

## The Magnetic Moments of the Proton and the Deuteron

### The Radiofrequency Spectrum of H<sub>2</sub> in Various Magnetic Fields<sup>1</sup>

J.M.B. KELLOGG, I.I. RABI and N.F. RAMSEY, Jr.

Columbia University, New York, New York

and J.R. ZACHARIAS

Hunter College, New York, New York

(Received July 31, 1939)

#### Abstract

The molecular-beam magnetic-resonance method for measuring nuclear magnetic moments has been applied to the proton and the deuteron. In this method the nuclear moment is obtained by observing the Larmor frequency of precession ( $\nu = \mu H/hI$ ) in a uniform magnetic field. For this purpose HD and D<sub>2</sub> molecules are most suitable because they are largely in the state of zero rotational momentum. Very sharp resonance minima are observed which makes it possible to show that the observed values of  $\nu/H$  are independent of  $H$ , and to make a very accurate determination of the ratio  $\mu_P/\mu_D$ . With molecules of ortho-hydrogen in the first rotational state a radiofrequency spectrum of six resonance minima was obtained. This spectrum when analyzed yields a set of nine energy levels from which are obtained (1) the proton moment from its Larmor precession frequency; (2) the proton moment from the magnitude of the dipole interaction between the two proton magnetic moments (the directly measured quantity is  $\mu_P/r^3$ ); and (3) the value of the spin orbit interaction constant of the proton moment with the rotation of the molecule or the magnetic field  $H'$  produced by the rotation of the molecule at the position of the nucleus. The numerical results are  $\mu_P = 2.785 \pm 0.02$  nuclear magnetons;  $\mu_D = 0.855 \pm 0.006$  nuclear magneton;  $(\mu_P/\mu_D) = 3.257 \pm 0.001$ ;  $H' = 27.2 \pm 0.3$  gauss;  $\mu_P/r^3 = 34.1 \pm 0.3$  gauss which gives  $\mu_P = 2.785 \pm 0.03$  nuclear magnetons. To within experimental error there is no disagreement of the

---

<sup>1</sup>Publication assisted by the Ernest Kempton Adams Fund for Physical Research of Columbia University.

results of these direct measurements with those from atomic beam measurements of the h.f.s.  $\Delta\nu$  of the ground states of H and D.

## Introduction

In this paper we shall describe experiments in which the magnetic moments of the proton and deuteron are measured to a much higher precision than heretofore. In addition there will be presented some experimental results which throw light on the inner dynamics of the hydrogen molecule, such as the magnetic field at the position of the protons which is produced by the rotation of the molecule as a whole. The magnetic moments will be deduced from two independent quantities: (1) the Larmor precession frequency of the proton or the deuteron in an externally applied magnetic field, (2) the mutual magnetic energy of interaction of the two proton moments in the hydrogen molecule. The first of these two measurements depends on principles briefly described in the first paragraph of the section on method and more adequately in a paper by Rabi, Millman, Kusch and Zacharias<sup>2</sup>. The results are given in the first part of the section "Evaluation of Experimental Results."

In a previous paper<sup>3</sup> called "The Gyromagnetic Properties of the Hydrogens," experiments were described which measured the h.f.s. separation of the normal states of atomic hydrogen and deuterium. The magnetic moments of the proton and the deuteron were evaluated from these measurements by the application of the Dirac theory of the hydrogen atom. These calculations depend on the assumption that the interaction of the nuclear spin with the external electron is purely electromagnetic in nature. The values which were obtained from this experiment were 2.85 and 0.85 nuclear magnetons for the proton and deuteron, respectively, with a precision of about 5 percent.

These values, particularly that of the proton are to be compared with the earlier value of 2.5 given by Estermann and Stern<sup>4</sup> as a result of a straightforward molecular beam deflection experiment with molecular hydrogen. Since this value was not claimed to be accurate to better than 10 percent the results of the two experiments, which differ entirely in principle, could be said to agree within the limits of error. A value of the proton moment was also given by Lasarew and Schubnikow<sup>5</sup> who measured the variation of

---

<sup>2</sup>I.I. Rabi, S. Millman, P. Kusch and J.R. Zacharias, Phys. Rev. **55**, 526 (1939).

<sup>3</sup>J.M.B. Kellogg, I.I. Rabi and J.R. Zacharias, Phys. Rev. **50**, 472 (1936)

<sup>4</sup>I. Estermann and O. Stern, Phys. Zeits. f. Physik **85**, 17 (1933).

<sup>5</sup>B.G. Lasarew and L.W. Schubnikow, Physik. Zeits. Sowj. **11**, 445 (1937).

the diamagnetic susceptibility of liquid hydrogen with temperature. They interpret the change in susceptibility as a paramagnetic effect of the nuclear moment and from measurements at three different temperatures obtain two values  $2.7 \pm 10$  percent and  $2.3 \pm 10$  percent. However, later experiments by Estermann, Simpson, and Stern<sup>6</sup> yield a value of  $2.46 \pm 3$  percent. They used the same method as in the previous experiments of Estermann and Stern, but with a more refined technique, which they applied to both H<sub>2</sub> and HD molecules.

The wide divergence between the values 2.85 and 2.46 is quite outside the sum of the limits of error. As an explanation the possibility of some sort of spin interaction between electron and proton not electromagnetic in character was suggested. Another possibility was a breakdown of the Dirac equation for the electron in the hydrogen atom.

These considerations which bring into question the fundamental entities of nuclear and atomic physics make a further experimental study of the proton moment a matter of great interest, particularly if the methods are independent. Further interest is added to these studies by recent theoretical investigations<sup>7</sup> of the nature of the proton and neutron moment and their composition in the deuteron.

## Method

The method we employ is the molecular-beam magnetic-resonance method<sup>1</sup> modified to apply to gas molecules. As used in our experiment this method provides a means of observing the reorientations of molecular and nuclear moments which may occur with respect to a constant homogeneous magnetic field when an oscillating or rotating magnetic field is superposed. In our experiments this oscillating magnetic field will be weak compared with the constant field and perpendicular to it in direction. In the absence of any interaction between the molecular constituents this reorientation will occur when the Larmor frequency of precession,

$$\nu = \mu H/hI \tag{1}$$

and the frequency of the oscillating field are in resonance.

More generally, when there are interactions between the molecular constituents, the resonance reorientations occur when the frequency of the os-

---

<sup>6</sup>I. Estermann, O.C. Simpson and O. Stern, *Phys. Rev.* **52**, 535 (1937).

<sup>7</sup>J. Schwinger, *Phys. Rev.* **55**, 235 (1939) *Abs.* **13**; H. Fröhlich, W. Heitler and N. Kemmer, *Proc. Roy. Soc.* **166A**, 154 (1938).

cillating field is in resonance with the frequency given by the Bohr relation

$$h\nu_{nm} = \Delta E_{nm} = E_n - E_m, \quad (2)$$

where  $E_n$  and  $E_m$  represent the energies of two states of the whole molecular system in the homogeneous magnetic field. There are selection rules which govern these transitions, and in the cases which we will discuss this selection rule is  $\Delta m = \pm 1$  where  $m$  is the magnetic quantum number of the system. It is to be emphasized that the method detects not only transitions from state  $n$  to  $m$ , but also the inverse transition  $m$  to  $n$ . One of these corresponds to absorption of radiation and the other to stimulated emission. As Einstein has shown these two processes are equally probable. The above two descriptions are equivalent in the absence of interactions within the molecule because the energy differences between the successive states of spin quantization are then all equal to  $\mu H/I$ , whence the Bohr frequency is the same as the frequency given by Eq. (1).

To detect the reorientations, a beam of molecules is spread by an inhomogeneous magnetic field and refocused onto a detector by a subsequent inhomogeneous field. The transitions between the states of different space quantization are produced in the homogeneous field of an electromagnet placed in the region between the two deflecting magnets. In the gap of this electromagnet is placed a loop of wire which is connected to a source of current of radio frequency to produce the oscillating field at right angles to

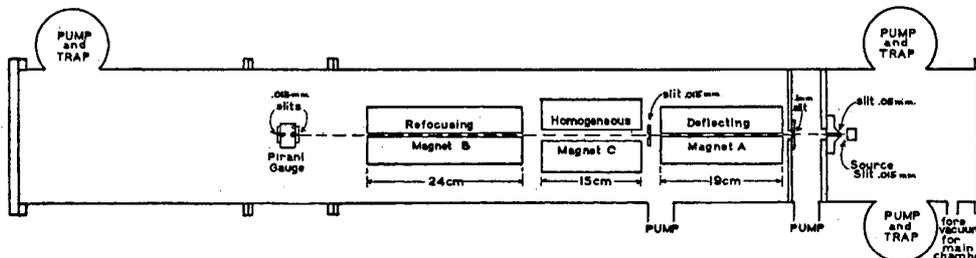


Figure 1: Schematic diagram of apparatus. Longitudinal dimensions from source to detector are drawn to scale. Flattened copper tubes 13.5 cm long to carry radiofrequency current are not shown. They should appear between the pole pieces of magnet  $C$ .

the steady field. If a reorientation of spin occurs in this field the subsequent conditions in the second deflecting field are no longer correct for refocusing and the intensity at the detector goes down. The experimental procedure

is to vary the homogeneous field while maintaining some given value of the frequency of the oscillating field until a resonance is observed by a drop in intensity at the detector and the subsequent recovery when the resonance value is passed.

