ERRATA IN PREVIOUS PAPERS

In Eq. (30) of reference 1, the factor in square brackets should read:

"[
$$k(2\kappa+k)(2\kappa+k-1)-4\alpha^2 Z^2(1-k)$$
]."

In reference 9, the last line of paragraph 4 should read : "(-0.80 ± 0.16), while we predict -5.3/(1.7+5.3)=-0.76."

The definition of the correction factor ζ (Eq. (47) of I) is incorrect since it neglects the effect of s electrons on the diagonal dipole matrix element.²¹ The proper formula for ζ can be evaluated with formulas given in

²¹ This error was pointed out to the author by Dr. Thomas Eck in private communication.

I, and the result can be written for a ^{2}P state (replacing Eq. (62) of I) as follows:

$$\zeta = 1 - \beta_{3/2} \left(1 + \frac{16}{5\xi} \right),$$

where $\beta_{3/2}$ is defined in reference 9 and some values are given in Table II of this paper. The octopole data in Table III have been corrected for this error.

Similarly, in Eq. (51) of I, the factor $\left[\Delta\nu/6(2I+1)\right]$ $\times \zeta(\xi/\theta)$ should be replaced by $(5/12)\xi\zeta a_{3/2}$, using this new formula for ζ . The correctly calculated values of R^{-1} still agree with the measured values within the experimental uncertainties.

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Electron g Value in the Ground State of Deuterium^{*+}

J. S. GEIGER, V. W. HUGHES, AND H. E. RADFORD Yale University, New Haven, Connecticut (Received July 6, 1956)

The ratio of the electron g_J in the deuterium ground state to the proton g_p in a cylindrical mineral oil sample has been measured. The measurement was made using the microwave magnetic resonance absorption method and apparatus which Beringer and Heald used to determine $-g_J/g_p$ for hydrogen. The three strong-field Zeeman transitions having $\Delta m_J = \pm 1$, $\Delta m_I = 0$ were observed at a frequency of 9200 Mc/sec. The accuracy was limited by the minimum observed line widths of 20 parts per million resulting principally from magnetic field inhomogeneities. When one uses the Breit-Rabi formula, the unweighted mean of 68 observations yields $-g_J(D)/g_p = 658.2162$ with an assigned error of ± 0.0008 . The ratio of this value to the value of $-g_J(H)/g_p$ obtained by Beringer and Heald, who used an identical mineral oil sample is $g_J(D)/g_J(H) = 0.9999983 \pm 0.0000015$, and to the value of $-g_J(H)/g_p$ of Koenig, Prodell, and Kusch, after suitable diamagnetic corrections, is $g_J(D)/g_J(H) = 0.9999997 \pm 0.0000023$. These values are in agreement with the theoretically expected value of $g_J(D)/g_J(H) = 1$ and with the less precise direct measurement of Nelson and Nafe.

1. INTRODUCTION

HE spin magnetic moment of the electron in the ground state of the hydrogen atom relative to the proton magnetic moment (or, in terms of the g value ratios, $g_J(H)/g_p$ has been measured in recent years^{1,2} to a precision of about 1 part per million (ppm). The quantity of theoretical interest is the ratio of the spin magnetic moment of the free electron to the orbital magnetic moment of the free electron (g_s/g_L) . The experimental value of $g_J(\mathbf{H})/g_L$ is obtained as the ratio of the value of $g_J(\mathbf{H})/g_p$ to the value of g_L/g_p , which is measured by comparing the cyclotron frequency of a free electron with the proton resonance frequency.³ The quantity g_s/g_L is obtained from $g_J(H)/g_L$ by making the

theoretical relativistic bound state correction^{4,5} g_s $=g_J(\mathbf{H})(1-\frac{1}{3}\alpha^2)$ in which α is the fine structure constant. The measurement of g_L/g_p has been made to an accuracy of only $12\ \rm ppm$ and thus limits the accuracy of the experimental value of g_s/g_L to about 12 ppm. The experimental values so obtained^{1,2} are in agreement with the theoretical value⁶ for the electron spin magnetic moment, which includes quantum electrodynamic radiative corrections to order α^2 .

One of the early radio-frequency measurements of electronic magnetism was a comparison of the electron spin magnetic moment in the ground states of hydrogen and deuterium by the atomic-beam magnetic resonance method.7 To within the experimental accuracy of 10 ppm, the ratio $g_J(\mathbf{H})/g_J(D)$ was found to be 1. In view

^{*} This research has been supported in part by the Office of Naval Research.

