frac{1}{2}, \frac{1}{2})$, are given in columns 1 and 2. The value of the magnetic field is entered in column 3. The observed half-width of the field independent line is in column 4. The

TABLE III. Results of weak field measurements of the h.f.s. of deuterium.

	$(\frac{3}{2},\frac{1}{2}\leftrightarrow\frac{1}{2},\frac{1}{2})$ (Mc)	$(\frac{3}{2},\pm\frac{1}{2}\leftrightarrow\frac{1}{2},\mp\frac{1}{2})$ (Mc)	Field (gauss)	$\frac{1}{2}$-Width (Mc)	Stability of freq. (Mc)	ν_D (Mc)	Mean ν_D (Mc)
Section 1	329.45±0.07	327.401	1.10	0.085	~±0.002	327.388	
		327.399	1.10	0.080	~±0.002	327.386	
		327.391	0.884	0.065	~±0.002	327.383	
	329.03±0.05	327.392	0.884	0.036	~±0.002	327.384	
		327.390	0.884	0.062	~±0.002	327.382	
							$327.384_6\pm0.003$
Section 2		327.399	1.12	0.044	<±0.002	327.385	
	329.47±0.05	327.397	1.12	0.046	<±0.002	327.384	
		327.396	1.12	0.044	<±0.002	327.383	
	328.35	327.388	0.514	0.050	<±0.002	327.385	
							$327.384_2\pm0.001$

estimate of the stability of the oscillator and the accuracy of the measurement of frequency, combined, is given in column 5 and ν_D in column 6. The average of these measurements is $\nu_D=327.384(6)\pm0.003$ Mc. The average deviation (0.003 Mc) of the 5 measurements from the mean is comparable to the accuracy with which the frequency was measured and is about 4 percent of the average half-width of the doublet line.

The second series of measurements was made with the 3-cm r-f loop which induced both π- and σ-transitions. In this series frequency could be measured to ±0.0005 Mc. The frequency of the oscillator was measured continuously, while the intensity of the beam was being measured, and its stability at every point was better than ±0.002 Mc. The oscillator output was attenuated and as a result the lines were narrowed and deepened. The expected minimum half-width of the lines is about 0.056 Mc. The results of these measurements are given in Section 2 of Table III. The value of ν_D is $327.384(2)\pm0.001$ Mc. The average deviation (0.001 Mc) of the 4 measurements from the mean is about 2 percent of the average half-width of the field independent line and is less than the average stability of the oscillator.

The accuracy of the determination of ν_D in any individual measurement was limited by the half-width of the doublet line and not by the stability of the oscillator, the accuracy of the measurement of frequency or the drift of the magnetic field. The mean of the 9 measurements of ν_D is

$$\nu_D=327.384\pm0.003$$

Mc, where the probable error has been estimated to be 5 percent of the mean half-width of the doublet line.

7. DISCUSSION OF RESULTS

The expression for the h.f.s. splitting of the $^2S_{\frac{1}{2}}$ state given by Eq. (1) may be rewritten by replacing the factors $\psi^2(0)$ and μ_0 by equivalent combinations of physical constants. The expression for ν becomes

$$\nu=4/3[(2I+1)/I](m_r/m_0)^3(m_0/M)\mu\alpha^2cR_\infty, \quad (7)$$

where μ is the nuclear magnetic moment in units of the nuclear magneton, m_0/M is the ratio of the electron to proton mass, m_r is the reduced mass of the electron, and m_0 the rest mass of the electron, $R_\infty=(2\pi^2m_0e^4)/h^3c$ is the Rydberg constant for infinite mass, and $\alpha=e^2/\hbar c$ is the fine structure constant. This equation has been used to compute the theoretical values of ν_D and ν_H shown in Table IV. Birge's[13] values of the natural constants were used in the computations. The proton moment has been measured by Millman and Kusch[7] and the deuteron moment obtained from this value and the ratio, μ_p/μ_d, measured by Bloch, Levinthal, and Packard.[14] The lack of

TABLE IV. H.f.s. separation of the ground state of H and D.