## Apparatus

The apparatus used in these experiments is similar to that used by R. M. K. Z.,<sup>1</sup> the chief modifications being those which result from the use of gas molecules in the beam. The present apparatus is shown schematically in Fig. 1. The outer 6" brass tube is divided into three parts to facilitate pumping, each part having its own high vacuum system. In the source chamber, where much gas emerges from the source, a pressure of  $4 \times 10^{-5}$  mm of mercury is maintained by two brass oil-diffusion umbrella-type pumps with dry-ice-cooled helical baffles. The pumping speed measured at the position of the source slit is 100 liters of air per second. In the separating chamber, which is connected to the source chamber only by a slit 0.05 mm wide and 3 mm high through which the molecular beam passes, and to the main chamber by a slit 0.1 mm wide and 6 mm high, the pressure is of the order of  $10^{-6}$  mm. The purpose of the separating chamber is to provide vacuum isolation of the main chamber from the gas in the source chamber. Finally in the main chamber, where the magnets are located and where the molecules are for the greatest length of time, a pressure of better than  $5 \times 10^{-7}$  mm is maintained with another brass oil-diffusion pump with a speed of 50 liters per second and with a glass pump of the Zabel design<sup>8</sup>. To diminish pressure fluctuations in this chamber, an extra section of brass tube 3 ft. long and 7" in diameter is added beyond the Pirani gauge detector to provide ballast volume. All the diffusion pumps of the separating and main chambers pump into a glass pump which in turn pumps into the source chamber which serves as its fore vacuum. The two brass pumps of the source chamber are backed by a glass pump which in turn pumps into a Leybold three stage mercury diffusion pump capable of pumping against 10 mm of pressure. The gas from the Leybold pump goes back to the source feed line so that it is used over again. With this recirculation system as little as 6 cc of gas at NTP is required for a day's run and, if desired, even that amount may be recovered at the end of the day for subsequent use.

The source is mounted at the bottom of an Invar Dewar to which it is soldered. The molecules being investigated must pass through a long 2-mm

---

<sup>8</sup>R.M. Zabel, Rev. Sci. Inst. **6**, 54 (1935).

tube in the Dewar before entering the source so their temperature becomes approximately that of the refrigerant in the Dewar. The Dewar is supported at the top by a ground brass joint so mounted that the trap can be moved both transversely and vertically under vacuum. The ground joint permits rotation about a vertical axis. This motion is necessary because of the canal effect of the slit jaws. In addition to the support at the top of the trap, two long Invar screws pass through the sides of the outer brass tube and are used to clamp the source rigidly in place. This was found to be necessary to prevent random 0.001 mm lateral motions of the source. The gas pressure inside the source is usually of the order of 4 or 5 mm of mercury. The source slit is 0.015 mm wide, 3 mm high, and 0.25 mm thick. Although the source slit is made vertical optically before the apparatus is pumped out, slight changes of its angle with the vertical can be made under vacuum by clamping the source box with the Invar screws and then moving the top of the Invar trap. This procedure bends the trap a bit and thus changes the angle of the slit with the vertical.

The collimator consists of two sharp slit jaws 0.015 mm apart mounted eccentrically on a vertical ground joint. Small rotations of the joint therefore make possible slight adjustments of the collimator position while large rotations completely remove the collimator from the path of the molecular beam. Although the geometry of the apparatus is such that the collimator cannot conveniently be put halfway between the source and the detector, it is placed as near to this position as possible, since, as pointed out by Manley<sup>9</sup>, this is the optimum position. The total beam length, source to detector, is 77 cm.

The detector is of the Stern-Pirani type and is shown diagrammatically in Fig. 2. The most important difference between this detector and the Pirani gauges previously used<sup>7</sup> is that use is made of all four arms of the Wheatstone bridge, two electrically opposite arms being in the detector chambers and two in the balancing chambers whereby the sensitivity is increased. Each set of gauge chambers, which must be of small volume to diminish the time lag of the detector, is formed by inlaying in solder two 1.6-mm (inside diameter) copper tubes in a rectangular trough cut in the surface of a brass block. A transverse hole is drilled from the outside through both tubes to form the interconnecting channel shown in the diagram. The faces of the block are then surface ground and lapped. The slit jaws shown in the diagram are carefully lapped brass blocks screwed to the lapped faces of the gauge block. The slit itself is formed by forcing these slit blocks together against 0.015

---

<sup>9</sup>J.H. Manley, Phys. Rev. **49**, 921 (1936).

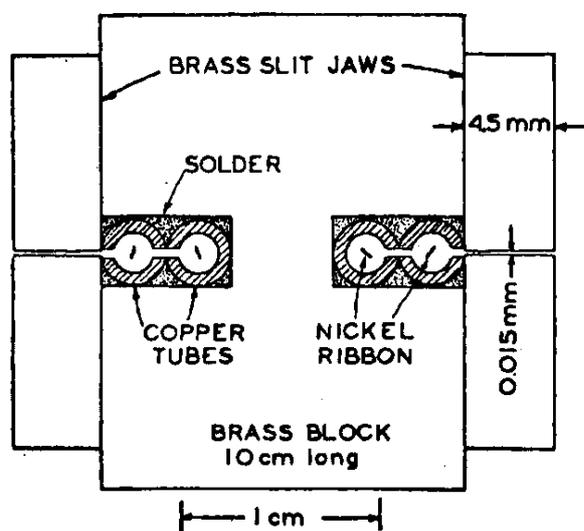


Figure 2: Horizontal cross section of the detector. The block and tubes are 10 cm long.

mm spacers of aluminum foil to form a channel 0.015 mm wide, 2 mm high, and 4.5 mm long. The gauge wires are made of nickel ribbon 9 cm long, 0.25 mm wide, and 0.004 mm thick. These ribbons are kept taut by small spiral springs of 6-mil nickel wire formed on the point of a needle. Nickel leads are brought out of the ends of the gauge chambers through small glass tubes which are ground to fit snugly into the copper tubes. The ends are then sealed with a drop of clear glyptal lacquer. Finally, the gauge is baked at a temperature of  $150^{\circ}$  for three days.

To prevent electrical disturbances in the detector circuit when the oscillator is turned on, the entire circuit is well shielded and by-pass condensers are attached between the leads of the hot wire arms of the bridge and ground.

The portion of the outer brass tube near the detector is surrounded with rubber tubing through which is circulated water from a large tank which stays at the average room temperature. The whole system is lagged with crumpled Alfol (aluminum foil) to provide thermal insulation. This is necessary to diminish the large galvanometer drifts which accompany even small changes of the detector temperature. After the apparatus has been opened to air, it takes about a week for the detector to outgas sufficiently for accurate measurements to be possible. Therefore one oil diffusion pump and a mechanical pump are left running all the time so that "sticking" vacuum

is maintained even when the apparatus is not in use.

The inhomogeneous deflecting magnets *A* and *B* (Fig. 1) are of the type described by Millman, Rabi, and Zacharias<sup>10</sup>. They are 19 cm and 24 cm long, respectively. The gaps are bounded by two cylindrical surfaces, one convex of radius 1.24 mm and the other concave of radius 1.47 mm. The gap width is 1.06 mm. Each magnet is wound with four turns of heavy, water-cooled copper. With 300 amperes the field is about 12,000 gauss and the gradient of the field about 90,000 gauss/cm.

The magnet *C* producing the homogeneous magnetic field is a single yoke magnet of Armco iron carefully annealed in a hydrogen atmosphere. It is wound with 9 turns of heavy, water-cooled copper. The surfaces of the air gap are 0.6 cm apart, 3.2 cm high, and 15 cm long. They are surface ground and lapped, and the gap is spaced with a ground and lapped spacer so that the air gap should be constant to about 0.05 percent.

Although the gradients of the two inhomogeneous magnetic fields must be in opposite directions for refocusing to be possible, it is essential<sup>1</sup> that all three magnetic fields be in the same direction and that the three magnets be close together to prevent reorientations of the molecules in the regions of weak rapidly changing field between the magnets. To further diminish these reorientations iron slabs are attached to the ends of the inhomogeneous magnets to increase the value of the magnetic field in the gaps between the magnets and to make the changes of field more gradual. With these precautions the refocused beam intensity in the present apparatus is about 95 percent of the beam intensity in the absence of the magnetic fields.