[†]To be submitted by J. S. Geiger in partial fulfillment of the Ph.D. thesis requirement at Yale University.
‡ Yale University Sterling Fellow, 1955–56.
¹ Koenig, Prodell, and Kusch, Phys. Rev. 88, 191 (1952).
² R. Beringer and M. A. Heald, Phys. Rev. 95, 1474 (1954).
³ J. H. Gardner, Phys. Rev. 83, 996 (1951).

⁴G. Breit, Nature 122, 649 (1928). ⁵N. F. Mott and H. S. W. Massey, *Theory of Atomic Collisions* (Clarendon Press, Oxford, 1949), second edition, p. 72. ⁶J. Schwinger, Phys. Rev. 73, 416 (1948); R. Karplus and N. M. Kroll, Phys. Rev. 77, 536 (1950). A further correction of

order α^3 to the magnetic moment of the electron in the hydrogen atom has been computed by E. H. Lieb, Phil. Mag. 46, 311 (1955). ⁷ E. B. Nelson and J. E. Nafe, Phys. Rev. 76, 1858 (1949).

of the importance of the value of the anomalous spin magnetic moment of the electron, the expectation that a more accurate experimental value of g_L/g_p will be attained by experiments in progress,⁸ and the unexplained values of the electron spin g values in the heavier alkalis,^{9,10} it has been felt desirable to remeasure the electron spin magnetic moment in the ground state of deuterium to the accuracy obtained in the recent $g_J(\mathbf{H})/g_p$ measurements. This paper reports a measurement of $g_J(\mathbf{D})/g_p$ by the microwave magnetic resonance absorption method to an accuracy of about 1 ppm. Comparison of this result with the experimental values for $g_J(\mathbf{H})/g_p$ yields values for $g_J(\mathbf{H})/g_J(\mathbf{D})$.

2. THE EXPERIMENT

2.1 Theory

The energies of the ground-state levels of deuterium in a magnetic field are given by Nafe and Nelson.¹¹ The present experiment is carried out under strong magnetic field conditions and the observed transitions correspond to a reorientation of the electron spin (i.e., $\Delta m_J = \pm 1$, $\Delta m_I = 0$, where m_J is the magnetic quantum number for electronic angular momentum and m_I is the magnetic quantum number for nuclear spin). These are the π_1 , π_2 , and π_3 transitions listed by Nafe and Nelson. Expressing the magnetic field strength H in terms of the corresponding proton resonance frequency, $\nu_p = -g_p(\mu_0 H/h)$ where μ_0 is the Bohr magneton and his Planck's constant, and solving for g_J/g_p in terms of the transition frequency ν , one obtains

 π_1 transition :

$$-\frac{g_J}{g_p} = \frac{\nu}{\nu_p} \frac{\nu + \nu_p (g_d/g_p) - \Delta \nu_d - \frac{2}{3} (\nu_p/\nu) (g_d/g_p) \Delta \nu_d}{\nu + \nu_p (g_d/g_p) - \frac{1}{3} \Delta \nu_d}$$

 π_2 transition:

$$-\frac{g_J}{g_p} = \frac{(\nu/\nu_p) + (g_d/g_p)}{\frac{1}{2} \left[(1+2/3x+1/x^2)^{\frac{1}{2}} + (1-2/3x+1/x^2)^{\frac{1}{2}} - \frac{g_d}{g_p} \right]},$$

 π_3 transition:

$$-\frac{g_J}{g_p} = \frac{\nu}{\nu_p} \frac{\nu + \nu_p (g_d/g_p) + \Delta \nu_d + \frac{2}{3} (\nu_p/\nu) (g_d/g_p) \Delta \nu_d}{\nu + \nu_p (g_d/g_p) + \frac{1}{3} \Delta \nu_d},$$

where

$$x = \left(-\frac{g_J}{g_p} + \frac{g_d}{g_p}\right) \frac{\nu_p}{\Delta \nu_d},$$

 g_d is the deuteron g value, and $\Delta \nu_d$ the deuterium ground-state hyperfine structure separation.