	Computed	Experimental
ν_H	1416.97±0.54 Mc	1420.410±0.006 Mc
ν_D	326.53±0.12 Mc	327.384±0.003 Mc
ν_H/ν_D	4.339385±0.00003	4.33867±0.00004

[13] R. T. Birge, Rev. Mod. Phys. **13**, 233 (1941).
[14] F. Bloch, E. C. Levinthal, and M. E. Packard, Phys. Rev. **72**, 1125 (1947).

precision in the computed values of ν_H and ν_D is due to the uncertainty in the values of α^2 and μ. The following values were used:

$$\alpha^2 = 5.3256 \pm 0.0013 \times 10^{-5} \quad (\pm 0.024 \text{ percent})$$
$$\mu_p = 2.7896 \pm 0.0008 \quad (\pm 0.029 \text{ percent})$$
$$\mu_d = 0.85644 \pm 0.00025 \quad (\pm 0.029 \text{ percent})$$
$$\frac{m_0}{M} = 1836.6 \pm 0.6 \quad (\pm 0.031 \text{ percent}).$$

The measured gyromagnetic ratios from which the values of the nuclear magnetic moments are obtained depend directly on the ratio of the quantities e/m_0c and e/Mc, and therefore on the ratio M/m_0. Thus the uncertainty in m_0/M contributes no significant error to ν_H or ν_D computed from Eq. (7) because the inverse of this ratio is contained in the values of μ_p and μ_d.[7]

The calculated values of ν_H and ν_D are less than the experimental values by 0.242 percent, for H and 0.259 percent, for D. This discrepancy is 5 times the sum of the published probable errors in the values of α^2 and μ_p (or μ_d).

The discrepancy in the absolute values of ν_H and ν_D may be attributed to a systematic error in the values of the natural constants, α^2 and R_∞, although the claimed probable error is very much smaller.

Note added in proof: The recent discovery by Kusch and Foley[15,16] that the magnetic moment of the electron is not μ_0 but $\mu_e = \mu_0(1+0.00118)$ explains the major part of this discrepancy with the theory of the absolute values of ν_H and ν_D, since both moments in Eq. (1) must be multiplied by this factor. This is in accordance with the ideas of Breit[17] and Schwinger.[18]

On the other hand, the theory of the hyperfine structure used to derive Eq. (1) did not take into account positron theory (pair production) or shifts in the position of energy levels such as may serve to explain the experiments of Lamb and Retherford,[19,20] nor did it take account of the effects of a possible interaction of the electron in the nucleus arising from the internal constitution of the nucleus or the elementary particles (meson theory). Another omission is the utilization of an exact relativistic Hamiltonian for the two-body problem. The justification for the term $(m_r/m_0)^3$ comes from the analogy with the occurrence of the reduced mass in the Rydberg for hydrogen, deuterium, and singly ionized helium. However, Halpern[21] has shown that an argument can be given for the occurrence of the reduced mass ratio to the $\frac{3}{2}$-power. A more rigorous justification of our assumption is given by Breit and Meyerott.[22]

The ratio ν_H/ν_D of the measured h.f.s. separations may be compared with the expected ratio found from Eq. (1) as modified by the introduction of the correct reduced mass dependence. The expected ratio is

$$\nu_H/\nu_D = 4/3(m_H/m_D)^3(\mu_p/\mu_d), \tag{8}$$

where m_H and m_D are the *reduced masses* of an electron in H and D, respectively.

The ratio of the moments is known much more accurately than either μ_p or μ_d from the recent work of Bloch, Levinthal, and Packard[14] and Roberts[23] which is more accurate than the earlier work of Kellogg, Rabi, Ramsey, and Zacharias.[10] From Bloch's values $\mu_p/\mu_d = 3.257195 \pm 0.00002$ the computed $\nu_H/\nu_D = 4.339385 \pm 0.00003$, which is to be compared with the experimental value $\nu_H/\nu_D = 4.33867 \pm 0.00004$. The latter is lower by 0.017 percent. The discrepancy exceeds the probable error of the measured h.f.s. ratio by a factor of 18. The close agreement may be considered to be an excellent justification for the gross and even many of the finer elements of the present theory of the h.f.s. The discrepancy in the two ratios although small seems to be well established and may be of important theoretical significance.

The authors wish to thank Professor I. I. Rabi, under whose direction the work was carried out, for his advice in the pursuit of the problem. We also wish to thank the other members of the molecular beam laboratory and members of the Columbia University Radiation Laboratory for assistance in technical matters relative to the experiment.

[15] P. Kusch and H. M. Foley, Phys. Rev. **72**, 1256 (1947).
[16] H. M. Foley and P. Kusch, Phys. Rev. **73**, 412 (1948).
[17] G. Breit, Phys. Rev. **72**, 984 (1947).
[18] J. Schwinger, Phys. Rev. **73**, 416 (1948).
[19] W. E. Lamb, Jr. and R. C. Retherford, Phys. Rev. **72**, 241 (1947).
[20] H. A. Bethe, Phys. Rev. **72**, 339 (1947).
[21] O. Halpern, Phys. Rev. **72**, 245 (1947).
[22] G. Breit and E. R. Meyerott, Phys. Rev. **72**, 1023 (1947).
[23] A. Roberts, Phys. Rev. **72**, 979 (1947).