The high frequency magnetic field within the air gap of the *C* magnet is produced by a radio-frequency current in a "hairpin" of the type described in detail by Millman<sup>11</sup>. The two horizontal wires between which the beam passes are of flattened 1/8 in. (outside diameter) copper tubing 13.5 cm long and 1 mm apart through which water flows for cooling purposes. This produces a magnetic field of about 3 gauss per ampere at the position of the beam. As much as 50 amperes of current at several megacycles have been used. The current comes from a single turn secondary inductively coupled to the tank coil of a conventional Hartley oscillator driven by an Eimac 250 TL tube. Frequencies between 0.5 and 16 megacycles have been used. The oscillator is sufficiently stable for the frequency to remain constant to 0.02 percent over the course of a day's run.

---

<sup>10</sup>S. Millman, I.I. Rabi and J.R. Zacharias, Phys. Rev. **53**, 384 (1938).

<sup>11</sup>S. Millman, Phys. Rev. **55**, 628 (1939).

## Calibration

The measurement of gyromagnetic ratios by the method of this experiment depends on the absolute measurement of only two quantities as is shown by Eq. (1): (a) the frequency of the oscillatory magnetic field and (b) the strength of the homogeneous magnetic field.

The frequency is measured with the same General Radio Type 620-A heterodyne frequency meter used by R. M. K. Z.<sup>1</sup> with which frequencies can be measured to 0.01 percent. In our laboratory this meter was compared with another meter of the same type and found to agree with it to 0.01 percent.

The homogeneous magnet  $C$  is calibrated as a function of the exciting current in the magnet windings. The current is measured by the potential drop across a shunt through which the current passes. This potential drop is measured to 0.01 percent with a type  $K$  potentiometer. As the same shunt is used in the calibration and in the measurement of moments, its absolute resistance is of no importance.

In the process of calibration it was found that the field accompanying a current in the windings depended on the way the magnet was demagnetized. Therefore a standardized demagnetization procedure was used in both the calibration and the subsequent measurements. Calibrations were made for several values of the current in the  $A$  and  $B$  magnets. When this procedure was followed, the magnetic fields were found to be reproducible to 0.2 percent.

The calibration of the magnet was performed with flip coils, ballistic galvanometer and mutual inductance in the manner described by R. M. K. Z.<sup>1</sup> Two Leeds and Northrup 50-millihenry mutual inductances were used in the calibration. The values of these two mutual inductances, rated by the manufacturer to  $\pm 0.5$  percent, were found to vary about 0.5 percent depending on humidity. This uncertainty together with a slight uncertainty in the area of the flip coil is the chief source of error in the experiment. The absolute calibration of the field and hence the absolute values of the magnetic moments should be good to about 0.5 percent.

Since the moments of a number of nuclei have been measured<sup>1 12</sup> on another apparatus with an independent field calibration, it is of interest to compare the results of the measurement of some one nuclear moment on the two apparatuses. For this purpose we chose fluorine which was available

---

<sup>12</sup>P. Kusch and S. Millman, Bull. Am. Phys. Soc. **14**, No. 3, Abs. 35; S. Millman and P. Kusch, Bull. Am. Phys. Soc. **14**, No. 3, Abs. 36; P. Kusch, S. Millman and I.I. Rabi, Phys. Rev. **55**, 1176 (1939).

to us in the form of  $\text{CCl}_2\text{F}_2$ . We found resonance minima which may be ascribed to fluorine. While these minima were not as narrow as those of hydrogen and could not be located as accurately, it was still possible to measure the moment of fluorine to an accuracy well within the limits of error claimed for the calibration of the magnets of either apparatus. The fluorine moment we obtain<sup>13</sup> is  $2.623 \pm 0.018$  nuclear magnetons. This is to be compared with the value  $2.622 \pm 0.013$  nuclear magnetons previously reported by R. M. K. Z.

## Procedure

Although the final values for the nuclear magnetic moments do not depend on the accuracy of the alignment of the apparatus or of the parallelism of the source, collimator, and detector slits, these adjustments must be carefully made in order that the beam intensity and deflecting power of the apparatus may be large enough. As in previous molecular beam experiments<sup>2,9</sup> much of the alignment is accomplished under vacuum with the beam, although part is done optically in advance. The three magnets are rigidly attached to a brass base plate which, together with the separating plate and foreslit between the separating and detector chambers, can be removed from the outer brass tube. As the magnets cannot be moved under vacuum, they, and the foreslit, are optically aligned on the base plate when it is outside the brass tube by running a tightly stretched number 40 copper wire down the line of the beam. The base plate and magnets are then inserted in the tube and clamped in position. The source slit, foreslits, collimator, and detector slit are approximately aligned optically and are carefully made vertical to make them parallel. The two wires which carry the high frequency current are set optically so that the beam passes between them. After these alignments have been made and the apparatus evacuated, gas is introduced into the source feed line and the beam is found by trial with the collimator removed from the beam path. The collimator is then introduced and the position of the beam relative to the magnetic field is found by moving the source, collimator, detector, and narrowest foreslit under vacuum. In this way the beam may be made to run parallel to the magnets and at any desired position in the air gap.

The best currents for use in the deflecting and refocusing magnets *A* and *B* are determined by trial. The ratio of the currents in the two magnets is

---

<sup>13</sup>J.M.B. Kellogg, I.I. Rabi, N.F. Ramsey, Jr. and J.R. Zacharias, Phys. Rev. **55**, 595 (1939), Abs. 24.

first selected so that the refocusing is a maximum. Then with this ratio preserved the total current is adjusted to a value large enough so that most of the molecules which have a constituent moment reoriented in the  $C$  field are not refocused, and small enough so that the deflections of the molecules are not too large to preclude good refocusing when no reorientations occur. A careful adjustment of the total current is particularly important in the measurement of the deuteron moment with HD where the deuteron magnetic moment being studied is in the same molecule with a much larger proton moment.

The resonance minima are observed by keeping the currents in the  $A$  and  $B$  magnets and the frequency of the oscillator constant and varying the current in the  $C$  magnet which produces the homogeneous field. A measure of the number of molecular reorientations produced by the oscillating field is obtained from the change in beam intensity which occurs when the oscillator is turned off or on. As there is always some drift (of the order of 1/2 cm a minute) of the detector galvanometer spot, observations of the change in beam intensity are made by turning the oscillator on and off at 15-second intervals for two minutes and then averaging the changes of the galvanometer deflection. In all of the experiments here described the Dewar to which the source is attached was filled with liquid nitrogen.

It is very important in these experiments that the correct high frequency current be used, since, as follows from the detailed theory of the reorientation probabilities as developed by Rabi<sup>14</sup>, the half-widths of the resonance minima are directly dependent on the strength of the oscillating magnetic field. If too much current is used the widths of the resonance minima increase proportionally to the current and if too little is used the depths of the minima decrease rapidly. The theoretical optimum strength of the oscillating field and the theoretical half-widths of the curves when this field is used are discussed in the next section. As is shown there, the optimum field depends both on the magnitude of the moment being measured and on the velocity and hence the mass of the molecule. In practice we usually determine the best values for the oscillatory current by trial. Since the positions of the minima are not affected by the magnitude of the oscillatory current, this determination is made only approximately.

---

<sup>14</sup>I.I. Rabi, Phys. Rev. **51**, 652 (1937).

## Experimental Results

In this section we shall present our data in the form of typical curves which represent beam intensity at the detector as a function of the value of the field in the  $C$  magnet while a fixed frequency and amplitude of the oscillating current is maintained. These curves we call resonance curves and the minima of intensity which are observed, resonance minima. Of physical interest are the numbers, locations, depths, half-widths, and asymmetries of these resonance minima.

These curves are closely analogous to the absorption and stimulated emission lines of spectroscopy except for two distinct differences. First, instead of measuring the absorption of the radiation we measure the fraction of molecules which make transitions. Second, we employ a definite fixed frequency and shift the positions of the energy levels to correspond to this frequency by varying the magnetic field rather than scanning the spectrum through a range of frequencies at a fixed value of the field. Thus our results are analogous to what would be obtained if one measured the Zeeman pattern of a spectral line by measuring the absorption of some narrow spectral line as a function of the magnetic field in which the absorber is placed. The Zeeman lines would successively pass across this frequency interval and one would obtain an unusual set of absorption lines from which the Zeeman levels could be deduced. In the present experiment with hydrogen molecules, as the strength of the magnetic field is varied the resonance minima occur in groups, the positions of the groups being such that the Larmor precession frequency of a constituent magnetic moment of the molecule is near the frequency of the oscillating field. Since the regions of field that are of-interest in the experiment are those in which the resonance minima occur, only these are included in the accompanying figures. It is to be emphasized, however, that between groups of minima there are large regions of the magnetic field intensity in which no resonance minima occur.