2.2 Experimental Procedure

The measurements reported in this paper were made using the microwave magnetic resonance absorption apparatus and technique employed by Beringer and Heald² (BH) for their hydrogen measurement, and the reader is referred to their article for a description of the apparatus and the details of the procedure. The magnetic field strength in the transition region within the microwave cavity is measured using a simulator proton resonance probe. A second regulator proton probe mounted outside the cavity is used to control the magnetic field strength. Calibration of the magnetic field strength in the cavity in terms of the regulator setting over the region of field strength in which a transition occurs is made before and after taking the microwave absorption data. The field shifts observed between these calibrations varied from 0 to 2 ppm with a mean of about 0.5 ppm. Use of a small-amplitude 30-cycle field modulation and a lock-in detector results in a detected microwave absorption signal approximating the first derivative of the absorption curve (see Fig. 1). The field corresponding to the crossover on the absorption derivative curve is obtained from the field regulator settings by interpolation between calibration runs based on a linear time drift. During more recent runs, the data have been obtained in a 30-minute period.

2.3 Line Width and Relaxation Mechanism

Magnetic field inhomogeneities are a major source of line broadening. During this experiment considerable effort was devoted toward improving the field homogeneity without marked success. Under good field conditions the proton line width, determined by observing the "derivative" of the proton line using the narrowband amplifier and lock-in detector, was 20 ppm. If this width is used as a measure of field homogeneity, the inhomogeneity is twice that quoted by BH, and a full width at half-maximum of 200 kc/sec is inferred for a non-field-broadened, non-power-broadened deuterium line.

The deuterium gas pressure is about 50 microns at the microwave cavity. Observation by BH on the



FIG. 1. Typical deuterium absorption line. Empirical relationship. The quantities a, b, c, and d are used as measures of the line shape.

⁸ Private communications from P. Franken (Stanford University) and E. Purcell and W. Hardy (Harvard University). ⁹ W. Perl, Phys. Rev. **91**, 852 (1953).

¹⁰ P. Kusch and H. Taub, Phys. Rev. **75**, 1477 (1949)

¹¹ J. E. Nafe and E. B. Nelson, Phys. Rev. **73**, 718 (1948).

Run	Field modulation in ppm	Microwave power at bolometer in milliwatts	Pressure at pump in microns	Line width in ppm	Line amplitude asymmetry	Line width asymmetry	$\begin{array}{c} -g_J/g_p \\ \text{(finite} \\ \text{cylindrical} \\ \text{mineral oil)} \end{array}$
1ª	33	0.03	9	31	+1.08	+1.04	658.2146
2	33	0.02	10	30	-1.13	-1.44	658.2171
3	33	0.055	15	34	+1.18	+1.02	658.2155
4ª	33	0.025	13	31	+1.59	+1.29	658.2104
5ª	23	0.023	10	25	-1.16	-1.15	658.2161
6	23	0.02	10	23	-1.03	-1.17	658.2152
7	23	0.02	5	22	+1.07	-1.13	658.2154
8ª		0.03	5	24	+1.26	+1.14	658.2172
9		0.03	6	23	+1.35	1.00	658.2170
10		0.03	5	23	+1.56	+1.50	658.2149
11ª		0.03	5	22	-1.08	-1.11	658.2199
12ª		0.03	5	23	-1.19	-1.30	658.2207
13ª	25	0.03	6	22	+1.09	+1.13	648.2147
14	25	0.03	6	22	+1.45	+1.26	658.2141
15	25	0.03	7	23	+1.54	+1.09	658.2090
16ª	25	0.03	9	22	+1.50	+1.20	658.2120
17	25	0.03	9	23	+1.18	+1.13	658.2137
18ª	25	0.03	9	22	-1.33	-1.22	658.2197
19	23	0.03	9	22	-1.52	-1.20	658.2199
20ª	23	0.03	8	22	-1.10	+1.11	658.2178
21ª	23	0.03	8	22	+1.10	+1.11	658.2165
22	23	0.03	8	21	-1.57	-1.32	658.2216
23ª	23	0.03	10	22	-1.61	-1.29	658.2217
24	23	0.03	7	23	-1.13	+1.05	658.2190
25ª	23	0.03	8	22	1.00	+1.11	658.2182

TABLE I. Summary of experimental data for deuterium π_1 line. In reducing the data, the values $\Delta v_d = 327.384\ 302\pm0.000\ 030\ Mc/sec$ [P. Kusch, Phys. Rev. 100, 1188 (1955)], and $g_d/g_p = 0.1535062 \pm 15$ [N. F. Ramsey, *Nuclear Magnetic Moments* (John Wiley and Sons, Inc., New York, 1953)] have been used. (Blanks indicate data not taken.)