The gases used in these experiments were  $H_2$ ,  $D_2$  and  $HD$ , the latter having been purified for us by Drs. Brickwedde and Scott of the National Bureau of Standards. All experiments were performed with the source at liquid nitrogen temperature. For equilibrium at this temperature, the distributions of the molecules in the different rotational states are as given in Table I. The resultant nuclear spins to be associated with the different rotational states of  $H_2$  and  $D_2$  are also included in the table. These are different for even and odd rotational states since, as is discussed

TABLE I. *Relative abundance of different rotational states at 78° K. To obtain the abundance of a state with given I and J ana,  $m_I$  and  $m_J$  divide the concentration given by the statistical weight. The calculations were made assuming an orlho-para ratio of 3 to 1 for  $H_2$  and 1 to 2 for  $D_2$ . For HD there is no quantum number of total spin.*

J	$H_2$			$D_2$			HD	
	Total Spin	Stat. Wt.	Rel. Conc.	Total Spin	Stat. Wt.	Rel. Conc.	Stat. Wt.	Rel Conc.
0	0	1	0.248	0.2	6	0.559	6	0.628
1	1	9	0.745	1	9	0.328	18	0.369
2	0	5	0.003	0.2	30	0.105	30	0.003
3	1	21	0.000	1	21	0.004	42	0.000

cussed in the theories of the rotational specific heat of homonuclear hydrogen molecules, only para- $H_2$  and ortho- $D_2$  may exist in the even rotational states and vice versa for odd.

Figure 3 is a resonance curve taken with HD molecules at a frequency of 4.000 million cycles in a region of magnetic field varied from about 900 to 1000 gauss. In this region the Larmor precession frequency of the proton is near the oscillator frequency. The very deep minimum arises from the reorientation of the proton in this molecule when the molecule is in a state of zero rotation as will be made clear in the next section. The small fine structure, on both sides is due to the same reorientation process, but in molecules which are in the first rotational state. The discussion of the results in the first rotational state and of the similar ones which arise from reorientations of the deuteron in the first rotational states of HD and  $D_2$  molecules will be reserved for another paper. Fig. 4 is a curve similar to that of Fig. 3 but taken in an entirely different region of frequency and magnetic field, the region being such that the Larmor frequency of the deuteron is near the oscillator frequency. Here again the deep minimum corresponds to reorientations of the deuteron when the molecule is in the zero rotational state white the structure on the two sides arises from similar transitions but in the first rotational state. Fig. 5 is a curve obtained with  $D_2$ . The deep central minimum arises from the reorientation of the deuteron in molecules in the zero rotational state and the structure on either side is due to molecules in the first rotational state.

All of these groups of resonance minima have been observed at more than one frequency. It is found that the ratios of  $f$ , the frequency of the oscillating field, to  $H$ , the magnitude of the homogeneous field at which the

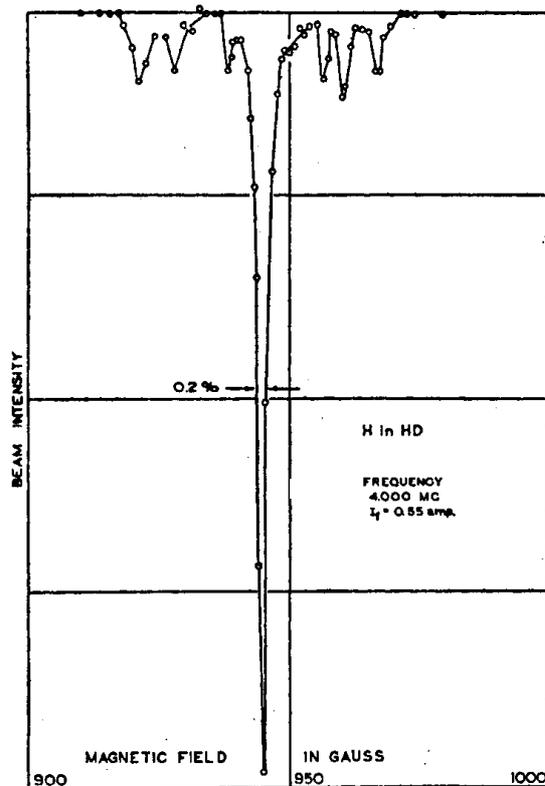


Figure 3: Resonance curve for HD molecules chiefly showing transition of the proton spin (or the zero rotational state).

principal minimum of any moment occurs, are constant. This constancy of  $f/H$  would be expected from Eq. (1) and is strong support for the assumption that the deepest minimum corresponds to the interaction of a magnetic moment with the applied magnetic field, since the constancy of  $f/H$  shows that the energy of interaction is proportional to the strength of the field.

The justification for identifying the resonance minima of Fig. 3 with proton reorientations and Fig. 4 with deuteron reorientations is that a group of minima with the same  $f/H$  as Fig. 3 is found in  $H_2$ , and a group with the same  $f/H$  as Fig. 4 in  $D_2$  (see Fig. 5).

Each of these curves alone is slightly asymmetrical as would be expected from the discussion of Millman<sup>10</sup>. As pointed out by Millman, the signs of

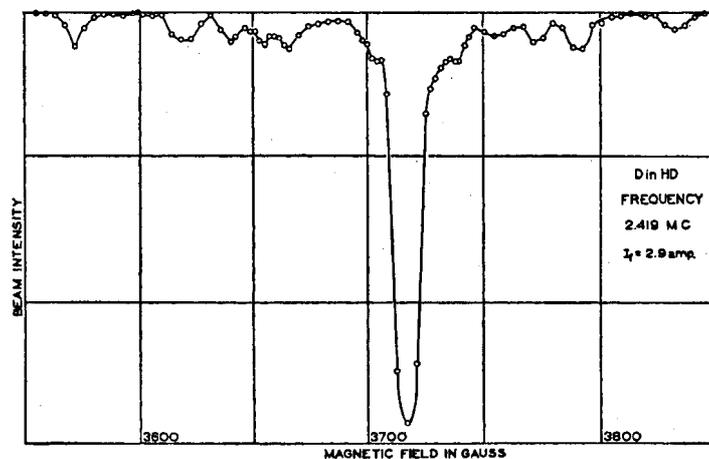


Figure 4: Resonance curve for HD molecules chiefly showing transition of the deuteron spin for the zero rotational state.

the moments can be deduced from the asymmetry. The signs of the proton and deuteron moments found in this way are positive in agreement with the results of K. R. Z.<sup>2</sup>

The depth of the minimum of H in HD corresponds to the occurrence of the reorientation process in about 75 percent of the molecules in the zero rotational state. That this quantity is not greater is to be expected on the basis of the theory given by Rabi and by R. M. K. Z. Since the molecules have a Maxwell distribution of velocity, some of the molecules are not under the influence of the oscillating field long enough, because of their high speed, to make the transition probability unity, while others, because of their low speed, are in the field too long and are partially returned to their original state. A discussion of the depths of the deuteron minima in HD and D<sub>2</sub> will be given in a later paper.

The minimal widths of the resonance minima are given approximately by the relation  $t\Delta\nu \cong 1$  where  $t = L/v$  is the time spent by the molecules in the oscillating field and  $\Delta\nu$  is related to the width of the minima in gauss by  $\Delta\nu = \mu\Delta H/hI$ . The minimal width of the resonance minima at half-intensity (half-depth) is therefore given by  $\Delta H \cong hIv/\mu L$ . If the resonance minima are considerably broader than this it is an indication of lack of resolution or of fine structure in the minima. If the oscillating field is made very weak, the depth of the resonance minimum decreases, but its width is

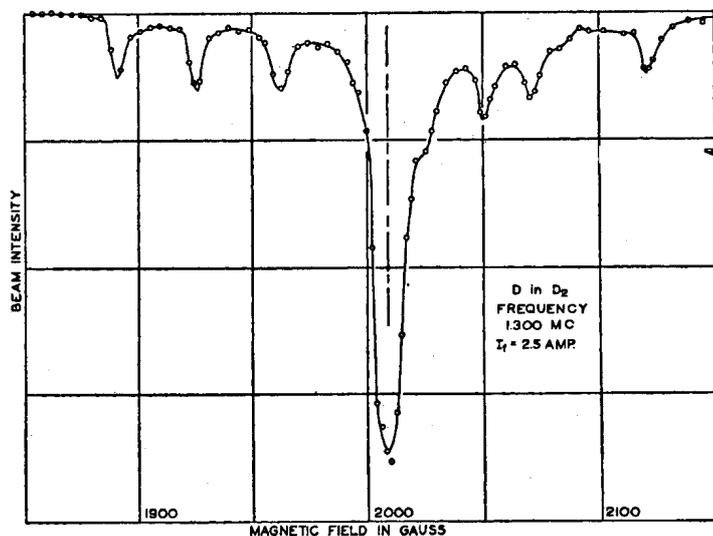


Figure 5: Resonance curve for  $D_2$  molecules showing transition of the resultant nuclear spin for the zero rotational state.

approximately unchanged; whereas, if the oscillating field is made too strong, the half-width of the minimum increases. The best value of the oscillating field for maximum depth of the resonance minimum and narrowest width when we deal with resolved lines is obtained when the amplitude of the oscillating field is approximately equal to  $hIv/\mu L$ . This relation was found to hold experimentally and is expected from the theory<sup>1</sup>.