* Magnetic field decreased through microwave line; increased on remaining runs.

atom concentration and the observed microwave signal strength suggest an atom density of 1015/cm3 as reasonable. If a kinetic mean free path of 0.1 cm is assumed, the expected reduced Doppler width¹² is 6 kc/sec. Wall collisions occur at a mean rate of about 10⁵/sec per atom, and, in addition to being an important source of line broadening, probably are the relaxation mechanism. The other collision process we believe to be of importance as a source of line broadening is the atomatom electron exchange collision discussed by Dicke and Wittke.¹³ A further discussion of gas collisions and relaxation processes is given in the Appendix.

3. RESULTS

3.1 Data

A representative set of experimental observations is tabulated in Table I. The values listed under the headings Line width, Line amplitude asymmetry, and Line width asymmetry are arrived at in the following way. The line width is the frequency separation between the zero-slope points on the "derivative" curve expressed in parts per million of the crossover frequency. The line amplitude asymmetry is the larger of deflections c and d, depicted in Fig. 1, divided by the smaller, a plus sign indicating that c > d. Similarly, for line

width asymmetry, the tabulated value is the ratio of the larger of a and b in Fig. 1 to the smaller, a plus sign indicating that a > b.

The line widths observed in the π_1 data are 1.5 times narrower than those for the π_2 and π_r lines. These narrower lines resulted from a decrease in the microwave power level together with improved magnetic field homogeneity. Power broadening made no contribution to the π_1 line widths.

The observed lines were in general asymmetric. A high correlation exists between the two measures of asymmetry listed in Table I, the two asymmetries of a line differing in sign in only 9 of 63 cases. No relation is found between these asymmetries and the direction in which the field was varied in taking the data. It is therefore likely that they do not result from changes with time of the atom density entering the microwave cavity, such as might arise from a nonequilibrium condition in the discharge.

Magnetic field inhomogeneity gives rise to a major part of the observed line width and is believed to be the principal cause of the asymmetries. A second source of line asymmetry, present only if the microwave frequency does not correspond accurately to the resonant value for the cavity, results from dispersion by the deuterium atoms. Further consideration will be given to these sources of line asymmetry in discussing possible systematic errors.

Unweighted and weighted mean values of g_J/g_p for the lines are given in Table II with standard errors. The

 ¹² R. H. Dicke, Phys. Rev. 89, 472 (1953).
 ¹³ J. P. Wittke and R. H. Dicke, Phys. Rev. 103, 620 (1956); P. Wittke, Ph.D. thesis, Princeton University, 1955 (unpublished). E. M. Purcell and G. B. Field, Astrophys. J. (to be published).

		Line amplitude asymmetry				Line width asymmetry				
Line	Number of runs	No. with +asym- metry	No. with -asym- metry	Mean +asym- metry	Mean —asym- metry	No. with +asym- metry	No. with -asym- metry	Mean +asym- metry	Mean —asym- metry	-gJ/gp (finite cylindrical mineral oil)
π_{2} π_{3} π_{1} All	23 20 25 68	12 12 13 37	11 7 11 29	1.17 1.18 1.31 1.22	1.29 1.11 1.27 1.24	15 12 14 41	8 5 10 23	1.12 1.12 1.16 1.13	1.08 1.06 1.23 1.14	$\begin{array}{c} 658.2173 \pm 0.0005 \\ 658.2147 \pm 0.0005 \\ 658.2165 \pm 0.0007 \\ 658.2165 \pm 0.0007 \\ 658.2162 \pm 0.0004 \end{array}$
					Weighted	mean values	5			
			(A) I	lines with	line amplitu	de asymmetr	y >1.20 d	liscarded		
π_2 π_3 π_1 All	14 15 14 43	9 8 6 23	5 6 7 18							$\begin{array}{c} 658.2171 {\pm} 0.0006 \\ 658.2154 {\pm} 0.0005 \\ 658.2168 {\pm} 0.0006 \\ 658.2164 {\pm} 0.0003 \end{array}$
			(B)	Lines wit	h line width	asymmetry	>1.10 dis	carded		
$egin{array}{c} \pi_2 \ \pi_3 \ \pi_1 \ \mathrm{All} \end{array}$	$\begin{array}{c}14\\12\\5\\31\end{array}$					7 5 4 16	7 4 0 11			$\begin{array}{c} 658.2176 \pm 0.0007 \\ 658.2155 \pm 0.0006 \\ 658.2150 \pm 0.0018 \\ 658.2162 \pm 0.0005 \end{array}$