In Fig. 6 we have a set of six resonance minima which arise from reorientations of the nuclei in  $H_2$  molecules in the first rotational state. Since, as is shown in Table I, the zero rotational state has zero resultant nuclear spin, this state has no resultant nuclear magnetic moment and consequently gives rise to no nuclear resonance minima. The observed resonance minima can be located to within 0.5 gauss. The depths of the minima are approximately equal. The sum of the depths of the resonance minima is approximately equal to the total intensity of ortho- $H_2$  molecules which reach the detector. This is less than the amount to be expected under ideal conditions since each minimum is due to transitions between two states and in our experiment transitions from  $b$  to  $a$  are counted as well as those from  $a$  to  $b$ . Since, as will be shown in the next section, there are nine states all told and since the molecules are equally distributed amongst the states, the depth of each minimum should represent  $2/9$  of the intensity and the sum of the six min-

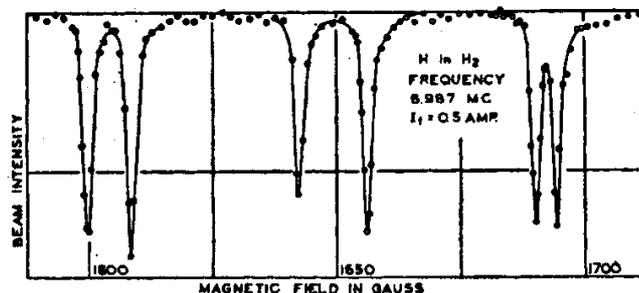


Figure 6: Radiofrequency spectrum of ortho- $H_2$  molecules arising from transitions of the resultant nuclear spin. The path of the beam in the radiofrequency field is 13.5 cm.

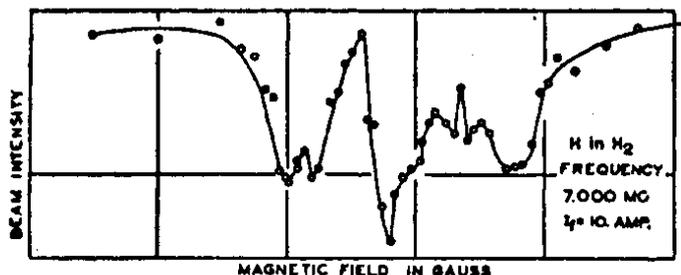


Figure 7: Radiofrequency spectrum of ortho- $H_2$  molecules arising from transitions of the resultant nuclear spin. The path of the beam in the radiofrequency field is only 2.7 cm. The radiofrequency current was too large.

ima  $12/9$  of the total intensity. The effect of the velocity distribution which was discussed above results in a 25 percent reduction of this intensity, so it is reasonable that the total depth should be approximately equal to the Intensity of ortho- $H_2$  molecules as found experimentally.

Figure 7 represents a curve which was obtained with  $H_2$  molecules in an earlier form of our apparatus in which the  $C$  magnet as well as the wires which produce the oscillating field were about a fourth as long as they are now. This curve was one of the first to be observed and a value of the oscillating field much greater than the optimum value discussed above was used. Fig. 8 is another curve on the same apparatus but with the use of the optimum oscillating field. A comparison of these two curves shows how the stronger oscillating field broadens the resonance minima and causes

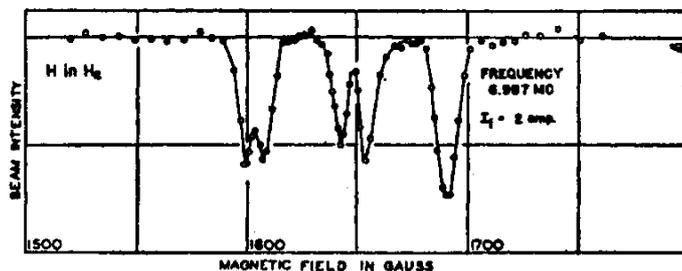


Figure 8: Radiofrequency spectrum for ortho- $H_2$  molecules arising from transitions of the resultant nuclear spin. The path of the beam in the radiofrequency field is 2.7 cm. Optimum r.f. current for this case is 2 amp.

the curious over-lappings which are responsible for the peculiar form of the curve in Fig. 7. By making the  $C$  magnet and the oscillating field four times longer, we were able to reduce the amplitude of the oscillating field by a factor of four since the time which the molecules are under its influence is four times as great. Fig. 6 when compared to Fig. 8 shows the effect of this improvement. The lines in Fig. 6 are much narrower and the resolution is consequently higher. There are six narrow and well separated minima, whereas in Fig. 8 there are only five separated minima.

Figure 9 shows how the positions of the  $H_2$  resonance minima shift when



Figure 9: Variation of radiofrequency spectrum with magnetic field to show the progress of the Paschen-Back effect. The spectra have been shifted to make the positions of  $H_0$  coincide.  $H_0$  was obtained directly by adding 10 percent of HD to the sample of  $H_2$ . In this way one can tell the shift in field of the individual lines.

observations are made at different frequencies. The vertical lines show the observed positions of the peaks at different frequencies. The positions of the different groups of minima in this figure are so adjusted that the field position marked zero is the position on the different groups at which the

Larmor frequency of a proton is equal to the oscillator frequency. The reason for the shifts in the peak positions will be discussed in the next section.

## Evaluation of Experimental Results

In this section we shall first deduce the magnetic moments of the proton and the deuteron from the locations in field and frequency of the deep resonance minima with HD and D<sub>2</sub> molecules as shown in Figs. 3, 4, and 5. Then we shall discuss in detail the results of the theory of the energy levels of ortho-H<sub>2</sub> in the first rotational state and apply them to the experimental results obtained from curves like Fig. 6. Finally we shall present a derivation of the formulae which we use. When the molecule of HD or D<sub>2</sub> is in the state with rotational angular momentum,  $J$ , equal to zero, the internuclear axis is oriented in every direction with equal probability. Since these molecules have no resultant electronic moment (<sup>1</sup>Σ state) all interactions between each nucleus and the rest of the molecule become independent of the orientation of the nucleus in the external magnetic field. This follows

TABLE II. *Summary of data taken during the spring of 1938 for the determinations of the proton and deuteron moments. The magnet used for these measurements was calibrated with a flip coil and mutual inductance. The path in the r.f. field was only 2,7 cm.*

Substance	Moment Measured	Frequency in Megacycles	Field in Gauss	Nuclear Moment
H <sub>2</sub>	H	5.662	1336	2.781
H <sub>2</sub>	H	7.000	1655	2.775
H <sub>2</sub>	H	8.923	2107	2.779
H <sub>2</sub>	H	14.007	3299	2.786
HD	H	10.420	2456	2.785
HD	H	10.420	2461	2.780
HD	H	10.430	2457	2.786
HD	H	13.535	3180	2.793
HD	H	13.190	3106	2.787
HD	H	13.212	3106	2.791
D <sub>2</sub>	D	2.103	3232	0.8536
D <sub>2</sub>	D	3.143	4832	0.8537
D <sub>2</sub>	D	2.103	3224	0.8560
HD	D	2.021	3106	0.8550

because the axis of the molecule has all orientations with equal probability independent of the nuclear spin orientation. Further, the magnetic interaction between the two nuclear magnets averages out to zero, because the mutual energy of two dipoles averaged over all possible orientations of the line joining them is zero. Therefore, each of the two nuclei in the molecule has a definite energy in the external magnetic field depending on its own orientation but independent of the orientation of the other nucleus. These are exactly the circumstances under which the theory of Eq. (1) may be applied as well as the rigorous theory<sup>13</sup> for the transition probability in the oscillating field.

The experimental results show that these predictions are indeed true and that the half-widths and depths of the minima are as to be expected and that the ratio  $f/H$  is constant. From these values of  $f/H$ , from Eq. (1), and from the known results that the spin of the proton is  $1/2$  and of the deuteron  $1$ , we compute the value of the magnetic moments. The results are tabulated in Table II, and show that those obtained for the deuteron with  $D_2$  and  $HD$ , and for the proton with  $H_2$  and  $HD$ , are in close agreement.

These measurements were made when the homogeneous field magnet was the small one permitting a length of path in the radiofrequency field of only 2.7 cm. However, this magnet is the one that is carefully calibrated so that our values of the moments depend on this calibration. The averages, obtained by weighting proportionally to frequency, are  $2.785 \pm 0.02$  nuclear magnetons and  $0.855 \pm 0.006$  nuclear magnetons for the proton and deuteron, respectively.

The longer magnet, put into the apparatus later, was not directly calibrated at all. Its field is known only in terms of the proton moment.

A very careful determination of the ratio  $\mu_P/\mu_D$  was made with the longer magnet. The result is  $\mu_P/\mu_D = 2570 \pm 0.001$ . This agrees with the value  $3.259 \pm 0.007$  obtained with the short magnet. The difference in the precisions of the two results is chiefly due to the difference between the lengths of the two radiofrequency fields.

When the rotational quantum number is greater than zero, the various interactions mentioned in the previous paragraph are no longer zero and the energy of a nucleus in the external magnetic field depends not only on its own orientation but also on the orientation of the other nucleus and on the orientation of the rotational angular momentum of the molecule. We shall discuss only ortho- $H_2$  in the first rotational state since, as discussed in the preceding section, this is the only state which contributes resonance minima when  $H_2$  is observed at  $78^\circ K$ .

In ortho- $H_2$  the two nuclei are in a state where the spins of the two

nuclei are “parallel,” that is, the total nuclear spin angular momentum is 1. Transitions between this state and the state in which the total spin is zero cannot occur in our experiment for two reasons. First, such a change in spin involves a change from ortho-H<sub>2</sub> to para-H<sub>2</sub> and hence a change in rotational quantum number for which the energy difference is so large that it involves a frequency thousands of times as great as those we employ. Second, this transition is highly forbidden because it is of the triplet to singlet type.

From these considerations we see that in an externally applied magnetic field, in which the energy of the protons due to interaction with the field is much larger than the magnetic energy of interaction between the two protons and of the protons with the molecular rotation, we obtain nine energy levels. These correspond to the three orientations of the total nuclear spin  $I$  with each of which three orientations of the rotation vector  $J$  are possible. The resonance minima shown in Fig. 6 arise from the six transitions and their inverses which can occur between these nine magnetic levels subject to the restriction  $\Delta m_I = \pm 1$ .

The theory of the location of these levels is very similar to that of the magnetic levels of a multiplet of the Paschen-Back effect. If we assume that the orientation dependent energy of the ortho-H<sub>2</sub> is due solely to interactions with the external field and to the spin-spin magnetic interaction between the nuclei and the magnetic interaction between the nuclear spins and the molecular rotation, then the theoretical expression for the total energy of the ortho-H<sub>2</sub> molecule in the magnetic field (apart from constants independent of the orientation) becomes

$$E = -\mu_P(\boldsymbol{\sigma}_1 + \boldsymbol{\sigma}_2) \cdot \mathbf{H} - \mu_R \mathbf{J} \cdot \mathbf{H} - \mu_P H' (\boldsymbol{\sigma}_1 + \boldsymbol{\sigma}_2) \cdot \mathbf{J} \\ + \frac{\mu_P}{r^3} \{ \boldsymbol{\sigma}_1 \cdot \boldsymbol{\sigma}_2 - 3(\boldsymbol{\sigma}_1 \cdot \mathbf{r})(\boldsymbol{\sigma}_2 \cdot \mathbf{r})/r^2 \}, \quad (3)$$

where  $\mu_P$  and  $\mu_R$  are the proton and rotational magnetic moments,  $\boldsymbol{\sigma}_1$  and  $\boldsymbol{\sigma}_2$  the Pauli matrices for the nuclear spins,  $J$ , the rotational angular momentum in units of  $h/2\pi$ , and  $r$  the radius vector joining the two nuclei. The first term is the energy of the two proton moments in the external magnetic field  $H$ , which we take in the  $z$  direction. This term can also be written as  $2\mu_P \mathbf{I} \cdot \mathbf{H}$  since, as has already been stated, the two proton spins, each of value  $1/2$ , combine to form a total proton spin  $I$  of value 1, and the two proton moments  $\mu_P$  combine to form a total moment equal to  $2\mu_P$ . The second term is the energy arising from the interaction of the rotational magnetic moment of the molecule with the external magnetic field. The third term is the energy of interaction between the proton moment and the

field  $H'$  caused by the rotation of the molecule at the position of the protons.

TABLE III. *Energy levels for the first rotational state of ortho- $H_2$  molecules in a magnetic field,  $\alpha = \mu_R/2\mu_P$ .*

$m_J$	$m_I$	Energy
1	1	$-2\mu_P\{H + \alpha H - H''/5 + H'\}$
1	0	$-2\mu_P\{\alpha H + 2H''/5 - 3H''/5 - H'^2/H(1-\alpha)\}$
1	-1	$-2\mu_P\{H + \alpha H - H''/5 - H' - [(3H''/5 + H')^2 + 2(3H''/5)^2]/H(1-\alpha)\}$
0	1	$-2\mu_P\{+2H''/5 + (3H''/5 - H')^2/H(1-\alpha)\}$
0	0	$-2\mu_P\{-4H''/5\}$
0	-1	$-2\mu_P\{-H + 2H''/5 - (3H''/5 - H')^2/H(1-\alpha)\}$
-1	1	$-2\mu_P\{H - \alpha H - H''/5 - H'[(3H''/5 + H')^2 + 2(3H''/5)^2]/H(1-\alpha)\}$
-1	0	$-2\mu_P\{-\alpha H + 2H''/5 + (3H''/5 - H')^2/H(1-\alpha)\}$
-1	-1	$-2\mu_P\{-H - \alpha H - H''/5 + H'\}$

This field is parallel to the rotational angular momentum  $J$ . The last term is the well-known expression for the interaction between two magnets separated by a distance  $r$ , which in this case is the internuclear distance.

From this form of interaction the energy-levels of the molecule may be obtained by the Schrodinger perturbation theory. The calculation is given at the end of this section. The results, good to the second-order perturbation theory, are given in Table III, where the resultant energy levels are classified by the quantum numbers  $m_I$  and  $m_J$ , which are the magnetic quantum numbers of the total nuclear spin and of the molecular rotation, respectively, where each takes the values 1, 0 and  $-1$ .

The terms involving  $(H')^2$  and  $(H'')^2$  represent corrections to the energies which are inversely proportional to the external field. They arise because the magnetic field is not sufficiently large for the Paschen-Back effect to be complete. These corrections though small, are nevertheless measurable. The quantity  $H''$  is the value of  $\mu_P/r^2$  and comes from the term which involves the mutual magnetic energy of the two protons and is independent of the value of the external field.  $H''$  is thus the field at one proton due to the magnetic moment of the other.

This set of energy levels plus appropriate selection rules will give the observed spectrum at frequencies equal to the energy differences divided by  $h$ , as is shown by Eq. (2). At high fields where the first three terms in the energy expression are much larger than the last two, we have rigorous selection rules, namely:

$$\Delta m_I = \pm 1,$$

or

$$\Delta m_J = \pm 1.$$

The first corresponds to a change in the orientation of the total proton spin by one unit while the component of the rotational angular momentum remains unchanged; while in the second the orientation of the nuclear spin remains fixed while the rotational  $m_J$  changes. Since the above mentioned corrections are small compared with the other terms we obtain two groups of lines, one of which corresponds to transitions in which  $m_I$  changes and the other when  $m_J$  changes. The first set (of six) is grouped around the region where  $f = 2\mu_P H/h$  and the other set of six around the region  $f = \mu_R H/h$ .

In this paper only the first group will be discussed. The second group does not yield any new information except the magnetic moment of rotation and will be discussed in a paper devoted to the rotational moments of  $H_2$ ,  $D_2$  and  $HD$ . The six lines which we will consider correspond to the energy differences given in energy units in Table IV.

We must now recall that we use a fixed oscillator frequency,  $f_0$ , and vary the magnetic field in the neighborhood of  $H_0$ , where  $H_0$  is defined by  $H_0 = hf_0/2\mu_P$ .  $H_0$  is thus the field at which the Larmor frequency of the proton would be equal to the oscillating frequency applied. Setting  $\Delta E$  as given in Table IV equal to  $2\mu_P H_0$  and dividing through by  $2\mu_P$  it can be seen that resonances will occur for the values of the magnetic field listed in Table V.

Except for the effect of the small last terms in Table V, we see that the resonances are symmetrical about the position  $H_0$ . This circumstance permits us to deduce a value of the proton moment from the center of the pattern formed by the six resonance minima with the results given in Table II.