TABLE II. Summary of results.

spread in the unweighted mean values for the individual lines is considerably in excess of that expected from the statistically calculated errors. In particular, the π_3 value falls considerably below that for the π_1 and π_2 lines. As indicated in the table, this value is based predominantly on lines of positive asymmetry which are expected to yield low values. When the three lines are taken as a group, the asymmetries tend to balance out. The histogram of Fig. 2 suggests that the data as a whole are of a random nature. The Gaussian curve has been matched in area to the histogram and has the root-mean-square deviation of the data.

In determining weighted mean values, the lines have been weighted in inverse proportion to their width, and lines of excess line amplitude asymmetry or line width asymmetry have been rejected as indicated in Table II. The π_3 value of g_J/g_p shows an increase in these cases and the scatter in the means for the three lines shows reasonable agreement with the statistical standard errors. The low value of g_J/g_p obtained for the π_1 line when runs are discarded on a line width asymmetry basis is based on only five runs, four of which show



FIG. 2. Histogram of g-factor ratio determinations for all the unweighted data. The solid curve is a Gaussian which has been matched in area to the histogram and which has the rms deviation of the data.

positive asymmetry. The three mean values of g_J/g_p for all the lines are in close agreement.

3.2 Possible Systematic Errors

As has been indicated, a major source of broadening of the microwave lines is magnetic field inhomogeneity. In order that the mean field measured with the simulator proton probe will be the mean field effective in the microwave experiment, it is necessary that the field region sampled and the weighting be the same in the two cases. Weighting differences which vary from about 0-20% over the sample volume result from differences of the rf field distribution in the cavity and in the solenoid containing the proton sample. To estimate these weighting differences, approximate numerical values of the solenoid field at points off its axis were found by representing each turn of the solenoid by a plane current loop and then superposing the fields of these loops. A second sampling difference results from the gas pressure gradient across the cavity length in the microwave experiment. The change in atom density between half-power positions in the cavity is estimated to be 10% or less. The sampling difference introduced by this effect will lead to different effective mean fields except in the case of static magnetic field distributions symmetric about the cavity center.

In order to reduce to a minimum any systematic error resulting from these sampling differences, the magnet was reshimmed each day and no more than two runs were made without some adjustment of the nickel shims. The cavity position along the horizontal center line of the magnet was shifted several times. The mechanical structure of the system prevented similar motion in the vertical direction. The pole caps were removed and their alignment altered twice during the course of this experiment.

Any line asymmetry arising from failure to set the

microwave frequency accurately to the resonant value for the cavity results in a shift in the crossover point on the "derivative" curve. In this experiment the microwave frequency was tuned to the cavity resonant value by using the power reaching the bolometer as a tuning indicator. For a chosen line shape, the shift in crossover position as a function of detuning can be calculated.¹⁴ For a Lorentz absorption curve and for small amounts of detuning, the shift is $\Delta \nu = \frac{1}{2} (a/\Delta f) \Delta \nu_0$, where $a = f - f_0$ measures the microwave detuning and Δf and $\Delta \nu_0$ are the cavity response width and the microwave line width respectively. The tuning method used is believed to limit $a/\Delta f$ to 5%, which in turn limits the line shift to about 1 ppm. The microwave frequency was retuned for each run and a random distribution of errors from this source is expected.

To eliminate frequency modulation of the proton-unit oscillators resulting from the beat effect seen as wiggles in the proton pattern, the units were designed² with separate oscillator and detector resonant circuits. The accurate alignment of these resonant circuits is necessary to eliminate line shifts similar to those just considered for the microwave case. This is achieved by modulating the oscillator frequency with a motordriven rotating capacitor and capacitively trimming the detector tank circuit for minimum output signal. The field was measured by adjusting the proton oscillator frequency for a symmetric proton pattern.

A 30-cycle field modulation frequency and a coherent oscilloscope sweep were used. At large modulation amplitudes, the observed proton pattern has many wiggles resulting from the persistence of coherence in the magnetic moment precession after passage through resonance.15,16 In this experiment, modulation amplitudes of about the observed proton line width were used.

Use of the sinusoidal field modulation, a coherent sinusoidal oscilloscope sweep, and care in aligning the proton resonance circuit results in a symmetric proton pattern^{16,3} for the frequency and field strength of the true line center.

A brief search for pressure dependence of the deuterium transition frequency indicated that any such shift is less than 0.5 ppm.

The only materials whose diamagnetic properties might alter the effective magnetic field in the two measurements are the Lucite container for the proton sample, the copper wire of the coil, and the quartz tubing which confines the deuterium gas to the center of the cavity. The cylindrical form of these structures results in a negligible shielding effect to the present precision provided the magnetic susceptibility of these materials is less than 10⁻⁴ cgs emu.¹⁷

In view of the indicated possible systematic errors, an error of twice the statistical standard error is assigned to the unweighted mean of all the data, giving

 $-g_J/g_p$ (finite cylindrical mineral oil)

 $= 658.2162 \pm 0.0008$.

3.3 Diamagnetic Corrections

In order to compare this result with the value obtained by Koenig, Prodell, and Kusch (KPK)¹ for hydrogen, a diamagnetic correction for the difference in the shapes of the mineral oil proton samples used must be applied to one of the values. Approximating the cylindrical sample used in this experiment by an ellipsold of revolution of the same axial dimensions (ratio 3 to 1) and using for the magnetic susceptibility of mineral oil the value $\chi = -0.73 \times 10^{-6}$, the increase in g_J/g_p necessary to convert the ratio from that for a finite cylindrical sample to a spherical sample is 1.0 ppm. The demagnetization factor for the finite cylinder can also be inferred from experimental data given by Dickinson.¹⁸ Use of this demagnetization factor leads to a conversion correction of 1.2 ppm. Since the magnetization is not uniform for a finite cylinder, the experimental arrangement can be expected to influence the effective demagnetization factor. Taking the diamagnetic correction to be 1.1 ± 0.2 ppm gives

 $-g_J/g_p$ (spherical mineral oil) = 658.2169 \pm 0.0009.

4. DISCUSSION

The experimental result can be directly compared with that of BH for hydrogen, $-g_J(H)/g_p = 658.2173$ ± 0.0002 , obtained by using this same apparatus and an identical mineral oil sample. The ratio of these values is $g_J(D)/g_J(H) = 0.9999983 \pm 0.0000015$. The ratio of the deuterium value of g_J/g_p , corrected to spherical mineral oil, to the hydrogen value of KPK, $-g_J(H)/g_p = 658.2171 \pm 0.0006$, is

 $g_J(D)/g_J(H) = 0.9999997 \pm 0.0000023.$

We do not regard the slight deviation from unity of the first of these ratios as significant.

The atomic g_J for the hydrogen and deuterium ground states are derived in present theory by calculating first the quantum electrodynamic radiative correction to the electron spin magnetic moment for a free electron in a uniform magnetic field.6 One then applies to the resultant spin moment the relativistic bound state correction of the Dirac theory^{4,5} which is the same for the two atoms. Nuclear effects,¹⁹ which would presumably differ for hydrogen and deuterium, are not believed to be sufficiently large to alter the g_J value to the

¹⁴ Gordon, Zeiger, and Townes, Phys. Rev. 99, 1264 (1955).

 ¹⁶ Bloembergen, Purcell, and Pound, Phys. Rev. 73, 679 (1948).
 ¹⁶ B. A. Jacobsohn and R. K. Wangsness, Phys. Rev. 73, 942

^{(1948).} ¹⁷ L. Page and N. I. Adams, Jr., *Principles of Electricity* (D. Van Nostrand Company, Inc., New York, 1949), second edition, p. 143.

 ¹⁸ W. C. Dickinson, Phys. Rev. 81, 717 (1951).
 ¹⁹ M. Phillips, Phys. Rev. 76, 1803 (1949); see also appendix of reference 1.

1

 T_1

present experimental precision. The observed value of 1 for $g_J(D)/g_J(H)$ confirms this belief.

It is a pleasure to thank Professor R. Beringer and Dr. M. A. Heald for helpful discussions.