A unique identification of the transitions producing the minima of the curve of Fig. 6 makes possible an evaluation of the interaction

TABLE IV. *Changes of energy associated with a change of the orientation of the total nuclear spin by  $\pm 1$  for ortho- $H_2$  molecules in the first rotational state.*

$m_J$	$\Delta m_I$	$\Delta E$
1	$0 \rightarrow 1$	$2\mu_P\{H - (3H''/5 - H') + (3H''/5 - H')^2/H(1 - \alpha)\}$
1	$-1 \rightarrow 0$	$2\mu_P\{H + (3H''/5 + H') + 6H''/5(3H''/5 + 2H')/H(1 - \alpha)\}$
0	$0 \rightarrow 1$	$2\mu_P\{H + 6H''/5 + (3H''/5 - H')^2/H(1 - \alpha)\}$
0	$-1 \rightarrow 0$	$2\mu_P\{H - 6H''/5 + (3H''/5 - H')^2/H(1 - \alpha)\}$
-1	$0 \rightarrow 1$	$2\mu_P\{H - (3H''/5 + H') + 6H''/5(3H''/5 + 2H')/H(1 - \alpha)\}$
-1	$-1 \rightarrow 0$	$2\mu_P\{H + (3H''/5 - H') + (3H''/5 - H')^2/H(1 - \alpha)\}$

TABLE V. *Magnetic fields at which resonances will occur for a fixed oscillator frequency  $f_0 = 2\mu_P H_0/h$ .*

$m_J$	$\Delta m_I$	Magnetic Fields		
1	$0 \rightarrow 1$	$H_0 + (3H''/5 - H')$	$+(3H''/5 - H')^2/H(1 - \alpha)$	
1	$-1 \rightarrow 0$	$H_0 - (3H''/5 + H')$	$-6H''/5(3H''/5 + 2H')/H(1 - \alpha)$	
0	$0 \rightarrow 1$	$H_0 - 6H''/5$	$-(3H''/5 - H')^2/H(1 - \alpha)$	q
0	$-1 \rightarrow 0$	$H_0 + 6H''/5$	$-(3H''/5 - H')^2/H(1 - \alpha)$	
-1	$0 \rightarrow 1$	$H_0 + (3H''/5 + H')$	$-6H''/5(3H''/5 + 2H')/H(1 - \alpha)$	
-1	$-1 \rightarrow 0$	$H_0 - (3H''/5 - H')$	$-(3H''/5 - H')^2/H(1 - \alpha)$	

constants  $H'$  and  $H''$ . This identification is made possible by the asymmetry of the positions of the two outermost minima which is especially noticeable in low field. In fact Fig. 9 and Table VI show clearly that the minima labeled  $A_L, B_L, A_R$  and  $B_R$  are symmetrically located about  $H_0$  at all frequencies, while  $C_L$  and  $C_R$  only approach symmetry at high frequency.

Setting  $(1 - \alpha) = 0.843 \approx 1$ , reference to Table V reveals two things. First, if *four* minima are symmetrical and two asymmetrical, the asymmetrically situated minima marked  $C_L$  and  $C_R$  on Fig. 6 must be assigned to the transitions  $m_J = 1, m_I = -1 \leftrightarrow 0$ , and  $m_J = -1, m_I = 0 \leftrightarrow 1$ . Second, the quantity  $(3/5H'' - H')^2/H$  must be small. Reference to Fig. 9 shows that the shifts from symmetry produced by this second-order term in a field of 1000 gauss must be less than 1 gauss. Hence  $(3/5H'' - H') < (1000)^{1/2}$ , and we must identify  $A_L$  and  $A_R$  with the transition  $m_J = 1, m_I = 0 \leftrightarrow 1$ , and  $m_J = -1, m_I = -1 \leftrightarrow 0$ . This leaves  $B_L$ , and  $B_R$  as the remaining minima, and they must be assigned to the other two transitions.

Once the transitions are identified, the determination of the separations in field between corresponding minima gives:

$$A_R - A_L = 2 \left( \frac{3}{5}H'' - H' \right) = 13.5 \text{ gauss},$$

$$B_R - B_L = (12/5)H'' = 81.8 \text{ gauss},$$

$$C_R - C_L = 2 \left( \frac{3}{5}H'' - H' \right) = 95.2 \text{ gauss},$$

This assignment satisfies the obvious requirement that  $(C_R - C_L) = (B_R - B_L) + (A_R - A_L)$ , and furthermore fixes the sign of  $H'$  as the same as that of  $H''$ , which is positive because the proton moment is positive. The experimental fact that at low fields the shifts of  $C_L$  and  $C_R$  are toward lower field serves only as a check on the correctness of the applicability of the theory.

The best values deduced from the results in Table VII are:

$$H' = 27.2 \pm 0.3 \text{ gauss} \quad \text{and} \quad \frac{3}{5}H'' = 20.5 \text{ gauss}$$

$$H'' = 34.1 \pm 0.3 \text{ gauss.}$$

These values can be used to account quantitatively for the asymmetry. In fact, the term  $(6/5)H'' (\frac{3}{5}H'' + 2H') / (1-\alpha)H = 3660/H$  if we use the value of the rotational moment given by Rafflsey<sup>15</sup>. We compare the expected shift of 3.8 gauss with the experimental value (see Table VI) of 4 gauss from  $(C_R + C_L)/2$  for the 4 Mc data.

The fact that the three intervals and the asymmetry can be accounted for to such accuracy by only two constants, strongly supports our theory. Furthermore, these values agree with similar results to be published by one of us (N. F. R., Jr.) using the resonances associated with transitions of the molecular rotation moment of H<sub>2</sub>. These values for these same constants are:

$$H' = 27.0 \text{ gauss}$$

$$H'' = 34.1 \text{ gauss}$$

The quantity  $H''$  is equal to  $\langle \mu_P / r^3 \rangle_{A_V}$ . We are indebted to Dr. Arnold Nordsieck for supplying us with the value of  $\langle r^{-3} \rangle_{A_V}$ , which he obtained from the band spectrum analysis of H<sub>2</sub> by C. R. Jeppeson<sup>16</sup>. The asymmetry of the potential even

TABLE VI. *Displacements in gauss of minima for H in H<sub>2</sub> from center (H<sub>0</sub>) obtained from H in HD. These displacements are considered reliable to  $\pm 0.5$  gauss. Note that only C<sub>L</sub> and C<sub>R</sub> are unequal; that they approach equality in high fields.*

	Displacements in Gauss for Oscillator Frequencies of		
	4.000 Mc	7.000 Mc	16.000 Mc
C <sub>L</sub>	-51.8	-49.3	-48.9
B <sub>L</sub>	-40.7	-40.8	-41.0
A <sub>L</sub>	-6.6	-6.9	-6.6
H <sub>0</sub>	942.3	1649.1	3769.0
A <sub>R</sub>	6.7	6.9	6.6
B <sub>R</sub>	41.0	41.2	41.0
C <sub>R</sub>	43.8	45.5	46.5

<sup>15</sup>N.F. Ramsey, Jr., Phys. Rev. **55**, 595 (1939), Abs. 26.

<sup>16</sup>C.R. Jeppeson, Phys. Rev. **44**, 165 (1933).

Table VII. *Displacements in gauss between corresponding minima of  $H$  in  $H_2$ . Note that the separations between corresponding minima are independent of oscillator frequency and that  $(A_R - A_L) + (B_R - B_L) = (C_R - C_L)$  as expected theoretically.*

	Displacements in Gauss for				Assigned Theoretical Expression
	Oscillator Frequencies of				
	4 Mc	7 Mc	16 Mc	Average	
$C_R - C_L$	95.5	94.8	95.4	95.2	$2(H' + 3H''/5)$
$B_R - B_L$	81.6	82.0	81.9	81.8	$12H''/5$
$A_R - A_L$	13.2	13.8	13.3	13.5	$2(H' - 3H''/5)$

for the lowest vibration state and the centrifugal effect of the first rotational level make the effective internuclear distance slightly larger than  $r_\epsilon$  the equilibrium internuclear distance. This value of  $\langle r^{-3} \rangle_{AV}$  of  $2.438 \times 10^{+24} \text{ cm}^{-3}$  combined with  $H'' = 34.1$  yields a value of  $\mu_P = 1.403 \times 10^{-23} \text{ erg/gauss}$  or  $2.785 \pm 0.03$  nuclear magnetons, in too perfect agreement with the value obtained from the  $\nu/H$  result. It is of interest to note that this serves as a check on the correctness of the calibration of the magnet, because if the calibration constant were changed the two values would change in opposite directions, and would disagree if the magnet were incorrectly calibrated.