APPENDIX. COLLISION LINE BROADENING AND **RELAXATION PROCESSES**

In analogy with the treatment of line widths and relaxation in nuclear paramagnetic resonance, it is useful to introduce into a discussion of electronic paramagnetic resonance the times T_1 and T_2^* , which are measures of the relaxation time and the inverse observed line half-width, respectively.²⁰ It has been pointed out that significant contributions to the microwave line width arise from field inhomogeneities, wall collisions, and gas collisions. If one assumes a Lorentzian line shape, the value of T_2^* corresponding to the observed 200-kc/sec line width is about 2×10^{-6} sec. The relaxation time T_1 can be determined from a study of the saturation of the power absorption as a function of the amplitude H_1 of the applied microwave field. The expression for the variation in the absorbed power at resonance P_a with H_1 , T_1 , and T_2^* , as given by formulas (6) and (13) of Bloembergen, Purcell, and Pound (BPP), is

$P_a \propto H_1^2 T_2^* / (1 + \gamma^2 H_1^2 T_1 T_2^*),$

where γ is the gyromagnetic ratio. In the present experiment T_1 is less than 10^{-4} sec.

$$= 1.6\pi N \gamma^4 \hbar^2 J (J+1) \\ \times \int_{2b}^{\infty} \frac{1}{r^4} \bigg\{ \frac{\tau_c}{1+4\pi^2 \nu_0^2 \tau_c^2} + \frac{2\tau_c}{1+16\pi^2 \nu_0^2 \tau_c^2} \bigg\} dr$$

where b ($\sim 10^{-8}$ cm) is the distance of closest approach, r is the dipole separation, ν_0 (=9.2×10⁹ cps) is the transition frequency, N is the number of atoms per cm³, and τ_c is the correlation time for dipoles separated by a distance r^{21} A reasonable correlation time for the low pressure gas is taken to be r/v, where v is the atomic velocity. This process gives a relaxation time of 0.2 sec, insufficient to account for the observed relaxation and resulting in very little line broadening. The wall collisions are sufficiently frequent in this experiment to account for the relaxation time observed. Impurities in the gas and those associated with the water vapor present in the discharge may also contribute to line broadening and relaxation.

The important gas collision process for line broadening is believed to be the atom-atom electron exchange collision discussed by Dicke and Wittke.13 In this collision process, the electrostatic interaction between the two atomic electrons results in an "exchange" of these electrons which is accompanied in the present highfield case by an interchange of the m_{J} 's of the atoms involved. This process is expected to have a cross section of order 10⁻¹⁵ cm², a value not inconsistent with the presently observed line widths in view of the accuracy with which the deuterium atom density is known.

A result of the transitions induced by the applied microwave power is an increase of the total m_J of the atomic gas sample. Since the electron exchange collisions in the present high-field case result only in an interchange of m_J 's by the atoms involved, the total m_J for the atomic gas is unchanged by this process and it does not produce relaxation. Due to the hyperfine structure interaction the strong field quantum numbers are only approximately applicable, and relaxation is produced by the exchange collisions in a higher approximation.

For a gas collision process to contribute appreciably to the line broadening, the cross section for the process must be of the order πa_0^2 , a_0 being the Bohr radius. The nature of the atom-molecule and atom-atom magnetic dipole interactions are such that these mechanisms result in relaxation as well as line broadening. Because the deuterium molecule has no net electronic magnetic moment, atom-molecule collisions have no significance for line broadening and relaxation. The relaxation time due to a magnetic dipole-dipole interaction between the electron spin magnetic moments in atom-atom collisions has been estimated in the analogous manner to that by which BPP evaluated the proton relaxation time in water. In this case relaxation results from magnetic dipole transitions induced by the rf field at an atom which arises from the thermal motion of the other gas atoms relative to it. If one assumes that the atomic dipoles are independent of one another, $1/T_1$

²⁰ Bloembergen, Purcell, and Pound, Phys. Rev. 73, 679 (1948).

²¹ The interaction in the present case is analogous to the interaction of the nuclei of neighboring water molecules in a water proton sample discussed in Sec. X of BPP. The above expression results from combining Eqs. (34) and (43) of BPP. A more detailed discussion of this type of interaction is given in N. Bloembergen's thesis, *Nuclear Magnetic Relaxation* (Drukkerij Fa. Schotanus and Jens, Utrecht, 1948), pp. 87 and 88.