## Derivation of Table III

We shall now sketch a derivation of the formulae which are used to construct Table III, the table of energy levels obtained from the energy expression of Eq. (3). Since we use a high value of the external field,  $m_I$  and  $m_J$  are “good” quantum numbers and we will use the  $m_I$  and  $m_J$  representation. The diagonal elements of the first three terms on the right of Eq. (3) in this representation are

$$-2\mu_P H m_I - \mu_R H m_J - 2\mu_P H' m_I m_J. \quad (4)$$

matrix elements of the fourth term

$$\mu_P^2 / r^3 (I J m_I m_J | \boldsymbol{\sigma}_1 \cdot \boldsymbol{\sigma}_2 - 3(\boldsymbol{\sigma} \cdot \mathbf{r})(\boldsymbol{\sigma}_2 \cdot \mathbf{r}) / r^2 | I J m'_I m'_J) \quad (5)$$

are evaluated from the nine wave functions of ortho- $H^2$ . To a high approximation these wave functions are written as a product of the symmetrical

spin functions of the two protons and the coordinate wave functions of the first rotational state. These wave functions are given by

$$\begin{aligned}\Psi_{m_I m_J} &= \varphi_{m_I} \psi_{m_J} & (6) \\ \psi_1 &= -\frac{1}{2}(3/2\pi)^{1/2} \sin \vartheta e^{i\varphi}, & \psi_0 &= \frac{1}{2}(3/2\pi)^{1/2} \cos \vartheta, \\ & & \psi_{-1} &= \frac{1}{2}(3/2\pi)^{1/2} \sin \vartheta e^{-i\varphi}, \\ \varphi_1 &= \alpha(1)\alpha(2), & \varphi_0 &= \sqrt{2}(\alpha(1)\beta(2) + \beta(1)\alpha(2))/2 \\ & & \varphi_{-1} &= \beta(1)\beta(2),\end{aligned}$$

where  $\alpha$  and  $\beta$  are the spin eigenfunctions for the spin components  $1/2$  and  $-1/2$ , respectively.

The evaluation of these matrix elements is simplified by use of the following identity which may readily be verified by expansion:

$$\begin{aligned}r^2 \boldsymbol{\sigma}_1 \cdot \boldsymbol{\sigma}_2 - 3(\boldsymbol{\sigma}_1 \cdot \mathbf{r})(\boldsymbol{\sigma}_2 \cdot \mathbf{r}) &= -(3z^2 - r^2)(3\sigma_{z_1}\sigma_{z_2} - \boldsymbol{\sigma}_1 \cdot \boldsymbol{\sigma}_2)/2 \\ &\quad - 3\left\{\frac{1}{4}(\sigma_{x_1} + i\sigma_{y_1})(\sigma_{x_2} + i\sigma_{y_2})(x - iy)^2\right. \\ &\quad \left. + \frac{1}{4}(\sigma_{x_1} - i\sigma_{y_1})(\sigma_{x_2} - i\sigma_{y_2})(x + iy)^2\right. \\ &\quad \left. + \frac{1}{2}[\sigma_{z_2}(\sigma_{x_1} + i\sigma_{y_1}) + \sigma_{z_1}(\sigma_{x_2} + i\sigma_{y_2})]z(x - iy)\right. \\ &\quad \left. + \frac{1}{2}[\sigma_{z_2}(\sigma_{x_1} + i\sigma_{y_1}) + \sigma_{z_1}(\sigma_{x_2} + i\sigma_{y_2})]z(x + iy)\right\} & (7)\end{aligned}$$

The matrix elements of the first term of Eq. (7) give all of the diagonal elements of Eq. (5) which are equal to<sup>17</sup>

$$(3m_J^2 - 2)(3\sigma_{x_1}\sigma_{x_2} - \boldsymbol{\sigma}_1 \cdot \boldsymbol{\sigma}_2)\mu_P^2/5r^3.$$

For ortho-H<sub>2</sub>, for which the three spin functions are symmetrical in the proton spin  $\boldsymbol{\sigma}_1 \cdot \boldsymbol{\sigma}_2 = 1$  and we then obtain for the diagonal elements of Eq.(5)

$$(3m_J^2 - 2)(3m_I^2 - 2)2\mu_P^2/5r^3.$$

The off diagonal matrix elements are used in our calculations to evaluate the second-order perturbations of the energies from complete Paschen-Back effect and give rise to the quantities listed in Table III. The off diagonal

---

<sup>17</sup>H.B.G. Casimir, "On the Interaction between Atomic Nuclei and Electrons," Prize Essay published by Teyler's Tweede Genootschap (1936), page 33.

elements of Eq. (S) are easily calculated from the three spin and three angular wave functions. The values of the nonvanishing elements are:

$$\begin{aligned}
& (m_I, m_J \text{ to } m_I - 1, m_J + 1) = (2m_I - 1)(2m_J + 1) \\
& \quad \times \{(m_I + 1)(2 - m_I)(1 - m_J)(2 + m_J)\}^{1/2} 3\mu_P^2/5r^3, \\
& (m_I, m_J \text{ to } m_I + 1, m_J - 1) = (2m_I + 1)(2m_J - 1) \\
& \quad \times \{(1 - m_I)(2 + m_I)(1 + m_J)(2 - m_J)\}^{1/2} 3\mu_P^2/5r^3, \\
& \quad (m_I, m_J \text{ to } m_I - 2, m_J + 2) \\
& \quad = \{(1 + m_I)m_I(2 - m_I)(3 - m_I)(1 - m_J) \\
& \quad \quad \times (-m_J)(2 + m_J)(3 + m_J)\}^{1/2} 3\mu_P^2/5r^3, \\
& (m_I, m_J \text{ to } m_I + 2, m_J - 2) = \{(1 - m_I)(-m_I)(2 + m_I)(3 + m_I) \\
& \quad \times (1 + m_J)(m_J)(2 - m_J)(3 - m_J)\}^{1/2} 3\mu_P^2/5r^3.
\end{aligned}$$

The off diagonal elements of the term  $\mu_P H'(\boldsymbol{\sigma}_1 + \boldsymbol{\sigma}_2) \cdot \mathbf{J}$  are:

$$\begin{aligned}
& m_I, m_J \text{ to } m_I + 1, m_J - 1 = \\
& \{(1 - m_I)(2 + m_I)(1 + m_J)(2 - m_J)\}^{1/2} \mu_P H', \\
& m_I, m_J \text{ to } m_I - 1, m_J + 1 = \\
& \{(1 + m_I)(2 - m_I)(1 - m_J)(2 + m_J)\}^{1/2} \mu_P H'.
\end{aligned}$$

The value of the perturbation energy which is to be added to the diagonal elements is obtained from the usual second-order perturbation theory. Since the only nonvanishing matrix elements are between states with the same value of  $m_I + m_J$  we have

$$W_{m_I, m_J} = \sum_{\delta} \frac{(m_I, m_J | E | m_I + \delta, m_J - \delta) \times (m_I + \delta, m_J - \delta | E | m_I, m_J)}{E_{m_I, m_J} - E_{m_I + \delta, m_J - \delta}}, \quad (8)$$

where the sum is over all permissible values of  $\delta$  except zero. Into this equation are inserted the appropriate nondiagonal elements listed above and for  $E_{m_I, m_J}$  the diagonal elements of Eq. (4) without the term which involves  $H'$ . The second-order terms of Table III are thus obtained.

## Discussion

The agreement between the measurements of the magnetic moment of the proton by two theoretically independent methods, i.e., the Larmor frequency in an external field and the magnetic interaction of the two proton moments makes our result quite certain. Our present result  $2.785 \pm 0.02$  nuclear magnetons is in agreement with the previous atomic beam measurement of the proton moment through the hyperfine-structure of the normal state of

atomic hydrogen. That result was  $2.85 \pm 0.15$  nuclear magnetons which is well within the limit of error. To this extent there is no reason for supposing some breakdown of the Dirac equation for the electron nor the assumption of any novel interaction between proton and electron. A similar discussion holds for the deuteron. If we assume that the neutron moment, is the difference<sup>18</sup> between the deuteron moment and the proton moment then its value is  $-1.93$  nuclear magnetons.

The quantity  $H'$  which is the constant of spin-orbit interaction or the magnetic field at a nucleus produced by the molecular rotation is 27.2 gauss. Although no exact theory of this quantity exists in the literature a rough consideration shows it to be quite reasonable. The magnetic field produced by the orbital motion of one proton at the position of the other is  $2ev/cr^2$  which can be written as  $(2e/Mc)(Mvr/r^3)$ . Setting  $Mvr$  equal to  $h/2\pi$  we obtain  $4\mu_n/r^3$  for this field, where  $\mu_n$  is one nuclear magneton. Inserting numerical values this becomes 49.0 gauss. The effect of the electrons is in the opposite sense. Since our results show that  $H'$  is positive the magnetic field produced by the electrons is somewhat less than half that of the nuclei.

Our results show that it is possible to apply exact spectroscopic principles and procedures to spectral regions which correspond to ordinary radio waves. The accuracy to which the laws of quantum mechanics hold and the necessity of their application in a region of frequency in which one is accustomed to think classically we consider a striking confirmation of the theory.

This research has been aided by grants from the Research Corporation and the Carnegie Institution of Washington.

---

<sup>18</sup>However, see J. Schwinger, reference 6, for a discussion of the effect of the deuteron quadrupole moment on these considerations.